Vinyl Acetate Emulsion Polymerization and Copolymerization With Acrylic Monomers

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Preface

Polyvinyl acetate and vinyl acetate-acrylic copolymer latices are very important in adhesives, paint, binders for nonwovens, paper and textile additive industries, and many related industries. Their production is growing steadily in both actual quantities and different applications. They also possess rather unique properties among emulsion polymers in general due to the high water-soluble nature of vinyl acetate monomer, its high monomer-polymer swelling ratio, and its high chain transfer constant. However, little work has been done on this subject outside of industrial laboratories, and comparatively few publications have been made in scientific periodicals. These publications have the disadvantage of presenting fragments of the field and never the total picture. Although many well-written texts have appeared on general emulsion polymerization in past years, no monograph devoted to polyvinyl acetate based latices has been published; there is only a symposium proceeding edited by M. S. El-Aasser and J. W. Vanderhoff in 1981. The need for an introductory and clear text in the field for visitors from industry or university students is quite evident.

The main objective of this book is to fill the above mentioned gap and provide a general background on understanding the mechanism and kinetics of emulsion polymerization initiated in the aqueous phase, and some of the practical problems of the latex production. This book is written mostly for newcomers to the field. It is designed as an introduction to research, and as a guide to anyone who wishes to use its contents in productive work. Throughout the book, considerable attention is devoted to experimental aspects, the contents of which should also serve as useful reference sources.

Chapter 1 summarizes the history of emulsion polymerization in general and the emulsion polymerization of vinyl acetate in particular. A short review of free radical addition polymerization is also presented to help the understanding of the kinetics of emulsion polymerization in the following chapters.

Chapter 2 presents essential concepts for the description of emulsion polymerization in general and the emulsion polymerization of water-insoluble hydrophobic monomers in particular. Inverse emulsion polymerization is also covered in this chapter.

Homopolymerization of vinyl acetate is treated in Chapter 3. A comprehensive survey on the open literature is conducted to enable readers to reach the related publications directly. Branching mechanisms of vinyl acetate homopolymerization, especially in the presence of polyvinyl alcohol protective colloid, are discussed. A survey of the literature on radiation-induced vinyl acetate emulsion homopolymerization is also presented.

Chapter 4 deals briefly with the role of the ingredients in vinyl acetate emulsion homo- and copolymerization. The properties of vinyl acetate monomer and polymer and the role and the properties of initiators, emulsifiers, protective colloids, process water, pH buffers, and ionic strength controllers are also discussed.

Chapter 5 presents the mechanism of vinyl acetate copolymerization with acrylic ester monomers, monomer reactivity ratios, and a literature survey on the emulsion copolymerization of vinyl acetate with selected acrylate monomers together with the results of the comonomer and emulsifier addition strategies and morphology of particles.

Chapter 6 reviews the most important aspects of the colloidal stability for both homo- and copolymers. Electrostatic as well as steric stabilization mechanisms and the reasons for undesired coagulations are discussed. Chapter 7 deals with the experimental determination of latex properties. Chapter 8 discusses the factors affecting the final properties of both homo- and copolymer latices.

Extensive references to the original literature are cited whenever possible throughout the text. This contribution cannot claim to be completely comprehensive; it is an attempt to join the fragments in order to see the total picture and judge the importance of the related factors. I am greatly indebted to my colleagues who encouraged me to write this book, and to my wife Ayse and my children for their patience and understanding throughout its preparation.

H. Yildirim Erbil

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1 Introduction

The industrial production of polyvinyl acetate homopolymer latices began in Germany around 1935 and has continued to the present, growing steadily over the years. In general, polyvinyl acetate emulsions are milk-white liquids containing 40–55% polymer solids, the balance being water and small amounts of emulsifiers, protective colloids, and other additives. Homopolymer latices prepared with polyvinyl alcohol stabilizers are still among the main products of the adhesive industry. Vinyl acetate (VAc) copolymers with ethyl and butyl acrylate, dibutyl maleate, versatic acid esters, and ethylene are available at low cost and have good durability properties. Emulsion copolymers of VAc have found increasing use in more sophisticated adhesives, exterior and interior paints, carpet backing, adhesives for clay coatings on paper, and numerous other applications. The use of these emulsions for paints eliminates the need for expensive, flammable, odorous, or toxic solvents. They are easy to apply, and the equipment used in application is readily cleaned with water when done promptly. These emulsions also offer the advantage of high solids content with fluidity since the viscosity of the emulsion is independent of the molecular weight of the resin.

Nevertheless, there are disadvantages of VAc copolymerization processes. VAc is a polar and very reactive monomer and requires special treatment to copolymerize with less polar and reactive monomers. The high solubility of VAc monomer in water leads to difficulties during copolymerization with more hydrophobic monomers since the relative concentrations of the copolymerizing monomers in the polymer and water phases are significantly different. Various monomer feed methods are employed to force random copolymerization with less reactive monomers. In addition, some effective initiator systems are required to homopolymerize or copolymerize the highly water soluble VAc monomer.

The thorough understanding of the mechanism and kinetics of polyVAc latices is important both industrially and scientifically and will enable a polymer chemist to make a VAc latex tailored for a specific end use; however, comparatively little work has been done on this subject outside of industrial circles. In addition, there are differences in the approaches toward this goal between the industry and academia. The application of kinetic results accumulated from dilatometer emulsion polymerization experiments to the industrial semicontinuous stirred tank or to continuous production processes is a very difficult task. Nevertheless, it is unavoidable because the thorough understanding of the industrial processes is impossible without it.

In industry, exact repeatability of emulsion polymerization processes within narrow limits is desirable, which means that the final solids content should be constant within ± 1%; the particle size, emulsion viscosity, and polymer average molecular mass should vary little from batch to batch; and any residual monomer should be maintained within minimum possible narrow limits. In order to achieve these conditions, the formulation of the emulsion polymerization should not be subject to variations such as minor changes of raw materials or of operative conditions. In addition, the formulation should give a reasonably satisfactory latex product even with substitute raw materials that are not entirely satisfactory, i.e., some lower grades or second-class raw materials can be used.

There are other restrictions of the emulsion polymerization process in industrial practice. The process should be completed in the shortest possible time; an overall time including loading the chemicals, polymerization, cooling, and unloading should be within 8–12 hours to allow working two or three shifts per day. It is desirable to prepare a latex at the highest concentration possible, usually >50%, to save time in production, unlike most theoretical work in laboratories. The upper limit of the maximum solids content is generally the high viscosity of the latex product which prevents proper stirring and heat transfer. In industry, the shapes of the universal emulsion polymerization reactors are nearly standard; cylindrical vessels with heights about double their diameters are generally used. However, the nature and shape of the stirrer and the rate of stirring vary from plant to plant, and that may affect the polymerization performance to a great extent. The most appropriate stirrer and agitation conditions are usually determined empirically. It is necessary to avoid excessive precipitation on the reactor walls and stirrer because that means loss of raw materials and wasted time due to reactor cleaning.

PolyVAc homopolymer latices are mostly produced by a delayed addition method in semicontinuous emulsion polymerization processes. In this method, 5–15% of the monomer is added into the reactor containing the water phase at the start, and some of the formulation ingredients and the balance of the monomer gradually. In some cases there is also gradual addition of water phase or water phase components. The delayed addition procedure avoids the coalescence of the monomer-swollen latex particles, thus attaining greater colloidal stability. On the other hand, copolymerization of VAc monomer requires the application of simultaneous monomer feeding methods due to the great differences between the VAc monomer and other comonomers. The monomers are mostly added in different streams so that comonomers are together in the polymerization reactor at any one time, forcing a homogeneous and uniform copolymer structure in the final product (see Sec. 5). Nevertheless, this is a complex method, and sometimes very heterogeneous copolymers are obtained comprising polyVAc homopolymers and copolymers of different structures (having different monomer sequences in the copolymer) at the end of the reaction. Thus, monomer feeding details are considered secrets of the companies in the industry, and that is one of the main causes of the separation between academic and industrial research practices.

Industrial laboratories are generally involved in both short- and long-term projects. Short-term duties include statistical experiments to understand batch-to-batch variations, scaling up problems from laboratory scale to pilot scale and from pilot scale to plant scale, the improvement of the final latex properties by minor variations in the chemical formulations, and monomer feeding procedures for the homopolymer and copolymerization reactions. Long-term duties include understanding the nature of particle formation, average particle size and particle size distribution control, the effects of the types and the concentrations of emulsifiers, initiators and stabilisators on the kinetics of the polymerization, and stabilization properties of the final latex products. The understanding of the mechanism of copolymerization in semicontinuous and continuous processes is also important. If the theory of all aspects of the homopolymerization and copolymerization of VAc had been developed, the industrial laboratories would avoid a large number of unnecessary empirical experiments. However, there is no such unified theory of the subject yet due to the complexity of the process and the different approaches of academic and industrial circles to the problem. Smith-Ewart kinetics is not valid for VAc homopolymerizations because of the appreciable solubility of the VAc monomer in the water medium, but the academic circles have published papers for years explaining the kinetic behavior of VAc emulsion polymerization as a deviation from Smith-Ewart general theory. Smith-Ewart and related theories may be applicable to nearly water-insoluble styrene monomer, and to some extent to acrylic ester monomers, but only the ideas and theories of aqueous initiation with propagation in both water and monomer swollen polymer particle phases is applicable for VAc kinetics. It is also a difficult task to extend these ideas to controlled monomer feed processes, which is the major practice in industry.

In general, industrial laboratories carried out most of the work done on vinyl acetate emulsion polymerization and copolymerization with acrylic monomers and both academic circles and industrial laboratories made comparatively few publications in scientific periodicals.

1.1 HISTORY OF EMULSION POLYMERIZATION

The patents originated from Farbenfabriken Bayer in the years 1909 to 1912 are the earliest literature references to the polymerization of diene monomers in the form of aqueous emulsions.[1-3] Hoffman and co-workers referred to the use of gelatin, egg white (protein), starch, flour, and blood serum as protective colloids in attempts to produce something resembling natural rubber latex. Polymerization was very slow and it took weeks to form a substantial amount of polymer. Initiation of polymerization depended on aerial oxygen. A further German patent by Klatte and Rollet in 1914 shows the use of oxygen-liberating compounds added as activators.[4] At that time, it was observed that all naturally occurring polydiene rubbers are found in the form of latices. It was therefore concluded that polymerization in the plant must take place under the relatively mild conditions of an aqueous system without the application of elevated temperatures and high pressures. Today, however, we know that the formation of naturally occurring polydiene proceeds by a condensation polymerization of a phosphate derivative of the diene instead of the addition polymerization of the corresponding monomeric diene. Without knowing that fact, the reproduction of the physiological conditions occurring in the plant was mentioned in some of these earlier patents, showing that the aim was the imitation of nature at that time.

In 1915, Gottlob[5] noted that a superior product was obtained if the butadiene or its homologues were emulsified or intimately mixed during the process of polymerization with aqueous colloidal solutions of substances such as egg albumin, starch, gelatin, etc. It was claimed that the emulsification or continuous stirring process resulted in a product similar to natural rubber latex. Hohenstein and Mark[6] repeated the polymerization reactions of Gottlob's patent in 1946 and observed an extremely slow, partial conversion of the monomer (isoprene and dimethylbutadiene) into a polymer latex, in some cases for as long as six weeks. They then concluded that these reactions were not emulsion polymerizations but "suspension polymerizations" in which the initiation of the reaction occurred by the action of atmospheric oxygen.

Dinsmore,[7] who was working for The Goodyear Tire & Rubber Company, was the first to be granted a patent to produce a synthetic rubber in 1929. In his patent disclosure, it was stated that "by treating the basic unsaturated hydrocarbon from which the rubber is to be produced with an emulsifying agent so as to break up the hydrocarbon into definite globules, a product much superior to any synthetic rubber heretofore produced is obtained." The reason for regarding it as an "emulsion polymerization" is the addition of soap, presumably added as an emulsifying agent in the first instance, as well as of a proteinaceous protective colloid. The polymer product obtained was tough, elastic, and could be cured by means of sulfur and a suitable accelerator of vulcanization in a manner similar to that employed to cure natural rubber. No initiating substance was added to the reaction mixture, resulting in extremely slow polymerization. The initiation probably occurs by way of *in situ* peroxide production by interaction between atmospheric oxygen and either the monomer or the fatty-acid soap.

Luther and Heuck[8,9] of I.G. Farbenindustrie A.G. were granted two very important patents in 1927 and 1932 in which hydrogen peroxide, sodium bisulphite, sodium hydrosulphite, sodium formaldehyde sulphoxylate initiator systems, acrylic ester monomers, Turkey-red oil, isobutylated napthalene-sulphonic acid emulsifiers, and acetic acid-sodium acetate or sodium phosphate buffer systems were first used in emulsion polymerization. The polymer product was to some extent lightened in color, and it was resistant to oxidative degradation. The original patent covering copolymerization of butadiene and styrene in emulsion to produce Buna S synthetic rubber was granted in 1933 to Tschunker and Bock.[10] General Tire & Rubber had already tested Buna S for tire production in 1933 but found it inferior to natural rubber. German production, however, increased from 300 tons per year in 1935 to 5000 tons per year in 1937, aiming to make the country independent of imported raw materials.

The oil resistant butadiene-acrylonitrile rubber (Buna N) created more interest in the U.S. and a pilot plant was in operation by the end of 1939. The U.S. government planned the construction of four plants with a total capacity of 40,000 tons per year, but after the Japanese occupation of Malaysia in 1942, which cut off supplies of natural rubber, the planned capacity was increased to 400,000 tons per year. The general-purpose butadiene-styrene 75/25 copolymer was designated GR-S (Government Rubber-Styrene) at that time. In 1944 production had increased to 669,000 tons. Subsequently, the mutual recipe was modified to a 72/28-monomer ratio in order to balance monomer consumption. Dunbrook summarized how the production of synthetic rubber was organized in the U.S. during the Second World War.[11] A better product was obtained by short-stopping the reaction at 72% conversion, and ammonium persulfate was used instead of the potassium salt; it is much more water soluble, which facilitates the preparation of a concentrated stock solution.[12]

Later, in 1948, "cold-SBR rubber" was produced at low temperatures using a redox initiating system and was found to have superior properties. A wide variety of initiating systems comprising a peroxide or hydroperoxide and a reducing agent were used. Initially, the variable and nonstandard composition of the emulsifier was a problem, but the solution was found by using disproportionated rosin acid salts.[12]

Very few papers on the subject were published in the scientific journals between 1910-1940. Whitby and Katz[13] reviewed the substances mentioned in patent literature as useful for effecting the emulsion polymerization of butadiene and its homologues in 1933. The advantages of this technique of initiating, propagating, and controlling the synthesis of polymers rapidly became apparent, though little or nothing was understood about the mechanism involved.

Ostromislensky[14,15] and Dogadkin and co-workers[16] were the first Russians to publish papers on the polymerization of butadiene monomer in the presence of soap, peroxides, and other initiators at varying temperatures. In 1938, Fikentscher[17] was the first to formulate the hypothesis that, contrary to popular belief, the principal locus of the emulsion polymerization reaction is within the aqueous phase and not within the monomer droplets. Trommsdorff[18] gave a brief description and interpretation of the emulsion polymerization in 1939.

Talalay and Magat[19] published a book on synthetic rubber production extracted from the Russian literature in 1945. Some information was also given concerning the kinetics of emulsion polymerization by showing the effect of increasing levels of both hydrogen peroxide and diazoaminobenzene on the rate of emulsion polymerization of butadiene.

In 1946, Hohenstein and Mark[6] reviewed the known facts and clearly presented the distinguishing features of the three types of free-radical addition polymerization, i.e., solution, suspension, and emulsion polymerization. The monomer can be present as monomer droplets, as a molecular solution in water, and also as a solubilisate within the micelles that exist in a soap solution of sufficient concentration. It was recognized that the amount of polymer formed in each of these three phases will depend primarily upon the way in which the monomer and initiator are distributed between these phases, and possibly to some extent upon the accessibility and reactivity of the monomer. The typical emulsion polymerization was clearly defined as one in which polymer formation occurs predominantly in the micellar phase. The impossibility of making hard-and-fast distinctions was noted because the so-called emulsion polymerization of vinyl acetate monomer, which is appreciably soluble in water, was recognized as being, in fact, a superposition of solution, suspension, and emulsion polymerization.

Bovey, Kolthoff, et al. reviewed most of the cooperative research in academic and industrial laboratories, much of which was published between 1945–1955.[20] Subsequently, emulsion polymerizations and copolymerizations involving polar monomers such as vinyl chloride, vinylidene chloride, vinyl acetate, methyl methacrylate, and butyl acrylate proved to be of industrial interest. Williams gave an extensive tabulation of the patent literature on emulsion polymerizations and copolymerizations published up to 1955, and also comparisons of the effects of alternative emulsifiers in the same polymerizations.[21] Warson's book gave the details of many emulsion polymerization formulations cited as examples in the patent literature up to 1970.[22] The literature relating to the mechanism of emulsion polymerization, and to many technical aspects up to 1973, is thoroughly reviewed in Blackley's book.[23] Emulsion polymerization of polar monomers is emphasized in the 1976 book by Eliseeva et al., of which an English edition was published in 1981.[24] Piirma edited a book that concentrates on developments between 1970–1980.[25] Buscall et al. edited a book emphasizing the colloid science relevant to emulsion polymerization.[26] Barton's and Capek's book covers developments of the kinetics and reaction mechanisms in the 1980s.[27] Napper and Gilbert reviewed the emulsion polymerization mechanisms in two publications, and later in a book.[28-30] Blackley expanded his previous book and published three comprehensive volumes on polymer latices in 1997.[31] In the same year, El-Aasser and Lovell edited a book on the theoretical and the practical aspects of emulsion polymerization.[32]

On the other hand, symposia on emulsion polymerization have been featured with increasing frequency in international scientific meetings since 1966, and the proceedings of many of them have been published collectively.[33-45] Papers presented at NATO Advanced Study Institutes have been published as four books.[46-49] Reprints of the full texts of papers presented at Plastics and Rubber Institute Conferences in London between 1978–1989 are also available.[50-53]

1.2 HISTORY OF EMULSION POLYMERIZATION OF VINYL ACETATE

The production of polyVAc latices using polyvinyl alcohol as an emulsifier began in Germany during the mid-1930s and has continued to the present, growing steadily through the years. The great number of patents and other literature up to 1969 dealing with the industrial production of polyvinyl acetate in emulsion, suspension, and solution form are collected in Hoelscher's book.[54] It was noted that VAc emulsion polymerization technology began in 1934 when Starck and Freudenberg assigned their patents to I. G. Farbenindustrie A. G. in Germany.[55] VAc emulsion polymerization recipes in use in Germany before and during World War II were originally disclosed in the BIOS (British Intelligence Objectives Subcommission) and the U.S. FIAT (Field Intelligence Agency Technical) reports and have been described in detail.[56-59] Manufacture of polyVAc latex paints was begun in England in 1948 on the basis of BIOS and FIAT report information, and most emulsion paint sold in Europe was of that type. On the other hand, in the U.S., latex paints based on butadiene-styrene copolymers dominated the market for years because of the presence of large plants to produce these types of latices to substitute for natural rubber during World War II. The patent literature on emulsion polymerization was summarized in Bartl's book, which was published in 1961.[60] The great number of emulsion polymerization patents up to 1969 was cited in Cogan's and Mantz's book.[61]

There were mainly two types of VAc emulsion polymers produced in 1970s: a fine particle size (0.1–0.2 microns) grade made by using anionic and/or nonionic emulsifiers and without a protective colloid, and a large particle size (0.5–3.0 microns) emulsion which is often only stabilized by protective colloids such as polyvinyl alcohol (88% hydrolyzed) and hydroxyethylcellulose. Two earlier patents for each case were assigned to the DuPont[62] and Gulf Oil[63] companies.

The understanding of the mechanism and kinetics of VAc emulsion homopolymerization and copolymerization with acrylic monomers has been an important aim for industrial as well as academic circles. The successful use of the Smith-Ewart Case II theory in explaining the emulsion polymerization of styrene monomer stimulated research in many other monomers. However, vinyl acetate is a highly water-soluble monomer and 2.5% by weight of the VAc dissolves in water at 28°C giving 1.75×10^{20} monomer molecules per ml of water, which is approximately 100 times more than the water solubility of styrene monomer.[64] Because of this, a different mechanism of emulsion polymerization should be operative for VAc polymerization.

The first papers on VAc emulsion polymerization were published in 1952 by Priest,[65] and in 1958 by O'Donnell et al.[66] and French.[67] Priest showed that the initiation occurred in the aqueous phase for VAc emulsion polymerization[65] so that a primary radical formed in the water phase could add monomer units much more readily than inside a micelle. Initiation in the aqueous phase was not considered important in the emulsion polymerization of styrene, but VAc is about 100 times more soluble in water than styrene, so that a primary radical formed in the water phase could add monomer units readily. These oligomeric radicals thus formed would grow until they reached their solubility limit in water and then precipitate to nucleate a polymer particle. In some cases, these particles upon precipitation would be destabilized and flocculate with other similar particles. O'Donnell et al.[66] and French[67] interpreted their data so that they assumed the application of the initiation-in-micelles hypothesis for VAc homopolymerization in terms of Smith-Ewart Case II theory despite some evidence to the contrary in industrial circles. French's paper was a very important historical paper that examined the emulsion polymerization of VAc with its relation to the emulsifier concentration and showing its large differences from the Smith-Ewart Case II kinetics[67] (see Secs. 2.3 and 3.2). In time, it was found that Smith-Ewart Case II theory fit the emulsion polymerization of styrene in only a narrow range of conditions, and was an even worse fit for the emulsion polymerization of other monomers.

The proposed mechanism was expanded and confirmed experimentally by Stannett et al.,[68] Napper and Alexander,[69] and Dunn and Taylor[70] between 1960-65. Gershberg has reviewed the emulsion polymerization kinetics of "relatively" water-soluble monomers and has found that the order of the polymerization reaction with respect to the micelle generating emulsifier concentration falls significantly as the solubility of the monomer in water increases.[71] His results showed that a broad correlation exists between the order of the reaction and the solubility of the monomer in water. Medvedev[72] developed the hypothesis of initiation in the adsorbed emulsified layer in 1957, and Ugelstad, El-Aasser, and Vanderhoff proposed the hypothesis of initiation in small monomer droplets in 1973.[73]

A symposium was devoted to the VAc emulsion polymerization at Lehigh University in 1980, and a book edited by El-Aasser and Vanderhoff[38] entitled *Emulsion Polymerization of VAc* was published in 1981. In this symposium, Zollars pointed out the importance of ionic strength on the stability and rate of polymerization and proposed a different particle formation mechanism depending on the coagulation rate which was calculated by DLVO theory.[74,75] Klein and Stannett[76] defended their previously published Litt, Patsiga, and Stannett (LPS) kinetic model;[68,77] however, Chang, Litt, and Nomura developed another model.[78-80] In this model, contrary to LPS theory and Zollars's suggestions, Chang, Litt, and Nomura determined that emulsion polymerization of VAc is independent of the emulsifier type, emulsifier concentration between 0–1% in seeded polymerizations, and ionic strength when twentyfold variable concentrations of potassium sulfate were added.[78] Vanderhoff reviewed the mechanism of emulsion polymerization in 1985.[81] On the other hand, Warson criticized the kinetic studies, which were conducted in dilatometers, and noted the need of the determination of reaction mechanisms in the industrially important semicontinuous and continuous emulsion polymerization processes.[82] In the semicontinuous (or delayed addition) process, the monomer (which may or may not be emulsified) and the other ingredients are added gradually to the stirred batch reaction vessel, which is fitted with a reflux condenser and heating and cooling jacket. Elgood, Gulbekian, and Kinsler were the first to report on the mechanism of VAc emulsion polymerization in semicontinuous process in 1964.[83] Gulbekian and co-workers published subsequent papers on the same subject until 1973.[84-86] Later, Warson summarized the developments on the semicontinuous process until 1983.[87] Donescu and co-workers also investigated the semicontinuous emulsion polymerization process in the 1980s.[88,89] El-Aasser, Makgawinata, and Vanderhoff reported the molecular weight distribution differences between batch and semicontinuous processes.[90]

The presence of a polyvinyl alcohol stabilizing agent in VAc emulsion homopolymerization greatly affects branching and reaction mechanism. Thus, considerable research results were published on this subject. O'Donnell, Mesrobian, and Woodward were the first to report the kinetics investigation of the VAc emulsion polymerization polyvinyl alcohol as a protective colloid in 1958.[66] Dunn and Taylor also showed that the addition of polyvinyl alcohol reduced the rate of polymerization and particle size.[70] Japanese research teams also investigated this subject in detail.[91-93] Gulbekian and Reynolds made a survey on the use of polyvinyl alcohol as an emulsifier and protective colloid in emulsion polymerization.[85] Warson,[87] as well as Dunn,[94] discussed the effect of the types of polyvinyl alcohol on the resultant polyVAc latex. Donescu and co-workers also investigated the effect of the presence of polyvinyl alcohol in VAc semicontinuous process.[88,89,95] Gilmore, Poehlein, and Schork modeled polyvinyl alcohol stabilized semicontinuous VAc emulsion polymerization96 and compared their model with experimental findings.[97] The branching of polyvinyl alcohol with polyVAc during emulsion polymerization is an important subject and was investigated by various researchers: Donescu and co-workers,[98] Okaya, Tanaka and Yuki,[93] Gilmore, Poehlein, and Schork[96,97] published papers on this subject. The branching of polyVAc during emulsion polymerization in the absence of the polyvinyl alcohol stabilizer due to the chain transfer to polymer and monomer is also a very important subject. Wheeler, Lavin, and Crozier were the first to propose a mechanism for branch formation in polyVAc in 1952 by applying degradative hydrolysis.[99] Stein,[100] in 1964, and Graessley and co-workers, between

1967 and 1977,[101-109] investigated the branching mechanism in detail. Later, Hamielec and co-workers re-examined this subject and developed a kinetic model to predict molecular weights after branching.[110-114] Tobita also developed a model to the kinetics of long-chain branching depending mainly on the chain transfer to monomer.[115]

Modeling of emulsion polymerization reactors is another research subject that is important industrially. Ugelstad and Mork derived such a model in 1969.[116,117] Min and Ray published a review on this subject in 1974.[118] Later, attempts were made to model the continuous processes. The continuous stirred tank reactor process (CSTR) uses one or more reactors similar to those used in the batch process, but with product overflowing to balance the feed of raw materials which must always include water to stabilize the polymer content. Poehlein and Dougherty published a review on the continuous emulsion polymerization in which 2 to 15 continuous stirred tank reactors (CSTR's) were connected in series.[119] Kiparissides, MacGregor, and Hamielec developed a model for VAc emulsion polymerization operating in CSTR conditions in a series of publications.[120-123] Later, Hamielec and MacGregor published a review on the design and operation of the batch and CSTR reactors under steady state and dynamic conditions.[124] Rawlings and Ray,[125] as well as Lee and Mallinson,[126,127] developed other models applicable to CSTR systems.

Meanwhile, Lanthier invented the loop continuous emulsion polymerization process while he was trying to determine the half-lives of redox initiator couples in 1966. He couldn't obtain accurate results in stirred glass flasks because of the too rapid decomposition of the materials. He then tried a steady state method by using a tube and circulation pump, and by equating the rate of overflow to the rate of arrival of new materials. During these experiments, the waste product (emulsion polymer) had accumulated to a significant extent and he realized that a new emulsion polymerization process had been born. Soon after, a small production unit was set up in Quebec, Canada, mainly from spare pumps and piping. The first production was used in the impregnation of textiles to give body and finish. The commercial latex range had opened to include polyVAc, VAc-butyl acrylate, VAc-vinyl versetate, and VAc-acrylamide copolymers between 1966–1968. Crown Paints opened a loop emulsion polymer production plant in the U.K. in 1977. It was realized that the pressure capability of pumps and pipework made the loop process ideal for handling gaseous monomers. A new reactor using a specially-developed circulation pump suitable for working at 7 MPa was installed and the production of VAc-ethylene emulsion copolymers (up to 18% ethylene) was started. On the other hand, VAc-vinyl versetate copolymers manufactured in the loop process gave an almost unique balance of good hiding power and good wet scrub resistance in medium pigment volume concentration. This may be due to the wide particle size distribution given by the loop process, coupled with the higher than usual molecular weight of the copolymers. When a narrow particle size distribution was achieved, semigloss paints without surface bloom were produced. Loop reactors are cheap, they cost approximately one-third as much as batch kettles and one-tenth as much as pressure reactors and can be housed in smaller buildings. This process requires no external heating and very little supervision. The system is automatic and the product properties can be monitored continuously by in-line methods. However, the annual tonnage from a single loop reactor is limited, not more than 5000 t/year. Geddes[128-130] and Khan,[131] and later Iabbadene and Bataille,[132] reported the results of emulsion polymerization in a tubular loop reactor.

1.3 A SHORT REVIEW OF THE FREE RADICAL ADDITION POLYMERIZATION

Vinyl monomers, such as vinyl acetate and acrylate esters, polymerize only by addition processes. In addition polymerizations, after chain initiation has begun there follows the successive addition of a large number of monomer molecules to the growing polymer chain. Eventually, this growth ends by a termination mechanism. The process of the addition polymerization is shown generally as:

$$n\left[CH_2 = CHR\right] \rightarrow \text{—}\left[CH_2 - CHR\right]_n\text{—} \tag{1.1}$$

Addition polymerizations are further characterized by the type of initiator used. They can be induced by free radical, ionic, or high-energy mechanisms. These mechanisms, however, are quite similar, including initiation, propagation, and termination steps.

A free radical is an extremely short-lived, highly energetic molecular fragment containing a single, unpaired electron. It reacts readily with the unsaturated vinyl double bond of a monomer molecule to begin a polymer chain growth. Radicals generally arise either by absorption of sufficient vibration energy by initiator precursors or by chemical reaction of a precursor with reducing agents involving a one-electron transfer. When the radical reacts with a monomer molecule a larger free radical is formed which, in turn, reacts with another monomer molecule, thus propagating the polymeric chain. While individual monomer addition reactions are almost instantaneous, the polymerization may take several hours to complete in the reaction mixture depending on the method and the temperature of polymerization. Growing polymer chains are finally terminated (free electrons coupled) in a variety of ways including disproportionation, biradical coupling, and one or more chain transfer mechanisms.

The following reactions show the stepwise sequence in free radical polymerizations:

1.3.1 INITIATION

The initiator (I) dissociates homolytically to yield a pair of free radicals ($R\cdot$), followed by addition of a free radical to the first monomer (M) molecule having a vinyl double bond to produce chain-initiating species ($M\cdot$).

$$I \xrightarrow{k_d} 2R\cdot \tag{1.2}$$

$$R\cdot \xrightarrow{k_i} RM\cdot \tag{1.3}$$

where k_d is the rate constant for the initiator dissociation and k_i is the rate constant for the initiation step. Free radicals can be generated by two processes: thermal cleavage through absorption of sufficient vibrational bond energy and chemical reaction involving electron transfer mechanisms. Although all chemical bonds will cleave if sufficient energy is absorbed, relatively few types of chemical bonds have the required bond dissociation energies to be useful as free radical precursors. If bond dissociation energies are too high, rates of free radical generation at reasonable temperatures are much too slow to be practical. If too low, rates of free radical generation are so rapid that storage and handling of the precursors presents problems. Two important chemical bonds meet the requirements of safety, practicality, and versatility: the peroxide (O–O) and azo (N=N) bonds. Typical homolytic cleavage of each of these bonds into free radicals is shown below:

Peroxide **Azo**

$$RO-OR' \xrightarrow{\Delta} RO\cdot + R'O\cdot \qquad RN=NR' \xrightarrow{\Delta} R\cdot + R'\cdot + N_2$$

The rate of thermal dissociation of an initiator, R_d, is given by,

$$R_d = 2fk_d[I] \tag{1.4}$$

where $[I]$ is the concentration of the initiator and f is the initiator efficiency. The initiator efficiency is defined as the fraction of the radicals produced in the dissociation reaction which initiates polymer chains. The value of f is usually less than unity due to wastage reactions. The use of the factor of 2 in the decomposition reaction follows the generally accepted convention for reactions producing radicals in pairs.

The second step where the primary radical adds to monomer is much faster than the first step. Therefore, the dissociation of the initiator is the rate-determining step in the initiation sequence, and the rate of initiation, R_i, is given by

$$R_i = 2fk_d[I] \tag{1.5}$$

1.3.2 PROPAGATION

Propagation is a process of the growth of $M\cdot$ by the successive addition of a large number of monomer molecules (n) as shown below.

$$RM\cdot + nM \xrightarrow{k_p} P_{n+1}\cdot \tag{1.6}$$

where k_p is the rate constant for propagation. In this step, a large number of monomer molecules is converted to polymer for each initial radical species produced in the first step. Monomer is consumed by the initiation reaction as well as by the propagation reactions. The rate of monomer consumption, which is synonymous with rate of polymerization is given by,

$$\frac{d[M]}{dt} = R_i + R_p \tag{1.7}$$

where R_p is the rate of propagation. However, the number of monomer molecules reacting in the initiation step is far less than the number in the propagation step for a process producing high polymer. The rate of initiation can be neglected and a very close approximation of the polymerization rate can be given simply by the rate of propagation:

$$\frac{d[M]}{dt} = R_p \tag{1. 8}$$

As a consequence, the rate of polymerization is the sum of all the individual propagation steps and, since the rate constants for all the propagation steps are the same as k_p, then the polymerization rate is given as:

$$\mathrm{R_p = k_p[M\cdot][M]} \tag{1.9}$$

where $[M]$ is the monomer concentration and $[M\cdot]$ is the total concentration of every size of chain radicals. However, radical concentrations are difficult to measure since they are very low and they should be eliminated from Eq. 1.9.

1.3.3 TERMINATION

The propagating polymer chain stops growing and terminates at some point. There are two mechanisms of termination:

1.3.3.1 Biradical Coupling

$$P_n\cdot + P_m\cdot \xrightarrow{k_{bc}} P_{n+m} \tag{1.10}$$

in which two polymeric radicals terminate each other by the occurrence of the annihilation of the radical centers.

1.3.3.2 Disproportionation

$$P_n\cdot + P_m\cdot \xrightarrow{k_{dp}} P_n + P_m \tag{1.11}$$

in which one polymeric radical abstracts a hydrogen atom from another, leaving it with a terminal vinyl double bond. Disproportionation occurs more rarely than biradical coupling. It results in the formation of two polymer molecules, one saturated and one unsaturated. Termination can also occur by a combination of bimolecular coupling and disproportionation. Bimolecular coupling termination always results in longer chains and thus higher molecular weight polymer than disproportionation.

In the above equations, k_{bc} and k_{dp} are the rate constants for termination by bimolecular coupling and disproportionation, respectively. If the particular mode of termination is not specified, rate constant for termination reaction is given as $k_t = k_{bc} + k_{dp}$. The propagation reaction would proceed indefinitely until all the monomer in a reaction system was exhausted if it were not for the strong tendency toward termination.

In polymerization kinetics, the steady state assumption is made that the concentrations of radicals increase initially but almost instantaneously reach a constant, steady state value. Then there is no change in the radical concentration during the course of polymerization. This means that the rates of initiation and the termination are equal:

$$R_i = R_t = -\frac{[R\cdot]}{dt} = 2k_t[M\cdot]^2 \tag{1.12}$$

Typical addition polymerizations achieve a steady state after an induction period which may be at most a few seconds. When Eq. 1.12 is rearranged,

$$[M\cdot] = \left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} \tag{1. 13}$$

and by combining Eqs. 1.9 and 1.13, one obtains the radical concentration-free expression for the rate of polymerization,

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} \tag{1. 14}$$

It is seen that the polymerization rate depends on the square root of the initiation rate. In other words, it depends on the square root of the initiator concentration so that

$$R_p = k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}} \tag{1. 15}$$

This dependence has been confirmed for many different monomer-initiator combinations over wide ranges of [*M*] and [*I*].

1.3.4 DEGREE OF POLYMERIZATION

The number-average degree of polymerization, DP, is the average number of monomer units per polymer molecule and is equal to the rate of chain growth divided by half the rate of chain termination. By combining Eqs. 1.9–1.14 one obtains,

$$DP = \frac{2R_p}{R_t} = \frac{2k_p[M][M\cdot]}{2k_t[M\cdot]^2} = \frac{k_p[M]}{\left(fk_dk_t[I]\right)^{1/2}} \tag{1.16}$$

DP is inversely dependent on the square root of the initiator concentration. Increasing the initiator concentration leads to smaller sized polymer molecules. Assuming all the termination reactions were bimolecular coupling only made the above derivation. The number-average molecular weight of a polymer is given by

$$\overline{M_n} = DP \cdot M_o \tag{1. 17}$$

where M_o is the molecular weight of the monomer. When termination by disproportionation occurs, the molecular weight of the polymer decreases. Nevertheless, most polymer radicals appear to terminate predominantly or entirely by bimolecular coupling.

1.3.5 CHAIN TRANSFER

The polymer weight is observed to be lower than predicted on the basis of termination by bimolecular coupling or disproportionation in many polymerizations. This effect is due to other mechanisms of premature termination that involve chain transfer in which growing polymeric radicals abstract hydrogen atoms from polymer, monomer, solvent, additives, impurities, or initiator. These radical displacement reactions are shown below:

Transfer to polymer: $$P_n\cdot + P_m \rightarrow P_nH + P_m\cdot \tag{1.18}$$

Transfer to monomer: $$P_n\cdot + M \rightarrow P_nH + M\cdot \tag{1.19}$$

Transfer to additive: $$P_n\cdot + A \rightarrow P_nH + A\cdot \tag{1.20}$$

Transfer to solvent: $$P_n\cdot + S \rightarrow P_nH + S\cdot \tag{1.21}$$

Transfer to initiator: $$P_n\cdot + I \rightarrow P_nH + R\cdot \tag{1.22}$$

In reactions 1.18 to 1.22, polymer chain growth is terminated, leaving a new free radical. The resulting new radical formed can initiate new polymer chain growth at the same rate as the primary radicals, at a slower rate, or not at all. If the effect of chain transfer is merely to reduce chain length (lower polymer molecular weight) with little or no effect on the rate of polymerization, the chemical agent is called a "modifier." When polymerization rate is slowed considerably, the chemical agent is called a "retarder." In both cases, nondegradative chain transfer is said to prevail. However, when the resulting free radical will not initiate polymerization, the agent is called an "inhibitor," and the chain transfer is referred to as degradative.

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2 General Emulsion Polymerization

2.1 BASIC ASPECTS

Emulsion polymerization is one of several processes by which a variety of unsaturated organic carbon compounds can be polymerized. This polymerization, which is an addition type, is carried out in liquid medium, which is almost always aqueous and produces a milky fluid called a latex. There is an important difference between suspension and emulsion polymerization: in the former the polymerization occurs in the organic or monomer phase, while in the latter it occurs in the water phase or medium.

There are four basic ingredients required for an emulsion polymerization. These are (1) the monomer, (2) the dispersion medium, (3) the emulsifier, and (4) the initiator. When correct amounts of the ingredients are mixed properly in a suitable container within a certain temperature range, an emulsion of monomer droplets is formed in the continuous dispersion medium. The initiator causes the monomer molecules to polymerize. When the polymerization is complete, a stable emulsion of polymer particles will remain.

1. Monomer: Organic monomers commonly polymerized using this process include vinyl acetate, acrylic and methacrylic acid, and especially their organic esters such as butyl and ethyl acrylates and methacrylates. In addition, acrylonitrile, butadiene, and styrene are very important monomers because of their use in making rubbers. It is quite common to produce copolymers using more than one monomeric substance.
2. Dispersion medium: It is possible to carry out emulsion polymerization in media other than water, but it is impractical. Besides its cheap price and environmental advantages, water provides an excellent heat sink so that the exothermic heat released by the polymerization reaction can be adequately dissipated.
3. Emulsifier: It may be comprised of a wide variety of surface-active agents or soaps. These materials solubilize the monomer to a certain extent, enable the formation or the emulsion of the organic monomer phase and the water phase, and then perform a stabilizing function in the polymer-water emulsion product.
4. Initiator: Emulsion polymerization occurs almost entirely following the radical mechanism. The function of the initiator is to cause the formation of the radicals, which in turn lead to the propagation of the polymer molecules. The active centers and propagation loci are located in the water phase and are isolated from each other. In these centers, the addition polymerization process proceeds by micellar mechanism.

Other substances may be included in the recipe of an emulsion polymerization process. However, any substance so included will be only to enhance or supplement the function of the four materials listed above (see Sec. 4).

In addition to the consideration that water as the dispersion medium contributes to low-cost, nonflammable, nontoxic, relatively odorless systems, emulsion polymerization offers many other advantages, for example:

1. In many applications the latex itself is in an ideal form for use, e.g., paints and surface coatings, adhesives, paper coating and impregnation, leather treatment, textile treatment, dipping, and latex foam rubber.
2. The production of a polymer of high molecular weight at a high rate of polymerization is possible; the molecular weight and degree of polymerization can be easily controlled so that a product having specific and reproducible properties can be obtained. For the other polymerization processes there is an inverse relationship between the polymerization rate and the polymer molecular weight. Large increases in molecular weight can only be made by decreasing the polymerization rate by lowering the initiator concentration or lowering the reaction temperature. Emulsion polymerization is a unique process in that it affords a means of increasing the polymer molecular weight without decreasing the polymerization rate. To a large extent, the molecular weight and polymerization rate can be varied independently of each other.
3. Better temperature control during polymerization can be achieved due to more rapid heat transfer in the low viscosity emulsion.
4. There is a minimum tendency toward coalescence of polymer particles, thereby preventing the formation of sticky and rubbery products.
5. The possibility of interrupting the polymerization at any stage is possible for the addition of other materials needed to modify the properties of the finished polymer.
6. Undesirable side reactions such as chain branching and cyclization can be minimized.
7. Many copolymerizations that are difficult to control in bulk or in any other method of polymerization can be carried out.
8. The control of the range and distribution of particle size within a particular system is possible.
9. The viscosity of a latex is independent of the molecular weight of the polymer. Thus the preparation of high solids content emulsions with low viscosity can be achieved in contrast to solutions of polymers. This facilitates the transfer of material through pumps and pipelines.

There are, however, some disadvantages of the emulsion polymerization. The presence of the emulsifier and possibly other constituents does not allow one to synthesize a pure polymer. For solid synthetic rubber production, the separation of the polymer from the dispersion medium is required, and the coagulation and recovery of the solid polymer is a multistep operation requiring additional materials and equipment.

2.2 EMULSION POLYMERIZATION OF HYDROPHOBIC MONOMERS

Styrene, esters of acrylic or methacrylic acids, butadiene, etc. are hydrophobic monomers. In many cases, although not in all, the hydrophobic monomer is only slightly soluble in water. In 1936, Dogadkin and co-workers[1,2] assumed that the latex particles were formed by polymerization of the emulsified droplets of monomer, but this hypothesis was abandoned as soon as it was observed that the latex particles were only about one-five-hundredth of the size of the emulsion droplets.[3,4] Fikentscher,[5] working in the Ludwigshafen laboratories of I. G. Farbenindustrie in 1938, showed that, contrary to popular belief, the principal locus of the emulsion polymerization reaction is within the aqueous phase and not within the monomer droplets. He described that the polymerization occurred in the aqueous phase by floating methyl methacrylate on a soap solution containing initiator when the aqueous layer became cloudy because of the formation of polymer latex particles as the volume of the monomer layer decreased. Gee et al.[6] showed in 1939 that butadiene vapor would polymerize in an aqueous solution of hydrogen peroxide. They also described that the initial rate was proportional to the square root of the peroxide concentration and the butadiene pressure (to which its concentration in solution would be proportional), showing that the reaction was occurring in the aqueous solution rather than at the interface.[6] Fryling concluded that the polymerization reaction was initiated from monomer solubilized in soap micelles.[7,8] Harkins demonstrated in the U.S. Rubber Company's laboratories in 1942 that if the latex can be stabilized electrostatically by ionic end-groups derived from the initiator, then the use of an emulsifier above its critical micelle concentration, CMC, is not essential.[4] Harkins proved that a latex can be formed when styrene vapor is passed into an aqueous solution of potassium persulfate; nevertheless, the latex particles were relatively large (150–200 nm in diameter) and the rate of polymerization was slow. Haward[9] showed in 1949 that the mutual termination reaction between the polymer radicals is eliminated by containing single radicals in isolated loci. Dunn and Taylor explained the high rate of polymerization during emulsion polymerization in their 1965 paper.[10] This is because a monomer which is miscible with its polymer partitions into the latex particles and increases the monomer concentration at the locus of polymerization.[10]

Harkins developed a qualitative theory on the emulsion polymerization of hydrophobic monomers.[4,11-13] In all cases, but particularly in the cases in which the monomer is only slightly soluble in water, the emulsifier or soap solubilizes the monomer in the water and enables more monomer molecules to be dissolved in the water phase. This action is attributed to the formation of micelles, which are tiny groups of perhaps 50 to 100 soap molecules[14] clumped together with their hydrophobic portions adjacent to each other and the hydrophilic portions adjacent to each other and in more intimate contact with the water. This juxtaposition of the soap molecules results in the formation of a tiny particle called a micelle in which there is a largely hydrophobic region that tends to attract the organic monomer molecules. Micelles take on a roughly spherical form with the hydrophobic portion of each molecule directed toward the center of the micelle. An average micelle will have a diameter of approximately 40-50°A and may be regarded within the colloidal dimensions. At the emulsifier concentrations normally employed in emulsion polymerization, one milliliter of solution will contain approximately 10^{18} micelles. Bovey, Kolthoff, Medalia, and Meehan calculated molecular weights of micelles of various surface-active agents.[15]

During the emulsion polymerization, mechanical agitation breaks the hydrophobic monomer phase into small droplets. The droplets are held in suspension by the action of the agitation and the emulsifier molecules, the hydrophobic portions of which are absorbed into the monomer droplets. The hydrophilic portions of the emulsifier molecules remain in the water phase. These droplets have quite large dimensions and are about 1 micron (10,000°A) in diameter. This means that an average droplet is about 200 times as large as an average micelle. Thus, in a typical emulsion polymerization system, there are at most 10^{10}–10^{11} monomer droplets per milliliter. The determination of particle size and particle number in emulsion systems is made by electron microscope, light scattering, and ultracentrifugation methods. Approximately 1% of the total monomer is actually solubilized by the micelles, which swell to about twice their original dimensions, having their diameters between 60 and100°A. With hydrophobic monomers such as styrene, only an insignificant amount of monomer (about 0.04%) is dissolved by water, which can be neglected in considering the kinetic mechanism. Thus, the system prior to initiation contains mainly three parts: the water phase, large monomer droplets dispersed throughout the water phase, and emulsifier micelles containing solubilized monomer.

After the emulsion of the monomer phase in the water phase and the presence of the emulsifier micelles are established, the initiator is added while the system is mechanically stirred. The initiator is chosen for its ability to break down into charged radicals. These radicals in turn react to form new radicals from the monomer molecules. These new radicals then combine with other monomer molecules following the addition polymerization procedure. One of the basic characteristics of emulsion polymerization is that polymerization occurs in the water phase and not in the monomer or organic phase.[16] This, indeed, is the primary difference between emulsion and suspension polymerization. Since most of the monomer molecules dissolved in the water phase are located within the micelles, most of the polymer molecules are initiated in the micelles. The micelles act as a meeting place for the oil-soluble monomer and the water-soluble initiator. The micelles are also favored as the sites of reaction because of their high monomer concentration and their high surface-to-volume ratio compared to the monomer droplets. There are, no doubt, comparatively few initiations that occur in the true aqueous phase outside of the micelles. Approximately 10^{13} free radicals per milliliters per second may be produced from a typical persulfate initiator at 50°C, and within a very short time radicals will meet the monomer-swollen micelles in which the polymerization then starts. After initiation, a new phase is formed in the emulsion polymerization system as the fourth part, namely polymer latex particles swollen with monomer.

The next step of polymerization is propagation. As polymerization proceeds, the micelles grow initially by the addition of monomer from the aqueous solution phase and subsequently from the monomer droplets. As the monomer molecules in the micelles combine with one another to give polymer chains, more will migrate (or diffuse) from the monomer drop through the water to the micelles. After initiation, polymerization inside the micelles proceeds rapidly and the polymer latex particles grow rapidly from within. Thus, the micelles grow from tiny groups of emulsifier and monomer molecules to larger groups of polymer molecules held in emulsion by the action of the emulsifier molecules located on the exterior surfaces of the particles. The hydrophobic monomer diffuses through the aqueous phase to supply the growing latex particles continuously from the monomer droplets. The latter gradually decrease in quantity as the polymerization proceeds, until at a conversion of approximately 50–85% they disappear completely. All the free monomer in the system has then diffused into the latex particles present. The monomer in the monomer-swollen latex particle is gradually used up from this point on and the polymerization rate will gradually decrease. Polymerization will cease completely when all the monomer in the particles is consumed.

The emulsifier is adsorbed on the surface of the growing latex particles. This adsorbed emulsifier acts as a protective colloid, preventing the latex particles from flocculating. The adsorption of the emulsifier on the rapidly and continually growing surface of the monomer-swollen latex particles reduces the concentration of dissolved emulsifier in the aqueous phase and also upsets the balance in the equilibrium between the dissolved emulsifier and the emulsifier in the inactivated micelles. The point is quickly reached at which the emulsifier concentration in solution falls below its critical micelle concentration, CMC. This is the concentration of emulsifier in solution which must be maintained in order to form and maintain micelles. When the concentration of emulsifier in solution falls below this value, the inactive micelles (those in which polymerization is not occurring) become unstable and disintegrate to restore the balance. At 2–15% conversion, depending on the particular polymerization system, the active micelles have grown much larger than the original micelles. They are no longer considered micelles, but monomer-swollen polymer latex particles. With time, all of the micelles disappear and the monomer droplets shrink in size. After a conversion of 10 to 20% of monomer to polymer has been reached, no micelles are left and essentially all of the emulsifier in the system has been adsorbed by the polymer particles. It is significant that at this point the surface tension of the aqueous phase increases because emulsifier-free water has a high surface tension of 72.8 mN/m. As a consequence, the monomer droplets are no longer stable and will coalesce if agitation is stopped. Polymerization proceeds homogeneously in the polymer particles as the monomer concentration in the particles is maintained at a constant concentration by diffusion of monomer from the monomer droplets. The number of monomer-swollen polymer particles remains constant throughout polymerization. The monomer droplets decrease in size as the size of the polymeric particles increase. Finally, at 50–80% conversion, the monomer droplets completely disappear and the polymer particles contain all the unreacted monomer and essentially all of the emulsifier molecules are also attached to the surface of polymer particles. After this stage no fresh latex particles can be formed since initiation of the polymerization reaction can take place only in monomer-swollen micelles. The number of latex particles is thus fixed from this point (approximately 10^{15} particles/ml) and further polymerization occurs only inside these latex particles. Polymerization continues at a steadily decreasing rate as the monomer concentration in the monomer-swollen polymer particles decreases. Final conversions of essentially 100% are usually achieved. The final polymer particles have diameters of the order of 500 to 2000°A and are intermediate in size between the initial micelles and initial monomer droplets.

It would appear from the foregoing that a successful emulsion polymerization process requires an acceptable emulsification system. As indicated earlier, an acceptable emulsification results from a combination of optimum agitation and the correct amount of the proper emulsifying agent or soap. For many polymerization systems a satisfactory degree of agitation includes a wide range of agitator speeds. However, some systems are more sensitive to agitation, and greater care must be exercised in determining the optimum agitator speed and the specific mechanical equipment being used. In general, the agitator speed must be high enough to break up the monomer phase into droplets, but not so high as to create so much shear that the emulsified polymer particles in the product are mechanically coagulated. A slimy mess is produced when polymerization occurs in a vessel in which the agitator speed was too low to break up the monomer phase into droplets. On the other hand, too high an agitator speed results in an excessive coagulum formation adhering tenaciously to the surfaces of baffles, agitator impellers, and vessel walls. The coagulum formation represents a loss in yield.

The emulsifying agent or soap has a multirole function to play in the emulsion polymerization process. First of all, the emulsifier must form the micelles which solubilize the monomer, and within which the initiation and early propagation of the polymer particles occur. The soap also helps to emulsify the monomer and stabilizes the emulsified polymer particles as they grow and in the final product. A large number of materials can be used as emulsifying agents. These materials are generally classified as anionic, cationic, or nonionic. By far the greatest number of emulsion polymerizations are carried out using anionic emulsifiers. Anionic soaps often used include carboxylates, sulfonates, and sulfates. Rosin acids and other types can also be used. Cationic emulsifiers are ordinarily used only in special situations. The anionic soap systems seem to be less subject to disturbances by minor changes in the other process variables; thus, they are more reliable in the sense of trouble-free operations. However, in special situations such as when an anionic system would be repelled by a surface to which it is to be applied, cationic systems are useful. Cetyltrimethyl-ammoniumbromide is probably the most commonly used cationic emulsifier. Many other compounds of a similar nature are referred to in the literature.

Nonionic emulsifiers are also used, most generally when ionic ones are not applicable for some special reason. One special advantage of nonionics is that they are insensitive to a wide range of pH. The structures of these emulsifiers commonly include long-chain alkyl groups attached through oxygen or nitrogen atoms to chains of ethylene or propylene oxide groups. Helin and coworkers[17] have considerable data concerning the performance of this type of emulsifier. Of immediate interest is the quantity of emulsifier to be used. The criterion for specifying the quantity of soap is that there must be sufficient soap present that the critical micelle concentration is exceeded. Shinoda[18] and Harkins[13] give critical micelle concentrations for various long-chain carboxylates and alkylbenzene-sulfonates as well as other types of emulsifiers. The critical micelle concentration concept comes from the observation that the surface free energy at the air-water interface or a dilute emulsifier solution decreases to a certain point as the concentration or the emulsifier increases. Beyond that point the surface free energy remains constant as additional soap is added. The theory is that the soap molecules align themselves at the interface until that is saturated and the additional soap molecules form the micelles. The work of Shinoda[18] resulted in the development of the equation,

$$\log_{10}[CMC] = ABn \tag{2.1}$$

where [CMC] stands for critical micelle concentration in moles per liter. The value for constant A proved to be close to 1.70 for most anionic and cationic emulsifiers investigated, while the value of constant B was close to 0.292. The number of carbon atoms in the hydrocarbon chain of the molecule is represented by n. Since the critical micelle concentration can be estimated, the question becomes how much emulsifier should be included in the recipe. The answer is that successful polymerizations have been carried out wherein the soap concentration was 10 times the critical micelle concentration. This concentration is lower than appears to be normal, however. A good, round number might be that sufficient soap should be used to exceed the critical micelle concentration by a factor of 50 to 100.

It should be noted at this point that the quantity of emulsifier present in the system affects not only the rate of polymerization but also the number and size of the polymer particles. The Smith-Ewart theory[19] and other quantitative treatments will be addressed later. The optimum quantity of soap is definitely influenced by whether a fine or coarse grain product is desired. In other words, if a product is desired that has a large number of relatively small particles, a relatively large amount of emulsifier should be used. Conversely, if the product should have a small number of large particles, less soap must be used.

Once the initiator generates a radical, the radical may be transferred to the propagating loci in more than one procedure. The initiator radical may react with other molecules in the water phase, including the water molecules, to create a different radical. It may react with a monomer molecule that is dissolved in the true water phase to create an active monomer radical. The initiator radical may also enter a micelle where it reacts with a monomer molecule to create an active monomer radical. Directly or indirectly, the initiator creates a propagating center in the micelles since the activated species that survive are absorbed into the micelles. Once the propagation proceeds far enough, the micelles are no longer micelles but polymer particles.

Initiators are generally divided into two broad classes, dissociative and redox. Possibly the most common initiator, potassium persulfate ($K_2S_2O_8$), will function in either classification. It will dissociate thermally to form the active sulfate radical (SO_4^{-2}) and may be reduced by a bisulfite salt to give the same radical while another radical (HSO_3^{-1}) is also formed (see 3.2). Actually, the persulfate salt is by far the most common dissociative initiator. Others include aromatic diazoamino compounds, aromatic diazothio ethers, and alkali metal aryl diazoates. Redox systems commonly include persulfate mercaptan systems, persulfate-bisulphite systems, chlorate bisulphite systems, hydrogen peroxide iron (3) salts, hydroperoxide-iron (2) salts, and other less common systems (see 3.2). Smith[20] demonstrates that, provided the number of reaction loci is fixed, variation in the quantity of initiator has no effect on the rate of polymerization. It has been noted, however, that the use of a redox initiator usually results in a significantly increased rate of polymerization. This is attributed to the sudden influx of a high concentration of radicals, thus causing the creation of new loci of propagation. The Smith-Ewart theory[19] accounts for this phenomenon. The real value of the redox system is that the polymerization can proceed at a higher rate at significantly lower temperatures compared to the temperatures required for the dissociative systems to proceed satisfactorily. Blackley[16] includes a lengthy discussion, and Bacon[21] presents a comprehensive review concerning redox systems.

The initial period of time before the micelles disappear is called "Interval I," the time between Interval I and the point where the monomer droplets disappear is "Interval II," and the time after the disappearance of the monomer droplets is "Interval III."

2.2.1 SMITH - EWART KINETIC THEORY

The theoretical calculations of Smith and Ewart[19,20] allow the derivation of the kinetic expressions for emulsion polymerization. These calculations are based on the rates of radical coupling reactions compared to the diffusion rates of radicals in water. It has been shown that the initiating radicals in emulsion polymerization systems do not terminate in the aqueous phase but are long-lived enough to diffuse into the polymer particles. Thus, essentially all of the radicals produced in the aqueous phase enter the polymer particles.

Emulsion polymerization follows the same kinetic laws as have been established for homogeneous free radical addition polymerizations in bulk or solution (see 1.3). There are, however, some special reaction conditions. In emulsion polymerization, the loci of polymerization are isolated from one another so that each small monomer-swollen latex particle (or each monomer-swollen micelle) is a homogeneous polymerization system independent of the multitude of others in the system. In addition, each latex particle is isolated from the bulk of the monomer. These two factors affect the polymerization kinetics so that:

1. There is a limit to the number of free radicals that can exist as such in the small volume of the latex particle. Thus, the rate of the termination reaction by biradical coupling (radical-radical interaction) will be less than conventional bulk or solution termination reactions. In addition, the high viscosity inside the latex particle may also hinder diffusion of the radicals. Consequently, the molecular weight or the degree of polymerization that will result is higher than in normal homogeneous reactions.
2. The concentration of monomer in the monomer-swollen latex particles is kept constant by diffusion through water phase from the monomer droplets (reservoirs) for the major part of the polymerization. Therefore, the rate of propagation in each particle will be constant, and the overall rate of

polymerization in the reaction system will depend on the number of latex particles.

The synthesis of emulsion polymers involves three intervals. The nucleation takes place in Interval I, polymer particle growth takes place in Interval II, and the termination reaction takes place in the absence of monomer droplets in Interval III. The molecular weight of the polymer chains formed in emulsion polymerization is influenced by these stages.

Harkins's conclusions relate to the emulsion copolymerization of butadiene and styrene, which are miscible with their polymers and which have very low solubilities in water, but which can be solubilized in larger quantities in the interior of the micelles of ionic surfactants. Model experiments concentrate on styrene homopolymerization because it can be handled more conveniently and is less toxic than some other common monomers. Basing their deliberations on Harkins's qualitative theory,[4,11-13] Smith and Ewart,[19,20] and later Haward,[22] developed an expression for the rate of polymerization in an "ideal" emulsion polymerization system. An "ideal" emulsion polymerization is a system where (a) monomer is completely insoluble in water phase, (b) initiator is only soluble in water phase and completely insoluble in monomer phase, (c) no inhibitors or shortstopping agents are present in the system, (d) no retarders and chain transfer agents are present, (e) there is no effect of colloidal stabilizers and the electrolytes on the polymerization kinetics, and (f) agitation rate is constant throughout the reaction. A simple quantitative explanation of the ideal emulsion polymerization kinetics is necessary in order to understand the deviations from the ideal case in actual emulsion polymerization processes.

According to the Smith-Ewart theory, under conditions where the concentration of the radicals is constant, the rate of initiation is equal to the rate of termination, ($R_i = R_t$) in the ideal emulsion polymerization, similar to the bulk and solution polymerization kinetics (see Sec. 1.3). That means the ideal emulsion polymerization obeys the steady-state kinetics since termination occurs immediately upon the entry of a radical into a polymer particle in which a polymer chain is propagating. However, allowance must be made for the small volume of the latex particles in which the reaction is occuring, and the limited number of radicals which can be accommodated in each particle for emulsion polymerization. Thus the termination rate is always lower than that given in Eq. 1.12.

Now, if n = number of radicals in reaction volume V and N_A = Avagadro's number, then

$$[M\cdot] = \frac{\left(n/N_A\right)}{V} \tag{2.2}$$

where $[M\cdot]$ is the concentration in moles of radicals in the reaction volume. Since in the conventional free radical addition polymerization kinetics the rate of termination is given by Eq. 1.12, then the rate of termination of an ideal emulsion polymerization becomes

$$R_t = 2k_t \frac{\left(n/N_A\right)^2}{V^2} \tag{2.3}$$

When the number of radicals in reaction volume V is large as in solution polymerization, the relationship in Eq. 2.3 is a very good approximation and the fact that a radical cannot react with itself can be ignored. However, when n is small in the small volume of the monomer-swollen latex particles, V, the exact relationship must be applied:

$$R_t = 2k_t \frac{\left(n/N_A\right)}{V} \cdot \frac{\left[(n-1)/N_A\right]}{V} \tag{2.4}$$

Thus, the rate of termination and, consequently, the molecular weight of the polymer depend on the distribution of radicals among the particles.

It is convenient to consider steady-state conditions after the inactive monomer micelles have disappeared and the number of polymer particles has become constant. In a typical emulsion polymerization system where there are 10^{14} polymer particles/ml and the radical production rate is 10^{13} radicals/ml per second, a radical diffuses into a polymer particle on an average of every ten seconds. It can be calculated that the radical concentration in a polymer particle is in the range of 10^{-6} molar or higher. This is a much higher radical concentration than in the homogeneous polymerization systems, and the radical lifetime here is only a few thousandths of a second. The entry of a second radical into the polymer particle results in immediate bimolecular termination. Thus, the polymer particle will have either one or zero radicals. The presence of two radicals in the same particle is synonymous with zero radicals since termination occurs so quickly. The particle is then dormant until another (the third) radical arrives approximately 10 seconds later. The particle is again activated and propagation proceeds until the next radical arrives in another ten seconds. The cycle of alternate growth and inactivity of the polymer article continues until the monomer conversion is essentially complete. Any polymer particle will be active half of the time and dormant the other half of the time. In other words, as Smith and Ewart proposed for the ideal case, at any given moment half of the monomer-swollen polymer particles contain one radical and are growing while the other half are inactive. The number of radicals per particle averaged over all the particles is one-half, and “zero-one” kinetics apply. Thus, statistically, the average number $\bar{n}$ of radicals per particle (in the V volume of monomer-swollen particle) is equal to ½. This is generally approximately correct for monomers such as styrene which have low transfer constants to monomer, which makes the rate of escape of radicals from particles almost negligible. If N is the total number of particles per liter, $N = \frac{\bar{n}}{V}$, then,

$$[M\cdot] = \frac{N}{2N_A} \tag{2.5}$$

is found. Then, the rate of termination becomes

$$R_t = k_t \frac{N^2}{2N_A^2}. \tag{2.6}$$

On the other hand, the rate of propagation in the conventional free radical addition polymerization kinetics is given by Eq. 1.9, and by combining Eqs. 1.9 and 2.5 one obtains

$$R_p = -\frac{d[M]_p}{dt} = \frac{\bar{n}Nk_p[M]_p}{N_A} = \frac{Nk_p[M]_p}{2N_A} \tag{2.7}$$

where $[M]_p$ is the equilibrium molar concentration of the monomer at the polymerization locus (the monomer-swollen latex particle) and k_p is the rate coefficient for the propagation step at the appropriate temperature. It is possible to determine R_p, N, and $[M]_p$ experimentally.

Inside the monomer-swollen polymer particle a radical propagates in the usual manner and the rate of propagation depends on the propagation rate constant k_p and the monomer concentration $[M]$ in the particle. The monomer concentration is usually quite high since in many cases the equilibrium swelling of the particle by monomer is of the order of 50% by weight. Values of $[M]$ as high as 5 molar are common.

The above equation indicates that the rate of polymerization is directly dependent on the number of monomer-swollen polymer particles, and is independent of the initiator concentration and the radical generation rate R_i in the ideal case. An increase in R_i simply results in an increased rate of alternation of activity and inactivity in each monomer-swollen latex particle. However, in actual practice the initiator concentration may affect the rate of polymerization and thus the molecular weight of the polymers since a reduction in the concentration of radicals would mean that the time interval between the successive entries of primary radical into the particle would be increased. Then the termination reaction would occur less frequently and the polymer chains would grow more before being terminated.

On the other hand, the monomer concentration in the particles is constant over a very large part of the polymerization, and, therefore, the rate of polymerization depends only on the number of particles present at a given temperature. However, the experimental determination of N with sufficient accuracy is difficult. N is usually calculated from measurements of average particle size and knowledge of the total mass of polymer. Burnett and Lehrle devised a method for the direct experimental determination of N.[23] Eq. 2.7 can be used to determine k_p independently of nonstationary state methods. However, Smith's k_p value for styrene monomer obtained in 1943[20] and that of Matheson et al. in 1951[24] was not consistent with contemporary values from bulk kinetics. The value of Matheson et al. was accepted as the most reliable available value for a long time, but this value was nearly half of the latest results of $k_p = 254$ dm^3 mol^{-1} s^{-1} at 50°C with an energy of activation $E_p = 29$ kJ mol^{-1}, which was found by applying the improved experimental techniques and theoretical interpretations between emulsion and bulk polymerization kinetics.[25] This was due to the fact that Matheson et al. neglected the primary radical termination in their calculations.[26]

Monomers which are more soluble in water than styrene, have high transfer constants, and produce highly active radicals (e.g., vinyl acetate and vinyl chloride) have $\bar{n} \ll \frac{1}{2}$ because of relatively facile transfer of radicals out of particles into the water phase.[27,28] When $\bar{n} = \frac{1}{2}$, N is the principal factor determining the rate of polymerization. When $\bar{n} \ll \frac{1}{2}$, the polymerization rate is much less sensitive to N. When the latex particles are large, although N is constant, an increase in $\bar{n}$ causes the rise in the rate of polymerization.[29] Dunn pointed out that although good reproducibility can be achieved under laboratory conditions, reproducibility of N under emulsion polymerization plant conditions can be poor.[30] This problem can be overcome by the use of "seeded polymerization" in which N is predetermined by dilution of completely polymerized seed latex with a small particle size. If the excessive dilution is avoided, then the renucleation cannot be permitted and reproducibility cannot be ensured.

Smith and Ewart assumed that the area occupied by an emulsifier molecule in a micelle and in a saturated monolayer at the polymer-water interface is the same. On the other hand, the number of radicals entering a particle should be proportional to the radius of the particle according to the diffusion theory. This means that the number of radicals entering a given area is inversely proportional to the radius of the spherical particle and, therefore, small particles are more effective than large particles in capturing radicals. However, this is a complex problem, and Smith and Ewart used the alternative assumptions to simplify this problem that either (1) the micelles capture all the radicals so long as they are present (which should give the maximum figure of the number of particles formed); or (2) the same interfacial area captures the same number of radicals regardless of particle size (which should give the minimum figure of the number of particles formed). Fortunately, these assumptions produce the same dependencies on emulsifier and initiator concentrations, differing only by a numerical factor.

The total number of particles per liter, N, is given by

$$N = F\left(\frac{\rho_i}{\mu}\right)^{2/5} \left(A_s[E]\right)^{3/5} \tag{2.8}$$

where ρ_i = rate of radical production from the initiator in molecules-per-unit volume ($\rho_i = dN/dt$), μ = rate of volume increase of a particle ($\mu = k_p/N_0$), N_0 = the number of particles containing 0 radicals, A_s = interfacial area occupied by one emulsifier molecule in the micelles, $[E]$ = concentration of emulsifier, and F = efficiency factor lying between 0.37 and 0.53.

Combining the last two equations derived a simple expression of the rate of polymerization for an ideal emulsion polymerization at a given temperature:

$$R_p = -\frac{d[M]}{dt} = K[I]^{2/5}[E]^{3/5}[M] \tag{2.9}$$

where $[I]$ is the initiator concentration and K is a constant. It should be noted that the initiator exponent of 2/5 and the emulsifier exponent of 3/5 are determined simply by the geometrical relation of the surface area to the volume of a sphere and cannot vary so long as zero-one kinetics apply. In these terms, $-d[M]/dt$ gives the rate of conversion or monomer to polymer in number of monomer molecules converted per second in a unit volume of aqueous phase. This expression holds only for that period during which the number of polymerization loci has reached its maximum and before the monomer droplets disappear in the steady-state situation. That means, in the above equation, the concentration of the monomer in the particles, $[M]$, is also constant up to the conversion at which monomer droplets disappear. Presuming the Harkins theory to be valid, the Smith-Ewart work leads to the conclusion that the rate of polymerization during this period is of the order of 0.4 with respect to the beginning initiator concentration, and of the order or 0.6 with respect to the concentration or the emulsifier. From the practical viewpoint, high polymerization rates are obtained by high initial rates of radical generation and high emulsifier concentrations. The above expression fits closely the experimental data for water insoluble hydrophobic monomers such as styrene and butadiene-styrene, and for initiators generating free radicals in the aqueous phase, such as potassium persulfate. The basic kinetics and the deviations from the ideal case were discussed in more detail by Bovey et al.,[15] Gerrens,[31] Van der Hoff,[32] Waterman,[33] Walling,[34] and Stockmayer.[35]

The above derivation is the simplest case of the ideal emulsion polymerization. However, there are three possibilities for kinetics of emulsion polymerizations according to Smith and Ewart[19] : Case I describes the situation where the number of free radicals per location is much less than unity and was applied to some polar monomers; Case II describes the situation where the number of free radicals equals approximately one-half the number of reaction loci; and Case III is the situation where the number of free radicals is very large. (The above classical kinetic derivation belongs to the Smith-Ewart Case II kinetics.) The derivation of Cases I and III kinetic equations was summarized by Dunn.[30]

Smith and Ewart did not consider the effect of the ionic strength of the aqueous phase and the valence of the counter-ions, which also affect the number of particles.[36,37] One of the main assumptions of their theory, i.e., the area occupied by an emulsifier molecule at the polymer-water interface would be the same as it is at the air-water interface and independent of the presence of monomer, has been found to be incorrect.[38]

2.2.2 GARDON KINETIC THEORY

A number of investigators made refinements to the Smith-Ewart work between 1957-1967.[35,39-41] However, between 1968–1971, Gardon, in a series of articles,[42-44] enlarged on the Smith-Ewart theory, producing an equation with which to calculate the number of particles produced in a polymerization. Gardon modified the Smith-Ewart equation (Eq. 2.9), by introducing the assumption that radicals entered latex particles by collisions rather than by diffusion, and cast the equations into convenient forms for numerical calculations. Gardon divided the emulsion polymerization into three stages: during the first period new polymer particles are being formed; in the second stage no new particles are being formed, but monomer still exists in droplets; in the third stage the monomer droplets have disappeared and the polymerization is proceeding in the particles formed during the first stage. It was necessary to have these three stages in order to allow for a mathematical treatment of the reaction system.

Gardon defined three parameters: *K*, *R*, and *S*. *K* is the volume growth rate of the particle and was given as:

$$K = \frac{dr^3}{dt} = \frac{(3/4)\left(k_p/N_A\right)\left(\rho_m/\rho_p\right)\phi_m}{1-\phi_m} \tag{2. 10}$$

where r is the particle radius; k_p is the rate coefficient of the monomer for the propagation; N_A is Avogadro's number; ρ_m and ρ_p are the densities of the monomer and polymer, respectively, and ϕ_m is the volume fraction of the monomer in the swollen-polymer particle at equilibrium.

R is the number of radicals per second produced in 1 cm^3 water by decomposition of the initiator and was given as

$$R = 2N_A k_d[I] \tag{2.11}$$

where $[I]$ is the initiator concentration and k_d is its decomposition rate coefficient.

S is the total area occupied in a saturated monolayer at the polymer-water interface by the surfactant molecules initially contained in 1 cm^3 water and was given as

$$S = N_A\, A_S\left([E]-\left[E_{CMC}\right]\right) \tag{2.12}$$

where A_S is the interfacial area occupied by one emulsifier molecule at the polymer-water interface, $[E]$ is the molar surfactant concentration, and $[E_{CMC}]$ is its critical micelle concentration under the conditions prevailing in the experiment.

Gardon gave the number of latex particles formed per cm^3 water as

$$N = 0.208 S^{3/5}\left(\frac{R}{K}\right)^{2/5} \tag{2.13}$$

and the root mean cube radius of the particle was given as

$$r_{rmc} = 1.05\left(\frac{m}{w}\right)^{1/3}\left(\frac{\rho_w}{\rho_p}\right)^{1/3}\left(\frac{1}{S^{1/5}}\right)\left(\frac{K}{R}\right)^{2/15} \tag{2.14}$$

where ρ_w is the density of water and (m/w) is the mass ratio of monomer to water. By assuming the number of average radicals per particle, $\bar{n} = {}^1/_2$, as Smith-Ewart Case II kinetics, the Interval II rate was given as

$$R_p = \frac{k_p N [M]_p}{2N_A}, \tag{2.15}$$

and by assuming that the Interval II rate was constant, the average molar mass of the produced polymer was given as

$$M_n = \frac{k_p \phi_m N \rho_m}{R}. \tag{2.16}$$

Gardon selected suitable values of the parameters for several monomers such as styrene, methyl methacrylate, and butyl acrylate ($K = 6.3 \times 10^{20}$ cm^3 s^{-1}, $k_p = 1.24 \times 10^{-5}$ cm^3 mol^{-1} s^{-1} for styrene monomer, and $K = 22.8 \times 10^{20}$ cm^3 s^{-1}, $k_p = 2.70 \times 10^{-5}$ cm^3 mol^{-1} s^{-1} was recommended for methyl methacrylate monomer, and $R = 5.8 \times 10^{-13}$ s^{-1} was figured out for 1% $K_2S_2O_8$ solution, all at 50°C).[43,44] Dunn and Al-Shahib obtained excellent agreement between calculated and observed sizes of latex particles by using some of Gardon's recommended values of the relevant parameters.[45] Later, Dunn criticized Gardon's approach, saying that these selected values differ from the latest results, and commented that there may be compensation of errors.[30] He cited that the assumption that A_S, which is the interfacial area occupied by one emulsifier molecule at the polymer-water interface, is independent of the nature of the polymer is not justified. Also, the assumption that the rate at which radicals enter latex particles can be found by dividing the number of particles by the rate of formation of radicals in the aqueous phase is wrong.[46] In addition, the rate of collision of radicals with particles does not seem what determines the radical entry rate.[30] In contrast to these views, Gardon suspected that the experimentally measured average particle size may be too large because of the failure to register the smallest particles, making the calculated particle number too small, and made comparisons with experimental data additional to those in his previous papers.[47,48]

2.2.3 OTHER KINETIC EFFECTS

2.2.3.1 The Effect of Electrolyte Concentration

When an ionic initiator such as potassium or ammonium persulfate is used, variation of the initiator concentration inevitably also changes the ionic strength of the aqueous phase. This effect has been widely overlooked.[30,36] When the ionic strength increases, the CMC of the emulsifier decreases, micelle size increases, and the amount of monomer solubilized increases. In addition, the adsorption of emulsifier on the surface of the polymeric particles increases, and this fact increases the surface charge density in the case of an ionic emulsifier. Also, with increasing ionic strength, the diffuse part of the electrical double layer is compressed and the coalescence rate of latex may be increased, producing a latex with a larger average particle size. The latex may be destabilized completely and will coagulate at a sufficiently high ionic strength.

2.2.3.2 Effect of the Structure of the Emulsifier

A_S, the area occupied by an emulsifier molecule in a saturated monolayer at the polymer-water interface, is directly proportional with N, the number of particles in unit volume and, consequently, the polymerization rate. It was determined that within a homologous series of emulsifiers, A_S decreases with increasing alkyl chain length. Then, logically, N should decrease. However, experimental results showed that N and R_p actually increase.[30,49] The reason is that CMC decreases with the increase of the alkyl chain length of the emulsifier, giving rise to the concentration of the micellar emulsifier. When equal concentrations of micellar emulsifiers are used, the same number of latex particles is produced with the same average particle size and the same particle size distribution.[50]

2.2.3.3 The Effect of Nonionic Emulsifiers

Nonionic emulsifiers impart colloidal stability by a steric mechanism and are different from the ionic emulsifiers, which impart colloidal stability by electrostatic mechanism. Nonionic emulsifiers are characterized by much lower CMC concentrations than comparable ionic emulsifiers because of the absence of electrostatic repulsion between the hydrophilic groups. The low CMC values of nonionic compounds correspond to high micellar weights, whereas the high CMC values observed with anionic surfactants correspond to low micellar molecular weights. That means that for equal concentrations of both kind of emulsifiers, anionic emulsifiers form many more micelles in water, thus giving more polymer particles with smaller particle size. In actual practice, minor portions of an anionic emulsifier can be used to reduce particle sizes. Several such mixed emulsifier systems have been found to produce a monodisperse latex at a particular ratio of nonionic to ionic emulsifier. No explanation has been offered as to why particular emulsifier mixtures produce monodisperse latices.[30] The probability of a latex particle being nucleated from a mixed micelle is great, and the combined effect of steric hindrance and electrostatic repulsion in retarding radical entry or preventing particle coalescence is minimum.[56] The effectiveness of electrostatic stabilization increases with ionic emulsifier concentration much more rapidly than the effectiveness of steric stabilization increases with nonionic emulsifier concentration.[30]

2.2.3.4 Monomer Solubilization and the Duration of Interval I

Interval I duration correlates with the amount of styrene solubilized by the micelles.[51] When the higher members of the homologous series of emulsifiers are used, larger micelles are formed which solubilize more monomer. Then, the duration of Interval I decreases as the homologous series increases. This behavior is in contrast with the identical Interval II rates, which are observed with styrene under conditions of equal micellar emulsifier concentration.[30]

The faster the initiation rate, the narrower should be the particle size distribution. It was commonly supposed that the breadth of the particle size distribution should be proportional to the duration of Interval I, but identical particle size distributions were obtained despite the variations in the duration of Interval I.[50]

2.2.3.5 The Effect of Monomer-to-Water Ratio

The monomer-to-water ratio is the weight ratio of the monomer to the water phase. In practice, the monomer-to-water-ratio chosen is that which gives the best rates of polymerization coupled with low viscosity to enable adequate heat and mass transfer. With styrene-butadiene copolymers, the monomer/water ratio is usually 1:2 to 1:3 for the preparation of general-purpose latex. According to Smith-Ewart kinetics, this ratio should have no influence on the rate of polymerization and the number of particles. In practice this is usually not the case, depending mainly on the solubility of the monomer in water and the polymer phases. When the amount of water, the concentration of emulsifier in the water, and the initiator concentration based on the water phase are kept constant, an increase in the amount of monomer results in the formation of larger particles. The increased number of monomer droplets obtained by increasing the amount of monomer requires more emulsifier at the water-monomer interface, so that somewhat less emulsifier is available for micelle formation. Thus, the initial number of micelles decreases. Furthermore, the polymer formed in the monomer-swollen particle swells to accommodate as much monomer as possible, and an increase in monomer concentration in the particle occurs. If the particle size is increased substantially, the average radical concentration inside the single particle can become more than the $^1/_2$ proposed by Smith-Ewart Case-II kinetics. Under such conditions, latex instability accompanied by flocculation may occur eventually owing to lack of sufficient emulsifier to protect the much larger amount of particle-water interface present.

When the amount of monomer is unusually low in relation to the emulsifier concentration, larger numbers of latex particles are formed.[52,53] This effect is used to prepare the seed latices with a high particle number, which will eliminate the oscillations otherwise experienced during the startup of continuous stirred-tank reactors for emulsion polymerization.[53-55]

2.2.3.6 The Effect of Temperature

The ideal kinetic mechanism has been derived assuming the polymerization temperature to be constant. However, the temperature will affect all the terms of the rate of polymerization equation. When the temperature of the reaction system increases, four changes will occur:

1. The rate of the initiation reaction and, thus, the concentration of the free radicals will increase.

2. The number of micelles produced by the emulsifier usually increases and, thus, the number of latex particles will increase.
3. The rate of diffusion of monomer from the monomer droplet to the latex particle and the amount contained by the monomer-swollen particle will both increase.
4. The rate of flux of radicals diffusing into the particles will increase.

Consequently, the overall result of the increase in the temperature in an ideal emulsion polymerization is to increase the rate of polymerization and reduce the degree of polymerization, i.e., molecular weight of the polymer formed. Nevertheless, one should be aware of the following possible side effects of the temperature increase:

1. The risk of the instability of the emulsion system increases, resulting in the occurrence of preflocculation, coagulation, or change in viscosity.
2. The risk of the production of the cross-linked, branched, and gelled polymer increases.
3. The structure of polymer and molecular weight distribution changes.
4. When chain-transfer agents are used to control the degree of polymerization and the polymer molecular weight, the efficiency of these agents alters.

2.2.3.7 The Effect of Agitation

The above ideal kinetic mechanism has been derived assuming the agitation pattern to be constant. When the speed of the stirrer of the reaction system increases, the overall reaction rate increases and the molecular weight of the polymer lowers. The main reason for this is the rate of monomer diffusion and the mass transfer increase by the increase of the agitation. The rate of agitation also affects the chain-transfer agent efficiencies.

2.2.3.8 The Effect of Conversion

For many kinds of hydrophobic monomers, the termination reaction results from total depletion of monomers inside the particles, and an emulsion polymerization is taken to 100% conversion or near to it. Polymerization of styrene and vinyl chloride, for example, may be taken to very high limiting conversions without detriment to the product properties. However, when butadiene or styrene-butadiene monomers are used in emulsion polymerizations and are taken to very high conversions, i.e., >80%, it may lead to profound changes in the polymer. In most cases, at the high conversions, deviations from the "ideal" emulsion polymerization occur and lead to such phenomena as latex instability, gelled polymer, branched polymer, and changes in composition in the case of copolymers. Shortstop-agents such as sodium polysulfide, sodium dimethyldithiocarbamate, hydroquinone, and phenylhydrazine, which inhibit and retard the polymerization reaction, are used to bring the reaction to a stop at the right conversion.

2.2.3.9 Gel Effect

If the medium is highly viscous, termination may be made more difficult so that quick termination does not occur even in particles smaller than 1000°A in diameter. The result is that the average radical concentration inside the particles can be higher than that proposed in the ideal kinetics. This is called the "Trommsdorf or gel effect." When this effect is present, the conditions inside the particle approach those in a homogeneous bulk reaction. With methyl methacrylate monomer the effect is quite pronounced at low conversions. This condition can occur to a relatively small extent in styrene and styrene-butadiene polymerizations taken to high conversions and resulting in very high molecular weight and branched and cross-linked polymer.

2.3 INVERSE EMULSION POLYMERIZATION

A hydrophobic monomer is emulsified in water with an oil-in-water emulsifier in the conventional emulsion polymerization, and usually a water-soluble initiator is used. Nevertheless, the reverse is also possible so that the emulsion polymerization can also be carried out with inverse emulsions. Here, an aqueous solution of a water miscible hydrophilic monomer such as arcylamide, acrylic acid, or methacrylic acid is emulsified in a hydrophobic oil phase with a water-in-oil emulsifier.[57] Polymerization can be initiated with either oil-soluble or water-soluble initiators to give a colloidal dispersion of submicroscopic, water-swollen polymer particles in oil. There are two aims to carry out inverse emulsion polymerization: (1) the achievement of the rapid polymerization rates combined with high molecular weights for water-soluble polymers, and (2) to transfer the water-swollen polymer particles to aqueous phase rapidly by inversion of the latex. Both purposes are important in the preparation and use of polyacrylamide-type flocculants.

Polyacrylamide polymers are water-soluble and are widely used for their thickening properties in paints, and as pushing fluids in tertiary oil recovery and drilling fluids, etc. These polymers should be of very high molecular weight to be most effective, and their manufacturing requires a process which overcomes the high exothermicity of the polymerization. As a consequence, it is essential to produce these polymers in water-in-oil dispersions. The free-radical polymerization is carried out with an oil-soluble or a water-soluble initiator to yield an inverse latex, i.e., a colloidal dispersion of water-swollen polymer particles in oil. High molecular weight polymers are obtained with very rapid polymerization rates. The achievement of low-viscosity media at high solids contents, easier handling, and dissolution are other advantages. For applications, the latice can be easily inverted by dilution with water, so that the high molar mass polymer dissolves rapidly contrary to solid-powder polymer, which forms gels or aggregates when added to water.

The stability of the particles in the inverse emulsions is generally less than that of the conventional emulsion polymerization system, due apparently to the different electrostatic forces operative in the two situations. In the inverse system, aromatic or aliphatic continuous phases such as toluene, xylene, heptane, isooctane, and cyclohexane are commonly used and the stabilization is essentially steric in origin.[58,59] In the conventional emulsion polymerization, the continuous phase is exclusively water and the particle stabilization is electrostatic and/or steric. Particle size (about 300 A°) in inverse emulsion polymerization is generally smaller than that encountered in conventional emulsion polymerization. Unusual variations in the number of particles with increasing emulsifier concentration and temperature are observed.

Acrylamide is the most readily available and inexpensive water-soluble monomer, and both benzoyl peroxide and AIBN (2,2′, azobisisobutyrilonitrile) are used as an oil-soluble initiator, and potassium persulfate is used as a water-soluble initiator. A monomer aqueous phase to oil phase weight ratio of about 70 to 30 is classically used.[60] The monomer content used in the formulations can vary between 30 to 42 wt% of the total mass. Apart from the pure toluene, xylene, heptane, isooctane, and cyclohexane solvents, deodorized kerosenes and low odor paraffin solvents are used as the oil phase in the industry. When water-soluble initiators are used, acrylamide polymerization proceeds within the monomer droplets regardless of the nature of the aromatic or aliphatic organic phase.[61-65] Each particle acts as a small batch reactor, and both monomer and initiator reside in the dispersed droplets. The process is essentially a suspension polymerization. When oil-soluble initiators are used in the inverse emulsion polymerization, the concepts of the conventional emulsion polymerization of hydrophobic monomers in water are applied. However, the results are, in many respects, contradictory and diversely interpreted, and a full comprehensive picture of the kinetic mechanisms occurring in these systems has not yet emerged.[66-72] Redox systems operating at low temperatures are preferred in industry, although they have not been studied systematically. The most commonly used initiator pair is *t*-butyl hydroperoxide-sodium metabisulfide, which generates radicals essentially in the oil phase in spite of the low solubility of *t*-butyl hydroperoxide in water.[73-76] Cumene hydroperoxide-sodium metabisulfite or thionyl chloride pairs are also used.[77]

The choice of emulsifier is important since it controls the stability of the emulsions during the emulsion polymerization and storage times. In practice, two types of emulsifiers are used: (a) ABA triblock copolymers where A is a polyester derived from 12-hydrostearic acid and B is a polyoxyethylene, and (b) nonionic emulsifiers such as fatty-acid esters of sorbitan and polyoxyethylene derivatives. The amount of surfactant is higher than that employed in conventional emulsion polymerization; it is between 2–5 wt% of the total mass. Latices prepared in inverse emulsions are less stable than conventional latices due to different electrostatic forces that are operative in both systems. Polymerization conditions have destabilizing factors such as vigorous stirring, temperature rise, and evolution of acrylamide content in the aqueous phase. Moreover, the very large differences in density between polymer particles (1.39 g/cm^3 for polyacrylamide) and the organic medium ($\approx$0.8 g/cm^3 for most oils) increase the flocculation tendency, especially in concentrated dispersions.[78] As a consequence, most inverse latices settle in a time which can vary from a few hours to a few weeks, and the sediment may be difficult to redisperse. Centrifuge tests are used to evaluate the settling stability of the inverse latices.

