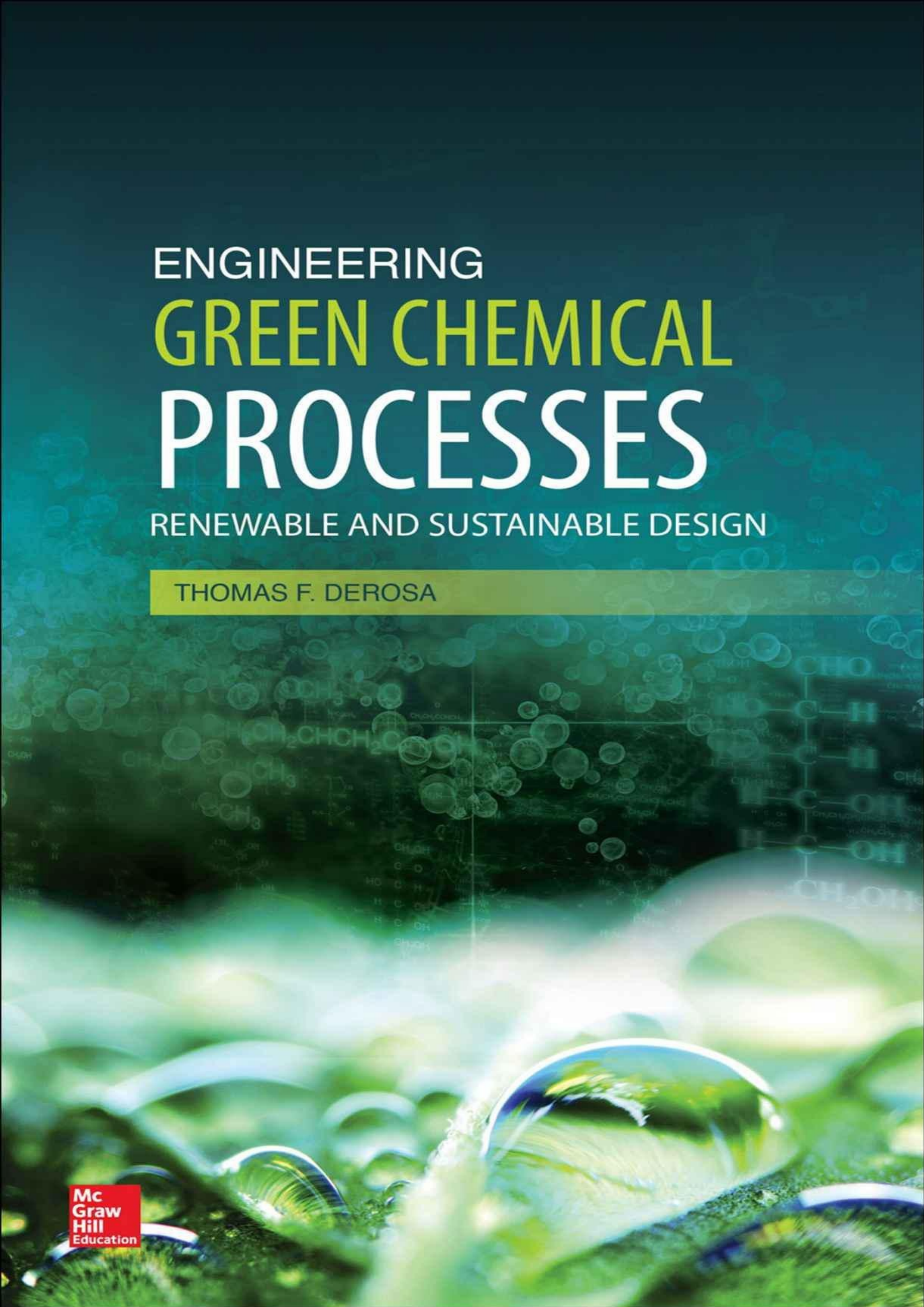

ENGINEERING GREEN CHEMICAL PROCESSES

RENEWABLE AND SUSTAINABLE DESIGN

THOMAS F. DEROSA

Mc Graw Hill Education

Engineering Green Chemical Processes

Renewable and Sustainable Design

Thomas F. DeRosa, Ph.D.

McGraw Hill Education

New York Chicago San Francisco Athens London
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This book is dedicated to my doctoral advisor and very, very dear friend,

Dr. Eli M. Pearce

ABOUT THE AUTHOR

Thomas F. DeRosa, Ph.D., a former senior scientist and senior intellectual property officer at Texaco, has published 49 U.S. patents relevant to new chemical methods, polymerization techniques, and product development. Before he was at Texaco, Dr. DeRosa was a senior chemist at AlliedSignal Corporation, where he worked on fluoropolymers and other polymers. He also worked at Pfizer Pharmaceuticals, Howmedica Division, as a project chemist, preparing urethane block copolymers. Dr. DeRosa has published five books and is currently an assistant professor at Borough of Manhattan Community College of the City University of New York. He received his B.S. in chemistry from Queens College of the City University of New York, his M.S. in organic chemistry from Adelphi University, and his Ph.D. in organic and polymer chemistry from Polytechnic Institute of New York.

Contents

Foreword

Engineering Green Chemical Processes: Renewable and Sustainable Design is educational, informative, and extremely challenging. The question arises: How is it possible to cover all possible areas under the general title of this book? Ordinarily, of course, this would be impossible. Instead, Dr. Thomas DeRosa has chosen a number of interesting and pertinent examples from the most current patents and used them to exemplify general principles that can be used in innovative synthetic and preparative methods. The text identifies areas of active research and development in both academic and industrial laboratories that are devising sustainable and renewable chemical methods. These laboratories are actively pursuing the development of the next generation of chemical agents that are cost effective and environmentally friendly. By using the most current patent literature, the author has spared no effort in identifying and illustrating research facilities that are producing industrially significant chemicals while reducing or eliminating chemical toxins and by-products associated with these processes.

In a dramatic and fundamental way, Dr. DeRosa has identified and illustrated sustainable chemical methods for the active chemist to safely prepare reagents, industrial materials, and polymers.

Engineering Green Chemical Processes: Renewable and Sustainable Design has devoted a considerable amount of effort toward the preparation of renewable consumer goods and products. The author illustrates how existing renewable chemical processes can be utilized to produce new consumer items or adapted to prepare existing consumer items.

The viability of renewable and sustainable chemistries and processes is completely dependent on economics. To address this concern, Dr. DeRosa provides numerous cost-effective product formulations containing renewable and sustainable compounds. In all cases, the consumer item is less expensively prepared and waste disposal and personnel protection concerns are eliminated. In addition, processing parameters for preparing consumer goods using formulations additized with renewable chemical agents require less energy input and generate products that do not require purification. It is my final objective in this foreword to challenge the reader to “think outside the box” to develop innovative and viable chemical methods.

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Acknowledgments

Although I thoroughly enjoyed learning, compiling, and reviewing the chemistries associated with this treatise, the process was extremely difficult and physically demanding since I am afflicted with and suffering from a spinal disorder. The pain associated with this disorder is chronic.

During this process my wife, Barbara DeRosa, and my dear friend, Eli Pearce, provided me with the emotional support I needed to compile and finish this scientific treatise. It is completely impossible for me to gauge the impact of their constant reassuring support and encouragement.

I certainly wish to thank my friend, Ed Immergut, for assisting me and reviewing the materials I provided him during the initial phase of this project. His input provided me with the technical direction this treatise would ultimately follow.

Finally, I wish to especially thank Yoon Sil Theresa Kim for completely rewriting the Introduction to this treatise. Her literary skills are absolutely amazing and incredible.

Thomas F. DeRosa, Ph.D.

Introduction

Engineering Green Chemical Processes: Renewable and Sustainable Design presents comprehensive coverage of engineering pertaining to green chemical processes with two technical objectives. The primary goal of the text is to provide the reader with solutions to contemporary and diverse environmental issues and challenges. The second objective is to provide the reader with a tool for monitoring future trends in any specific area of interest.

Both objectives were achieved using databases from the U.S. Patent and Trademark Office and of U.S. patent applications. All technical entries and topics appearing and analyzed in this treatise came from either issued patents or patent applications obtained from the following website:

http://www.uspto.gov

Readers interested in identifying high-yielding synthetic methods required to prepare chemical agents or polymers for either research or industrial applications will benefit greatly from this text. It is important to note that all of the chemical agents and polymers synthesized in this treatise were those that did not rely on petrochemicals as co-reagents. Instead, they were obtained solely through synthetic methods that generate an absolute minimum amount of toxic organic waste. In addition, the text will provide the reader with the most diverse and creative synthetic selections that are currently under investigation in both academic and industrial research facilities around the world. The criteria or guidelines used for selecting a patent or patent application for *Engineering Green Chemical Processes: Renewable and Sustainable Design* are listed below. To ensure that the reader is comfortable with the selection method, two examples have been provided in each selection category. Each example is extensively discussed in this treatise.

Selection Process

1. The investigation must directly address a persistent environmental problem.
    - Bisphenol-A Replacement Monomers
    - Porphyrin Sensitizers for Solar Panels
2. The method for preparing a chemical agent or polymer must be innovative, must not require the use of petrochemicals, and must not be energy intensive.
    - Remediation of Municipal Waste Using Natural Non-Pathogenic Microbes
    - Non-Yellowing Eyeglass Lenses Using Isosorbide Polycarbonates
3. The product produced and the process used must be low or non-toxic.
    - Asphalt Recycling Using Fatty Acid/Esters
    - Dextrose-Derived Polyfarnesenes
4. The synthesis of any chemical agent, polymer, or additive must be renewable or sustainable.
    - Estolide Pour Point Depressants
    - Recycled Yarn

5. A patent or patent application must not have exceeded 18 months since its publication.
    - Glycerol, Triglycerides, and Lactic Acid Bitumen Binders
    - Renewable cis-Isoprene

Finally, I can think of no better illustration to conclude this Introduction than two synthetic preparations of the identical antibiotic, Bryostatin 1.

Organic Synthetic Route (Non-Renewable)

In March of 2008, a research team synthesized Bryostatin 1 in 31 steps over a period of 5 years. In this chemical investigation, it was estimated that for every purified milligram of Bryostatin 1 produced, approximately 27 L of toxic organic waste products were generated.

Microbial Synthetic Route (Renewable)

In January of 2013, researchers isolated Bryostatin-1-producing bacteria present in Bugula sand in the Gulf of Mexico. After the sand was immersed in a standard aqueous inorganic growth medium, 0.75 g of Bryostatin 1 were isolated in approximately 90 minutes. The process produced no toxic side products or wastes. The safety and the success of this simple process led to the installation of additional Bryostatin-1 growing stations to harvest larger quantities of Bryostatin 1, which were monitored by high school students. This microbial synthetic route of Bryostatin 1 is discussed at length in this treatise.

Finally, it is my hope that readers will use *Engineering Green Chemical Processes: Renewable and Sustainable Design* as a key to access other areas in their academic or industrial pursuits.

Thomas F. DeRosa, Ph.D.

Chapter

1

Antibiotics

Bryostatin 1

Author Thomas J. Manning

Patent Title ***Green chemical process to produce natural products,*** U.S. Patent Application 20130004993 (January 3, 2013)

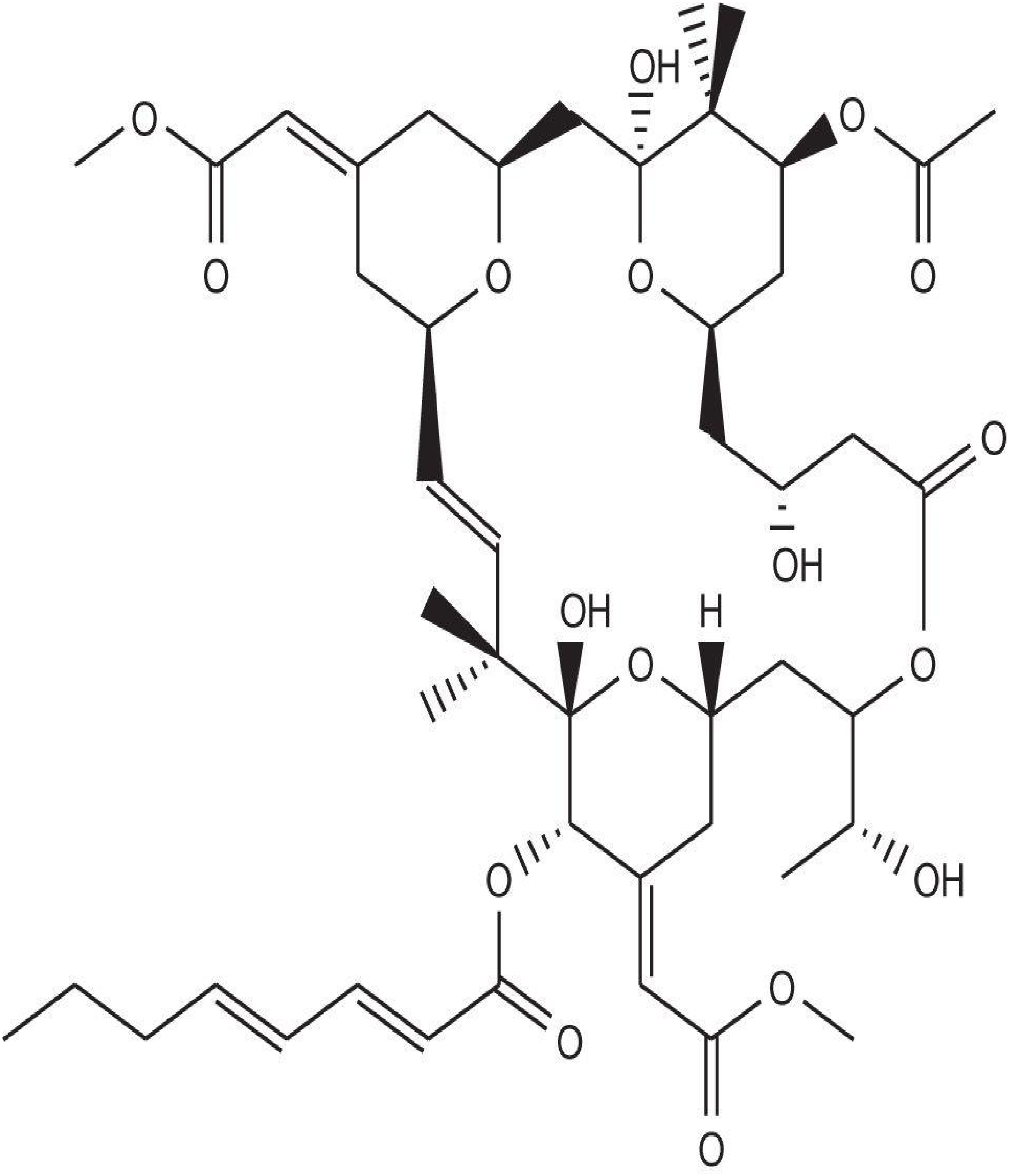
Product Application

Bryostatins are antiviral chemical agents that are used to control latent HIV-1 infections. These chemical agents appear to be particularly beneficial adjuncts in the treatment of HIV-infected patients since they purge latent viruses from different cellular reservoirs such as in the brain and lymphoid organs.

Significance of Current Application

Bryostatin 1, (I), is an unusually potent antiviral agent previously prepared by Keck.[1] The process entailed a 31-step convergent synthesis, made extensive use of toxic solvents, produced an excessive amount of toxic solvent waste, and made the commercialization of Bryostatin 1 an extremely difficult challenge. Moreover, current synthetic methodologies beyond this green process are viewed as commercially unviable because of their complexity and cost. The current application addresses these synthetic shortcomings by describing a single-step technique for preparing Bryostatin 1. This method entails utilizing Bryostatin 1–producing bacteria, then harvesting the antibiotic from a growing broth. The procedure is simple, does not require dangerous chemicals or generate toxic reaction waste products, and is potentially a commercially viable process.

Structure of Bryostatin 1, (I)



Bryostatin 1

(I)

Figure 1.1

Experimental

1. Preparation of Bryostatins 1 and 16 derived from Bugula sand. The experimental method was designed to best mimic the Gulf of Mexico location where the Bugula sand was collected and Bryostatins 1 and 16 were produced. In this process, growing nutrients, bacteria, and Bugula sand were placed into a glass container where the sand was soaked for several hours and was then gently stirred.

After several weeks of storage at 31°C, the laden ecosystem mixture was returned to the lab. Sample aliquots were routinely removed, analyzed from the reaction vessel, and consumed-growth nutrient components were replaced to ensure the optimum biosynthesis of Bryostatins 1 and 16.

The product was then harvested by decanting the sand and evaporating the water under a very high vacuum. The product mixture was isolated after extracting with n-butyl alcohol. The nutrient composition used in this process is provided in Table 1.1.

TABLE 1.1 Growth medium used to maintain a bacterial ecosystem that produced a mixture of Bryostatins 1 and 16 using Bugula sand as the host.

Component	Mass (g)
Water	1000
Sand (Bugula host ecosystem)	454
Chloride ion	19.29
Sodium ion	10.78
Calcium carbonate	5
Sodium silicate	5
Na_2NTA	3.0
Iron(III) chloride	2.5
Sulfate ion	2.6
Magnesium ion	1.5
Wood dust (cellulose/lignin)	1
Potato (starch)	1
Steel wool	1
Calcium chloride	0.5
Potassium ion	0.42
Glucose	0.4
Peptone	0.25
Bicarbonate ion	0.21
Sodium succinate	0.15
Yeast	0.1
Chitin	0.1
Sodium nitrate	0.075
Bromide ion	0.056
Sodium acetate	0.05
Boric acid	0.0257
Zinc sulfate hydrate	0.022
Sodium phosphate	0.01
Cobalt chloride hydrate	0.01
Strontium chloride hydrate	0.01
Potassium molybdenum hydrate	0.0063
Folic acid (B9)	0.002
Fluoride ion	0.001
Vitamin C	0.0007
Thiamin (B1)	0.0007
Riboflavin (B2)	0.0005
Niacin	0.0005
Vitamin B6	0.0005
Pantothenic acid	0.0005
Vitamin E	0.0002
Copper ion	0.00002
Vitamin A	0.00001
Folate	0.000002
Iodine	0.0000015
Chromium ion	0.0000012
Vitamin B12	0.0000006
Vitamin B7	0.000001
Vitamin K	0.00000025
Selenium ion	0.0000002
Vitamin D	0.0000001

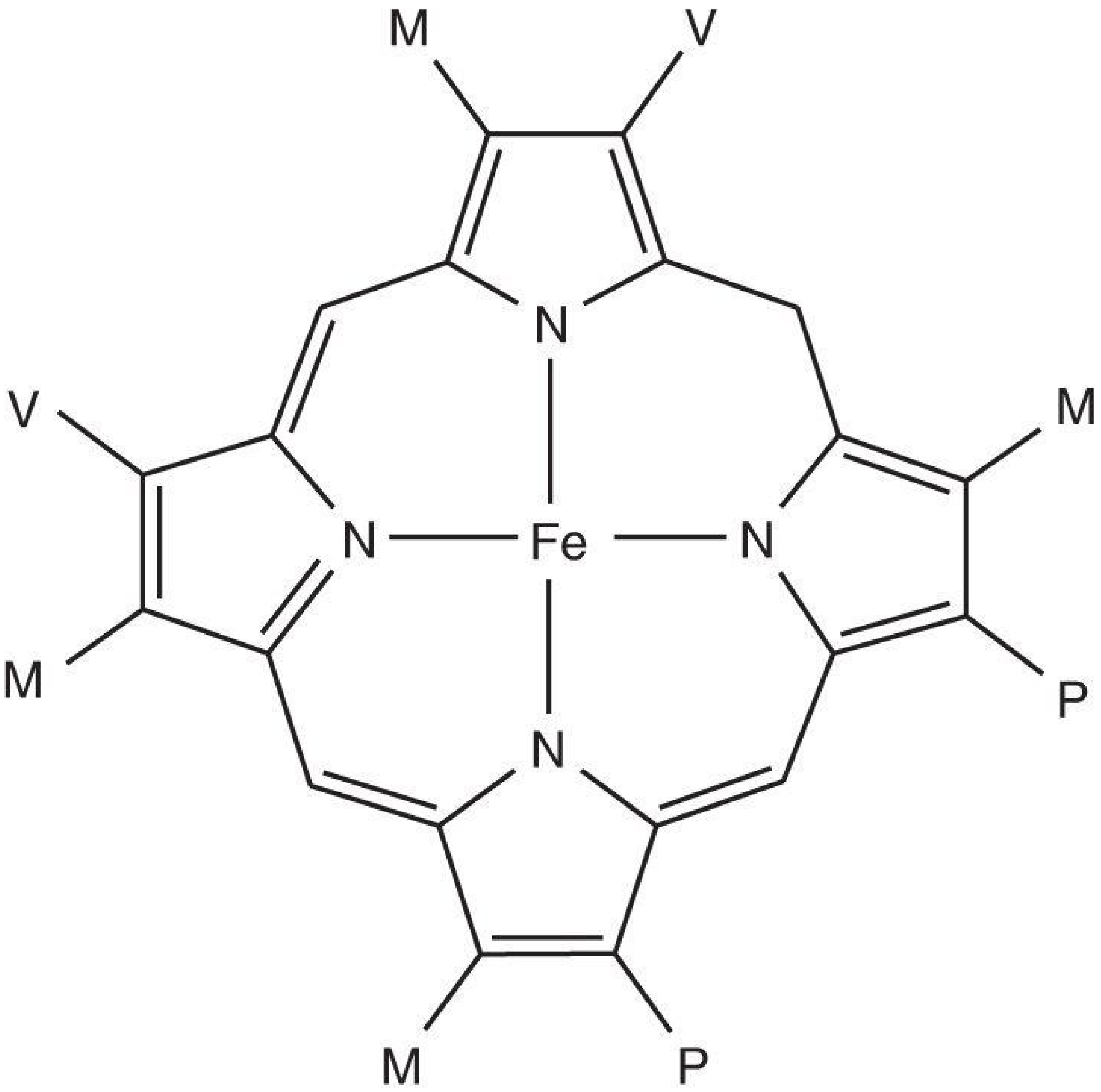
Notes and Observations

1. Majmudar[2] prepared a two-component topical skin composition that was designed to minimize the facial appearance of chronological age, chronic exposure to adverse environmental factors, and malnutrition. The topical skin composition consisted of a marine-botanical extract of codium tomentosum extract blended with Aosaine®, which was the hydrolysis product of seaweed proteins from algae Ulva lactuca.

2. Dillon[3] grew Porphyridium sp. [strain UTEX 637] and Porphyridium cruentum [strain UTEX 161] in artificial seawater and prepared microalgal compositions that were determined to be useful in improving the health and appearance of skin. The sonified microalgal composition also contained monosaccharides, particularly glucose, and unspecified insoluble polysaccharides.

3. Shin[4] isolated Salmonella bacteriophage from a chicken slaughterhouse, which was found to be effective in treating salmonella bacteria from Salmonella enteritidis, Salmonella typhimurium, Salmonella gallinarum, and Salmonella pullorum. This invaluable bacteriophage was isolated from slaughtered chickens by centrifuging the mixture at 4000 rpm for 10 minutes and then filtering the supernatant through a 0.45-mm porous glass filter.

4. Pendrak[5] used Candida albicans yeast to produce derivatives of α-biliverdin, (II), which were then used in the treatment of cancer, cardiovascular disease, inflammation, and Alzheimer’s disease. (See Fig. 1.2.)



α-biliverdin (II)

Figure 1.2

References

1. G. E. Keck et al., *Convergent assembly of highly potent analogues of bryostatin 1 via Pyran annulation: Bryostatin look-alikes that mimic phorbol ester function*, JACS, 2008, May 28; 130(21), pp. 6600-1

2. Gopa Majmudar, *Compositions of marine botanicals to provide nutrition to aging and environmentally damaged skin*, U.S. Patent 8,318,178 (November 27, 2012)

3. Harrison F. Dillon et al., *Microalgae-derived compositions for improving the health and appearance of skin*, U.S. Patent 8,277,849 (October 2, 2012)

4. Soo An Shin et al., *Salmonella bacteriophage and antibacterial composition*

comprising the same, U.S. Patent 8,293,515 (October 23, 2012)

5. Michael L. Pendrak et al., *Methods for the production of biliverdin*, U.S. Patent 8,344,019 (January 1, 2013)

Chapter

2

Automotive

Anti-Flocculation Agent in Diesel Using 5-Acetoxy-Methylfurfural

Author Gerardus Johannes Maria Gruter

Patent Title ***Method for the synthesis of organic acid esters of 5-hydroxymethylfural and their use,*** U.S. Patent 8,242,293 (August 14, 2012)

Relevant Prior Patents by Author

5-Substituted 2-(alkoxymethyl) furans, U.S. Patent 8,231,693 (July 31, 2012)

Method for the synthesis of 5-alkoxymethylfurfural ethers and their use, U.S. Patent 8,133,289 (March 13, 2012)

Product Application

5-Acetoxymethylfurfural is effective as a diesel fuel additive to minimize flocculation problems.

Significance of Current Application

The primary purpose for preparing a reaction mixture consisting of 10 wt% 5-hydroxymethylfurfural and 90% 5-acetoxymethylfurfural was as a diesel fuel additive to minimize flocculation. 5-Acetoxymethylfurfural is a biomass-derived chemical agent obtained from sucrose. The successful and inexpensive method for preparing 5-acetoxymethylfurfural from biomass-derived sucrose is both unique and economical so that multi-ton quantities of this diesel fuel anti-flocculation additive can be prepared by this route. Finally, the reaction-product mixture generated from this process does not require purification in order to remain effective as an anti-flocculation agent.

This investigation also addresses a second area of industrial concern. Furandicarboxylic acid is currently being used as a replacement monomer for terephthalic acid in the preparation of polyesters for both performance and cost considerations. Industrially generated derivatized furans, however, are currently produced exclusively using fructose which is considerably more expensive as a reagent then either glucose or sucrose. In the current investigation, 5-hydroxymethylfurfural and 5-acetoxymethylfurfural produced using sucrose can be readily converted into furan-dicarboxylic acid. The simplicity and ease of synthesizing derivatized furans as a source of furandicarboxylic acid from glucose or sucrose make these renewable reactions industrially viable.

Product Formation

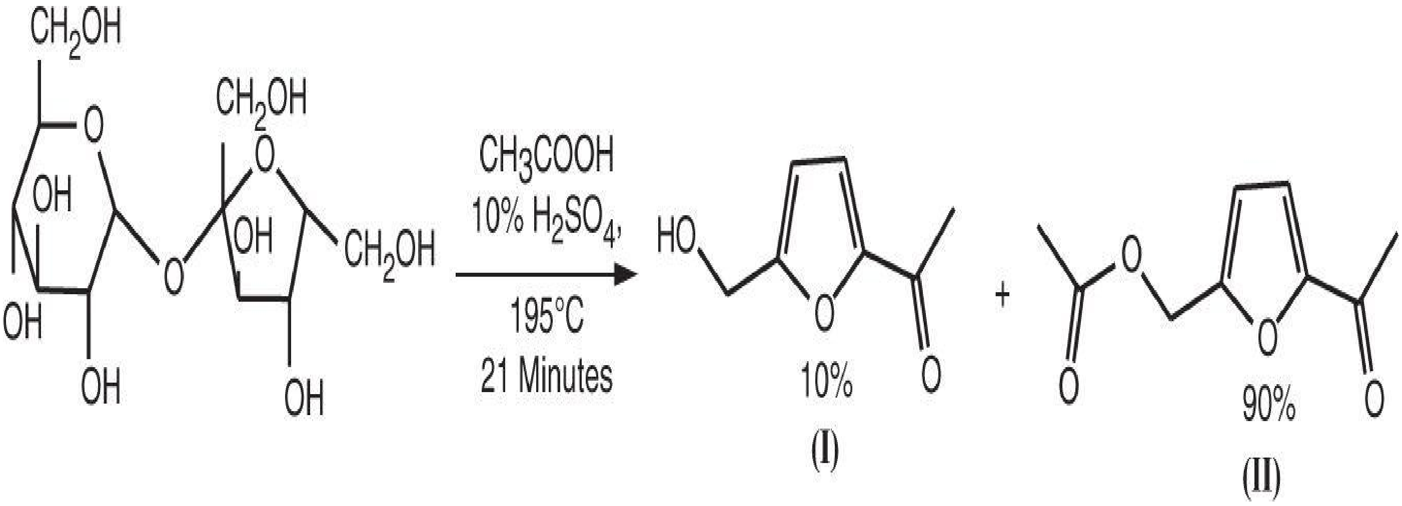


Figure 2.1

Experimental

1. Preparation of a 1:9 mixture of 5-hydroxymethylfurfural, (I), and 5-acetoxymethylfurfural, (II), using a biomass-generated sucrose feed. In a continuous-flow reactor, sucrose containing acetic acid, 10% sulfuric acid, and bio-derived sucrose were added at 10 mmol/L. The mixture was then heated to 195°C with a residence time of between 6 and 60 seconds at a nitrogen flow rate of 3.33 mL/min. After 21 minutes the products were separated, isolated, and analyzed by high pressure liquid chromatography (HPLC) and mass spectrometry that identified the reaction products as 5-hydroxymethylfurfural, (I), and 5-acetoxymethylfurfural, (II), with a selectivity of 1:9, respectively, in a 25% yield. Purified reaction products were further characterized using [1]H- and ^{13}C-nuclear magnetic resonance (NMR).

Testing

A. Diesel fuel testing. A small-scale model diesel engine was fueled with diesel fuel additized with 1 wt%, 2 wt%, 3 wt%, 5 wt%, and 10 wt% of a commercially available diesel additive containing a mixture of varying ratios of 5-hydroxymethylfurfural, (I), and 5-acetoxymethylfurfural, (II). At 2 wt% treatment, the commercially additized fuel became opaque. When additized with equivalent amounts of the experimental mixture containing 90 wt% 5-acetoxymethylfurfural, the fuel remained clear at treatment levels of up to 15 wt%.

Notes and Observations

1. 5-Hydroxymethylfurfural and 5-acetoxymethylfurfural were initially prepared by Tyrlik[1] by dehydration of glucose as well as by the reaction of 4-acetylbutyrolactone with glucose, trioxane, and aluminum chloride, respectively.

2. Lightner[2] used 10% sulfuric acid at 100°C in the hydrolysis of biomass-derived sucrose and isolated 5-hyroxymethylfurfural, (I), and furfural, (III). Further treatment of the reaction products with sulfuric acid produced levulinic acid, (IV), and formic acid, (V), by a heterocyclic ring opening reaction. This experimental mixture was marginally successful when used as an anti-flocculation additive in diesel fuel. (See Fig. 2.2.)

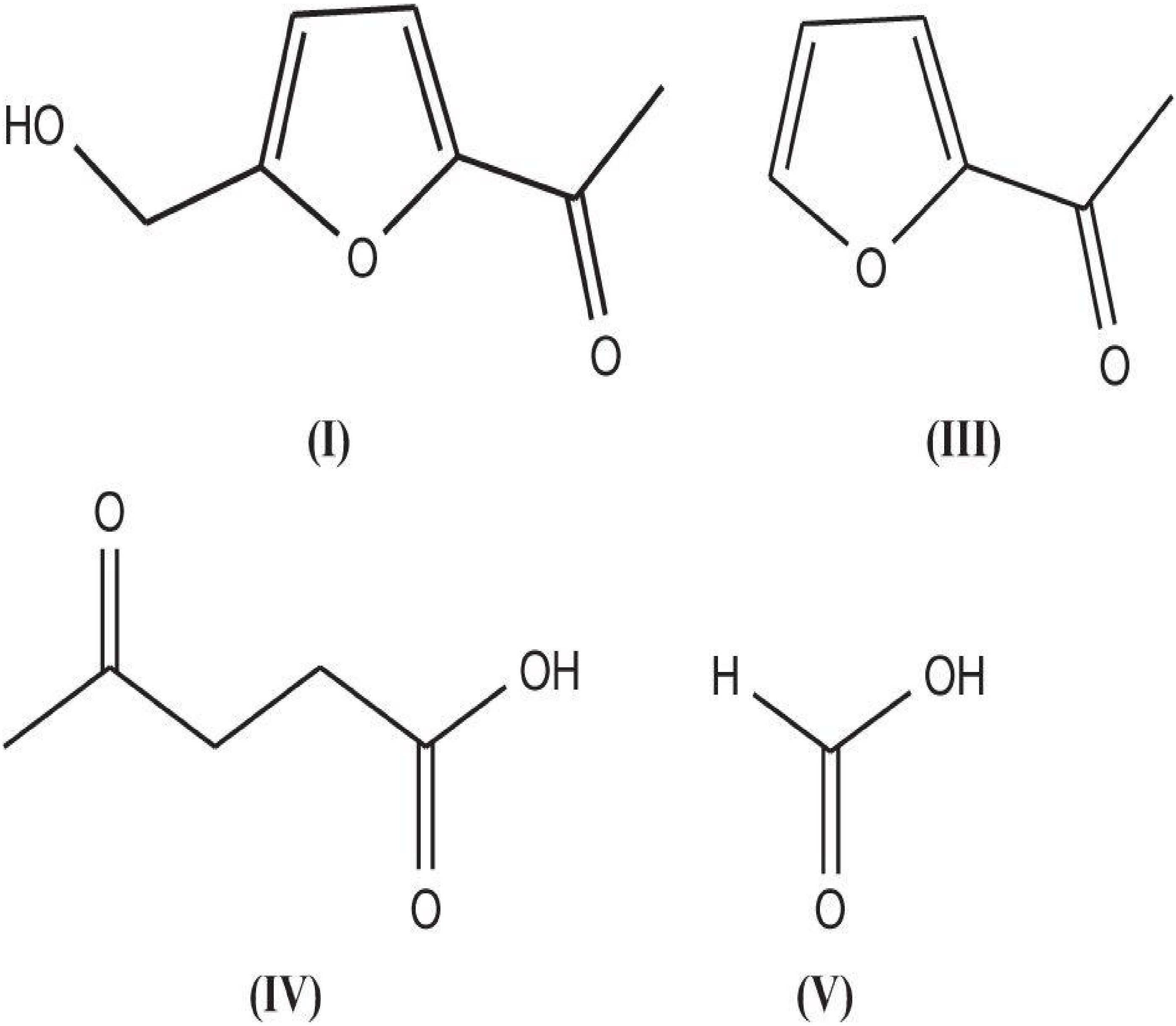
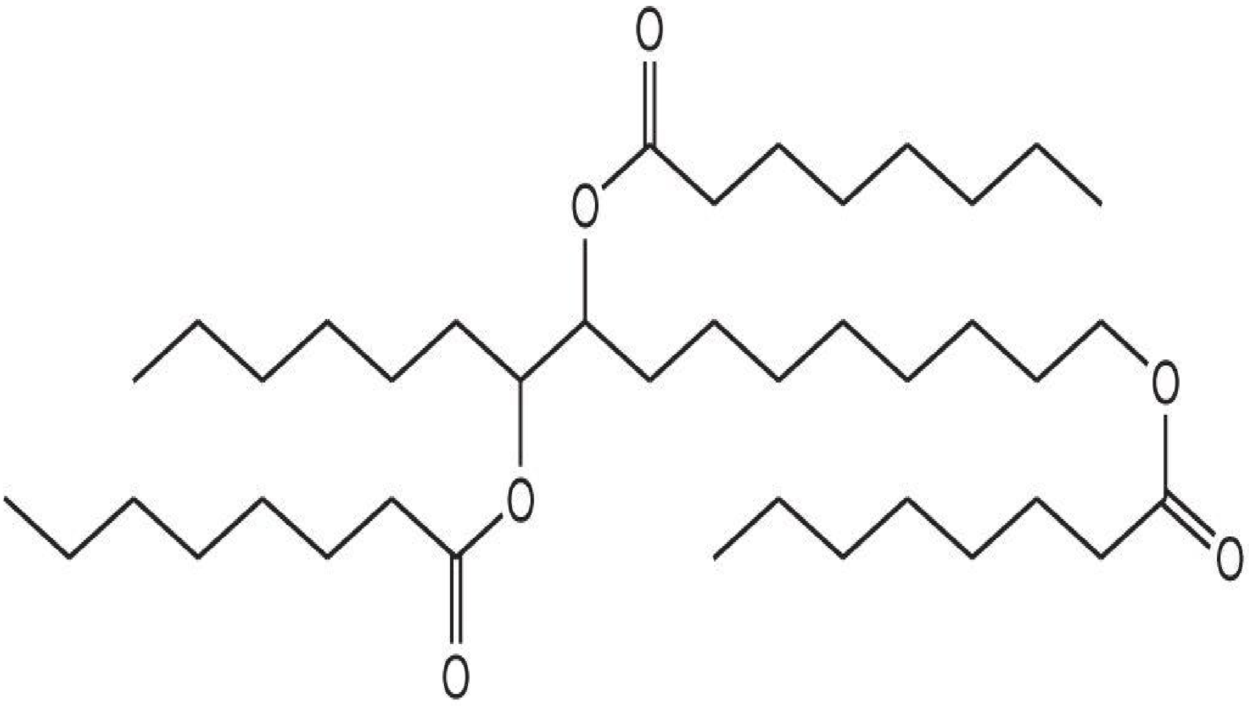


Figure 2.2

3. Triester lubricant additives, notably octadecane-1,9,10-triyl trioctanate, (VI), and octadecane-1,9,10-triyl trisdecanoate, (VII), were prepared by Elomari[3] utilizing a biomass precursor and then used as the lubricity additive in diesel fuel. (See Fig. 2.3.)



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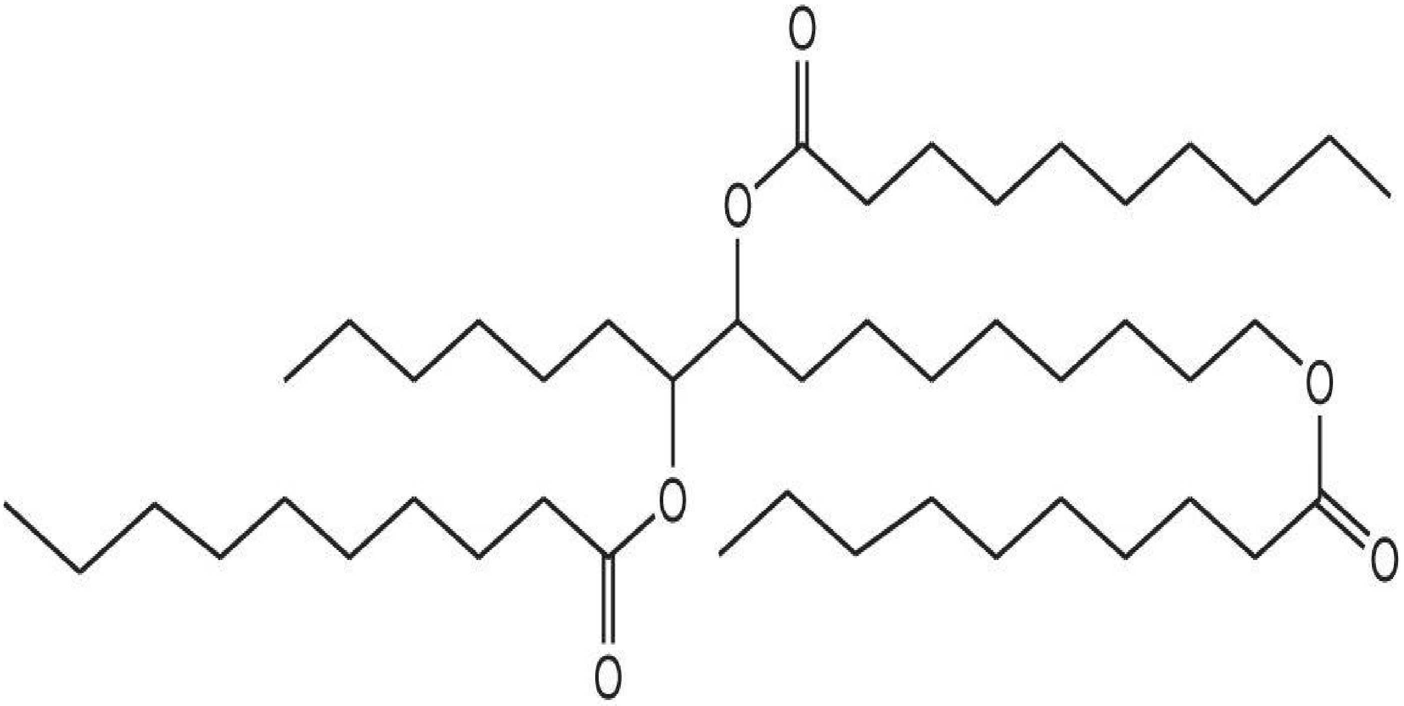
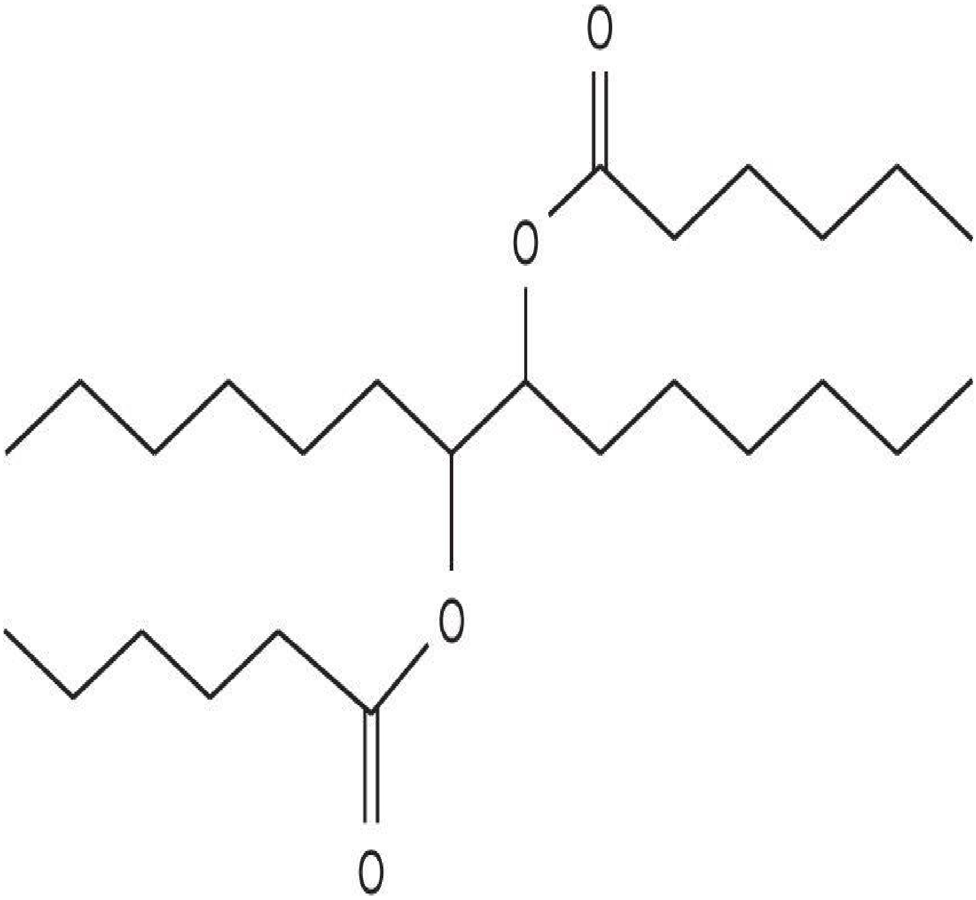


(VII)

Figure 2.3

4. In a separate investigation by Elomari,[4] bio-derived esters, particularly hexanoic acid, 2-hexanoyloxy-1-hexyl-octyl ester, (VIII), and 9,10-bis-decanoyloxy-octadecanoic acid decyl ester, (IX), were determined to be effective as refrigeration lubricants. (See Fig. 2.4.)



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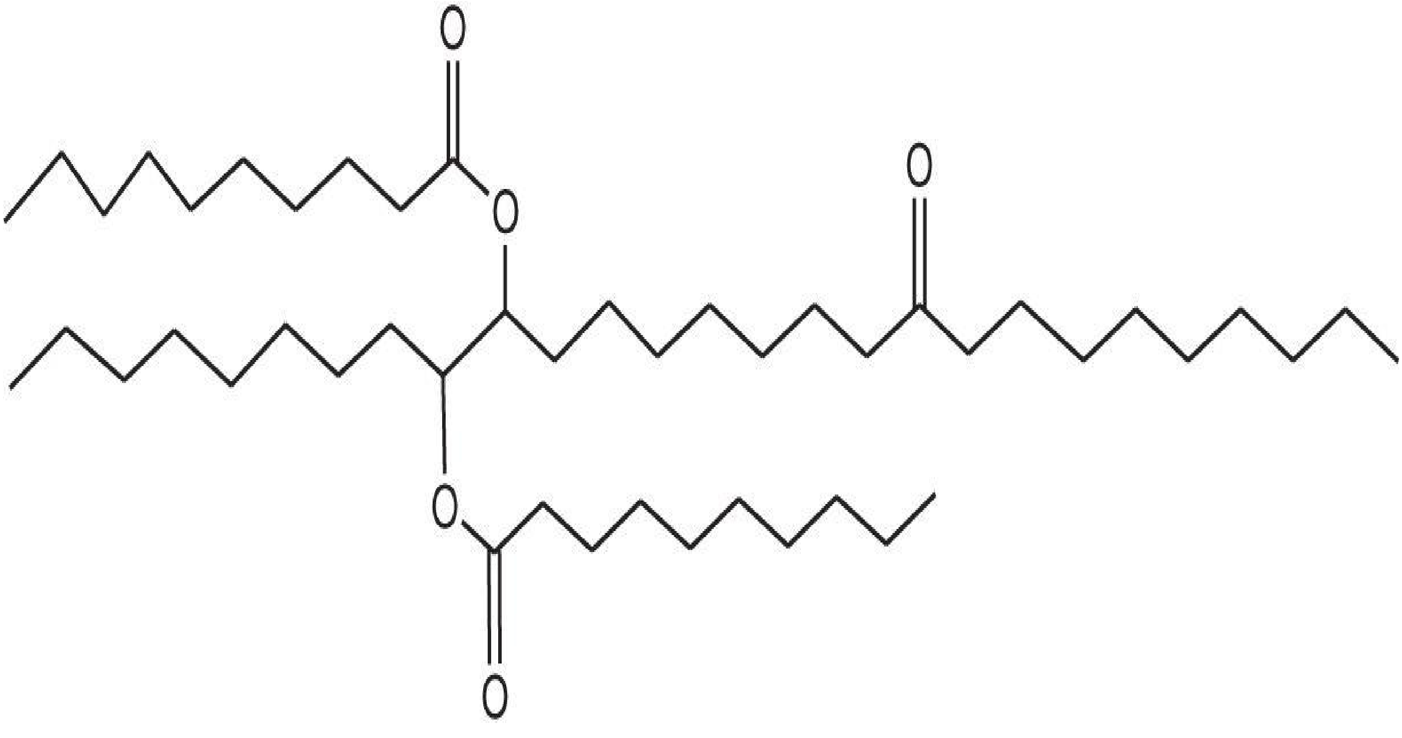

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Figure 2.4

References

1. S. Tyrlik et al., *Selective dehydration of glucose to 5-hydroxymethylfurfural and a one-pot synthesis of a 4-acetylbutyrolactone from glucose and trioxane in solutions of aluminum salts*, Carbohydrate Research, vol. 315, pp. 268-272, 1999; ibid, Carbohydrate Research, vol. 315, 268-272, 1999

2. Gene E. Lightner, *Additives derived from biomass extracted by biodiesel fuel oil*, U.S. Patent 7,520,905 (April 21, 2009)

3. Saleh A. Elomari et al., *Biolubricant esters from the alcohols of unsaturated fatty acids*, U.S. Patent 8,304,574 (November 6, 2012)

4. Saleh A. Elomari et al., *Refrigeration oil from gas-to-liquid-derived and bio-derived diesters*, U.S. Patent 8,268,187 (September 18, 2012)

Biodiesel Fuel

Author Monica Bhatia et al.

Patent Title ***Reduction of the toxic effect of impurities from raw materials by extractive fermentation,*** U.S. Patent 8,313,934 (November 20, 2012)

Product Application

A method for producing biodiesel fuel in relatively high yields with inexpensive and readily available carbohydrates using genetically engineered strain of E. coli, LS9-ID1.

Significance of Current Application

In the initial phase of the potentially ongoing investigation, the genetically engineered strain of E. coli, LS9-ID1, was found to be effective in producing non-fossil-fuel generated diesel fuel. The E. coli strain used in this investigation appears effective in generating biodiesel from contaminated sucrose, starch, or carbohydrates. Finally, preliminary observations indicate that E. coli, LS9- ID1, is a versatile strain that can be used to produce other industrial-significant bio-organic products when used in modified fermentation broths.

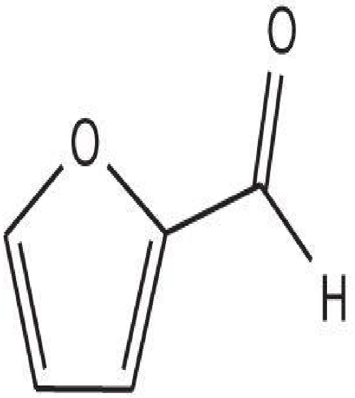
Experimental

1. Preparation of biodiesel using fermenting carbohydrates in contaminant-free broths. A culture of a genetically engineered strain of E. coli, LS9-ID1, was transferred from a frozen stock and incubated in Luria-Bertani broth for approximately three hours. The culture was then transferred to a mineral medium commonly used for E. coli, M9, which was buffered and supplemented with thiamine and trace minerals. The culture was further incubated and used to inoculate the same fermentation media with 50 g/L containing either glucose, fructose, or pentose. Culture growth was then induced using isopropyl-β-D1-thiogalactopyranoside and the mixture was treated with 10 mL/L of either methanol or ethanol in shake flasks to initiate the fermentation process and subsequent formation of biodiesel fuel. In a typical reaction, glucose, or another carbohydrate, was exhausted in approximately 24 to 40 hours where the formation of biodiesel was maximized. During the fermentation process, the reaction extent was monitored by optical density measurements at 600 nm. The reaction extent could also be monitored using HPLC to determine carbohydrate degradation and ester formation.

2. Preparation of biodiesel using extractive fermentation with contaminated broths. The ability to prepare biodiesel was also performed by extractive fermentations using the engineered strain of E. coli, LS9-ID1, which improved the performance of the fermentation in the presence of toxins. In this process the experimental protocol described in Preparation 1 was used. In the current process, however, two sets of duplicate flasks were prepared with different concentrations of the broth containing the selected toxin. One set served as the control, which included the toxin without the hydrophobic solvent extract. In the second set, the extract was added in a ratio volume of 1:3 solvent/per 3 volumes of fermentation broth. The flasks were then inoculated at 37°C in agitated shakers. When the optical density measurements at 600 nm reached a value of one, the cultures were treated with 1 mM of isopropyl-β-D1-thiogalactopyranoside and 20 mL/L methanol. Cell growth and production of fatty acid methyl esters were then measured after 24 hours. In the control culture lacking a hydrophobic solvent, the optical density measurements at 600 nm was measured directly in the fermentation broth. The optical density of flasks containing the hydrophobic solvent was measured after the broth was centrifuged and the cell pellet was re-suspended in the same volume of distilled water.

Testing Results

Carbohydrate solutions fermented with the engineered strain of E. coli, LS9-ID1 in solutions containing the organic contaminants including furfural, (I), syringealdehyde, (II), 4-hydroxy-benzaldehyde, (III), 5-hydroxymethylfurfural, (IV), and guaiacol, (V), in the presence of fatty acid methyl esters were approximately 85% as effective as control samples containing the identical toxin but not the hydrophobic solvent in generating biodiesel. (See Fig. 2.5.)



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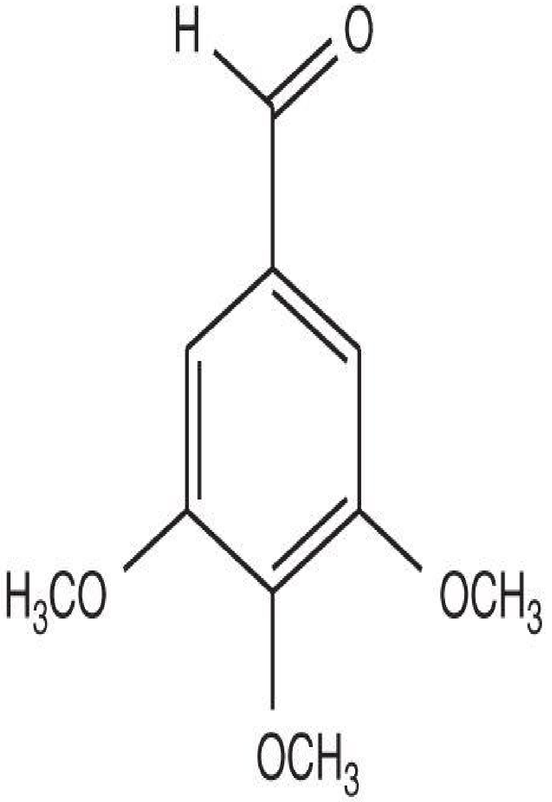

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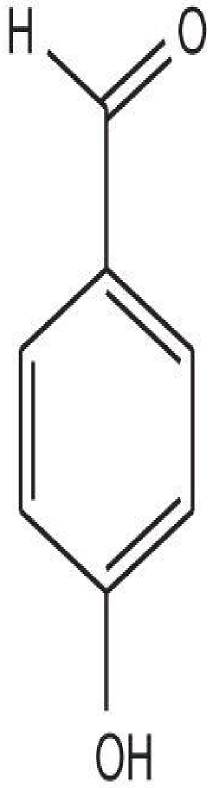

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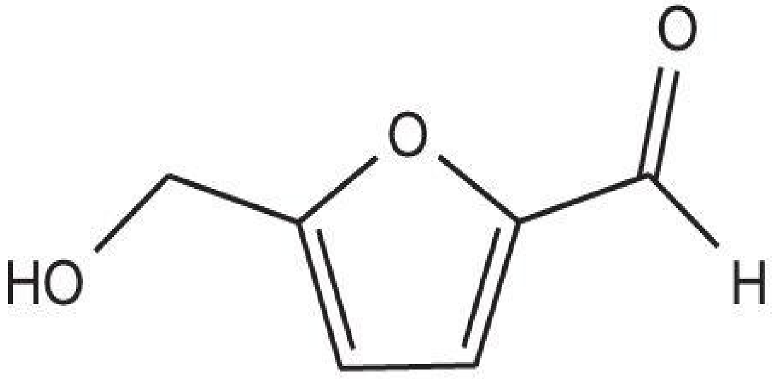

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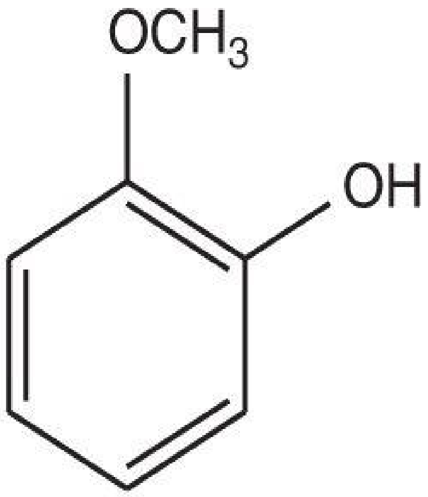
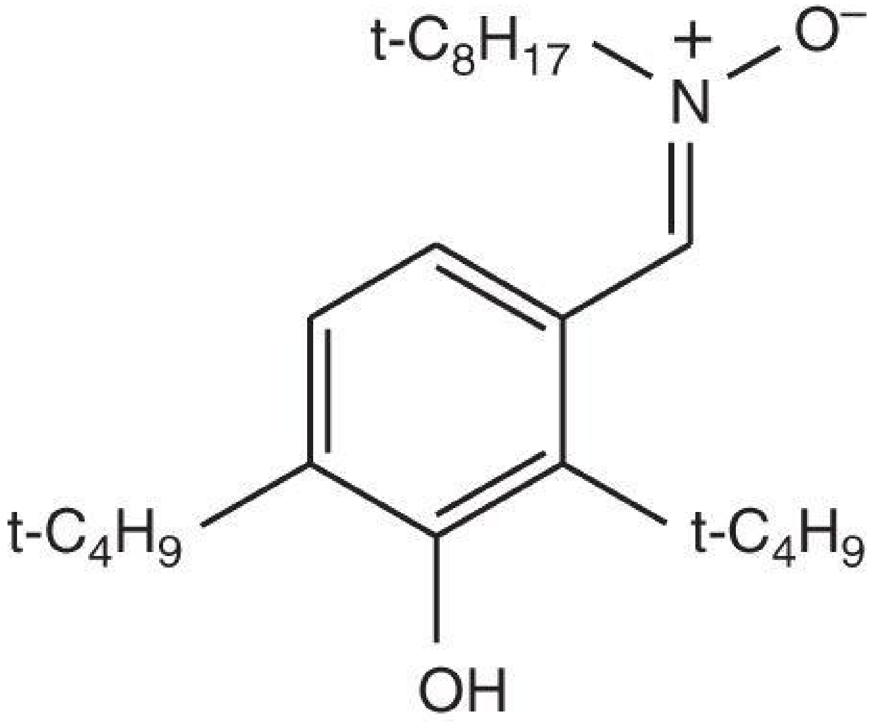


(V)

Figure 2.5

Notes and Observations

1. Banavali[1] determined that 2,6-di-t-butyl-4-(N-t-octyl) nitronyl phenol, (VI), was a particularly effective anti-oxidant for biodiesel. (See Fig. 2.6.)



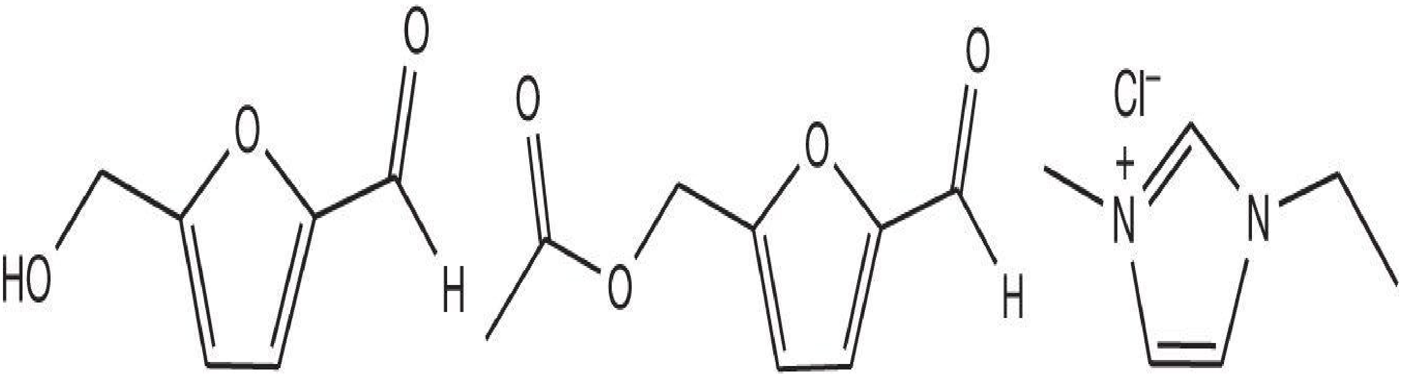
(VI)

Figure 2.6

2. Kalel[2] treated wet algal biomass with green microalgae Scendesmus dimorphus to recover fatty acid esters that were used as components in biodiesel fuel blends.

3. A photobioreactor apparatus containing genetically enhanced photoautotrophic, particularly cyanobacteria and algae, was prepared by Woods[3] to generate large quantities of bioethanol. Bioethanol produced from this process was subsequently used as blending component in the industrial production of biofuels.

4. Gruter [4] used glucose and fructose to prepare bio-hydroxymethylfurfural, (VII), and bio-5-acetoxy methylfurfural, (VIII), in high yields by treating acetic acid containing chromium (II) chloride in the presence of the ionic solvent, 1-ethyl-3-methylimidazolium chloride, (IX). Bio-hydroxymethylfurfural and bio-5-acetoxymethylfurfural obtained from this process were used as components of biodiesel. (See Fig. 2.7.)



(VII) (VIII) (IX)

Figure 2.7

References

1. Rajiv Manohar Banavali et al., *Preparation of nitrones*, U.S. Patent 8,329,949 (December 11, 2012)

2. Aniket Kalel, *Methods of extracting neutral lipids and recovering fuel esters*, U.S. Patent 8,318,018 (November 27, 2012)

3. R. Paul Woods et al., *Closed photobioreactor system for continued daily in situ production of ethanol from genetically enhanced photosynthetic organisms with means for separation and removal of ethanol*, U.S. Patent 8,323,958 (December 4, 2012)

4. Gerardus Johannes Maria Gruter et al., *Hydroxymethylfurfural ethers and esters prepared in ionic liquids*, U.S. Patent 8,314,260 (November 20, 2012)

Ethylene Glycol

Author Tao Zhang et al.

Patent Title ***Method for producing ethylene glycol from polyhydroxy-compounds,*** U.S. Patent 8,324,433 (December 4, 2012)

Relevant Prior Patents by Author or Coauthors

Tungsten carbide catalysts, their preparation and application in synthesis of ethylene glycol from cellulose, U.S. Patent 8,338,326 (December 25, 2012)

Method of using tungsten carbide catalysts in the preparation of ethylene glycol, U.S. Patent Application 20120283487 (November 8, 3012)

Mesoporous carbon supported tungsten carbide catalysts, preparation and applications thereof, U.S. Patent Application 20120178974 (July 12, 2012)

Methods for preparing ethylene glycol from polyhydroxycompounds, U.S. Patent Application 20120172633 (July 5, 2012)

Product Application

This investigation is designed to provide automotive vehicles with renewable ethylene glycol. In addition, it is also designed as an industrial source of renewable C_3 and C_4 polyhydroxyl aliphatic compounds.

Significance of Current Application

The conventional method for preparing aliphatic polyols requires (a) oxidation of an olefin to an expoxide using a peracid followed by (b) the acid catalyzed hydrolysis to epoxides. The method uses non-renewable reagents and generates a significant amount of futile by-products, particularly oligomeric ethylene oxide. In the current investigation, an effective route for preparing ethylene oxide uses renewable and sustainable polyhydroxy aliphatics such as starch, hemicellulose, glucose, sucrose, fructose, and fructan. The process involves a hydrogenative-degradation reaction using catalysts containing tungsten and either cobalt, ruthenium, rhodium, palladium, iridium, or platinum on activated carbon to generate this glycol. The most probable synthetic route for forming polyhydroxyl aliphatics is through hydrogenative dehydration of the renewable sugars or polysaccharides.

Catalyst Formation

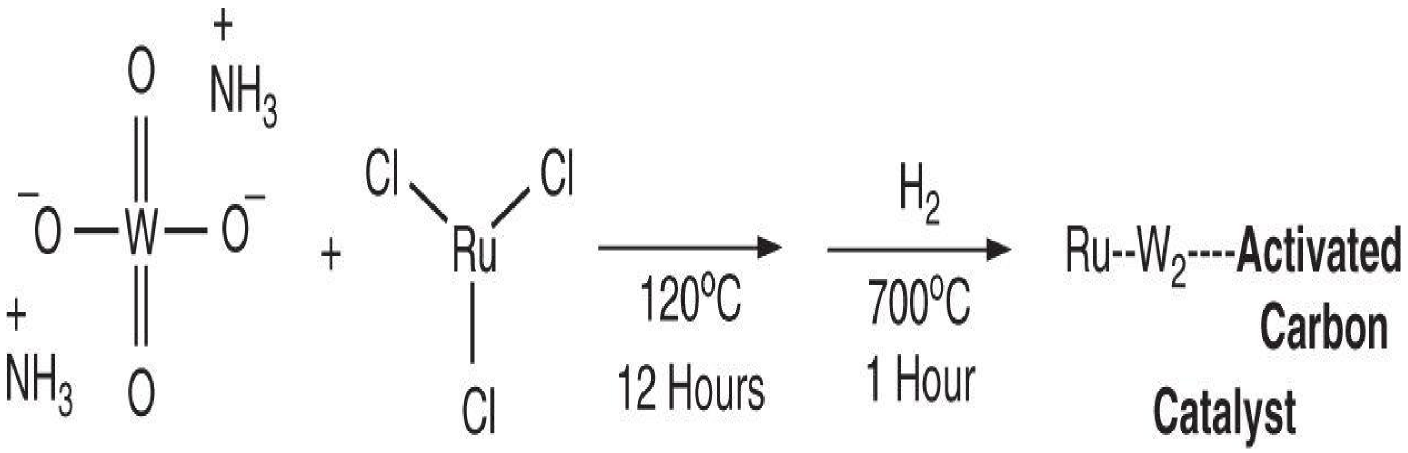


Figure 2.8

Product Formation

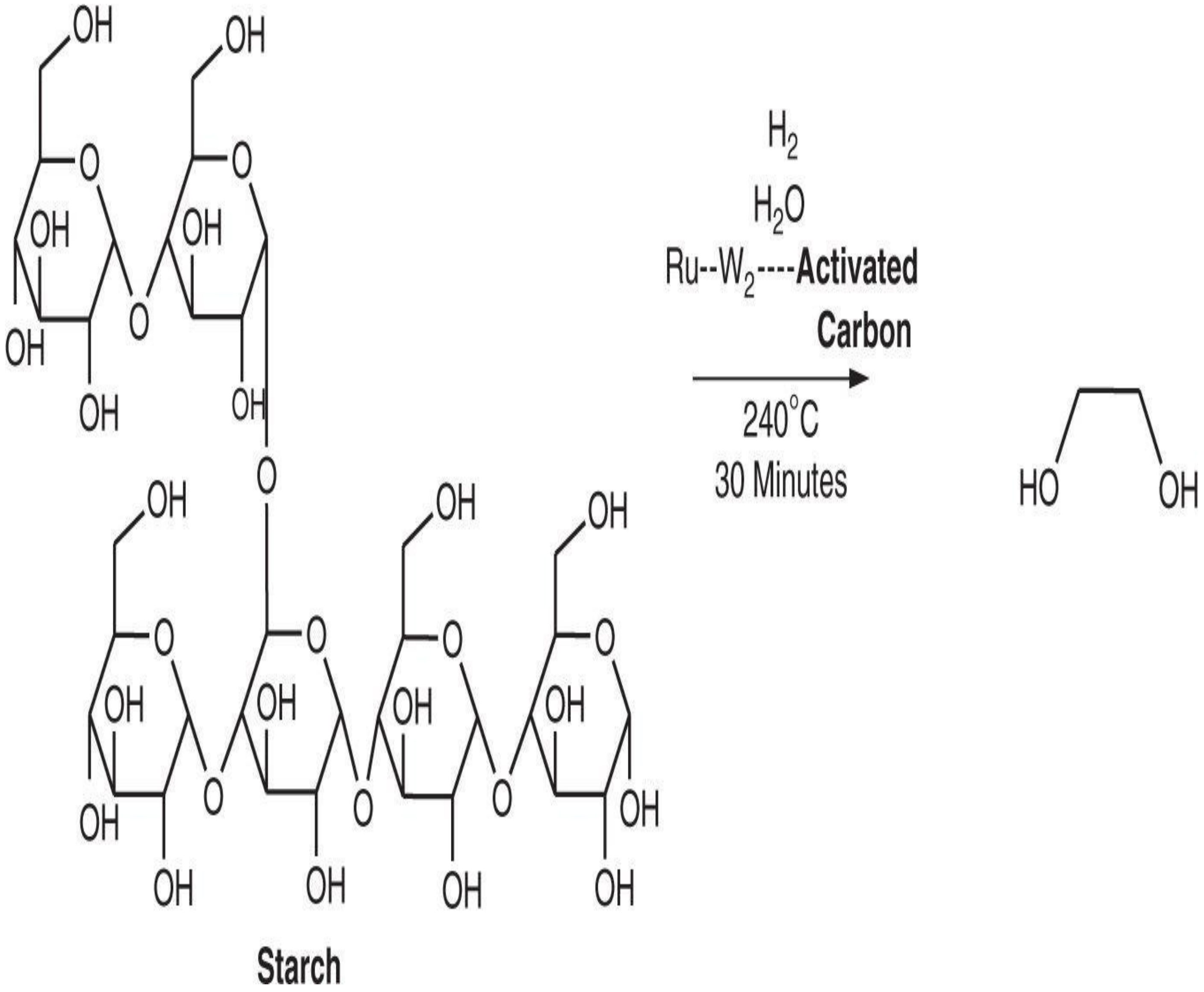


Figure 2.9

Experimental

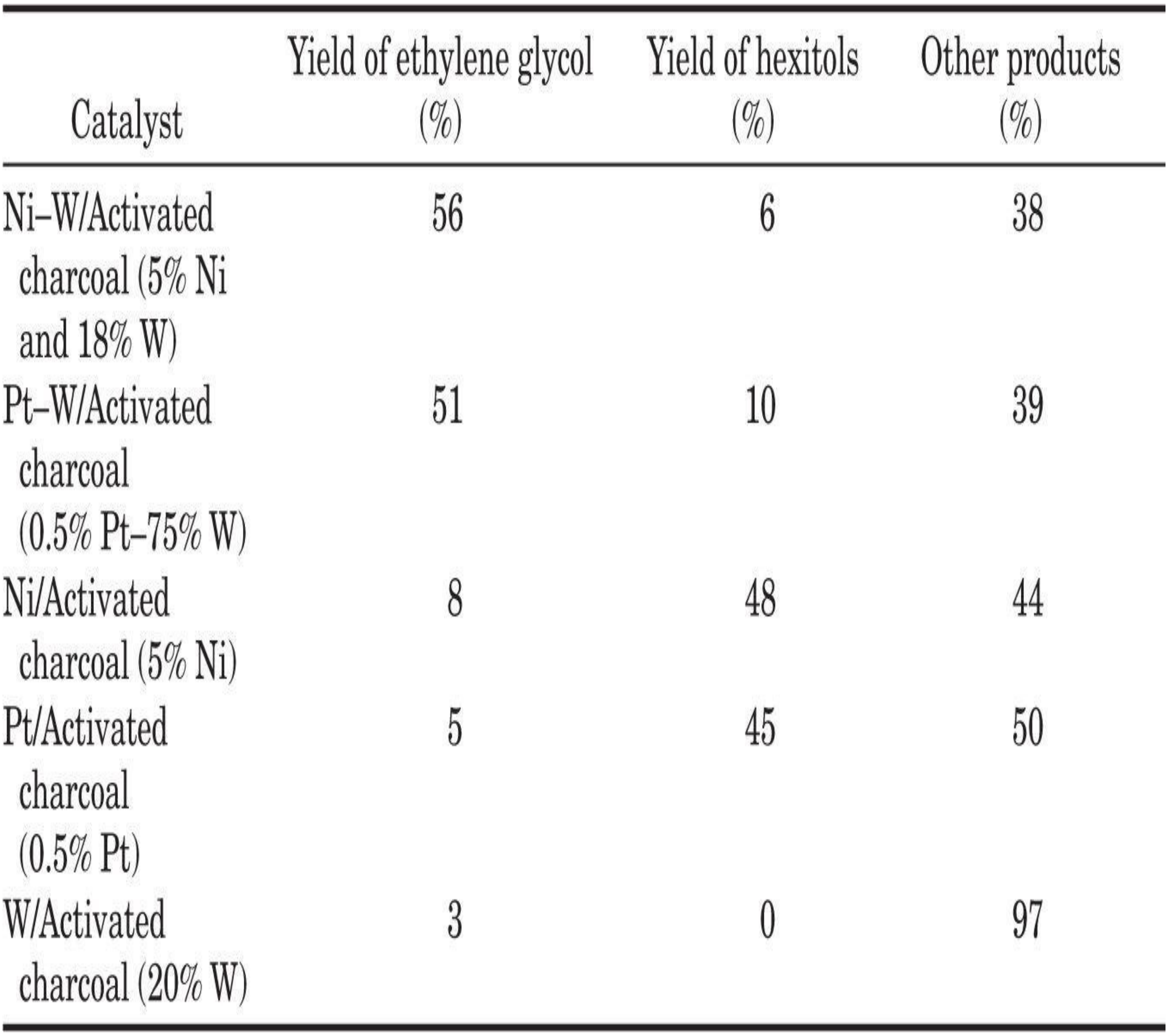
1. Preparation of the hydrogenative-degradation platinum-tungsten catalyst. Activated charcoal was soaked in a solution containing ruthenium trichloride and ammonium metatungstate and then dried in an oven at 120°C for 12 hours. The intermediate was then reduced in a carbo-thermal reaction in the presence of hydrogen at 700°C for 1 hour and the product, Ru–W_2C—activated charcoal, isolated as a black solid containing 5 wt% ruthenium and 10 wt% tungsten.

2. Preparation of ethylene glycol from the hydrogenative-degradation of starch. A 200 mL stainless steel reactor was charged with 1.0 g of either a sugar or polysaccharide, 0.3 g of a catalyst described in Step 1, and 100 mL of water. The reactor was filled with hydrogen and vented three times to remove air. Thereafter, the reactor was charged with 200 MPa of hydrogen and the temperature increased to 240°C for thirty minutes then slowly cooled to ambient temperature. The mixture was then centrifuged and the supernatant isolated. The supernatant was then analyzed using HPLC containing a calcium ion exchange column with a refractive index detector. Analysis indicated that ethylene glycol had been formed in 47% yield. Other reaction by products included sorbitol, mannitol propylene glycol, butantetraol, and ethanol.

Reaction Scoping Studies and Results

Selected hydrogenative-degradation reactions using starch with a variety of catalysts and reaction conditions are provided in Table 2.1.

TABLE 2.1 Conversion of starch to ethylene glycol in the presence of selected catalysts. A mixture of sorbitol, mannitol propylene glycol, butantetraol, and ethanol were also produced in the reaction but were not quantified.



Catalyst	Yield of ethylene glycol (%)	Yield of hexitols (%)	Other products (%)
Ni–W/Activated charcoal (5% Ni and 18% W)	56	6	38
Pt–W/Activated charcoal (0.5% Pt–75% W)	51	10	39
Ni/Activated charcoal (5% Ni)	8	48	44
Pt/Activated charcoal (0.5% Pt)	5	45	50
W/Activated charcoal (20% W)	3	0	97

Notes and Observations

1. Kalnes[1] prepared ethylene glycol using feedstock derived from the short rotation of forestry, industrial wood waste, forest residue, and agricultural residue by heating the mixture at elevated temperatures with either tungstic acid, phosphotungstic acid, or cellulose metatungstate.
2. Zhang[2] successfully converted cellulose into ethylene glycol by hydrogenative degradation using tungsten carbide that contained up to ~1% of a co-catalyst consisting of either ruthenium, rhodium, palladium, osmium, iridium, platinum, or copper. Optimum conversion results were observed when the co-catalyst was supported on a porous substrate particularly activated charcoal, alumina, silica, or titanium dioxide.
3. Kalnes[3] produced ethylene glycol using an effluent stream derived from biomasses such as waste material, recycled material, industrial wood waste, and agricultural residue. In this process the biomass was passed over a catalyst bed consisting of tungsten carbide containing trace amounts of nickel. Side products that were generated by this process included alcohols, carboxylic acids and aldehydes, polysaccharides, glycerol, and depolymerized lignin.

4. Chen[4] used either tungstic acid or molybedic acid containing trace amounts of vanadium oxides, metavanadates, chromium oxides, chromium sulfate or titanium ethoxide supported on alumina, and silica or zeolites to convert cellulose or hemicellulose into a mixture of ethylene glycol and propylene glycol. The typical yield of ethylene glycol and propylene produced in these reactions was 11 parts and 2 parts, respectively.

References

1. Tom N. Kalnes et al., *Process for generation of polyols from saccharide containing feedstock*, U.S. Patent 8,222,463 (July 17, 2012)

2. Tao Zhang et al., *Methods of using tungsten carbide catalysts in preparation of ethylene glycol*, U.S. Patent Application 20120283487 (November 8, 2012)

3. Tom N. Kalnes, *Continuous catalytic generation of polyols from cellulose with recycle*, U.S. Patent Application 20110313212 (December 22, 2011)

4. John Q. Chen et al., *Catalyst system for generation of polyols from saccharide containing feedstocks*, U.S. Patent Application 20110312488 (December 22, 2011)

Chapter

3

Biosolvents

Ethyl Lactate

Author Nadine Essayem et al.

Patent Title ***Method for obtaining compositions of biosolvents by esterification and contained compositions of biosolvents,*** U.S. Patent Application 20130105738 (May 2, 2013)

Relevant Prior Patents by Author or Coauthors

Process for transformation of lignocellulosic biomass or cellulose by tungsten-based solid Lewis acids, U.S. Patent Application 20130053601 (February 28, 2013)

Method for preparing a mixture of biofuels, U.S. Patent Application 20110146137 (June 23, 2011)

Tungsten catalysts, U.S. Patent 7,851,401 (December 14, 2010)

Catalytic method of producing alkyl mercaptans by adding hydrogen sulphide to an olefin, U.S. Patent 7,339,083 (May 4, 2008)

Catalytic method of producing mercaptans from thioethers, U.S. Patent Application 20060025633 (February 2, 2006)

Product Application

Esters are used in medicinal, agricultural, cosmetic, ink, and cleaning formulations.

Significance of Current Application

Esters are industrially prepared by reacting an acid with an alcohol in the presence of a catalyst in a high-boiling point oil-derived petroleum solvent. Esters produced though this route, however, are energy intensive, require extensive purification before they can be used, and generate toxic organic waste products. To address these concerns, the current investigation has identified biosolvents that selectively dissolve esters during the esterification process. As a result of this selective solubility, the ester reaction kinetics became more favorable, leading to higher yields of product at shorter reaction times and at lower reaction temperatures. Esters produced using biosolvents generate considerably less organic waste products, are less energy intensive, and can be used to produce a wide variety of industrially significant esters.

Renewable Reagents

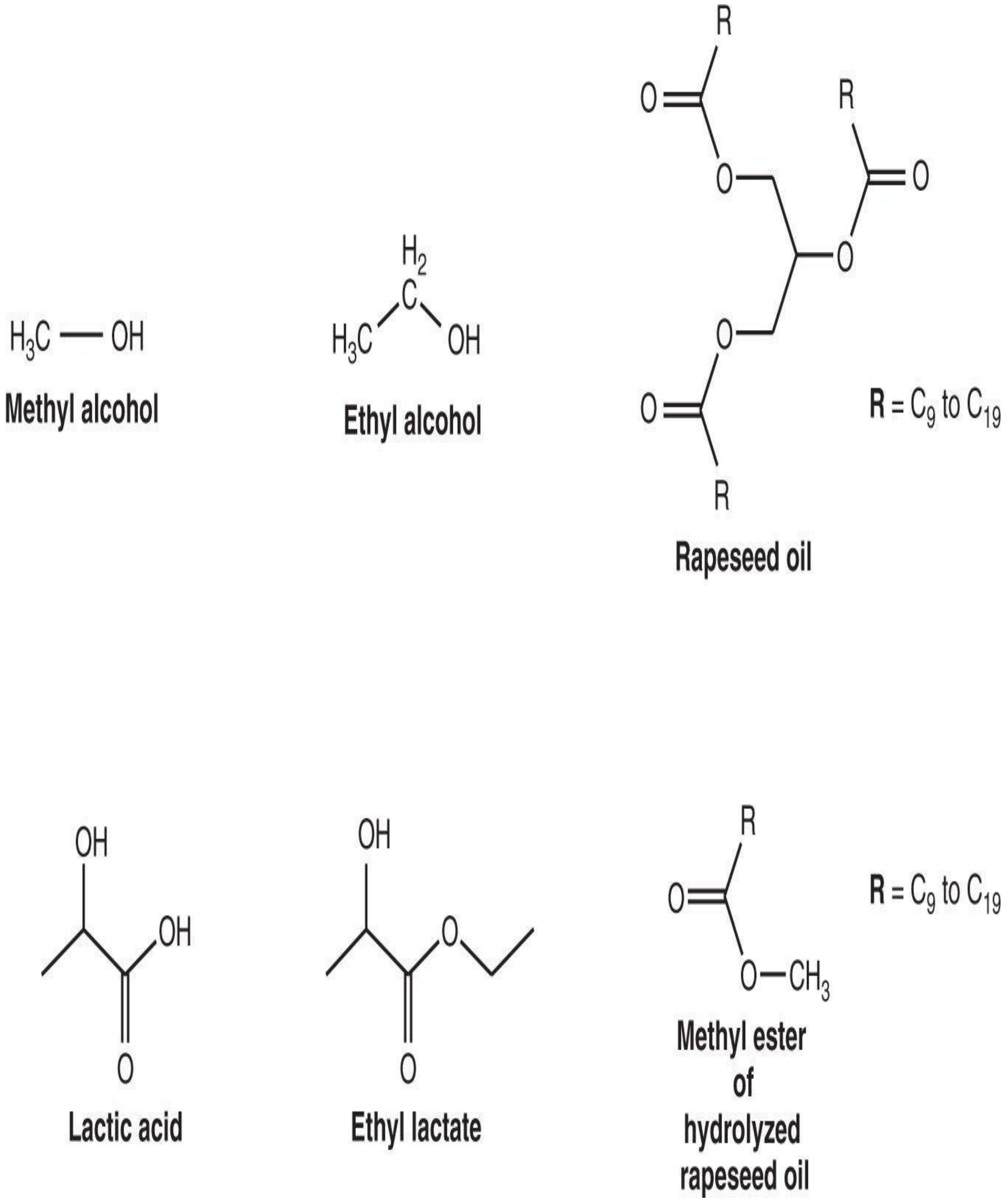
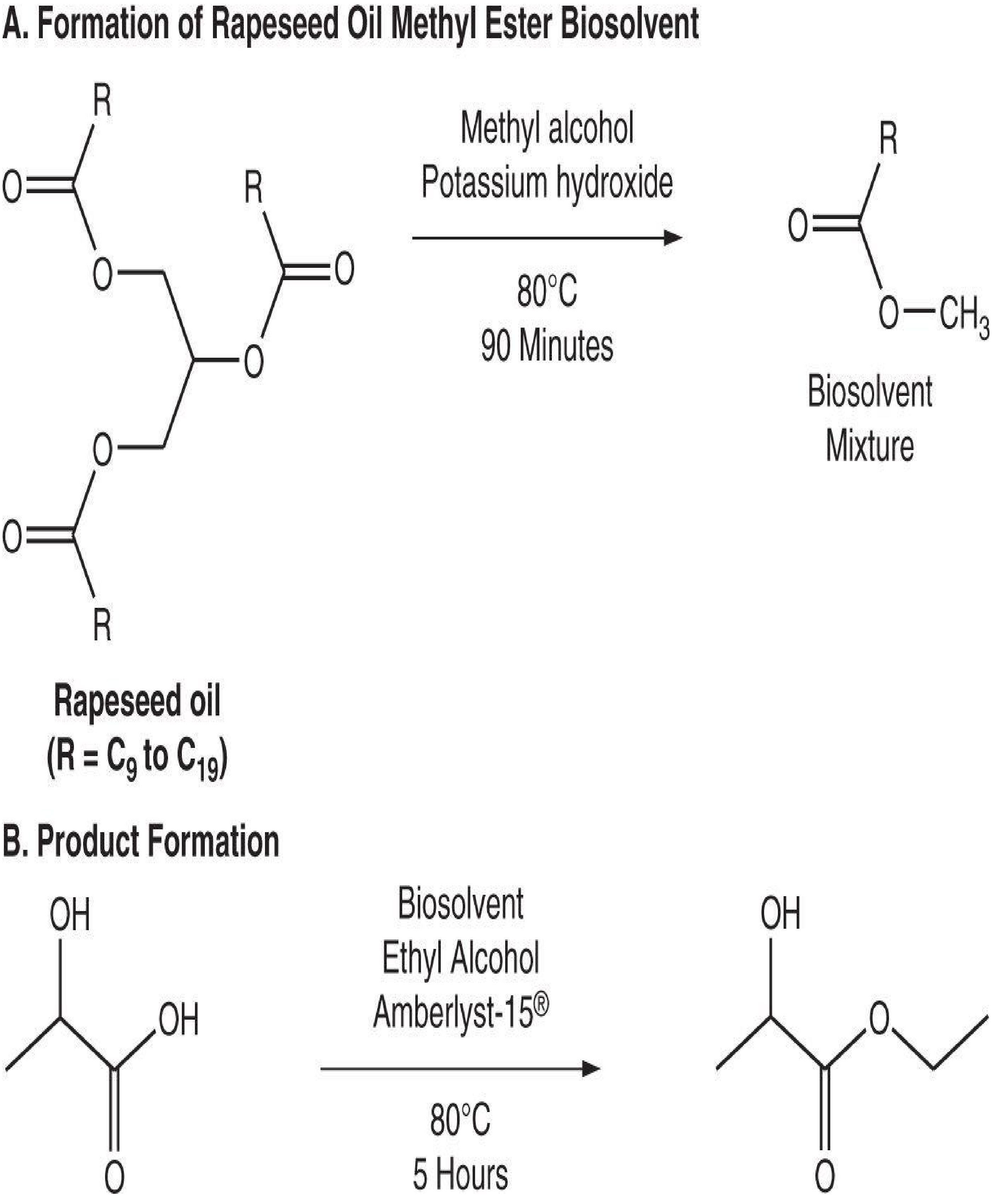


Figure 3.1

Product Formation


A. Formation of Rapeseed Oil Methyl Ester Biosolvent

B. Product Formation

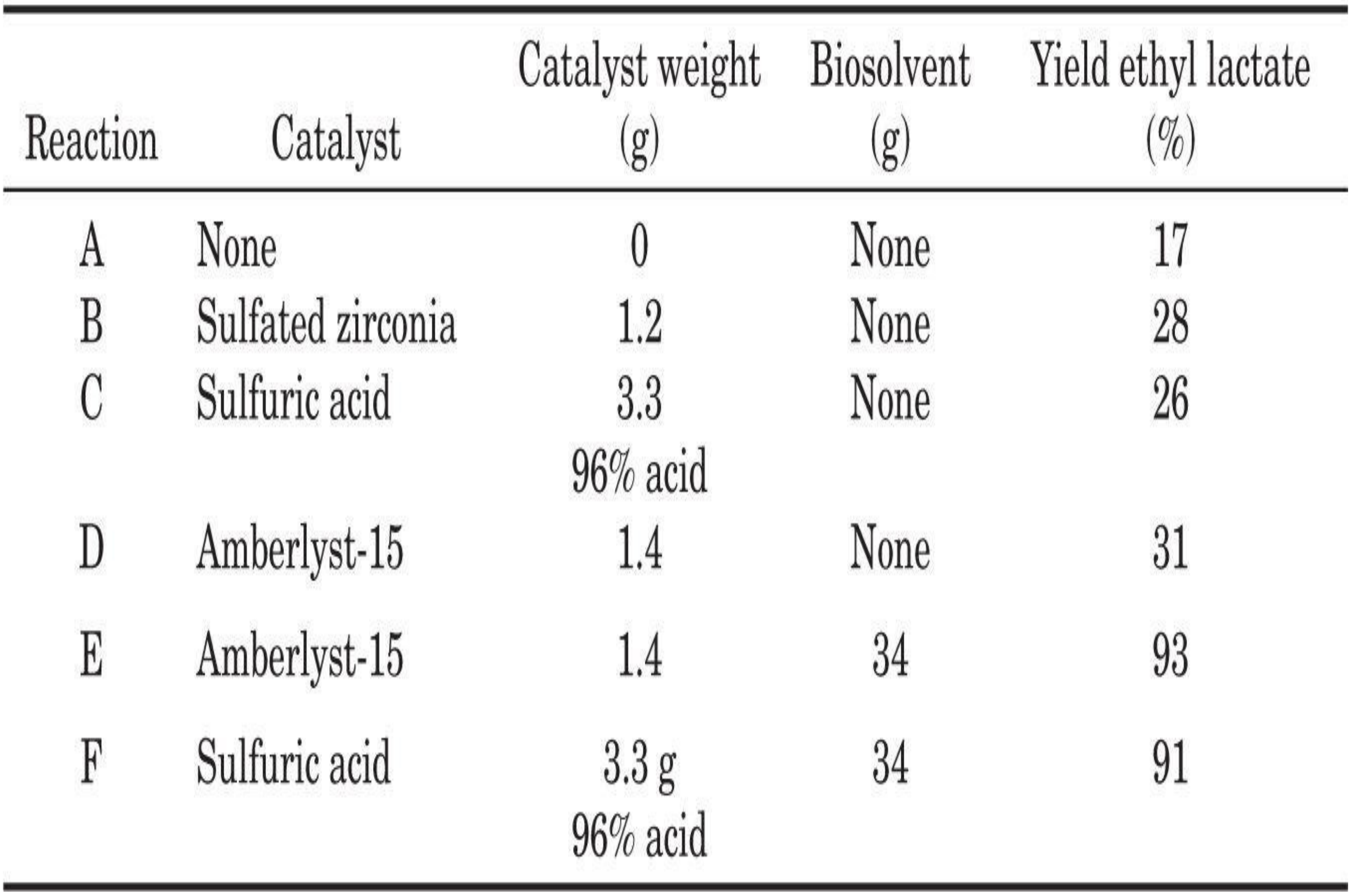
Figure 3.2

Experimental

1. Preparation of biosolvent. A Pyrex® flask was charged with 330 g of rapeseed oil, 120 g of methyl alcohol, and 3 g of potassium hydroxide then heated to 80°C while stirring using the reaction mixture using a mechanical stirrer. The reaction was stopped after approximately 90 minutes, and the methyl ester mixture separated from glycerol by decantation. Gas chromatography indicated that the rapeseed oil was completely consumed by the transesterification reaction and a mixture of methyl esters were obtained.