Hydrophilic monomers other than acrylamide, such as sodium p-vinylbenzenesulfonate, were also used in inverse emulsion polymerization. Sodium p-vinylbenzenesulfonate was initiated by either benzoyl peroxide or potassium peroxydisulfate and polymerized in xylene as the continuous phase.[57] Sorbitan monostearate was found to be a suitable surfactant for producing a water-in-oil emulsion.

Microemulsion polymerizations were developed in the last two decades, and inverse microemulsion polymerization was carried out after 1980 in order to produce thermodynamically stable latices in the nanosize range (<50 nm). Acrylamide was polymerized in sodium 1, 4-bis (2-ethylhexyl) sulfosuccinate reverse micelles where the organic phase was toluene, benzene, decane, or heptane.[79-85] These microemulsions are characterized by a high surfactant-to-monomer ratio (2.5–3.0). Each final particle contains a very small number of macromolecules, with the particle size independent of the nature of the free radical initiator.[85] This is in strong contrast with latices prepared in normal inverse emulsion polymerizations. The stability of the inverse microemulsion latex strongly depends on suitable formulation. A good chemical compatibility between the organic phase and emulsifiers leads to perfectly transparent, stable, and fluid latices, the size of which remains unchanged over years with no evidence of flocculation, even at high volume fractions more than 60%.[86]

Copolymerization is also used in the inverse microemulsion technique. Most industrial applications require the use of copolyelectrolytes based on acrylamide. Such copolymers are obtained in water-in-oil dispersions either by partial hydrolysis of polyacrylamide[87] or, more often, by radical copolymerization of acrylamide by ionic monomers.[88-92]

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3 Emulsion Homopolymerization of Vinyl Acetate

3.1 GENERAL ASPECTS

Vinyl acetate monomer can be polymerized with bulk, solution, emulsion, and suspension polymerization processes. However, there are some technical restrictions in the industrial practice. The heat of polymerization of VAc monomer has been determined several times to be 21 ± 0.5 kcal/mole.[1] The difficulty of removing the heat of polymerization and therefore of controlling the polymerization reaction, as well as the occurrence of branching at high polymer-monomer ratios which can lead to insolubilization of the polymer, have made bulk polymerization of VAc unattractive. In industry, most of the polyVAc sold commercially is made by emulsion polymerization, with suspension and solution polymerization following in order of importance. Commercially, solution polymerizations are preferred when the polyVAc is to be sold as a solution polymer directly, for example, for adhesive applications in ethyl acetate or toluene solvents, or when the polyVAc is only an intermediate product as it is in polyvinyl alcohol preparation in methanol solvent. Suspension polymerization of VAc is also carried out to produce intermediate homopolymer in polyvinyl alcohol manufacturing.

There are three important processes for preparing emulsion polymers: batch, semicontinuous (semibatch or delayed addition), and continuous. In the batch process, all of the ingredients are added initially to the reactor. Heat is applied to the system until the azeotropic temperature of 65–66°C for VAc-water pair is obtained. After some time at this temperature, the polymerization becomes exothermic and the reaction mixture may require cooling. By proper control, the polymerization is completed at a temperature of approximately 90°C. Emulsion polymer prepared in this manner is usually characterized by high molecular weight and large particle size.

The need to avoid a runaway exothermic reaction leading to uncontrollable boiling and consequent foaming or destabilization has led to the "delayed addition" process and later to continuous processes. In the semicontinuous process the monomer (which may or may not be emulsified) and the other ingredients are added gradually to the stirred batch reaction vessel, which is fitted with a reflux condenser and heating and cooling jacket. This is the most commonly used process in the industrial practice of VAc emulsion polymerization. In this approach, most of the water and stabilizers and some of the initiator are added together with 0–10% of the VAc monomer. The initiator decomposes upon heating the reactor contents to a suitable temperature, and the monomer polymerizes. The exothermic heat output rises in temperature to a degree which is allowed as the optimum temperature for the process. The remaining monomer and initiator are added incrementally during the polymerization period at a temperature higher than 75°C (usually between 75–85°C) over a period of 3–5 hours. The rate at which monomer can be introduced depends on the rate of polymerization and the cooling available. Emulsions prepared in this manner appear to be more stable and show smaller particle size than emulsions prepared by the batch process. Many variations can be made in preparing polyVAc emulsions by the processes described above. For example, in the semicontinuous technique 5 to 30 percent of the monomer may be charged initially to the reactor, and the remaining monomer may be added during a polymerization period of two to six hours (usually four hours). Delayed addition of some of the initiator and/or some of the emulsifier may be made during the course of the polymerization. Or, a portion of finished emulsion may be recycled to act as a seed or heel for another delayed addition type polymerization. Changes in temperature and rates of agitation also affect the properties of the finished emulsion. Refluxing in a condenser is a very effective way of cooling, but the amount of reflux varies greatly with the availability of the monomer, which is not polymerized, agitation rate, and temperature. In addition, the achievement of stabilization of the reaction temperature is very difficult in these circumstances.

In a typical delayed addition recipe for a large particle size (0.5–3.0 microns), 42.75% (by wt.) water is charged to a reactor; 2% hydroxyethylcellulose, 0.05% emulsifier are dissolved in the water phase; and the reaction mixture is heated to 80°C within one hour to complete the dissolution, and then cooled down to 30°C . To this reaction mixture, 5.5% VAc monomer, 0.15% sodium bicarbonate, and 0.05% potassium persulfate are added and it is heated to 70–75°C. The remaining 49.5% vinyl acetate is added incrementally over 4 hours while the reaction temperature is maintained at 80°C by the controlled removal of the exothermic heat. After all the monomer has been added, the emulsion is heated to 90°C for 30 minutes and cooled, and the coarse particles are filtered. The solids content is approximately 56–57%, the viscosity 3000 cP, and the pH 5.0.[2]

The continuous stirred tank reactor process (CSTR) uses one or more reactors similar to those used in the batch process, but with product overflowing to balance the feed of raw materials which must always include water to stabilize the polymer content. In the cascade type of continuous reactor system, all ingredients are added to one reactor with minimal stirring and the monomer is polymerized to a fixed level and then transferred to a second, or possibly into a third or even subsequent reactor until polymerization is substantially complete. The partially polymerized polymer is moved continuously to the additional finishing kettles for completion of polymerization.[3,4] Monomer is added at constant polymer ratio, and initiators and stabilizers are added correspondingly. The finished latex is withdrawn at the same rate as the ingredients enter. There is considerable latex nonhomogeneity in the primary reactor. Monomer is absorbed by the existing particles. There is wide particle scatter. Considerable intergrafting and chain branching occurs within existing particles. There will be appreciable new nucleation from grafted polyvinyl alcohol giving self-stabilized particles.

In the loop reactor continuous process, the reaction mixture is recirculated by a pump through pipework fitted with cooling jackets, or sprayed with variable water jets. The heat is removed throughout the piping. The ratio of water phase to monomer and the total input volume can be controlled, as can the rate of recirculation. Redox initiators are usually employed, one component dissolved in the monomer and the other in the water phase. The two streams are kept separate until they are mixed within the reactor. Loop reactors use a reaction volume of 50 to 100 liters and, depending on the cooling water, production rates of 400–1000 kg/h are possible. The flow of cooling water is automatically controlled since overcooling may retard the reaction. If the built-up monomer suddenly polymerizes, it is not possible to control the exothermic reaction. If overheating is applied, the initiator decomposes too rapidly, leading to loss of reaction later in the process or even destabilization of the polymer particles. It is easier to control the reaction temperature in the loop process with such a small reaction volume and the absence of reflux.

On a plant scale, polyVAc emulsion homopolymerization and copolymerization with other liquid monomers can be carried out in universal polymerization reactors from 1 to 30 m^3 volume capacity. The only limiting factor to reactor size is the efficient removal of the heat of polymerization, and reactors having their volume capacities between 5 to 15 m^3 are conventional in industrial practice. The control of the average particle size, particle size distribution, copolymerization rate, and heat transfer are complex processes on a large scale.[5,6] Monomer storage is either above ground or underground in carbon steel tanks. The colloids, such as polyvinyl alcohol and hydroxyethylcellulose, are dissolved in water by heat (usually by steam) in a separate, agitated stainless steel vessel and then transferred to the polymerization reactor. The reactor is made of stainless steel and is either fully jacketed or equipped with stainless steel, steam, or cooling water circulation pipes on the outer side of the reactor body to enable rapid heating or cooling when required. When a fully jacketed reactor is used, there may be additional cooling coils in the reactor.

Chain transfer reactions in VAc polymerization is important because the chain transfer process retards the rate of polymerization of VAc much more than in the case for styrene or methyl methacrylate. Since the transfer constants to polymer of VAc are larger than those for most other common monomers, branching of polyVAc is of great practical and industrial importance. The properties, not only of the polyVAc, but even more those of the derived polyvinyl alcohols are profoundly affected by branching (see Sec.3.3).

Most applications of polyVAc latices lead to the isolation of the polymer by the removal of water. The polymer acts as a binder between particles of pigment; as an adhesive for wood, paper, or other surfaces; or as a decorative and protective film on the surface. The state of division of the polymer has a strong influence on its properties, even in the dry state. The key stage in many applications is the transition between wet, dispersed polymer and dry film. The polymer should have a glass transition temperature below the temperature of drying, or should be plasticized by suitable solvent.

3.2 LITERATURE SURVEY ON THE MECHANISM OF VINYL ACETATE EMULSION HOMOPOLYMERIZATION

Vinyl acetate monomer differs from most of the emulsion polymerizable hydrophobic monomers with its high water-solubility, but it also differs in respects other than its solubility in water. VAc has a high equilibrium monomer-polymer swelling ratio (up to 7:1), a high chain transfer constant, and its radical has a strong tendency to abstract hydrogens from previously formed homopolymer to form branches. PolyVAc is also different from other polymers in many respects: it shows some hydrophilicity although it is generally hydrophobic, it can be solubilized in emulsifier solutions, and it can be hydrolyzed to form polyvinyl alcohol which stabilizes the polyVAc polymer in water in the absence of any emulsifier.

The high water-solubility of the vinyl acetate monomer can be expected to have two effects. In the first place, it will favor the solution polymerization in the water phase relative to polymerization in the particles. Secondly, it will increase the tendency for propagating radicals to become desorbed from the particles because the more soluble a monomer is in water, the more hydrophilic its polymer tends to be. Further complications arise from the greater reactivity of the polyvinyl acetate free radical as compared with the polystyrene free radical. Therefore, chain transfer reactions to other components of the polymerization system become correspondingly more important. All these factors affect the kinetics and mechanism of VAc emulsion polymerization.

In 1965, Gershberg reviewed the emulsion polymerization kinetics of "relatively" water-soluble monomers and found that the order of the polymerization reaction with respect to the micelle-generating emulsifier concentration falls significantly as the solubility of the monomer in water increase.[7] According to his paper, styrene monomer shows $[E]^{0.6}$ dependency whereas butyl methacrylate shows $[E]^{0.5}$; butyl acrylate, $[E]^{0.4}$; methyl methacrylate, $[E]^{0.3}$; vinyl acetate, $[E]^{0.25}$; and acrylonitrile, $[E]^{0.2}$, dependencies with increasing water solubility. These results show that a broad correlation exists between the order of the reaction and the solubility of the monomer in water. Medvedev[8] developed the hypothesis of initiation in the adsorbed emulsified layer in 1957. The hypothesis of initiation in small monomer droplets was proposed by Ugelstad, El-Aasser, and Vanderhoff in 1973.[9]

VAc emulsion polymerization differs from other relatively water-soluble monomers in one more aspect: in industrial practice it has been customary to use a "protective colloid," notably polyvinyl alcohol or hydroxyethyl cellulose, as the principal surface-active material in the polymerization system rather than the micelle generator emulsifiers. Some emulsifiers may also be added to the system, but their role seems to be secondary to that of the protective colloid. In 1958, O'Donnell, Mesrobian, and Woodward reported the kinetics investigation of the VAc emulsion polymerization at 70°C using potassium persulfate as initiator and polyvinyl alcohol as protective colloid.[10] The initial quantity of the monomer was always considerably in excess of that required to saturate the aqueous phase at 70°C. The initiator concentration and the amount of monomer were kept constant and only polyvinyl alcohol concentrations were changed during the experiments. It was observed that, after an induction period of about 30 minutes, the conversion-time relationship was essentially linear up to conversions of at least 60 to 70%, indicating that the reaction rate was of zero order with respect to total monomer concentration. The increase in the polyvinyl alcohol concentration increased the rate of polymerization and there was a near constant of the ratio of the rate of polymerization to the 3/5th power of the polyvinyl alcohol concentration.[10] O'Donnell, Mesrobian, and Woodward kept the levels of initial monomer and the polyvinyl alcohol concentration constant and varied the potassium persulfate initiator concentration. After an induction period, which increased as the amount of initiator decreased, it was found that the polymerization rate was constant up to at least 60% conversion. The relationship between the logarithm of the steady rate and that of the initiator concentration was found to be linear, and the slope of this relationship indicates an order of reaction of $[I]^{0.7}$, almost double the order of 0.4 predicted by Smith-Ewart Case II kinetics. Light-scattering measurements failed to provide evidence of micelle formation, and O'Donnell, Mesrobian, and Woodward concluded that each molecule of polyvinyl alcohol might be a locus for the emulsion polymerization reaction.[10]

In 1952, Priest reported the particle growth mechanism in the emulsion polymerization of VAc.[11] The latices were made in capped bottles tumbled at 15 rpm in a thermostat at 50°C using potassium persulfate as initiator. He examined the latices by electron microscope. The particle size distribution measurements were made on 100 particles per cm^3 by averaging the sizes of 10 particles measured. Priest pointed out that polymerization of VAc in water is the initial process when water-soluble initiators are decomposed. With the growth of a given polymer chain, a point is reached at which the polymer is no longer soluble in water and should separate from solution. Since solution polymerization of VAc continues to occur throughout the whole range of conversion to monomer, new particles should form at a constant rate so long as monomer concentration is maintained at saturation. The maximum number of primary particles to be developed in the solution polymerization of VAc in water leading to a latex is equal to the number of polymer chains long enough to give water-insolubility formed throughout the course of polymerization. However, the number of particles actually found at the completion of an emulsion polymerization is the total number of primary particles less the reduction caused by coalescence during the course of reaction. The coalescence of particles is dependent on the quantity and efficiency of the material employed as stabilizer. Thus, the higher the concentration of the added sodium lauryl sulfonate anionic emulsifier, the smaller the average particle size.[11]

Priest determined that when no stabilizer and emulsifier are added during emulsion polymerization, the polyVAc latex particles are prevented from coagulating by adsorption of small quantities of sulfate groups derived during the cleavage of persulfate initiator. Average particle sizes were found to be large, on the order 0.1–1.0 micron in diameter, and having a narrow size distribution. The ultimate particle size in mixtures having the same monomer-to-water ratio is a function of the relative number of sulfate groups per particle. Therefore, as the concentration of persulfate initiator is increased, a decrease in the particle size is expected. This fact was not confirmed experimentally. The reason was the simultaneous increase of the ionic strength of the reaction system due to increasing the initiator concentration, which created an opposite effect. Experimentally, the higher the ionic strength, the higher the average particle size found. Since the particles are stabilized by electrostatic charges, these charges become effectively screened in the presence of electrolytes and, consequently, more coalescence takes place in the system, resulting in larger average particle size. Thus, the net effect of increasing the initiator concentration could not be predicted in advance. By increasing the temperature of the polymerization reaction, the average polymer chain length is shortened and the number of sulfate end-groups is increased. Therefore, a decrease in average particle size with an increase in reaction temperature is expected, which was confirmed experimentally.[11] It was determined that the increase in the monomer-to-water ratio resulted in the increase of the average particle size in the resultant latex.

In general, if single polymer molecules are the primary nuclei, Priest calculated that each particle should increase in size by a factor of about 1000 during the polymerization period. However, the number of particles decreased during the course of polymerization by a factor of at least 360 in the self-stabilized polymerization due to the inter-combination of particles. The intercombination rate decreases as the particles become larger.[11]

French published a paper in 1958, reporting the effect of nonionic emulsifier in VAc emulsion polymerization.[12] He used potassium persulfate initiator and nonionic ethylene oxide-propylene oxide block copolymer emulsifier (Pluronic) as micelle generators in VAc emulsion polymerization. This is an important paper to examine the rate of VAc polymerization and its relation with the emulsifier concentration, and showing its large differences from Smith-Ewart Case II kinetics. The polymerization recipes contained 55 parts of VAc monomer, which was hydroquinone-inhibited, at a concentration of 15 ppm (which is concordant with the industrial practice), 45 parts of deionized water, 0.041 parts of potassium persulfate, and varying amounts of non-ionic surfactant. Emulsion polymerizations were run at 65 to 70°C by a batch technique using a stirred, 1-liter glass reactor. Particle size measurements were carried out by electron microscope. French examined the number of particles as a function of conversion to see if the number of latex particles remained constant during the polymerization reaction as is the case with styrene polymerization. The number of particles in the reaction system was observed to decrease rapidly over the first 20% of conversion, but thereafter remained constant between 20 to 100% conversion, within experimental error. With the increase of the emulsifier concentration, the number of the latex particles in the same unit weight of latex rose much more sharply than what was expected from Smith-Ewart Case II kinetics at 65-70°C.[12] French also examined how much monomer was present in the latex particles by centrifuging the short-stopped latex samples. VAc monomer droplets are comparatively large, have a density of 0.93 g/cm^3, and will cream on centrifuging. Polymer particles, on the other hand, are much smaller, have a higher density, and will not rise to the top in the centrifuge tube. It is possible to determine the ratio of monomer to polymer in the centrifuge tube after a centrifugation time of 20 minutes at 1300 rpm. It appeared that the monomer diffused into the polymer particles by the time 13.5% conversion was reached but was largely in separate droplets at 7.7% conversion. This result contrasts with the situation in styrene-butadiene polymerization where the monomer does not diffuse into the polymer particle until well above 30% conversion. French concluded that latex particles containing polymer-plus-monomer have reached their maximum diameters by 13.5% conversion, and thereafter they change in diameter only as a result of the shrinkage accompanying polymerization.[12] In addition, French determined how the average particle size, number of particles, and total surface area changed with variation in surfactant concentration. Polymerizations were run to 99–100% conversions at 65°C. It was apparent that the particle size decreases and the number of particles increases with increasing surfactant concentration, but these relationships were not linear. However, the total surface area of the particles per 100 g of polymer was a linear function of the emulsifier concentration. French also pointed out that there was a linear relationship between the logarithms of the effective molecular area of various types of surfactants and their molecular volumes. It is evident that the effective molecular area increases with the increase of the molecular volume of the surfactant, and that the efficiencies of surfactants in emulsion polymerization systems on the basis of equal surface areas which the surfactants can occupy is a fair basis for comparison.[12]

According to French, there was another difference between the styrene and VAc emulsion polymerization: at low concentrations of styrene, the polymer particles are smaller. However, polystyrene particles continue to grow after the total polymer area is equal to the surfactant area. Styrene monomer continues to diffuse into polymer particles after the micelles have disappeared and no new particles can form. Therefore, one should take the total polystyrene surface area per 100 g of polymer at the point where soap micelles disappear to compare the efficiencies of surfactants in polymerization rather than near 100% conversion. In styrene emulsion polymerization, the number of particles formed has an $[E]^{0.6}$ dependency, whereas in vinyl acetate polymerization there is an $[E]^3$ dependency. French explained this dependency by assuming that all the VAc monomer has been imbibed within the polymer particles by the time emulsified micelles have been consumed. Gerrens has given a similar proposal.[13] For the simplest case where the particles are spheres of uniform size, the argument can be presented as follows: a system contains E grams of emulsifier in a unit volume (i.e., in 100 ml latex). Let the adsorption area of the emulsifier be φ, then the total adsorption area will be $= E\ \varphi$. If this total adsorption area of the emulsifier is equal to the surface area of the polymer particles (i.e., the interfacial area between the polymer and water phases) at the point when all the micelle disappears, then the maximum number, N, of particles that will form will be related to their radii, r, by the equation

$$\varphi E = 4\pi r^2 N \tag{3.1}$$

and the radius of the latex particle is given as

$$r = \left(\frac{\varphi E}{4\pi N}\right)^{1/2} \tag{3.2}$$

If one assumes that all the VAc monomer is imbibed within the polymer latex particles by the time micellar soap has been consumed, then there is a relation with the amount of the monomer and the radius of the particle. If the system contains, initially, M grams of monomer of density ρ, then the volume of the total monomer is, $V_T = M/\rho$. Then, one must have that

$$\frac{M}{\rho} = \frac{4}{3}\pi r^3 N \tag{3.3}$$

and the radius of the latex particle is given as

$$r = \left(\frac{3M}{4\pi\rho N}\right)^{1/3}. \tag{3.4}$$

Dividing Eq. 3.4 by Eq. 3.2 gives the volume-to-surface ratio particle radius:

$$r = \frac{3M}{\rho\varphi E} \tag{3.5}$$

By combining Eqs. 3.1 and 3.5, one obtains for the number of particles in the system

$$N = \frac{\rho^2\varphi^3 E^3}{36\pi M^2} \tag{3.6}$$

This derivation is an oversimplification of the process, but it is very useful to show the relation between N and $[E]^3$. French finally concluded that the divergence in detail between VAc and styrene emulsion polymerizations can be adequately explained by the greater water solubility of VAc, which enables the monomer to diffuse completely into the growing polymer particles very early in the reaction.[12]

French also reported the variation of the viscosity of the final latex with particle size. He used latex samples containing a total polymer content of 52% and measured their Brookfield viscosities. The higher the emulsifier concentration, the higher the viscosity that was found.[12] It is a known fact that the viscosity of a latex at a constant solids content increases with decreasing particle size. When the average particle size decreases for the constant amount of polymer, it is evident that the total surface area of the polymer particles increases. This means that the increase in the latex viscosity corresponds to an increase in the total surface area, and, because the surfactant concentration is proportional to the total surface area, the result of the increase in the latex viscosity with the increase in the surfactant concentration is reasonable. French plotted the logarithm of latex viscosity against the surfactant concentration; a straight line resulted which fit most of the experimental data. When the logarithm of the latex viscosity against the total surface area was plotted, another straight line, parallel to the first one, resulted. Furthermore, if the viscosity of the water phase is increased by addition of a water-soluble polymer (for example, by the addition of polyvinyl alcohol etc.), the viscosity of the latex is also increased for the same total polymer surface area. French derived a simple relationship to express the variation of latex viscosity with particle size:

$$\log \frac{\eta}{\eta_o} = \frac{k}{D} \tag{3.7}$$

where η is the viscosity of latex, η_o is the viscosity of water, k is a constant and D is the volume-to-surface ratio of particle diameter in microns. On the other hand, Maron, Meadow, and Krieger showed that there is a relation between the viscosity of the latices and the volume fraction of the polymer phase so that[14]

$$\log \frac{\eta}{\eta_o} = \frac{a\phi}{(1 - b\phi)} \tag{3.8}$$

where ϕ is the volume fraction of polymer phase, $(1 - \phi)$ is the volume fraction of the water phase, and a and b are constants. French then combined the two factors in a general equation to express the viscosity as a function of both particle size and total solids:

$$\log \frac{\eta}{\eta_o} = \frac{k_1 a\phi}{D(1 - b\phi)} \tag{3.9}$$

where k_1 is a new constant. Experimentally, the constant $b = 1$ was found. Furthermore, ϕ/D is proportional to the total polymer surface area per unit volume of latex so that, after evaluation of k_1, Eq. 3.9 reduces to Eq. 3.10, which states that the logarithm of viscosity is proportional to the polymer surface area divided by the water volume fraction:

$$\log \frac{\eta}{\eta_o} = 6.7x10^{-8} \frac{A}{(1 - \phi)} \tag{3.10}$$

where A is polymer surface area (cm^2/100 ml latex).

Okamura and Motoyama compared the emulsion polymerization behaviors of vinyl acetate, styrene, and vinyl caproate in 1962.[15] Vinyl caproate was chosen as a monomer which resembles vinyl acetate monomer in chemical nature, but styrene monomer in water-solubility. They showed that vinyl acetate polymerized even when no added emulsifiers were present and that the polymerization rate was insensitive to the concentration of the added emulsifier, whereas the styrene polymerization rate increased sharply as the concentration of the added emulsifier exceeded that required for micelle formation. They found that vinyl caproate resembled styrene rather than vinyl acetate in obeying the Smith-Ewart kinetics, thereby providing convincing evidence that the “anomalous” behavior of vinyl acetate is due to its high water-solubility, not to its chemical nature.[15] The similarity between the behavior of styrene and vinyl caproate in emulsion polymerization was also confirmed by Litt, Stannett, and Vanzo in 1972.[16]

Napper and Parts polymerized VAc in the aqueous phase at pH = 3.80 without using any stabilizing agents.[17] They maintained this pH by using an acetic acid-sodium acetate buffer and carried out the polymerization at 40°C for one week. All experiments were conducted with the dilatometer immersed in a bath thermostat. They used potassium peroxydisulfate as initiator. Polymer was formed as an extremely stable suspension, proving the stabilizing effect of the sulfate ions absorbed by the polymer. The typical conversion-time curve shows an initial region of accelerating rate followed by a region of decelerating rate, there being no significant region of constant rate. The relationship between the square root of the conversion and the time of the reaction was found to be approximately linear during the period of acceleration. There was proportionality between the slope of this plot and the square root of the initiator concentration.[17] The number of particles present was independent of conversion beyond about 16% and was independent of the monomer concentration. In the same year, Napper and Alexander examined the effect of the addition of low concentrations of emulsifiers to the emulsion polymerization of VAc, having their concentrations so low that they did not allow the formation of micelles in the aqueous phase.[18] They used anionic, nonionic, and cationic emulsifiers. Nonionic emulsifiers were found to have little effect on the polymerization reaction. Anionic emulsifiers accelerated the reaction, the effect increasing with the length of the hydrophobic part of the emulsifier, whereas cationic emulsifiers retarded the reaction and there was no effect of chain length of the emulsifier on this retardation behavior. In addition, anionic emulsifiers increased the particle concentration, whereas the cationic emulsifiers caused a decrease in the number of particles and gave a very broad distribution of sizes.[18] These effects were explained in terms of the ionic interactions between the emulsifier and the negatively charged oligomeric vinyl acetate radical species propagating in the aqueous phase. According to their description, the hydrophobic part of the anionic emulsifier molecule was adsorbed onto the polymer and then discouraged aggregation of polymer particles. When anionic emulsifiers having long hydrophobic chains were used, the tendency of the emulsifier molecule to be adsorbed onto the polymer was increased. The reason is simple: both the anionic emulsifier and the polymer particle were negatively charged and the presence of the long hydrophobic chain of the emulsifier had a screening effect on the Coulombic forces, which prevented the emulsifier adsorption. Therefore, the higher the chain length of the hydrophobic part of the emulsifier, the higher the emulsifier adsorption on the polymer. Instead, cationic emulsifiers increased the aggregation of the particles by a charge-neutralizing effect.[18]

In 1965, Dunn and Taylor confirmed the formation of stable suspension of polyVAc when polymerization was carried out in the absence of added emulsifier and colloids by using persulfates as emulsifiers at 60°C.[19] The polymer suspension was so stable that it did not settle unless centrifuged at high speed. The reaction occurred in three stages: an initial acceleratory stage where a solution polymerization took place, a stage of maximum and constant rate between 20–45% conversion in which the polymerization occurred in the monomer-swollen polymer particles, and then a final period of deceleration. Stirring had no effect upon either the polymerization rate or the average size of the particles. The maximum polymerization rate was found to be of the order of 0.64 with respect to initiator concentration, and to increase with initial monomer concentration when the initiator concentration was kept constant.[19] The number of particles increases with the increase of initiator concentration, whereas increasing monomer concentration produces fewer but larger particles. The size of polyVAc particles is some ten times larger than those formed in styrene emulsion polymerization. This large size of particles may allow the coexistence of several polymer radicals. Knowing the number of particles and the monomer concentration in the particles, and assuming a value for the rate coefficient for the propagation step, Dunn and Taylor estimated the number of radicals per particle. This value increased with conversion and with the increase of the initiator concentration, ranging from 0.17 to 61.5 as shown in Figure 3.1. Since the number of radicals per particle is 0.5 in ordinary styrene emulsion polymerization, obeying Smith-Ewart Case II kinetics, then the calculated number of active centers appears implausibly high. However, it is conceivable that such a large number of growing radicals could coexist in a particle which was so viscous as to prevent mutual termination between polymer radicals, and in which the only alternative termination process involves the approach of a charged sulfate radical to a particle of similar charge.[19] Monomer concentrations in the swollen particles were found to be very low when compared with conventional styrene emulsion polymerization. In addition, the reaction was different from ordinary emulsion polymerization in that the monomer concentration in both polymer and water phases decreased continually throughout the reaction. The addition of a neutral salt such as potassium sulfate decreased the reaction rate, a stable suspension was not formed, and the latex precipitated. The addition of the polyvinyl alcohol stabilizer reduced the maximum rate of polymerization and the particle size. The average particle diameters decreased from 0.3 micron to 0.1 micron by the addition of 0.24% w/v polyvinyl alcohol. It was proposed that chain transfer reactions between vinyl acetate and polyvinyl alcohol could occur giving a graft copolymer and retard the rate of polymerization because of the introduction of an alternative termination. Since the approach of a charged radical to a charged particle is not involved, the termination between polyvinyl acetate and polyvinyl alcohol may be favored.[19]

In 1962, Elgood, Gulbekian, and Kinsler presented experimental results on the mechanism of vinyl acetate emulsion polymerization in which monomer, emulsifier, and initiator were all added continuously to the reactor, similar to the industrial delayed-addition practice.[20] They used a 1-liter flask equipped with a mechanical stirrer and reflux condenser, inhibited vinyl acetate monomer (with 20 ppm hydroquinone), two nonionic emulsifiers (ethoxylated nonyl phenol with 16 and 20 moles of oxyethylene units), an anionic emulsifier (sodium dodecyl benzene), and ammonium persulfate-sodium formaldehyde sulphoxylate dihydrate initiator pair in their two different recipes. No buffer system was used. The emulsion was gently purged with nitrogen throughout the process. Samples were removed at 15-minute intervals, polymer concentrations were determined gravimetricaly, and average particle sizes were determined by turbidimetry which was precalibrated by electron microscopy. Particle volumes, numbers, and total surface areas were then calculated from the measured solids contents, weight-average particle diameters, and taking the density of polyVAc in emulsion to be 1.1.[20] The results are given in Figures 3.2–3.4. The number of particles was found to be in accordance with those of French,[12] who applied batch emulsion polymerization. In the first recipe only nonionic emulsifier (ethoxylated nonyl phenol with 16 moles of oxyethylene units) was used, whereas in the second recipe both nonionic and anionic emulsifiers (ethoxylated nonyl phenol

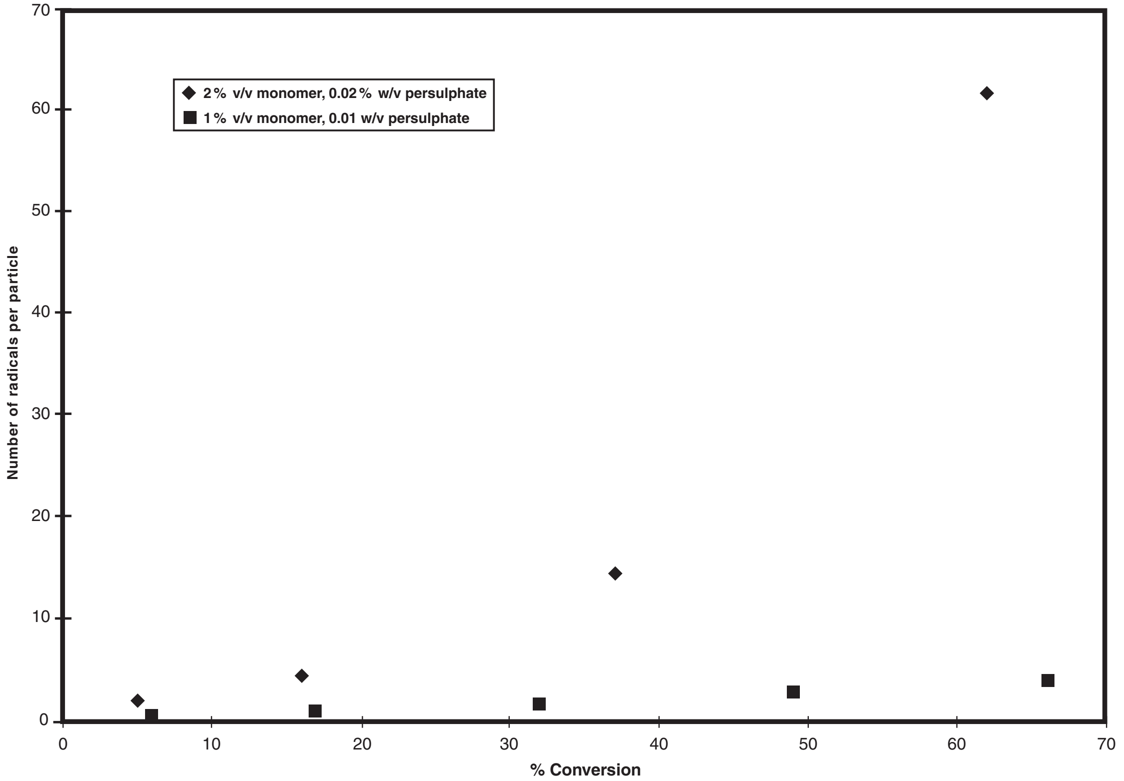


FIGURE 3.1 Variation of the number of vinyl acetate radicals per particle with conversion (data from Dunn and Taylor[3.19]).

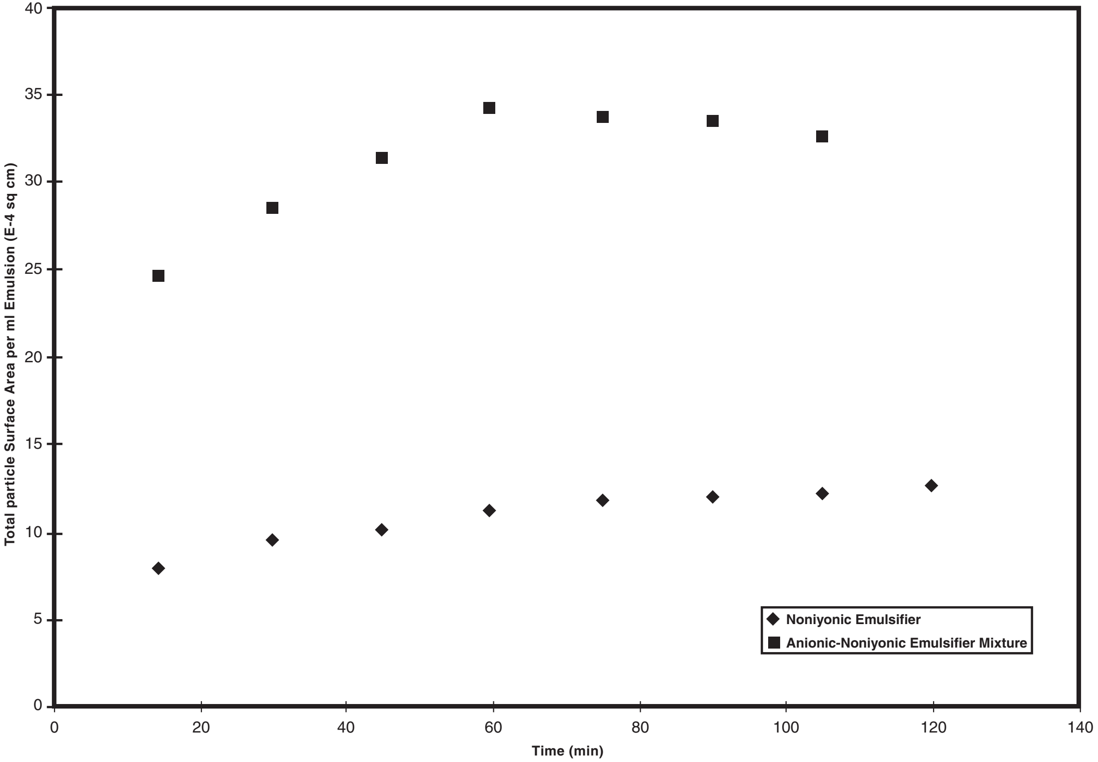


FIGURE 3.2 Variation of total surface area of particles per ml of latex with time (data from Elgood, Gulbekian, and Kinsler[3.20]).

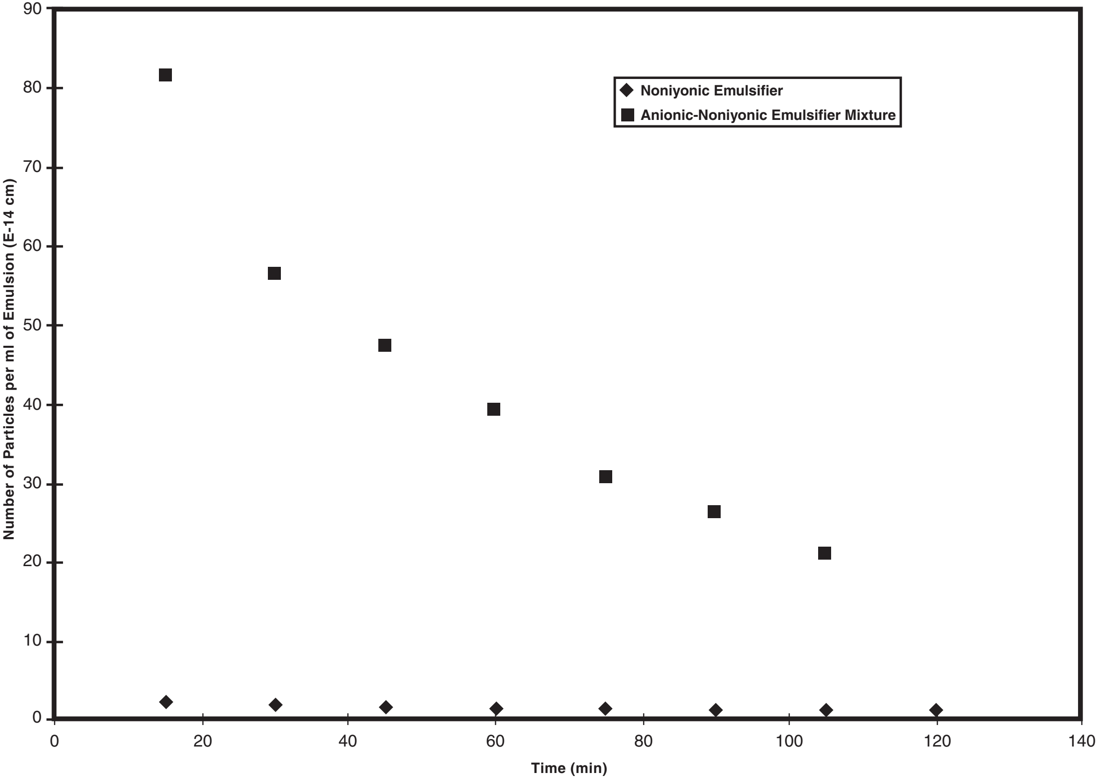


FIGURE 3.3 Variation of the number of particles per ml of latex with time (data from Elgood, Gulbekian, and Kinsler[3.20]).

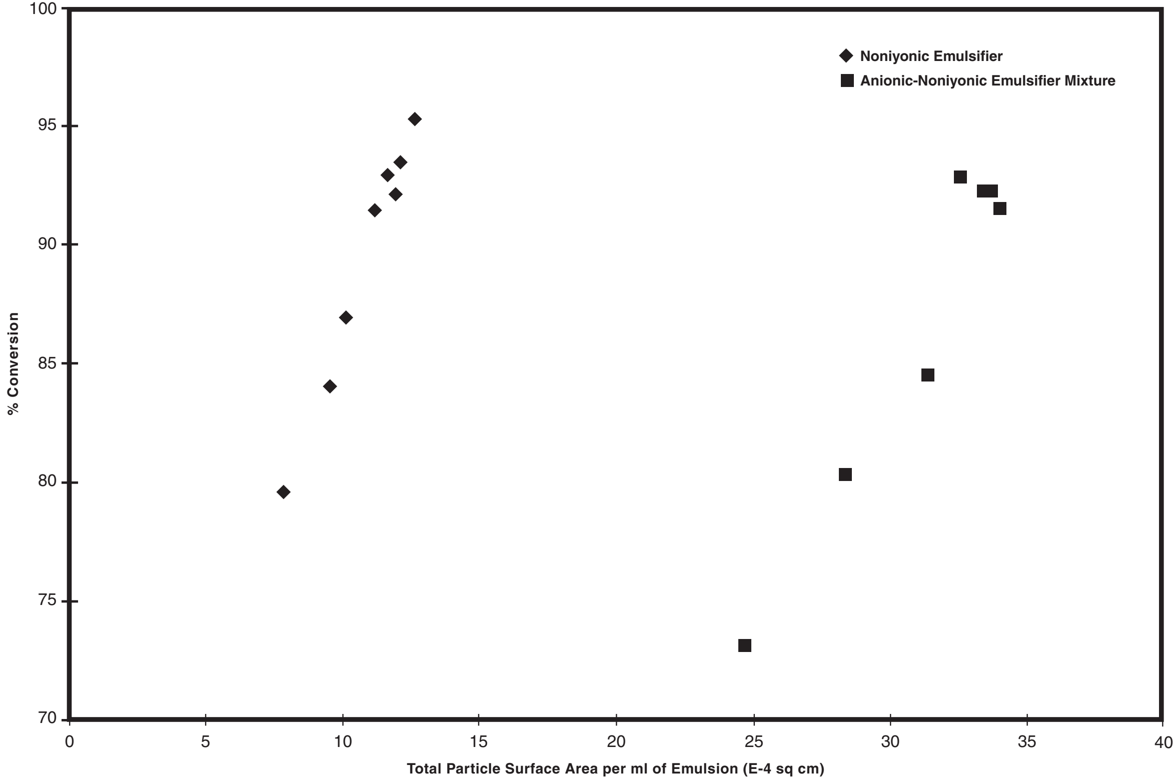


FIGURE 3.4 Variation of conversion percent with total particle surface area (data from Elgood, Gulbekian, and Kinsler[3.20]).

with 20 moles of oxyethylene units and sodium dodecyl benzene) were used. They determined that the number of particles was approximately 40 times more in the second recipe than in the first, and the number of particles decreased as polymerization proceeded for both recipes. However, in the first recipe it remained constant over the last three quarters of the process, whereas in the second recipe it diminished throughout the reaction. In contrast to this, in the first run the total particle surface area per ml of emulsion increased throughout the process, while in the second run it remained constant over the last three-quarters. In both runs, the % monomer converted to polymer appeared to be most closely related to the total particle surface area per ml of emulsion. Elgood, Gulbekian, and Kinsler concluded that the total particle area was the most important parameter to control the rate of polymerization of the high water-soluble VAc monomer.[20]

In order to investigate the rate of polymerization, seeded emulsion polymerizations were carried out. The paper by Patsiga, Litt, and Stannett, which was published in 1960, compares the emulsion polymerization of vinyl acetate at 60°C with that of styrene at 60°C using, in both cases, potassium persulfate as initiator and seed latices.[21] In the first step, the seed latices were prepared by using sodium lauryl sulfate as the micelle generator. In the second step, the seeded polymerizations were carried out under conditions such that no new particles were formed during the reaction. For styrene monomer, good agreement was obtained with the Smith-Ewart Case II kinetics. For VAc monomer, there was a direct proportionality between the rate of polymerization and the 0.2th power of the number of particles. They also realized that there was a positive polymerization rate when no particles were present. Such a relationship is reasonably explained by the simultaneous occurrence of polymerization reaction in both water phase and particles. Furthermore, the relative magnitudes of the two rates are consistent with the view that most of the polymerization occurs in the aqueous phase.[21] Patsiga, Litt, and Stannett described the polymerization mechanism as soluble polyvinyl acetate molecules are produced which are stabilized by the emulsifier, and these function as nuclei for further polymerization and form the monomer-swollen polymer particles. When the total surface area of the particles exceeds the covering power of the emulsifier, the remaining polymer macromolecules and microparticles are destabilized and can be swept up by larger particles. The number and size of the particles are constant during the main part of the reaction, between 20–85% conversion. Chain transfer to monomer and polymer probably occurs in the water phase, and polymerization in a particle proceeds until chain transfer to monomer occurs. The monomer free radical ($M\cdot$) diffuses out of the particle and polymerization continues in the water phase until new polymer molecules are again swept up. It was also concluded that the radical would spend only 4–20% of its time in the polymer phase. The constancy of the polymerization rate between 20–85% conversion was attributed mainly to the monomer-swollen latex particles acting as reservoirs of monomer, by contact with which the aqueous phase remains saturated.[21]

Litt, Patsiga, and Stannett published another paper on the same subject some ten years after the first and developed their mechanistic ideas more fully.[22] They used dilatometry to follow the kinetics at 60°C under an atmosphere of nitrogen and presented additional data for both seeded and nonseeded polymerizations. They also examined the effect of the presence of the electrolytes such as potassium sulfate and found that it increases the polymerization rate in nonseeded systems. In seeded systems, an order of reaction of 0.8 was observed for initiator (potassium persulfate) compared with about unity for the nonseeded systems. In addition, a two-fold variation of the monomer-to-water ratio produced no change in rate of polymerization rate in the case of nonseeded systems. The zero-order dependence of rate of polymerization upon monomer concentration over most of the reaction is explained in terms of propagation occurring in the particles and termination in the aqueous phase.[22] They presented a polymerization mechanism: polymerization is initiated in the aqueous phase; it picks up emulsifier as the polymer grows and becomes a polyelectrolyte. After many collisions, the polymer with an average degree of polymerization between 50 and 300 is swept by a particle. Activation energy is necessary for breaking through the ionic double layers of the polymer and the particle. Growth of the now nonsolvated radical continues in the particle until chain transfer to monomer occurs. The monomer radical passes into the aqueous phase and usually reinitiates chain growth there. Termination occurs mainly in the aqueous phase. As the monomer concentration in the particle decreases, the rate of chain transfer to monomer decreases also. Thus, radicals stay in particles longer and their concentrations increase almost inversely to monomer concentration. Then, the rate of polymerization remains almost constant. At about 90% conversion, the monomer concentration in the aqueous phase starts decreasing rapidly, radical termination is favored, and the rate of polymerization decreases.[22]

Vanzo, Marchessault, and Stannett developed a vapor pressure method to determine the solubility of VAc monomer in both the aqueous phase and the polymer particles in 1965.[23] Although latex polymers are actually soluble in monomer, they swell only to a well-defined limit in the latex system, even in the presence of excess monomer. The osmotic driving force is balanced by the interfacial tension at the polymer-water interface and equilibrium swelling is attained. In emulsion polymerization systems, the presence of emulsifier greatly lowers the interfacial tension and allows a substantial amount of swelling. The vapor pressure measurements permit an estimation of the partial molar free energy of the monomer-polymer system. A thermodynamic treatment yields a relationship from which the monomer-polymer interaction parameter and the interfacial tension can be obtained simultaneously. The increased solubility of monomer in the polymer (such as VAc) is reflected in a lowering of the interaction parameter. For VAc-polyVAc system, the monomer-polymer interaction parameter decrease with the increase in temperature, whereas the interfacial tension is calculated nearly constant and is equal to 3.1 mN/m.[2,23]

In 1973, Klein, Kuist, and Stannett examined the effect of the ionic strength of the water phase and of temperature upon the solubility of vinyl acetate monomer in the monomer-swollen polymer particles, which were stabilized by the adsorption of ionic species.[24] The ionic strength was controlled by the addition of potassium sulfate solution. It was determined that the interfacial tension between the particle and the aqueous phase decreased, and the solubility of the VAc monomer in the monomer swollen-latex particle increased sharply with increasing ionic strength. The polymer-solvent interaction parameter was not affected by variation in ionic strength. This was explained in terms of decrease in interfacial surface free energy associated with partial collapse of the electrical double layer at the interface. In contrast to this, the solubility of monomer in the aqueous phase was found to be nearly constant with varying ionic strength. The solubility of the monomer in the monomer-swollen polymer also increased with the temperature. The variations of interfacial tension with temperature were found to be complex, but entirely dependent on the entropic consideration of adsorption. The polymer-solvent interaction parameter had a linear inverse temperature dependence.[24]

In an important publication, published in 1968, Gulbekian pointed out that the examination of the kinetics of VAc emulsion polymerization had usually been carried out in one-stage processes in which all the ingredients were added at the start. Instead of the one-stage approach, he investigated the emulsion polymerization system with uniform continuous addition of VAc monomer, nonionic emulsifier (propylene oxide-ethylene oxide block copolymer), and ammonium persulfate initiator.[25] He explained that in the one-stage process, the overall concentration of the monomer, the ratio of emulsifier to monomer, and the particle size would vary during the polymerization, resulting in a very complex kinetic picture. He proposed that in order to reduce the number of the uncontrolled variables, a system involving continuous addition of monomer, emulsifier, initiator, and alkali buffer was required. This process was expected to yield a narrow distribution of particle diameters in the final latex. He used a stainless steel pilot reactor with a volume of 16 liters and suitably equipped with a stirrer, temperature recorder, and three controlled flow lines. VAc monomer inhibited with 15 ppm hydroquinone was used, similar to industrial practice.[25] After the addition of the first 10% portion of the total monomer-emulsifier solution plus some parts of water and initiator and the remaining monomer-emulsifier solution, the initiator and the NaOH solution were added to the reactor continuously by separate streams at uniform rates over about four hours, and the temperature was kept at around 71°C. Small samples were taken every 30 minutes; the nonvolatiles were determined gravimetrically and the weight average particle sizes by turbidimetry. The quantity of the emulsifier was varied between 2 and 20% by weight on VAc monomer. The increase of the weight-average particle diameter ($2r$ in Figure 3.5), the decrease of the total number of particles per gram emulsion (N/W in Figure 3.6), and the near constancy of the total particle surface area per gram emulsion (A/W in Figure 3.7) with polymerization times are given in Figures 3.5–3.7 for varying emulsifier/monomer weight ratios. Since there is a direct proportionality between the polymerization time and the weight of the emulsion, the increase of the total particle surface area per unit weight of emulsion (A/W) with the increase of the emulsifier/monomer weight ratio, which is proportional to $[E]$, was calculated from the mean values of (A/W) and is given in Figure 3.8. Gulbekian concluded that in a continuous-addition process, the total particle surface area of polymer per unit weight of emulsion varied directly as the emulsifier-monomer weight ratio.[25] This relationship can be shown as

$$\frac{A}{W} = 4\pi r^2 \frac{N}{W} \propto [E] \tag{3.11}$$

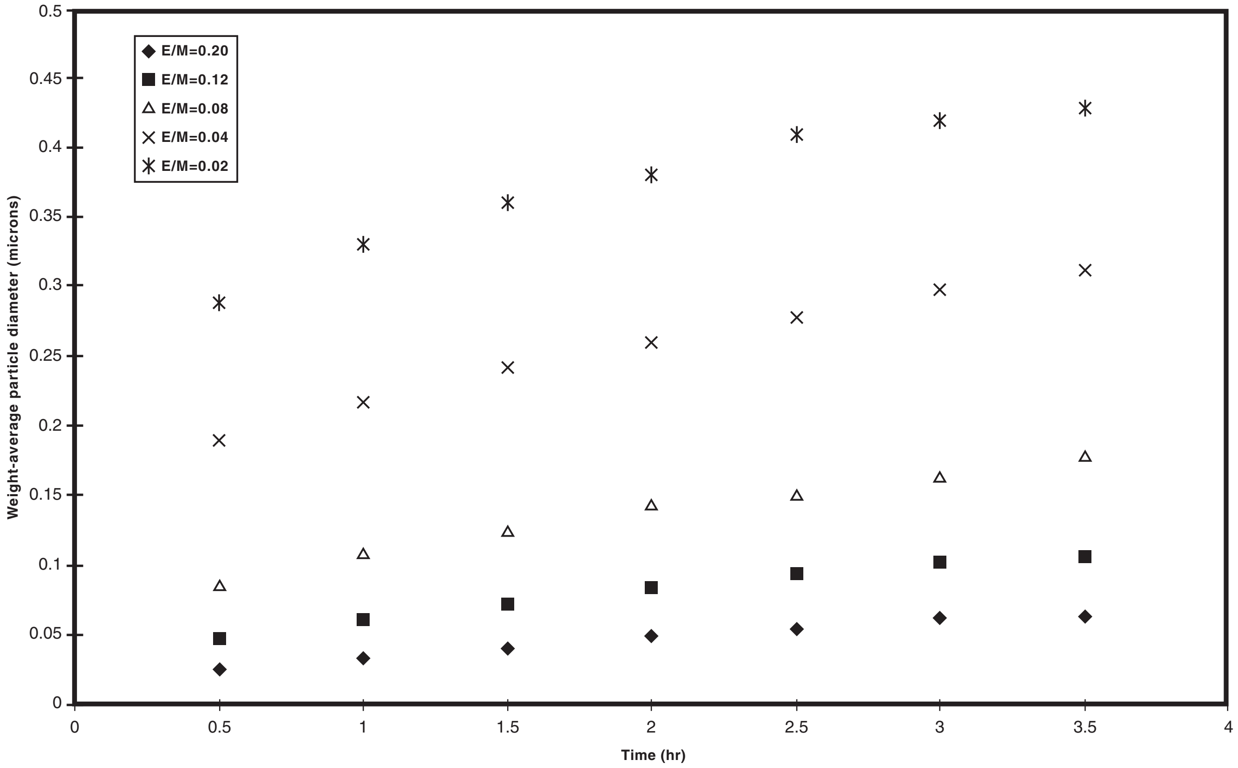


FIGURE 3.5 The increase of weight-average particle diameter with time (data from Gulbekian[3.25]).

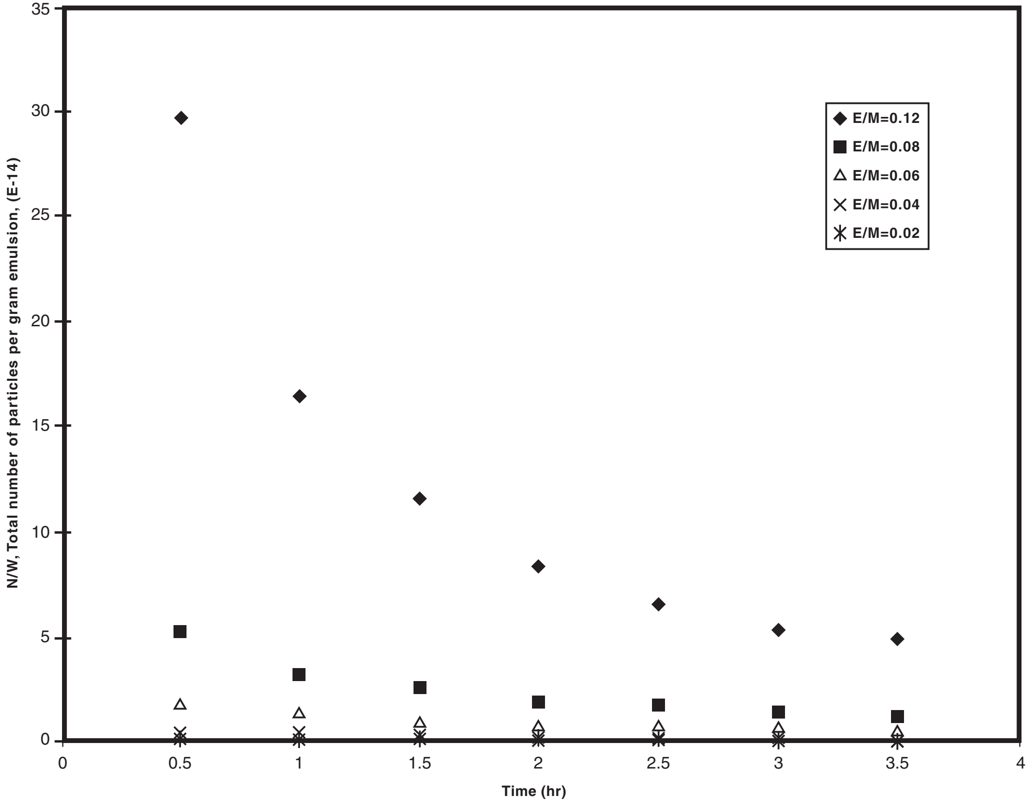


FIGURE 3.6 The decrease of the total number of particles per gram of latex with time (data from Gulbekian[3.25]).

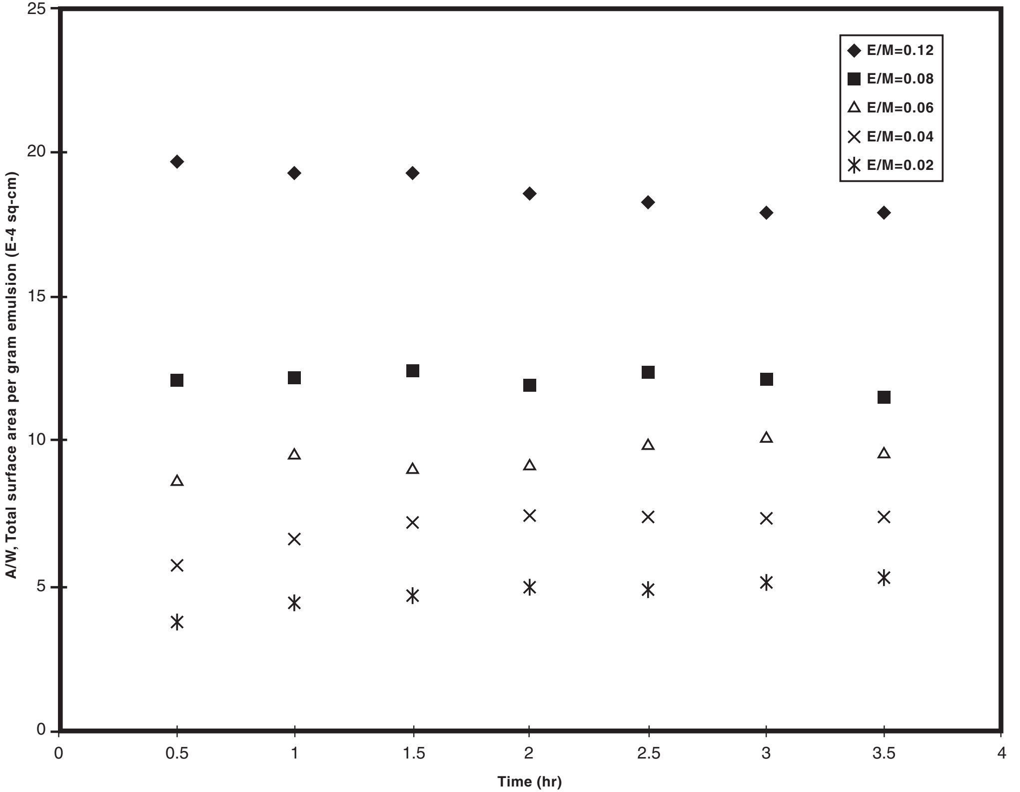


FIGURE 3.7 Variation of total surface area of particles per gram of latex with time (data from Gulbekian[3.25]).

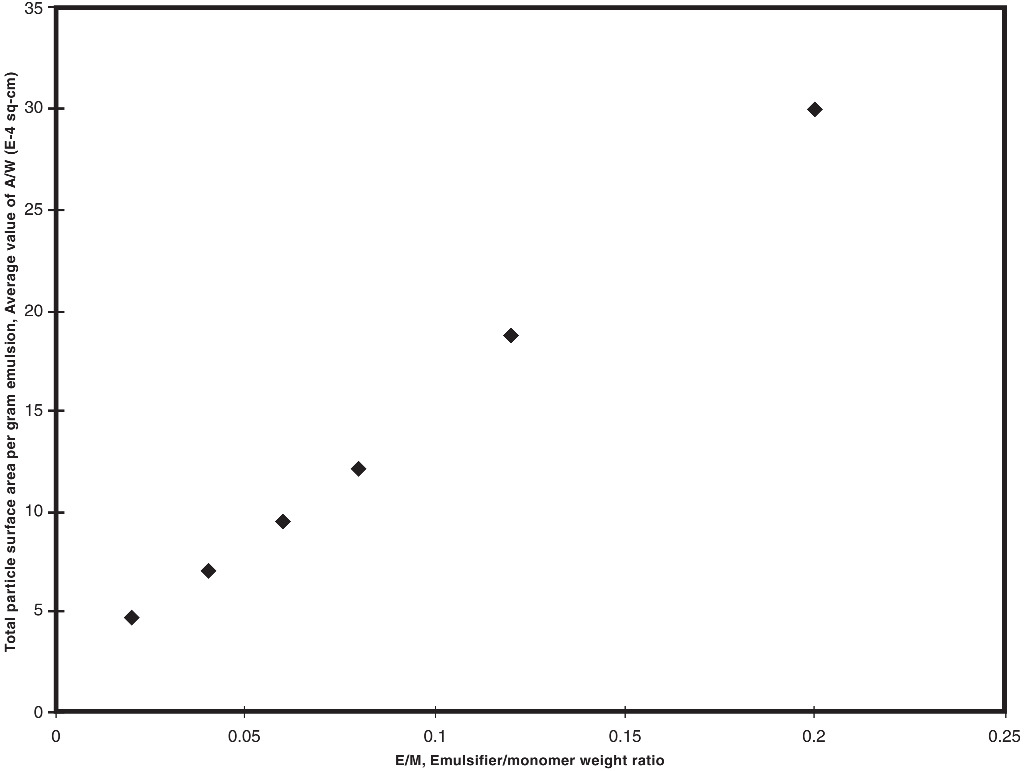


FIGURE 3.8 The increase of total surface area of particles per gram of latex with emulsifier/monomer weight ratio (data from Gulbekian[3.25]).

This equation is in agreement with the assumption that a minimum quantity of adsorbed surfactant per unit particle surface is necessary for stability.[26] In the system studied, Gulbekian calculated 2.0 – 2.4 × 10^{12} molecules of nonionic emulsifier were required to stabilize 1 cm^2 of polyVAc in emulsion. Since at a constant polymer-emulsion weight ratio one may write

$$\frac{4}{3} = \pi \, r^3 \rho \frac{N}{W} = const. \tag{3.12}$$

then, by dividing Eq. 3.12 by Eq. 3.11, one obtains

$$r \propto \frac{1}{[E]} \tag{3.13}$$

The above expression indicates that a smaller particle radius is obtained by the use of higher concentrations of the emulsifier, thus resulting in higher latex viscosity. The particle size is determined by the surface area that the given concentration of surfactant is able to stabilize. Alternatively, by combining Eqs. 3.11–3.13, one obtains

$$\frac{N}{W} \propto [E]^3 \tag{3.14}$$

which is in agreement with French's one-stage VAc emulsion polymerization process for the same kind of nonionic emulsifier.[12] It was shown that, for continuous-addition processes, the above relationship applies also to other monomers, regardless of their solubility in water, such as styrene and methacrylate esters.[25]

Gulbekian also concluded that the water phase was the main locus of polymerization when water soluble initiators such as persulfates were used and the rate of polymerization was dependent on the solubility of the monomer in the water phase. He proposed that $[M]$ should be regarded as the monomer concentration in the water phase, and not the monomer concentration in the latex particle as in styrene polymerizations. The solubility of VAc monomer in a range of nonionic emulsifier solutions was determined, and the emulsifier concentration was found to have a much greater effect on the less water-soluble monomers such as styrene than on the more soluble ones such as VAc.[25]

Netschey, Napper, and Alexander have described that the rate of polymerization of VAc in seed latices is affected by the nature of the stabilizing layer surrounding the seed particle.[27] They thought that, when the seed concentration is sufficient to prevent new nucleation, the emulsifiers that are adsorbed on the latex particles have an effect on the rate of polymerization. They then prepared three types of stabilized polyVAc seed latices: first, an electrostatically stabilized seed latice was prepared by the aqueous solution polymerization of VAc monomer in the presence of sodium hexadecyl sulfate; second, an amphipathic steric stabilizer (nonionogenic) poly(ethylene oxide-block-vinyl acetate) was synthesized by polymerizing vinyl acetate onto preformed polyethylene oxide, using benzoyl peroxide as initiator; third, seed particles stabilized by a combination of electrostatic and steric mechanisms were prepared by adsorption of the steric stabilizer on the surface of the electrostatically stabilized particles.[27] Then, polymerizations were carried out by using these seed latices with potassium persulfate as initiator. It was determined that polymerizations occurred much more slowly in seed latices protected by an adsorbed steric, nonionogenic stabilizer than in those stabilized electrostatically. Polymerization in seed latices stabilized by a combination of steric and electrostatic molecules occurred even more slowly.[27] Although electrostatic stabilization by adsorbed anions should discourage the ingress of the negatively charged oligomeric free radical species into the particle, it evidently provides a less formidable barrier than does the electrically neutral but rather viscous layer which surrounds the particles when a nonionogenic stabilizer is used. When a combined stabilizer system is used, the presence of both viscous and electrostatic barriers is evidently more formidable than either is separately, and gives an even slower rate of polymerization. Netschey, Napper, and Alexander proposed that the foregoing concepts are obviously relevant to the understanding of the kinetics of VAc emulsion polymerization. They criticized most of the earlier studies that ignored the profound kinetic influences of stabilizing barriers.[27]

Noro published a paper on VAc emulsion polymerization in relation to the chemical structure of polyvinyl alcohol used as the protective colloid.[28] Emulsion polymerization does not occur with polyvinyl alcohol synthesized by acid hydrolysis, but a fairly stable emulsion was obtained with reacetylated polyvinyl alcohol, although the viscosity was low. When fully hydrolyzed polyvinyl alcohol was used as an emulsifier in order to improve water resistance, the storage stability was found to be poor. Results showed that the viscosity, particle size, stability, and freeze-thaw stability of the final latex were determined largely by the fine chemical structure of the polyvinyl alcohol used in the polymerization.[28]

Hayashi, Iwase, and Hojo carried out the emulsion polymerization of vinyl acetate in the presence of polyvinyl alcohol using a dilatometer.[29] They stated that the use of potassium persulfate initiator resulted in sulfate end groups in the polymer chains, which impart extreme stability to the final latex. However, when hydrogen peroxide initiator was used, the hydroxyl groups were linked to the end groups, resulting in a destabilized latex that precipitates in the absence of polyvinyl alcohol.[29] They determined that the rate of polymerization increased during the formation of polymer particles (first stage), remains constant because the number of polymer particles is kept constant (second stage), and finally becomes first order with respect to the monomer concentrations (third stage). They found that the maximum rate of polymerization reaction with respect to the polyvinyl alcohol concentration was found to be zero, independent of the initiator concentration when potassium persulfate was used as initiator. However, when hydrogen peroxide was used as the initiator, the maximum rate of polymerization was proportional to 0.22 power of polyvinyl alcohol concentration. They then studied the influence of the variation in the potassium persulfate concentration on the rate of polymerization and found that the maximum rate of polymerization varied at the power 0.42 with the initiator concentration, close to the theoretical predictions of 0.5 by Litt et al.[22] Finally, Hayashi, Iwase, and Hojo described the emulsion polymerization of VAc in the presence of polyvinyl alcohol as follows: the polymerization of VAc is initiated by water soluble initiators in the aqueous solution, even in the absence of any emulsifiers. When the polymer particles are formed in water, most of the end groups of the polymer chains exist on the surface of the resulting particles, and these groups contribute to the stabilization of the latex particles through both electrical repulsion and hydration effects. The sulfate end group originating from persulfate initiators has both effects whereas the hydroxyl end group has only a hydration effect, resulting in less stabilized latices. They concluded that the formation and stabilization of latex particles is not related to the effect of polyvinyl alcohol as emulsifier, but more to the effect of the sulfate end group.[29]

Gulbekian and Reynolds made a survey on the use of polyvinyl alcohol as an emulsifier and protective colloid in the emulsion polymerization of VAc and other monomers.[30] They examined the optimum properties of the polyvinyl alcohol types, i.e., their degree of hydrolysis, the average molecular weight on the emulsion polymerization mechanism, and the stability of the final latices. They stated that maximum conversion and minimum precipitate were obtained when 82.6–91.5% hydrolyzed polyvinyl alcohol with the maximum molecular weight in 4% (of the weight of the monomer) was used in conjunction with half of the amount of 10 mole ethoxylated nonyl phenol emulsifier. Gulbekian and Reynolds also pointed out the interactions of polyvinyl alcohol with the persulfate initiators, which degrades the polyvinyl alcohol macromolecule by oxidation reaction resulting in a loss in emulsion viscosity.[30]

Netschey and Alexander published two papers in 1970 that examined the effect of free monomer distribution on the particle size of VAc latices[31] and the effect of preformed latex upon polymerization kinetics.[32] They prepared seed latices by using potassium persulfate initiator and sodium hexadecyl sulfate emulsifier. The seed latex was then dialyzed to remove any free initiator and surfactant. They determined the sizes of these seed latices. Later, kinetics of emulsion polymerizations initiated by potassium persulfate were studied by dilatometry, with different concentrations of seed latex, both in the absence and in the presence of sodium hexadecyl sulfate surfactant.[32] It was found that even with the lowest concentration of seed latex (approximately 7×10^{11} particles/ml) no new particles are formed. There was no sign of any fine particles at the end of a run. They believe that the emulsion polymerization of VAc occurs exclusively in particles of polymer swollen by monomer. When seed latex was added in the presence of the emulsifier, there was clearly a dramatic difference between the high and low concentration of the seed systems; no fresh nuclei were formed with the high concentration of seed latex, whereas fresh nucleation occurred with the low concentration of the seed latex.[32] They explained that with the high seed system the seed particle surface was clearly not saturated with emulsifier, even at the commencement of polymerization. Therefore, any oligomer molecules forming in the aqueous phase could not be stabilized by surfactant adsorption before they were incorporated by a seed particle. No new nuclei were formed and all polymers were deposited on the seed particle. With the low seed system, at the start there was clearly a considerable excess of emulsifier. Only about 15% is required to saturate the surface of the seed particles and, under those conditions, oligomers forming in the aqueous phase are rapidly stabilized by adsorption of surfactant, leading to fresh nucleation and a consequent small particle size in the final latex.[32] Netshey and Alexander also indicated that the effect of sulfate anions was minimal. Based on a degree of polymerization of approximately 2000, and assuming two sulfate anions per chain, the surface coverage of the latex particle was insufficient to substantially affect the above conclusions.

Netschey and Alexander determined the distribution of the VAc monomer between the aqueous phase and in polyVAc polymer at 20° and 40°C.[31] When the partition coefficients of VAc monomer between aqueous phase and polymer is determined, it is possible to calculate the monomer concentration, $[M]$. Napper and Parts were the first to measure this figure by centrifugation of the latex and estimation of the VAc in the supernatant solution by bromometric titration.[17] However, Netschey and Alexander used an interferometer to determine the concentration of the residual VAc in the aqueous phase. Known mixtures of the resulting latex and monomer were allowed to equilibrate for standard data derivation. The latex was then coagulated by addition of 0.5 mg hexadecyltrimethyl ammonium bromide, and the clear supernatant was used for interferometric analysis. The uptake of monomer in grams-per-gram of polymer was then calculated.[31] They also measured the density of the polymer particles swollen by monomer, the particle size in the presence of the monomer, and the saturation concentration of VAc monomer in water in order to obtain a complete picture of the process. The partition coefficient, K is defined as

$$K = \frac{\textit{Vinyl acetate in polymer}\left(g/g\right)}{\textit{Vinyl acetate in aqueous phase}\left(g/g\right)} \tag{3.15}$$

It was found that there was a sharp increase in the VAc uptake in polymer particles with the increase in the VAc concentration in the aqueous phase, and K fluctuates between 10 and 50 for 40°C.[31] The diameters of particles have been measured by means of the analytical ultracentrifuge. Comparison of the diameters so measured with those calculated from the monomer distribution data showed quite reasonable agreement. The variation of number of particles with percentage conversion showed that the number of latex particles had stabilized and reached a nearly constant value by about 10% conversion.[31]

Friis and Nyhagen reported the kinetics of VAc polymerization at 60°C in the presence of sodium lauryl sulfate as emulsifier and potassium persulfate as initiator.[33] The rate of polymerization was found proportional to the 0.5th power of the initiator concentration and the 0.25th power of the number of particles. The number of particles was, in turn, proportional to the 0.5th power of the emulsifier concentration. The conversion-time curve is linear for much of the course of the reaction.[33]

Elgood and Gulbekian investigated the redox-initiated emulsion polymerization of VAc at 50°C. The initiator system comprised a combination of ammonium persulfate, a reducing agent, and a salt of a metal of variable valency.[34] They used three reducing agents — sodium formaldehyde sulphoxylate, sodium hydrophosphite, and hydrazine hydrate — in combination with the chlorides of titanium (III), iron (III), cobalt (II), and copper (II). Nonionic ethoxylated nonyl phenol and anionic sodium dodecyl benzene sulfonate emulsifiers were also present in the reaction systems. Sodium formaldehyde sulphoxylate was found to work with all four metal ions; the other two reducing agents worked only with copper (II) ions.[34] Elgood and Gulbekian determined that if the metal ion concentration was reduced below a certain critical level, polymerization occurred only very slowly at temperatures below a minimum polymerization temperature. For maximum conversion of monomer to polymer, it is necessary to adjust the pH of the system. The initial pH was 3.5 and dropped, as the reaction proceeded, to about 2.2 at completion unless adjusted by the addition of small amounts of alkali such as potassium hydroxide. For each metal ion, there was an optimum final pH for maximum conversion. The optimum was especially pronounced for systems containing copper (II) and occurred at about pH = 4. The need to increase the pH as reaction proceeds was associated with an increase in the ratio of polymer to water. According to Elgood and Gulbekian, as this ratio increases, a greater proportion of the available monomer will partition into the polymer particles, and in order to polymerize it the locus of polymerization must transfer progressively from the water phase to the polymer particle. It is thus necessary to reduce the solubility of the metal compound in the aqueous phase and increase its solubility in the polymer particles. This is achieved by increasing the pH of the system, hence favoring the formation of the less water-soluble metal emulsifier. They showed experimentally that the solubility decrease of the metal-emulsifier formed from the anionic emulsifier (dodecylbenzene sulfonate) in the water phase resulted in increasing effectiveness in promoting conversion.[34]

In spite of the economic importance of emulsion polymerization reactors, the mathematical modeling of these reactors became an important activity only after the development of the Harkins theory in 1945. The particle morphologies had gained importance until then. Initially, the polymer particle was considered a uniform mass of monomer and polymer with no internal structure. However, it was shown that the particles have a definite internal structure. Morton et al.[35] examined the thermodynamics of the particle swelling by monomer in 1954. They showed that a swelling equilibrium is reached when the change in the free energy of mixing and the change in the surface free energy balance, using Flory-Huggins theory for mixing and the Kelvin equation for surface free energy.[35] Gardon showed that the prediction of monomer concentration in a swelled polymer particle from the thermodynamic theory was consistent with experimental results obtained by either equilibrium swelling or monomer drop disappearance.[36] On the other hand, nonuniform particle theories were developed: Medvedev et al. postulated that the site of the polymerization reaction was in the adsorbed micelle layer on the surface of the particle.[37,38] According to his view, the interior of the particle contains only monomer and dead polymer, the rate of reaction is proportional to the total surface area in the system, and for fixed amounts of emulsifier this has been considered constant. Medvedev suggested that the constant rate of polymerization observed by many workers in Interval II was a strong verification of his theory.[37] Later, Williams and co-workers presented experimental evidence to support the view of nonuniform particles.[39-41] They showed that the monomer concentration in the particle decreases with conversion in Interval II, while the polymerization rate remains constant. They proposed a core-shell model of the polymer particle with a polymer rich core and a monomer-rich shell, and assumed that the polymerization took place at the growing polymer-monomer interface.

However, when no emulsifier is used in emulsion polymerization, a new approach is needed in order to model the polymerization. Fitch postulated a mechanism for such processes in which those radicals were formed and later grew in the aqueous phase.[42] When these oligomers exceed their solubility limit they precipitate out and form polymer particles. This theory was used to explain the mechanism in which particles were formed in the absence of emulsifiers by Dunn et al.[19] for VAc, by Eliseeva et al.[43] for acrylates, by Ohishi[44] for vinyl chloride, and by Robb[45] and Schulz et al.[46] for styrene monomers.

Earlier emulsion polymerization models were developed for batch reactors. However, in industry most of the latex manufacturers use semicontinuous reactor systems, which involves a continuous feeding of monomer or monomer with emulsifier after a part of the recipe has been charged. Naidus was the first to report experimental investigation on semicontinuous reactors in 1953.[47] Others reported experimental as well as theoretical treatments of this type of system.[48-51] It was understood that the qualitative nature of the emulsion polymerization largely depends on monomer solubility in water and in polymer, and the polymer solubility in water. The extent of monomer-water solubility varies considerably from monomer to monomer and determines both the principal reaction loci and the mechanism of particle formation. For highly water-soluble monomers such as VAc, with a water solubility of 2.4% at 20°C, experimental evidence indicates that the particle formation begins in the water phase. The degree to which the monomer is soluble in the polymer, i.e., the degree of swelling of polymer by monomer also varies quite widely. For polymers which can imbibe large quantities of monomer, such as polystyrene and polyVAc, there will be appreciable growth of the polymer particles with conversion. On the other hand, for polyvinyl chloride, which has very small capacity for monomer, very little growth of particle occurs during polymerization. The solubility of the polymer in water also influences the locus of polymerization and the mechanism of particle formation. For polymers with high water solubility, such as polyVAc, there may be appreciable amounts of both growing and dead polymer in the aqueous phase. In summary, the high water solubility of VAc, as well as the presence of polar carboxyl groups in the polymer structure, contribute the main deviations from the Smith-Ewart theory: the rate of VAc emulsion polymerization does not depend linearly on the number of particles but shows 0.14 to 0.12 power dependence.[21] The rate of polymerization shows almost zero dependence on the emulsifier concentration,[52,53] while the number of particles is an increasing function of emulsifier concentration.[12,19] The rate of polymerization is directly proportional to the monomer concentration in the aqueous phase.[54] The number of particles increases sharply to a maximum within 10% conversion and decreases continuously during the period of constant reaction rate.[54] This large number of particles is formed in a short time even when micelles are absent.[19] The conversion-time curve is of sigmoidal shape.[22,29]

Regarding the modeling of the emulsion polymerization of VAc, Napper and Parts[17] correlated only the conversion-time curve with Smith-Ewart's recursion equation and Stockmayer's solution of the average number of radicals in a particle. Their model does not include the chain transfer reaction, desorption of radicals, particle formation in the aqueous phase, or agglomeration of the particles. Harriott[55] suggested that both the chain transfer reaction to monomer and the desorption of short chain length radicals from the particles were so rapid that one can consider the total particle phase of the emulsion system as a bulk system. He also correlated the rate of polymerization using standard bulk kinetics in the total polymer phase with the approximation that radicals in a particle can react with other radicals in another particle with rapid chain transfer reaction and desorption.[55] Litt et al.[21,22] correlated only the conversion-time curve with the inclusion of radical desorption and the chain transfer reaction, but without allowing coalescence of particles or the possibility of more than one radical in a particle. Dunn and Chong suggested that the surface of the latex particles was the major locus of polymerization and an adsorption equilibrium relationship existed in the polymerization system between monomer concentrations on the particle surface and in the aqueous phase.[54] They suggested that the aqueous phase could not be the main locus of VAc polymerization reaction because of the low (5% of maximum rate) portion of the total observed reaction rate. Warson proposed that the stability of the polyVAc particles was strongly governed by the electrical charge of the polymer end groups existing mostly on the surface of the particle.[56] Hayashi et al. concluded that the rate of polymerization dependence on the emulsifier concentration was governed by the presence or absence of the stabilization by the polymer end groups coming from the initiator.[29]

Min and Ray published a review on the modeling of the emulsion polymerization reactors in 1974.[57] After reviewing the published literature on VAc emulsion polymerization mechanisms and models thoroughly, they concluded that no generally acceptable model existed at that time because none of the published models adequately explained the wide variability of the dependence of the rate of polymerization on experimental conditions.[57] They postulated a reaction mechanism for VAc emulsion polymerization so that (1) radicals are generated in the aqueous phase, (2) radicals grow in the aqueous phase to form oligomers having 50- to 200-unit chain length, (3) these oligomers form new particles by micellar initiation and by precipitation in the aqueous phase, (4) small particles coalesce easily with a large particle, (5) polymer radicals propagating in the particles form the major reaction locus, (6) there is significant chain transfer reaction to monomer in the particle, (7) there is significant rate of radical desorption from particles, (8) radicals terminate in the aqueous phase as well as within the polymer particles, and (9) the amount of available emulsifier is augmented by the growing number of end groups on the surface of polymer particles. Min and Ray also developed a general modeling framework to represent all the aspects of batch and continuous emulsion polymerization. They suggested that the application of this more detailed model in its fullest form to several specific emulsion polymerization systems was possible.[57]

In 1969, Ugelstad derived a polymerization rate expression for vinyl chloride emulsion polymerization that explained the effect of reaction parameters such as initiator concentration, particle number, and monomer-to-water ratio on rate and the shape of the conversion-time curve in 1969.[58,59] There are some similarities between emulsion polymerization of vinyl acetate and vinyl chloride: for both processes, polymerization takes place exclusively in the polymer particles, and the average population of free radicals per particles is much less than unity. Nomura et al.[53] and Friis and Nyhagen[33] showed that the kinetic expression after Ugelstad could also explain the behavior of VAc polymerization and the kinetics of the two systems with regard to monomer consumption rates that are essentially identical. Friis and Hamielec reexamined the kinetics of vinyl chloride and vinyl acetate and confirmed the validity of Ugelstad's model for systems with high desorption rate.[60] The kinetics of these systems bear several similarities: (1) the rate of polymerization is half-order with respect to initiator concentration, (2) the number of polymer particles is independent of initiator concentration, (3) the number of polymer particles becomes constant at 5–10% conversion, (4) the order of reaction with respect to particle number is small and lies between 0.05 and 0.20, (5) the average population of free radicals per particle is of the order of 0.01–0.001, and (6) the molecular weight of the polymers produced is independent of particle number and size and initiator concentration.[60] In the VAc system, the monomer dissolves with relatively high concentration in its polymer and the separate monomer phase is therefore exhausted early, already at 20% conversion. Hence, the monomer-swollen polymer particles retain an almost constant volume after 20% conversion. The polymerization rate is practically constant in the interval 20–85%, which is in accordance with Ugelstad's expression. There is a balance between a decreasing monomer concentration in the particles and an increasing average number of radicals per particle, which results in a decrease in the desorption and termination rate constants.[60] With respect to molecular weight and branching development, polyVAc has a large polydispersity ratio, and at high conversions the polymer becomes highly branched. The transfer reaction to monomer, polymer, and terminal double-bond polymerization is all molecular weight controlling. The molecular weight distribution broadens strongly with increasing conversion. The increase in M_n with conversion is due to terminal double-bond polymerization, while the increase in M_w is mainly due to transfer to polymer. At ordinary initiation rates, termination rates are unimportant for molecular weight development, and therefore molecular weight is independent of number and size distribution of polymer articles and of initiator and emulsifier level.[60]

Hayashi and Hojo[61] reported in 1976 that when polyVAc latex is dried below its minimum film-forming temperature (MFT, at 5°C), the polymer particles could be observed exactly with a scanning electron microscope. A great deal of space between the polymer particles is seen, which is different from the case of the transparent film formation above MFT. They found that for constant initiator concentration, the radii of particles are in good agreement with the cube root of the charged monomer weight ratio. They concluded that for constant initiator concentration, the number of polymer particles formed in each experiment is approximately equal, even if different amounts of monomer are charged.[61]

Poehlein and Dougherty published a review on the continuous emulsion polymerization in which 2 to 15 continuous stirred tank reactors (CSTRs) were connected in series.[62] They presented theories that could be used for prediction of particle size, particle formation, rate of polymerization and molecular weight for styrene continuous emulsion polymerization. They pointed out that the data for other monomers do not follow theoretical predictions as closely as styrene. VAc latices have a large number of small particles that may account for a large fraction of the total.[63] In the CSTR data for VAc emulsion polymerization, the start-up procedure involved a gradual increase in emulsifier and initiator concentrations until a steady state was achieved.[64] The increase in initiator concentration resulted in the increase of conversion with a slope of 0.72, which could not be considered exact as there were few data points. This figure was intermediate between Litt et al.'s 1.0 exponent[22] and Harriot's 0.5 exponent.[55] The increase in emulsifier concentration resulted in a slight conversion increase.[64]

Bataille, Van, and Pham studied the semicontinuous (delayed addition) emulsion polymerization of VAc in 1978.[65] In industry, the semicontinuous process is usually applied to lengthen the particle-generating period and slow the growth rate of the particle by regulating the rate of addition of reactants to the reactor. Then, high solids contents and small particle-size latices having high viscosities can be obtained. Many commercial latices are produced in two semicontinuous processes. The first is the monomer addition process where water, emulsifier, initiator, and part of the monomer (usually 10% by weight) are charged into the reaction vessel and polymerization is started. The remaining monomer is fed into the reaction vessel at a constant rate. The second is the emulsion addition process where part of the whole batch is put into the reaction vessel; the rest is fed as a monomer-emulsion, after which the polymerization is started. Finkentscher et al. were the first to report on both the monomer addition and emulsion addition techniques using acrylic ester monomer.[66] Bataille, Van, and Pham used a 2-liter glass reactor, redox initiators of tert-butyl hydroperoxide and sodium bisulfite, and nonionic ethylene oxide-propylene oxide surfactants and carried out the polymerization at 40°C.[65] Samples of the reaction mixture were taken at various intervals. These samples were relatively small so that the overall composition in the reactor was not seriously affected. Once a sample was removed, it was short-stopped with hydroquinone and precipitated in order to determine the conversion gravimetrically. Polymerizations were run at different feed rates, all other variables being held constant. For all the runs, the conversion-time curves were linear and dependent on the feed rates. When the rate of polymerization was plotted against time, the experimental points were represented by points calculated based on the theory of solution polymerization. The conversion of monomer to polymer was found to be a first-order reaction and autoacceleration was not present, unlike the situation in the polymerizations of other monomers. A linear increase in the rate of polymerization with an increase in the number of particles per cm^3 of latex was seen. In addition, similar to Elgood et al.,[20] a linear increase in the rate of polymerization with the increase in the surface area of particles per cm^3 of latex was also found.[65] The increase in the particle diameter and the decrease in the number of particles per cm^3 of latex with time are given in Figure 3.9. It was proposed that many of the micelles originally formed broke down and migrated to monomer-swollen polymer particles in their growth stages where the emulsifier molecules were needed to stabilize these new particles. When the time of growth for an individual particle was considered, those particles formed early in the reaction had a longer growth period compared to particles that formed later in the polymerization reaction. It follows that the "older" particles would then be larger than the "younger" particles. However, when semicontinuous technique was applied, the period of particle formation was extended, which would tend to raise the number of smaller particles and have a broadening effect on particle size distribution. Evidence of fresh nucleation was observed in the electron micrographs taken 60 minutes

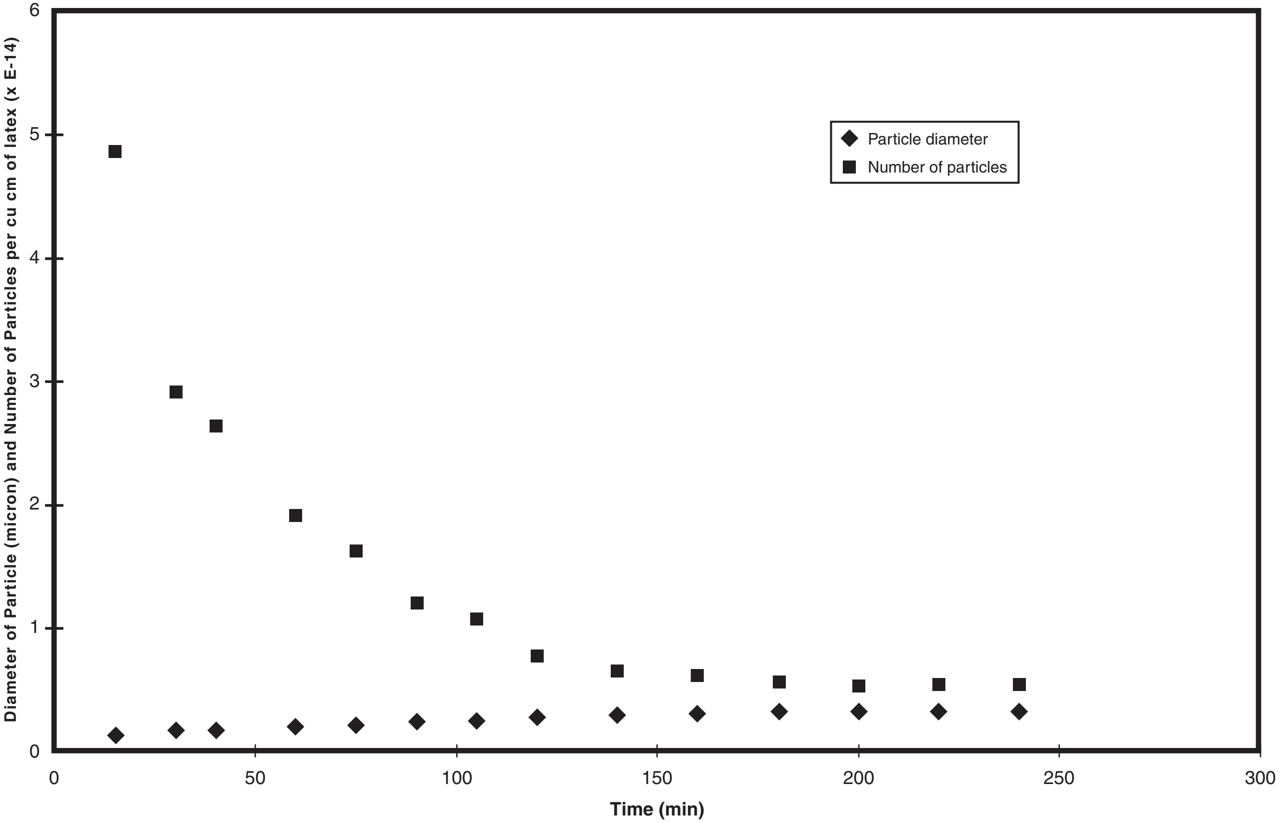


FIGURE 3.9 Variation of particle diameter and number of particles per ml of latex with time (data from Bataille, Van, and Pham[3.65]).

after starting. It was obvious that particles were formed continuously as monomer, initiator, and emulsifier were fed into the reactor. It was proposed that the locus of polymerization was both in the aqueous phase and in the micelles. The oligomers thus formed attained a certain size and then were precipitated from the aqueous phase. During precipitation, oligomeric particles released the emulsifier that kept them in equilibrium in the aqueous phase. The emulsifier release formed micelles to generate new particles. This theory explained the decrease in the number of particles during the course of reaction, and the fresh nucleation of particles even at high conversion.[65] When semicontinuous emulsion polymerization kinetics was applied, the average number of radicals per particle was found to be much greater than 0.5, so Smith-Ewart Case II theory was not applicable. When the number and the weight-average molecular weights were calculated, an increase in the polydispersity with conversion was observed, indicating an increase in the density of chain branching.[65]

In 1979, Zollars published an important paper on the kinetics of the batch emulsion polymerization of VAc.[67] He tried to obtain a more complete understanding of the effects of the initiator level, ionic strength, and particle diameter on the rate of generation of latex particles in batch polymerization of VAc. He pointed out that these data were especially necessary for the description of semicontinuous and continuous processes. He used a 3-liter, glass-jacketed resin flask which was charged with all the water and the desired levels of sodium lauryl sulfate emulsifier and potassium sulfate ionic strength controller. All the inhibitor-free VAc monomer was added to the reactor and the system was thoroughly purged with nitrogen. Then, potassium persulfate initiator was added. The reaction temperature was kept constant either at 50 or 60°C. Ten-milliliter samples of the reaction mixture were removed at prescribed intervals throughout the reaction and short-stopped with hydroquinone. The samples were analyzed for residual monomer by dissolving the latex in methanol and using a gas chromatograph. The average particle diameter was determined by using a light-scattering technique, giving a weight-average particle number, and by multiplying with a polydispersity factor of 2.6;[33] the number-average particle number was found that could be used in kinetic calculations.[67]

Zollars presented the results of the previous investigators using similar VAc polymerization systems and pointed out that the one major point of disagreement was the dependence of the polymerization rate and particle number on the initiator concentration. The reaction rate order on the initiator concentration varied between 0.5 and 1.0, and the particle number order on the initiator concentration between 0 and 1.2.[67] The general characteristics of a VAc emulsion polymerization were also observed in this study: (1) the separate monomer phase disappeared at about 20% conversion, (2) a constant rate period was observed between about 20% and 80% conversion, and (3) the emulsifier level was observed to have no significant effect on the polymerization rate. A number of polymerizations were carried out under conditions simulating those used by Litt[22] or by Friis[33] because those studies represented the two extremes in VAc kinetics. Litt et al.[22] proposed an aqueous phase termination model indicating that the reaction was first-order for reaction rate and 1.2 order for particle number, while Friis and Nyhagen[33] proposed a polymer phase termination model indicating that the reaction was half-order for reaction rate and zero order for particle number. Zollars reported that at 50°C, in the range of initiator concentrations studied by Friis, from 1×10^{-3} to 4×10^{-3} M, the rate of polymerization was proportional to the initiator concentration to the 0.65 ± 0.07 power. Friis reported the dependence to be to the 0.56 ± 0.03 power. On the other hand, at 60°C, in the range of initiator concentrations studied by Litt, the polymerization rate was dependent on the initiator concentration to the 0.88 ± 0.14 power, while Litt reported a value of 0.93 ± 0.12. Then, Zollars concluded that the results of both investigator groups were reproducible in the same piece of equipment using the same source of reactants.[67] Zollars also concluded that the emulsifier concentration had no effect on the reaction rate at either 50° or 60°C, in agreement with the results of Litt. He reported that there was no effect of the alkyl chain length of emulsifier on the rate of polymerization by comparing the results of sodium lauryl sulfate and sodium cetyl sulfate emulsifiers. He pointed out that the opposite comment of Napper and Alexander[18] on this point was due to the fact that they used very low monomer concentrations which were less than the solubility of VAc in water, and emulsifier concentrations less than the CMC. In addition, the level of agitation, within reasonable bounds, had no observable effect on the polymerization rate. When the ionic strength was kept constant by using K_2SO_4 in combination with $K_2S_2O_8$, the increase of ionic strength resulted in the decrease of the order of polymerization rate at either temperature.

Zollars reported that the number of particles increased with increasing conversion at all levels of initiator. This is in contrast with the reports of Friis[33] and Priest,[11] who reported that the number of particles remained constant beyond 20% conversion. Zollars suggested that these workers used electron micrography to determine the particle number, which was very insensitive to small particles, and thus any new generation of particles may have gone unnoticed.[67]

Zollars criticized that both kinetic models of Litt and Friis did not take into account the changes in the dependence of the particle number with changes in the initiator concentration and ionic strength. Proposed mechanisms that a change in the rate constants for the “sweep-up” of aqueous oligomers is responsible for the change in the reaction rate order have ignored the observed changes in the particle number. He proposed a different particle formation mechanism depending on the coagulation rate.[67] The rate of coagulation of latex particles was calculated by DLVO theory.[54] Particle stability increased with increasing surface potential or particle diameter but decreased exponentially with increasing ionic strength of the suspending medium. Now, for the standard emulsion polymerizations in which the initiator was the only salt added, low initiator levels produced low ionic strengths and, therefore, high particle stability. For this situation, coagulation would not play an important role in determining the particle number. A first-order dependence between particle number and initiator concentration was feasible for low initiator concentrations. As the initiator level increased, ionic strength increased and coagulation played a more important role in the determination of the particle number. Two opposing effects resulted from the increase of the initiator concentration. The rate of coagulation brought on by higher ionic strength would not allow the increase of the particle number by the increase of the initiator concentration. However, after a while, a further increase in particle number at high initiator levels was observed which was due to the "salting out" effect of the emulsifiers at high ionic strength. When polymerizations were carried out at constant ionic strengths by using K_2SO_4 in combination with $K_2S_2O_8$, the constant coagulation rate gave rise to a constant particle number, showing that the coagulation was the dominant factor at high ionic strengths.[67]

Zollars carried out a set of experiments to derive an empirical particle number kinetic model. He applied a multiple linear regression analysis to all the data obtained and gave the equation below for the weight-average particle number:

$$\begin{aligned} N_w \times 10^{-17} = {} & 18.64 + 4.972 \times 10^{8} f k_i [I] - 1.081 \times 10^{3} \\ & (\textit{ionic strength}) - 5.405 \times 10^{-2} T - 1.1 \times 10^{10} f k_i [I] (\textit{ionic strength}) \\ & + 3.276 (\textit{ionic strength}) T + X (0.7847 + 14.63 [E]) \end{aligned} \tag{3.16}$$

where X is the fractional conversion, N_w has units of number of particles/liter H_2O, T is the temperature in Kelvin, and all other variables are as known before. Zollars urged that the extension of this empirical model beyond the initiator and emulsifier ranges and types studied was questionable and proposed that when this model was used in combination with the reaction model proposed by Friis, it fit all previous data and could be used for reactor simulation purposes. Zollars preferred the kinetic model of Friis using the termination step in polymer because this model yielded consistently better predictions for the conversion-versus-time histories over a much wider range of reaction variables than did Litt's water phase termination model.[67]

Kiparissides, MacGregor, and Hamielec reported a model of the emulsion polymerization of VAc in a continuous stirred tank reactor operating under conditions of sustained oscillations.[68] They used the experimental results previously reported by Greene et al.[64] When these oscillations are present, they lead to emulsifier levels too small to adequately cover polymer particles, with the result that excessive agglomeration and fouling could occur. Furthermore, excessive branching and poor processability could take place. In order to control the production rate and latex properties in the production of polyVAc in CSTR, two models were developed: a comprehensive one that used the age distribution of particles, and an approximate model that accounted for discrete nucleation periods. In both models, it was considered that polymer particles were generated by both micellar and homogeneous mechanisms. According to these models, sustained oscillations are mainly caused by the particle formation mechanisms. The rapid generation of particles results in the formation of a large surface area. This new surface area is then covered with emulsifier at a rate that exceeds the feed rate of fresh emulsifier to the reactor. The reactor is thus depleted of free emulsifier and, consequently, of micelles. Furthermore, as the number of particles increases, the rate of radical capture into polymer particles increases and, at some time, the homogeneous nucleation ceases. Then a long period starts where particles are not generated. The duration of this period depends on the feed rate of emulsifier and the residence time of polymer particles.[68]

The basic assumptions made in modeling this reaction in a continuous stirred tank reactor were (1) the reactor is uniformly mixed, (2) density change in a reaction mixture is negligible, (3) the extent of particle flocculation and breakup is negligible, (4) particles are generated by micellar and homogeneous mechanisms, and (5) monomer volume fraction in a particle is assumed to be independent of particle size and age; in other words, monomer diffuses into particles independently of their size or age. Particle growth rates are generally considered a function of monomer concentration in the particle, particle size, and rates of radical adsorption and desorption. In a CSTR, particles can be generated continuously, leading to distributions of particle size and age. The aqueous phase initiator and oligomeric radical balances can be written as

$$\frac{d[I]_w}{dt} = \frac{1}{\theta}\left([I]_{feed} - [I]_w\right) - k_d[I]_w \tag{3.17}$$

$$\begin{aligned}\frac{d[R]_w}{dt} = {} & \frac{1}{\theta}\left([R]_{feed} - [R]_w\right) + 2fk_d[I]_w - k_{ab}A_p[R]_w k_v \\ & - k_m A_m [R]_w k_v - k_h[R]_w - k_{tw}[R]_w^2 + \int_0^t k_{de} n(t,\tau)\,\bar{q}(t,\tau)\,d\tau\end{aligned} \tag{3.18}$$

where $[I]_{feed}$ and $[R]_{feed}$ are the initiator and radical concentrations in the feed stream (molecules/liter emulsion), $[I]_w$ and $[R]_w$ are the initiator and radical concentrations in the aqueous phase, θ is the mean residence time (sec), k_d is the initiator decomposition rate coefficient (sec^{-1}), f is the efficiency of initiator decomposition, k_{ab} is the overall transport coefficient for radical transfer from the aqueous phase into polymer particles (dm/sec), k_v is the volume of emulsion phase over the volume of aqueous phase (liter emulsion/liter), k_m is the rate coefficient of micellar nucleation (dm/sec), k_h is the rate coefficient of the homogeneous nucleation (sec^{-1}), k_{tw} is the rate coefficient of termination in aqueous phase (it is assumed equal to zero), k_{de} is the rate coefficient of radical escape from the polymer particles (sec^{-1}), A_p is the total surface area of polymer particles (dm^2/liter emulsion), A_m is the total surface area of micelles (dm^2/liter emulsion), $n(t, \tau)$ is the number of particles at time t which are born in the time interval $(\tau, \tau + d\tau)$ (1/liter emulsion), and $\bar{q}(t, \tau)$ is the average number of particles per particle of the class $n(t, \tau)\,d\tau$.

A_m can be expressed by

$$A_m = S_T - S_{CMC} - A_p \tag{3.19}$$

where S_T is the total emulsifier concentration and S_{CMC} is the critical micelle concentration (converted to dm^2/liter). The change of S_T with time is given as

$$\frac{dS_T}{dt} = \frac{\left(S_{feed} - S_T\right)}{\theta} \tag{3.20}$$

where S_{feed} is the emulsifier concentration in the feed. In this treatment, it was assumed that the termination took place exclusively in polymer particles, similar to Ugelstad and Hansen,[69] and that the rate of radical capture was proportional to the total surface available for radical capture, similar to Gardon[70] and Fitsch and Tsai.[42] The last term in Eq. 3.18 denotes the total desorption rate of radicals from the polymer particles.

Kiparissides, MacGregor, and Hamielec published three consecutive papers on the continuous emulsion polymerization of VAc in 1980.[71-73] In the first paper of the series, experimental studies were presented in detail.[71] Experimental investigations in CSTRs have shown that the conversion, number of polymer particles, and other related properties often oscillate widely with time. In other words, a steady state is never achieved. These oscillations can lead to emulsifier levels too small to adequately cover polymeric particles, with the possible result of excessive agglomeration and reactor fouling. Excessive branch formation is another problem at high conversions. They used a 2-liter, jacketed glass reactor with an overflow arm attached to its side to give a reactor volume of 1.2 liters at an agitation rate of 320 r/min. The reactants were stirred using a flat blade paddle stirrer driven by a variable speed motor. The stainless steel cooling coil inside the reactor provided baffling to ensure proper mixing. There were two polyethylene storage tanks to hold the raw materials. Both tanks were blanketed with nitrogen to reduce oxygen retardation. The larger, 22-liter tank contained distilled and inhibitor-free VAc monomer (4 parts), distilled water (7 parts), and sodium lauryl sulfate surfactant, and was stirred with a flat blade paddle. The small 9-liter tank contained the rest of the recipe's water (3 parts) and the total amount of initiator. The potassium persulfate initiator was predissolved and the solution was purged with nitrogen for one hour before the reaction was started. The two separate feeds were fed to the reactor at constant rate. The reactor start-up consisted of filling the reactor with distilled water prior to introducing any feed streams. For all experiments, the emulsion recipe comprised 100 ml water, 400 ml VAc, varying amounts of initiator (0.005–0.030 mol/liter water), and emulsifier (0.01–0.06 mol/liter water). The continuous overflow was collected in a 22-liter drum, which contained a hydroquinone solution to quench the polymerization.[71]

Kiparissides, MacGregor, and Hamielec reported that sustained oscillations appeared at low emulsifier concentrations and a steady-state value could be obtained for high emulsifier concentrations. When sustained oscillations were present, this mechanism was offered: at the beginning of the reaction, a rapid generation of a large number of particles and surface area consumes the available emulsifier. Then, the free micelles quickly disappear. This leads to a period where particle generation rate is close to zero. This period depends on the feed rate of the emulsifier, the washout rate of polymer particles, and the growth of organic surface. Eventually, the emulsifier concentration saturates the organic surface and free emulsifier is again available for particle generation. This mechanism leads to the formation of discrete particle populations and fluctuations in the number of particles, polymerization rates, and conversion.[71] In general, the rate of polymerization was found proportional to the initiator concentration.

They also examined the effect of stirring rates between 220 and 500 r/min on conversion under a nitrogen blanket. The increase in the agitation rate resulted in a decrease in the conversion. When the liquid-air surface generated by stirring increased, a rise in the coagulation rate resulted. In addition, a larger liquid-air interface increased the oxygen content in water and thus reduced the radical generation rate, resulting in slow polymerization rates. Kiparissides, MacGregor, and Hamielec also investigated reactor fouling due to excessive agglomeration, referring to the DLVO theory, and concluded that a high ionic strength of the reaction system, because of the high initiator concentration and the existence of the small and large particles together, were probably the main reasons for fouling. As Bierman[74] and later Mathews et al.[75] pointed out previously, those colloids that are most different in size will have the greatest chance of attracting and, hence, coagulating.

In the second paper of the series,[72] Kiparissides, MacGregor, and Hamielec applied their previously developed simulation models for VAc continuous emulsion polymerization data[68] to their experimental conversion-time plots.[71] The number of latex particles, the total surface area of particles, and the free soap concentrations were predicted by these models, and sustained oscillations in CSTR reactors were explained.[72]

In the third paper of the series,[73] Kiparissides, MacGregor, Singh, and Hamielec reported an experimental evaluation of turbidity spectra, and of liquid exclusion chromatography for the online and offline monitoring of polymer particle size during the continuous emulsion polymerization of vinyl acetate. It has been shown that turbidity spectra may be used to monitor online polymer particle size during the latex production. By monitoring continuously the absorbance at even a single wavelength (for example at 350 nm), one can determine whether the reactor operates at a steady-state or sustained oscillations mode. It is important that turbidity measurements be carried out in the absence of multiple scattering as a very dilute solution is required. Latex streams from a CSTR reactor were diluted 100 to 500 times before measuring the absorbance in the spectrophotometer over the wavelength region 350–700 nm.[73] Another important feature of turbidity spectra analysis was the determination of the rate and extent of particle flocculation. Liquid exclusion chromatography was used to follow secondary particle nucleation in an offline mode. When a unimodal chromatogram is obtained, it corresponds to steady-state conditions in which there is a continuous generation of particles. When a bimodal chromatogram is observed, it shows discrete particle generation and sustained oscillations.[73]

In 1980, a symposium was held on emulsion polymerization of vinyl acetate at Lehigh University, and a book entitled *Emulsion Polymerization of VAc* was published which was edited by M. S. El-Aasser and J. W. Vanderhoff. Some of the thirteen papers presented in this symposium summarized the up-to-date knowledge on the mechanism of VAc emulsion polymerization. Warson pointed out that VAc was not polymerized commercially in dilatometers, and that there should be a bridge between theory and practical emulsion polymerization.[76] He presented the specific problems of the industrial production so that exact repeatability within narrow limits is desirable; the final solids content should be constant ±1%, and the particle size, emulsion viscosity, polymer molecular weight, and residual free monomer should be maintained within narrow limits. He pointed out that it is normally desirable to prepare a latex at the highest concentration possible, usually >50%, unlike theoretical work. In practice, the nature and shape of the stirrer may affect production performance, and this is determined by trial-and-error. Sometimes baffles are desirable to improve mixing, especially with viscous and thixotropic latices. It is necessary to avoid excessive foaming and precipitation either in the reactor or on the reactor walls and stirrer. There are scaling-up problems in industry. In many cases, successful laboratory processes had failed unpredictably and irregularly on a production scale, with heavy precipitation.[76] Warson also pointed out the importance of the type and properties of polyvinyl alcohol stabilizer used in the emulsion polymerization of VAc. He stated that when one polyvinyl alcohol type that was suitable for a process was replaced by another, reputedly of better quality, from the same manufacturer, the process failed completely from the colloidal stability aspect. By experience, he concluded that when polyvinyl alcohol has a broad molecular weight and molecular species distribution it gives more stable latices. Warson discussed that usually 88% hydrolyzed polyvinyl alcohol is used as a stabilizer in the VAc polymerization, but the variations in the structure, branching, tacticity, and production methods of polyvinyl alcohol resulted in latices having different properties.[76] He suggested that VAc polymer has a tendency to graft onto polyvinyl alcohol in the delayed-addition (or semi-continuous) process, and sometimes excessive grafting would cause instability when nonionic emulsifiers are added since the overall molecules of polyvinyl alcohol are not sufficiently hydrophilic after grafting unless some ionic groups have been introduced.

Warson also pointed out that a rapid method of testing is essential for residual monomer in the semicontinuous method so that, if necessary, the rates of addition of monomers and the additional water phase can be adjusted. If the emulsifier is also added gradually, it helps to attain the stability of latex because this level of emulsifier is just sufficient to maintain stability as the particle size increases without creating new nucleation, and the stabilizer present is adequate to prevent particle coalescence.[76]

Dunn reviewed the polymerization of aqueous solutions of VAc monomer.[77] He stated that persulfate initiator provides ionic end-groups capable of stabilizing latex particles in the absence of surfactants, although sulfate end-groups are liable to acid catalyzed hydrolysis, giving hydroxyl end-groups that may possibly be oxidized to carboxyl by the persulfate. Dunn recalled that although VAc is relatively highly soluble in water (2.8% at 60°C), polyVAc is not and precipitates as soon as it is formed. Monomer is then partitioned between the phases according to the relationship

$$\left(M_p\right) = 13.7\left(M_w\right)^2 \tag{3.21}$$

where (M_p) and (M_w) are monomer concentrations by weight in the polymer and water phases, respectively.[19] The form of this relation has been confirmed independently by Napper and Parts.[17] Dunn also discussed the effect of ionic strength on colloidal stability: when ionic strength is increased, the electrostatic energy barrier is reduced and the latex coagulates, however, when emulsifier is present this factor is less obvious. Emulsifier may stabilize small particles by adsorption, but in the absence of emulsifier, small particles are less stable than the large particles with which they coalesce. Thus, when particles are nucleated by oligomeric precipitation in the absence of emulsifier, a monodisperse particle size distribution is obtained. Of course, new particles continue to be formed throughout the reaction, but they are unstable and they coalesce with the pre-existing large particles rather than with each other. Thus, the number of particles soon becomes constant.[77]

Dunn criticized the use of dilatometry in kinetic studies of VAc emulsion polymerization because, at 60°C, the percentage contraction corresponding to 100% conversion of VAc monomer into polyVAc is 15.7%. This means that when a solution of VAc polymerizes, the solvent (water) expands partially, compensating the contraction due to polymerization. When a separate VAc monomer phase is also present in the system, intermediate values of the percentage contraction are applicable, which makes it difficult to apply the dilatometric method of determining polymerization rates.[77]

Dunn also reviewed the effect of polyvinyl alcohol on polymerization of VAc. He stated that polyvinyl alcohols are polymeric emulsifiers, and the type which was preferred for emulsion polymerization application was that with about 12 mole% residual acetyl groups produced by alkaline methanolysis of polyVAc (88% hydrolyzed type). He cited the work of Tubbs,[78] that the residual acetyl groups were not randomly distributed but occurred in short blocks. The presence of polyvinyl alcohol reduced the rate of polymerization of VAc to about half its original value, even at a concentration of only 0.36%. However, this effect is dependent on the type and the nature of polyvinyl alcohol, small differences in the structure have a profound effect on the properties of the polyVAc latex obtained. Polyvinyl alcohol also acts as a thickener for the aqueous phase during emulsion polymerization. The viscosity of polyVAc latices is very sensitive to the properties of the polyvinyl alcohols used in their preparations. Increased adsorption of polyvinyl alcohol will result in a reduction of average particle size, thus increasing latex viscosity. An anionic emulsifier such as sodium dodecyl sulfate is much more effective than polyvinyl alcohol in reducing the size of polyVAc latex particles, but it has little effect on the rate of polymerization reaction.[77]

Zollars reported the effects of particle number and initiator concentration on the kinetics of VAc polymerization.[79] He repeated all the experimental findings and discussions in his previous publication[67] and presented the same empirical model in his paper. Nevertheless, Zollars stressed that much of the kinetic information presented by previous investigators appeared to be contradictory, which was not a consequence of variations in experimental techniques or materials. Instead, he suggested that the variability is a result of changes in the particle number with changes in the ionic strength of the aqueous phase.[79]

Klein and Stannett defended their previously published Litt, Patsiga, and Stannett (LPS) kinetic model[22] against Zollar's suggestions on the change of particle number with the variation of ionic strength.[67,79] Nevertheless, they accepted that there is no single kinetic model that explains all the trends.[80] They cited their publication where the state of the art for persulfate initiated polymerizations in the presence of sodium lauryl sulfate emulsifier was critically reviewed.[81] They stated that the LPS model has a single adjustable parameter which is the rate constant for radical capture by existing particles, while the Friis model[33] contains two such parameters. The LPS model is based on the existence of oligomeric radicals in the aqueous phase onto which emulsifier molecules have adsorbed, dispersed, and stabilized, but which undergo coagulation with increasing ionic strength.[82] In the LPS model, a monomer radical polymerizes to 50 to 300 degrees of polymerization in the aqueous phase, and at the same time the ionic emulsifier is adsorbed onto the polymer molecule, transforming it into a solubilized polymeric chain. These radical-containing active chains will be swept up by monomer-swollen particles. Within the particles, the monomer concentration is high and the captured polymeric radical will further grow or chain transfer to a monomer molecule. This chain transfer rate is high for VAc monomer. The monomer radical inside the particle will cyclize to a preferred butyrolactonyl radical that is preferentially partitioned in the aqueous phase where it grows into a new chain, is stabilized by adsorbed emulsifier, and is swept up by another particle. The termination step is postulated to occur mainly in the aqueous phase between polymeric chains and butyrolactonyl radicals. The unique feature of the LPS mechanism is the rate constant for sweep-up of the solubilized aqueous polymer radicals by the particles.

Klein and Stannett used dilatometry for their kinetic studies.[21,22,80] Particle size distribution was measured with an electron microscope using a freeze-drying technique with carbon replication in order to harden the otherwise soft polyVAc particles in the electron beam.[83] They prepared seed latices first, measured their particle size distribution, and used these seed latices in dilatometric polymerization rate measurements. They tried to investigate the effect of ionic strength and pH on the polymerization rate, but there were two problems: (1) at low ionic strength, the buffer capacity was inadequate to keep the pH reasonably constant; and (2) at high ionic strength, even with the post addition of 0.2% sodium dodecyl sulfate emulsifier, the latex became unstable. They decided to test moderate ionic strengths, less than 0.075 M, between pH = 3.40–7.75 by using potassium dihydrogen phosphate solution as a buffer. They evaluated the oligomeric radical capture rate constant as a function of ionic strength and pH. The radical capture rate constant was decomposed into a stability factor term and an ionic strength independent rate constant. The pH effect on the stability factor was suggested in terms of association between the acetic acid and hydroxyl at the particle surface, both of which are the products of polymer hydrolysis.[80]

Chang, Litt, and Nomura reinvestigated the kinetics of VAc emulsion polymerization in three separate publications.[84-86] In the first paper of the series, they examined the variation of the polymerization rate with changes in particle concentration, type of emulsifier, emulsifier concentration, persulfate initiator concentration, ionic strength, and monomer volume.[84] Initially, they reported that there was some agreement in the previous literature about the following features of the reaction: (1) the rate of polymerization is approximately independent of monomer concentration, at least from 20 to 85% conversion; (2) the number of particles is roughly independent of conversion after 30% conversion in unseeded polymerizations; (3) the polymerization rate depends on the particle concentration to about 0.2 power; (4) dependence of the polymerization rate on the emulsifier concentration is small, with a maximum of 0.25 power; and (5) molecular weights are independent of all variables and mainly depend on chain transfer to monomer. They stated that they would reinvestigate the order of dependence of the rate on persulfate initiator concentration, and the dependence of the number of particles on the initiator concentration.[84]

Chang, Litt, and Nomura used dilotometry (under nitrogen blanket) in their polymerization rate determinations. They used inhibitor-free distilled VAc, potassium persulfate initiator, sodium lauryl sulfate, sodium lauryl ether sulfate, and sodium tridecyl sulfate emulsifiers. All the results reported were concerned only with the seeded emulsion polymerizations because the number of particles in the latex could be better controlled by using seed, thus simplifying the analysis. Consequently, the mechanism of particle formation could not be considered in the work.[84] There were four steps in the growth mechanism: (1) persulfate ion radical enters the particle where it either initiates or terminates the polymerization depending on whether the particle contains a radical or not — nevertheless, as only 1 to 2% of particles contain radicals, it usually initiates polymerization; (2) a radical in a particle can chain transfer to monomer, generating a stable monomer radical — the chain transfer occurs on vinyl hydrogen, contrary to the popular belief that the major chain transfer site is on the acetyl hydrogens of vinyl acetate, this radical reinitiates relatively slowly, and thus the radical can escape from the particle (or diffuse easily out of the particle) to become an aqueous radical; (3) an aqueous monomer radical can be swept up by a dead particle, or it can react with initiator to generate a sulfate ion radical which will then enter a particle and initiate or terminate the polymerization, or it can be swept up into a particle containing a radical, thus usually it terminates; and (4) the escape from particles and diffusion back in continues for the monomer radical until it either reinitiates or terminates — the major termination step is the reaction of monomer radical with polymer radical in a particle.[84]

Contrary to the LPS theory, Chang, Litt, and Nomura determined that the VAc emulsion polymerization rate is independent of the emulsifier type, emulsifier concentration between 0% and 1% in seeded polymerizations, and ionic strength when twentyfold variable concentrations of potassium sulfate are added.[84] The effect of potassium persulfate initiator concentration was examined by keeping the ionic strength constant at 3 × 10 in each run by the addition of potassium sulfate, and the rate of polymerization was found to depend on the initiator concentration to the 0.6 power, a value which was intermediate between the previously published figures of 0.5 to 1.0.[21,22,33,67] The dependence of polymerization rate on initiator concentration when sodium lauryl sulfate was used as emulsifier was also studied and a power dependence of 0.62 was found. The dependence of polymerization rate on the volume of VAc monomer phase per unit volume of aqueous phase was determined and a power dependence of 0.39 was found.[84] The dependence of polymerization rate on particle concentration was studied by polymerizing VAc at a given initiator concentration while varying the number of particles in the seed. Enough monomer was added to give 25 wt% of polymer plus monomer. Small amounts of emulsifier (0.1%) were added to stabilize the particles. The number average diameters were measured using quasi-elastic laser light scattering, and then the number of particles in unit latex volume were calculated. The number of particles remained unchanged within experimental error before and after polymerization for all runs except those at very low particle concentrations. It was explained that at very low particle concentrations the added emulsifier is above its critical micelle concentration and may stabilize new particles, whereas at high particle concentrations the emulsifier is adsorbed onto the particles. Then, the dependence of polymerization rate on particle concentration was determined by keeping the ionic strength and monomer-to-water-phase ratio constant, and an average dependence to the 0.12 power was found.[84] This value was intermediate between the previously reported zero to 1.2 power dependence, but also far away from the previous 1.2 value of the LSP theory.[22] In addition, it was determined that the rate of polymerization was almost independent of monomer concentration in the monomer-swollen particles until 85% conversion.[84]

Chang, Litt, and Nomura stated that the LSP model was inconsistent in many respects and they developed another model mainly because the kinetically important chain transfer was on vinyl hydrogen.[84] They refused the reinitiation of polymerization after chain transfer via butyrolactonyl radical mechanism, which was developed by LSP theory.[22] In this model, they derived an equation for the rate of VAc emulsion polymerization:

$$R_p = C_1\left(1 + C_2\frac{d}{[M]^{1/2}}\right)^{1/2}[M]^{1/4}\left(\frac{V_{org}}{V_{aq}}\right)^{1/3}[P]^{1/6}[I]^{1/2}\left(1 + C_3[I][M]^{1/2}\right)^{1/2} \qquad (3.22)$$

where d is particle diameter, $[M]$ is monomer concentration in the particles, V_{org} is the volume of organic (monomer) phase contained in the particles, and V_{aq} is the volume of aqueous phase. $[P]$ is the number of particles/liter of H_2O and $[I]$ is initiator concentration. The three C's were given as:

$$C_1 = 3.09 \times 10^{-8}\left(\frac{k_2\left(f k_1 k_4\right)^{1/2}}{k_3^{1/2}}\right)\left(\frac{[M_o]}{D_o^{1/2}}\right) \qquad (3.23)$$

$$C_2 = \frac{1.42 \times 10^{23} D_o}{k_{80}} \qquad (3.24)$$

$$C_3 = \frac{0.072\ k_7\ D_o}{k_4 D_a d^3 [P]\, P_e \left[M_o\right]^2} \qquad (3.25)$$

where k_1 is unimolecular decomposition constant of potassium persulfate, k_2 is propagation rate constant of VAc, f is efficiency factor of unimolecular persulfate decomposition, k_3 is chain transfer constant of growing radical to monomer, k_4 is reinitiation rate constant due to chain transferred monomer radical adding to monomer, $[M_o]$ is monomer concentration in organic phase, D_o is diffusion constant of monomer radical in particles before disappearance of separate monomer phase, k_{80} is termination rate constant for monomer radical in a particle at or before 30% conversion, k_7 is induced decomposition rate constant due to attack by monomer radical on potassium persulfate in the aqueous phase, D_a is diffusion constant of monomer radical in aqueous phase, and P_e is probability of escape of monomer radical from particle. The integration of Eq. 3.22 was also carried out for two sections where a separate monomer phase is present between 0 and 30%

conversion, and where it is totally consumed and disappears at 30% and higher conversions by applying the required modifications.[84]

In the second paper of the series, Litt and Chang investigated the induced decomposition of the persulfate initiator as a function of conversion, organic-to-water-volume ratio, initiator concentration, and the number of particles.[85] Kolthoff and Miller reported that the first-order rate constant of decomposition for potassium persulfate in a neutral aqueous medium is 3.0×10^{-4} min^{-1} at 60°C.[87] Decomposition is more rapid at low pH as a result of the induced decomposition by hydrogen ion present. Patsiga reported that the first-order rate constant of decomposition for potassium persulfate in an aqueous 0.67% sodium lauryl sulfate emulsifier solution was 5.07×10^{-4} min^{-1} at 60°C.[88] Patsiga also found that the decomposition was ten times more rapid in the presence of VAc than with emulsifier. Litt and Chang determined persulfate concentration by reacting the residual initiator in the samples (after centrifugation) with ferrous ammonium sulfate and potassium thiocyanate, and by following the red color with a spectrophotometer at 470 nm.[86] The initiator concentration decreased as a function of time and conversion. The rate constant for induced decomposition of initiator by the monomer radicals was found to be 2.1 × 10 liter/mole-sec. The high rate constant shows diffusion control of the reaction and implies that the reaction of persulfate with monomer radicals in the aqueous phase proceeds through an electron transfer mechanism. The rate of induced decomposition reaction is dependent on the number of particles to the 0.11 power and the volume of organic phase-to-aqueous volume ratio to the –0.64 power.[85] The dependencies found agreed well with those predicted in their previous model.[84]

In the third paper of the series, Litt and Chang investigated the major chain transfer site of VAc in emulsion polymerization.[86] Since there is no dependence of molecular weight on the persulfate initiator concentration above 30% conversion, the chain transfer of growing radical to the monomer is a very important factor. They synthesized vinyl trideuteroacetate (CD_3–CO–O–CH=CH_2) and trideuterovinyl acetate (CH_3–CO–O–CD=CD_2) and compared their polymerization properties with undeuterated vinyl acetate (CH_3–CO–O–CH=CH_2). The polymer molecular weights and rates of polymerization of the three monomers were determined under identical conditions. The bulk and emulsion polymerization rate of trideuterovinyl acetate was found to be 1.78 times that of vinyl acetate. The molecular weight of poly(trideuterovinyl acetate) was 2.59 times that of poly(vinyl acetate). Chain transfer was shown to be 94% on the vinyl hydrogens and only 6% on the acetyl hydrogens. Thus, vinyl radical, CH_3–CO–O–$\dot{C}$=CH_2 is the major monomer radical formed, and is a stable radical which reinitiates relatively slowly compared to the propagation step. The major termination step in bulk polymerization, which was previously assumed to be growing radical reacting with another growing radical, was found to be almost completely the reaction of monomer radical with growing radical.[86]

Donescu, Gosa, Diaconescu, Mazare, and Carp examined the emulsion polymerization rate of VAc in the presence of hydroxyethylcellulose (HEC) protective colloid.[89] Unlike most other protective colloids such as polyvinyl alcohols, hydroxyethylcellulose macromolecule undergoes scission due to the oxidative degradation effect of the persulfate initiator used. Since HEC and the potassium persulfate initiator pair are usually used in the production of VAc-acrylic copolymer emulsion paints, there is a need to evaluate this oxidative degradation mechanism. After potassium persulfate addition at 70°C, the viscosity of HEC solution, or the ratio of viscosity/initial viscosity, showed a decrease and attained to a constant value after some time. Carbonyl groups were formed on HEC chains after oxidative degradation, which could be followed by UV absorbance at 263 nm.[89]

On the other hand, concentration of HEC has a strong effect on the decomposition reaction rate of potassium persulfate. As was specified for polyvinyl alcohol protective colloid[90] or small molecular alcohols,[91,92] the decomposition rate of potassium persulfate rises strongly in the presence of HEC. In addition, HEC forms a redox system with the initiator. The rate of oxidative cleavage is given by the equation:

$$\frac{-\left[K_2S_2O_8\right]_o}{dt} = K\left[K_2S_2O_8\right]_o \left[HEC\right]_o^{0.25} \tag{3.26}$$

where K is a constant. The kinetics of emulsion polymerization of VAc in the presence of HEC has certain distinctive aspects due to this degradative process. When the number of carbonyl groups on the HEC chain increased, some reactive centers (free radicals) were formed. These free radicals may act as growing centers, which yield graft-copolymers with VAc. At the same time, as oxidative degradation is accompanied by the scission of the chain, free radicals are formed at the ends of HEC fragments as well. VAc addition to these radicals may cause the formation of block copolymers.[93] The evidence of the formation of HEC-polyVAc graft copolymers was shown by transmission electron micrographs of the benzene soluble fractions of the latex polymers and viscometric measurements.[89]

In 1981, ten years after their first publication,[53,94] Nomura and Harada published a paper on the theoretical estimation of the rate coefficient for radical desorption in emulsion polymerization of VAc.[95] In a high monomer conversion range, the diffusion coefficient of radicals in a polymer particle, D_p, will decrease markedly with the progress of polymerization due to an increase in the viscosity inside the polymer particles. The rate coefficient for radical desorption from a polymer particle, k_f, is written as

$$k_f = \frac{2D_p}{d^2}\left(\frac{k_{mf}}{k_p}\right) \tag{3.27}$$

where d is diameter of polymer particle, k_{mf} is rate constant for chain transfer to monomer, and k_p is propagation rate constant. The k_f coefficient involves only known parameters. Correspondingly, the rate of emulsion polymerization, R_p, was formulated for high monomer conversion range as

$$R_p \propto N_T^{1/6}\, I_o^{1/2}\, V_p^{1/3} \tag{3.28}$$

where N_T is the total number of polymer particles per unit volume of water, I_o is initial initiator concentration, and V_p is the total volume of polymer particles per unit water volume. Nomura and Harada reported that Eq. 3.28 predicted the R_p of emulsion polymerization of VAc.[94] Nomura also published the detailed derivation of the equations in their theory.[96]

Yeliseva published an important review on the emulsion polymerization of polar monomers in 1982.[97] He pointed out that the dependency of the polymerization rate to the emulsifier concentration was a function of the area occupied by the emulsifier molecule in the saturated adsorption layer on the polymer particles. He examined the interfacial characteristics of the latices prepared from polar monomers such as acrylic, methacrylic esters, VAc, and vinyl chloride in order to evaluate the overall surface area relationship with the polymerization rate. First of all, the interfacial free energy between water and monomers, as well as polymers obtained from these monomers, were examined. The adsorption of the emulsifiers onto the monomer-aqueous phase interface, polymer-aqueous phase interface, and latex particle-aqueous phase interface are very important parameters in order to understand the emulsion polymerization of polar monomers. Yeliseyeva pointed out that each monomer has its own specific features in emulsion polymerization, and attempts to put various emulsion reaction systems into one physicochemical model or theoretical scheme have therefore failed.[97] In general, the emulsifier activity at the water-organic phase interface is determined by the structure of the emulsifier molecule and polarity and other molecular interaction properties of the organic phase. He cited the former version of the geometric mean relation of Fowkes[98] and geometric-harmonic-mean relation of Wu[99] in order to calculate the interfacial tension between water and organic phases by applying the surface tension components theory. According to the geometric-mean relation, provided that only London dispersion forces exist between the phases, the interfacial tension at the boundary of the two phase, γ_{12}, is

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\gamma_1^d - \gamma_2^d\right)^{1/2} \tag{3.29}$$

where γ_1 and γ_2 are the surface tension of the first and the second phases and γ_1^d and γ_2^d are the dispersion components of the surface tension. Wu derived an equation for boundary phases which relates γ_{12} not only to dispersion interactions but also to polar interactions:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left[\left(\gamma_1^d - \gamma_2^d\right)^{1/2} - \frac{4\gamma_1^p\,\gamma_2^p}{\left(\gamma_1^p + \gamma_1^p\right)}\right] \tag{3.30}$$

where γ_1^p and γ_2^p are the polar components of the surface tension. The dispersion and polar components of surface tension of liquids can be experimentally measured by a variety of methods.[100,101] Wu reported that there is considerable contribution of the polarity to the surface tension of polymers, such as 33% for polyVAc, 28% for polymethyl methacrylate, and 11% for polychloroprene.[99] Since polar contribution is a very important factor to determine the interfacial free energy, the polarity of polymers in emulsion strongly influences (1) adsorption of surfactants, (2) mechanism of particle formation, (3) particle flocculation, and (4) configurational behavior of the forming polymer chains.[102]

The difference in polarity between boundary phases, which determines the interfacial free energy, is the main factor affecting the extent of adsorption. For adsorption of a third component by the interface, the polarity of the third component should lie between the polarities of the two boundary phases. Thus, it is important to know the adsorption characteristics of the emulsifier on the monomer-aqueous phase and polymer-aqueous phase interfaces.[97] When two liquids are considered, asymmetric molecules of some liquids display a molecular orientation on the interface which is indicative of their structure.[100] Thus, interfacial tension between octane-water interface is 50.5 mN/m, whereas between octanol-water interface it is only 8.8 mN/m. Reduction of interfacial tension in the latter case is due to the orientation of octanol hydroxyl groups toward water, in other words, to the structure and the polarity of the interfacial layer. Because of such an orientation, the stimulus for adsorption of other asymmetric molecules of a third component on the interface is decreased. On the other hand, interfacial tension cannot serve as the only criterion of emulsifier adsorption. The greater the difference in polarity between boundary phases, the steeper the orientation of surfactant molecule at the interface, and the larger the reduction in free energy of the system due to adsorption. For example, the surfactant molecules are less oriented at the octanol-water interface than octane-water interface.[97] The consideration of the adsorption kinetics of emulsifier is very important in an estimation of its effectiveness under the dynamic conditions of emulsion polymerization. A period is needed for the establishment of adsorption equilibrium, and this period varies between 15 and 120 seconds.[97]

The general conclusions developed for adsorption of surfactants on liquid-liquid and liquid-air interfaces cannot be completely applied to adsorption on liquid-solid interfaces. Because of the dispersion, polar, orientation, and hydrogen bonding interactions, the emulsifier molecules adsorbed onto the solid phase-liquid interface may acquire a nonvertical orientation; they may be arranged with greater planarity the higher the interaction acts upon the polar part of the emulsifier molecule.[97] Thus, Wolfram[103] found that the adsorption area of a sodium dodecylsulfate emulsifier molecule on paraffin surface is 0.41; on polyethylene, 1.21; on polymethyl methacrylate, 1.32; and on polyethylene, terephtalate 1.42 nm^2. Wolfram determined these values from the wetting angle on planar polymer surface, however, Paxton[104] applied adsorption titration method to the particles of aqueous polymer dispersions and found similar results as Wolfram such that the area occupied by a sodium dodecylbenzylsulfonate molecule in a saturated adsorption layer, A_{Slim}, on polymethyl methacrylate surface is 1.31 nm^2; on polystyrene, 0.53 nm^2. Dunn and Chong[54] determined that A_{Slim} = 1.24 nm^2 for sodium dodecylsulfate on polyVAc latex particles, which is 2.4 times higher than the minimum adsorption area. Piirma and Chen[105] reported that electrolyte concentration, temperature, and particle size should also be considered when determining the adsorption areas of surfactant molecules on latex particles.

Yeliseyeva reported that with increasing monomer solubility in water, the size of particles decreases and their distribution broadens. The emulsifier adsorption decreases with increasing polarity of the interface. Therefore, less emulsifier is consumed for the formation of a given surface, which facilitates the increase of the overall surface area and the decrease in particle size. For acrylic acid esters, the broadest particle size distribution was observed for the most polar monomer methyl acrylate.[97] This corresponds to the longest period of particle formation due to the increased critical size of radicals and the smallest emulsifier consumption. The lower stability of smaller particles, which follows from the DLVO theory, resulted in limited flocculation of particles during VAc emulsion polymerization. Dunn and Chong concluded that flocculation throughout the process occurs between small, newly formed particles and larger, "old" particles.[54] According to data obtained by Okamura and Motoyama, adsorption of anionic emulsifiers such as sodium dodecyl sulfate and dioctylsulfosuccinate by the PolyVAc latex particles was limited, that is, an increase in emulsifier concentration above a certain limit did not produce an increase in adsorption.[106] Yeliseyeva concluded that latex particles of polar monomers were the result of limited flocculation of primary particles, which were the precipitates of the polymeric radicals grown in the aqueous phase.[97] This limited flocculation of primary particles depends on the ratio of the rate of formation of their overall surface area, S, to the rate of establishment of equilibrium adsorption, Γ, of the emulsifier by the surface:

$$\frac{d\Gamma}{dt} = K\frac{dS}{dt} \tag{3.31}$$

where K is a proportionality constant for the equilibrium adsorption. When this equation is applied, the surface of the polymer phase is stabilized by the adsorbing emulsifier, and the formed particles may remain discrete at high degrees of conversion. Then, the number of particles may be assumed constant. In reality, however, it may occur for polar polymers that

$$\frac{d\Gamma}{dt} \langle K\frac{dS}{dt}\,. \tag{3.32}$$

In this case, the surface activity of the emulsifier on the polar polymer surface is low and particles appear with their surfaces insufficiently covered by the emulsifier at high polymerization rates. Under conditions of high temperature and agitation, such particles rapidly flocculate with each other and an equilibrium adsorption of the emulsifier is established at the formed aggregate latex particles.[97]

Yeliseyeva found that there was an inverse relationship between the dependence of the rate of polymerization to the emulsifier concentration and A_{slim}. This means that for styrene monomer having its A_{Slim} = 0.53 nm^2, its polymerization rate has a higher power dependency to the emulsifier concentration (0.5) than methyl acrylate having its A_{Slim} = 1.51 nm^2 with a 0.13 power dependency when sodium dodecyl sulfate is used as an emulsifier. Since A_{Slim} = 1.24 nm^2 for sodium dodecylsulfate on polyVAc, it should also have low power dependency of the rate of polymerization to the emulsifier concentration. Thus, the role of emulsifier in polymerization kinetics decreases with the decease in its ability to create the overall interfacial area.[97]

Hamielec and MacGregor published a review on the state of the art of emulsion polymerization reactor principles.[107] They considered the design and operation of the batch and continuous stirred tank reactors (CSTR) under steady-state and dynamic conditions. They assumed that emulsion polymerization of VAc follows Smith-Ewart Case I kinetics with the production of polymer with long-chain branching, and that styrene follows Case II kinetics. They presented kinetic derivations for both mechanisms for comparison. In addition, they summarized the online control methods of continuous latex reactors, giving examples of instrumentation for online enthalpy control around the reactor by cooling water, online latex density control, on-line turbidity spectra, and online surface tension control.[107]

Warson briefly summarized the industrial practice of the batch, semicontinuous (delayed addition), and continuous (cascade type) emulsion polymerization of VAc.[108] He stated that it is not possible to expect the same latex properties when the same polymerization recipe is used for every type of process. The reason is the great difference in the particle environment and the physical equilibrium during polymerization, and the possibility of grafting reactions taking place to different extents. Warson criticized that the attempts to force applying Smith-Ewart kinetics to the highly water-soluble VAc monomer system had clouded a proper understanding of VAc polymerization mechanism. He gave a clear picture of the mechanism: with a water-soluble initiator, the initiation takes place in the water phase and oligomeric aqueous polymer is formed. It is solubilized in water by its end groups, but it becomes insoluble as polymerization proceeds. The polymer particles formed absorb monomer and when conversion becomes about 14%, the rest of the monomer is absorbed substantially into the polymer particles. Then the polymerization proceeds in the particles, which can be treated as a compartmentalized system. For PolyVAc, because of the relatively large particle size (0.3–1 micron), there is more than one growing radical per particle most of the polymerization time, with a varying mechanism for chain termination.[108]

Warson presented the differences in each polymerization system for comparison. For batch polymerization, the monomer substantially absorbed into polymer particles at about 14% conversion, but there was excess monomer in the environment throughout. Particle formation is probably complete by 14% conversion; further initiation in water phase is limited and, hence, further nucleation. However, the number of particles is probably balanced by particle coalescence. The initiator decomposes by a first-order reaction, but the radical flux is probably constant, and the R_p dependence on initiator is probably about 0.5. When polyvinyl alcohol is used as the protective colloid, its concentration is constant in batch process, but a considerable fraction is adsorbed onto the polymer particles. Grafting on polymer particles is probably very limited because of the excess monomer present in the reaction system.[108]

For semicontinuous (or delayed-addition) polymerization processes, only a limited quantity of monomer, i.e., 2 to 5% is present in the system throughout the reaction. This is a *de facto* "seed" process, the seed quantity depending on the extent of the original addition of initial monomer and other ingredients. As long as the monomer weight percentage relative to monomer plus polymer is below 14%, there will be no monomer drops as separate entities. Particle formation is complete at an early stage, stabilized by adsorption of polyvinyl alcohol, with possible extra stabilization due to initiator residues. Particle sizes increase by monomer absorption and by adsorption of initiated radicals from the water phase. Sometimes bimodal molecular distribution occurs indicating two different modes of polymerization; one is in the monomer-swollen particles and the other is the result of aqueous or surface initiation. Monomer starvation and high temperature conditions result in high grafting to polyvinyl alcohol, or possibly on polymer molecules. Excessive grafting to polyvinyl alcohol causes an increase in latex viscosity and instability.[108] A high initiator concentration with a low monomer concentration should give optimum conditions for the formation of graft copolymer. Grafting increases the actual weight of the polyvinyl alcohol stabilizer, which will cause an increase in the size of the hydration shells.

In the cascade type of continuos reactor system, all ingredients are added to one reactor having minimal stirring and the monomer is polymerized to a fixed level and transferred to a second reactor where the reaction will be substantially completed or, possibly, into a third or even subsequent reactor until polymerization is substantially complete. Monomer is added at constant polymer ratio and initiators and stabilizers are added correspondingly. The finished latex is withdrawn at the same rate as the ingredients enter. This system can be used to produce VAc-acrylate copolymers where the comonomers are added at the desired stage. There is considerable non-homogeneity in the primary reactor. Monomer is absorbed by the existing particles. There is direct initiation of the monomer in the water phase, but the equilibrium point is not known. The growing radicals are partially swept up by the existing particles in this non-equilibrium condition. There is wide particle scatter. Considerable intergrafting and chain branching occurs within existing particles. There will be an appreciable amount of new nucleation from grafted polyvinyl alcohol, giving self-stabilized particles. With minimal stirring, the reduced mixing leads to a greater tendency of particles to agglomerate and, thus, to a greater scatter in particle size.[108]

Taylor and Reichert examined the influence of the process type (batch and continuous) on the molecular weight distribution in VAc polymerization.[109] Chain branching affects the molecular weight distribution of polymer produced. Branch points are introduced by reaction of growing radicals with polymer chains formed previously, and by terminal double bond polymerization. Branching broadens the molecular weight distribution of the final latex. Branching reactions are highly dependent on residence time and mixing effects. In the batch reactor all polymer molecules will have the same length of reaction time, but monomer and initiator concentrations will change with time, which causes broadening of molecular weight distribution. In the continuous reactor, reaction products will have a distribution of times in the reactor, but monomer and initiator concentrations will be constant. Models were developed employing a complex kinetic scheme including polymer transfer and terminal double bond polymerization without neglecting initiation and termination steps.[109]

Donescu, Gosa, Ciupitoiu, and Languri[110] examined the semicontinuous emulsion polymerization of VAc using polyvinyl alcohol as aprotective colloid and ethoxylated (20 moles) cetyl alcohol as a coemulsifier. Polymerizations were carried out in 1- or 2-liter glass reactors. The initial charge consisting of 10% monomer, approximately 40% water, all the polyvinyl alcohol, and some amount of coemulsifier was fed at 65°C and the "de facto" seed polymer was prepared within 30 minutes by using potassium persulfate emulsifier. The remaining monomer-initiator solution and the coemulsifier solutions were fed for 4 hours at 70°C. Emulsion films were obtained by drying at room temperature and were subjected to successive extractions in water and benzene, boiling for 8 hours each. The amounts of water-soluble, benzene-soluble, and insoluble fractions were determined gravimetrically.[110] Water-soluble fractions contain small quantities of ungrafted polyvinyl alcohol, coemulsifier, and a very small amount of polyVAc homopolymer, while benzene-soluble fractions contain ungrafted poly VAc and graft copolymer with a high content of polyVAc, and insoluble fractions are polyVAc crosslinked with polyvinyl alcohol. They examined the effect of stirring speed on the size of particles and the conversion percentage. Up to 400 rpm, which can be accepted as normal for a 1-liter reactor, a nearly linear decrease of the particle diameter was found by the increase of stirring rate. Conversion was also decreased from 85% to 82% by the increase of stirring rate. This may be due to the increase of the mechanical and surface coagulation with the application of intense shear, thereby reducing the total number of polymer particles.[110]

Donescu, Gosa, Ciupitoiu, and Languri also reported the distribution of the coemulsifier between the initial charge and the remaining monomer. If all the coemulsifier was fed in the initial charge, small particle sizes were obtained. If the amount of coemulsifier fed continuously with the remaining monomer was high, the final particle sizes were large. In addition, there was a sharp decrease in the insoluble fraction, from 50% down to 10%, with the increase of the coemulsifier in the initial charge up to 50%. This means that polyVAc crosslinked with polyvinyl alcohol fraction decreases to reasonable levels if at least half of the coemulsifier is introduced in the initial charge.[110]

Vanderhoff published a review outlining the mechanism of emulsion polymerization in 1985.[111] He pointed out that the preparation of polymer latices is both science and art. It is a science from the kinetic mechanism point of view, whereas it is an art in that the formulator uses a recipe which comprises monomer, water, emulsifier, initiator, and other ingredients, and the quality of the latex obtained depends upon small variations in the polymerization parameters as well as the skill of the preparer.

Vanderhoff reported that, for the initiation-in-the-aqueous phase mechanism, the rate of particle nucleation is initially the rate of radical generation, R_i, but shortly thereafter a steady state is reached between the initiation and capture of the oligomeric radicals, R_c and the flocculation of the latex particles R_f,

$$\frac{dN}{dt} = R_i - R_c - R_f \,. \tag{3.33}$$

Thus, the nucleation of particles continues throughout the course of the polymerization but is moderated by the capture of the precipitating oligomeric radicals and the flocculation of primary and mature particles.[111] The principal function of the emulsifier is to stabilize the oligomeric radicals as they precipitate from the aqueous phase. Thus, the initiation and propagation of polymerization in the aqueous phase follows the general kinetic scheme for mass, solution, and suspension polymerization, and the expression for the number-average degree of polymerization, $\bar{X}_n$, is

$$\bar{X}_n = \frac{R_p}{R_i} = k_p[M]\left(\frac{1}{R_i k_t}\right)^{1/2} \tag{3.34}$$

Taking for the rate coefficient of the 0.1% potassium persulfate initiator at 60°C as[87] $k_i = 3.0 \times 10^{-4}$ min^{-1} and the values of k_p and k_t are, 2300 and 2.9×10^7 l/mol-sec, respectively, and assuming that the polymer does not precipitate from aqueous solution before it is terminated and the termination occurs by termination mechanism; it was found that, $\bar{X}_n$ = 1320, the number-average molecular weight, M_n = 1.14×10^5, the diameter of the primary spherical particle, D = 6.8 nm, and the surface charge of the spherical particle = 0.22 μC/cm^2. When these calculations were done for the styrene monomer which polymerizes with initiation-in-micelles mechanism, it was found that the primary polyVAc particles have significant molecular weight (approx. 120 times larger than polystyrene primary particles), and particle diameter (approx. 5 times larger than polystyrene primary particles), and much lower surface charge (approx. 23 times less than polystyrene primary particles). The surface charge is found to be 0.22 μC/cm^2 for polyVAc, and it is smaller than the critical value for stability of 0.32 μC/cm^2 found according to the DLVO theory.[111] Thus, VAc monomer would be expected to yield primary polymer particles comprised of single polymer molecules. However, it may be argued that precipitation of the primary particles would result before the first polymer molecule is terminated; the polymeric radical would assume a spherical form and absorb monomer from the aqueous phase. Then, the size of the polymer particle is increased before termination, which will decrease the probability of termination because of creating a new barrier for the terminating radical. Moreover, monomer absorption would decrease the surface charge. For example, for a 1:1 monomer/polymer ratio, the diameter of the particle would increase from 6.8 to 8.7 nm and its surface charge would decrease from 0.22 to 0.13 μC/cm^2. Thus, stability is decreased making the particle more likely to flocculate with other primary particles, as well as with mature particles. On the other hand, the rate of polymerization is increased because of the higher monomer content.[111]

It is known that polyVAc is solubilized by emulsifier solutions, and that the high emulsifier level in the beginning of the polymerization would favor solubilization of the polymer.[112-114] The tendency of polymer precipitation depends upon the ability of the emulsifier to solubilize the growing radical.[111] Vanderhoff examined the conditions to produce monodisperse polyVAc latices. The shorter the particle nucleation stage relative to that of the particle growth stage, the narrower will be the latex particle size distribution. The primary particles generated early in the reaction must act as nuclei to capture all primary radicals formed thereafter, and these nuclei must grow without flocculation until the end of the polymerization.[111] If there is no emulsifier, the sulfate end-groups introduced by the persulfate initiator are often sufficient to stabilize latex particles at relatively low monomer-water ratios to produce a monodisperse latex.[17,115-117] If emulsifier is present, the lower its concentration, the higher the tendency to obtain monodisperse latex. In practice, seeded polymerization using a monodisperse seed latex allows the preparation of larger monodisperse latices of different size.[118,119]

Rawlings and Ray developed a class of simplified emulsion polymerization models for continuous stirred-tank reactor systems exhibiting unwanted oscillations for emulsion polymerization of monomers such as styrene, styrene-butadiene, vinyl chloride, methyl methacrylate, and vinyl acetate.[120] Their model showed that radical desorption, chain transfer agents, and certain types of impurities should have a strong influence on reactor stability. Later, Lee and Mallinson developed a model to predict the molecular weight of polyVAc in continuous stirred-tank reactor emulsion polymerization systems by using a moment method.[121] The molecular weight oscillations, which are often observed in continuous emulsion polymerization and are associated with a heterogeneous initiation mechanism that involves radical desorption and absorption phenomena. It was found that the observed oscillations are closely related to the radical diffusion and desorption rates in the water phase. Lu and Brooks investigated the effects of start-up procedure of VAc emulsion polymerization in a continuous flow, back mixed reactor.[122] In many cases, although the continuous flow reactor is isothermal and the feed rate is steady, monomer conversion and the number of polymer particles oscillate with time and a steady state cannot be obtained.

It was found that, for a given feed stream, the average particle size and the number of particles could depend on the start-up procedure, even when the monomer conversion was the same. The start-up procedures can be changed by altering the initial charges, which are: distilled water; water and emulsifier; water, emulsifier, and monomer; water, emulsifier and initiator; water, emulsifier, and monomer and initiator. In each case, the reactor is full of liquid initially, but this reactor charge can be varied. The proportions of the ingredients in the initial reactor contents are the same as those in the feed, but when a particular component is absent initially it is replaced by an equivalent amount of water. Sodium dodecyl sulfate is used as emulsifier and ammonium persulfate is used as initiator.[122] Lu and Brooks reported that soon after the start-up, particle nucleation in the reactor appeared to cease. In addition, a gel effect was not required to produce the oscillations in monomer conversion and particle size. Lu and Brooks concluded that the idealized reactor models are inapplicable and future model developments must include non-classical particle nucleation and particle coalescence.[122]

Hayashi, Komatsu, and Hirai investigated the seeded polymerization of VAc using monodisperse polyVAc seed, prepared in the absence of emulsifiers, with potassium persulfate.[123] They pointed out that Patsiga et al.[21] did not attempt to seek evidence for new particle formation during seeded polymerization. In addition, Napper and co-workers[17,18] reported that a constant number of particles is attained at very early conversion in the absence of emulsifiers, which means that no additional new particles are formed after this stage. In contrast, Hayashi, Komatsu, and Hirai reported that new small particles were formed in the emulsion polymerization system containing a small amount of seed particles, whereas no new particles were observed in the system containing a large amount of seed particles.[123] Both seed particles and the seeded polymerizations were carried out in a 1-liter stirred glass reactor. Potassium persulfate initiator was used at 70°C in an emulsifier-free reaction system to obtain seed particles of 0.04 microns. They were dialyzed in running water for one week to remove any excess persulfate initiator. The constant number of seed particles was used in seeded polymerization in order to examine the effect of rate of stirring, and it was found that the diameters of seed particles and newly formed small particles increase with increasing rotational speed of the stirrer. The number of the new small particles decreases with the stirring rate. On the other hand, the effect of stirring rate on the unseeded polymerization was also examined. It was found that the diameter of the particles increases with the increase of the stirring rate. Higher stirring rates lead to coagulation of more small particles during the initial stage of polymerization where the small particles form.[123]

When constant stirring rate was applied, the number of seed particles was varied in the experiments, and it was seen in the electron micrographs that there were both large particles that arose from the increase in the volume of seed particles and small particles that were newly formed in the water phase.[123] As the number of seed particles increases, the diameter of large particles increases suddenly and, after passing through a maximum value, decreases slowly. The diameters of the new particles increase and the number of new particles decreases linearly with the increase in the number of seed particles. When large amounts of seed particles are used in seeded polymerizations, no new particles are observed in the system. In this case, the diameter of the grown seed particles agrees with the theory that all the VAc is polymerized within seed particles, as proposed by Netschey and Alexander.[32] Hayashi, Komatsu, and Hirai commented that the total surface area of the seed latex is the decisive parameter for the formation of the newly formed small particles. The limiting total surface area of seed particles, at which no more new small particles are formed, was found to be 6.1×10^{-2} m^2/g-latex. It means that all small radicals formed in the water phase are absorbed by the original seed particles when the total surface area is greater than 6.1×10^{-2} m^2/g-latex.[123]

Donescu, Gosa, and Languri examined the semicontinuous emulsion polymerization of VAc in the presence of polyvinyl alcohol stabilizer in 1989.[124] Hydrogen peroxide and a ferrous sulfate redox initiator system were used. At low rates of monomer addition, the monomer inflow controls the rate of polymerization, whereas at high rates of monomer addition the emulsion polymerization system is flooded, the rate of polymerization is no longer determined by the rate of addition, and the amount of the unreacted monomer increases with time. At a moderate feed rate, the polymerization rate is controlled by the monomer addition rate, and the polymerization rate becomes proportional to the introduced monomer. The diameters of the particles increase and the amount of insoluble polymer decreases with increasing feed rate. This means that when the monomer feed rate increases, the ratios of monomer/particle and monomer/active reaction centers also increase. The increase of the monomer feed rate also results in the increase of the benzene soluble fraction of the final polymer, which demonstrates the low extent of grafting and crosslinking.[32,117]

Contrary to the findings of Hayashi, Komatsu, and Hirai,[123] Donescu, Gosa, and Languri reported that the conversion of the reaction and the particle diameter decrease with increasing stirring speed.[124] However, they employed a stirring rate of 200 to 500 rpm for a 2-liter reactor, whereas, Hayashi, Komatsu, and Hirai used a stirring rate of 22 to 150 rpm for a 2-liter reactor. Donescu, Gosa, and Languri reported the presence of a vortex at 400 rpm. As stirring rate increases, the average particle size decreases nearly linearly. They explained that the decrease of the conversion with the increase of the stirring rate was due to the particle coagulation and the reaction inhibition with oxygen. At the same time, the fraction of the insoluble polymer (crosslinked polymer) also decreased with the increase in the stirring rate. They speculated that the transfer reaction of active centers to oxygen, the concentration of which increases with stirring rate, causes the decrease of the final content of the crosslinked polymer.[124]

Lee and Mallinson improved their previous model[121] to predict the molecular weight of polyVAc in continuous stirred-tank reactor emulsion polymerization systems by using a moment method, developed an explicit equation for the molecular weight distribution from the mass balances, and compared the results of their model with experimental data taken from gel permeation chromatography.[125] They described the kinetic mechanism as having a very complex nature which includes radical transfer effects and multiple propagation steps, i.e., the terminal double-bond reaction and the method of solution of the two mass balances for dead polymer and living polymer chains. They pointed out that these two mass balance equations couldn't be solved without a consideration of the heterogeneous initiation mechanism.[125] In the experimental observations, the higher surfactant concentration gave higher weight average molecular weights, $\overline{M}_w$, but lower number average molecular weights, $\overline{M}_w$, which shows large polydispersity ratios. Their distribution equation fit the experimental data, and it was shown that the large polydispersity ratios are strongly dependent upon the monomeric radical concentration in the particles and the terminal double bond rate constant.[125] Lee and Mallinson also determined that the molecular branching from multiple propagation and radical transfer appeared significant experimentally, and this caused a rapid increase in the higher molecular weight fractions. However, they could not include this phenomenon in the theoretical size distribution equation.[125]

Badran, Moustafa, Yehia, and Shendy examined the emulsion polymerization of VAc initiated by the potassium persulfate-cyclohexanone sodium bisulfite redox pair system.[126] Emulsion polymerization reactions were carried out at 1°C in a 250 ml stirred flask with a stirring rate of 500 rpm. The rate of polymerization was found to be dependent on the initiator, monomer, and emulsifier concentrations to the 0.88, 0.22, and 0.20 powers, respectively. They also reported that the potassium persulfate-sodium bisulfite redox pair system decreases the maximum conversion and doesn't form a stable emulsion.[126]

Bataille, Dalpe, Dubuc, and Lamoureux investigated the effect of agitation on the conversion of VAc emulsion polymerization.[127] They criticized that rather conflicting results were obtained on the effect of agitation on the emulsion polymerization conversions by the previous workers. They varied the rate of agitation and the level of sodium lauryl sulfate emulsifier in the batch emulsion polymerization of VAc in a 1-liter glass reactor at 60°C by using potassium persulfate initiator, and the latices obtained were characterized for the conversion and the molecular weight.[127] Three levels of agitation were studied: 75, 150, and 220 rpm. First, they reported an increase in the reaction rate and conversion with the increase in the emulsifier level. They obtained weight average molecular weights of $\overline{M}_w$ = 1 000 000 – 3 600 000 with an agitation rate of 150–220 rpm, which were much higher than the ones obtained at an agitation rate of 75 rpm. They commented that this was due to the lower diffusion associated with the lower agitation.[127] The polydispersity of the polymers obtained varied between 1.6 and 7.5; it increased with increasing conversion. They pointed out that if one operates at abnormal agitation conditions (too low or too high), the level of emulsifier has little influence on the polymerization rate.[127]

Hergeth, Lebek, Kakuschke, and Schmutzler reported the formation of oligomers in VAc emulsion polymerization.[128] They examined the emulsifier-free VAc polymerization where the monomer polymerizes in the aqueous phase to form short-chain oligomers. These oligomers are surfactants because of their ionic head groups arising from the potassium persulfate initiator and hydrophobic hydrocarbon chain. The monomer was added dropwise to a 0.5-liter reaction flask in "monomer starved" conditions, where the monomer concentration is far below its saturation concentration in water. The monomer addition rate was lower than the polymerization rate. The surface tension of the oligomeric solutions was measured and the adsorption of the oligomers on highly dispersed quartz (silica) powder particles was determined. Particle diameters and molecular weights of the oligomers were also reported. It was found that the primary particle formation in the aqueous phase is due to an oligomeric micellization, which can be seen in the sharp decrease of the surface tension of the solution.[128] They obtained a number-average degree of polymerization of 9–11 for PVAc oligomers during nucleation stage, and compared the predicted value of approximately 1300 by Vanderhoff.[111] They suggested that the rate of termination in the aqueous phase is high as compared to termination in the latex particle, and this is the primary cause of the discrepancy. They also speculated that the formed short-chain PVAc oligomers ultimately micellize, resulting in a process that transforms from homogeneous nucleation to heterogeneous nucleation.[128] PolyVAc oligomers were strongly adsorbed onto silica particles in the aqueous phase. In general, quartz powder forms large aggregates in aqueous media; however, if VAc emulsion polymerization is carried out in the presence of quartz powder, it loses its aggregative tendency and is dispersed in aqueous phase in an ideal manner.[128]

Donescu and Fusulan investigated the decomposition of the potassium persulfate initiator during the semicontinuous polymerization of VAc, using polyvinyl alcohol and hydroxyethyl cellulose as protective colloids, and ethoxylated cetyl alcohol with 20 mol ethylene oxide and sodium sulfosuccinate of nonylphenol ethoylated with 6 mol ethylene oxide as emulsifiers.[129] It was found that the rate of potassium persulfate decomposition is higher in the aqueous phase containing a protective colloid and surfactant. The decomposition rate is low in the presence of VAc monomer. When the monomer addition rate was increased, the quantity of the decomposed persulfate was also increased.[129]

Levy and Hinojosa reported the effect of oxygen on VAc polymerization.[130] Oxygen reacts with vinyl monomers to form less reactive poroxy radicals, resulting in a slower rate of propagation compared to that in the absence of oxygen. On the other hand, peroxidic compounds are also formed, which lead to initiation of vinyl monomer. The global effect of oxygen gas on the rate of polymerization will depend on the relative importance of these two opposing effects. The impact of oxygen becomes even more complicated when inhibitors are added to stabilize the VAc monomer. Levy and Hinojosa examined the effect of oxygen concentration in the gas blanket atmosphere on the VAc monomer in three grades; one is inhibitor free, one is inhibited with 3–5 ppm hydroquinone, and another is inhibited with 14–17 ppm hydroquinone. They found that when stabilized with 3-5 ppm of hydroquinone, both air-saturated and oxygen-free VAc exhibit adequate thermal stability at normal transport and storage temperatures (25–50°C). Oxygen destabilization of VAc is not caused by the oxidation of acetaldehyde impurity, but is probably due to the relatively low stability of VAc polyperoxides.[130]

Urquiola, Dimonie, Sudol, and El-Aasser investigated the emulsion polymerization of VAc using a polymerizable surfactant, sodium dodecyl allyl sulfosuccinate, in three subsequent papers.[131-133] They pointed out that the conventional surfactants are held on the particle surface by physical forces and thus adsorption/desorption equilibrium always exists, which may not be desirable as a surfactant leaching out upon contact with water or interfering with adhesion to a substrate.[131] They suggested using polymerizable surfactants to bind the polyVAc particles chemically to obtain more stable latices. In this manner, these surfactants cannot be desorbed from the particle surface or exuded from a dried film. They can also confer stability over a wide pH range. Urquiola, Dimonie, Sudol, and El-Aasser carried out a comparative study of the emulsion polymerization kinetics using the reactive sodium dodecyl allyl sulfosuccinate surfactant and its nonpolymerizable counterpart — its hydrogenated derivative that does not have the double bond required for polymerization. CMC and interfacial tension with water properties of both of these surfactants were found to be very close. Emulsion polymerizations were carried out at 60°C in a glass reactor under nitrogen atmosphere by using sodium persulfate initiator. Reaction kinetics were determined by following the fractional conversion of the VAc. The rate of polymerization was found to increase with decreasing concentration of the polymerizable surfactant. This is the opposite of the usual behavior found in conventional emulsion polymerization. The increase in the surfactant concentration lead to smaller particle sizes as measured by transmission electron microscopy. These results suggested that the reactive surfactant does not act only as an emulsifier, but it may also copolymerize with VAc, or may act as a chain transfer agent.[131] They examined the polymerization mechanism in their second paper and reported that both the aqueous phase forming water-soluble oligomers and particle/water interface were found to be loci for copolymerization.[132] It was found that the reactions at the particle/water interface are more important, and a relationship exists between the particle/water interface and the polymerization rate.[132] A mathematical model was also developed in order to understand the growth of latex particles in this system.[133] A combination of copolymerization and chain transfer to reactive surfactant was found to provide a good fit for the experimental results.[133]

Okaya, Tanaka, and Yuki compared the physical properties of the films obtained by the batchwise and semicontinuous emulsion polymerizations of VAc.[134] Polyvinyl alcohol that was 88% hydrolyzed was used as protective colloid, and 40 moles of ethoxylated nonyl phenol nonionic surfactant was the emulsifier in both systems. Branched polyVAc was obtained in both systems when the polymerization was carried out at high conversions. In the batchwise polymerization, long branches and higher molecular weight chains were formed with increasing conversion with high degrees of polymerization. Short branches and low degrees of polymerization were obtained in the semicontinuous polymerization due to the higher chain-transfer reactions. In the batchwise polymerization, higher mechanical properties and improved water resistance of the polymer films were seen due to the higher entanglement of the long polyVAc macromolecules. Latices prepared in the presence of polyvinyl alcohol resulted in higher tensile strengths than those prepared with nonyl phenol ethoxylates, presumably due to the formation of a reinforcing polyvinyl alcohol structure.[134]

Brooks and Wang examined the kinetics of seeded and nonseeded emulsion polymerization of VAc without adding any emulsifier and using potassium persulfate as the initiator.[135] Batch polymerizations were carried out in a 1-liter glass flask under nitrogen blanket. When seed latices were prepared, they were transferred into a cellophane dialysis tube to remove excess initiator and its by-products. Monomer conversion was determined gravimetrically, and particle size was determined by using a transmission electron microscope.[135] It was determined that the number of stable particles does not increase after the early stages of polymerization. The polymerization rate was proportional to the 0.69 power of the initial monomer concentration. The particles were stabilized by initiator fragments. In seeded polymerizations, the polymerization rate depends on the 0.6 power of initiator concentration but is independent of the monomer-to-polymer ratio. When the monomer-to-polymer ratio is high, new stable particles can be formed without leading to significant increase in the polymerization rate. When the rate of stirring is increased, there is no effect on the polymerization rate within 50–150 rpm, unless the stirring rate is very high. At a rate of stirring of about 300 rpm the polymerization rate is reduced.[135]

Gilmore, Poehlein, and Schork modeled polyvinyl alcohol stabilized, semicontinuous VAc emulsion polymerization[136] and compared their model with experimental findings.[137] The model accommodates the particle nucleation, growth, and grafting onto the polyvinyl alcohol backbone during nucleation and polymeric stabilization. When emulsion recipe, process conditions, and kinetic parameters are supplied, the model predicts the conversion, particle size, and number profiles.[136] Their mathematical model is comprised of 244 equations, only nine of which are differential. The cumulative number of unknown variables is 297, and thus 53 variables in addition to the nine initial conditions for the ordinary differential equations must be specified to solve the model. Of the 53 unspecified variables, 22 are provided by the polymerization recipe or literature estimates, while the remaining 31 must be inferred or hypothesized based on probable mechanisms. These figures give an idea of the complexity of the semicontinuous emulsion polymerization of VAc.[136] In the experiments, 88% hydrolyzed, low molecular weight ($\overline{M}_v =$ 11 000–31 000) polyvinyl alcohol and commercial 3–5 pmm hydroquinone-inhibited

VAc monomer were used.[137] Polymerizations were conducted at 60°C in a 1-liter glass reactor where hydrogen peroxide initiator was added continuously. Ferrous sulfate was added as a co-initiator. An N_2 blanket was maintained during the polymerization to minimize O_2 inhibition. Semibatch simulations indicate that independent increases in the vinyl acetate, polyvinyl alcohol, and initiator levels raises the primary grafted particle population. The model was found useful in predicting the relative importance of polyvinyl alcohol grafting during nucleation. The model suggests that when the molar ratio of VAc to polyvinyl alcohol is high, grafted primary particles do not contribute significantly to the total primary particle concentration, and physical adsorption of polyvinyl alcohol onto the latex particle is a more important process.[137] These findings are in contrast with the reports of many workers in the field (See sec. 3.3).

Donescu, Ciupitoiu, Gosa, and Languri examined the hydration properties of polyVAc in the presence of water.[138] They obtained polyVAc latices in the semicontinuous process in the presence of polyvinyl alcohol. The glass transition temperature of polyVAc decreases due to the hydration process, and water may be considered a true plastifier. Using DTG and TGA measurements during the evaporation of polyVAc latices, they reported the existence of bound water on the polymer particles. These particles are subjected to more frequent flocculation, due either to an insufficient emulsifier concentration or to a high stirring rate. In addition, it was postulated that the migration of the monomeric radical to the water phase is favored by the presence of the bound water, thus decreasing the water-polymer barrier.[138]

Gossen and MacGregor reported a method to measure mean particle diameter from on-line measurements of latex density and dilute latex turbidity during the continuous production of polyVAc emulsion polymer.[139] The solids fraction was calculated from density, all flow rates into the reactor, and knowledge or estimates of all constituent densities. Mean particle diameter was calculated from the solids fraction and the UV turbidity of a diluted sample. PolyVAc latex, the refractive index of which is only 1.1 times that of water, has been the source of many unsuccessful particle diameter measurements. However, Gossen and MacGregor were able to calculate the relationship between the specific turbidity and the particle diameter by applying the Mie theory. Unfortunately, no electron microscopy results were given for comparison.[139]

Lepizzera and Hamielec investigated the particle nucleation mechanism in seeded emulsion polymerization of VAc in both the presence and absence of polyvinyl alcohol.[140] They pointed out that the particle nucleation is the most important step because of its effect on polymerization kinetics, particle size distribution, and emulsion viscosity. Two different grades of polyvinyl alcohols which were approximately 88% hydrolyzed but with different weight average molecular weights (26 000 and 103 000) were used. Potassium peroxodisulfate was used as initiator, and sodium hydrogen carbonate was used as buffer. The seeded emulsion polymerization was performed at 60°C in a 1-liter glass reactor with a stirring speed of 250 rpm. Lepizzera and Hamielec followed the polymerization of only a small amount of VAc monomer because they used 600 g water, 300 g seed latex, and only 60 g VAc and 3–12 g polyvinyl alcohol in their experimental recipe. They also did not use electron micrography for particle diameter measurements due to the shrinkage of polyVAc particles when exposed to the electron beam. Instead, they applied disc centrifuge sedimentation to determine the average particle diameters.[140] In the absence of polyvinyl alcohol, no new nucleation was observed by electron microscopy, while in its presence new particles were formed, giving a bimodal particle size distribution. The number of new particles was greater with the higher molecular weight polyvinyl alcohol. The introduction of higher molecular weight polyvinyl alcohol increases the rate of polymerization, whereas a lower molecular weight one decreases it. Lepizzera and Hamielec proposed that nucleation of new particles occurs via precipitation of "copolymer" polyvinyl alcohol-polyVAc radicals in the water phase.[140] In the particle growth stage there is a constant number of polymerization centers in the presence of monomer source. Seeded emulsion polymerization can be utilized to determine the rate of polymerization in this stage since the particle number should not change. The number of radicals entering per growth center is given below:

$$\bar{n} = n_o \frac{N_A}{k_p\left[M_p\right]N_p}\left(\frac{dx}{dt}\right) \tag{3.35}$$

where $\bar{n}$ is the average number of radicals per growth center (particle), n_o the initial amount of monomers (in moles), N_A the Avagadro number, k_p the propagation rate coefficient, (liter/mol-s), $[M_p]$ the monomer concentration in the growth centers (mol/liter), N the number of seed particles per liter, and x the conversion of monomer. Lepizzera and Hamielec measured the number of radicals per particle indirectly through the use of kinetic models and determined that VAc polymerization follows Smith-Ewart Case III kinetics, with the number of radicals per particle increasing with conversion.[140]

The mechanism of the propagation of VAc polymerization is a controversial subject. Dunn[77] suggested that VAc emulsion polymerization should be a Case I scenario due to the high water solubility of VAc monomer and its oligomers, and the ability of polymer radicals to chain transfer to monomer. On the other hand, Leppizera and Hamielec[140] and, independently, Lange et al.[154] defended that VAc emulsion polymerization follows Case III kinetics with the number of radicals per particle increasing with conversion. They suggested that since large particle size latices were used, the effect of large particles dominates n and, thus, Case III kinetics would apply.

Tobita applied his simulation model to the kinetics of long-chain branching in VAc emulsion polymerization.[141] He investigated the effect of compartmentalization on the kinetics by application of the kinetic parameters and experimental data reported by Friis et al.[60,142] Tobita discussed the chain transfer to polymer and terminal double bond polymerization. He assumed that the loci of polymerization are the polymer particles, with diameters usually in the submicron range. It was found that the method of moments conventionally applied clearly overestimates the weight average chain lengths, and the effect of compartmentalization must be accounted for in VAc emulsion polymerization.[141]

Kshirsagar and Poehlein examined the radical entry into particles during seeded VAc emulsion polymerization.[143] They pointed out that since the rate of free radical entry into the polymer particles cannot be equated with the rate of free radical generation, the process of entry of free radicals acquires fundamental importance. They used the postulate of Maxwell et al.[144] that the aqueous-phase growth of the free radicals to a critical size is the rate-determining step for entry. Kshirsagar and Poehlein tried to validate this model by experimentally determining the critical size of oligomeric radicals that enter particles. They isolated the oligomers and determined their molecular weight by applying Fourier transform infrared spectroscopy, thin-layer chromatography, and fast atom bombardment-mass spectroscopy. Though the experimental techniques failed to give definitive values of the size of VAc oligomers, approximations have been obtained that closely match the predicted values.[143] They obtained an estimated size of 5–6 units for radical oligomers entering particles, with an upper bound of 12–14 units created by mutual termination of radicals in the aqueous phase. This is similar to Maxwell et al.'s estimated values of 7–8 and 15–18, respectively.[144] These values are also in the range of Hegerth et al.'s estimated values of 9-11.[128]

Iabbadene and Bataille reported the results of VAc emulsion polymerization in a tubular loop reactor.[145] Tubular loop reactors have many advantages — low investment costs, better heat transfer, and reduction in downtime — however, there are problems such as plugging of the reactor, and the optimum conversion is usually lower than the one obtained by the batch process. In order to improve the conversion of VAc monomer to polymer, silver ions (AgNO3) were added to the reaction system. Potassium persulfate was used as initiator and sodium lauryl sulfate was used as emulsifier. Reactions were carried out in a Teflon tube reactor with an inside diameter of 2.2 cm surrounded by stainless steel mesh. A variable speed pump with a progressive cavity was used to assure the circulation of the reaction mixture inside the tube.[145] Up to 82% conversion was obtained in these circumstances. The molecular weight and the molecular weight distribution of the polymer were determined, as well as its particle size. It was found that agitation or flow rate has an important effect on VAc emulsion polymerization in a tubular loop reactor. The particle size may be preselected by varying the flow rate and reaction time. The formation of small particles was not observed at high conversions. A bimodal molecular distribution was observed, confirming that two different mechanisms are at play and are independent of the reactor design.[145]

Sarkar, Adhikari, Banerjee, and Konar studied the decomposition rate of the conventional thermal initiator, potassium persulfate, in the presence of VAc.[146] They worked with initiator and monomer concentration ranges, which are commonly encountered in industrial polymerization of VAc. They discovered that the initial rate of potassium persulfate decomposition in the presence of VAc was dependent to the 1.49th power on the initial persulfate concentration, and 0.05th power to the initial monomer concentration. The initial concentrations studied for potassium persulfate were 0.0185 to 0.00185 mol/liter, while initial monomer concentration ranged from 0.054 to 0.270 mol/liter. The presence of sodium dodecyl sulfate and polyVAc did not increase the rate of decomposition of the initiator.[146]

On the other hand, Donescu, Fusulan, and co-workers searched the influence of the potassium persulfate initiator concentration on the semicontinuous emulsion polymerization of VAc in the presence of sodium salt of the sulfosuccinic acid semiester with 25 moles of ethoxylated nonyl phenol emulsifier.[147,148] They determined that the presence of the emulsifier actually increased the rate of persulfate decomposition. The monomer conversion was determined gravimetrically, and the fraction of non-decomposed initiator present in the reaction medium was determined by ceriometry. It was found that potassium persulfate has a higher decomposition rate than in water, even after consumption of monomer. The initiator reacts either with free surfactant molecules or with those grafted onto polyVAc chains. The reaction order of the polymerization and of initiator decomposition, compared to the initiator, ranged from 0.1–0.33.[148]

In a subsequent publication, Donescu, Fusulan, and Gosa reported on the interactions between initiator and emulsifier monomer during VAc emulsion polymerization.[149] Again, potassium persulfate was used as initiator, and sodium salt of the sulfosuccinic acid semiester with 25 moles of ethoxylated nonyl phenol was used as emulsifier. Batch and semicontinuous emulsion polymerizations were applied. Due to emulsifier-initiator and emulsifier-monomer interactions, the CMC of the emulsifier was found to be higher and the electrical conductivity decreased sharply at emulsifier/initiator molar ratio = 1. The emulsifier-monomer interaction reduces the concentration of free surfactant in the reaction medium and, consequently, the rate of initiator decomposition.[149]

Lepizzera and Hamielec reported that all grades of polyvinyl alcohol increased the rate of decomposition of potassium persulfate, and the higher molar mass polyvinyl alcohol materials increased the rate of decomposition more effectively than the molar mass materials at equal loading.[140]

Craig reviewed the publications on the effect of the presence of hydroxyethylcellulose on the decomposition of persulfate initiator during the emulsion polymerization of VAc and suggested that HEC forms a redox pair with persulfates, which increases the rate of persulfate decomposition.[150]

Magallanes, Gonzalez, Dimonie, Sudol, Yue, Klein, and El-Aasser characterized polyvinyl alcohol stabilizer during VAc emulsion polymerization in the presence of polyvinyl alcohol.[151] In this work, they quantify and characterize the polyvinyl alcohol-graft-polyVAc formed during the emulsion polymerization by using the Gel Permeation Chromatography, Fouler Transform Infrared, and Nuclear Magnetic Resonance techniques. Since particle formation and, therefore, the properties of the final latex will depend on the degree of grafting, the analysis of these water-insoluble graft copolymers is important. PolyVAc polymer present in the latex was extracted by acetonitrile so that the latex and acetonitrile were kept in a rotary evaporator at 76°C until all the water present was distilled as an acetonitrile/water mixture. At the end of this operation the acetonitrile-insoluble polyvinyl alcohol was in the form of a precipitate in the polyVAc-acetonitrile solution. This precipitate was then separated by ultracentrifugation.[151] This method was reported as a reliable technique to quantitatively separate polyVAc homopolymer from water-soluble and water-insoluble polyvinyl alcohol. FTIR and NMR analyses were applied to calculate the acetate content of polyvinyl alcohols. It was determined that only a small fraction of the polyvinyl alcohol chains (about 22.5 wt%) were grafted by polyVAc when a batch emulsion polymerization recipe of 7.3% by wt. VAc monomer was used with 3.1% polyvinyl alcohol that was 87.6% hydrolyzed.[151]

Badran et al. investigated the effects of other bisulfite adducts on the polymerization of VAc with potassium persulfate through the addition of sodium bisulfite to the carbonyl functionality on benzaldehyde, acetaldehyde, octyl aldehyde, methyl propyl ketone, and acetone.[152] When emulsifier-free polymerization was applied at 40°C, the rate of polymerization in the presence of these bisulfite adducts was found to be a function of initiator concentration to the 0.54, 0.66, 0.95, 1.0, and 1.1 powers, respectively. These figures are somewhat different from an order dependence of 0.60 for potassium persulfate as reported by Chang et al.[84] The types of bisulfite adduct also influenced the final monomer conversion and latex particle size. When acetone was used, higher conversions were obtained, which was attributed to the lower steric hindrance. When longer carbon adducts was used, smaller particle size latices were produced, which was attributed to increased emulsifying tendencies.[152]

Song and Poehlein reported that the molecular weight development of any emulsion polymer is a function of a number of factors including the solubility of the monomer in water.[153] The high water solubility of VAc monomer allows for a longer critical chain length to be obtained before the polymer chain becomes water insoluble and collapses upon itself. The critical chain length decreases rapidly as particles form, and then it remains constant.[153]

El-Aasser, Makgawinata, and Vanderhoff examined the difference between batch and semicontinuous VAc emulsion homo- and copolymerization.[155] They determined that batch homopolymerization produced a narrower molecular weight distribution than the semicontinuous process. The semicontinuous process produced a bimodal molecular weight distribution having a high molecular weight fraction, which was attributed to chain transfer to polymer due to monomer-starved conditions and a substantial amount of low molecular weight fraction.[155]

Lee and Mallinson showed that, some emulsifiers could influence the molecular weight distribution.[156] When sodium bis-ethylhexyl sulfosuccinate was used instead of sodium dodecyl sulfate in VAc emulsion polymerization, it could broaden the molecular weight distribution. They reported an increase in polydispersity from 4.2 to 14, which was attributed to significant chain transfer effects of this emulsifier.[156]

Between 1983–1995, Vandezande, Smith, and Bassett reviewed problems peculiar to VAc emulsion homo- and copolymerization such as reactivity and water solubility and the consequences regarding particle formation, growth, and stabilization.[157]

Ayoub, Nasr, and Rozik studied the polyoxyethylene emulsifier composition on the course of VAc emulsion polymerization.[158] Three different emulsifier types from methoxypolyoxyethylene and VAc monomer were prepared in the presence of benzoyl peroxide using a macroradical initiator technique. These emulsifiers were used in the emulsion polymerization of VAc with sodium persulfate as initiator. The rate of polymerization was found proportional to the 0.33, 0.40, and 0.44 power of emulsifier concentration for 65, 73, and 81 wt percent polyoxyethylene, respectively. The particle size was observed to decrease with increasing emulsifier concentration.[158]

Cao, Gan, Wang, Xu, and Ke investigated the radical desorption in emulsion homopolymerization of VAc.[159] A model to calculate the radical desorption rate constant was developed to study the effects of the reaction temperature, emulsifier concentration, initiator concentration, monomer conversion, and phase ratio. They concluded that the desorption of radicals from latex particles to aqueous phase must be taken into account in the modeling of the kinetics of VAc emulsion polymerization.[159]

DeBruyn, Gilbert, and Ballard also examined the radical loss by transfer to a monomeric species which is very slow to propagate and the radical activity of which is lost by exit and termination, either in the aqueous phase or when it enters a particle containing a growing radical.[160] This behavior results in the polymerization rate independence on monomer concentration in the emulsion polymerization of VAc. Since the transfer step is the rate determining, the rate of this process is proportional to monomer concentration, which cancels the dependence on monomer concentration in the overall polymerization rate expression. Gamma-radiolysis relaxation studies are used to determine the radical loss rates, which fit the model well.[160]

Moustafa, AbdElHakim, and Mohamed studied the kinetics of emulsifier-free emulsion polymerization of VAc using a potassium persulfate-potassium metabisulfite redox initiation system.[161] The apparent activation energy of the polymerization reaction was calculated, and the effect of some inorganic substances on the rate of polymerization was revealed.