2. Preparation of ethyl lactate using a biosolvent and catalyzed by Amberlyst-15®. A Pyrex flask was charged with 66.7 g of ethanol and 39.1 g of lactic acid so that the ethanol/lactic ratio was 3.3. This mixture was further treated with 34 g of the Step 1 biosolvent, and 1.4 g of dried Amberlyst-15. The mixture was then heated to 80°C for 5 hours while stirring using a magnetic stirrer then cooled to ambient temperature. Gas chromatography indicated that 93% of ethyl lactate was prepared. Other ethyl lactate esterification reaction results using other catalysts in the presence or absence of a biosolvent are provided in Table 3.1.

TABLE 3.1 Product formation of ethyl lactate after reacting the mixture for 5 hours at 80°C. In all cases the reagent ratio of ethanol/lactic acid was 3.3.



Reaction	Catalyst	Catalyst weight (g)	Biosolvent (g)	Yield ethyl lactate (%)
A	None	0	None	17
B	Sulfated zirconia	1.2	None	28
C	Sulfuric acid	3.3 96% acid	None	26
D	Amberlyst-15	1.4	None	31
E	Amberlyst-15	1.4	34	93
F	Sulfuric acid	3.3 g 96% acid	34	91

Testing Results

The formation of ethyl lactate was investigated using the same ratio of lactic acid and ethyl alcohol. Different reaction catalysts were used in the presence or absence of the rapeseed oil methyl ester mixture biosolvent. The results are summarized in Table 3.1.

Notes and Observations

1. Chabot[1] used biosolvents consisting of methanol, ethanol, sorbitol, and mannitol to extract two sweetening agents, steviosides, and rebaudiosides found in the leaves of stevia. In addition to behaving as sweetening agents, both steviosides and rebaudiosides also had high antioxidant properties.

2. Methyl alcohol was used by Yoon[2] as both a reagent and biosolvent in converting glycerol into methyl lactate, as illustrated in Eq. 1. The product was then reacted with N,N-diethylamine dissolved in the biosolvent methyl alcohol and the amide isolated in quantitative yield, as illustrated in Eq. 2. (See Fig. 3.3.)

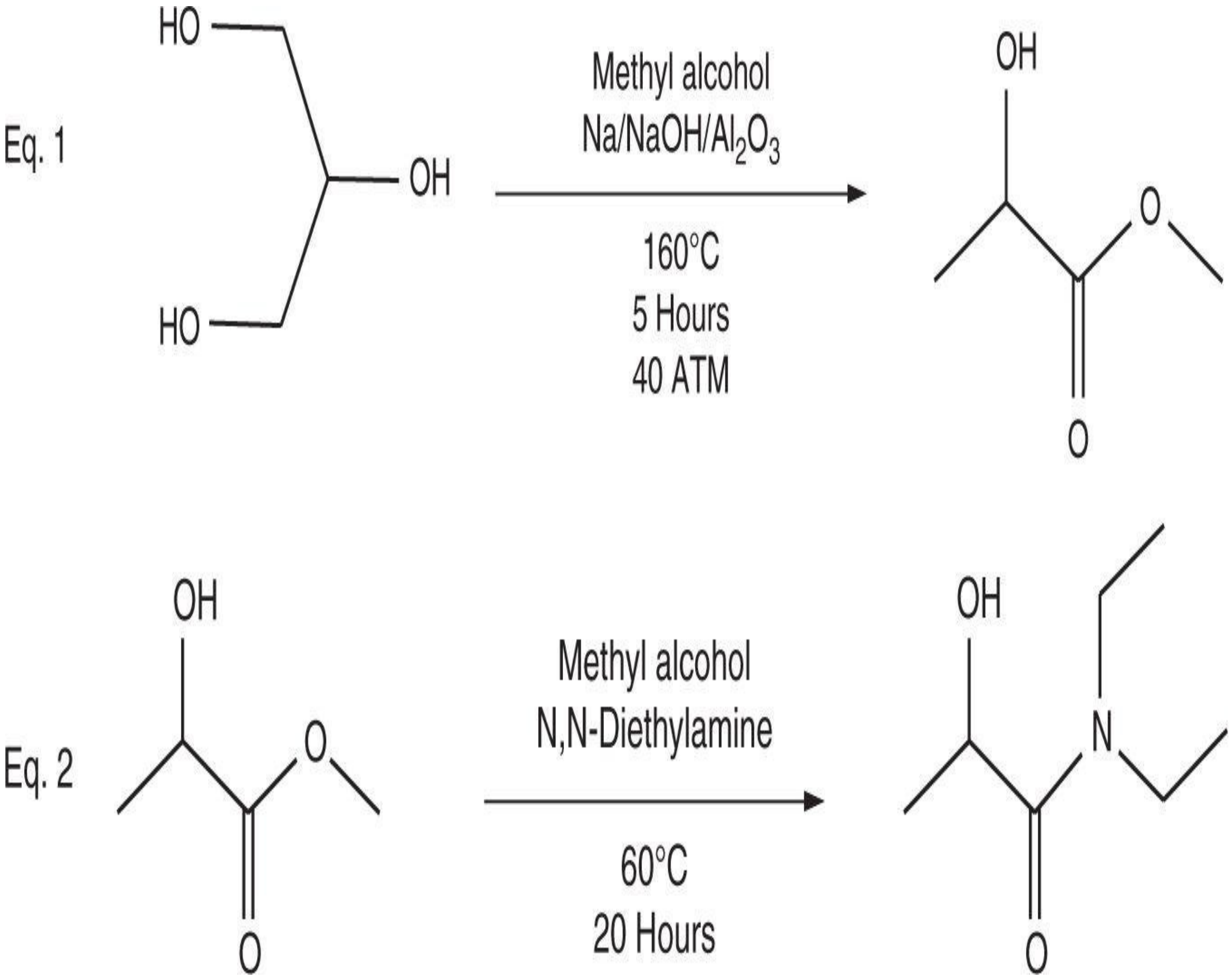


Figure 3.3

3. Consumer cleaning detergents prepared by Datta[3] containing C_3 to C_6 aliphatic alcohols dissolved in the biosolvent ethyl lactate had enhanced cleaning and solvent properties. In addition, the cleaning formulation was essentially odorless when lactate esters and related ester biosolvents were used in the presence of tertiary amines.

4. Datta[4] replaced methyl ethyl ketone and methyl iso-butyl ketone present in general cleaning and wiping solvent formulations with the biosolvent ethyl lactate to reduce the toxicity of the product. Other lactate biosolvents, including methyl lactate, n-propyl lactate, isopropyl lactate, n-butyl lactate, sec-butyl lactate, isobutyl lactate, and t-butyl lactate, were used as ketone replacements.

References

1. Sophie Chabot et al., *Extraction method for providing an organic certifiable Stevia Rebaudiana extract*, U.S. Patent Application 20130108718 (May 2, 2013)

2. Sung-Cheol Yoon et al., *Method for preparing alkyl lactate and a method for preparing lactamide using the same*, U.S. Patent Application 20130079547 (March 28, 2013)

3. Rathin Datta et al., *Composition of lactate esters with alcohols with low odor and enhanced performance*, U.S. Patent 7,754,104 (July 13, 2010)

4. Rathin Datta et al., *Solvent blend for replacement of ketones,* U.S. Patent Application 20110315929 (December 29, 2011)

Chapter

4

Candles

Low-Smoke-Emitting Candles

Author	Timothy A. Murphy et al.
Patent Title	***Triacylglycerol-based alternative to paraffin wax,*** U.S. Patent 8,202,329 (July 19, 2012)

Relevant Prior Patents by Author or Coauthors

Triacylglycerol based candle wax, U.S. Patent 8,070,833 (December 6, 2011)

Wax compositions and methods of preparing wax compositions, U.S. Patent Application 20100024281 (February 4, 2010)

Wax and wax-based products, U.S. Patent 7,833,294 (November 16, 2010)

Hybrid wax compositions for use in compression molded wax articles such as candles, U.S. Patent Application 20100205851 (August 19, 2010)

Prilled waxes comprising small particles and smooth sides compression candles made therefrom, U.S. Patent Application 20100132250 (June 3, 2010)

Candle and candle wax containing metathesis and metathesis-like products, U.S. Patent Application 20090217568 (September 3, 2009)

Triacylglycerol based wax for use in container candles, U.S. Patent 7,637,968 (December 29, 2009)

Triacylglycerol based candle wax, U.S. Patent 7,462,205 (December 9, 2008)

Product Application

Low-smoke-emitting candles with emissions that are essentially odorless.

Significance of Current Application

Conventional candles are made from paraffin wax. Although these candles are inexpensive, they emit excessive smoke and a burning foul-smelling odor, as well as a large amount of particles or soot. Moreover, particulates and soot generated from burning these candles are similar to exhaust particles given off by burning diesel fuel in diesel engines. The current investigation has identified renewable materials and mixtures that can be easily molded into candles. These materials consist of blends from the hydrogenation products of soybean oil and fatty acids. When molded into candles, they are essentially smokeless and odorless while emitting equivalent amounts of light for similar periods to that of paraffin-based candles.

Renewable Agents

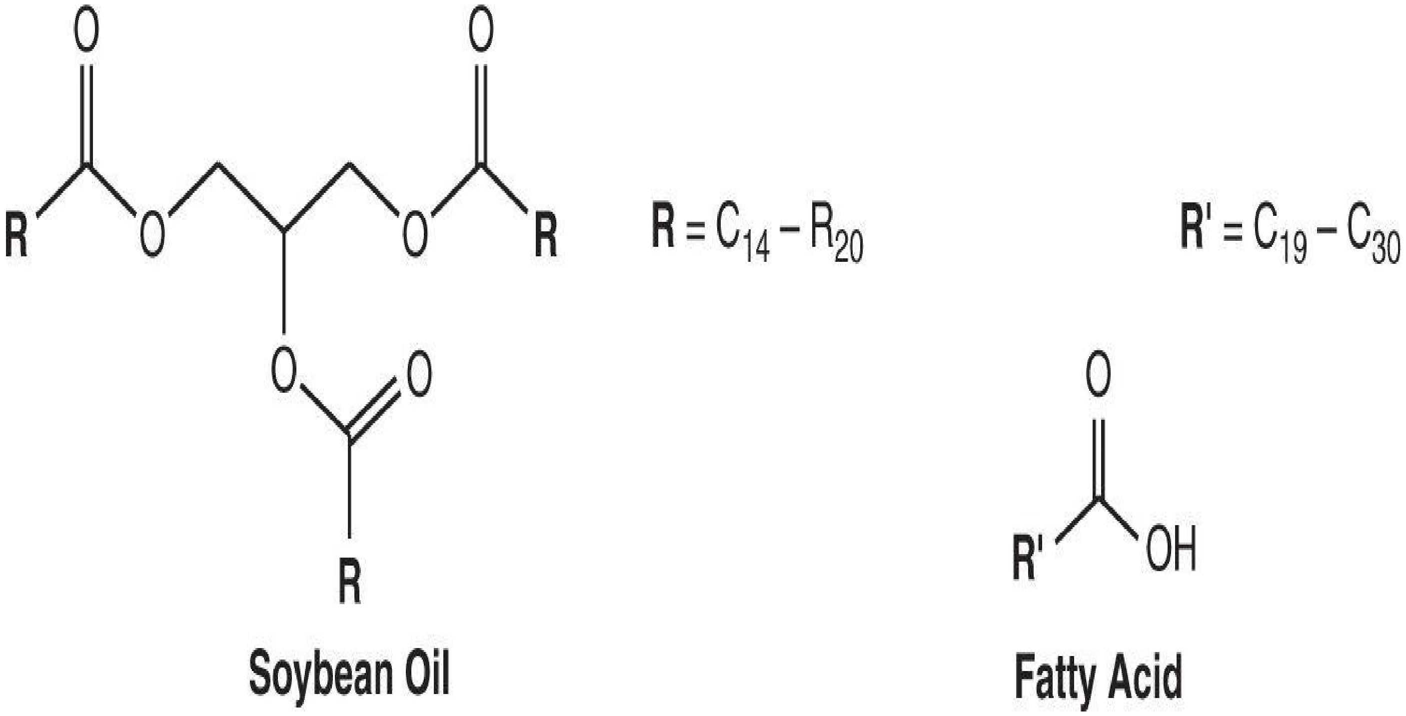


Figure 4.1

Product Formation

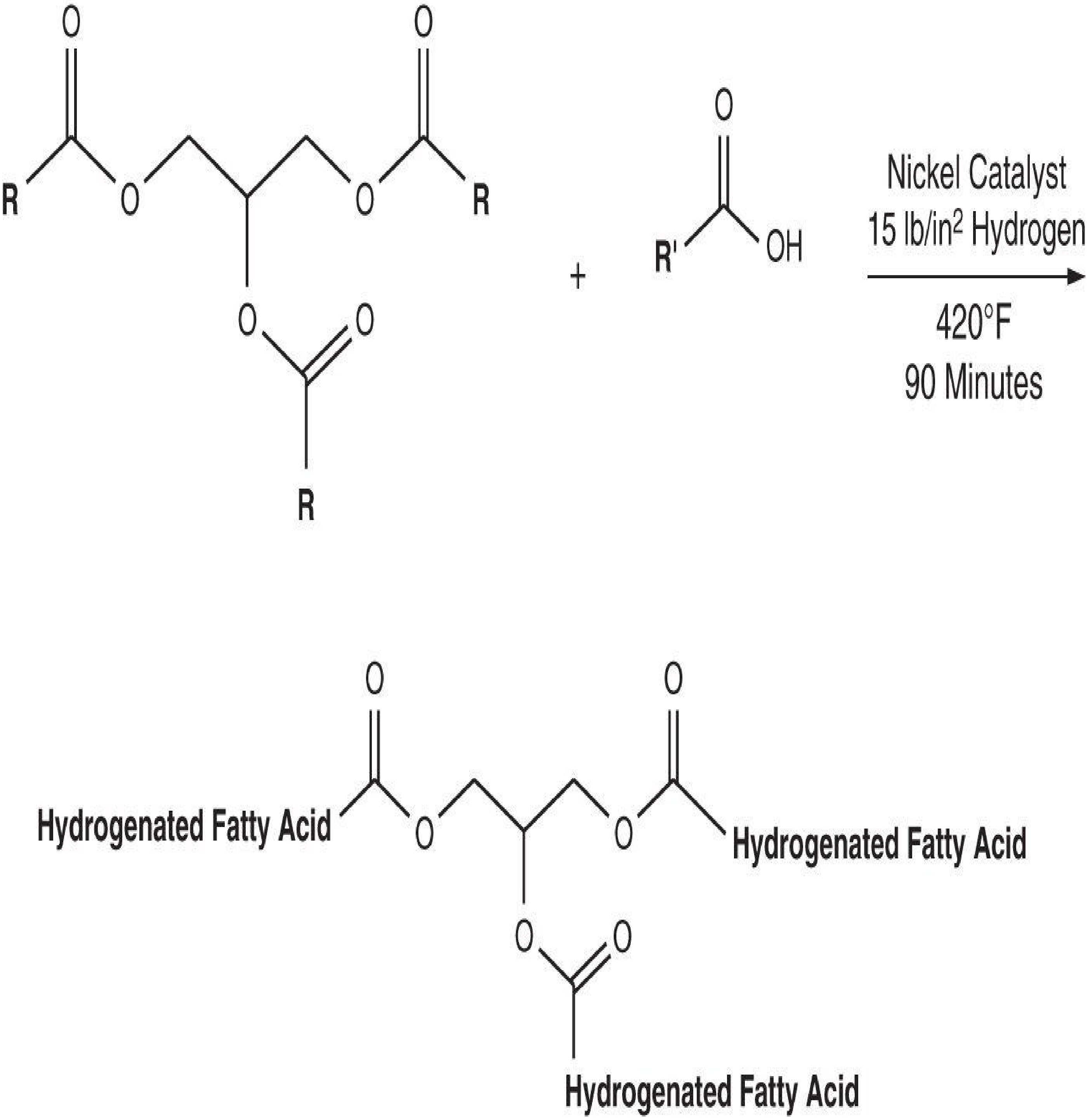


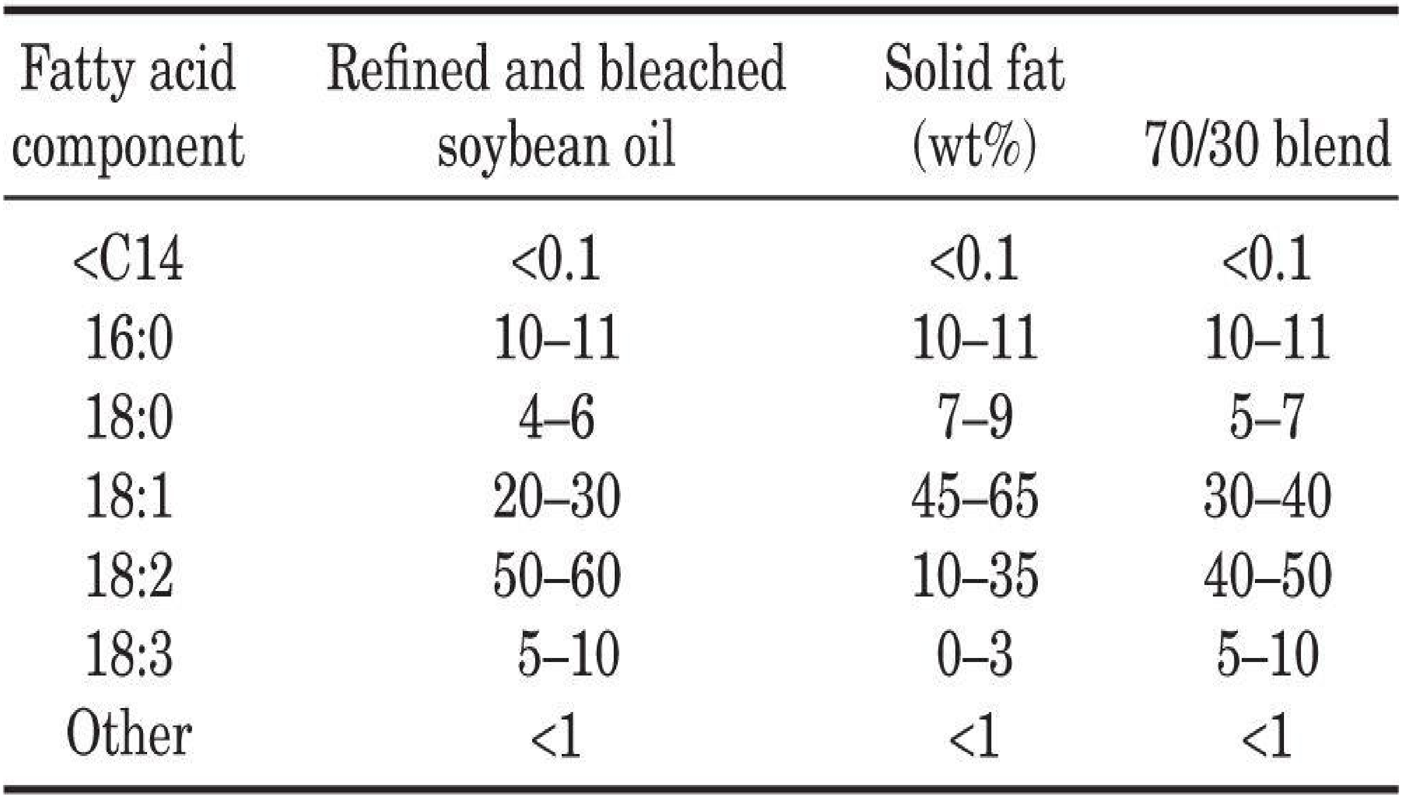
Figure 4.2

Experimental

1. Preparation of hydrogenated fatty acid glycerol triester suitable for making candles. A reactor was charged with 70 wt% refined and bleached soybean oil and then blended with 30 wt% of a hard-fat fraction obtained by chilling deodorized soybean oil to 38°F. The fatty acid composition for these two reagents is provided in Table 4.1. After the two-component mixture was thoroughly blended, it was hydrogenated. The hydrogenation process was performed at 420°F using 15 lb/in^2 of hydrogen with a nickel catalyst. Throughout the process, sample aliquots were periodically removed, and once the reaction intermediate attained an Iodine Value of 66-69, the reaction was stopped. The product was then removed from the reaction chamber, and the melting point was determined to be 106°F to 108°F. The chemical profile of the fatty acid glycerol triester is provided in Table

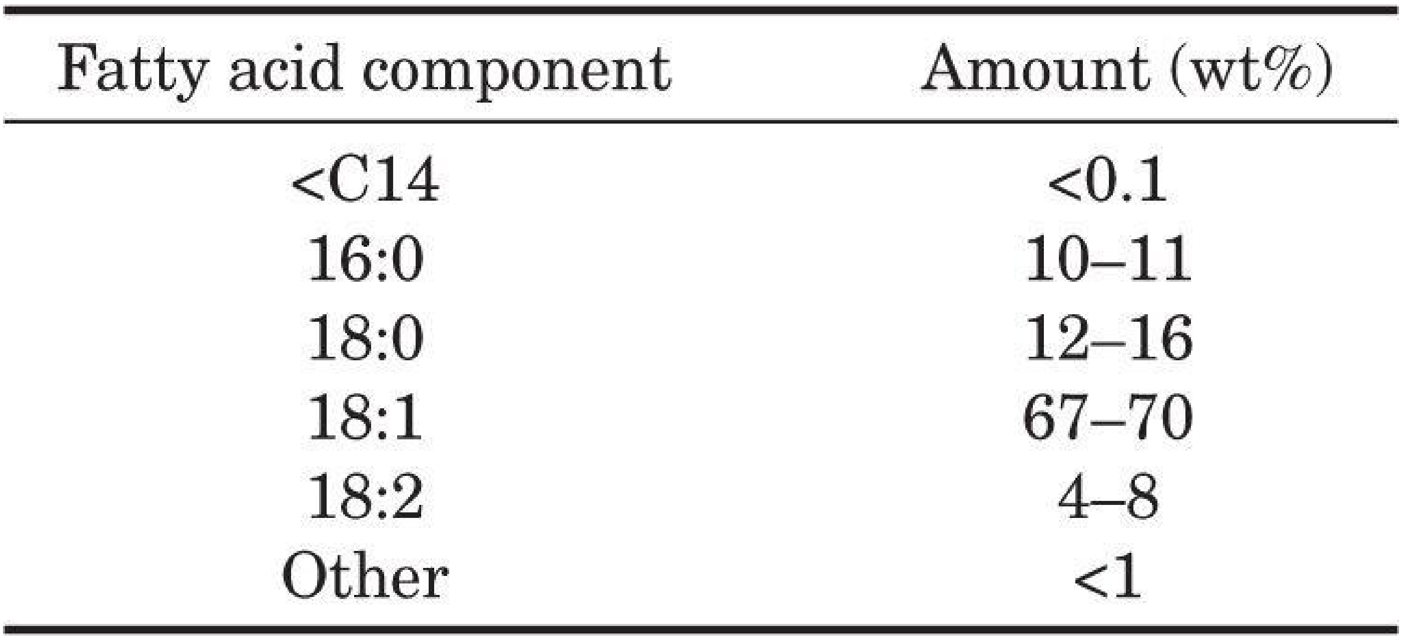
4.2. Hydrogenated soybean oil properties are provided in Table 4.3.

TABLE 4.1 The fatty acid compositions using refined and bleached soybean oil containing a “hard fat” co-component and then used in preparing smokeless candles.



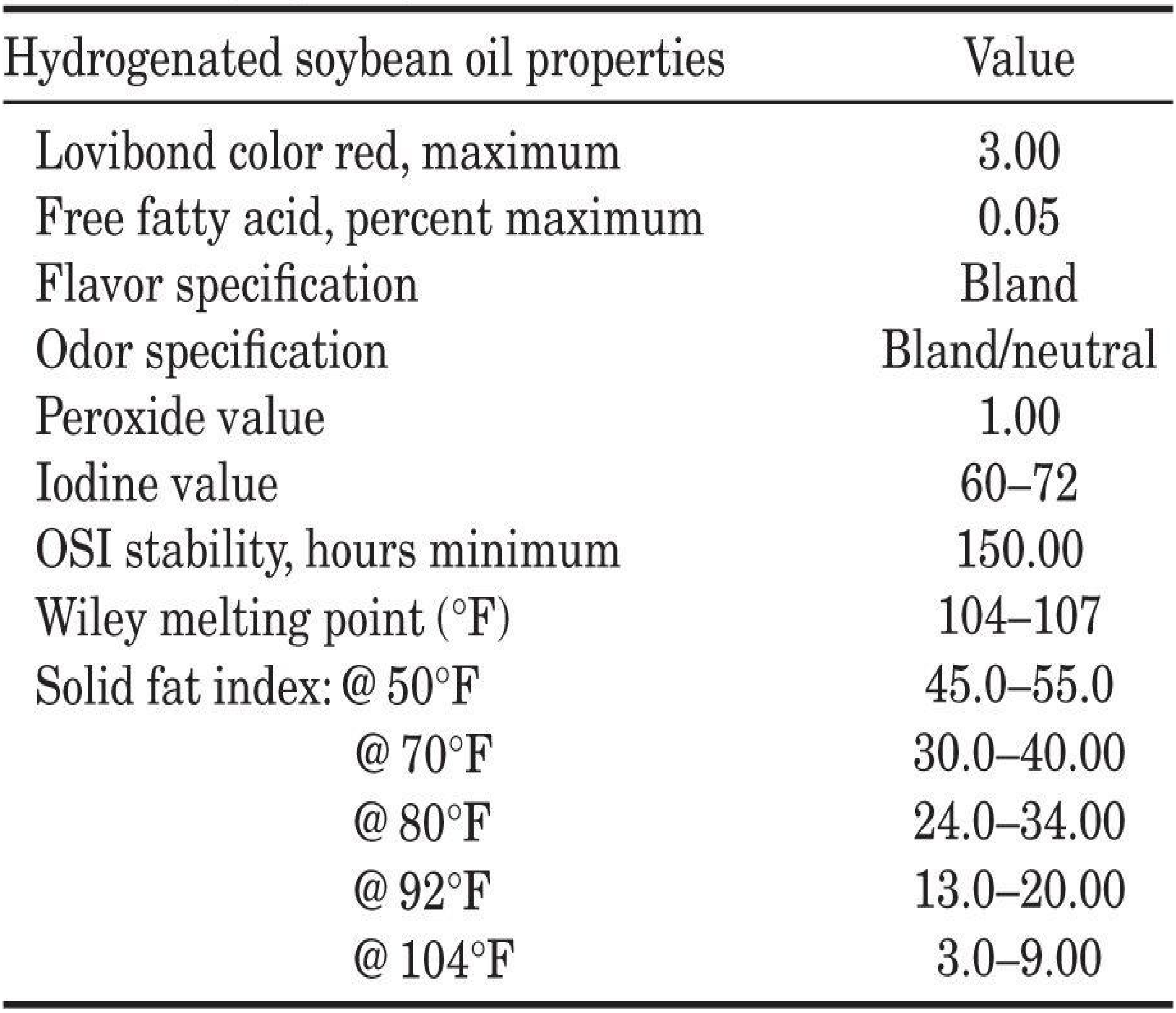
Fatty acid component	Refined and bleached soybean oil	Solid fat (wt%)	70/30 blend
<C14	<0.1	<0.1	<0.1
16:0	10–11	10–11	10–11
18:0	4–6	7–9	5–7
18:1	20–30	45–65	30–40
18:2	50–60	10–35	40–50
18:3	5–10	0–3	5–10
Other	<1	<1	<1

TABLE 4.2 Fatty acid profile used to prepare fatty acid glycerol trimesters for use in smokeless and odorless candles.



Fatty acid component	Amount (wt%)
<C14	<0.1
16:0	10–11
18:0	12–16
18:1	67–70
18:2	4–8
Other	<1

TABLE 4.3 Physical properties of hydrogenated soybean oil used in preparing smokeless and odorless candles.

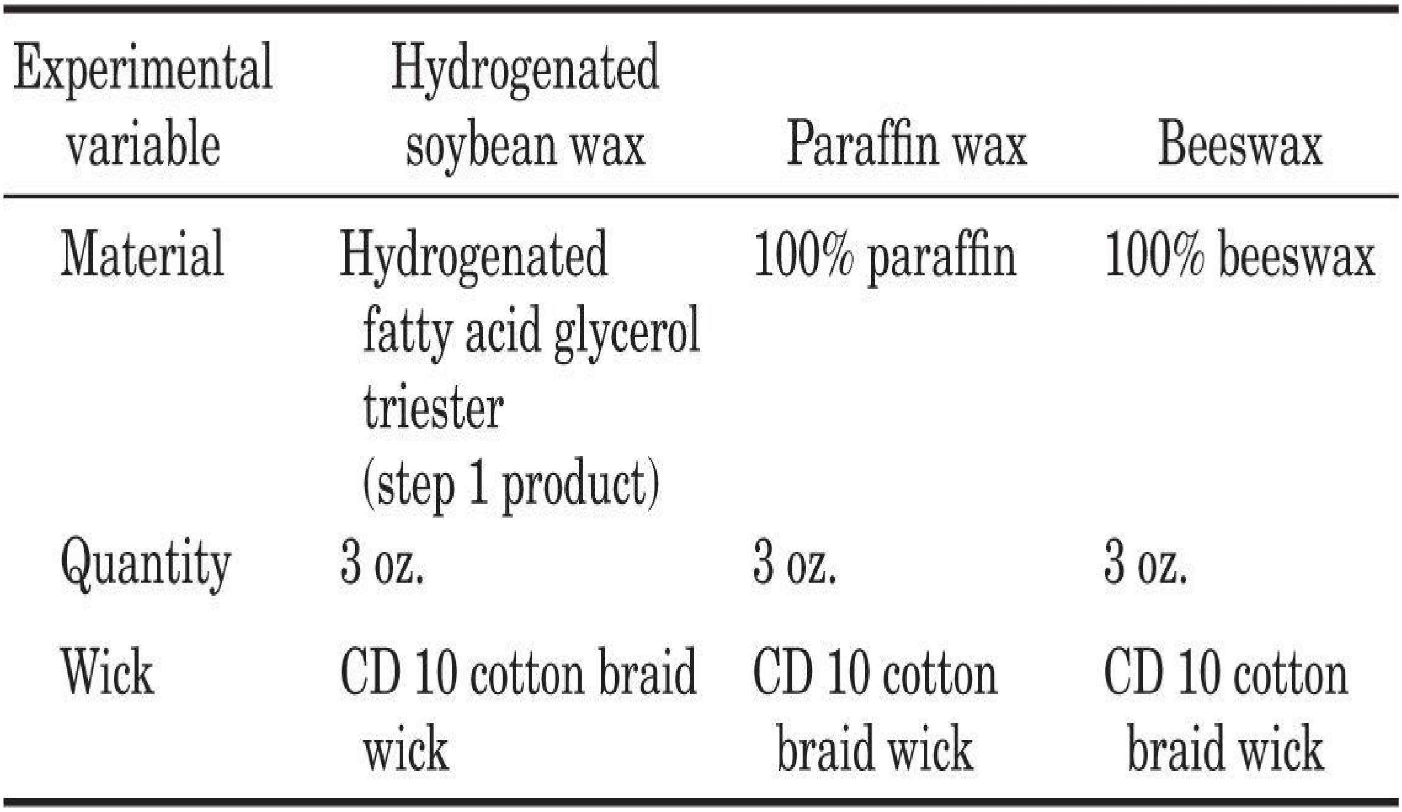


Hydrogenated soybean oil properties		Value
Lovibond color red, maximum		3.00
Free fatty acid, percent maximum		0.05
Flavor specification		Bland
Odor specification		Bland/neutral
Peroxide value		1.00
Iodine value		60–72
OSI stability, hours minimum		150.00
Wiley melting point (°F)		104–107
Solid fat index:	@ 50°F	45.0–55.0
	@ 70°F	30.0–40.00
	@ 80°F	24.0–34.00
	@ 92°F	13.0–20.00
	@ 104°F	3.0–9.00

Testing

A. Burn testing. A comparison-burn test of votive candles was performed using paraffin wax and beeswax placed in identical glass votive containers. In all cases, votives were set up in front of three identical china plates that served as soot barriers to capture emissions from candle flames during the burn test. Testing variables are provided in Table 4.4.

TABLE 4.4 Experimental parameters used to assess the smoke, odor, and particulate formation properties of burning candles.

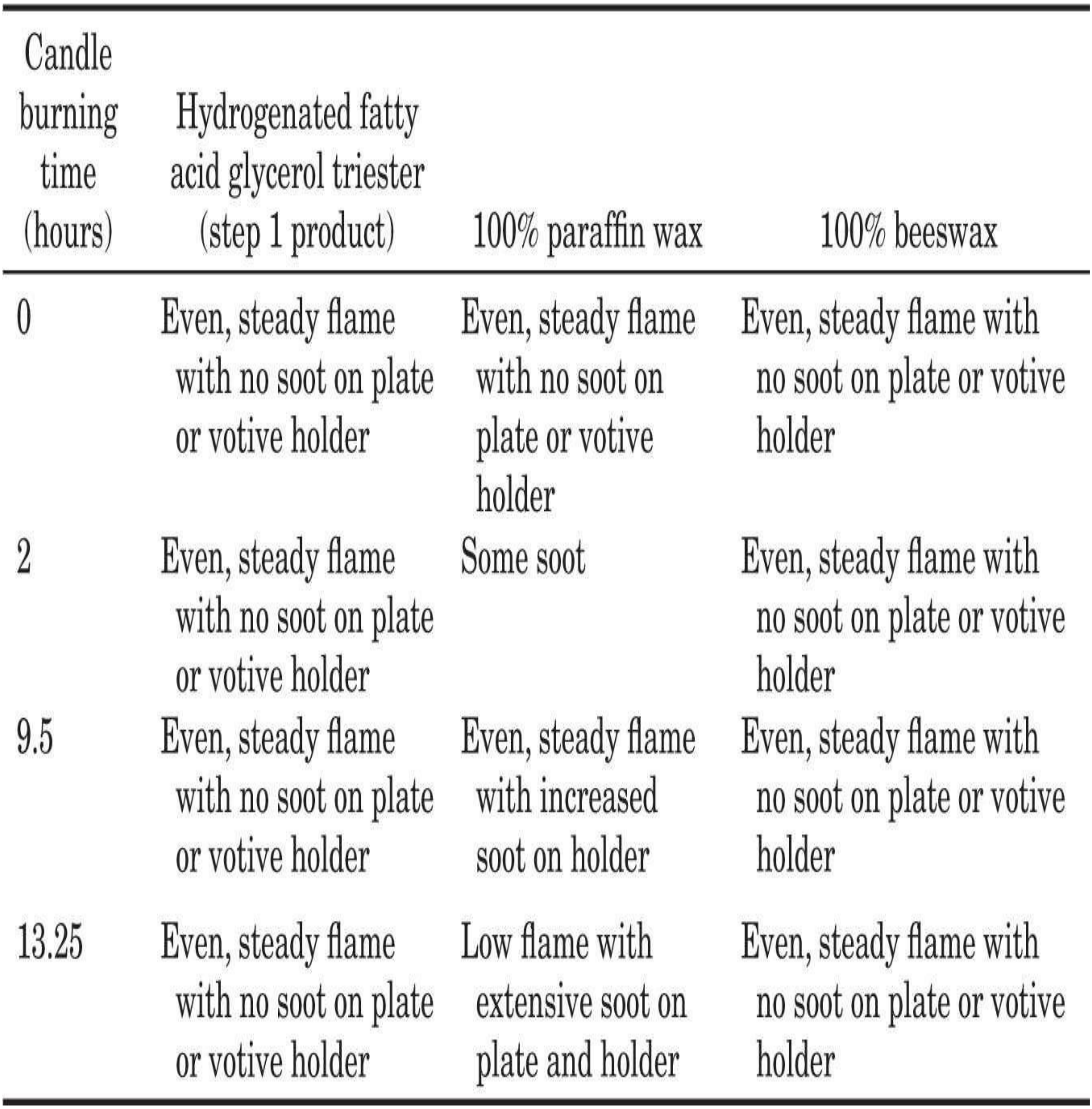


Experimental variable	Hydrogenated soybean wax	Paraffin wax	Beeswax
Material	Hydrogenated fatty acid glycerol triester (step 1 product)	100% paraffin	100% beeswax
Quantity	3 oz.	3 oz.	3 oz.
Wick	CD 10 cotton braid wick	CD 10 cotton braid wick	CD 10 cotton braid wick

Testing Results

A. Burn-testing results

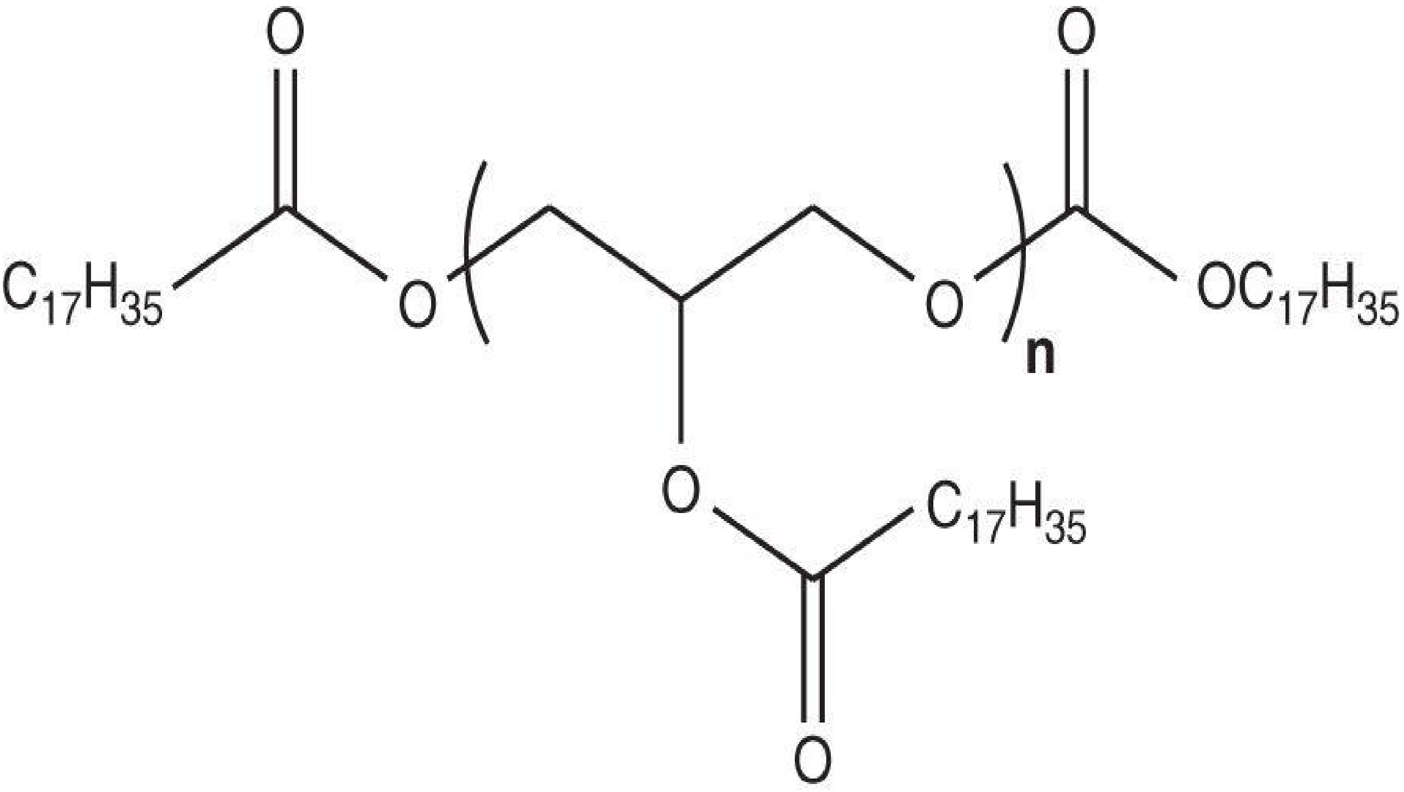
TABLE 4.5 Burn testing results of burning candles prepared from hydrogenated fatty acid glycerol triesters, paraffin wax, and beeswax. Testing indicated that candles consisting of either hydrogenated fatty acid glycerol triesters or beeswax were sootless while paraffin wax-containing candles produced extensive soot.



Candle burning time (hours)	Hydrogenated fatty acid glycerol triester (step 1 product)	100% paraffin wax	100% beeswax
0	Even, steady flame with no soot on plate or votive holder	Even, steady flame with no soot on plate or votive holder	Even, steady flame with no soot on plate or votive holder
2	Even, steady flame with no soot on plate or votive holder	Some soot	Even, steady flame with no soot on plate or votive holder
9.5	Even, steady flame with no soot on plate or votive holder	Even, steady flame with increased soot on holder	Even, steady flame with no soot on plate or votive holder
13.25	Even, steady flame with no soot on plate or votive holder	Low flame with extensive soot on plate and holder	Even, steady flame with no soot on plate or votive holder

Notes and Observations

1. Kondo[1] prepared polyglycerol stearate, (I), and related polyglycerol fatty acid esters to prepare stable emulsions useful as food, pharmaceutical, and cosmetics additives. The solid polyglycerol fatty acid esters were also used as a component in smokeless and odorless candles. (See Fig. 4.3.)



(I)

Figure 4.3

2. Tischendorf [2] prepared smokeless and odorless candles using fat or fatty oil mixtures as the starting reagent. An essential aspect of this investigation is that all candle-forming reagents were refined and converted into solids. Oils and fats, which were particularly useful, included blends of soy oil, palm oil, palm kernel fat, rapeseed oil, linseed oil, and animal fats and oils.

3. Uptain[3] prepared low-soot producing candles by thoroughly blending together 52 wt% of paraffin wax with 48 wt% of hydrogenated natural oils. The blended composition was then converted into candles by compression molding.

4. Murphy[4] prepared a four-component vegetable-oil-based wax that was suitable for making smokeless and odorless votive candles. The components consisted of:

   a. 82 wt% hydrogenated refined, bleached soybean oil.
   b. 5 wt% partially hydrogenated refined, bleached soybean oil.
   c. 10 wt% fully hydrogenated soybean oil.
   d. 3 wt% monoglycerol esters of a mixture of fatty acids derived from hydrolysis of hydrogenated soybean oil commercially available as Dimodan®.

References

1. Naoki Kondo et al., *Polyglycerol fatty acid ester and composition containing same*, U.S. Patent 8,324,423 (December 8, 2009)

2. Dieter Tischendorf, *Method for producing candles consisting of vegetable or animal oils or fats*, U.S. Patent 7,601,184 (October 13, 2009)

3. Kevin D. Uptain et al., *Hybrid wax compositions for use in compression molded wax articles such as candles*, U.S. Patent Application 20100205851 (August 19, 2010)

4. Timothy A. Murphy, *Triacylglycerol based wax for use in container candles*, U.S. Patent 7,637,968 (December 29, 2009)

Chapter

5

Chemical Additives

Organoleptic Agents to Biodegrade Polymers

Author John Allen Lake et al.

Patent Title ***Chemical additives to make polymeric materials biodegradable,*** U.S. Patent Application 20130011906 (January 10, 2013)

Relevant Prior Patents by Author or Coauthors

Chemical additives to make polymeric materials biodegradable, U.S. Patent 8,222,316 (July 17, 2012)

Biodegradable films and sheets suitable for use as coatings, wraps and packaging materials, U.S. Patent 7,297,394 (November 20, 2007)

Biodegradable polymer blends for use in making films, sheets and other articles of manufacture, U.S. Patent 7,241,832 (July 10, 2007)

Biodegradable polymeric mixtures based on thermoplastic starch, U.S. Patent 6,235,815 (May 22, 2001)

Product Application

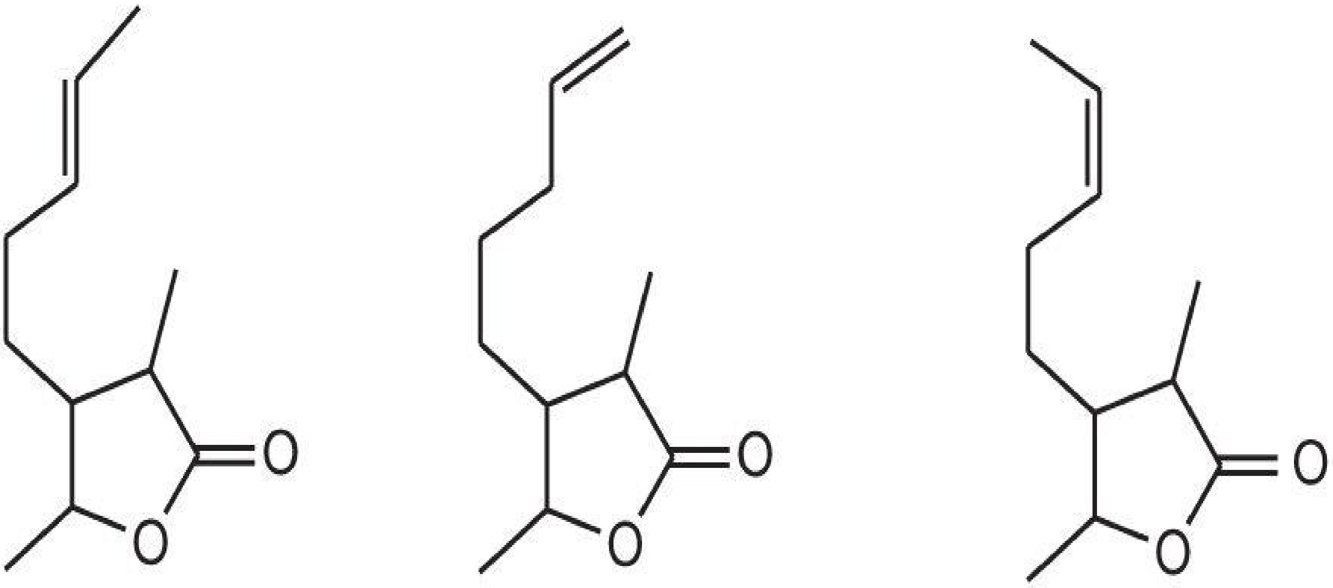
The present invention describes a method to biodegrade commercially available polymers using non-toxic agents. Its key application is as a method of eliminating unwanted plastics.

Significance of Current Application

Chemical additives designed to biodegrade plastics using microbes attracted to an organoleptic agent have been successfully used to degraded polyethylene, polypropylene, polyvinyl acetate, poly (lactic acid), polycaprolactones, poly (glycolic acid), polyvinyl chloride, polystyrene, polyterethalate, polyesters, and polyamides. The additive is particularly useful in degrading selective plastics present in landfills since it remains active in the presence or absence of oxygen to initiate biodegradation.

Organoleptic Agents

Organoleptic additives designed to attract microbes to digest polymers are illustrated in (I) through (III).



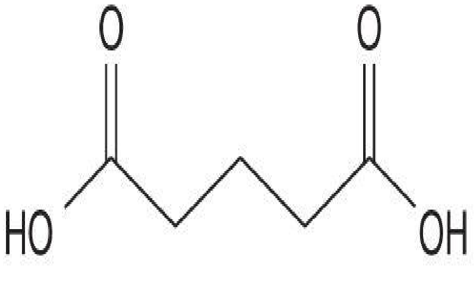
(I) (II) (III)

Three 3,5-dimethyl-pentenyl-dihydro-2(3H)-Furanone isomers

Figure 5.1

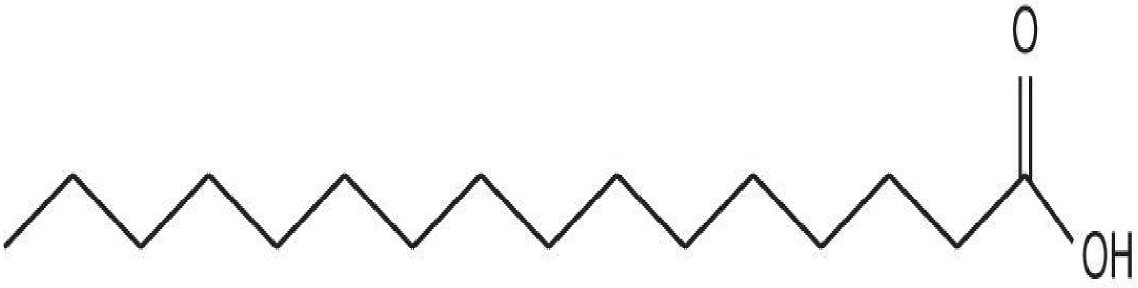
Organoleptic Carrier Resin Co-Components

Seven carrier-resin co-components were blended with the organoleptic isometric additives 3,5-dimethyl-pentenyl-dihydro-2(3H)-furanones. The seven co-components are illustrated in (IV) through (X).



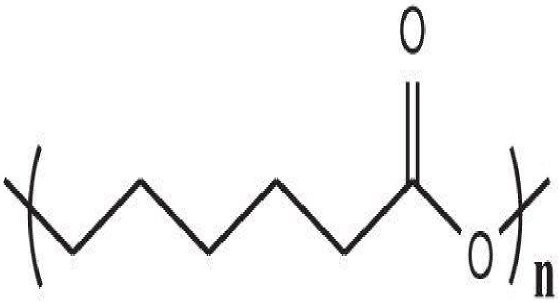
(IV)

Glutaric acid



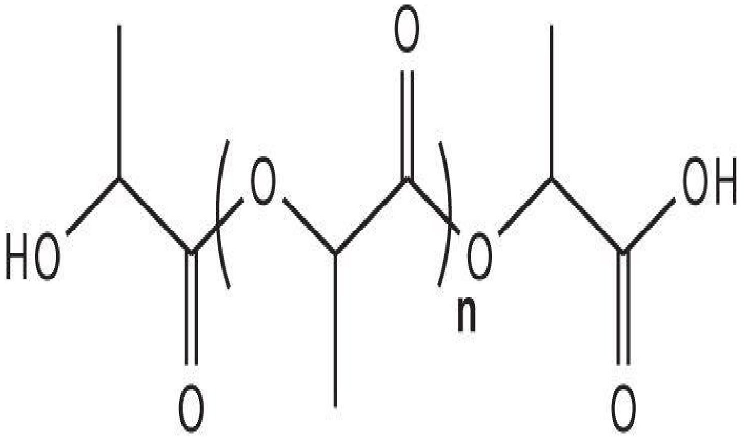
(V)

Hexadecanoic acid



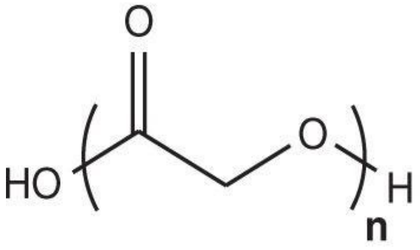
(VI)

Polycaprolactone



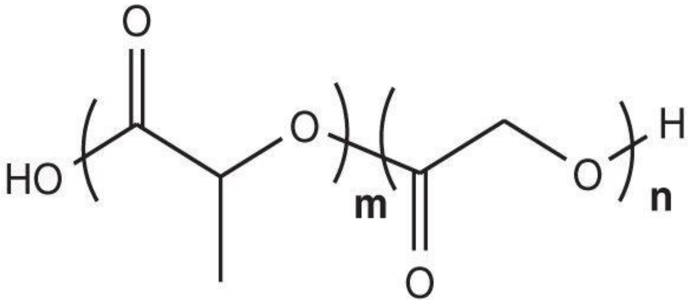
(VII)

Poly(lactic acid)



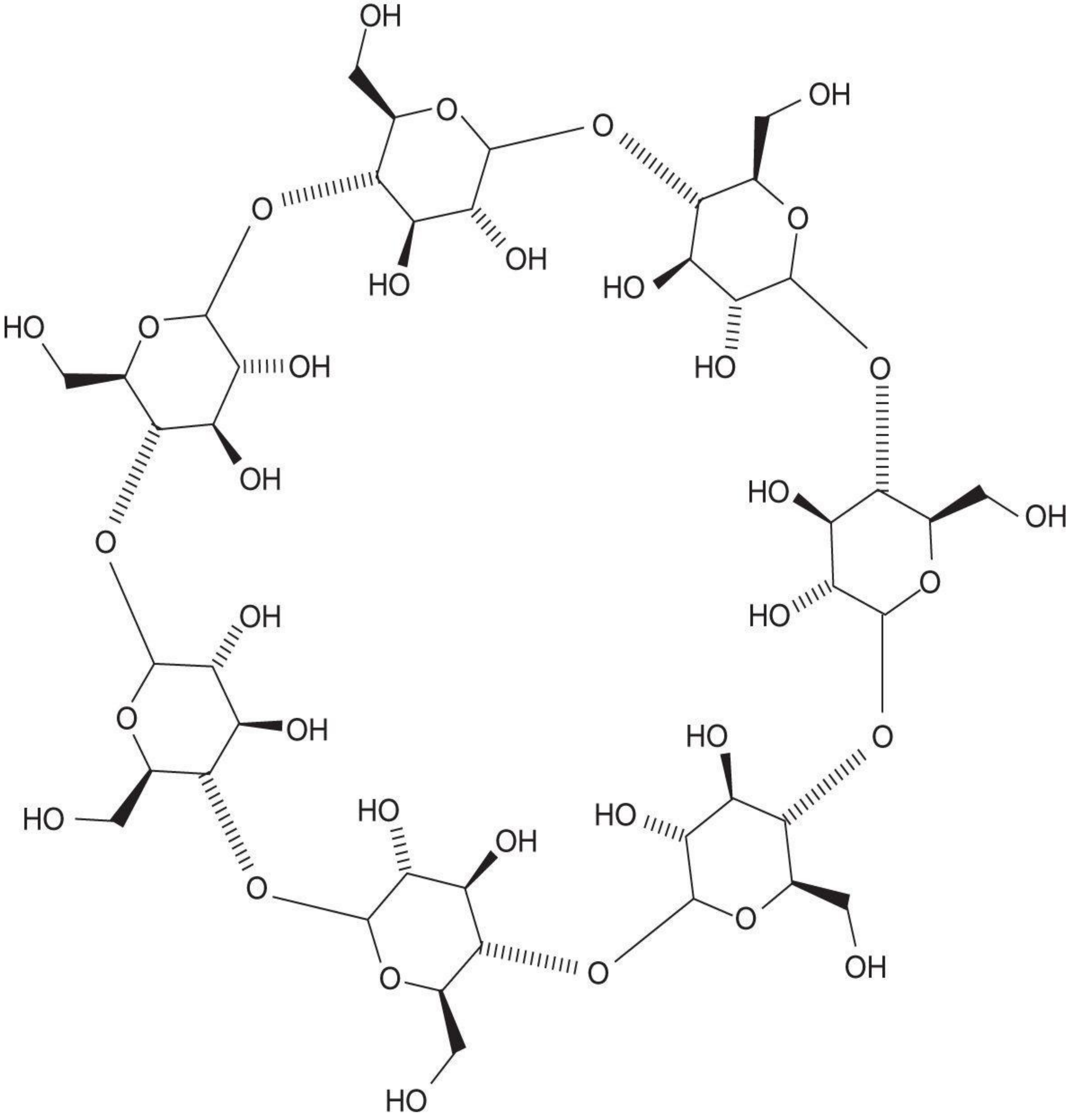
(VIII)

Poly(glycolic acid)



(IX)

Poly(lactic-co-glycolic acid)



Cyclodextrin

(X)

Figure 5.2

Experimental

1. Preparation of organoleptic degradation additive blend. Twenty percent of the three isomeric organoleptic 3,5-dimethyl-pentenyl-dihydro-2(3H)-furanone organoleptic agents were blended with seven co-components, (IV) through (X). Each of the seven co-components was blended in approximate equal weight percentages. After the mixtures were thoroughly combined, they were then blended with poly(vinylchloride) foam and used immediately to biodegrade high-density polyethylene.

2. Degradation of polyethylene using the ten-component degradation additive blend. A sample of polyethylene was completely coated with the poly(vinylchloride) foam containing the ten-component degradation additive. The coating remained undisturbed on polyethylene for 24 hours at ambient temperature. The coating was then removed, and scanning electron microscopy was used to evaluate the extent of the polymer degradation. The same coating process was then repeated on polystyrene.

Testing Results

A. Polyethylene biodecomposition. After a 24-hour exposure to the ten-component additive mixture containing the three isometric organoleptic additives, SEM identified cracks, as well as both shallow and deep depressions present in the film. SEM also identified biofilms and colonies present in large continuous depressions of moderate depth that were assumed to be both Rhodococcus and B. borstelensis attracted by the organoleptic agent mixture containing the three isomeric organoleptic furanones.

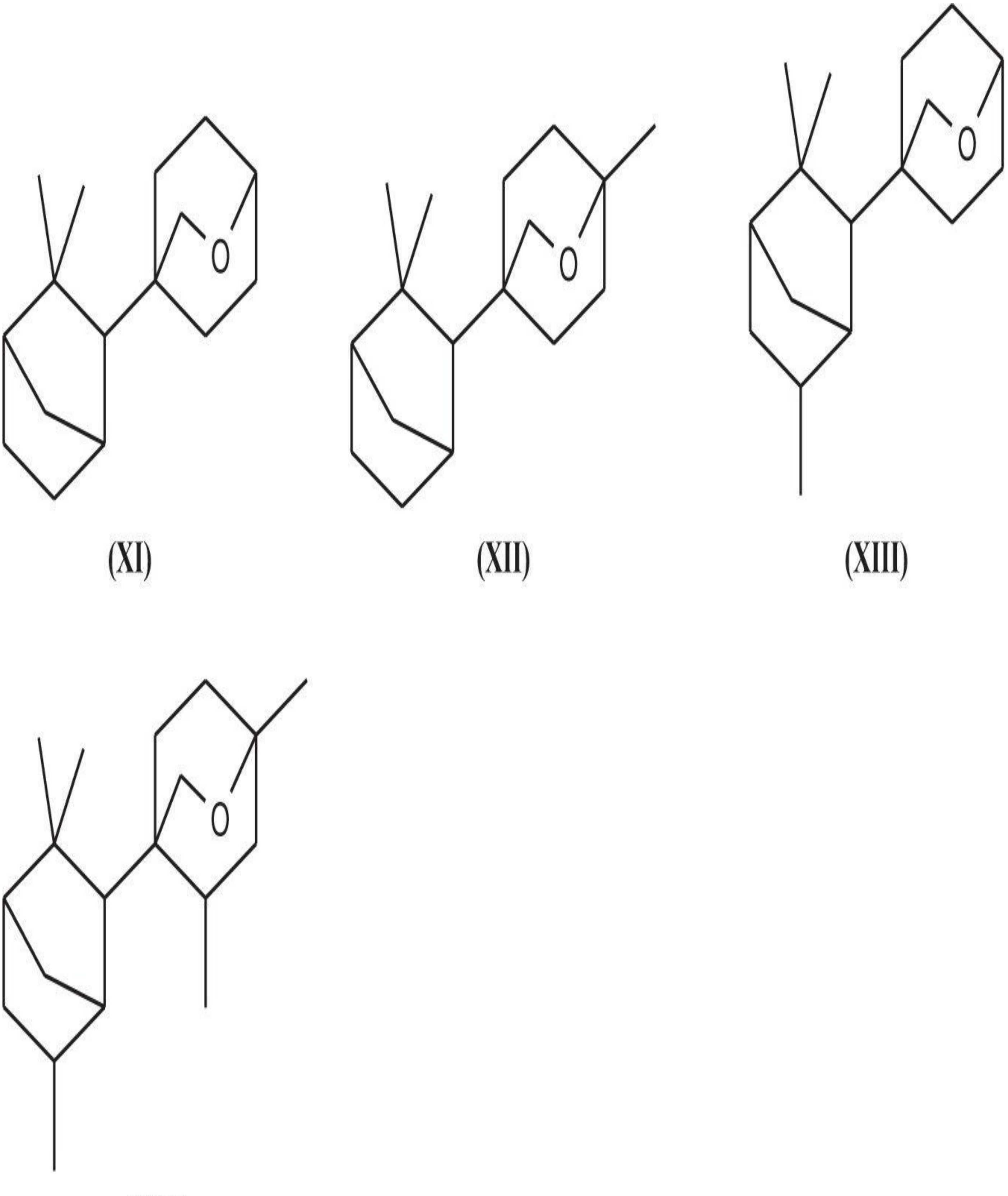
B. Polystyrene decomposition. Although polystyrene film was moderately degraded using the ten-component additive mixture containing the three isometric organoleptic additives, considerably more degradation was so observed when using either expanded polystyrene foam or polystyrene bubble wrap.

Notes and Observations

1. In an earlier investigation by Lake,[1] high-impact-polystyrene nursery plant labels were degraded using a ten-component additive that contained the isometric organoleptic agent mixture, 3,5-dimethyl-pentenyl-dihydro-2(3H)-furanones. The extensive degradation of high-density polystyrene was believed to be a result of the organoleptic agents attracting the polystyrene degradation microbe, C. violaceum.

2. Otome[2] prepared an organoleptic mixture consisting of lemon perfume, curry powder, ginger powder, cinnamon powder, and an unspecified tea. When polyethylene succinate, polybutylene succinate adipate, or polyethylene succinate were coated with the organoleptic mixture, plastic packing material consisting of these polymers was completely degraded in one month.

3. Narula[3] prepared four isomers of 2-oxa-bicyclo[2.2.2]octane, (XI), (XII), (XIII), and (XIV), which were effective as organoleptic agents. (See Fig. 5.3.)



(XI)

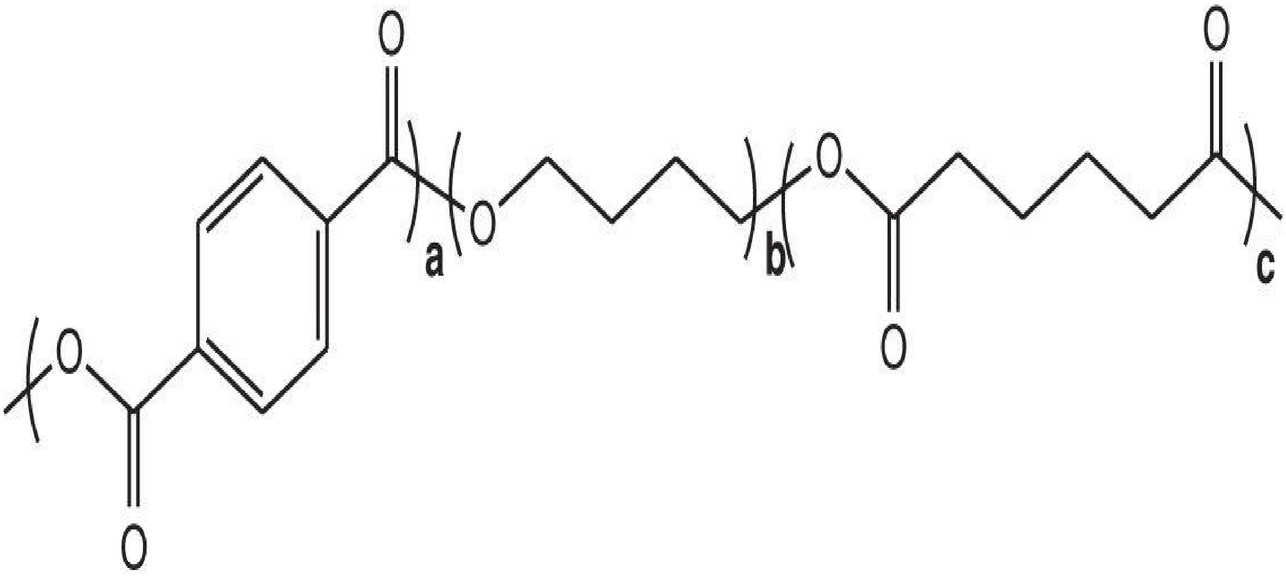
(XII)

(XIII)

(XIV)

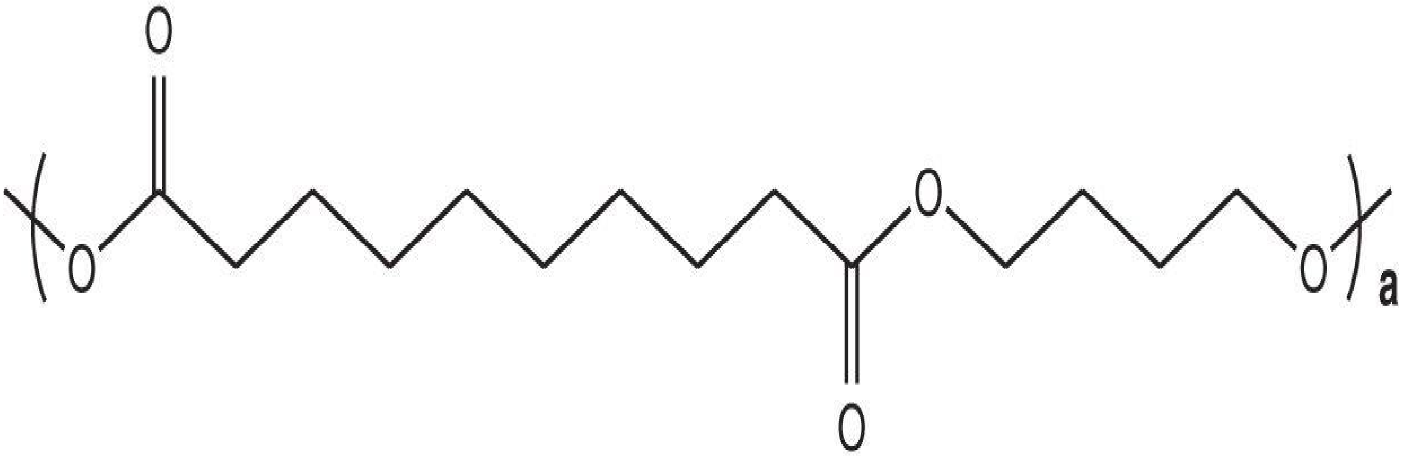
Figure 5.3

4. Bastioli[4] prepared terpolymers consisting of Ecoflex® 0700, (XV), polybutylene-sebacate, (XVI), made from sebacic acid and butandiol, and 10% polylactic acid polymer, (XVII), which when blended together functioned as an organoleptic agent. (See Fig. 5.4.)



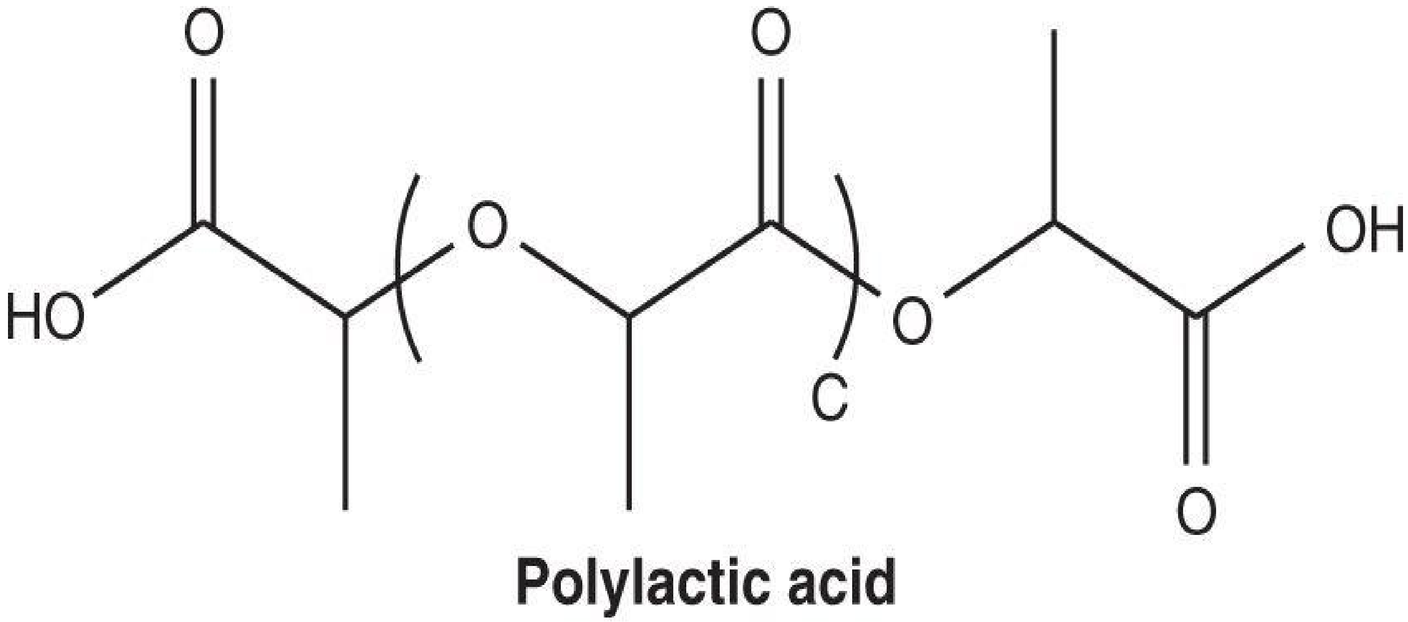
Ecoflex® 0700

(XV)



Poly(sebacic acid)-co-butandiol

(XVI)



(XVII)

Figure 5.4

References

1. John Allen Lake et al., *Chemical additives to make polymeric materials biodegradable*, U.S. Patent 8,222,316 (July 17, 2012)

2. Shigeo Otome, *Packaging material*, U.S. Patent Application 20050181157 (August 18, 2005)

3. Anubhav P. S. Narula et al., *Organoleptic compounds*, U.S. Patent 8,183,200 (May 22, 2012)

4. Catia Bastioli et al., *Ternary mixtures of biodegradable polyesters and products manufactured from them*, U.S. Patent 7,067,596 (June 27, 2006)

Chapter

6

Coatings

Macromolecular Hazard-Free Paint Coating Additive

Author	Neal St. John Williams et al.
Patent Title	***Triglyceride macromonomers***, U.S. Patent 8,283,483 (October 9, 2012)

Relevant Prior Patents by Author or Coauthors

Paint compositions, U.S. Patent Application 20110124786 (May 26, 2011)

Aqueous dispersion of addition polymer particles, U.S. Patent Application 20030130408 (July 10, 2003)

Process for making poly (urethane-urea)/addition polymer composite particles, U.S. Patent Application 20020058751(May 16, 2002)

Product Application

Macromolecular agents prepared in this investigation are useful as additives in paint, varnish, and wood stain coating formulations that can readily form aqueous dispersions.

Significance of Current Application

Renewable palm, safflower, sunflower, rapeseed, and soya bean oils were chemically converted into macromonomers in quantitative yield using a single-step reaction employing inexpensive reagents. When the product mixture was blended into aqueous paint latex formulations, the reaction polymer appeared as microparticles having mean particle diameters from 0.05 microns to 2 microns. Dried painted surfaces containing these polymer microparticles were strong, stable, dried quickly, devoid of toxic co-reagents, and resisted pealing on metal, plastic, and wood.

Product Formation

Phase 1. Isomerization of Olefins in Palm Oil

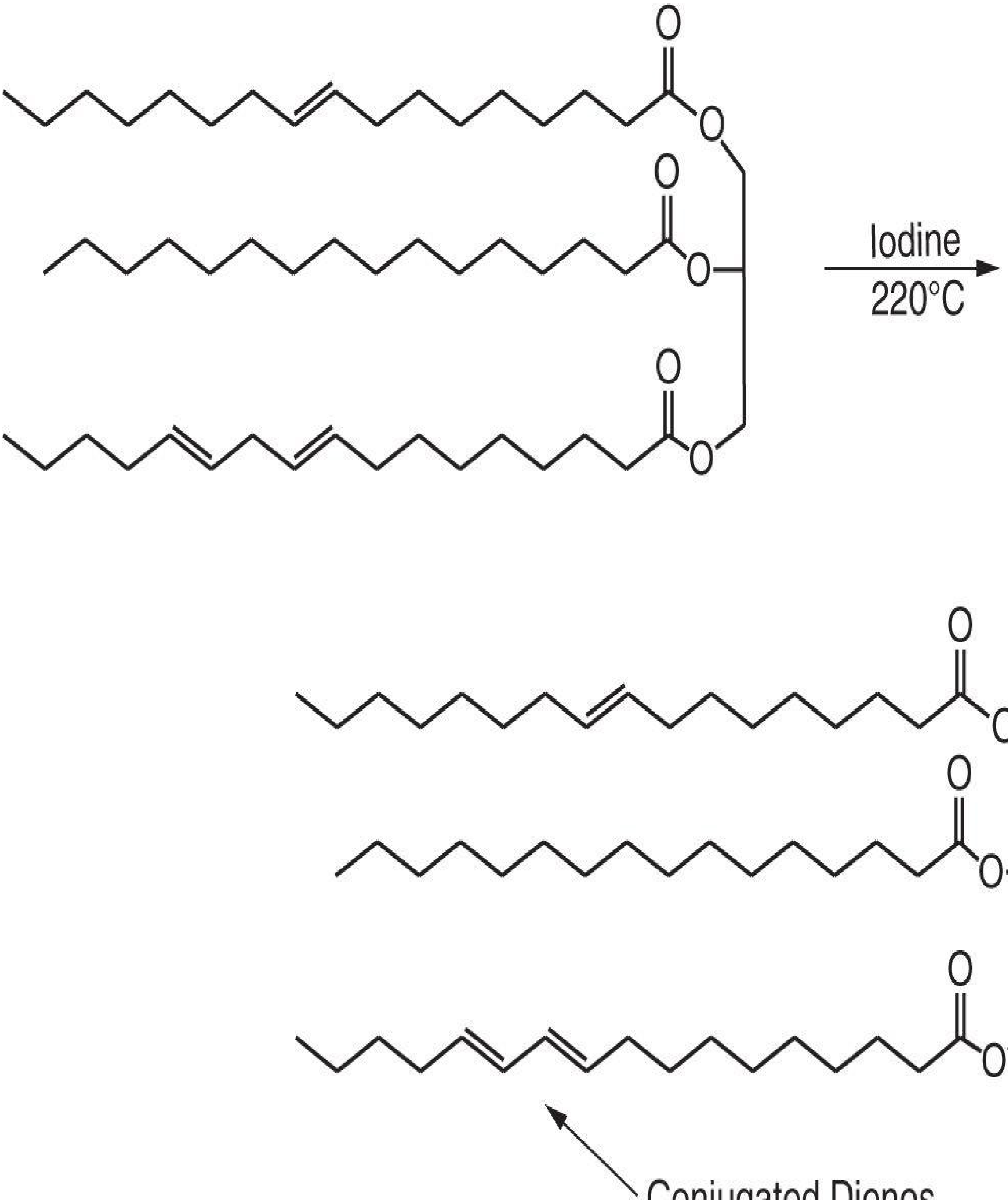
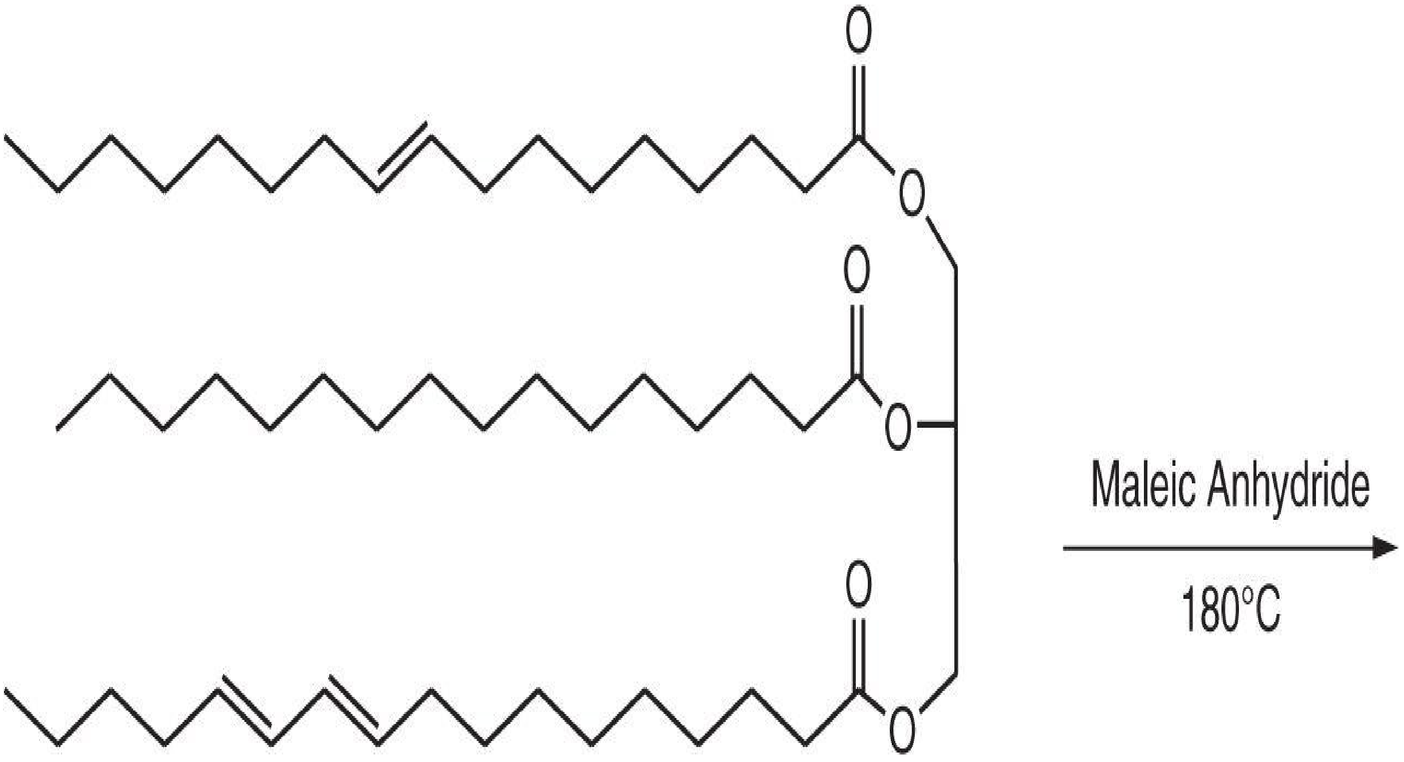


Figure 6.1

Phase 2. Diels-Alder/Maleic Anhydride Addition Reaction


Maleic Anhydride
180°C

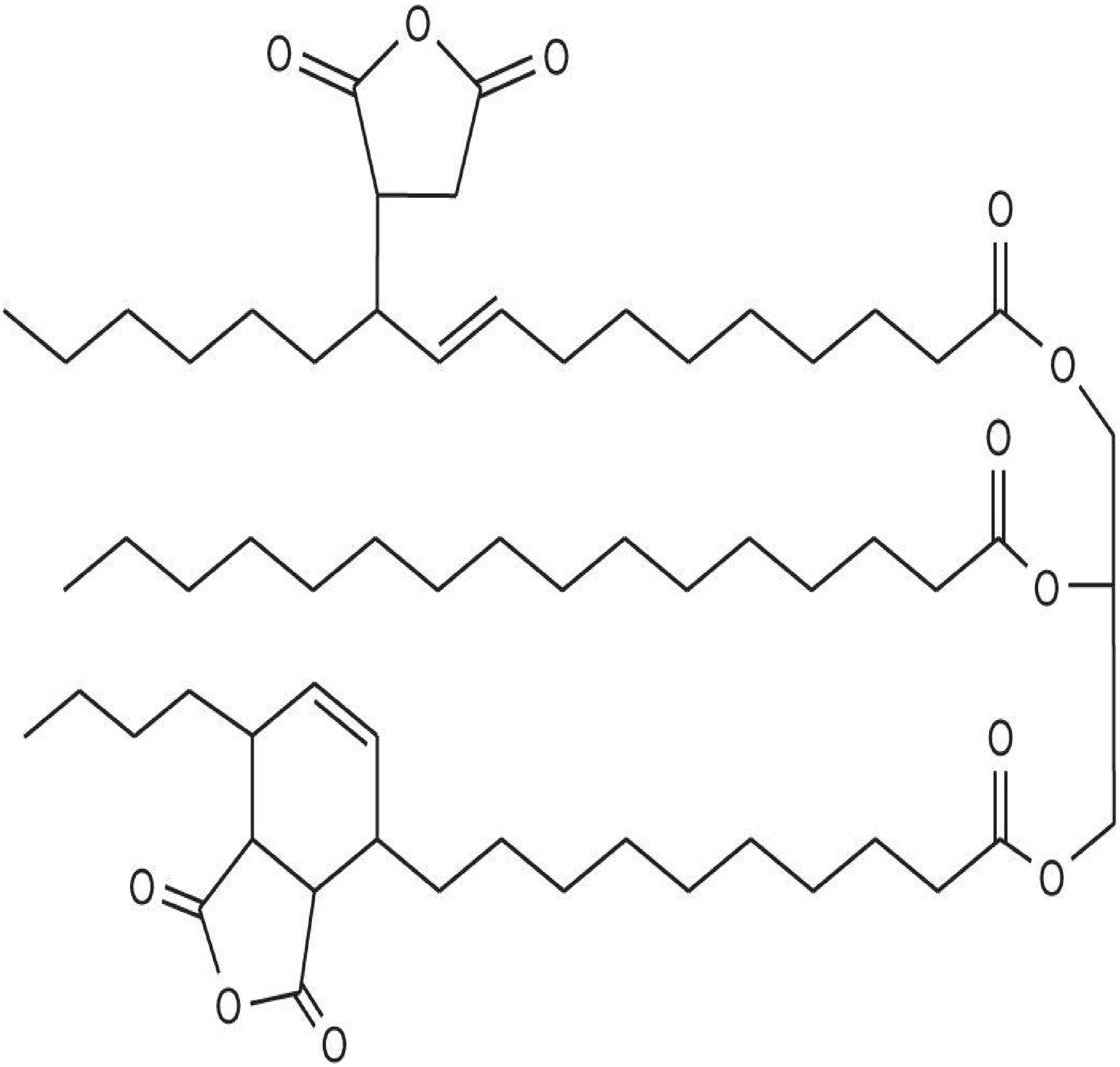


Figure 6.2

Phase 3. Partial Esterification of Palm Oil/Succinic Anhydride Intermediate with Hydroxylmethyl Methacrylate

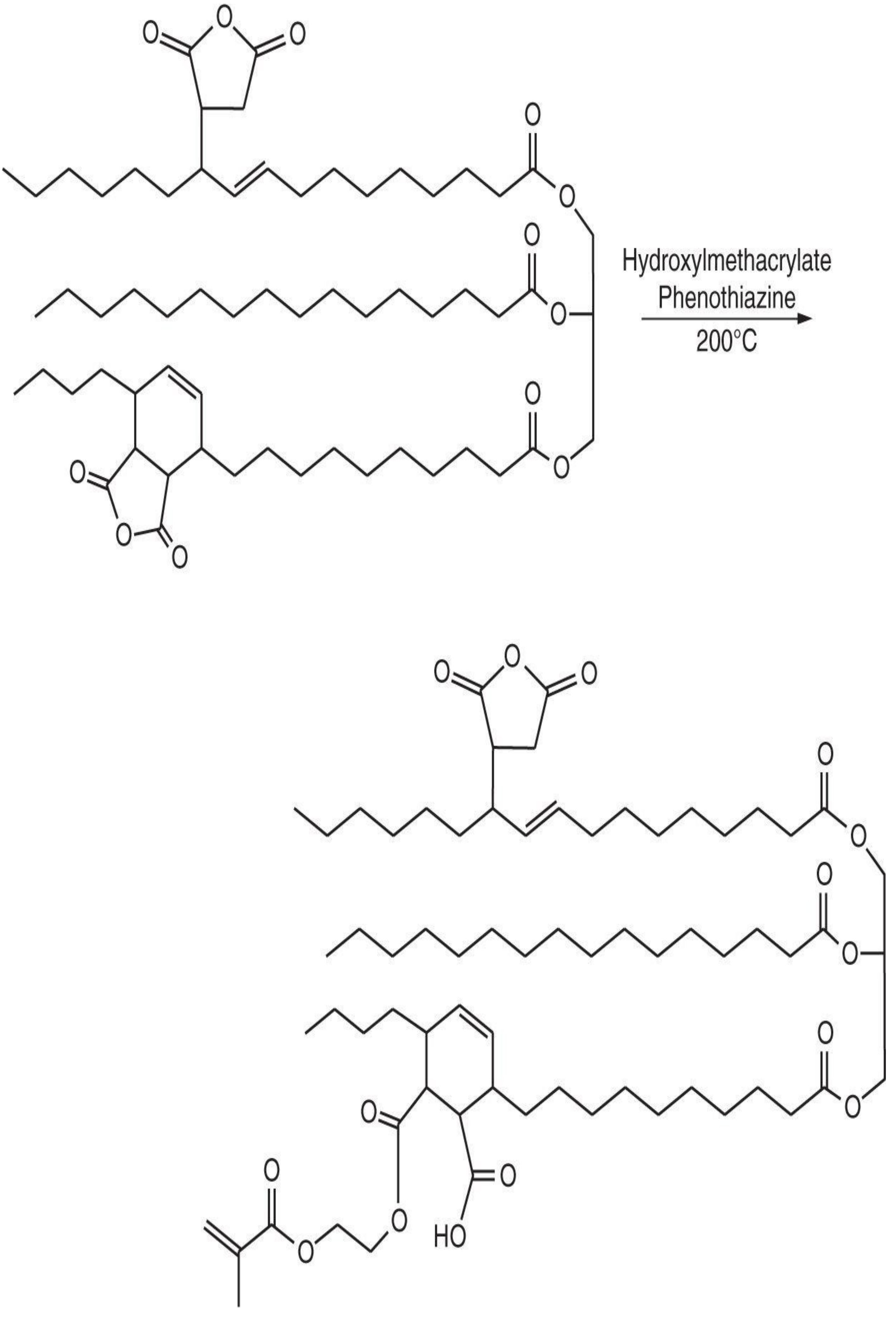

Hydroxylmethacrylate
Phenothiazine
200°C

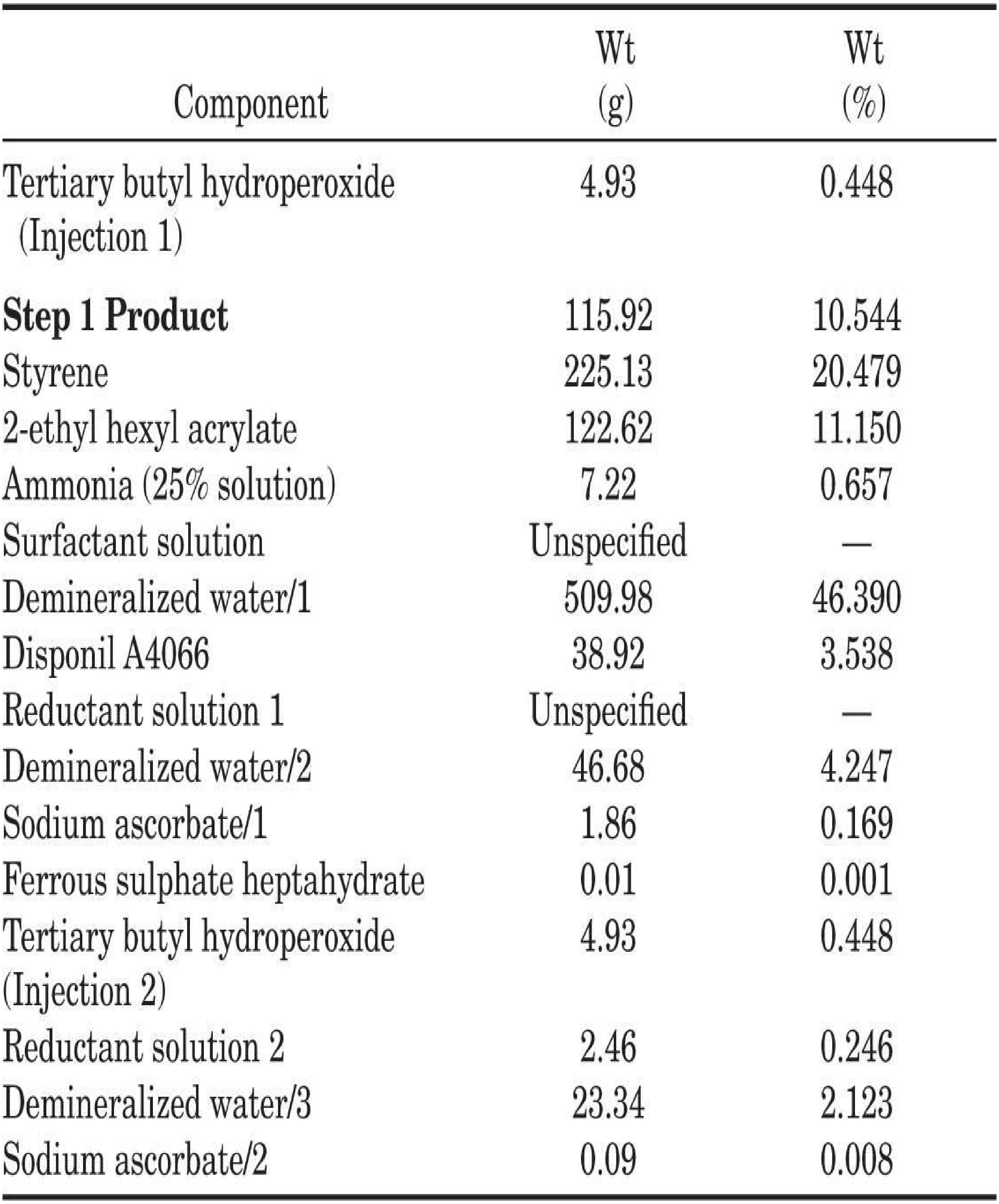
Figure 6.3

Experimental

1. (Generic) One-pot macromolecule synthesis. A five-liter round-bottomed flask fitted with a water-cooled condenser, a nitrogen protective blanket, and a stirrer operating at 75 rpm was charged with RD Palm oil (available from Hampshire Commodities, Fleet, Hampshire, U.K., GU51 3SR) and maleic anhydride, then heated to 100°C and treated with iodine. The temperature was maintained at 100°C for 30 minutes, then increased to 200°C for 30 minutes, and then further increased to 220°C for 5 hours and 30 minutes. The mixture was then cooled to 200°C and treated with phenothiazine and hydroxyl ethyl methacrylate over a period of 15 minutes while maintaining the temperature at 200°C for 60 minutes. Thereafter, glycerol was added at 200°C and the reaction mixture cooled to 80°C. The mixture was then further treated with 2-ethyl hexyl acrylate as the copolymerizating monomer. After filtering through lambswool at 80°C, a viscous yellowish solution was isolated in quantitative yield.