Guan and Gilbert published their kinetic study of seeded emulsion polymerization of VAc in Chinese.[162] In this dilatometric study based on the data of conversion Vs time, the entry and exit rate coefficients were calculated and it was shown that these rates over bar increased linearly with initiator concentration. Lee and Shin examined the soap-free emulsion polymerization of VAc in the presence of polyvinyl alcohol-mono thiol, which was initiated by a redox initiator pair containing potassium persulfate and sodium bisulfite.[163]

Moustafa, AbdElHakim, Sayyah, and Mohamed investigated the effect of the presence of sodium, calcium and aluminum chloride, sodium sulfate, and ammonium phosphate electrolytes on the emulsifier-free emulsion polymerization of VAc using a potassium persulfate-sodium bisulfite redox initiator system at 50°C.[164] Shaffie, Moustafa, Mohamed, and Badran determined the effect of redox initiation systems of different persulfate cations such as sodium, potassium, and ammonium persulfate; each of them was coupled with an acetone sodium bisulfite adduct.[165] The stability and morphology of the latices were also studied.

Britton, Heatley, and Lovell investigated the chain transfer to polymer during polymerization by C-13 NMR spectroscopy.[166] Bulk and emulsion homopolymerizations of VAc were conducted. The branching in the polyVAc obtained by emulsion polymerization was found to be much higher than the polyVAc obtained by bulk polymerization due to the fact that emulsion polymerizations proceed almost exclusively within the latex particles and at high instantaneous conversions.[166]

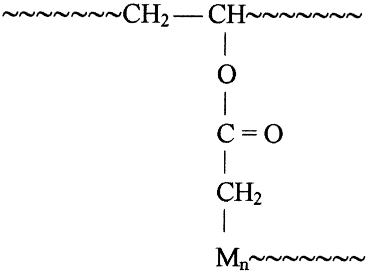
Shaffie, Ayoub, Ismail, and Badran examined the kinetics of VAc emulsion polymerization using redox initiator pairs containing potassium persulfate and different sodium bisulfite adducts such as acetone, methyl propyl ketone, octyl aldehyde, acetaldehyde, benzaldehyde, salicylaldehyde, and cyclohexanone.[167] Their effect on polymerization rate and particle size was determined.

Ohmura, Kataoka, Watanabe, and Okubo studied the controllability of particle size distribution of continuous VAc emulsion homopolymerization in CSTR.[168] The emulsifier concentration was varied below the critical micelle concentration, and the periodical oscillations in monomer conversion were monitored. The authors suggest that particles can be formed intermittently owing to the temporal variation of the concentration of free emulsifier in the condition below CMC.[168]

3.3 BRANCHING MECHANISMS IN VINYL ACETATE EMULSION POLYMERIZATION

Branching reactions during polymerization generally lead to a broadening of the molecular weight distribution, and it is often difficult to distinguish between the effects of branching and polydispersity. The extent of branching is great for polyVAc, which has a very reactive propagating radical. PolyVAc has a transfer to polymer value, C_P, which is probably in the range $1–5 \times 10^{-4}$. Further, VAc monomer has a high transfer-to-monomer value, C_M, of about $1.75–2.8 \times 10^{-4}$. Transfer to monomer yields radicals at the acetoxy methyl group which can initiate polymerization at its radical end, and can also enter into the propagation reaction of some other propagating radical. The result of this behavior is the formation of a branched polymer. Thus, extensive branching occurs in polyVAc since a branch is formed for each act of transfer to either monomer or polymer.

A number of studies have been made to elucidate the branching mechanism. Wheeler, Lavin, and Crozier proposed a mechanism for branch formation in polyVAc in 1952 by applying degradative hydrolysis.[169] This method assumes that chain transfer of polymer occurs at the acetoxy methyl group, leading to polymer branches which can be cleaved



$$\sim\sim\sim\sim\sim\sim CH_2 - \underset{\begin{array}{c} | \\ O \\ | \\ C=O \\ | \\ CH_2 \\ | \\ M_n\sim\sim\sim\sim\sim\sim \end{array}}{CH}\sim\sim\sim\sim\sim\sim$$

from the original polymer molecule by ester hydrolysis of the linkage. They prepared polyVAc with a very slow bulk photopolymerization, which was initiated by a sun lamp at 70°C to different degrees of conversions and solution polymerization in benzene, which was initiated by acetyl peroxide. The alcoholysis of the resulting polymers was carried out in methanolic potassium hydroxide solution to obtain polyvinyl alcohol. Then, acetylation of the resulting polyvinyl alcohol was conducted in pyridine-acetic acid and acetic anhydride solution. The concentration of polymeric double bonds was determined by iodine-sodium thiosulfate titration and the results were reported as monomer units per double bond. The number average degrees of polymerization were estimated by quantitative determination of the double-bond end groups. A simplified kinetic analysis gives the degree of branching in terms of six rate constant ratios. These rate constants were estimated from viscosity measurements, and the frequency of branching at 70°C was expressed in terms of monomer units per hydrolyzable branch and nonhydrolyzable branch.[169] However, there are conflicting data which indicate that all of the transfer to polymer does not take place at the acetoxy methyl site. Howard found that most transfer to polymer takes place at the α or β hydrogens, leading to nonhydrolyzable branches.[170] In contrast, Imoto found that the methyl group of the acetate was the principal transfer point, 40 times more so than the α or β hydrogen of the backbone of the polymer.[171]

Stein found that the double bond at the end of the polymer molecule, introduced by transfer to monomer, is almost as reactive as the monomer itself; this means that the large polymer molecule does not shield this double bond effectively.[172] PolyVAc samples were prepared by polymerization to different degrees of conversion at 60°C. Measurements of osmotic pressure and light scattering were done, and number and weight average molecular weights were found. The transfer constant to polymer was calculated from the variations of the molecular weights with increasing conversion and $C_P = 1.8 \times 10^{-4}$ was found. It was determined that the number of branches per polymer molecule increases very rapidly after a conversion of 80%.[172]

Schulz and Roberts-Nowakowska have shown that VAc polymerizations can be conducted such that branching occurs by a few relatively simple reactions.[173] These reactions are so effective that the influence of radical initiation and termination on average chain length can be made negligible.

Graessley and Mittelhauser applied bulk VAc polymerization at 60°C by using azobisisobutyronitrile initiator.[174] The polymerization rate was kept so low that the molecular weight distribution should be independent of the radical initiation and termination rates. Intrinsic viscosity, light scattering, and osmotic pressure were measured on solutions of dried polymer samples. $C_P = 1.2 \times 10^{-4}$ and $C_M = 1.9 \times 10^{-4}$ values were found. Average branching densities were then calculated for each sample, and ranged as high as 1.5 branch points/molecule. Then, Graessley and Mittelhauser examined whether the relative decrease in intrinsic viscosity caused by branching is independent of the nature of the solvent. Intrinsic viscosities were measured in three systems: a theta-solvent, a good solvent, and one that was intermediate in solvent interaction. The results were compared with calculated viscosities, which would have been observed if all the molecules had been linear. The ratio between measured branched and calculated linear intrinsic viscosities were substantially the same in all three solvents, showing that branching is independent of the nature of the solvent.[174]

In a subsequent publication, Graessley, Hartung, and Uy applied bulk polymerization of VAc for two temperatures: 60 and 72°C. The calculated branch points per polymer molecule were found to be slightly higher at 72°C for all conversions.[175] Selected samples were saponified and reacetylated to determine the amount of branching through the acetate group. They found that 25–37% of the branches were not hydrolyzable. Molecular weights extrapolated to zero conversion appear to be unchanged by saponification and reacetylation, showing that short-chain branching through the acetate group is very infrequent.[175]

Saito, Nagasubramanian, and Graessley investigated the molecular weight distribution of branched polyVAc theoretically.[176] They developed new distribution functions to calculate the fraction of molecules with r repeating units and the number of branch points contained in molecules with r repeating units. This new approach showed that branching will increase the proportions of both high and low molecular weight components in the systems.[176]

Nagasubramanian, Saito, and Graessley also developed a method to determine the intrinsic viscosity in branched polyVAc.[177] They pointed out that the intrinsic viscosity depression caused by branching is different than predicted by various viscosity theories[174] and there is a need to explain this difference. The intrinsic viscosity ratio between measured branches and the linear intrinsic viscosity was recalculated as a function of average branching density for trifunctionally branched polymers. Using realistic distributions of molecular weights and branches, calculations were made for structure-sensitive parameter, g, and the ratio of hydrodynamic radii, h. Experimental data on branched polyVAc lay between the curves obtained from the $g^{1/2}$ and h^3 relations.[177]

Nagasubramanian and Graessley developed a model to apply to the continuous polymerization reactors with branching[178] and compared the experimental results on VAc solution polymerization with this model.[179] Their model indicates that when branching occurs, the product from a continuous stirred reactor should have a broader distribution than that from batch polymerization. The continuous polymer should also be more highly branched.[178] In the experiments, t-butanol was used as solvent and azobisisobutyronitrile was used as initiator. Stirred tank solution polymerizations were conducted at 60°C with conversions ranging from 13 to 63%.[179] At low conversions, the molecular weights of the continuous samples were lower than the batch samples. These molecular weight reductions were attributed to the presence of trace impurities in the continuous feed mixture. The molecular weight distributions obtained in a continuous reactor were found to be broader than those from batch polymerizations. At any given conversion, the continuous polymer is more highly branched than the corresponding batch sample.[179]

Nozakura, Morishima, and Murahashi investigated the long branching in polyVAc and polyvinyl alcohol.[183,184] They distinguished two forms of branching. Hydrolyzable branch at the acetoxy methyl group is so named because, during hydrolysis of the polyVAc to polyvinyl alcohol, the branched chain is released. Thus, a decrease in molecular weight results upon saponification, and branching of this type during polymerization does not result in branching in polyvinyl alcohol. On the other hand, the abstraction of an α-hydrogen of the polyVAc would result in a nonhydrolyzable long chain branch that remains in the derived polyvinyl alcohol. They reported that the crosslinked polyVAc gel could be decrosslinked to give soluble polymers by the reaction of partially hydrolyzed polyVAc and toluene diisocyanate.[183] It was found that the hydrogen atoms in the α-position are more reactive than those on the acetoxymethyl group. The chain transfer constant to polymer (main chain) was calculated as $C_{P,1} = 3.03 \times 10^{-4}$, but the chain transfer to polymer (acetoxy methyl group) was calculated as $C_{P,1} = 1.27 \times 10^{-4}$, both at 60°C.[184] On the other hand, the polymerization of the terminal double bond, which is the product of the monomer transfer, gives a trifunctional branch point. Nozakura, Morishima, and Murahashi calculated chain transfer constant to monomer (acetoxy methyl group) as $C_M = 2.26 \times 10^{-4}$ at 60°C and found that the chain transfer constant to the α- or β-position in the monomer was negligible. The formation of nonhydrolyzable branches by the terminal double bond can also be neglected. This fact indicates that all of the long branching is formed by transfer to polymer mechanisms.[184]

Friis, Goosney, Wright, and Hamielec derived a model to explain the branching and molecular weight developments in VAc emulsion polymerization.[185] This model expresses the leading moments of distribution as function of conversion, and it can calculate the number of branch points as a function of conversion. It was determined that molecular weight and branching development are largely controlled by transfer to polymer and monomer, and the average molecular weights are functions of only temperature and conversion. The particle number and initiator concentration does not affect the molecular weights. Furthermore, when the polymerizations are carried out at the same temperature, the average number of branch points per molecule is larger in emulsion than in bulk polymerization.[185]

Friis and Hamielec modified the kinetic equations for molecular weight and branching development after Graessley for the case of VAc emulsion polymerization using sodium lauryl sulfate as emulsifier.[60] It was noted that commercial polymerization rates could be obtained in emulsion polymerization at much lower rates of initiation than in solution or bulk polymerization.

Gavat, Dimonie, Donescu, Hagiopol, Munteanu, Gosa, and Deleanu investigated the grafting process in VAc emulsion polymerization in the presence of polyvinyl alcohol and nonionic emulsifiers such as ethylene oxide-propylene oxide block copolymers.[186] Films were obtained by drying at room temperature from the latex samples taken in the course of polymerization. These films were subjected to successive extractions in water and in benzene at boiling for 5-6 hours each, finally obtaining three fractions, which were determined by gravimetry: polymer soluble in water (mainly polyvinyl alcohol), soluble in benzene (mainly polyVAc), and insoluble in benzene and water (mainly graft copolymers). Graft copolymers of the VAc monomer on polyvinyl alcohol and ethylene oxide-propylene oxide emulsifiers were formed. The number of grafting reactions increases with the rise in initiator concentration.[186]

Hamielec and Ouano derived a generalized universal molecular weight calibration parameter in gel permeation chromatography.[187] They reported that in the commonly used GPC universal calibration parameter, the intrinsic viscosity multiplied by the weight average molecular weight ($[\eta] M_w$) is incorrect. When branching is present the error could be very large. They suggested that the number average molecular weight should be used instead of the weight average molecular weight so that $([\eta]M_n)$ should be used as GPC universal calibration parameter for all polymer systems.[187]

In a subsequent paper, Hamielec, Ouano, and Nebenzahl characterized branched polyVAc by gel permeation chromatography and laser light scattering photometry.[188] When low angle laser light scattering (LALLS) was coupled to a GPC chromatograph, they gave self-consistent data on the molecular weight distribution of linear polymers. In this work, Hamielec, Ouano, and Nebenzahl applied this technique to study the chain branching of polyVAc prepared by bulk polymerization. The new GPC universal calibration parameter was successfully applied as $([\eta]M_n)$, and at low initiator concentrations agreement was obtained for the number average molecular weight distribution with classical light scattering measurements.[188] Hamielec,[189] and later Axelson and Knapp,[190] reported the use of gel permeation chromatography and a low angle laser light scattering detector to characterize polymers with long chain branching.

Later, Hamielec reviewed the developments concerning the kinetics of polyVAc molecular weight and long chain branching development in bulk, solution, and emulsion polymerization.[191] He stated that Graessley and co-workers found their proposed kinetic mechanism was consistent with measured number and weight average molecular weights up to intermediate conversion levels for very low initiation rates, and these permitted the numerical estimation of the chain transfer constants to polymer, monomer, and the number of long chain branches per polymer molecule, $\bar{B}_N$. The saponification and reacetylation studies showed that about 70% of the long branches were on the acetate group.[174-182] Hamielec criticized that Graessley and co-workers did not attempt to measure $\bar{B}_N$ experimentally. He pointed out that commercial polymerization rates can be obtained in emulsion polymerization at much lower rates of initiation than in solution or bulk polymerization. Consequently, the kinetic scheme after Graessley can be applied to accurately predict molecular weight and branching development in commercial emulsion polymerizations.[60,182] Hamielec noted that the kinetic model would not apply when the polymerization is conducted in the presence of polyvinyl alcohol stabilizer, as chain transfer to polyvinyl alcohol leads to insoluble copolymers. He noted that due to the unpublished study of Jenkins and Porter, who examined the mechanical (high speed stirring) and chemical (saponification and reacetylation) degradation of branched polyVAc, some conclusions were drawn on branching mechanisms: (1) the branches through the acetate group are long and are ruptured preferentially on shearing, (2) the branches through the α- and β-carbon are long and are not broken on shearing, (3) the extent of long branching through the acetate group is about 67% of total branching, (4) 80% of the decrease in molecular weight results from the main chain scission on shearing, and (5) the branched polyvinyl alcohol contains a smaller but nevertheless significant amount of branching. Hamielec stated that the monomer or polymer concentrations are taken as constant in Stages I and II of emulsion polymerizations, and the equations for molecular weight and branching development are given as

$$\overline{M}_N = \frac{M_R}{C_M}\left(1 + \frac{K\,X_C}{1 - X_C}\right) \tag{3.36}$$

$$\overline{M}_W = \frac{2M_R\left(1 + \frac{K\,X_C}{1 - X_C}\right)^2}{\left[C_M + \frac{C_P\,X_C}{1 - X_C} - \left(\frac{2C_P\,X_C}{1 - X_C}\right)\left(1 + \frac{K\,X_C}{1 - X_C}\right)\right]} \tag{3.37}$$

$$\overline{B}_N = \left(\frac{X_C}{1 - X_C}\right)\left[\frac{C_P}{C_M}\left(1 + \frac{K\,X_C}{1 - X_C}\right) + K\right] \tag{3.38}$$

where, $\overline{M}_N$ is the number average molecular weight; $\overline{M}_W$ is the weight average molecular weight; $\overline{B}_N$ is the number average number of long chain branches per polymer molecule; M_R is the molecular weight of the monomer repeat unit; C_M and C_P are the chain transfer constants to monomer and polymer, respectively; X_C is the conversion where Stage II ends or weight fraction of polymer in monomer; and K is the terminal double bond reaction rate constant.[191] The kinetic parameters determined for VAc emulsion polymerization are given as[60,182] $K = 0.49$,

$$C_M = 0.2\,e^{\left(\frac{-4290}{RT}\right)} \tag{3.39}$$

$$C_P = 0.076\,e^{\left(\frac{-3340}{RT}\right)} \tag{3.40}$$

As an example, at 60°C and $X_C = 0.2$, it was found that $C_M = 3 \times 10^{-4}$, $C_P = 4.8 \times 10^{-4}$, and $\overline{B}_N = 0.6$. This value of long chain branches per polymer molecule is appreciable at 20% conversion. To calculate these values in Stage III one must use the moments method.[191] Hamielec reminded that the whole polymer is a mixture of linear polymer chains and polymer chains with one, two, or more long branches per polymer molecule. The branch lengths on the average are assumed to be the same as the average main chain length. However, if the emulsion polymerization temperature were allowed to increase with time, and if a chain transfer agent was added at higher conversion levels, then the branches would be shorter than the main chains on the average. When gel permeation chromatography was applied, one would deal with polymers the size of which in solution depends on both molecular weight and branching structure. Hamielec recommended the calibration of a gel permeation chromatography instrument via nuclear magnetic resonance spectroscopy, which is an absolute method of long chain branching frequency.[191]

Warson reported that monomer starvation and high temperature conditions result in high grafting to polyvinyl alcohol or possibly onto polymer molecules during semicontinuous emulsion polymerization of VAc.[108] Excessive grafting to polyvinyl alcohol causes an increase in latex viscosity and instability. A high initiator concentration with a low monomer concentration should give optimum conditions for the formation of graft copolymer. He pointed out that grafting increases the actual weight of the polyvinyl alcohol stabilizer, which will cause an increase in the size of the hydration shells.[108]

Okaya, Tanaka, and Yuki used 88% hydrolyzed polyvinyl alcohol as protective colloid, and 40 moles ethoxylated nonyl phenol nonionic surfactant as emulsifier in VAc batchwise and semicontinuous emulsion polymerization.[134] When the polymerization was carried out at high conversions, branched polyVAc was obtained in both systems. In the batchwise polymerization, long branches and higher molecular weight chains were formed with increasing conversion, whereas short branches were obtained in the semi-continuous polymerization due to the higher chain-transfer reactions. In the batchwise polymerization, higher mechanical properties and improved water resistance of the polymer films were seen due to the higher entanglement of the long polyVAc macromolecules.[134]

Gilmore, Poehlein, and Schork studied polyvinyl alcohol stabilized semicontinuous VAc emulsion polymerization.[136,137] Their model accommodates the particle nucleation, growth, and grafting onto the polyvinyl alcohol backbone during nucleation and polymeric stabilization. In addition, it is comprised of 244 equations, only nine of which are differential.[136] When emulsion recipe, process conditions, and kinetic parameters are supplied, the model predicts the conversion, particle size, and number profiles.[136] In the experiments, 88% hydrolyzed, low molecular-weight ($\overline{M}_v$ = 11,000–31,000) polyvinyl alcohol and commercial 3–5 pmm hydroquinone-inhibited VAc monomer were used.[137] Semibatch simulations indicate that independent increases in the vinyl acetate, polyvinyl alcohol, and initiator levels increase the primary grafted particle population. The model was found useful in predicting the relative importance of polyvinyl alcohol grafting during nucleation. It suggests that when the molar ratio of VAc to polyvinyl alcohol is high, grafted primary particles do not contribute significantly to the total primary particle concentration, and physical adsorption of polyvinyl alcohol onto the latex particle is a more important process.[137]

Tobita developed a model of the kinetics of long-chain branching in emulsion polymerization depending mainly on the chain transfer to polymer.[192] Later, by the application of the kinetic parameters in his model and the experimental data reported by Friis et al.,[60,142] he investigated the effect of compartmentalization on the kinetics of VAc emulsion polymerization.[141] He assumes that the loci of polymerization are the polymer particles, with diameters usually in the submicron range. Tobita found that the method of moments conventionally applied by many workers in the field[174-182,185,191] clearly overestimates the weight average chain lengths when branching frequency is high and the effect of compartmentalization must be accounted for in VAc emulsion polymerization.[141]

Magallanes, Gonzalez, Dimonie, Sudol, Yue, Klein, and El-Aasser quantified and characterized the polyvinyl alcohol-graft-polyVAc formed during VAc emulsion polymerization by using the gel permeation chromatography, Fourier transform infrared, and nuclear magnetic resonance techniques.[151] PolyVAc polymer present in the latex was extracted by acetonitrile solvent, and the acetonitrile-insoluble polyvinyl alcohol was in the form of a precipitate in the polyVAc-acetonitrile solution. Then, this precipitate was separated by ultracentrifugation. FTIR and NMR analyses were applied to calculate the acetate content of grafted polyvinyl alcohols. It was determined that only a small fraction of the polyvinyl alcohol chains (about 22.5 wt%) was grafted by polyVAc when a batch emulsion polymerization recipe was applied. The properties of the final latex, such as latex viscosity and adhesion, can be correlated with the degree of grafting by using this new characterization method.[151]

Britton, Heatley, and Lovell determined the chain transfer to polymer during bulk and emulsion homopolymerizations of VAc by C-13 NMR spectroscopy.[166] Structural features such as normal and inverted repeat unit placements chain transfer to polymer and hydrolysis of acetate side groups were investigated. The chain transfer to polymer via methyl side groups dominates. The mole percent branches increased steadily with overall conversion. Since emulsion polymerization proceeds almost exclusively within the latex particles and at high instantaneous conversions, the branching in the polyVAc obtained by emulsion polymerization was found to be much higher than the polyVAc obtained by bulk polymerization.

3.4 RADIATION-INDUCED VINYL ACETATE EMULSION POLYMERIZATION

In general, chemical initiators, potassium, ammonium, or sodium persulfates are used to initiate emulsion homo- or copolymerizations of VAc in industry. The use of high-energy radiation to initiate this reaction is not practiced on an industrial scale and has been studied comparatively little. Cobalt-60 gamma radiation is used as a source of high-energy radiation. It has a high degree of penetration and ease of estimating the dose-depth characteristics. When Cobalt-60 is used as the radiation source, it is possible to obtain radical fluxes comparable to those used with chemical initiation.

Allen et al. carried out the earliest study of gamma radiation of VAc emulsion polymerization in 1956.[193,194] They prepared polyVAc latex in order to use the trapped radicals remaining after the radiation source was removed to generate block copolymers by the subsequent addition of methyl methacrylate. The conversion curves were found linear for about 15–70% polymerization, and the molecular weights were of the order of 10^6. It was assumed that fewer than 0.5 radicals per particle were present and that the mechanism was closer to Smith-Ewart Case I kinetics.[194]

Okamura, Inagaki, and co-workers studied the effect of emulsifiers on the radiation-induced emulsion polymerization of VAc.[195,196] They used anionic (sodium lauryl benzene), nonionic (polyoxyethylene lauryl ether), and cationic (cetyl pyridinium chloride and stearyl ammonium chloride) emulsifiers. At the same emulsifier concentration and radiation dose rate, the relative rate of polymerization was found to be anionic > nonionic > cationic emulsifiers. The reaction rates increased with increasing dose, but with an unspecified dependency. The dependence of the reaction rate and the molecular weight of the polymer on the emulsifier concentration were found to be between 0.14 and 0.40 power. Okamura and co-workers investigated the stability of radiation-initiated polyVAc latices and, when cationic emulsifiers were used, stable latices were obtained up to solids contents of 50% by weight.[197,198]

Stannett, Gervasi, Kearney, and Araki reported radiation-induced emulsion polymerization of VAc by using sodium lauryl sulfate emulsifier in order to compare the results with the potassium persulfate initiator systems.[199] They examined the results of changing the variables such as dose rate, emulsifier concentration, water-to-monomer ratio, and temperature on the polymerization rate, molecular weight, and the number of particles. The reaction rates were rapid, and 99% conversions can be obtained within 40–50 minutes by applying a 0.02 Mrad/h radiation dose rate at 30°C.[199] The conversion-time plot was essentially linear up to about 85% conversion. When the irradiation source was removed for 30 minutes and then returned, it was seen that the polymerization stopped almost immediately and then continued to proceed at the normal rate on restoration of the radiation source. Friis determined similar results on his pilot plant flow polymerization system; he determined a very small increase in conversion followed by a cessation of polymerization.[200] Sunardi also investigated the radiation-induced VAc emulsion polymerization under intermittent conditions.[201]

The rate of polymerization dependence on the concentration of the emulsifier was found to be 1.0 power for sodium lauryl sulfate and 0.9 for dioctyl sodium sulfosuccinate.[199] The effect of the radiation dose on the polymerization rate was found to be 0.7 order at 0°C, and 0.9 at 50°C. When seeded polymerizations were applied, the order of reaction rate decreased to 0.26 at 50°C.[199] In general, the orders obtained from radiation-induced polymerizations approach the Smith-Ewart values more than the persulfate-initiated systems. When seeded polymerizations were applied, the order of reaction rate was found to be of 0.7 order with the number of particles.[199]

Stannett, Gervasi, Kearney, and Araki found that the molecular weights of polyVAc were almost independent of the dose rate, emulsifier concentration, and monomer-to-water ratio, consistent with the determining factor being chain transfer to monomer.[199] Similarly, O'Neill, Pinkava, and Hoigne, reported that the molecular weights were relatively insensitive to the dose rate and emulsifier concentration.[202] The presence of branching was determined by hydrolysis and reacetylation of the resultant polymers. Friis found that molecular weight was independent of the emulsifier content and the number of particles, but it decreases slightly with increasing dose rate, probably due to some bimolecular termination at the higher dose rate.[200]

Stannett, Challa, Drew, and Stahel reviewed radiation-initiated VAc emulsion polymerization.[203] In summary, radiation-induced polymerizations can be conducted at any temperature without resorting to complex redox systems. The activation energy drops from about 20 kcal/mole for persulfate initiation to approximately 7 kcal/mole. When low temperature VAc emulsion polymerization is applied, high molecular weight polymers can be obtained with considerable advantages for some paint and coating applications.

The radicals produced by the radiolysis of water are mainly hydroxyl radicals. These are neutral and highly reactive radicals leading to highly efficient initiation. This gives higher surface tension latices with lower ionic strengths and higher pHs, often eliminating the need for adding buffers. No contamination with residual initiator fragments occurs. This method also allows the use of cationic emulsifiers which often interact with chemical systems in persulfate-initiated VAc polymerizations.[203]

Nevertheless, there are disadvantages to the use of radiation initiation: (1) less stable latices form due to the lack of anionic end groups of persulfate initiator: (2) radiation attacks all the components in the reaction system, particularly the emulsifier, the monomer, and the polymer already formed, which leads grafting, branching, and even cross-linking and acetate scission; (3) polymer builds up on the walls of the reaction vessel due to the diminishing flow rate near the walls, and the radiation is at its most intense near the radiation source.[203]

Stannett, Stahel, and co-workers carried out pilot plant studies to produce radiation-initiated polyVAc latices.[204,205] The reaction medium is circulated from a stirred vessel away from the radiation source. O'Neill, Pinkava, and Hoigne used a semicontinuous radiation-initiated polymerization system which was essentially an all-glass apparatus.[202] Friis also applied a different semicontinuous radiation-initiated polymerization system.[200] Neutron Products, Inc. attempted to build a large-scale pilot plant as a model for a commercial scale radiation-initiated emulsion polymerization facility.[203] The plant had heat exchangers and pumps capable of handling high-viscosity polymeric emulsions, multiple-stage processing, and the capability for continuous operation. The pilot plant consisted of four complete reactor loops. All the chemicals used in latex formulations were of commercial grade with no purification prior to reaction. They tried to produce polyVAc latex suitable for production of high molecular weight, high quality paints. Both semibatch and continuous production were carried out in this pilot plant. Good quality latices were obtained.[203] However, two problems remained: (1) the residual free-monomer was higher than commercially acceptable levels, and (2) polymer build-up inside the process lines occurs. Economic analysis indicates that capital and operating costs for radiation initiation and conventional persulfate initiation plants would be about the same.[203]

Stannett reviewed radiation-initiated emulsion polymerization in general.[206] She summarized the laboratory results of VAc, styrene, acrylonitrile, methyl methacrylate, and vinyl chloride monomers, and some pilot plant studies. She cited that Kamiyama used an electron accelerator for the emulsion polymerization of VAc using sodium lauryl sulfate as the emulsifier. Close to 90%, conversions were obtained in a few seconds with degrees of polymerization of about 2500, almost independent of the dose rate. The resulting latices had a semitransparent appearance, suggesting very small particle sizes.[207] Hayashi and Okamura studied emulsion polymerization in a flow system with electron beam irradiation.[208] In VAc polymerization, 60% conversion was reached in 200 seconds, at 40°C, at a dose rate of 0.1 Mrad/sec. Trimodal molecular weight distributions were obtained at peaks of about 400; 40,000; and 400,000. The highest peak may have been cross-linked or highly branched.[208]

Yamamoto, Seki, Fukae, Sangen, and Kamachi produced high molecular weight polyvinyl alcohol through photo-emulsion polymerization of VAc in 1990.[209,210] Since it is desirable to produce high molecular weight polyvinyl alcohol fibers having high modulus and strength, it is necessary to produce high molecular weight polyVAc, which was polymerized at low temperatures. They used polyoxyethylene nonyl phenyl ether sodium sulfate and sodium dodecyl sulfate emulsifiers. The polymerizations were conducted between –5 to 5°C in sealed 30 ml Pyrex Kjeldahl flasks, and the mixture was irradiated with a high-pressure mercury lamp for 10 hours. Basic hydrolysis was then applied to the polyVAc thus synthesised to obtain polyvinyl alcohol. High molecular weight polyVAc having a 21000 number average degree of polymerization, and corresponding polyvinyl alcohol having a 12800 number average degree of polymerization after hydrolysis, were obtained. The characteristics of the polyvinyl alcohol were similar to those of usual polyvinyl alcohol synthesized by usual chemical routes.[210]

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4 Properties and Roles of Ingredients in Vinyl Acetate Emulsion Homopolymerization

PolyVAc latices are composed of dispersions of extremely fine polymer particles in water. They are prepared from vinyl acetate monomer, water, initiators, emulsifiers (surfactants), protective colloids, acidity buffers, modifiers, antifoaming aids, and other ingredients. A brief review of the properties and the role of each component follows.

4.1 VINYL ACETATE MONOMER

Vinyl acetate monomer (CH_2=CH–OOC–CH_3) is the raw material of the extremely fine polyVAc polymer particles in the latex. It is a reactive, unsaturated chemical and is subject to polymerization by light, heat, and chemical initiators. A large number of books and reviews have been published on the synthesis and chemistry of VAc monomer.[1-20]

4.1.1 SYNTHESIS AND MANUFACTURE OF VINYL ACETATE MONOMER

VAc monomer was probably first synthesized by the Russian chemist Miasnikoff in 1860.[21] Wohl and Mylo prepared α-chloro and α-bromovinyl acetate.[22] Mylo then suggested that the corresponding VAc could be obtained from the α-halogen aldehydes.[23] Klatte isolated vinyl acetate as a by-product during the ethylidene diacetate synthesis in 1912.[24] The first commercial production of vinyl acetate based on the reaction of acetylene and acetic acid was piloted by Herrmann at the Consortium (Wacker-Chemie) in 1924. This success led to the first commercial production of polyVAc in 1928 by Wacker-Chemie. This was followed by Hoechester Farbwerke, and then by Shawinigan Chemicals of Canada.

At present, most of the commercially made vinyl acetate is produced by three processes. In the first process (modified liquid-phase Wacker Process), ethylene gas and air slightly above atmospheric pressure are passed into glacial acetic acid in the presence of a palladous chloride-cuprous chloride catalyst system.[25] The main reactions are:

$$H_2C = CH_2 + PdCl_2 + CH_3COOH \rightarrow CH_3COO{-}CH{=}CH_2 + Pd + 2\,HCl \qquad (4.1)$$

$$H_2C = CH_2 + H_2O + PdCl_2 \rightarrow CH_3CHO + Pd + 2\,HCl \qquad (4.2)$$

$$Pd + 2\,CuCl_2 \rightarrow PdCl_2 + 2\,CuCl \qquad (4.3)$$

$$2\,CuCl + 2\,HCl + {}^1\!/\!{}_2\,O_2 \rightarrow 2\,CuCl_2 + H_2O \qquad (4.4)$$

The cupric chloride then oxidizes the palladium back to palladous chloride and is itself reduced to cuprous chloride. The air oxidizes the cuprous ion back to cupric. There are severe corrosion problems associated with the production of HCl gas and the use of glacial acetic acid, and thus the large sections of the plant downstream from the reactor should be built of titanium metal, resin-graphite composites, or special ceramics. The products, i.e., vinyl acetate monomer and acetaldehyde, are separated from the existing gas stream in a series of distillation columns.[26] When only air oxidation is considered, this reaction can be written as

$$H_2C = CH_2 + CH_3COOH + {}^1\!/\!{}_2\,O_2 \rightarrow CH_3COO{-}CH{=}CH_2 + H_2O \qquad (4.5)$$

Overall yields are 90% based on ethylene, and 95% based on acetic acid. Producers estimate that the use of ethylene instead of acetylene for VAc monomer manufacture led to a 20% reduction in raw material costs. As a result, essentially all post-1980 production capacity for VAc monomer is based on ethylene feed.

The vapor-phase ethylene-acetic acid process differs from the above described liquid-phase process in that very little acetaldehyde forms during the reaction. A gaseous mixture of acetic acid, ethylene, and oxygen is blown over a catalyst of 0.1–2 wt% palladium metal on an inert support at 175–200°C in a tubular reactor. The exit stream containing vinyl acetate, unreacted starting materials, water, and small amounts of acetaldehyde, carbon dioxide, and other by-products is separated by a combination of scrubbers and distillation stages. In contrast to the liquid-phase process, corrosion is not a problem and the normal materials required for hot acetic acid are used in plant construction.

In the second process, acetylene adds directly to acetic acid either in liquid or vapor-phase process.[27,28] In the vapor-phase process, acetylene and acetic acid vapors are passed over a zinc acetate on charcoal support catalyst at 180-210°C at atmospheric pressure. The reaction is exothermic and cooling is necessary.

$$HC \equiv CH + CH_3COOH \rightarrow CH_3COO{-}CH{=}CH_2 \qquad (4.6)$$

The overall yields are 92–98% based on acetylene, and 95–99% based on acetic acid. VAc is purified by distillation in a series of columns which also separate the unreacted acetylene and acetic acid for recycling. Stainless steel is used extensively because of the corrosive operating conditions; copper still pots are used to prevent polymerization during distillation.

In the third process, which was produced by Celanese Corp., there are ten steps in which acetic anhydride is combined with acetaldehyde forming ethylidene diacetate, which is then pyrolyzed to vinyl acetate and acetic acid.[20]

$$(CH_3CO)_2O + CH_3CHO \rightarrow CH_3CH(CH_3COO)_2 \tag{4.7}$$

$$CH_3CH(CH_3COO)_2 \rightarrow CH_3COO{-}CH{=}CH_2 + CH_3COOH \qquad \text{(75\% yield)} \tag{4.8}$$

$$CH_3CH(CH_3COO)_2 \rightarrow (CH_3CO)_2O + CH_3CHO \qquad \text{(25\% yield)} \tag{4.9}$$

Separation and purification of VAc and acetic acid are carried out in a number of distillation steps.

4.1.2 PHYSICAL PROPERTIES OF VINYL ACETATE MONOMER

Some physical properties of vinyl acetate monomer are listed in Table 1 in Appendix 1. The vapor pressure of VAc at various temperatures can be calculated by using the following equation:[29]

$$\log_{10} P_{mm} = \frac{(0.05223)\,(34433)}{T} - 8.091 \tag{4.10}$$

Some other physical properties have been calculated and plotted as a function of temperature, such as heat of vaporization, vapor heat capacity, liquid heat capacity, liquid density, vapor viscosity, liquid viscosity, surface tension, vapor thermal conductivity, and liquid thermal conductivity.[30]

Solubility diagrams for the ternary systems such as VAc-acetic acid-water,[31] VAc-2-propanol-water,[32] VAc-acetaldehyde-water,[33] VAc-acetic acid-acetaldehyde,[34] and binary systems such as VAc-water[32,36] and VAc-acetylene[35] have been reported.

The composition and boiling points of the azeotropes containing VAc are listed in Table 2 in Appendix 1.[32,36-38] The heat of mixing of VAc with some organic compounds is given in Table 3[39] in Appendix 1.

The distribution of VAc monomer between water and polyVAc was found to obey the following relationship:

$$W_{polymer} = 13.7\, W_{water}^2 \tag{4.11}$$

where $W_{polymer}$ is the wt% of VAc in the polyVAc and W_{water} is the wt% of VAc in water at equilibrium at 25°C.[40] The vapor pressure of VAc above its aqueous solutions has been reported.[41] The presence of the surfactants in water increase the VAc solubility in the solution. For example, the solubility of VAc in the aqueous solution containing 0.01 g/ml 10 mole nonylphenol-ethylene oxide condensate is 3.12 wt%, whereas it increases to 5.33% when 0.08 g/ml of the same surfactant is dissolved in the aqueous solution.[42]

4.1.3 CHEMICAL PROPERTIES OF VINYL ACETATE MONOMER

VAc monomer acts both as an organic ester and an olefinic compound. Hydrolysis, transesterification, and addition are important reactions of VAc.

4.1.3.1 Hydrolysis of Vinyl Acetate

The hydrolysis of VAc was studied for the first time in 1927,[43] and the hydrolysis of VAc was reviewed in detail several times.[44,45] VAc hydrolyzes readily when treated with acid or alkali to give acetic acid (or sodium acetate) and acetaldehyde.

$$CH_3COO\text{–}CH{=}CH_2 + H_2O\left(H^+ \text{ or } OH^-\right) \rightarrow CH_3COOH + \left[HO\text{–}CH{=}CH_2\right] \qquad (4.12)$$

$$\left[HO\text{–}CH{=}CH_2\right] \rightarrow CH_3CHO \qquad (4.13)$$

The produced vinyl alcohol is unstable, and acetaldehyde instantaneously forms by tautomeric rearrangement. Thus, it was found that under alkaline conditions, VAc hydrolyzes 1000 times as fast as does its saturated analogue, ethyl acetate, whereas in ethyl alcohol solution the rates of hydrolysis are similar.[44] The rate of hydrolysis in an aqueous system is lowest at a pH of 4.44. The alkaline hydrolysis rate of VAc was determined as 2.6 liters/mole-sec.[46] The acid hydrolysis rate of VAc is much slower than alkaline hydrolysis.[44] At low acid concentrations, the hydrolysis mechanism was found to be very similar to that of saturated esters, namely acyl-oxygen fission mechanisms.[47] However, at high acid concentrations, the reaction mechanism seems to change and involves an olefin-protonation step.[48] When mercury ions are used to catalyze the hydrolysis reaction, the kinetics are similar to those of acid catalysis with the exception that the mercury ions are not regenerated.[49] VAc hydrolyzes rapidly when catalyzed by palladium chloride in acidic medium.[50] Hermann and Haehnel obtained acetyl aldoxan on saponification of VAc.[51] Marvel reported that VAc reacts with acetaldehyde in the presence of sodium to form the same cyclic acetal.[52]

4.1.3.2 Transesterification of Vinyl Acetate

High-vinyl esters can be made from VAc by transesterification reactions in the presence of mercuric salts in acidic medium.[54] A carboxylic acid reacts with VAc to give the desired vinyl carboxylate:

$$\begin{gathered} CH_3COO\text{–}CH{=}CH_2 + RCOOH\ (H^+, Hg^{+2}) \rightarrow \\ RCOO\text{–}CH{=}CH_2 + CH_3COOH \end{gathered} \qquad (4.14)$$

These reactions may be catalyzed by palladium (II) chloride in the presence of sodium or lithium chloride.[55] Vinyl ethers have been prepared by the reaction of VAc and alcohols.[56] Vinyl succinimide and phthalimide esters can also be prepared.[57]

4.1.3.3 Addition Reactions

Chemical reactions involving the addition of a reagent to the double bond have been done. Hydrogenation as a 1,2-addition reaction in the presence of 5% platinium gives ethyl acetate.[65] VAc reacts with hydrogen bromide or chloride to form α-haloethyl acetate, which can be distilled under vacuum without decomposition.[78] VAc can be brominated in the presence of sodium acetate and acetic anhydride to give glycol aldehyde triacetate.[79,80] This bromination reaction is used to determine the VAc content in polyVAc latices. However, the method has to be used cautiously because side reactions occur which interfere with the quantitative bromination.[81] Bromination of the double bond can be effective with dioxane dibromide in 78% yield.[82] Chlorine forms the dichloro ethyl acetate which hydrolyzes easily in water.[83] Chlorination in ethanol gives a chloroacetal in good yield.[84] Methyl or buthyl mercaptan add to VAc to form thio compounds in good yields:[85]

$$CH_3COO{-}CH{=}CH_2 + C_4H_9SH \rightarrow C_4H_9S{-}CH_2CH_2{-}OOCCH_3 \qquad (4.15)$$

Benzyl mercaptan and mercaptoethanol add to VAc to give the corresponding sulfides.[86,87] Carboxylic acids such as stearic acid,[88] benzoic acid,[20] acrylic acid,[89] pentanoic acid,[90] and dimethyl malonate[20] add to VAc under the influence of sulfuric acid to form ethylidene esters.

4.1.3.4 Oxidation of Vinyl Acetate

Oxidation of VAc monomer in an inert solvent in the presence of a free-radical source is quite slow. Styrene monomer is oxidized ten times faster than VAc under the same conditions.[91] Glycol aldehyde is formed when VAc is oxidized with hydrogen peroxide.[92,93] VAc-oxygen adducts form in different media.[94-98] The peroxide of VAc was synthesized by reacting VAc with hydrogen peroxide and sodium hydroxide. This peroxide can be used to initiate the polymerization of vinyl monomers.[53] An ozonide of VAc has been made which is explosive when dry.[28]

4.1.3.5 Decomposition of Vinyl Acetate

VAc begins to decompose at 360°C, without polymerizing at this temperature.[58] When the temperature reaches up to 500°C, the pyrolysis of VAc takes place, giving β-ketoaldehydes in addition to acetic acid, acetylene, propylene, ketene, acetaldehyde, carbon monoxide, carbon dioxide and dimethylketene.[59]

4.1.3.6 Other Reactions of Vinyl Acetate

Paraformaldehyde reacts with VAc to give acrolein and acetic acid.[60] VAc reacts with aromatics to give a number of addition products, for example, 9,10-dimethylanthracene and 2,7,9,10-tetramethylanthracene.[61] By use of diiodomethane with a zinc-copper couple, a methylene is added to VAc yielding cyclopropyl acetate.[62] The reaction of VAc with acid chlorides gives 1,3-diketones.[63] Thiols add across the double bond with

Lewis acid catalysis and by a free-radical-catalyzed reaction to form thioacetates, and similar additions are known for ammonia, amines, silanes, and metal carbonyls.[20]

4.1.4 INHIBITION OF VINYL ACETATE MONOMER

VAc monomer may polymerize during storage by the effect of oxygen in air. In order to prevent this undesired polymerization, suitable inhibitors are dissolved in the commercial monomer after synthesis and stabilization for shipment and storage is ensured. VAc is available with either hydroquinone or diphenylamine inhibitors. There are three main grades:

1. The first grade contains p-hydroquinone, which is regularly furnished in a concentration of 3–7 ppm. This level of inhibitor has been found effective for control of quality under normal storage conditions if it is expected to be used within two months of delivery.
2. A grade containing 12-17 ppm p-hydroquinone is also available for those who store the monomer up to four months before polymerization. Also, p-hydroquinone-inhibited grades need not be distilled before use.
3. If long-term storage is desired (more than one year), a diphenylamine-inhibited grade is used. This grade contains 200–300 ppm diphenylamine inhibitor. This is the common level of diphenylamine used in VAc monomer. This inhibitor must be removed by distillation before polymerization can be effected.

4.1.5 STORAGE AND HANDLING OF VINYL ACETATE MONOMER

4.1.5.1 Bulk Storage in the Plant

Since vinyl acetate is a volatile, flammable liquid having low flash point and auto-ignition temperature, the normal precautions for handling such materials should be observed. The flammable limits of VAc vapor in air are 2.6–13.4 vol%. At normal storage temperatures an explosive vapor-air mixture can exist in the vapor space of a storage tank unless air is excluded, thus, nitrogen blanketing should be considered. This is a red-label product as defined by international regulations. It is very important that all containers and connecting units involved in the transfer of this material be adequately grounded. A common system having all equipment connected to a buried water line or a similar ground facility is recommended. Any electrical apparatus in the vicinity should be explosion-proof. Open fires or spark-producing devices of any form must be excluded from the operational area. For working near open containers, spark-proof tools are recommended.

As a general rule, vinyl acetate should be stored under moderate temperature conditions. It is known that inhibited VAc has good storage stability at normal temperatures, i.e., below 30°C. Outside storage is quite adequate, but it is recommended that it not be placed close to heat-generating sources such as furnaces or similar facilities. A white or aluminum outer paint coat on the facilities will help considerably in keeping the temperature of the contents as low as possible. For aboveground tanks, water-spray cooling is sometimes used to minimize storage temperatures during hot summer weather.

4.1.5.2 Materials of Construction

Carbon steel is a very satisfactory material of construction for the storage of vinyl acetate. Tanks and piping should be as free of rust as possible. While clean rust does not show any appreciable effect on the quality of the material, a physical pickup could be detrimental to the polymeric end-product. Carbon steel tanks are frequently treated with chemical compounds of the phosphate type, which both remove rust and have an inhibiting effect on additional rust formation. Baked-phenolic-coated steel, aluminum or stainless steel materials, and glass-lined reactors can be used, but under most circumstances the cost is not justified. Copper and bronze or brass fittings are not recommended on storage facilities as traces of copper tend to inhibit the polymerization of vinyl acetate.

4.1.5.3 Tank Cars, Trucks, and Drums

Top unloading of a tank car containing vinyl acetate is recommended. However, if circumstances require, bottom unloading is considered an acceptable practice. The material should be unloaded by means of a pump, gravity, siphon, or inert gas pressure. Under no circumstances should air pressure be used.

As mentioned in the general comments, grounding systems should be used in the handling of drums containing vinyl acetate. Great care should be exercised in the handling of empty vinyl acetate drums, as the residual material when mixed with air can be explosive and dangerous. These drums can be readily cleaned by washing with water and steaming. It is desirable to store drums away from heat and direct sunlight.

4.1.5.4 Physiological Properties

Vinyl acetate is only moderately toxic orally or by absorption through the skin.[20,110,111] It is an irritant on contact with skin or eyes, and sometimes blisters form. VAc vapor causes reddening of the eyes during prolonged contact. No report of long-term chronic effects in man are known to exist.[20] However, as with all organic solvents, prolonged or repeated contact with the skin should be avoided. The vapor is not especially irritating to the nose and throat, but good industrial hygiene practices should be followed and adequate ventilation provided. Repeated or prolonged exposure should be avoided. No maximum allowable concentration has been suggested, but it seems probable that a concentration in excess of 400 parts per million by volume of the vapor in the air should not be exceeded for continued exposure. First aid should be administered to persons having taken VAc monomer internally, usually by inducing vomiting after giving half-liters of solution containing 2 tablespoons of salt.

4.1.6 ANALYSIS OF VINYL ACETATE MONOMER

The specifications of commercial vinyl acetate monomer are given in Appendix 2. Commercial VAc monomer is very pure and generally does not have to be treated to remove impurities.[20] ASTM D-2190-65, D-2086-65, D-2191-65, and D-2193-66 methods and their upgrades are used to specify the VAc monomer. The purity of VAc is best determined by gas or liquid chromatography.[99-102] UV and IR spectroscopy can also be used to determine monomer purity.[103] The determination of VAc in mixtures of other monomers can be carried out by thin-layer chromatography.[104] In wet analysis, VAc concentration can be determined by determining olefin unsaturation. These involve different types of reactions: bromination,[105,106] addition of iodine monochloride to determine iodine number,[20] and addition of mercury (II) salts which can be determined polarographically.[107] The wet analysis methods of commercial VAc monomer are given in Appendix 3. The polymerization activity of VAc monomer is measured by various so-called activity tests.[20,108,109] Briefly, the method utilizes a dilatometer in which a VAc sample is polymerized at 50°C using 0.5% benzoyl peroxide as initiator. Most commercial monomers have an activity time of 90–120 minutes using this test.[20]

4.2 POLYVINYL ACETATE POLYMER

Polyvinyl acetate is an amorphous, non-crystalline, thermoplastic polymer.[112-115] It is isomeric with polymethyl acrylate. Although unbranched polyVAc can be prepared by polymerizing at low temperatures, the industrially prepared polyVAc is branched due to transfer reactions. PolyVAc of various tacticities were synthesized by reacetylating stereospecific polyvinyl alcohols.[116] PolyVAc absorbs 3 to 6 wt% water between 20 to 70°C within 24 hrs.[7,117,118]

4.2.1 PHYSICAL AND MECHANICAL PROPERTIES

The density of polyVAc is 1.191 g/cm^3 at 20°C. The density decreases with the increase in the temperature, so that it is 1.190 at 25°C, 1.170 at 50°C, 1.110 at 120°C, and 1.050 g/cm^3 at 200°C.[7,20,119] Its specific volume is 0.841 dm^3/kg and can be expressed with the equation, $0.823 + 6.4 \times 10^{-4}$ T, for T = 100–200°C.[120-124] Its molar volume at 25°C is 74.25 cm^3/mol.[125] The index of refraction of polyVAc is 1.4669 at 20.7°C, and 1.4480 at 80°C.[119,126] The heat capacity of polyVAc is 1.465 kJ/kg at 30°C.[127] The softening temperature and the glass transition temperature (T_g) of polyVAc depend on the molecular weight of the polymer. The higher the molecular weight, the higher softening temperature and T_g are obtained. Its softening temperature is found to be 35–50°C,[128] its decomposition temperature is 150°C,[119] and its glass transition temperature for medium molecular weight varies between 28–31°C,[129] and is also found to be 34–39°C when polyVAc is completely dry, and less than 30°C when it is wet.[117,119] The cubical coefficient of thermal expansion of polyVAc is 6.7×10^{-4} K^{-1}, whereas the linear coefficient of thermal expansion above glass transient temperature is 22×10^{-5} K^{-1}, and below glass transient temperature it is 7×10^{-5} K^{-1}.[119,129,130] The thermal conductivity is 0.159 J/sec-m-K.[131] The surface tension of polyVAc was calculated to be 36.5[120,132] or 42.85[133] mN/m at 20°C, and it decreases to 27.9 mN/m at 150°C.[119] The interfacial tension of polyVAc with polyethylene is 14.5 mN/m, and with polyisobutene it is 9.9 mN/m at 20°C.[120] The hardness of polyVAc is L 80–85 Shore units at 20°C.[119] Its internal pressure was calculated as 2.554×10^8 at 0°C, 2.847×10^8 at 20°C, and 4.187×10^8 J/m^3 at 60°C.[134,135] The dielectric constant of polyVAc is 3.5 at 20°C and 8.3 at 150°C with both at 2×10^3 kHz.[136]

The mechanical properties of the polyVAc depend on the molecular weight. The Young modulus of polyVAc is 600 N/mm^2 at 25°C with 50% relative humidity.[137] Its tensile strength varies from 29.4 to 49.0 N/mm^2 at 20°C.[119] The modulus of elasticity is 1274–2255 N/mm^2 according to ASTM-D-256, the rubbery shear modulus is 13 N/mm^2, and the notched impact strength is greater than 100 cm-kg/cm^2.[119] The elongation at break of polyVAc is between 10–20% at 20°C.[119] Its compressibility is 18×10 cm^3/g-atm in the glassy state.[138]

4.2.2 SOLUBILITY IN SOLVENTS AND FRACTIONATION

The solubility of polyVAc in various solvents is given in Appendix 4. PolyVAc is soluble in aromatic, ketone, and ester solvents. It is also soluble in some alcohols, such as methanol, 95% ethanol, 90% 2-propanol, and 90% butanol. Chlorinated hydrocarbons such as chloroform, carbon tetrachloride, trichloroethylene, and methylene chloride are good solvents. PolyVAc is insoluble in anhydrous ethanol and higher alcohols, aliphatic hydrocarbons, water, carbon disulfide, and cyclohexane. The solubility parameter of polyVAc is 18.6–19.9 (MPa)$^{0.5}$ [139] and, when three-component solubility parameters are considered, the dispersion forces' contribution is $\partial_d = 19.0$, the polar forces' contribution is $\partial_p = 10.2$, and the hydrogen bonding contribution is $\partial_h = 8.2$, thus the total three-component solubility parameter is calculated from $\partial^2 = \partial_d^2 + \partial_p^2 + \partial_h^2$ and is found to be $\partial = 23.1$ (MPa)$^{0.5}$.[131] The cohesive energy density of polyVAc is 369 J/cm^3.[140]

Most fractionation research was carried out to determine intrinsic viscosity-molecular weight relationships and also the molecular-weight distribution of polyVAc and polyvinyl alcohol.[20] Some studies were conducted to find how the branching in polyVAc affects the fractionation. Acetone-water and methy acetate-petroleum ether, solvent-nonsolvent pairs, were used and different molecular-weight distributions were obtained for the same highly-branched polyVAc in these different pairs.[141] Gel permeation chromatography (GPC) was applied for rapid fractionation and molecular-weight distribution determination by using tetrahydrofuran as solvent.[142-144]

4.2.3 POLYMER MOLECULAR WEIGHT DETERMINATION BY VISCOMETRY

The viscosity of polyVAc solution depends on both the solvent type and the molecular weight of the polymer. It has been found that the heat of mixing is independent of molecular weight. The variation of the viscosity of polyVAc with the concentration in diethyl phthalate solution is given as $\eta_o = -28.518 + 5.599 \log c$.[145] The viscosity of dilute solutions of polyVAc has been measured to determine the molecular weight-intrinsic viscosity relationship. This relationship is very sensitive to changes in the polydispersity of the polymer and to branching. K and values of the Mark-Houwink equation, $[\eta] = K M^a$, are given as $K = 21.4 \times 10^5$, $a = 0.69$ for acetone solvent at 25°C,[146] $K = 22 \times 10^5$, $a = 0.65$ for benzene solvent at 30°C,[147] and $K = 20.3 \times 10^5$, $a = 0.72$ for chloroform solvent at 25°C.[146] Fractionation experiments have proved that branches are split off during saponification. However, these branches are still high in molecular weight. The intrinsic viscosity at equal molecular weight is lower for branched than for linear polyVAc.[20] The concentration dependence of the reduced viscosity, η_{sp}/c, was found to be independent of the degree of branching.[148] In general, the more solvated the macromolecule the higher the intrinsic viscosity. Intrinsic viscosity was determined as 0.66 dl/g for acetone, 0.69 dl/g for chlorobenzene, 0.92 dl/g for chloroform, 0.42 dl/g for methanol, 0.46 dl/g for toluene, and 0.75 dl/g for dioxane.[145] The theta solvents and theta temperatures for polyVAc were found to be carbon tetrachloride, 46.4°C; methanol, 6°C; ethanol, 56.9°C; ethyl butyl ketone, 29°C; ethyl isoamyl ketone, 66°C; ethyl n-butyl ketone, 29°C; and 3-heptanone, 26.8°C.[20] The intrinsic viscosity of polyVAc is markedly dependent on the shearing stress during the viscosity measurement, especially at high molecular weights and in good solvents.[149]

The specific viscosity (η_{sp}), intrinsic viscosity $[\eta]$, and the polymer concentration in the solvent can be related by Huggins's equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \tag{4.16}$$

Huggins's constant, k', depends on solvent type, shear rate, temperature, and the molecular weight of the polymer. Huggins's constant was found to be 0.37 for acetone, 0.41 for chlorobenzene, 0.34 for chloroform, 0.47 for methanol, 0.50 for toluene, 0.37 for benzene, and 0.34 for dioxane.[131] Its dependence on the branching of polyVAc is controversial.[20]

4.2.4 Hydrolysis

The chemical properties of polyVAc are those of an aliphatic ester. PolyVAc hydrolyzes to give polyvinyl alcohol and acetic acid, or the acetate of the basic cation.[20,150,151] It was determined that neither a side-group-induced reaction nor an unzipping reaction takes place during hydrolysis.[150] The rate of hydrolysis is slightly higher for low-molecular weight polyVAc than for the high-molecular weight one.[116] Industrially, polyvinyl alcohol is produced by a base-catalyzed ester interchange with methanol where methyl acetate forms in addition to the polymeric product. The treatment of polyvinyl alcohol with aldehydes leads to the formation of polyvinyl acetals such as polyvinyl formal and polyvinyl butyral. These products are amorphous resins, the rigidity and softening point of which depend on the aldehyde used. Polyvinyl acetals may be made either from polyvinyl alcohol or directly from polyVAc without separating the alcohol. Polyvinyl formal is used as a wire enamel in conjunction with a phenolic resin. Polyvinyl butyral is used as a safety glass interleaver because of its high adhesion to glass, toughness, light stability, and clarity and moisture insensitivity.

When it is used as a glass interleaver, a very pure product is required, and this is most conveniently prepared from polyvinyl alcohol rather than by the direct process from polyVAc.

4.2.5 MECHANICAL AND THERMAL DEGRADATION

The mechanical degradation of polyVAc takes place by shearing and mastication, and the polymer molecular weight decreases. The shear degradation of polyVAc in solution does not occur in the main chain but rather at ester linkages on branch points.[152,153] Both rate of shear and temperature lead to lower molecular weight. Suprisingly, very little change occurs when polyVAc is masticated in an oxygen atmosphere.[154]

The thermal degradation of polyVAc starts at 150–220°C.[119,155] The polymer can be heated at 125°C for hours without changing, but at 150°C it gradually darkens, and at over 225°C it liberates acetic acid, forming a brown, insoluble resin. The volatilization occurs very rapidly at 300°C.[156] It was found that the thermal degradation rate was independent of the molecular weight of polyVAc.[20] The pyrolysis products of polyVAc depend on the pyrolysis temperature. The decomposition occurs in two stages; in the first stage only acetic acid is lost. During the second stage, the polyene decomposes giving off hydrogen, methane, carbon dioxide, carbon monoxide, and C_2 hydrocarbons[157,158] as well as acetaldehyde, ethanol, vinyl acetate, butyraldehyde, benzene, toluene, and cyclohexane.[159] Pyrolysis-GC analysis and pyrolysis-GC-mass spectroscopy and differential thermal analysis (DTA) of polyVAc give very good results.[20]

PolyVAc becomes brittle on cooling below room temperature, i.e., at 10–15°C. This is the main reason to add plasticizers to polyVAc homopolymers in order to prevent brittleness during winter.

4.2.6 LIGHT STABILITY AND BIOLOGICAL DEGRADATION

Light stability is important for polyVAc because large amounts of homo- and copolymers are used in the surface coatings industry. PolyVAc has excellent light stability. When it is used as a paint, it shows good tint retention and good mechanical stability after a weathering test.[20] Under the influence of ultraviolet radiation, polyVAc cross-links to varying degrees. The presence of oxygen reduces cross-linking. Although it also undergoes chain scission under the influence of UV radiation, the free radicals produced are usually very active so that they either recombine immediately or terminate by hydrogen abstraction. Since degradation and cross-linking are a continuing process, the molecular weight decreases and, especially when oxygen and water are present, a complete deterioration of the polyVAc film will result. PolyVAc has been found to be fairly resistant to UV degradation.[160-163]

PolyVAc also degrades biologically. It supports the growth of various microorganisms that can be used as the side chain; a degradation of the main chain does not occur.[20] Additives such as emulsifiers, protective colloids, and plasticizers support bacterial and fungal growth, thus affecting the final properties of the polymer.[164-165]

4.3 INITIATORS

The function of the initiator is to generate free radicals, thereby initiating the polymerization reaction. Emulsion polymerizations have been restricted almost entirely to catalysis by free-radical initiation. Use of water-soluble, free-radical precursors predominates over oil-soluble types in aqueous emulsion polymerization practice. The initiators fall into two broad classifications: (1) the dissociative initiators which arise through thermal bond scission (dissociation) of the free-radical precursor without interacting with any other molecule, and (2) the redox initiators which comprise at least two types of molecules and are generated by electron transfer mechanisms involving free-radical precursors and reducing agents (reduction-oxidation or redox).

4.3.1 THERMAL DISSOCIATION TYPE FREE RADICAL INITIATORS

All chemical bonds rupture if sufficient energy of vibration of the atoms is attained. However, only a limited range of bond dissociation values is feasible to allow practical rates of free-radical generation. If too low, undue decomposition of monomer during storage results. If too high, rates of decomposition are inordinately long. A very important class of compounds, characterized by O–O and N=N bonds within the molecule, exhibit bond dissociation energies falling with 30–35 kcal/mole. These decompose at very convenient temperatures (generally between 60–85°C) and at rates commensurate with efficient polymerization times. A thermally dissociative initiator must be stable at normal temperatures and it is inevitable that emulsion polymerization reactions using these initiators require the temperature to be raised above their decomposition temperatures, typically to 50–70°C. Therefore, it is not generally possible to carry out emulsion polymerizations at ambient or subambient temperatures using these initiators.

The main types of free radicals which dissociate thermally are:

a. Persulfates $S_2O_8^{-2} \rightarrow SO_4\cdot^{-1} + SO_4\cdot^{-1}$ (4.17)

b. Hydrogen peroxide $HO - OH \rightarrow HO\cdot + HO\cdot$ (4.18)

c. Organic peroxides $RO - OR' \rightarrow RO\cdot + R'O\cdot$ (4.19)

d. Hydroperoxides $RO - OH \rightarrow RO\cdot + HO\cdot$ (4.20)

e. Diacyl peroxides $(RCOO)_2 \rightarrow R\cdot + R\cdot + 2\,CO_2$ (4.21)

f. Peracids $RCOOOH \rightarrow R\cdot + HO\cdot + CO_2$ (4.22)

g. Peresters $RCOOOR' \rightarrow R\cdot + R'O\cdot + CO_2$ (4.23)

h. Azo compound $RN = NR' \rightarrow R\cdot + R'\cdot + N_2$ (4.24)

4.3.1.1 Persulfates

The most commonly used initiators for the preparation of polyVAc emulsions are of the water-soluble, free-radical-producing persulfates (peroxodisulfates), usually in the form of potassium, sodium, and ammonium persulfate. They are used in the temperature range of 50-90°C. Persulfate initiator is insoluble in VAc and in most water-immiscible monomers.

Persulfate ion decomposes in the aqueous phase thermally to give sulfate ion-radicals, which initiate polymerization either in that phase or in the monomer-swollen polymer phase after diffusing across the interface.

$$S_2O_8^{-2} \rightarrow 2 \cdot OSO_3^{-1} \tag{4.25}$$

The decomposition of persulfates is accelerated at acid pH; however, the acid-catalyzed decomposition does not yield free radicals.[166,167] When anionic emulsifiers are used, the emulsifier anions are adsorbed onto the monomer-swollen polymer particles and monomer-containing micelles, and also onto the monomer droplets. Then they form a repulsion barrier to the diffusion of sulfate ion radicals through that interface. Thus, the initiation of polymerization in the water phase is the more likely reaction, with the oligomeric sulfate ion radical adding monomer units until it was adsorbed at the interface between the monomer-swollen polymer and water phases, with the radical end oriented toward the monomer-swollen polymer phase.

The sulfate ion-radical may react with water to form bisulfate ions and hydroxide radicals as follows:

$$\cdot OSO_3^{-1} + H_2O \rightarrow HSO_4^{-1} + HO\cdot \tag{4.26}$$

Therefore, the initiation of polymerization may occur by reaction of a vinyl monomer molecule either with a sulfate ion-radical or with a hydroxyl radical. The propagating polymer chain has a hydrophilic moiety at the end in either case since the initiating radical is hydrophilic.

When an oligomeric VAc radical is formed in the water phase, it grows with the following steps: first, an oil-in-water emulsifier forms in water phase, later, if this was not adsorbed onto a particle surface, a water-in-oil emulsifier forms where water molecules are kept in oligomer, and, finally, a polymer chain forms in water which is long enough to precipitate from water phase.

As we know from the polymerization kinetics, when less initiator is used in the polymerization, a higher molecular weight polymer is obtained, and vice versa. The rate of polymerization, R_p, is primarily a function of initiator concentration, $[I]^n$, and Chang et al. reported an order dependence of $n = 0.60$ for potassium persulfate.[168] Sarkar et al. derived an equation for the initial rate of potassium persulfate decomposition in the presence of VAc monomer in the ranges of industrial VAc polymerizations.[169] They studied the range of $[S_2\,O_8^{-2}]_i = 1.85 \times 10^{-2} - 1.85 \times 10^{-3}$ mol/dm,^{3}

while the $[VAc]_i = 0.054 - 0.270$ mol/dm^3. However, it was determined that the decomposition rate of potassium persulfate is also affected by the type of the surfactant employed in the polymerization.

Donescu and Fusulan reported that when the disodium salt of the sulfosuccinic acid monoester was used with nonylphenol ethoxylated with 25 moles of ethylene oxide, these surfactants increased the rate of persulfate decomposition when copolymerizing VAc with dibutyl maleate.[170] In addition to surfactants, the presence of protective colloids, polyvinyl alcohols (PVOH), and hydroxyethyl cellulose (HEC) also affects the rate of initiator decomposition. Lepizzera and Hamielec found that all grades of PVOH increased the rate of decomposition of the initiator.[171] They reported that the higher molecular weight PVOH types increased the rate of decomposition more than the lower molecular weight PVOH at equal loading. Craig studied the effect of HEC to increase the decomposition rate of the initiator, compared his results with a number of previous researchers, and concluded that HEC forms a redox pair with persulfates.[172]

4.3.1.2 Peroxides

$$HO - OH \rightarrow HO\cdot + HO\cdot \tag{4.27}$$

$$RO - OR' \rightarrow RO\cdot + R'O\cdot \tag{4.28}$$

Hydrogen peroxide and other peroxides are soluble in both the aqueous and monomer-swollen polymer phases and thus distribute themselves between the two phases. In principle, hydroperoxides could decompose in either phase to form a hydroxyl radical and another oxygenated radical according to the particular hydroperoxide used. The distribution of any hydroperoxide between the two phases may be changed by dissolving suitable ingredients in both phases.

When hydrogen peroxide is used to initiate VAc emulsion polymerization, it decomposes in the aqueous phase to form hydroxyl radicals, which are uncharged. Thus, an adsorbed layer of anionic emulsifier would not present a repulsion barrier to the diffusion of the uncharged hydroxyl radicals, and these radicals initiate polymerization in the water phase or diffuse across the interface to initiate polymerization in monomer-swollen polymer particles or micelles as well as monomer droplets. Polymerization in the aqueous phase would give oligomeric radicals with a hydrophilic but uncharged end group, which would reach a critical chain length and then be adsorbed at the monomer-swollen polymer and water interface.

Infrequently, only oil-soluble benzoyl peroxide initiator is used in emulsion polymerization. It partitions preferentially into the monomer or monomer-swollen polymer particles and generates the free-radical in that confined space. It was postulated that the dissolution of emulsifier increased the solubility of benzoyl peroxide in the water phase and the rapid diffusion of primary radicals from the particles to the water phase.

4.3.2 REDOX TYPE FREE RADICAL INITIATORS

Initiators of the redox type generate free radicals through an oxidation-reduction reaction at relatively low temperatures. The components of a redox initiation system are unreactive at normal ambient temperatures, provided that they are kept separate from each other. Redox initiators can be used at near-ambient temperatures, and at subambient temperatures such as 5°C. The advantage of a redox initiation system lies in the much lower activation energy for bond scission, about 10 kcal/mole compared to 30–35 kcal/mole required in thermal scission. Typical of such systems are potassium persulfate-sodium bisufite[173,174] and hydrogen peroxide-ferrous sulfate.

For many reasons free radical generation by thermal scission may be undesirable in emulsion polymerization. Most obvious, of course, is the need to conduct polymerizations at temperatures well below those at which the precursor decomposes rapidly enough for utility. The use of redox initiators has many advantages. Lower temperature polymerizations are possible, resulting in higher molecular weight polymers. Lower temperature polymerizations favor more linear polymers due to suppression of high temperature-accelerated chain transfer (as chain transfer to solvent, monomer, and polymer) and termination reactions, resulting in low levels of polymer branching. In addition, better control of polymerization rates and more efficient catalyst activity result when redox systems are used.

Redox catalysis systems use both a primary initiator precursor and a chemical reducing agent. One electron transfer from the reducing agent to the precursor occurs, giving rise to a free radical or free radical ion which may react as such or decompose further to another free radical, and a stable ion or molecule. Some of these redox systems, very important catalysts in industrial VAc homopolymerizations and copolymerizations with acrylic monomers, are shown below:

a. Persulfate - Bisulfite

$$S_2O_8^{-2} + HSO_3^{-1} \rightarrow SO_4\cdot^{-1} + SO_3\cdot^{-1} + HSO_4^{-1} \tag{4.29}$$

b. Persulfate - Thiosulfate

$$S_2O_8^{-2} + 2\,S_2O_3^{-2} \rightarrow 2\,SO_4\cdot^{-1} + S_4O_6^{-2} \tag{4.30}$$

c. Persulfate - Formaldehyde Sulfoxylate

$$S_2O_8^{-2} + HOCH_2SO_2^{-1} + OH^{-1} \rightarrow 2\,SO_3\cdot^{-1}(HCHO) + H_2O \tag{4.31}$$

d. Peroxide - Formaldehyde Sulfoxylate

$$2\,H_2O_2 + HOCH_2SO_2^{-1} \rightarrow 2\,HO\cdot + HOCH_2SO_3^{-1} + H_2O \tag{4.32}$$

Some examples of such systems are tertiart-butyl hydroperoxide/sodium formaldehyde sulphoxylate or potassium persulfate/sodium bisulfite/iron (2) compounds which allow low temperature polymerizations.[175]

e. Peroxide - Metallic Ion (reduced state)

$$H_2O_2 + Fe^{+2} \rightarrow HO\cdot + OH^{-} + Fe^{+3} \tag{4.33}$$

f. Persulfate - Metallic Ion (reduced state)

$$S_2O_8^{-2} + Fe^{+2} \rightarrow SO_4\cdot^{-1} + SO_4\cdot^{-2} + Fe^{+3} \tag{4.34}$$

Other effective metallic ions in which the metal ion is in a reduced state include Cr^{++}, Cu^{+}, and Ti^{++}

g. Organic redox systems may also be used such as cumyl hydroperoxide - benzene sulfinic acid

$$\begin{aligned} &2C_6H_5C(CH_3)_2OOH + C_6H_5SO_2H \rightarrow \\ &\quad 2C_6H_5C(CH_3)_2O\cdot + C_6H_5SO_3H + H_2O \end{aligned} \tag{4.35}$$

h. Benzoyl peroxide-benzene phosphinic acid

$$(C_6H_5CO_2)O + C_6H_5P(OH)_2 \rightarrow 2\,C_6H_5\cdot + C_6H_5P(O)(OH)_2 + 2\,CO_2 \tag{4.36}$$

4.3.2.1 Persulfate - Bisulfite

One of the most widely used redox systems is the persulfate-bisulfite reaction:

$$S_2O_8^{-2} + HSO_3^{-1} \rightarrow SO_4^{-2} + \cdot OSO_3^{-1} + \cdot OSO_2H \tag{4.37}$$

The polymerization is initiated by both the sulfate ion-radicals and bisulfite radicals and the polymers thus formed contain both sulfonate and sulfate end groups.

4.3.2.2 Peroxide - Iron (II) Salt

The oxidation of iron (II) cation by the hydrogen peroxide produces hydroxyl radicals which initiate the emulsion polymerization.

$$H_2O_2 + Fe^{+2} \rightarrow HO\cdot + OH^{-} + Fe^{+3} \tag{4.38}$$

Initially, hydroxide radicals are generated too rapidly; only a small proportion of these radicals initiate polymerization. Subsequently, the rate of generation decreases considerably as the components are consumed. In order to prevent this effect, oil-soluble organic hydroperoxides are used, the concentrations of reactants in the aqueous phase are limited, and the generation of radicals proceeds at a uniform rate. Instead of hydroxyl radicals, predominantly alkoxy radicals are produced:

$$ROOH + Fe^{+2} \rightarrow RO\cdot + OH^{-1} + Fe^{+3} \tag{4.39}$$

where R is an organic group such as tert-butyl, p-methane, p-methylisopropylbenzene (p-cymene), isopropylbenzene (cumene). The hydroperoxide usually partitions in the oil phase, whereas the iron compound is dissolved in the aqueous phase. The initiation rate can be controlled through limitation of the rate at which two components of the redox couple are brought together. This redox initiation system is capable of great diversification because of the wide range of available organic hydroperoxides, and also the possibility of controlling the availability of iron (II) ions by using preformed complexes or very insoluble iron (II) salts such as iron sulfide. The iron (II) component can be added in the form of a complex with either pyrophosphate or EDTA (ethylenediaminotetraacetic acid) anions. Reducing sugars such as glucose or dextrose may be added to convert the iron (III), which is formed back to iron (II) without reacting with the hydroperoxide. However, there are disadvantages to using hydroperoxide-iron (II) redox couple: the presence of traces of iron sometimes cause staining, discoloration, and oxidative degradation of the produced polymer.

Combinations of reducing agents can also be used, and, for example, persulfate-pyrosulfite-thiosulfate with copper sulfate co-catalyst at near neutral pH was found to be the most effective initiating system for VAc.[176] Latex producers try to obtain their products with the lowest residual monomer content. The search of the new initiator systems for VAc emulsion polymerization is done mainly to satisfy this need. Potassium persulfate/sodium bisulfite/acetone[177] and potassium persulfate/sodium bisulfite/benzaldehyde, acetaldehyde, methyl propyl ketone[178] initiator systems were tried for this purpose. The types of bisulfite adduct influenced the order dependence of the rate of polymerization to the initiator concentration where $n = 0.54 - 1.10$, and also the latex particle size distribution and the extent of the monomer conversion. The acetone adducts resulted in higher conversions due to lower steric hindrance, whereas the longer carbon adducts resulted in smaller particle size latices due to increased emulsifying tendencies.

4.3.3 OTHER FREE RADICAL INITIATORS

Infrequently, oil-soluble free-radical-producing compounds such as benzoyl peroxide and azobisisobutyronitrile (AIBN) are employed as initiators in emulsion polymerization.[179,180] Since these are not soluble in water, they cannot be considered as true emulsion polymerization initiators. However, the water-soluble derivatives of AIBN such as 4,4′-azobis-4-cyanopentanoic acid and disodium 2,2′-azobis-2-cyanopropane-1-sulfonate can be used to initiate emulsion polymerization. Other diazo compounds used to initiate emulsion polymerizations are aromatic diazoamino compounds, aromatic diazothioethers, and alkali-metal aryl diazates.

4.3.4 OTHER METHODS OF INITIATION

High-energy radiation initiation of polymer processes has been studied quite extensively with heavy emphasis on both electron bombardment and gamma radiation from cobalt-60 source (see Sec. 3.4), and ultrasonic methods. It is generally thought that absorption of high energy gives rise to free radicals *in situ*, such as hydroxyl radicals in water phase which initiate polymerization. Radiation polymerization of vinyl acetate and other vinyl monomers, including the acrylate esters, has been successfully demonstrated. Irradiation of both dilute and concentrated monomer solutions, pure liquid monomer, pure solid monomer, and gaseous monomer have led to high molecular weight polymer. Radiation grafting of monomers on polymer chains is an interesting newer development. Physical and chemical modification of the substrate polymer in this way gives rise to improved special properties.

4.4 WATER

Water not only provides the dispersing medium for the final emulsion particles, but serves as a solvent and diffusing medium for small quantities of monomers, as solvent for surfactant, initiator (and activator, if used), protective colloid, and ionic species such as salts and buffers. In addition, it is a dispersing medium for monomer droplets, the reservoirs for feeding the growing polymer chains either in "micelles" or in monomer-polymer particles. Most importantly, it functions as an excellent heat transfer medium, allowing large amounts of the exothermic heat of polymerization to be quickly dissipated.

Natural water has inorganic (mineral), organic, and gas components. Calcium and magnesium cations—which give hardness to water—and sodium, potassium cations, chloride, sulfate nitrate, nitrite, fluoride, phosphate, and borate anions can be mentioned as primary minerals. The presence of the multivalent cations can influence particle nucleation and stability during the synthesis of anionically stabilized latices (see Sec. 3.2 and 6). Variation in the hardness of water will often yield variation in particle size and can contribute instability. For this reason, the use of deionized water is preferred in industry. Ion-exchange columns having both anionic and cationic ion exchangers are used to deionize the reaction water. Another deionization method is reverse osmosis, but the ion exchange process is more economical. Water deionization is usually monitored by measurement of electrical resistivity. A water quality of 5×10^4 to 1×10^7 ohm-cm, which is equivalent to less than 0.05 mg/liter of sodium chloride, can be obtained by applying a suitable choice of ion-exchange resins and bed configurations.

The organic components in water are usually analyzed in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), organic carbon, detergents, oil and greases, pesticides, and trihalomethanes. In general, the organic components in water can be neglected because of their low concentrations. Only the dissolved oxygen gas in water is considered in emulsion polymerization practice. If the oxygen gas concentration in water is high, it may delay the start of polymerization because oxygen gas is a free-radical scavenger. This can be avoided by sparging with nitrogen prior to polymerization to deoxygenate the reaction water.

The proportion of water quantity to monomer quantity is also a factor that should be considered in polymerization kinetics. The monomer-to-water ratio is the weight ratio of the monomer to the water phase. In practice, the monomer-to-water-ratio chosen is that which gives the best rates of polymerization coupled with low viscosity to enable adequate heat and mass transfer.

4.5 EMULSIFIERS

Emulsifying agents in emulsion polymerizations serve to reduce the interfacial tension between the monomer phase and the water phase so that, with agitation, the monomer is dispersed (or emulsified) in the water phase. In general, the amount of emulsifier used influences the average size of the final latex particle. As a rule, a large quantity of emulsifier will produce small polymer particles, and a small amount of emulsifier will produce large polymer particles. Thus, in order to decrease the particle size and increase latex viscosity, an increase in the quantity of emulsifier is required. Anionic and nonionic emulsifiers in concentrations of 0.05 to 2.00% by weight are generally added for the emulsion polymerization of vinyl acetate. These concentrations correspond to 0.1 to 4.0% by weight to monomer (lower concentrations for the anionic emulsifiers and higher for the nonionics).

Emulsifiers (or surfactants, soaps, dispersing agents, detergents) perform the most important function of all in producing fine particle dispersions. They act to stabilize the monomer droplets in an emulsion form, serve to solubilize monomer within micelles, stabilize the formed monomer-swollen polymer particle during propagation and after the polymerization process, act to solubilize the polymer in aqueous phase to a lesser extent, sometimes serve as the site for the nucleation of particles, and sometimes act as chain transfer agents and retarders.[181]

Emulsifiers owe their unique properties to the presence in one molecule of two well-separated groups: a nonpolar (hydrophobic or oil-soluble) group and a polar (hydrophilic or water-soluble) group. At a concentration above a minimum (critical micelle concentration), characteristic of every surfactant, aggregation of the discrete molecules occurs to form micelles. These micelles are composed of a certain number of surfactant molecules in which the oil-soluble ends (tails) are directed inward toward the center, with the water-soluble ends (heads) on the periphery nearest the water atmosphere. Monomer diffuses from droplets in the mixture through the aqueous phase and into the micelles. Micelles continue to swell as polymer is formed and more of the monomer diffuses in. Finally, the micelle structure is destroyed and the surfactant molecules remain on the polymer particles as unimolecular absorbed layers. Monomer will then continue to diffuse into these particles and polymerize until conversion is complete.

Emulsifiers can be classified into four main types: anionics, cationics, nonionics, and amphoterics (zwitterionics) depending on the electrical charge (or absence of charge).[182] Nonionic and anionic emulsifiers are the most widely used types because of enhanced compatibility with negatively charged polyVAc particles as a result of persulfate initiator fragments as compared to the cationic or amphoteric emulsifiers. The mixtures of different kind of surfactants (i.e., mixtures of nonionic and anionic emulsifiers) are often used together in a synergistic manner to control the particle size and to impart enhanced colloidal stability to the latex with regard to electrolyte differences, extremes in temperatures, and mechanical shearing effects. There is an enormous variety of commercial surfactants that are employed in the formulation of emulsion polymerizations. McCutcheon's publishes an extensive compilation listing a wide variety of surfactants and their manufacturers' information.[183] Commercial emulsifiers often comprise a distribution of many different homologue molecules (i.e., in ethoxylated nonionic emulsifiers with ethylene oxide (EO) units present, the number of EO units per emulsifier molecule may vary, as can the alkyl lengths). This often results at the emulsifier manufacturing step where a distribution of EO and alkyl chain lengths in the emulsifier feed stock is used. The presence of the distribution of these homologues, and the by-products in the commercial emulsifier resulting from the manufacturing process (e.g., salts, alcohols, fats, etc.), may influence the kinetics of emulsion polymerization and, thus, the properties of the final latex.

There is a need for a method to predict the efficiency of emulsification for a given surfactant. HLB [hydrophile-lipophile (hydrophobe)] balance of the polar hydrophilic head and nonpolar lipophilic tail components in an emulsifier molecule system developed for this purpose in the late 1940s expresses the size and strength of the water-soluble and oil-soluble portions of the molecule.[184]

HLB method is represented by an arbitrary scale in which the least hydrophilic materials have low HLB values, and increasing HLB corresponds to increasingly hydrophilic character. In general, emulsifiers with low HLB values (numbers less than 6 or 7) are defined as hydrophobic and are used as water-in-oil emulsifiers, while those with high HLB values (numbers greater than 8) are hydrophilic and good for oil-in-water emulsions such as polyVAc latices. The use of this system for selecting emulsifiers to be used in emulsion polymerization formulations has met mixed success. In general, emulsifier selection is still quite empirical and the experience of the formulator or trial-and-error approaches dominate in this field. In the 1990s it was found that surfactant adsorption energies were strongly correlated with the latex particle size obtained from emulsion polymerization, which may be a promising method for the future.[185]

4.5.1 ANIONIC EMULSIFIERS

The hydrophilic head groups of the anionic surfactants are negatively charged and comprise sulfate, sulfonate, sulfosuccinate, or phosphate groups which are attached to an extended hydrophobic backbone. The nature of the negatively charged hydrophilic group is important because it influences the extent of electrostatic stabilization, the behavior of the emulsifier as a function of solution pH, and the variation of the polyVAc latex stability with time, electrolyte, and temperature conditions. The nature of the hydrophobic backbone affects the critical micelle concentration (CMC) value of the emulsifier, the interfacial tension between the water and the monomer which influences the emulsification of the monomer, the adsorption behavior of the emulsifier on the latex particle surface, and the extent of steric stabilization.

4.5.1.1 Sodium Alcohol Sulfate

Sodium lauryl (dodecyl) sulfate, $[C_{12}H_{25}OSO_3^- Na^+]$, is one of the most commonly used anionic emulsion polymerization surfactants having a sulfate ionic group. It has a CMC of 0.060–0.085 wt% in water, according to the manufacturer.

4.5.1.2 Alkyl Aryl Sodium Sulfonate

Sodium dodecylbenzene sulfonate, $[C_{12}H_{25}C_6H_4SO_3^- Na^+]$, has a sulfonate ionic group. Its CMC varies between 0.10–0.12 wt% according to the manufacturer. Two sulfonate groups per emulsifier molecule were also synthesized. Alkylated disulfonated diphenyl oxide emulsifiers with C6–C16 hydrophobic groups (both linear and branched) are manufactured with CMC's ranging from 0.05 to 1.90 wt% depending on the hydrophobic group.

Sulfonate emulsifiers have an advantage over sulfate emulsifiers in that they are less susceptible to hydrolysis under acidic conditions. The hydrolysis reaction separates the polar hydrophilic group from the hydrophobic group by cleavage of the C-O-S bond in the sulfates, and thus destroys its function as an efficient emulsifier. However, the equivalent bond in sulfonates is C-S, which is not so susceptible to acid hydrolysis.

4.5.1.3 Dialkyl Ester of Sodium Sulfosuccinic Acid

Sodium dioctyl sulfosuccinate, $[(C_8H_{17}\ COOCH_2)_2SO_3^-\ Na^+]$, is a very commonly utilized emulsifier and has a CMC of 0.07 wt%, whereas its homologues, sodium dihexyl sulfosuccinate with its CMC = 1.0 wt% and sodium diamyl sulfosuccinate with its CMC = 1.2 wt%, are also used in emulsion polymerizations. Another derivative of sulfosuccinate is a polymerizable emulsifier, sodium dodecyl allyl sulfosuccinate, which was studied extensively by Urgiola et al. in the emulsion polymerization of VAc.[186] They determined that a significant degree of chain transfer to the emulsifier occurs, which explains the decrease in the polymerization rate with increasing emulsifier concentration. This behavior is opposite to the usual observation with conventional emulsifiers.

4.5.1.4 Fluorinated Anionic Emulsifiers

A series of fluorinated anionic emulsifiers was synthesized in which a fluorocarbon group replaced the hydrophobic tail in the emulsifier molecule containing a sulfonate hydrophilic group. Ammonium perfluoroalkyl sulfonate can be used in acrylic-based emulsions, which lower the surface tension of the aqueous phase much larger than equivalent hydrocarbon-based emulsifiers.

4.5.1.5 Phosphate Ester Anionic Emulsifiers

When ethoxylated nonyl phenol groups are combined with phosphate anionic groups, phosphate ester anionic emulsifiers are obtained such as nonyl phenol ethoxy (6) phosphate ester with a CMC of 0.022 wt%. This emulsifier can be used in the emulsion polymerization of VAc and VAc-acrylic copolymers.[188]

4.5.2 CATIONIC EMULSIFIERS

Cationics are used in specialty applications where it is desirable to impart a positive charge on emulsion particles. Cationic emulsifiers are only infrequently used in VAc emulsion polymerization because they are not compatible with anionic emulsifiers or negatively charged latex particles. Examples of cationic surfactants are quaternary salts such as acetyl dimethyl benzyl ammonium chloride and hexadecyl trimethyl ammonium bromide. Both of the above ionic species are characterized by a long chain alkyl (oil-soluble) group and a water-soluble portion which carries the electronic charge, with a counter-ion of opposite charge attached.

Salts of long chain amines, polyamine salts, polyoxyethylenated long-chain amines and their quarternized derivatives, and amine oxides are also used as cationic emulsifiers.[189]

4.5.3 NONIONIC EMULSIFIERS

Nonionic emulsifiers, which carry essentially no charge, overcome the incompatibility exhibited by ionic emulsifiers when certain additives are used in compounding. They usually produce latices of rather large particle size.

Nonionic emulsifiers are generally characterized by a simple method called "cloud-point determination." The cloud-point is a measure of the inverse solubility of the nonionics with temperature, and is usually determined by heating 1 wt% solution of the emulsifier in water in a test tube until it clouds, and then measuring the temperature at which clearing occurs as the solution cools. In most cases, no difference is found between a cloud-point measured in rising or falling temperature. At the cloud-point, the sudden onset of turbidity of the nonionic solution takes place, and at somewhat higher temperatures the solution begins to separate into two phases. In one of them, the emulsifier concentration is enriched, whereas in the other it is depleted. The cloud-point method determination serves both as a control method and as a specification for nonionic emulsifiers.

4.5.3.1 Polyoxyethylenated Alkylphenol Nonionic Emulsifiers

Ethylene oxide adducts of alkyl aryl phenols are examples of this type. Nonylphenol polyoxyethylene glycol, $[C_9H_{17}C_6H_4O\text{–}(CH_2CH_2\text{–}O)_nH]$, and octylphenol polyoxyethylene glycol, $[C_8H_{15}C_6H_4O\text{–}(CH_2CH_2\text{–}O)_n H]$, are the main members of this group. The number of ethylene oxide units, (n), may be varied from a few to about 100 (typically from 1 to 70 EO units), which characterize the distribution of polyEO chain lengths for each specific emulsifier and produce a wide range of surfactant properties. The lower EO unit numbers are oil-soluble, while the higher are water-soluble. As the length of the ethylene oxide side chain is increased, uses gradate from water-in-oil emulsions through wetting agents, oil-in water emulsions, and detergents to solubilizers. These emulsifiers are supplied having various activities ranging from 20 to 100%. The CMC value of 30–40 moles of EO for octylphenol is in the 0.03–0.04 wt% range, whereas the CMC value of 9–100 moles of EO for nonylphenol is in the 0.005–0.100 wt% range.[188] The HLB value increases with the increase in EO units in the emulsifier. Typically, the HLB value of 4 moles ethoxylated nonylphenol emulsifier is 8.7, whereas it increases up to 18 for the 40 moles ethoxylated one. Thus, all the nonylphenol emulsifiers having more than 4 EO units are considered essentially hydrophilic. The higher adducts containing 20 to 100 moles of ethylene oxide are used in the emulsion polymerization of VAc and acrylates.

By judicious choice of these nonionics, or by use of blends of high, intermediate, and low ethylene oxide substituted ones, it is possible to alter latex properties such as particle size, viscosity, freeze-thaw stability, film clarity, water resistance, and rates of monomer conversion. However, most emulsifiers are water soluble and contribute to the water sensitivity of a film deposited from the emulsion. If, therefore, the end use of the emulsion is to prepare water-resistant films, the emulsifier concentration used should be kept at a minimum.

4.5.3.2 Polyoxyethylenated Alcohol Nonionic Emulsifiers

Ethylene oxide adducts of straight chain primary alcohols such as n-decanol, n-dodecanol, n-tetradecanol, and n-octadecanol are examples of this type, $[RO–(CH_2CH_2O)_n H]$. These emulsifiers can be biodegradable and are favored due to environmental aspects. Ethylene oxide adducts of fatty alcohols are also used as surfactants in emulsion polymerization because of their tolerance for hard water and their imparting shear resistance to latex.

4.5.3.3 Ethylene Oxide-Propylene Oxide Block Copolymer Nonionic Emulsifiers

Polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymers are examples of this type: $[H–(OCH_2CH_2)_a–(OCH_3CH–CH_2)_b–(OCH_2CH_2)_a–OH]$. The polyethylene oxide portion constitutes between 10 and 80% of the copolymer. Emulsifiers having their HLB value greater than 24 are used in emulsion polymerizations. Their use in industry is due in part to their low foam level, and in part on their preventing the agglomeration of pigment particles on addition to aqueous systems when the latex is used as a paint binder. Using polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymer surfactant as the sole emulsifier in VAc emulsion polymerization, the molecular weight of the VAc polymer increases and the latex particle size decreases as the concentration of the surfactant containing 80 wt% polyoxyethylene (HLB value = 27) is increased from 2.5 to 7.5%.[188]

Tetrafunctional block copolymers are also synthesized by the polycondensation of polypropylene oxide and polyethylene oxide on ethylene diamine: $[H(C_2H_4O)_y(C_3H_6O)_x]_2–N–CH_2–CH_2–N–[(C_3H_6O)_x (C_2H_4O)_y H]_2$. The addition of these emulsifiers decreases the water sensitivity and enhances freeze-thaw, shear, and electrolyte stability. They also result in low foam formation during emulsion polymerization.[188]

4.5.3.4 Other Nonionic Emulsifiers

Polyoxyethylenated fatty acid esters, alkanolamine condensates, tertiary acetylenic glycols, alkylpolyglycosides, polyoxyethylenated mercaptans, polyoxyethylenated silicones, n-alkylpyrollidones, polyoxyethylenated alkylamides, and amines are considered nonionic emulsifiers.

4.5.4 AMPHOTERIC EMULSIFIERS

Amphoteric (zwitterionic) emulsifiers show anionic properties at high pH and cationic properties at low pH. They are mainly alkylamino or alkylimino propionic acids. These surfactants are not commonly used in emulsion polymerization recipes.

4.6 PROTECTIVE COLLOIDS

Protective colloids are used to increase the particle stability in latices against coagulation (see Sec. 6.2). Certain water-soluble hydrophilic compounds may be used as protective colloids. These colloids are used in emulsion polymerization of polyVAc to prevent agglomeration of the polymer particles as they are formed. These substances are not absorbed within the polymer particles but remain on the surface and prevent agglomeration by enveloping the polymer. These water-soluble polymers coat the emulsion particles and are solvated or surrounded by water molecules. A part of the protective colloid polymer chain is anchored or strongly adsorbed on the particle surface, while the major part must be extended into the aqueous phase (see Sec. 2, 3.2, 3.3, and 6.2). This prevents polymer-polymer interaction leading to coagulation or agglomeration of particles. This kind of stabilization is also known as steric stabilization. Protective colloids also increase the viscosity of the water phase, prevent the close proximity necessary for particles to agglomerate, reduce the sedimentation rate of the solid particles, and produce a stabilizing effect on the latex. However, although they are used largely in the polyVAc latex industry, protective colloids are not always necessary or desirable components of a latice. Similarly, stable latices may be made without surfactants, but only with protective colloid.

There are some disadvantages of protective colloids. Since they are water-soluble, they impart water sensitivity to a film deposited from the latex. In addition, since they are not absorbed within the polymer particles, they may impart haziness and low scrub resistance to a film. For these reasons it is desirable to keep the concentration of the protective colloid as low as possible. The amount of protective colloid required is usually in the range of 1 to 5 wt% in solution. In actual experience, the behavior of emulsifiers and protective colloids is not as clear-cut as has been theorized. Emulsifiers have some of the properties of protective colloids, and the reverse is also true. Therefore, emulsions can be made using only one of either type material. However, the most usual procedure is to use both as adjuncts, and quite frequently more than one of each type. The selection of an emulsifier-protective colloid system having the right balance of each component is critical for an emulsion of specific properties and stability. The correct balance in the emulsifier-protective colloid system can be found only by considerable experimentation.

Protective colloids are generally of two types: (1) natural or modified-natural products such as gum agar, gum arabic, gum tragacanth, water soluble starches, pectin, gelatin, and alginates, and modified cellulosics such as hydroxylethyl cellulose and carboxymethyl cellulose; and (2) synthetic products such as polyvinyl alcohol, polymethacrylamide, polyvinyl pyrollidone, sulfonated polystyrene, and alkali salts of polymethacrylic and polyacrylic acids. The two most widely used protective colloids are polyvinyl alcohol and hydroxyethyl cellulose.

4.6.1 POLYVINYL ALCOHOL

Hydrolysis of polyvinyl acetate yields water-soluble, high molecular weight polyvinyl alcohol polymer.[151,190] Partially hydrolyzed (87–89%) grades are commonly used as protective colloids in the industrial emulsion polymerization of VAc. It fulfills the dual function of emulsifying the monomer and stabilizing the polymer particles formed during the process. The properties of polyvinyl alcohol may be modified widely depending upon the chain length of the polyvinyl acetate selected and the extent of hydrolysis. Industrial grades include the fully hydrolyzed (98–99 mol%), intermediate hydrolyzed (93–97 mol%), and partially hydrolyzed (85–90 mol%) forms of polyVAc, and, thus polyvinyl alcohol always contains an unhydrolyzed residual polyVAc. Partially hydrolyzed polyvinyl alcohols contain 10–15 mol% acetyl groups, and these grades have a block copolymer structure. The distribution of residual acetyl groups is critically affected by the hydrolysis procedure adopted. The "blockiness" of the copolymer can be increased by adding a proportion of benzene to the alkaline hydrolysis solvent.

The physical properties of polyvinyl alcohol are controlled by its molecular weight and its degree of hydrolysis. At the constant degree of hydrolysis, the increase of the molecular weight increases the solution viscosity in water; increases the tensile strength, water and solvent resistance, and adhesive strength of the resultant polyvinyl alcohol film; and decreases the ease of solvation in water. At constant molecular weight, the increase in the degree of hydrolysis increases water and solvent resistance, crystallinity, tensile and adhesive strength, and the ability to adhere to hydrophilic surfaces of the of the resultant polyvinyl alcohol film. Since hydrolysis and molecular weight can be independently controlled in the manufacturing process, a product matrix has evolved that provides the property balance needed for different applications. Polyvinyl alcohol product matrix has three key hydrolysis levels, which were given previously, and four different molecular weight ranges. The four general molecular weight ranges are described with their nominal number average molecular weights, M_n, and aqueous solution viscosity of 4 wt% solution at 20°C measured with a Brookfield viscometer. These grades of polyvinyl alcohol are low (M_n = 25,000, solution viscosity 4–7 cPs), intermediate (M_n = 40,000, solution viscosity 13–18 cPs), medium (M_n = 60,000, solution viscosity 26–30 cPs), and high (M_n = 100,000, solution viscosity 48–65 cPs). Mixtures of these grades can also be used for the desired final properties and there is no limit to the viscosity that can be generated by blending the available grades. Grades of different degrees of hydrolysis can also be blended to develop particular performance characteristics that are between these grades, i.e., intermediate solubility. The surface tension of polyvinyl alcohol solutions in water increase linearly with the degree of hydrolysis from 88 to 98%, but then increase sharply above 98%.

Solid polyvinyl alcohol powder must be completely dispersed in water at room temperature or lower prior to heating. Good agitation is necessary to prevent lump formation during addition of the solid polyvinyl alcohol to water. A large diameter, low-speed agitator is preferred to provide good turnover of the liquid surface without excessive air entrapment. Water should never be added to the dry solid. After dispersion of the polyvinyl alcohol, the slurry temperature should be increased by direct steam injection, if possible. This eliminates the potential for polyvinyl alcohol build-up on steam coils or heated surfaces caused by localized water evaporation. When heat-set, this polyvinyl alcohol is difficult to remove, which greatly reduces the heat-transfer rate. Solubility in water is also influenced by the particle size, surface area, and crystallinity of the polyvinyl alcohol. Decreasing the particle size and molecular weight improves the solubility rate. Antifoam agents are usually required while preparing polyvinyl alcohol solutions. Silicone antifoams are the most effective, but this effectiveness is not long lasting and, in some cases, decreases the wettability of aqueous solutions. They are, therefore, not recommended. The nonsilicone antifoam agents based on octyl alcohol and tributyl phosphate (NOPCO 1497-V of Nopco Chemical Co.) are equally effective. Amounts equal to 0.01 to 0.05 wt% of the aqueous solutions are usually added. Polyvinyl alcohol solutions show a high tolerance to many electrolytes; small additions of strong inorganic acids and bases do not precipitate polyvinyl alcohol from solution, but the hydrolysis reaction continues to completion at extreme pHs. Up to 50 wt% of lower alcohols can be added to polyvinyl alcohol solutions without causing precipitation. Polyvinyl alcohol cannot be dissolved by most common organic solvents.

Aqueous solutions of polyvinyl alcohol are stable upon storage but must be protected from rust contamination and bacterial growth. Plastic or stainless-steel containers are recommended for long-term storage. Sodium nitrite may be added in 0.05–0.20 wt% solution to prevent rust in iron containers. Formaldehyde is an efficient and inexpensive biocide if added at 500 ppm to polyvinyl alcohol solutions. Sodium propionate and other biocides can also be used to prevent mold development.

Polyvinyl alcohol undergoes chemical reactions in a manner similar to other secondary polyhydric alcohols. It forms polyvinyl acetals with aldehydes such as polyvinyl formal and polyvinyl butyral. Polyvinyl alcohol can be readily cross-linked with glyoxal, urea-formaldehyde, and melamine-formaldehyde. Ammonium sulfate or chloride is necessary with the formaldehyde cross-linkers. The controlled gelation of polyvinyl alcohol solution is important where penetration into a porous substrate is undesirable, e.g., paper coatings and adhesives. Boric acid and borax form complexes with polyvinyl alcohol and are widely used industrially as gelling agents. A 0.1 wt% borax can cause thermally irreversible gelation by forming a bisdiol complex with polyvinyl alcohol. Boric acid forms a weaker monodiol complex and is preferred for controlled partial gelation of polyvinyl alcohol. The reaction is very sensitive to pH, and full gelation occurs above pH = 6.[190]

The wide range of chemical and physical properties of polyvinyl alcohol has led to their broad industrial use. The excellent adhesion of polyvinyl alcohol to cellulosic materials such as paper, cardboard, and cellophane makes it useful as an adhesive and coating for these materials. Polyvinyl alcohols are also used as textile warp sizes. They are highly resistant to solvents, oil, and grease. They form tough, clear films that have high tensile strength and abrasion resistance. Their oxygen-barrier qualities are very high; however, they must be protected from moisture, which greatly increases the gas-transmission rate.

The use of different grades of polyvinyl alcohols as protective colloids in the emulsion polymerization of VAc was studied, good stability was achieved only with partially hydrolyzed grades, and the stability increased with the acetyl content and with the blockiness of the distribution of the acetate groups[151] (see Sec. 3.2 and 3.3). The choice of the polyvinyl alcohol grade is important to control the viscosity of the final polyVAc latex. Intermediate and medium viscosity grades of partially hydrolyzed (usually 88 mol%) are generally used in VAc emulsion polymerization, and the low and high viscosity grades are added to affect the viscosity of the final latex when required. Latex viscosity increases with the degree of acetylation, degree of blockiness, and molecular weight of the polyvinyl alcohol used, and with its quantity.[151] As an example, when 18–88 grade of polyvinyl alcohol is used (88% hydrolyzed type with a solution viscosity of 18 cps in 4% solution), the typical polyVAc latex viscosities are about 12,000 cPs for 2 wt% concentration, and about 80,000 cPs for 4 wt% concentration.[191,192] It is sometimes observed that the viscosity of polyvinyl alcohol-based polymer emulsions tends to rise on storage owing to the formation of structure by the colloid. The same effect was seen in 10% solutions of polyvinyl alcohol itself, but the addition of aliphatic monobasic alcohols diminished this tendency.[151] Fully hydrolyzed polyvinyl alcohol grades are normally not used during industrial emulsion polymerizations, but may be added after the polymerization is complete to increase the water resistance of the latex films.

Polyvinyl alcohol is sometimes used in conjunction with micelle-forming emulsifiers, and the presence of such emulsifiers is essential if a fully hydrolyzed grade is used in the formulation.[151] The function of the emulsifier will depend on the extent to which it is adsorbed onto the polyvinyl alcohol. If it is not adsorbed, it fulfills an independent role. When sodium dodecyl sulfate is used in conjunction with polyvinyl alcohol, adsorption occurs, a complex is formed, and it behaves like a polyelectrolyte.[151] The emulsifier interacts with the acetyl groups of polyvinyl alcohol. It was also found that the solubility of ionic surfactants, i.e., sodium n-hexadecyl sulfate in water, is increased by the presence of polyvinyl alcohol.[193]

Polyvinyl alcohol interacts with the initiators. In the absence of VAc monomer, it was determined that hydrogen peroxide caused oxidation of polyvinyl alcohol at 60°C, and the carbonyl content was increased.[194] Oxidation with ammonium persulfate at 60°C also yielded carbonyl groups, the number increasing with the quantity of persulfate.[195]

In a system where monomer is polymerized in the presence of a polymer under homogeneous conditions, it is possible for graft copolymerization to occur by transfer mechanisms. VAc monomer exhibits high grafting tendency, and it is likely that initiator-radical attack on polyvinyl alcohol produces a macroradical, which itself initiates VAc polymerization[196,197] (see also Sec. 3.2 and 3.3). In emulsion polymerization, the extent of graft copolymerization increases with increasing acetyl content of the polyvinyl alcohol, however the reverse is true for grafting in homogeneous solution, in agreement with the chain transfer constants.[196] This process emphasizes the peculiarities associated with the heterogeneous system of emulsion polymerization.[151] It can be explained that, in the early stages of the emulsion polymerization of VAc, polyvinyl alcohol is dissolved in water phase, and more hydroxyl groups and fewer acetyl groups may be available for radical attack owing to clustering of the acetyl groups of partially hydrolyzed polyVAc in aqueous solution. Later in the process, polyvinyl alcohol is adsorbed onto the surface of polyVAc particles, and the preferentially adsorbed acetyl groups of the polyvinyl alcohol may be nearer to the locus of polymerization at the surface of the particle, thus resulting in higher grafting onto the polyvinyl alcohol having higher acetyl content.[151]

When tert-dodecyl mercaptan was incorporated as a chain-transfer agent in the emulsion polymerization of VAc containing polyvinyl alcohol as colloidal stabilizer, the final molecular weight and the polydispersity of the graft-copolymer fraction were both reduced.[198]

The minimum temperature at which a polymer emulsion will form a continuous film (MFT) is another property dependent on both polymer and colloid stabilizer. MFT is found to decrease with increasing quantities of polyvinyl alcohol between 3 and 11% of the weight of the VAc monomer. Since MFT of polyVAc latices lies between 15° and 21°C, and the films are brittle at room temperature, it is usually necessary to include a plasticizer such as dibutyl phthalate or a coalescing solvent such as 2-butoxyethanol. PolyVAc latices based on polyvinyl alcohol generally have good stability to the post addition of solvents of this nature.[151] On the other hand, the rate of film formation decreased with an increase of polyvinyl alcohol content.[199] The dried latex films were investigated by light scattering, and with highly polydisperse latices it was found that polyVAc particles were embedded in a polyvinyl alcohol cement.[151]

4.6.2 HYDROXYETHYL CELLULOSE

Hydroxyethyl cellulose is a water-soluble, nonionic polymer manufactured by reacting purified cellulose with ethylene oxide. It is a hydroxyethyl ether of cellulose, and it is possible to synthesize several molecular weight grades. Each anhydroglucose unit in the cellulose molecule has three reactive hydroxyl groups, and ethylene oxide polymerizes to form a side chain on each hydroxyl group. In commercial hydroxyethyl cellulose products, 1.8 or 2.5 moles of ethylene oxide attach to each anhydroglucose unit in cellulose. Hydroxyethyl cellulose protective colloid is compatible with all four types of emulsifiers used in emulsion polymerizations. However, it has the disadvantage of being readily degraded biologically.

Due to its nonionic nature, hydroxyethyl cellulose possesses an outstanding tolerance for salts and other electrolytes. Solutions of hydroxyethyl cellulose are stable within the wide pH range of about 2 to 12. The solutions of hydroxyethyl cellulose are pseudoplastic, that is, they vary in viscosity depending upon the amount of stress applied.

Hydroxyethyl cellulose[200,201] and hydrophobically-modified hydroxyethyl cellulose[202] have been used for increased stability in latices, as well as for rheology control. They provide a hydrated shell around particles for steric stabilization. Hydroxyethyl cellulose is preferentially used in latices for architectural coatings. Grafting reactions take place between hydroxyethyl cellulose and VAc to form prepolymers, which subsequently collapse to form particles encapsulated by a hydrated polymer shell.[203,204] Grafting to polyVAc is less extensive for hydroxyethyl cellulose than polyvinyl alcohol and is accompanied by oxidative degradation of the cellulose backbone.[205] Consequently, the protective layer around the polymer particles is not thick, and extreme latex viscosities can be avoided.

The emulsion polymerization rate of VAc in the presence of hydroxyethyl cellulose protective colloid was investigated in detail.[204] Hydroxyethyl cellulose macromolecule underwent scission due to the oxidative degradation effect of the persulfate initiator used. Carbonyl groups were formed on hydroxyethyl cellulose chains after oxidative degradation, which could have been followed by UV absorbance at 263 nm.[204]

On the other hand, concentration of hydroxyethyl cellulose has a strong effect on the decomposition reaction rate of potassium persulfate.[206] The kinetics of emulsion polymerization of VAc in the presence of hydroxyethyl cellulose has certain distinctive aspects due to this degradative process. When the number of carbonyl groups on the hydroxyethyl cellulose chain increased, some reactive centers (free radicals) were formed. These free radicals may act as growing centers which yield graft-copolymers with VAc. At the same time, as oxidative degradation is accompanied by the scission of the chain, free radicals are formed at the ends of hydroxyethyl cellulose fragments as well. VAc addition to these radicals may cause the formation of block copolymers.[207] The evidence of the formation of hydroxyethyl cellulose-polyVAc graft copolymers were shown by transmission electron micrographs of the benzene-soluble fractions of the polymers, and by viscometric measurements.[204]

4.7 PH AND IONIC STRENGTH CONTROLLERS

Emulsion systems are sensitive to pH, and each system has a definite pH for optimum conversion and latex stability. The range for polyvinyl acetate emulsions appears to be pH = 4.5–5.5, which can be obtained by buffering the reaction medium with buffer systems such as sodium bicarbonate, sodium acetate-acetic acid, or diphosphate-monophosphate (monosodium phosphate). In connection with pH there is also the problem of hydrolysis of the vinyl acetate monomer and polymer. The rate of hydrolysis of polyvinyl acetate to polyvinyl alcohol is negligible in the usual finished emulsion, however, the hydrolysis of VAc monomer may be significant by excessive acidity arising from initiator residues. In weakly acidic or basic media VAc is hydrolyzed to yield acetic acid and acetaldehyde. In order to keep the hydrolysis of vinyl acetate monomer to a minimum during emulsion polymerization, it is best to maintain the system as close to a neutral pH as possible. In addition, most initiator decomposition rates are pH dependent. Under acidic conditions, decomposition of persulfate initiators are accelerated, which can lead to a reduction in the number of free radicals in the polymerizing system with a resulting decrease in conversion.[208] For these reasons it is desirable to maintain the acidity or pH during polymerization within a narrow range, generally between 4.5 and 5.5. The rate of hydrolysis, K, is calculated from the equation

$$\log \frac{1}{(1-X)} = 2.303\, K\, t \tag{4.40}$$

where X is the fraction of vinyl acetate hydrolyzed, and t is the time in minutes. K was found as follows: 0.3 at 25°C, 2.3 at 60°C, and 7.8 at 80°C.[7]

Control of pH during emulsion polymerization is important; however, buffers are salts, and, as such, they can influence the colloidal stability of the latex and the particle size (see also Sec. 6).

4.8 OTHERS

4.8.1 CHAIN TRANSFER AGENTS

Chain transfer agents can be included in emulsion polymerization systems to terminate propagating polymer chains and to prevent polymer chains from growing too large, which leads to difficulty in subsequent processing. Changing the concentration of such modifiers or chain transfer agents during emulsion polymerization leads to control of average molecular weight, molecular weight distribution, branching, and cross-linking of the polymer. The extent of chain transfer can be predicted if the chain transfer constants (Cs) are known for a given monomer system. It should also be emphasized that monomer or emulsifier can undergo chain transfer reactions which will also influence the molar mass of the final polyVAc latex. Chain transfer constants for VAc monomer to various chemicals are given in some sources.[209,210]

Examples of chain transfer agents used in emulsion polymerization include mercaptans (tert-butyl mercaptan), aldehydes, chlorinated aliphatics, disulfides, sulfur, amines, chloroform, carbon tetrachloride, nitroso compounds, and other carbonyl compounds. When tert-dodecyl mercaptan was used as a chain-transfer agent in the VAc emulsion polymerization containing polyvinyl alcohol as colloidal stabilizer, the final molecular weight and the polydispersity of the graft-copolymer fraction were both reduced.[198] In some instances chain transfer, with its resulting lowering of polymer molecular weight, is undesirable and an effort should be made to avoid it.

4.8.2 RETARDERS

Sometimes emulsion polymerization is so rapid that control of exothermic heat of polymerization is difficult. It is necessary to use agents called “retarders” to slow the propagation rates. These retarders actually enter the polymerization to produce less reactive (to monomer) radical chain ends. If carried to extremes and propagation rates are reduced to zero, the retardation actually becomes inhibition. The growing chain radical end will be unreactive to further monomer addition and reaction will cease. Examples of retarders include ortho-nitrophenol, conjugated dienes and trienes, and even some vinyl monomers.

4.8.3 ANTIFOAMS

Use of surfactants in certain process conditions may lead to excessive foam in the emulsion product. Ideally, it would be desirable to maintain conditions to minimize air entrapment. This is not always possible, and use must be made of antifoam additives. Most defoamers sold are proprietary in composition but are believed to contain some aliphatic solvents, silicone oils, and possibly heavy metal soaps. Excessive reliance on additives of this kind may lead to additional problems — film properties and the compounding ability of the emulsions may be severely impaired.

Antifoam agents are usually required while preparing polyvinyl alcohol containing polyVAc latices. Silicone antifoams are the most effective, but this effectiveness is not long lasting, and in some cases decreases the wettability of latices, which is undesirable. The nonsilicone antifoam agents based on octyl alcohol and tributyl phosphate (NOPCO 1497-V of Nopco Chemical Co.) are equally effective and their use is recommended. Amounts equal to 0.01 to 0.05 wt% of the aqueous solutions are usually added.

4.8.4 PLASTICIZING AND COALESCING AIDS

Plasticizers such as dibutyl phthalate and tricresyl phosphate may be added to the system during or after emulsion polymerization. These plasticizers aid in film coalescence and flexibility. Frequently, certain properties may be achieved by incorporating plasticizers and coalescing aids to polyVAc latices after polymerization is complete.[211] In many coating applications film formation has to be rapid, requiring low glass transition, (T_g) polymer, and the final polymer film properties must be hard and resistant, representing high T_g. Coalescing aids, such as hexylene glycol, 2,2,4-trimethyl 1,3-pentane diol monoisobutyrate, and various alkyl esters of carbitol are generally used in the emulsion polymerization industry. Coalescing aids evaporate after film formation, restoring the film to the original polymer T_g. For example, glycols are added to latices to improve freeze-thaw stability and wet-edge characteristics. Plasticizers generally behave in a similar manner except they stay with the polymer for a considerably longer time.[212,213] MFT is the minimum temperature at which a polymer emulsion will form a continuous film, and it has relationship with the T_g of the polymer. Since MFT of polyVAc latices lies between 15° and 21°C, and the films are brittle at room temperature, it is necessary to add a plasticizer such as dibutyl phthalate, or a coalescing solvent such as 2-butoxyethanol, in order to ensure the film formation and to prevent brittleness of homopolyVAc films by increasing the T_g of the polymer films produced. Plasticizers such as tricresyl phosphate are also added to latices to give films fire-retardancy.

4.8.5 BIOCIDES AND FUNGICIDES

PolyVAc coatings and latices are prone to microbiological contamination and deterioration. At present, the environmentally driven trend in latex production is to lower the residual free monomer which was once used to prevent bacterial growth and maintain microbiological stability. Thus, there is a need to add biocides and fungicides. The choice of these agents should be made on the basis of the specific microbe present. Formaldehyde is an efficient and inexpensive biocide if added to polyvinyl alcohol based polyVAc latices. Phenolics and halogen compounds such as pentachlorophenol, o-phenylphenol; amines and nitriles such as tetrachloroisophthalonitrile and nitro derivatives; organo sulfur compounds such as 2-*n*-octyl-4-isothiazolin-3-one; and sulfur nitrogen compounds are used as common antimicrobial agents.[214]

4.8.6 ANTIOXIDANTS AND ULTRAVIOLET LIGHT ABSORBERS

Free radicals form in polymer films by exposure to ultraviolet (UV) radiation, and the oxidative degradation of polymers proceeds by a free-radical mechanism. The spectral energy between 300–400 nm breaks covalent chemical bonds to form radicals. Sunlight supplies radiation in the wavelength of 300–800 nm, and UV degradation is linked to oxidative degradation via free-radical-initiated auto-oxidation mechanisms. Thus, every polymer needs UV stabilization depending on the nature of the polymer and the required length of service in a given environment. Antioxidants are produced to prevent UV degradation, and they act as effective free radical scavengers. Some examples of often-used UV stabilizers are 2-hydroxybenzophenone; phenyl salicylate; 1,3,5-tris(2′-hydroxyphenyl)triazine; and 2-(hydroxyphenyl)benzotriazole.[188] Commercial antioxidants are numerous and a list is given.[212]

4.8.7 LATEX POSTADDITIVES

Some chemicals added to a latex after polymerization is complete are called "post-additives." Apart from antifoams and plasticizing and coalescing aids, biocides and fungicides, and antioxidants and UV absorbers, which are also post-additives, anionic and/or nonionic emulsifiers are also added after polymerization is complete to enhance the colloidal (shear) stability of the latex prior to pumping operations, or to improve freeze-thaw stability in winter months. This additional emulsifier is not added during polymerization itself since this would decrease the particle size in the latex. The pH of the final latex may also be adjusted after polymerization.

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5 Vinyl Acetate Copolymerization with Acrylic Monomers

5.1 MODIFICATION OF POLYVINYL ACETATE LATEX PROPERTIES BY COPOLYMERIZATION

PolyVAc homopolymer has a glass-transition temperature, T_g, of approximately 30°C and a minimum film-forming temperature, MFT, of approximately 20°C. These values make polyVAc latices unsuitable for many applications because the MFT is too high for this polymer to act as an effective binder for pigments and fillers at normal ambient temperatures, whereas the T_g is too low for the polymer to be useful as a rigid plastic at normal ambient temperatures. It is usual to lower the T_g of polyVAc by plasticization to make the polymer more suitable for application as a binder and an adhesive. Some characteristics of polyVAc can be altered for specific end uses by the incorporation of plasticizers such as phthalate diesters and/or other additives. These "external modifiers", while useful, frequently lose their effect because of the tendency to leach out during weathering or aging. They also migrate into substrates, with adverse consequences for both the polymer and the substrate, and sometimes the extraction of the plasticizer from the polymer by organic liquids. A more satisfactory approach to the modification of properties is by the copolymerization of vinyl acetate with other monomers to lower the T_g by internal plasticization. The homopolymers of these comonomers should have a T_g of well below normal ambient temperatures. Typical of such compounds with which vinyl acetate is commercially copolymerized are vinyl chloride, vinyl propionate, higher vinyl esters such as vinyl versatate, acrylates, methacrylates, maleates, fumarates, ethylene, and acrylonitrile. Terpolymers of vinyl acetate are also widely used. The selection of the comonomer to be used to produce latices for any given application depends principally upon the functional suitability of the comonomer and its cost. Copolymers and terpolymers produce resins which retain, to certain extents, some of the properties of the homopolymers of the starting monomers. By a judicious choice of monomers for copolymer reaction, it is possible to "tailor-make" a resin to fit the particular end use. These resins, being "internally-modified," weather or age without losing desirable properties due to the exudation of a critical component. For example, copolymers of vinyl acetate with dibutyl fumarate or dibutyl maleate exhibit good flexibility and water resistance in films deposited from the emulsions, and they are important for surface-coating applications. Copolymer emulsions of vinyl acetate and acrylonitrile produce films having high heat stability and toughness. Copolymers of vinyl acetate and acrylates (especially n-butyl and 2-ethylhexyl acrylate) in latex form are excellent for interior and exterior paints and are superior to either homopolymer alone. The copolymerization of softer acrylic monomers add durability to the copolymer, but high concentrations of these monomers increase the tack of the final copolymer films. It is therefore advantageous to add a third monomer, for example methyl methacrylate (MMA), to increase the T_g of the copolymer. The T_g of polyMMA is 106° C, and thus small amounts effectively decrease tackiness of softer latex films. Minor amounts of carboxylic acid monomers such as acrylic acid and methacrylic acid are sometimes copolymerized into VAc-acrylic latices, chiefly for introducing a viscosity response to changes in pH. Some other vinyl monomers are also copolymerized with VAc. Vinyl versatate monomer, a commercial product of Shell Chemicals (VEOVA), is a branched vinyl neodecanoate, and its copolymer with VAc is used as paint binder in large quantities in Europe. Internal plasticization of polyVAc occurs by two mechanisms: (1) some comonomers increase the inherent flexibility of the copolymer chain, and (2) some comonomers create more space in which those copolymer chains can move.

In industry, the emulsion copolymerization of VAc with other comonomers should be as complete as possible because it is not economically feasible to remove unpolymerized monomers. There are two reasons: (1) if the residual free monomer content exceeds 0.5 ppm, it gives bad odor, especially if the comonomer is an acrylic ester; (2) residual VAc will hydrolyze to give acetic acid during storage, which will decrease the pH of the latex. The products of this hydrolysis are acetic acid and acetaldehyde, which can subsequently oxidize to acetic acid.

5.2 ACRYLIC MONOMERS

"Acrylic monomers" comprise the monomeric alkyl esters of acrylic acid and methacrylic acid but also include the free acids themselves and derivatives such as their amides and nitriles, as well as amides and esters bearing functional groups on the side chain such as hydroxyl. Acrylic ester emulsion homopolymers are prepared from acrylic monomers and are used as exterior or interior coatings; binder for leather, textiles, and paper; and as adhesives, laminates, elastomers, PVC plasticizers, and floor polishes. These latices are stable, have good pigment binding and durability characteristics, and copolymerization versatility. Acrylic monomers copolymerize either with styrene or vinyl acetate (but not together) in an enormous range of accessible copolymer compositions modifying the final properties of the prepared latex films such as glass transition temperature, minimum film-forming temperature, solubility, and morphology design.

The number of acrylic monomers that have been homopolymerized or copolymerized with VAc monomer is too large to list here. There are three general restrictions on polymerizable acrylic ester monomers. First, the monomers must become finitely, but not completely, soluble in the aqueous surfactant solution. Second, the monomers should be polymerizable at the temperatures where this solubilization occurs. Third, the monomers should be unreactive to any significant degree with water, surfactant, or other additives. When copolymerizations are conducted, difficulty may arise if one monomer is too highly soluble in water compared to the others. Monomers, of course, ultimately become the finely dispersed polymer particles in emulsion polymers.

Some physical and thermodynamic properties of selected acrylic monomers are given in Table 5.1.

TABLE 5.1
Physical and Thermodynamic Properties of Selected Acrylic Monomers

Monomer	Density (g/cm³)	Solubility in Water (g/100g)	Specific Heat (J/g°C)	Heat of Polym. (kJ/mol)	Copolym. Parameters Q	e
Methyl Acrylate	0.950	5.20	2.01	78.7	0.45	0.64
Ethyl Acrylate	0.917	1.51	1.97	77.8	0.41	0.55
Butyl Acrylate	0.894	0.20	1.92	77.4	0.38	0.85
2-Ethylhexyl Acrylate	0.881	0.01	1.92	60.7	0.37	0.24
Acrylic Acid	1.045	∞	2.10	77.0	0.83	0.88
Methyl Methacrylate	0.939	1.59	1.88	57.7	0.78	0.40
Methacrylic Acid	1.015	∞	2.10	56.3	0.98	0.62

5.2.1 INHIBITION OF ACRYLIC MONOMERS

Acrylate esters are supplied commercially with small amounts of inhibitors. Together with dissolved oxygen, these prevent premature spontaneous polymerization during shipment and storage. It was shown that the relatively large amounts of inhibitors traditionally used generally are no longer necessary. In fact, methyl, ethyl, butyl, and 2-ethylhexyl acrylates with only 15 ppm (0.0015%) methyl ether of hydroquinone (MEHQ) have excellent stability. No color and polymer buildup or change in inhibitor concentration was noted after six months' storage at 43°C. These very low inhibitor grades, while affording more than adequate protection, eliminate the need for inhibitor removal in many applications levels. The regular and alternate inhibitor commercially available for each acrylic ester monomer are given in Table 5.2.

TABLE 5.2
Regular Inhibitor Grades of Acrylate Ester and Acrylic Acid Monomers

	Methyl Acrylate	Ethyl Acrylate	Butyl Acrylate	2-Ethyl Hexyl Acrylate	Acrylic Acid
Methyl Ether of Hydroquinone, ppm	15–20	15–20	15–20	15–20	200 ± 20
Hydroquinone, ppm	1000 ± 100	100 ± 100	100 ± 10	100 ± 10	—

5.2.1.1 Inhibitor Selection

If the process is one in which inhibitor may be present during polymerization, the low inhibitor concentration (15 ppm) methyl ether of hydroquinone is preferred because of economic and technical advantages of shorter processing cycles, smoother and more reproducible copolymerizations, and superior color properties. If the process requires use of inhibitor-free monomer, hydroquinone (100 ppm) is preferred since it is more easily and completely removed than its methyl ether. If storage requirements indicate higher levels of inhibitor for processes not requiring inhibitor removal, then higher concentrations of the methyl ether of hydroquinone (50 ppm) are recommended. If color of end product is an important consideration and inhibitor removal is not desired, the methyl ether of hydroquinone (15 ppm) is preferred. Hydroquinone tends to cause discoloration of polymers much more so than does the methyl ether. Inhibitor removal from acrylic acid monomer is not recommended.

5.2.1.2 Inhibitor Removal by Distillation

It is sometimes desirable to remove all traces of inhibitor before reaction. Both hydroquinone and the methyl ether of hydroquinone may be removed by simple flash distillation, or by the use of a fractionation column. Sufficient inhibitor should be added to the still pot to bring the inhibitor level to a minimum of 0.10 percent before the distillation operation is begun. If a distillation column is used, inhibitor should be added to the top of the column in the reflux pans to prevent plugging and polymer build-up inside the column. The distillations should be carried out at as low a pressure as the temperature of available cooling water to condensers will allow. Suitable vacuum equipment such as a steam jet ejector is needed for reduced pressure operation. It is recommended that a small stream of air be injected at the bottom of the column or still to provide the inhibiting effect of oxygen in the still and overhead condenser. The use of a fractionation column will effect complete removal of hydroquinone and the methyl ether of hydroquinone inhibitors. A simple pot still with no trays or reflux will produce distillate containing up to 20 ppm inhibitor. The use of flash distillation equipment will more effectively remove hydroquinone than methyl ether of hydroquinone since hydroquinone is the less volatile of the two. Stainless steel equipment is recommended for all distillation operations. Equipment such as the still, fractionation column, vapor line, condenser, and overhead receiver should be designed and constructed for ease of dismantling for inspection and cleaning. The vapor line and other associated equipment should be designed in such a way that the “dead spots” that allow the uninhibited monomer to accumulate are completely eliminated. Sharp bends or loops in piping should also be avoided. A tube and shell condenser should be used and designed for monomer condensation inside the tubes to facilitate the removal of any polymer that may form.

The distillation equipment should include adequate pressure-relieving devices such as relief valves or rupture discs. Low steam pressure should be employed in the heating coils or reboiler to avoid high skin temperatures on the heat transfer surface. The overhead receiver from the distillation equipment should be one of small volume to maintain a low residence time of uninhibited monomer in the receiver, preferably less than two hours. Receiver temperature should be below 25°C. Subsequent cooling should be provided to chill the monomer to 5°C or below if it is not to be used immediately.

5.2.1.3 Inhibitor Removal by Washing

A suitable procedure for washing one metric ton of acrylic ester monomer is as follows: wash twice with 20 kilograms of a solution containing 5 kg sodium hydroxide and 25 kg sodium chloride per 100 kg solution, and wash three times with 50 kg of water. The washing operation should be done at 20-25°C. This procedure will lower the inhibitor concentration to the 10-20 ppm range. Equipment needed for such an operation includes a wash tank fitted with an agitator, sight glass, cooling coils, suitable rupture discs or relief valve, vent lines, and flame arrestors. The wash tank and associated equipment should be of stainless steel construction. Monomer losses up to 5 weight percent of the wash water (in the case of methyl acrylate) can result from the foregoing procedure because of the solubility of the monomer in water. The degree of inhibitor removal may be determined by measuring the amount of inhibitor still present.

5.2.1.4 Inhibitor Removal by Ion-Exchange

Both hydroquinone and its methyl ether, as phenolic inhibitors, may be removed by use of strongly basic, macroreticular ion-exchange resins.

5.2.2 ACRYLIC HOMOPOLYMER PROPERTIES

The versatility in properties of the four acrylic homopolymers that are largely used in the latex industry are shown in Table 5.3. A formulator can tailor a copolymer (or terpolymer) composition and structure from this broad range to meet customer application requirements.

TABLE 5.3
Properties of Acrylate Ester Homopolymers

Monomer	Tackiness	Hardness	Tensile Strength	Elongation	Water Absorption	T_g (°C)
Methyl Acrylate	Almost Tack-free	Fairly Soft	Moderate	Moderate	Fairly High	22
Ethyl Acrylate	Tacky	Soft, Plastic	Low	Very High	Slight	–8
Butyl Acrylate	Very Tacky	Very soft, Plastic	Very Low	Extremely High	Very Small	–43
Methyl Methacrylate	Tack-free	Fairly Hard	High	Low	Slight	105

The quality of water used is important in emulsion copolymerization of acrylics with VAc monomer. Polyvalent cations present in natural water can have a strong inhibitory effect on the polymerization reaction and lead to flocculation. Even excessive amounts of univalent ions can influence the formation of micelles and, ultimately, polymer particle size in the latex. Consequently, either deionized or softened water is recommended for emulsion copolymerizations in industry.

Redox type free radical initiators such as persulfate-bisulfide systems are generally used in industry. Copolymerization can be conducted by batch mode, semicontinuous (gradual monomer addition) mode, or a combination of the two. Generally, semicontinuous emulsion copolymerization is preferred because of the difficulty of the control of the exothermic batch reactor temperature, and in order to obtain homogeneous distribution of the copolymers in the macromolecule. In this method, the comonomer mix is prepared neat, or pre-emulsified, with emulsifiers and water. Agitation of the pre-emulsified mix is required to maintain stable monomer droplet formation. The copolymerization temperature in the reactor depends on the selection of soap and catalyst, which is ultimately dictated by particle size. An increase in reaction temperature generally increases the polymerization rate, reducing both molecular weight and particle size.

Heat liberation during emulsion copolymerization is dependent on both copolymer composition and polymer-to-water ratio. For high solids emulsions, an extended gradual addition time is required. Stainless steel or glass-lined reactors are used in copolymerizations. Glass reactors have been preferred due to cleanability since wall fouling occurs in stainless-steel reactors. In some recipes, the agitation rate is increased with time to improve heat and mass transfer, and to compensate for the increased reactor load. Precautions should be taken to avoid separation of the monomer/water mixture for those emulsions in which the comonomer mix is pre-emulsified.

5.3 COPOLYMERIZATION AND REACTIVITY RATIOS

5.3.1 COPOLYMERIZATION

Radical chain polymerizations can be conducted with mixtures of two monomers to form copolymer products with two different structures in the polymer chain. A copolymer is not an alloy of two homopolymers but contains units of both monomers incorporated into each copolymer molecule. The two monomers enter into the copolymer in a relatively random manner in overall amounts determined by their relative concentrations and reactivities. Copolymerization is useful to tailor-make a polymer product with specifically desired properties. Copolymerization allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two monomer units in the copolymer product.

The composition of a copolymer is usually found to be different from that of the comonomer feed from which it is produced. Different monomers have differing tendencies to undergo copolymerization. There is no relation between the reactivity of a monomer in its homopolymerization and its copolymerization with other monomers. Further, a few monomers such as maleic anhydride undergo facile copolymerization although they have no tendency to undergo homopolymerization. Thus, the composition of a copolymer cannot be determined from a knowledge of the homopolymerization rates of the two monomers. There is also the composition drift of copolymers. For example, if an equimolar mixture of vinyl acetate and vinyl chloride are copolymerized, the chemical composition of the copolymer product varies throughout the reaction, and the ratio of chloride to acetate in the copolymer changes from 9:3 to 7:3 to 5:3 to 5:7. This composition drift is attributed to the greater reactivity of one of the monomers in the mixture. Thus, it is necessary to distinguish between the composition of a copolymer being formed at any one time in the copolymerization reaction and the overall composition of all the polymer formed at a given degree of conversion.

A variety of copolymer structures can be obtained even in the simplest case, that of copolymerizing two monomers: (1) random copolymers are formed when irregular propagation occurs and the two units enter the chain in a random fashion. This is the most commonly encountered structure. (2) Alternating copolymers are obtained when equimolar quantities of two monomers are distributed in a regular alternating fashion in the chain. (3) Linear block copolymers are formed when long sequences of one monomer join to another sequence or block of the second instead of having a mixed distribution of the two units. (4) A nonlinear graft copolymer (or branched block copolymer) is formed by attaching chains of one monomer to the main chain of another homopolymer. In general, block and graft copolymers possess the properties of both homopolymers, whereas the random and alternating copolymers have characteristics that are more of a compromise between the extremes.

5.3.2 COPOLYMER COMPOSITION EQUATION

If we consider the case for the copolymerization of the two monomers M_1 and M_2, there will be two propagating species — one with $M_1\cdot$ radical at the propagating end and the other with $M_2\cdot$ radical. By assuming the chemical reactivity of the propagating chain in a copolymerization to be dependent only on the monomer unit at the growing end and independent of the chain composition preceding the last monomer unit, only four propagation reactions are then possible:

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_2\cdot \tag{5.1}$$

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1\cdot \tag{5.2}$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_1\cdot \tag{5.3}$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2\cdot \tag{5.4}$$

where k_{11} is the rate constant for a propagating chain radical $M_1\cdot$ adding to monomer M_1, and so on; k_{11} and k_{22} are called as the rate constants for the "self-propagating" reactions; and k_{12} and k_{21} are the corresponding "cross-propagation" rate constants. The monomers are then consumed according to the following equations:

$$-\frac{d[M_1]}{dt} = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1] \tag{5.5}$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2] \tag{5.6}$$

The above rates of disappearance of the two monomers are synonymous with their rates of entry into the copolymer. By combining Eqs. 5.5 and 5.6, one obtains,

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]}{k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]} \tag{5.7}$$

A steady-state concentration is assumed for each of the reactive radicals separately in order to remove the concentration terms $M_1\cdot$ and $M_2\cdot$ in Eq. 5.7. When a steady-state condition prevails, the rates of interconversion must be equal for the constant radical concentrations, so that

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2] \tag{5.8}$$

The manner in which a copolymerization proceeds depends upon the "monomer reactivity ratios," r_1 and r_2, i.e, the relative tendencies of the two monomers to add to a polymer radical ending in one or the other of the monomer units. If, $r_1 = k_{11} / k_{12}$ and $r_2 = k_{22} / k_{21}$ are defined where r_1 and r_2 are the reactivity ratios for the given monomers, then the above equation becomes

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\left(r_1[M_1] + [M_2]\right)}{[M_2]\left([M_1] + r_2[M_2]\right)} \tag{5.9}$$

which is called the "copolymer composition equation." The copolymer equation shows that if monomer M_1 is more reactive than M_2, then M_1 will enter the copolymer more rapidly. Consequently, the feed becomes progressively poorer in M_1 and composition drift occurs. The equation is then an "instantaneous" expression, which relates only to the feed composition at any given time.

If r_1 is small (less than unity), it means that $M_1\cdot$ preferentially adds M_2. An r_1 value greater than units means that $M_1\cdot$ preferentially adds M_1 instead of M_2. An r_1 value of zero means that M_1 is incapable of undergoing homopolymerization. When $r_1 r_2 = 1$, the monomers add at the same ratio to $M_1\cdot$ or $M_2\cdot$. In this case, the above equation can be simplified to

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]}{[M_2]} = \frac{[M_1]}{r_2[M_2]} \tag{5.10}$$

This is the special case of "ideal copolymerization." Nevertheless, $r_1 r_2$ is usually less than 1. As the values of r_1 and r_2 decrease, the tendency to form an alternating polymer increases. In the limiting case, where $r_1 = r_2 = 0$ perfect alternation results in the copolymer, i.e., $\sim M_1M_2M_1M_2M_1M_2\sim$. For terpolymers the situation is much more complicated.

5.3.3 Experimental Determination of Reactivity Ratios

One must obtain reliable values of r_1 and r_2 if the copolymerization is to be completely controlled because these figures are the factors which control the composition of the copolymer. This can be achieved by analyzing the composition of the copolymer formed from a number of comonomer mixtures with various $[M_1]/[M_2]$ ratios at low (5 to 10%) conversions. Low conversions are preferred because monomer reactivities do not differ greatly within this range. The techniques used for copolymer analysis include elemental analysis, radioisotopic tagging, and ultraviolet, infrared, and nuclear magnetic spectroscopy.

In the first analysis method, the instantaneous copolymer composition versus the comonomer feed composition is plotted, and then which theoretical curve would best fit the data by trial-and-error selections of r_1 and r_2 is determined. This is a tedious procedure and it is usually easier to solve Eq. 5.9 simultaneously for the different sets of the data.

Mayo and Lewis suggested[1] a rearranged form of eq. 5.9:

$$r_2 = \frac{[M_1]}{[M_2]}\left\{\frac{\boldsymbol{d}[M_2]}{\boldsymbol{d}[M_1]}\right\}\left(1 + \frac{r_1[M_1]}{[M_2]} - 1\right) \tag{5.11}$$

For each experiment with a given feed, the data for the copolymer compositions are substituted into Eq. 5.11 and r_2 is plotted as a function of various assumed values of r_1. Each experiment yields a straight line, and the intersections of the lines for different feeds give the best values of r_1 and r_2. Any variations observed in the points of intersection of various lines are a measure of the experimental errors in the composition data.

Fineman and Ross suggested another very useful method for data analysis.[2] If we now define $\boldsymbol{f}_1$ and $\boldsymbol{f}_2$ as mole fractions of monomers M_1 and M_2 in the feed, and $\boldsymbol{F}_1$ and $\boldsymbol{F}_2$ as mole fractions of monomers M_1 and M_2 in the copolymer at any given time, then by definition,

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \tag{5.12}$$

and

$$F_1 = 1 - F_2 = \frac{d\left[M_1\right]}{d\left[M_1\right] + d\left[M_2\right]} \tag{5.13}$$

Combining Eq. 5.9 with Eqs. 5.12 and 5.13 yields

$$F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}} \tag{5.14}$$

By rearranging Eq. 5.14 one obtains

$$\frac{f_1}{f_2}\left(\frac{F_2}{F_1} - 1\right) = r_2 + \left\{\left(\frac{f_1}{f_2}\right)^2 \frac{F_2}{F_1}\right\} r_1 \tag{5.15}$$

and a plot of $\frac{f_1}{f_2}\left(\frac{F_2}{F_1} - 1\right)$ against $\left\{\left(\frac{f_1}{f_2}\right)^2 \frac{F_2}{F_1}\right\}$ will give a straight line having r_1 as the slope and r_2 as the intercept. Tidwell and Mortimer compared the relative merits of the different methods for analyzing feed-copolymer data to determine r_1 and r_2 and the use of computational methods.[3] Kelen and Tudos developed a new method to determine reactivity ratios of monomers,[4] which was further extended by Raiter and Kohn.[5]

Vinyl acetate radical is very reactive and thus gives very high k_{12} rate constant with many comonomers, resulting in very small r_1 reactivity ratios. The overall conclusion is VAc does not copolymerize easily. Copolymerization reactivity values of some monomer with VAc are given in Table 5.4 below.[6] The major outlet for VAc copolymers is in paints and adhesives, as textile coatings, and as binders for pigmented coatings and binders in the paper industry. The major comonomers for these applications are ethylene, acrylates, and maleates and fumarates. Ethyl, butyl, and 2-ethylhexyl acrylate are important comonomers for VAc. The reactivity ratio of VAc is given as $r_1 = 0.05$, and BuA as $r_2 = 3.1$ in the *Polymer Handbook*.[7] Bataille and Bourassa made a detailed study of the determination of reactivity ratios of VAc and n-butyl acrylate in copolymerization,[47] and Noel, Van Altveer, Timmermans, and German determined reactivity ratios of methyl acrylate-VAc and methyl acrylate and other vinyl monomers during copolymerization[54] (see Sec. 5.3).

5.3.4 VARIATION OF COPOLYMER COMPOSITION WITH CONVERSION

The copolymer equation gives the "instantaneous" copolymer composition, which is the composition of the copolymer formed from a particular comonomer feed composition at very low conversion degrees, such as less than 5%, where the

TABLE 5.4
Copolymerization Reactivity Ratios of VAc (M_1) and Comonomers (M_2)[6]

Comonomer (M_2)	r_1	r_2	Temp. (°C)
Acrylamide	0.07	7.5	50
Acrylic Acid	0.01	10.0	70
Acrylonitrile	0.061	4.05	60
n-Butyl Acrylate	0.0388	5.529	50
n-Butyl Methacrylate	0.127	62.1	60
Chloroprene	0.01	50	65
Crotonic Acid	0.33	0.01	68
Diallyl Phthalate	0.72	2.0	
Diethyl Fumarate	0.011	0.444	60
Diethyl Maleate	0.17	0.043	60
Diisopropyl Maleate	0.17	0.043	60
Dimethyl Maleate	0.12	0.028	60
2-Ethylhexyl Acrylate	0.04	7.5	60
Heptyl Methacrylate	0.271	60.4	60
2-Hydroxypropyl Methacrylate	0.033	23.83	
Maleic Anhydride	0.072	0.01	
Methacrylic Acid	0.01	20	70
Methacrylonitrile	0.01	12	70
Methyl Acrylate	0.029	6.7	60
Methyl Cyanoacrylate	0.005	0.5	60
Methyl Methacrylate	0.015	20	60
Butyl Maleate	0.011	0.398	65
Methyl Maleate	0.0345	0.522	65
Vinyl Chloride	0.6	1.8	40
Vinylidene Chloride	0.1	6	68
Vinyl Versatate VV9	0.93	0.90	60
Vinyl Versatate VV10	0.99	0.92	60
Vinyl Versatate VV13	1.25	0.93	60

comonomer feed is relatively unchanged from its initial value. However, in actual practice, the comonomer feed changes in composition as one of the monomers preferentially enters the copolymer, and the less reactive monomer concentration increases as the degree of conversion increases. In these circumstances, in order to determine the instantaneous copolymer composition as a function of conversion, an integrated form of copolymer equation is needed. Meyer et al.[8,9] developed a solution for such systems.

When *dM* moles of monomers are copolymerized, the polymer will contain F_1 dM moles of M_1 and the feed will contain $(M - dM)(f_1 - df_1)$ moles of M_1. A material balance for monomer 1 requires that

$$Mf_1 - (M - dM)(f_1 - df_1) = \boldsymbol{F}_1\, dM \tag{5.16}$$

If we neglect the small ($df_1\ dM_1$) term and convert the above equation in its integral form, we obtain

$$\int_{M_o}^{M} \frac{dM}{M} = \ln \frac{M}{M_o} = \int_{(f_1)_o}^{f_1} \frac{d\boldsymbol{f}_1}{\boldsymbol{F}_1 - \boldsymbol{f}_1} \tag{5.17}$$

where M_0 and $(\boldsymbol{f}_1)_0$ are initial values of M and $\boldsymbol{f}_1$. By combining Eqs. 5.14 and 5.17, one can integrate Eq. 5.17 graphically or numerically to calculate variations in the comonomer feed and copolymer composition with the degree of conversion $(1 - M/M_0)$.

Meyer et al. integrated Eq. 5.17 to closed form so that[8,9]

$$1 - \frac{M}{M_o} = 1 - \left[\frac{f_1}{(f_1)_o}\right]^{\alpha} \left[\frac{f_2}{(f_2)_o}\right]^{\beta} \left[\frac{(f_1)_o - \delta}{f_1 - \delta}\right]^{\gamma} \tag{5.18}$$

where

$$\alpha = \frac{\boldsymbol{r}_2}{(1-\boldsymbol{r}_2)}, \quad \beta = \frac{\boldsymbol{r}_1}{(1-\boldsymbol{r}_1)}, \quad \gamma = \frac{(1-\boldsymbol{r}_1\,\boldsymbol{r}_2)}{(1-\boldsymbol{r}_1)(1-\boldsymbol{r}_2)}, \quad \delta = \frac{(1-\boldsymbol{r}_2)}{(2-\boldsymbol{r}_1-\boldsymbol{r}_2)} \tag{5.19}$$

Computer calculations of the compositions yield graphical results.[9] In industrial copolymerizations, two general methods are used to obtain a copolymer structure with a narrow distribution of composition. One involves stopping the copolymerization before 100% conversion such as styrene-butadiene emulsion polymerization, and the second involves maintaining the feed composition constant by the continuous addition of the more reactive monomer such as butyl acrylate-VAc semicontinuous emulsion copolymerization.

5.3.5 THE Q-*e* SCHEME

Monomer-radical reactions depend on resonance, steric, and polarity effects and are very complicated. However, it is desirable to predict the monomer reactivity ratios for comonomer pairs which have not yet been copolymerized. Alfrey and Price developed the Q-*e* scheme for this purpose.[10,11] They wrote the rate constants for a radical ($M_1\cdot$)-monomer (M_2) reaction so that

$$k_{12} = \boldsymbol{P}_1\,\boldsymbol{Q}_2\ \exp(-\boldsymbol{e}_1\,\boldsymbol{e}_2) \tag{5.20}$$

where $\boldsymbol{P}_1$ is a measure of the general reactivity of the radical, $\boldsymbol{Q}_2$ is a measure of the general reactivity of the monomer, and $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are measures of the polarities of the radical and monomer, respectively. The $\boldsymbol{P}$ and $\boldsymbol{Q}$ terms primarily define the resonance effects in radical and monomer. By assuming that the same *e* value applies to both monomer and its radical, it is possible to write expressions for k_{11}, k_{22}, and k_{21} analogous to Eq. 5.20. Thus, these are combined to yield monomer reactivity ratios in the forms

$$r_1 = \frac{Q_1}{Q_2} \exp\left[-e_1\left(e_1 - e_2\right)\right] \tag{5.21}$$

$$r_2 = \frac{Q_2}{Q_1} \exp\left[-e_2\left(e_2 - e_1\right)\right] \tag{5.22}$$

The **Q-*e*** scheme is a semiempirical approach to placing monomer reactivity on a quantitative basis. With the application of this method, monomer reactivity is separated into a **Q** parameter which describes mainly the resonance factor (and to some extent the steric factor), and the *e* parameter which describes the polar factor. Values of **Q** and ***e*** have been assigned to monomers based on their *r* values and the arbitrarily chosen reference values of $Q = 1$ and $e = -0.80$ for styrene monomer. Although this approach has many disadvantages and is unsound theoretically, it has proved to be a useful approximation in a qualitative way. $Q = 0.026$ and $e = 0.22$ were found for VAc monomer.[7]

5.3.6 Comonomer and Emulsifier Addition Strategies

The above copolymer equations were derived for uncomplicated homogeneous-phase reactions. In an emulsion copolymerization, differences in solubilities of the monomers in the water phase, differences in solubilizing effect of the emulsifier on the monomers, and the different solubilities of the monomers in the polymer particle all affect the course of the reaction and result in deviations. In addition, since the reactivity ratios of VAc-acrylate mixtures favor a heterogeneous copolymer composition when a batch polymerization is made, most industrial processes use a delayed addition semicontinuous emulsion polymerization technique. In semicontinuous emulsion, only part of the total reaction formulation is introduced at the beginning of the polymerization reaction, the remainder being added, according to a predetermined schedule, during the course of polymerization. The controlled introduction of monomer to the reaction vessel facilitates great control over the homogeneity of the copolymer formed, the rate of polymerization, the rate of heat generation, and the properties and morphology of the polymer particles formed. There may be many strategies for monomer addition: comonomers may be added neat as a mixture or by different streams or emulsifiers may be fed as a different stream or added to the reaction mixture initially. Another alternative is the addition of pre-emulsified comonomers so that the emulsifier is also fed to the reactor in a programmed manner. The addition choice of the emulsifier is very important to determine the particle size of the copolymers and the colloidal stability of the latex produced.

In general, whichever type of semicontinuous process is used, 5–10% of the total comonomers are added initially to allow complete conversion of this comonomer, which may be considered as the seed stage. The addition of the remaining 90–95% comonomers, either directly or as an emulsion, provides for growth of particles formed in the seed stage. The objective is to use the seed stage to give control over particle size and particle size distribution, which will be narrow if the seed stage is short. However, if the level of emulsifier is too high or the number of seed particles is too low, new particles can be formed during the addition of comonomers, giving rise to undesired broad particle size distributions. This is known as "secondary nucleation." Conversely, if insufficient emulsifier is used which results in low surface charge density of particles, limited coagulation of latex particles can occur, leading to reductions in the number of particles. If all of the emulsifier is added initially, then the number of particles formed in the seed stage will be greater than in the process where emulsion is added continuously. It is possible to control the latex particle size distribution by introducing the emulsifier at particular times during the emulsion copolymerization. For example, if a further addition of surfactant is made late in the reaction to generate a new crop of particles, a bimodal particle size distribution will be obtained.

5.3.7 EFFECTS OF COMONOMER ADDITION RATES

5.3.7.1 Control of Copolymerization Rate

The maximum rate of polymerization, $R_{\max}$, is obtained when the saturation concentration of monomer in particles, $[M]_{\max}$, is achieved. The feed rate of comonomers, $\boldsymbol{F}$, is of crucial importance for all semicontinuous emulsion polymerizations because it controls the availability of monomer for copolymerization and, hence, the concentration of monomer, $[M]$, in the monomer swollen particles. Two cases may be considered:

1. $\boldsymbol{F} > R_{\max}$, which results in $[M] = [M]_{\max}$ and a build-up of monomer in the reaction vessel with excess monomer forming into droplets. This is called "monomer-flooded condition" and the semicontinuous copolymerization is essentially indistinguishable from the equivalent batch reaction because $R = R_{\max}$ in these conditions.
2. $\boldsymbol{F} < R_{\max}$, the concentration of comonomers in the particles falls below the saturation value and is controlled directly by $\boldsymbol{F}$. This situation is called "monomer-starved condition." In industry, monomer-starved conditions are generally used to control the reaction kinetics parameters.

Wessling analyzed the relation of rate of polymerization, R_p, with the monomer feed rate, F, for semicontinuous polymerization operating under monomer-starved conditions.[12] He found that

$$R_p = F\,\phi_p \tag{5.23}$$

where ϕ_p is the volume fraction of the polymer in the monomer-swollen latex particles. Thus, it is possible to control R_p by adjusting F. This analysis is applicable only when a steady state exists during the semicontinuous emulsion polymerization. It is thus an oversimplification of the real situation and it sometimes fails, although good correlation has been observed with experimental results. For example, a finite time is required before the steady-state value of comonomer concentration in the monomer-swollen particle is attained at the beginning of the addition of comonomers. Therefore, R_p gradually increases initially as the value of $[M]$ in the particle increases to its steady-state value. In addition, the average number of radicals per particle also increases with conversion, and this factor results some deviations from Eq. 5.23.

Dimitratos, El-Aasser, Georgakis, and Klein refined Wessling's analysis and applied it to the copolymerizations of VAc with BuA[13] (see Sec. 5.3).

Monomer partitioning in polymer particles is an important factor that affects the polymerization kinetics in both batch and semicontinuous emulsion polymerization. If we assume that the thermodynamic equilibrium is established during comonomer addition, the changing masses of the unreacted monomers and copolymer are related to monomer partitioning. Morton et al. were the first to describe the importance of monomer partitioning in emulsion polymerization systems.[14] German, Maxwell, and co-workers investigated monomer-partitioning thermodynamics in detail.[15-20] Complete analysis of the partitioning of monomers between the aqueous phase, monomer droplets, and latex particles is a very complex process and requires knowledge of many quantities such as interaction parameters and interfacial tensions, which are difficult to measure.[21] Thus, in practice, system-specific approaches that involve the use of experimentally determined partition coefficients are sometimes used.[22,23] If the two monomers have significantly different solubilities in water, then partitioning is sometimes neglected. This is especially true when the more water-soluble monomer is included as a relatively small proportion of the comonomer mixture, since a high proportion of this monomer will be dissolved in the water phase and a relatively low proportion in the latex particles, which are the loci for formation of the copolymer.[25]

5.3.7.2 Control of Copolymer Composition

In general, the instantaneous conversion of comonomers is very high, typically above 90% at any time during the addition of comonomers. That means that comonomers are almost immediately copolymerized upon entering the reactor under monomer-starved conditions. Then, the copolymer formed must have the same overall composition as that of the comonomer mixture added. Therefore, it is possible to produce copolymers of uniform composition by feeding a comonomer mixture of constant composition under monomer-starved conditions in semicontinuous emulsion copolymerization. When the reaction is conducted using a batch process, a heterogeneous copolymer is obtained.

Bassett and Hoy developed a new approach by varying the monomer feed composition continuously to achieve a controlled composition drift, which was called "power feeds."[24,25]

Monomer-starved, semicontinuous emulsion polymerization is also used to prepare latices having core-shell structures. First, particles of a homopolymer are prepared. Then another monomer is polymerized sequentially on the first core homopolymer. In this case, two different glass transition temperatures are obtained belonging to each homopolymer.

There are disadvantages of working under monomer-starved conditions. The low monomer feed rates give rise to low rates of copolymerization and increase the average molecular weight of the copolymers formed. Then, individual monomers are fed separately so that the comonomer composition in the reactor will be kept constant.[25] The concentration of each monomer in the reactor is monitored online by gas or liquid chromatography. However, feedback control cannot be done properly since the time required for analysis is significant. Another method is the application of the optimum monomer addition rate profiles. In this method, monomers are added at rates that vary with time to maintain the comonomer composition constant. This method requires thorough knowledge of partitioning, reactivity ratios, rate coefficients, etc. Two strategies have been employed: (1) independent addition of both monomers using precalculated rate-time profiles, and (2) less reactive monomer is added completely to the reaction vessel at the beginning of the growth stage of the emulsion polymerization, followed by feeding the more reactive monomer using pre-calculated rate-time profiles. These control strategies are specific to a particular emulsion polymerization reaction, it is not possible to predict the optimum addition rate profiles directly, and considerable experimental effort is required to establish optimum values of parameters for each system.[25-28]

Chain transfer agents are added to control the average molecular weight and the molecular weight distribution of the copolymers. When the chain transfer agent is dissolved in the monomer to be added, the depletion of chain transfer agent during polymerization can be avoided and more uniform molecular weight distribution is obtained. Alternatively, polymers with broad and/or multimodal molecular weight distributions can be formed by manipulating the rate and/or time at which chain transfer agent is fed to the reaction system.[25] The importance of chain transfer to polyVAc homopolymer is well known (see Sec. 3.5). Lowell et al. showed that chain transfer to polymer is also important in emulsion polymerization of n-butyl acrylate, leading to long-chain branches.[29,30] In addition, cross-linking can occur if propagating branches terminate by coupling, which has effects upon mechanical properties, particularly in the viscoelastic region.

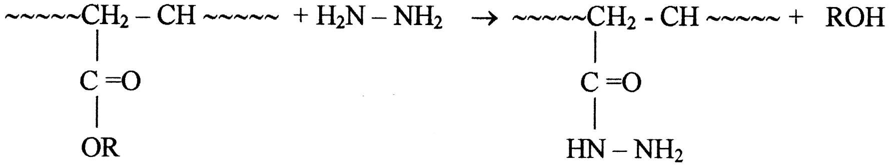
5.3.7.3 Coagulum Formation

Undesired coagulum may form during and after the copolymerization. In industry, coagulum formation can be tolerated only at very low levels as parts per million of latex, otherwise both the wastage of chemicals and the reactor downtime for cleaning would make the process economically intolerable. When polymerization takes place in monomer droplets, the polymer resulting from bulk polymerization of the monomer in the droplets eventually becomes coagulum. These droplets become large, swollen polymer particles of low colloidal stability and act as nuclei for further coagulum formation. However, if monomer-starved conditions are applied properly during the emulsion polymerization, the monomer droplets are absent and no coagulum forms.

5.4 VINYL ACETATE/ACRYLIC BATCH AND SEMICONTINUOUS EMULSION COPOLYMERIZATIONS

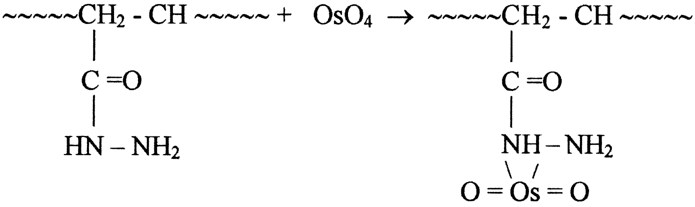
Chujo, Harada, Tokuhara, and Tanaka applied various monomer addition methods to emulsion copolymerization of VAc and n-Butyl acrylate with the same overall composition of VAc/BuA (70/30) in 1969.[31] Nonionic emulsifiers and 88% hydrolyzed polyvinyl alcohol were used. The homogeneities and the grafting efficiencies of the copolymers were determined by acetone-hexane fractionation and dynamic viscoelasticity measurements of copolymers. Heterogeneity values were found to differ very much with the change of monomer addition method. Continuous comonomer addition methods yield nearly homogeneous copolymer. Stepwise monomer addition yields less homogeneous copolymer. If all the comonomer is added at the beginning of the reaction, it yields a very heterogeneous copolymer. It was determined that the homogeneity of the copolymer had great influence on hardness and adhesive properties. When homogeneity increases, hardness decreases.

Misra, Pichot, El-Aasser, and Vanderhoff prepared films of VAc-BuA copolymer latices and investigated film properties in detail in 1979.[32] They dried the latex in glass Petri dishes pretreated with a mold release agent at 22°C. The morphology of these films was studied after aging for 40–50 days at room temperature. Microtomed sections of 60–100 nm thickness were deposited on 20 mesh stainless-steel specimen substrates and exposed to hydrazine vapors by suspending them for 105 minutes over 85% aqueous hydrazine solution in a closed vessel at 45°C. Acrylate esters present in the copolymer structure formed hydrazide as shown below:



$$\sim\sim\sim\sim\sim\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{OR}}}{\mathrm{CH_2}}-\mathrm{CH}\sim\sim\sim\sim\sim + \mathrm{H_2N-NH_2} \rightarrow \sim\sim\sim\sim\sim\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{HN-NH_2}}}{\mathrm{CH_2}}-\mathrm{CH}\sim\sim\sim\sim\sim + \mathrm{ROH}$$

The specimens were dried under vacuum for 12–14 hours to remove all moisture, and then exposed to osmium tetroxide vapors for 5 minutes in the absence of water to stain the acrylate ester-containing regions. Staining is a result of complex formation:



$$\sim\sim\sim\sim\sim\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{HN-NH_2}}}{\mathrm{CH_2}}-\mathrm{CH}\sim\sim\sim\sim\sim + \mathrm{OsO_4} \rightarrow \sim\sim\sim\sim\sim\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{NH-NH_2}\\ \backslash\ /\\ \mathrm{O=Os=O}}}{\mathrm{CH_2}}-\mathrm{CH}\sim\sim\sim\sim\sim$$

The stained specimens were examined by transmission electron microscope using cold stage. The low temperature holder was cooled with liquid nitrogen to prevent the degradation and melting of the polymer film upon exposure to electron beam. Stained polyBuA showed dark regions, whereas polyVAc homopolymer stained in the same manner showed no dark regions. 63:37 VAc-BuA copolymers prepared by batch and semicontinuous emulsion copolymerization were compared by this staining method. Since BuA is by far the more reactive monomer, batch emulsion polymerization should produce compositions ranging from a BuA-rich fraction containing more BuA than the monomer mixture composition, to polyVac homopolymer after all the BuA has been exhausted. On the other hand, the semicontinuous copolymerizations which were conducted under "monomer-starved conditions," that is, where the monomer mixture was added at a rate equal to or less than the rate at which it could polymerize, produced a homogeneous distribution of compositions representative of the 63:37 ratio of the monomer mixture. In the electron micrographs of the stained microtomed films, the darker BuA-rich regions of the batch polymerized sample are more than twice as large as those of the semicontinuous polymerized sample.

Dynamic mechanical spectroscopy of the films prepared from the batch polymerized latices showed two peaks in the loss modulus spectra, indicating the second-order transition temperature (glass transition temperature, T_g) of a BuA-rich copolymer and polyVAc homopolymer corresponding to an inhomogeneous composition. In comparison, films prepared from the semicontinuous method showed a single peak indicating a more homogeneous composition.

The batch-polymerized latex has a larger average particle size and narrower particle size distribution than the semicontinuous polymerized latex. An analysis showed that the BuA-rich core comprises 18–23% of the value for the batch-polymerized particles, and only 1.7–9.8% for the semicontinuous polymerized particles. Thus, the electron micrographs confirmed that batch-polymerized particles have a heterogeneous structure comprising a relatively large BuA-rich core surrounded by a polyVAc-rich shell. In comparison, the semicontinuous polymerized particles have a more homogeneous structure comprising a much smaller BuA-rich core surrounded by a shell of VAc-BuA copolymer.[32]

Pichot, Llauro, and Pham studied the compositions and sequence distributions of VAc-BuA copolymers obtained with batch and semicontinuous emulsion copolymerizations by using proton and ^{13}C nuclear magnetic resonance (NMR) Spectroscopy.[33] Batch copolymerizations were applied as bottle polymerizations, where all the ingredients except the initiator were charged before starting the polymerization. In the semicontinuous process, the monomer mixture was slowly added at a constant rate to a reaction vessel charged with water, emulsifier, and initiator. After obtaining high conversion degree (95–100%), copolymers were precipitated from latices by the addition of acetone, followed by a large excess of methanol-water mixture, and dried under vacuum. Copolymer samples were dissolved (5 wt.%) in a mixture of deuterated benzene and tetrachloroethylene. ^1H NMR spectra were recorded. This method allows quantitative determination of the copolymer composition based on the examination of the methine and methylene carbon resonances. ^{13}C NMR spectra were also recorded at 70°C. Copolymer samples were examined as 15–20% solutions in a mixture of deuterated benzene and tetrachloroethylene (50/50 by volume) using tetramethyl silane (TMS) as internal reference. The copolymer composition calculated from the ^{13}C NMR carbonyl resonances is in fairly good agreement with ^{1}H NMR results. The authors pointed out that the copolymerization reactivity ratios are strongly affected by the polymerization conditions (temperature, solvent, polymerization procedure, etc.), and they determined the reactivity ratio of VAc is 0.04 whereas the reactivity ratio of BuA is 5.529.[33] They concluded that the batch process gives heterogeneous copolymers having long homosequences while, in the semicontinuous one, the copolymers obtained have a better statistical distribution of comonomers.

El-Aasser, Makgavinata, Vanderhoff, and Pichot copolymerized VAc-BuA comonomer mixtures having various compositions by batch and semicontinuous emulsion processes.[34,35] Homopolymer VAc and BuA latices, as well as copolymer latices, were characterized with respect to molecular weight, particle size, anionic end groups on particle size, and colloidal stability against electrolytes after cleaning by ion exchange in the aqueous phase. Similar to Chujo et al.[31] and Misra et al.,[32] homogeneous copolymer compositions could be obtained only by semicontinuous emulsion processes, whereas heterogeneous copolymer compositions were obtained by batch processes.

For homopolymer polyVAc and polyBuA, when batch polymerization is applied, a broad molecular weight distribution is seen due to the long-chain branching at high conversion, with a polydispersity ratio of 14.7 for polyVAc and 11.5 for polyBuA. When semicontinuous emulsion polymerization is applied, both homopolymers exhibit a bimodal molecular weight distribution. The small value obtained is the indication of the presence of a large quantity of low-MW oligomers, which are initiated in the aqueous phase. The high MW fraction is caused by long-chain branching. For VAc-BuA copolymers, the MW distributions for batch copolymers are only slightly dependent upon the BuA content, and a broad distribution is seen. The molecular weight distribution for semicontinuous copolymers, on the other hand, show a bimodal distribution.[34,35]

The average particle size of batch latices was independent of comonomer composition, whereas for semicontinuous latices it decreased with the increase in BuA content and was always lower than that of the corresponding batch latex. The locus of initiation plays an important role in the batch process and the initiation step is suggested to take place predominantly in micelles swollen with monomers, thus the particles are initially formed over a short period of time. On the other hand, for the semicontinuous emulsion process, particle nucleation is assumed to take place predominantly in the aqueous phase. Thus the particles are formed over the entire duration of the polymerization process, and particle growth takes place predominantly by coalescence of smaller-size particles or low-MW oligomers with larger-size particles. When the comonomer mixture is rich in the relatively more hydrophobic BuA monomer, favorable adsorption of emulsifier onto the particle surface results in a high level of colloidal stability of the newly formed small size latex particles. Thus, the final latex system comprised particles with small average size and broader distribution.[34,35]

The surface functional groups on the latex particle surface results from (1) initiator fragments as sulfate or hydroxyl groups, (2) hydrolysis of polyVAc chains giving hydroxyl groups, and (3) hydrolysis of BuA chains giving carboxylic acid groups. It was determined that the total surface concentration of carboxylic and sulfate acidic groups on semicontinuous latex particles is much higher than on batch latex particles, and more dependent on the copolymer composition. Acid-induced hydrolysis results in a drastic change in the type and concentration of the surface groups of semicontinuous latex particles.[34,35]

The colloidal stability of the ionically cleaned latices against NaCl, $BaCl_2$ and $Al(NO_3)_3$ electrolytes showed that both electrostatic (due to surface acid groups) and steric (due to the presence of the polyvinyl alcohol at the surface) mechanisms are contributing. However, for semicontinuous latices, the decrease in BuA content less than 50 mole% resulted in a proportional increase and, ultimately, dominant role of steric stabilization.[34,35]

Misra, Pichot, El-Aasser, and Vanderhoff investigated the morphology and mechanical properties of the Vac-BuA copolymer latex films of various copolymer compositions.[34,36] The filming ability is better in semicontinuous copolymer latex films compared to batch latex films and is enhanced for both films with increased BuA content. Surface morphology of these thin latex films cast on Teflon slides was studied through single-stage carbon-platinum replicas. The surface replicas were prepared by shadowing the surface of the film with Pt followed by a coating of carbon, and dissolving the copolymer films in toluene. The replicas were examined by transmission electron microscope. The bulk morphology was investigated by staining 60–100 nm-thick microtomed film sections through the hydrazine-osmium tetroxide technique. Batch copolymer latex films showed domains of polyBuA dispersed on polyVAc matrix; the domain sizes were increased with increased BuA content. Semicontinuous latex films were much more homogeneous in composition.

Glass-transition, T_g, of copolymer films was measured by differential scanning calorimeter, DSC, and dynamic mechanical spectrometer. Two different T_g were found for the batch latex films, and the difference between these T_g was found to increase with increased BuA content in the copolymer. However, only one T_g was found for the corresponding semicontinuous copolymer latex film.[36,37] Tensile properties of the batch copolymer films showed a higher ultimate tensile strength, higher Young's modulus, and lower percent elongation to break compared to semicontinuous latex films. It was suggested that the reason is the presence of continuous polyVAc matrix in the batch latex films.[34,36]

Donescu, Gosa, Languri, and Ciupitoiu investigated the semicontinuous emulsion polymerization of VAc with dibutyl maleate.[37] Polyvinyl alcohol protective colloid and 20 moles ethoxylated cetyl alcohol emulsifier were used in the copolymerizations. The overall conversion, copolymer particle size, and latex film properties were reported. Vanderhoff[38] summarized the previous experimental findings on the copolymerization of vinyl acetate with butyl acrylate.[32,34-36,39-41] He reported that the water solubilities are 290 and 11 mM for VAc and BuA, respectively, and the copolymerization reactivity ratios are r_1 = 0-0.04 for VAc and r_2 = 3-8 for BuA monomer. These ratios show that BuA is much more reactive in copolymerization so that, in a batch copolymerization, a polyBuA-rich copolymer is formed until the

BuA monomer is exhausted, and polyVAc is formed thereafter to give a two-peaked distribution of copolymer composition.

The number average MW of the batch latices were higher than those of the semicontinuous latices, and their MW distributions were unimodal and narrower. The broader distribution and bimodal character of the semicontinuous MW distributions were attributed to the low concentration of monomer present in the particles during copolymerization, and the higher probability of branching. For batch latices, the number average MW and the number of surface end groups per polymer molecule increased with increased BuA content.[38]

Vanderhoff reported the results of semicontinuous emulsion copolymerization of 80:20 VAc-BuA. The aqueous phase containing the dissolved emulsifier and initiator was mixed with 8% of the comonomer mixture and polymerized in batch at 60°C; the remaining 92% of the monomer was added continuously at varying rates. Batch copolymerizations were carried out using the same monomer mixtures for comparison. It was determined that the rate of polymerization increases with increasing rate of monomer addition, approaching the rate observed for batch polymerization.[38]

Cavaille, Jourdan, Kong, Perez, Pichot, and Guillot reported the micromechanical behavior of copolymer films obtained from VAc-BuA copolymer latices prepared by different emulsion processes.[42] They applied (1) conventional batch copolymerization, (2) core-shell polymerization in which the more reactive VAc monomer was polymerized on a polyBuA seed latex, and (3) a simple blend of two homopolymer latices obtained by batch homopolymerization. Micromechanical measurements were conducted by using an inverted, forced oscillation pendulum. The real dynamic shear modulus, G', the imaginary part of the dynamic shear modulus, G'', and the internal friction ($\tan \delta = G''/G'$) of these films were measured as a function of the temperature. Large differences were found to exist between batch copolymer and simple homopolymer blends. Core-shell morphology showed the presence of a copolymer with the homopolymer zones.[42]

Delgado, El-Aasser, and Vanderhoff applied miniemulsion copolymerization of VAc and BuA and compared their results with conventional emulsion copolymerization.[43] The monomer droplets are not considered to be loci of polymerization in conventional emulsion polymerization because monomer droplet size is large and its surface area is relatively small compared to that of the monomer-swollen micelles. For the same total volume of monomer, if the size of the monomer droplets is reduced to 100–400 nm in diameter, then the total area of the droplets is increased, approaching that of the monomer-swollen micelles. Therefore, the probability of initiation in monomer droplets increases as the droplet size decreases. The authors described a miniemulsion system of a mixture of Vac and BuA using sodium hexadecyl sulfate as surfactant and hexadecane as a cosurfactant.[43] Ammonium persulfate was used as the initiator. All copolymerizations were conducted in a batch process using a glass reactor equipped with a stirrer and reflux condenser. Sodium hexadecyl sulfate and sodium bicarbonate was dissolved in water, and hexadecane was either mixed with monomers or emulsified in aqueous solution by applying sonification at 50°C. Comonomer mixture containing 50:50 molar ratio of VAc-BuA was added slowly to the reactor under strong agitation and nitrogen flow. Once the addition was completed, the miniemulsion was transferred to an Omni mixer and stirred for 9 minutes. It was then transferred back to the glass reactor and ammonium persulfate initiator solution was injected at 60°C.