2. Microparticle latex paint formulation. The Step 1 macromolecular product was blended with the components provided in Table 6.1, then heated to 50°C with vigorous mixing for 60 minutes as the latex was isolated.

TABLE 6.1 Latex paint formulation containing the Step 1 macromolecular product. Upon curing, polymer microparticles that formed had mean particle diameters between 0.05 to 2 microns.



Component	Wt (g)	Wt (%)
Tertiary butyl hydroperoxide (Injection 1)	4.93	0.448
Step 1 Product	115.92	10.544
Styrene	225.13	20.479
2-ethyl hexyl acrylate	122.62	11.150
Ammonia (25% solution)	7.22	0.657
Surfactant solution	Unspecified	—
Demineralized water/1	509.98	46.390
Disponil A4066	38.92	3.538
Reductant solution 1	Unspecified	—
Demineralized water/2	46.68	4.247
Sodium ascorbate/1	1.86	0.169
Ferrous sulphate heptahydrate	0.01	0.001
Tertiary butyl hydroperoxide (Injection 2)	4.93	0.448
Reductant solution 2	2.46	0.246
Demineralized water/3	23.34	2.123
Sodium ascorbate/2	0.09	0.008

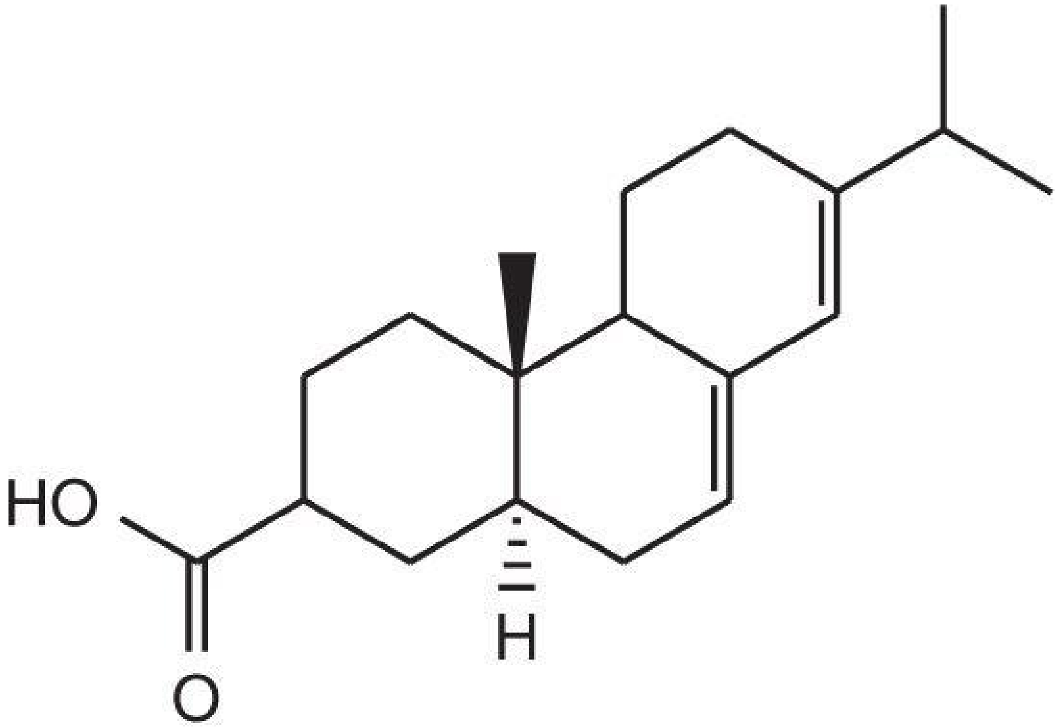
Testing Results

Testing results not supplied by the author.

Notes and Observations

1. Bricout[1] prepared paint and varnish coating formulation containing the renewable vegetable binder rosin, (I), which was then esterified using either glycerol or pentaerythritol. In addition, paint formulations were also prepared containing “agro-

solvents” such as rosin esterified with glycerol or pentaerythritol, soya bean, linseed, sunflower, rapeseed, grapeseed, peanut, olive, canola, safflower, coconut, wheat germ, corn, walnut, almond, palm, sesame, china-wood or “tung,” castor, and cottonseed oils, and their mixtures, which dramatically reduced painted surface volatile organic emissions. (See Fig. 6.4.)



Abretic Acid,
a Component of Rosin

(I)

Figure 6.4

2. Williams[2] prepared aqueous ‘green’ paint formulations using renewable animal or vegetative sources containing arachidic, behenic, palmitic, or myristic acids. When applied to a surface, paint formulations containing these renewable additives formed into a self-supporting, dimensionally stable paint body with thixotropic rheology properties.
3. Franklin[3] used the fatty acyl carrier protein (ACP) thioesterase gene derived from Elaeis, Arabidopsis, Gossypium, Vitis, Garcinia, Brassica, Madhuca, Oryza, or Ulmus to prepare fatty acid oils having chain lengths from C_8, C_{10}, C_{12} to C_{14} from microalgae. Products prepared from these renewable sources were used as paint, gasoline, and diesel fuel additives.
4. In an effort to completely eliminate volatile organic components in non-aqueous paint formulations, Williams[4] prepared a hard poly(urethane-urea) addition polymer of composite particles that was then used for coating wood compositions at ambient temperature. Paint formulations containing the poly(urethane-urea) additive also

contained neopentyl glycol and a polyester diol having an Mn ~1,000 daltons to improve paint flow properties.

References

1. Xavier Bricout et al., *Use of solvents derived from renewable resources, paints and coating including them, method for preparing them*, U.S. Patent 8,317,911 (November 27, 2012)

2. Neal St. John Williams, *Paint compositions*, U.S. Patent Application 20110124786 (May 26, 2011)

3. Scott Franklin, *Renewable chemical production from novel fatty acid feedstocks*, U.S. Patent Application 20120283460 (November 8, 2012)

4. Neal St. John Williams, *Process for making poly (urethane-urea)/addition polymer composite particles*, U.S. Patent Application 20020058751 (May 16, 2002)

Chapter

7

Cosmetics

Deodorants Containing 1,4-Dioxan-2-One Derived from Lactic Acid

Author	Sergey Selifonov
Patent Title	***Preparation of lactic acid derivatives and their use***, U.S. Patent 7,211,693 (November 1, 2007)

Relevant Prior Patents by Author

Glyceryl ether compounds and their use, U.S. Patent 8,318,814 (November 27, 2012)

Glycerol levulinate ketals and their use, U.S. Patent 8,178,701 (May 15, 2012)

Glyceryl ether compounds and their use, U.S. Patent 8,084,635 (December 22, 2011)

Glycerol levulinate ketals and their use, U.S. Patent 8,053,468 (November 8, 2011)

Product Application

3-Methyl-1,4-dioxan-2-ones and derivatives are useful as additives in deodorant formulations.

Significance of Current Application

There are inherent environmental concerns in the preparation of dioxanones when used as additives in deodorants formulations. Methods for their preparation include the use of halogenated raw materials and solvents, formation of undesired by-products, and expensive, synthetic multi-steps.

Moreover, in all cases the chemical reagents used in the preparation of dioxanones are non-renewable and are typically produced using petroleum-based reagents. A final concern in the preparation of dioxanones is the large amount of toxic chemical waste generated in each synthetic step. The current investigation has addressed all of these concerns by using carbohydrate fermentation-derived (S)-ethyllactate with a high yielding single-step reaction.

An additional advantage associated with this process is that the reaction appears to have extremely favorable kinetics at ambient temperature.

Product Formation

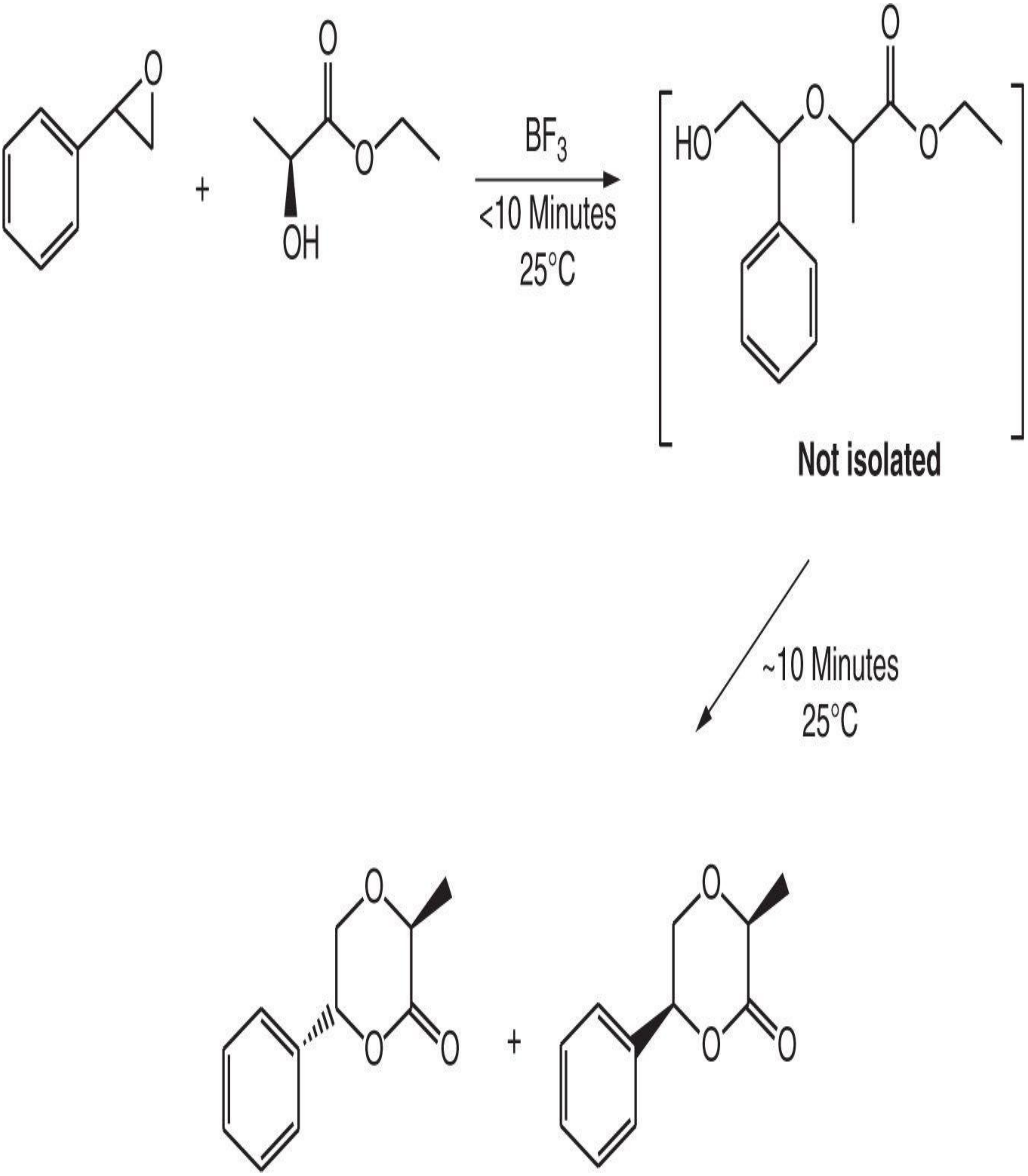


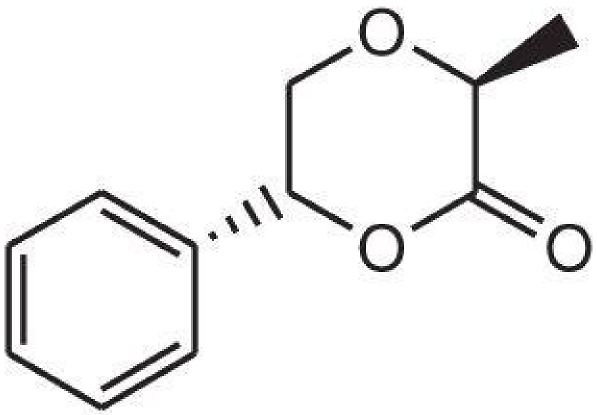
Figure 7.1

Experimental

Case I. Non-Renewable Route

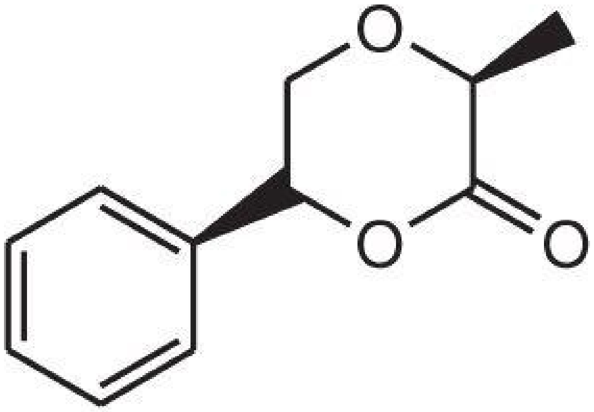
1. Preparation of 3,6-cis- and 3,6-trans-isomers of 6-phenyl-3-methyl-1,4-dioxan-2-one isomers.

A microreactor was charged with 1 μL of boron trifluoride dietherate dissolved in 1 mL of ethyl S (-) lactate and then rapidly treated with 0.05 mL of racemic styrene epoxide. The mixture was then vigorously stirred for 2 minutes at ambient temperature. An aliquot of the reaction mixture was then taken and diluted with ethyl acetate and immediately analyzed by GC-MS and GC-FID. The analysis showed the complete conversion of styrene oxide into two reaction products consisting of approximately equivalent amounts of 3,6-cis- and 3,6-trans-isomers of 6-phenyl-3-methyl-1,4-dioxan-2-one. The combined yield of isomers formed in this reaction was 81%. Mass-spectra electron ionization at 70 eV for each isomer is provided in Fig. 7.2.



trans-Isomer

MS 192 (20, M$^+$), 162 (8), 133 (9), 119 (3), 104 (100), 91 (21), 77 (16), 65 (4), 56 (35).



cis-Isomer

MS 192 (8, M$^+$), 162 (5), 133 (6), 119 (2), 104 (100), 91 (18), 77 (15), 65 (4), 56 (32).

Figure 7.2

Minor reactions of other products which also generated from this reaction are provided in Fig. 7.3.

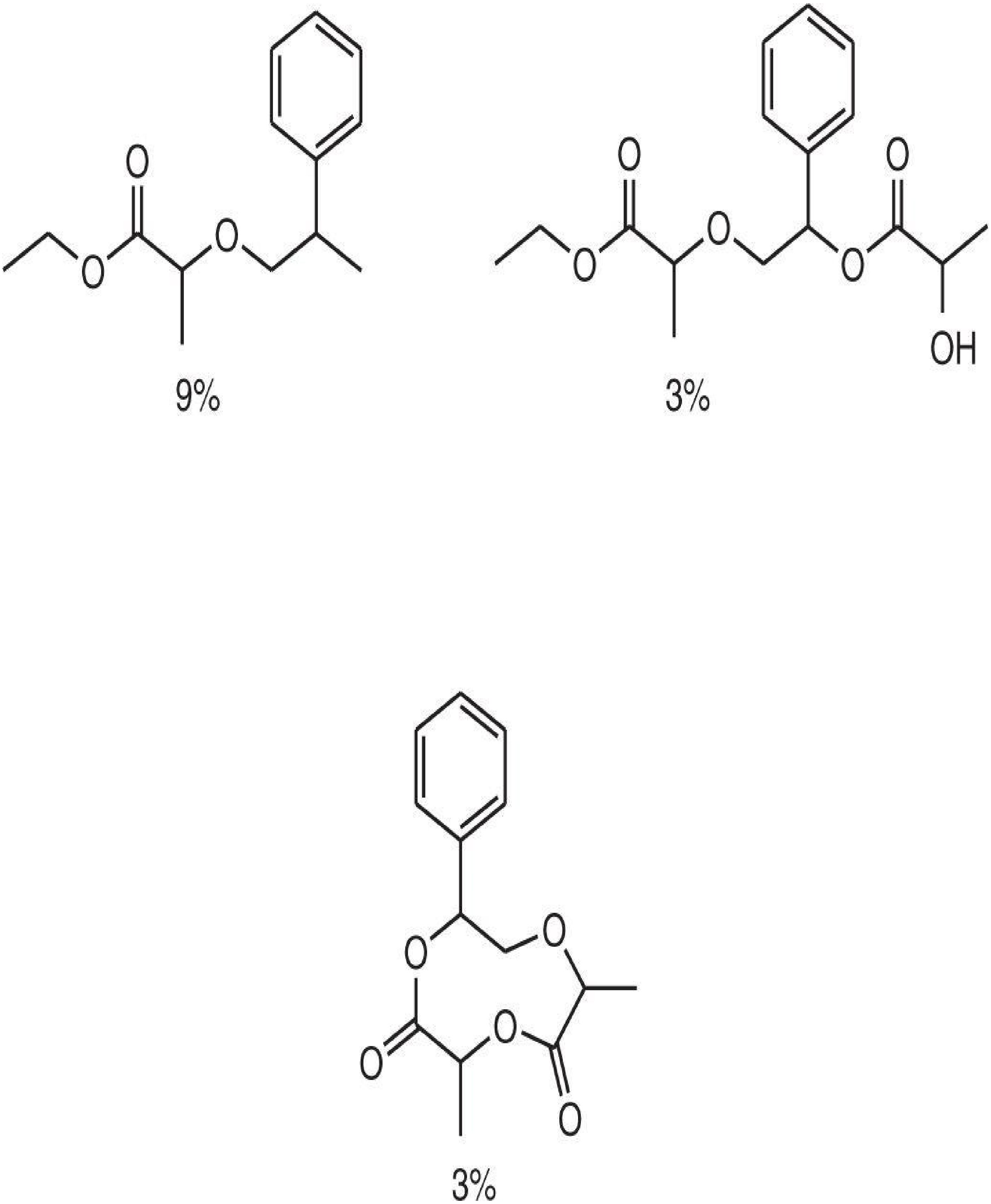


Figure 7.3

Case II. Renewable Route

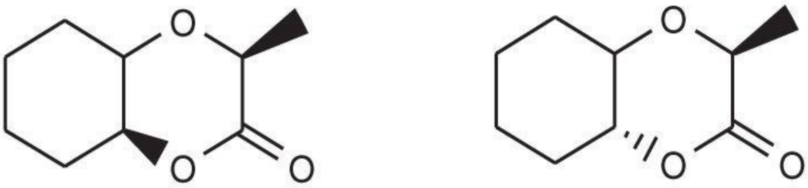
2. Preparation of 3,6-cis- and 3,6-trans-isomers of 6-phenyl-3-methyl-1,4-dioxan-2-one isomers. In this process, the exact experimental procedure from Step 1 was used with carbohydrate-derived (S)-ethyllactate. Although an eight-component mixture was generated in this process, components were easily separated into individual 1,4-dioxan-2-

ones using chromatographic methods. Products generated from corresponding reaction yields are illustrated in Fig. 7.4.

94%

(I)

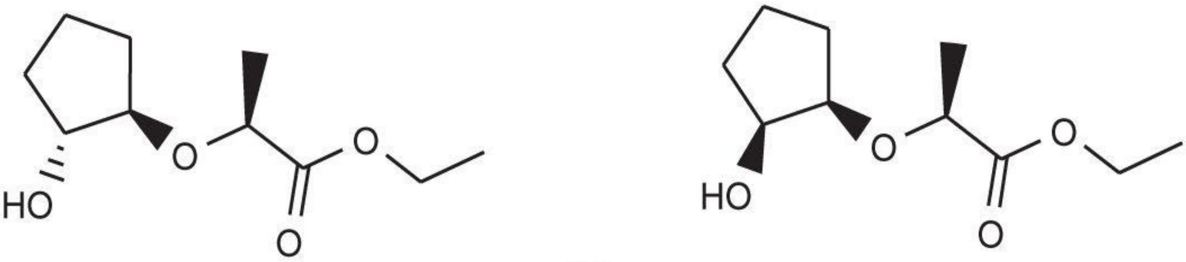
+



3%

(II)

+



2%

(III)

+

1%

(IV)

Figure 7.4

Notes and Observations

1. Binder[1] obtained 3-hydroxymethylfurfural, (V), in up to 65% yield by heating a 10 wt% solution of fructose dissolved in N, N-dimethylacetamide containing lithium chloride at ~100°C. Hydroxymethylfurfural was then modified to produce industrially significant intermediates or as a component in automotive fuel formulations. Conversion processes are provided in Fig. 7.5.

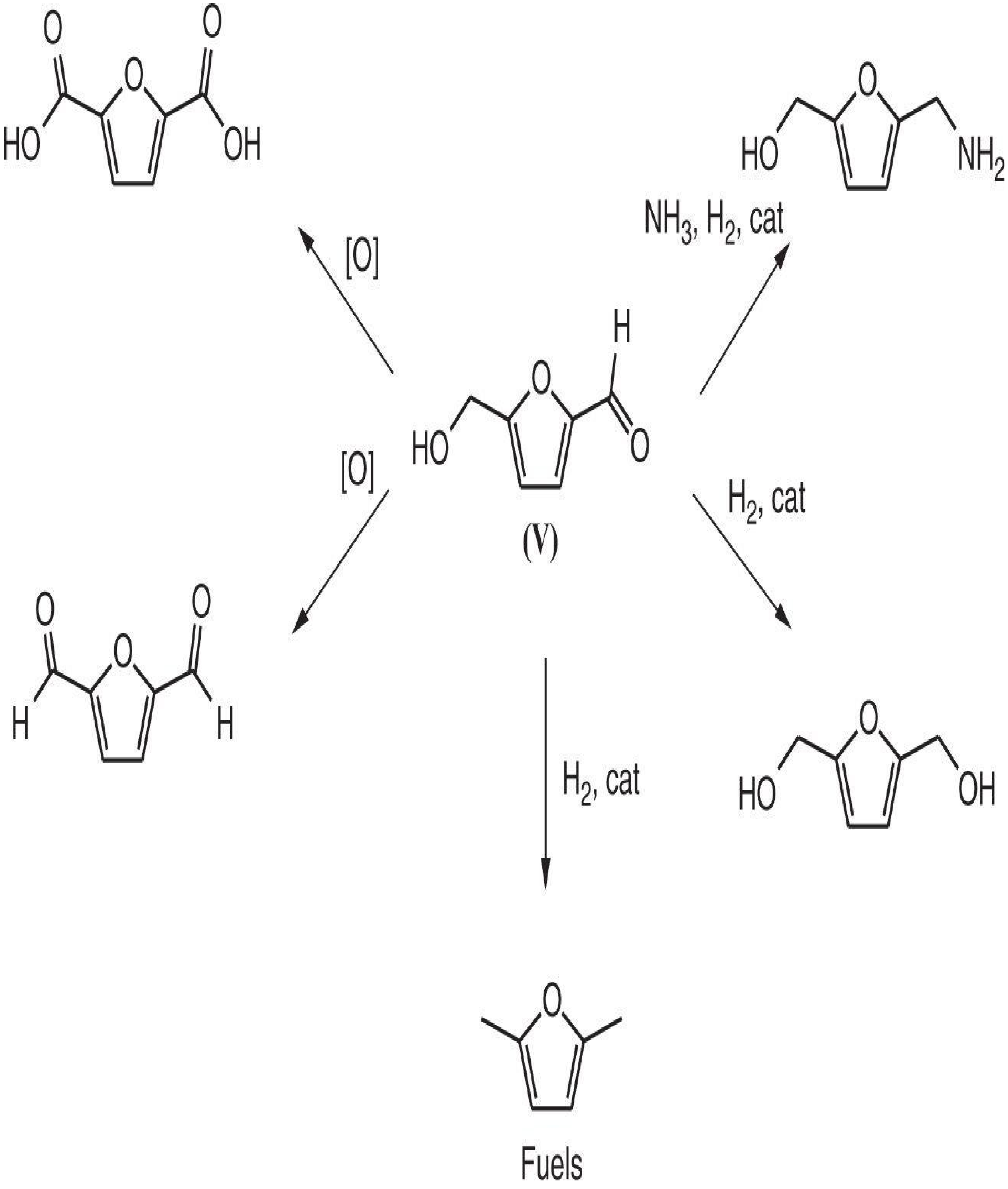
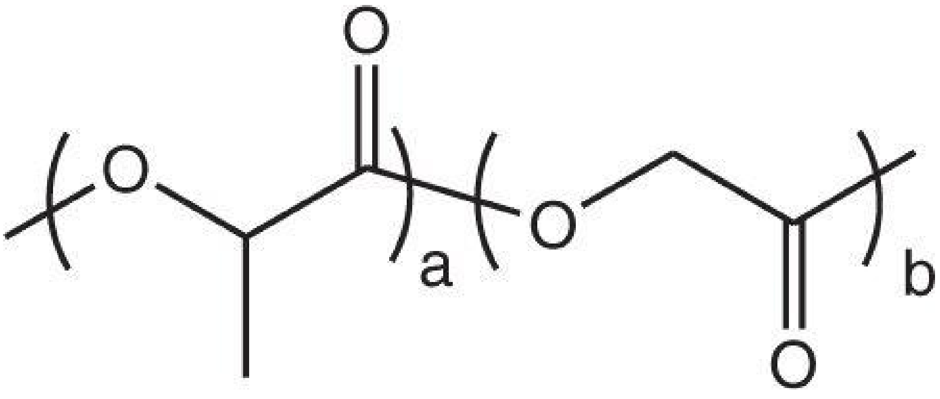


Figure 7.5

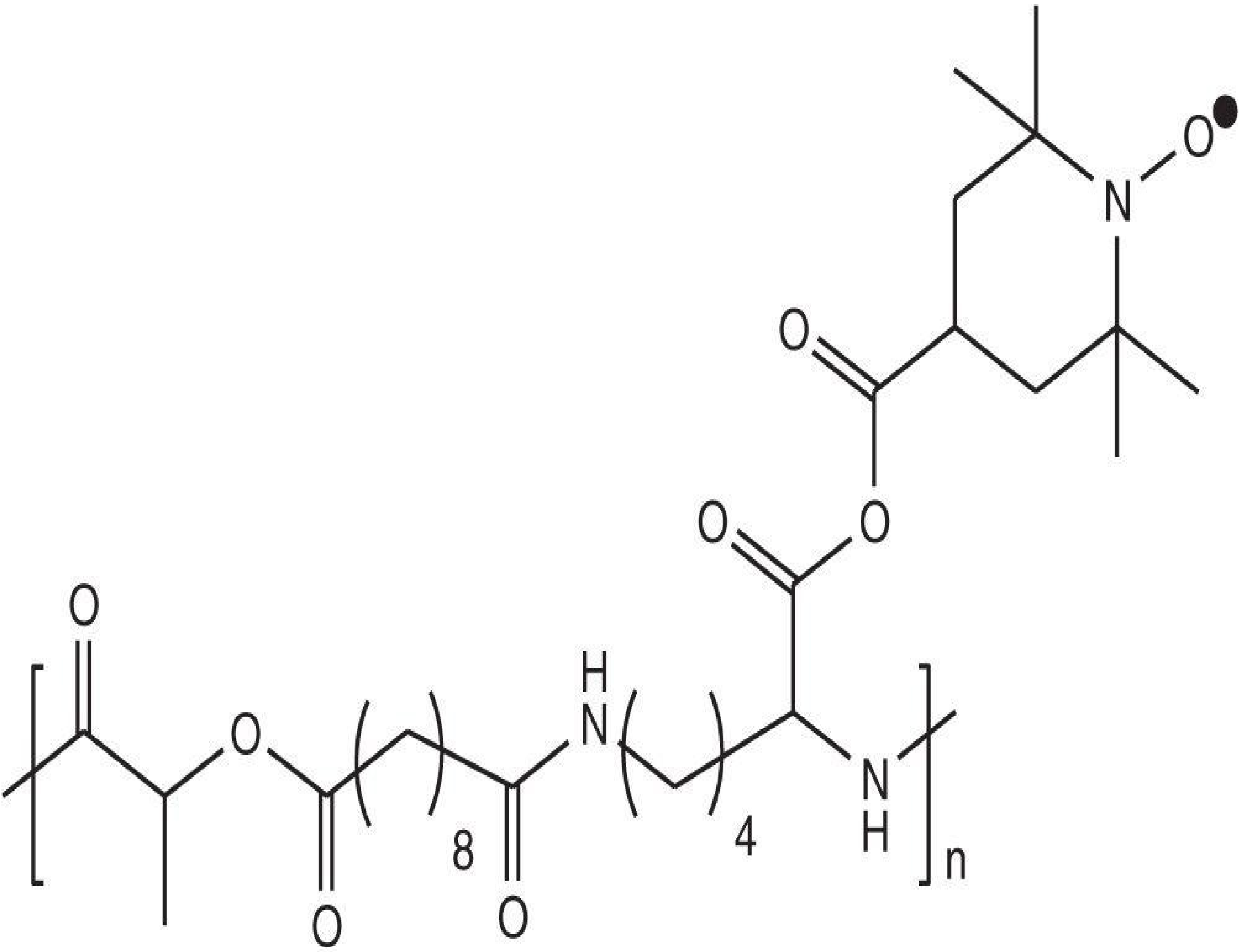
2. Biomass-derived lactic acid and glycolic acid were converted into the biodegradable microparticle copolyester, poly(d,l-lactic-co-glycolic acid, (VI),[2] having an Mn ~110,000 daltons, and used as a drug delivery agent, particularly for heparin. (See Fig. 7.6.)



(VI)

Figure 7.6

3. Hossainy[3] prepared oxidant-resistant medical articles containing amide/ester terpolymers, (VII), using bio-derived lactic acid and lysine that were and then reacted with butane-1,4-diol, sebacic acid. 4-Carboxy-2,2,6,6-tetramethylpiperidine-1-oxyl 4-carboxy was also incorporated into the polymer as the antioxidant. (See Fig. 7.7.)



(VII)

Figure 7.7

4. Hoshino[4] prepared a series of cross-linkable polyesters using biomass-derived glycolic acid, lactic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid, and 6-hydroxycaproic acid. Polyesters were prepared by condensing with biomass-derived tri-alcohols including trimethylol-propane, glycerin, and pentaerythritol. Polyesters derived from these reactions were then used to prepare either moldable plastics or engineered polymers.

References

1. Joseph Bartholomew Binder et al., *Chemical transformation of lignocellulosic biomass into fuels and chemicals*, U.S. Patent 8,324,376 (December 4, 2012)

2. Gun Poong Kim et al., *Biodegradable polymer microparticles and preparation method thereof*, U.S. Patent 8,329,856 (December 11, 2012)

3. Syed F. A. Hossainy et al., *Polymers containing poly(hydroxyalkanoates) and agents for use with medical articles and methods of fabricating the same*, U.S. Patent 8,329,157 (December 11, 2012)

4. Toyomasa Hoshino et al., *Aliphatic polyester resin and its production method*, U.S. Patent 8,318,893 (November 27, 2012)

Facial Creams Containing Biologically Based Mono- and Di-Esters

Author	Gyorgyi Fenyvesi et al.
Patent Title	***Personal care and cosmetics compositions comprising biologically based mono- and di-esters,*** U.S. Patent 8,309,116 (November 13, 2012)

Relevant Prior Patents by Author or Coauthors

Personal care composition containing bio-derived 1,3-propanediol and its conjugate esters, U.S. Patent 8,048,920 (November 21, 2011)

Heat transfer compositions comprising renewably-based biodegradable 1,3-propanediol, U.S. Patent 7,988,883 (August 2, 2011)

Deicing and anti-icing compositions comprising renewably-based, biodegradable 1,3-propanediol, U.S. Patent 7,972,530 (July 5, 201)

Synthesis of mono- and di-esters from biologically produced 1,3-propanediol, U.S. Patent 7,960,575 (June 14, 2011)

Bio-derived 1,3-propanediol and its conjugate esters as natural and non-irritating solvents for biomass-derived extracts, fragrance concentrates, and oils, U.S. Patent 7,759,393 (June 20, 2010)

Product Application

Propanediol distearate is used in cosmetic formulations including facial lotions, skin care, conditioning agents, skin cleansing compositions, and eye shadow.

Significance of Current Application

In this investigation, mono- and propanediol distearate were used as the essential components in cosmetic formulations. In the preparation of both mono- and propanediol distearate, 1,3-propanediol was prepared and isolated from bio-based and renewable resources. Furthermore, production costs for preparing this renewable intermediate were considerably lower than conventional chemical-based methods since d-glucose was used as the diol renewable agent, costs associated with toxic-waste disposal were eliminated, and purities in excess of 99.9+% were obtained by simple distillation.

Product Formation

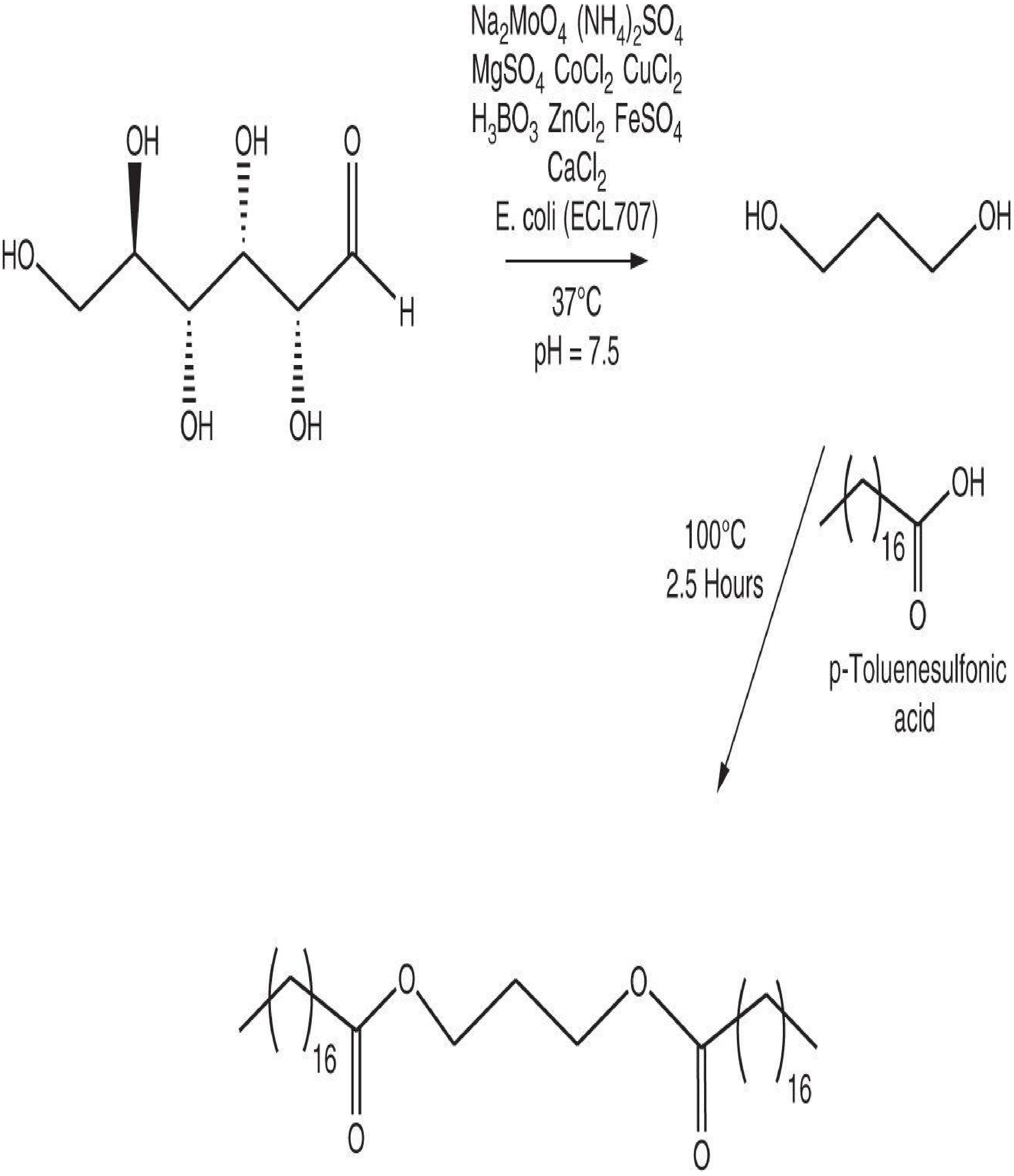


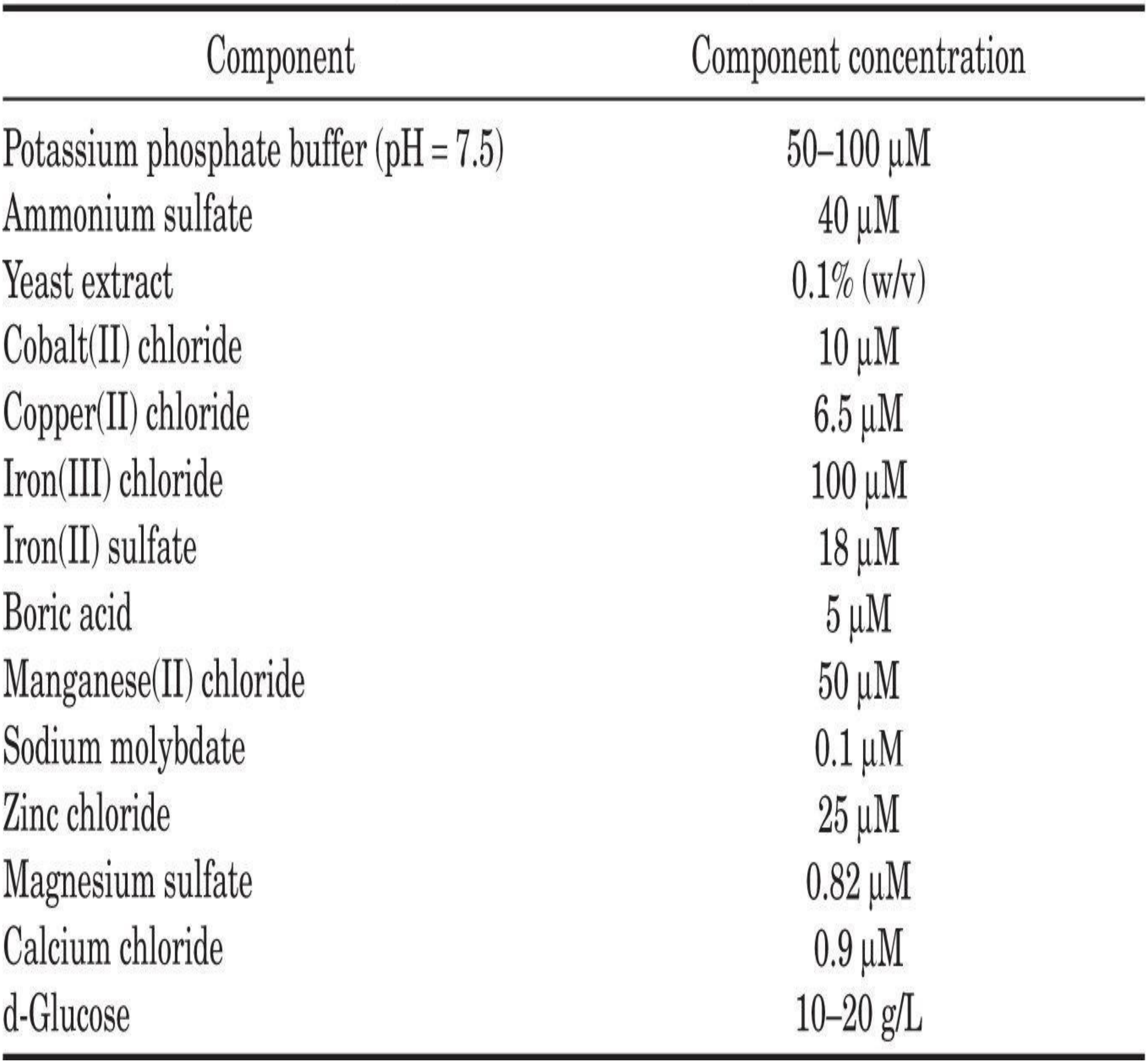
Figure 7.8

Experimental

1. Preparation of biologically derived 1,3-propanediol by fermentation. E. coli strain ECL707 containing the K. pneumoniae dha regulon cosmids pKP1 or pKP2, the K. pneumoniae pdu operon pKP4, or the Supercos vector alone, were grown in a 5-L Applikon fermenter and the batch was then used to produce 1,3-propanediol from d-glucose. Components comprising the growing medium are provided in Table 7.1.

TABLE 7.1 Growing medium used for converting d-glucose into 1,3-propanediol

using E. coli strain ECL707 containing the K. pneumoniae dha regulon cosmids pKP1 or pKP2.



Component	Component concentration
Potassium phosphate buffer (pH = 7.5)	50–100 µM
Ammonium sulfate	40 µM
Yeast extract	0.1% (w/v)
Cobalt(II) chloride	10 µM
Copper(II) chloride	6.5 µM
Iron(III) chloride	100 µM
Iron(II) sulfate	18 µM
Boric acid	5 µM
Manganese(II) chloride	50 µM
Sodium molybdate	0.1 µM
Zinc chloride	25 µM
Magnesium sulfate	0.82 µM
Calcium chloride	0.9 µM
d-Glucose	10–20 g/L

As the fermentation process progressed, additional d-glucose was intermittently added to the growing medium so that the d-glucose concentration was consistently in excess. During the biosynthesis, the temperature was maintained at 37°C while the pH was maintained at 7.5 using 5M potassium hydroxide or sodium hydroxide. In addition, appropriate antibiotics were included for plasmid maintenance. Anaerobic fermentations were performed at 0.1 vvm where nitrogen was initially used to sparged throughout the reactor. When the d_O setpoint was 5%, 1 vvm air was also sparged through the reactor and the medium supplemented with vitamin B_{12}. Reaction aliquots were routinely removed and the concentration of 1,3-propanediol ranged from 8.1 g/mL to 10.9 g/mL. Once the fermentation process was stopped, the reaction yield of 1,3-propanediol from d-glucose ranged from 4% to 17% with 99% purity after microdistillation.

2. Preparation of propanediol distearate using biologically derived 1,3-propanediol.

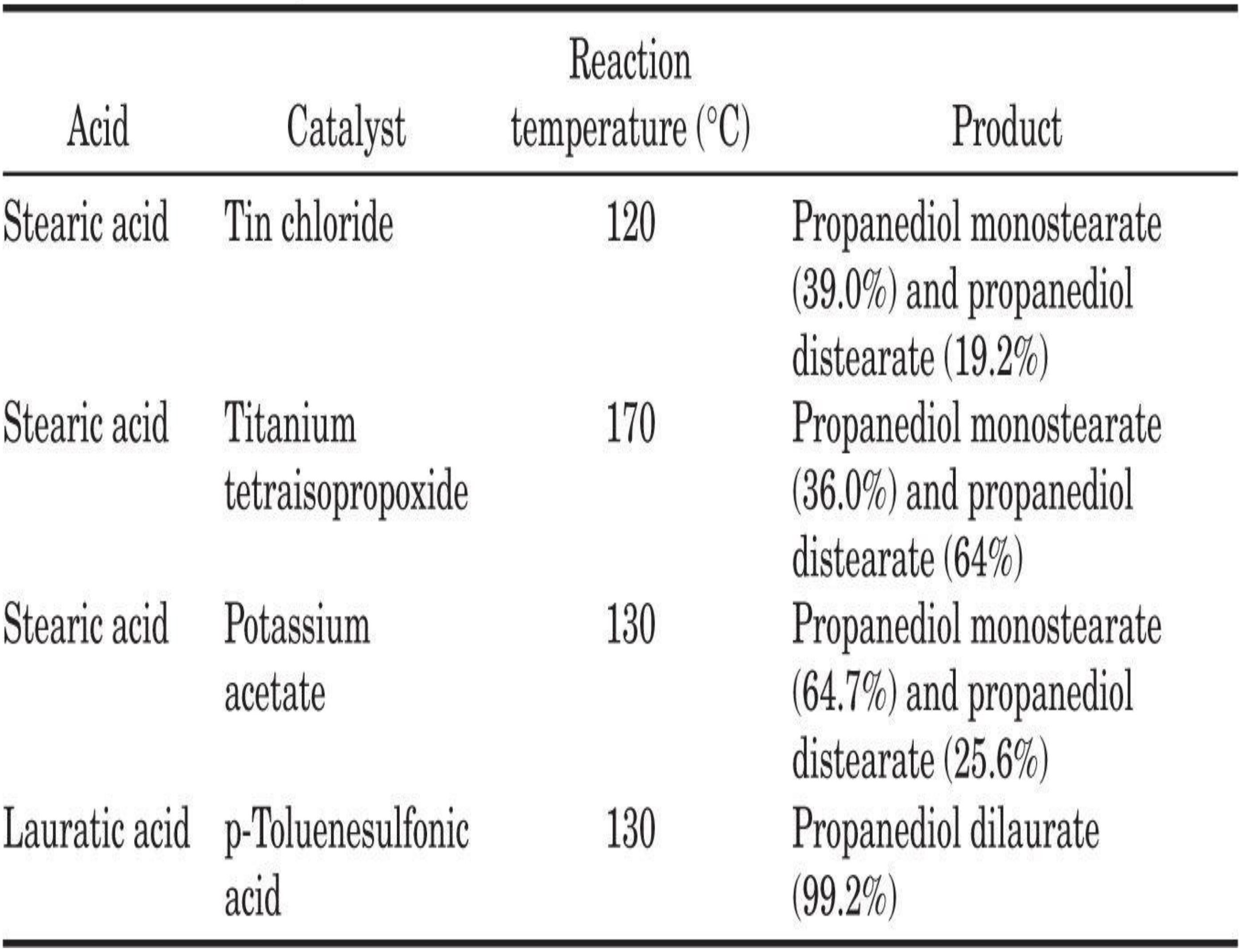
A reactor was charged with 2.58 g of the Step 1 product, 19.45 g of stearic acid, and 0.2125 g of p-toluenesulfonic acid, then purged using dry-nitrogengas to remove moisture for 15 minutes. The reaction temperature was then raised to 100°C while thoroughly stirring the mixture for 2.5 hours. After the reaction was completed, the mixture was cooled to about 35°C and the product was transferred into a beaker and purified by treating it with 100 mL of water. While the mixture was being mechanically stirred between 45°C and 60°C for 15 minutes, it formed an emulsion. The mixture was then further cooled to ambient temperature and the product isolated by filtration.

^{1}**H-NMR** (d-chloroform) δ 0.88 (t, CH_3–CH_2, 6H), 1.26 (t, CH_2–CH_2–CH_2, 28H), 1.61 (t, $CH_2$2–CH_2-C=O, 4H), 1.97 (t, –O–CH_2–CH_2–CH_2–O, 2H), 2.28 (t, CH_2-C=O, 4H), 4.15 (t, C(=O)–O–CH_2–4H)

DSC Tm = 66.4°C and Tc = 54.7°C

3. Effect of different catalysts on formation of Step 2 product provided in Table 7.2

TABLE 7.2 The effect on product formation of mixtures of mono- and di-esters using biologically derived 1,3-propanediol with different reaction catalysts, temperatures, and different carboxylic acids.



Acid	Catalyst	Reaction temperature (°C)	Product
Stearic acid	Tin chloride	120	Propanediol monostearate (39.0%) and propanediol distearate (19.2%)
Stearic acid	Titanium tetraisopropoxide	170	Propanediol monostearate (36.0%) and propanediol distearate (64%)
Stearic acid	Potassium acetate	130	Propanediol monostearate (64.7%) and propanediol distearate (25.6%)
Lauratic acid	p-Toluenesulfonic acid	130	Propanediol dilaurate (99.2%)

Notes and Observations

1. Mixtures of sesame oil containing Candida antarctica lipase were used by Price[1] to

catalyze the formation of hydrazides from C-glycosides, (I), as illustrated in Eq. 1. Materials generated from this process were used as eco-friendly detergents. (See Fig. 7.9.)

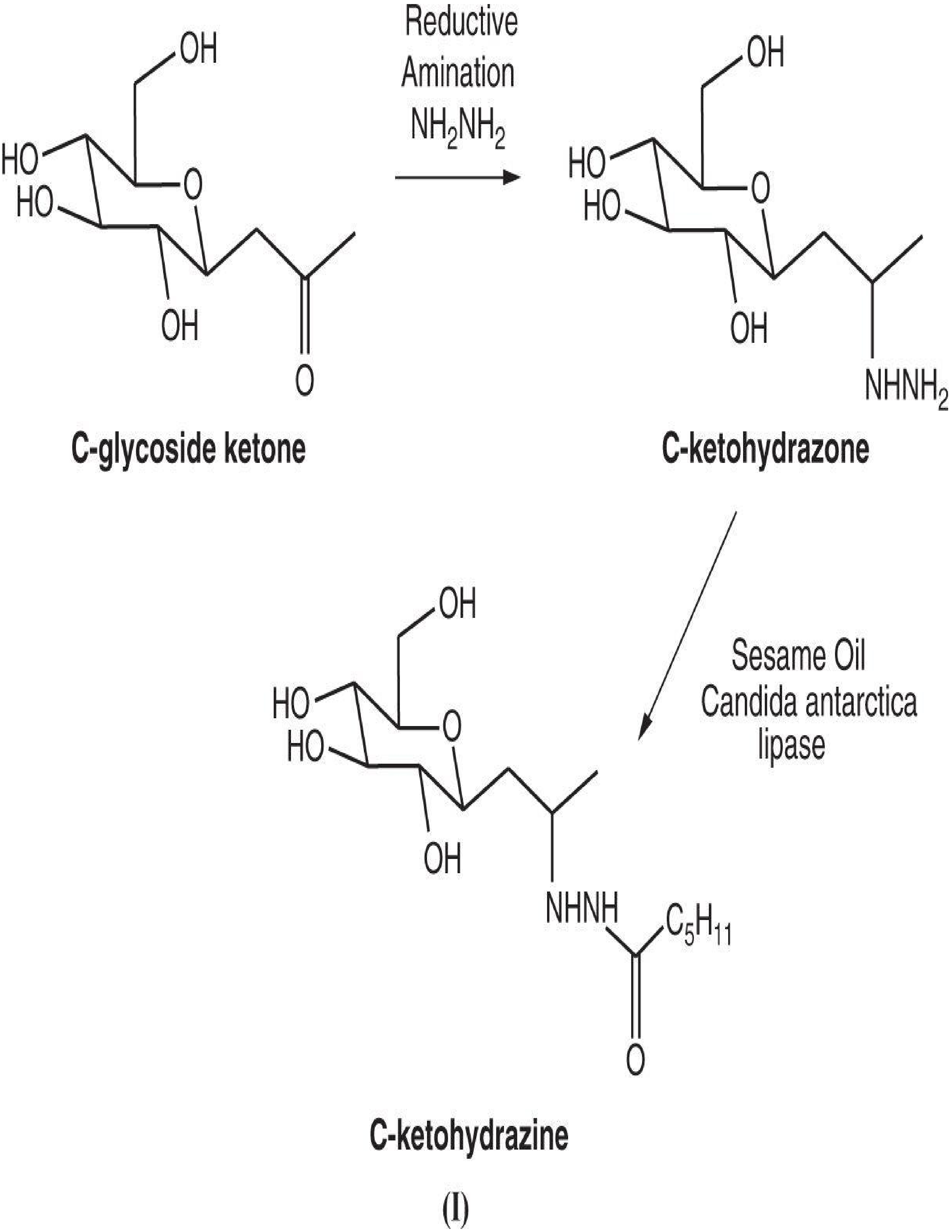
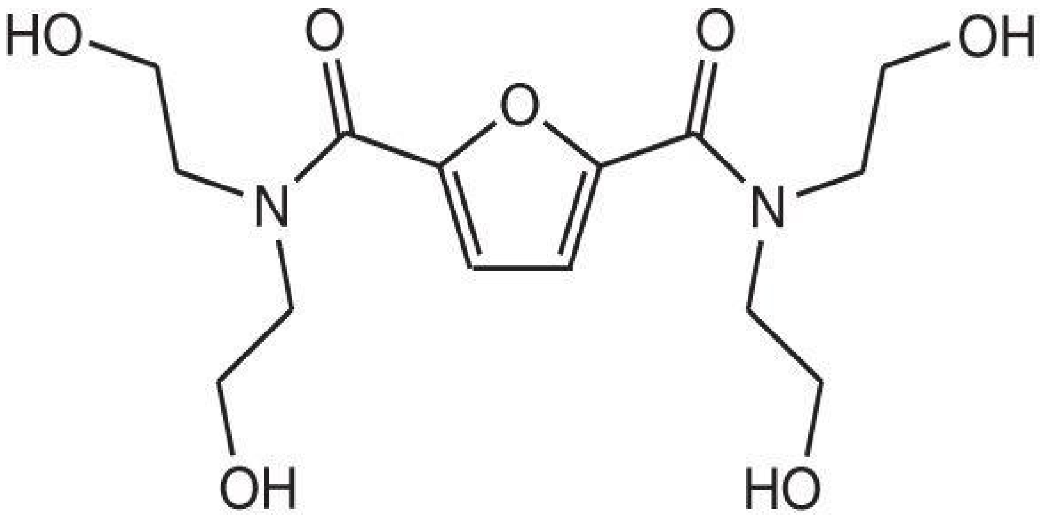


Figure 7.9

2. Benecke[2] used heat-curable aqueous compositions containing naturally occurring furan-based polyols, (II), III), and (IV), in book and fiberglass binding formulations as a replacement for formaldehyde to limit toxic formaldehyde emissions during manufacturing processing. (See Fig. 7.10.)



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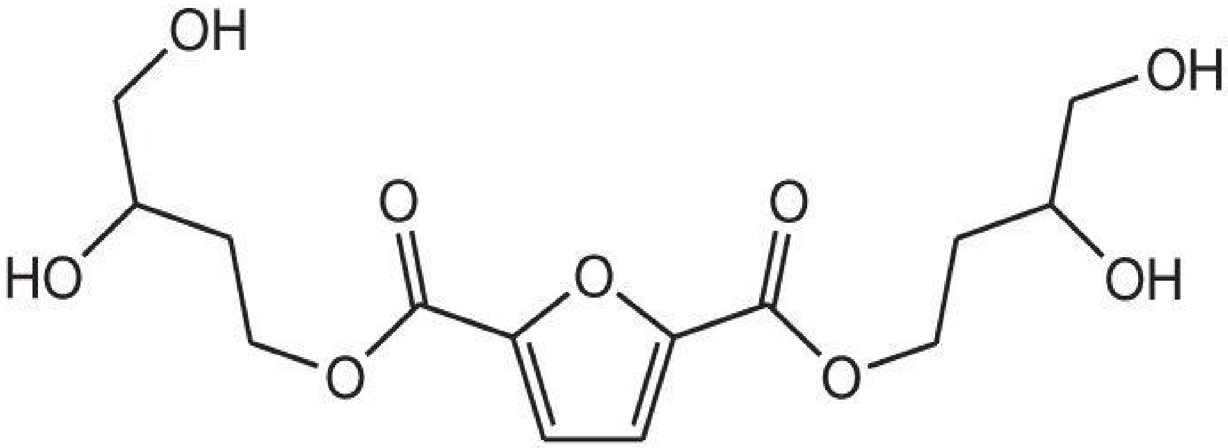
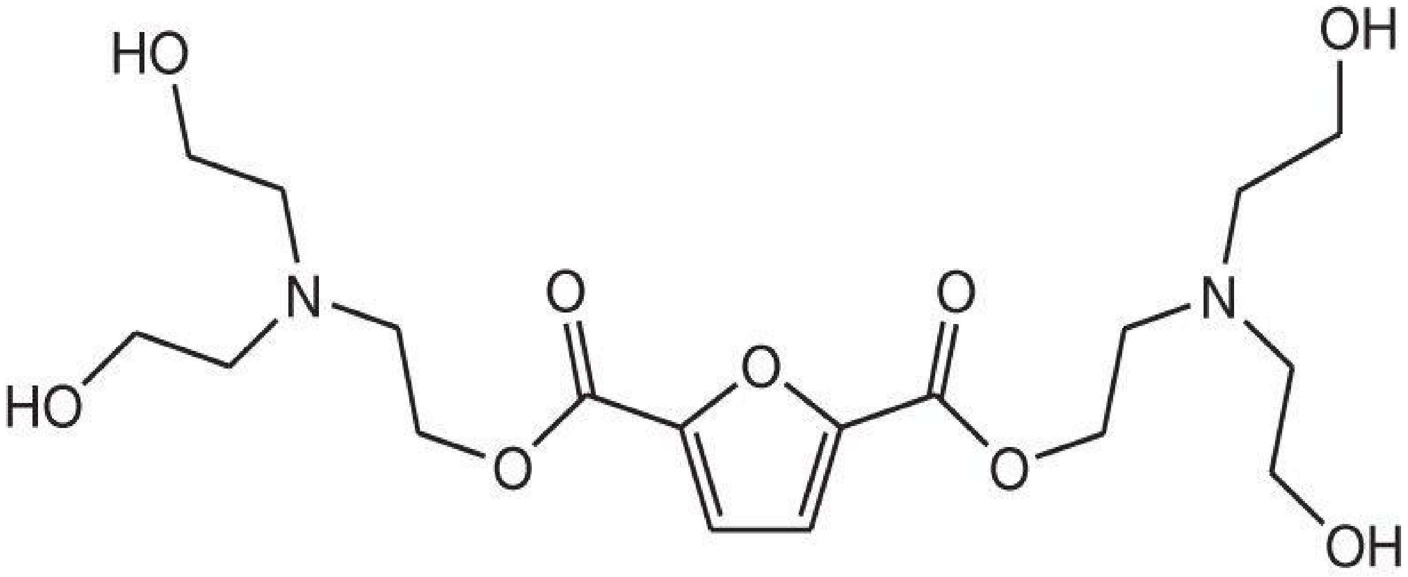


(III)

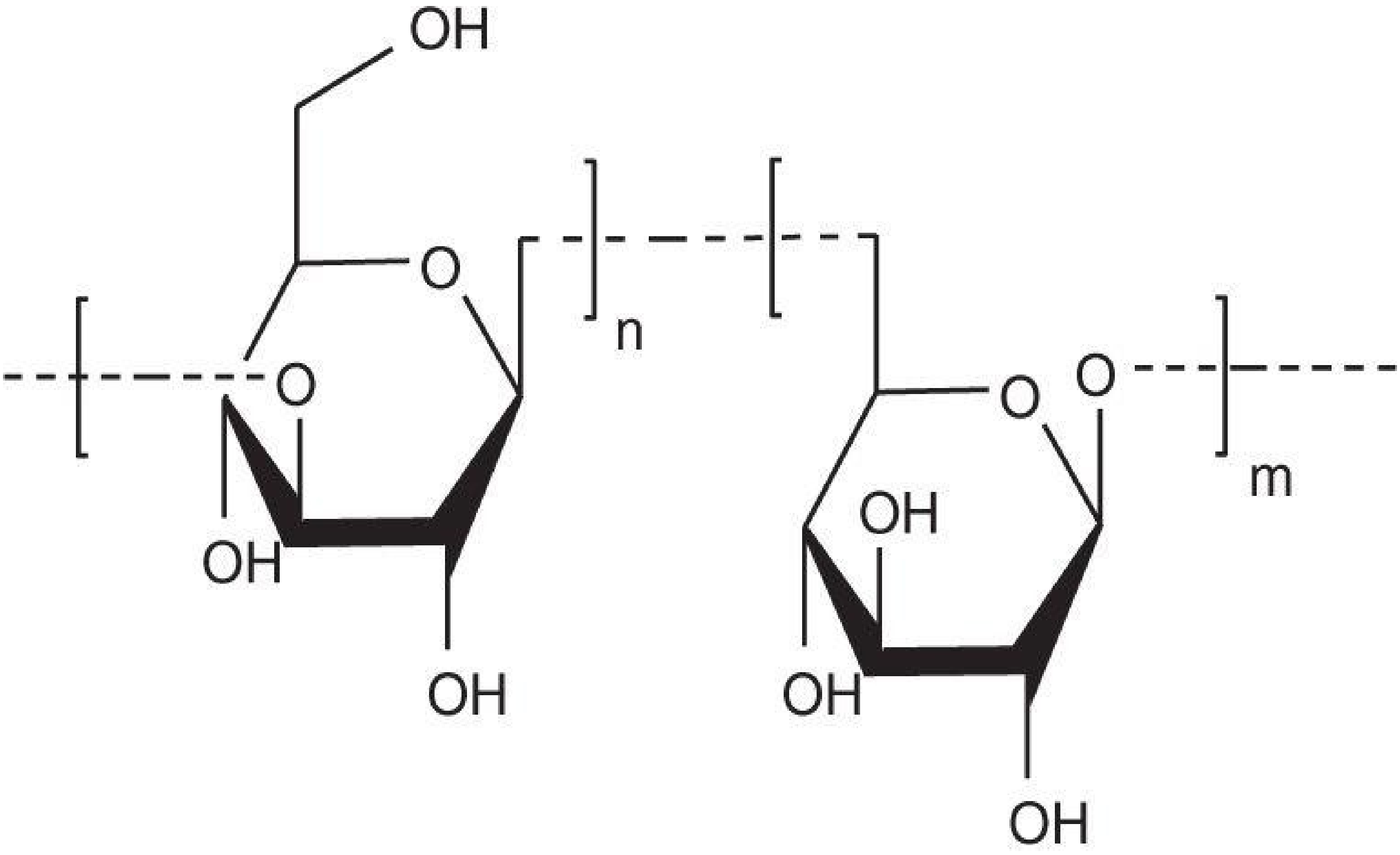


(IV)

Figure 7.10

3. Diner[3] treated a cellulose-ethyl alcohol mixture with saccharification enzymes Spezyme

CP, Multifect CX12L, and Novozyme 188 to extract glucan, (V), and xylan, (VI). Both sugars are fermentable and are utilized for the production of other industrial and renewable chemical agents. (See Fig. 7.11.)



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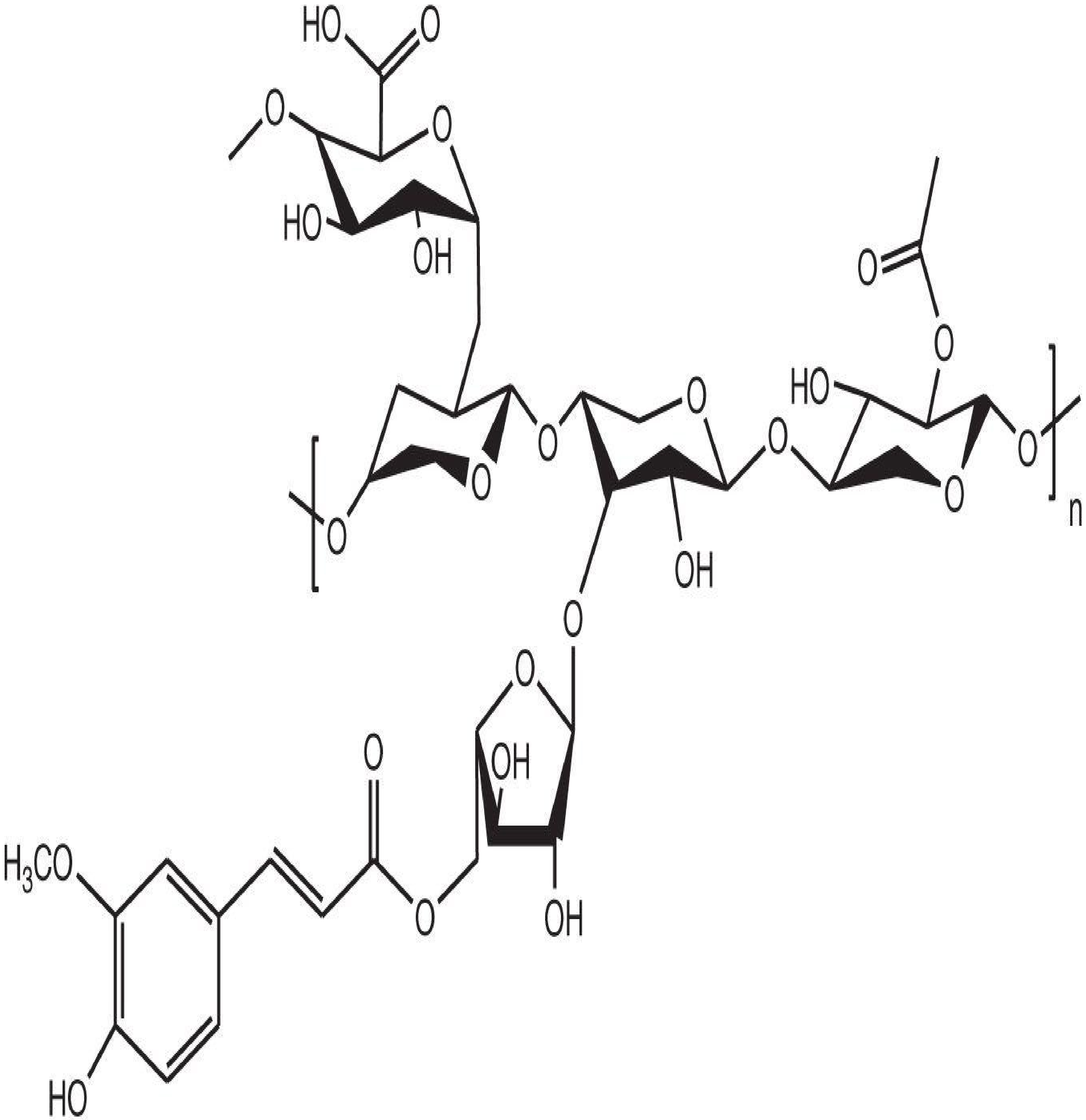


(VI)

Figure 7.11

4. Boy[4] prepared an aqueous glucose solution using maize or maize gluten powder with α-amylase. The process entailed:
   a. Fractionating by dry milling of maize kernels so that the maize kernels are separated into a maize-starch-comprising endosperm fraction, a high-oil germ fraction, and optionally, a bran fraction.
   b. Enzymatical liquefaction and saccharification of the maize starch containing an aqueous suspension of the endosperm fraction using α-amylase that then provided an aqueous glucose solution. This process is continued until the maize gluten and bran are consumed.

References

1. Neil P. Price, *Green detergents from agriculture-based lipids and sugars*, U.S. Patent 8,314,219 (November 20, 2012)
2. Herman P. Benecke et al., *Formaldehyde-free binders*, U.S. Patent 8,309,676 (November 13, 2012)
3. Bruce A. Diner et al., *Organic solvent pretreatment of biomass to enhance enzymatic saccharification*, U.S. Patent 8,304,213 (November 6, 2012)
4. Matthias Boy et al., *Method for the production of an aqueous glucose solution*, U.S. Patent 8,293,504 (October 23, 2012)

Chapter

8

Detergents

Biodegradable Isosorbide Glyceryl Additized Detergents

Author Catherine Breffa et al.

Patent Title ***Isosorbide glyceryl ether derivatives and their use in household applications***, U.S. Patent 8,420,588 (April 16, 2013)

Relevant Prior Patents by Author or Coauthors

Isosorbide monoesters and their use in household applications, U.S. Patent 8,389,465 (March 5, 2013)

Anionic isosorbide derivatives and their use, U.S. Patent 8,420,588 (April 16, 2013)

Use of isosorbide ethers in detergents and cleaners, U.S. Patent Application 20110059884 (August 30, 2011)

Use of isosorbide ethers in detergents and cleaners, U.S. Patent 8,008,246 (August 30, 2011)

Anionic isosorbide derivatives and their use, U.S. Patent Application 20100324153 (December 23, 2010)

Isosorbide derivatives that can be used in detergent compositions for gasoline-type fuels, U.S. Patent 6,527,816 (March 4, 2003)

Product Application

Isosorbide glyceryl alkyl ether derivatives are designed to be used as cleaning additives in both consumer household products, particularly laundry and cleaning detergents, and in cosmetic formulations.

Significance of Current Application

Isosorbide derivatives may represent the next generation additive contained in consumer home-cleaning detergents. They are active in cleaning formulations that is either alkaline or acidic. Moreover, isosorbide glyceryl alkyl ethers are readily isolated from renewable non-animal biomasses. In addition, isosorbide glyceryl alkyl ethers could potentially replace cleaning-agent additives in cosmetics since these derivatives are non-irritating and non-corrosive.

Product Formation

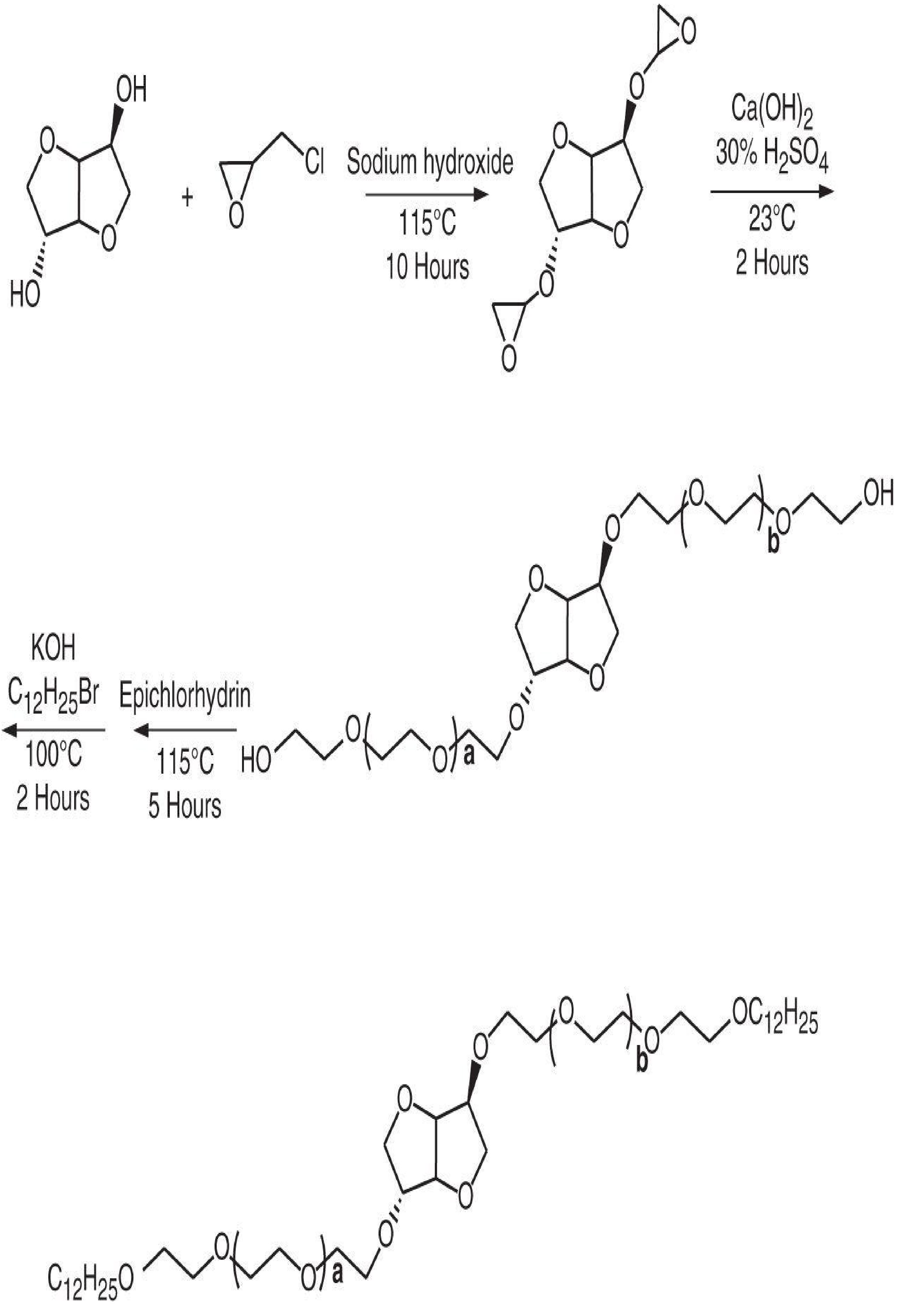

OH
HO
+
Cl
Sodium hydroxide
115°C
10 Hours
$Ca(OH)_2$
30% H_2SO_4
23°C
2 Hours
OH
b
HO
a
KOH
$C_{12}H_{25}Br$
100°C
2 Hours
Epichlorhydrin
115°C
5 Hours
$OC_{12}H_{25}$
b
$C_{12}H_{25}O$
a

Figure 8.1

Reagent Bio-Renewability Sources

Isosorbide was derived from d-glucose while glycidol was derived from biomass sources before being converted into epichlorohydrin.

Experimental

1. Preparation of isosorbide bisglycidylether. A reactor was charged with 73.5 g of isosorbide and 370 g of epichlorohydrin then heated to 65°C for 10 hours. During this period the reaction mixture was incrementally treated with 81 g of 50% aqueous sodium hydroxide. After the addition had been completed the mixture was heated to 150°C under vacuum to distill off both water and excess epichlorohydrin from the reaction intermediate. The crude mixture was then extracted with acetone, filtered, and then washed with water. After drying, the product was isolated.

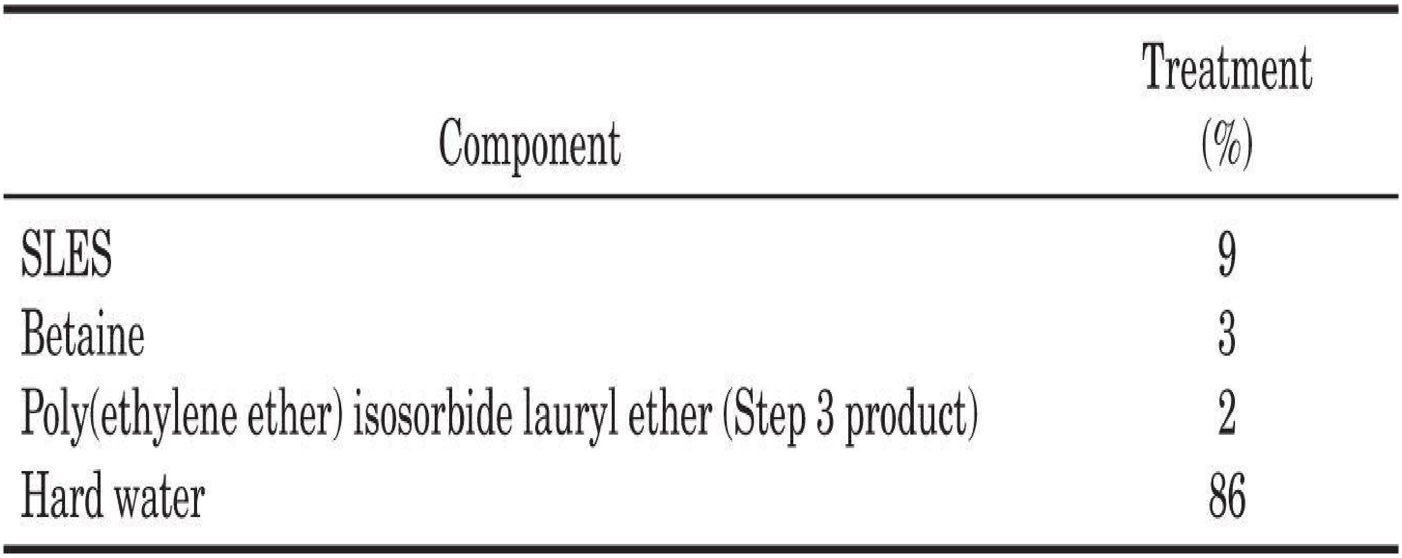
2. Preparation of poly(ethylene ether) isosorbide. A reactor was charged with a solution consisting of 26.9 g of the Step 1 product dissolved in 22 mL of water and ethylene oxide, and then treated with a dropwise addition of 2 mL of 30% sulfuric acid. After reacting at 115°C for 3 hours, the mixture was cooled to ambient temperature and neutralized by the addition of an aqueous slurry of 0.8 g of calcium hydroxide. The mixture was then filtered, distilled under vacuum, and 20 g of product were isolated as a light-yellow oil.

3. Preparation of poly(ethylene ether) isosorbide lauryl ether. One equivalent of the Step 2 product was treated with two equivalents of epichlorohydrin and heated for 5 hours at 115°C. The reaction intermediate was then treated with 182 g of dodecanol and 3.65 g of potassium hydroxide and then further heated to 100°C for 3 hours. The mixture was cooled, filtered, and the unreacted dodecanol was removed by vacuum distillation. After vacuum drying, 48 g of the product were isolated as a yellow paste, and the surfactants of this reaction product were evaluated. Testing results are provided in the Results Section.

Testing

A. Foam stability testing. A foaming test solution to evaluate poly(ethylene ether) isosorbide lauryl ether was prepared to determine the surfactant effectiveness of the Step 3 product illustrated in Table 8.1. Components were thoroughly blended using a mechanical stirrer and the mixture was immediately evaluated.

TABLE 8.1 Cleaning formulation used to evaluate the foam stability of the renewable experimental detergent, poly(ethylene ether) isosorbide lauryl ether.



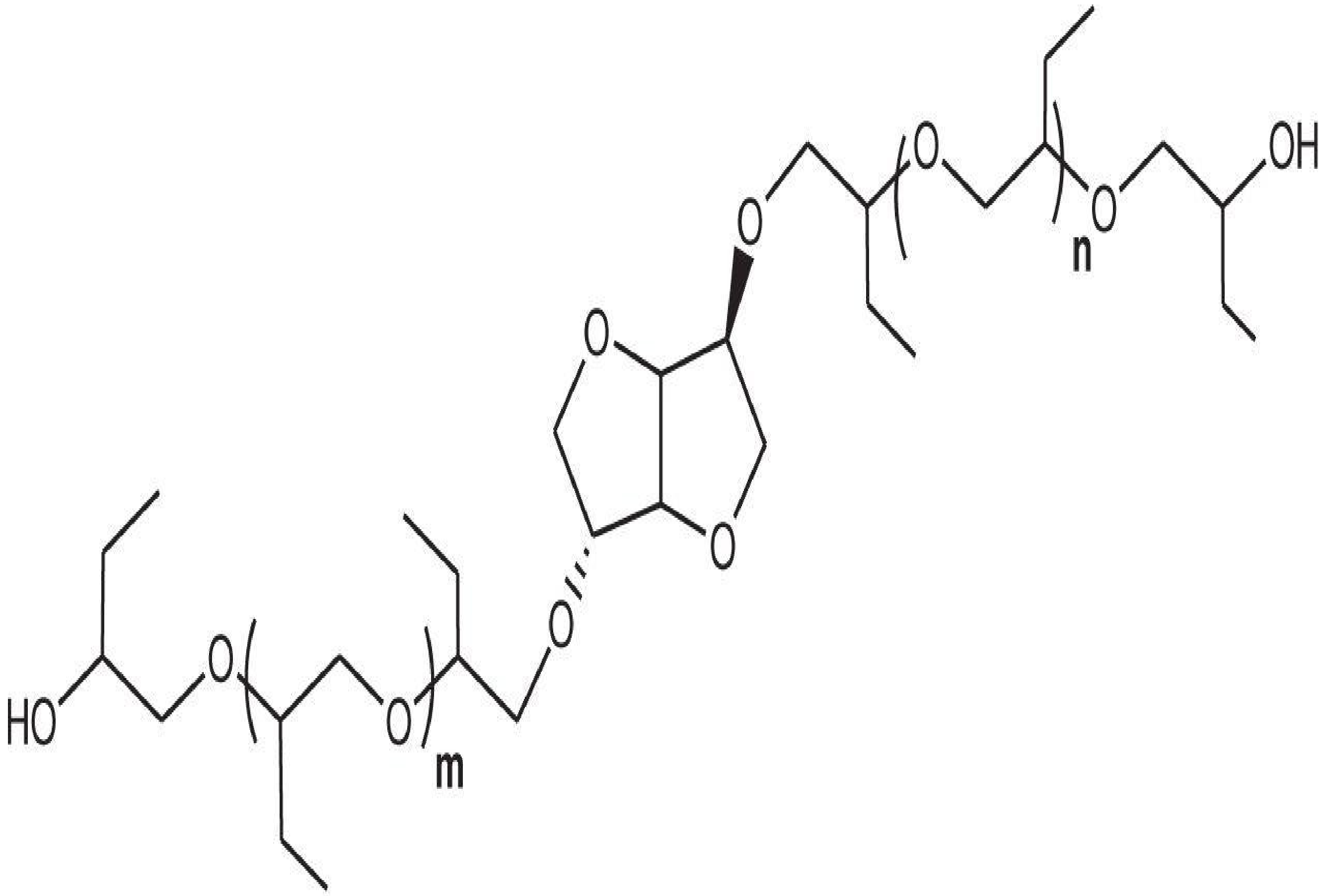
Component	Treatment (%)
SLES	9
Betaine	3
Poly(ethylene ether) isosorbide lauryl ether (Step 3 product)	2
Hard water	86

Testing Results

A 2.0 wt% aqueous solution of the surfactant mixture provided in Table 8.1 was stirred in a beaker for 10 seconds at 2,000 rpm, and the resulting foam properties were evaluated. The generated foam was dense, did not readily collapse, and had a stable foam height of 5.5 cm. This evaluation was then repeated using commercial cleaners. Foams produced using these products were airy and readily collapsed. The typical foam height for commercial detergents was only 1.1 cm.