The use of hexadecane had several results: the polymerization rate was slowed down, the final latex particle size was larger, and the amount of coagulum formed during the polymerization was diminished. The copolymer formed in miniemulsion process showed a lower content in VAc monomeric unit up to 70% conversion. The dynamic mechanical properties of the copolymer films showed less mixing between the BuA-rich core and VAc-rich shell in the miniemulsion latices compared to the conventional latex films. Two glass-transition temperatures, T_g, were seen in both processes, one for polyBuA-rich domains and the other for polyVAc-rich domains.[43]

Delgado, El-Aasser, Silebi, and Vanderhoff reported on the role of hexadecane cosurfactant in the miniemulsion copolymerization of VAc and n-BuA.[44,45] They carried out a miniemulsion copolymerization of 50:50 molar ratio of VAc-BuA comonomer mixture. Even though hexadecane affects the distribution of the monomers between the different phases, its presence in the bulk monomer does not greatly affect the polymerization kinetics unless a microemulsification process is used. In this case, the heaxadecane stabilizes the submicron droplets formed in the miniemulsification process. The submicron droplets become the main loci of particle generation with the result of a drastic change in the profile of the kinetics.[45]

Delgado, El-Aasser, Silebi, Vanderhoff, and Guillot developed a mathematical model for the monomer transport between monomer droplets and the aqueous phase and polymer particles during the course of both conventional emulsion and miniemulsion copoymerization of VAc-BuA.[46] Equilibrium swelling thermodynamics were used in the model to provide the magnitude of the driving force for the mass transfer to occur. The model does not consider the transfer of monomer as a result of the collision process. The increase in polyVAc-rich domains was related to mass transfer rate. The model confirms that the dispersion of monomers in small droplets increases the swellability of polymer particles. The presence of hexadecane cosurfactant in the monomer droplets increases the amount of retained monomers originally present in particles upon the entry of radicals and the formation of copolymer.[46]

Bataille and Bourassa determined the reactivity ratios for VAc and BuA monomers during batch copolymerization.[47] They used proton NMR for the determination of copolymer composition; r_1 for Vac was found to be 0.024 and r_2 for BuA as 10.67 by using the integrated Meyer-Lowry copolymer equation,[8] and the r_2/r_1 value was found to be 439 with this method. When the Finemann-Ross equation[2] is applied it goes to 734, and the Alfrey-Price method[10] gives 223. The authors concluded that for copolymerizations where the monomers have about the same reactivity, the copolymer equation linearization does not create too many problems. However, for copolymerizations where there is a large difference in reactivity, such as VAc-BuA copolymers, the integrated Meyer-Lowry equation should be used.[47]

Erhart, Dimonie, El-Aasser, and Vanderhoff studied the grafting reactions of polyvinyl alcohol in the emulsion copolymerization of VAc-BuA.[48,49] Polyvinyl alcohols of different degrees of hydrolysis were used as the sole emulsifiers in the copolymerizations. It was determined that the grafting reactions of polyvinyl alcohol and VAc in the aqueous phase affect overall polymerization kinetics. The grafted copolymers were analyzed by Fourier transform infrared spectroscopy (FTIR). A limiting value was determined for the amount of VAc to graft onto polyvinyl alcohol to maintain water solubility.[48]

Donescu, Gosa, and Languri investigated the semicontinuous emulsion copolymerization of VAc with 2-ethylhexyl maleate (80:20 by volume)[50] and compared their results with their previous study on the semicontinuous emulsion copolymerization of VAc with 2-ethylhexyl acrylate.[51] Hydroxyethyl cellulose (HEC) was used as the protective colloid, sodium sulfosuccinate of 6 moles ethoxylated nonyl phenol as emulsifier, and n-butanol as chain transfer agent. The comonomer addition rate was high; it was nearly in "flooded conditions." The evolution of the amount of copolymer was nearly linear with time,[50] and this result is similar to VAc-2-ethylhexyl acrylate copolymerization.[51] The oscillations in the particle number, conversion, and latex surface tension occurred throughout the reaction due to the flocculation and nucleation of new particles. The authors suggested that HEC splits its chain in the presence of the initiator, thus continuously stabilizing the new particles formed.[50]

The stirring rate effect on the system was also examined. The higher the stirring rate, the higher the latex vortex volume, and the higher the oxygen content in the polymerization system. Oxygen gas acts as an inhibitor and reduces the copolymerization rate and conversion. The higher the stirring rate, the smaller the average particle size found up to 600 rpm stirring rate.[50]

The inclusion of the chain transfer agent n-butanol lowers the content of the cross-linked copolymer. The presence of n-butanol decreases the average particle diameter. n-Butanol is different from conventional chain transfer agents such as t-dodecyl mercaptan; it is highly water-soluble and ensures a high splitting rate of potassium persulfate initiator. This fact results in a complex behavior of this chain transfer agent.[50]

Dimitratos, El-Aasser, Georgakis, and Klein published an important paper in 1990 reporting the pseudo-steady states in seeded semicontinuous copolymerization of an 80:20 VAc-BuA (wt/wt) system[13] (see also Sec. 5.2.7.1). They refined Wessling's[12] and Gerren's[52] semicontinuous copolymerization analyses and derived a unified equation that can be used both for water-soluble and sparingly water-soluble monomers.[13] First of all, they distinguished two kinds of monomer feed rates: (1) "flooded conditions" in which the monomer feed rate is large enough to maintain the saturation value of monomer concentration in the latex particles, $[M^p]$, and (2) "monomer-starved conditions" in which the feed rate is below this value. When flooded conditions are applied, the rate of polymerization is at maximum and is independent of the monomer feed rate. When monomer-starved conditions are applied, the polymerization rate approaches a constant value which depends on the monomer addition rate.[13]

Although both Wessling's and Gerren's analyses use only Smith-Ewart Case II kinetics, the authors derived a more general polymerization rate equation comprising every kind of emulsion polymerization system that does or does not obey Smith-Ewart Case II kinetics (where the average number of radicals per particle, $n = 0.5$). The general equation for the pseudo-steady state is as follows:

$$R_i = \frac{F_i}{\left[1 + \frac{1}{Kb_i}\,\frac{d}{dt}\left(\frac{f_i\,V_R}{N\,\bar{n}}\right)\right]} \tag{5.24}$$

where

R_i = Rate of polymerization (kmol/sec)
F_i = Monomer feed rate (kmol/sec)
$K = (k_{p11}\ k_{p22})\ /\ N_A$
k_{p11} = Reaction rate constant for the first monomer
k_{p22} = Reaction rate constant for the second monomer
N_A = Avagadro's number
$b_i = (r_1\ m + 1)/(\ k_{p22}\ r_1\ m + k_{p11}\ r_2)$
r_1 = Reactivity ratio for the first monomer
r_2 = Reactivity ratio for the second monomer
m = Ratio of monomer concentration $[M_1^p]$ over $[M_2^p]$
V_R = total volume of latex in the reactor (m^3)
N = Total number of particles
$f_i = [M_i^R]\ /\ [M_i^p]$
$[M_i^R]$ = unreacted monomer (i) concentration in the reactor (kmol/m^3 latex)

Pseudo-steady state was defined so that it is not a steady state in the strict sense, but due to the transient nature of the semicontinuous process, some variables behave as if at a steady state. The authors analyzed only neat comonomer feeding, and pre-emulsified comonomer feeding was not included. It was assumed that no polymer is dissolved in the aqueous phase, nor water in the polymer particles. The polymer phase volume includes the volume of the pure polymer as well as the volume of monomer in the monomer-swollen particles. A necessary condition to obtain pseudo-steady-state behavior for both monomer consumption rates is that the ratio m of the monomer concentrations in the polymer phase assumes a constant volume.[13]

In the case of sparingly water-soluble monomers, almost all the monomer resides in the monomer-swollen particles, and, thus, $f_i = V_P/V_R$, where V_P is the volume of the polymer phase. As the particle size increases, the radical concentration increases and approaches a constant value. The system will behave more or less like continuous addition bulk or solution polymerization with constant radical concentration. In this case, we have

$$\frac{N\,\bar{n}}{V_p} = const. \tag{5.25}$$

When these findings are inserted in the main equation (Eq. 5.24), we have

$$R_i = F_i \tag{5.26}$$

The authors suggested that the particle size needed to achieve conditions of constant radical concentration might be out of the range usually encountered in emulsion polymerization systems.

In seeded, sparingly water-soluble monomer systems, the total number of particles, N, will be constant. Then the main equation can be rearranged into

$$\frac{1}{R_i} = G_i + \frac{1}{F_i} \tag{5.27}$$

with constant G_i, which is similar to Wessling's treatment. G_1 and G_2 can be written as

$$G_1 = \frac{1}{K\, b_1 N\, \bar{n}} \left(\frac{MW_1}{d_1} + \frac{MW_2}{\mu d_2} \right) \tag{5.28}$$

$$G_2 = \frac{1}{K\, b_2 N\, \bar{n}} \left(\frac{\mu MW_1}{d_1} + \frac{MW_2}{d_2} \right) \tag{5.29}$$

where

MW_i = Molecular weight of the monomer
d_i = Density of the monomer (kg/m^3)
μ = Monomer feed ratio = F_1/F_2

Therefore, the dependence of the reaction rate on monomer feed rate is linear with the slope of unity, again as in the case of fixed radical concentration which was treated as above.

In the case of highly water-soluble monomers such as VAc, if the monomer partition coefficients between the polymer and the aqueous phase are proportional to the volume r ratio of the aqueous phase to the polymer phase,

$$\frac{V_a}{V_p a_i} = const. \tag{5.30}$$

where

V_a =Volume of the aqueous phase (m^3)
V_p =Volume of the polymer phase (m^3)
a_i =Partition coefficient

Then, by differentiating Eq. 5.24, one obtains $R_i = F_i$ again. This condition basically suggests that the amount of monomer in each phase does not change at the pseudo-steady state. For a seeded, highly water-soluble monomer system with constant n

and a_i, we can also derive Eq. 5.27 again. Correspondingly, for homopolymerization of a single monomer in semicontinuous process, by setting $m = 0$ and $\mu = 0$, one obtains

$$R = \frac{F}{\left[1 + \frac{N_A}{k_p N \bar{n}}\left(\frac{MW}{d}\right)F\right]} \tag{5.31}$$

The authors concluded that, under certain assumptions, the relationship between the monomer consumption rates and the monomer feed rates is the same for both water-soluble and water-insoluble monomers. For the very slow monomer feed rates (under monomer-starved conditions), $R_i = F_i$ can be easily obtained. If we rearrange Eq. 5.27 so that

$$R_i = \frac{F_i}{\left(1 + F_i\, G_i\right)} \tag{5.32}$$

then, F_iG_i becomes very small and $R_i = F_i$ is obtained again. The authors compared the feed rates of many previous publications and concluded that these monomer feed rates were indeed extremely small to allow for the application of the above equation. This conclusion is also in good agreement with the well-established experimental fact that the resulting copolymer composition is very close to the comonomer feed composition with very low feed rates.

The authors tested their theoretical model against experimental data from the seeded copolymerization of 80:20 VAc-BuA. Both batch and semicontinuous runs were conducted. When the feed rates exceeded the maximum values for monomer-starved conditions (in the flooded region), the conversion-time curves overlapped with the batch test curves, confirming the fact that the batch copolymerization rate is the maximum rate that can be achieved. The conversion and the overall polymerization rate rise by increasing the feed rates in monomer-starved conditions. The proportionality constant between the reaction rate and the monomer feed rate was found to be equal to 0.82 for VAc and 0.99 for BuA. The deviation of VAc from unity can be attributed to its high water solubility. This copolymer system does not obey Smith-Ewart Case II kinetics, and n varies between 9.91 and 10.91, which was found to be fairly constant. Partition constants for VAc and BuA were also determined to be fairly constant. The authors concluded that their experimental findings fit their theoretical model well.[13]

Urquiola, Arzamendi, Leiza, Zamora, Asua, Delgado, El-Aasser, and Vanderhoff investigated the semicontiniuous seeded emulsion copolymerization of VAc and methyl acrylate.[53] Both monomer-starved and semi-starved neat comonomer feeding were applied. In the case of the starved process, both monomers, but mainly VAc, accumulated in the reactor, and this preferential accumulation resulted in a drift of the copolymer composition. The decrease of the feed rate or the increase of the amount of seed initially charged in the reactor resulted in a decrease of the compositional drift in the copolymer. The total number of particles reached a plateau value, which was nearly the same in all of the experiments conducted for both starved and semi-starved processes. It was found that a polyVAc-rich copolymer was formed when a low methyl acrylate feed was used, whereas a polymethyl acrylate-rich copolymer was obtained at high methyl acrylate feed rates for the semi-starved process. A mathematical model was also developed to analyze the experimental results.[53]

Makgawinata, El-Aasser, Vanderhoff, and Pichot discussed the preparation of VAc-BuA copolymer latices and reported that the feed rates of the monomer mixtures have an effect on the final properties of the latex.[54] They concluded that semicontinuous copolymerizations provide better control over compositional heterogeneity than batch copolymerizations. The particle size and distribution varied with comonomer composition and feed method, with the smallest particle size obtained in the BuA-rich copolymers. The semicontinuous process produced smaller particles than did batch polymerizations.[54]

Donescu and Fusulan copolymerized VAc with dibutyl maleate using a semicontinuous process.[55] They also noticed a decrease in particle size with increasing dibutyl maleate comonomer. Similar to Makgawinata et al.,[54] they concluded that the more hydrophobic monomer is responsible for reducing particle size. The increased hydrophobicity allows for greater stability of the first-formed particles since surfactant is more easily adsorbed onto the surface. They determined that dibutyl maleate comonomer also had a retarding effect on the copolymerization rate.[55]

Noel, Van Altveer, Timmermans, and German determined the monomer reactivity ratios of methyl acrylate (MA) and VAc; vinyl 2,2-dimethyl propionate (VEOVA-5 of Shell); and vinyl 2-ethyl hexanoate (V2EH).[56] They used a nonlinear optimization technique which was applied to the monomer feed-copolymer composition data obtained from low conversion bulk polymerization reactions using AIBN as initiator. The copolymer compositions were determined by proton-NMR spectroscopy. They applied the nonlinear optimization techniques to determine monomer reactivity ratios that were developed by Hautus et al.[57] and Dube et al.[58] They found the following reactivity ratios: $r_{MA} = 6.9 - r_{VAc} = 0.013$, $r_{MA} = 5.5 - r_{VEOVA\text{-}5} = 0.017$, and $r_{MA} = 6.9 - r_{V2EH} = 0.093$. They concluded that the three vinyl esters can be described with one set of reactivity data. This greatly simplifies any potential for compositional drift since interphase partitioning of the monomer is the only variable that must now be dealt with.[56]

Donescu, Fusulan, Gosa, and Ciupitoi studied the semicontinuous copolymerization of VAc with acid comonomers such as fumaric acid, crotonic acid in order to improve the stability and adhesion properties.[59] They used HEC as protective colloid and 6 moles ethoxylated nonyl phenol sulfosuccinic disodium salt as emulsifier in their experiments. It was determined that the presence of acid comonomers decreases the rate of reaction and increases particle size.[59]

Urretabizkaia, Asua, et al. investigated the optimal monomer feed policy for composition control of VAc-methyl methacrylate (MMA)-BuA terpolymer.[60,61] They used an open-loop emulsion polymerization system to obtain a 55% solids terpolymer latex. The effect of feed flow rate, emulsifier concentration, and initiator concentration were examined. Reducing the monomer feed rate and increasing that for the initiator reduced the rate of terpolymer composition drift. The terpolymer composition was estimated by determining the monomer concentrations in the reactor using gas chromatography. Increased emulsifier levels only increased the number of particles but not the reaction rate, causing the authors to conclude that the reaction system operates under Smith-Ewart Case 3 conditions with negligible aqueous phase termination, and thus the polymerization rate was independent of the number of polymer particles.[60] A mathematical model was developed for reactors with and without limited heat removal capacity.[61] The model allows the calculation of the composition of the initial charge of the reactor and time-dependent monomer addition rates required. When a reactor with limited heat removal capacity is used, the optimal monomer addition policy requires only a fraction of the three monomers to be included in the initial charge, and the remaining monomers can be fed at a controlled flow rate. It was determined that even in the case of long feed times, the starved-feed process produced a more heterogeneous product than the optimal controlled process.[61]

Canu, Canagallo, Morbidelli, and Storti examined the optimal comonomer feed policy to control the composition of the copolymers in a semicontinuous emulsion copolymerization.[28] A mathematical model was developed to produce a given amount of copolymer with a constant instantaneous composition and complete monomer depletion within a minimum reaction time. This model uses only the comonomer reactivity ratios and the interphase partition laws. The reliability of the model has been tested by comparison with the optimal policies given in the literature for methyl methacrylate-ethyl acrylate, styrene-methyl acrylate (MA), and VAc-MA comonomer systems. They used the data reported by Arzamendi and Asua for VAc-MA copolymer system.[62] Both of the monomers are highly water soluble in this system, and the copolymerization reaction was conducted in monomer-starved conditions throughout the entire process due to the significant amount of seed initially charged in the reactor. When the above model is applied, a practically constant MA monomer flow rate is found as a function of conversion, with mass of MA fed to the reactor per unit mass of polymer produced ranging from 0.435 to 0.442 g/g. The amount of MA initially introduced to the reactor is predicted from the model as 19.1 g, and this figure is in good agreement with the corresponding experimental figure of 18.5 g.[28]

Gugliotta, Arotcarena, Leiza, and Asua developed a new approach to estimate conversion and the cumulative copolymer composition in batch and semicontinuous emulsion polymerization based on online calorimetric measurements.[63] The method was validated for two different copolymerization systems, VAc-BuA and BuA-styrene. The method uses a simple mathematical model of the semicontinuous emulsion polymerization containing four parameters that have to be known previously: reactivity ratios, monomer partition coefficients, propagation rate constants, and enthalpy of homopolymerization reaction of each monomer involved. (It was assumed that the enthalpy of cross-propagation is equal to the enthalpy of homopolymerization.) The concentration of monomers in the monomer-swollen polymer particles are calculated using the equilibrium equations, and the overall material balances by means of an iterative algorithm applied by Urretabizkaia and Asua et al.[60,61,64] The equilibrium equations were written in terms of partition coefficients, which can be obtained from the literature or from independent measurements. The authors derived equations to calculate the amount of unreacted monomer in the reactor, the fractional conversions, the overall gravimetric conversion, and the cumulative copolymer conversion.

The estimated values of conversion and copolymer composition obtained from calorimetric data were compared with the experimental measurements of conversion and cumulative copolymer composition by gravimetry, gas chromatography, and proton-NMR spectroscopy for both VAc-BuA and BuA-styrene systems.[63] Good agreement was obtained for both systems; however, in the VAc-BuA system, the compositional drift was found to be greater than for the BuA-styrene system.

The authors proposed that this model could be useful to implement closed-loop copolymerization composition control strategies. For this purpose, an automatic sampling system was also developed to handle high solids content latices (55% by wt.), and which was used for online terpolymer composition control in the emulsion terpolymerization of VAc-BuA MMA.[65]

Urretabizkaia, Sudol, El-Aasser, and Asua compared two methods of continuous determination of copolymer concentrations and conversion of VAc polymers.[64] An online calorimetric determination was compared with offline gravimetric and gas chromatographic methods. Good agreement was obtained for VAc-BuA copolymer, whereas the calorimetric measurements predicted a more homogeneous composition than the offline GC measurements for VAc-MMMA copolymer.[64]

Gugliotta, Arzamendi, and Asua investigated various monomer partitioning models including VAc-BuA and VAc-methyl acrylate.[66] The partitioning of monomers in the various phases changes the local monomer concentrations, and this is reflected in the composition of the final product. The authors determined the optimal models for three polymerization types: batch, starved, and optimal-starved. They used partitioning models of Morton,[14] Maxwell et al.,[15,16] and Noel et al.[67] However, Canu, Canegallo, Morbidelli, and Storti[28,68] developed a different approach to compositional control that requires the knowledge of only the monomer reactivity ratios and interphase partitioning laws. In this approach, the continuous monitoring of conversion is also needed. The above models for polyVAc and its acrylic copolymers employ the classical terminal model described by Mayo-Lewis.[1]

Ma, Won, Kubo, and Fukuda examined the propagation and termination of the VAc-MMA copolymerization reaction by considering the penultimate unit effect when calculating the reactivity ratios and comparing it to the terminal model.[69] The data fit the terminal model within experimental error; however, penultimate effects were observed for chain radicals with a terminal MMA unit.

Gajria and Vijayendran investigated the pH response of acrylic acid (AA) and methacrylic acid (MAA)-modified VAc-BuA copolymer latices.[70] These latices are used in the pressure-sensitive adhesives industry. The authors determined that feeding the acid in the monomer feed as opposed to a water solution feed produced a greater viscosity response upon pH adjustment. Most acid groups were found to locate on the surface of the latex, with some buried in the particle. No polymeric acid was found in the aqueous phase, contrary to styrene or pure acrylic latices.[70]

Huo, Hamielec, and McGregor also studied the effect of AA incorporation into 2-ethylhexyl acrylate-VAc-AA terpolymers.[71] They noticed a dependence of latex swelling with polymerization procedure. The addition of sodium chloride effectively reduced the pH-thickening response curve.

Smith, Bassett, and co-workers reported that VAc copolymers with branched vinyl esters such as vinyl versatate (or vinyl neodecanoate or trade name VEOVA-10 of Shell) have the potential to outperform VAc-acrylic copolymers due to the random copolymerization nature of the first set.[72,73] Branched vinyl esters are resistant to hydrolysis, both as monomers and in polymers, due to their neighboring group steric effect. VAc copolymers with VEOVA monomers have a hydrolytic stability with increasing concentrations of branched vinyl ester. The hydrocarbon chains from VEOVA monomer shield neighboring VAc groups from hydrolytic attack by water. One monomer unit of VEOVA-10 protects two to three VAc units.[72,73] The branched vinyl esters tend to form random copolymers with VAc since the r_1 and r_2 values are near unity in each case. However, the large disparity in reactivity ratios of the acrylates with VAc indicates a high tendency to form separate acrylate and vinyl blocks which contribute to the poor alkaline stability of VAc-BuA copolymers.[73] Branched vinyl esters are strongly resistant to saponification, water absorption, and UV degradation. Combining them with VAc or VAc-acrylic copolymers will improve water and alkali resistance and exterior durability.[73]

McKenna, Graillat, and Guillot studied the polymerization rate constants for VAc and BuA homopolymerization and VAc-BuA solution copolymerization in ethyl acetate solvent using benzoyl peroxide as initiator.[74] They also investigated the oxygen inhibition on the observed rate of polymerization. The reactions were conducted at 70°C, both with and without nitrogen purge. A decrease in the rate of polymerization in the second instance was attributed to the presence of dissolved oxygen in the solution. They reported $(k_p)/(k_t^{1/2}) = 0.978$ for BuA homopolymerization, and $(k_p)/(k_t^{1/2}) = 0.279$ for VAc homopolymerization when the gel effect is neglected.[74]

Two semicontinuous solution copolymerization reactions were also conducted in different reactor systems in order to confirm the validity of the rate constant data reported. They recommended the use of their polymerization rate constant data when oxygen may be continuously present, especially in continuous industrial reactors.[74]

Abad, DeLa Cal, and Asua investigated the similarities and differences between the continuous loop reactor and the continuous stirred tank reactor (CSTR) systems when redox-initiated, high solids emulsion copolymerization of VAc and VEOVA-10 was applied.[75] Inhibited commercial comonomers, $K_2S_2O_8$ – $Na_2S_2O_5$ redox initiator systems, HEC protective colloid, and anionic-nonionic emulsifier systems were used in the experimental formulations. The copolymerization reactions were conducted under similar macromixing, feed composition, and space-time conditions. It was found that when the heat-removal capacity of the reactor exceeds the heat generation rate, there are no differences between the loop reactor and the CSTR in terms of conversion, particle size and number, and molecular weight distributions. However, when the heat generation rate is high, a thermal runaway occurred in the CSTR reactor, whereas the loop reactor temperature is easily controlled. In addition, it was determined that the steady-state results were independent of the start-up procedures.[75]

Dube and Penlidis published four papers on the systematic study of terpolymerization of VAc-BuA-methyl methacrylate (MMA) monomers.[76-79] In the first paper, bulk copolymerizations of BuA-MMA, BuA-VAc, and VAc-MMA were carried out in glass tubes in order to determine the monomer reactivity ratios during copolymerization.[76] Both the initial and complete conversion experiments were conducted, and the copolymer compositions were determined by proton-NMR spectroscopy. The analysis of the data was performed by using two different computational tools: (1) an in-house program employing the Mayo-Lewis equation[1] was used, (2) a program that applies the Meyer-Lowry integrated equation[8] was used. The second approach is preferred and $r_{BuA} = 5.9582 - r_{VAc} = 0.01443$, $r_{MMA} = 26.1975 - r_{VAc} = 0.1526$, $r_{BuA} = 0.2936 - r_{MMA} = 1.7773$ was found by the integrated Meyer-Lowry copolymer equation. These results were compared with the previously published data. On the other hand, the molecular weight distributions of the copolymers were determined by gel permeation chromatography (GPC) and a double gel-effect was found for VAc-acrylic copolymerizations. It was suggested that gel effect of polyVAc and polyacrylics were present simultaneously.[76]

In the second paper of the series, the solution copolymerizations of the same monomer pairs were carried out, and the determined parameters were compared with the bulk copolymerization partameters.[77]

In the third paper of the series, emulsion homopolymerization of individual monomers, copolymerizations of the above-mentioned pairs, and terpolymerization of the three monomers were conducted in a 5-liter stainless-steel reactor in batch type polymerizations.[78] First of all, a search for a stable emulsion recipe was conducted and, after many trials resulting in catastrophic coagulation of the latex, some stable recipes were obtained. It was found that the molecular weights of the copolymers obtained from monomer pairs were too high to reasonably characterize all of the samples; however, only terpolymerization yielded low molecular weight material. Thus, the authors could make only some qualitative comments on the terpolymer system.[78]

In the fourth paper of the series, optimal Bayesian design for the emulsion terpolymerization in a pilot plant reactor was conducted. This design procedure was claimed to improve subjective judgment of the process results.[79]

Cooper, Grieser, and Biggs studied the synthesis of VAc-BuA copolymer latex using ultrasound as an initiator in the absence of any added initiators at room temperature.[80] The passage of an ultrasonic wave through a liquid medium generates free radicals because of the physical process of acoustic cavitation. Small voids are formed in the liquid structure which periodically collapse, leading to transient regions of high temperature (≈5000°K) and pressure (≈500 atm) within the liquid. These localized extreme conditions are sufficient to cause free radical formation. In water, primarily hydrogen gas and hydroxyl radicals are produced.[80] The authors investigated homo- and copolymerization of VAc and BuA by the use of ultrasound initiator. Sodium dodecyl sulfate and sodium di-(2-ethylhexyl) sulfosuccinate anionic emulsifiers were used in 0.5 wt% to prepare 100 g emulsions containing monomers in water. After initiation, polymerization was completed and stable latices were obtained. Then the conversions, average particle sizes, molecular weights, and surface charges of particles were determined. Small latex particles (≈5–30 nm) were observed for BuA homopolymer and VAc-BuA copolymer latices, whereas VAc homopolymerization gave anomalously large particle sizes (≈350 nm). Molecular weights were found to be relatively high (3×10^6 g/mol). Polymer degradation was observed at prolonged sonication times.[80] Polymerization rate was found to depend upon the monomer concentration dissolved in the aqueous phase and its vapor pressure. VAc is the more volatile monomer and showed a markedly lower polymerization rate at equivalent monomer concentrations when compared to BuA. This was attributed to monomer evaporation into the cavities formed by the ultrasound, causing a dampening of the cavitation process and, hence, a lower radical density.[80]

Poehlein and Schork reviewed the continuous emulsion and miniemulsion homo- and copolymerization systems between 1993–1996.[81] The review included loop reactors, continuous stirred tank reactors (CSTRs), the methods to avoid oscillations in some latex properties during manufacture, methods to obtain the desired particle characteristics, and methods to achieve low residual monomer concentrations. This review shows the extent of developments after the publication of their first review in 1993.[82]

Donescu and Fusulan examined the copolymerization of VAc with some acid comonomers such as crotonic acid, maleic acid, maleic monoesters, and 25 moles ethoylated monononyl phenol maleate. As a different approach, they also followed the splitting reaction of the potassium persulfate initiator in the presence of these acid comonomers.[83]

Tang, Weng, and Pan investigated the batch emulsion terpolymerization of VAc and methyl acrylate, acrylic acid and acrylamide at 25°C with a redox initiator system, and a coplex emulsifier.[84] The structure of the resulting terpolymer, as well as the particle size and number density of the latices, were determined as a function of time and conversion. The optimum concentration of the initiator was found to be 0.2 wt% and the emulsifier, 2.0 wt%. The results showed that the terpolymerization process has a three-stage feature and the particle size changed drastically, finally reaching a limiting value of 110 nm.[84]

Kwark, Lyoo, and Ha studied the kinetics of emulsion copolymerization of VAc with vinyl pivalate.[85] Both homo- and copolymerizations of these monomers were conducted by using low temperature redox initiators. A mathematical model was developed to estimate the polymerization kinetics, and good agreement with the experimental data was obtained when the partitions of monomers in different phases were considered.[85]

Erbil investigated the surface energetics of films of VAc-BuA copolymers made by the semicontinuous emulsion polymerization process.[86] Nonionic emulsifiers and ammonium persulfate-sodium formaldehyde sulfoxylate redox initiators were used at 50°C. Molar compositions of copolymers were determined by proton-NMR analysis, and it was found that copolymer compositions deviated by only 0.7 – 5.2 mole% from the feed comonomer compositions when the semicontinuous method was applied. A decrease of average particle size and glass-transition temperature was found by the increase of BuA content in the copolymer.[86] Viscosity average molecular weights of the copolymers increased up to 40 mole% BuA, then decreased. Copolymer latex films were obtained by drying the latex at room temperature. Contact angle measurements of several liquids were then carried out on these films. Van Oss's and Good's "Surface Tension Components" approach[87,88] was applied to evaluate the contact angle data. The apolar (Lifshitz-Van der Waals) surface tension component was found to be fairly constant by the change in BuA content; however, electron donor surface tension component (basic) decreased considerably with BuA increase. The thermodynamic work of adhesion was calculated for cellulosic substrate-latex film interfaces, and the work of adhesion was found to decrease with the increase of BuA content.[86]

DeBruaga, Echevarria, Armitage, Delacal, Leiza, and Asua improved the calorimetric online control method that was previously developed[61] for semicontinuous copolymerization of VAc-BuA.[89] The conversion and the copolymer composition were estimated by online calorimetry. It was shown that the feedback control was able to avoid monomer accumulation in the reactor and, hence, potentially dangerous thermal runaways. The use of the same method in the emulsion copolymerization of VAc with VEOVA-10 of Shell was also presented.[89]

Hydrolysis of VAc copolymers in latex form was first investigated by Davies and Reynolds,[90] and later by Martin, Smith, and Bassett.[91] Blackley summarized and discussed their results in detail.[92] Although polyacrylates and polymethacrylates render their ester groups less susceptible to hydrolysis than the ester groups in polyVAc, there is a marked tendency for VAc-acrylic copolymers to undergo hydrolysis when in contact with aqueous media. The principal reaction is the splitting off of the acetate moiety of the units derived from vinyl acetate to give attached hydroxyl groups. In industry, the alkaline hydrolysis of copolymer latices is more important because most of the surface coating latices come into contact with plaster, cement, etc. to maintain alkaline conditions. Davies and Reynolds studied the hydrolysis of VAc-vinyl caprylate-vinyl caprate, VAc-VEOVA, and VAc-BuA copolymers.[90] VAc-VEOVA copolymer was found to be most resistant to alkaline hydrolysis. They also showed that the incorporation of small concentrations of copolymerized carboxylic-acid units such as acrylic acid in the copolymer increases the alkaline hydrolysis too much. They offered two mechanisms for this purpose: (1) the equilibrium water content of the particles was increased, thereby increasing the ease of entry of ions into the particles; (2) steric protection was reduced by replacement with smaller units, which also created local domains of relative hydrophilicity adjacent to hydrolyzable units.[92]

Sun, Liu, and Zhao simulated the development of the particle morphology of VAc-BuA emulsion copolymers.[93] For the semicontinuous process, the final particle morphology revealed microphase separation structure; the faster the feed rate of comonomers, the greater the separation. During the slowest feeding of comonomers, a multicore-shell structure is formed.[93]

Donescu, Fusulan, and co-workers published five papers on the copolymerization of VAc between the years 1997 and 1999.[94-98] In the first paper of the series, microemulsion copolymerization of VAc with a reactive surfactant (monomaleate of nonyl phenol ethoxylated with 25 moles of ethylene oxide) was carried out.[94] In the second paper, the authors examined the copolymer-water interaction for VAc-maleate diester copolymer latices. The amount of water bound to copolymer particles decreases with the increase of comonomer hydrophobicity.[95] In the third paper, microemulsion copolymerization of VAc with 2-ethylhexyl acrylate was carried out in the presence of n-propanol cosurfactant, 25 mole ethoxylated nonyl phenol emulsifier, or the maleic monoester of this emulsifier.[96] In the fourth paper, the emulsion homopolymerization of VAc and copolymerization of VAc with bis(2-ethylhexyl)maleate in the presence of maleic-modified and unmodified silica were studied.[97] In the fifth paper, microemulsion copolymerization of VAc with acrylic acid was investigated in the presence of maleic monoester of 25 moles ethoxylated nonyl phenol emulsifier. Conductometric and refractometric investigations have shown the existence of some aqueous/organic, bicontinuous, and organic/aqueous microemulsions.[98]

5.5 PARTICLE MORPHOLOGY OF COPOLYMERS

The formation of composite latex particles having specific morphological and physical properties is important industrially to meet a variety of molecular and colloidal requirements. Composite latices are used as architectural and automotive coatings, as impact modifiers in adhesives to provide an optimum peel strength, and in biotechnology.[99] These latices containing composite particles exhibit a wide variety of particle morphologies such as "core-shell," "hemispherical," "particles with fragmented inclusions," and "inverted core-shell particles." Composite latices having "core-shell" structure are synthesized by stepwise emulsion polymerization with different monomer types where the second monomer is polymerized in the presence of seed latex particles. In this structure, initially polymerized homopolymer is located at the center of the particle, and the second formed polymer becomes incorporated into the outer layer. The seed particles used in this process may be prepared in a separate step or formed *in situ* during emulsion polymerization. "Inverted" core-shell particles are synthesized with the second polymer at the center of the particle and the seed polymer on the periphery of the particle.

Thermodynamic and kinetic factors control particle morphology development. Thermodynamic factors determine the equilibrium morphology of the final composite particle, while kinetic factors determine the ease with which this morphology can be achieved. Torza and Mason pioneered the study of the interfacial behavior of systems containing various types of three mutually immiscible liquids.[100] They measured interfacial tensions among the three liquids present in the emulsion polymerization system, calculated the spreading coefficients, and then observed the results in the actual three-phase systems. They determined that, in most cases, predictions of engulfing based on calculations for spreading pressure were satisfactory. Sundberg, Casassa, Pantazopoulos, Muscato, Kronberg, and Berg[101] developed a thermodynamic analysis for the morphology of a variety of types of polymers by applying Torza's and Mason's approach. They showed that the interfacial tension of each phase is the determining factor for the type of microcapsules formed. Chen, Dimonie, and El-Aasser[102] derived a mathematical model to describe the free energy changes corresponding to five different particle morphologies very similar to Sundberg et al.'s thermodynamical analysis using Gibbs-free energy considerations. Only core-shell, inverted core-shell, and hemispherical particles are found to be stable thermodynamically, and all other reported morphologies are non-equilibrium, kinetically controlled structures prepared under conditions in which the polymerization kinetics proceed faster than do the phase separation kinetics.[99] In kinetically controlled morphologies, the key factor determining the final particle morphology is the amount of second monomer present in the particle during polymerization. The control of the monomer flow rate in the semicontinuous polymerization process allows one to obtain the desired morphology in the final particle. Monomer solubility in water differences, monomer reactivity ratio disparity, selection of the emulsifier, chain transfer agents, and the presence of a cross-linking agent in the emulsion polymerization system are also important factors in controlling particle morphology.

Some core-shell particles are obtained unintentionally due to the water solubility and reactivity ratio differences of VAc monomer with acrylic monomers. Misra, Pichot, El-Aasser, and Vanderhoff investigated the morphology and mechanical properties of the VAc-BuA copolymer latex films of various copolymer composition.[34,36] Surface morphology of these thin latex films cast on Teflon slides were studied through single-stage carbon-platinum replicas. The surface replicas were prepared by shadowing the surface of the film with Pt followed by a coating of carbon and dissolving the copolymer films in toluene. The replicas were examined by transmission electron microscope. The bulk morphology was investigated by staining 60–100 nm-thick microtomed film sections through the hydrazine-osmium tetroxide technique. Batch copolymer latex films showed domains of polyBuA dispersed on polyVAc matrix; the domain sizes were increased with increased BuA content. Semicontinuous latex films were much more homogeneous in composition. Glass-transition, T_g, of copolymer films were measured by differential scanning calorimeter, DSC, and dynamic mechanical spectrometer. Two different T_g were found for the batch latex films, and the difference between these T_g was found to increase with increased BuA content in the copolymer. However, only one T_g was found for the corresponding semicontinuous copolymer latex film, showing that it is homogeneous.[36,37] Batch copolymer films showed a higher ultimate tensile strength, higher Young's modulus, and lower percent elongation to break compared to semicontinuous latex films. It was suggested that the reason is the presence of continuous polyVAc matrix in the batch latex films.[34,36]

Cavaille, Jourdan, Kong, Perez, Pichot, and Guillot studied the micromechanical behavior of copolymer films obtained from VAc-BuA copolymer latices prepared by conventional batch copolymerization and core-shell polymerization.[42] In addition, a simple blend of two homopolymer latices obtained by batch homopolymerization was also investigated for comparison. Micromechanical measurements were conducted by using an inverted forced oscillation pendulum. The real dynamic shear modulus, G'; the imaginary part of the dynamic shear modulus, G''; and the internal friction ($\tan \delta = G''/G'$) of these films were measured as a function of the temperature. Large differences were found to exist between batch copolymer and simple homopolymer blends. Core-shell morphology shows the presence of a copolymer with the homopolymer zones.[42]

Jourdan, Cavaille, and Perez,[103] and independently Kong, Pichot, and Guillot,[104] showed that semicontinuous processes produce homogeneous latex films by using soap titration methods. DeLaCal, Urzay, Zamora, Forcada, and Asua investigated the polyVAc homopolymer formation on VAc-BuA copolymer seed.[105] They determined that when particles are small, the polymerization takes place throughout a significant portion of the latex particle. However, when the particle grows larger, polymerization is confined to the latex surface only, and the last formed polymer resides on the surface of the latex particle.

Okaya, Tanaka, and Yuki investigated the VAc polymers produced in the presence of polyvinyl alcohol.[106] Latices produced in the presence of polyvinyl alcohol resulted in higher tensile strengths than those produced with only nonylphenol ethoxylate emulsifiers, presumably due to the formation of a reinforcing polyvinyl alcohol network structure. However, this network is also responsible for the poor water resistance of the films prepared from this latex.[106]

Some particle morphologies are formed intentionally, such as interpenetrating network and core-shell composite particles. In order to synthesize an interpenetrating network, a second monomer is copolymerized in the presence of a first-formed homopolymer and a di- or polyunsaturated monomer. The first polymer is a cross-linked product and has also been copolymerized with a di- or polyunsaturated monomer. Yan, Xu, Zhang, Yao, and Qian used interpenetrating network techniques to produce a composite vinyl-acrylic latex.[107] They copolymerized VAc and divinyl benzene to produce the first polymer and used BuA-divinyl benzene copolymer as the second polymer. In both cases, the cross-linking agent divinyl benzene was added at 0.4 wt%. Dynamic mechanical measurements and C-13 NMR spectroscopy were used for the determination of compatibility between phases.[107]

Vandezande and Rudin described a method in which a core-shell vinyl-acrylic latex is produced with a VAc core by using an inverted core-shell process.[108] This process is the reverse of the thermodynamic expectations. In general, the rather high water solubility of VAc as compared to other monomers such as BuA results in the polyVAc migrating to the surface of the latex particle. Since polyVAc has a T_g that is lower than the practical polymerization temperature of most monomers, the polyVAc is free to migrate to its most thermodynamically favorable position. Vandezande's and Rudin's method employs polymerizable surfactants to prepare seed VAc-BuA latex in the first step. VAc monomer is then polymerized in the presence of these seed latex particles using a hydrophobic nonionic initiator. They suggested that these latices will outperform homogeneous copolymers of similar overall monomer composition since the more water-sensitive polyVAc is surrounded by a more hydrophobic shell material. On the other hand, since only a part of the more costly BuA is employed in the production of these inverted core-shell particles, the total material cost of the latex is cheaper.[108]

5.6 FILM PROPERTIES OF COPOLYMERS

Polymer latices are extensively applied as water-borne coatings. During drying, the latex originally present as a colloidal dispersion of particles in water is transformed into a void-free and mechanically coherent polymer film. In this process, the application temperature must exceed the minimum film forming temperature (MFT) of the system. The MFT commonly corresponds to T_g of the latex polymer in the presence of water. The extent of the contribution of various forces involved with the film formation from latices is a subject under much debate.[73,109] The reason for this debate is there is no single mechanism of film formation from latices. The drying mechanism will probably depend upon whether or not the particles form an ordered dispersion before they dry, especially in the late stages of drying. In addition, the nature of the particle deformation process may be different in different systems. The particle deformation may be driven by osmotic forces or by surface and/or interfacial tension forces, depending on whether water loss precedes or accompanies full densification of the films. However, this is in relation to the drying temperature compared to the wet T_g of the latex polymer and the rate of water loss. On the other hand, the presence of polar groups or water-swellable polymers at the surface of the particles can lead to formation of a membrane phase in the newly formed latex film. This phase, if present, acts as a barrier to retard interparticle polymer diffusion.[109]

There are three stages in the film formation. First, evaporation of water brings the polymer particles into close contact. Second, as more water evaporates, the particles undergo deformation to form a void-free solid structure which is still mechanically weak. At this stage the temperature must be above or equal to the MFT. Finally, fusion occurs among adjacent particles to give a mechanically strong film. At this stage the temperature should be above T_g. Latex paints dry as a moving front, with a dry region surrounding the wet dispersion. The diameter of the wet region decreases with time. There is some indication that the propagating front expels salts and surfactant from the spaces between the individual latex particles. A consequence of this drying mechanism is that these constituents of the dispersion tend to become concentrated in the last spot to dry.[109,110] At low ionic strength, latices of uniform particle size tend to form a colloidal crystalline phase. Ordering is promoted by Coulombic repulsions, which operate over significant distances. The structure of the dispersion determines the packing of the particles at close contact, and this structure is retained in the dried film. They tend to dry uniformly, there is no drying front, and these films are normally flat across their entire surface.[111,112]

During drying, water is lost initially at a constant rate, and then the rate slows until water loss is complete. There are several factors to contribute to this drying process: (1) as the particles deform and limit the surface area of the air-water interface, the evaporation rate slows, and eventually coalescence leads to closing of the surface; (2) the area of the wet portion of the film contracts during drying; (3) when the latex has sufficient polar polymer in its shell, it forms a continuous membrane in the film as it dries, only the water loss through this membrane with varying mechanisms may predominate; (4) a dry porous layer may form over the film—this phase is initially thin and becomes thicker as the drying proceeds, and this porous layer may control the drying rate. Depending upon the above arguments, several models were developed to explain the drying process.[113-116] While these models capture certain features of the latex drying, they are neither general nor complete.[109] Several new techniques are now used to examine the drying process such as small angle neutron scattering (SANS),[112,117] UV-visible transmission,[118] and optical microscopy.[119] Winnik summarized the effects of morphology of latices, the type and quantity of emulsifier and salts present in the latices, and the problems encountered with the definition and the measurement of MFT to the evaluation of drying mechanism of synthetic latices.[109]

There are several forces resisting and driving particle deformation and film formation during the compaction step of film formation. The resisting forces to particle deformation are viscoelastic in nature.[120, 121] Larger particles require larger extents of deformation to form void-free solid films. The driving forces to particle deformation are surface tension and capillary forces.[122] Particle compaction might also occur under water, in which case the polymer-water interfacial tension would minimize the surface area.[123] Capillary force exerts a vertical compression on the system. Thermodynamically, there is no distinction between the osmotic pressure and the mean capillary pressure which develops when the meniscus intercepts the surface of the particles.[109,124,125] There will be some contribution of capillary forces to osmotic pressure as the system becomes more concentrated before the particles come into contact. Ultimately, osmotic pressure must converge to mean capillary pressure once the particles are in contact. Crowley, Sanderson, Morrison, Barry, Morton-Jones, and Rennie determined that when the osmotic pressure increases 1% of the equilibrium vapor pressure of the water, the force should be sufficient to densify the film.[125] Dobler, Pith, Holl, and Lambla designed experiments that allowed latices to coalesce in the presence of water but in the absence of evaporating water. They pointed out the importance of capillary action during evaporation and concluded that the forces due to polymer-water interfacial tensions were very small.[123,126] However, Sperry, Synder, O'Dowd, and Lesko reported the reverse is true, that capillary action does not significantly affect the coalescence process.[127]

Vandezande reported that water can substantially plasticize more hydrophilic vinyl acetate-acrylate latices.[73] As a result, the modulus of a wet vinyl acetate-acrylate copolymer latex film is considerably lower than that of a dried latex film. On the other hand, the polar and acidic groups at the surface of the latex particle associate in the dried film causing pseudo-crosslinks to form, increasing the T_g and changing the viscoelastic properties of the dry film. Although water significantly affects the coalescence process of polyVAc latices due to hydroplasticization, polymer-water interfacial tensions are not expected to contribute significantly to film formation due to the very hydrophilic nature of the polymer.[73]

The emulsifier present in the latex could either become solubilized by the latex polymer or remain as domains of a separate phase within the film. Many emulsifiers were exuded to the surface of polymer films upon drying. As a general rule, nonionic emulsifiers are often miscible with common acrylate and methacrylate polymers, whereas anionic emulsifiers are not.[109] Fourier Transform Infrared (FTIR) and atomic microscopy (AFM) techniques are used to characterize the emulsifier migration on polymer surfaces.[110,128]

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6 Colloidal Stability of Vinyl Acetate Homopolymer and Acrylic Copolymer Latices

6.1 BASIC PHENOMENA

Colloidal systems are referred as being either "stable" or "unstable." They are rather "metastable" according to the basic thermodynamics. However, it is often inconvenient and confusing to use the term "metastable" for practical purposes since its meaning can be somewhat ambiguous. Thermodynamically, at a constant temperature, a system will tend to change spontaneously in a direction, which will lower its total free energy. Latices have a tendency to phase separately because aggregation and coalescence of the particles are accompanied by a loss of interfacial area between two phases, and the interfacial free energy between the two phases is positive. Therefore, aggregation and coalescence of the particles is accompanied by a reduction in the total Gibbs free energy of the system. Passage to a state of lower free energy will therefore tend to occur spontaneously unless there is a substantial energy barrier preventing the elimination of the colloidal state. The term "colloidal stability" refers to the tendency for a latex system to remain unchanged as a colloidal dispersion as time elapses. The particles will remain dispersed as single entities for long periods of time. According to the basic thermodynamical definition, a colloid is stable if it remains in the energetically metastable state for some arbitrary or functionally determined length of time. However, if conditions are adjusted so that the energy barrier becomes negligibly small, or disappears altogether, the colloid becomes "unstable." The colloid begins to lose its initial colloidal properties such as its degree of dispersion or size before that predetermined time has passed. Thus, when stable colloids are required, the latex should be prepared in such a way that it has adequate free-energy barriers to prevent the breakdown of the colloidal state. The energy necessary to carry a system over the energy barrier comes from the Brownian motion of the particles, which results from the random bombardment of the surface of the particles by molecules of the dispersion medium (by water molecules for VAc homopolymer and copolymer latices). Thermal motion of the dispersion medium molecules transfers momentum to the polymer particles and maintains them in constant motion. The average translational energy imparted to a colloidal particle due to such a mechanism is approximately 5×10^{-21} J at room temperature. The energy involved in a collision of two particles will be about 10^{-20} J. This value will be for average particles; however, the actual energy of a given particle in a given collision may be much smaller or much higher since the distribution of energies is in accordance with the Maxwell-Boltzman distribution. Brownian motion is an inevitable concomitant of the molecular nature of the dispersion medium, and it is a mechanistic pathway determining the stability of the colloidal system. If some barriers are present between particles which discourage their close approach, then the occurrence of aggregation and coalescence is prevented and the latex is stable. These barriers arise from the balance between the various attractive and repulsive forces which are operative between two particles as they approach each other closely. The higher the barrier, the more stable the colloid. The resultant potential-energy barrier between the neighboring particles is conveniently expressed as the variation of the potential energy of a pair of particles with their separation. A reference system is used in colloid science so that the potential energy is taken zero for infinite interparticle separation. This means that the attractive free energy becomes increasingly negative as the surfaces approach each other. It is usually assumed that the contributions to total free energy from attractive and repulsive forces are additive, so that depending on the range and relative strengths of these two contributions, a variety of resultant total free-energy curves may result.

It should be kept in mind that the major factors that contribute to colloidal behavior are particle size and shape, the nature of the solid/liquid interface, and the interactions between the particles themselves and between the particles and the liquid medium. Polymer latices can often be subjected to conditions which may lead to instabilization, such as addition of various electrolytes, high temperatures, freeze-thaw cycles, high shear, etc. The surface properties of the particles in the latex play a major role in determining the colloidal behavior of the particles. They are usually controlled by the synthetic method used for the preparation of the latex (i.e., emulsion polymerization), but post-treatment can also be used to produce the desired effect. A polymer colloid particle contains a substantial number of polymer chains within the particle. These can be arranged in a crystalline, amorphous, rubbery, or glassy state. Monomer can also be retained by the particles and, hence, the particles may be swollen extensively (or minutely) with monomer. The surface groupings can arise from the initiator used, adsorbed or grafted emulsifier, use of specific comonomers, or adsorbed or grafted polymeric species. The physical state of the polymer particles is important in colloidal and hydrodynamic interactions and in drying processes. For example, if particles are soft, coalescence of particles can occur to give continuous film formation, whereas with hard particles their individuality is retained in the dry state.

An extensive literature exists relating to colloidal stability of latices, and most of the published materials are reviewed in many good books.[1-28] Thus, in this chapter a short summary of basic principles will be given, and then attention will be focused on colloidal stability of VAc homo- and copolymer latices.

6.1.1 ELECTRICAL DOUBLE LAYER INTERACTION ENERGIES

Most polymer colloids carry an electric charge in aqueous medium. This arises from ionizable groups on the particle surface, depending on the method used to prepare the polymeric particles. For VAc homopolymer and copolymer particles in latex form, anionic groups such as sulfate or carboxylate supply this electrical charge.

Surface charge on the particle influences the distribution of nearby ions in the polar medium. To maintain electroneutrality, ions of opposite charges (counter-ions) are attracted towards the surface, and ions of like charge (co-ions) are repelled away (less important) from the surface. This process, together with the mixing tendency of thermal motion, leads to the formation of an electrical double layer made of the charged surface and a neutralizing excess of counter-ions over co-ions distributed in a diffuse manner in the polar medium. This diffuse double layer is the result of thermal motions of the ions which prevent a compact ion arrangement. The net result is that close to the charged surface there is an excess of counter-ions over co-ions, the difference decreasing until, in bulk solution, they are equivalent or maintain electroneutrality. The theory of electrical double layer deals with this distributions of ions and, hence, with the magnitude of the electrical potentials that occur in the locality of the charged surface.

According to Coulomb's electrostatics law, the force between two electric charges q_1 and q_2 is separated by a distance d in a vacuum in the form

$$F = \frac{q_1 q_2}{4\pi\varepsilon_0 d^2} \tag{6.1}$$

where ε_0 is the permittivity of free space (vacuum). If q_1 and q_2 have the same sign, the force is a repulsion; if they are of opposite sign, the force is an attraction.

In the presence of a medium surrounding both charges, the force is reduced by a factor $\varepsilon_r = \varepsilon/\varepsilon_0$, the *relative permittivity* (or *dielectric constant*) of the medium. The work done in bringing two charges together from infinite separation to a distance d in a medium of permittivity ε measures the electrostatical free energy of the system relative to that at infinite separation and is given by

$$\Delta W = -\int_{\infty}^{d} F\, dh = \frac{q_1 q_2}{4\pi\varepsilon d} \tag{6.2}$$

The charge q_1 may be thought of as producing an electric field at a point d. The work needed to bring a unit charge to this point is called "electrical potential" at d due to the charge q_1 and is denoted by Ψ. Electrical potential at d is given as

$$\Psi = \frac{q_1}{4\pi\varepsilon d} \tag{6.3}$$

The work done to bring up a charge q_2 to this point is $q_2\Psi$ and is positive if q_2 is positive and vice versa. For the understanding of the electrostatistics of electrolyte solutions, we need Boltzmann's distribution law, which relates the probability of particles being at a given point at which they have a potential energy, or free energy, ΔG, relative to some chosen reference state. This probability may be expressed in terms of the average concentration, c, at the point considered relative to that, c^0, at the reference level, taken as the zero of energy. If the temperature is, T, then

$$c = c^0 \exp\left(-\frac{\Delta G}{kT}\right) \tag{6.4}$$

Boltzmann's law indicates that if at some point in an electrolyte solution there is an electrical potential, Ψ, then in the region of that point the concentration of the positive ions will be

$$c\,(+) = c^0 \exp\left(-\frac{z_+ e\Psi}{kT}\right) \tag{6.5}$$

where z_+ is the valency of the positive ion, e is the elementary charge, and c^0 is the concentration of positive ions in a region where $\Psi = 0$. Similarly, we can write for negative ions

$$c\,(-) = c^0 \exp\left(-\frac{z_- e\Psi}{kT}\right) \tag{6.6}$$

There will therefore be an imbalance of electrical charges in this region, which in the case where $z_+ = z_- = 1$ is

$$c\,(+) - c\,(-) = c^0\left[\exp\left(-\frac{e\Psi}{kT}\right) - \exp\left(-\frac{e\Psi}{kT}\right)\right] \tag{6.7}$$

If the region under consideration is close to a negative ion, then Ψ will be negative and [c(+) – c(–)] will be positive. This means that around a negative ion there will be an excess of positive charge, which is called "charge cloud" or "ionic atmosphere." Since the electrolyte solution as a whole is electrically neutral, the integral [c(+) – c(–)] dv taken over the whole volume (v) of the solution outside the negative charge must exactly balance that charge. In colloid science, we are particularly interested in the ionic atmosphere, which is developed around a charged colloid particle rather than around a single ion. In this context it is usual to call this ionic atmosphere an "electrical double layer." It is convenient for a treatment of an electrical double layer to assume that the particle surface is smooth and that the charges (point charges) are uniformly spread over the surface according to the Boltzmann distribution. The dispersion medium (water) is assumed to influence the double layer only through its dielectric constant, which is assumed to have the same value throughout the diffuse part.

The thermal motion causes the counter-ions to be spread out in space, forming a "diffuse double layer" in which the local concentration is determined by Equation 6.7. The electrical potential in the solution falls off exponentially with distance from the surface. For the plane surface case

$$\Psi = \Psi_0 \exp(-\kappa x) \tag{6.8}$$

($1/\kappa$) is called the "thickness of the double layer." At a distance ($1/\kappa$), the electrical potential drops by a factor of ($1/e$). The thickness of the double layer depends markedly on the ionic concentration. As the concentration increases, the thickness of the double layer decreases rapidly.

In latex stability, we have to consider not only the nature of a single double layer but also the way in which the double layers surrounding two colloid particles interact with one another when they come together. When two similarly charged colloid particles with their associated double layers move toward one another, they will begin to "feel" one another's presence. Two ionic charge clouds of the same sign repel one another in much the same way as do the electron clouds around atoms and molecules. Alternatively, the double layers may be thought of as screening the charges on the colloid particles from one another. A charged particle with its neutralizing double layer looks like an uncharged entity, seen from a sufficient distance. At closer separations, the screening is incomplete and each particle sees the other one as a partially charged particle of the same sign, and as a consequence the particles repel one another. Mathematical approximations and physical simplifications are required in order to obtain a solution to this phenomenon. The repulsion energy is dependent on the charge of the particle and, hence, on the electrical potential at its surface and on the electrolyte concentration.

6.1.1.1 Surface Charge Density

The "surface charge density" is a fundamental quantity for any charged surface and is given by

$$\sigma_0 = v\, e\, N_S \tag{6.9}$$

where the subscript zero denotes that this is the location of the surface, N_S is the number of charged sites per unit area, e is the fundamental unit of electricity (1.6×10^{-19} Coulomb), and v is the magnitude of the charge of the ion (the valency of the ion), i.e. 1, 2, or 3, depending on its chemical nature. The actual values of surface charge density normally lie between about 0.5 – 12.0 μC–cm^{-2}. For $\sigma_0 = 10.0$ μC–cm^{-2}, the average occupied per charged site is 1.6 nm^2.

In order to estimate the surface charge density, an acidic latex in the Na^+ form can be converted into the H^+ form by passing it through an ion-exchange resin column. The latter ions can then be titrated with a standard alkali solution either potentiometrically or conductimetrically. Provided a known weight of latex particles is used for the titration and the surface area is known, the number of charges per unit area of surface, N_S, can be determined and σ_0 calculated.[28,29]

6.1.1.2 Surface Potential

The surface of a particle acquires a surface electrostatic potential of magnitude Ψ_0 which can be either positive or negative depending on the chemical nature of the surface groups. The electrical double layer is often divided into two parts with one layer of counter-ions close to the surface at a distance, δ, (Stern layer thickness) of approximately the radius of a hydrated ion; the rest of the counter-ions are spread out in a spatial domain, the extension of which depends on the salt concentration in the bulk of the electrolyte solution. Thus, Ψ_0 denotes the electrostatic potential at the particle surface, and Ψ_S the potential just outside the layer of the bound counter-ions at the beginning of the diffuse layer. Ψ_S controls the colloidal stability of the system for most of the latices. Eq. 6.8 shows the distribution of cations and anions in the diffuse layer obeying the Boltzmann distribution law. Similarly, for low potentials ($\Psi_S < 25$ mV) for a spherical particle of radius R at a distance r from the center of the particle, the surface potential is given as

$$\Psi_r = \Psi_S \, R \exp\left[\kappa\left(R - r\right)\right] \big/ r \tag{6.10}$$

The parameter, κ, has dimensions of reciprocal length and is given by

$$\kappa^2 = \frac{2\mathrm{n_0 v^2 e^2}}{\varepsilon_r \varepsilon_0 \mathrm{kT}} = \frac{\mathrm{N_A\ e^2 I}}{\varepsilon_r \varepsilon_0 \mathrm{kT}} \tag{6.11}$$

where n_0 is the number of ions of each type present per unit volume of the bulk phase, v the magnitude of the charge of the ion (the valency of the ion), I is the ionic strength of the electrolyte solution, ε_0 is the permittivity of free space 8.85×10^{-12} F m^{-2}, ε_r is the relative permittivity of the medium, N_A is Avogadro's number, k is the Boltzmann constant, and T is the absolute temperature. $(1/\kappa)$ is often called "double layer thickness."

The parameter, κ, can be determined experimentally by direct measurement of the electrostatic force of repulsion between two crossed mica hemicylinders.[30,31] The electrostatic force of repulsion, F_{el}, is given for this situation as

$$\ln\left[\frac{F_{el}}{2\pi R_h}\right] = \ln\left[\frac{64 n_0 kT}{\kappa}\gamma^2\right] - \kappa h \tag{6.12}$$

where R_h is the radius of curvature of the hemicylinder, h is the distance between the surfaces, and

$$\gamma = \frac{\left[\exp\left(\dfrac{\mathrm{v e}\Psi_S}{2\mathrm{kT}}\right) - 1\right]}{\left[\exp\left(\dfrac{\mathrm{v e}\Psi_S}{2\mathrm{kT}}\right) + 1\right]} \tag{6.13}$$

The force is measured by using a transducer and the separation distance using a multiple-beam interferometer. When a ln $[\mathrm{F_{el}}/2\,\pi\, R_h]$ versus h (in nm) plot is drawn, a value of κ can be obtained from the gradient, and a value of γ from the intercept. Surface potential may also be estimated by using Eq. 6.12, but it is more convenient to apply electrokinetic experiments, particularly electrophoresis, even with simple equipment. Electrophoresis is the movement of a charged particle plus attached material relative to a stationary liquid by an applied electric field. When an electrical force is applied to a particle having a charge of q, the viscous force of the medium opposes the movement of the particle. The two opposing forces are equal when the particle is in a state of steady-state motion so that

$$u = \frac{qE}{6\pi\eta R} \tag{6.14}$$

where u is the speed of the particle, E is the electric field strength, η is the viscosity of the medium, and R is the radius of the particle. Now the electrokinetic or zeta potential (ξ) at the surface of a sphere of radius R and carrying a charge q is defined as

$$\xi = \frac{q}{4\pi\varepsilon R} \tag{6.15}$$

where ε is the permittivity of the medium in which it is immersed. By combining Eqs. 6.14 and 6.15 and taking $\varepsilon = \varepsilon_0\, \varepsilon_r$ by definition, one obtains

$$u = \frac{3}{2}\frac{\varepsilon_0\varepsilon_r\xi}{\eta}E \qquad for \qquad \kappa R \langle\langle 1 \tag{6.16}$$

and

$$u = \frac{\varepsilon_0\varepsilon_r\xi}{\eta}E \qquad for \qquad \kappa R \rangle 100\,. \tag{6.17}$$

The exact location of the shear plane (which, in reality, is a region of rapidly changing viscosity) is an unknown feature of the electrical double layer. In fact, the exact nature of zeta potential is still a matter of some discussion and, theoretically, $\xi \le \Psi_S$ relationship should hold. In tests of electrical double layer theory it is customary to assume the identity of Ψ_S and ξ. The bulk of experimental evidence suggests that errors introduced through this assumption are usually small. Any difference between Ψ_S and ξ will clearly be most pronounced at high potentials and at high electrolyte concentrations. If the particle under investigation is in the form of a reasonably stable emulsion containing microscopically visible particles, the electrophoretic behavior can be observed and measured directly. The electrophoresis cell usually consists of a horizontal glass tube of either rectangular or circular cross-section with an electrode at each end. The electrophoretic velocity is found by timing individual particles over a fixed distance on a calibrated eyepiece.

Zeta potential, ξ, is a useful and readily accessible practical quantity despite its limited theoretical understanding. It establishes whether the particle is positively or negatively charged or has no apparent charge. It can also be used to monitor changes in mobility with pH, with variation in electrolyte concentration, and with addition of various additives such as emulsifiers, polymers, polyelectrolytes, etc.[28] The measurement of particle mobility as a function of pH and p(conductivity) was suggested to identify the nature of the surfaces of colloidal polymer particles.[32,33]

6.1.2 VAN DER WAALS ATTRACTION ENERGIES

van der Waals recognized the existence of attractive forces between nonpolar molecules in 1873, and London described how they could be calculated by a quantum mechanical discussion of the interaction between fluctuating dipoles arising from the motions of the outer electrons on the two molecules. van der Waals attraction forces (or London dispersion forces) increase in magnitude as the molecules approach one another, and at a separation of r between the nuclei of atoms (or the center of mass of roughly spherical molecules) they are proportional to the inverse seventh power of the separation. The work done in separating reversibly a pair of molecules from a distance d to infinity can be calculated by integrating this attractive force between this range:

$$\Delta W = -\int_d^{\infty}\left(-\frac{A}{r^7}\right)dr = \frac{A}{6d^6} = \frac{A'}{d^6} \tag{6.18}$$

Since the energy at infinite separation is zero, the free energy of attraction between a pair of molecules at a separation d is

$$\Delta G^{att} = -\Delta W = -\frac{A'}{d^6} \tag{6.19}$$

The constant A' is a quantum mechanical quantity and is related to the nature of individual molecules. London gives A' for the interaction of two identical molecules in the form

$$A' = \frac{3}{4}h_p\, v\alpha^2 \tag{6.20}$$

where α is the electronic polarizability of the molecule, h_P is Planck's constant (6.63×10^{-34} Js), and v is a characteristic dispersion frequency identified with that corresponding to the first ionization potential.

The attractive force increases and the free energy becomes increasingly negative as the atoms approach one another. However, at close distances, their electron clouds begin to interact. If the electrons are in nonbonding orbitals of the molecules, this gives rise to a repulsive force and an increase in free energy which becomes effectively infinite when the electron clouds interpenetrate. This repulsion is called "Born

Repulsion." Its contribution to the intermolecular potential is given approximately, for a distance d apart as

$$\Delta G^{rep} = \frac{B'}{d^{12}} \tag{6.21}$$

Lennard-Jones assumed that the total potential energy of interaction between a pair of molecules is equal to the sum of the contributions from attractive and repulsive forces

$$\Delta G^{Tot} = \Delta G^{rep} + \Delta G^{att} = \frac{B'}{d^{12}} - \frac{A'}{d^{6}} \tag{6.22}$$

This is known as Lennard-Jones potential between a pair of molecules.

When the potential energy between two particles is considered, it is assumed that every molecule in one particle interacts with each molecule in the other according to a Lennard-Jones potential, and the total free energy of interaction is obtained by summing the contributions from all possible pairs of molecules. Born repulsion is neglected in these circumstances except for those molecules on opposing surfaces. Hamaker calculated the simplest case is that of two hard, flat, effectively infinite plates a distance, h apart.[34] For unit area of surface

$$\Delta G^{att} = -\frac{A_H}{12\pi h^2} \tag{6.23}$$

where, A_H is called a Hamaker constant. It is related with London's A' constant so that

$$A_H = A'\pi\, q^2 = \frac{3}{4}\, h_P\, v\alpha^2\, \pi^2\, q^2 \tag{6.24}$$

where q is the number of molecules in unit volume of particles.

The above equations given for particle interactions were derived for the situation in which the interacting units were separated by a vacuum. However, interacting particles are separated by some medium in real conditions. This medium itself contains atoms or molecules that will impose their own effects on the system as a whole. The particle surfaces will experience a reduced mutual attraction due to the presence of the units of the third (medium) component. This situation is very complex theoretically. However, for most practical cases, a simple approximation of a composite Hamaker constant is found to be sufficient. Then, for this situation, A_H has to be rewritten as a composite constant A_c in the form

$$A_c = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2 \tag{6.25}$$

with A_{11} as the constant for the polymeric particles and A_{22} the value for the medium. When $A_{22} = 3.70 \times 10^{-20}$ J is assumed for water, $A_{11} = 8.84 \times 10^{-20}$ J is calculated for polyVAC, and 7.11×10^{-20} J for polyMMA.[28,35] An important result of the relationship in Eq. 6.25 is that as the vacuum Hamaker constants for 1 and 2 become closer in value, A_c tends toward zero and the free energy of attraction between the particles tends toward zero. This means that since the force of attraction is decreased, any repulsive term necessary to maintain an adequate value of ΔG_{max} is also reduced. This fact can be used to manipulate the stability of colloids.

When two spherical particles in a vacuum are considered, Hamaker found that the energy of attraction can be expressed as

$$V_A = -\frac{A_H}{12}\left[\frac{1}{x^2+2x} + \frac{1}{x^2+2x+1} + 2\ln\left(\frac{x^2+2x}{x^2+2x+1}\right)\right] \qquad (6.26)$$

where, $x = h/2R$, h is the distance of surface-to-surface separation, and R is the particle radius. For the condition that $R \gg h$, this reduces to[5,28]

$$V_A = -\frac{A_H\, R}{12\, h} \qquad (6.27)$$

Another approximation is given as[36]

$$V_A = -\frac{A_H}{12}\left[\frac{L}{h} + 2\ln\frac{h}{L}\right] \qquad (6.28)$$

where $L = R + 3h/4$. At values of h beyond 100 nm, a “retardation effect” starts which weakens the attraction between particles. The interactions resulting from fluctuating dipoles is effectively instantaneous at close distances. However, for long distances, the time required for the electromagnetic signal of one unit to travel to its neighbor (at light speed), polarize the local electron cloud, and receive the return signal of said polarization is long relative to the “lifetime” of the original dipole. This retardation effect is generally ignored for atoms or molecules; however, for larger units such as colloidal particles, this effect is significant. An approximate equation is given for the retardation effect by Kitchener and Schenkel.[37]

6.1.3 POTENTIAL ENERGY CURVES

According to the classic DLVO theory which was developed by Derjaguin and Landau[38] and Verwey and Overbeek[1] in the 1940s, the stability of colloidal particles having surface charges can be explained using the potential energy diagram. It is assumed that the contributions to the total free energy from attractive and repulsive forces are additive, so depending on the range and relative strengths of these two contributions, a variety of resultant total free-energy curves may result. The particles are usually assumed to be spherical, and they are commonly said to display "hard-sphere" interaction.

Following the DLVO hypothesis and including the Born repulsion, when smooth spherical particles with charged surfaces are considered, the total potential energy of interaction, V_T, is composed of three terms, so that

$$V_T = V_R + V_A + V_B \tag{6.29}$$

where V_R = repulsion electrostatic energy, V_A = van der Waals' attraction energy, and V_B = Born repulsion energy. V_T is evaluated as a function of separation distance, h.

The force of electrostatic repulsion between two charged, crossed, hemicylindrical surfaces is given by Eqs. 6.12 and, 6.13. This is, in fact, equivalent to interactions between a sphere and a flat plate. When Eq. 6.12 is integrated, it directly leads to the potential energy of electrostatic repulsion,

$$V_R = \int_0^\infty F_{el}\, dh = \left[\frac{64 n_0\, kT\gamma^2}{\kappa} \ \exp(-\kappa h) \right] \frac{2\pi R_h}{\kappa} \tag{6.30}$$

where R_h is the radius of curvature of the hemicylinder and the term in square brackets is the expression for interaction between flat plates. When only two spherical colloidal particles are considered, the expression can be changed into a form containing the terms of particle radius, R, and either the distance of surface-to-surface separation, h, or the center-to-center distance between the particles, r. For the condition that $\kappa R < 3$, then[28]

$$V_R = 4\pi\varepsilon_r\varepsilon_0\Psi_S^2\, R^2 \ \ \exp(-\kappa h)/(h + 2R) \tag{6.31}$$

or

$$V_R = 4\pi\varepsilon_r\varepsilon_0\Psi_S^2\, R^2 \ \ \exp(2\kappa R) \ \ \exp(-\kappa r)/r \tag{6.32}$$

For $\kappa R > 10$, then

$$V_R = 2\pi\varepsilon_r\varepsilon_0\Psi_S^2\, R \ \ln\left[1 + \exp(-\kappa h)\right] \tag{6.33}$$

and for intermediate values where $3 < \kappa R < 10$,

$$V_R = 2\pi\varepsilon_r\varepsilon_0 \left(\frac{4kT}{e} \right)^2 R\gamma^2 \ \exp(-\kappa h)/v^2 \tag{6.34}$$

V_R is frequently divided by kT and expressed as V_R/kT to give the magnitude in dimensionless unit.

V_A is the van der Waals attraction energy, and one of the Eqs. 6.26 to 6.28 is used according to the conditions of the colloid.

V_B is the Born repulsion energy. As already explained, it is a very short range repulsion which arises at close approach for molecular orbital overlap. Born repulsion causes the potential energy to increase to very large positive values at very small interparticle separations. The Born repulsion is usually represented as a cutoff potential at a distance of about one atomic diameter from the origin.[14]

The total potential energy expression depends on a number of assumptions such as neglect of ion size, the approximate nature of Hamaker constant, assumption of a smooth surface, and a smeared-out surface charge. However, the potential energy curve provides an excellent working hypothesis for understanding the complex behavior of colloidal dispersions. The form of this curve is given in Figure 6.1 for interaction between two spherical particles. It has some characteristic features to help the understanding of colloidal stability:

A- *Primary Minimum*: At small separations, the attraction is the dominant effect. This deep minimum determines the closest approach, h_0, at short distances of surface separation. The depth is related to twice the dispersive contribution to the surface energy.

B- *Primary Maximum*: The electrostatic repulsion can be larger in magnitude than the electrostatic attraction at intermediate distances and, hence, a maximum seen in the potential energy curve. The magnitude of the primary maximum is represented by V_{Max}. When it is greater than about 10 kT, i.e., an order of magnitude larger than the average kinetic energy of the particles, conditions are favorable for the formation of a stable colloid.

C- *Secondary Minimum*: The potential energy curve is influenced by the exponential decay of the repulsion relative to the $1/h$ dependence of the attraction at large distances. It follows that the attraction must again dominate at large distances because an exponential fall-off is much faster than the inverse power. Consequently, another minimum can occur in the curve, which is called a secondary minimum, and its magnitude is shown by V_{SM}. A colloid in this region may be subjected by weak or secondary minimum flocculation. Because of the shallow nature of the secondary minimum, the flocculants formed are held together rather weakly and tend to be unstable, that is, they can be broken up by rather small energy inputs such as gentle stirring.[39] For very small particles having diameters less than 200 nm, the secondary minimum may be so shallow that Brownian motion prevents flocculation altogether. In other cases a dynamic equilibrium may develop between small flocs and individual colloidal particles.

D- *Activation Energy of Particle Approach*: $\Delta V_f / kT$.

E- *Activation Energy of Particle Separation*: When two particles are located in the primary minimum, the activation energy to separate and redisperse them is ΔV_b. In general, $\Delta V_b >> \Delta V_f$, and, once particles are brought together in a primary minimum, considerable energy is needed to redisperse them.

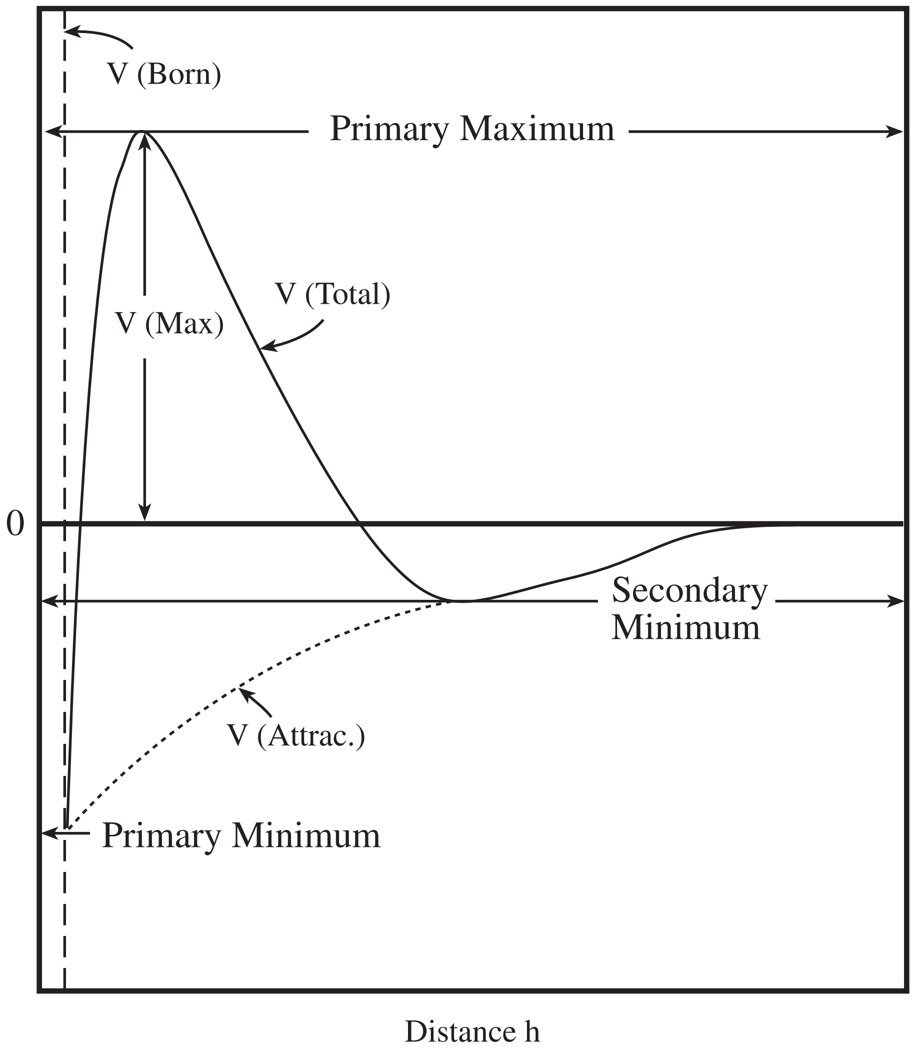

FIGURE 6.1 Potential energy variation with distance between two spherical particles.

The total interaction energy, V_T, is always attractive for very small and very large distances. It may be attractive for all distances, and then the system is unstable. Alternatively, there may be a range of distances over which the repulsion dominates. The energy barrier represented by V_{Max} prevents the particles from coming together. In practice, as two charged particles approach each other, their electrical double layers will begin to overlap. Since the electrical double layers are of the same sign, their interaction will be repulsive, leading to an increase in the electrical potential and, thus, in the total free energy of the system. In summary, such interactions will represent an energy barrier to the approach of the two particles. In order for aggregation to occur, two particles must collide, and do so with sufficient force that the collision will be effective, or "sticky." If they cannot approach sufficiently because of the repulsive energy barrier, they cannot form aggregates or coagulum. The height and thickness of this barrier are very important. It turns out that coagulation behavior is determined almost entirely by the height of the barrier, V_{Max}. The value of V_{Max} depends on the magnitude of Ψ_0 and $1/\kappa$ and hence will be reduced by increasing the concentration and valency of the electrolyte in the system. In practice it is well known that addition of sufficient electrolyte to stable colloid usually leads to coagulation.

Since a colloidal particle is undergoing Brownian motion because the surrounding solvent molecules are bombarding it, it can either be knocked toward the second particle or knocked in the opposite direction and will be more easily driven away than driven toward the second particle. Nevertheless, there is a finite probability that it can finally fight its way over the barrier. As the concentration of the electrolyte is increased, the electrostatic potential is lowered, making it easier for particles to pass into the primary minimum so that the barrier becomes lowered; a point is reached at which it just disappears, which is the critical coagulation concentration (c.c.c.). At critically high electrolyte concentrations, the energy barrier is removed and the total potential energy remains negative at all times, so the particles attract one another at all separations (see Sec. 6.3.1).

6.2 STERIC STABILIZATION

6.2.1 MECHANISM OF STERIC STABILIZATION

Colloidal particles having no surface charges are stabilized with a different mechanism called "steric stabilization." The mechanism involves the presence of a hydrophilic (or lyophilic) macromolecule (usually a synthetic polymer) which adsorbs onto the colloidal particle surface and provides a stabilization mechanism. It has been known empirically that the addition of certain natural biopolymers such as gelatin can stabilize colloids. The earliest example is the use of natural gums by the ancient Egyptians to prepare inks 2000–3000 years ago.

In industry, many colloids are prepared by emulsion polymerization with the help of a stabilizing action provided by added hydrophilic colloids (or protective colloids) during manufacture. PolyVAc homo- and copolymer latices, which are prepared in the presence of water-soluble macromolecules such as polyvinyl alcohol, hydroxyethyl cellulose protective colloids, and nonionic emulsifiers, are also stabilized with the steric stabilization mechanism.

Steric stabilizers need not carry an electrical charge in order to be effective. They should at least be partially soluble in the liquid medium and possess a high molecular weight to prevent close approach of the particles. One portion of their macromolecule should be relatively insoluble in the dispersion medium (water for polyVAc colloids) and have a high tendency to adsorb firmly onto the particle surface. For example, for partially hydrolyzed polyvinyl alcohol protective colloids, the nonhydrolyzed polyvinyl acetate portion (about 12%) adsorbs on to the polyVAc particles, whereas the water-soluble, completely hydrolyzed polyvinyl alcohol portion (about 88%) is soluble in water medium. The layer of bound macromolecule should be of sufficient density to provide steric interference when particles approach each other closely, but should not be too dense because dense layers do not provide effective repulsive forces between the particles.

Polymeric protective agents or steric stabilizers must be strongly anchored to the particle surface at a minimum of one point or, even better, several points. If single-point attachment is involved, the result will be a system with a free-swinging "tail" projecting into the dispersion medium (see Figure 6.2). If two or more points are involved, the result will be the formation of various "loops" and, possibly, some tails as well. There are also "trains" lying on the surface. For the same polymer chain length, one can think intuitively that, in a system of tails, the distance the protective layer extends into the solution will be greater than a comparable system of loops, and a single-point attachment would provide better stabilization. However, for loops, once interpenetration begins, there will be twice as many units affected by the volume restriction effect, leading to a stronger entropic effect. In most practical situations both tail and loop configurations are operative and it is difficult to comment which configuration is better than another. Nevertheless, the net result is the formation of a relatively thick adsorbed layer that can impose the stability of the colloid. Heller and Pugh were the first to use the "steric protection" term and to offer a mechanism to their colloidal stability phenomenon.[40]

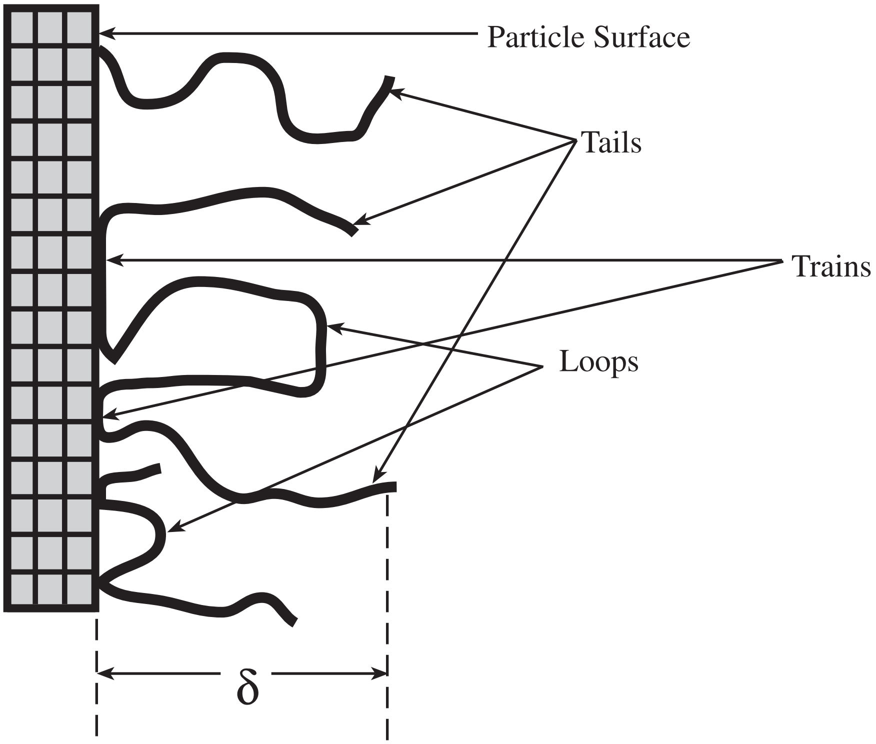

FIGURE 6.2 Adsorption of polymers on particle surface: types of attachments. δ is the average thickness of the absorbed layer.

If two colloidal particles have an adsorbed layer of a hydrophilic polymer, as they approach each other those layers begin to interpenetrate (see Figure 6.2). Then, the increase of the local concentration of the adsorbed polymer segments between the two particles causes an osmotic effect that will force the dispersion medium into the region between the surfaces to reduce the segment concentration and drive the surfaces apart. In reality, the local osmotic pressure in the interpenetrating region will increase over that in the solution; consequently, to maintain equilibrium it becomes necessary to draw water molecules from an external region. Secondly, the volume restriction decreases the local entropy because the interaction species begin to lose certain degrees of freedom due to crowding. The movement of adsorbed polymeric chains is constrained, leading to a reduction in the number of configurations they can adopt, which implies a reduction in the local entropy. This contribution to the intermolecular potential is called "entropic repulsion." From the stabilization point of view, the decrease of entropy is unfavorable. On the other hand, the osmotic effects may be accompanied by an unfavorable enthalpic effect due to desolvation of the more closely packed polymer units. Thermodynamically, in order to regain the lost entropy, the particles must move, allowing them more freedom of movement, while the dispersion medium moves to resolvate the units. Consequently, the result is an energy barrier retarding the approach of particles and providing an effective mechanism for stabilization.

The steric stabilization mechanism contrasts with electrostatic stabilization in certain important respects. It is relatively insensitive to the presence of electrolytes dissolved in the dispersion medium, and it can be conferred even if the dispersion medium is of low polarity and low permittivity. It is generally more sensitive to changes of temperature than is electrostatic stabilization, partly because entropic effects make a greater contribution in the Gibbs free energy change than they do in electrostatic stabilization, and partly because the solvency of water for water-soluble macromolecules can be very temperature-sensitive. However, steric stabilizers possess a very important practical property: they prevent the coagulation of colloidal dispersions on freezing because, without them, the electrolyte concentration increases in the equilibrium solution phase with the separation of ice crystals. Steric stabilizers can be effective under conditions where diffuse electrical double layers are compressed to such an extent that they are almost unable to confer colloidal stability. Thus, steric stabilization is the most effective way of stabilizing hydrophobic colloids, which have aqueous dispersion media of high ionic strength.

Stabilizing macromolecules should be firmly anchored to the particle surface in order to prevent desorption or lateral movement of the stabilizer as two particles approach each other. Anchoring may be done either by strong adsorption or by covalent bonds. However, there are instances where weak adsorption can occur by way of hydrophilic groups by interaction with other hydrophilic groups which are firmly bound to the surface in low concentration. An example is the adsorption of polyethylene oxide from aqueous medium onto the surface of nonpolar solids; a possible attachment mechanism is hydrogen bonding between some of the hydrophilic units of macromolecules and polar groups, such as hydroxyl and carboxyl, which are either covalently bonded at the solid surface or are themselves strongly adsorbed.

If the stabilizer macromolecule is bound by adsorption, then the hydrophilic-hydrophobic balance of the macromolecule in relation to the aqueous dispersion medium should be such that an adequate mixing tendency is combined with an adequate binding tendency. Otherwise, if the hydrophilic tendency is too great, the macromolecule will desorb from the surface; if the hydrophobic tendency is too great, the macromolecule will collapse against the particle. The more effective macromolecular steric stabilizers usually have amphipatic character such as block and graft copolymers. The comb-type of graft copolymer has been used with considerable success. Backbone adsorbs at the particle surface and the "teeth" have a strong tendency to extend into the dispersion medium.

The layer of bound macromolecules should be of sufficient thickness to prevent the close approach of the particles. Other things being equal, the effectiveness of a steric stabilizer will increase with increasing molecular weight. It also implies that the effectiveness of a steric stabilizer will increase with increasing solvency of the dispersion medium for the hydrophilic segments of the macromolecule, because the latter will then adopt a more expanded conformation.