Notes and Observations

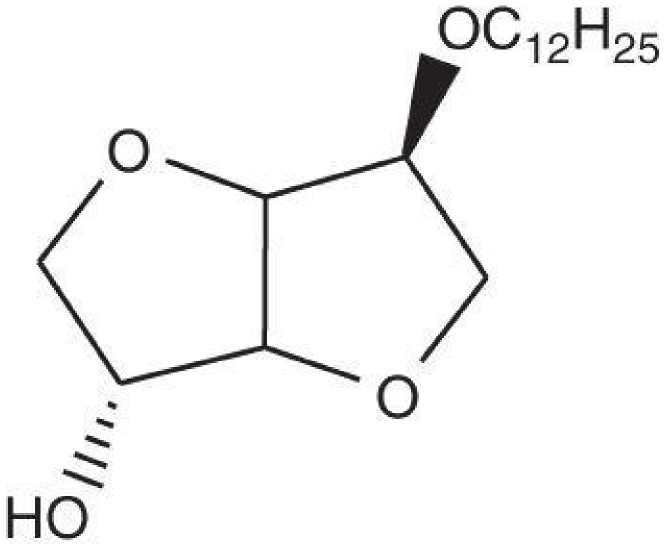
1. In an earlier investigation by Deflort,[1] a gasoline engine detergent, (I), was prepared by condensing isosorbide with 1,2-epoxybutane. Fuel treatment levels as low as 20 mg/L were determined to be sufficient in limiting deposits on engine components. (See Fig. 8.2.)



(I)

Figure 8.2

2. Breffa[2] prepared isosorbide laurylmonoether, (II), which was effective as both a detergent and a thickening agent when used in aqueous solutions. (See Fig. 8.3.)

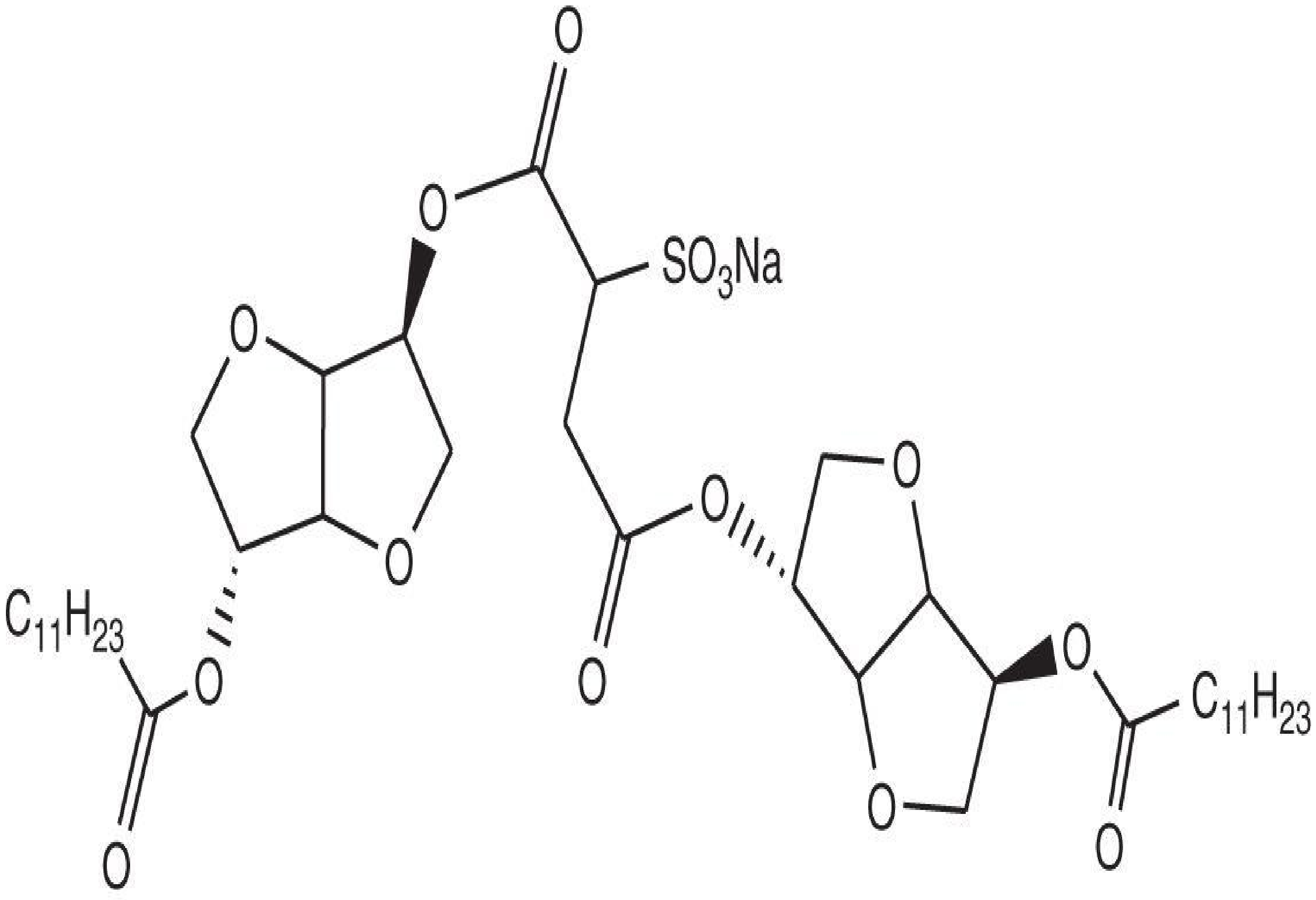


(II)

Figure 8. 3

3. Breffa[3] prepared the isosorbide lauroylester of sodium sulfosuccinate, (III), which was moderately effective as a surfactant but extremely effective as a thickening agent in

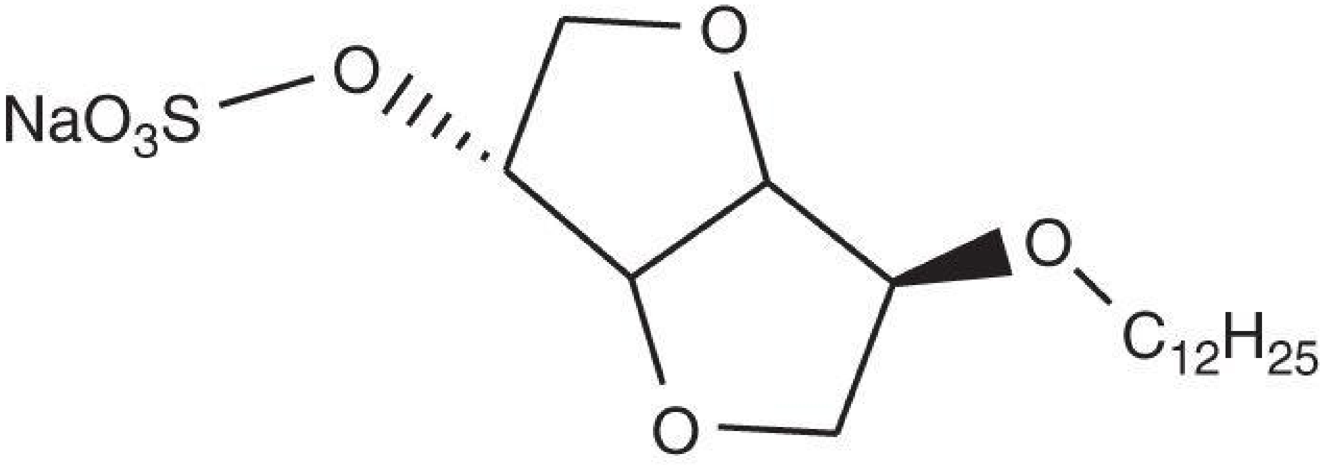
aqueous solutions containing detergents. (See Fig. 8.4.)



(III)

Figure 8.4

4. Behler[4] prepared the sodium sulfate of isosorbide monododecylether, (IV), in a two-step reaction initially using sulfonyl chloride. When the sulfate ester was dissolved in water it showed very similar foam properties to partially renewable Texapon® N70, which consists of a C_{12} to C_{14} diethylene oxide sodium sulfate salt. (See Fig. 8.5.)



(IV)

Figure 8.5

References

1. Bruno Deflort et al., *Isosorbide derivatives that can be used in detergent compositions for gasoline-type fuels*, U.S. Patent 6,527,816 (March 4, 2003)
2. Catherine Breffa et al., *Use of isosorbide ethers in detergents and cleaners*, U.S. Patent 8,008,246 (August 30, 2011)
3. Catherine Breffa et al., *Anionic isosorbide derivatives and their use*, U.S. Patent 8,334,318 (December 8, 2012)
4. Ansgar Behler et al., *Anionic isosorbide derivatives and their use*, U.S. Patent Application 20100324153 (December 23, 2010)

Methylglycine-N,N-Diacetic Acid-Containing Detergents

Author	Somerville Roberts et al.
Patent Title	***Aminocarboxylic builder particle,*** U.S. Patent 8,357,650 (January 22, 2013)

Relevant Prior Patents by Author or Coauthors

Process for making a detergent composition comprising a hydrophilic silica and a copolymer containing a carboxylic acid monomer and a sulfonic acid monomer, U.S. Patent 8,288,333 (October 16, 2012)

Catalytic laundry detergent composition comprising relatively low levels of water-soluble electrolyte, U.S. Patent 8,211,848 (July 3, 2012)

Detergent composition, U.S. Patent 8,183,196 (May 22, 2012)

Low-builder, highly water-soluble, low-density solid laundry detergent composition, U.S. Patent 8,080,509 (December 11, 2011)

Particle for imparting a fabric-softening benefit to fabrics treated therewith and that provides a desirable suds suppression, U.S. Patent 8,003,592 (August 23, 2011)

Solid laundry detergent composition comprising anionic detersive surfactant and calcium-augmented technology, U.S. Patent 7,910,533 (May 22. 2011)

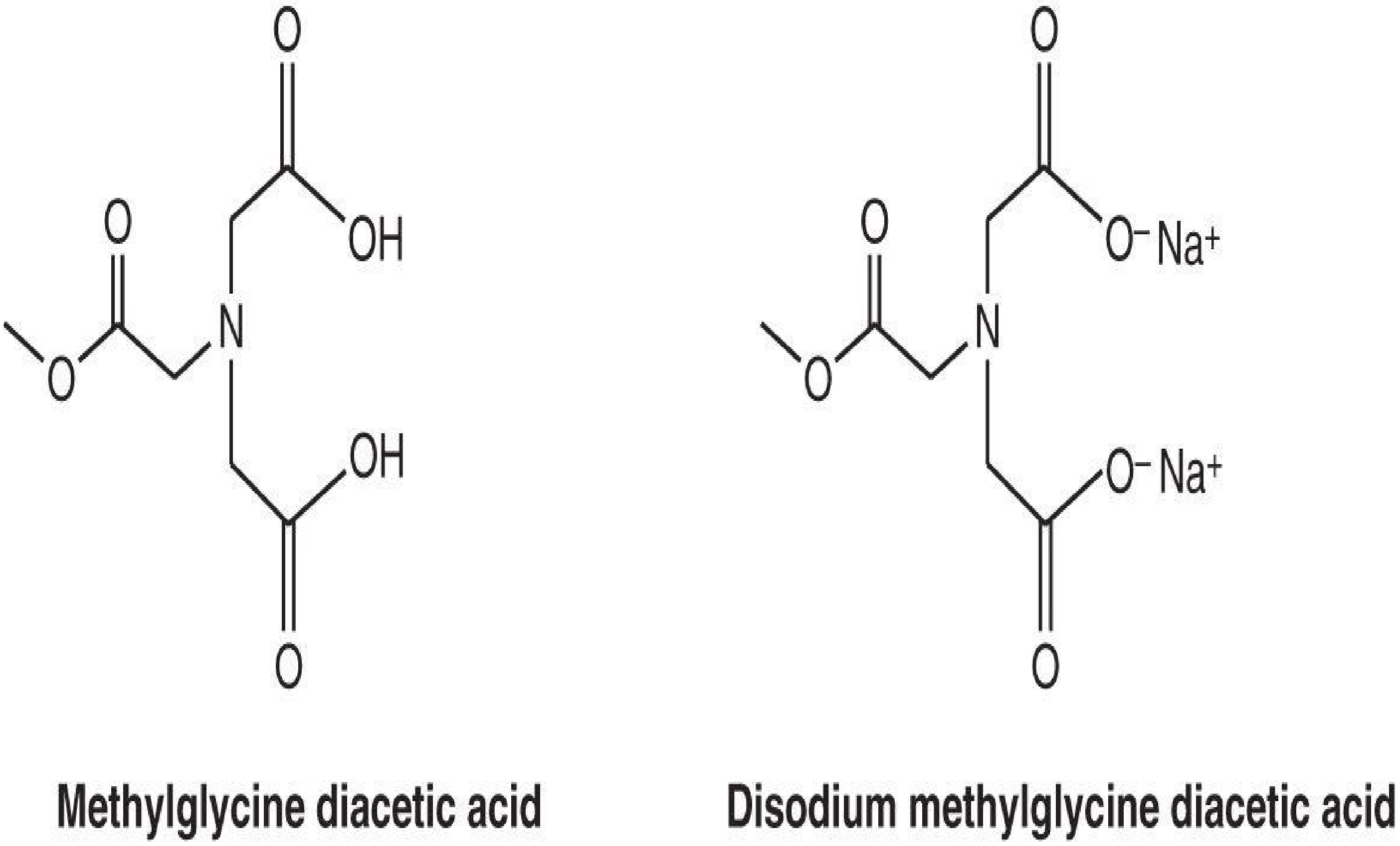
Product Application

Methylglycine-N,N-diacetic acids and their alkali metal salts were prepared and evaluated as replacements for phosphates in consumer and industrial detergent formulations. Methylglycine-N,N-diacetic acid derivatives are completely biodegradable and are effective as all-purpose cleaning additives that can be used in either liquid or solid detergent formulations.

Significance of Current Application

It is the objective of this investigation to replace environmentally non-degradable and moderately toxic phosphate builders in detergent formulations with biodegradable, non-toxic, and cost-effective material alternatives. Two hurdles, however, had to be addressed before a viable phosphate replacement could be identified. First, phosphates are excellent moisture sinks that contribute to both moisture management and the stability of the detergent package. Experimentally, the author has demonstrated in this study that alkali metal salts of methylglycine-N,N-diacetic acid and derivatives exhibit the identical moisture management properties. A second consideration is that when phosphates have been removed from the detergent package, detergency of the product must remain unchanged. This requirement was also experimentally demonstrated by the author using the environmentally friendly methylglycine-N,N-diacetic acid. The detergent package containing methylglycine-N,N-diacetic acid was as effective at lower additive treatment levels to obtain phosphate cleaning equivalency.

Renewable Components



Methylglycine diacetic acid

Disodium methylglycine diacetic acid

Figure 8.6

Sodium or potassium salts of methylglycine-N,N-diacetic acid are particularly preferred because of their low hygroscopicity and their high solubility in water. The preparation of methylglycine-N,N-diacetic acid is described by Greindl,[1] while the general preparation of other alkyldiacetic acid derivatives is described by Schneider,[2] as illustrated in Fig. 8.7 for α-D l-alanine-N,N-diacetic trisodium salt, (I), beginning with iminodiacetonitrile, (II). Finally, methylglycine diacetic acid and analogues can be used as phosphate-replacement additives in a wide variety of consumer cleaning products.

Product Formation

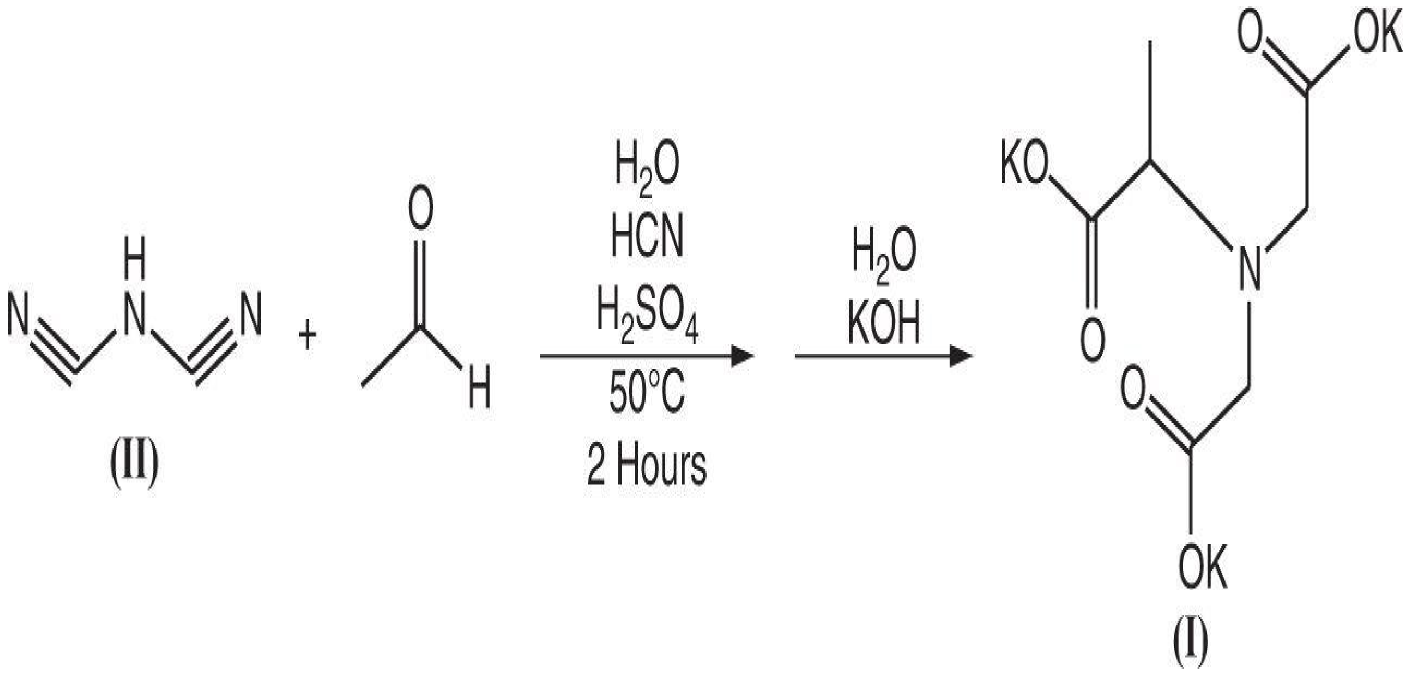


Figure 8.7

Experimental

1. Preparation of quick-dissolving methylglycine-N,N-diacetic acid and alkali metal salt. The process for preparing quick-dissolving methylglycine-N, N-diacetic acid and salts involves a five-step procedure entailing:

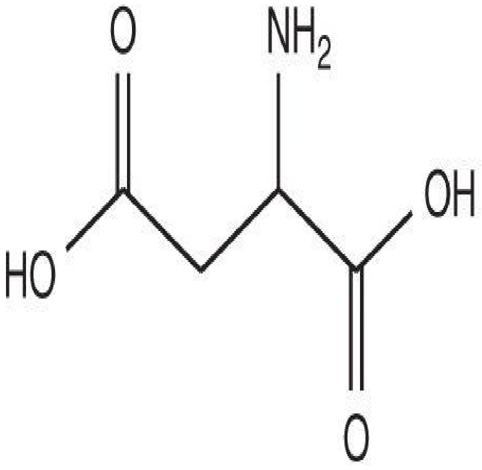
1. An aqueous solution between 25 wt% and 40 wt% of the aminocarboxylic builder salt is prepared.
2. The Step 1 solution was then treated with a sufficient amount of sulphuric acid at 20°C to obtain a solution pH range between 3 and 5. The solution was then treated with acetaldehyde and heated at 50°C for 2 hours.
3. The Step 2 solution was then further treated with sulphates or citrates in order to lower the hygroscopicity of methylglycine-N, N-diacetic acid and to produce micronized particles.
4. The Step 3 solution was then dried by evaporation and methylglycine-N,N-diacetic acid was isolated.
5. Methylglycine-N,N-diacetic acid was then dissolved in water to make a 45% solution that neutralized with a slight excess of potassium hydroxide.

Testing

No testing data was supplied by the author.

Notes and Observations

1. Preuschen[3] prepared a biodegradable automatic dishwashing cleaner by heating a mixture of aspartic acid, (III), adenosine diphosphate, (IV), and polyethelyneglycol. The product mixture formed from this reaction was not characterized. (See Fig. 8.8.)



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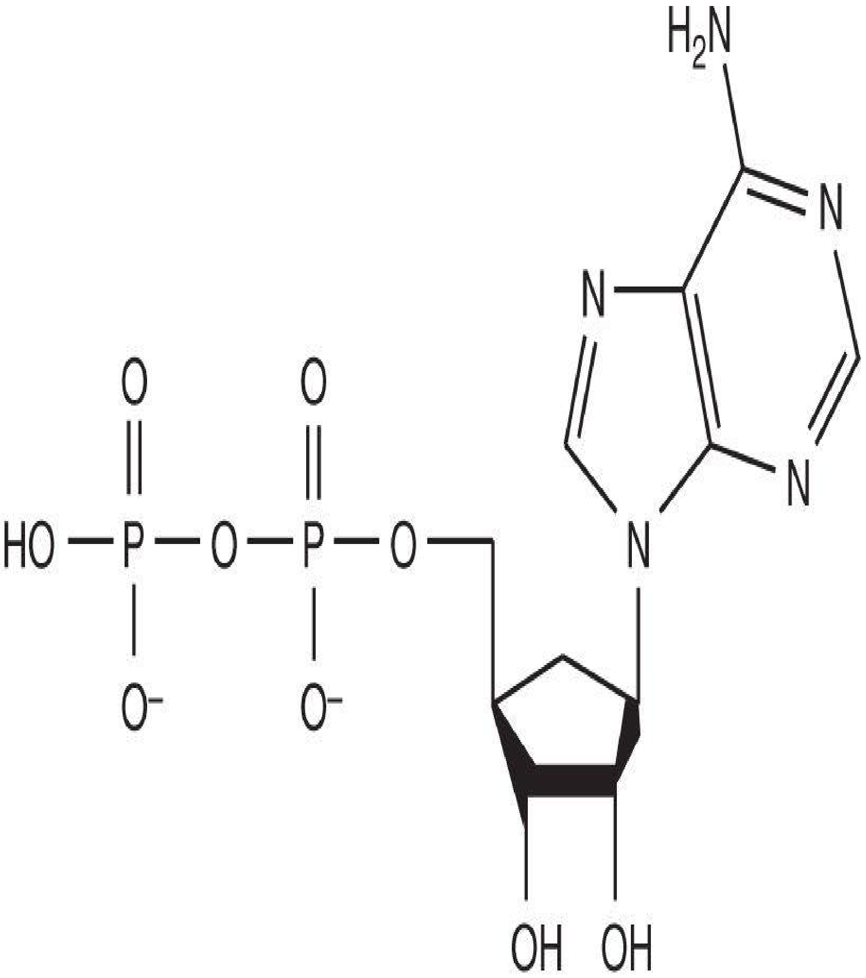

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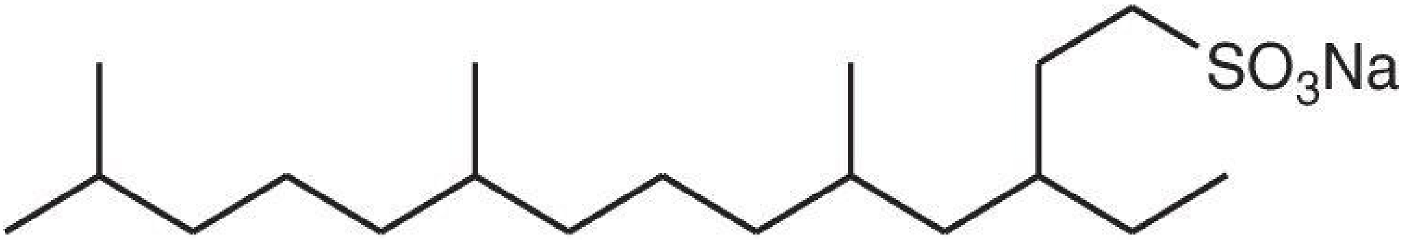

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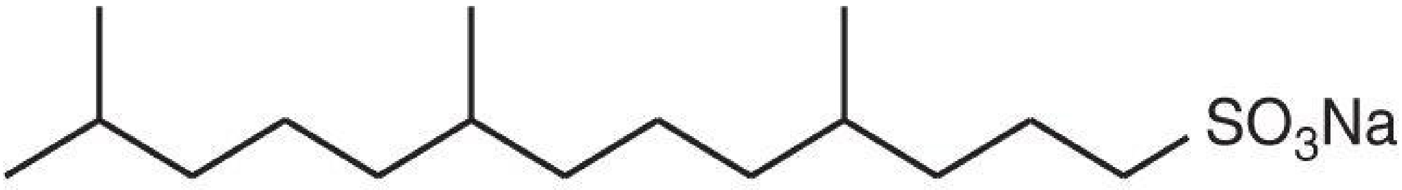
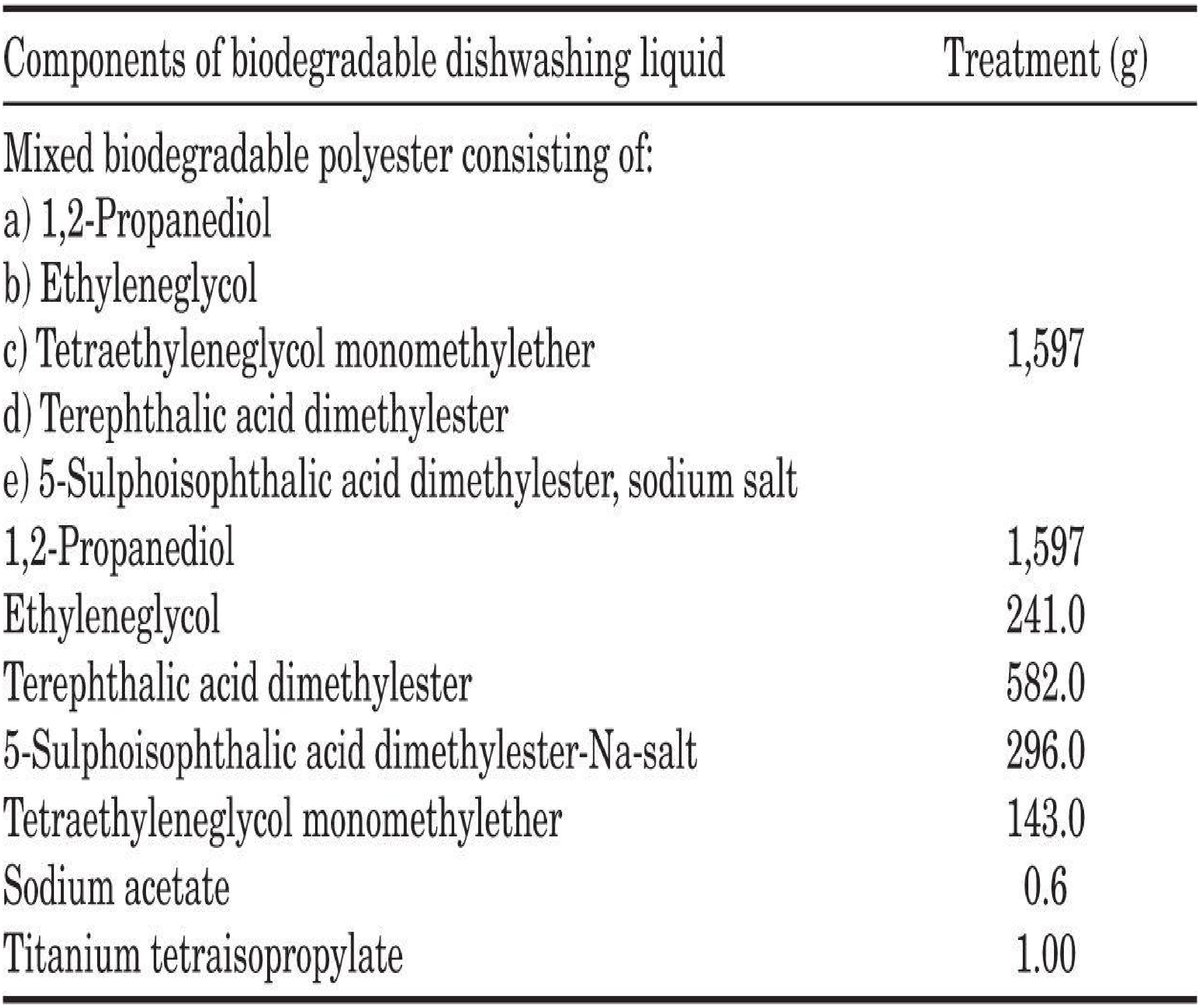


(VI)

Figure 8.8

2. Geret[4] prepared a biodegradable automatic dishwashing detergent tablet containing a five-component biodegradable polyester, as illustrated in Table 8.2.

TABLE 8.2 Composition of biodegradable dishwashing liquid detergent containing a five-component biodegradable polyester (comprising (a)–(e). Dishwashing tablets prepared from this formulation contained 9 wt% of the biodegradable polymer.



Components of biodegradable dishwashing liquid	Treatment (g)
Mixed biodegradable polyester consisting of:	
a) 1,2-Propanediol	
b) Ethyleneglycol	
c) Tetraethyleneglycol monomethylether	1,597
d) Terephthalic acid dimethylester	
e) 5-Sulphoisophthalic acid dimethylester, sodium salt	
1,2-Propanediol	1,597
Ethyleneglycol	241.0
Terephthalic acid dimethylester	582.0
5-Sulphoisophthalic acid dimethylester-Na-salt	296.0
Tetraethyleneglycol monomethylether	143.0
Sodium acetate	0.6
Titanium tetraisopropylate	1.00

3. Scheibel[5] prepared biodegradable laundry detergent formulations containing highly branched aliphatic anionic surfactants, (V) and (VI), as cleaning agents. The highly branched anionic surfactants, however, required four synthetic steps to prepare, and the essential intermediates were isolated in modest-to-moderate yields, as illustrated in Eq. 1. (See Fig. 8.9.)

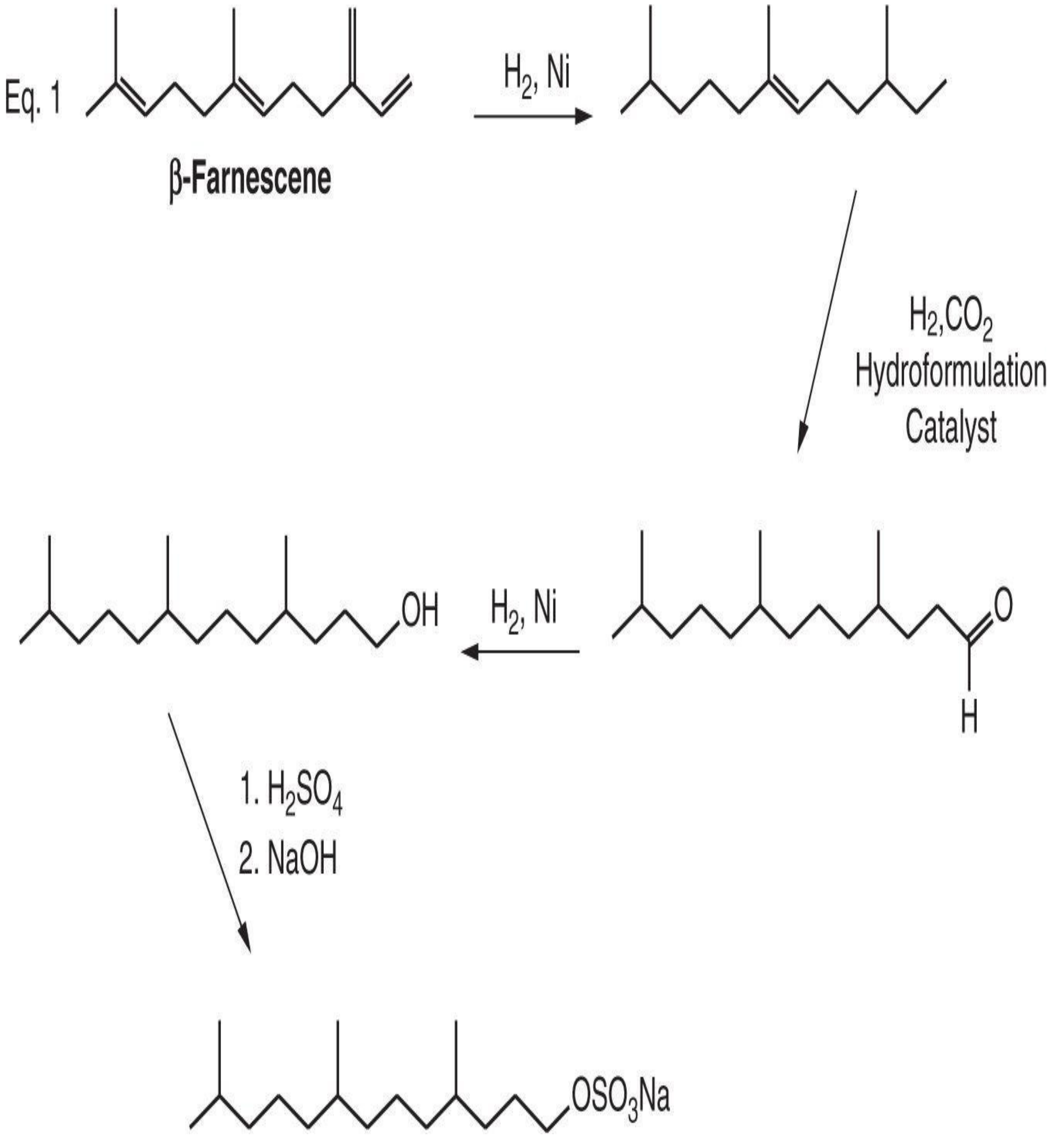
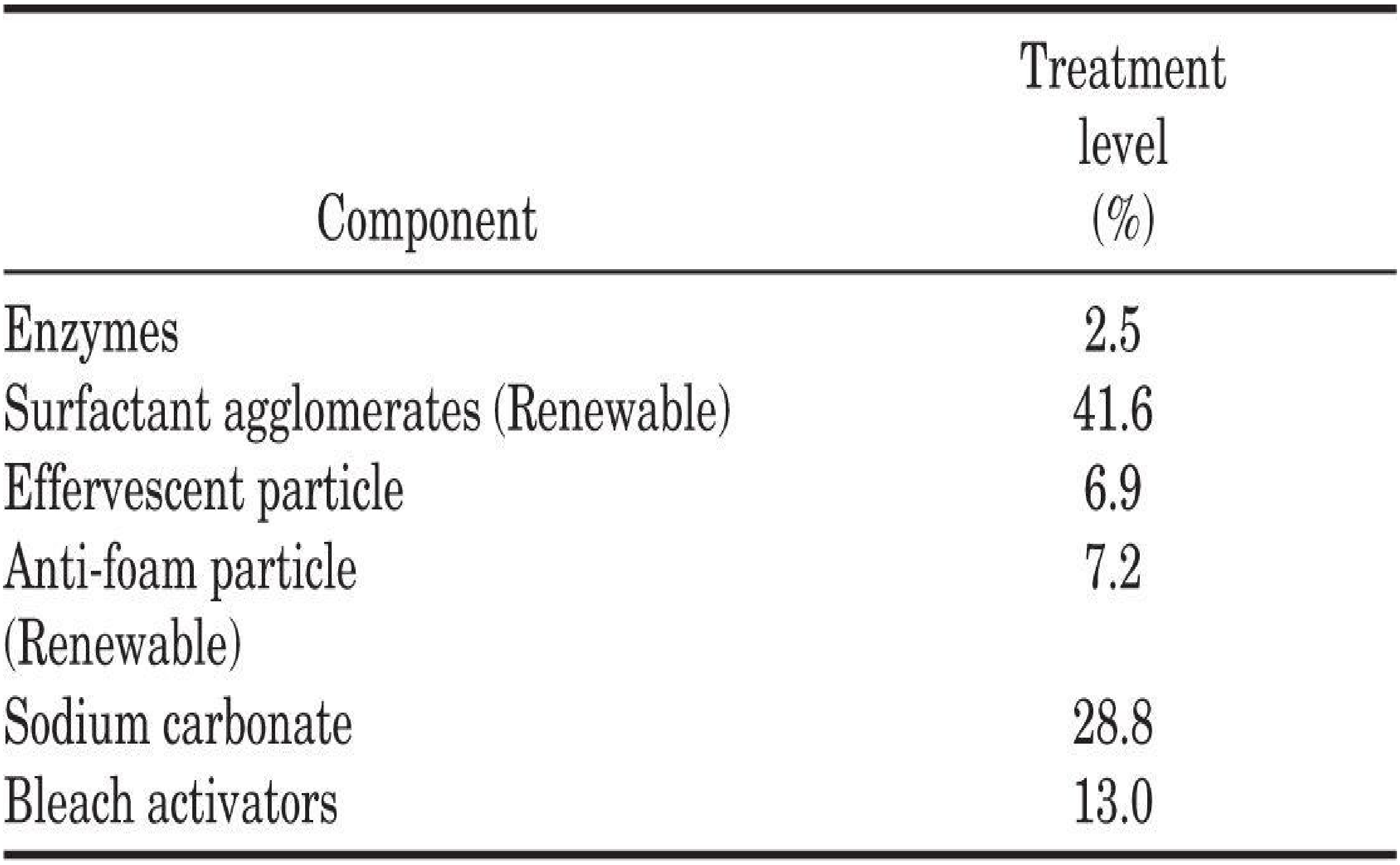


Figure 8.9

4. In an earlier investigation by the author,[6] biodegradable laundry formulations were prepared and then placed in perforated pouches to slowly disperse renewable components over a three-cycle wash. Components of this formulation are provided in Table 8.3.

TABLE 8.3 Detergent formulation contained in renewable laundry pouches that were designed to deliver components over a three-cycle wash.



Component	Treatment level (%)
Enzymes	2.5
Surfactant agglomerates (Renewable)	41.6
Effervescent particle	6.9
Anti-foam particle (Renewable)	7.2
Sodium carbonate	28.8
Bleach activators	13.0

References

1. Thomas Greindl et al., *Preparation of glycine-N,N-diacetic acid derivatives*, U.S. Patent 5,849,950 (December 15, 1998)

2. Juergen Schneider et al., *Use of glycine-N,N-diacetic acid derivatives as biodegradable complexing agents for alkaline earth metal ions and heavy metal ions and process for the preparation thereof*, U.S. Patent 5,786,313 (July 28, 1998)

3. Judith Preuschen et al., *Composition*, U.S. Patent Application 20110053819 (March 3, 2011)

4. Laurence Geret et al., *Detergent composition*, U.S. Patent Application 20100197546 (August 5, 2010)

5. Jeffrey John Scheibel et al., *Specific branched aldehydes, alcohols, surfactants, and consumer products based thereon*, U.S. Patent Application 20100137649 (June 3, 2010)

6. Somerville Roberts et al., *Pouched compositions*, U.S. Patent Application 20050049164 (March 3, 2005)

Chapter

9

Diesel Fuel

Anti-Flocculation Diesel Fuel Additive

Author Gerardus Johannes Maria Gruter

Patent Title ***Method for the synthesis of organic acid esters of 5-hydroxymethylfural and their use***, U.S. Patent 8,242,293 (August 14, 2012)

Relevant Prior Patents by Author

5-Substituted 2-(alkoxymethyl)furans, U.S. Patent 8,231,693 (July 31, 2012)

Method for the synthesis of 5-alkoxymethyl furfural ethers and their use, U.S. Patent 8,133,289 (March 13, 2012)

Product Application

5-Acetoxymethylfurfural is effective as a diesel fuel additive to minimize flocculation problems.

Significance of Current Application

The primary purpose of this investigation was to identify diesel fuel anti-flocculating agents. A mixture consisting of 10 wt% of 5-hydroxymethylfurfural and 90 wt% of 5-acetoxymethylfurfural was subsequently identified and empirically shown to minimize flocculation in diesel fuel. The biomass-derived renewable reagent that was used to generate the diesel fuel anti-flocculation compound was sucrose.

Furfural derivatives prepared using inexpensive sucrose have never been used in the preparation of this chemical route, and it is anticipated that multi-ton quantities will be generated and used in diesel fuel formulations. Finally, since the reaction product mixture does not require purification before being used as an anti-flocculation agent, the process becomes even more cost effective.

A secondary purpose of this investigation was to identify a direct route for preparing furan dicarboxylic acid derivatives from sucrose for use as a terephthalic acid replacement monomer when preparing polyesters. Derivatized furans are currently bio-generated almost exclusively using fructose, which is relatively expensive when compared to either glucose or sucrose. The current investigation also addresses this concern by preparing chemically modifiable 5-hydroxy-methylfurfural and 5-acetoxymethylfurfural in moderate yields using sucrose.

Product Formation

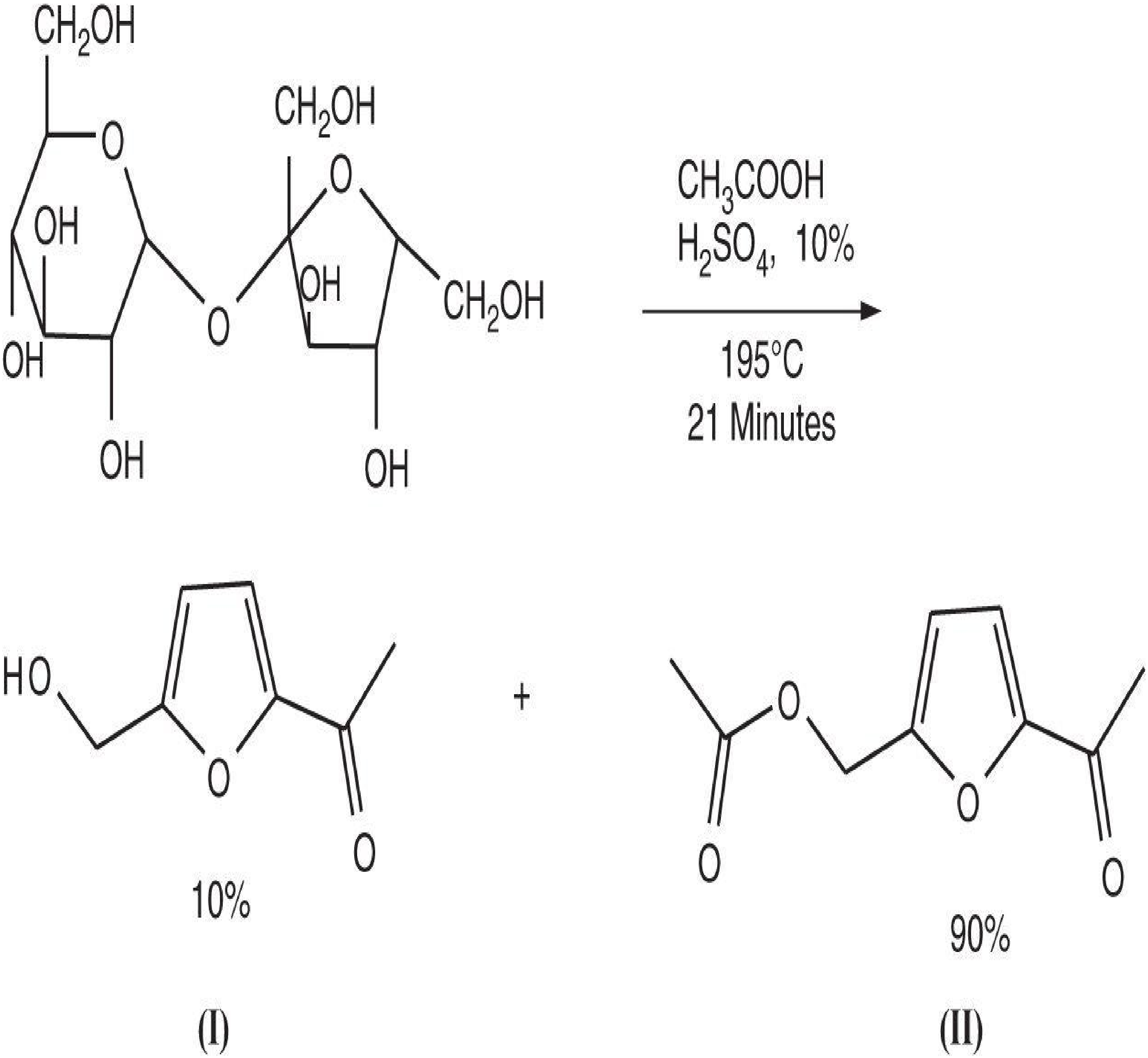


Figure 9.1

Experimental

1. Preparation of 5-hydroxymethylfurfural and 5-acetoxymethylfurfural. In a continuous-flow reactor, sucrose-containing acetic acid and 10% sulfuric acid was added to the reactor at 10 mmol/L. The mixture was heated to 195°C with a residence time between 6 and 60 seconds at a flow rate of 3.33 mL/min/reactor. After 21 minutes, the products were separated and isolated by HPLC and mass spectrometry, which were used to identify the reaction-product mixture as 5-hydroxymethylfurfural, (I), and 5-acetoxymethylfurfural, (II). The mixture had a product selectively of 1:9 with a combined product yield of 25%. Structural characterization of both reaction products was then performed using ^{1}H- and ^{13}C-NMR.

Testing

A. Blending properties. A small-scale model diesel engine was fueled with normal diesel fuel additized with 1 wt%, 2 wt%, 3 wt%, 5 wt%, and 10 wt% of a commercially available diesel additive containing a mixture of varying ratios of 5-hydroxymethylfurfural, (I), and 5-acetoxymethylfurfural, (II). At 2 wt% treatment, the commercially additized fuel became opaque. When additized with equivalent amounts of the experimental mixture generated in Step 1, which contain 90 wt% of 5-acetoxymethylfurfural, the fuel remained clear at treatment levels of up to 15 wt%.

Notes and Observations

1. 5-Hydroxymethylfurfural and 5-acetoxymethyl-furfural were initially prepared by Tyrlik[1] by the dehydration of glucose. In the same investigation, mixtures of 5-hydroxymethylfurfural and 5-acetoxymethylfurfural were also prepared by reacting 4-acetylbutyrolactone with glucose, trioxane, and aluminum chloride.

2. Lightner[2] used 10% sulfuric acid at 100°C to hydrolyze biomass-derived sucrose and isolated a mixture of 5-hyroxymethylfurfural, (I), and furfural, (III). Further treatment of the product mixture with sulfuric acid produced heterocyclic-ring-opening that generated levulinic acid, (IV), and formic acid, (V). The experimental four-component mixture was marginally effective when used as an anti-flocculation agent in diesel fuel. (See Fig. 9.2.)

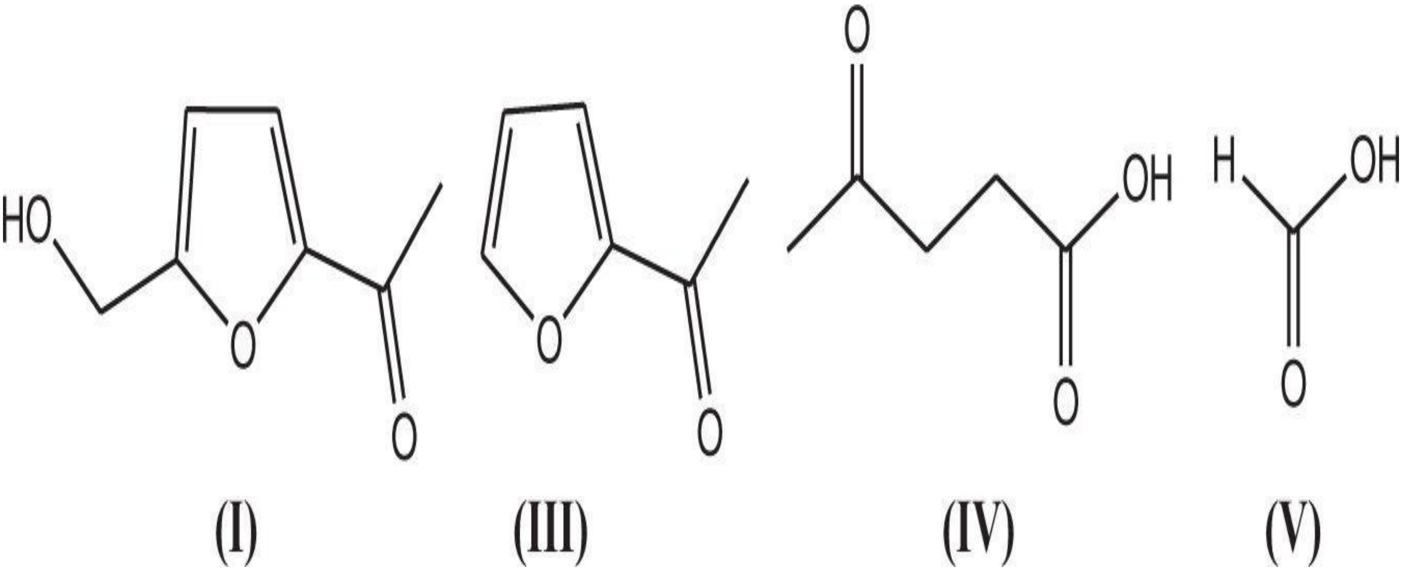
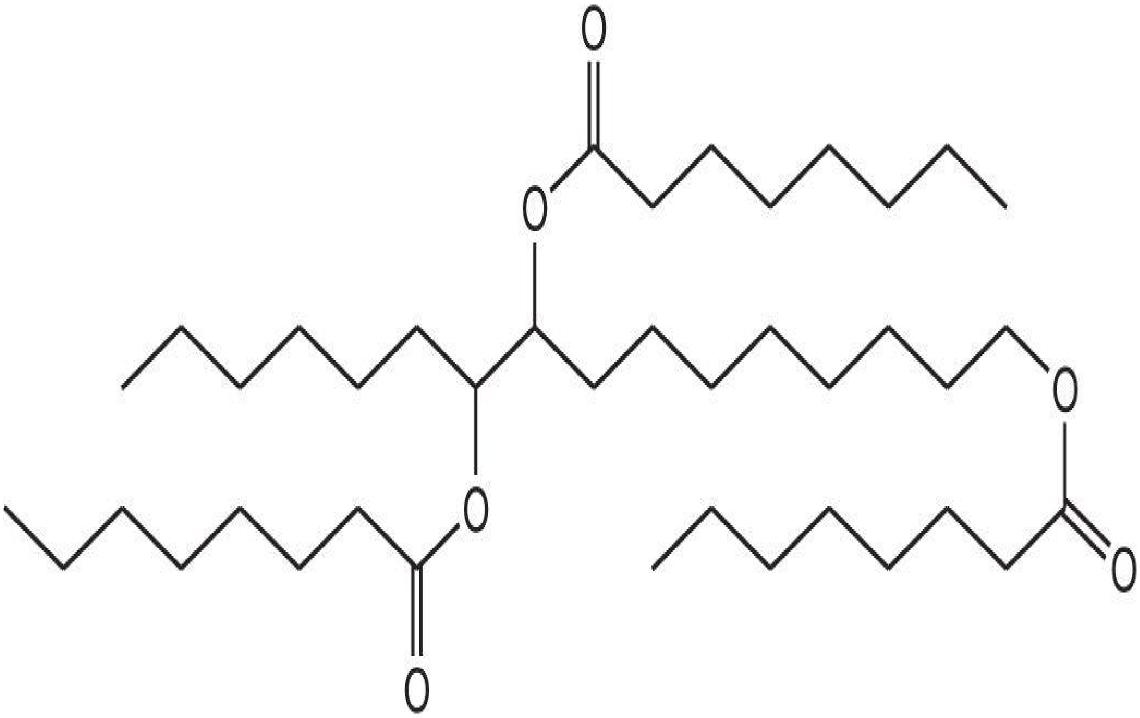


Figure 9.2

3. Triester lubricant additives, notably octadecane-1,9,10-triyl trioctanate, (VI), and octadecane-1,9,10-triyl trisdecanoate, (VII), were prepared by Elomari[3] utilizing a biomass precursor and then used to improve the lubricity of diesel fuel. (See Fig. 9.3.)



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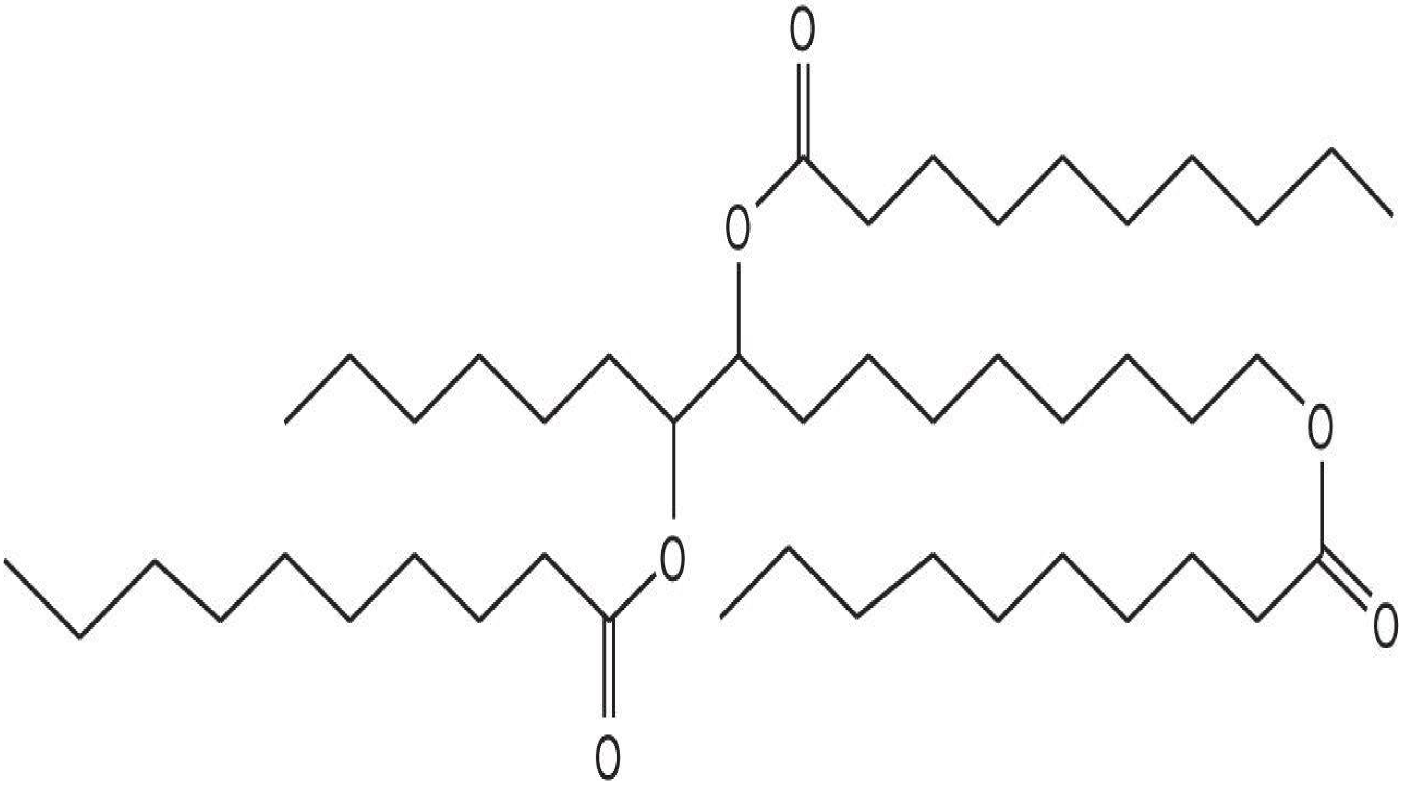
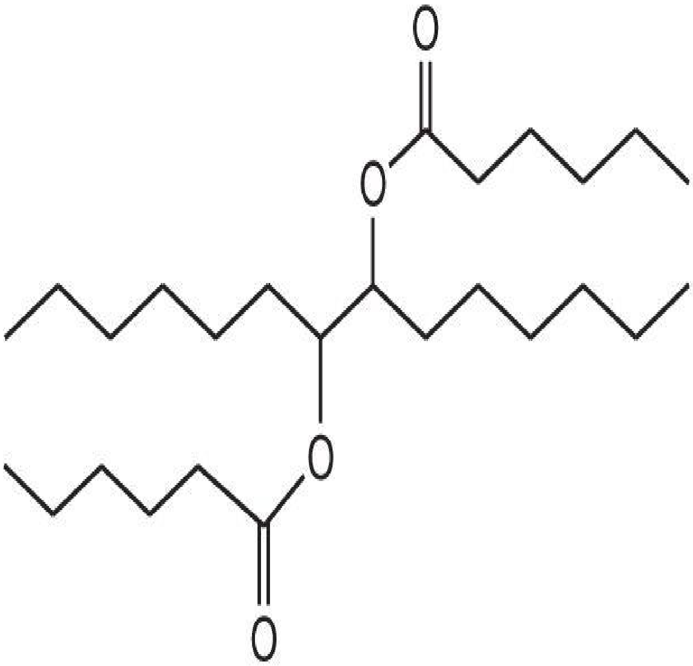


(VII)

Figure 9.3

4. In a separate investigation by Elomari,[4] bio-derived esters, particularly hexanoic acid 2-hexanoyloxy-1-hexyl-octyl ester, (VIII), and 9,10-bis-decanoyloxy-octadecanoic decyl ester, (IX), were determined to be effective as refrigeration lubricants. (See Fig. 9.4.)



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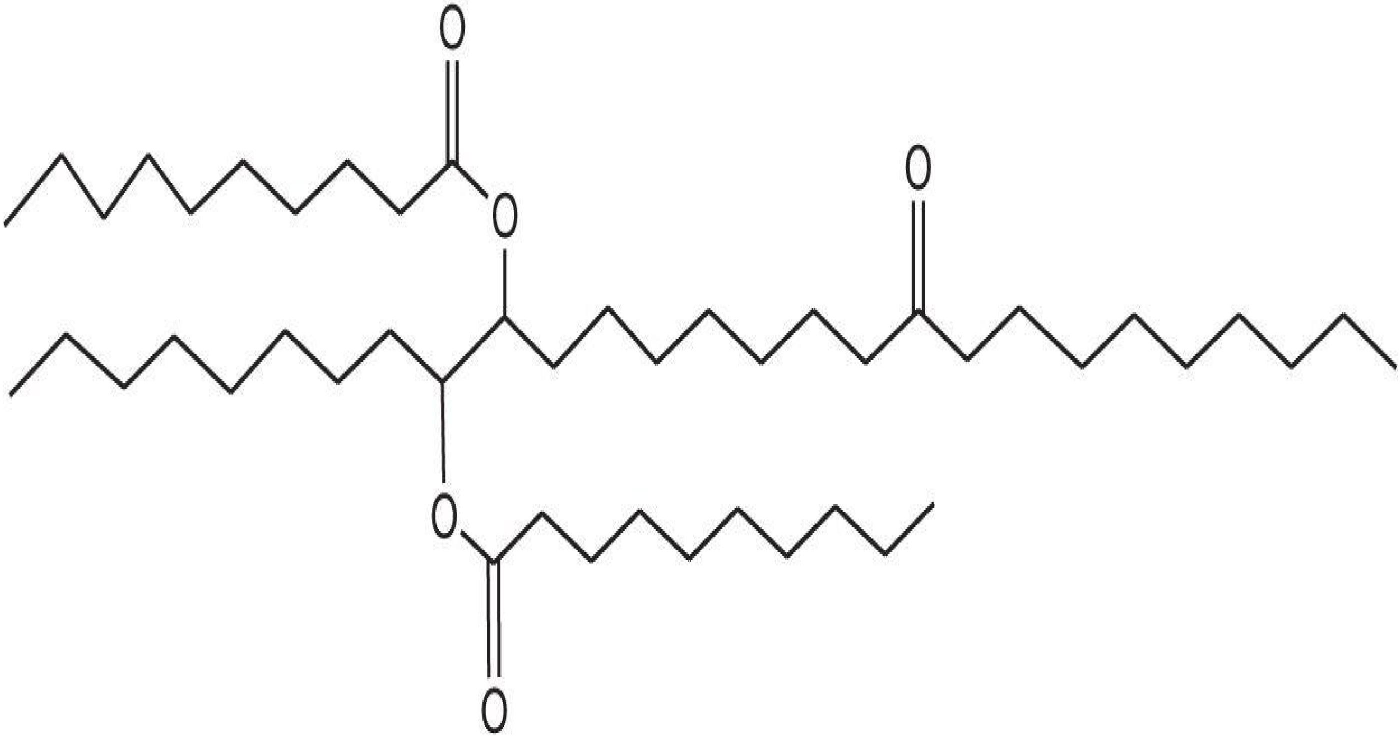


(IX)

Figure 9.4

References

1. S. Tyrlik et al., *Selective dehydration of glucose to 5-hydroxymethylfurfural and a one-pot synthesis of a 4-acetylbutyrolactone from glucose and trioxane in solutions of aluminum salts*, Carbohydrate Research, vol. 315, pp. 268–272, 1999; ibid, Carbohydrate Research, vol. 315, 268–272, (1999)

2. Gene E. Lightner, *Additives derived from biomass extracted by biodiesel fuel oil*, U.S.

Patent 7,520,905 (April 21, 2009)

3. Saleh A. Elomari et al., *Biolubricant esters from the alcohols of unsaturated fatty acids*, U.S. Patent 8,304,574 (November 6, 2012)

4. Saleh A. Elomari et al., *Refrigeration oil from gas-to-liquid from bio-derived diesters*, U.S. Patent 8,268,187 (September 18, 2012)

Biologically Derived Diesel Fuel

Author Monica Bhatia et al.

Patent Title ***Reduction of the toxic effect of impurities from raw materials by extractive fermentation,*** U.S. Patent 8,313,934 (November 20, 2012)

Relevant Prior Patents by Author or Coauthors

Transesterification of biodiesel feedstock with solid heterogeneous catalyst, U.S. Patent 8,580,119 (November 12, 2013)

Process for the production of fatty acid alkyl esters, U.S. Patent 8,580,986 (November 12, 2013)

Conversion of saponifiable lipids into fatty esters, U.S. Patent 8,569,530 (October 29, 2013)

Enclosed bioreactor system and methods associated therewith, U.S. Patent 8,569,050 (September 24, 2013)

Product Application

Biodiesel fuel for use in private and commercial vehicles was prepared in relatively high yields using inexpensive and readily available carbohydrates when fermented with the genetically engineered strain of E. coli, LS9-ID1.

Significance of Current Application

In the initial phase of this ongoing investigation, the genetically engineered strain of E. coli, LS9-ID1, was empirically determined to be effective in producing non-petroleum generated diesel fuel from either glucose, fructose, or pentoses. In addition, the E. coli strain also is effective in generating biodiesel from contaminated sugar, starch, or carbohydrates. It is further anticipated that E. coli, LS9-ID1, will be used to generate other bio-products in modified fermentation reactions.

Experimental

1. Preparation of biodiesel using carbohydrates in non-contaminated broth. A culture of the genetically engineered strain of E. coli, LS9-ID1, was transferred from a frozen stock and incubated in Luria-Bertani broth for approximately three hours. The culture was then transferred to a mineral medium commonly used for E. coli, M9, which was buffered and supplemented with thiamine and trace minerals. The culture was then further incubated and used to inoculate the same fermentation media with 50 g/L containing either glucose, fructose, or mixed pentoses.

Culture growth was then induced using IPTG and the mixture treated with either 10 mL of methanol or ethanol in shake flasks to initiate the fermentation process and subsequent formation of biodiesel fuel. In a typical reaction, glucose and other carbohydrates were consumed within 24 to 40 hours where the formation of biodiesel was maximized. During the fermentation process, the reaction extent was monitored by optical density measurements at 600 nm. The reaction was also monitored using HPLC to determine carbohydrate degradation.

2. Preparation of biodiesel using contaminated broth. Biodiesel was also prepared by extractive fermentations using the engineered strain of E. coli, LS9-ID1, which is designed to improve the performance of the fermentation process in the presence of toxins. In this process, biodiesel was prepared using the Step 1 procedure. In addition, two sets of duplicate flasks were prepared containing different concentrations of toxic agents illustrated in (I) through (V). The first set served as the control, which included the toxin without the hydrophobic solvent extract. In the second set, the hydrophobic solvent extract was added in a volume ratio of 1:3 solvent-to-fermentation broth, respectively. The flasks were then inoculated and incubated at 37°C in agitated shakers. When optical density measurements at 600 nm reached a value of 1, the cultures were treated with 1 mM of IPTG and 20 mL/L methanol. Cell growth and the production of fatty acid methyl esters were then measured after 24 hours. In the control set lacking a hydrophobic solvent, optical densities at 600 nm were obtained by direct measurements of the fermentation broth. Optical densities of flasks containing a hydrophobic solvent were measured after the broth was centrifuged and the cell pellet re-suspended in the same volume of distilled water.

Testing Results

Carbohydrates solutions fermented with the engineered strain of E. coli, LS9-ID1 in solutions containing the organic contaminants including furfural, (I), syringealdehyde, (II), 4-hydroxybenzaldehyde, (III), 5-hydroxymethylfurfural, (IV), and guaiacol, (V), in the presence of fatty acids methyl esters were approximately 85% as effective in generating biodiesel as fermentations conducted in contaminated-free broth.

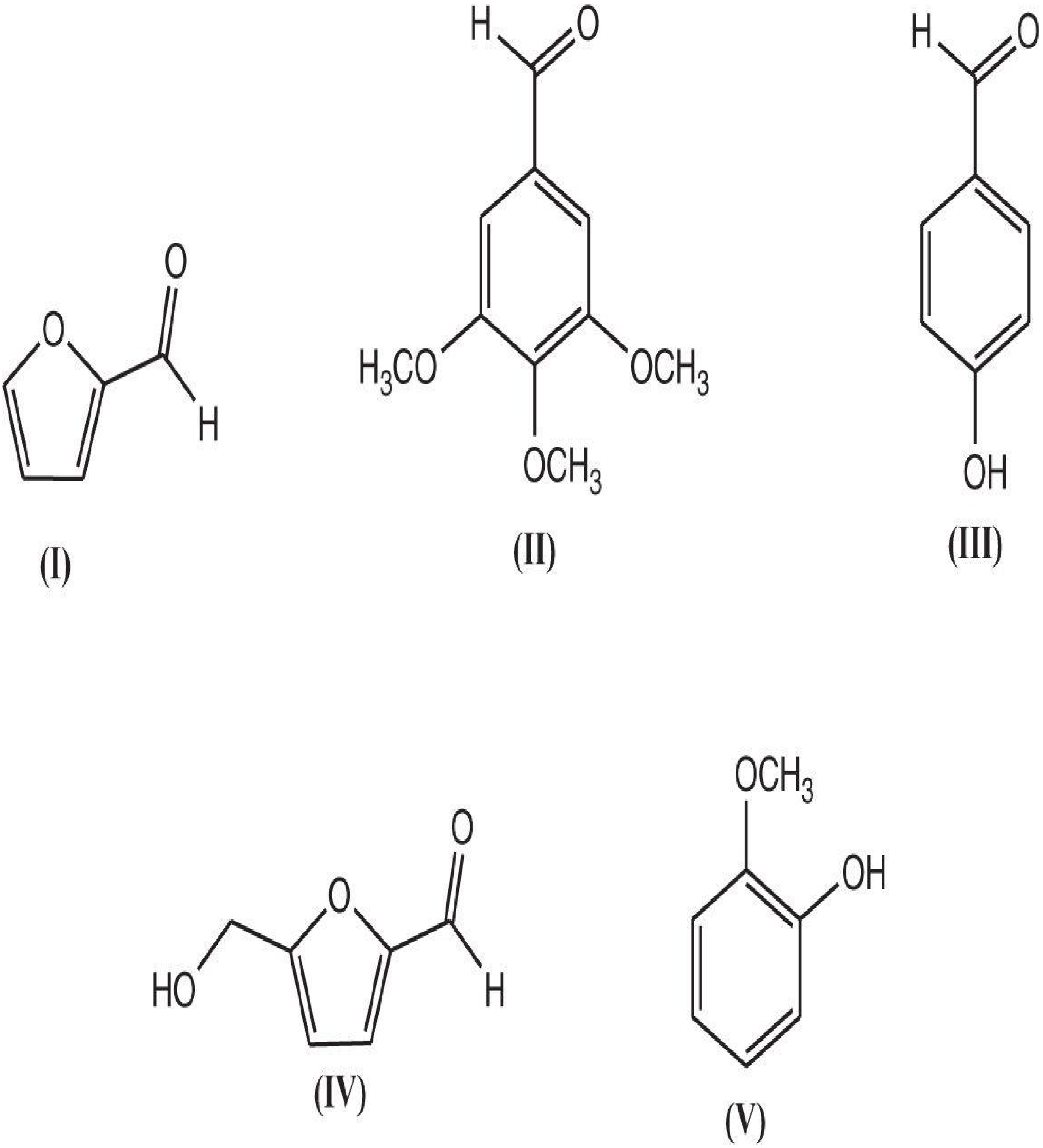
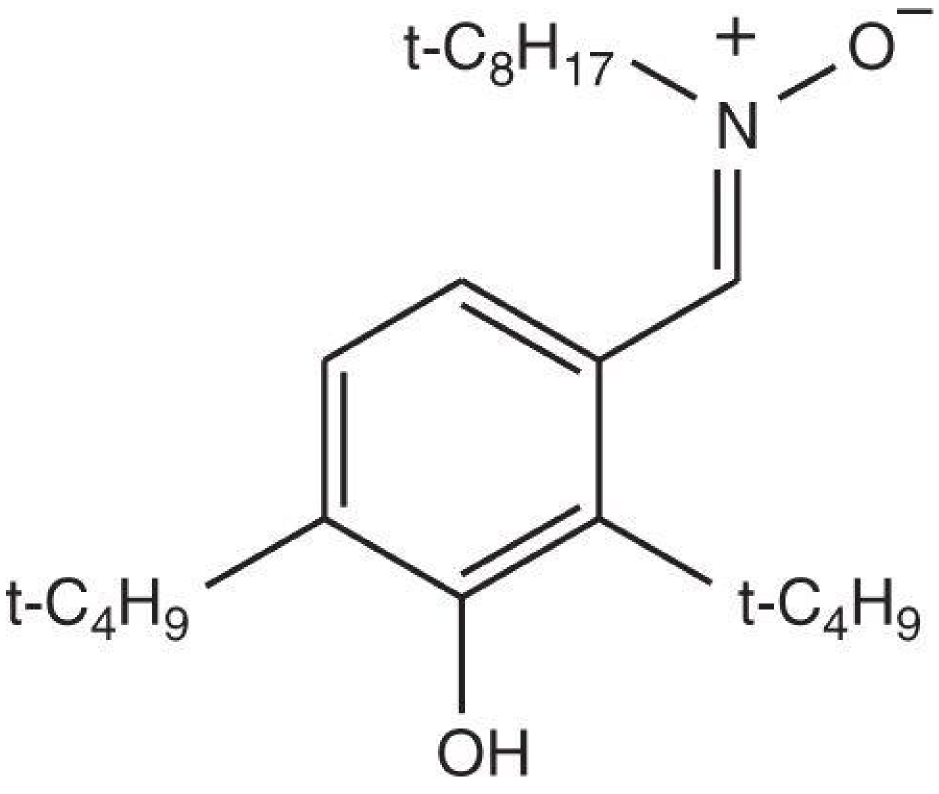

(I) (II) (III) (IV) (V)

Figure 9.5

Notes and Observations

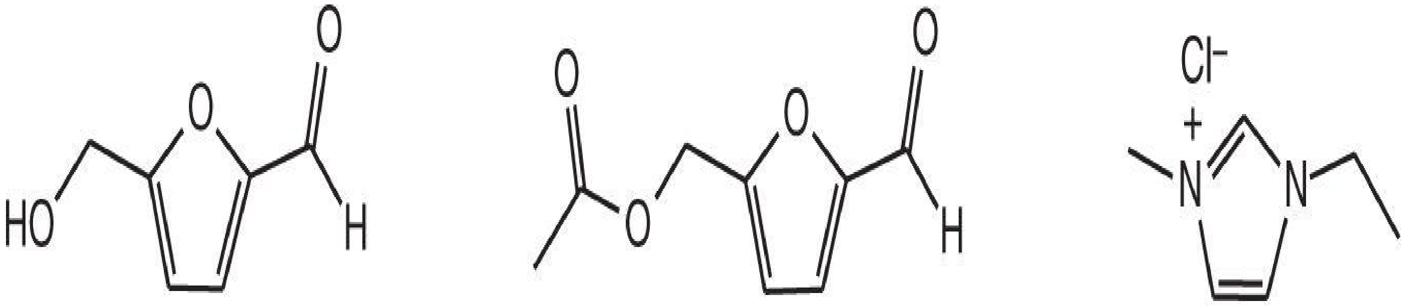
1. Banavali[1] determined that 2,6-di-t-butyl-4-(N-t-octyl) nitronyl phenol, (VI), was a particularly effective anti-oxidant for biodiesel. (See Fig. 9.6.)



(VI)

Figure 9.6

2. Kalel[2] treated wet algal biomass with green microalgae Scendesmus dimorphus to recover fatty acid esters that were used as components in biodiesel fuel blends.
3. A photobioreactor apparatus containing genetically enhanced photoautotrophic agents, cyanobacteria and algae was prepared by Woods[3] and used to prepare large quantities of ethanol. Ethanol produced from this process was subsequently used as blending component in biofuel formulations.
4. Gruter[4] used glucose and fructose to prepare both hydroxymethylfurfural, (VII), and 5-acetoxy methyl furfural, (VIII), in high yields by treating acetic acid containing chromium (II) chloride in the presence of the ionic solvent, 1-ethyl-3-methylimidazolium chloride, (IX). Products obtained from this process were used as components in both biodiesel and automotive fuel formulations. (See Fig. 9.7.)



(VII) (VIII) (IX)

Figure 9.7

References

1. Rajiv Manohar Banavali et al., *Preparation of nitrones*, U.S. Patent 8,329,949 (December 11, 2012)

2. Aniket Kalel, *Methods of extracting neutral lipids and recovering fuel esters*, U.S. Patent 8,318,018 (November 27, 2012)

3. R. Paul Woods et al., *Closed photobioreactor system for continued daily in situ production of ethanol from genetically enhanced photosynthetic organisms with means for separation and removal of ethanol*, U.S. Patent 8,323,958 (December 4, 2012)

4. Gerardus Johannes Maria Gruter et al., *Hydroxymethylfurfural ethers and esters prepared in ionic liquids*, U.S. Patent 8,314,260 (November 20, 2012)

Chapter

10

Eyeglasses

Non-Yellowing Eyeglass Lenses Using Isosorbide Polycarbonates

Author	Jean Francois Morizur
Patent Title	***Isosorbide-containing polycarbonates and their preparation,*** U.S. Patent 8,372,943 (February 12, 2013)

Relevant Prior Patents by Author

Isosorbide-based polycarbonates, method of making, and articles formed therefrom, U.S. Patent 8,273,849 (September 25, 2013)

Polycarbonate graft copolymers, U.S. Patent 8,426,532 (April 23, 2013)

Polycarbonate polymers containing bisphenol compounds, U.S. Patent 8,207,287 (June 26, 2012)

Bisphenol compounds and methods of making, U.S. Patent 8,202,960 (June 19, 2012)

Method for making carbonates and esters, U.S. Patent 7,977,447 (July 12, 2011)

Polyetherimide/polyphenylene ether sulfone blends, U.S. Patent 8,034,857 (October 11, 2011)

Method of making isosorbide polycarbonate, U.S. Patent 7,863,404 (July 4, 2011)

Polycarbonate resins method of manufacture, and articles formed there from, U.S. Patent 7,858,728 (December 25, 2010)

Method for making carbonates and esters, U.S. Patent 7,977,447 (July 12, 2011)

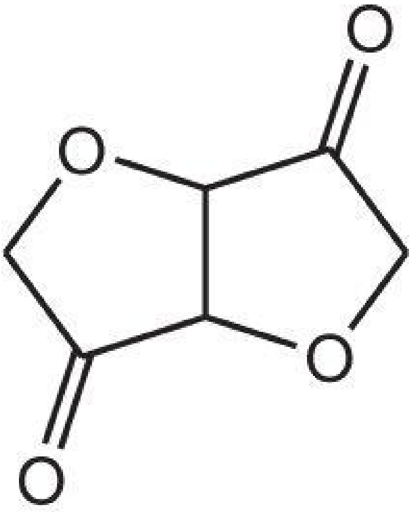
Product Application

Polycarbonate copolymers containing renewable isosorbide are intended for use as both eyeglass lenses and safety glass.

Significance of Current Application

The preparation polycarbonates involves a number of trade-offs. For example, low reactivity of monomers can be compensated by increasing catalyst concentration or either reaction time or temperature. This invariably produces polycarbonates with varying degrees of yellowness in the transparent material. To address this concern the incorporation of isosorbide as a reaction monomer was used in preparing homo- or co-polycarbonates. Lenses generated using this monomer were found to both colorless and easily processed using molding or extrusion methods. Finally molecular weights of isosorbide homo- or co-polycarbonates was determined to be acceptably high for commercial applications.

Renewable Agent

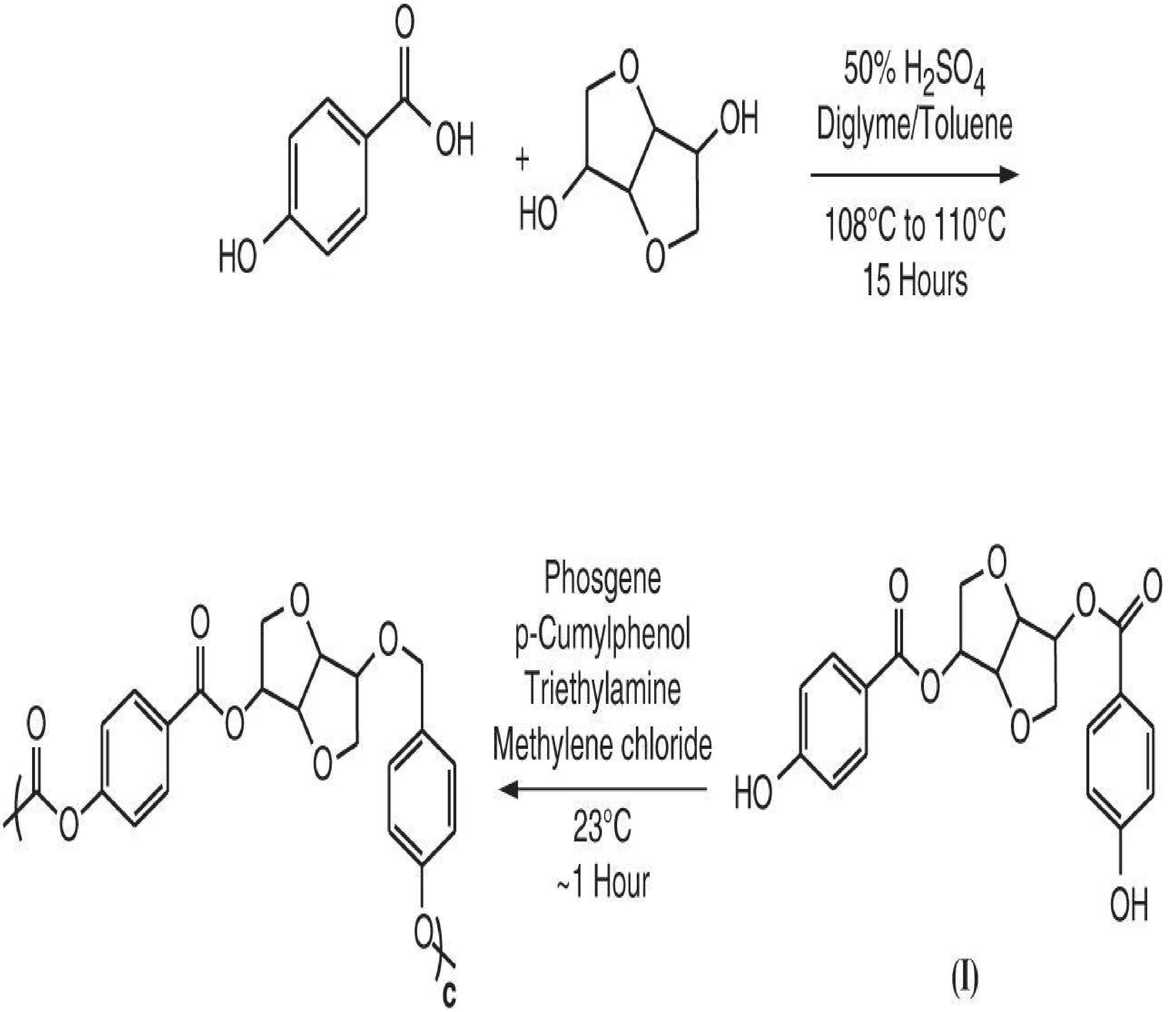


Isosorbide

Figure 10.1

Product Formations

Case I. Isosorbide Homopolymer



Case II. Isosorbide Copolymer

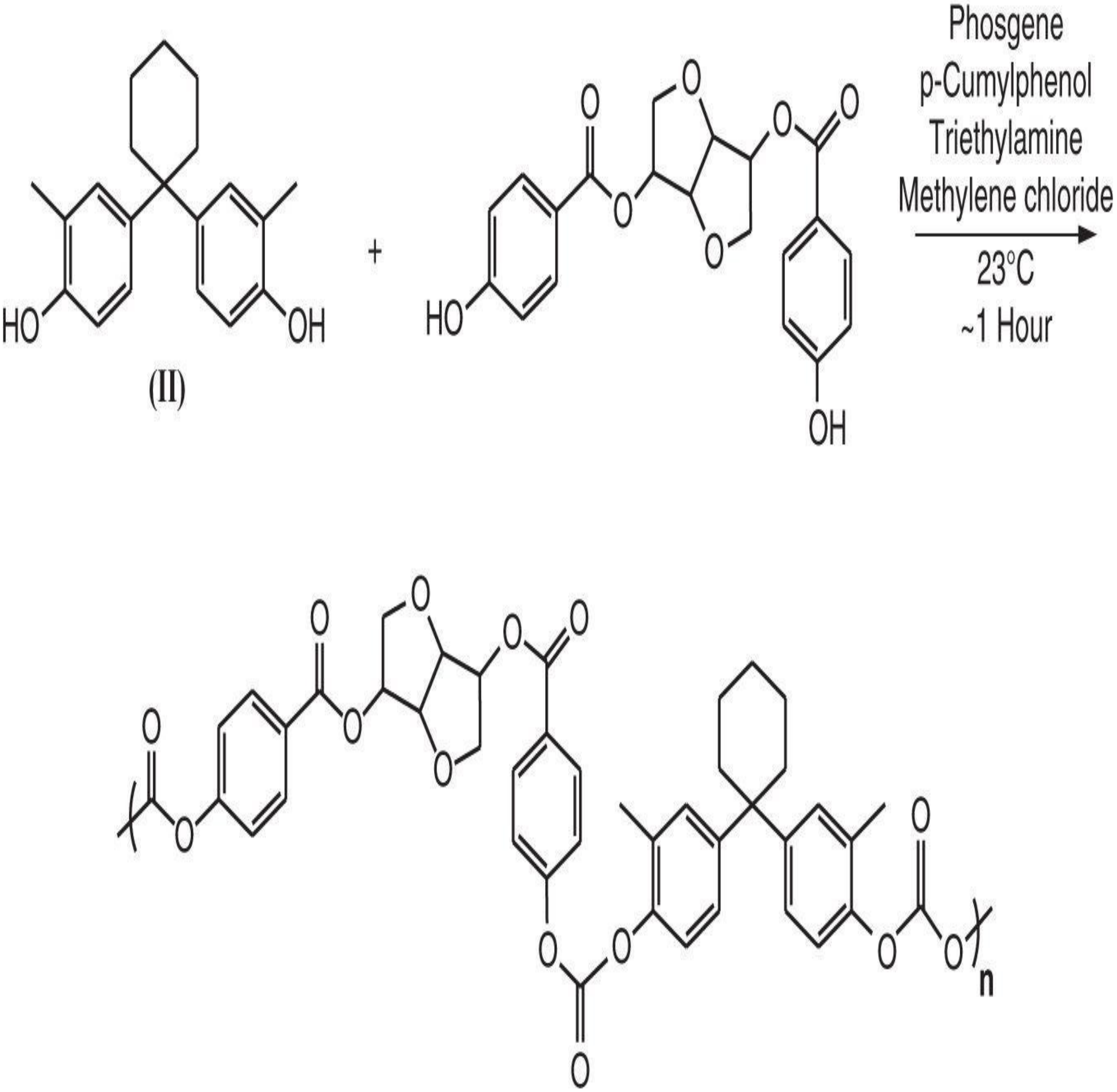


Figure 10.2

Experimental

Case I. Homopolymer

1. Preparation of poly(isosorbide-bisphenol) homopolymer. A two-liter glass reactor equipped with an overhead condenser, a phosgene inlet, and a pH probe to monitor pH during the course of the reaction was charged with 10.73 g of isosorbide-bisphenol A, (I), 0.31 g of p-cumylphenol, 0.10 mL of triethylamine, 500 mL of methylene chloride, and 300 mL of de-ionized water. The reaction was then stirred for 10 minutes at ambient temperature while maintaining a pH of 8 by the dropwise addition of 30 wt% sodium hydroxide solution. The mixture was then treated with 10.14 g of phosgene at 2 g/min followed by the incremental addition of 30 wt% sodium hydroxide solution so the reaction pH was maintained between 9 and 10. After the phosgene addition was completed, the reaction mixture was purged with nitrogen gas and the organic layer extracted. The extract was initially washed once with dilute hydrochloric acid, three times with ambient temperature water, and then the reaction product precipitated in hot water. The polymer was dried in an oven at 110°C and isolated as a colorless solid. Analytical test results are provided below: Mn = 58,637 daltons

PDI = 2.30

Tg = 167°C

Elastic modulus = 1969 MPa

Case II. Copolymer

2. Preparation of poly(isosorbide-co-1,1-bis(4’hydroxy-3’methylphenyl)-cyclohexane) copolymer. The copolymer of isosorbide-bisphenol, A monomer, (I), and 1,1-bis(4’hydroxy-methylphenyl)cyclohexane, (II), was prepared using interfacial polymerization. A two-liter glass reactor equipped with an overhead condenser, a phosgene inlet, and a pH probe, which permitted monitoring the pH during the course of the reaction, was charged with 10.73 g of 1,1-bis(4’hydroxy-3’methylphenyl)cyclohexane, (II), 14 g of isosorbide- bisphenol, (I), 0.41 g of p-cumylphenol, 0.10 mL of triethylamine, 23 L of methylene chloride, and 10.8 L of water. The reaction was then stirred for 10 minutes at ambient temperature while the pH was maintained at 8 by the incremental addition of 30 wt% sodium hydroxide solution. The mixture was then treated with 0.21 g of phosgene at 2 g/min while the reaction pH was maintained between 9 and 10 by the incremental addition of 30 wt% sodium hydroxide. After the phosgene addition was completed, the reaction assembly was purged with nitrogen gas and the organic layer was extracted. The extract was washed once with dilute hydrochloric acid and three times deionized water at ambient temperature. The organic layer was precipitated into hot water and the polymer was dried in an oven at 110°C then isolated as a colorless solid. Analytical test results are provided below:

Mn = 37,976 daltons

PDI = 1.69

Tg = 154°C

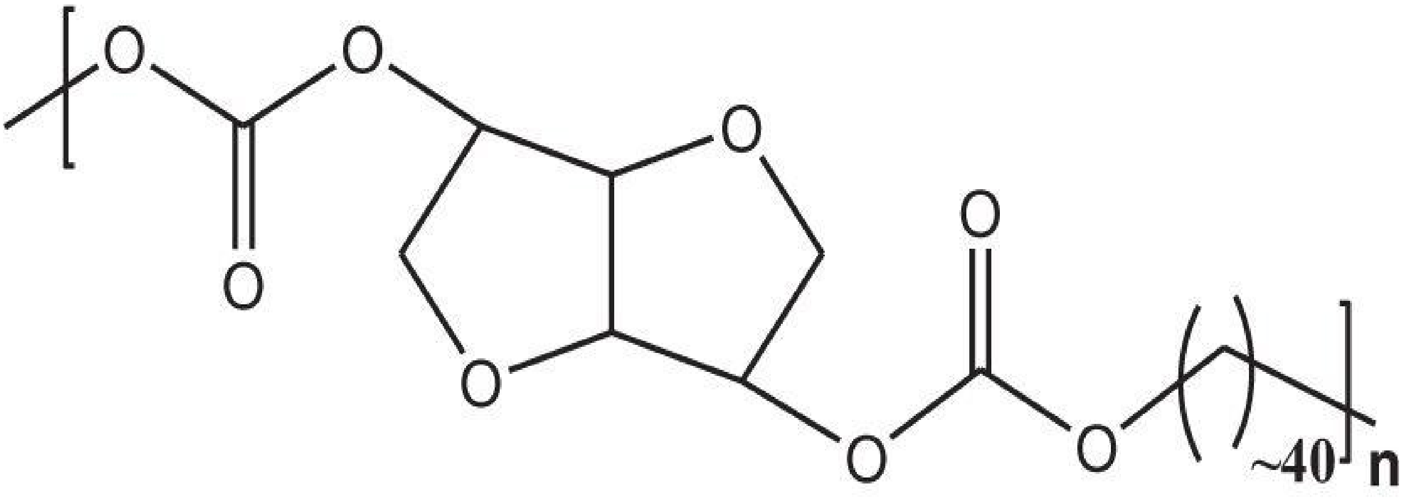
Elastic modulus = 1654 MPa

Testing

Testing was limited to polymer characterization as provided in Steps 1 and 2.

Notes and Observations

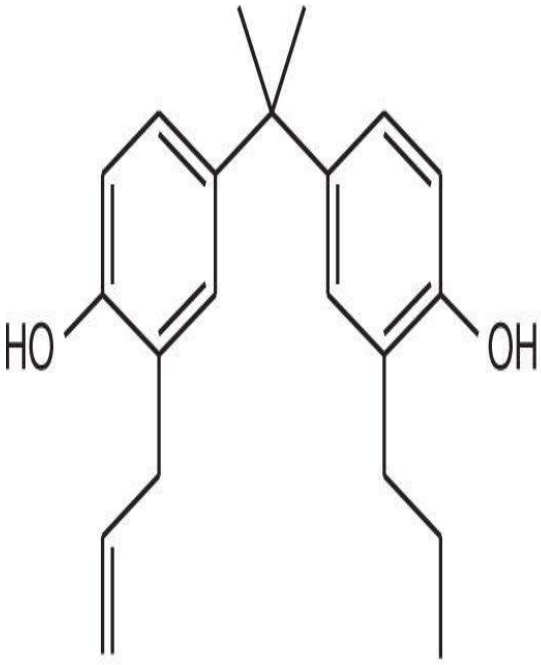
1. Kamps[1] prepared isosorbide-aliphatic polycarbonates, (III), using amorphous and renewable oligomeric di-alcohols having molecular weights of approximately 2,000 to 3,000 daltons. Isosorbide copolycarbonates generated from this process was colorless, had a notched Izod-impact strength greater than 13 kJ/m[2] at 23°C, and had a heat deflection temperature of approximately 150°C. (See Fig. 10.3.)



(III)

Figure 10.3

2. Huang[2] prepared a series of graft copolymers beginning with 2,2’diallylbisphenol A, (IV), which was initially converted into a polycarbonate, (V), by reacting with phosgene. This polycarbonate was then converted into the graft polycarbonate, (VI), by the free radical addition of methylmethacrylate using either 2,2’-azobisisobutyronitrile or benzoyl peroxide as free radical initiators. The graft co-polymer had excellent anti-fog and anti-scratch properties. These materials are particularly useful in coating applications where a lower contact angle was needed. (See Fig. 10.4.)



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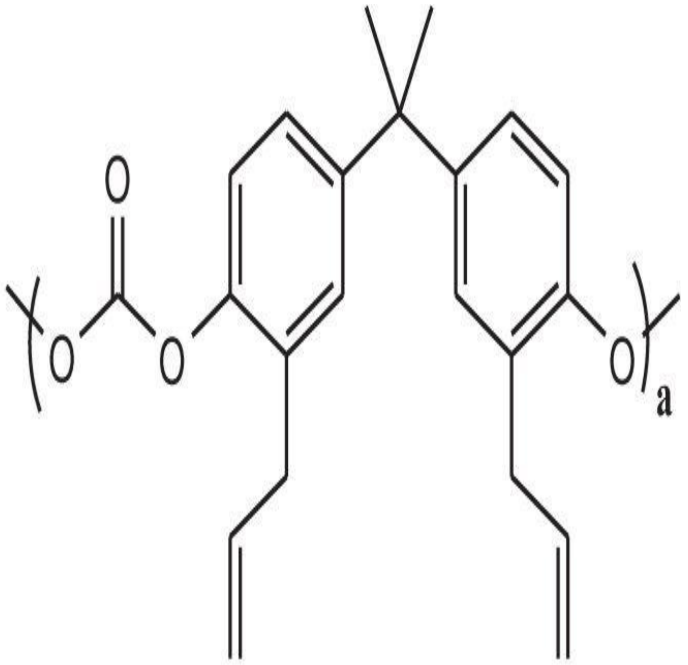

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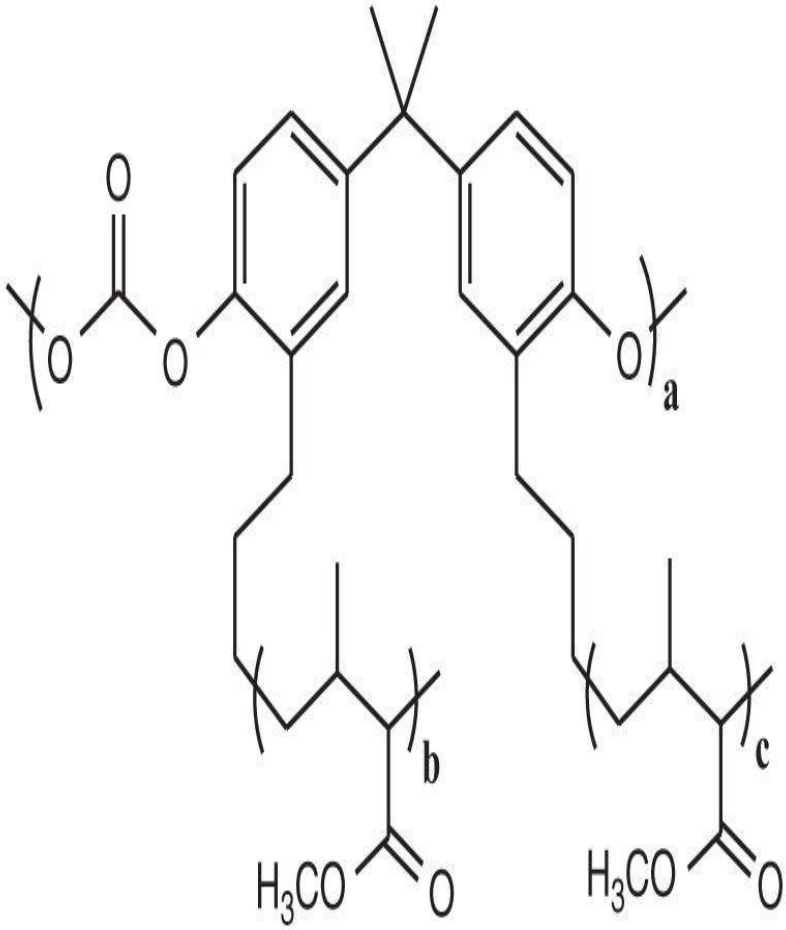
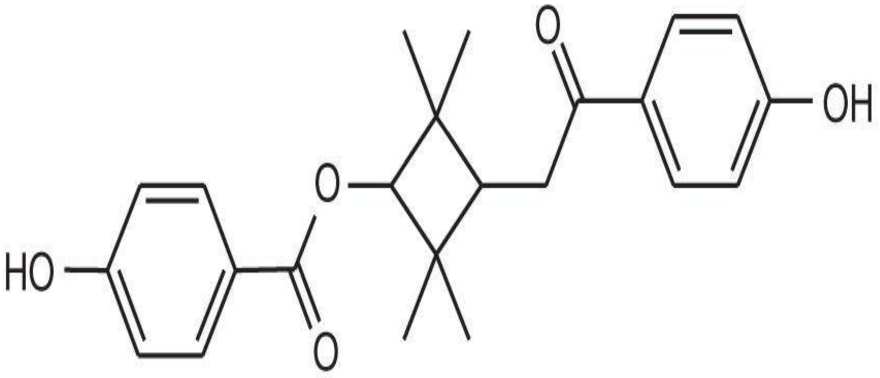


(VI)

Figure 10.4

3. Morizur[3] prepared a series of cyclobutylpolycarbonates that were designed to improve the optical properties of lenses without incurring a yellowing penalty. In the first instance, tetramethylcyclobutyldiol-2,5-bis(4-hydroxybenzoate), (VII), was prepared and converted into the polycarbonate homopolymer, (VIII), by reacting with phosgene at ambient temperature. In the second instance, the cyclobutyl intermediate was condensed with bisphenol A, (IX), in the presence of phosgene at ambient temperature to prepare a polycarbonate copolymer, (X). In both cases, polymers were isolated in quantitative yields. (See Fig. 10.5.)



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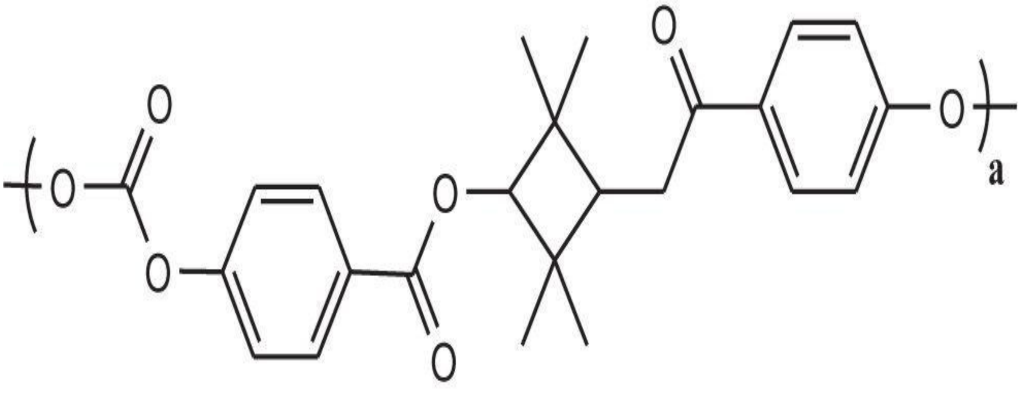

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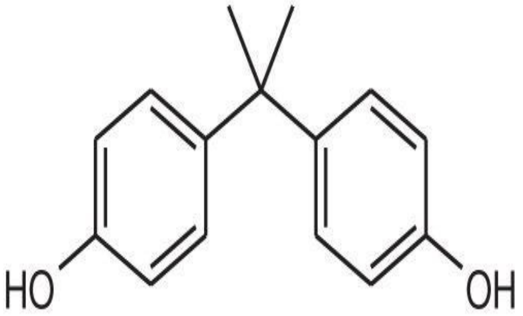

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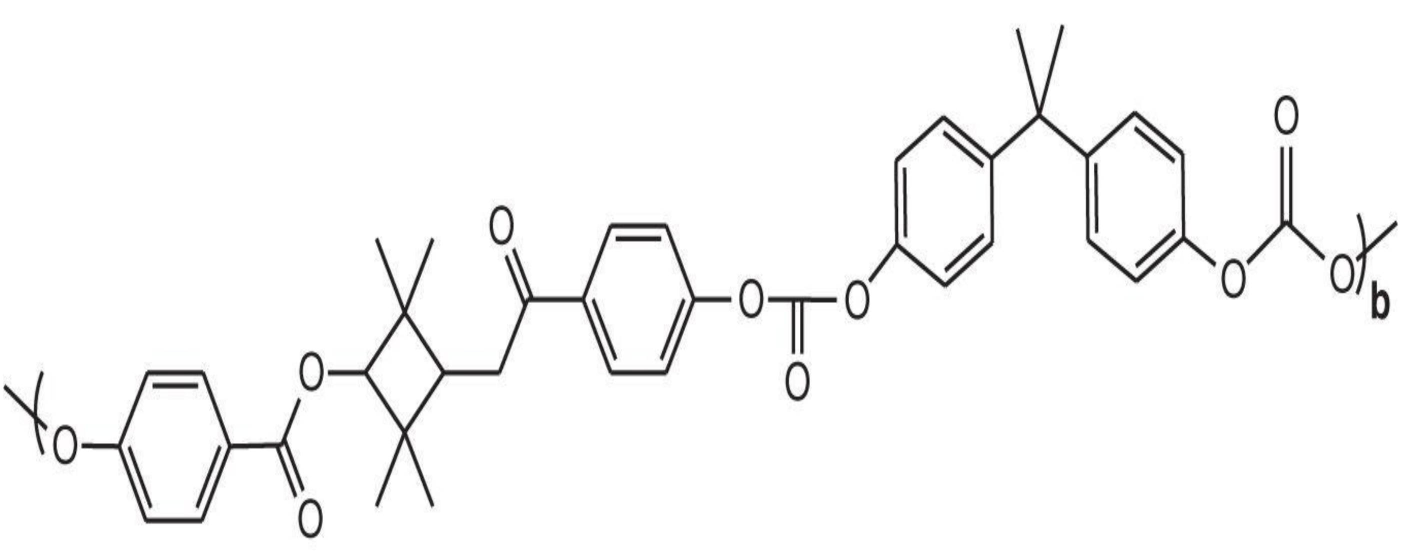
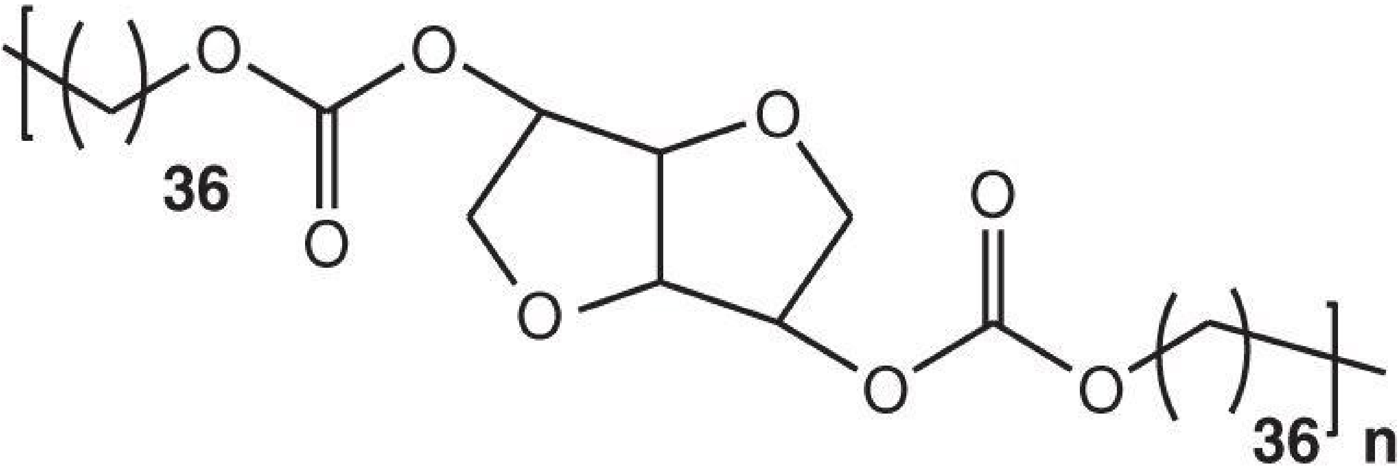


(X)

Figure 10.5

4. Brack[4] prepared an isosorbide-containing polycarbonate copolymer, (XI), by reacting a mixture of isosorbide and the fatty diol, $C_{36}H_{72}(OH)_2$, with phosgene. The presence of the fatty acid in the copolycarbonate reduced the color of the copolymer and improved the range of solubility of the material in organic solvents. In this instance, both isosorbide and the fatty-alcohol were bio-renewable reagents. (See Fig. 10.6.)



(XI)

Figure 10.6

References

1. Jan Henk Kamps et al., *Isosorbide-based polycarbonates, method of making, and articles formed therefrom*, U.S. Patent 8,273,849 (September 25, 2013)

2. Rubin Huang et al., *Polycarbonate graft copolymers*, U.S. Patent 8,426,532 (April 23, 2013)

3. Jean-Francois Morizur, *Polycarbonate polymers containing bisphenol compounds*, U.S. Patent 8,207,287 (June 26, 2012)

4. Hans-Peter Brack et al., *Method of making isosorbide polycarbonate*, U.S. Patent 7,863,404 (July 4, 2011)

Chapter

11

Fibers

Recycled Yarn

Author Alon Weiser et al.

Patent Title ***Process of making recycled polyamide yarn***, U.S. Patent 8,366,977 (February 5, 2013)

Relevant Prior Patents by Author or Coauthors

Process for making polyamide textile articles bearing designs in different colors, U.S. Patent 7,597,722 (October 6, 2009)

Yarns, particularly yarns incorporating recycled material, and methods of making them, U.S. Patent Application 200601853437 (August 24, 2006)

Spandex covered tightly with shrinkable nylon and process for producing it, U.S. Patent 7,152,390 (December 26, 2006)

Process for the manufacture of polyamide yarns dyeable in melange shades, U.S. Patent 6,524,503 (February 26, 2003)

Product Application

The current application provides a method to recycle polyamide yarn containing high-carboxylic-acid termini with polyamides containing high amine termini content. In this process, new polyamide links are formed so that the discarded yarn can be used in other fabric applications.

Significance of Current Application

The present method of recycling discarded yarn uses a strategy of chemically combining two polymeric fibers by termini interaction and each fiber termini with the other fiber termini. In this process, an aliphatic diamine and aliphatic carboxylic acid are mixed to form a salt. The mixture is then heated and a high amine polymer is formed. This material is then heated with a high acid terminated yarn and nested; and the yarn is incorporated into the extended polyamide. This process can be repeated with fiber or other material. Recycling can be achieved by termini bonding interactions of some discarded material with a suitable difunctional chemical agent. For example, discarded materials containing high levels of hydroxyl termini could be readily recycled by using difunctional aliphatic or oligomeric carboxylic acids to form a polyester, anhydrides to also form a polyester, phosgene to form polycarbonates, or olefins to form ethers.

Product Formation

Blending Component 1

High Amine Termini Content Nylon 66 Oligomer

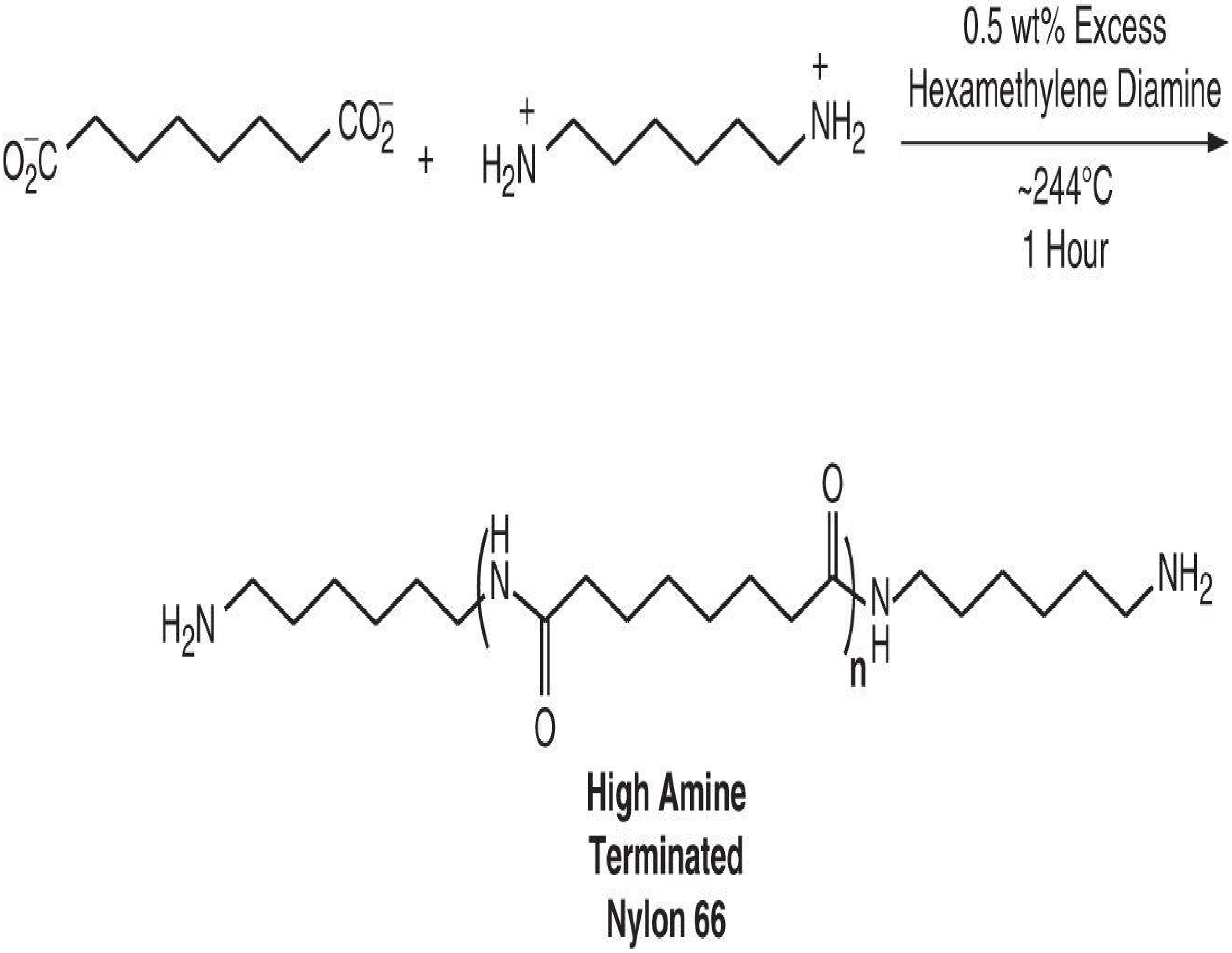
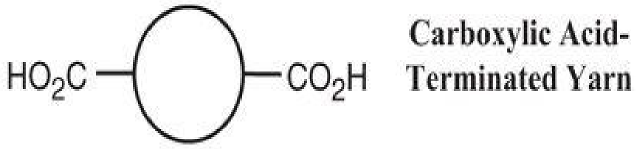


Figure 11.1

Blending Component 2

High Carboxylic Acid Terminated Yarn



Recycling

Recycling High Carboxylic Acid Terminated Yarn
With
High Amine Termini Content Nylon 66

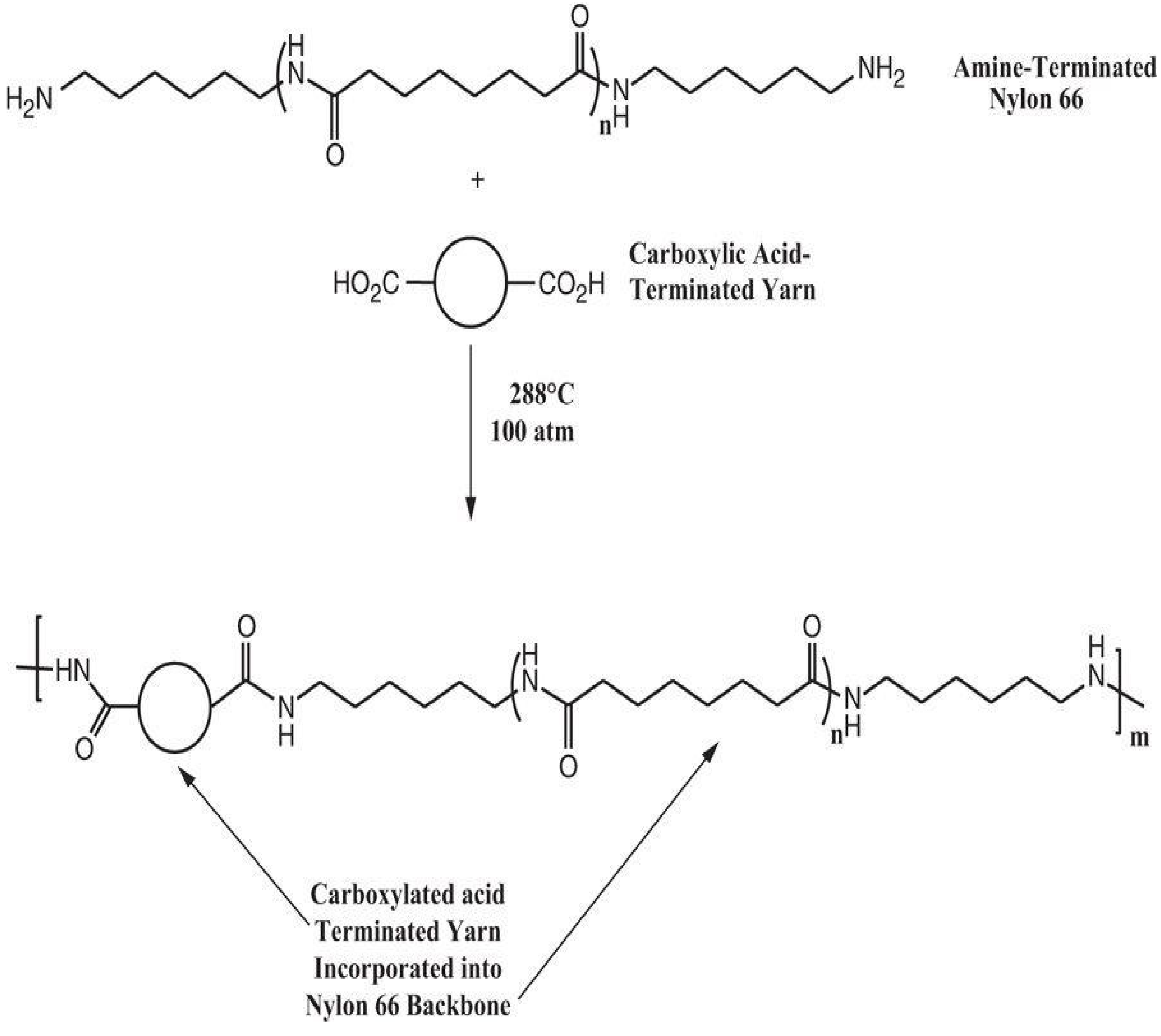


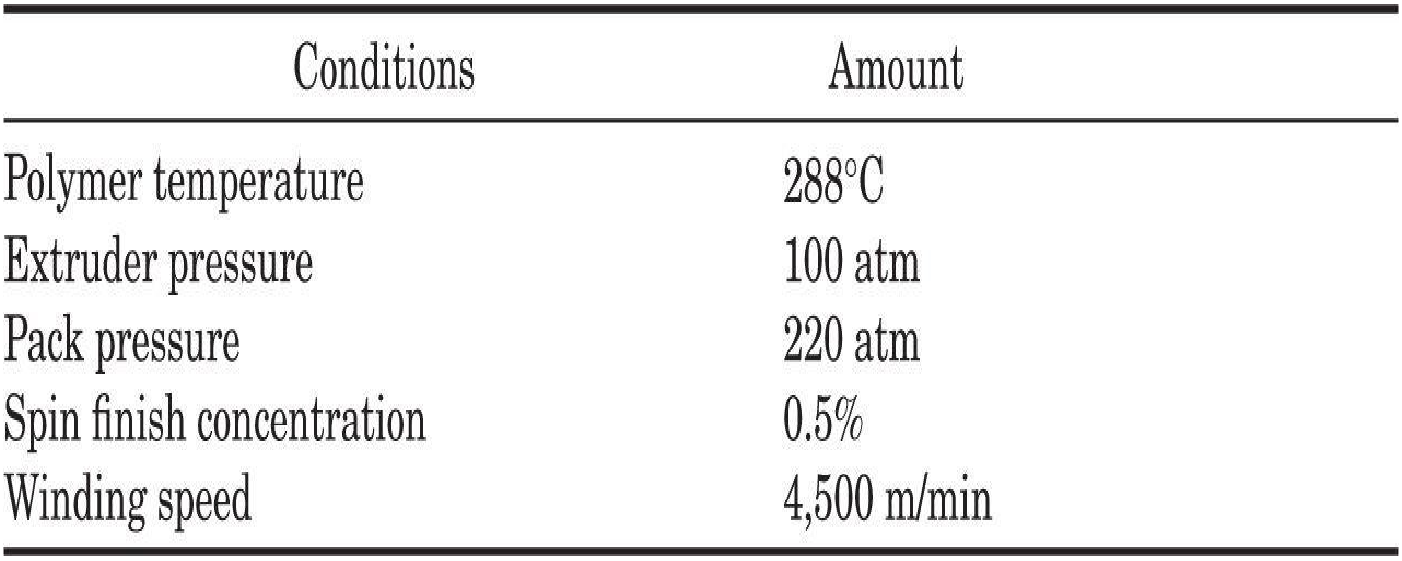
Figure 11.2

Experimental

1. Preparation of Nylon 66 oligomer. Aqueous solutions of hexamethylene diammonium adipate and 0.5 wt% excess hexamethylene diamine were charged into a stainless steel batch autoclave under a nitrogen blanket then heated sufficiently to distill off water. Once the autoclave temperature reached 244°C, the pressure was gradually lowered and the reaction product removed from the vessel. After cooling the polymer with ice water, the polymer was chopped into chips. The polyamide was characterized as having a relative viscosity between 46 Pa.s and 48 Pa.s with an amine-termini content of between 80 and 89 meq/kg.

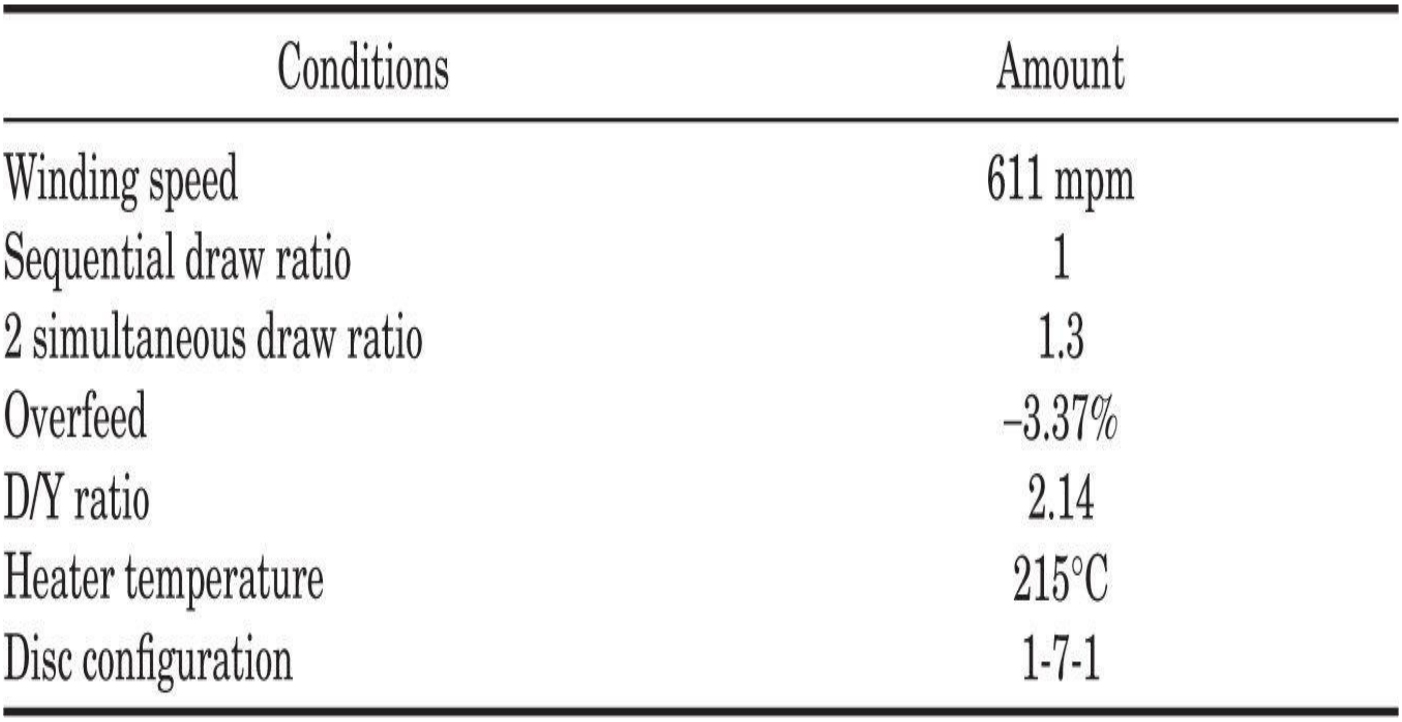
2. Process for recyclable polyamide yarn. Blending parameters used to recycle discarded high carboxylic-acid-content polyamide yarn with high-amine-content Nylon 66 are provided in Table 11.1. Physical, spinning, and texturing properties of the recycled yarn are provided in Table 11.2.

TABLE 11.1 Blending parameters used to recycle through amidation high carboxylic-acid-content polyamide yarn with high amine-content Nylon 66.



Conditions	Amount
Polymer temperature	288°C
Extruder pressure	100 atm
Pack pressure	220 atm
Spin finish concentration	0.5%
Winding speed	4,500 m/min

TABLE 11.2 Texturing parameters used to process an amidative blend of discarded high carboxylic-acid-content yarn with high amine-content Nylon 66.



Conditions	Amount
Winding speed	611 mpm
Sequential draw ratio	1
2 simultaneous draw ratio	1.3
Overfeed	−3.37%
D/Y ratio	2.14
Heater temperature	215°C
Disc configuration	1-7-1

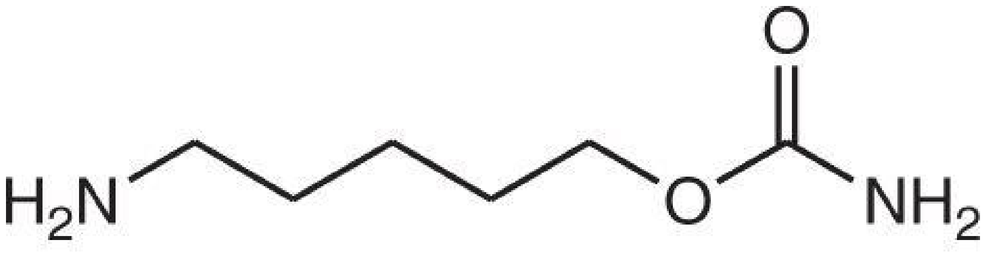
Testing Results

Yarn regenerated from recycled high carboxylic-acid-content yarn with high amine-content Nylon 66 was considered to be of high quality and had physical properties consistent with industrial standards. Ten test subjects who used the recycled yarn indicated that the textured yarn was smooth, easily manipulated, and did not form clumps or snags when used. Neither heat nor cold appeared to affect the recycled yarn and, when wet and subsequently dried, the physical properties of the material remained unchanged.

Notes and Observations

1. Coombs[1] prepared enhanced-performance yarns by preparing spun staple fibers of recycled plastic. In this process, the core of the fiber consisted of recycled polyethylene terephthalate that contained medium to high levels of contamination and then wrapped it with recycled polyamide yarn. Fibers from this process were used to prepare ripstop yarn, which is in the grid of ultra-high strength fabrics.

2. Leboeuf [2] developed a two-step process for recycling Nylon 66 from post-industrial and post-consumer products. In this process, waste nylons were initially depolymerized by mixing them with methanol and then heating the mixture to 195°C for 1 hour under 900 psi. The depolymerized polyamide was then filtered and treated with either 1,6-hexamethylene diamine or hexamethylene diamine monocarbamate, (I), to selectively functionalize the termini. The functionalized depolymerized polyamide was then post-reacted with a selected dicarboxylic-acid monomer and a new polyamide obtained. After processing, the recovered polyamide was used to prepare consumer-oriented products. (See Fig. 11.3.)



(I)

Figure 11.3

3. Jackson[3] dyed a blend containing a mixture of recycled and virgin Nylon 66. Dyeless post-industrial waste Nylon 66 was obtained from off-specification yarn. The unusable fiberstock was processed through an extruder and then chopped and converted into flakes. A blend consisting of sulfur, recycled polyamide flakes, and virgin flakes was then prepared by thoroughly mixing in a blender and then melt-extruding the mixture into flakes. The extruded flakes were then treated with cationic dyes designed to couple with the amine terminus of the polyamide. The mixture of a selected dye and extruded flakes was then re-extruded, and the colored Nylon 66 flakes were isolated. Erionyl dyes, which were particularly effective, included Black MR, Blue P2R, Red A-3B, and Yellow A3G. Irgalan dyes, which were also as effective as Nylon 66 dyes, included Black BGL, Blue 3GL, Bordeaux EL 200, Red B, and Yellow 2GL KWL 250.

4. Mckinnon[4] developed a four-step process to recover carpet waste that consisted of 92% Nylon 66 while 8% consisted of a mixture containing latex and polypropylene. The four processing steps consisted of:

   1. The carpet was mixed and dissolved in either methanol or ethanol and heated to 210°C under a pressure of at least 350 psig. This phase was designed to both dissolve the polyamide as well as to partially depolymerize it to less than 90% of its original average molecular weight.
   2. The solution was then filtered to remove latex and polypropylene so that the methanol or ethanol solution contained predominately Nylon 66 oligomers.
   3. The depolymerized polyamide was then recovered from the solution by distilling off either methanol or ethanol.
   4. Once the solvent had been removed, Nylon 66 oligomers were isolated and re-polymerized to make other consumer and industrial products.

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1. Timothy S. Coombs, *Yarns, particularly yarns incorporating recycled material, and methods of making them*, U.S. Patent 7,841,162 (November 30, 2010)

2. Christian Leboeuf, *Process for the solution recovery of nylon with high reactivity and articles made therefrom*, U.S. Patent Application 20040249001 (December 9, 2002)

3. Craig A. Jackson et al., *Colorable filaments from polymer blend*, U.S. Patent Application 20040053047 (March 18, 2004)

4. Michael S. Mckinnon, *Solvent-based recovery and recycle of polyamide material*, U.S. Patent 7,319,113 (January 15, 2008)

Triacylglyceride Thermoset Fibers

Author Ekaterini Korovessi et al.

Patent Title ***Copolyamides compositions from triacylglycerides,*** U.S. Patent Application 20130048136 (February 28, 2013)

Relevant Prior Patents by Author or Coauthors

Process for making linear dicarboxylic acids from renewable resources, U.S. Patent Application 20110300594 (December 8, 2011)

Preparation of levulinic acid esters and formic acid esters from biomass and olefins, U.S. Patent Application 20050118691 (June 2, 2005)

Preparation of levulinic acid esters and formic acid esters from biomass and olefins; compositions prepared thereby; and uses of the compositions as fuel additives, U.S. Patent Application 20030233011 (December 18, 2003)

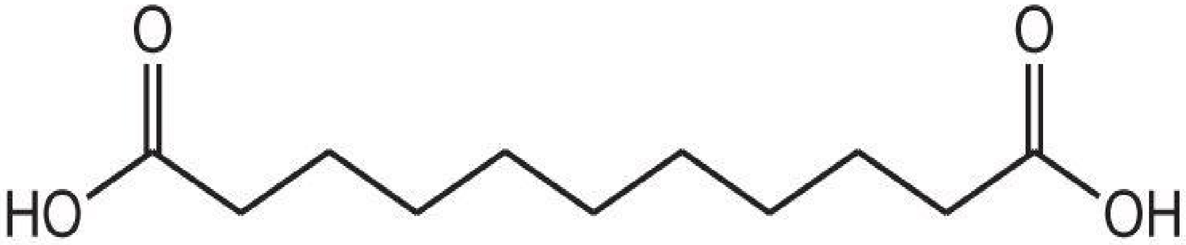
Product Application

Mixed polyamides prepared from this investigation were designed to be used in automotive applications. These materials are particularly useful as ultra-high-strength polyamide fibers, thermoplastics, and thermosets that are resistant to both salt stress and corrosion cracking.

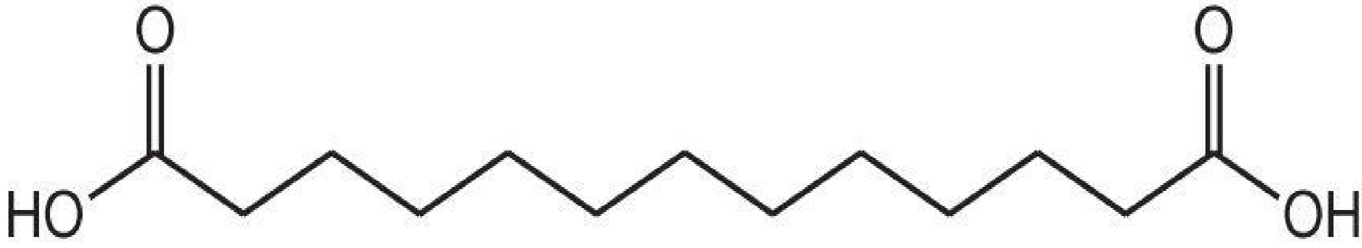
Significance of Current Application

Motor vehicles containing Nylon-6,6, -6, -6,10, and -6,12 as exteriorautomotive components have a limited lifetime because they become stressed or corroded by salt. In addition, corrosion of metallic fittings and frame supporting the vehicle further add to concerns of whether the vehicle can be safely driven or whether it is unsafe and potentially unusable. This investigation has determined that polyamides derived from a single diamine and two separate aliphatic dicarboxylic acids are considerably more resistant to stress and corrosion. Aliphatic dicarboxylic acids used in this process were prepared by fermentation of d-glucose and inoculum of the Candida maltosa strain, ATCC 74430.

Biologically Diacids Derived from Fermentation

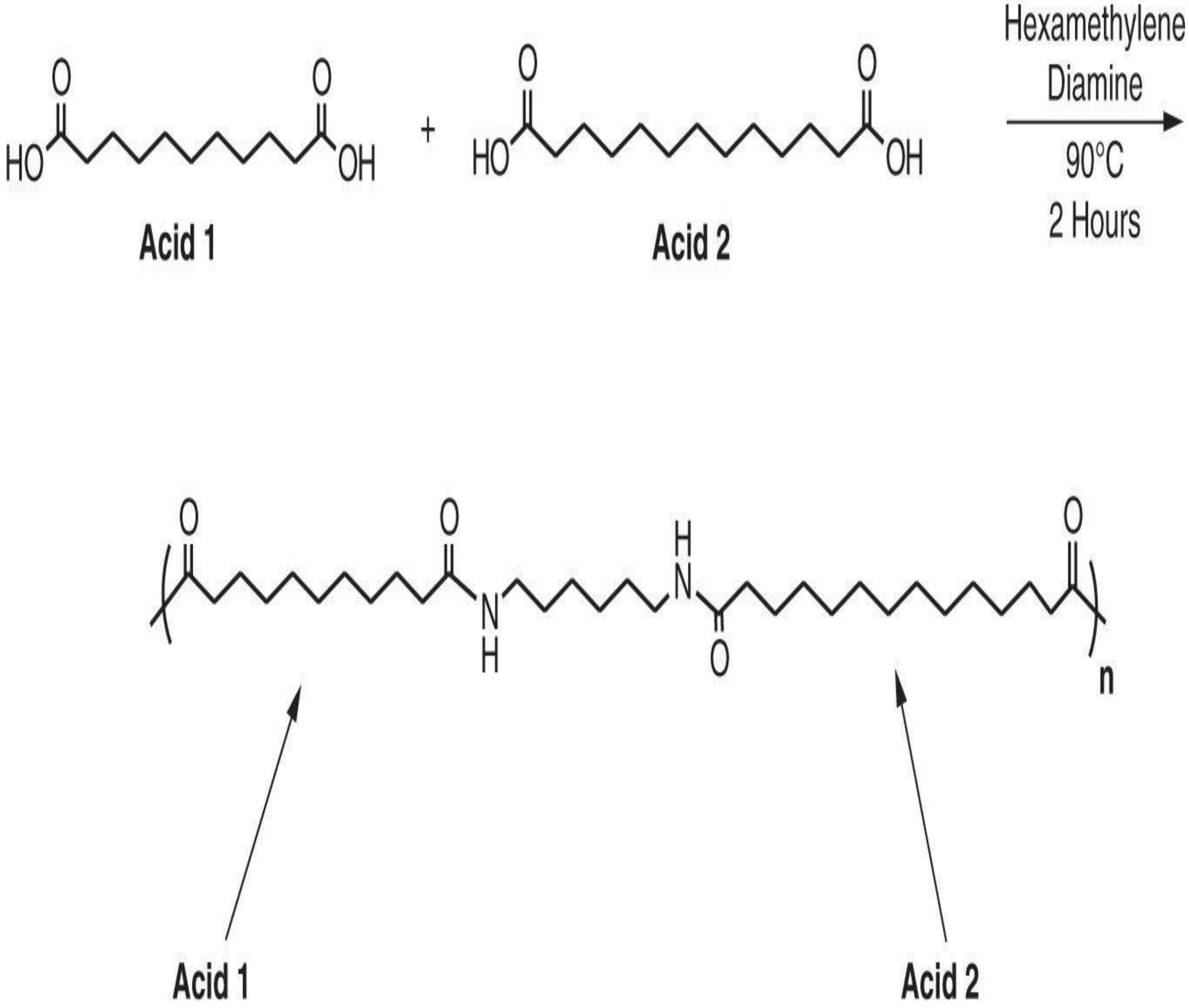


Dedecanedioic acid



Tetradecanedioic Acid

Product Formation



Experimental

1. Preparation of dodecanedioic acid and tetradecanedioic acid. A 10-mL seed inoculum of Candida maltosa strain ATCC 74430 was grown for 24 hours at 30°C while shaking at 250 rpm in a solution containing 10 g/L of yeast extract, 20 g/L of peptone, and 20 g/L of glucose. The cell suspension was then inoculated in a 700-mL solution of yeast medium having a pH of 5. The yeast-growth medium composition is listed below:

3 g/L Ammonium sulfate

6.6 g/L Potassium dihydrogen phosphate

0.4 g/L Dipotassium phosphate

0.6 g/L Anhydrous magnesium sulfate

4 g/L Yeast extract

75 g/L Glucose

100 mg/L Biotin

13 mg/L Iron sulfate pentahydrate

51–120 mg/L Copper sulfate

20 mg/L Zinc sulfate pentahydrate

6 mg/L Manganese sulfate monohydrate

0.2 mg/L Cobalt nitrate hexahydrate

3 mg/L Sodium molydate

1.6 mg/L Potassium iodide

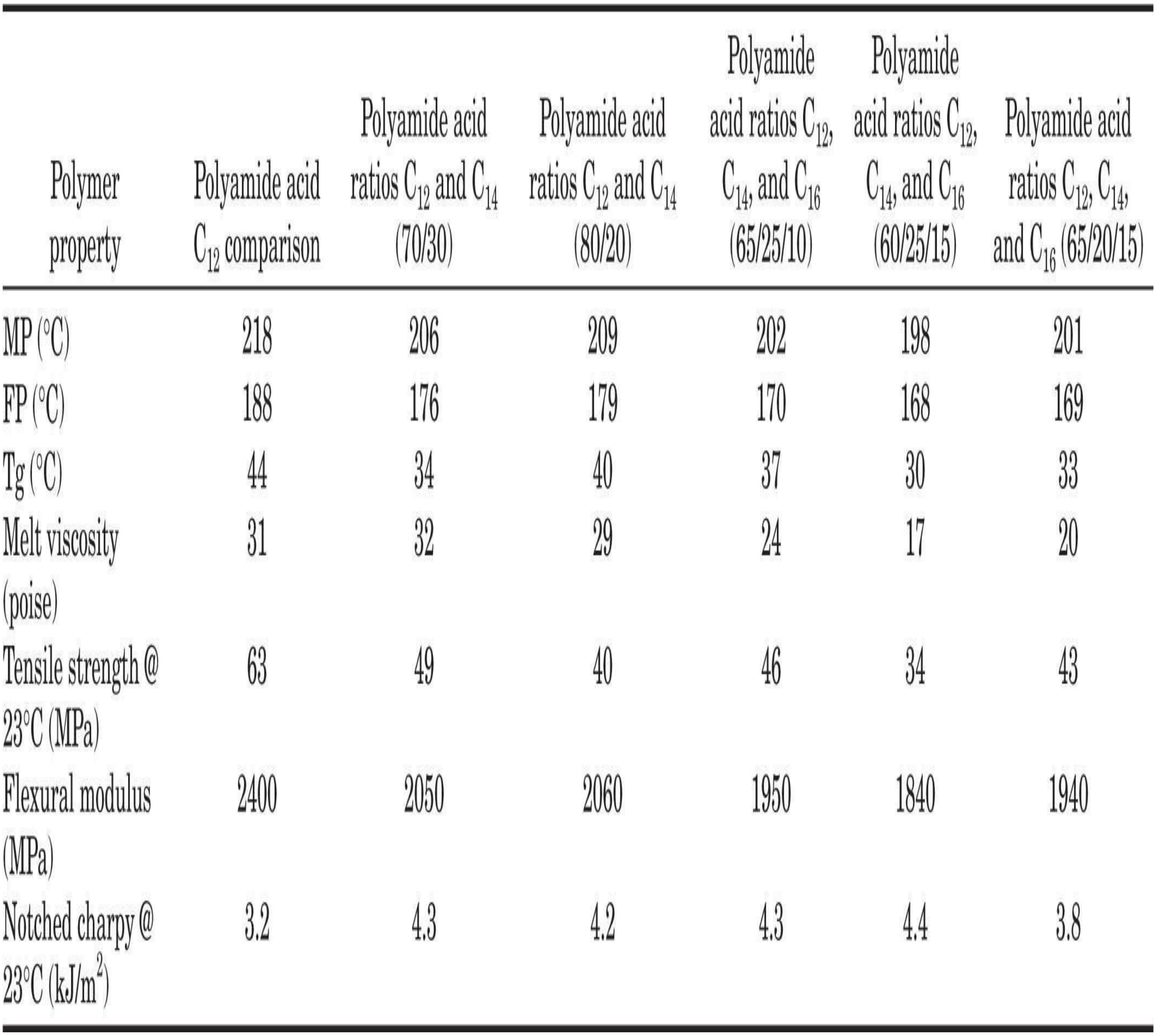
The yeast and growth mixture was then mixed for 24 hours at 30°C with shaking at 250 rpm. A fermenter containing 7 L of water at a pH of 5 was then mixed with yeast and then inoculated with 525 mL of the overnight culture. The fermenter was maintained at minimal airflow and agitation continued until dissolved oxygen reached 20% of atmospheric oxygen levels. The dissolved oxygen was then increased to approximately 80% of atmospheric oxygen and maintained using the fermenter control of aeration up to 2 vvm and agitation speeds up to 1400 rpm at 30°C. The mixture was then treated with 10% w/v ammonium hydroxide to provide nitrogen for cell growth while maintaining a pH of the medium at 5. After approximately 18 hours, the glucose concentration reached zero and an alkane mixture was added to obtain a concentration of 20 g/L. The pH of the medium was then adjusted to 7.5 through using 20% potassium hydroxide throughout the fermentation process. Approximately 51 hours after the alkanes were added to the reactor, two mixed diacids were harvested. The reactor provided 80 g of dodecanedioic acid (C_{12}) and 48 g of tetradecanedioic acid (C_{14}) of the diacid product mixture which were used without purification.

2. Preparation of poly[(dodecanedioic acid-co-hexamethylene diamine)-co-(tetradecanedioic acid-co-hexamethylene diamine)]. A large steel reaction vessel was charged with 39.3 pounds of dodecanedioic acid, 11 pounds of tetradecanedioic acid, and an aqueous solution containing 24.7 pounds of hexamethylene diamine dissolved in 120 pounds of water. The solution was then heated to 90°C for 2 hours. After all reagents were dissolved, the solution pH was adjusted to 7.6. After an additional hour of heating at 90°C, the solution was treated with 66.3 g of glacial acetic acid to lower the pH to 5.1 and 0.7 g of Carbowax® 8000. After thoroughly mixing, the reaction contents were transferred to an autoclave having an agitator rate of 10 rpm while pressurized to 265 psia. The mixture was then heated and steam generated from this process was vented to maintain the pressure at 265 psia. During the heating process, the internal reaction temperature increased to 248°C and remained there for 60 minutes. The reaction pressure was then reduced to 13 psia over 20 minutes and the autoclave was flooded with nitrogen. Molten polymer was extruded into strands and fibers and quenched with cold water.

Testing

The physical properties of experimental amides and a comparison polyamide are provided in Table 11.3. Testing results provided by the author were limited to quantitative observations only to more precisely assess differences between each polyamide. Corrosion testing indicated that experimental fibers and sheets derived from mixed aliphatic dicarboxylic acids were considerably more improved than polyamide analogues prepared from a single aliphatic dicarboxylic acid.

TABLE 11.3 Physical properties of mixed polyamides in varying stoichometric ratios. The polyamide derived from C_{12} alone provided as a comparison.

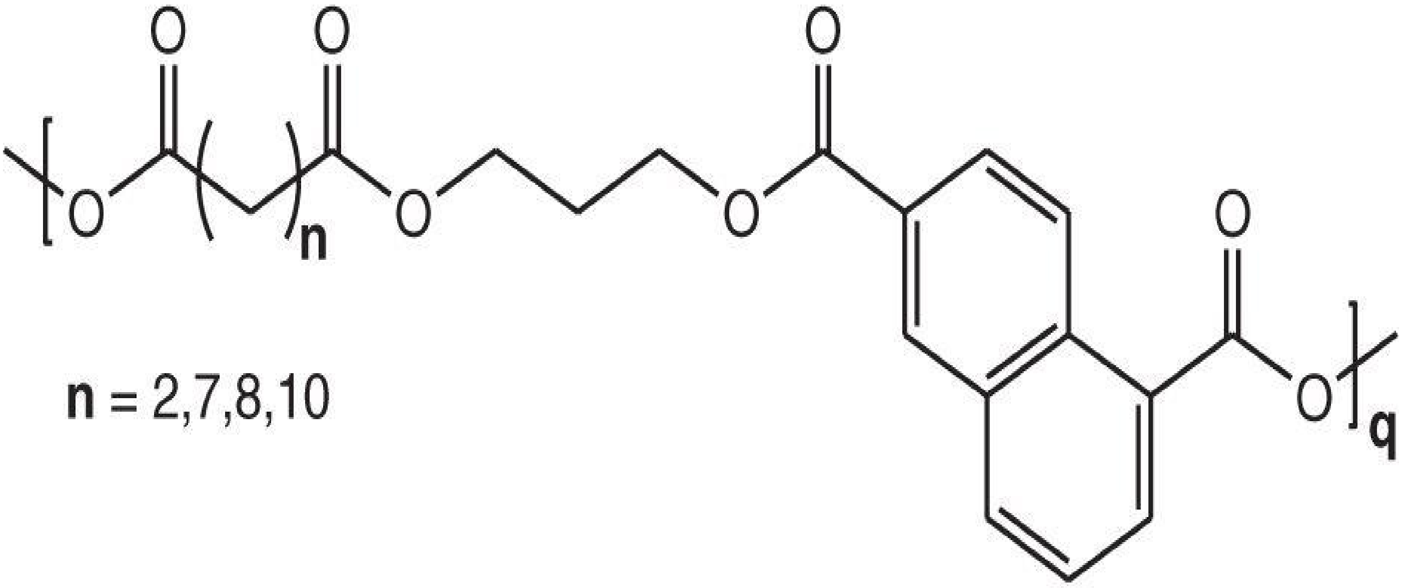


Polymer property	Polyamide acid C_{12} comparison	Polyamide acid ratios C_{12} and C_{14} (70/30)	Polyamide acid ratios C_{12} and C_{14} (80/20)	Polyamide acid ratios C_{12}, C_{14}, and C_{16} (65/25/10)	Polyamide acid ratios C_{12}, C_{14}, and C_{16} (60/25/15)	Polyamide acid ratios C_{12}, C_{14}, and C_{16} (65/20/15)
MP (°C)	218	206	209	202	198	201
FP (°C)	188	176	179	170	168	169
Tg (°C)	44	34	40	37	30	33
Melt viscosity (poise)	31	32	29	24	17	20
Tensile strength @ 23°C (MPa)	63	49	40	46	34	43
Flexural modulus (MPa)	2400	2050	2060	1950	1840	1940
Notched charpy @ 23°C (kJ/m^2)	3.2	4.3	4.2	4.3	4.4	3.8

Notes and Observations

1. Dudley[1] used Candida tropicalis to convert hexadecyl pelargonate, castor oil, hexadecyl acetate, dodecene, tetradecene, hexadecene, and octadecene into a mixture of a 1,2-diol and aliphatic fatty dicarboxylic acids by biooxidation. Extensive toxicity testing of all organic solvents and reagents was a key part of the investigation to ensure that the culture broth of Candida tropicolis was not being subjected to inhibition of growth, unacceptable amounts of cell death, or undue interference with the bioconversion process.
2. Korovessi[2] utilized a transformed Pichia pastoris strain SW64/65 identified as ATCC 74409 to convert dodecane and tetradecane into dodecanedioic acid and tetradecanedioic acid by a fermentation process. Similar conversions were also made by hydrotreating coconut oil, stearic acid, soybean oil, palm kernel oil, and chickenfat products using an alumina-supported pre-sulfurized tri-metallic hydrotreating catalyst consisting of cobalt/nickel/molybdenum. Fatty alcohols products were then bio-converted into the corresponding diacids using Pichia pastoris strain SW64/65.
3. Gohil[3] prepared mixed polyesters, (I), (II), using biologically generated sebacic acid,

adipic acid, 1,12-(I), (II) dodecanedioic acid, and succinic acid. (See Fig. 11.6.)



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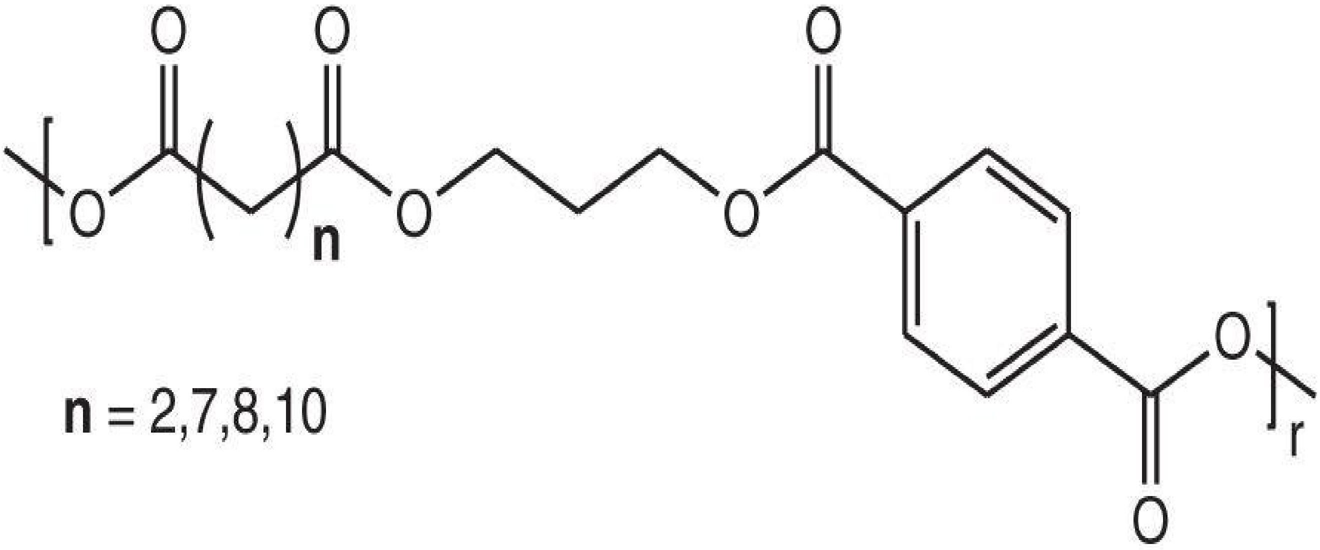

(II)

Figure 11.6

4. Picataggio[4] used Yarrowia lipolytica containing at least one gene that encoded both a delta-17 desaturase and at least one gene of a delta-5 desaturase. The gene has a SEQ ID NO:126 sequence and was designed to biosynthesize polyunsaturated omega fatty acids. In this process, the following four transformations were prepared in good yields. (See Fig. 11.7.)

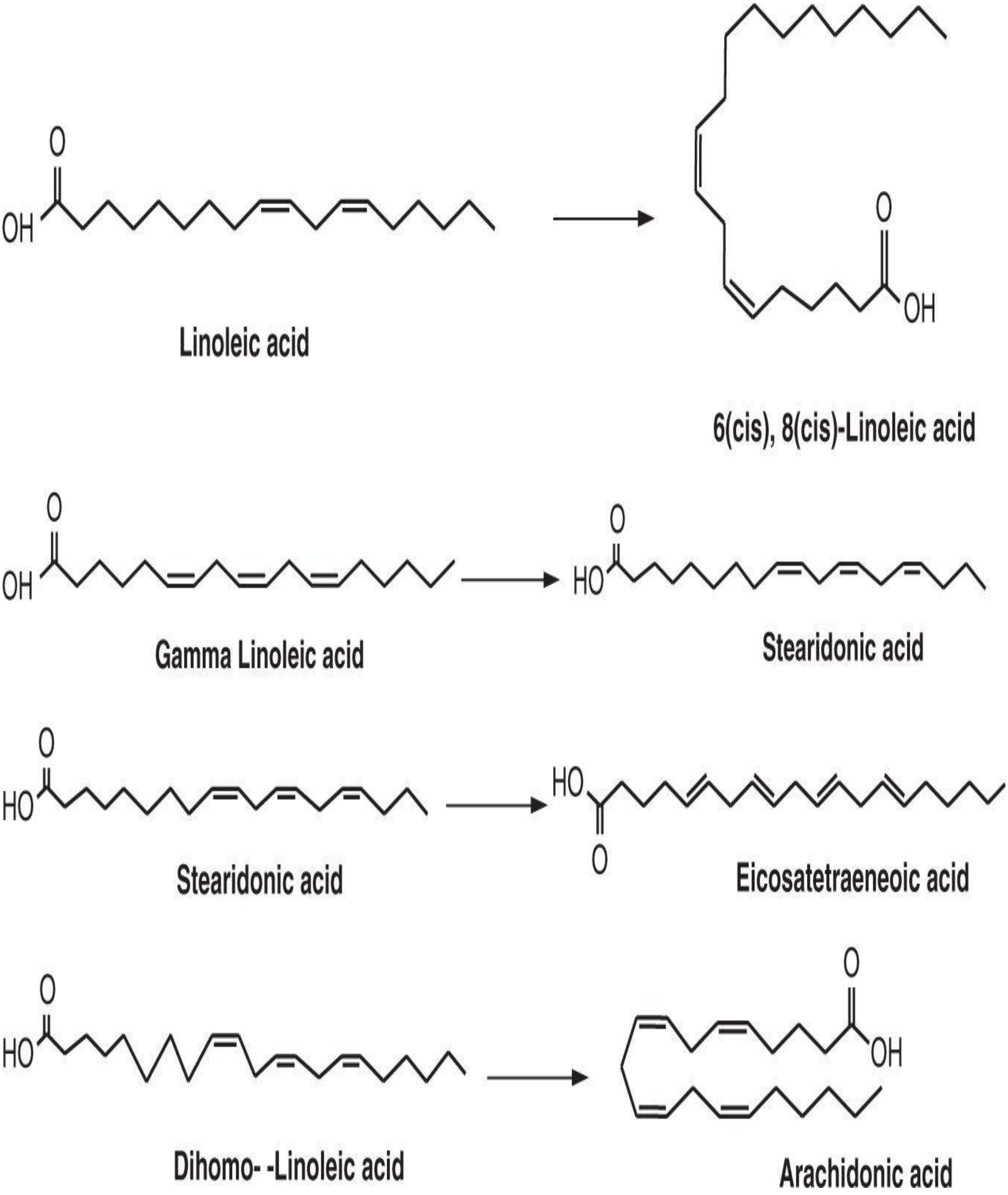

Figure 11.7

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2. Ekaterini Korovessi et al., *Process for making linear dicarboxylic acids from renewable resources,* U.S. Patent Application 20110300594 (December 8, 2011)

3. Rameshchandra M. Gohil, *Polyester compositions from biologically-derived materials*, U.S. Patent 8,273,850 (September 25, 2012)

4. Stephen K. Picataggio, *Production of polyunsaturated fatty acids in oleaginous yeasts*, U.S. Patent 7,238,432 (July 3, 2007)

Chapter

12

Food Packaging

Starch/Starch Nanoparticle and Glycerol Composites

Author Carol Smith et al.

Patent Title ***Biodegradable, biocompatible and non-toxic material, sheets consisting of said material and the use thereof in food, pharmaceutical, cosmetic, and clearing products***, U.S. Patent Application 20130034638 (February 7, 2013)

Product Application

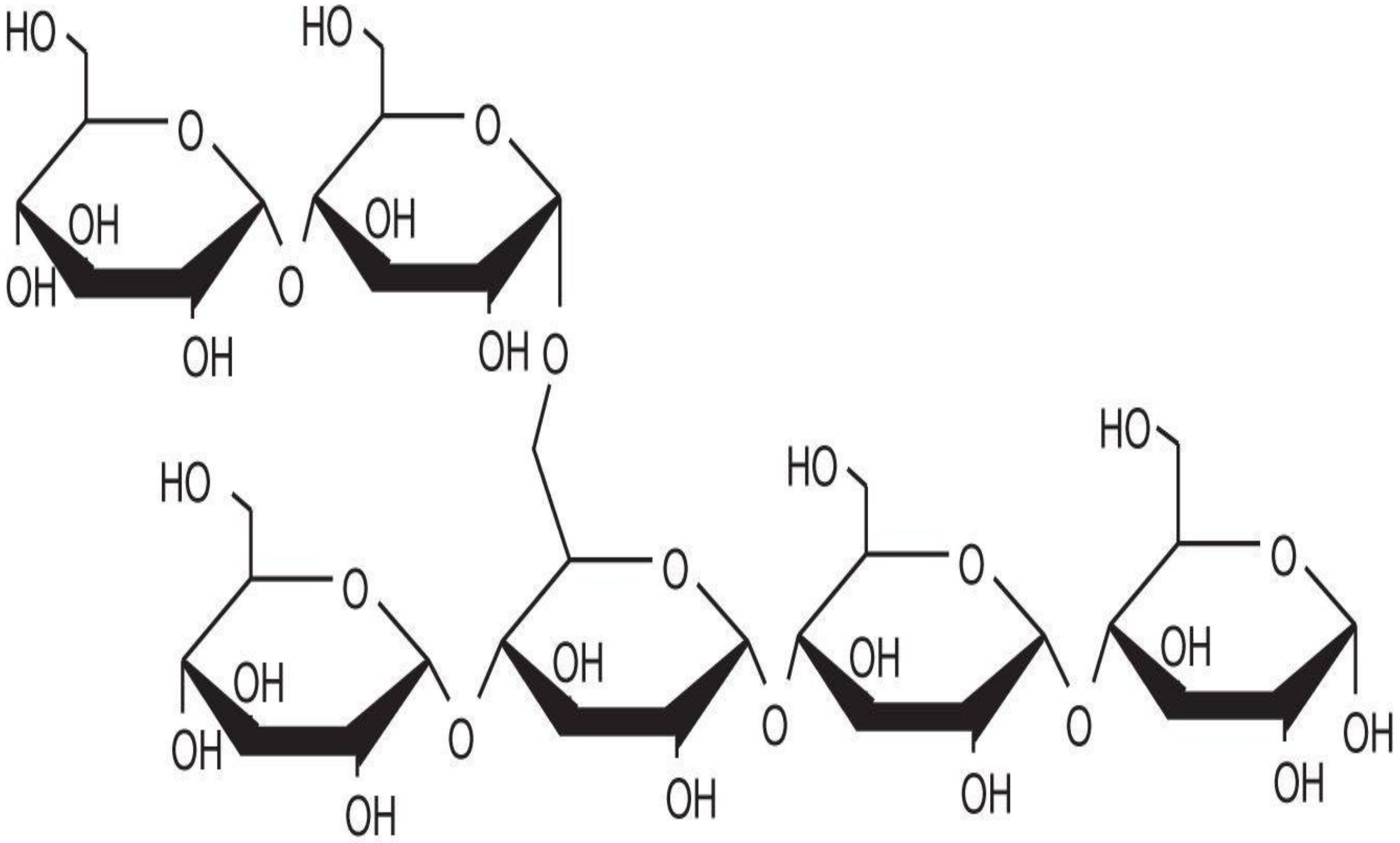
Biodegradable and biocompatible sealable sheets were prepared by blending together waxy starch, glycerol, and starch nanocrystals. These materials are considered non-toxic and are intended to be used for packaging perishable foods.

Significance of Current Application

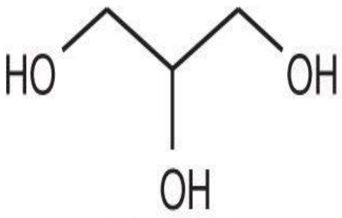
The current investigation has developed a method for preparing a solid blend consisting of starch nanoparticles and glycerol that can be readily converted into renewable sheets and containers. Sheets and containers generated from this solid blend are non-toxic and are suitable for use as packaging materials for perishable foods, drug capsules, or additives in cosmetic and cleaning formulations. Sheets and containers were formulated using renewable starch nanoparticles and glycerol, both of which were isolated from biomass sources and used after processing. These non-toxic thermoplastic composites are both biodegradable and biocompatible and can be readily converted into any shape because of their flexibility and low-thermal processing requirements. Finally, both solid starch and starch nanoparticles can also be used in the manufacturing of other non-toxic synthetic polymers.

Components

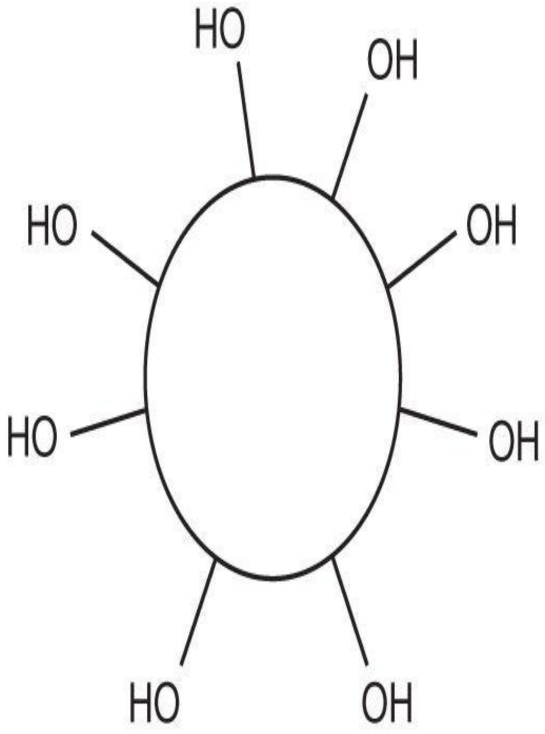
Structural depictions of renewable starch, glycerol, and starch nanocrystals are illustrated in Figure 12.1.



Starch



Glycerol



Starch Nanocrystals

Figure 12.1

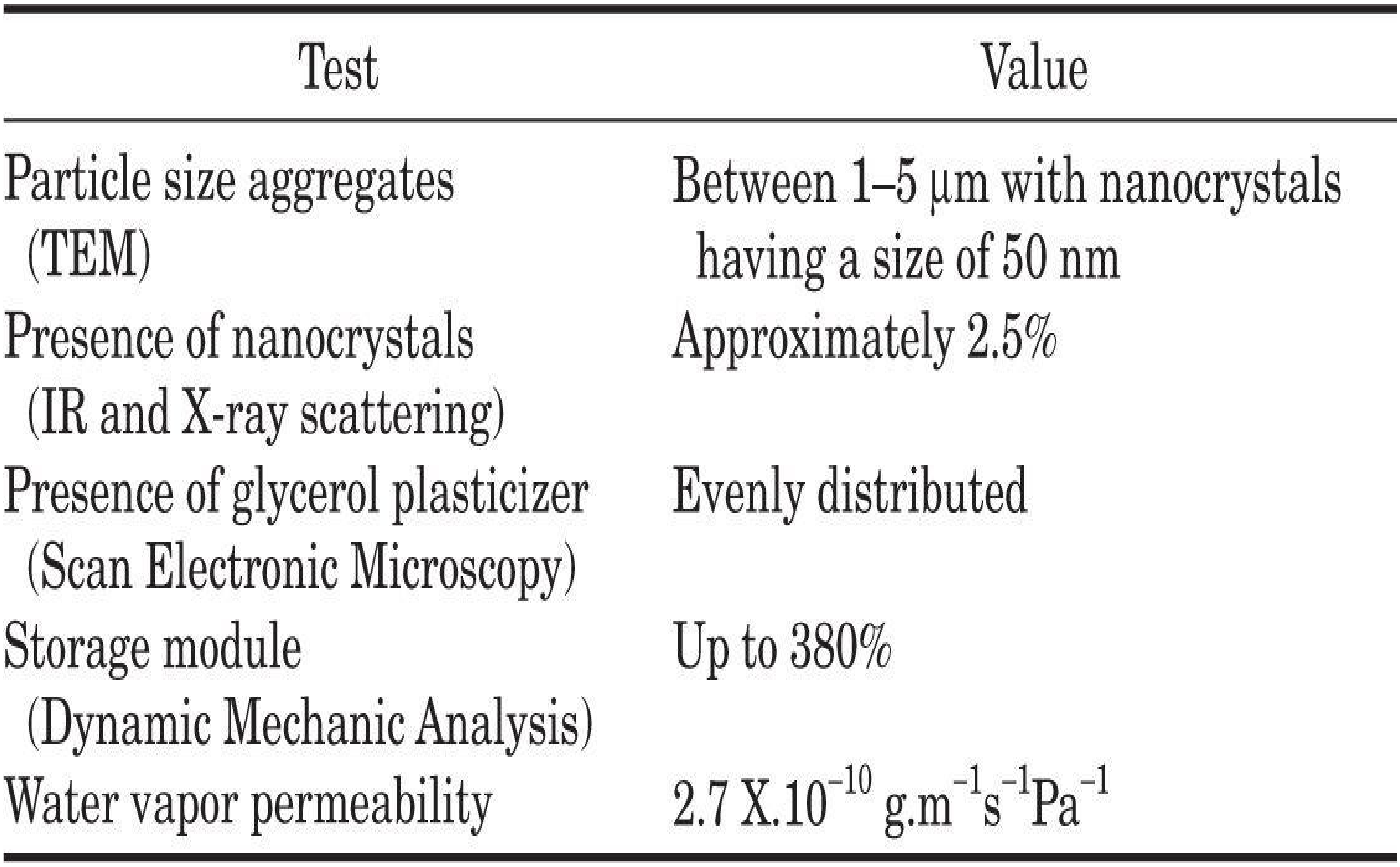
Experimental

1. Preparation of starch nanocrystals by acid hydrolysis. A large vessel charged with 36,725 g of waxy corn starch was treated with 250 mL of 3.16 M sulfuric acid and then mixed for five days at 40°C. Crude crystals generated from this process were isolated and continuously washed with distilled water until a neutral pH was obtained. White nanoparticles were isolated by filtration, dried, and then treated with several drops of an anti-microbial agent, re-dried, and stored at 4°C until needed.

2. Preparation of renewable films. A vessel containing a 2:1 wt/wt ratio of 15 g of starch and water was treated with 185 g of distilled water that formed a dispersion and was then treated with 2.5 wt% of glycerol. The mixture was then heated at a rate of 1.59°C/minute for 28 minutes where the mixture jellified at 70°C. The jellified mixture was then degassed for 30 minutes using a mechanic pump and then treated with 2.5 wt% to 5 wt% of starch nanocrystals obtained from the Step 1 process. At this point the mixture was stirred for 10 minutes at 250 rpm and then further degassed for an additional hour. The slurry was then poured into Petri dishes to form films and foils and cured at 50°C for 24 hours. Dried, whitish sheets isolated from these processing conditions had a thickness that ranged from 150 to 300 μm.

3. Preparation of renewable bags and related shapes. Sheets obtained from the Step 2 process were converted into bags by heat sealing. In this process, heat sealing was performed using a bag sealing device. A sealing temperature of approximately 90°C was typically used and was applied to the sheets for 1–2 minutes along the borders of both sheets. Borders of the sheets were between 5 to 20 cm in width or length and could be prepared in any other desired shape. Depending upon the application of the shape, a vacuum of 0.015 mm Hg or pressurization using a gas or a mixture of gases could be applied as part of the processing. Physical properties of the sheets are provided in Table 12.1.

TABLE 12.1 Physical properties of sheets prepared using a blend of processed glycerol, starch, and starch nanoparticles.



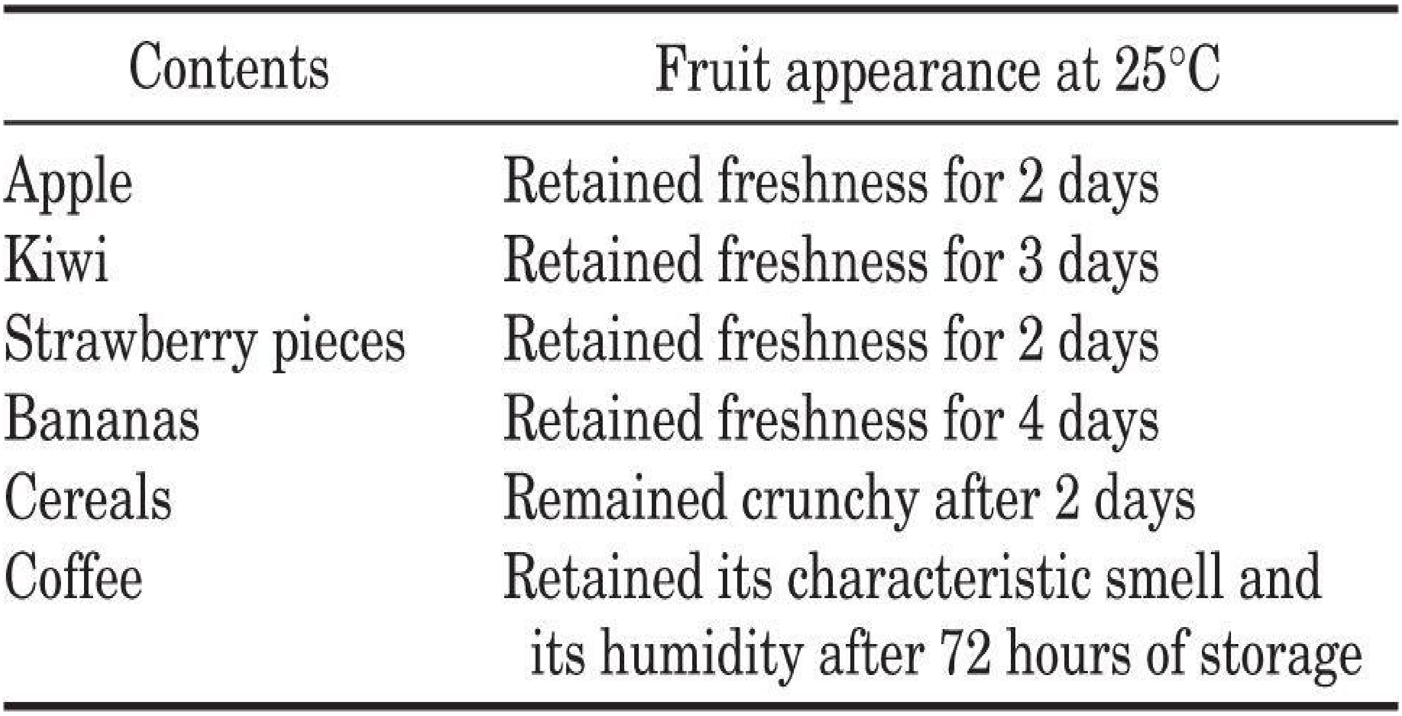
Test	Value
Particle size aggregates (TEM)	Between 1–5 µm with nanocrystals having a size of 50 nm
Presence of nanocrystals (IR and X-ray scattering)	Approximately 2.5%
Presence of glycerol plasticizer (Scan Electronic Microscopy)	Evenly distributed
Storage module (Dynamic Mechanic Analysis)	Up to 380%
Water vapor permeability	$2.7 X.10^{-10}$ $g.m^{-1}s^{-1}Pa^{-1}$

Testing

Storage stability properties.

Storage stability properties of selected fruits, coffee, and cereals were performed that were designed to assess both the freshness and robustness of the stored item. Items placed into food storage containers were stored at ambient temperature and evaluated daily for both freshness and robustness. Testing results are provided in Table 12.2.

TABLE 12.2 Storage properties of fruit, cereals, and coffee when stored in biodegradable bags prepared in Step 3.

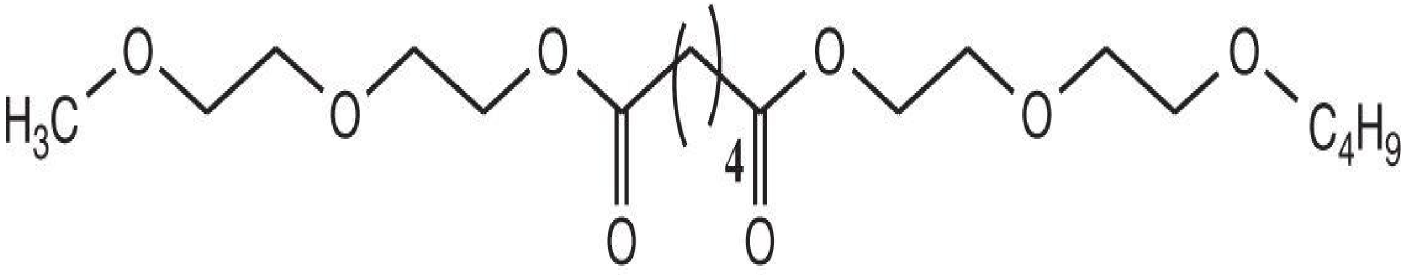


Contents	Fruit appearance at 25°C
Apple	Retained freshness for 2 days
Kiwi	Retained freshness for 3 days
Strawberry pieces	Retained freshness for 2 days
Bananas	Retained freshness for 4 days
Cereals	Remained crunchy after 2 days
Coffee	Retained its characteristic smell and its humidity after 72 hours of storage

Notes and Observations

1. Kellett[1] prepared renewable polymers for use in multi-component fibers containing thermoplastic polyethylene and polypropylene. In this process, a blend of 60 wt% polyethylene, 30 wt% thermoplastic starch, and 10 wt% ethyl acrylic acid were heated to 60°C for 12 hours so that the starch covered the polyethylene surface. Thereafter, the mixture was extruded through a Perkins twin screw at 400 rpm at 150°C in all zones and the fibers isolated.