6.2.2 STERIC INTERACTION ENERGY

As explained in Section 6.1.2 and shown in Figure 6.1, van der Waals attraction energy decreases with the increase of the separation distance between particles. In addition, as explained by Eq. 6.25, if the particles have a surrounding layer with a Hamaker constant similar to the dispersion medium, this surrounding layer simply acts as a spacer and prevents the surfaces of core particles from approaching close to each other. When steric stabilizer macromolecules are adsorbed onto the polymeric particles with radius R, they form a surrounding layer with a thickness of δ. Initially, this layer was thought to prevent the surfaces of the core particles from approaching to a distance of less than 2δ. Vold was the first to investigate the influence of a uniform layer of thickness, δ, on the energy of attraction, V_A. He obtained expressions which showed that a reduction of attraction could be achieved by this mechanism.[41] This theory was improved by several authors.[23,25,28,42] It was found that both the adsorbed and grafted layers on the particle surface are producing a repulsion greater than that expected on the basis of electrostatic effects. When the particles approach each at a distance less than 2δ, an overlap region forms; that is, the length of core particle separation, h, is shorter than δ. Depending on the surface concentrations of the groups, the chains either have to interpenetrate or change their conformation by bending backwards, leading to "*denting*" of the surface. If two colloidal particles begin to interpenetrate (see Figure 6.2), the increase of the local concentration of the adsorbed polymer segments between the two particles causes an increase in the local osmotic pressure in the interpenetrating region. Consequently, it becomes necessary to draw water molecules from an external region to maintain thermodynamic equilibrium. In addition, the volume restriction decreases local entropy because the interaction species begin to lose certain degrees of freedom due to crowding. The movement of adsorbed polymeric chains is constrained, leading to a reduction in the number of configurations they can adopt, which implies a reduction in the local entropy.

The V_S term is used to represent the potential energy of steric repulsions. The relation between V_S, h, and δ is very complex, and universal agreement has not yet been reached.[9,15-18,24,27,28] A simple approach, depending mainly on Ottewill's publications,[8,27] will be presented here.

When the adsorbed layers are assumed to be uniform, then the overlapping of the two layers causes a decrease of the local volume and an increase in the osmotic pressure, which is termed as "excess osmotic pressure," π_e. Thus, when the particles are far apart it can be considered that the solution is ideal and of chemical potential, μ_0; when overlap occurs it becomes nonideal and of chemical potential, μ; so that

$$\mu - \mu_o = \pi_e \bar{V}_1 \tag{6.35}$$

where $\bar{V}_1$ is the partial molar volume of the solvent. The excess osmotic pressure is then related directly to the second virial coefficient, B, for interaction between the molecules in the overlap region, giving

$$\pi_E = B\,R\,T\,c_g^2 \tag{6.36}$$

where c_g is the mass concentration of the material in the overlap region. Then, V_S is expressed in terms of c_g, h, δ and B so that

$$\frac{V_S}{kT} = 2\,B\,N_A c_g^2 \left[\left(\delta - \frac{h}{2}\right)^2 \left(3R + 2\delta + \frac{h}{2}\right)\right] \tag{6.37}$$

with the first term being the interaction term and the second, in square brackets, the geometric factor. It seems that there is little repulsion with the adsorbed layers far apart, but very strong repulsion takes place once the layers start to overlap. Thus, for well-packed and uniform adsorbed layers, the interaction becomes very close to that of "hard-spheres."

When the Flory-Krigbaum equation is used to evaluate the second virial coefficient, B, it gives

$$\frac{V_S}{kT} = \frac{4\pi c_g^2}{3\bar{V}_1 \rho_2^2}\left(\psi_1 - \chi_1\right)\left(\delta - \frac{h}{2}\right)^2 \left(3R + 2\delta + \frac{h}{2}\right) \tag{6.38}$$

where ψ_1 is an entropy parameter for the mixing of molecules in the overlap region and is taken as 0.5 for ideal mixing, and χ_1 is the polymer-solvent interaction parameter which characterizes the interaction of the adsorbed polymer molecule with water. When ψ_1 is assumed to be 0.5, then if $\chi_1 = 0.5$, V_S becomes zero, if $\chi_1 > 0.5$, V_S is negative, and if $\chi_1 < 0.5$, V_S is positive.

The adsorption of macromolecules on particle surface causes the surface excess, Γ_2. The concentration term, c_g, can be directly related to in a layer of thickness, δ, since

$$c_g = \frac{\Gamma_2 M_2}{\delta} \tag{6.39}$$

where Γ_2 is in moles per unit surface area, and M_2 the molar mass of adsorbed macromolecules

.It should be noted that the thickness of the adsorbed layer, *δ*, is not a quantity that can be precisely defined. It depends on the segment-density distribution for a macromolecule which is adsorbed at a solid surface and extends into a liquid phase. The segment–density distribution function, denoted by $\rho(u)$, characterizes the manner in which the segment, concentration varies with distance from the surface. $\rho(u)$ is defined as the concentration of polymer segments in the dispersion medium at a distance u from the surface. Correspondingly, δ can be defined as the minimum value of u at which $\rho(u)$ becomes effectively zero.

The above derivations only take account of molecular mixing in the overlap region. Napper discussed other factors such as configurational changes of macromolecules on compression and the elasticity of the surrounding layer.[9] Napper described the region $2\delta > h > \delta$ as the "inter-penetration domain," and the region $\delta > h$ as the "inter-penetration plus compression domain." Statistical mechanics were also applied to this problem.[23]

The potential energy of steric interactions should be included in the total potential energy expression, so that Eq. 6.29 becomes

$$V_T = V_R + V_A + V_B + V_S \tag{6.40}$$

The V_R term is neglected if the surface of the colloidal particles are uncharged. In this case, the potential energy-separation distance plot is given in Figure 6.3, where the long-range repulsive potential arises from only steric contributions, V_S. It is seen in this figure that the stability is attained for Curve 1 but not for Curve 2; the thickness and/or density of the steric layer is insufficient to prevent the coagulation of the latex.

6.2.3 EFFECT OF THE SIZE OF PARTICLE AND STABILIZING POLYMER

When a polymer is dissolved in a solvent, its size is best described with a constant radius of gyration, R_G. When we compare the R_G with the mean radius of the colloidal particle, R, there are three possibilities:

1. $R >> R_G$
   The added macromolecule can adsorb onto the particle surface and act as a stabilizer. This is the case explained above.
2. $R \approx R_G$
   There is the possibility that the various possible points of attachment will encounter two different particles rather than attach to the same particle. Attachment of the same polymer chain to two particles essentially ties

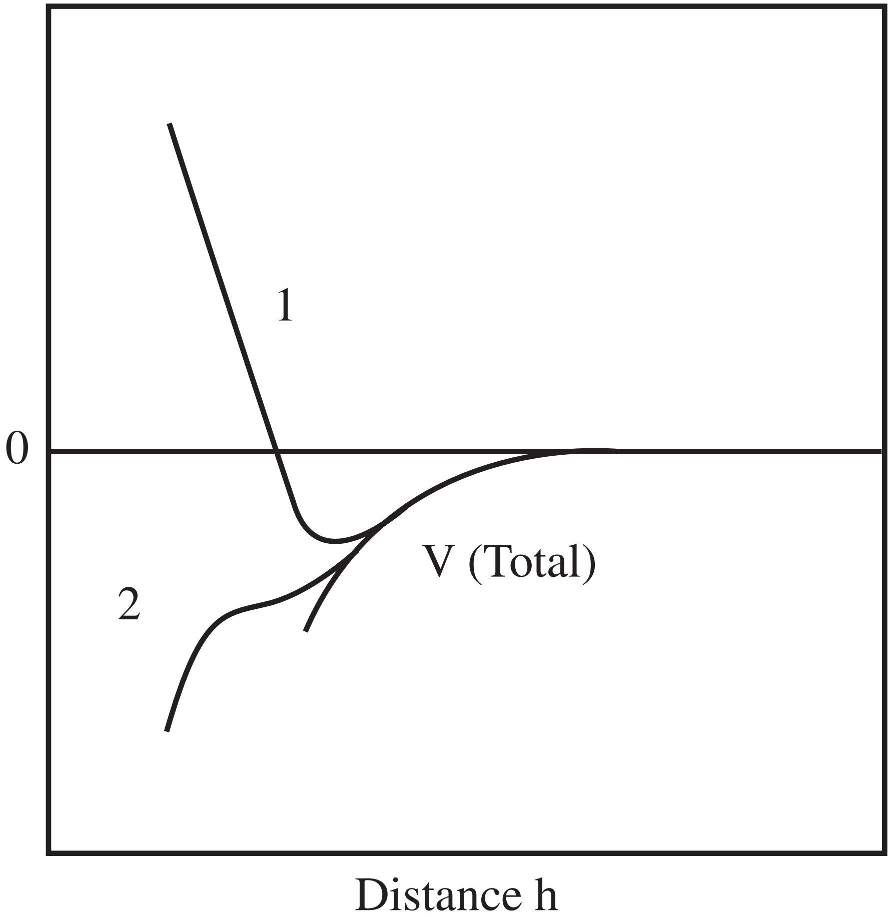

FIGURE 6.3 The total interaction energy curve between colloidal particles. Curve 1 shows stable colloids whereas Curve 2 shows unstable colloids.

them together and brings them closer, then "bridging flocculation" results. That is especially the case where there is a large excess of particles relative to the concentration of polymer. Bridging flocculation is a potential hazard in the formulation of sterically stabilized colloids; it may also have its positive uses. For example, the addition of small amounts of a high molecular weight acrylamide polymer to water leads to the flocculation of particulate matter that may be difficult to remove otherwise.

3. $R_G >> R$
   When large-sized, water-soluble polymer chains are added to a colloid having only very small particles, then many points of attachment are possible and lead to network formation and, hence, flocculation or gel formation.

In summary, it is important to consider the size of the particles and stabilizer macromolecules, even the coil-globule behavior of the macromolecule.

6.2.4 DEPLETION FLOCCULATION

The presence of an excess of nonadsorbed macromolecules can result in flocculation which is called "depletion flocculation." If the polymer chains are not adsorbed or are poorly adsorbed onto the particles, as the two colloidal particles approach, polymer chains become squeezed out of the area of closest approach, leaving bare surfaces that are attracted in the normal way. Then the water molecules flow from between the particles out into the solution by osmotic forces. The net effect on the particles is that they are drawn together by the water flow, resulting in a loss of stability and flocculation. Actually, the situation is more complex because of the configurational entropic effects and concentration effects of the added macromolecule. In practice, at low dissolved polymer concentrations, the colloidal particles and the added polymer form a stable dispersion. However, on adding more polymer after a critical concentration, the colloid separates into a particle-rich phase in equilibrium with a second phase dilute in particles. This process is reversible and the particles redisperse upon removing the polymer or diluting the system.

Depletion flocculation was seen with aqueous latices containing particles with grafted polyoxyethylene chains[43] and sterically stabilized polyMMA particles.[44] This volume exclusion mechanism was examined in detail by various authors.[45-49]

6.3 COAGULATION OF POLYMER COLLOIDS

Coagulation involves the aggregation of particles without the destruction of their individuality. When attraction potential energy dominates, the particles stick together in clumps and the process is referred as "coagulation." When these clumps are formed, it results in the loss of the independent translational motion of the individual particles which causes a decrease in the entropy of the system and, hence, an increase in the total free energy. However, for rapid coagulation which occurs in the primary minimum region, the entropy term is neglected because of the dominant free energy term. If the coagulation (or flocculation) occurs in the secondary minimum region, then the entropy effects are of major importance.

6.3.1 COAGULATION OF ELECTROSTATICALLY STABILIZED COLLOIDS

The coagulation of electrostatically stabilized colloids by the addition of electrolyte is a well-known process. In 1882, Schulze determined that the coagulating effect of salts on a number of inorganic dispersions increased markedly with the charge number of the cations.[50] Hardy, in 1900, found for positively charged particles that the coagulation ability was dependent on the charge of the anions.[51] The result is the "Schulze-Hardy Rule," which states that coagulation is controlled mainly by the nature of the ion of the added electrolyte carrying a charge of opposite sign to the surface charge on the colloidal particle, and the effectiveness is strongly dependent on the valency of this counter-ion. The nature and valency of the ion of the same sign as the particle (co-ion) were found to be of secondary importance. The DLVO approach in Section 6.1. gave the first theoretical understanding of this effect.

The early relationship indicated that the critical coagulation concentration (c.c.c.) varied as the inverse sixth power of the valency. Experimental results obtained under carefully controlled conditions gave ratios for electroltytes; for valency 2, the exponent is 6.27 and for valency 3, the exponent is 5.85. It was found that for monovalent ions, the effectiveness for coagulating negatively charged colloids has the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, while for divalent cations the order is $Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2}$.

6.3.1.1 Critical Coagulation Concentration

The term c.c.c. is the concentration of the minimum electrolyte necessary to bring the colloidal system into the regime of rapid coagulation. It is an approximate measure because it should be applied under specified conditions of particle concentration, rate of addition of electrolyte, temperature, etc.

According to the DLVO theory, the increase in electrolyte concentration leads to a lowering of the energy barrier to coagulation. As the concentration of the electrolyte is increased, the electrostatic potential is lowered, making it easier for the particles to pass into the primary minimum so that the barrier becomes lowered. When a point is reached at which it just disappears, that is the critical coagulation concentration (c.c.c.). When Born repulsion, V_B, is ignored at the c.c.c. point, $V_T = V_M = 0$ should be obtained giving

$$V_R = -V_A \tag{6.41}$$

and

$$\frac{dV_R}{dh} = -\frac{dV_A}{dh} \tag{6.42}$$

By using Eq. 6.34 for V_R and Eq. 6.27 for V_A, and taking $h = 1/\kappa$ under these conditions, one obtains

$$\kappa_{coag}\left(m^{-1}\right) = 2.039 \times 10^{10} \frac{\gamma^2}{Av^2} \tag{6.43}$$

In addition, κ can be directly related to the electrolyte concentration in mol/lt at c.c.c. so that

$$c.c.c.\left(mol\ lt^{-1}\right) = 3.853 \times 10^{-39} \frac{\gamma^4}{A^2 v^6} \tag{6.44}$$

where A is in Joules. Eq. 6.44 predicts that c.c.c. depends inversely on the sixth power of the valency of the electrolyte ions. The fact that DLVO theory predicts the

Schulze-Hardy Rule would seem to confirm the validity of the theory. It is also possible to derive an expression between c.c.c and the ξ–potentials, which is often experimentally

$$c.c.c.\left(mol\ lt^{-1}\right) = 3.451 \times 10^{-3}\,\frac{\varepsilon^4}{A^2 v^2} \tag{6.45}$$

It has to be recognized that the above equation is at best only semiquantitative because of the several assumptions made.

6.3.1.2 Effects of Organic Electrolytes

Some ionic organic surfactants act as both stabilizers and coagulants for polymer latices. The addition of an ionic surfactant of opposite sign to the charge on the colloidal particle causes coagulation, whereas an ionic surfactant of the same sign enhances stability. For a negatively charged particle, if a cationic surfactant such as alkyltrimethyl ammonium bromide having varying alkyl lengths is added, coagulation at low concentrations of added surfactant, particularly for longer chain surfactants, occurs. However, restabilization of particles also occurs beyond the critical coagulation concentration, especially for longer chain surfactants.[52,53] The c.c.c. values for surfactants are very low if compared with an inorganic electrolyte such as potassium bromide. The mechanism of restabilization is as follows: initially, opposite-charges result in coagulation; however, when more opposite charged surfactant is added, the hydrophobic portions of the surfactant adsorbs onto the particle surface and the new cationic head groups now maintain the colloidal stability. Thus, when surfactants having chain lengths of C_4 or lower are used, they do not produce restabilization due to the lack of strong adsorption onto the particle surface.

Addition of a surfactant having the same charge as that of the particle surface enhances the colloidal stability with a similar mechanism.[54] The organic hydrophobic portions of the surfactant adsorb onto the particle surface and the charged head groups further increase particle stability.

During emulsion polymerization, the adsorption of emulsifier onto the particle surface occurs at the earlier stages of particle growth. Thus, when the surfactant concentration is high with low monomer concentrations, small particles are formed favorably. In contrast, large-sized particles are formed in emulsifier-free polymerizations also possessing lower molecular weight polymer than the former process.

6.3.2 COAGULATION OF STERICALLY STABILIZED COLLOIDS

In order to coagulate a sterically stabilized colloid, a reduction in the range of repulsive forces should be obtained. One way to do that is the addition of a nonsolvent for the protective polymer to the medium. Then, the nature of the medium and the composite Hamaker constant are changed. Polymer segment-medium interactions are decreased and at some critical concentration of the additive, the segment-segment interactions dominate, leading to a more dense polymer layer and a reduction in the layer thickness, δ. This behavior is a direct consequence of the so called "θ-transition.” Thus, an extended and relatively open, random-coil polymer chain in “good” solvent will transform and collapse into a more compact configuration in a “poor” solvent at the “θ” point. It is therefore expected that the concentration of added nonsolvent needed to cause coagulation should correlate with that to reach the θ-point in a bulk polymer solution. Alternatively, this point may be reached by increasing the temperature. The increase of temperature decreases the interactions between the medium and the polymer segments because of the decreasing density of the medium, and thus segment-segment interactions dominate when an “upper coagulation temperature” is reached. This is analogous to those bulk polymer solutions that undergo a phase separation as the temperature is raised. There is also a “lower coagulation temperature.” This is due partly to the Brownian motion no longer being able to maintain the dispersed state, and partly because the protective polymer chains “freeze” on the particle surface and no longer act as a steric barrier.

On the other hand, if the nature of the solvent is changed such that it becomes a better solvent for the protective polymer, then the chains will be more weakly adsorbed, providing the possible onset of depletion flocculation or related phenomena.

6.3.3 Coagulation of Colloids by Freezing and Thawing

Freeze-thaw destabilization of latices is of considerable practical importance because of the need to store and transport these latices within cold countries during winter. When the temperature is reduced to a degree where the dispersion medium begins to freeze, then a third phase (ice) forms in the system. As freezing proceeds, the volume of water available to the latex particles progressively decreases. Later, the particles become entrapped between the growing crystals of solidified dispersion medium. Then the particles are forced into contact with each other. However, there is a vague point in freeze-thaw experiments: the effect of colloidal destabilization by freezing is usually apparent after the latex is subsequently thawed. Thus, it is not entirely clear to what extent coagulation occurs in the freeze or thawing steps. For this reason it is better to define this process as “freeze-thaw destabilization” in general.[26]

Some external factors affect the extent of coagulation during the freeze-thaw cycle. These are the duration of freezing, the magnitude of temperature decrease, and the rate of thawing. Some properties of the latex also influence the extent of coagulation. These are the extent to which the polymer has been plasticized, either by additives or by residual monomer; the inherent colloidal stability of the latex; the chemical nature of the colloid stabilizers that are present; and the presence of freeze-thaw stabilizer additives.

It is unlikely that much interparticle coalescence will occur during the freezing step if the temperature of the latex is rapidly decreased below the minimum film-forming temperature, although it might during the subsequent thawing. Latices based on styrene copolymers are generally reported in the published experimental investigations on freeze-thaw coagulations,[56-60] and for these copolymers the expectations are broadly fulfilled.

In industry, the copolymerization of minor amounts of hydrophilic monomers such as acrylic and methacrylic acid would be expected to improve the freeze-thaw stability of acrylic-based copolymer latices. This is expected because these acidic groups should concentrate near the surface of the particles and prevent interparticle coagulation. King and Naidus used methacrylic acid in the ethyl acrylate-methyl methacrylate emulsion copolymerization.[61] They assumed that a latex is freeze-thaw stable if it has survived three cycles of freezing and thawing without obvious signs of coacervation, and without the viscosity of latex increasing by more than half of the initial value. It was determined that there is a minimum level of copolymerized methacrylic acid required to impart freeze-thaw stability. The minimum level of methacrylic acid required correlated well with the glass-transition temperature of the copolymer, increasing progressively with the increasing ratio of ethyl acrylate/methyl methacrylate.[61]

Naidus and Hanzes used styrene-ethyl acrylate-methacrylic acid copolymer latices.[58] They also demonstrated that the presence of a methacrylic acid group greatly improves freeze-thaw stability.

Some freeze-thaw stability agents are added to prevent the coagulation during the cold winter season. The addition of glycols such as butyldiglycol depresses the freezing point and reduces the likelihood of ice crystals forming in the water phase. However, they also reduce the overall colloid stability through the reduction of the permittivity of the water phase, reducing the solvency of the water phase for stabilizer macromolecules, and reducing the degree of hydration of the particle surface.

6.3.4 EFFECT OF A SHEAR GRADIENT ON COLLOID STABILITY

In industry, the mechanical stability of latices is an important property. A latex must have sufficient stability during pumping, transportation, and even in the stage of manufacture by emulsion polymerization.

For colloidal-sized particles, the effect of gravity is completely outweighed by the thermal motion of the particles. As the particle size increases up to suspension range, particles tend to precipitate under the influence of the gravity. Brownian motion cannot prevent them from precipitation. When agitation is applied as an external shear force, some latices coagulate. The collision frequency and average kinetic energy of particles increase. Thus the particles have the ability to surmount any potential-energy barrier between them. The term "ortho-kinetic coagulation" is used to denote colloidal destabilization by mechanical agitation.

There are two experimental methods to determine the mechanical stability of latices: either the time required to effect obvious and gross coagulation, or the amount of coagulum produced after agitating the latex for a fixed time under controlled conditions of agitation. The second method is mostly used and the greater the amount of coagulum produced, the less is the latex mechanically.

The effect of applying a shear gradient is to produce a reduction in the potential energy barrier, and, thus, at a certain rate of shear the onset of instability can occur.[26,28] Small particles are rather insensitive to shearing forces, whereas larger particles having their radius greater than 0.5 micron can often be coagulated by stirring.

Zeichner and Schowalter,[62,63] and later Zollars and Ali, investigated the hydrodynamic interactions between the polystrene particles.[64] Husband and Adams determined that shear coagulation is sensitive to pH for carboxylated styrene-butyl acrylate-ethyl acrylate terpolymer particles between pH 5.5 and 7.0.[65] They considered the balance between DLVO repulsive forces and hydrodynamic forces to estimate the shear rate at which the onset of coagulation occurred.

The addition of water-soluble hydrophilic polymers such as hydrocolloids to latices increases the mechanical stability markedly. The enhancement of mechanical stability is due to the steric and hydration effects. Hydrocolloids are high molecular-weight polymers having low surface activity. Methyl cellulose had been used for this purpose.[66]

6.4 COAGULATION DURING THE PROCESS OF PARTICLE FORMATION

Once nucleation has occurred to form the first particles in an emulsion polymerization, it is probable that these particles would be unstable as a consequence of a small particle size and a low surface charge. Consequently, coagulation occurs over a short period of time to form particles of a size and surface charge which renders them colloidally stable.[28,67-70] Nucleation and subsequent coagulation processes are consecutive.

If no steric stabilizers are present in the emulsion polymerization system, the size of the first stable colloidal particle formed is controlled to a large extent by the ionic strength of the dispersion medium. The higher the electrolyte concentration, the larger the particle size obtained. For the same initial monomer concentration and for the same percentage of monomer, the final latex particle diameter in the medium of higher ionic strength will be the larger because the size of the initial stable particles controls the number of particles in the latex during the monomer diffusional growth period.

Electrolyte concentration-particle size relationship can be derived in a simple way by applying certain assumptions[28,69]: if each polymer chain has the same molecular weight, M_w, and two charged end-groups, and all the end-groups are anchored at the surface of completely spherical particles, it follows that the number of polymer chains per particle, N_c, is given by

$$N_c = \frac{4\pi R^3 \rho_L N_A}{3M_w} = \frac{m_p}{M_w} N_A \tag{6.46}$$

where m_p is the mass of the particle, R is the particle radius, and ρ_L is the particle density. Since the number of charged end-groups per particle is $2N_c$ from these considerations, and since each end-group has a charge e, then the surface charge density is given by

$$\sigma_S = \frac{2N_c e}{4\pi R^2} \tag{6.47}$$

and thus the surface potential by

$$\psi_S = \frac{\sigma_S R}{\left[\varepsilon_r \varepsilon_0 (1 + \kappa R)\right]} \tag{6.48}$$

Depending on the above simplistic assumptions, we can now calculate values of V_T from equations 6.26 or 6.27 and 6.31 or 6.32, and it is possible to compare stability on a quantitative basis. For example, at 4×10^{-4} mol/lt electrolyte concentration, the stability of latex is achieved with a particle radius of $R = 3.7$ nm, whereas to achieve the same result at 4×10^{-3} mol/lt electrolyte concentration, R has to grow to 11.3 nm.[28] These predictions are confirmed by experimental results, and it is possible to use the electrolyte concentration to control the ultimate particle size during emulsifier-free polymerizations where the surface charges are originated from the initiator decomposition products.[70] Gilbert applied these basic ideas on the coagulation during the process of particle formation into the treatment of emulsion polymerization kinetics.[71]

6.5 COLLOIDAL STABILITY OF VINYL ACETATE HOMO- AND COPOLYMER LATICES

In 1952, Priest determined that polyVAc latex particles are prevented from coagulating by adsorption of small quantities of sulfate groups derived during the cleavage of persulfate initiator when no emulsifier and polyvinyl alcohol stabilizer is added during emulsion polymerization.[72] Average particle sizes were found to be large, of the order of 0.1–1.0 micron in diameter, having a narrow size distribution. The ultimate particle size in mixtures having the same monomer-to-water ratio is a function of the relative number of sulfate groups per particle. Thus, a decrease in the particle size is expected as the concentration of persulfate initiator is increased. However, this fact was not confirmed experimentally and the higher the ionic strength, the higher the average particle size was found. The reason is the simultaneous increase of the ionic strength of the reaction system by increasing the initiator concentration, which creates an opposite effect. Priest commented that since the particles are stabilized by electrostatic charges, these charges become effectively screened in the presence of electrolytes, and, consequently, more coalescence takes place in the system, resulting in larger average particle size.[72]

Ten years later, Napper and Alexander examined the effect of the addition of low concentrations of emulsifiers to the emulsion polymerization of VAc, having their concentrations so low that they do not allow the formation of micelles in the aqueous phase.[73] Nonionic emulsifiers were found to have little effect on the polymerization reaction. Anionic emulsifiers accelerated the reaction, the effect increasing with the length of the hydrophobic part of the emulsifier. In addition, anionic emulsifiers increased the number of particles. These effects were explained in terms of the ionic interactions between the emulsifier and the negatively charged oligomeric vinyl acetate radical species propagating in the aqueous phase. The hydrophobic part of the anionic emulsifier molecule was adsorbed onto the polymer and then discouraged aggregation of polymer particles. When anionic emulsifiers having long hydrophobic chains were used, the tendency of the emulsifier molecule to be adsorbed onto the polymer was increased. The authors suggested that both the anionic emulsifier and the polymer particle were negatively charged, and the presence of the long hydrophobic chain of the emulsifier had a screening effect on the Coulombic forces which prevents the emulsifier adsorption. Therefore, the higher the chain length of the hydrophobic part of the emulsifier, the higher the emulsifier adsorption on the polymer.[73]

Dunn and Chong applied the DLVO theory of colloid stability to particle formation in emulsifier-free polymerization of VAc in 1970.[74] They also examined the VAc emulsion polymerization where anionic sodium dodecyl sulfate emulsifier is used. It was found that the polymeric particles are stabilized by ionic end-groups derived from potassium persulphate initiator. Electrical forces of repulsion between particles were calculated. The Hamaker constant, which defines the magnitude of van der Waals attraction forces, has also been estimated so that, $A_P = 8.84 \times 10^{-20}$ J for polyvinyl acetate and $A_W = 3.37 - 3.28 \times 10^{-20}$ J for water, both at 20°C. The dependence of the stability of the polymer dispersion formed on the concentrations of initiator and the anionic emulsifier was investigated and a good fit with DLVO theory was found. Palit's dye partition method was used to determine the ionic end-groups and adsorbed anions on the particle surface. Since the magnitude of electrical repulsive forces between particles and the stability of the polymer dispersions depend, in part, on the ionic strength of the continuous phase, then a new series of experiments was conducted in order to discriminate the variation of initiator or anionic emulsifier concentration. Surface charge density, σ, was calculated by assuming all the end-groups are on the surface of the particles. The Poisson-Boltzmann equation was used to relate the surface potential, ψ_o, to the σ. The total energy of interaction was calculated as the sum of repulsion and attraction energies as a function of interparticle distance. It was determined that the small particles are unstable with respect to coalescence with larger particles. The increase of ionic strength reduces the height of the energy barrier for the particles produced at the same initiator concentration, from 22.25×10^{-20} J at the lower ionic strength of 2.4×10^{-3} M to 2.22×10^{-20} J at the higher ionic strength of 10.1×10^{-3} M. The authors suggested that the surface of the polymer particles is the principal locus of polymerization. Diffusion of monomer from the interior of particles to the surface would lead to an increase in the monomer concentration at the surface. The rate of particle coalescence during the polymerization depends primarily on the stabilization of the polymer particles, and is only indirectly related to the rate of polymerization.[74]

Litt, Patsiga, and Stannett examined the effect of the presence of the electrolytes such as potassium sulfate and found that it increases the polymerization rate in nonseeded systems.[75] Klein, Kuist, and Stannett investigated the effect of the ionic strength of the water phase and of temperature upon the solubility of vinyl acetate monomer in the monomer-swollen polymer particles, which were stabilized by the adsorption of ionic species, in 1973.[76] The ionic strength was controlled experimentally by the addition of potassium sulfate solution. It was determined that the interfacial tension between the particle and the aqueous phase decreased, and the solubility of the VAc monomer in the monomer swollen-latex particle increased sharply with increasing ionic strength. The polymer-solvent interaction parameter was not affected by variation in ionic strength. This was explained in terms of decrease in interfacial surface free energy associated with partial collapse of the electrical double layer at the interface. In contrast to this, the solubility of monomer in the aqueous phase was found to be nearly constant with varying ionic strength.[76]

Netschey, Napper, and Alexander have described that the rate of polymerization of VAc in seed latices is affected by the nature of the stabilizing layer surrounding the seed particle.[77] They prepared three types of stabilized polyVAc seed latices. First, an electrostatically stabilized seed latice was prepared by the aqueous solution polymerization of VAc monomer in the presence of sodium hexadecyl sulfate. Second, an amphipathic steric stabilizer, poly (ethylene oxide-block-vinyl acetate) was synthesized by polymerizing vinyl acetate onto preformed polyethylene oxide, using benzoyl peroxide as initiator. Third, seed particles stabilized by a combination of electrostatic and steric mechanisms were prepared by adsorption of the steric stabilizer onto the surface of the electrostatically stabilized particles.[77] Polymerizations were carried out by using these seed latices and potassium persulphate as initiator. It was determined that polymerizations occurred much more slowly in seed latices protected by an adsorbed steric, nonionogenic stabilizer than in those stabilized electrostatically. Polymerization in seed latices stabilized by a combination of steric and electrostatic molecules occurred even more slowly.[77] The authors suggested that, although electrostatic stabilization by adsorbed anions should discourage the ingress of the negatively charged oligomeric free radical species into the particle, it evidently provides a less formidable barrier than does the electrically-neutral but rather viscous layer that surrounds the particles when an amphipathic stabilizer is used. When a combined stabilizer system is used, the presence of both viscous and electrostatic barriers is evidently more formidable than either is separately and gives an even slower rate of polymerization.[77]

Hayashi, Iwase, and Hojo described the emulsion polymerization of VAc in the presence of polyvinyl alcohol.[78] When the polymer particles are formed in water, most of the end groups of the polymer chains exist on the surface of the resulting particles, and these groups contribute to the stabilization of the latex particles, through both electrical repulsion and hydration effects. They concluded that the formation and stabilization of the latex particles would not be related to the effect of polyvinyl alcohol as emulsifier, but more to the effect of the sulfate end group.[78]

Zollars proposed a different particle formation mechanism depending on the coagulation rate.[79] According to the DLVO theory, particle stability increased with increasing surface potential or particle diameter but decreased exponentially with increasing ionic strength of the suspending medium. In many VAc emulsion polymerizations, the initiator is the only salt added, and low initiator levels produced low ionic strengths and, therefore, high particle stability. Thus, coagulation would not play an important role in determining the particle number for these situations. A first-order dependence between particle number and initiator concentration was feasible for low initiator concentrations. As the initiator level increased, ionic strength increased and coagulation played a more important role in the determination of the particle number. Two opposing effects resulted from the increase of the initiator concentration. The rate of coagulation brought on by higher ionic strength would not allow the increase of the particle number by the increase of the initiator concentration. However, after a while, a further increase in particle number at high initiator levels was observed which was due to the "salting out" effect of the emulsifiers at high ionic strength. Zollars showed that when polymerizations were carried out at constant ionic strengths by using K_2SO_4 in combination with $K_2S_2O_8$, the constant coagulation rate gave rise to a constant particle number, indicating that coagulation was the dominant factor at high ionic strengths.[79]

Dunn reviewed the polymerization of aqueous solutions of VAc monomer in 1981.[80] He stated that persulphate initiator provides ionic end groups capable of stabilizing latex particles in the absence of surfactants, although sulfate end groups are liable to acid-catalyzed hydrolysis, giving hydroxyl end groups which may possibly be oxidized to carboxyl by the persulphate. Dunn pointed out that when ionic strength is increased, the electrostatic energy barrier is reduced and the latex coagulates. However, when emulsifier is present this factor is less obvious. Emulsifier may stabilize small particles by adsorption, but in the absence of emulsifier small particles are less stable than large particles with which they coalesce. Therefore, a monodisperse particle size distribution is obtained when particles are nucleated by oligomeric precipitation in the absence of emulsifier. The number of particles in the polymerization system soon becomes constant because, although new particles continue to be formed throughout the reaction, they are unstable and coalesce with the preexisting large particles rather than with each other.[80]

Klein and Stannett extended their previously published Litt, Patsiga, and Stannett (LPS) kinetic model, which is based on the existence of oligomeric radicals in the aqueous phase onto which emulsifier molecules have adsorbed, dispersed, and stabilized, but which undergo coagulation with increasing ionic strength.[81]

Vanderhoff calculated the surface charge for polyVAc to be 0.22 $\mu C/cm^2$ in 1985.[82] He stated that this value is smaller than the critical value for stability of 0.32 $\mu C/cm^2$ according to the DLVO theory. Therefore, VAc monomer would expect to yield primary polymer particles comprised of a single polymer molecule. However, the precipitation of the primary particles would result before the first polymer molecule is terminated; the polymeric radical would assume a spherical form and absorb monomer from the aqueous phase. Then, the size of the polymer particle is increased before termination, which will decrease the probability of termination because of creating a new barrier for the terminating radical. In addition, monomer absorption would decrease the surface charge. Vanderhoff calculated that for a 1:1 monomer/polymer ratio, the diameter of the particle would increase from 6.8 to 8.7 nm and its surface charge would decrease from 0.22 to 0.13 $\mu C/cm^2$. Thus, the stability is decreased, making the particle more likely to flocculate with other primary particles as well as with mature particles.[82]

Hayashi, Komatsu, and Hirai investigated the rate of stirring on the seeded polymerization of VAc using monodisperse polyVAc seed, prepared in the absence of emulsifiers, with potassium persulfate.[83] The constant number of seed particles was used in seeded polymerization in order to examine the effect of stirring rate and it was found that higher stirring rates lead to coagulation of more small particles during the initial stage of polymerization when the small particles form.[83]

In general, if there is no emulsifier, the sulfate end groups introduced by the persulfate initiator are often sufficient to stabilize latex particles at relatively low monomer-water ratios to produce a monodisperse latex.[84,85-87] If emulsifier is present, the lower its concentration, the higher the tendency to obtain monodisperse latex. In practice, seeded polymerization using a monodisperse seed latex allows the preparation of larger monodisperse latices of different sizes.[88,89]

The quality of water used is important in emulsion copolymerization of acrylics with VAc monomer. Polyvalent cations present in natural water can have a strong inhibitory effect on the polymerization reaction and lead to flocculation. Even excessive amounts of univalent ions can influence the formation of micelles and, ultimately, polymer particle size in latex. Consequently, either deionized or softened water is recommended for emulsion copolymerizations in industry.

El-Aasser, Makgavinata, Vanderhoff, and Pichot characterized homopolymer VAc and BuA latices as well as VAc-BuA copolymer latices having various compositions with respect to anionic end groups on particle size and colloidal stability against electrolytes after being cleaned by ion exchange in the aqueous phase.[90,91] For semicontinuous emulsion polymerization processes, particle nucleation is assumed to take place predominantly in the aqueous phase. Thus, the particles are formed over the entire duration of the polymerization process and particle growth takes place predominantly by coalescence of smaller-size particles or low-MW oligomers with larger-size particles. Favorable adsorption of emulsifier on the particle surface results in a high level of colloidal stability of the newly formed small-size latex particles when the comonomer mixture is rich in the relatively more hydrophobic BuA monomer. Thus, the final latex system comprised particles with small average size and broader distribution.[90,91] The controlled introduction of monomer to the reaction vessel facilitates great control over the homogeneity of the copolymer formed. There may be many strategies for monomer addition: comonomers may be added neat as a mixture or by different streams, or emulsifiers may be fed as a different stream or added to the reaction mixture initially. Another alternative is the addition of pre-emulsified comonomers so that the emulsifier is also fed to the reactor in a programmed manner. The addition choice of the emulsifier is very important to determine the particle size of the copolymers and colloidal stability of the latex produced.[90,91] El-Aasser, Makgavinata, Vanderhoff, and Pichot showed that surface functional groups on the latex particle surface result from (1) initiator fragments as sulfate or hydroxyl groups, (2) hydrolysis of polyVAc chains giving hydroxyl groups, and (3) hydrolysis of BuA chains giving carboxylic acid groups. It was determined that the total surface concentration of carboxylic and sulfate acidic groups on the semicontinuous latex particles is much higher than on the batch latex particles, and more dependent on the copolymer composition. Acid-induced hydrolysis results in a drastic change in the type and concentration of the surface groups of semicontinuous latex particles.[90,91] The colloidal stability of the ionically-cleaned latices against NaCl, $BaCl_2$, and $Al(NO_3)_3$ electrolytes showed that both electrostatic (due to surface acid groups) and steric (due to the presence of the polyvinyl alcohol at the surface) mechanisms are contributing. However, for semicontinuous latices, the decrease in BuA content less than 50 mole % resulted in a proportional increase and, ultimately, dominant role of steric stabilization.[90,91]

Erhart, Dimonie, El-Aasser, and Vanderhoff determined that the grafting reactions of polyvinyl alcohol and the VAc in the aqueous phase affect the overall polymerization kinetics and colloidal stability in the emulsion copolymerization of

VAc-BuA.[92,93] Polyvinyl alcohol of different degrees of hydrolysis was used as the sole emulsifier in the copolymerizations. A limiting value was determined for the amount of VAc to graft onto polyvinyl alcohol to maintain water solubility.[92]

Donescu, Gosa, and Languri examined the semicontinuous emulsion copolymerization of VAc with 2-ethylhexyl maleate[94] and compared their results with their previous study on the semicontinuous emulsion copolymerization of VAc with 2-ethylhexyl acrylate.[95] They used hydroxyethyl cellulose, HEC, as the protective colloid; sodium sulfosuccinate of 6 moles ethoxylated nonyl phenol as emulsifier; and *n*-butanol as chain transfer agent. The comonomer addition rate was high; it was nearly in "flooded conditions." The authors suggested that HEC splits its chain in the presence of the initiator, thus continuously stabilizing the new particles formed. Oscillations in the particle number, conversion, and latex surface tension occurred throughout the reaction due to the flocculation and nucleation of new particles.[94] Donescu and Fusulan also copolymerized VAc with dibutyl maleate using a semicontinuous process.[96] They noticed a decrease in particle size with increasing dibutyl maleate comonomer. They concluded that the more hydrophobic monomer was responsible for reducing particle size, similar to Makgawinata et al.[97] Since the emulsifier is more easily adsorbed onto the surface, the increased hydrophobicity allows for greater stability of the first-formed particles.

Donescu, Fusulan, Gosa, and Ciupitoi investigated the semicontinuous copolymerization of VAc with acid comonomers such as fumaric acid and crotonic acid in order to improve stability and adhesion properties.[98] They used HEC as protective colloid and 6 moles ethoxylated nonyl phenol sulfosuccinic disodium salt as emulsifier, and determined that the presence of acid comonomers decreases the rate of reaction and increases the particle size.[98]

Gajria and Vijayendran examined the pH stability of acrylic acid (AA) and methacrylic acid (MAA)-modified VAc-BuA copolymer latices.[99] The authors determined that most acid groups were found to locate on the surface of the latex, with some buried in the particle. When the monomeric acids were fed in the monomer feed as opposed to a water solution feed, the resultant latex had a greater viscosity response upon pH adjustment.[99]

Huo, Hamielec, and McGregor also studied the effect of AA incorporation to 2-ethylhexyl acrylate-VAc-AA terpolymers.[100] The addition of sodium chloride effectively reduced the pH-thickening response curve.

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7 Experimental Determination of Latex Properties

7.1 TOTAL SOLIDS CONTENT

The total solids content of a latex is the percentage by mass of the whole, which is nonvolatile at 105°C for 2 hours in an open atmosphere oven. A quantity of latex is weighed in a flat-bottomed glass dish (m_0) and dried in an oven at 105 ± 5°C to the constant weight in 2 hours, and the remaining polymer film is weighed again to find the quantity of the weight of the residue (m). The ratio of the remaining solids over the total initial weight ($100m/m_0$) gives the total solids content.[1,2] Preferably, a flat-bottomed, lipless dish about 6 cm in diameter and having a cover is used according to ISO procedure.[3] The dish and cover should be weighed to the nearest 1 mg, and a 1.5–2.5 g latex sample is poured into the dish, the cover replaced, and the dish, cover, and sample are weighed to the nearest 1 mg. The dish is then swirled to ensure that the test sample is spread over its entire bottom. The test sample in the dish, uncovered, is dried at 105 ± 5°C for 2 hours. The dish is then allowed to cool in a dessicator, the cover replaced, and the dish, cover, and dried sample are weighed. The cover is then removed and the uncovered dish heated for 15 minutes at the same temperature. It is again cooled at the dessicator, the cover replaced, and then reweighed. This procedure is repeated until the constant weight is obtained showing the weight loss between successive weighings is less than one mg.[3]

7.2 DENSITY

A pyknometer having a volume of 50 cm^3 is used to determine the density of latices, when required, at 20 or 25°C. Density of polyVAc is greater than 1 g/cm^3, similar to all the water-based latices. Special hydrometers are also used for rapid determination of latex density. Density value is important for the transport and shipment of the manufactured latices; it has fewer scientific drawbacks.

7.3 PH

pH is usually measured by a pH-meter having a glass electrode in conjunction with a saturated calomel electrode.[4,5] Calibration of the pH-meter using aqueous solutions of known pH is always necessary. According to ISO procedure, the pH-meter is calibrated at 23 ± 1°C, and successive readings are to agree within 0.05 pH unit.[4] The pH-meter should be recalibrated at no more than 30-minute intervals if a series of determinations is being made. Care should be taken to wash the glass electrode completely free of adhering polymer after a measurement has been made. Glass electrode is washed with water, wiped dry with soft absorbent paper, and immersed in the test sample. Determinations are to be conducted in duplicate; the readings should agree within 0.1 pH unit.

Universal pH indicator papers may be used for rough pH determinations. The opacity of the latex obscures the immediate color change, and that is the reason for the roughness of the pH measurement.

7.4 VISCOSITY

Viscosity is the ratio of shear stress to shear rate, and it is determined by applying a known shear stress to a liquid and measuring the resulting shear rate. Generally, the viscosity of a latex at any given total solids content decreases with increasing particle size and with increasing broadening of the particle-size distribution. When the particle size increases in a monodisperse latex, the average shortest distance between the surfaces of neighboring particles is also increased, thus decreasing the tendency of a particle to interfere with the motion of its neighbors resulting in a reduction of latex viscosity. The broadening of the particle size distribution increases the packing efficiency of the particles where the smaller particles can be accommodated in the spaces between the larger particles. This effect increases the fluidity of the latex and decreases its viscosity. By experience, it is determined that the viscosity of a blend of two or more relatively monodisperse latices of different particle sizes is less than that of any of the individual latices at the same volume fraction of dispersed polymer.[6-15]

Viscosity measurement is an indication of the flow properties and latex rheology and is of great practical relevance for their industrial applications. It is also important for the transportation and handling of the latices. Barnes, Hutton, and Walters[16] discussed the application of viscosity measurements, and Macosko[17] provided an extensive review of the current state of viscometry. Many different kinds of viscometers are used to determine the viscosity of polymer latices, and only viscometers that are in wide industrial use will be mentioned here.

7.4.1 BROOKFIELD VISCOMETERS

Brookfield viscometers are used for rapid viscosity measurements with limited accuracy. They consist of a rotating cylinder spindle driven by a synchronous electric motor through a berillium-copper torque spring. The viscous drag on the cylinder causes an angular deflection of the torque spring, which is proportional to the viscosity of the latex in which the disc is rotating. The torque, and thus the viscosity, is indicated by means of a pointer and scale. The pointer is attached to the cylinder spindle and the scale is attached to the drive spindle above the spring, so that both pointer and scale rotate. They must be clamped together to obtain a reading and the rotation stopped when the pointer is opposite a window cut in the casing. A range of rotating speeds and spindles is available so that a wide range of viscosity can be covered. For practical comparisons, the same number spindle is used at constant temperature (25°C) with the same rotating speed. The spindle is immersed in the latex to a specified depth.[2,18,19] This method enables one to detect small changes in latex viscosity. Since the temperature affects the latex viscosity inversely, the use of a constant temperature thermostat is required.

Two types of instruments are specified: Type R, to be used for latices having viscosities up to 200mPa-s, and Type L up to 2000 mPa-s. The respective rotational frequencies are $20 \pm 0.2\ \mathrm{m}^{-1}$ and $60 \pm 0.2\ \mathrm{m}^{-1}$.

Brookfield viscometers have limited accuracy to follow continuously the viscosity changes caused by temperature changes or associated with non-Newtonian flow behavior. In addition, Brookfield viscometer readings are affected by turbulence and, to some extent, by the angle of immersion of the spindle.

7.4.2 CONE-PLATE AND DOUBLE-CONE VISCOMETERS

In cone-plate viscometers, the latex is contained within the space between a flat plate and a cone of very obtuse angle. The torque required to drive the cone at a definite angular speed is determined. The whole of the test latex is subjected to shear all the time, and the strain rate is uniform throughout the latex. Cone-plate viscometers are used to determine latex viscoelastic properties since a well-defined shear rate and stress can be maintained throughout the test sample. In addition, they are very easy to clean and very little test latex is required. However, heat may be generated in the latex during measurement faster than it can be dissipated, leading to troublesome temperature rises. Gorton and Swinyard described the use of the Ferranti-Shirley cone-plate viscometer.[20]

In the double-cone viscometer, the latex is sheared in the space between two coaxial cones as one cone is rotated at uniform angular speed about their common axis relative to each other. The torque transmitted to the other cone is masured.[2]

7.4.3 RHEOGONIMETERS

The Weissenberg rheogonimeter measures the viscosity at constant rate of shear with extreme accuracy.[2,21] It is a sophisticated instrument used for the detailed investigation of viscoelastic properties. Various types of shearing can be applied upon the test latex, such as cone-plate and parallel-plate geometry, and a wide range of rotational frequencies is available.[2]

7.4.4 ORIFICE-TYPE VISCOMETERS

A shear stress may be applied to a liquid (latex) by allowing it to flow through an orifice of known diameter at the bottom of a container under the pressure of the head of liquid in the container. These are also called “cup-type viscometers.” The time required is measured for a definite volume of latex to efflux under a standard (atmospheric) pressure. Redwood, Engler, and Ford-Cup viscometers are of this type. These have been widely used for the determination of latex viscosity as they are cheap and easy to handle. It is preferable to filter small pieces of coagulum present in the latex through a wire-mesh screen and then allow it to stand for a period to eliminate air bubbles.

Cup-type viscometers are not suitable for the precise viscosity determination of non-Newtonian latices because the rate of shear strain varies throughout the period of measurement due to the continuously decrease of driving pressure. The capillary viscometer is an improvement that provides a flow path, the length of which is much longer than its diameter so that entrance and exit effects are minimized, allowing better calculation of the average shear rate.[22] However, the use of capillary viscometers with polymer latices is not recommended because when they are used, cleaning is very difficult and they tend to become fouled with latex deposits.[2]

7.5 SURFACE TENSION

The surface-active materials present in latex lower the surface tension of the water medium from its pure value of 72.8 mN/m to a value which indicates the wettability of latex against various substrates such as textile, paper fibers, metal, and wood surfaces. Surface tension (or surface free energy) of a latex also shows the extent of interactions between the particle surfaces and the surrounding aqueous phase according to the principles of equilibrium thermodynamics.

The surface tension of the interface between air and the latex aqueous phase is usually determined by the ring-pull method. For this purpose, the du Nouy ring tensiometer[23] is used and ASTM D 1417-57 T or ISO Standard 1409[24] is applied. The force additional to its weight is measured, which is required to pull a small platinum wire ring of circular cross-section out of the surface of the liquid.[25,26] The force of detachment, F, is roughly related to the surface tension, γ, of the latex by the equation

$$F = 4\,\pi\,R\,\gamma \tag{7.1}$$

where R is the radius of the ring. Harkins and Jordan[27] developed a correction factor which was discussed by Freud and Freud[28] and Zuidema and Waters.[29] The correction factor is a function of R and r, where r is the radius of the ring wire. It is preferable to calibrate the instrument with a series of liquids having known surface tensions. The ring and the cup should be very clean during measurement. The platinum ring is cleaned by washing with water and then heating in the oxidizing section of a Bunsen flame, taking care to avoid distorting the ring. The tensiometer should be protected from air currents during measurement. According to ISO Standard 1409, the latex test sample should have a total solids content of 40% or less, and the measurement should be done at 25 ± 1°C with a platinum ring of 40 mm in diameter.[24]

The latex surface tension may be used as a measure of the unbound emulsifier (free-emulsifier) concentration. Gas bubble tensiometers are used for the continuous measurement of this parameter. Gas bubbles are released below the surface of the latex from two orifices of different diameters, and the differential back pressure between two orifices is measured, which is related to surface tension. Free emulsifier concentration is a critical parameter to control the steady-state oscillations in continuous stirred tank reactors (CSTR) and in preventing coagulation during polymerization.

7.6 MEAN PARTICLE SIZE AND PARTICLE SIZE DISTRIBUTION

The knowledge of mean particle size and particle size distribution in a polymer latex is of primary importance because these properties affect almost all properties of the latex (stability, rheology, optical, and electrical). For emulsion polymerization, an accurate measurement of mean particle size and particle size distribution is essential in dealing with polymerization kinetics associated with particle initiation, particle formation, particle growth, and agglomeration. In addition, the drying mechanism of latices and the formed polymer film properties are a function of particle size and particle size distribution. Mean particle size and particle size distribution are important parameters related to the stability of latices where the colloidal stability decreases with increasing particle size.

In general, latex particles are regarded as spherical unless there is strong evidence to the contrary. However, the particles may be ellipsoidal or flat platelets in shape, or they may be essentially spherical initially but, due to partial agglomeration, particles of irregular shape may be formed. Particle diameter (or radius) is used for particles, which are spherical, and a hypothetical equivalent spherical diameter (or radius) is used for nonuniform particle sizes. There are other measures of particle size such as surface area and volume; however, the relationship between these various measures of particle size are simple only if the particles are of simple size. In addition, the magnitude of an average particle size for a particular latex depends upon how the average is defined. If all the particles of a latex are the same size, there would be no need to consider averages; however, in practice, all the latices have a distribution of particle sizes, and thus it is essential to define an average size. There are number average, weight average, harmonic average, geometric average, turbidity average, Z average, light scattering average, surface area average, volume average, volume/surface area average, and volume/diameter average expressions. All of these averages generally have different numerical values.

Particle size distribution indicates how the total population of particles is distributed among the various particle sizes. The particle size distribution may be expressed as differential or cumulative. Distributions may be normal, narrow, broad, skewed, bimodal, multimodal, or anything in between. There are many different methods of reporting distributions, and since most particle size equipment is computer-driven, there is some confusion in this area.

There is extensive literature relating to mean particle size and particle size distribution measurements. Comprehensive books on this subject include those by Orr and Dallavalle,[30] Cadle,[31] Orr,[32] Groves,[33] Beddow,[34] Butters and Wheatley,[35] Bohren and Huffman,[36] Stanley-Wood and Allen,[37] Dahnneke,[38] Barth,[39] Provder,[40] Allen,[41] Provder,[42] Chu,[43] Stanley-Wood and Lines,[44] and Brown.[45] Review papers and book chapters on this subject include those by Gordon and Pendle,[46] Barth and Sun,[47-49] Rowell,[50] Ottewill,[51] Blackley,[2] and Collins.[52]

The variation in latex sampling, the changes in particle size during dilution, and the shifts due to outsized particles are known as common problems for all the methods. The obtaining of a representative latex sample is very important and is often underestimated.[2,52] Since latices have a tendency to form a sediment and skin, the sampling is more difficult as the sample source increases in size, it is easier to obtain a representative sample from a 500 ml laboratory reactor than it is to obtain one from a rail tank car. The contents of drums are homogenized by stirring, otherwise by rolling of the drum until conformity with a specified criterion of homogeneity is attained, such as the total solids content of samples taken from the top and bottom of any drum or tank shall differ less than a specified amount, such as 0.5%. The final sample shall contain contributions from as many levels in the container as possible, and exposure of the latex to air should be minimized and air introduction avoided. The sampling bottles, with screw caps, should be made of glass or chemically-inert plastic, and the void space in the filled sample bottle should be 2–5%.

Assuming a representative latex sample has been obtained, it should be highly diluted prior to particle size analysis. Before the dilution, it is to be stirred and filtered through a stainless-steel wire cloth having an average aperture of 180 ± 10 μm in order to remove outsized particles.[2] The interference from outsized particles is a serious problem, especially for light-scattering and chromatographic methods where the results are strongly influenced by a few large particles. The dilution of sample is best carried out by using the serum which is obtained from simple membrane dialysis or centrifugation of the original latex. However, this step is frequently bypassed by making dilutions with deionized water containing 0.1% of a suitable nonionic surfactant. Care should also be exercised in the amount of shear used to mix the sample prior to and during the dilution procedure because excessive shear, in some cases, leads to agglomeration or flocculation.[52]

There is no universal particle size determination method or instrument that can satisfy all the varied criteria and needs. In general, microscopy-based techniques (dark field microscopy, electron microscopy, SEM and TEM), scattering techniques (classical light, quasi-elastic, X-rays, photon correlation, turbidity), chromatographic methods (size exclusion chromatography, SEC; hydrodynamic chromatography, HDC; capillary hydrodynamic fractionation, CHDF; sedimentation field flow fractionation, SFFF), and other methods (fractional creaming, soap titration, electrozone sensing Coulter particle counter, and acoustics) are used to determine the mean particle size and particle size distribution. It should be kept in mind that different particle size methods yield different results. The size range, precision, the need for relative or absolute data, the time required for measurement, the cost of instrument, and results format options are the factors that should be considered to select the appropriate instrument for a specific task. Since the subject is very wide, descriptions of only a limited number of methods which are relevant to polyVAc and polyacrylate latices will be presented here.

7.6.1 OPTICAL MICROSCOPY - DARK FIELD MICROSCOPY

The limit of resolution for an ordinary optical microscope is about 0.4 μm, and, thus, latices containing particles with mean diameters less than 2 μm are usually not subjected to optical microscopy for particle size analysis. When ultraviolet light is used instead of visible light, a much higher resolving power can be achieved; this approach was used by Lucas in 1938 to investigate the particles in natural rubber latex.[53] It is necessary, however, that the object should transmit UV light sufficiently for this purpose.

In order to increase the resolving power of an optical microscope, a dark-field condenser was used with a phase-contrast objective in 1955.[54] This method was later called "dark field microscopy." The inventors of this method, Schoon and Phoa, hardened the natural rubber particles by bromination to prevent flattening, a method discovered by Brown in 1947.[55]

The dark field microscopy method consists of depositing a sample on a glass slide and measuring the intensity of light scattered from individual particles viewed in dark field illumination, and visually accessed or recorded on photographic film for subsequent image analysis. It has a useful size range of 0.05–0.80 μm. The principle is based on the Mie theory of light-scattering with the particles acting as point sources. This method provides an indication of the breadth or narrowness of the size distribution, the presence of outsized and agglomerated particles, and the presence of floc and/or second-generation particles.[52,55,56] The method is sensitive to dust and dirt on microscope slides, and special precautions are required to maintain absolute cleanliness.

7.6.2 ELECTRON MICROSCOPY

Mean particle size and particle-size distribution are measured most frequently by electron microscope.[2,58-70] The latex particles are mounted on a support film, dried, and subjected to electron bombardment in the dehydrated condition. However, the particles of rubbery polymers tend to flatten or agglomerate during drying, and a slight increase in some particle volume is also seen. Thus, Brown tried to harden the particles by bromination to prevent such differences in size.[55] Soft polymers of acrylates cannot be hardened by bromination; they can be hardened by exposure to high-energy radiation. There is another problem encountered with the electron microscopy of latex particles: the scattering power of latex particles for electrons is not much greater than that of the substrate on which they are mounted, resulting in poor shape definition. Metal shadow–casting techniques, especially the formation of a gold film of approximately 0.8 nm thickness around the particles, is necessary. Another problem is the reliability of the latex sampling. In actual practice, a very small drop is diluted and only a small fraction of the diluted sample is investigated by electron microscopy. Furthermore, in any one field view, only a very small proportion of the total number of particles is visible. The extent of the representation of this field view for the whole latex sample is always a question. Replication of observation is necessary to increase the reliability of the data. A discussion of possible errors in the latex particle size determination by using electron microscopy was given by Davidson and Haller.[56] Monodisperse polystyrene latices of known particle size have been used as standards for the calibration of electron microscopes.[2]

Priest was the first to report particle size determination of polyVAc by electron microscopy in 1952.[59] Later, many researchers applied this method to polyVAc latex reserach.[64,67,69] Klein and Stannett used a freeze-drying technique with carbon replication in order to harden otherwise soft polyVAc particles under electron bombardment.[69] Lepizzera and Hamielec criticized the use of electron microscopy to determine polyVAc particle size due to the considerable shrinkage when exposed to the electron beam. Instead, they applied a disc centrifuge sedimentation method in 1994.[71]

7.6.3 FRACTIONAL CREAMING

Fractional creaming is a very simple and practical particle size determination method that dates back to 1939.[72] Schmidt and co-workers derived a universal calibration curve for this method showing the variation of the maximum particle number with the concentration of the creaming agent in the aqueous phase after creaming, notwithstanding differences in the nature of the polymer particles.[73,74] It is a largely overlooked method and is particularly suitable for latex systems having polymers with low glass transition temperatures.[2,52] Experimentally, the usual creaming agent, sodium alginate, is added to a series of aliquots of the diluted latex dispersion (usually 10% by weight) in increasing amounts to cream the particles. The total solids content of each sample is adjusted to 2.5%. The system is gently mixed after the addition of sodium alginate and allowed to stand 24 to 48 hours to complete the total creaming at ambient temperature. Then, a sample of skim layer is withdrawn and analyzed for polymer content. At the same time, the concentration of the sodium alginate present in the aqueous phase of the aliquot is determined. The difference between the polymer content in the skim and that initially present in the latex is indicative of the mass fraction of polymer present as particles less than a certain critical size. A fractional creaming universal calibration curve is used to determine the critical particle size by using the concentration of sodium alginate in the aqueous phase that is determined experimentally. Then, a cumulative distribution curve is obtained showing the mass fraction of polymer dispersed as particles with sizes less than a series of values.[2,73,74]

This method depends on the fact that the size of the largest particle found in the skimmed latex decreases progressively as the amount of creaming agent increases. With the initial addition of the creaming agent, the particles having the largest sizes decrease sharply, and eventually a limiting particle size is attained so that no significant further decrease in maximum particle size occurs by increasing the concentration of the creaming agent. Schmidt and co-workers used electron microscopy to determine the maximum particle size present in latex skims.[74]

7.6.4 SOAP TITRATION

Surface area and mean particle size of latices are measured by soap titration, which was applied by Maron, Elder, and co-workers.[75-80] The particles were assumed to be spherical, and the particle size given by this method is a volume-to-surface-area diameter. The method involves the titration of a weighed test sample of latex of known polymer content with a standard aqueous solution of a surface-active material until the critical micelle concentration of the surfactant is attained. This method is applied to synthetic latices, which are prepared using cationic surface-active substances. A latex test sample of 25–50 cm^3 is suitable. The solids content of latex should not exceed 10%, otherwise the changes that accompany the addition of the soap are usually too small to give sharp discontinuity in slope at the point of micelle formation. The concentration of the surface-active material should be between 0.05–0.25 mol/lt. The titration is carried out at 50°C to prevent gelation or curd separation. It is assumed that any soap present in the particles is completely displaced from the surface by the added soap during soap titration. Two techniques are used to determine the titration end point: surface tension and electrical conductance after each addition of the soap. A time interval should elapse between each addition of solution and the corresponding measurement to allow equilibration. The du Nuoy ring-pull method is used for surface tension determination. Both methods give identical results. The effective molecular area of the soap at the particle surface, which is required in the calculation of particle area, has been independently determined by electron microscopy.

Cockbain,[81] and later Chen,[82] applied this method to natural rubber latex by using anionic surfactants. Blackley presented a detailed discussion on the use of this method.[2] In summary, soap titration is a quick method with limited accuracy.[61,83]

7.6.5 LIGHT SCATTERING

When a beam of electromagnetic radiation is passed through a colloidal dispersion a proportion is transmitted, another portion is absorbed by one of the phases in the system, and the remainder appears as scattering radiation emerging from the dispersion in directions other than the incident direction, as well as in the incident direction. This scattered radiation is emitted as waves by fluctuating electric dipoles induced in the particles by the incident radiation. It usually has essentially the same frequency and wavelength as the incident radiation, and its intensity depends upon direction. The nature of the scattered radiation depends upon the size, shape, nature, and concentration of the dispersed particles. If a particle is small compared to the wavelength, the scattering intensity will be the same in both forward and backward directions. For larger particles, those that are comparable in size to the wavelength, there will be more scattering in the forward than in the backward direction because of the interference taking place in the scattering from different parts of the particle. It is thus possible to determine the size of particles accurately by making precise measurements of the angular variation of the scattered intensity in the forward direction. Classical light-scattering uses electromagnetic radiations of wavelengths within the range for visible light. X-ray scattering is used similarly for the determination of particle properties.

The theory of light-scattering was first developed by Lord Rayleigh,[84] and subsequently improved by Mie[85] and Debye.[86] Several comprehensive books and book chapters have been published on the theory and application of light-scattering.[2,36,43,45,50-52,87-90] An unpolarized beam of light—usually a laser—is used as light source after being filtered, expanded, collimated, and passed through a dilute suspension. Diffracted and transmitted light is collected by a Fourier optical system and focused onto a light-sensitive ring or radial diode array detector positioned in the focal plane of the lens. Since small particles scatter at large angles, and large particles scatter at small angles, a series of concentric diffraction rings consistent with the various particle sizes is obtained. The signal is then processed using Mie and Fraunhofer scattering theories. Usually, weight-average particle size distribution is obtained for the size range of 0.1–50 μm. Azzopardi outlines the limitations of light scattering.[91] Dunn and Chong determined the particle size of diluted polyVAc latex by classical light-scattering in 1970.[92] Zollars determined the weight-average particle number of polyVAc by light-scattering and multiplied these values with a constant polydispersity factor of 2.6 to obtain number–average particle size distribution.[93]

7.6.6 QUASI-ELASTIC LIGHT SCATTERING (PHOTON CORRELATION SPECTROSCOPY)

Quasi-elastic light scattering (QELS) is also known by names such as,"photon correlation spectroscopy," "dynamic light scattering," "laser scattering," "light beating spectroscopy," and "laser Doppler velocimetry." QELS is based on the time and frequency fluctuations in the scattered intensity caused by Brownian motion of the scatterers, in contrast to classical light-scattering which is concerned with the average intensity of the scattered light. The information on the number, size, shape, and charge of particles in space can be obtained by analyzing the intensity fluctuations.

A monochromatic beam of laser light is focused onto a diluted latex and the scattering intensity is measured at some angle by a photon counting detector. Since the particles in the latex are in constant Brownian motion, scattered light will result that is spectrally broadened by the Doppler effect. The smaller the particles, the more rapidly they move under the influence of Brownian motion. The particle diffusivity is determined by analyzing the intensity fluctuations, or frequency fluctuations and the diffusion coefficient is related to particle diameter with the well-known Stokes-Einstein equation. The rate of movement of the particles is inferred from the rate of autocorrelation decrease. Autocorrelation expresses the degree to which two dynamic properties are related over some time period. The smaller the particles, the more rapid is the decay of autocorrelation. Detailed information can be found in a number of comprehensive books and reviews.[38-40,89-91,94-97]

The particle size range of QELS is 0.003-5 μm; only refractive index and viscosity of the dispersing media are required. No calibration is required, and a 2-ml latex sample size is enough to obtain precise results. However, QELS cannot be used for latices with multimodal particle size distributions, and particles must be spherical for accurate data analysis.

7.6.7 TURBIDITY

When a diluted latex test sample is placed in an optical cell of known path length (l), and the ratio of the intensities of the incident (I_0) and transmitted (I) beams are determined at an appropriate wavelength using a spectrophotometer, the turbidity (τ) is calculated from

$$\tau = (1/l)\ln(I_0/I) \tag{7.2}$$

Basically, turbidity of a latex is a quantitative measure of the overall loss of energy during the transmission of electromagnetic radiation through the latex, notwithstanding the mechanism or direction. If the system is sufficiently dilute to preclude multiple scattering, the turbidity at various wavelengths can be related to the particle size distribution by a number of semiempirical equations.[2,98-101] The method involves only sample dilution followed by turbidity analysis by a UV-visible spectrophotometer. Gulbekian determined the mean particle size of polyVAc latex by turbidimetry in 1968.[102] Kiparissides, MacGregor, Singh, and Hamielec used turbidity for particle size determination of vinyl acetate latices.[103]

7.6.8 HYDRODYNAMIC CHROMATOGRAPHY

Hydrodynamic chromatography is the elution of latex particles in an order of decreasing size from a column containing nonporous spherical beads of a suitable polymer. It is similar to gel permeation chromatography, which is applied for polymer molecular weight determination. This method was invented by Small in 1974.[104] The latex should be highly diluted (0.01% by wt.) and the method depends upon the velocity profile, which develops in the dispersion medium as it flows through the capillaries formed by the packing. Each void acts as a small capillary. The velocity is maximum at the center; the larger particles tend to locate at the center and elute more rapidly, whereas the smaller particles elute slowly because they tend to locate at the walls of the column.[105-111] The particle size range is 0.015–1.50 μm.[52] The columns are calibrated by measuring the rate of transport of colloidal particles of known size. It is a rapid method, requires small samples, and yields a particle size distribution directly. However, sometimes column blocking occurs. Column calibration and detector response corrections are frequently required.

7.6.9 SIZE EXCLUSION CHROMATOGRAPHY

In this method, a column packed with porous beads is used. The elution mechanism is the steric exclusion of particles from pores of certain sizes, causing the small particles to spend more time in pores than the larger ones. The separation is more efficient than the hydrodynamic chromatography. The particle size range is 0.015–1.50 μm, except that the upper limit for efficient separation is determined principally by the pore size of the beads.[2] Kiparissides, MacGregor, Singh, and Hamielec compared the turbidity data with the size exclusion data for polyVAc latices.[103]

7.7 FREE MONOMER CONTENT

In order to determine the unpolymerized free monomer remaining in the latex, the volatile unsaturates are distilled from the latex with methanol, and the quantity of

VAc and/or acrylic ester is best analyzed by gas chromatography. If wet analysis is required, VAc concentration can be determined by finding olefin unsaturation. This involves four different types of reactions, bromination, addition of iodine monochloride to determine iodine number, and addition of mercury (II) salts which can be determined polarographically.

The presence of free monomer should preferably be below 0.5% by weight because of the irritating odor of both VAc and acrylic ester monomers, and because of health and environmental considerations.

7.8 COAGULUM CONTENT

The quantity of material retained by a mesh of an average aperture width of 180±10 μm under specified conditions of filtration is called "coagulum content." According to ISO procedure,[113] 200 g latex is diluted with 200 ml of a 5% aqueous solution of an appropriate surfactant such as nonionic alkyl phenol ethoxylate and filtered through a cloth having average aperture width of 180 ± 10 μm. The residue on the cloth is washed with latex dilution solution, then water and the coagulum are dried for 30 minutes at 100 ± 5°C, allowed to cool, and weighed. Duplicate results should agree within 0.01% by wt.

7.9 MERCAPTAN CONTENT

n-dodecyl mecaptan can be titrated with standard aqueous iodine solution under acidic conditions. Otherwise, amperometric titration with Ag can be carried out.[112]

7.10 COLLOIDAL STABILITY

7.10.1 CHEMICAL STABILITY

Suitable chemicals, e.g., ZnO, $CaCl_2$, $MgCl_2$, and $BaCl_2$ aqueous solutions are added, and time for coagulum to form with specified amount is measured. The chemical stability is the ability of the latex to withstand chemical colloid-destabilizative effects.[2] These tests provide an indication of the decrease of the potential energy barrier by specified chemical influences. The numerical results of the chemical tests are strongly dependent upon the experimental procedure for the test. These tests are primarily designed for natural rubber latex but are applied to synthetic latices as well.

7.10.2 MECHANICAL STABILITY

High-speed mechanical shear agitator to produce shear between surfaces is applied to a latex having a specified total solids content for a specified time, and the mass of coagulum produced is then determined by filtration and weighing.[2,114,115] The results are expressed as percentage of the mass of the latex test sample, or as the actual mass of dried coagulum over the initial mass of the latex. Mechanical stability is the ability of the latex to withstand colloid-destabilizative effects of mechanical processes such as shearing and agitation.

Although high-speed stirring tests for mechanical stability are applied to synthetic latices, it is widely recognized that the results of such tests do not necessarily provide a reliable indication of mechanical stability against the effects of high shear.[2] If an indication of the latter is required, a rubbing test should be considered. Murphy proposed a test that simulates the hand-rubbing test long used by latex technologists to obtain a rough indication of mechanical stability.[116] Maron and Ulevitch described a test in which the latex is subjected to shear stress imposed by a metal disc rotating under a load and in contact with a polyethylene surface.[117]

7.11 MONOMER CONVERSION DURING POLYMERIZATION

Gravimetric analysis of the polymer formed is the classical method to determine monomer conversion during homopolymerization. A latex sample is weighed first and then dried in a steam bath, a conventional or microwave oven, or infrared drying equipment and its solids content is determined. After correction for the nonvolatile components in the formulation, the result is converted to the weight of homopolymer formed in the reactor.

In the case of copolymerizations, additional information is required to obtain partial conversions of each monomer on a molar basis. Average copolymer composition is determined by infrared (IR), nuclear magnetic resonance (NMR) spectroscopy and, high performance liquid chromatography (HPLC) elemental analysis, and sometimes the titration of specific groups present in the copolymer.[118] On the other hand, the ratio of the comonomers in the reactor can also be used for this purpose. The ratio of comonomers can be determined by gas chromatography, either of the latex[119] or of the gas phase above the latex in the reactor. Gas chromatography can directly give the partial conversions of the comonomers if an internal standard is used or the sample size is known, but this method is not accurate.

Control of comonomer composition requires intelligent comonomer addition strategies which rely on the monitoring of monomer conversions. The required conversion-time relation is then obtained by online measurements.[120,121] Hergeth published an excellent overview of online methods.[122]

GC determination of conversion of the latex[123] or the gas phase above the latex[124] can be applied online. The gas phase measurements sometimes give improper results because the space should be in equilibrium with latex, which requires a separate, smaller vessel that is accurately thermostatted.

Polymer content can be determined by online monitoring of the polymerization reactors by ultrasound sensors having frequencies between 20 kHz and 100 Mhz. The propagation of ultrasound is sensitive to both density and compressibility of the medium. The wave speed is dependent on the properties of the two constituents as well as their relative amounts in a latex system.[125,126] The measuring devices are not very sensitive to fouling.

It is also possible to measure the rate of polymerization from measurements of the exothermic heat flux by a calorimeter.[127,128] The volume of the reactor contents is monitored with dilatometry.[129] Dilatometry shows the reduction of the partial molar volume of the monomer when it forms the polymer. Instead of dilatometry, density measurements are also carried out, especially with Paar digital densitometers[130] and bubble densitometers.[131] When both density and GC measurements are applied simultaneously, better reliability is gained.[132] Raman spectroscopy can also be used to monitor monomer conversion online.[133,134]

7.12 LATEX CLEANING

In a latex system there are three separate regions: the aqueous phase (serum) of latex, the latex particles, and the surface of latex particles. If the polymer characterization in any of these regions will be done, latex cleaning is of crucial importance.[118,135] The latex may be coagulated by destabilizing with the addition of an electrolyte and then filtered and washed with water, but oligomers, water-soluble polymers, and electrolytes can still be present in the polymer coagulum. Thus, latex cleaning by serum replacement or dialysis methods are required in order to obtain a clean polymer.[136] In serum replacement technique, the latex particles are stirred in a cell separated by a filtration membrane, and the serum of the latex is also obtained. The conductivity of the serum after each replacement is measured in order to monitor the extent of washing.[137] Regenerated cellulose membranes are used for dialysis and hollow fiber dialysis of latices.[138] Dialysis removes the electrolytes but is not very efficient in removing oligomers and residual monomer. Steam stripping is sometimes used to remove residual monomer.[139]

Ion-exchange columns are also used to clean the latices.[140] Other cleaning methods are repeated centrifugation with replacement of serum[118] and gel filtration.[135]

After latex cleaning, the oligomers present in serum, particle surface, or in the particles are characterized because of their importance for polymerization kinetics.[118,141-145] In addition, VAc oligomers adsorb strongly onto highly dispersed silica particles in the aqueous phase, which leads to a disintegration of the filler particle agglomerates during application.[143]

Several particle surface characterization techniques such as conductometric and potentiometric titrations are also used to monitor the latex cleaning process.[118] Surface end-group characterization techniques are applied to reveal the influence of the monomer addition profiles on the distribution of SO_3^- and COO^- groups.[146]

7.13 AVERAGE MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

In principle, the molecular weight determination of emulsion polymers could be achieved by using approaches and techniques similar to those available for polymers in general.[147-150] Absolute methods such as osmotic pressure, light scattering, and ultracentrifugation measure the mean molecular weight without any calibration procedure. Every method gives a particular average molecular weight.

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[illegible] HT-SCATTERING METHODS

[illegible] light-scattering method is applied to measure the weight average molecular weights, $\bar{M}_w$, of polymers in the range 10,000–10,000,000. The light intensity scattered per weight concentration of polymer in solution is measured. The scattering pattern of electromagnetic radiation caused by the polymer sample solution is investigated. In the earlier days several electromagnetic radiation sources were used,[151,152] but at present laser beam or neutrons are used, and these new analysis methods are called “static light scattering” (SLS), “small-angle X-ray scattering” (SAXS), and “small-angle neutron scattering” (SANS). In combination with a fractionation method, light scattering methods can be used to determine the molecular weight distribution of polymers.[118,153]

7.13.3 VISCOMETRY

In order to determine the viscosity average molecular weight of polymers, $\bar{M}_v$, the intrinsic viscosity of the polymer in a solvent is determined by using a capillary viscometer, and the Mark-Houwink equation is applied.[154,155] The intrinsic viscosity is the limiting value of the reduced viscosity as the concentration of the polymer in solution is extrapolated to zero. The value of $\bar{M}_v$, is intermediate to those of $\bar{M}_n$ and $\bar{M}_w$, but is always closer to $\bar{M}_w$. Viscometry can be applied in the molecular weight range of 1,000–10,000,000. Formerly, the Vistex method was applied for practical situations in industry.[156] In this method, the intrinsic viscosity of latex dissolved in Vistex solvent (85/15 benzene/isopropyl alcohol) is determined.

7.13.4 ULTRACENTRIFUGATION

Ultracentrifugation is also an absolute method and is used in the range of 1,000-1,000,000 molecular weight, especially for heterogeneous polymer samples. It gives

of graft copolymer.[172] Ultracentrifugation was also applied to characterize the graft copolymers.[173, 174]

It is possible to separate the grafts from the polymer backbone by chemical cleavage using oxidizing agents when the polymer backbone has residual double bonds.[175, 176] The free graft polymers can be analyzed as for conventional polymers.[177,178] Saponification and reacetylation are applied to study long-chain branching on the polyVAc.[179-187] Determination of short chains and side groups can be carried out by IR and NMR spectroscopy.

The comparison of solution and melt viscosities gives an indication of the degree of branching. The Weissenberg rheogonimeter is used for this purpose.

7.14.2 Cross-Linked Polymer Content

Cross-linked polymer content is the insoluble polymer (or the polymer having infinite molecular weight) part of the total polymer. The separation of the insoluble gels is subject to errors and the experimental criteria strongly depend on the experimental procedure.[188,189] Donescu and co-workers extracted dry polyVAc films successively in boiling water and benzene for 8 hours and determined the amount of water-soluble, benzene-soluble, and insoluble fractions gravimetrically. The insoluble fraction was considered as cross-linked polymer.[190,191] NMR analysis was found to be useful to determine cross-linking during polymerization.[118]

7.15 CHEMICAL COMPOSITION OF COPOLYMERS

IR, NMR spectroscopy, and pyrolysis-GC are used to determine the average chemical composition of copolymers. UV spectroscopy can also be applied to copolymer analysis (rarely) if a characteristic, undisturbed UV peak is available. After determining the average copolymer composition, chemical composition distribution is sometimes required to obtain the relative abundance of copolymer chains.

7.15.1 Infrared Spectroscopy

IR spectroscopy is one of the main methods used to characterize polymers and copolymers.[147,192-193] Core-shell latex particles of polyVAC and polystyrene are analyzed with IR and Raman spectroscopy. Fourier-transform IR (FTIR) has higher sensitivity and resolution than the conventional IR and is used extensively for polymer analysis.[194] Attenuated total reflectance FTIR (ATR-FTIR) is also a suitable method to analyze drying latex films that still contain some water.[195-197]

7.15.2 Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy is usually appropriate to determine the composition and the microstructure of copolymers because the characteristic signals of the different monomer units are much more pronounced in NMR than in IR. Both proton and carbon-13 NMR spectroscopy can be applied to copolymer analysis.[192,198,199] Arzamendi and Asua determined the composition of VAc-methyl acrylate[200] and methyl methacrylate-ethyl acrylate copolymers,[201] whereas Bataille and Bourassa[202] and Erbil[203] determined VAc-butyl acrylate by using NMR spectroscopy.

7.15.3 Pyrolysis Gas Chromatography

In this method, a known amount of copolymer sample (usually a dried film) is heated to temperatures above 400°C instantaneously. Thermal degradation of the sample occurs at this temperature. Then, the degradation products (in some cases the monomers) are separated and analyzed by GC.[118, 204] Copolymer samples of known composition are required to calibrate this analysis method.

7.15.4 Chemical Composition Distribution

As stated above, the chemical composition distribution of copolymers gives the relative abundance of copolymer chains. The copolymer chains with different chemical compositions have to be separated before their compositions can be analyzed. Thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), and high-performance precipitation liquid chromatography (HPPLC) are used for this purpose. German and co-workers published an excellent review on this subject.[118]

7.15.5 Monomer Sequence Distribution

When various feed strategies are applied during emulsion copolymerization, experimental data on monomer sequence distribution of a copolymer chain are required to confirm the validity of the approach. Monomer sequence distribution data are also needed for comparison of the theoretical kinetic copolymerization models. Proton or carbon-13 NMR is used to determine the monomer sequence distribution.[118,205] Since both co-isotacticity of copolymers and the physical mixing of two homopolymers should also be taken into account during NMR analysis, the determination of the monomer sequence distribution is a very complicated process. Sometimes the comparison of theoretically calculated sequences is used for NMR peak assignment.[118]

7.16 SURFACE TENSION OF DRIED LATEX FILMS

The surface tension of polymers cannot be measured directly because of the elastic and viscous restraints of the bulk solid phase, and thus the use of indirect methods is required.[206,207] The laws of capillarity of liquids cannot be applied to solid polymers because the mobility of the surface molecules in polymers are exceedingly small when compared with the liquids. Most polymeric films are incapable of adjusting to such equilibrium conformations, and in practice their surface structure will be largely a frozen-in record of an arbitrary past history where some imperfections, humps, and surface waves are present.

The only general method is the rather empirical one of estimating polymer surface tension from that of the contacting liquid. This is a useful method and has many practical consequences in the surface coating, ink, detergent, lubricant, adhesive, emulsifier, etc. industries.

In most instances, when a liquid is placed on a polymer, it will not wet it but will remain as a drop having a definite angle of contact, θ, between the liquid and polymer phases. Polymers are low-energy surfaces and they attract the molecules of the liquid with less force than that with which the liquid molecules attract one another. Therefore, the molecules in the liquid next to the surface have a weaker force field than in the liquid surface.[207] The liquid molecules at the interface are pulled more strongly into the bulk of the liquid than they are by the polymer. There is a tension in the layer adjacent to the polymer, and the liquid molecules are somewhat separated owing to the one-sided force field. The situation is analogous to the behavior of a drop of one liquid on another immiscible liquid, the drop liquid having the higher surface tension than that of the lower liquid.

Contact angles can be measured by static methods such as direct measurement with a goniometer eye-piece, captive bubble, tilting plate, drop dimensions, and Wilhelmy plate methods, or by various dynamic methods.[207]

7.16.1 CRITICAL SURFACE TENSION OF POLYMER

An empirical organization of contact angle data on polymers was introduced by Zisman and co-workers.[208,209] They measured θ for a series of liquids on the same polymer sample, and they plotted cos θ versus surface tension (γ_L) of the liquids (Fox and Zisman plot). Even for a variety of nonhomologous liquids, the graphical points fell close to a straight line or collected around it in a narrow, rectilinear band. Each line extrapolated to zero θ at a certain γ_L value, which Zisman called the "critical surface tension of polymer," γ_c. They proposed that as γ_L decreases toward γ_c, the interfacial tension between the polymer and the liquid (γ_{SL}) will approach zero, and when γ_{SL} reaches zero, γ_L will be equal to γ_c (but not the surface tension of polymer, γ_{SV}). Zisman warned that $\gamma_c \neq \gamma_{SV}$, and γ_c is an empirical value characteristic of a given solid; however, γ_{SV} is a thermodynamic quantity.[209]

The critical surface tension concept was found to be useful to classify the polymer surfaces. However, there are objections to this method because the value of γ_c is often uncertain since the extrapolation is quite long, and considerable curvature of the empirical line is present for solids on which a wide range of liquids form nonzero contact angles.[210] It is generally believed that when dealing with liquids where van der Waals forces are dominant, γ_c of the polymeric solid is independent of the nature of liquid and is a characteristic of the solid alone.[209, 211] However, when dipolar and hydrogen bonding interactions contribute to the polymer/liquid interactions, γ_c may depend on both the nature of the liquids and the polymer. This reality led to the concepts of surface and interfacial tension components theory.

7.16.2 SURFACE TENSION COMPONENTS OF POLYMERS

Good and Gririfalco[212, 213] developed a theory of liquid–liquid interfacial tension in 1957, based on the theory of solubility of nonelectrolytes[214] and the Berthelot "geometric mean"[215] hypothesis for the attractive constant in the van der Waals equation. The proposed theory was that the free energy of adhesion between two phases might be given by the geometric mean of the free energies of the cohesion of the separate phases. This approach was found to be a good approximation for fluorocarbon–hydrocarbon systems, but not for many immiscible water–organic liquid systems where hydrogen bonding is dominant. In 1957, Bondi and Simkin[216] proposed to separate the heat of vaporization, ΔH_v, of water into two terms: one is the London dispersion interaction term and the other is hydrogen-bonding. Since surface tension [or surface free energy] is related to the heat of vaporization through the cohesive energy density concept of Hildebrand,[217] Fowkes[218] hypothesized that the surface tension of a liquid or solid could be separated in a similar manner into additive components. Fowkes suggested that interfacial interactions between two bulk phases can only occur between forces of the same type, i.e., dispersion–dispersion, polar–polar, hydrogen bonding–hydrogen bonding. In the case when London dispersion forces dominate at the interface, Fowkes further proposed that it can be expressed by a geometric mean equation.[218,219]

van Oss, Good, and Chaudhury[206,210,220] developed a more advanced approach after 1985, based on the Lifshitz theory[221] of the attraction between macroscopic bodies to estimate the free energy of adhesion between two condensed phases. An important result is that the contribution of dipole-dipole attraction on interfacial interactions, γ^p, and the dipole-induced dipole attraction, γ^i, were far smaller relative to γ^d than had been thought. They then, suggested that a solid surface consists of two terms, one is Lifshitz-van der Waals interactions, γ^{LW}, comprising dispersion, dipolar, and induction forces, and the other term is the acid-base interaction term, γ^{AB}, comprising all the electron donor-acceptor interactions such as hydrogen-bonding. They thought that the Lifshitz calculations yield γ^{LW}, that is the consequence of all the electromagnetic interactions taken together, whether due to oscillating temporary dipoles (γ^d), permanent dipoles (γ^p), or induced dipoles (γ^i). The general contact angle equation was derived as

$$\gamma_L(1+\cos\theta) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right) \tag{7.3}$$

In this derivation, van Oss and co-workers adopted Small's[222] combining rule for acid-base interactions, which is not a geometric mean:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+\gamma_i^-} \tag{7.4}$$

where γ_i^+ is the Lewis acid, and γ_i^- is the Lewis base parameter of surface tension. If both γ_i^+ and γ_i^- are present, the polymer surface is termed as "bipolar." If one of them is not present (equals to zero), the polymer surface is termed "monopolar." If both γ_i^+ and γ_i^- are absent, the polymer surface is termed "apolar." Therefore, $\gamma_i^{AB} = 0$ for apolar and monopolar substances, and γ_i^{AB} is present only for bipolar substances.

The total interfacial tension between the polymer and the contacting drop liquid is given as

$$\gamma_{SL} = \left(\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}}\right)^2 + 2\left(\sqrt{\gamma_S^+} - \sqrt{\gamma_L^+}\right)\left(\sqrt{\gamma_S^-} - \sqrt{\gamma_L^-}\right) \tag{7.5}$$

The most important consequence of Eq. 7.5 is that the contribution of acid-base interaction results in negative total interfacial tension (or free energy) in some circumstances. This occurs if $\gamma_L^+ \rangle \gamma_S^+$ and $\gamma_L^- \langle \gamma_S^-$, or if $\gamma_L^+ \langle \gamma_S^+$ and $\gamma_L^- \rangle \gamma_S^-$, and if $\left|\gamma_{SL}^{AB}\right| \rangle \left|\gamma_{SL}^{LW}\right|$. A solid-liquid system may be stable although it has negative γ_{SL}.[210, 223]

In order to use the general contact angle equation (Eq. 7.3) in determining solid surface tension components, a set of values of γ_L^{LW}, γ_L^+, and γ_L^- for reference liquids are determined arbitrarily. The values of all acid-base parameters derived therefrom are relative to those of water.[220]

After having the reference liquid values, there are two methods to calculate the polymer surface values of γ_S^{LW}, γ_S^+, and γ_S^-. In the first method, three forms of Eq. 7.3 are solved simultaneously by using the contact angle data of three different liquids, with two of them being polar. In the second method, γ_S^{LW} can be determined first by using an apolar liquid, then two other polar liquids are used to determine γ_S^+ and γ_S^-. It is recommended that if polar liquids are employed, water should always be used, otherwise, if only two polar liquids other than water are used (e.g., ethylene glycol and formamide), highly variable γ_S^+ and γ_S^- may be obtained.[210, 224]

van Oss-Good methodology was successfully applied to protein and polymer interactions with liquids, polymer solubility prediction in solvents, critical micelle concentration estimation of surfactants, polymer phase separation, and microemulsion formation.[225-227] This methodology was applied to liquid-liquid interactions[228] as well as polyVAc-butyl acrylate copolymer surface tension determinations[203] and found very useful to interpret the interactions at the interfaces. A nonlinear programming method was also developed for the application of geometric-mean relation to the polymer surface tension determination.[229]

7.17 THERMAL PROPERTIES OF LATEX FILMS

Glass transition temperature (T_g) and crystalline melting temperature (T_m) are two properties that characterize polymers and copolymers thermally. When a polymer cools down below its T_g, the amorphous domains of this polymer cease thermal motions and then rigidity, brittleness, and stiffness are introduced to the polymer. T_m is the melting temperature of the crystalline domains. Both T_g and T_m are related to the microstructure of the copolymer chain, chain rigidity, molecular symmetry, and intermolecular forces due to pendant groups. In addition, when a polymer (or copolymer) is cross-linked, its T_g increases with increasing cross-link density.

In order to determine these thermal transitions, differential scanning calorimetry (DSC) and dynamic thermal analysis (DTA) methods are used. These methods depend on the changes in specific volume and heat capacity of the polymer.

T_g of a copolymer is roughly proportional to the weight fractions and T_g values of the homopolymers of which it is formed. The T_g of a copolymer film is highly influenced by the copolymer composition distribution and the average copolymer composition. Several semi-empirical equations have been proposed to correlate between T_g values and copolymer composition.[230-234] Since VAc homopolymer has a T_g of +29°C and can easily emulsion copolymerize with acrylic monomers having their homopolymer's T_g between –85°C (poly-2-ethylhexyl acrylate) to +100°C (polymethyl methacrylate), the T_g values of the produced copolymer films can be tailor-made for specific applications. Then, it is necessary to check the T_g values of the copolymers experimentally.[203]

7.18 MECHANICAL PROPERTIES OF LATEX FILMS

The mechanical properties of homo- and copolymer latex films are very sensitive to their structure and the details of the emulsion polymerization procedure.[235-244] The polymer film samples are subjected to tensile strength, elongation at break, elastic modulus (by which is meant stress at a prescribed elongation), tear strength, and impact strength tests. Stresses are conventionally calculated using initial cross-sectional areas, which for polymeric films are considerably greater than the cross-sectional areas after stretching. Factors such as humidity, temperature, surface cleaning, handling procedure, etc. all affect the results of mechanical property determinations and should be carefully controlled. There is also the matter of drawing inferences concerning material quality from the mechanical test results of thin films obtained from latices. Usually, arithmetic mean of up to 13 sample results are taken to report the test data. Quality assurance by sampling is an important subject industrially.[245]

Emulsion copolymer films with the same average composition but with strongly varying microstructures give very different dynamic moduli results.[246] It was found that chemical composition distribution has a tremendous effect on mechanical properties such as elastic modulus, elongation at break, and impact strength.[247] Cavaille and co-workers investigated the mechanical properties of VAc-butyl acrylate copolymer films obtained from latices prepared according to different emulsion polymerization processes.[248, 249] They reported that high-resolution mechanical spectrometry is very useful in investigating structure-property relationships.

Cross-linking and polymer interdiffusion also have influences on the mechanical properties of polymer films. The viscoelastic properties of cross-linked latex films, such as storage and loss moduli, and the loss tangent behave in a similar manner as the properties of corresponding homogeneous cross-linked polymers.[250]

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8 Factors Affecting the Final Properties of Polyvinyl Acetate-Based Latices

8.1 PRACTICAL APPROACHES TO DESIRED PVAc LATEX PROPERTIES

8.1.1 Brief Description of VAc Emulsion Polymerization

The initiation takes place in the water phase with a water-soluble persulphate initiator, and an oligomeric aqueous polymer is formed. It is solubilized in water by its end groups, but it becomes insoluble as polymerization proceeds. The polymer particles formed absorb monomer, and, when conversion becomes about 14%, the rest of the monomer is absorbed substantially into the polymer particles and the separate monomer phase disappears at about 14–20% conversion. The polymerization proceeds in the particles, which can be treated as a compartmentalized system. Since polyVAc particles are relatively large in size (0.2–1.0 μm), there is more than one growing radical per particle most of the polymerization time, with a varying mechanism for chain termination. A constant polymerization rate period is observed between about 20% and 80% conversion, which is approximately independent of monomer concentration. The polymerization rate depends on the number of particles to about 0.2 power, and on the emulsifier concentration to between 0 to 0.25 power. The molecular weights of polyVAc are independent of all variables and mainly depend on chain transfer to monomer. The number of particles in the reaction system is observed to decrease rapidly over the first 20% of conversion, but thereafter to remain constant between 20 to 100% conversion, within experimental error. However, some authors believe the number of particles decreases continuously during the period of constant reaction rate after 10–14% conversion. It was proposed that the loci of polymerization are both in the aqueous phase and in the micelles. The oligomers thus formed attain a certain size and are then precipitated from the aqueous phase. During precipitation, oligomeric particles release the emulsifier that kept them in equilibrium in the aqueous phase. The emulsifier release forms micelles to generate new particles. This theory explains the decrease in the number of particles during the course of reaction, and the fresh nucleation of particles even at high conversion.

The number of particles in the same unit weight of latex is an increasing function of emulsifier concentration. The percentage of monomer converted to polymer appears to be most closely related to the total particle surface area per ml of emulsion. The total particle area is the most important parameter to control the rate of VAc emulsion polymerization. When the total surface area of the particles exceeds the covering power of the emulsifier, the remaining polymer macromolecules and microparticles are destabilized and can be swept up by larger particles.

No single emulsifier has been found suitable for all uses in emulsion polymerization of VAc. Nonionic emulsifiers give better shelf and freeze-thaw stability, and resistance to electrolytes. Anionic emulsifiers are used to produce finer particles; however they cause more grafting on polyVAc. Blends of anionic and nonionic emulsifiers are used to give balanced properties. The emulsifier adsorption onto the particle surface decreases with increasing polarity of the polymer surface. Depending on the extent of the dispersion, polar, orientation, and hydrogen-bonding interactions, the emulsifier molecules adsorbed onto the polymer phase-liquid interface may acquire a nonvertical orientation; they may be arranged with greater planarity the higher the interaction on the polar part of the emulsifier molecule. Therefore, less emulsifier may be consumed for the formation of a given polyVAc surface, which facilitates the increase of the overall surface area and the decrease in particle size.

The chemical groups located on the particle surface maintain its colloidal stability. sulfate ionic groups from peroxide initiator decomposition, hydroxyl groups from sulfate hydrolysis, from the adsorption of polyvinyl alcohol, and from the hydrolysis of polyVAc during polymerization, and carboxyl ionic groups from the sulfate oxidation may be present on the surface of the polyVAc particle. If it is not prevented, the hydrolysis reactions decrease the pH of the medium, and thus it is necessary to adjust the pH of the reaction medium. The initial pH is 3.5 and drops, as the reaction proceeds, to about 2.2 at completion unless adjusted by a suitable buffer system or by the addition of small amounts of alkali such as potassium hydroxide.

The increase in the reaction temperature decreases the mean-particle size, increases the rate of polymerization and the rate of chain transfer, decreases the molecular weight of polymer chains, and alters the molecular weight distribution. It also increases the monomer diffusion rate and, correspondingly, the amount of the monomer in the monomer-swollen latex particle increases. The increase in the reaction temperature may also cause easy flocculation and the formation of cross-linked and/or branched polymer.

Only sufficient constant agitation rate to keep the monomer and other constituents suitably dispersed is required during polymerization. A higher agitation rate decreases the particle size, increases the polymerization and monomer diffusion rate, and, more important, the chain transfer rate. Excessive agitation destabilizes the latex mechanically. In industrial practice, the nature and shape of the stirrer may affect the production performance, and this is usually determined by trial and error. It is necessary to avoid excessive foaming and precipitation either in the reactor or on the reactor walls and stirrer.

Semicontinuous emulsion polymerization is usually applied in industry in order to lengthen the particle-generating period and slow the growth rate of the particle by regulating the rate of addition of reactants to the reactor. Only part of the total reaction formulation is introduced at the beginning of the polymerization reaction, the remainder being added, according to a predetermined schedule, during the course of polymerization. The conversion-time curves are linear and dependent on the feed rates. High solids contents and small particle size latices having high viscosities can be obtained with this process. The conversion of monomer to polymer is found to be a first-order reaction. A linear increase in the rate of polymerization, with the increase in the number of particles per cm^3 of latex, is also seen in these circumstances. In the semicontinuous process, if the monomer addition rate is slower than the rate of reaction, the rate of polymerization is controlled by the monomer feed rate only. If heat removal is sufficient, the conversion is complete within the predetermined time and no free monomer remains. Otherwise, refluxing is required after the normal production time, which causes side reactions and sometimes agglomeration of the latex. If the feed rate is too slow, a broader particle size distribution usually results. (This is sometimes a desirable property in indoor paint binder applications.) The slow feeding rate also results in low quantities of monomer in monomer-swollen particles. This condition gives rise to higher molecular weights, branching, and increased polydispersity.

Only a limited quantity of monomer, i.e., 2 to 5%, is present in the system throughout the reaction for semicontinuous polymerization processes. In practice, this is a *de facto* "seed" process, the seed quantity depending on the extent of the original addition of initial monomer and other ingredients. As long as the monomer weight percentage relative to monomer plus polymer is below 14%, there will be no monomer drops as separate entities. Particle formation is complete at an early stage, stabilized by adsorption of polyvinyl alcohol (if present in the formulation), with possible extra stabilization due to initiator residues. Particle sizes increase by monomer absorption and by adsorption of initiated radicals from the water phase. It is obvious that particles are formed continuously as monomer, initiator, and emulsifier are fed into the reactor. However, the particles formed early in the reaction have a longer growth period compared to the particles formed later in the polymerization reaction. It follows that the "older" particles would then be larger than the "younger" particles. Nevertheless, when semicontinuous technique is applied, the period of particle formation is extended, tending to raise the number of smaller particles and have a broadening effect on particle size distribution. The semicontinuous process usually produces a bimodal molecular weight distribution having a high molecular weight fraction—attributed to chain transfer to polymer due to monomer-starved conditions—with a substantial amount of low molecular weight fraction.

Some plasticizers, such as dibutyl phthalate and tricresyl phosphate, are added to aid in film coalescence and flexibility (usually after the polymerization is completed). Tricresyl phosphate also improves fire-retardancy. Glycols such as butyl glycol and butyl glycol acetate are added to latices to improve freeze-thaw stability and wet edge characteristics.

Many papers have been published to explain the mechanisms of VAc emulsion polymerization which are given in Section 3.3. Nevertheless, when all of them are considered, many controversial subjects arise, depending mostly on the different polymerization conditions applied by different workers, but they also help one understand clearly the many points on the mechanism of VAc emulsion polymerization. Some of the important papers are outlined below.

Priest reported the particle growth mechanism in the emulsion polymerization of VAc in 1952.[1] The number of particles actually found at the completion of an emulsion polymerization is the total number of primary particles less the reduction caused by coalescence during the course of reaction. The coalescence of particles is dependent on the quantity and efficiency of the material employed as stabilizer. Thus, the higher the concentration of the added sodium lauryl sulfonate anionic emulsifier, the smaller the average particle size that resulted.[1]

French investigated the effect of nonionic ethylene oxide-propylene oxide block copolymer emulsifier in VAc emulsion polymerization in 1958.[2] The number of particles in the reaction system was observed to decrease rapidly over the first 20% of conversion, but thereafter remained constant between 20 to 100% conversion, within experimental error. With the increase of the emulsifier concentration, the number of the latex particles in the same unit weight of latex increased greatly. French concluded that latex particles containing polymer-plus-monomer have reached their maximum diameter by the time of 13.5% conversion, and thereafter the change in diameter is only as a result of shrinkage accompanying polymerization.[2] It was apparent that the particle size decreases and the number of particles increases with increasing emulsifier concentration, but these relationships were not linear. Instead, the total surface area of the particles per 100 g of polymer was a linear function of the emulsifier concentration. French also reported the variation of the viscosity of the final latex with particle size: the higher the emulsifier concentration, the higher the viscosity that was found.[2] The viscosity of a latex at a constant solids content increases with decreasing particle size. When the average particle size decreases for the constant amount of polymer, it is evident that the total surface area of the polymer particles increases. This means that the increase in the latex viscosity corresponds to an increase in the total surface area, and because the surfactant concentration is proportional to the total surface area, the result of the increase in the latex viscosity with the increase in the surfactant concentration is reasonable. When the logarithm of the latex viscosity against the emulsifier concentration is plotted, a straight line results which fits most of the experimental data. When the logarithm of the latex viscosity against the total surface area is plotted, another straight line, parallel to the first one, is found when the logarithm of the latex viscosity against the total surface area is plotted.

Napper and Alexander examined the effect of the addition of anionic, nonionic, and cationic emulsifiers to the emulsion polymerization of VAc.[3] The concentration of all the emulsifiers was kept so low that they did not allow the formation of micelles in the aqueous phase. Nonionic emulsifiers were found to have little effect on the polymerization reaction. Anionic emulsifiers accelerated the reaction, the effect increasing with the length of the hydrophobic part of the emulsifier, whereas cationic emulsifiers retarded the reaction and there was no effect of chain length of the emulsifier on this retardation behavior. In addition, anionic emulsifiers increased the number of particles, whereas the cationic emulsifiers caused a decrease and gave a very broad distribution of sizes.[3]

Dunn and Taylor also determined that the emulsion polymerization of VAc was different from ordinary emulsion polymerization in that the monomer concentration in both polymer and water phases decreased continually throughout the reaction when the reaction was carried out in the absence of added emulsifier.[4]

Elgood, Gulbekian, and Kinsler investigated the semicontinuous emulsion polymerization of VAc similar to the industrial process in 1962.[5] They compared the results of two different recipes where only nonionic emulsifier was used in the first one, and both nonionic and anionic emulsifiers were used in the second. They determined that the number of particles was approximately 40 times more in the second recipe than in the first, and the number of particles decreased as polymerization proceeded for both recipes. In contrast, in the first run, the total particle surface area per ml of emulsion increased throughout the process, whereas in the second run it remained constant over the last three-quarters. In both runs, the % monomer converted to polymer appeared to be most closely related to the total particle surface area per ml of emulsion. They then concluded that the total particle area was the most important parameter to control the rate of polymerization of the high water-soluble VAc monomer.[5]

Patsiga, Litt, and Stannett determined that soluble polyVAc molecules are produced which are stabilized by the emulsifier, and these molecules function as nuclei for further polymerization and form the monomer-swollen polymer particles.[6] When the total surface area of the particles exceeds the covering power of the emulsifier, the remaining polymer macromolecules and microparticles are destabilized and can be swept up by larger particles. The number and size of the particles are constant during the main part of the reaction, between 20–85% conversion.

Elgood and Gulbekian investigated the redox-initiated emulsion polymerization of VAc at 50°C and determined that, for maximum conversion of monomer to polymer, it is necessary to adjust the pH of the system.[7] The initial pH was 3.5 and dropped, as the reaction proceeded, to about 2.2 at completion unless adjusted by the addition of small amounts of alkali such as potassium hydroxide.

Bataille, Van, and Pham found that the conversion-time curves were linear and dependent on the feed rates for all the runs in the semicontinuous emulsion polymerization of VAc.[8] The conversion of monomer to polymer was found to be a first-order reaction. A linear increase in the rate of polymerization was seen with the increase in the number of particles per cm^3 of latex. In addition, similar to Elgood et al.,[5] a linear increase in the rate of polymerization with the increase in the surface area of particles per cm^3 of latex was also found.[8] It was obvious that particles were formed continuously as monomer, initiator, and emulsifier were fed into the reactor. However, the particles formed early in the reaction have a longer growth period compared to particles formed later in the polymerization reaction. It follows that the "older" particles would then be larger than the "younger" particles. Nevertheless, when semicontinuous technique was applied, the period of particle formation was extended, tending to raise the number of smaller particles and to have a broadening effect on particle size distribution. Evidence of fresh nucleation was also observed in the electron micrographs. It was proposed that the loci of polymerization were in both the aqueous phase and the micelles. The oligomers thus formed attained a certain size and were then precipitated from the aqueous phase. During precipitation, oligomeric particles released the emulsifier that kept them in equilibrium in the aqueous phase. The emulsifier release formed micelles to generate new particles. This theory explained the decrease in the number of particles during the course of reaction, and the fresh nucleation of particles even at high conversion.[8]

Zollars[9] observed the general characteristics of a VAc emulsion polymerization so that (1) the separate monomer phase disappeared at about 20% conversion, (2) a constant rate period was observed between about 20% and 80% conversion, and (3) the emulsifier level was observed to have no significant effect on the polymerization rate. He pointed out that the opposite comment of Napper and Alexander[3] on this point was due to the fact that they used very low monomer concentrations, which were less than the solubility of VAc in water, and emulsifier concentrations less than the CMC. Zollars reported that the number of particles increased with increasing conversion at all levels of initiator.[9]

Warson presented the specific problems of industrial production. So that exact repeatability within narrow limits is possible, the final solids content should be constant ±1%, and the particle size, emulsion viscosity, polymer molecular weight, and residual free monomer should be maintained within narrow limits.[10] He pointed out that it is normally desirable to prepare a latex at the highest concentration possible, usually >50%, unlike theoretical work. In industrial practice, the nature and shape of the stirrer may affect production performance, and this is usually determined by trial and error. It is necessary to avoid excessive foaming and precipitation either in the reactor or on the reactor walls and stirrer. In many cases, successful laboratory processes had failed unpredictably and irregularly on a production scale, with heavy precipitation.[10]

Chang, Litt, and Nomura examined the variation of the polymerization rate with changes in particle concentration, type of emulsifier, emulsifier concentration, persulphate initiator concentration, ionic strength, and monomer volume.[11] They reported that there was some agreement in the previous literature about the following features of the reaction: (1) rate of polymerization is approximately independent of monomer concentration, at least from 20 to 85% conversion; (2) the number of particles is roughly independent of conversion after 30% conversion in unseeded polymerizations; (3) the polymerization rate depends on the particle concentration to about 0.2 power; (4) dependence of the polymerization rate on the emulsifier concentration is small with a maximum of 0.25 power; and (5) molecular weights are independent of all variables and mainly depend on chain transfer to monomer.[11]

Yeliseva pointed out that the dependency of the polymerization rate on the emulsifier concentration was a function of the area occupied by the emulsifier molecule in the saturated adsorption layer on the polymer particles.[12] Depending on the extent of the dispersion, polar, orientation, and hydrogen-bonding interactions, the emulsifier molecules adsorbed onto the solid phase-liquid interface may acquire a nonvertical orientation; they may be arranged with greater planarity the higher the interaction on the polar part of the emulsifier molecule. The emulsifier adsorption decreases with increasing polarity of the polymer surface. Therefore, less emulsifier may be consumed for the formation of a given surface such as polyVAc, which facilitates the increase of the overall surface area and the decrease in particle size.[12]

Warson gave a clear picture for the VAc emulsion polymerization mechanism:[13] with a water-soluble initiator, the initiation takes place in the water phase and oligomeric aqueous polymer is formed. It is solubilized in water by its end groups, but it becomes insoluble as polymerization proceeds. The polymer particles formed absorb monomer, and, when conversion becomes about 14%, the rest of the monomer is absorbed substantially into the polymer particles. The polymerization then proceeds in the particles, which can be treated as a compartmentalized system. Since polyVAc particles are relatively large in size (0.3–1.0 micron), there is more than one growing radical per particle most of the polymerization time, with a varying mechanism for chain termination.[13] For semicontinuous polymerization processes, only a limited quantity of monomer, i.e,. 2 to 5%, is present in the system throughout the reaction. This is a *de facto* "seed" process, the seed quantity depending on the extent of the original addition of initial monomer and other ingredients. As long as the monomer weight percentage relative to monomer plus polymer is below 14%, there will be no monomer drops as separate entities. Particle formation is complete at an early stage, stabilized by adsorption of polyvinyl alcohol with possible extra stabilization due to initiator residues. Particle sizes increase by monomer absorption and by adsorption of initiated radicals from the water phase. Sometimes bimodal molecular distribution occurs, indicating two different mode of polymerization; one is in the monomer-swollen particles and the other is the result of aqueous or surface initiation.[13]

Hayashi, Komatsu, and Hirai reported that new small particles were formed in a VAc emulsion polymerization system containing a small amount of seed particles, whereas no new particles were observed in the system containing a large amount of seed particles.[14] It was found that the diameter of the seed particles and the newly formed small particles increase with increasing rotational speed of the stirrer. The number of new, small particles decreases with the stirring rate. On the other hand, it was found that the diameter of the particles increases with the increase of the stirring rate in the unseeded polymerization. Higher stirring rates lead to coagulation of more small particles during the initial stage of polymerization where the small particles form.[14]

El-Aasser, Makgawinata, and Vanderhoff examined the difference between batch and semicontinuous VAc emulsion homo- and copolymerization.[15] They determined that batch homopolymerization produced a narrower molecular weight distribution than the semicontinuous process. The semicontinuous process produced a bimodal molecular weight distribution having a high molecular weight fraction attributed to chain transfer to polymer due to monomer-starved conditions — with a substantial amount of low molecular weight fraction.[15]

8.1.2 TO REDUCE PARTICLE SIZE

The following actions will decrease the particle size of latex:

1. Increasing the concentrations of emulsifier and protective colloid
2. Increasing the concentration of initiator
3. Feeding the monomer more slowly
4. Increasing the temperature of polymerization
5. Increasing the monomer-to-water ratio

8.1.3 TO INCREASE PARTICLE SIZE

The following actions will increase the particle size of the latex:

1. Decreasing the concentrations of emulsifier and protective colloid
2. Decreasing the rate of addition of emulsifier and protective colloid

3. Decreasing the concentration of initiator
4. Decreasing the rate of addition of initiator
5. Decreasing the temperature of polymerization

8.1.4 To Increase Latex Viscosity

The following actions will increase the viscosity of the latex:

1. Decreasing particle size
2. Increasing the concentrations of emulsifier and protective colloid
3. Increasing the solids concentration
4. Increasing the temperature of emulsion polymerization

The viscosity of latex is independent of the molecular weights of the polymer it contains, and it is mostly dependent on the mean particle size and particle size distribution. The higher the emulsifier concentration, the higher the viscosity.

8.1.5 To Increase Molecular Weight of Polymer

The following actions will increase the molecular weight of the polymer film produced by drying the latex:

1. Avoiding chain transfer agents
2. Decreasing the temperature of polymerization
3. Using a redox-type initiator at low temperatures
4. Decreasing the concentration of initiator
5. Increasing initial charge of monomer to 15–20%
6. Increasing the rate of addition of monomer

The control of molecular weight by varying the emulsifier, initiator temperature, or agitation speed is usually impractical. In industry, the nature and concentration of chain transfer agent is important for this purpose. If no chain transfer agent is used, the produced polyVAC is usually highly branched because of the high degrees of conversion of commercial latices. These branches in the polymer structure also have high molecular weights.

8.1.6 Conditions for Unstable Latices

If a latex is colloidally unstable, the following reasons may be the cause:

1. There is insufficient emulsifier concentration.
2. The pH varies beyond the usual range during and after the emulsion polymerization.
3. Large quantities of electrolytes such as KCl, NaCl, $CaCl_2$, and $MgCl_2$ are present in the aqueous medium, and the particles are specifically stabilized with electrostatic mechanism. When $Al_2(SO_4)_3$ is added, it usually coagulates the latex.

4. The presence of low-molecular-weight alcohols such as methanol and ethanol desorb the steric stabilizers from the surface of the particles, resulting in coagulation. High-molecular-weight alcohols and polyhydroxy compounds do not act in this manner, and some of them are used as steric stabilizers.
5. Too high and too low temperatures cause instability because of the decrease of the energy barrier.
6. High-speed agitation and any kind of mechanical shear remove the stabilizers from the water-particle interface.

8.2 THE EFFECT OF THE TYPE OF THE POLYVINYL ALCOHOL AND CELLULOSIC PROTECTIVE COLLOIDS ON PVAc HOMOPOLYMERS

In industrial practice, it has been customary to use a "protective colloid," notably hydroxyethyl cellulose (HEC) or polyvinyl alcohol, as the principal surface-active material in the VAc homopolymerization system rather than the micelle generator emulsifiers. Some emulsifiers may also be added to the system, but their role seems to be secondary to that of the protective colloid. Protective colloids increase the viscosity of the water phase and impart water-sensitivity, haziness, and low scrub resistance to the film obtained by drying the latex.

HEC is generally used in the manufacture of VAc-based indoor paint binders because it imparts higher tolerance to the latices to mix with cheap inorganic extenders, such as calcite, than does the polyvinyl alcohol containing latices. Several types of HEC are available in the chemical industry, depending mainly on the degree of ethyl substitution and molecular length. In general, the higher the molecular weight of HEC, the higher the latex viscosity obtained. There are very few publications relating to HEC containing VAc homopolymer latices.

Donescu, Gosa, Diaconescu, Mazare, and Carp examined the emulsion polymerization rate of VAc in the presence of HEC protective colloid.[16] HEC macromolecule undergoes scission due to the oxidative degradation effect of the persulphate initiator used. After potassium persulphate addition at 70°C, the viscosity of HEC solution, or the ratio of viscosity/initial viscosity, showed considerable decrease and attained a constant value after time. Carbonyl groups were formed on HEC chains after oxidative degradation, which could be followed by UV absorbance at 263 nm.[16]

Donescu and Fusulan investigated the decomposition of potassium persulphate initiator during the semicontinuous polymerization of VAc, using polyvinyl alcohol and hydroxyethyl cellulose as protective colloids in the presence of nonionic and anionic emulsifiers.[17] It was found that the rate of potassium persulphate decomposition is higher in the aqueous phase containing a protective colloid and surfactant. The decomposition rate is low in the presence of VAc monomer.

Craig reviewed publications on the effect of the presence of HEC on the decomposition of persulphate initiator during the emulsion polymerization of VAc and suggested that HEC forms a redox pair with persulphates, which increases the rate of persulphate decomposition.[18]

The addition of polyvinyl alcohol protective colloid to the VAc emulsion polymerization system has many consequences, which have been studied much more than HEC addition. The experimental results showed that the viscosity, particle size, colloidal stability, and freeze-thaw stability of the final latex were determined largely by the fine chemical structure of the polyvinyl alcohol used in the polymerization. First of all, the final viscosity of polyVAc latices is very sensitive to the properties of the polyvinyl alcohols used in their preparations. Increased adsorption of polyvinyl alcohol will result in a reduction of average particle size and thus an increase in latex viscosity. Second, the addition of polyvinyl alcohol reduced the maximum rate of VAc polymerization and the particle size. The presence of polyvinyl alcohol in the polymerization system reduced the rate of polymerization to about half its original value, even at a concentration of only 0.36%. However, this effect is dependent on the type and nature of polyvinyl alcohol; small differences in the structure have profound effects on the properties of the polyVAc latex obtained.

Several types of polyvinyl alcohols are available in the chemical industry. Generally, 88% hydrolyzed polyvinyl alcohol types having varying molecular weights are preferred to produce polyVAc latices. These types give the maximum conversion and minimum polymer precipitate, but variations in the structure, branching, tacticity, and production methods of polyvinyl alcohol resulted in latices having different properties. In most instances, experience gained by trial-and-error guides because when one polyvinyl alcohol type, which is suitable for a process, is replaced by another, reputedly of better quality from the same manufacturer, the process may fail completely from the colloidal stability aspect. It is generally believed that when polyvinyl alcohol has a broad molecular weight and molecular species distribution, it gives more stable polyVAc latices. Fully hydrolyzed polyvinyl alcohol (95–98% hydrolyzed grades) was also used in order to improve water resistance of the final film; however, the storage stability of the produced latex was found to be poor. Similar to HEC behavior, but less in extent, persulphate initiators degrade the polyvinyl alcohol macromolecule by oxidation reaction, resulting in a loss in emulsion viscosity.

Some anionic and nonionic emulsifiers are used in conjunction with polyvinyl alcohol protective colloids in emulsion polymerization of VAc. It was determined that the solubility of some anionic emulsifiers in water increases in the presence of polyvinyl alcohol. The roles and effects of these emulsifier-polyvinyl alcohol pairs depend on their nature and reaction conditions and are generally examined as case studies in the open literature. Some related publications are outlined below.

O'Donnell, Mesrobian, and Woodward reported the kinetics investigation of VAc emulsion polymerization at 70°C using potassium persulphate as initiator and polyvinyl alcohol as protective colloid in 1958.[19] The initial quantity of the monomer was always considerably in excess of that required for saturating the aqueous phase at 70°C. The initiator concentration and the amount of monomer were kept constant, and only polyvinyl alcohol concentrations were changed during the experiments. It was observed that the increase in the polyvinyl alcohol concentration increased the rate of polymerization and there was a near constant of the ratio of the rate of polymerization to the 3/5th power of the polyvinyl alcohol concentration.[19] The authors kept the levels of initial monomer and the polyvinyl alcohol concentration constant, and varied the potassium persulphate initiator concentration. After an induction period, it was found that the polymerization rate was constant up to at least 60% conversion. The relationship between the logarithm of the steady rate and that of the initiator concentration was found to be linear, and the slope of this relationship indicates an order of reaction of $[I]^0$. Light-scattering measurements failed to provide evidence of micelle formation, and O'Donnell, Mesrobian, and Woodward concluded that each molecule of polyvinyl alcohol might be a locus for the emulsion polymerization reaction.[19]

Dunn and Taylor confirmed the formation of stable suspension of polyVAc when polymerization was carried out in the absence of added emulsifier in 1965.[4] The addition of the polyvinyl alcohol stabilizer reduced the maximum rate of polymerization and the particle size. The average particle diameters decreased from 0.3 micron to 0.1 micron by the addition of 0.24% w/v polyvinyl alcohol. It was proposed that chain transfer reactions between vinyl acetate and polyvinyl alcohol could occur giving a graft copolymer and retard the rate of polymerization because of the introduction of an alternative termination. Since the approach of a charged radical to a charged particle is not involved, the termination between polyvinyl acetate and polyvinyl alcohol may be favored.[4]

Noro published a paper on VAc emulsion polymerization in relation to the chemical structure of polyvinyl alcohol used as the protective colloid.[20] Emulsion polymerization does not occur with polyvinyl alcohol synthesized by acid hydrolysis, but a fairly stable emulsion was obtained with reacetylated polyvinyl alcohol, although the viscosity was low. When fully hydrolyzed polyvinyl alcohol was used as an emulsifier in order to improve water resistance, the storage stability was found to be poor. Results showed that the viscosity, particle size, stability, and freeze-thaw stability of the final latex were determined largely by the fine chemical structure of the polyvinyl alcohol used in the polymerization.[20]

Gulbekian and Reynolds made a survey of the use of polyvinyl alcohol as an emulsifier and protective colloid in the emulsion polymerization of VAc and other monomers.[21] They examined the optimum properties of the polyvinyl alcohol types, i.e., degree of hydrolysis, the average molecular weight on the emulsion polymerization mechanism, and the stability of the final latices. They stated that maximum conversion and minimum precipitate were obtained when 82.6–91.5% hydrolyzed polyvinyl alcohol with the maximum molecular weight in 4% (of the weight of the monomer) was used in conjunction with the half of 10-mole ethoxylated nonyl phenol emulsifier. Gulbekian and Reynolds also pointed out the interactions of polyvinyl alcohol with the persulphate initiators, which degrades the polyvinyl alcohol macromolecule by oxidation reaction, resulting in a loss of emulsion viscosity.[21]

Warson pointed out the importance of the type and properties of polyvinyl alcohol stabilizer used in emulsion polymerization of VAc.[10] He stated that when one polyvinyl alcohol type, which is suitable for a process, is replaced by another, reputedly of better quality from the same manufacturer, the process may fail completely from the colloidal stability aspect. By experience, he concluded that when polyvinyl alcohol has a broad molecular weight and molecular species distribution, it gives more stable polyVAc latices. Warson discussed that usually 88% hydrolyzed polyvinyl alcohol is used as a stabilizer in the VAc polymerization, but variations in the structure, branching, tacticity, and the production methods of polyvinyl alcohol resulted in latices having different properties. He suggested that VAc polymer has a grafting tendency onto polyvinyl alcohol in the semicontinuous process, and sometimes excessive grafting would cause instability when nonionic emulsifiers are added since the overall molecules of polyvinyl alcohol are not sufficiently hydrophilic after grafting unless some ionic groups have been introduced.[10]

Dunn[22] reviewed the effect of polyvinyl alcohol on polymerization of VAc. He stated that polyvinyl alcohols are polymeric emulsifiers, and the type preferred for emulsion polymerization application was with about 12 mole% residual acetyl groups produced by alkaline methanolysis of polyVAc (i.e., 88% hydrolyzed type). He cited the work of Tubbs[23] that the residual acetyl groups were not randomly distributed but occurred in short blocks. The presence of polyvinyl alcohol reduced the rate of polymerization of VAc to about half its original value, even at a concentration of only 0.36%. However, this effect is dependent on the type and nature of polyvinyl alcohol; small differences in the structure have a profound effect on the properties of the polyVAc latex obtained. Polyvinyl alcohol also acts as a thickener for the aqueous phase during emulsion polymerization. The final viscosity of polyVAc latices is very sensitive to the properties of the polyvinyl alcohols used in their preparations. Increased adsorption of polyvinyl alcohol will result in a reduction of average particle size, thus increasing latex viscosity. An anionic emulsifier such as sodium dodecyl sulfate is much more effective than polyvinyl alcohol in reducing the size of polyVAc latex particles, but it has little effect on the rate of polymerization reaction.[22]

Donescu, Ciupitoiu, Gosa, and Languri determined that the glass transition temperature of polyVAc decreases due to formation of a hydration shell when polyVAc latices are obtained in the semicontinuous process in the presence of polyvinyl alcohol.[24] They reported the existence of bound water on the polymer particles by using DTG and TGA measurements during the evaporation of polyVAc latices. Water was considered a true plastifier. In addition, it was postulated that the migration of the monomeric radical to the water phase is favored by the presence of the bound water, thus decreasing the water-polymer barrier.[24]

Lepizzera and Hamielec investigated the particle nucleation mechanism in seeded emulsion polymerization of VAc in the presence and absence of polyvinyl alcohol.[25] Two different grades of polyvinyl alcohols, which were approximately 88% hydrolyzed but had different weight average molecular weights (26,000 and 103,000), were used. In the absence of polyvinyl alcohol no new nucleation was observed by electron microscopy, while in its presence new particles were formed, giving a bimodal particle size distribution. The number of new particles was greater with the higher-molecular weight polyvinyl alcohol. The authors proposed that nucleation of new particles occurs via precipitation of "copolymer" polyvinyl alcohol-polyVAc radicals in the water phase.[25]

The presence of polyvinyl alcohol results in extensive grafting (see Sec. 3.3). Some researchers suggest that the adsorption of the polyvinyl alcohol onto the particle surface is a more dominant mechanism than grafting. Since grafting affects many final latex and film properties, some of the important papers are outlined below.

Warson suggested that when polyvinyl alcohol is used as the protective colloid, a considerable fraction is adsorbed onto the polymer particles. Grafting on polymer particles is probably very limited because of the excess monomer present in the reaction system.[13] In the semicontinuous process under monomer-starved and high temperature conditions, high grafting to polyvinyl alcohol or possibly onto polyVAc molecules occurs. Excessive grafting to polyvinyl alcohol causes an increase in latex viscosity and instability. A high initiator concentration with a low monomer concentration should give optimum conditions for the formation of graft copolymer. Grafting increases the actual weight of the polyvinyl alcohol stabilizer, which will cause an increase in the size of the hydration shells.[13]

Donescu, Gosa, Ciupitoiu, and Languri[26] examined the semicontinuous emulsion polymerization of VAc using polyvinyl alcohol as protective colloid and ethoxylated (20 moles) cetyl alcohol as a co-emulsifier. They reported the distribution of the co-emulsifier between the initial charge and the remaining monomer. If all the co-emulsifier was fed in the initial charge, small particle sizes were obtained. If the amount of co-emulsifier fed continuously with the remaining monomer was high, the final particle sizes were large. In addition, there was a sharp decrease in the insoluble fraction from 50% to 10% with the increase of the co-emulsifier in the initial charge to 50%. This means that polyVAc crosslinked with polyvinyl alcohol fraction decreases to reasonable levels if at least half of the co-emulsifier is introduced in the initial charge.[26]

Donescu, Gosa, and Languri examined the semicontinuous emulsion polymerization of VAc in the presence of polyvinyl alcohol stabilizer and hydrogen peroxide-ferrous sulfate redox initiator system in 1989.[27] At a moderate feed rate, the polymerization rate is controlled by the monomer addition rate, and the polymerization rate becomes proportional to the introduced monomer. The mean particle diameter increases and the amount of insoluble polymer decreases with increasing feed rate. This shows that when the monomer feed rate increases, the ratios of monomer/particle and monomer/active reaction centers also increase. The increase of the monomer feed rate also results in the increase of the benzene-soluble fraction of the final polymer, which demonstrates the low extent of grafting and crosslinking.[28,29]

Okaya, Tanaka, and Yuki used 88% hydrolyzed polyvinyl alcohol and 40 moles ethoxylated nonyl phenol nonionic surfactant as emulsifier in the semicontinuous polymerization of VAc.[30] Short branches and a low degree of polymerization resulted due to higher chain-transfer reactions. Polymer films obtained from the latices prepared in the presence of polyvinyl alcohol resulted in higher tensile strengths than those prepared with only nonyl phenol ethoxylates, presumably due to the formation of a reinforcing polyvinyl alcohol structure.[30]

Gilmore, Poehlein, and Schork modeled polyvinyl alcohol-stabilized semicontinuous VAc emulsion polymerization[31] and compared their model with experimental findings.[32] Their model suggests that, when the molar ratio of VAc to polyvinyl alcohol is high, physical adsorption of polyvinyl alcohol onto the latex particle is a more important process than grafting.[32]

Nozakura, Morishima, and Murahashi investigated the long branching in polyVAc and polyvinyl alcohol.[33,34] They distinguished two forms of branching: (1) hydrolyzable branch at the acetoxy methyl group, and (2) the abstraction of a α-hydrogen of the polyVAc. Thus, a decrease in molecular weight upon saponification and branching of the first type during polymerization does not result in branching in polyvinyl alcohol. On the other hand, the abstraction of a α-hydrogen of the polyVAc would result in a non-hydrolyzable long chain branch that remains in the derived polyvinyl alcohol. It was found that the hydrogen atoms in the α-position are more reactive than those on the acetoxymethyl group.[34]

Gavat, Dimonie, Donescu, Hagiopol, Munteanu, Gosa, and Deleanu investigated the grafting process in VAc emulsion polymerization in the presence of polyvinyl alcohol and nonionic emulsifiers such as ethylene oxide-propylene oxide block copolymers.[35] The number of grafting reactions increases with the rise in initiator concentration.

Hamielec proposed that the kinetic model would not apply when the polymerization is conducted in the presence of polyvinyl alcohol stabilizer, as chain transfer to polyvinyl alcohol leads to insoluble copolymers.[36] He presented some conclusions on branching mechanisms: (1) the branches through the acetate group are long and are ruptured preferentially on shearing; (2) the branches through the α- and β-carbon are long and are not broken on shearing; (3) the extent of long-branching through the acetate group is about 67% of total branching, 4–80% of the decrease in molecular weight results from the main chain scission on shearing; and (5) the branched polyvinyl alcohol contains a smaller but nevertheless significant amount of branching.[36]

8.3 THE CHOICE AND THE ROLE OF ACRYLIC ESTER COMONOMERS AND STABILIZATION OF POLYVAc COPOLYMER LATICES BY MONOMERIC CARBOXYLIC GROUPS

The selection of the acrylic ester comonomer to be used to produce copolymer latices for any given application depends principally upon the functional suitability of the comonomer and its cost. The homopolymers of these acrylates should have a T_g of well below normal ambient temperatures in order to lower the T_g of the VAc copolymer by internal plasticization. PolyVAc homopolymer has a T_g of 27–28°C and an MFT of 14–20°C according to its molecular weight and the degree of branching. The properties of the four acrylic homopolymers which are largely used in the latex industry are shown in Table 5.3. A formulator can tailor a copolymer (or terpolymer) structure from this broad range to meet customer application requirements. For example, when 20% by weight BuA is incorporated into a VAc-BuA copolymer, T_g becomes 11–15°C and MFT 6–8°C; when 40% BuA is present, T_g becomes 0 to –6°C; and when 60% BuA is present, T_g becomes –20 to –40°C. In addition, the particle size of the copolymer latex decreases sharply with the increase of the BuA monomer content. Hardness in the resultant polymer films can be varied at will, from very hard and tack-free to soft and tacky. The copolymerization of comparatively soft acrylic monomers adds durability to the VAc copolymer, but high concentrations of these monomers increase the tack of the final copolymer films. BuA imparts softness and tackiness, whereas ethyl acrylate imparts moderate softness but no tackiness. Methyl methacryclate imparts hardness and no tackiness. PolyMMA has a T_g of 106°C, and it is sometimes advantageous to add MMA monomer to a VAc-acrylic ester copolymer structure to increase the T_g of the terpolymer and, thus, small amounts of MMA effectively decrease tackiness of softer latex films. The potential applications of these VAc-acrylic ester copolymers are unlimited and other new uses are sure to follow as a result of the resourcefulness and imagination of the chemist.

Copolymers of vinyl acetate and n-butyl and 2-ethylhexyl acrylate in latex form are excellent for interior and exterior paints and are superior to either homopolymer alone. Copolymers of vinyl acetate with dibutyl fumarate or dibutyl maleate exhibit good flexibility and water resistance in films deposited from the emulsions, and they are important for surface-coating applications. The incorporation of acrylate ester copolymers improves water and abrasion resistance of copolymer film. Color retention is also better in paints made by copolymerizing acrylate esters.

Polyvinyl alcohol protective colloid can be used in the copolymerization of acrylic esters with VAc, but its presence has an adverse effect when the latex is mixed with inorganic extenders such as calcite. Thus, hydroxyethyl cellulose (HEC) is usually preferred as protective colloid when steric stabilization is required. However, persulphate initiators degrade both polyvinyl alcohol and HEC above 70°C, and high decreases in the solution viscosity can be seen. Thus, persulphate initiators should be added after or at the same time as the monomer and, preferably, the copolymerization should be conducted at 50°C with the addition of redox initiators.

The nature and the concentration of the chemical groups on the particle surface are very important to stabilize the latex and to impart good mixing characteristics with extenders and pigments in many applications. sulfate ionic groups from peroxide initiator decomposition, hydroxyl groups from sulfate hydrolysis, or from the adsorption of polyvinyl alcohol, and/or from the hydrolysis of polyVAc during polymerization, and carboxyl ionic groups from the sulfate oxidation may be present on the surface of the homopolymer PolyVAC particle surface. In addition, carboxylic groups can be formed by the hydrolysis of polyBuA or polyethyl acrylate for VAc-acrylate copolymers. The properties of the monomeric acetate, butyl, ethyl, and acrylate groups should also be considered in order to predict the behavior of the latices.

Minor amounts of carboxylic acid monomers such as acrylic acid and methacrylic acid are sometimes copolymerized into VAc-acrylate latices, chiefly for introducing a viscosity response to changes in pH. When involved in the copolymer structure, these groups act as effective thickeners and impart good blending properties with inorganic extenders such as calcite. Carboxylic groups are generally located on the particle surface and form an ionic shell around the particle at high pH values, which imparts high pH and stability. However, if the latex is cooled or heated beyond its stability limits, coagulation occurs by desolvation and the collapse of the shell around the particles.

Donescu, Fusulan, Gosa, and Ciupitoi studied the semicontinuous copolymerization of VAc with acid comonomers such as fumaric acid, crotonic acid in the presence of HEC and anionic emulsifiers in order to improve the stability and adhesion properties.[37] It was determined that the rate of polymerization decreased and the mean particle size increased in the presence of acid comonomers.[37]

Gajria and Vijayendran investigated the pH response of acrylic acid and methacrylic acid-modified VAc-BuA copolymer latices.[38] These latices are used in the pressure-sensitive adhesives industry. Feeding the acidic monomer with the main monomer feed as opposed to a water solution feed produced a greater viscosity response upon pH adjustment. Most acid groups were found to locate on the surface of the final latex, with some buried in the particle. No polymeric acid was found in the aqueous phase.[38]

Huo, Hamielec, and McGregor studied the effect of acrylic acid incorporation into 2-ethylhexyl acrylate-VAc-acrylic acid terpolymers.[39] The addition of sodium chloride effectively reduced the pH-thickening response curve.

Minor amounts of n-methylol methacrylamide are sometimes used to impart cross-linking and heat-set properties to the VAC-acrylate copolymers, especially in textile printing binder applications.

8.4 THE ROLE OF MONOMER ADDITION METHODS AND FEED RATES ON PVAc-ACRYLATE COPOLYMER COMPOSITION IN THE SEMICONTINUOUS PROCESS

In semicontinuous emulsion polymerization, only part of the total reaction formulation is introduced at the beginning of the polymerization reaction, the remainder being added, according to a predetermined schedule, during the course of polymerization. The controlled introduction of monomer to the reaction vessel facilitates great control over the homogeneity of the copolymer formed, the rate of polymerization, the rate of heat generation, and the properties and morphology of the polymer particles formed. Generally, it is difficult to control the exothermic reactor temperature, and the heat liberation during emulsion copolymerization is dependent on both copolymer composition and polymer-to-water ratio. For high solids latices, an extended gradual addition time is required. In some recipes, the agitation rate is increased with time to improve heat and mass transfer, and to compensate for the increased reactor load.

There may be many strategies for monomer addition. Comonomers may be added neat as a mixture or by different streams. Emulsifiers may be fed as a different stream or else added to the reaction mixture initially. Another alternative is the addition of pre-emulsified comonomers so that the emulsifier is also fed to the reactor in a programmed manner to maintain stable monomer droplet formation. Precautions should be taken to avoid separation of the monomer/water mixture for those emulsions in this case. The addition choice of the emulsifier is very important to determine the particle size of the copolymers and colloidal stability of the latex produced.

In industrial practice, whichever type of semicontinuous process is used, 5–10% of the total comonomers are added initially to allow complete conversion of the comonomer, which may be considered as seed stage. The addition of the remaining 90–95% comonomers, either directly or as an emulsion, provides for growth of particles formed in the seed stage. The objective is to use the seed stage to give control over particle size and particle size distribution, which will be narrow if the seed stage is short. However, if the level of emulsifier is too high or the number of seed particles is too low, new particles can be formed during the addition of comonomers, giving rise to sometimes undesired broad particle size distributions. This is known as "secondary nucleation." Conversely, if insufficient emulsifier is used, which results in low surface charge density of particles, limited coagulation of latex particles can occur, leading to reductions in the number of particles. If all of the emulsifier is added initially, the number of particles formed in the seed stage will be greater than for the process where emulsion is added continuously. It is possible to control the latex particle size distribution by introducing the emulsifier at particular times during the emulsion copolymerization. For example, if a further addition of surfactant is made late in the reaction to generate a new crop of particles, a bimodal particle size distribution will be obtained.

If semicontinuous process is not applied in emulsion copolymerization, there could be many adverse consequences. For example, in batch emulsion copolymerizations where all the chemicals are added at the beginning of the reaction, the composition of a copolymer is usually found to be different from that of the comonomer composition from which it is produced. Different monomers have differing tendencies to undergo copolymerization. The more reactive monomer preferentially enters the copolymer and the less reactive monomer concentration increases in the reactor as the degree of conversion increases. In addition, the differences in solubilities of the monomers in the water phase, differences in solubilizing effect of the emulsifier on the monomers, and the different solubilities of the monomers in the polymer particles all affect the course of the reaction and result in deviations. Thus, a formulator achieves control of the copolymer structure and monomer sequence distribution when the semicontinuous addition method is applied.

Basically, two types of monomer addition rates can be applied during semicontinuous emulsion copolymerization:

1. The feed rate is less than the maximum rate of copolymerization reaction. Then the concentration of comonomers in the particles falls below the saturation value and is controlled directly by the feed rate. This situation is called the "monomer-starved condition." The conversion and the overall polymerization rate rise by increasing the feed rates in monomer-starved conditions. In industry, monomer-starved conditions are generally applied for better control of the reaction parameters. However, theoretically, the control of reaction rate can be applied only when a steady state exists during the copolymerization; the control of reaction rate by the feed rate is thus an oversimplification of the real situation, but it is a very useful approach in industrial practice.
2. The feed rate is higher than the maximum rate of copolymerization reaction. This situation is called the "monomer-flooded condition" (or the monomer-flooded region). When the feed rates exceed the maximum values for monomer-starved conditions, the conversion-time curves overlap with the batch test curves, confirming the fact that the batch copolymerization rate is the maximum rate that can be achieved. There is no effect of increasing comonomer feed rate on copolymerization rate in this case.

In general, the instantaneous conversion of comonomers is very high, typically above 90% at any time during the addition of comonomers. That means that comonomers are almost immediately copolymerized upon entering the reactor under monomer-starved conditions. Then, the copolymer formed must have the same overall composition as that of the comonomer mixture added. Therefore, it is possible to produce copolymers of uniform composition by feeding a comonomer mixture of constant composition under monomer-starved conditions. Conversely, when the reaction is conducted using a batch process, a heterogeneous copolymer is obtained.

In kinetically-controlled morphologies, the key factor determining the final particle morphology is the amount of second monomer present in the particle during polymerization. The control of the monomer flow rate in the semicontinuous polymerization process allows one to obtain the desired morphology in the final particle. Monomer solubility in water differences, monomer reactivity ratio disparity, selection of the emulsifier, chain transfer agents, and the presence of a cross-linking agent in the emulsion polymerization system are also important factors in controlling particle morphology.

Monomer-starved emulsion copolymerization is also used to prepare latices having core-shell structures. First, particles of a homopolymer are prepared, and then another monomer is polymerized sequentially on the first core homopolymer. In this case, two different glass transition temperatures are obtained, one for each homopolymer.

Thermodynamic and kinetic factors control particle morphology development. Thermodynamic factors determine the equilibrium morphology of the final composite particle, while the kinetic factors determine the ease with which this morphology can be achieved. Torza and Mason pioneered the application of the interfacial behavior of systems containing various types of three mutually-immiscible liquids to emulsion copolymer systems.[40]

Nevertheless, there are disadvantages to working under monomer-starved conditions. Low monomer feed rates give rise to low rates of copolymerization and increase the average molecular weight of the copolymers formed. If the feed rate is too slow, the branching and secondary reactions are high. Under monomer-starved conditions, the polymer/monomer ratio in the polymerization loci is very high and polymer chain transfer reactions are likely to occur. In order to overcome such adverse effects, individual monomers are fed separately so that the comonomer composition in the reactor will be kept constant.[41] The concentration of each monomer in the reactor is monitored on line by gas or liquid chromatography. However, sometimes feedback control cannot be done properly since the time required for analysis is significant. Another method is the application of the optimum monomer-addition-rate profiles. In this method, monomers are added at rates which vary with time to maintain the comonomer composition constant. This method requires thorough knowledge of partitioning, reactivity ratios, rate coefficients, etc. Two strategies have been employed: (1) independent addition of both monomers using precalculated rate-time profiles, and (2) less reactive monomer is added completely to the reaction vessel at the beginning of the growth stage of the emulsion polymerization, followed by feeding of the more reactive monomer using precalculated rate-time profiles. These control strategies are specific to a particular emulsion polymerization reaction, and considerable experimental effort is required to establish optimum values of parameters for each system.[41-44]

When the thermodynamic equilibrium is established during comonomer addition, the changing masses of the unreacted monomers and copolymer are related to monomer partitioning. If the two monomers have significantly different solubilities in water, then partitioning is sometimes neglected. This is especially true when the more water-soluble monomer is added as the minor part of the comonomer mixture, since a high proportion of this monomer will be dissolved in the water phase and a relatively low proportion in the latex particles which are the loci for formation of the copolymer.[41]

The copolymerization temperature in the reactor depends on selection of emulsifier and initiator, which is ultimately dictated by particle size. An increase in reaction temperature generally increases the polymerization rate, reducing both molecular weight and particle size.

Chain transfer agents such as dodecyl mercaptan and other sulphur- and halogen-containing compounds are added to control the average molecular weight and the molecular weight distribution of the copolymers. When the chain transfer agent is dissolved in the monomer to be added, the depletion of chain transfer agent during polymerization can be avoided and more uniform molecular weight distribution obtained. Alternatively, polymers with broad and/or multimodal molecular weight distributions can be formed by manipulating the rate and/or time at which the chain transfer agent is fed to the reaction system.[41] The importance of chain transfer to polyVAc homopolymer is well known (see Sec. 3.5). In addition, Lowell et al. showed that chain transfer to polymer is also important in emulsion homopolymerization of n-butyl acrylate, leading to long-chain branches.[45,46] Cross-linking can also occur if propagating branches terminate by coupling, which has effects upon film mechanical properties, particularly in the viscoelastic region.

Chujo, Harada, Tokuhara, and Tanaka compared the various monomer addition methods to emulsion copolymerization of VAc and *n*-Butyl acrylate with the same overall composition in 1969.[47] Similar to industrial practice, they used nonionic emulsifiers and 88% hydrolyzed polyvinyl alcohol in the copolymerizations. Heterogeneity values were found to differ very much with the change of monomer addition method. For example, continuous comonomer addition methods yield nearly homogeneous copolymer, whereas stepwise monomer addition yields less homogeneous copolymer. If all the comonomer is added at the beginning of the reaction, it yields a very heterogeneous copolymer. It was determined that when homogeneity increases, hardness decreases.[47]

Bassett and Hoy developed an approach by varying the monomer feed composition continuously to achieve a controlled composition drift, which was called "power feeds."[41,48]

Semicontinuous polymerized particles were found to have a more homogeneous structure, comprising a much smaller BuA-rich core surrounded by a shell of VAc-BuA copolymer.[49] The molecular weight distribution for semicontinuous copolymers shows a bimodal curve.[50,51] The mean particle size decreased with the increase in BuA content and was always lower than that of the corresponding batch latex. Particle nucleation is assumed to take place predominantly in the aqueous phase for semicontinuous emulsion process. Thus, the particles are formed over the entire duration of polymerization, and particle growth takes place predominantly by coalescence of smaller-sized particles or low-MW oligomers with larger-size particles. When the comonomer mixture is rich in the relatively more hydrophobic BuA monomer, favorable adsorption of emulsifier onto the particle surface results in a high level of colloidal stability of the newly formed small-size latex particles. Thus, the final latex system comprised particles with small average size and broader distribution.[50,51]

Donescu, Gosa, and Languri studied the semicontinuous emulsion copolymerization of VAc with 2-ethylhexyl maleate[52] and compared their results with their previous publication on the semicontinuous emulsion copolymerization of VAc with 2-ethylhexyl acrylate.[53] The comonomer addition rate was high, nearly in the "flooded region." The evolution of the amount of copolymer is nearly linear with time,[52] and this result is similar to VAc-2-ethylhexyl acrylate copolymerization.[53] The authors suggested that when HEC is present as protective colloid, its chain is split in the presence of the persulphate initiator and, thus, continuously stabilizes the new particles formed. The inclusion of n-butanol as chain transfer agent lowers the content of the cross-linked copolymer. n-Butanol is different from the conventional chain transfer agents, such as t-dodecyl mercaptan, in that it is highly water-soluble and ensures a high splitting rate of potassium persulphate initiator. The presence of n-butanol also decreases the average particle diameter.[52]

Dimitratos, El-Aasser, Georgakis, and Klein reported the relationship between the monomer consumption rates and the monomer feed rates in the pseudo-steady-states in seeded, semicontinuous copolymerization of VAc-BuA.[54] The authors analyzed only neat comonomer feeding and pre-emulsified comonomer feeding was not included. The authors concluded that, under certain assumptions, the relationship between the monomer consumption rates and the monomer feed rates is the same for both water-soluble and water-insoluble monomers. Thus, the resulting copolymer composition should be very close to the comonomer feed composition with very low feed rates.[54]

Urquiola, Arzamendi, Leiza, Zamora, Asua, Delgado, El-Aasser, and Vanderhoff investigated the semicontiniuous seeded emulsion copolymerization of VAc and methyl acrylate.[55] Mainly VAc accumulated in the reactor in the case of the monomer-starved process, and this preferential accumulation resulted in a drift of the copolymer composition. The decrease of the feed rate or the increase of the amount of seed initially charged in the reactor resulted in a decrease of the compositional drift in the copolymer. It was found that a polyVAc-rich copolymer was formed when a low methyl acrylate feed was used, whereas a polymethyl acrylate-rich copolymer was obtained at high methyl acrylate feed rates in the semistarved process.[55]

Makgawinata, El-Aasser, Vanderhoff, and Pichot reported that the feed rates of the monomer mixtures have many effects on the final properties of the VAc-BuA copolymer latex.[56] They concluded that the particle size and distribution varied with comonomer composition and feed method, with the smallest particle size obtained in the BuA-rich copolymers.

Donescu and Fusulan noticed a decrease in particle size with increasing dibutyl maleate during VAc-dibutyl maleate semicontinuous polymerization.[57] They concluded that the more hydrophobic monomer is responsible for reducing particle size, similar to what Makgawinata et al.[56] concluded. Since the emulsifier is more easily adsorbed onto the surface, the increased hydrophobicity allows for greater stability of the first-formed particles.[57]

Canu, Canagallo, Morbidelli, and Storti developed a mathematical model for the optimal comonomer feed policy to control the composition of the copolymers in a semi-continuous emulsion copolymerization.[58] The model uses only the comonomer reactivity ratios and interphase partition laws. The reliability of the model has been tested by comparison with the optimal policies given in the literature for VAc-methyl acrylate and methyl methacrylate-ethyl acrylate comonomer systems.

Gugliotta, Arotcarena, Leiza, and Asua developed a new method to estimate the conversion and cumulative copolymer composition in either batch or semicontinuous emulsion copolymerizations. Their method is based on online calorimetric measurements.[59] The method was validated for two different copolymerization systems: VAc-BuA and BuA-styrene.

Erbil used nonionic emulsifiers and ammonium persulphate-sodium formaldehyde sulphoxylate redox initiators at 50°C in the semicontinuous emulsion copolymerization of VAc-BuA.[60] It was found that copolymer compositions deviated by only 0.7–5.2 mole% from the feed comonomer compositions. A decrease of average particle size and glass-transition temperature was found by the increase of BuA content in the copolymer.[60]

Sun, Liu, and Zhao simulated the development of the particle morphology of VAc-BuA emulsion copolymers.[61] The final particle morphology revealed a microphase separation structure for the semicontinuous process, and the faster the feed rate of comonomers, the greater the separation that occurred. A multicore-shell structure is formed during the slowest feeding of comonomers.[61]

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Appendix 1

Properties of Vinyl Acetate Monomer

TABLE 1
Physical Properties of Vinyl Acetate Monomer

Property		Value	Reference
Molecular Weight		86.091	
Boiling Point,	(760 mmHg)	72.7°C	4.64
	(300 mmHg)	47.0°C	4.32
	(50 mmHg)	9.0°C	4.32
	(10 mmHg)	–18.0°C	4.32
Melting Point		–92.8°C	4.20
Freezing Point		–100.2°C	4.65
Liquid Density,	(9°C)	0.9459 g/ml	4.66
	(20°C)	0.9342 g/ml	4.66
	(30°C)	0.9181 g/ml	4.66
	(40°C)	0.8920 g/ml	4.20
Specific Gravity,	(20/20°C)	0.9342	4.4
	(10/20°C)	0.9455	4.4
Vapor Density	(air = 1.0)	2.97	4.37
Liquid Viscosity	(0°C)	0.55 mPa-s	4.30, 4.67
	(20°C)	0.43 mPa-s	
	(40°C)	0.35 mPa-s	
	(80°C)	0.25 mPa-s	
	(120°C)	0.18 mPa-s	
Surface Tension	(20°C)	25.5 dyn/cm	4.30
	(40°C)	22.8 dyn/cm	
	(80°C)	18.3 dyn/cm	
Interfacial Tension to Water,	(20°C)	16.5 dyn/cm	4.20
Parachor		204.7	4.66
Refractive Index, n_D,	(20°C)	1.3953	4.20
	(25°C)	1.3949	4.64
Solubility in Water,	(20°C)	2.3 wt%	4.20
	(50°C)	2.1 wt%	4.68
	(70°C)	3.5 wt%	4.68
Solubility of Water,	(20°C)	0.9 wt%	4.38
	(66°C)	1.9 wt%	

TABLE 1 (continued)

Property	Value	Reference
Solubility Parameter	9.05	4.69
Cohesive Energy Density	83.8 cal/cm^3	4.13
Flash Pt., (Tag Open Cup, ASTM D1310)	–5°C	4.37
Flash Pt., (Closed Cup)	7.8°C	4.20
Auotoignition Temperature	427°C	4.20
Coefficient of Cubical Expansion per °C	1.52×10^{-3} (20–40°C)	4.37
Explosive Limit in Air (lower)	2.6 vol%	4.37
(upper)	13.4 vol%	
Dielectric Constant, 25°C	5.8	4. 38
Trouton's constant	23.8	4. 29
Magnetic Susceptibility	-46.2×10^{-5}	4.71
Redox Potential (in 0.1 N H_2SO_4)	0.3	4.72
Supersonic Velocity (134°C, 95.98 kHz)	202.7 m/sec	4.73
Critical Temperature	240.8°C	4.73
	228.9°C	4.29
	252°C (estimated)	4.30
Critical Pressure	45.67 atm	4.73
	4.19 atm (estimated)	4.30
Critical Volume	0.265 liters/mole	4.20
Critical Density	0.324 g/ml	4.30
Liquid Specific Heat (20°C)	0.46 cal/g-°C	4.32
(60°C)	0.48 cal/g-°C	
(100°C)	0.505 cal/g-°C	
Vapor Specific Heat (1 atm 20°C)	22.5 cal/g-°C	4.74
(1 atm, 100°C)	27.3 cal/g-°C	4.74
(1 atm, 134°C)	29.5 cal/g-°C	4.73
Vapor Heat Capacity (1 atm, 20°C)	22.5 cal/sec-cm-°C	4.20
(1 atm, 100°C)	27.3 cal/sec-cm-°C	
Thermal Conductivity (23.1°C)	3.70×10^{-4} cal-mole-°C	4.75
(48.2°C)	3.37×10^{-4} cal-mole-°C	
(67°C)	3.26×10^{-4} cal-mole-°C	
Heat of Vaporization (72.7°C)	7.8 kcal/mole (0.379 kJ/g)	4.28
Heat of Melting	2.87 kcal/mole	4.20
Heat of Polymerization	21.3 kcal/mole (1.035 kJ/g)	4.76, 4.77
Heat of Combustion	495 kcal/mole (24.06 kJ/g)	4.28
Heat of Hydrogenation (at 43°C)	–30.95 kcal/mole (–1.504 kJ/g)	4.65
Heat of Formation		
(from acetylene and acetic acid, at 200°C)	–29.6 kcal/mole (–1.439 kJ/g)	4.25
(from ethylene and acetic acid, at 120°C)	–41.1 kcal/mole (–1.998 kJ/g)	4.25
Adiabatic Compressibility	90×10^{12} egs	4.20
Dipole Moment, (25°C, in benzene)	1.75 Debye	4.20
(25°C, in carbon tetrachloride)	1.79 Debye	4.70
Molar Kerr Constant,		
(in carbon tetrachloride at 25°C)	3.61×10^{-12}	4.70

TABLE 2
Composition and Boiling Point of Azeotropes Containing Vinyl Acetate[4.32,4.36-4.38]

Compound	Azeotrope B.P. (°C at 1 atm)	VAc wt%
Ethanol	67.3	74.0
Methanol	58.8	63.4
2-propanol	70.8	77.6
Water	66.0	92.7
Benzene	72.4	96.1
Toluene	72.6	96.0
Cyclohexane	67.4	61.3
Heptane	72.0	83.5

TABLE 3
Heat of Mixing of Vinyl Acetate with Some Compounds[4.39]

Compound	Heat of Mixing (kJ/m^3)
Acetone	3389.0
Methanol	22007.8
90% Methanol	50208.0
90% Ethanol	68617.6
Butanol	71964.8
90% Butanol	61504.8
Ethyl Acetate	3430.9
Acetic Acid	4895.3
Benzene	14393.0
Nitrobenzene	4727.9
Chloroform	–49789.6
Trichloroethylene	–4686.1
Carbon tetrachloride	23848.8

Appendix 2

Commercial Vinyl Acetate Specifications

TABLE 4
Commercial Vinyl Acetate Specifications

Property	Range
Vinyl acetate, wt%, min.	99.8–99.9
Carbonyls as acetaldehyde, wt%, max.	0.010–0.013
Acidity, as acetic acid, wt%, max	0.005–0.007
Water content, wt%, max	0.04
Distillation range, °C	72.5–73.0
Specific gravity, 20/20°C	0.9335–0.9340
Color, APHA system	0–5
Suspended matter	none
Activity time* (H Grade inhibited), minutes	130–150

Appendix 3

Wet Analysis of Vinyl Acetate Monomer

1. **Specific gravity.** Determine specific gravity by employing a pycnometer accurate to the fourth decimal place. The constant temperature bath is to be maintained at 20 ± 0.05°C.
2. **Acetaldehyde.** Pipette 50 ml of freshly prepared 0.44% sodium bisulfite solution into each of two glass-stoppered 250-ml Erlenmeyer flasks containing ice. Add 100 ml of sample to one flask by means of a pipette. Shake flasks continually for 10 ± 1.0 minutes to mix contents thoroughly. Add 0.5 ml of stable starch indicator to blank and sample. Titrate with standardized 0.1 N iodine solution until the deep blue color of the indicator just appears and persists for at least 15 seconds. There should be ice remaining in the flask at the end of the titration. Calculate acetaldehyde content by equation:

$$\textit{Weight percent aldehyde} = \frac{(\textit{blank} - \textit{sample titration}) * \textit{N of iodine} * 0.02202 * 100}{\textit{ml of sample} * \textit{specific gravity}}$$

3. **Acidity.** Measure 50 ml of methanol into a 250-ml Erlenmeyer flask containing ice. Add 1 ml of bromthymol blue indicator and neutralize with 0.05 N sodium hydroxide to a dark green end-point. Carefully pipette a 100-ml sample into flask. Titrate rapidly to the first end-point (dark green) using 0.05 N sodium hydroxide. Do not allow temperature of the sample to rise appreciably during the titration. There should be ice remaining in the flask at the end of the titration. Calculate acidity by equation:

$$\textit{Weight percent acetic acid} = \frac{\textit{ml NaOH} * N * 0.060 * 100}{\textit{ml of sample} * \textit{specific gravity}}$$

4. **Water.** Pipette 10 ml of Karl Fischer reagent into the titrating chamber and titrate to the "dead stop" end-point with standard water-in-methanol solution to obtain the blank. Again pipette 10 ml of the Fischer reagent into the chamber and add 20 ml of sample by means of a pipette. Titrate to the end-point with standard water-in-methanol solution. This is the sample titration. Calculate water content by equation:

$$Weight\ percent\ water = \frac{(blank - sample\ titration) * Factor * 100}{ml\ of\ sample * specific\ gravity}$$

Factor = strength of reagent, grams of water per 100 ml of standard water solution.

5. **Distillation range.** The apparatus, procedure, and calculating outlined in ASTM D1078-56T entitled "Method of Test for Distillation Range of Lacquers, Solvents and Diluents" shall be employed for this determination.
6. **Color.** Introduce 100 ml of sample into a Nessler tube and compare the sample with a 5 APHA color standard. The comparison shall be made by looking vertically downward through the tubes upon a white or mirrored surface at such an angle that light is reflected through the column of liquid.
7. **Inhibitor content.** It is advisable that inhibitor content be determined every three months to maintain specification limits (hydroquinone, 14–17 ppm; diphenylamine, 200 ppm). Polymer content is also a rapid means for checking stability of vinyl acetate. Presence of more than 0.10% polymer content would indicate addition of inhibitor should be made.
8. **Hydroquinone content.** Beckman spectrophotometer method.

   Standardization: Prepare solutions containing 5, 10,15, 25, and 35 ppm hydroquinone in methanol. Determine the optical densities of these solutions with a Beckman spectrophotometer. Points when plotted from the data on rectangular coordinate paper should lie in a straight line.

   Procedure: Pipette 50 ml of sample into a 250 ml flask having a standard taper joint. Connect flask to a water aspirator and place in a water bath at a temperature of 50 ± 5.0°C and evacuate for 30 minutes to flash off all the vinyl acetate. The hydroquinone remains as a residue in the flask. Do not exceed 55°C or 30 minutes flash-off time.* Carefully repressure the flask, remove from the water bath, and cool to room temperature. Add 50 ml of methanol to the flask containing the residue of the sample just before the optical density is measured. Gently swirl the flask to insure complete dissolution of the hydroquinone. Transfer the methanol-dissolved residue to one of two matched 10-mm silica absorption cells. Obtain optical density of the sample.

   Report. Read the ppm of hydroquinone from the working curve, or use the equation:

$$Hydroquinone,\ ppm = optical\ density * 1 / slope$$

* It is necessary to observe caution where connections are used in the vacuum system. Rubber should not be used where it is possible for the vinyl acetate to condense and make contact with the rubber in returning to the flask. Vinyl acetate has a solvent action on rubber, and the dissolved rubber components will cause interference with the test.

9. **Hydroquinone content.** Ceric oxidation method.

Standardization: To prepare 0.002 N ceric sulfate, dissolve 0.6889 grams of ceric ammonium nitrate in 1 N sulfuric acid. Heat until all red fumes are drawn off. Make up to one liter with 1 N sulfuric acid. To standardize, titrate 1-ml portions of the hydroquinone standard (0.200 grams dissolved and diluted in 100 ml of water) with ceric sulfate solution, using one drop of diphenylamine indicator, to a faint end-point.

Procedure: Pipette 50 ml of sample into a 250-ml flask. Connect flask containing sample to a water aspirator and place in a water bath at a temperature of 50 ± 5.0°C. Flash the vinyl acetate to dryness within 30 minutes. The hydroquinone remains as a residue in the flask. Do not exceed 55°C or 30 minutes flash-off time.*

Carefully repressure the flask, remove from the water bath, and cool to room temperature. Add 5 ml of water to the flask. Add a drop of diphenylamine indicator (0.1 gram of diphenylamine dissolved in 100 ml of concentrated sulfuric acid) and titrate with ceric sulfate solution to a faint violet end-point.

Report. Calculate hydroquinone concentration from the equation:

$$Hydroquinone,\ ppm\ =\ \frac{ml\ Ce(HSO_4)_4 * titer\ Ce(HSO_4)_4 * 1000}{50 * 0.934}$$

* It is necessary to observe caution where connections are used in the vacuum system.

10. **Diphenylamine content.** Beckman spectrophotometer method.

Standardization: Prepare known amounts of diphenylamine in the range of 10 to 80 ppm in methanol. Determine the optical densities of these solutions with a Beckman spectrophotometer. The data, plotted on rectangular coordinate paper, should be a straight line.

Procedure: Pipette 10 ml of sample into Pyrex glass 250-ml flask having a standard taper joint. Connect to a water aspirator vacuum source and place in a water bath at a temperature of 50 ± 5.0°C and evacuate, flashing the vinyl acetate to dryness within 30 minutes. The diphenylamine remains as a residue in the flask. Carefully repressure the flask, remove from the water bath, and cool to room temperature. Pipette 50 ml of methanol into the flask containing the residue of the sample just before the optical density is measured. Gently swirl the flask to insure complete dissolution of the diphenylamine in the residue sample. Transfer the methanol-dissolved residue sample to one of two matched 10 mm silica absorption cells. Obtain optical density of the sample.

Report. Read the parts per million of diphenylamine from the working curve and multiply by five, or calculate from the slope of the curve:

$$Diphenylamine,\ ppm\ =\ optical\ density * 5 / slope$$

11. Polymer content

Procedure: Determine to the nearest milligram the weight of a 125-ml Erlenmeyer flask that has been previously dried in an oven at 110 ± 5°C and cooled for one hour in a desicator. Measure 100±1 ml of vinyl acetate, by means of a graduate, into the weighed Erlenmeyer flask. Connect flask to a water aspirator and lower into water bath heated to 50 ± 5°C and evacuate for one hour. Polymer remains as a residue in the flask. Glassware with ground glass joints is desirable to prevent contamination of the sample. Purge flask with dry air or nitrogen. Cool flask and weigh to the nearest milligram.

Report. Correct for inhibitor content as noted in calculation:

$$Weight\ percent\ polymer = \frac{(wt\ flask + polymer) - wt\ flask - \dfrac{ppm,\ inhibitor}{1000}}{sp\ gr\ of\ sample} \times 100$$

Appendix 4

Solubility of Polyvinyl Acetate in Various Solvents

TABLE 5
Polyvinyl Acetate Solubility in Solvents

Solvent	Description
Methanol	Partially soluble
Acetone	Partially soluble
V. M. & P. Naptha	Insoluble
Ethyl acetate	Partially soluble
Ethylene glycol	Insoluble
Carbon tetrachloride	Partially soluble
Methylene chloride	Soluble
Xylene	Insoluble
Butanol	Insoluble
Benzene	Soluble
Methyl ethyl ketone	Partially soluble
Ethylene glycol diacetate	Partially soluble
Toluene	Soluble

Solubility is judged following attempts to dissolve 10% by weight of polyvinyl acetate in the solvent. The polyvinyl acetate is prepared by heating 50 grams of vinyl acetate monomer and 0.10 grams of benzoyl peroxide at 70°C for two hours. One gram of the solid polymer is added to 9 grams of solvent. The mixture is heated to 60°C for a few minutes and is then left standing for several days. The sample is then observed and the solubility rated by appearance as follows:

Soluble — A clear solution of increased viscosity.
Partially soluble — Some gelled, swollen particles remaining out of solution, but otherwise clear solution of increased viscosity.
Insoluble — Large amount of gelled particles remaining out of solution with no apparent change in viscosity of solvent.

Appendix 5

Polyvinyl Acetate Latex Specifications

TABLE 6
Polyvinyl Acetate Latex Specifications

Property	Range
Solids Content, wt%	48–55
Viscosity, mPa-s (= cP)	200–4500
pH	4–6
Residual Monomer, % max.	0.5
Particle Size, microns	0.1–3.0
Particle Charge	Neutral or Negative
Density at 25°C, g/cm^3	0.92
Borax Stability	Stable or Unstable
Mechanical Stability	Good or Excellent

Appendix 6

Acrylic Ester Monomer Specifications

1. **Storage, Handling, and Safety:** The problems involved in the storage and handling of the lower acrylate monomers are essentially the same as those encountered with any other volatile and flammable chemical of comparable flash point and boiling range. Methyl and ethyl acrylates should be handled as red-label solvents. Butyl and 2-ethyihexyl acrylates are less volatile and flammable.

   All acrylates, however, are polymerizable monomeric compounds and, although they are supplied commercially properly stabilized and inhibited, proper precautions must be taken to avoid contamination with any foreign material that could catalyze a polymerization reaction. Peroxides are the most commonly used polymerization catalysts and should therefore be avoided; however, metallic salts, strong acids, or bases can also act as catalysts. Steps, therefore, should be taken to avoid contamination with these types of compounds as uncontrolled bulk polymerization can be explosive and violent. To prevent the catalysis of potentially violent polymerization reactions, acrylate esters should be stored only in containers that exclude sunlight or other ultraviolet energy sources.

   Acrylates, especially methyl and ethyl among the lower members of the series, are toxic chemicals and must be handled with adequate precautions. Butyl and 2-ethylhexyl acrylates are very similar in their physiological effects, but are somewhat less toxic. Oral ingestion, inhalation of vapors, and skin and eye contact with liquid and vapor are to be avoided. While oral ingestion is an unlikely hazard in the industrial handling of a chemical substance, care must be exercised to avoid accidental swallowing. If such an accident should occur, induce vomiting and, as soon as possible, call a physician.

   For handling operations inside a plant or building, vapor-proof goggles should be worn and adequate ventilation provided. For outside handling or unloading, ventilated goggles or safety glasses will suffice. In the event of excessive vapor concentrations due to a spill, suitable organic vapor gas masks should be worn. The leak or spill, of course, should be stopped immediately and the spilled monomer washed away with large quantities of water.

As acrylate monomer vapors are quite irritating to the eyes, nose, and throat, concentrations of vapor in operating areas should be maintained below 10 ppm for methyl acrylate, and 25 ppm for ethyl acrylate. No value for vapor concentration in air has been suggested as yet for butyl or 2-ethylhexyl acrylates. Exposure to excessive vapor concentrations can cause drowsiness accompanied by nausea, headache, or extreme irritation to the respiratory tract. In the event such symptoms do occur, the person should be removed from the area; the ill effects will subside after a few hours. There are no residual harmful effects from limited overexposure. Some persons are extremely sensitive and susceptible to irritation by vapors of acrylate monomers. Individuals with this unusual susceptibility should not work in unloading or processing operations.

The liquid monomer has a definite irritating effect to the skin and should therefore be washed off immediately if it comes into contact with the skin. Clothing that becomes saturated or contaminated should be removed and thoroughly washed before being worn again. Rubber gloves which are damaged, or the inside of which have been contaminated with monomer, should be discarded. If liquid is splashed into the eyes it should, of course, be washed immediately with water for 15 minutes and a physician should be contacted. Here, again, some individuals are much more sensitive than others.

Normal adequate precautions should be taken, as with any potentially dangerous organic chemical, and the rules of good industrial housekeeping should be followed. Careful planning and common sense will prevent mishaps, spills, or overexposure.

2. **Storage of uninhibited monomer:** If the process requires inhibitor to be removed from the monomer prior to use, the monomer should be used immediately or as soon after such removal as possible. If, however, it is necessary to store uninhibited monomer, the material should be chilled to 5°C or less and held at this temperature during the storage period. It is recommended that the uninhibited monomer not be stored for periods exceeding 24 hours. Extreme precautions must be taken to avoid contamination of stored uninhibited monomer. Polymerization reactions may be catalyzed quite readily with no inhibitor present. In the event that it is not possible to use the uninhibited monomer as early as was anticipated, the monomer should be re-inhibited for the extended storage period.

Appendix 7

Wet Analysis of Acrylic Ester Monomers

1. **Acidity:** Measure 50 ml of reagent-grade methanol into a 250-ml Erlenmeyer flask containing ice. Add 1 ml of 0.1% bromthylmol blue indicator in alcohol.

   Neutralize with 0.05 N standardized reagent grade sodium hydroxide to a dark-green end-point, using a calibrated 10-ml. burette graduated in 0.01-ml. subdivisions. Pipette carefully a 100-ml sample into the flask. Titrate rapidly to the first end-point (dark green) using 0.05 N sodium hydroxide. The temperature of the sample should not be allowed to rise appreciably during the titration.

   Note: If available, a potentiometric titration system may be used.

   Report: $$\text{Acid, wt\%} = \frac{\text{ml.NaOH} \times \text{N} \times \text{miliequivalent wt.}}{\text{ml.sample} \times \text{specific gravity}} \times 100$$

   The milliequivalent weight of acetic acid is 0.06005, and of acrylic acid, 0.07206.
2. **Color:** Prepare suitable platinum-cobalt color standards as specified by ASTM D l209-54. Introduce 100 ml. of sample into one of two tall-form 100-mi. Nessler tubes. These should be matched for uniformity of color and selected so that the graduated scales will not vary more than 2 millimeters in height. Compare the sample with a series of platinum-cobalt color standards by looking vertically downward through the tubes upon a white or mirrored surface at such an angle that light is reflected through the columns of liquid. Report as the color the number of the platinum-cobalt color standard that most nearly matches the sample; in the range of 0 to 40, report to the nearest one color unit; in the range of 41 to 100, to the nearest five-color unit.
3. **Propionate content:** Refer to chromatographic assay method for determination of impurities, including propionate ester content.
4. **Refractive index:** Determine the refractive index of the acrylate esters at 20°C using Abbe or similar refractometer instrument.

5. **Specific gravity:** Use a Reischauer or equivalent pycnometer calibrated at the temperature at which the sample is to be determined. Use water bath having a depth of at least 30 cm, capable of maintaining temperatures constant at 20°C ± 0.05°C, and provided with suitable holders for pycnometers.
6. **Water:** Make blank determination by pipetting fresh or stabilized Karl Fischer reagent into the titrating chamber of an electrometric dead-stop titration apparatus. Titrate to the "dead-stop" end point with a standard water-in-methanol solution. The point at which the "magic eye" first closes is taken as the end point. The foregoing steps should be repeated and fresh reagents used at regular intervals, such as for each set of determinations or approximately every four hours, and whenever reagents are changed. Reagents must, of course, be protected from atmospheric moisture. Recommended blank and sample sizes for approximate water content, if known, are as follows:

up to	1.0%	10 ml blank	10 ml sample
1.0 to	5.0%	20 ml blank	2 ml sample
5.0 to	10.0%	20 ml blank	1 ml sample
Over	10.0%	50 ml blank	1 ml sample

   As was done for the blank, pipette an appropriate amount of Karl Fischer reagent into the titrating chamber. Add the sample to the Karl Fischer reagent with a pipette and titrate to the end-point with standard water-in-methanol solution. This is the sample titration (see *Note*).

   $$\frac{(\text{blank} - \text{sample titration}) \times F}{\text{ml of sample}} = \text{grams per 100 ml. water}$$

   $$\frac{(\text{blank} - \text{sample titration}) \times F \times 100}{\text{grams of sample}} = \text{weight percent water}$$

   F (Factor) = Strength of reagent, grams of water per 100 ml of standard water solution.

   Note: Upon the addition of sample to the reagent, the deep brown color of the Karl Fischer reagent must persist to indicate an excess of the reagent. If the color fades, reduce the sample size, increase the amount of reagent, or both.
7. **Distillation range:** Follow procedures and calculations using apparatus outlined in ASTM D1078-56T "Method of Test for Distillation Range of Lacquers, Solvents and Diluents" for this determination. Use a Tirrill-type gas burner to supply heat, or an electric heater only after it has been proven to give similar results. Use suitable thermometers that conform to ASTM specifications. Observe caution in using the apparatus for immediate reuse; cool the heating unit to room temperature before starting a test.

8. **Inhibitor Contents:**

   8.1. **Hydroquinone content:** Visible Spectrophotometer is used for this purpose.

   Standardization: Morpholine, methanol, hydroquinone, and reference acrylates must be of reagent grade, preferably American Chemical Society grade if available, for all tests. Prepare morpholine solution No.1 by mixing 600 ml morpholine with 1000 ml methanol and dilute with water to one gallon. Prepare morpholine solution No. 2 by mixing by volume four parts morpholine, four parts methanol, and eight parts water. Prepare 1000-ppm standards by weighing appropriate amounts of hydroquinone and dilute with the proper acrylate to the 100-ml mark in volumetric flasks. Prepare standard curves in ranges indicated by making appropriate dilutions and reacting the solutions according to the procedure given below. Plot optical density versus ppm hydroquinone using the designated morpholine solution as reference and using the appropriate instrument.

   Procedure: Referring to the foregoing table, pipette the designated number of milliliters of morpholine solution into a 400-ml beaker. Pipette the sample into the solution. Bubble air through the solution for 20 minutes. Determine optical density with the appropriate instrument, using the given wave length and the correct morpholine solution as reference. Read the optical density and concentration in ppm from the proper curve.

   8.2. **Methyl ether of hydroquinone content:**

   Standardization: Prepare standard curves for each of methyl, ethyl, butyl, 2-ethylhexyl acrylate, and acrylic acid. In solutions of the appropriate uninhibited acrylate ester or acid make up weight percent curves plotting optical density versus ppm in the range indicated in table of sample sizes shown below.

   Procedure: Shake 10-ml sample of acrylate with 10 ml of 1.25 N sodium hydroxide. If a light brown color develops, the sample contains hydroquinone. The color developed by less than 40 ppm hydroquinone may be disregarded, as it will not significantly change the methyl ether of hydroquinone reading obtained by the following procedure: Pipette 25 ml glacial acetic acid reagent grade into a 50-ml volumetric flask. Pipette the appropriate sample size of acrylate monomer into the flask. Add 5 drops of saturated solution of sodium nitrite to the mixture and swirl. Dilute to volume with acetic acid. The color develops immediately. Read the optical density at 420 m~ in the colorimeter using acetic acid as a reference. Read the concentration from the appropriate curve for each acrylate or acrylic acid prepared from known concentrations of methyl ether of hydroquinone.

9. **Analysis of acrylate esters by gas chromatography:** The sample is introduced into a gas-liquid partition column, the compounds are separated as they pass through the column with a carrier gas, and their presence in the effluent is detected and recorded as a chromatogram. The component

content is determined from the chromatogram by comparing the height of the component peak in the sample with the height of the same component in a known standard, any difference in attenuation being taken in consideration. A Carbowax 20 M column. (Ucon 50 HB 2000 having a maximum recommended temperature of 200°C for ethyl acrylate). A flux-calcined diatomaceous earth solid support (50–60 mesh) which has been acid-washed, such as Chromosorb W, Acid-Washed, or Gas Pack WA, Acid-Washed.

Column preparation: Clean an indicated length of appropriate O. D. copper or aluminum tubing with acetone or methylene chloride and dry with a stream of clean, dry air or inert gas. Bend the tubing into a V-shape for filling. Fasten the tubing to a rigid support. For methyl acrylate, dissolve 30 grams of Carbowax 20 M and 0.1 gram of Poly Tergent J-300 in 100 ml of chloroform in a beaker. For ethyl acrylate, dissolve 10 grams of Ucon 50 HB 2000 in 75 ml of methanol in a beaker. For butyl acrylate and 2-ethyihexyl acrylate, use 120 ml of support. Weigh out enough Carbowax 20 M to be equal to 25% of the support weight and dissolve in 100 ml of chloroform. Add this solution to the 120 ml of dry support in a 600-ml beaker. Stir gently to evenly coat the support. Pour the coated support onto a nonabsorbing surface. Spread and let dry at room temperature. Plug one end of the coiled tubing with copper turnings or glass wool. Attach this end to a vacuum source. Introduce the coated material at the other end of the column and tap the column to compact the support. Plug with copper turnings or glass wool. Condition the column at a temperature of 200°C by passing carrier gas through it at a rate of 50 ml per minute for 16 hours (35 ml. per minute for ethyl acrylate).

Primary standard: When preparing the standard, use acrylate that is at least 99.9% pure. The other components added should be 98% pure. Scan the acrylate used to prepare the standard. Weigh out the standard components on an analytical balance, adding the components other than acrylate (and 3-methyl-2-butanone for ethyl acrylate test only) in amounts sufficient to give maximum deflection on the recorder when scanned at the same attenuation as the sample. (The 3-methyi-2-butanone is prepared in a separate standard.) Scan the prepared standards. Measure the peak height in the original material and subtract from the peak height in the scan of the prepared standards. The difference is divided into the weight percent added to make up the standard and to obtain the factor. This factor is multiplied times the total peak height in the standard to give the corrected weight percent in the standard. (The factor for 3-methyl-2-butanone is divided by the factor for acetal to determine the ratio of their sensitivities. The factor for 3-methyl-2-butanone is then determined by multiplying the factor for acetal by the ratio of their sensitivities. This is necessary because the 3-methyl-2-butanone and acetal peaks are not completely resolved.)

Standardization: Inject an appropriately-sized sample of the primary standard into the chromatograph. Adjust the attenuation to give maximum peak height-to-noise ratio, but keeping all peaks on scale. Allow to run five minutes after last peak has emerged.

Analysis: Inject a similar size sample of the material to be analyzed under the same conditions as those used for standardization.

Calculations:

$$\text{Wt\%} = \frac{\text{Peak Height of Component in Sample} \times \text{Percent of Component in Standard}}{\text{Peak Height of Component in Standart}}$$