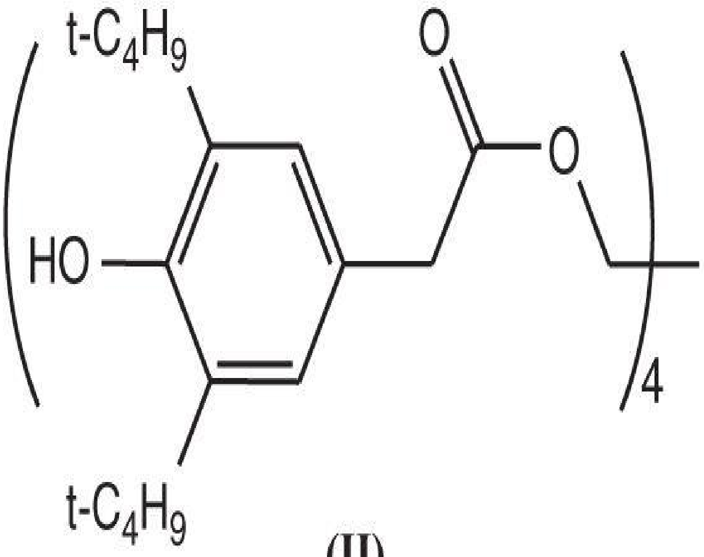
2. Fujita[2] used the mixed alcohol ester, methyl diglycol butyldiglycol adipate, (I), as a plasticizer for renewable and biodegradable polylactic acid sheets used to prepare food storage containers. (See Fig. 12.2.)



(I)

Figure 12.2

3. Polyethylene glycol having an Mn~4000 daltons was used by Gagliardi[3] as a plasticizer for disposable sanitary napkin formulation. In this process, the plasticizer was blended with a degradable hydrophilic polyurethane polymer, polyethylene glycol having an Mn ~4,000 daltons. The tetrakis[methylene-3 (3’,5’-di-tert-butyl-4-hydroxyphenyl)propionate] methane, (II), and the thermal stabilizer, tris(2,4-di-tert-butylphenyl) phosphite, (III), were used as anti-oxidants. (See Fig. 12.3.)



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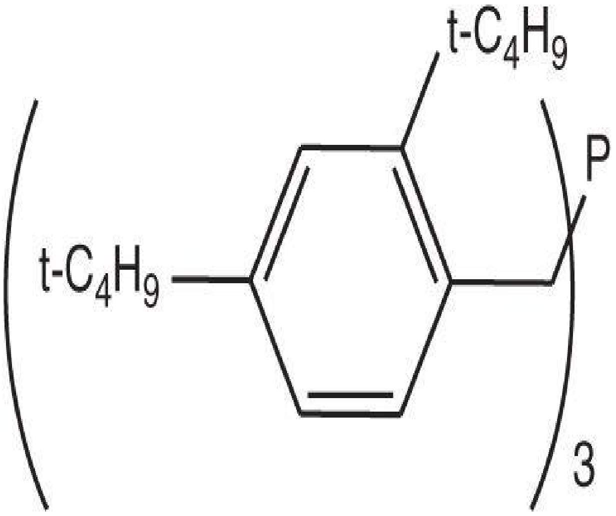

(III)

Figure 12.3

4. Rashti[4] prepared a biodegradable and disposal mouth clip to improve oral hygiene. The

mouth clip consisted of a semi-rigid biodegradable polyurethane biopolymer foam that was prepared by reacting either an aliphatic polyol or polyvinyl alcohol with a diisocyanate. Rigid biodegradable polyurethane foam prepared by this process could also be used for toothbrush handles or bristles.

References

1. Patti Jean Kellett et al., *Bio-polymers in multicomponent fibers*, U.S. Patent Application 20130023608 (January 24, 2013)

2. Yasunori Fujita et al., *Ester compound, plasticizer for biodegradable aliphatic polyester resin, and biodegradable resin composition*, U.S. Patent 7,166,654 (January 23, 2007)

3. Ivano Gagliardi et al., *Liquid absorbent thermoplastic composition comprising superabsorbent material particles of substantially angle-lacking shape*, U.S. Patent 7,321,007 (January 22, 2008)

4. Sean A. Rashti, *Disposable mouth chip-DMC*, U.S. Patent Application 20130034833 (February 13, 2013)

Chapter

13

Gasoline

Gasoline Containing Ethyl Alcohol Additives Derived from Fermentable Sugars

Author Ish Kumar Dhawan et al.

Patent Title ***Compositions and methods for production of fermentable sugars,*** U.S. Patent 8,309,328 (November 13, 2012)

Relevant Prior Patents by Author or Coauthors

Compositions and methods for production of fermentable sugars, U.S. Patent 8,236,551 (August 7, 2012)

Endoglucanases, U.S. Patent 8,206,960 (June 26, 2012)

Endoglucanases, U.S. Patent 8,293,792 (January 3, 2012)

Endoglucanases, U.S. Patent Application 20120315676 (December 13, 2012)

Endoglucanase variants, U.S. Patent Application 20120208235 (August 16, 2012)

Fungal strains, U.S. Patent Application 20120107880 (May 3, 2012)

Product Application

Myceliophthora thermophile fungal cells were effective in converting diverse sources of renewable biofeed stock into glucose. Glucose prepared by this route was then converted into ethyl alcohol using existing fermentation methods and used as either an automotive fuel or fuel additive.

Significance of Current Application

A method is provided that utilizes genetically modified Myceliophthora thermophile fungal cells to convert lignocellulose biofeeds derived from cellulose into glucose. Once lignocellulose biofeeds are converted into the intermediate oligosaccharides by steam treatment, they are then converted into glucose or related glucose intermediates. At this juncture both glucose of related glucose intermediates are readily converted into bio-ethyl alcohol by enzymatic processes for subsequent use as either an automotive fuel or an automotive fuel additive. The investigation is particularly significant since the biofeed stock was derived from a multitude of sources including wood pulp, wood chips, sawdust, hardwood, softwood, newsprint, cardboard, paper pulp, corn fiber, corn grain, corn cobs, corn husks, corn stover, grasses, wheat, wheat straw, barley, barley straw, and oat straw. The fermentable conversion of these biofeed sources provided high yields of fermentable glucose in relatively short reaction and processing times.

Strains

Strain CF-400 (Δcdh1) was a derivative of C1 strain (UV18100f Δalp1 ΔELTA.pyr5) that was then modified with a deletion of cdh1, wherein cdh1 comprised the polynucleotide sequence of SEQ ID NO:5.

Strain CF-401 (Δcdh1 Δcdh2) was a derivative of the C1 strain which was then modified with a deletion of both a cdh1 and a cdh2, where cdh2 comprised the polynucleotide sequence of SEQ ID NO:7.

Strain CF-402 (+bgl1) was a derivative of the C1 strain that was then modified with the overexpression of an endogenous beta-glucosidase 1 enzyme (bgl1).

Strain CF-403 was a derivative of the C1 strain that was then modified with a deletion of cdh1 and then further modified to overexpress bgl1.

Strain CF-404 was a derivative of the C1 strain that was then modified to overexpress bgl1 with a deletion of both cdh1 and cdh2.

Experimental

1. Biofeed pre-treatment. Wheat straw was initially steam treated so that the hemicelluloses was hydrolyzed into the relatively large intermediate oligosaccharides. Acetyl groups on the hemicellulose were also hydrolyzed into acetic acid, which further aided in the hydrolysis process. Following this pre-treatment, 0.5% of sodium benzoate was added as a preservative. The pre-treated material was then washed with six volumes of water at 35°C and the intermediate was isolated by filtration.

2. Enzymatic treatment of oligosaccharides. A portion of steam-treated wheat straw from the Step 1 process was then further hydrolyzed using cellulolytic enzymes Strain CF-401 through Strain CF-404. Steam-treated wheat straw was hydrolyzed using a treatment level of 30 mg of cellulolytic enzymes/g of cellulose at 50°C at a pH of 5.0 with 250-rpm orbital shaking.

3. Preparation and quantification of glucose. During the enzymatic treatment of the oligosaccharides phase described in Step 2, 1 mL sample aliquots were periodically removed and the enzymatic reaction terminated by heating the sample to 100°C for 5 minutes. The glucose concentration in the supernatant was then determined by using a coupled enzymatic assay based on glucose oxidase and horseradish peroxidases according to the method of Trinder.[1]

Testing Results

Glucose conversion of the biomass varied from 78% to 96% conversion. Although automotive fuel formulations were provided by the author, testing results were omitted.

Notes and Observations

1. Abbas[2] used enzymatic methods to convert carbohydrates into ethyl alcohol at elevated temperatures using yeast cells obtained from the genus H. polymorpha which contained an inactive acid trehalase gene containing an overexpression of xylulokinase with an

overexpression of heat-shock protein 104.

2. Fungal C1 strain β-glucosidase had at least a 5-fold thermo-activity greater than the unmodified Bgl1 strain, which had previously been prepared by Yang.[3] Fungal C1 strain β-glucosidase was used to convert renewable biomass into a fermentable sugar for subsequent conversion into either bio-ethyl alcohol or other bio-fuels.
3. Modified fungal α-amylase derived from either Aspergillus oryzae or B. licheniformis α-amylase was prepared by Svendsen[3] and then used to prepare fructose syrups.
4. Cascao-Pereira[4] treated insoluble cornstarch with covalently linked Remazol Brilliant Blue R with α-amylases isolated from Bacillus subtilis and prepared both glucose and bio-ethyl alcohol.

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3. Jie Yang et al., *Recombinant β-glucosidase variants for production of soluble sugars from cellulosic biomass*, U.S. Patent 8,323,947 (December 4, 2012)
4. Allan Svendsen et al., *α-Amylase mutants*, U.S. Patent 8,323,946 (December 4, 2012)
5. Luis G. Cascao-Pereira et al., *Variant α-amylases from Bacillus subtilis and methods of uses, thereof*, U.S. Patent 8,323,945 (December 4, 2012)

Automotive Fuel Derived from Lignocellulosic Waste

Author Jeffrey S. Tolan

Patent Title ***Method for the production of glucose from lignocellulosic feedstocks,*** U.S. Patent 8,298,796 (October 30, 2012)

Relevant Prior Patents by Author or Coauthors

Process of removing calcium and obtaining sulfate salts from an aqueous sugar solution, U.S. Patent 8,273,181 (September 25, 2012)

Method of obtaining inorganic salt and acetate salt from cellulosic biomass, U.S. Patent (August 21, 2012)

Enzyme compositions and methods for the improved enzymatic hydrolysis of cellulose, U.S. Patent 8,202,709 (June 19, 2012)

Method for glucose production using endoglucanase core protein for improved recovery and reuse of enzyme, U.S. Patent 8,012,721 (September 6, 2011)

Method of processing lignocellulosic feedstock for enhanced xylose and ethanol production, U.S. Patent 7,993,463 (August 9, 2011)

Product Application

A method is described for producing bio-ethyl alcohol from high cellulose-containing feedstocks that is then used as either a fuel or fuel additive in gasoline-powered automobiles.

Significance of Current Application

The objective of this investigation was to expand the source of agriculturally derived ethyl alcohol from biomasses. In the process of producing bio-ethanol, agricultural waste products, such as forestry wastes and grasses, were used as the bio-feedstock. Agricultural waste products not used in bio-feedstock processes to produce bio-ethyl alcohol were disposed of in landfills. The current invention has devised treatment methods that broaden agricultural bio-feedstock sources for generating bio-ethyl alcohol by using lignocellulosic waste. This is an effective method since lignocellulosic waste products are readily available, inexpensive, and comprise as much as 55% of most feedstocks. Using a hydrolysis/fermentation/hydrolysis experimental route, three biofeeds consisting of lignocellulosic waste, hemicellulose waste, and lignin were converted into bio-ethyl alcohol in approximately 78% yield. The relatively large and inexpensive bio-ethyl alcohol produced in this process was then used in consumer automotive fuel formulations.

Experimental

1. Isolation and purification of ethyl alcohol from wheat straw. Moisture-free wheat straw that was used had a 750 t/d with 12% moisture content. The wheat straw consisted of 35.9% of cellulose, 17.5% of xylan, 22.1% of lignin, and inorganic cations such as 1.1% of potassium, 0.13% of calcium, 0.06% of magnesium, and 0.01% of sodium. The wheat bales used were initially broken up and fed into a dilute sulfuric-acid-solution pretreatment vessel, and the slurry that formed was sent over a decanter centrifuge to separate the sugar stream from the pretreated wheat straw solids. The sugar stream had a flow rate of 121,000 L/h and consisted of a mixture of 26 g/L of xylose, 2.5 g/L of arabinose, 7.4 g/L of glucose, 1.7 g/L of galactose, and 0.9 g/L of mannose. Other soluble organic compounds detected in the stream included 3.5 g/L of acetic acid, 1.2 g/L of glucuronic acid, 0.7 g/L of galacturonic acid, and 2.2 g/L of furfural. The sugar stream also contained 7.3 g/L of sulfuric acid, 1.7 g/L of potassium cations, 0.2 g/L of calcium cations, 0.12 g/L of magnesium cations, and 0.02 g/L sodium cations. The sugar stream was then treated with 62.7 kg/hr of carbon dioxide at a rate designed to precipitate out both calcium and magnesium cations. Carbon dioxide was then fed into the vessel to react with both calcium and magnesium cations in the stream. In this process, sulfuric acid was generated and was then neutralized with a stream of 493 kg/hr of ammonium hydroxide and the precipitate removed by filteration. In this process, 52% of calcium carbonate and 48% of magnesium carbonate were prepared by filtration. The filter cake containing these materials was then concentrated to ~25% solids and resolubilized in water by treating it with dilute sulfuric acid. Once this process was completed the pH of the filtered sugar stream containing residual calcium carbonate and other cations was lowered to ~5. The wheat straw slurry was then treated with a cellulase enzyme for 96 hours at pH 5.0 at 50°C to enzymatically hydrolyze the sugar solution mixture. The slurry mixture was then transferred into a 4 to 5 million liter vessel and agitated using an 0.8 hp/1000 gal of power source. The cellulase enzyme treatment level during the hydrolysis process was approximately 25 mg/gram of cellulose.

Following the hydrolysis process, the slurry composition consisted of an aqueous sugar solution and unconverted wheat-derived solids that were subsequently removed using a filter press so that a clear aqueous stream solution resulted. The clear aqueous stream was then further fermented to convert residual glucose and xylose into ethanol using cellulase enzymes followed by re-treatment with dilute sulfuric acid. Thereafter, a still-bottom-stream distillation process was performed on the re-fermented clear aqueous phase, and bio-ethyl alcohol was distilled over and isolated in 77.8% yield in greater than 95% purity.

Notes and Observations

1. Foody[1] developed a high-yielding method for preparing bio-ethyl alcohol from lignocellulosic feedstock by first removing inorganic salts from the biomass. The salt-removing process and bio-ethyl alcohol consisted of the following five-step treatment process:

   a. Pretreating the lignocellulosic feedstock with one or more acids to produce a lignocellulosic feedstock containing at least a portion of hemicellulose in the feedstock that was then hydrolyzed to a sugar mixture consisting of xylose, arabinose, mannose, galactose, and/or any combination.
   b. Removing the sugar-acid mixture from the pretreated lignocellulosic feedstock.
   c. Adding base to the sugar-acid mixture and then recovering residual inorganic salts.
   d. Treating the sugar-acid lignocellulosic feedstock with one or more water-soluble

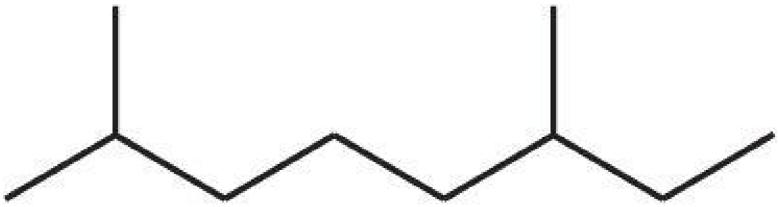
inorganic bases to adjust the lignocellulosic feedstock pH to between 4.0 and 6.0 or to obtain a neutralized feedstock.

e. Enzymatically hydrolyzing the neutralized feedstock to produce a sugar stream and an enzyme hydrolyzed feedstock.

f. Fermenting the sugar stream to produce a fermentation broth and distilling and isolating bio-ethyl alcohol from the filtered solution.

2. Rusek[2] developed a two-step method for preparing non-petroleum high-octane aviation fuel derived from biomass sources. In the initial phase, biomass feedstocks were converted into sugars and then fermented using microorganisms or mutagens to prepare bio-ethyl alcohol or acetic acid. In the subsequent phase, bio-ethyl alcohol or acetic acid were converted into acetone that was then catalytically converted into mesitylene and isopentane using niobium, iron, silver, or manganese oxides-based catalysts. When used as an additive in jet fuel formulations, high-octane aviation fuel was obtained.

3. Martin[3] processed an exogenous gene encoded with 3 hydroxy-3-methyl-glutaryl-CoA reductase with lignocellulosic feedstocks to obtain 2,6-dimethyloctane, (I), which was used to prepare high-octane automotive fuels. (See Fig. 13.1.)



(I)

Figure 13.1

4. Lantero[4] used the microorganism Rhizopus for producing bio-ethyl alcohol by mixing a ground slurry of uncooked corn starch for 72 hours with Rhizopus enzymes at ambient temperature. In this process, glucose converted into bio-ethyl alcohol in quantitative yields.

References

1. Brian Foody, *Recovery of inorganic salt during processing of lignocellulosic feedstocks*, U.S. Patent 8,247,203 (August 21, 2012)

2. John J. Rusek, *Renewable engine fuel and method of producing same*, U.S. Patent 8,313,540 (November 20, 2012)

3. Kevin V. Martin et al., *Dimethyloctane as an advanced biofuel*, U.S. Patent 8,309,323 (November 13, 2012)

4. Oreste Lantero et al., *Methods for producing ethanol from carbon substrates*, U.S. Patent 8,293,508 (October 23, 2012)

Chapter

14

Industrial Chemicals

Acrolein

Author Jean-Luc Dubois

Patent Title ***Method for producing acrolein by means of dehydration of glycerol***, U.S. Patent 8,324,432 (December 4, 2012)

Relevant Prior Patents by Author

Process for manufacturing acrolein or acrylic acid from glycerin, U.S. Patent 8,252,960 (August 28, 2012)

Method for preparing acrylic acid from glycerol, U.S. Patent 8,212,070 (July 3, 2012)

Method for synthesis of acrolein from glycerol, U.S. Patent 8,143,454 (March 27, 2012)

Acrylic acid preparation method, U.S. Patent 7,880,034 (February 1, 2011)

Process for the preparation of acrylic acid comprising a partial oxidation of propane to propylene, U.S. Patent 7,732,639 (June 8, 2010)

Acrolein Preparation Method, U.S. Patent 7,531,699 (May 12, 2009)

Product Application

Acrolein is used in the preparation of acrylic acid that, when polymerized alone or as an esterified analogue, is used to prepare alkyl polyacrylates. Acrolein is also a key intermediate in the synthesis of the synthetic amino acid, methionine, which is used as a replacement for fish meal in animal food supplements.

Significance of Current Application

The non-renewable industrial method for preparing acrolein relies upon steam or catalytically cracking selected petroleum fractions to initially prepare propylene, which is subsequently non-selectively oxidized at elevated temperatures to form the desired product. This process, however, requires extensive purification of the oxidation-reaction product mixture before acrolein can be isolated and converted into acrylates, methionine, acrylonitrile, or related fine chemicals. The current investigation has developed a method to prepare acrolein by dehydrating renewable glycerol using an acid-gas mixture with a tungstated zirconia catalyst. This process uses biobased glycerol, is not energy intensive, and generates minimal amount of organic-reaction waste products.

Product Formation

A. Reaction catalyst. The tungstated-zirconia dehydration catalyst was purchased from Daiichi Kigenso KK, Z1044. These catalysts are characterized as containing enough surface tungsten oxide to give a monolayer on the zirconia support that behaves as the catalytic surface. It is also active as a dehydrating agent and can be regenerated after poisoning.

B. Product formulation.

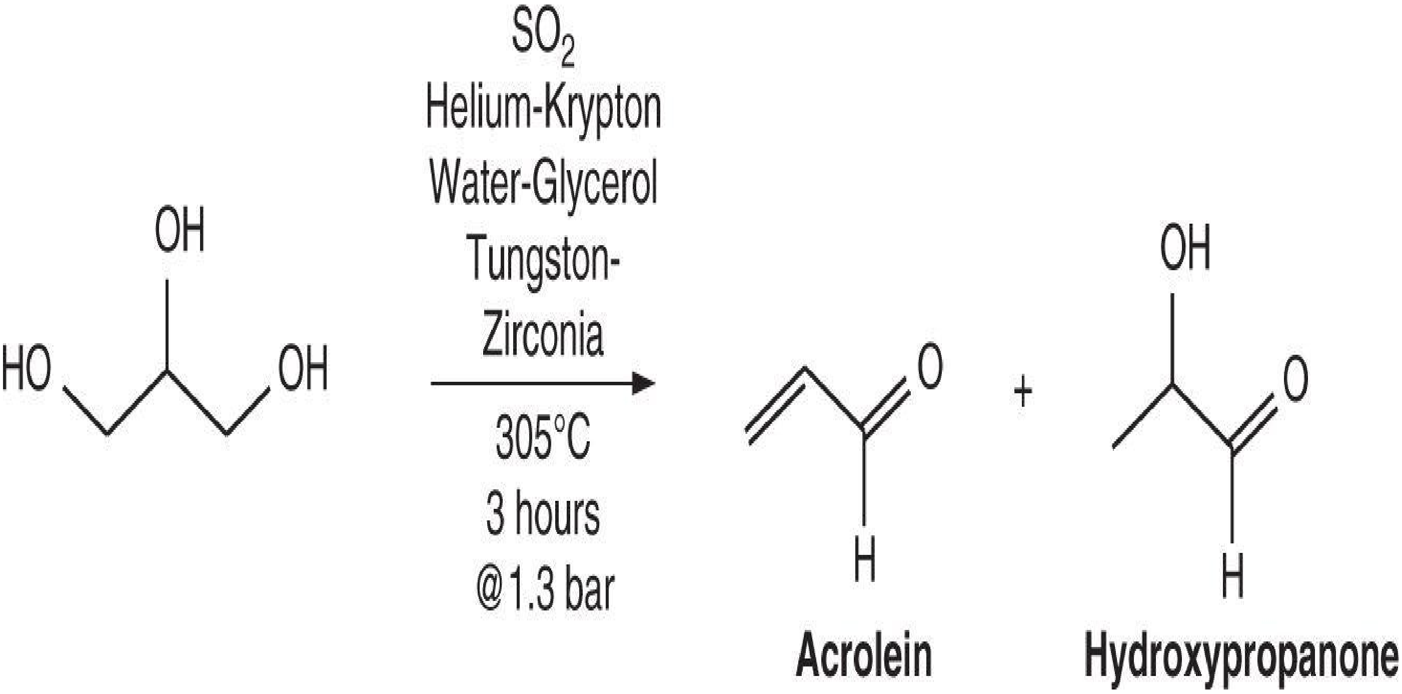


Figure 14.1

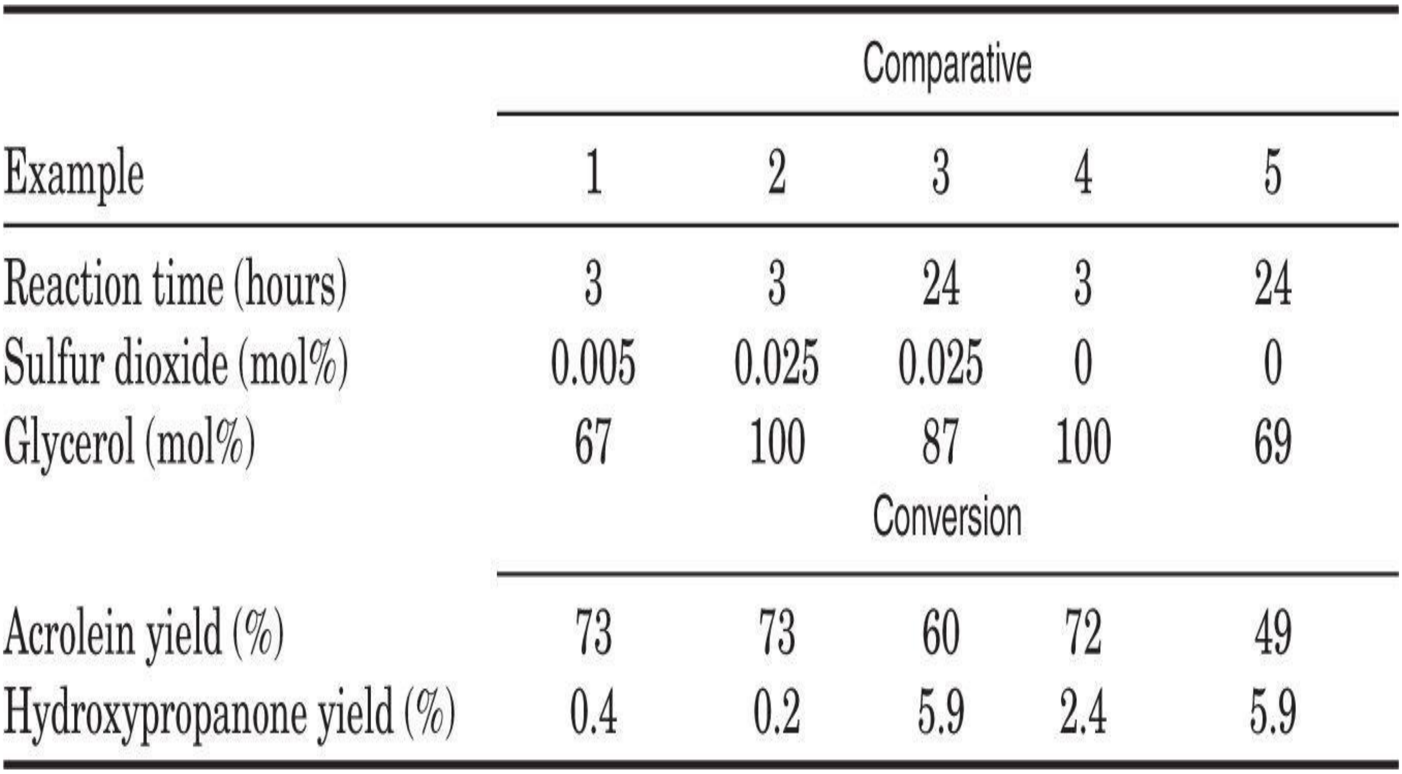
Experimental

1. Preparation of the dehydration catalyst. A Pyrex reactor containing a catalytic bed held on a sintered glass was treated with 6.6 g of tungstated zirconia having a particle size of between 0.1 mm and 0.15 mm with 7 mL of silicon carbide having an average particle size of 0.125 mm. The glass reactor was then placed into an oven and heated to 305°C for 4 hours. After cooling, 7.2 g of the dehydration catalyst was isolated as a blackish solid and used immediately.

A. Preparation of acrolein. The reactor and catalyst described in Step 1 was immediately treated with a mixture of helium-krypton/SO_2/water-glycerol at 1.3 bar pressure then heated to 305°C for 3 hours. The helium-krypton gas mixture contained 4.92% of krypton while the water-glycerol mixture contained 67 mol% of glycerol. Sulfur dioxide levels were maintained at 0.005 mol% throughout the reaction. Effluents formed during the reaction were separated from non-condensable materials using a cold trap at 0°C, and acrolein and hydroxypropanone levels were quantitatively determined using chromatographic methods. After distillation, acrolein was isolated in 73% yield in 98% purity. Other stoichiometries used to prepare acrolein and product conversions are provided in Table 14.1.

TABLE 14.1 Summary of reaction stoichiometries and formation of acrolein and hydroxypropanone. Comparative reactions performed in the absence of sulfur

dioxide resulted in very low product yields.



	Comparative				
Example	1	2	3	4	5
Reaction time (hours)	3	3	24	3	24
Sulfur dioxide (mol%)	0.005	0.025	0.025	0	0
Glycerol (mol%)	67	100	87	100	69
			Conversion		
Acrolein yield (%)	73	73	60	72	49
Hydroxypropanone yield (%)	0.4	0.2	5.9	2.4	5.9

Testing Results

Notes and Observations

1. At 200°C, Suppes[1] dehydrated renewable glycerol with the hydroxyacetone intermediate, (I), using a copper-chromite catalyst. The intermediate was then hydrogenated and propylene glycol, (II), was isolated, as illustrated in Eq. 1. (See Fig. 14.2.)

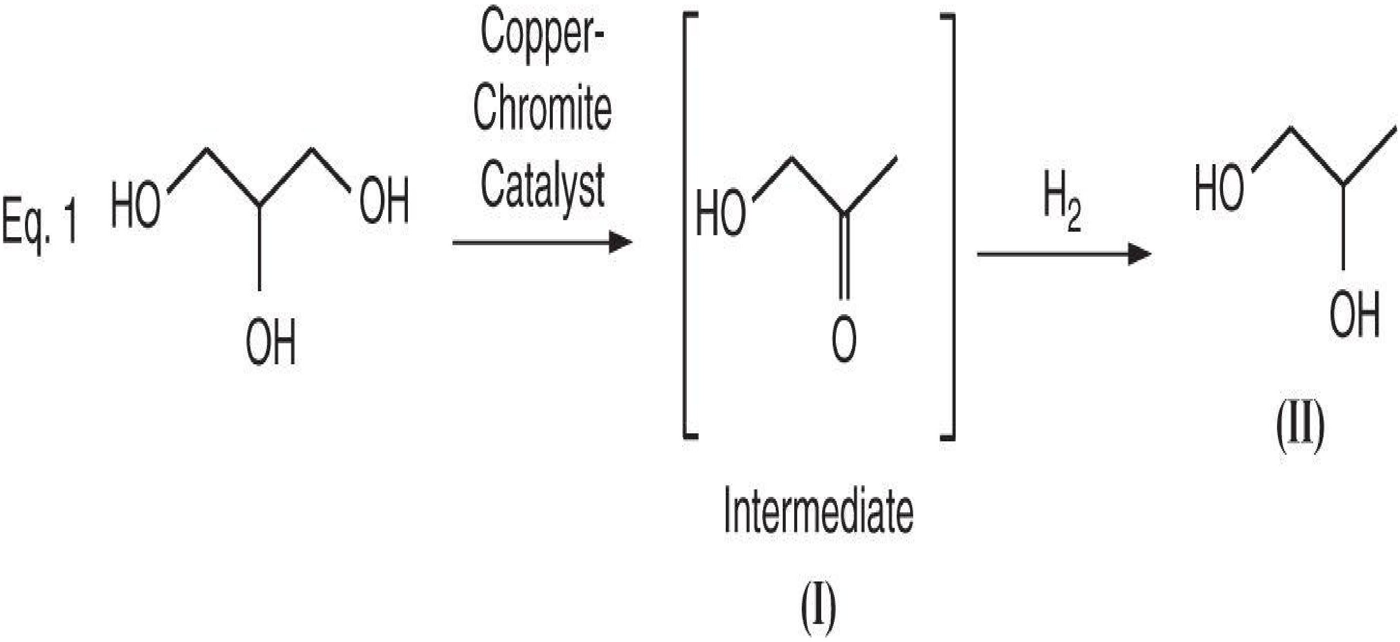


Figure 14.2

2. In an earlier investigation by the author,[2] a dehydration catalyst consisting of the cesium salt of tungstophosphoric acid, $Cs_3[PW_{12}O_{40}]\cdot nH_2O$, n ~ 30, was used to prepare both acrolein and acrylic acid through the dehydration of renewable glycerol. In this process,

gasified glycerin was passed through a fixed-catalyst bed of $Cs_3[PW_{12}O_{40}] \cdot nH_2O$, n ~ 30 containing air at a reaction temperature ranging from 260°C to 350°C. Product conversions were not provided by the author, however.

3. In a two-step process, the author[3] initially dehydrated renewable glycerol into acrolein using a fixed-catalytic bed consisting of silicate zirconias at a reaction temperature ranging from 250°C to 320°C. The reaction mixture was then purified by distillation and converted into acrylic acid by air oxidation using either a ruthenium or rhodium oxide catalyst. These reactions are summarized in Eq. 2. (See Fig. 14.3.)

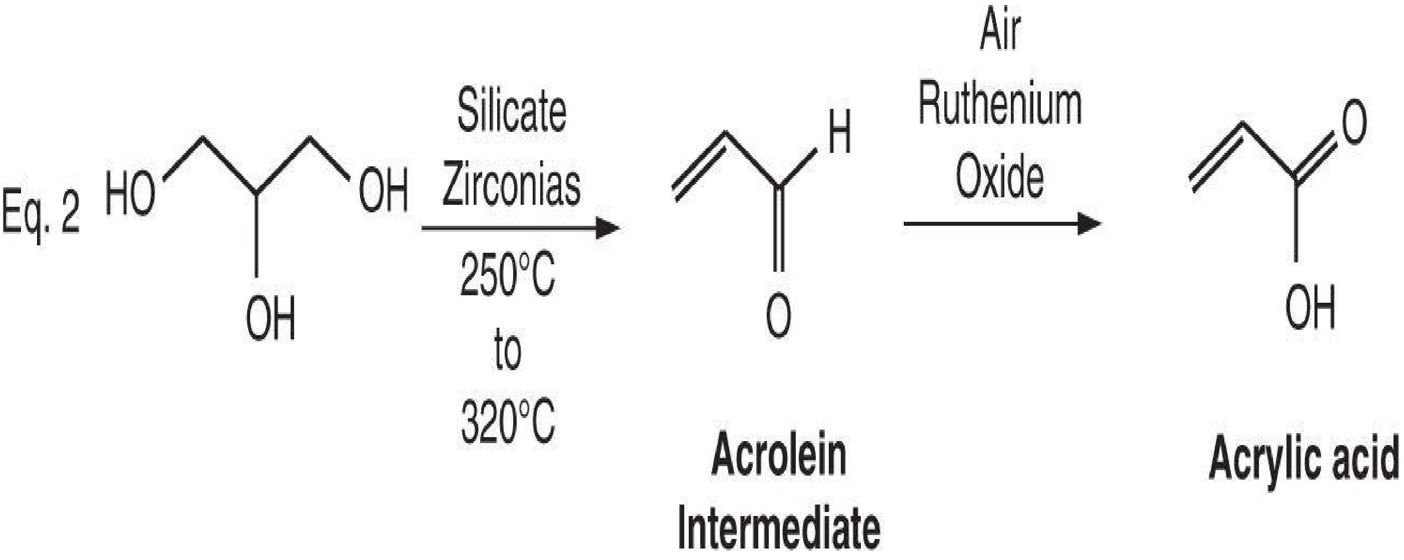


Figure 14.3

4. Kuppinger[4] prepared acrylic acid by the dehydration of 3-hydroxypropionic acid that was then used to prepare polyacrylic acid. In this process, a mixture of 3-hydroxypropionic acid, baker’s yeast, and renewable glucose were heated to 140°C under a pressure of 8 bar over a dwell time of 8 minutes in the presence of between 1 part to 5,000 parts of phosphoric acid. Acrylic acid yields for this reaction typically exceeded 62%.

References

1. Galen J. Suppes, *Method of producing lower alcohols from glycerol*, U.S. Patent 8,252,961 (August 28, 2012)

2. Jean-Luc Dubois, *Process for manufacturing acrolein or acrylic acid from glycerin*, U.S. Patent 8,252,960 (August 28, 2012)

3. Jean-Luc Dubois, *Method for preparing acrylic acid from glycerol*, U.S. Patent 8,212,070 (July 3, 2012)

4. Franz-Felix Kuppinger et al., *Process for preparing acrylic acid purified by crystallization from hydroxypropionic acid and apparatus therefore*, U.S. Patent 8,198,481 (June 12, 2012)

6-Aminocaproic Acid

Author Brian M. Baynes et al.

Patent Title ***Biological synthesis of 6-aminocaproic acid from carbohydrate feedstocks,*** U.S. Patent 8,404,465 (March 26, 2013)

Relevant Prior Patents by Author or Coauthors

Methods and systems of producing dicarboxylic acids, U.S. Patent Application 20120259138 (October 11, 2012)

Process for purifying an organic acid, U.S. Patent Application 20030171615 (September 11, 2003)

Process for purifying an organic acid, U.S. Patent Application 20030155298 (April 21, 2003)

Process for obtaining an organic acid from an organic acid ammonium salt, an organic acid amide, or an alkylamine organic acid complex, U.S. Patent Application 20030029711 (February 13, 2003)

Process for production of esters, U.S. Patent 6,664,413 (December 16, 2003)

Process for production of organic acids and esters thereof, U.S. Patent 6,291,708 (September 18, 2001)

Product Application

6-aminocaproic acid is the precursor to nylon and nylon copolymers, polyesterpolyols, plasticizers, and is used in food blends as an acidulant.

Significance of Current Application

In 2005, the global demand for 6-aminocaproic acid was approximately 2.7 million metric tons. This entire amount of 6-aminocaproic acid, however, was derived from non-renewable fossil fuels. This investigation represents the first example of preparing 6-aminocaproic acid from renewable lysine and a recombinant microorganism, which is not energy intensive. This method generates 6-aminocaproic acid in both high and in very high purity.

Experimental

1. Preparation of 6-aminocaproic acid. A recombinant microorganism was used in the preparation of producing 6-aminocaproic acid from lysine. The recombinant microorganism consisted of a recombinant nucleic acid encoded with a polypeptide that catalyzes a substrate-to-product conversion of 6-amino-3-hydroxyhexanoyl-CoA to 6-aminohex-2-enoyl-CoA. A vessel was charged with a selected recombinant microorganism and lysine then placed into a growth medium consisting of:

TABLE 14.2

Component	Mass (g)
Water	1000
Chloride ion	19.29
Sodium ion	10.78
Calcium carbonate	5
Sodium silicate	5
Na_2NTA	3.0
Iron(III) chloride	2.5
Sulfate ion	2.6
Magnesium ion	1.5
Calcium chloride	0.5
Potassium ion	0.42
Bicarbonate ion	0.21
Sodium succinate	0.15
Sodium nitrate	0.075
Bromide ion	0.056
Sodium acetate	0.05
Boric acid	0.0257
Zinc sulfate hydrate	0.022
Sodium phosphate	0.01
Cobalt chloride hydrate	0.01
Strontium chloride hydrate	0.01
Potassium molybdenum hydrate	0.0063
Folic Acid (B9)	0.002
Fluoride ion	0.001
Vitamin C	0.0007
Thiamin (B1)	0.0007
Riboflavin (B2)	0.0005
Niacin	0.0005
Vitamin B6	0.0005
Pantothenic acid	0.0005
Vitamin E	0.0002
Copper ion	0.00002
Vitamin A	0.00001
Folate	0.000002
Iodine	0.0000015
Chromium ion	0.0000012
Vitamin B12	0.0000006
Vitamin B7	0.000001
Vitamin K	0.00000025
Selenium ion	0.0000002
Vitamin D	0.0000001

The mixture was then fermented for 48 hours at 23°C and 6-aminocaproic acid was isolated using chromatographic methods. After re-crystallization, the product was isolated in 91% yield having a 96% purity.

Notes and Observations

1. Raemakers-Franken[1] metabolized 6-aminohex-2-enoic acid into 6-aminocaproic acid using either Escherichia coli, Bacillus, or Corynebacterium glutamicum microorganisms.
2. Dehydrogenase L-lactate dehydrogenase (EC1.1.1.28) or D-lactate dehydrogenase (EC1.1.1.27) were used by Senkpeil[2] to prepare chiral α-hydroxy-carboxylic acids including (2R)- or (2S)-2-hydroxypentanoic acid, (2R)-or (2S)-2-hydroxyhexanoic acid, (2R)- or (2S)-2-hydroxy-3-methylpentanoic acids.
3. Cheng[3] used a gene cluster isolated from an Acinetobacter sp. that encoded enzymes to convert cyclohexanol to adipic acid. Yields in this process were moderate to substantial.
4. Brzostowicz[4] prepared the adipic acid intermediate, 6-hydroxy hexanoic acid, using a host cell containing the chimeric gene. Host cells included those that were isolated from the groups of genera consisting of Escherichia, Bacillus, Brevibacterium, Corynebacterium, Mycobacterium Rhodococcus, Arthrobacter, Nocardia, Streptomyces, and Actinomyces microorganisms.

References

1. Petronella C. Raemakers-Franken et al., *Biochemical synthesis of 6-amino caproic acid*, U.S. Patent 7,491,520 (February 16, 2009)
2. Richard F. Senkpeil et al., *Production of α-hydroxy-carboxylic acids using a coupled enzyme system*, U.S. Patent Application 20040053382 (March 18, 2004)
3. Qiong Cheng et al., *Biological method for the production of adipic acid and intermediates*, U.S. Patent 6,498,242 (December 24, 2002)
4. Patricia C. Brzostowicz et al., *Genes and enzymes for the production of adipic acid intermediates*, U.S. Patent 6,365,376 (April 2, 2002)

Furfural, Furfurol, Levulinic Acid, and γ-Valerolactone

Author	James Dumesic et al.
Patent Title	***Method to produce, recover, and convert furan derivatives from aqueous solutions using alkylphenol extraction,*** U.S. Patent 8,389,749 (March 5, 2013)

Relevant Prior Patents by Author or Coauthors

Production of levulinic acid, furfural, and gamma valerolactone from C5 and C6 carbohydrates in mono- and biphasic systems using γ-valerolactone as a solvent, U.S. Patent 8,399,688 (March 19, 2013)

Hydroxymethylfurfural ethers and esters prepared in ionic liquids, U.S. Patent 8,314,260 (November 20, 2012)

Mixture of furfural and 5-(alkoxymethyl)furfural derivatives from sugars and alcohols, U.S. Patent 8,277,521 (October 2, 2012)

Process for converting cellulose in a liquid biofuel using N-methyl, imidazolium chloride, U.S. Patent 8,247,581 (April 23, 2012)

Photobioreactor systems and methods for treating CO_2 enriched gas and producing biomass, U.S. Patent 8,110,395 (February 7, 2012)

Production of levulinic and levulinate esters from biomass, U.S. Patent Application 20100312006 (December 9, 2010)

Product Application

Furfural, furfurol, levulinic acid, and γ-valerolactone are valuable industrial chemical intermediates. They are particularly useful in preparing polymeric materials and chemical additives.

Significance of Current Application

The objective of this investigation was to develop methods for preparing furfural, furfurol, levulinic acid, and γ-valerolactone using renewable and sustainable biosources. This investigation also addresses a greater concern associated with the future availability of chemical resources since petrochemical resources used to produce them continue to diminish.

To address these to concerns, this investigation has developed renewable and sustainable sources to prepare furfural, furfurol, levulinic acid, and γ-valerolactone, four industrially significant which are needed in industrialized societies. Beginning with the sugar xylose, which was derived from renewable and sustainable corn-stover biomasses, the author was able to prepare these four compounds in relatively high yields, moderate energy intensity, and with moderate organic-reaction toxic-waste formation. Furfural, (I);

furfuryl alcohol, (II); levulinic acid, (III); and γ-valerolactone, (IV), can be used to prepare polymers, additives, and pharmaceutical intermediates. (See Fig. 14.4.)

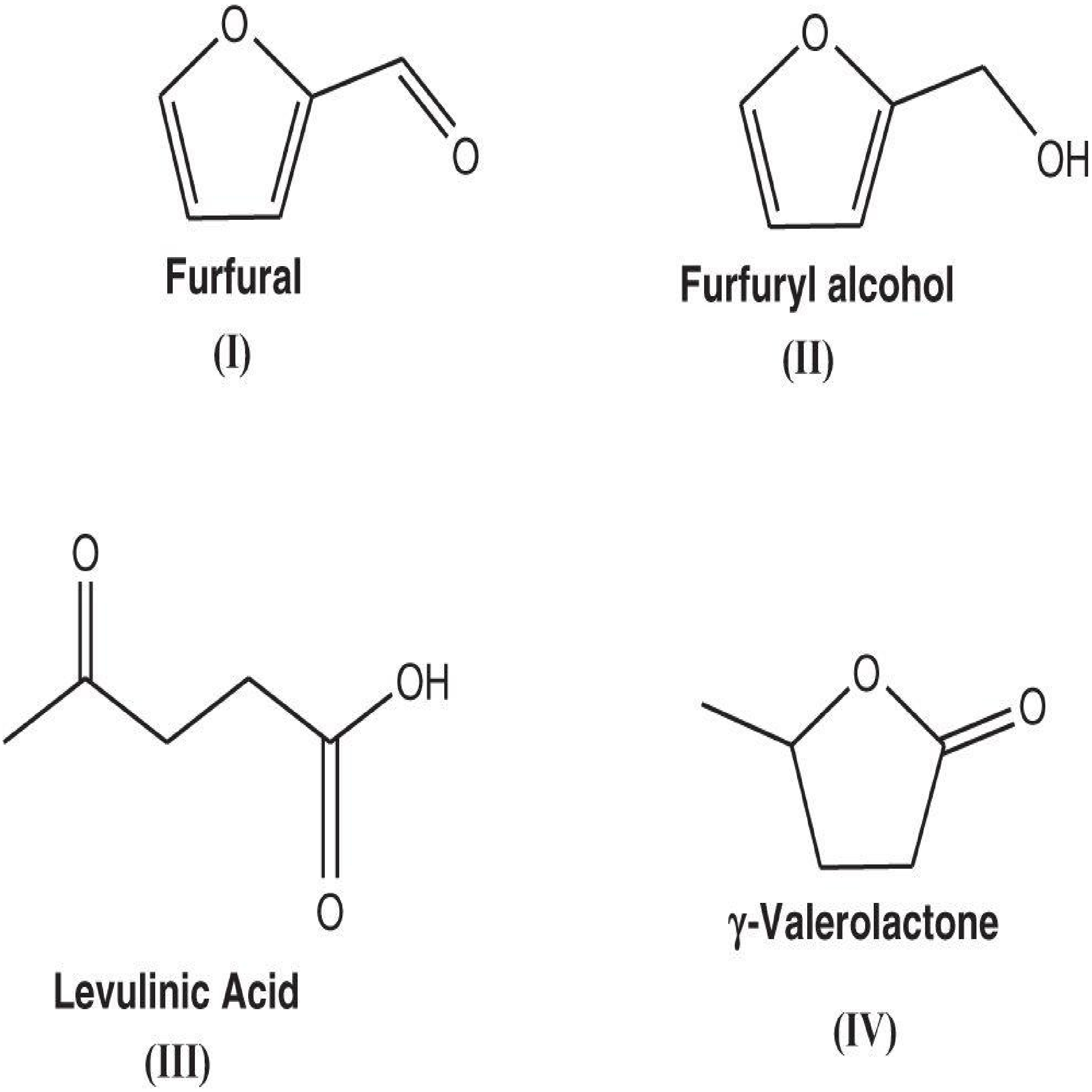


Figure 14.4

Product Formation

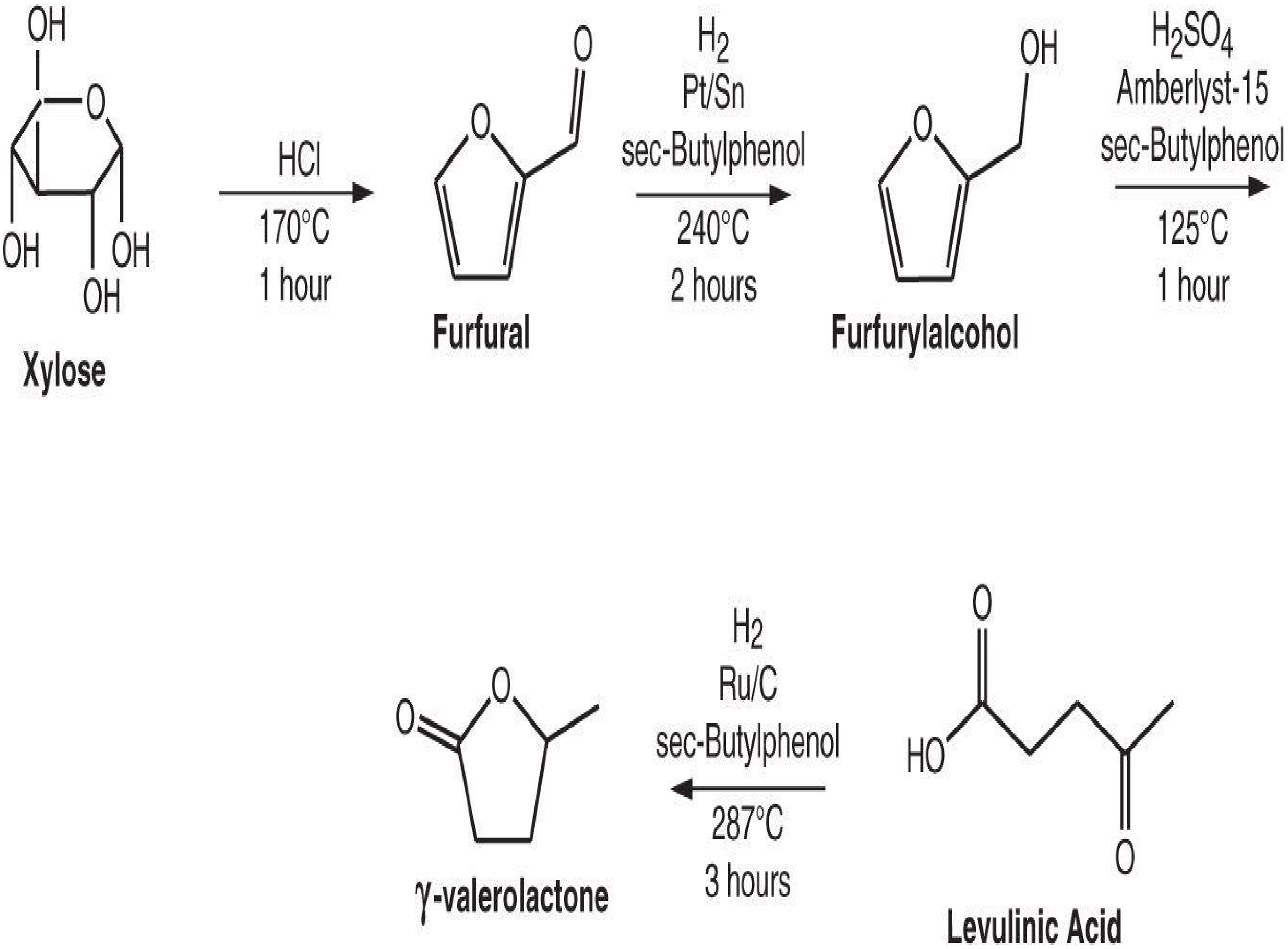


Figure 14.5

Aromatic Partition Coefficients

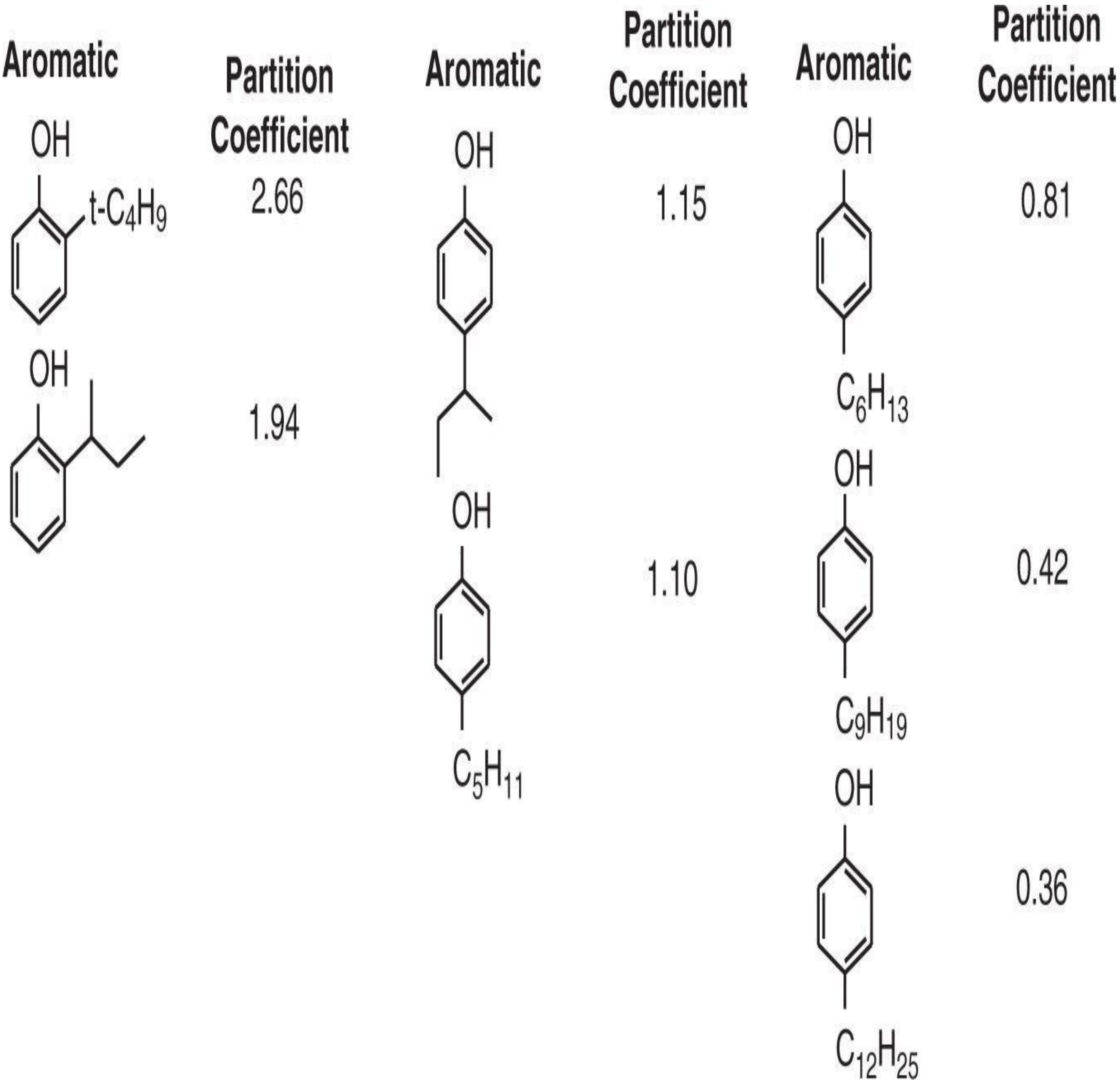


Figure 14.6

Experimental

1. Preparation by dehydration of xylose. Dehydration of xylose was conducted in water containing xylose, 0.1 M hydrochloric acid, and the organic extracting solvent, 2-sec-butylphenol. In a typical reaction, a glass reactor was charged with 2.5 g of xylose, 47.5 mL of water, 10 mL of 0.1 M hydrochloric acid, and 25 mL of 2-sec-butylphenol. The biphase solution was then heated to 170°C for approximately one hour and the solutions were separated. The 2-sec-butylphenol solution was distilled and furfural was isolated in 71%.

2. Preparation of furfuryl alcohol by hydrogenation using Pt/Sn bimetallic catalyst. A glass reactor was charged with 25 g of furfural isolated from Step 1, 45 g of 2-sec-butylphenol, and 0.5 g of bimetallic Pt/Sn catalyst on a SiO_2 support. The mixture was then heated to 240°C. After the mixture was cooled to ambient temperature it was extracted with 2-sec-butylphenol. After removal of 2-sec-butylphenol by distillation, furfuryl alcohol was isolated in 97.8% yield.

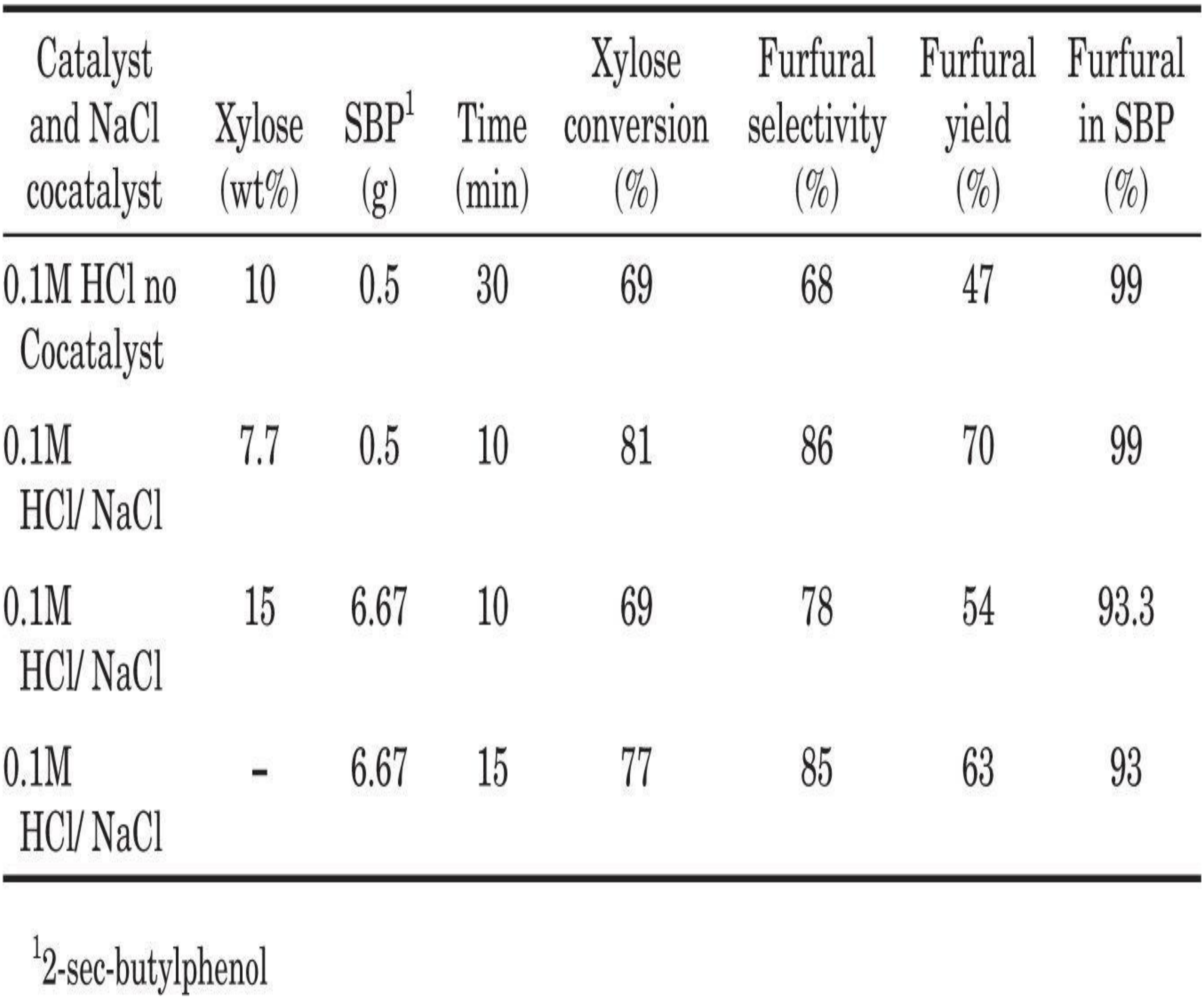
3. Preparation of levulinic acid from furfuryl alcohol. A reactor was charged with 50 g of the Step 2 product, 12 M hydrochloric and 18 M sulfuric acids, 3 g of Amberlyst-15, and 70 g of 2-sec-butylphenol. The reaction temperature was then increased to 125°C for approximately one hour and then cooled. The organic phase was then isolated, distilled, and levulinic acid was isolated in 94% yield.

4. Preparation of γ-valerolactone from levulinic acid by hydrogenation. A round-bottom flask was charged with 1.0 g of 5 wt% Ru/C, 10 g of levulinic acid from Step 3, and 35 g of 2-sec-butylphenol as the extraction solvent. While adequately stirring the mixture the temperature was increased to 287°C for 3 hours under a steady stream of hydrogen gas. After cooling to ambient temperature, 2-sec-butylphenol was isolated, distilled, and γ-valerolactone was isolated in 78% yield.

Testing Results

Reaction scooping results for the formation of furfural using renewable xylose are provided in Table 14.3.

TABLE 14.3 Scoping reactions for the formation of furfural from the dehydration of xylose conducted at 170°C in a biphasic system using 2-sec-butylphenol (SBP) as the extracting solvent.



Catalyst and NaCl cocatalyst	Xylose (wt%)	SBP[1] (g)	Time (min)	Xylose conversion (%)	Furfural selectivity (%)	Furfural yield (%)	Furfural in SBP (%)
0.1M HCl no Cocatalyst	10	0.5	30	69	68	47	99
0.1M HCl/ NaCl	7.7	0.5	10	81	86	70	99
0.1M HCl/ NaCl	15	6.67	10	69	78	54	93.3
0.1M HCl/ NaCl	-	6.67	15	77	85	63	93

[1] 2-sec-butylphenol

Notes and Observations

1. Lake[1] developed a novel method for isolating levulinic acid from biomass. In this process biomass was placed into a sealed recovery module and then heated to approximately 175°C for 30 minutes or longer using a pressurized refiner. Levulinic acid was then extracted in high yields using furfural. Biomasses useful for this process include sludges from paper manufacturing process, agricultural residues, molasses, aqueous oak wood extracts, rice hull, oats residues, wood sugar slops, fir sawdust, cotton balls, wood flour, straw, and corn husks.

2. In an earlier biphase investigation by Dumesic[2] an aqueous solution of fructose containing DMSO or butanol was dehydrated into furan and the product extracted using either cyclobutanone, cyclopentanone, or cyclohexanone.

3. In a subsequent investigation by Shearer,[3] cellulose or xylose was used to prepare levulinic acid, furfural, or γ-valerolactone. In this process, cellulose or xylose was mixed in a single-phase aqueous-reaction medium containing 0.1 M hydrochloric acid and then heated under pressure to 170°C. The mixture was then extracted with water-immiscible γ-valerolactone and levulinic acid, furfural, or γ-valerolactone was isolated.

4. Gruter[4] prepared 2-hydroxymethylfurfural, (V), from the acid-catalyzed reaction of

fructose present in biomass and then converted it into 5-(ethoxymethyl)furfural, (VI), and 2-(ethoxymethyl)-5-methylfuran, (VII). All biomaterials generated from this process were used in gasoline-powered engines as octane boosters. (See Fig. 14.7.)

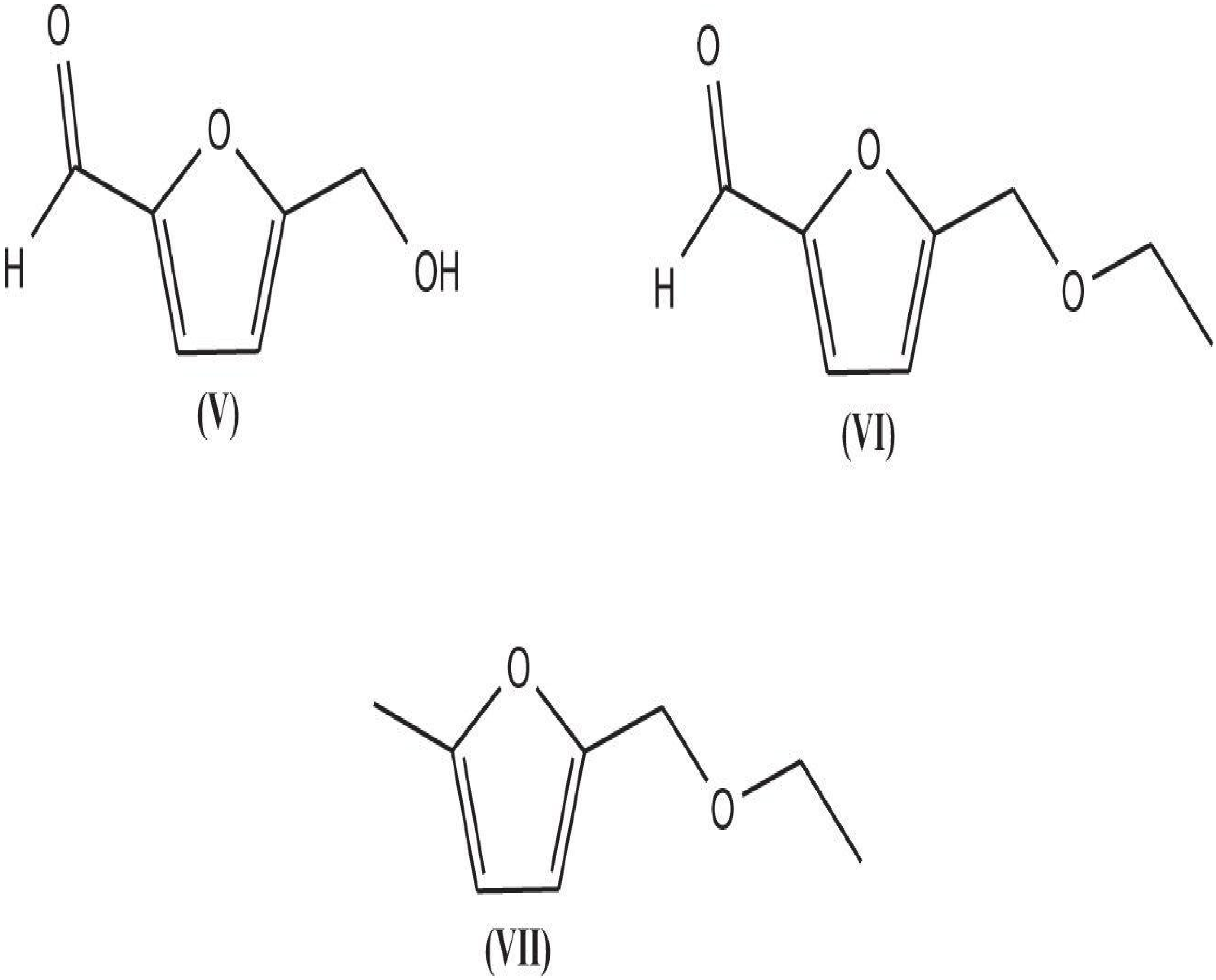


Figure 14.7

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1. Michael A. Lake et al., *Production of levulinic acids and levulinate esters from biomass*, U.S. Patent Application 20100312006 (December 9, 2010)

2. James A. Dumesic et al., *Catalytic process for producing furan derivatives in a biphasic reactor*, U.S. Patent 7,572,925 (August 11, 2009)

3. David Shearer et al., *Production of levulinic acid, furfural, and γ-valerolactone from C_5 and C_6 carbohydrates in mono- and biphasic systems using γ-valerolactone as a solvent*, U.S. Patent 8,399,688 (March 19, 2013)

4. Gerardus Johannes Maria Gruter, *5-Substituted 2-(alkoxymethyl)furans*, U.S. Patent 8,231,693 (July 31, 2012)

Hydrazides

Author George Anello Chiarello et al.

Patent Title ***Processes for making hydrazides,*** U.S. Patent 8,383,857 (February 26, 2013)

Relevant Prior Patents by Author or Coauthors

Processes for making hydrazides, U.S. Patent 8,110,705 (February 7, 2012)

Scalable process for the preparation of a rapamycin 42-ester from a rapamycin 42-ester boronate, U.S. Patent 7,622,578 (November 24, 2009)

Product Application

This investigation describes a method for selectively preparing monohydrazides while minimizing the formation of bis-hydrazide by-products. In this process, mono-3-methyl-3-mercaptobutanoic acid hydrazide was prepared by performing the hydrazide reaction at –78°C to isolate the product in 97% yield. In both cases, the identical chemical reagents used in the selective synthesis of hydrazides, contained monohydrazides of bis-hydrazide.

Significance of Current Application

It is synthetically very difficult to prepare monohydrazides while minimizing the formation of bishydrazide by-products. This is of particular concern in the preparation of calicheamicins, which are a new class of enediyne antineoplastic agents. The ability to produce these monohydrazide derivatives of this chemical agent is considered essential since calicheamicins appear effective in the treatment of non-solid tumor cancer associated with myeloid leukemia. This investigation has identified that the formation of monohydrazides is temperature sensitive, which can be used to prepare calicheamicins in quantitative yields.

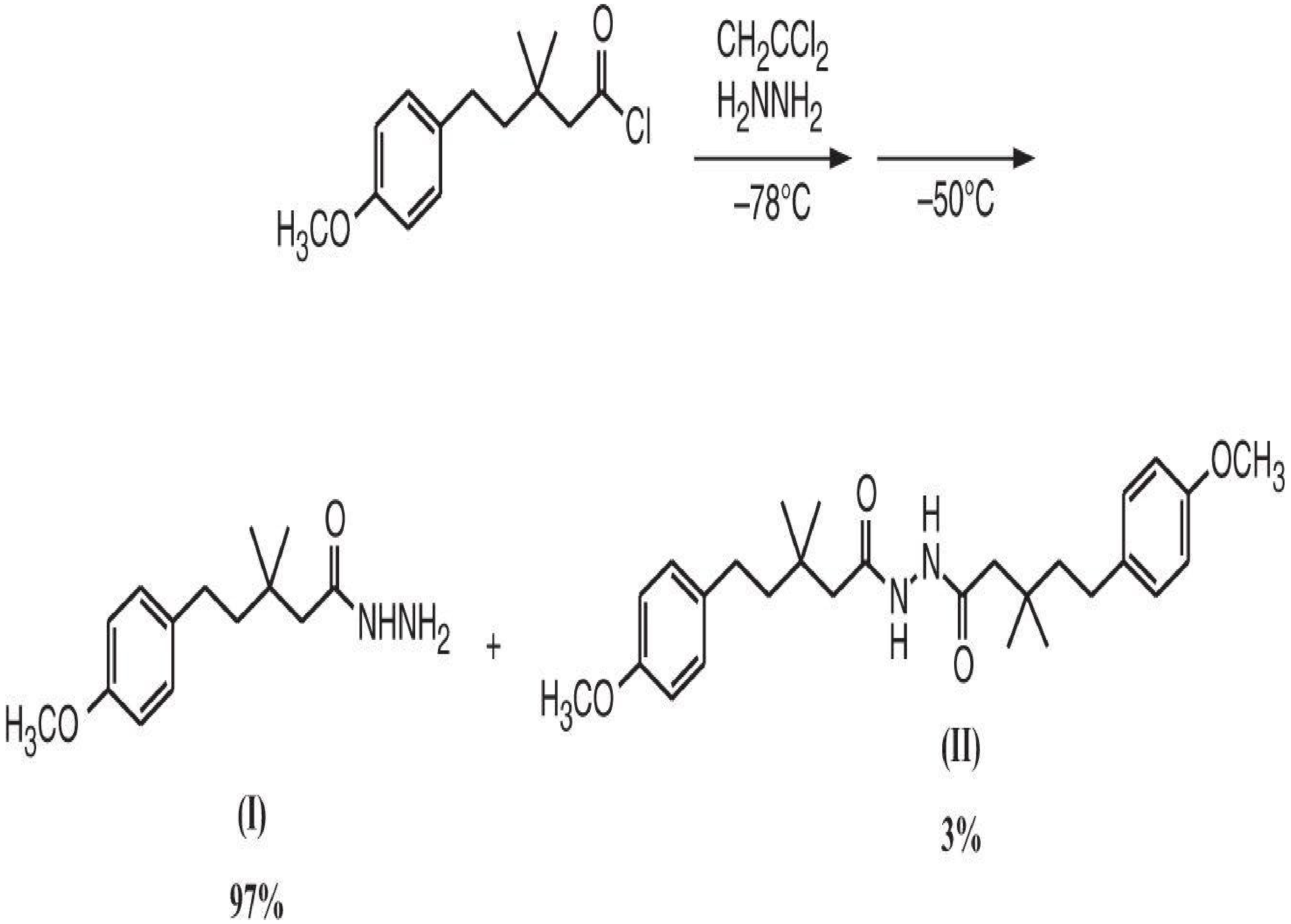


Figure 14.8 Product Formation 1: High yield preparation of mono-p-methoxybenzylthioether hydrazide, (I).

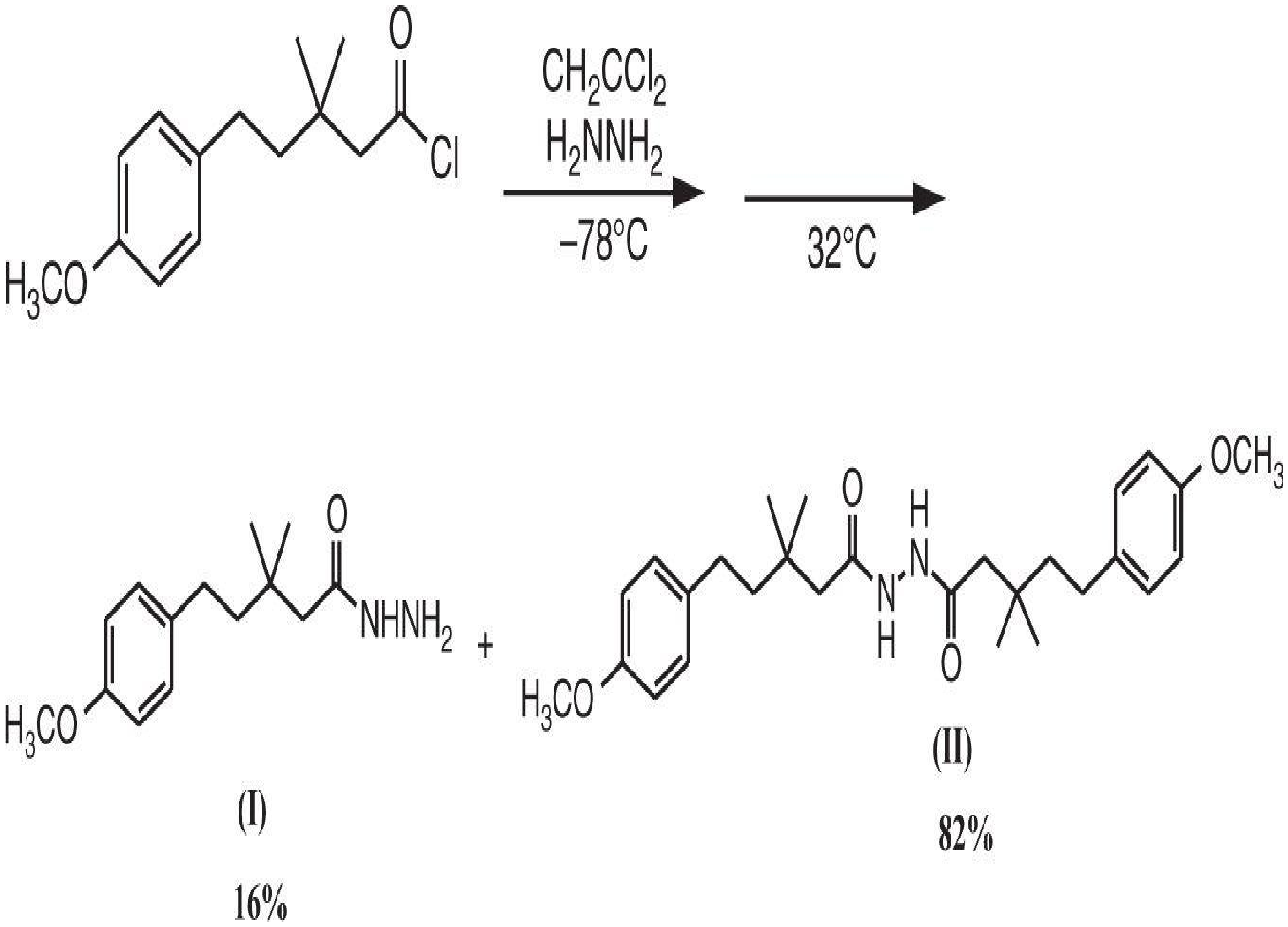


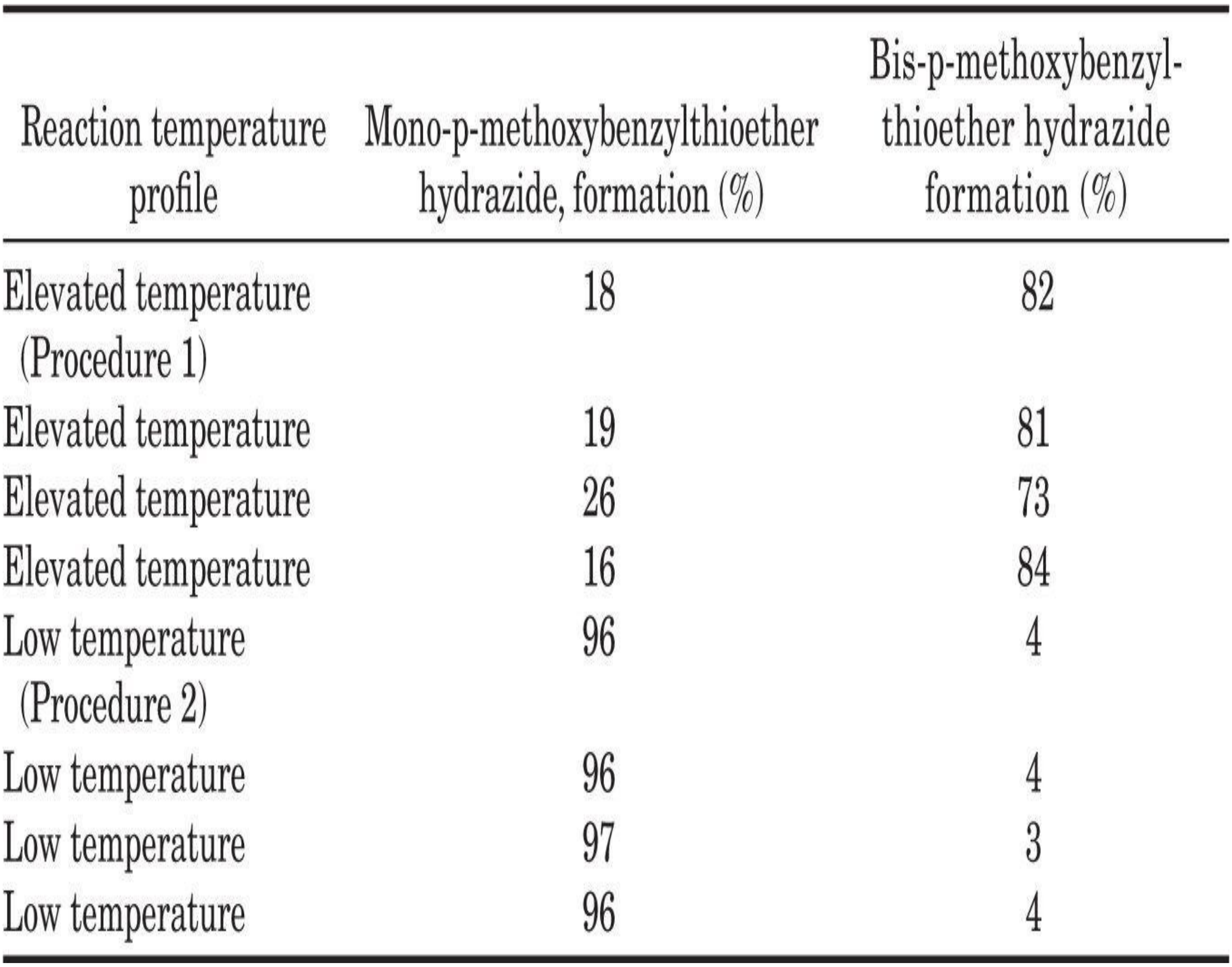
Figure 14.9 Product Formation 2: High yield preparation of bis-methoxybenzylthioether hydrazide, (II).

Experimental

1. Preparation bis-methoxybenzylthioether hydrazide. In a separate vessel, p-methoxylbenzylthioether acid was dissolved in a glass reaction vessel containing 500 mL of methylene chloride and additional methylene chloride was added so that a total volume of 1,300 mL was obtained. A second vessel was charged with 7.8 mol of anhydrous hydrazine and 250 mL of methylene chloride. This second mixture was then cooled to –72°C using a dry-ice acetone bath and then added dropwise to the first vessel while constantly stirred. The addition of hydrazine required approximately 2 hours, after which the mixture was stirred for approximately 30 minutes between –68°C to –72°C. The reaction mixture was then concentrated in vacuo using a rotary evaporator containing a bath temperature between 32°C and 36°C and having a pressure between 25 to 28 in of Hg. In this workup process, a total of 630 g of crude p-methoxylbenzylthioether hydrazide was isolated. Crude p-methoxylbenzylthioether was then swirled in 1,580 mL of methanol at –28°C and then treated with 1312 g of 4% sodium hydroxide methanol solution and filtered to obtain a clear solution. The mixture was then concentrated under reduced pressure and 622.7 g of crude p-methoxybenzylthioether hydrazide were isolated. The solid was then re-dissolved in 2100 mL of methylene chloride, dried using magnesium sulfate, filtered, re-concentrated, and 643 g of semi-pure product obtained. The solid was again re-dissolved in 400 mL of methylene chloride then heated to between 32°C and 40°C for 5 minutes and treated with 4,260 mL of diethyl ether while stirring between 0°C and –10°C. The stirring rate was increased and the mixture was treated with 1070 mL of heptane. A precipitate formed, which was isolated by filtration, and 429 g of product were isolated after vacuum drying. Yields of purified bis-p-methoxybenzylthioether hydrazide isolated using this experimental method varied from 73% to 82%, as summarized in Table 14.4.

2. Preparation of mono-p-methoxybenzylthioether hydrazide. Stoichiometry and the Step 1 procedure were repeated at –78°C where the hydrazine/methylene chloride solution which initially produced an un-stirrable frozen mixture. Viscous lumps stuck to the reaction flask while the blade decelerated. A solution of thioether acid chloride/methylene chloride was then added dropwise to the mixture while keeping the reaction temperature at approximately –72°C HPLC analysis, however, indicated that at the end of the addition only a moderate amount of product had been generated. When the reaction mixture was warmed to approximately –50°C, a stirrable heterogeneous mixture developed, followed by a rapid exotherm that quickly caused the temperature to increase to –28°C causing a color change to the mixture from yellow to off-white. After work up, the yields of both p-methoxybenzylthioether hydrazide and bis-p-methoxybenzylthioether hydrazide were quantified. The results are summarized in Table 14.4.

TABLE 14.4 The formation of mono-p-methoxybenzylthioether hydrazide and bis-p-methoxybenzyl-thioether hydrazide using p-methoxylbenzylthioether acid and hydrazine but prepared at two reaction temperatures.



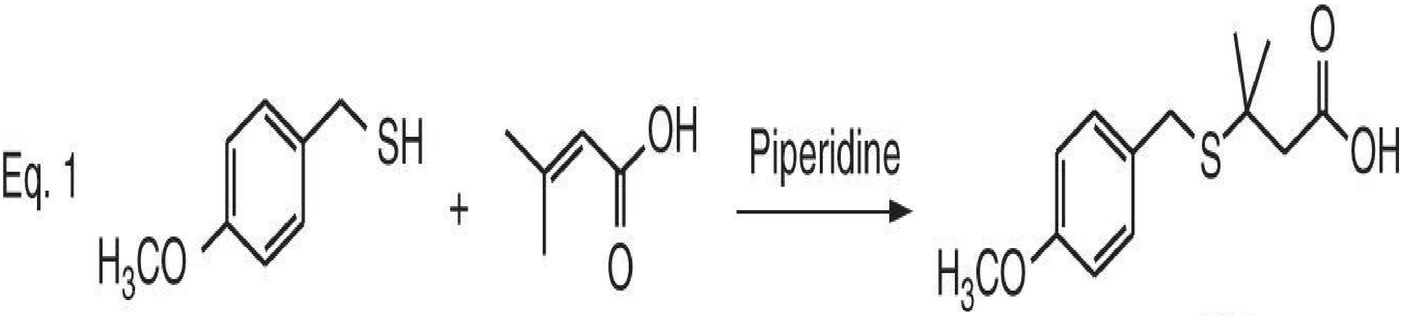
Reaction temperature profile	Mono-p-methoxybenzylthioether hydrazide, formation (%)	Bis-p-methoxybenzyl-thioether hydrazide formation (%)
Elevated temperature (Procedure 1)	18	82
Elevated temperature	19	81
Elevated temperature	26	73
Elevated temperature	16	84
Low temperature (Procedure 2)	96	4
Low temperature	96	4
Low temperature	97	3
Low temperature	96	4

Testing Results

Table 14.4 provides a summary of the formation of mono-p-methoxybenzylthioether hydrazide and bis-p-methoxybenzylthioether hydrazide using p-methoxylbenzylthioether acid and hydrazine using two separate synthetic routes. The mono-p-methoxybenzylthioether hydrazide adduct is preferred.

Notes and Observations

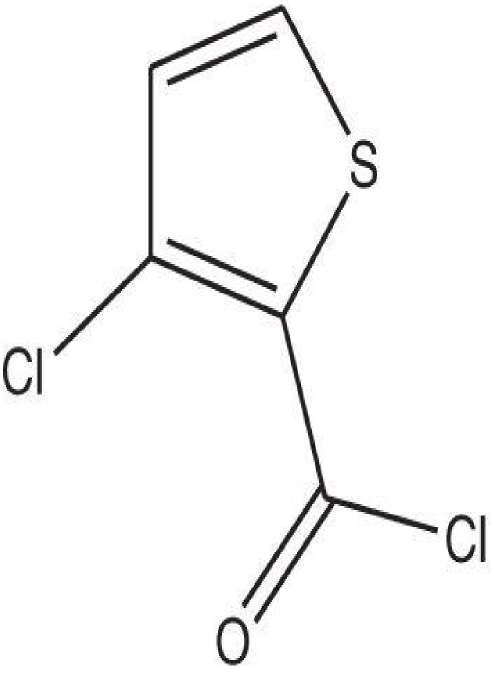
1. 3-Methyl-3-mercaptobutanoic acid, (III), is a DMH linker, or CL-332258, and was developed to link calicheamicin to monoclonal antibodies. This agent was previously prepared by the author[1] and is illustrated in Eq. 1. (See Fig. 14.10.)



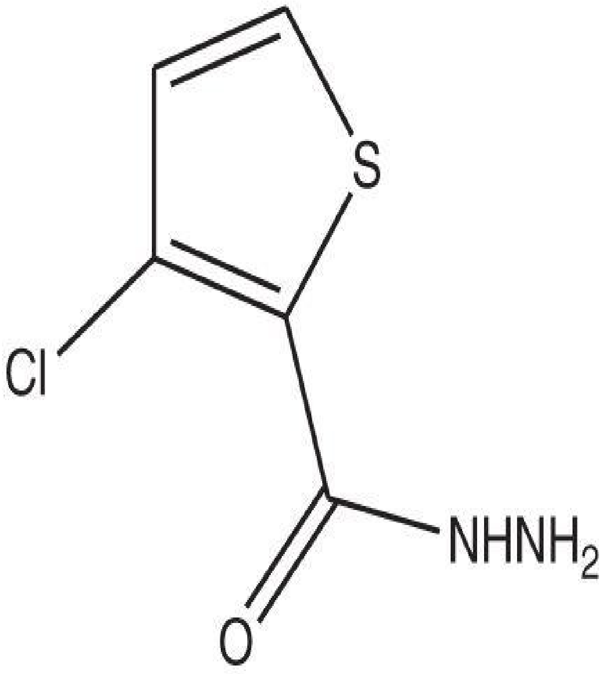
(III)

Figure 14.10

2. Using the hydrazide method of the current investigation, Cai[2] converted 3-chlorothiophene-2-carbonyl chloride, (IV), into the corresponding hydrazide, (V), using hydrazine at 30°C in high yields. This synthesized material was subsequently used as an intermediate in preparing activators of caspases and inducers of apoptosis. (See Fig. 14.11.)



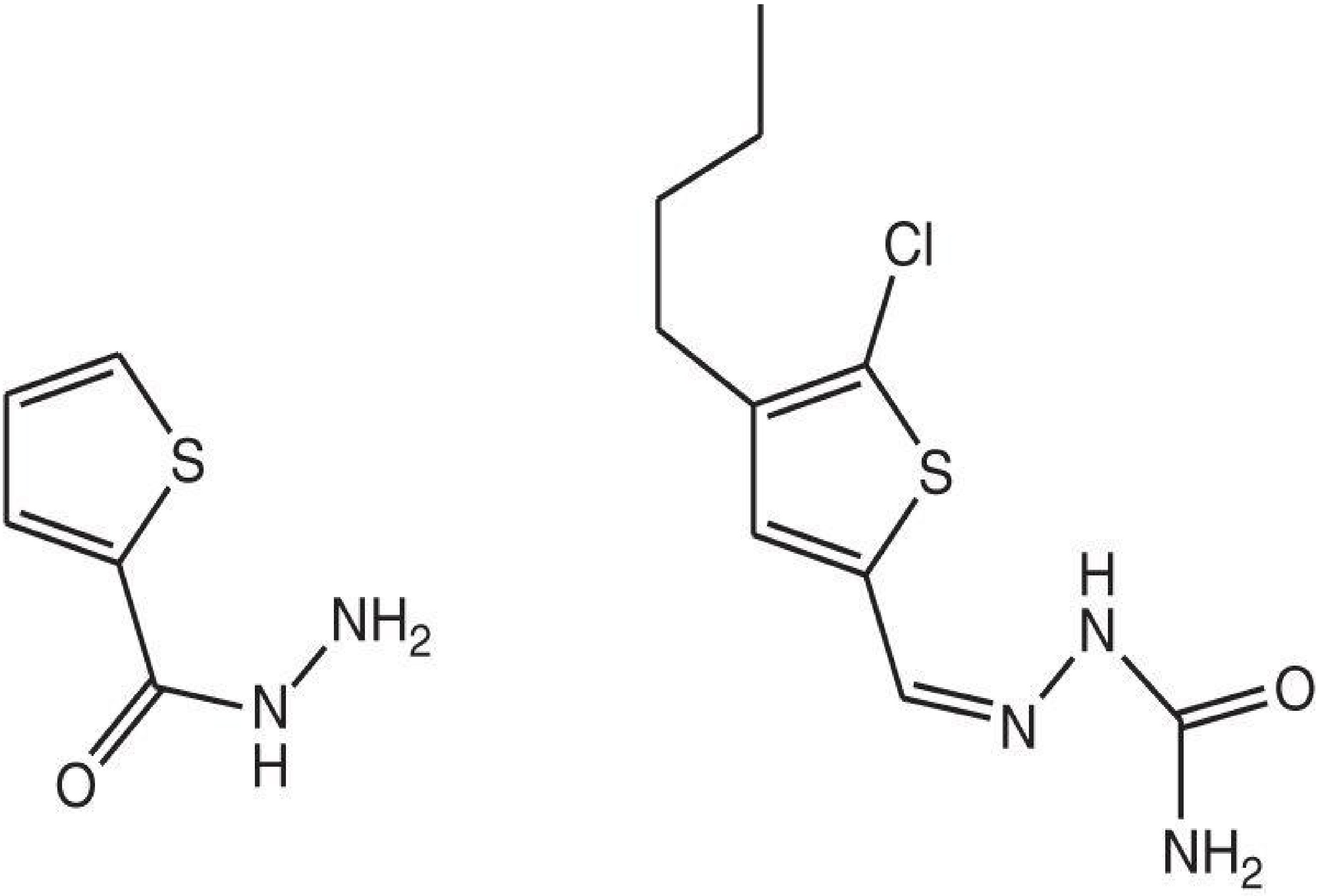
(IV)



(V)

Figure 14.11

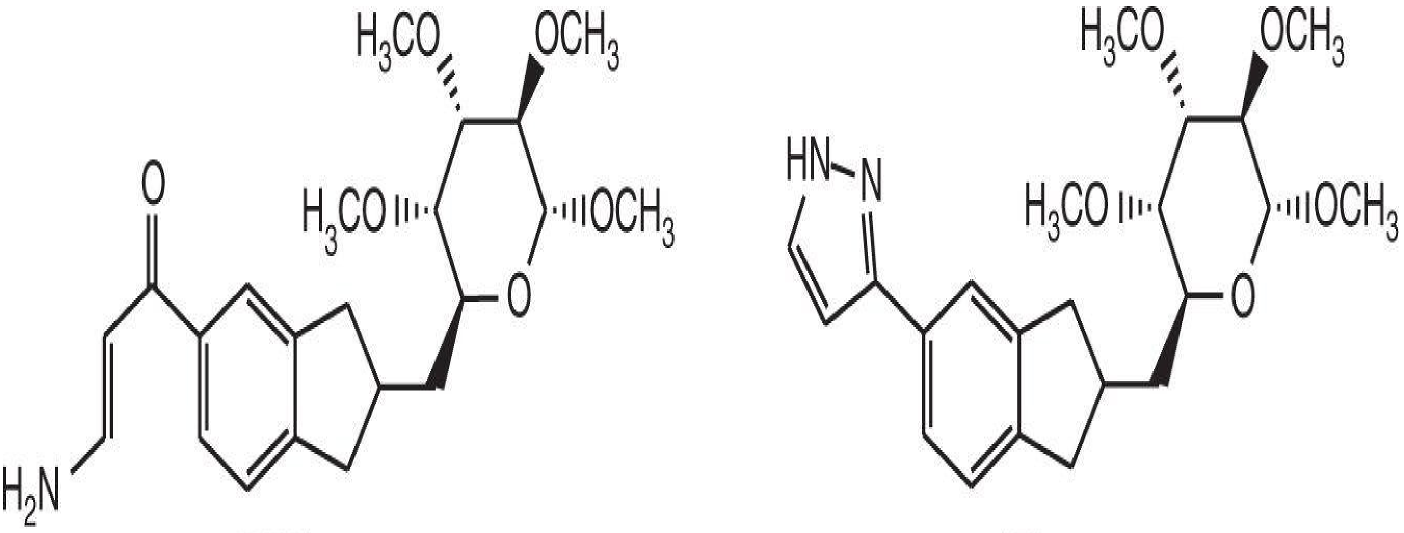
3. Fernandez-Po[3] converted 2-thiophenecarboxylic acid into the corresponding hydrazine, (VI), in quantitative high yield at –70°C, which was then converted into 4-butyl-3-chloro-2-thiophenecarboxylic acid thiosemicarbazone, (VII), which is effective in treating proliferative diseases. (See Fig. 14.12.)



(VI) **(VII)**

Figure 14.12

4. Crouse[4] reacted with anhydrous hydrazine at ambient temperature to convert an indole intermediate, (VIII), into a 1H-pyrazole derivative, (IX). The cyclization reaction required 8 hours of stirring and the product was isolated in 94% yield. The product was subsequently used in pesticide formulations. (See Fig. 14.13.)



(VIII) (IX)

Figure 14.13

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1. George Anello Chiarello et al., *Processes for making hydrazides*, U.S. Patent 8,110,705 (February 7, 2012)

2. Sui Xiong Cai et al., *3,5-Disubstituted-[1,2,4]-oxadiazoles and analogs as activators of caspases and inducers of apoptosis and the use thereof*, U.S. Patent Application 20040127521 (July 1, 2004)

3. Jose A. Fernandez-Po et al., *Pharmacological agents and methods of treatment that inactivate pathogenic prokaryotic and eukaryotic cells and viruses by attacking highly conserved domains in structural metalloprotein and metalloenzyme targets*, U.S. Patent 6,803,379 (October 12, 2004)

4. Gary D. Crouse et al., *Pesticidal compositions*, U.S. Patent 8,383,786 (February 26, 2013)

Hydrogen

Author Raghunath V. Chaudhari et al.

Patent Title ***Polyol hydrogenolysis by in situ-generated hydrogen,*** U.S. Patent 8,415,511 (April 9, 2013)

Relevant Prior Patents by Author or Coauthors

Hydrogenolysis of glycerol and products produced therefrom, U.S. Patent 8,153,847 (April 10, 2012)

Methods and systems for generating polyols, U.S. Patent 8,198,486 (June 12, 2012)

Hydrogenolysis of glycerol and products produced therefrom, U.S. Patent 7,928,148 (April 19, 2011)

Methods and systems for generating polyols, U.S. Patent 7,767,867 (August 3, 2010)

Modified Pt/Ru catalyst for ring opening and process using the catalyst, U.S. Patent Application 20070078289 (April 5, 2007)

Product Application

This investigation has developed a method for preparing in situ hydrogen using renewable glycerol as the hydrogen source to obtain a mixture of gas-phase-hydrogenation products including methane, ethane, propane, and pentane, which are useful in automotive fuel formulations. In addition, this method is useful in preparing aliphatic alcohols and diols, which are useful as solvents and in the preparation of polymers and intermediates, respectively.

Significance of Current Application

There are increasing demands placed on the limited supplies of fossil fuels, both as a source of automotive fuels and as a source of petrochemicals. In the current investigation, the renewable chemical agent, glycerol (previously derived from cellulosic sources), was reduced into alcohols and diols as isolated in the liquid phase, and then into methane, ethane, propane, and pentane in the gas phase which are both useful as mixed biofuels. The catalysts used in this hydrogenation method consisted of both/or 5% Ru/Al_2O_3 and 5% Pt/Al_2O_3. Each of these catalysts converted bioglycerol into a source of in situ hydrogen. Moreover, following the hydrogenolysis procedure unused, hydrogen produced from this process was separated and used in other hydrogenation reactions to generate alcohols and other biofuel mixtures.

Catalysts

A. 5% Ru/Al_2O_3 as powders ranging in size from 75 µm to 150 µm.

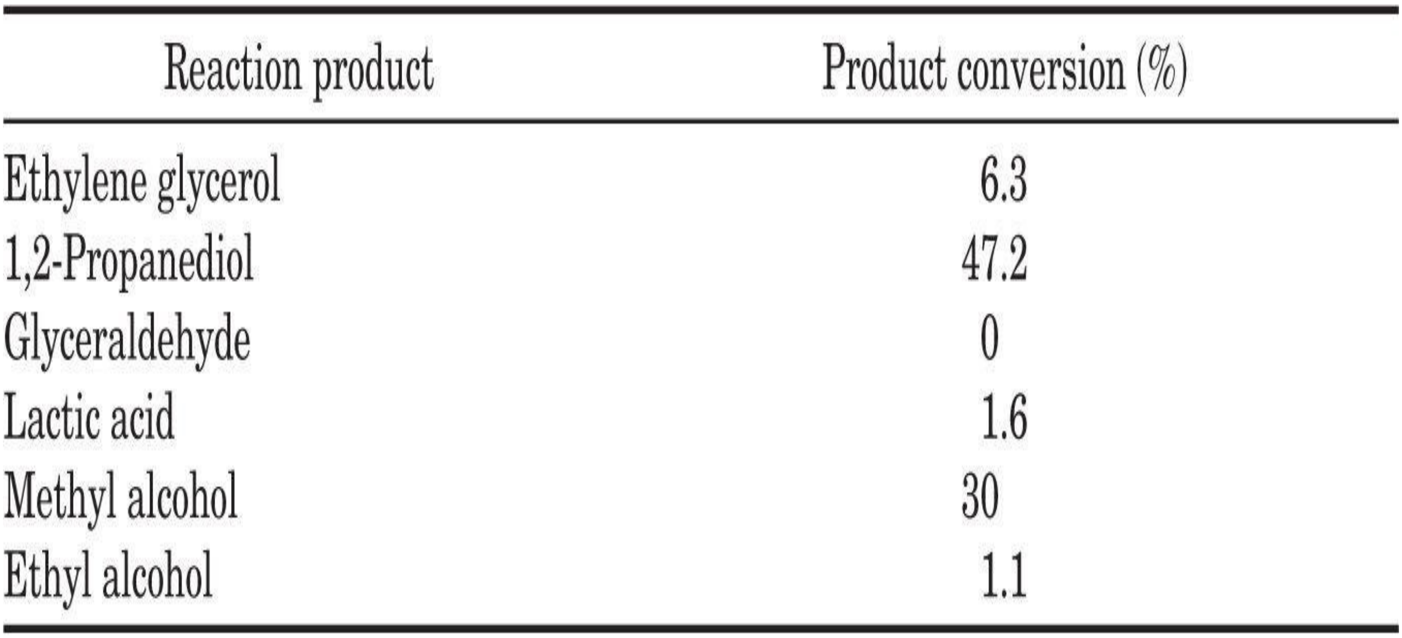
B. 5% Pt/Al_2O_3 as powders ranging in size from 100 µm to 125 µm.

Experimental

1. Preparation of hydrogenolysis products of glycerol without the use of external hydrogen. A high-pressure hydrogenation reactor was charged with a known amount of glycerol dissolved in water and 2 wt% of 5% Ru/Al_2O_3 and 5% Pt/Al_2O_3 alone or used as a catalytic mixture. After sealing the chamber, the reactor was placed into heating slots and then purged three times with nitrogen at ambient temperature. The reactor was then heated to a temperature of 200°C under low agitation at a nitrogen pressure of 14 bar for approximately 6 hours. Once the reaction was terminated and the mixture cooled to ambient temperature, both gas-and liquid-phase samples were obtained and analyzed by gas chromatography. Product formation in the liquid and gas phases are provided in Tables 14.5 and 14.6, respectively.

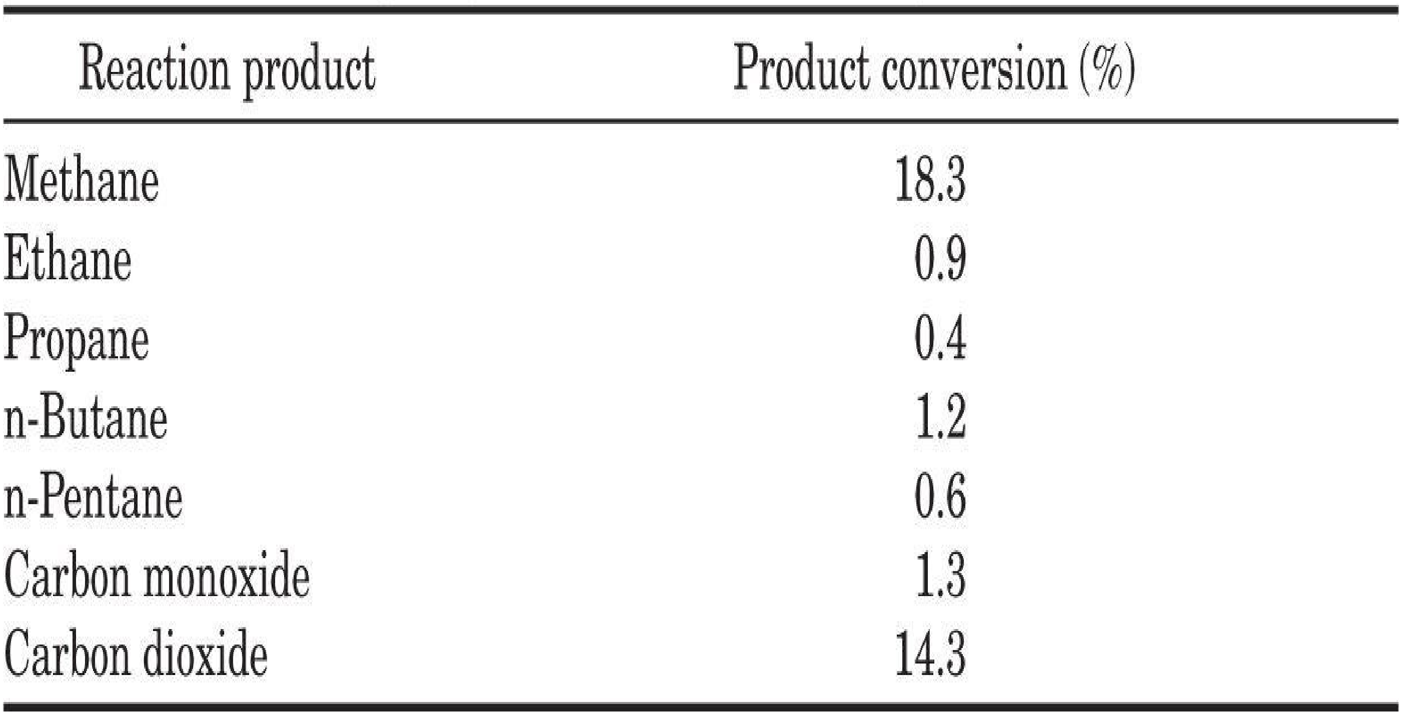
Testing Results

TABLE 14.5 Liquid-phase product formation using hydrogenolysis of glycerol without an external hydrogen source under a nitrogen pressure of 14 bar.



Reaction product	Product conversion (%)
Ethylene glycerol	6.3
1,2-Propanediol	47.2
Glyceraldehyde	0
Lactic acid	1.6
Methyl alcohol	30
Ethyl alcohol	1.1

TABLE 14.6 Gas-phase product formation using hydrogenolysis of glycerol without an external hydrogen source under a nitrogen pressure of 14 bar.

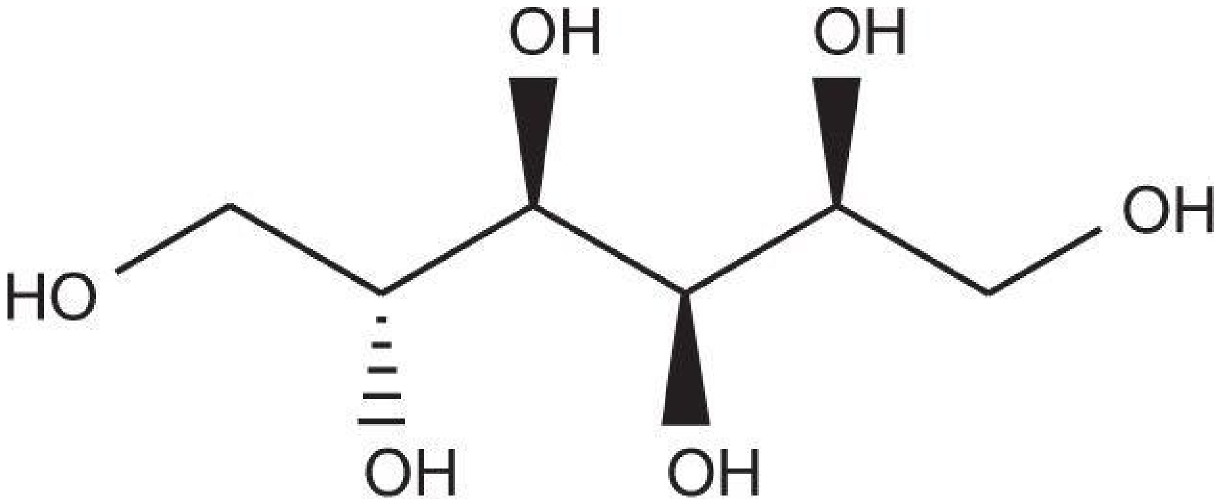


Reaction product	Product conversion (%)
Methane	18.3
Ethane	0.9
Propane	0.4
n-Butane	1.2
n-Pentane	0.6
Carbon monoxide	1.3
Carbon dioxide	14.3

Notes and Observations

1. Bloom[1] used in situ-generated hydrogen from bio-based glycerol in the absence of external hydrogen at approximately 190°C using either nickel or ruthenium on carbon as catalysts to prepare 1,2-propanediol in high yields.

2. Chopade[2] used in situ-generated hydrogen from the polyol, sorbitol, (I), in the absence of external hydrogen using either nickel on carbon or ruthenium on carbon as a reaction catalyst and prepared a mixture of ethylene glycol and 1,2-propanediol in good yields. (See Fig. 14.14.)



(I)

Figure 14.14

3. Suppes[3] used the copper-chromite catalyst, $(CuO)_x(Cr_2O_3)_y$, to convert glycerol in high yields to 1,2-propanediol containing trace amounts of ethylene glycol. The reaction was conducted at 210°C in the absence of external hydrogen and under a nitrogen initial

pressure range of 0.05 to 1.2 bar to a final pressure between 0.1 and 0.3 bar.

4. Arredondo[4] converted glycerol into hydroxyacetone under nitrogen gas in the absence of an external hydrogen source using the copper-chromite catalyst, $(CuO)_x(Cr_2O_3)_y$. The hydrogenation product was then converted into 2-amino-1-hydroxypropane by reacting with ammonium hydroxide.

References

1. Paul Bloom, *Hydrogenolysis of glycerol and products produced therefrom*, U.S. Patent 8,153,847 (April 10, 2012)

2. Shubham P. Chopade et al., *Catalysts and process for hydrogenolysis of sugar alcohols to polyols*, U.S. Patent 6,291,725 (September 18, 2001)

3. Galen J. Suppes, *Method of producing lower alcohols from glycerol*, U.S. Patent 8,252,961 (August 28, 2012)

4. Victor Manuel Arredondo et al., *Process for the conversion of glycerol to propylene glycol and amino alcohols*, U.S. Patent 7,619,118 (November 27, 2009)

l-Lactic Acid

Author	Masateru Ito et al.
Patent Title	***Lactic acid production method,*** U.S. Patent 8,349,597 (January 8, 2013)

Relevant Prior Patents by Author or Coauthors

Sugar derivatives and applications of same, U.S. Patent 8,350,024 (January 8, 2013)

Method for producing butanol, U.S. Patent Application 20120253086 (October 4, 2012)

Method for producing diol or triol, U.S. Patent Application 20120253082 (October 4, 2012)

Method for producing oxidized phenol sulfides, U.S. Patent Application 20120253054 (October 4, 2012)

Method for continuously producing oxidized phenol sulfides, U.S. Patent Application 20110028737 (February 3, 2011)

Product Application

Ultra-pure l-lactic acid and poly-l-lactic acid were prepared and used in the preparation of biodegradable prostheses. l-Lactic acid was also used in the preparation of biodegradable plastics and fine chemicals.

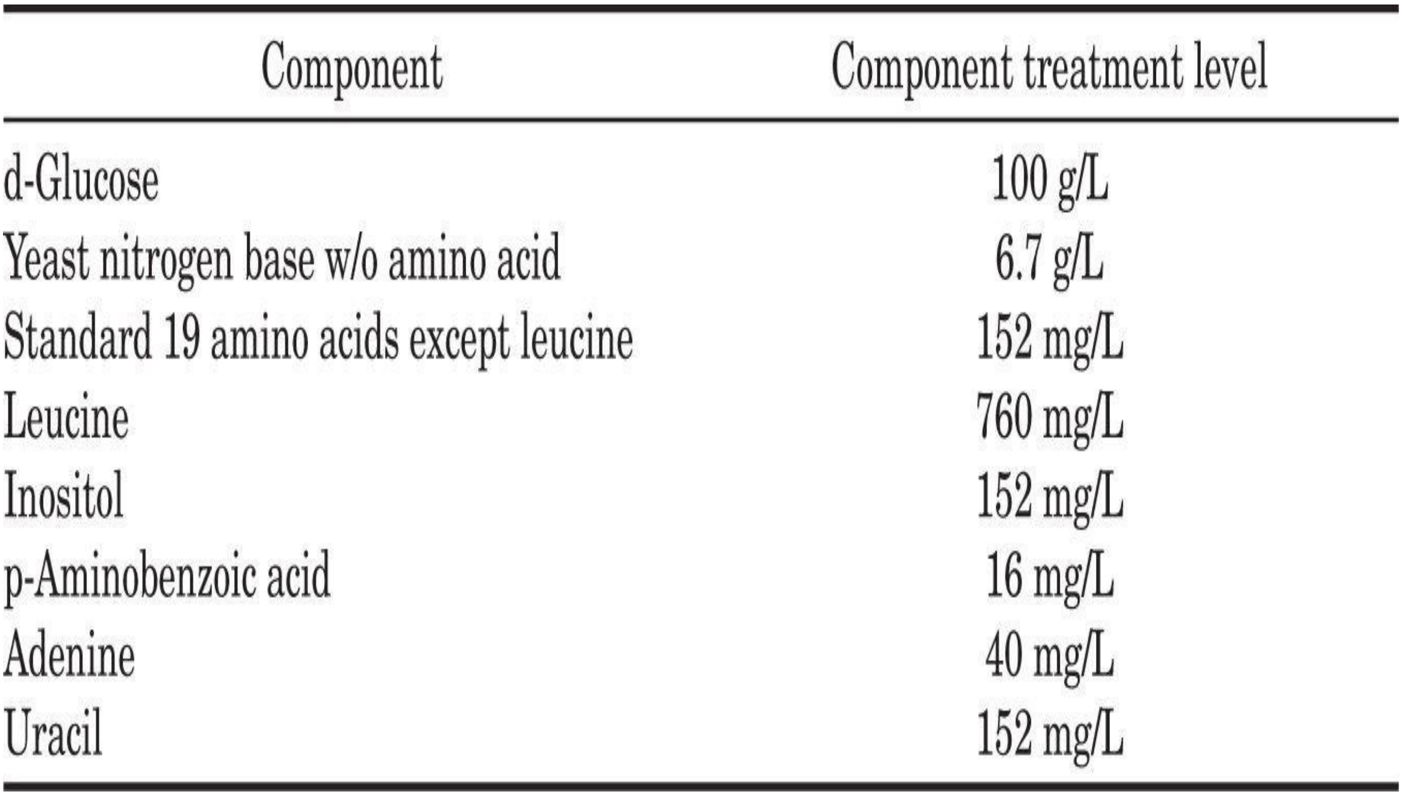
Significance of Current Application

The current investigation describes a simple and direct method for preparing ultra-pure l-lactic acid using fermentation synthesis. This level of purity is required for medical applications, particularly when preparing biodegradable prostheses. This investigation also provides a new and extremely effective method for isolating ultra-pure monomers using low-energy nano-membrane purifications as a replacement for distillation purification methods.

Experimental

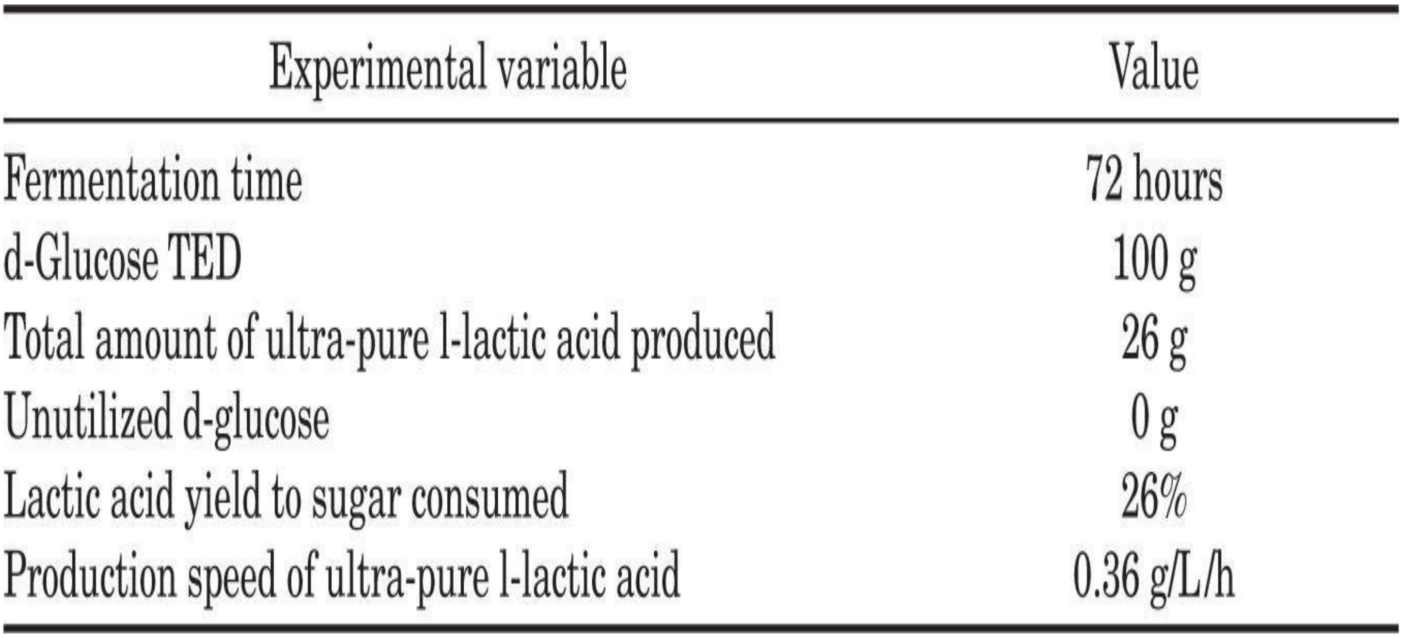
1. Preparation of l-lactic acid by batch fermentation. The batch fermentation synthesis of l-lactic acid using d-glucose was conducted using an l-lactic acid fermentation medium provided in Table 14.7. The medium was used after glassware was high-pressure steam sterilized for 15 minutes at 121°C. The medium was then treated with yeast SW-1 strain and the reaction conducted in a 2-L flask at 30°C. During this 72-hour reaction the airflow was maintained at 0.2 L /min with a stirring speed of 400 rpm while maintaining the pH at 5 using 1 M of calcium hydroxide. Finally, the reaction extent for l-lactic acid formation was evaluated by systematically removing aliquots and measuring d-glucose levels. Results for this synthesis are provided in Table 14.8.

TABLE 14.7 Fermentation medium used to grow l-lactic acid using d-glucose.



Component	Component treatment level
d-Glucose	100 g/L
Yeast nitrogen base w/o amino acid	6.7 g/L
Standard 19 amino acids except leucine	152 mg/L
Leucine	760 mg/L
Inositol	152 mg/L
p-Aminobenzoic acid	16 mg/L
Adenine	40 mg/L
Uracil	152 mg/L

TABLE 14.8 Experimental conditions and results in the preparation of ultra-pure lactic acid using yeast strain SW-1.



Experimental variable	Value
Fermentation time	72 hours
d-Glucose TED	100 g
Total amount of ultra-pure l-lactic acid produced	26 g
Unutilized d-glucose	0 g
Lactic acid yield to sugar consumed	26%
Production speed of ultra-pure l-lactic acid	0.36 g/L/h

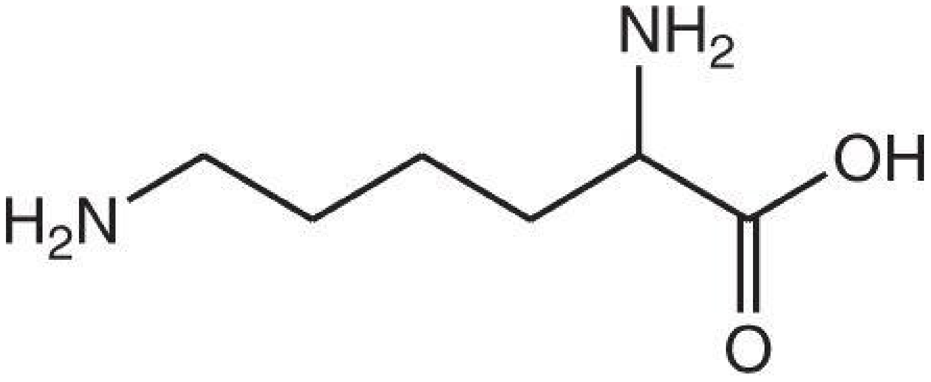
2. Preparation of ultra-pure l-lactic acid using a nano-filtration membrane. The entire contents of the Step 1 product mixture was poured into a membrane filtration apparatus at 25°C containing a UTC60 90 ϕ nano-filtration membrane manufactured by Toray Industries, Inc. The pressure of the high-pressure pump was adjusted at 0.5 MPa and the permeated liquid was recovered. The concentration of l-lactic acid which permeated through the membrane was quantified by an ion chromatography at 35°C. Analytical results and l-lactic acid product conversion are provided in Table 14.8.

Testing Results

Notes and Observations

1. Suzuki[1] developed a method for preparing ultra-pure polyethers using crude aliphatic cyclic oxides by polymerizing them in the presence of zinc hexacyanocobaltate, $Zn_3[Co(CN)_6]_2$. Once the purified polyether was isolated, it was post-reacted with semi-purified hydroxyaliphatics, particularly 2-hydroxyacetic acid l-lactic acid or 2-hydroxy-2-ethyl butyric acid, to produce ultra-pure polyethers containing ester termini.

2. In an investigation by Kaneko[2] it was determined that when Aphanothece sacrum was treated with mild base, a derivatized sugar extract was produced. The extract that was formed produced liquid crystal gels and liquid crystals when treated with ytterbium salts, Yb^{+3}, and then chemically crosslinked these sugar derivatives in the presence of the diamine of L-lysine, (I). (See Fig. 14.15.)

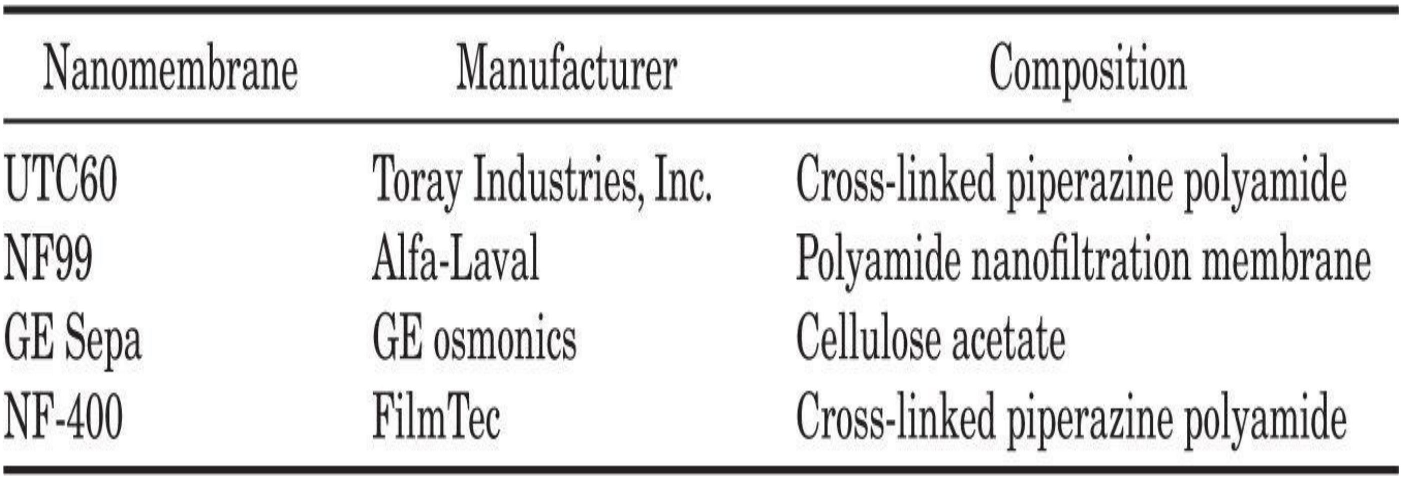


(I)

Figure 14.15

3. In a subsequent investigation by the author,[3] impure butanol was ultra purified by passing through a nanofiltration membrane which did not utilize traditional distillation methods. Membranes which were particularly effective are provided in Table 14.9.

TABLE 14.9 Nanofiltration membranes which were effective in purifying crude butanol. All purifications were conducted at 25°C at 1 MPa.

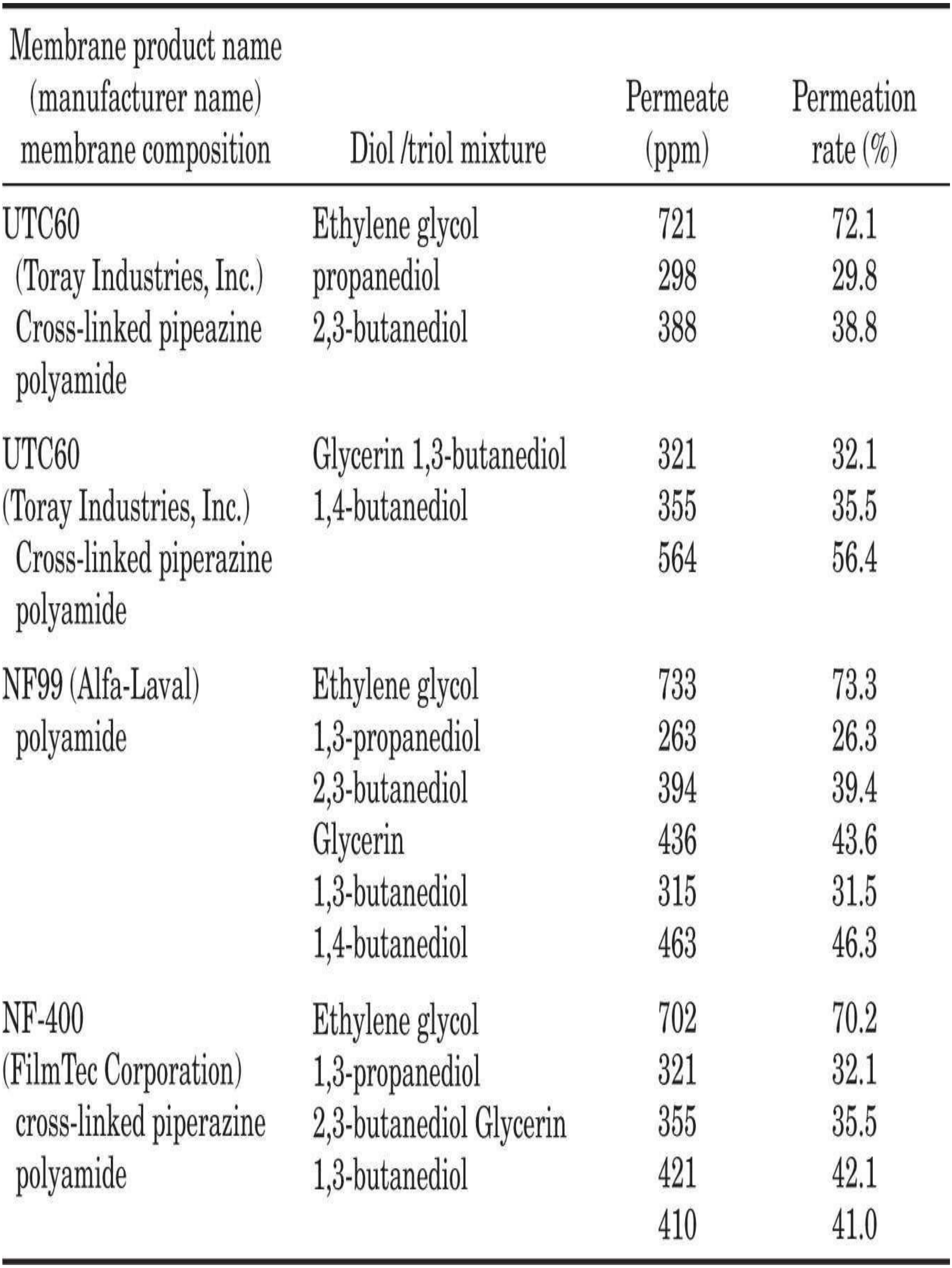


Nanomembrane	Manufacturer	Composition
UTC60	Toray Industries, Inc.	Cross-linked piperazine polyamide
NF99	Alfa-Laval	Polyamide nanofiltration membrane
GE Sepa	GE osmonics	Cellulose acetate
NF-400	FilmTec	Cross-linked piperazine polyamide

4. In a subsequent investigation by the author,[4] complex mixtures of aliphatic diols and

triols were successfully separated at 25°C and at 1 MPa using nanomembranes. This represents the first successful purification of a mixture of aliphatic diols and triols that did not require the use of energy-intensive distillation. The results of aliphatic diols and triols separations and separation parameters are summarized in Table 14.10.

TABLE 14.10 Separations of aliphatic diols and triols using selected nanomembranes. All separations were conducted at 25°C without the application of external heat or the use of traditional distillation purification methods.



Membrane product name (manufacturer name) membrane composition	Diol /triol mixture	Permeate (ppm)	Permeation rate (%)
UTC60	Ethylene glycol	721	72.1
(Toray Industries, Inc.)	propanediol	298	29.8
Cross-linked pipeazine	2,3-butanediol	388	38.8
polyamide			
UTC60	Glycerin 1,3-butanediol	321	32.1
(Toray Industries, Inc.)	1,4-butanediol	355	35.5
Cross-linked piperazine		564	56.4
polyamide			
NF99 (Alfa-Laval)	Ethylene glycol	733	73.3
polyamide	1,3-propanediol	263	26.3
	2,3-butanediol	394	39.4
	Glycerin	436	43.6
	1,3-butanediol	315	31.5
	1,4-butanediol	463	46.3
NF-400	Ethylene glycol	702	70.2
(FilmTec Corporation)	1,3-propanediol	321	32.1
cross-linked piperazine	2,3-butanediol Glycerin	355	35.5
polyamide	1,3-butanediol	421	42.1
		410	41.0

References

1. Chitoshi Suzuki et al., *Process for purifying polyether*, U.S. Patent 8,354,559 (January 15, 2013)

2. Tatsuo Kaneko et al., *Sugar derivatives and application of same*, U.S. Patent 8,350,024 (January 8, 2013)

3. Izumi Morita et al., *Method of producing butanol*, U.S. Patent Application 20120253086 (October 4, 2012)

4. Izumi Morita et al., *Method of producing diol or triol*, U.S. Patent Application 20120253082 (October 4, 2012)

Levulinic acid and γ-Valerolactone

Author James Dumesic et al.

Patent Title ***Method to produce and recover levulinic acid and/or γ-valerolactone from aqueous solutions using alkylphenols,*** U.S. Patent 8,389,761 (March 5, 2013)

Relevant Prior Patents by Author or Coauthors

Method to produce, recover and convert furan derivatives from aqueous solutions using alkylphenol extraction, U.S. Patent 8,389,749 (March 5, 2013)

Hydroxymethylfurfural ethers and esters prepared in ionic liquids, U.S. Patent 8,314,260 (November 20, 2012)

Process for converting cellulose in a liquid biofuel using N-methyl imidazolium chloride, U.S. Patent 8,247,581 (August 21, 2012)

Method for producing bio-fuel that integrates heat from carbon-carbon bond-forming reactions to drive biomass gasification reactions, U.S. Patent 8,153,698 (October 12, 2012)

Production of methyl-vinyl ketone from levulinic acid, U.S. Patent 7,960,592 (June 14, 2011)

Product Application

Both levulinic acid and γ-valerolactone are important industrial materials useful in the preparation of polyether-based prosthetic devices, fine chemicals, and in the preparation of chemical intermediates.

Significance of Current Application

Levulinic acid and γ-valerolactone are both significant industrial reagents. Levulinic acid is prepared by heating sucrose with 12 M hydrochloric acid, whereas γ-valerolactone is prepared from converting levulinic acid into γ-hydroxypentanoic acid, which then cyclizes into a three-component mixture. The desired product is then isolated by separation methods. The current investigation has developed a method for directly preparing these materials using a single-step route in excellent yields. The route is a renewal since it uses cellulose deconstruction at ambient temperature while generating only nominal amounts of toxic organic-reaction by-products.

Reagents

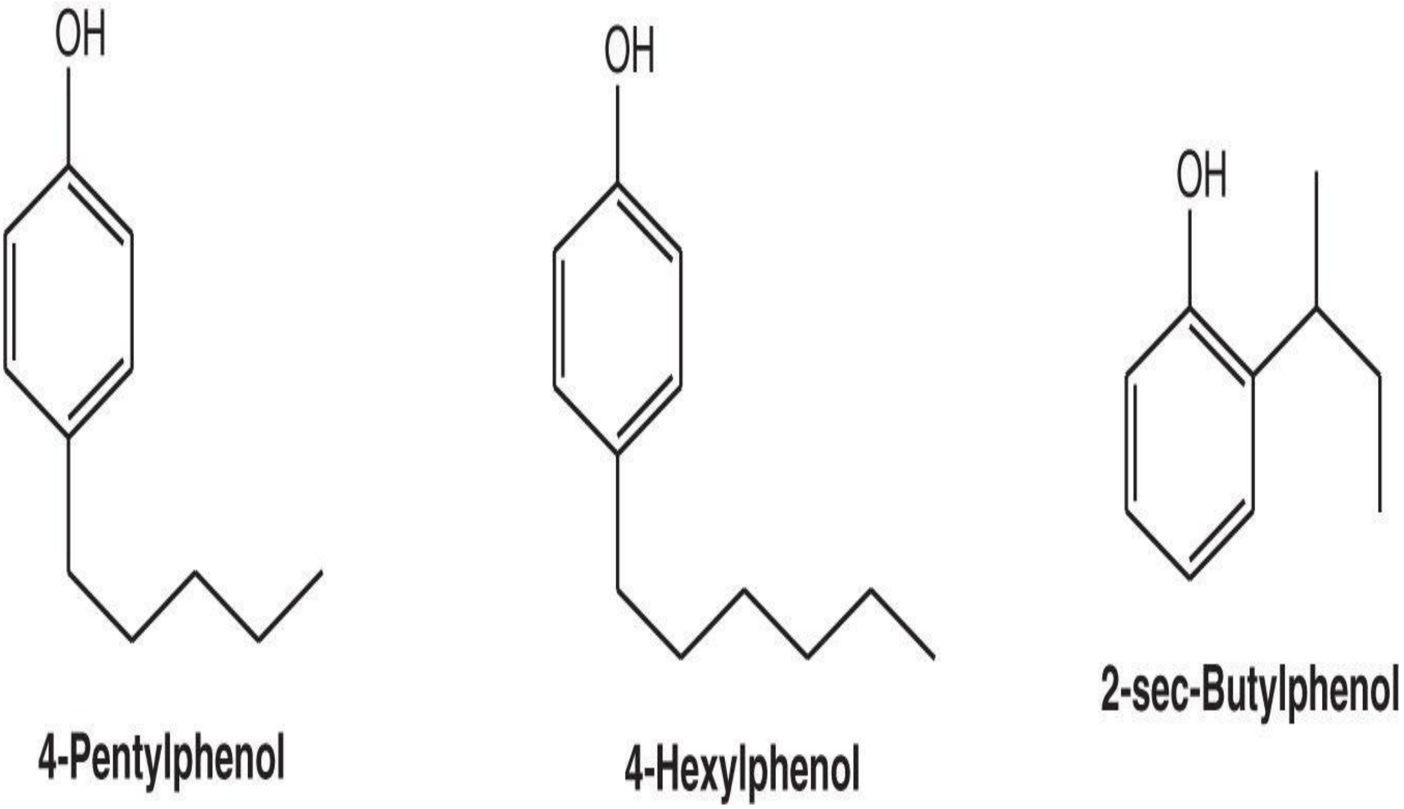


Figure 14.16

Products

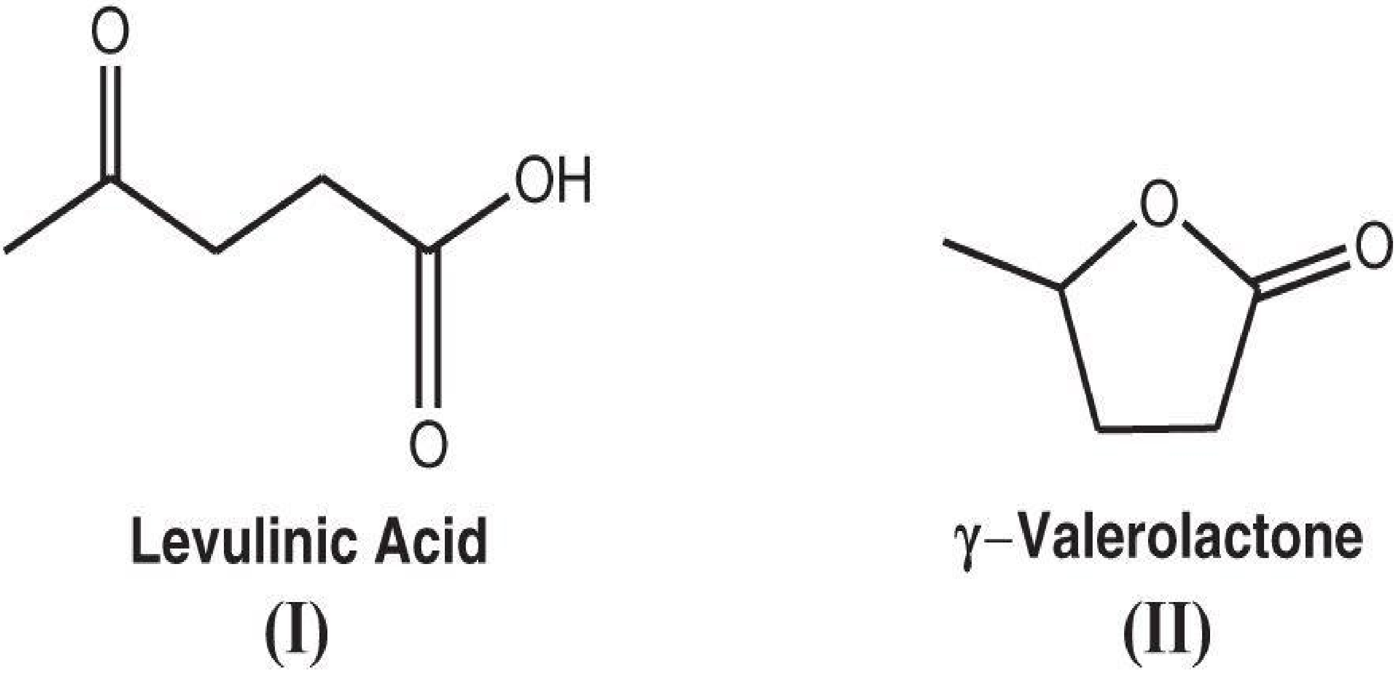


Figure 14.17

Experimental

1. Preparation of levulinic acid and γ-valerolactone using a non-renewable model reaction. Liquid–liquid extractions were carried out in glass vials. In a typical reaction, the vial was charged with 4 g of 0.5 M sulfuric acid, levulinic acid, formic acid, and γ-valerolactone. The vial also contained 1.35 g each of 2-sec-butylphenol, 4-n-pentylphenol, and 4-n-hexylphenol as well as γ-valerolactone. The mixture was then vigorously shaken for one minute and two phases appeared. When separated, the organic top phase contained

2-sec-butylphenol, γ-valerolactone, levulinic acid, and formic acid. The lower aqueous phase consisted of a combination of water, sulfuric acid, formic acid, and the remaining γ-valerolactone, levulinic acid. After phases were separation and extraction, they were analyzed by gas chromatography and the difference between the initial and final amounts of levulinic acid and γ-valerolactone in the aqueous phase was increased by be 47% for levulinic acid and 32% for γ-valerolactone.

2. Preparation of levulinic acid and γ-valerolactone using cellulose deconstruction. The aqueous phase from a cellulose deconstruction reactor was mixed with an equal mass of 2-sec-butylphenol in a 500-mL separatory funnel at ambient temperature and then shaken for 1 minute. After remaining undisturbed overnight the phases separated and the organic phase transferred to a Parr reactor was then hydrogenated using a RuSn/C catalyst. After hydrogenation the solution was filtered to remove the catalyst and the mixture was transferred to a 500-mL separatory funnel and the aqueous phase extracted using sec-butylphenol. The amounts of levulinic acid γ-valerolactone that were isolated from the aqueous phase were determined by using sec-butylphenol and were then quantified using chromographic methods where levulinic acid was increased by 91.9% yield and γ-valerolactone by 73.1%.

Testing

Structural characterization for both levulinic acid and γ-valerolactone isolated by extraction from the aqueous phase using sec-butylphenol was also provided by the author.

Notes and Observations

1. Lake[1] developed a process for isolating levulinic acid and its esters from biomass. In this process, the biomass was heated to a refining-treatment temperature followed by hydrolyzing the biomass mixture with water. The process produced a mixture of sugars that were subsequently converted into levulinic acid, formic acid, and furfural and then isolated by solvent extraction using reaction-generated furfural.

2. Dumesic[2] devised a method for preparing high quantities of furan, (III), 2-methylfuran, (IV), 2,5-dimethylfuran, (V), hydroxymethylfurfural, (VI), and 2,5-dimethyltetrahydrofuran, (VII), from biomass derived from plant material, vegetation, or agricultural waste. In this process, a two-phase aqueous- and organic-phase system was used. Initially, the reactor was charged with fructose, dimethylsulfoxide, poly(1-vinyl-2-pyrrolidinone) having an Mn~10,000 daltons, methyl isobutyl ketone, 2-butanol, hydrochloric acid, sulfuric acid, and phosphoric acid. An activated zeolite ion-exchange resin with a 1:1 wt/wt fructose-resin ratio was then added and the mixture heated to 198°C for about 8 to 12 hours to ensure at least a 75% fructose conversion. After cooling to ambient temperature, the product mixture was isolated by extraction using hydroxylmethylfuran. Sufficient quantities of these products were produced and used as additives in gasoline formulations. (See Fig. 14.18.)

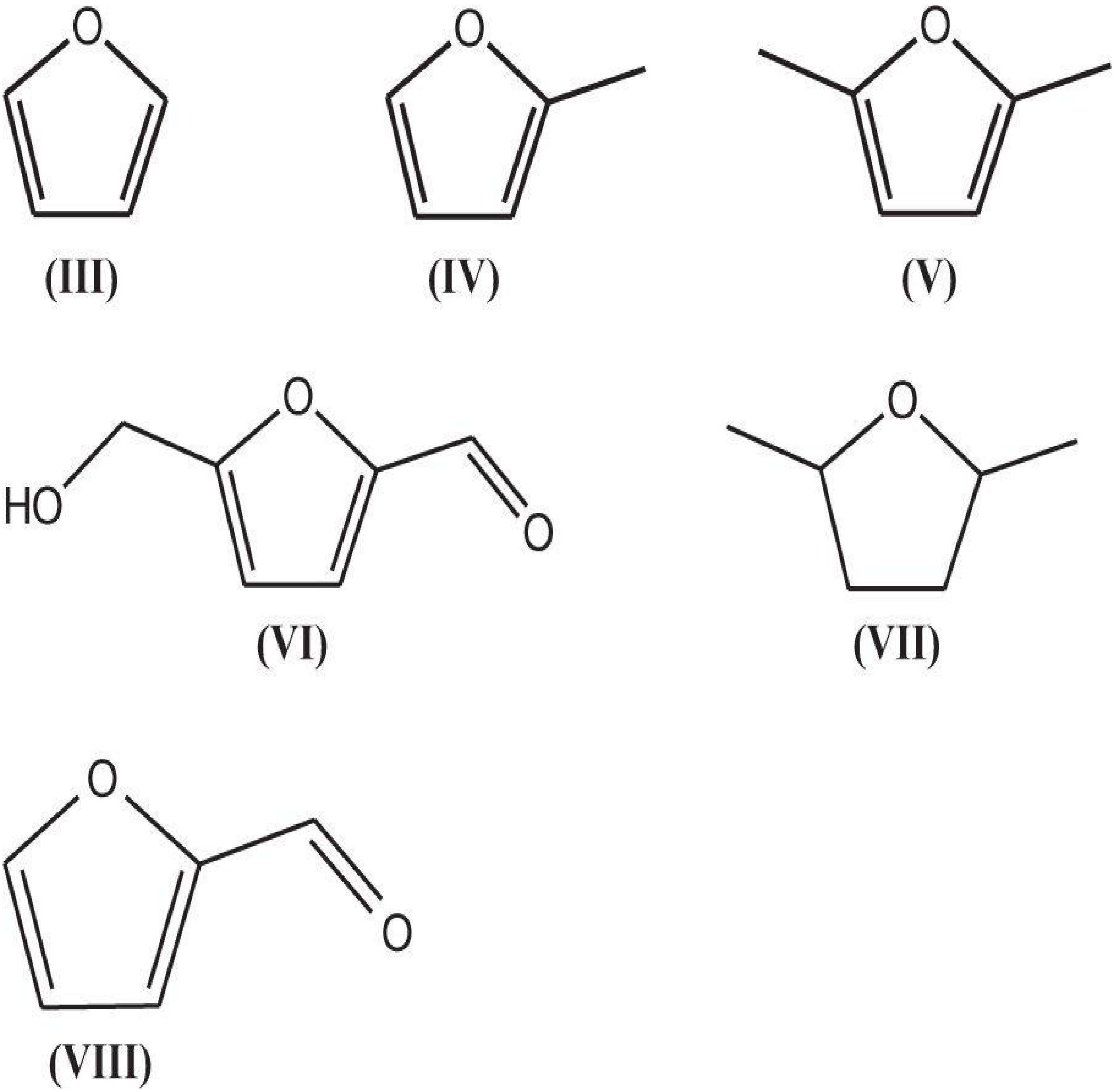
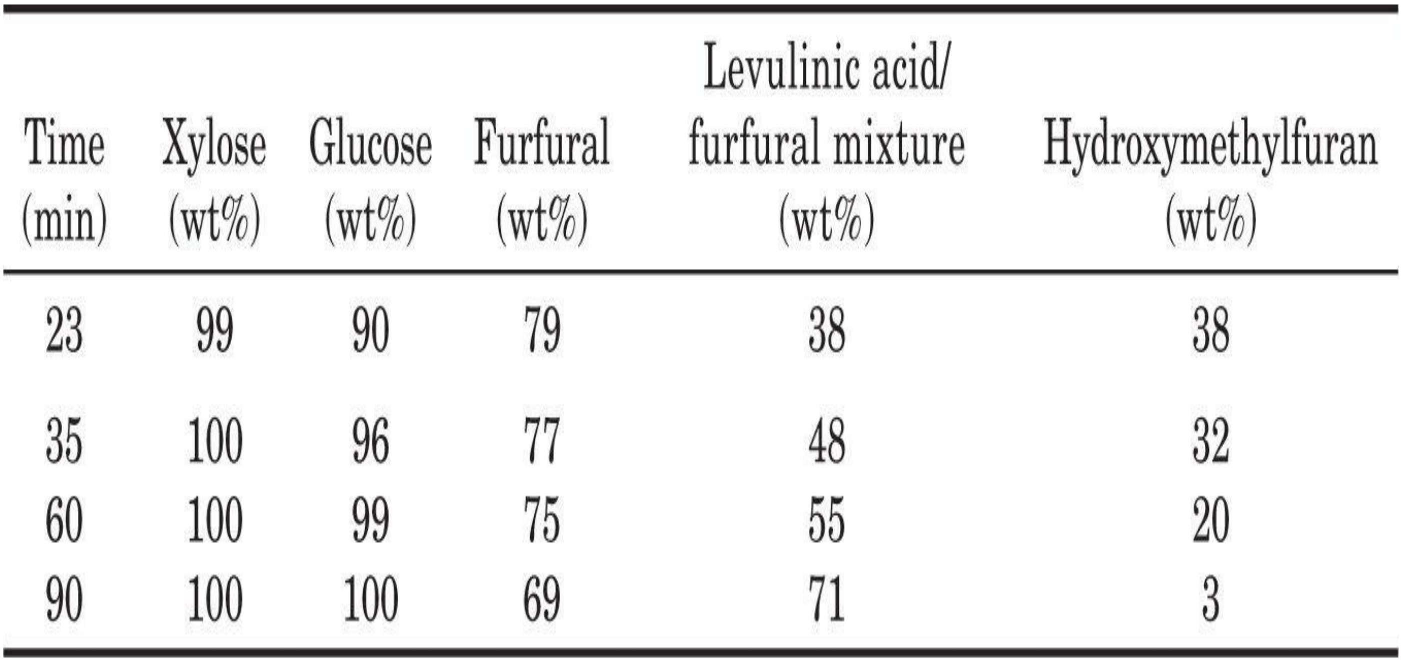


Figure 14.18

3. Lignocellulosic feedstocks were used by Dumesic[3] to isolate glucose and xylose as a precursor to preparing levulinic acid, (I), γ-valerolactone, (II), hydroxymethylfurfural, (VI), and furfural, (VIII). In this process, xylose and glucose were dehydrated by heating the mixture to 175°C containing a selected zeolite H-mordenite as a solid acid in mixtures typically containing 35 wt% xylose and 10 wt% sulfuric acid dissolved in γ-valerolactone. Chemical agents produced from this process were then used as additives in gasoline formulations. Yields for this process are provided in Table 14.11.

TABLE 14.11 Results of xylose and glucose dehydrations conducted at 175°C using a biphasic reactor and γ-valerolactone as the exacting solvent.



Time (min)	Xylose (wt%)	Glucose (wt%)	Furfural (wt%)	Levulinic acid/ furfural mixture (wt%)	Hydroxymethylfuran (wt%)
23	99	90	79	38	38
35	100	96	77	48	32
60	100	99	75	55	20
90	100	100	69	71	3

4. Dumesic[4] used biomass-derived materials from either cellulose or lignocellulose to prepare both levulinic acid and γ-valerolactone without the need for purification. In this method, sulfuric acid was used to depolymerize lignocellulose, hemicellulose, glucose, or xylose. The initial process produced levulinic acid. After levulinic acid was extracted using either distillation or extraction methods, it was then converted into γ-valerolactone in 90.5% yields using hydrogenation with 5 wt% ruthenium on carbon.

References

1. Michael A. Lake et al., *Production of levulinic acid and levulinate esters*, U.S. Patent Application 20100312006 (December 9, 2010)

2. James A. Dumesic et al., *Catalytic process for producing furan derivatives in a biphase reactor*, U.S. Patent Application 20080033188 (February 7, 2008)

3. James A. Dumesic et al., *Production of levulinic acid and* γ-*valerolactone from C5 and C6 carbohydrates in mono- and biphasic systems using* γ-*valerolactone as a solvent*, U.S. Patent Application 20120302767 (November 29, 2012)

4. James A. Dumesic et al., *Solute-enhanced production of* γ-*valerolactone from aqueous solutions of levulinic acid*, U.S. Patent Application 20120302766 (November 29, 2012)

Methacrylic Acid

Author Anthony P. Burgard et al.

Patent Title ***Microorganisms for the production of methacrylic acid,*** U.S. Patent 8,241,877 (August 14, 2012)

Relevant Prior Patents by Author or Coauthors

Microorganisms for producing butadiene and methods related thereto, U.S. Patent Application 20130011891 (January 10, 2013)

Microorganisms for producing propylene and methods related thereto, U.S. Patent Application 20120329119 (December 7, 2012)

Microorganisms for producing 1,3-butadiene and methods related thereto, U.S. Patent Application 20120329113 (December 27, 2012)

Microorganisms for producing cyclohexanone and methods related thereto, U.S. Patent Application 20120329111 (December 27, 2012)

Microorganisms for producing adipic acid and other compounds, U.S. Patent Application 20120309062 (December 6, 2012)

Microorganisms and methods for the biosynthesis of adipate, hexmethylenediamine and 6-aminocaprotic acid, U.S. Patent Application 20120282661 (November 8, 2012)

Microorganisms and methods for the biosynthesis of fumarate, malate, and acrylate, U.S. Patent Application 20120237990 (September 20, 2012)

Product Application

Methacrylic acid is used to prepare polymers and fine chemicals. The application for biologically produced methacrylic acid described in this investigation is somewhat restricted. However, because of the limited amounts of methacrylic acid produced.

Significance of Current Application

Beginning with succinyl-CoA, a five-step biosynthesis using a non-naturally occurring nucleic acid encoded with a 3-hydroxyisobutyric acid pathway was used to prepare methacrylic acid. This current investigation represents ongoing studies by Genomatica Incorporated to biologically prepare commercially viable amounts of industrial-significant reagents including fumarates, malates, acrylates, adipate, hexmethylenediamine, 6-aminocaprotic acid, adipic acid, cyclohexanone, 1,3-butadiene, and propylene. Although these studies do not generate industrially required amounts of these reagents, the methods used to prepare them utilize only renewable chemical precursors and requires minimal energy input. Finally, the biological methods used to prepare these fine chemicals and polymer precursors do not generate any toxic organic waste by-products.

Product Formation

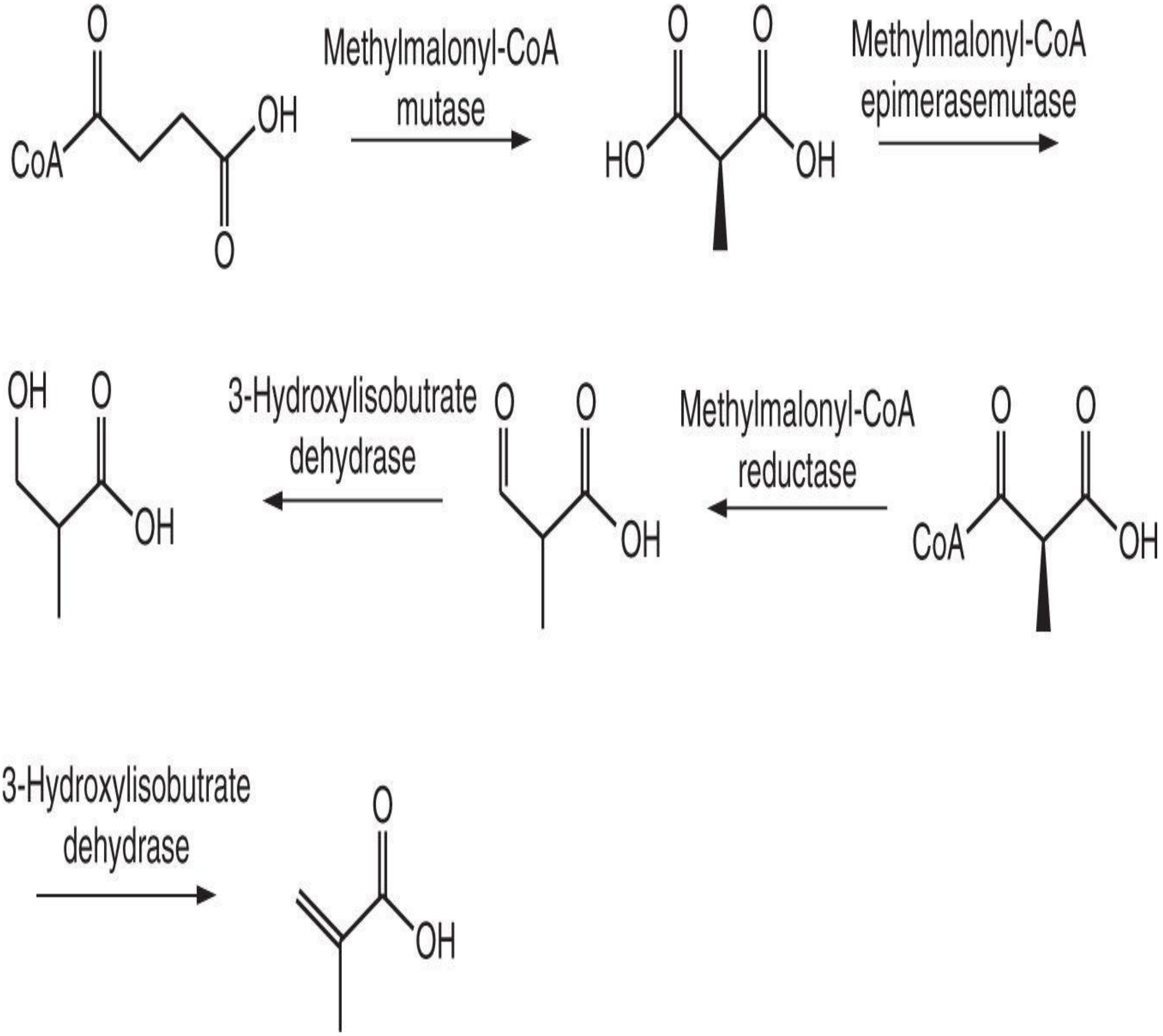


Figure 14.19

Experimental

1. Preparation of methacrylic acid from succinyl-CoA to methacrylic acid via 3-hydroxyisobutyrate (reaction overview). In this biosynthetic process, a maximum amount of methacrylic acid was generated using 1.33 mol of succinyl-CoA per mol of glucose under anaerobic conditions without generating any toxic organic water by-products. The synthetic pathway was energetically efficient and generated 0.5 moles of ATP per mole of glucose that was metabolized to methacrylic acid only if phosphoenolpyruvate and carboxykinase activity were assumed to be irreversible. The pathway entails converting succinyl-CoA to (R)-methylmalonyl-CoA, which was subsequently converted into (S)-methylmalonyl-CoA by an epimerase. Thereafter, (S)- or (R)-stereoisomers of methylmalonyl-CoA were reduced to either (R)- or (S)-3-hydroxyisobutyrate, respectively, by a pair of enzymes or by using a single enzyme that exhibited acyl-CoA reductase and alcohol-dehydrogenase activities. Succinyl-CoA was then converted into 3-hydroxyisobutyrate and methacylic acid was isolated in high yields after dehydration.

Notes and Observations

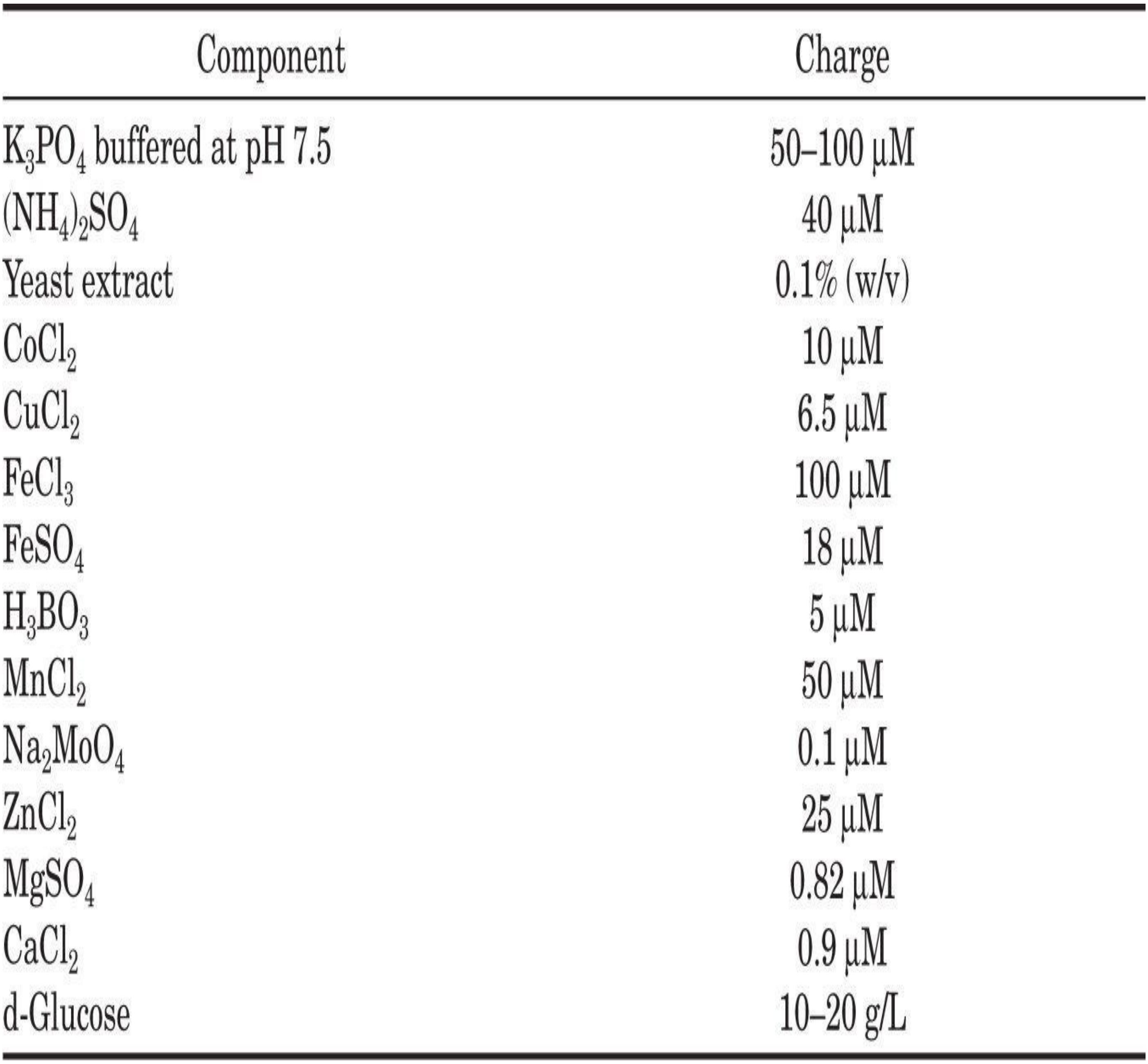
1. The biological preparation of 1,4-butanediol was previously prepared by Burgard[1] in a two-step process. Initially, poly(4-hydroxybutrate), (I), was treated with either poly(4-hydroxyalkanoate) dehydrogenase or a coenzyme-A derivative to generate 4-hydroxybutanoic acid, (II). The latter product was then isolated and treated with E. coli, and 1,4-butanediol (III), was isolated. (See Fig. 14.20.)

(I) (II)

Figure 14.20

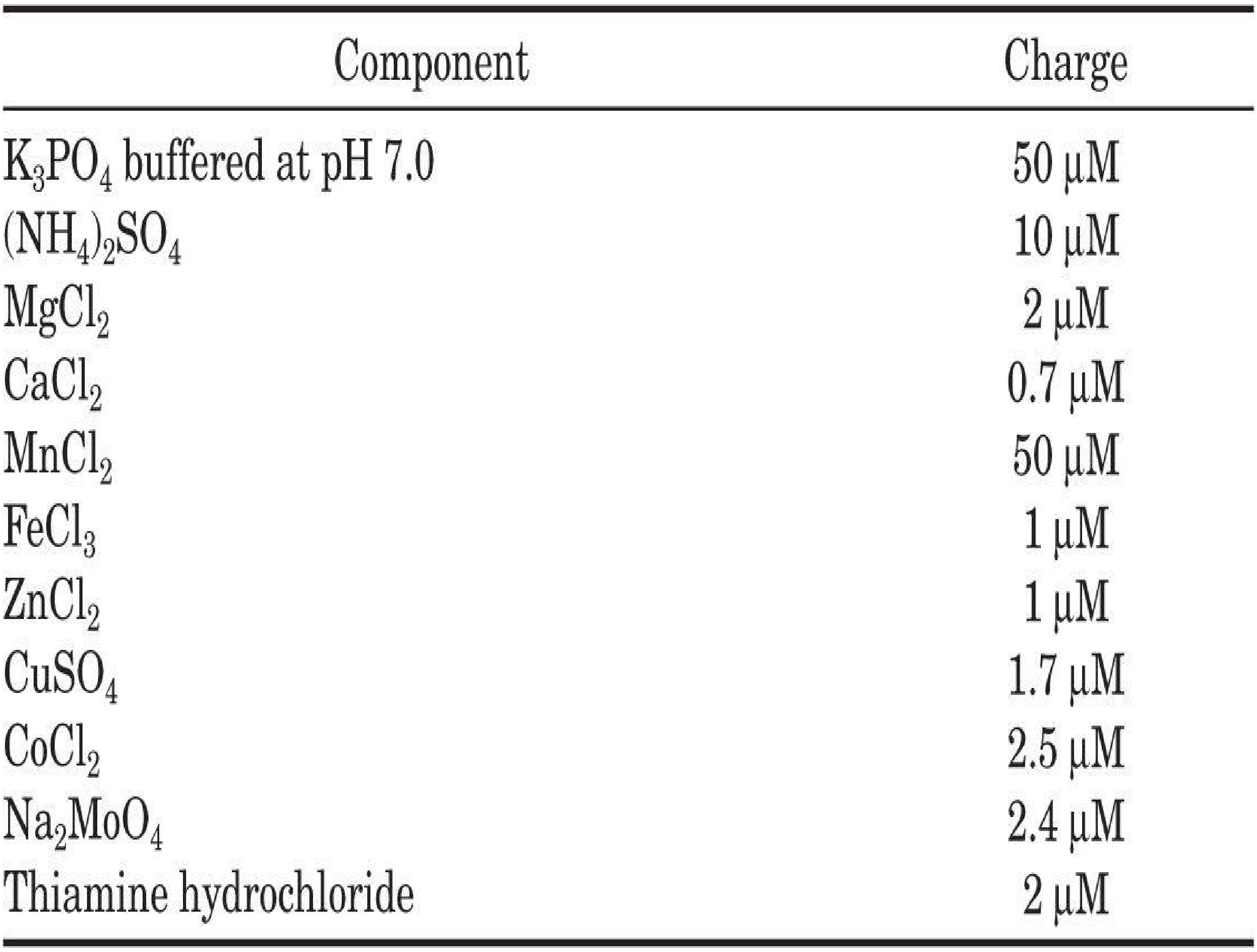
2. Joerger[2] used E. coli strain ECL707 containing the Klebsiella pneumoniae dha regulon cosmids pKP1 to convert d-glucose into 1,3-propanediol under fermentation conditions. The medium used in the process is provided in Table 14.12.
3. Viitanen[3] prepared the xylose-fermenting zymomonas mobilis strain, ZW658, and then biologically prepared ethanol in 93% yield or 0.46 g ethanol/g sugar using a mixed sugar feed consisting of 90% xylose, 10% glucose, and 0.6% acetic acid at 37°C at pH = 5.5.
4. Using E. coli transformed with the K. pneumoniae dha regulon genes dhaR or fY, dhaT, orfX, orfW, dhaB1, dhaB2, dhaB3, and orfZ, Emptage[4] biologically converted glycerol to 1,3-propanediol in yields exceeding 80% using the growth medium provided in Table 14.13.

TABLE 14.12 Growing medium used for the biological synthesis of 1,3-propanediol from d-glucose using the E. coli strain ECL707 containing the K. pneumoniae dha regulon cosmids pKP1.



Component	Charge
K_3PO_4 buffered at pH 7.5	50–100 µM
$(NH_4)_2SO_4$	40 µM
Yeast extract	0.1% (w/v)
$CoCl_2$	10 µM
$CuCl_2$	6.5 µM
$FeCl_3$	100 µM
$FeSO_4$	18 µM
H_3BO_3	5 µM
$MnCl_2$	50 µM
Na_2MoO_4	0.1 µM
$ZnCl_2$	25 µM
$MgSO_4$	0.82 µM
$CaCl_2$	0.9 µM
d-Glucose	10–20 g/L

TABLE 14.13 Medium used for biologically preparing 1,3-propanediol using glycerol with modified E. coli.



Component	Charge
K_3PO_4 buffered at pH 7.0	50 µM
$(NH_4)_2SO_4$	10 µM
$MgCl_2$	2 µM
$CaCl_2$	0.7 µM
$MnCl_2$	50 µM
$FeCl_3$	1 µM
$ZnCl_2$	1 µM
$CuSO_4$	1.7 µM
$CoCl_2$	2.5 µM
Na_2MoO_4	2.4 µM
Thiamine hydrochloride	2 µM

References

1. Anthony P. Burgard et al., *Methods and organisms for the growth-coupled production of 1,4-butanediol*, U.S. Patent 7,947,483 (May 24, 2011)

2. Melissa Joerger et al., *Personal care composition containing bioderived 1,3-propanediol and its conjugate esters*, U.S. Patent 8,048,920 (November 1, 2011)

3. Paul V. Viitanen et al., *Ethanol production in fermentation of mixed sugars containing xylose*, U.S. Patent 7,629,156 (December 8, 2009)

4. Mark Emptage et al., *Process for the biological production of 1,3-propanediol with high titer*, U.S. Patent 7,504,250 (March 7, 2009)

Peracids

Author Robert Dicosimo et al.

Patent Title ***Production of peracids using an enzyme having perhydrolysis activity,*** U.S. Patent 8,329,441 (December 11, 2012)

Relevant Prior Patents by Author or Coauthors

Enzymatic peracid production using a cosolvent, U.S. Patent 8,304,218 (November 6, 2012)

Production of peracids using an enzyme having perhydrolysis activity, U.S. Patent 8,298,808 (October 30, 2012)

Production of peracids using an enzyme having perhydrolysis activity, U.S. Patent 8,293,792 (October 23, 2012)

Enzymatic peracid generation formulation, U.S. Patent 8,293,221 (October 23, 2012)

Production of peracids using an enzyme having perhydrolysis activity, U.S. Patent 8,288,136 (October 16, 2012)

Perhydrolase for enzymatic peracid production, U.S. Patent 8,222,012 (July 17, 2012)

Product Application

Peracids generated from this investigation are designed to be used as additives in bleaching formulations in consumer laundry detergent products.

Significance of Current Application

Low levels of peracids present in consumer laundry detergent products are effective as mild bleaching agents. The current industrial method to prepare peracids involves reacting a carboxylic acid with hydrogen peroxide catalyzed with a strong inorganic acid, such as concentrated sulfuric acid. Although this method is effective in producing peracids, it is extremely dangerous and produces very high levels of toxic organic waste by-products. In the current investigation, the next generation for producing peracids is described. In this enzymatic method, Bacillus subtilis ATCC 31954® was used as a replacement for concentrated sulfuric acid. It was determined in this investigation that under identical reaction conditions and stoichiometries, catalyzing the peracid-forming reaction with Bacillus subtilis as a replacement for sulfuric acid generated up to six times the amount of peracid. In addition, reaction waste produced in this method was laboratory-processable and re-cycled, while storage and handling concerns associated with using Bacillus subtilis ATCC 31954® were eliminated.

Product Formation

A. Peracetic acid formation in the absence of Bacillus subtilis (control).

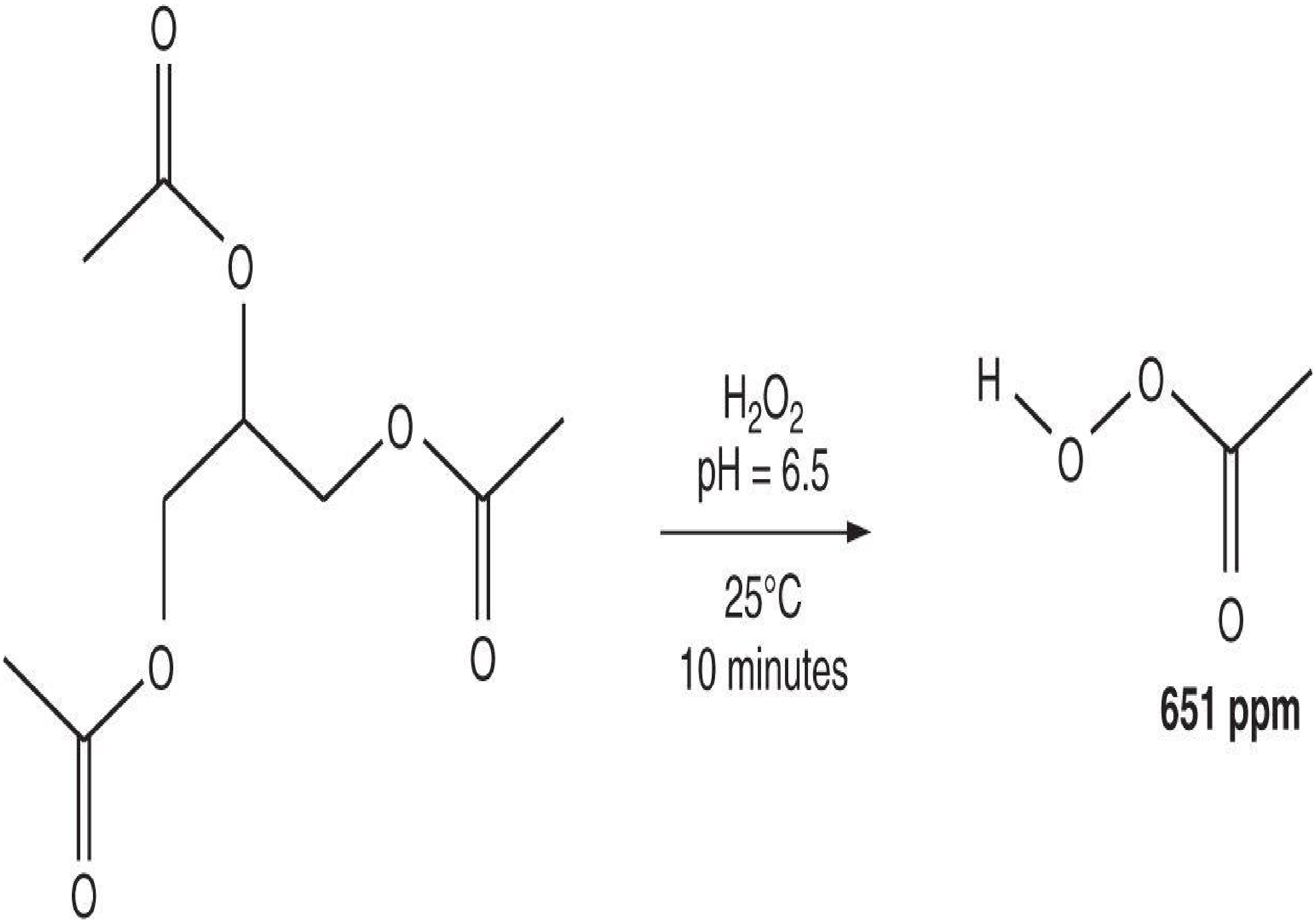


Figure 14.21

B. Peracetic acid formation catalyzed with Bacillus subtilis.

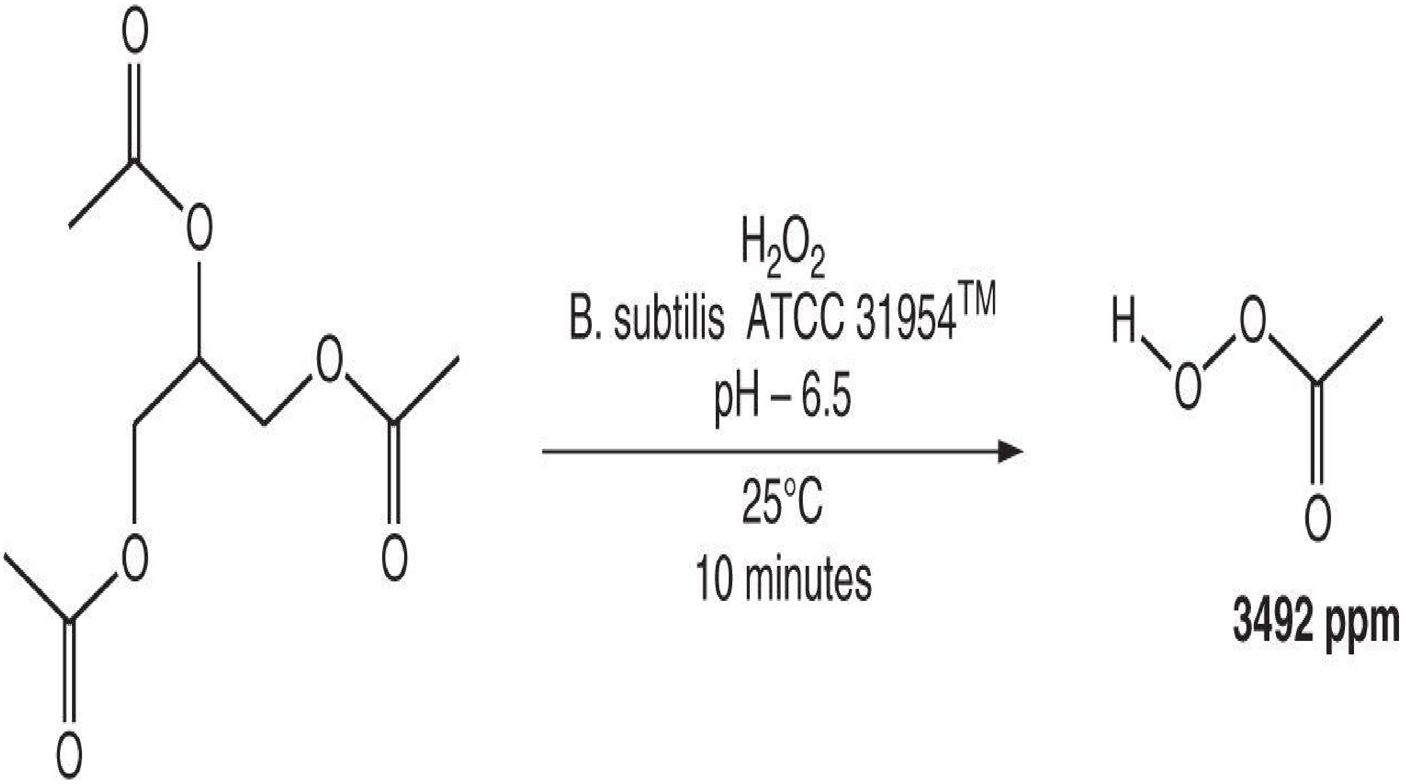


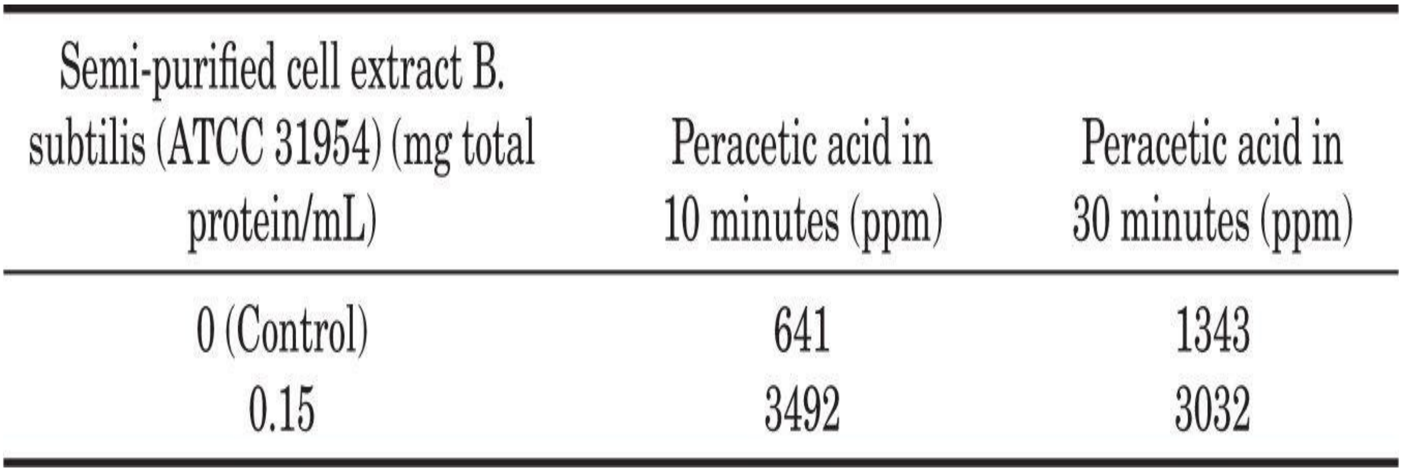
Figure 14.22

Experimental

1. Preparation of cell extract from Bacillus subtilis ATCC 31954®. A culture of Bacillus subtilis ATCC 31954® was revived following suspension of the dried culture in 5 mL of nutrient broth that was then incubated for three days at 30°C. After the third day of incubation an aliquot was streaked onto a trypticase soy agar culture plate and further incubated at 35°C for 24 hours. Thereafter, several single colonies were scraped onto a 1-µL inoculation loop and transferred into 50 mL of Lactobacillus MRS broth and grown at a 200-rpm agitation rate for 12 hours at 30°C. A 2-mL sample of this culture was then transferred into an unbaffled 500-mL shake flask containing 100 mL of MRS broth for growth at 30°C at a 200-rpm agitation rate for 12 hours to 14 hours. The cells were then harvested and then isolated by centrifugation at 15,000 rpm for 25 minutes at 5°C, and the cell paste was stored at −80°C. For cell extract preparation, 0.9 g of cell paste was suspended at 25wt% in 0.05 M of a potassium phosphate buffer at pH 7.0 containing 1 mM of dithiothreitol and 1 mM of EDTA. The cell suspension was then passed twice through a French press having a working pressure of 16,000 psi, and the crude extract was centrifuged at 20,000 rpm to remove cellular debris. Once a clear cell extract was obtained, it was assayed for total soluble protein and then re-frozen and stored at −80°C.

2. Perhydrolysis activity of semi-purified cell Bacillus subtilis ATCC 31954® extract. A 1-mL aliquot of Bacillus subtilis ATCC 31954® cell extract containing 10 mg of total protein/mL was prepared using the Step 1 procedure and then diluted with an equal volume of 50 mM phosphate buffer at pH 7.0 and then filtered through a 100,000 molecular weight-cutoff centricon membrane. Thereafter, 100 mL of semi-purified cell extract (0.15 mg extract total protein) in 50 mM phosphate buffer at pH 6.5 was then added to a small, round beaker containing 250 mM triacetin and 2.5 M hydrogen peroxide and stirred at 25°C for either 10 minutes or 30 minutes. In addition, a control reaction was also conducted by substituting 50 mM phosphate buffer at pH 6.5 for semi-purified cell extract. Product-formation testing results for peracid formation are provided in Table 14.14.

TABLE 14.14 Peracetic acid produced by a reaction of 250 mM triacetin and 2.5 M and hydrogen peroxide at pH 6.5 in the presence or absence of the semi-purified cell extract B. subtilis ATCC 31954®.



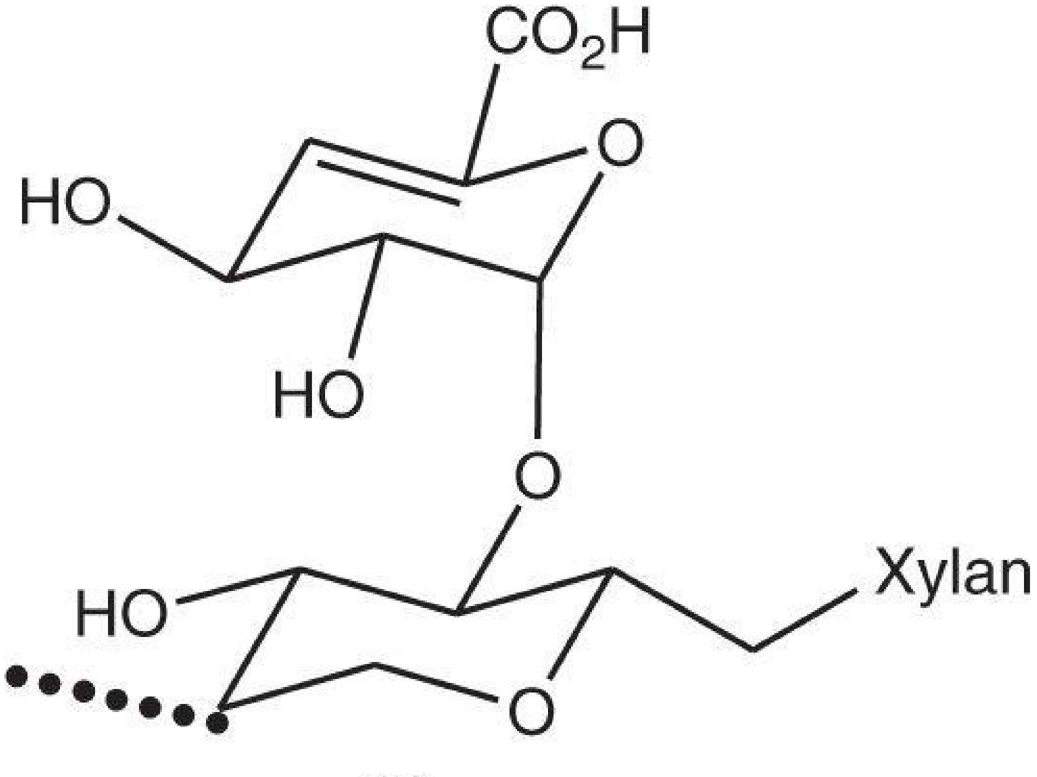
Semi-purified cell extract B. subtilis (ATCC 31954) (mg total protein/mL)	Peracetic acid in 10 minutes (ppm)	Peracetic acid in 30 minutes (ppm)
0 (Control)	641	1343
0.15	3492	3032

Testing Results

Notes and Observations

1. In an earlier investigation by DiCosimo[1] carboxylic acid esters monoacetin, triacetin, monopropionin, dipropionin, tripropionin, monobutyrin, dibutyrin, tributyrin, glucose pentaacetate, xylose tetraacetate, acetylated xylan, acetylated xylan fragments, β-D-ribofuranose-1,2,3,5-tetraacetate, tri-O-acetyl-D-galactal, tri-O-acetyl-glucal, and propylene glycol diacetate were all enzymatically converted into the corresponding peracids in high yields using Bacillus subtilis ATCC 29233®. Formulations that generated peracids were subsequently used in consumer disinfectant and bleaching formulations.

2. Iori Tomoda[2] developed a chlorine-dioxide-free method for bleaching pulp by removing hexeneuronic acid, (I). In this process, mashed pulp was treated with in situ-generated peroxomonosulfuric acid that caused the pulp to have a luster improvement of at least 54.8%, a kappa value of 8.5, and a pulp viscosity of 19.7 mPas. (See Fig. 14.23.)



(I)

Figure 14.23

3. Enzymes from both B. Stearothermophilus α-amylase and Bacillus pullulanase were used by Svendsen[3] to generate in situ peracid-forming bleach activators which were then used in consumer cleaning and laundry formulations.

4. Disinfectant and laundry detergents formulations containing spray-dried CE-7 enzyme powder were prepared by DiCosimo[4] to generate alkyl peracids.

References

1. Robert DiCosimo et al., *Enzymatic peracid generation formulation*, U.S. Patent 8,293,221 (October 23, 2012)

2. Iori Tomoda et al., *Process for producing bleached pulp*, U.S. Patent 8,268,123 (September 8, 2012)
3. Allan Svendsen et al., *Alpha-amylase variant with altered properties*, U.S. Patent 8,252,573 (August 28, 2012)
4. Robert DiCosimo et al., *Enzyme powder comprising spray-dried formulation comprising a CE-7 enzyme*, U.S. Patent 8,252,562 (August 28, 2012)

Terephthalates

Author	Seiko Sato
Patent Title	***Biomass plastic alternative to polyethylene terephthalate and method for producing the biomass plastic,*** U.S. Patent Application 20130066039 (March 14, 2013)

Relevant Prior Patents by Author

None

Product Application

Polyethylene terephthalate is used in forming molded products such as beverage or food containers, as well as in preparing fibers for clothing.

Significance of Current Application

Polyethylene terephthalate is ordinarily prepared by the chemical reaction of petroleum-derived terephthalic acid with ethylene glycol. This process is energy intensive, generates excessive unusable chemical-waste products, and relies exclusively on non-renewable petrochemicals. The current investigation addresses these concerns by preparing polyethylene terephthalate, requiring low energy input and uses biomass-derived reagents. The method uses Bacillus subtilis, Bacillus pumilus, Bacillus thuringiensis, and Corynebacterium glutamicum microorganisms with Kaoliang starch to produce biodegradable polyethylene terephthalate without any dependence on fossil-derived intermediates.

Product

Figure 14.24

Product Formation

1. A microorganism mixture consisting of Bacillus subtilis, Bacillus pumilus, and Bacillus thuringiensis was cultured at approximately 45°C for up to three days in a starch and silicic-acid medium.

2. The growing microorganism mixture from Step 1 was then treated with Corynebacterium glutamicum and the mixture was cultured an additional three days at approximately 40°C.
3. The microorganism mixture from Step 2 was used to prepare polyethylene terephthalate that was then isolated from the mixture.

Experimental

1. Preparation of the microorganism mixture for the biosynthesis of polyethylene terephthalate. A biomass was prepared consisting of 1 kg of Kaoliang starch, ground fruit-pulp of jujube, and approximately 100 g of magnesium silicate derived from coral fossil powder or shell powder containing between 10 wt% to 15 wt% of water. The biomass was then treated with a 3:5:2 weight ratio of Bacillus subtilis, Bacillus pumilus, and Bacillus thuringiensis to make about 10 wt% slurry. It was then cultured for several days at approximately 45°C. The biomass was then treated with Corynebacterium glutamicum and the mixture was further cultured for up to three days at 40°C.

2. Preparation of polyethylene terephthalate biomass plastic. After the Step 1 mixture reacted for approximately 36 hours, polyethylene terephthalate was identified as a gel-like precipitate. It was isolated by vibrating the culture container which caused the polymer to fall from the floating cellular residues. After isolating the lower polymer layers, the gel-like polymer was dried and then ground to powder.

Testing

A. Polymer identification. The biomass plastic was identified using infrared spectroscopy. Infrared spectra of bio-derived and petrochemically derived polyethylene terephthalate samples were identical.

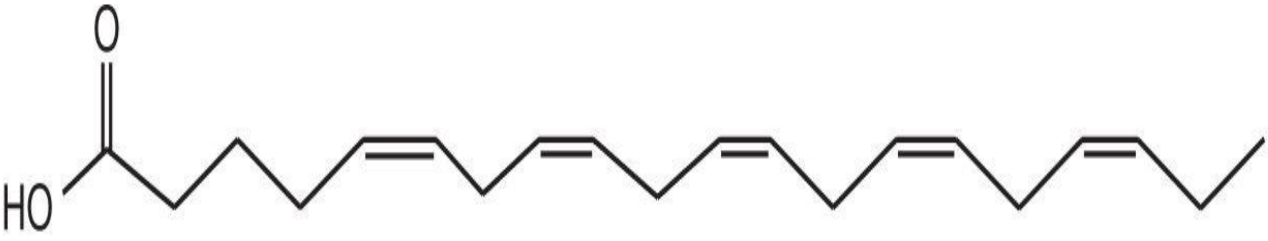
B. Physical testing. Selected physical testing of petrochemically and bioderived polyethylene terephthalate samples was conducted and the results are summarized in Table 14.15.

Notes and Observations

1. Singh[1] biosynthesized eicosapentaenoic acid, (I), docosapentaenoic acid, (II), and docosahexaenoic acid, (III), in good yields using Pavlova salina CS-4 plasmids incorporated into yeast cells by heat shock. (See Fig. 14.25.)

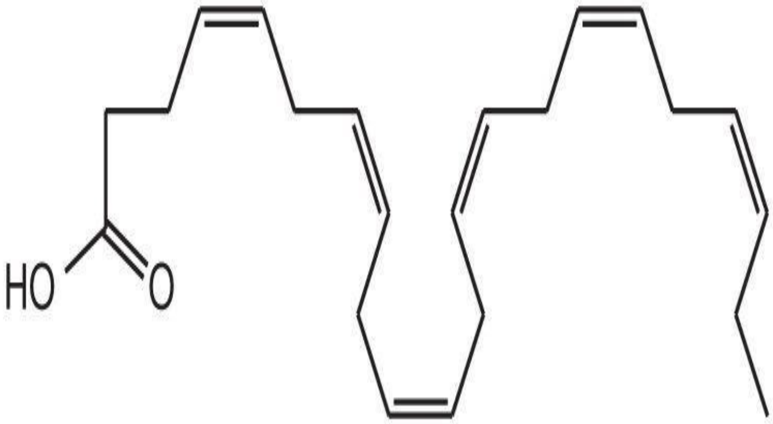
TABLE 14.15 Results of physical testing of non-annealed, annealed, and bioderived polyethylene tere-phthalate samples. Physical properties of annealed bio- and petrochemically derived polyethylene terephthalate samples were essentially identical.

Test items	Non-annealed Bio-PET 1	Annealed Bio-PET 1	Annealed petrochemically-derived PET
IZOD impact strength (kgf cm/cm)	4.5	6	6.7
Flexural strength (kgf/cm^2)	915	723	718
Flexural modulus (kgf/cm^2)	24,300	22,800	21,400
Maximum tensile stress (kgf/cm^2)	556	567	535
Elongation at break (%)	Necking was observed	Necking was observed	Necking was observed
Density (g/cm^3)	1.34	1.34	1.34
Intrinsic viscosity	0.72 ± 0.015	0.76 ± 0.015	0.8 ± 0.015
VICAT softening point (°C)	79	81	81



(I)

(II)

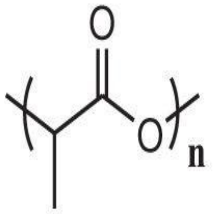


(III)

Figure 14.25

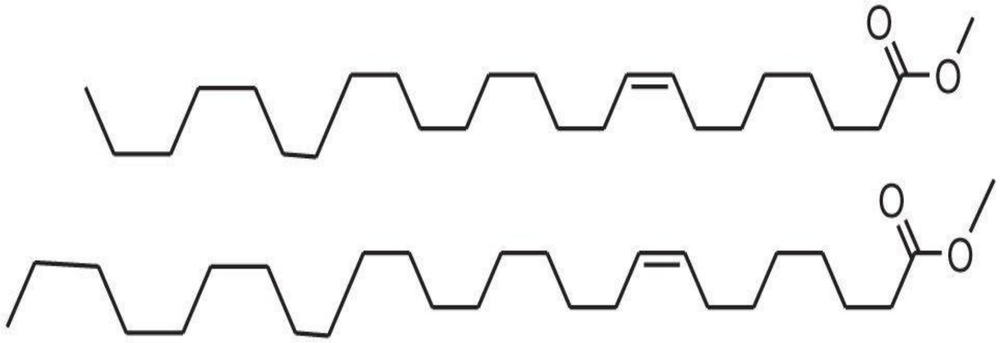
2. Riebel[2] formed biolaminates and bioadhesives using biologicallyderived polylactic acid, (IV), with soybean oil, (V). The blends from this mixture were then used in wood-paneling applications. In this application, bioplasticizers, (VI) to (IX), were added to polylactic acid and soybean oil mixture blends, heated to at least 150°C, and then pressed for 2.5 minutes with 50 lb/in^2 to ensure a strong contact with the bioadhesive. (See Fig. 14.26.)

Adhesive Components



Polylactic Acid

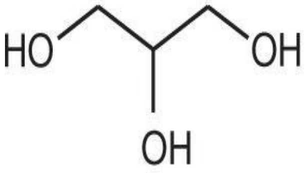
(IV)



Two Components of Soybean oil

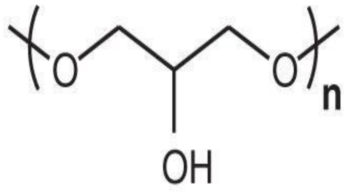
(V)

Adhesive Plasticizer Components



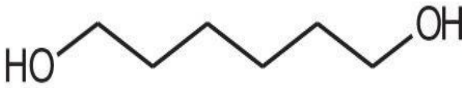
Glycerin

(VI)



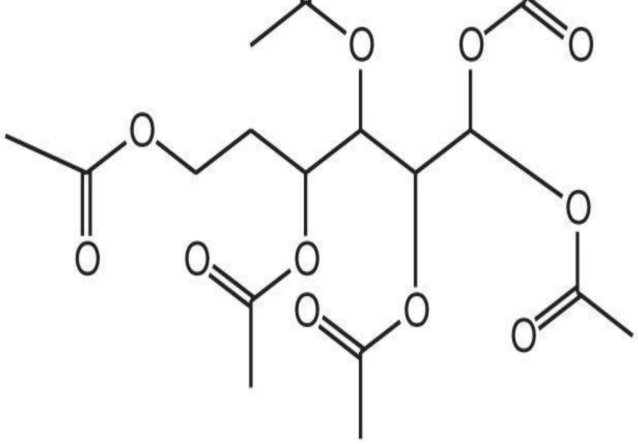
Polyglycerin

(VII)



1.6-Hexanediol

(VIII)



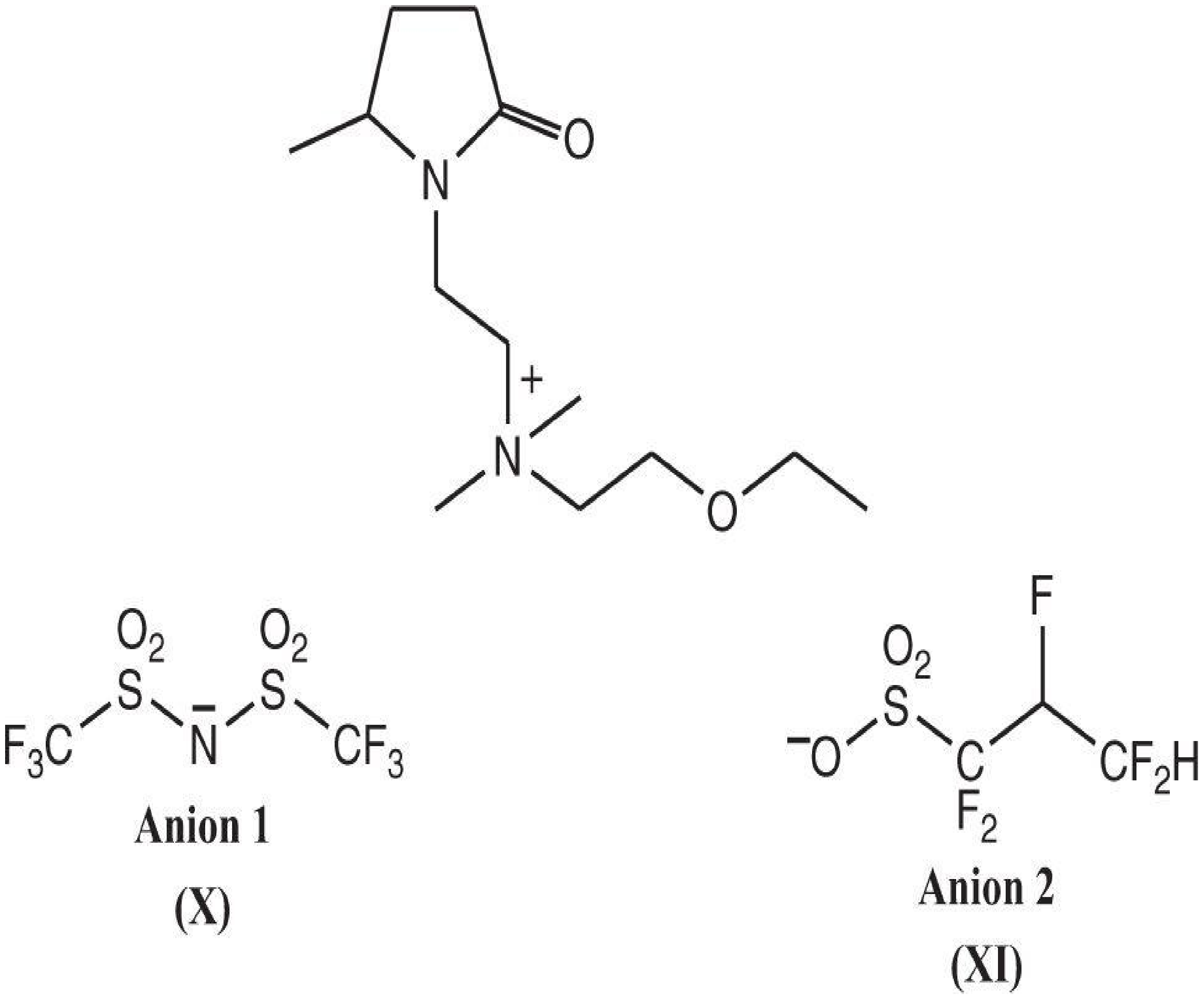
Sorbitol Hexaacetate

(IX)

Figure 14.26

3. Shearer[3] pyrolysized biomasses derived from cellulosic materials, lignin-containing materials, animal by-products, organic wastes, landfill matter, marine waste, agricultural waste (animal or human) to 450°C and 525°C, in the absence of air, to form a semi-brittle biochar. The biochar was used exclusively as a bioremediation agent in addressing chemical spills.

4. Foo[4] greatly increased the amount of levulinic acid and levulinic acid derivatives from inexpensive renewable biomass feedstock by treating the feedstock with 5-methyl-pyrrolidin-2-one ionic liquid derivatives, (X) to (XI), and then heating the mixture to approximately 100°C for several hours. (See Fig. 14.27.)



Anion 1

(X)

Anion 2

(XI)

Figure 14.27

References

1. Surinder Pal Singh et al., *Synthesis of long-chain polyunsaturated fatty acids by recombinant cell*, U.S. Patent Application 20130060053 (March 7, 2013)

2. Michael J. Riebel et al., *Cellulosic biolaminate composite assembly and related methods*, U.S. Patent 8,389,107 (March 15, 2013)

3. David Shearer et al., *Biochar*, U.S. Patent 8,361,186 (January 29, 2013)

4. Thomas Foo, *Functionalized N-substituted pyrrolidonium ionic liquid*, U.S. Patent 8,350,056 (January 8, 2013)

Succinic Acid

Author	Roger L. Bernier et al.
Patent Title	***Biobased compositions of diammonium succinate, monoammonium succinate, and/or succinic acid and derivatives thereof,*** U.S. Patent Application 20130072714 (March 21, 2013)

Relevant Prior Patents by Author or Coauthors

Processes for producing succinic acid from fermentation broths containing diammonium succinate, U.S. Patent 8,246,792 (August 21, 2012)

Methods and systems of producing dicarboxylic acids, U.S. Patent Application 20120259138 (October 11, 2012)

Process for purifying an organic acid, U.S. Patent Application 20030171615 (September 11, 2003)

Process for purifying an organic acid, U.S. Patent Application 20030155298 (April 21, 2003)

Process for obtaining an organic acid from an organic acid ammonium salt, an organic acid amide, or an alkylamine organic acid complex, U.S. Patent Application 20030029711 (February 13, 2003)

Process for production of esters, U.S. Patent 6,664,413 (December 16, 2003)

Process for production of organic acids and esters thereof, U.S. Patent 6,291,708 (September 18, 2001)

Product Application

Succinic acid is a precursor for preparing polyesters, engineered plastics, and polyimides.

Significance of Current Application

Sugar fermentation for preparing succinic acid is considered a replacement for petroleum-derived materials. Succinic acid was readily prepared in both high yield and purity by the reaction of microorganisms E. coli with monosaccharides such as fructose or glucose. This biological method for preparing succinic acid required low energy and did not generate toxic organic-reaction waste products. Finally, since no specific equipment was required for this biosynthesis, it inherently becomes a more industrially viable method for preparing this material.

Product Structure

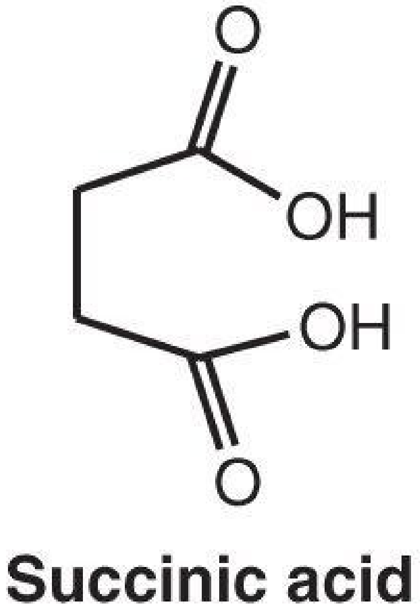


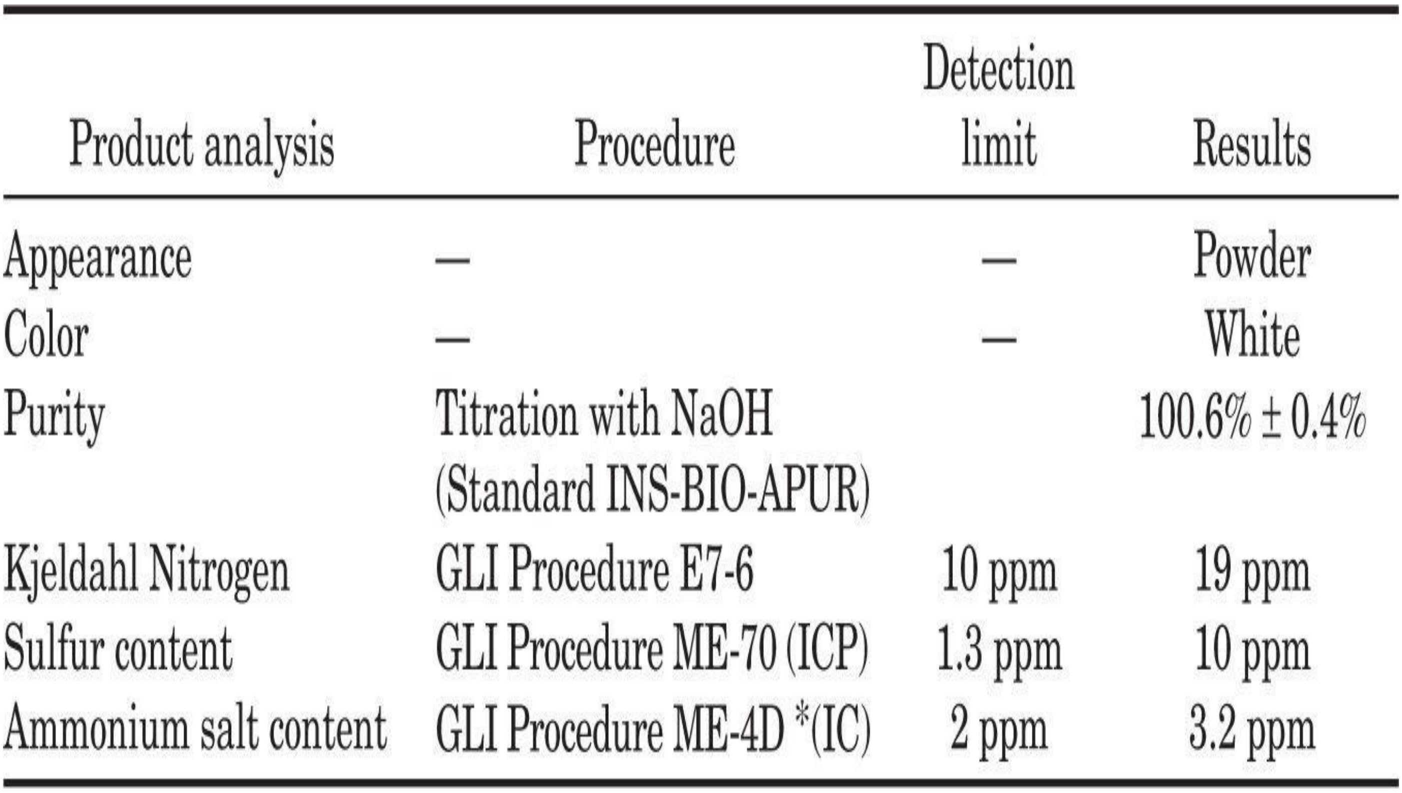
Figure 14.28

Experimental

1. Preparation of succinic acid. A fermentation reactor with aeration containing an E. coli strain was used to prepare cell mass. A total liquid volume of 75,000 L was used. A minimal amount of bio-based succinic acid salt medium was added for cell growth that contained 1211 kg of salts. After the cell mass growth had been completed, the entire liquid contents were combined and then transferred to a conversion vessel and additional liquid was added. Sugar solutions in the form of purified hydrolyzed-wheat-starch solution were then gradually added, as well as agents for pH control. Thereafter, biobased carbon dioxide sparging was then introduced which was obtained from a commercial beer or ethanol fermentation. The final volume of the reaction kettle contained over 300,000 L of crude biogenerated succinic acid, as well as some ammonium salts at neutral pH. Overall purity of the biobased succinic acid and the ammonium salt mixture at neural pH on a water-free basis was of the order of 80–85%. For commercial use, however, the succinic acid solution containing a mixture of ammonium salts had limited industrial applications and it became necessary to convert succinic acid salts into purified succinic acid. To address this concern, the reaction product mixture was further processed by cell removal using 150 kDa Kerasep ceramic membranes at 40°C with a volume concentration factor of at least 15 times. In addition, demineralization with the chelating-type resin Applexion XA 6043 Na aminomethylphosphonic at 40°C was needed for ammonium salt removal. Purification of the solution also required base removal using the biopolar membrane electrodialysis EUR40B-BIP V2 operating at 40°C, as well as using the strong cation exchange Applexion XA 2033 Na resin operating at 40°C. After these processes were applied, both mono- and diammonium succinates were removed. The purified succinic acid solution was then filtered through a nanofiltration unit at 20°C, and 800 kg bags of dried and purified succinic acid were isolated. The physical properties of the 97% yield purified succinic acid crystals are summarized in Table 14.16.

Testing

TABLE 14.16 Analytical testing of biogenerated succinic acid prepared to Step 1.



Product analysis	Procedure	Detection limit	Results
Appearance	—	—	Powder
Color	—	—	White
Purity	Titration with NaOH (Standard INS-BIO-APUR)		100.6% ± 0.4%
Kjeldahl Nitrogen	GLI Procedure E7-6	10 ppm	19 ppm
Sulfur content	GLI Procedure ME-70 (ICP)	1.3 ppm	10 ppm
Ammonium salt content	GLI Procedure ME-4D *(IC)	2 ppm	3.2 ppm

Notes and Observations

1. Fruchey[1] developed a method for selectively converting biogenerated diammonium succinate into monoammonium succinate using a similar fermentation method. In this process, an aqueous solution of diammonium succinate was refluxed in water containing concentrated acetic acid. During this heating process, water was directly distilled off so that the internal temperature of the reaction was approximately 110°C. Upon cooling moderately large monoammonium succinate crystals were isolated which did not require additional purification.

2. In an attempt to prepare a gasoline component and a chemical intermediate, Gruber[2] fermented a mixture of glucose-effected E. coli and yeast extract for approximately 9 hours under a stream of oxygen and isolated isobutanol as the reaction product. Isobutanol was then treated with a γ-alumina catalyst on a fixed-bed tubular reactor for 6 hours, which produced isobutylene in over 95% yield as the dehydration product and a small amount of linear butanes. Isobutylene was then used in gasoline fuel formulations.

3. Bradin[3] fermented a mixture consisting of corn-derived glucose, xylose, or fructose with the bacteria Clostridium tyrobutyricum. In this ambient temperature process, butyric acid was isolated as the single reaction product. The intermediate was then subjected to the Kolbe[4] electrolysis to form hexane that was then used in gasoline or diesel fuel formulations. In the same investigation, a limited amount of butyric acid was isomerized into mixed octanes and used as octane enhancers in gasoline fuel formulations.

4. Cervin[5] prepared isoprenein in high yield by using the protein sequence for the kudzu Pueraria Montana isoprene synthase gene that was introduced into E. coli by thermal shock. In a typical reaction, the fermentation media per L of fermentation medium consisted of 13.6 g of potassium hydrogen phosphate, 2 g of magnesium sulfate

pentahydrate, 2 g of citric acid monohydrate, 0.3 g of ferric ammonium citrate, 3.2 g of ammonium sulfate, 5 g of yeast extract, and 1 mL of an unspecified trace metal solution. The six-component mixture was then dissolved in water and the pH adjusted to 6.8 with potassium hydroxide. The solution was then treated with glucose and, after reacting for 6 hours at ambient temperature, isoprene was isolated in moderate yield by distillation.

References

1. Olan S. Fruchey et al., *Processes for the production of hydrogenated products*, U.S. Patent 8,399,687 (March 13, 2013)

2. Patrick R. Gruber et al., *Renewable compositions*, U.S. Patent 8,378,160 (February 19, 2013)

3. David Bradin, *Production of gasoline from fermentable feedstocks*, U.S. Patent 8,241,881 (August 14, 2012)

4. The Kolbe electrolysis, or Kolbe reaction, is a decarboxylative dimerisation reaction that occurs by a free radical mechanism:

$$R_1COO^- + R_2COO^- \rightarrow R_1\text{-}R_2 + 2\ CO_2$$

5. Marguerite Cervin, *Compositions and methods for preparing isoprene*, U.S. Patent Application 20130071908 (March 21, 2013)

1,3,5-Trihydroxybenzene Derivatives Phloroglucinols

Author	John W. Frost
Patent Title	***Biosynthesis of phloroglucinol and preparation of 1,3,5-trihydroxybenzene therefrom,*** U.S. Patent 8,329,445 (December 11, 2012)

Relevant Prior Patents by Author

Compositions and methods for production of fermentable sugars, U.S. Patent 8,236,551 (August 7, 2012)

Endoglucanases, U.S. Patent 8,206,960 (June 26, 2012)

Endoglucanases, U.S. Patent 8,293,792 (January 3, 2012)

Endoglucanases, U.S. Patent Application 20120315676 (December 13, 2012)

Endoglucanase Variants, U.S. Patent Application 20120208235 (August 16, 2012)

Fungal Strains, U.S. Patent Application 20120107880 (May 3, 2012)

Product Application

Phloroglucinol intermediates that were biosynthesized from glucose in moderate to good yields include 1,3,5-trihydroxylbenzene, 2-acetyl-1,3,5-trihydroxylbenzene (phloroglucinol), and 2,6-diacetyl-1,3,5-trihydroxylbenzene. All of these materials are useful as pharmaceutical and chemical additive intermediates.

Significance of Current Application

Phloroglucinol, and derivatives thereof, are widely used in pharmaceutical applications as antispasmodics; in industrial applications as explosive precursors; chemical additives; and in fabric-dye formulations. The traditional method for preparing phloroglucinol derivatives is synthetically challenging and expensive. Their preparation involves the use of multi-step reactions requiring the use of non-renewable reagents, which subsequently generates extensive amounts of toxic organic-reaction waste materials. In this investigation it was empirically determined that the anabolic enzymatic catalysis of renewable d-glucose to the malonyl-CoA analogue could be feasibly used to prepare phloroglucinols at low cost and without generating toxic organic reaction waste products.

Phloroglucinols Prepared Using Enzymatic Catalysis

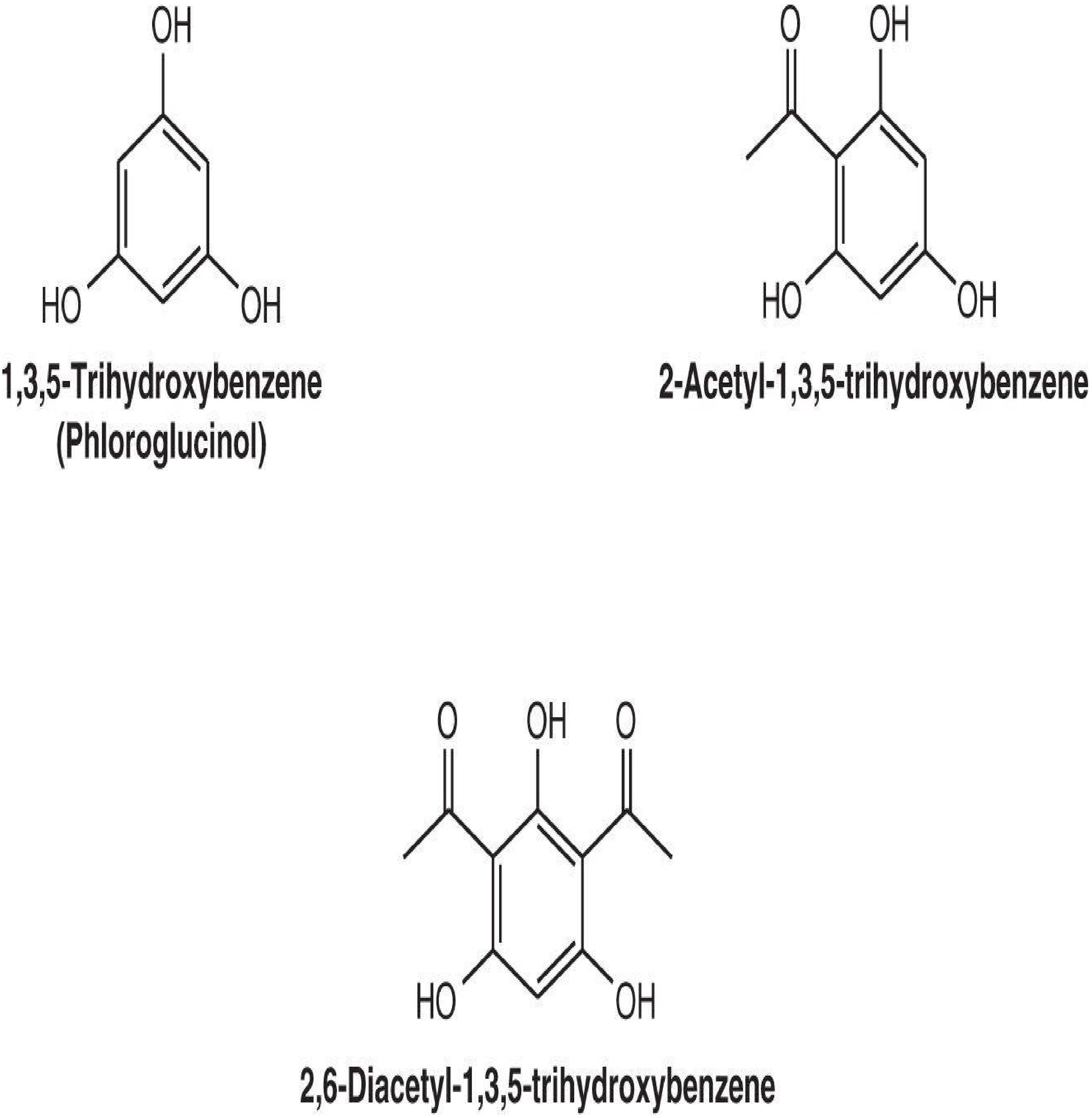


Figure 14.29

Experimental

1. Preparation of enzymes by cell culturing. Cells were cultured in either a TB or YM medium under shaken-flask conditions and then fermented under electronically controlled conditions. Harvested cells were subsequently isolated, washed and filtered in purified water, and then re-suspended in M9 minimal salts and then stored until needed.

2. Preparation of phloroglucinols by fermentation using glucose. In a typical fermentation reaction, a glass reaction chamber at 36°C containing a selected host/plasmid strain (illustrated in Table 14.17) was continuously treated with a d-glucose and pO_2 cascade while maintaining a steady state of carbon dioxide. During this process, the temperature was then lowered to between 25°C and 30°C and the reaction continued between 15 and 60 hours. Reaction aliquots were routinely removed from the glass reactor vessel and analyzed by TLC and quantified using HPLC. Testing results are provided in Table 14.17.

Testing Results

TABLE 14.17 Bioformation of phloroglucinol, 2-acetylphloroglucinol, and 2,6-diacetyl phloroglucinol using enzymes expressing phlACBDE genes.

Phloroglucinol formation

Entry	Host/plasmid phloroglucinols (mg/L)	Plasmid inserts	Phloroglucinol (mg/L)	2-acetyl-phloroglucinol (mg/L)	2,6-diacetyl-phlorogluinol (mg/L)
1	P. fluorescens Pf-5/ pME6031	None	10	23	35
2	P. fluorescens Pf-5/ pJA2.232	phlACBDE	470	500	790
3	E. coli BL21(DE3)/ pJA3.085	phlACBDE	32	14	0 4
4	E. coli BL21(DE3)/ pIA3.156	phlACBD	22	13	0
5	E. coli BL21(DE3)/ pJA2.042	phlD	720	0	0
6	E. coli JWF1(DE3)/ pJA3.131A	phlD	780	0	0
7	E. coli BL21(DE3)/ pJA3.169	phlACB	0	0	0
8	E. coli BL21(DE3)/ pJA3.169	phlACB	39	17	2

Notes and Observations

1. Burgard[1] used glucose to prepare the nonnatural microbial organism, 3-hydroxyisobutyryl-CoA synthetase, with 3-hydroxyisobutyric acid via a hydroxybutyryl-CoA mutase pathway to generate methacrylic acid. The process yielded 1.33 moles of methacrylic acid per mole of glucose under anaerobic conditions without the formation of reaction by-products.
2. In an earlier investigation by Burgard,[2] an E. coli strain was engineered to produce adipate acid by encoding the nucleic acids to prepare enzymes previously used in a 2-hydroxyadipyl-CoA to adipate pathway.
3. Microbially produced C_6 to C_{26} fatty alcohols were produced from renewable fatty carboxylic acids or fatty acid derivatives using the genetically engineered host cell FadD.acyl-CoA synthase. Alcohols prepared from this process were subsequently used by Scheibel[3] in detergent and cosmetic formulations.
4. Nonnaturally occurring microbial organisms consisting of trans, trans-muconate decarboxylase and trans-2,4-pentadienoate decarboxylase or cis, trans-muconate, cis-decarboxylase and trans-2,4-pentadienoate decarboxylase were used by Osterhout[4] to prepare phloroglucinol derivatives.

References

1. Anthony P. Burgard et al., *Microorganisms for the production of methacrylic acid,* U.S. Patent 8,241,877 (August 14, 2012)
2. Anthony P. Burgard et al., *Microorganisms for the production of adipic acid and other compounds*, U.S. Patent 8,088,607 (January 3, 2012)
3. Jeffrey John Scheibel et al., *Detergent compositions comprising microbially produced fatty acid alcohols and derivatives thereof,* U.S. Patent Application 20120172281 (July 5, 2012)
4. Robin E. Osterhout et al., *Microorganisms and methods for the biosynthesis of aromatics, 2,4-pentadieneoate and 1,3-butadiene,* U.S. Patent Application 20120021478 (January 23, 2012)

γ-Valerolactone

Author Anna Maria Cornelia Francisca Castelijns et al.

Patent Title ***Process to produce valerolactone from levulinic acid,*** U.S. Patent Application 20120329981 (December 27, 2012)

Relevant Prior Patents by Author or Coauthors

Process for the Preparation of cis-1-ammonium-4-alkoxycyclohexane carbonitrile salts, U.S. Patent Application 20120197035 (August 2, 2012)

α-*Substituted* α,β-*unsaturated E- or Z-aldehydes, use thereof, and process for their preparation*, U.S. Patent Application 20110301365 (December 8, 2012)

Synthesis routes to 2(S),4(S),5(S),7(S)-2,7-dialkyl-4-hydroxy-5-amino-8-aryl-octanoyl amides, U.S. Patent 8,088,955 (January 3, 2013)

Process for producing cinnamaldehyde derivatives, use thereof and the like, U.S. Patent 7,141,263 (November 28, 2006)

Product Application

γ-Valerolactone is a valuable chemical intermediate used in the preparation of adipic acid. In combination with diamines, Nylon 4,6 and Nylon 6,6 are prepared.

Significance of Current Application

The current industrial method for production of adipic acid begins with the oxidation of benzene derived from non-renewable fossil fuel. During the oxidation phase, however, nitric oxides are generated, which are subsequently vented into the air where, in combination with hydrocarbons and sunlight, generate smog. To address these problems, this investigation has developed a method to produce adipic acid using renewable levulinic acid to prepare the γ-valerolactone as the key intermediate. The current method is attractive since atmospheric-toxic nitric oxides are not produced during the process.

Product Formation

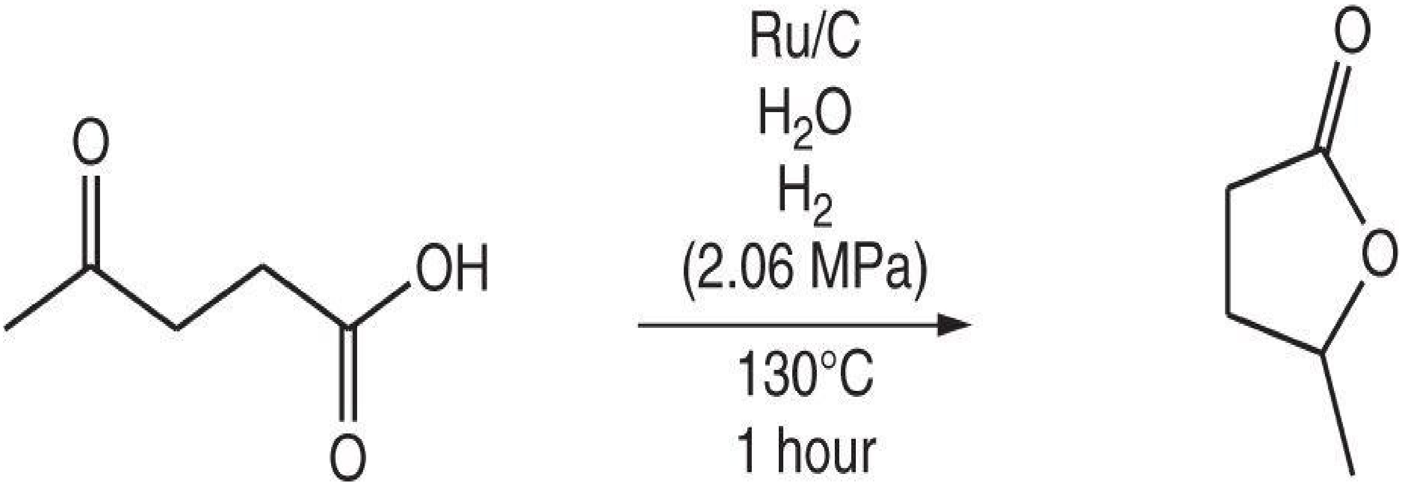


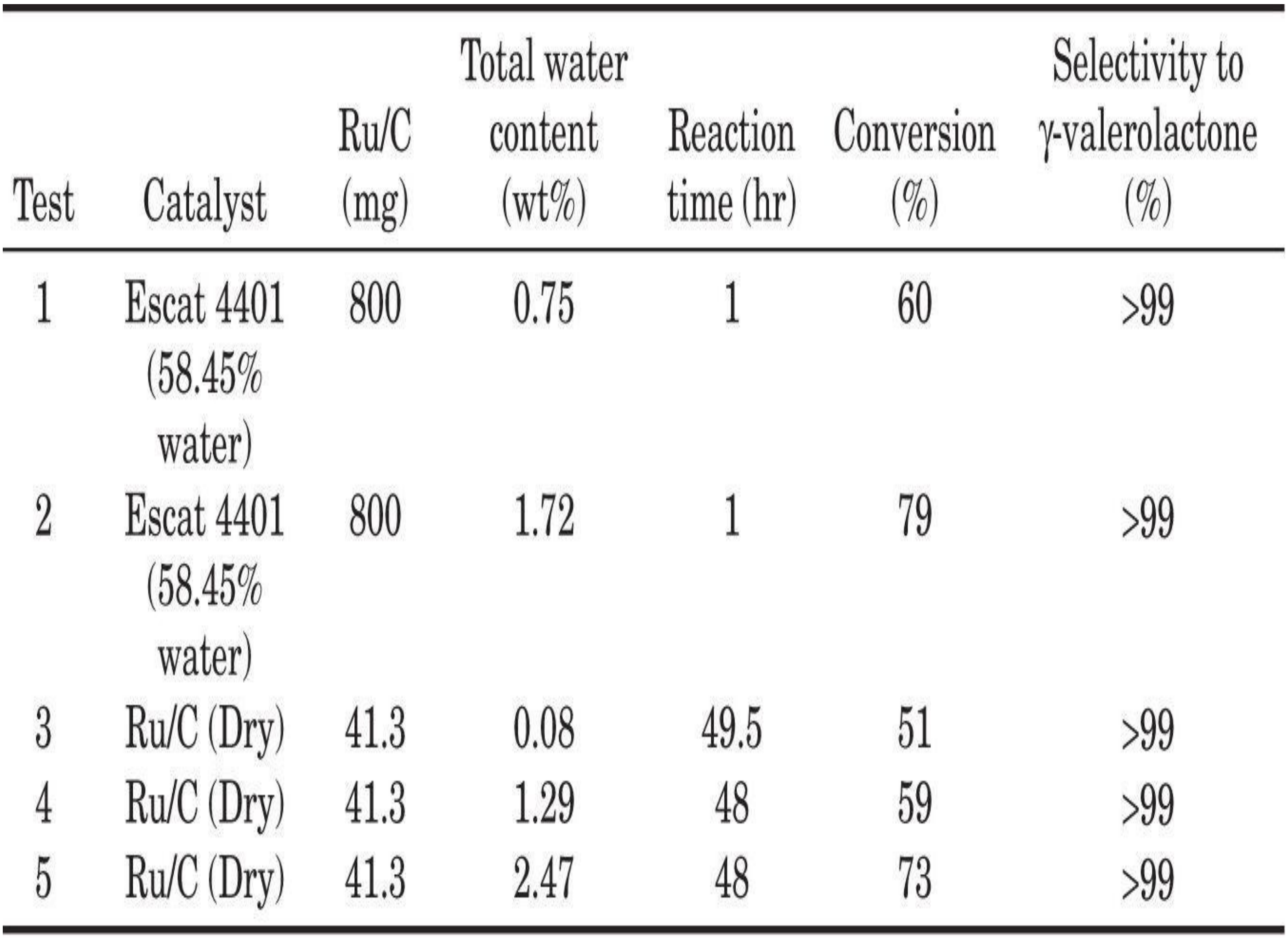
Figure 14.30

Experimental

1. Preparation of γ-valerolactone. A 150-mL autoclave was charged with 80 g of levulinic acid previously obtained from the method of Hachimama.[1] The ruthenium-carbon catalyst (described in Table 14.18) was then added to the reaction vessel where the ratio of ruthenium-to-carbon was 1:20, respectively. The reaction vessel was then treated with water, and the autoclave was purged three times with nitrogen and three times with hydrogen. The reaction container was then heated to 130°C at a pressure of 2.06 MPa hydrogen and γ-valerolactone was isolated in 79% yield and in <99% selectivity. A summary of similar conversions in varying reactions stoichiometries is provided in Table 14.18.

Testing Results

TABLE 14.18 Stoichiometric effects for converting levulinic acid into γ-valerolactone using varying ruthenium-carbon catalyst levels and water content. All hydrogenations were conducted at 2.06 MPa at 130°C.



Test	Catalyst	Ru/C (mg)	Total water content (wt%)	Reaction time (hr)	Conversion (%)	Selectivity to γ-valerolactone (%)
1	Escat 4401 (58.45% water)	800	0.75	1	60	>99
2	Escat 4401 (58.45% water)	800	1.72	1	79	>99
3	Ru/C (Dry)	41.3	0.08	49.5	51	>99
4	Ru/C (Dry)	41.3	1.29	48	59	>99
5	Ru/C (Dry)	41.3	2.47	48	73	>99

Notes and Observations

1. Dumesic[2] used acetic aqueous dispersions of biomasses derived from either cellulose or lignocellulose to prepare and selectively extract in high purity levulinic acid and γ-valerolactone. Although minor amounts of alkylphenols were also isolated using this

method, neither levulinic acid nor γ-valerolactone required purification before use.

2. Olson[3] developed a biorefinery to prepare automotive fuel using cellulose biomass. In the process, ethyl levulinate, (I), was isolated and then self-condensed under basic conditions to form higher molecular weight-branched alkanes, (II). Upon hydrogenation, the biofuel, (III), was formed. (See Fig. 14.31.)

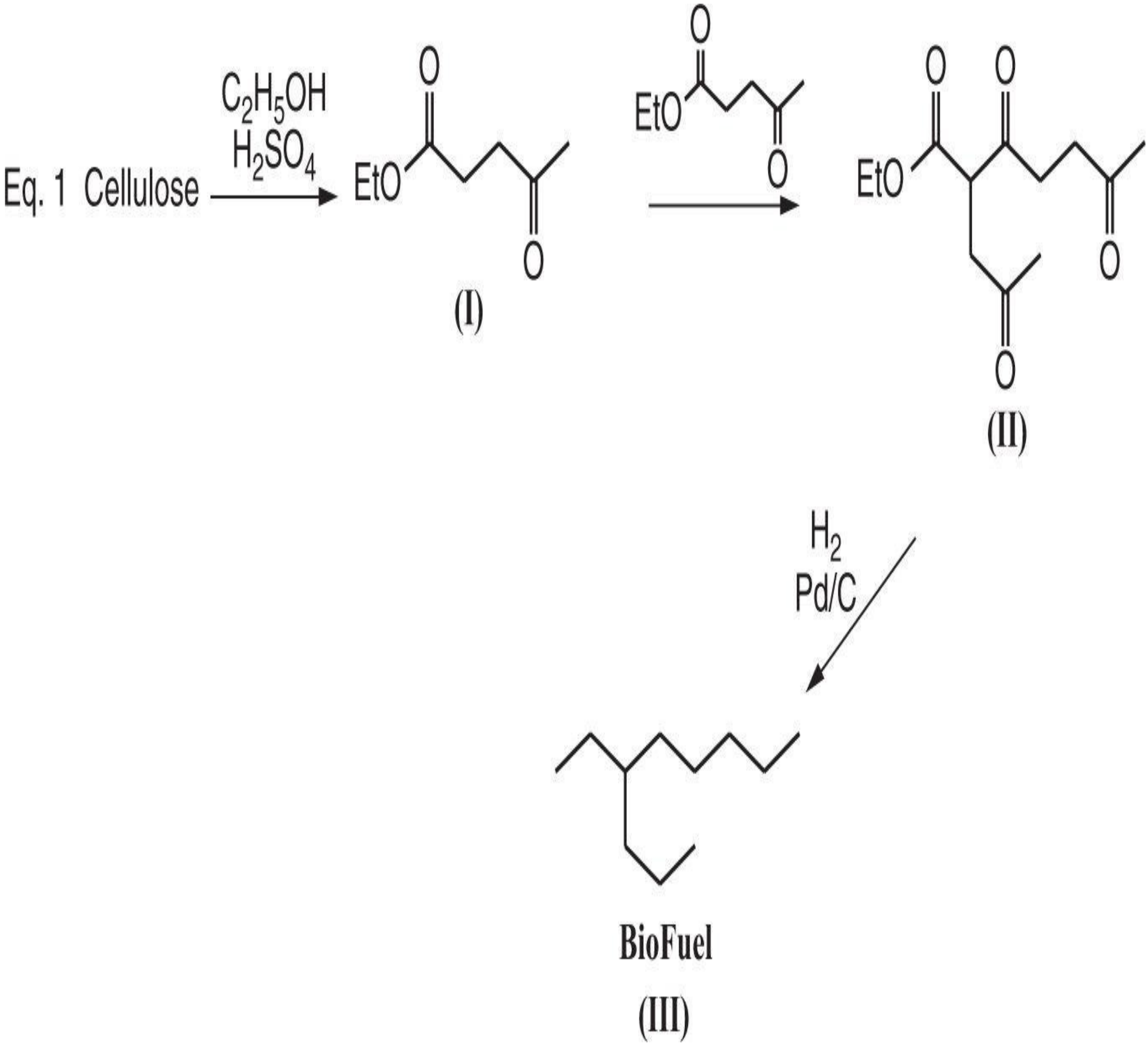
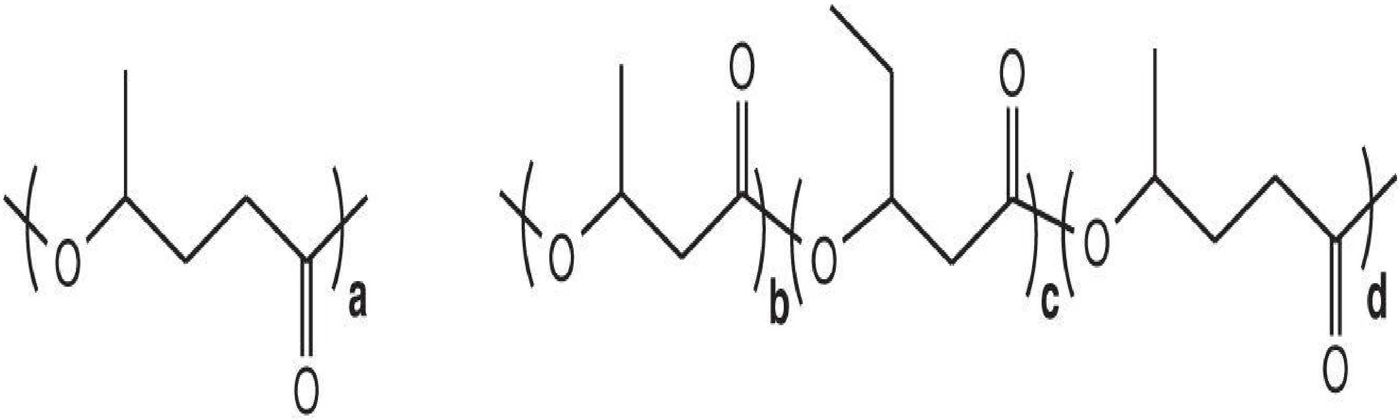


Figure 14.31

3. Although the objective of the investigation by Skraly[4] was to identify and either delete or inactivate genes encoding undesirable activities, E. coli MBX 1177 carrying the plasmid pFS 30 cells that were precultured with sodium ampicillin, sodium 5-hydroxyvalerate, glucose, LB broth powder containing potassium phosphate at pH 7 and δ-valerolactone were also used to prepare poly(5-hydroxyvalerate), (IV), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate-4-hydroxyvalerate), (V). (See Fig. 14.32.)



(IV) (V)

Figure 14.32

4. Van De Graaf [5] used an autoclave reactor to convert a mixture of ethyl and furfuryl alcohols into levulinic acid or ethyl levulinate using acetic resins Amberlyst 46, Amberlyst 36 W, or Dowex 50 WX4.

References

1. Yoshikazu Hachimama et al., *Studies on the preparation of plasticizers from carbohydrate sources, I. levulinic acid esters, II. sorbide esters*," Technology Reports of the Osaka University, vol. 3, No. 72, pp. 191–200 (1953)

2. James A. Dumesic et al., *Solvent-enhanced production of gamma-valerolactone from aqueous solutions of levulinic acid*, U.S. Patent Application 20120302766 (November 29, 2012)

3. Edwin S. Olson et al., *Multiproduct biorefinery for synthesis of fuel components and chemicals from lignocellulosics via levulinate reactions*, U.S. Patent Application 20120283493 (November 8, 2012)

4. Frank A. Skraly et al., *Polyhydroxyalkanoate biopolymer compositions*, U.S. Patent 8,093,022 (January 10, 2012)

5. Wouter David Van De Graaf et al., *Process for the conversion of furfuryl alcohol into levulinic acid or alkyl levulinate*, U.S. Patent 7,265,239 (September 4, 2007)

Chapter

15

Lubricants

Algal-Oil-Derived Synthetic Lubricants

Author Jeffrey A. Brown et al.

Patent Title ***Synthetic compositions obtained from algae***, U.S. Patent 8,273,694 (September 25, 2012)

Relevant Prior Patents by Author or Coauthors

Diester-based lubricants and methods of making same, U.S. Patent 8,324,423 (December 4, 2012)

Biolubricant esters from the alcohols of unsaturated fatty acids, U.S. Patent 8,304,574 (November 6, 2012)

Oligomerization of olefin feed comprising propylene and propane to produce base oil, U.S. Patent 8,207,389 (June 26, 2012)

Biolubricant esters from the alcohols of unsaturated fatty acids, U.S. Patent 8,188,019 (May 29, 2012)

Isolation and subsequent utilization of saturated fatty acids and α-olefins in the production of ester-based biolubricants, U.S. Patent 8,097,740 (January 17, 2012)

Production of biofuels and biolubricants from a common feedstock, U.S. Patent 7,815,694 (October 19, 2010)

Triester-based lubricants and methods of making same, U.S. Patent 7,544,645 (January 9, 2009)

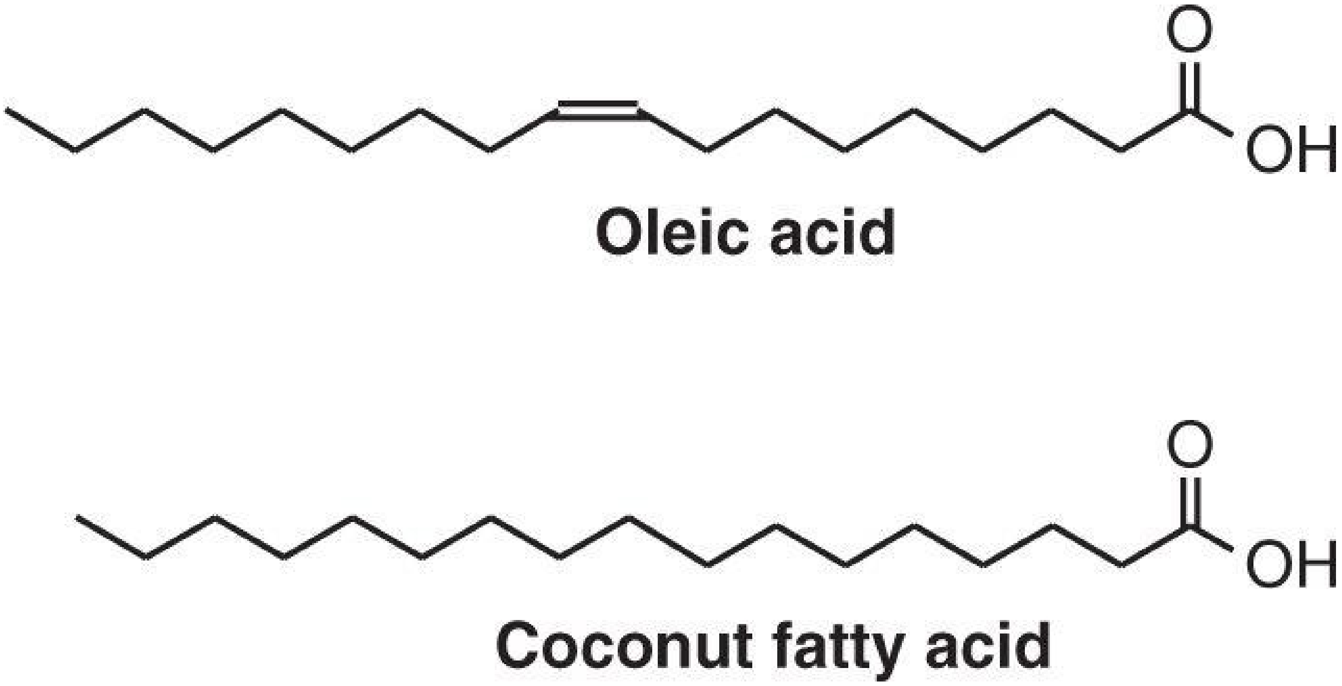
Product Application

Synthetic oils derived from algae are designed to be used as drilling fluids, penetrating oils, fuel additives, and as base-stock blends for use in crankcase oil formulations in two- and four-stroke engines.

Significance of Current Application

Petroleum-derived base stock oils require excessive performance-enhancing additives such as antioxidants and friction modifiers to have optimum effectiveness. These same oils, however, pose serious environmental concerns. One persistent environmental concern is that used crankcase oil is not biodegradable. A second serious concern is that these oils are petroleum derived. The current investigation has identified a method for inexpensively preparing renewable base stock lubricating oils that are biodegradable and derived from renewable oil-enriched algae. Chemically modified algal oils provide lubricating oils in high-yielding and non-polluting processes that are as effective as high-performance lubricants. These oils meet or exceed manufacture requirements while remaining bio-renewable and biodegradable. In addition, lubricating oils prepared using oil-enriched algae are more cost effective and appear to have greater versatility than petroleum-derived oils.

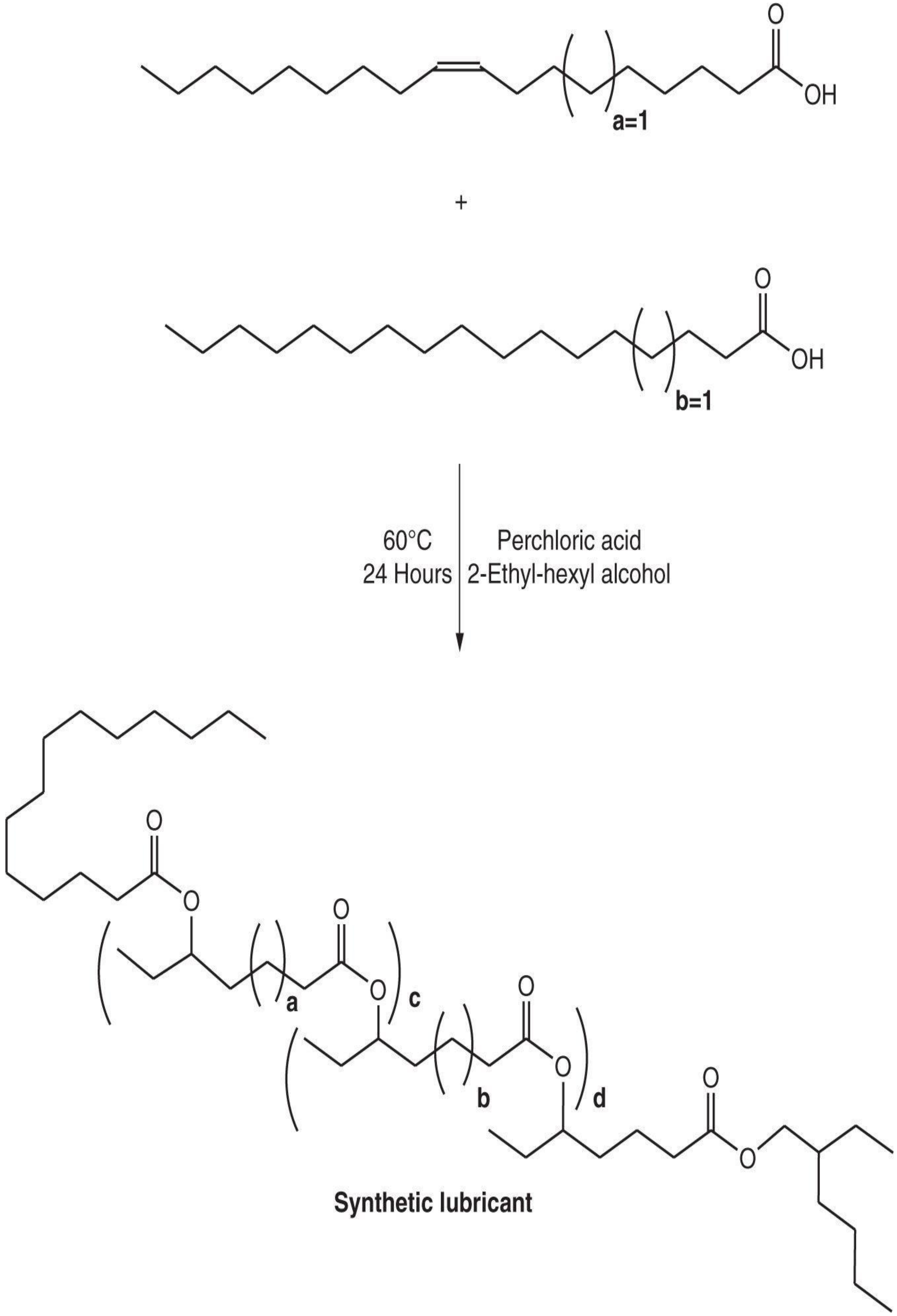
Renewable Agents


Oleic acid

Coconut fatty acid

Figure 15.1

Product Formation



Synthetic lubricant

Figure 15.2

Experimental

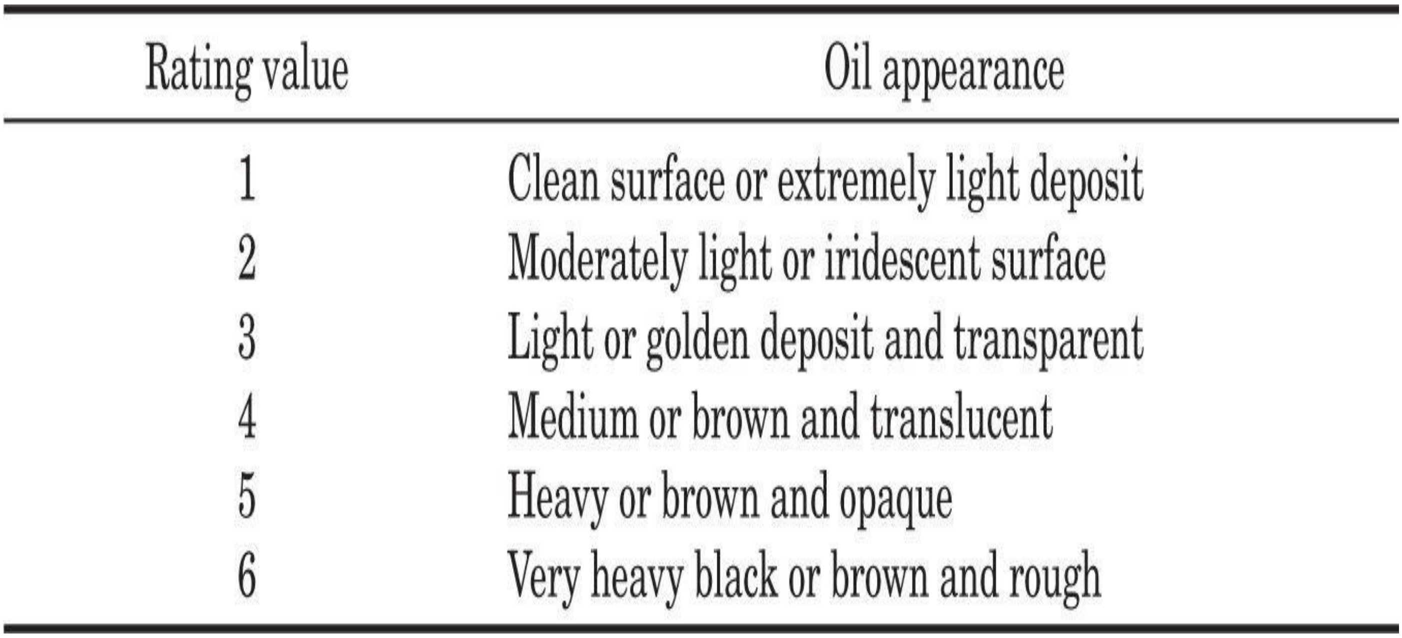
1. Preparation of a synthetic lubricant. A 1-L three-neck round-bottom flask containing an overhead stirrer was charged with 170 g of high oleic-acid-content algal oil and 200 g of coconut fatty acids and then heated to 60°C and pressurized to 10 tons. After the reaction had proceeded for several hours, a 70% aqueous solution of perchloric acid was incrementally added to the reaction mixture for about 5 minutes. After 24 hours, the pressure was lowered to 760 mm Hg and the mixture was treated with 1.2 equivalents of 2-ethyl-1-hexanol. A vacuum was then applied to the reaction vessel while heating was continued for an additional hour. Once the mixture cooled it was quenched by treating with 4.77 g of potassium hydroxide dissolved in 50 mL of water, and the two layers that formed slowly separated. The crude product was decanted from the aqueous phase and reaction by-products were removed from the oil by distillation at 180°C to 190°C at a pressure of 0.2 to 0.5 torr. After cooling, the product was isolated as a viscous, yellowish oil.

Testing

A. Anti-oxidancy testing. Anti-oxidants were not used in this test. The Step 1 product was tested for resistance to high temperature oxidation and deposit formation. In this test, a custom apparatus called the “Rotating Thin-Film and Bulk Thermo-Oxidation Test” was used, and eight test samples were simultaneously evaluated. Samples were placed in individual glass vials and then put into a heating block at 160°C. The test was run at an atmospheric pressure of 2 rpm and samples were evaluated for viscosity properties every 24 hours. The test was run until all samples had a 200% increase in viscosity and were then visually rated. The rating system used to evaluate the oil anti-oxidancy is provided in Table 15.1, and the anti-oxidancy test results are provided in Table 15.2.

Testing

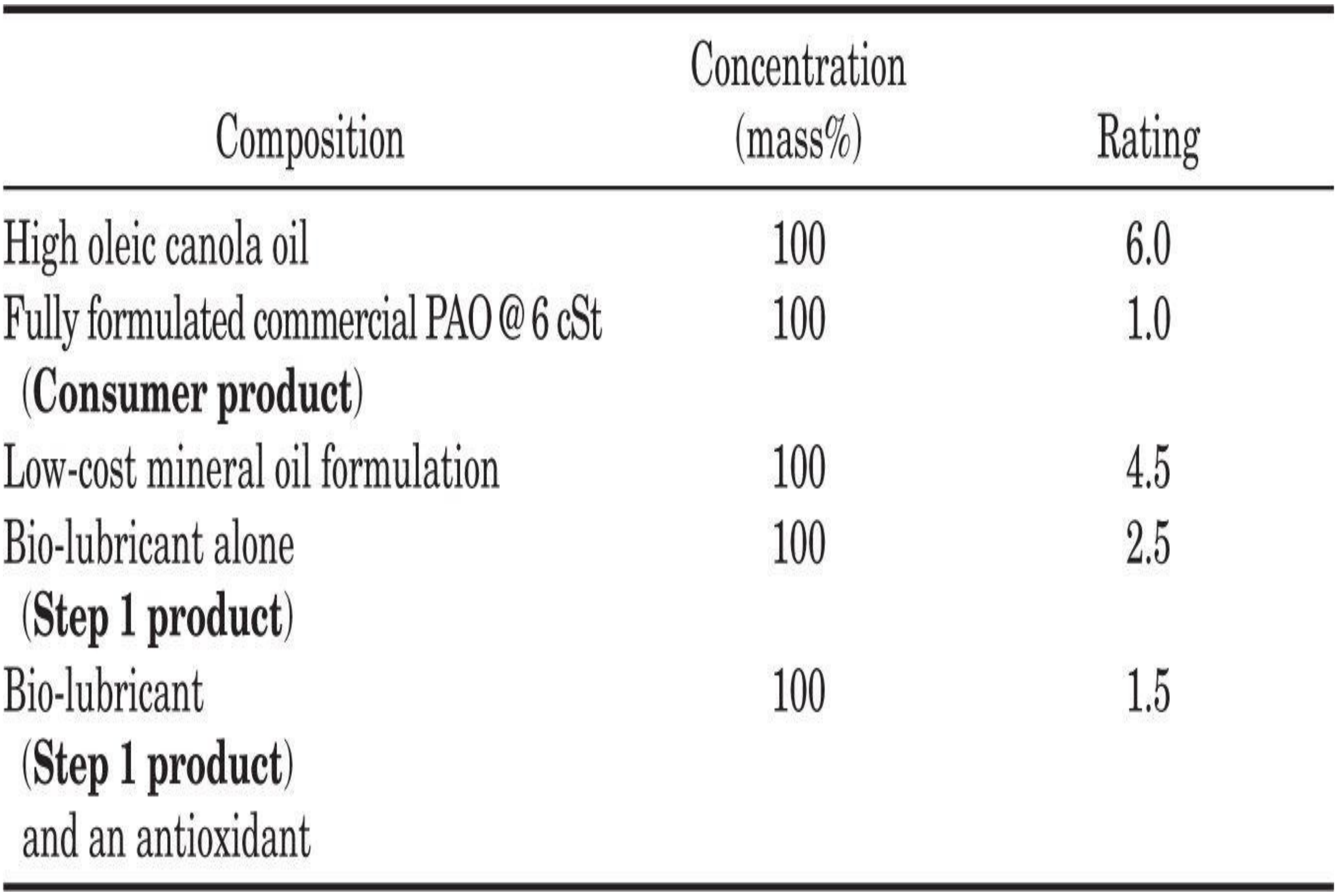
TABLE 15.1 Test evaluation used to rate the oil oxidation and degradation properties of the biolubricant.



Rating value	Oil appearance
1	Clean surface or extremely light deposit
2	Moderately light or iridescent surface
3	Light or golden deposit and transparent
4	Medium or brown and translucent
5	Heavy or brown and opaque
6	Very heavy black or brown and rough

Testing Results

TABLE 15.2 Deposit-formation test results for the neat bio-lubricant with one containing an antioxidant. The fully formulated consumer sample was renewable but not biodegradable.



Composition	Concentration (mass%)	Rating
High oleic canola oil	100	6.0
Fully formulated commercial PAO @ 6 cSt (**Consumer product**)	100	1.0
Low-cost mineral oil formulation	100	4.5
Bio-lubricant alone (**Step 1 product**)	100	2.5
Bio-lubricant (**Step 1 product**) and an antioxidant	100	1.5

Notes and Observations

1. Miller[1] prepared diester-based lubricant compositions using the Fischer-Tropsch reaction with the α-olefin biomass precursor, 1-tetradecene, (I), as illustrated in Eq. 1. (See Fig. 15.3.)

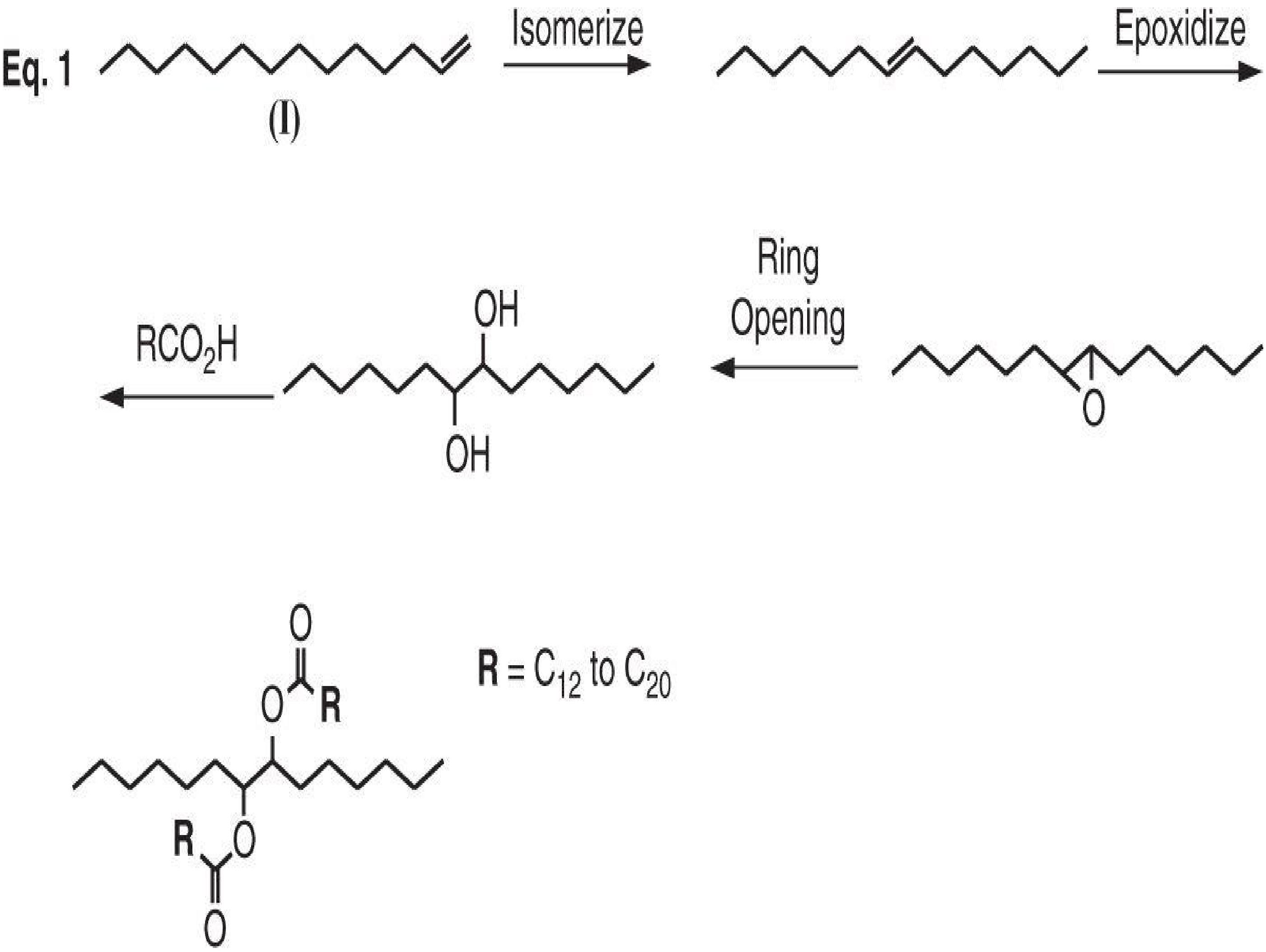


Figure 15.3

2. Elomari[2] used biomass-derived mono-unsaturated fatty acids that were subsequently reduced to form triesters, (II). Bio-lubricants containing triesters were effective as lubricants when used in lubricant formulations as well as being more cost effective then poly α-olefin compositions. (See Fig. 15.4.)

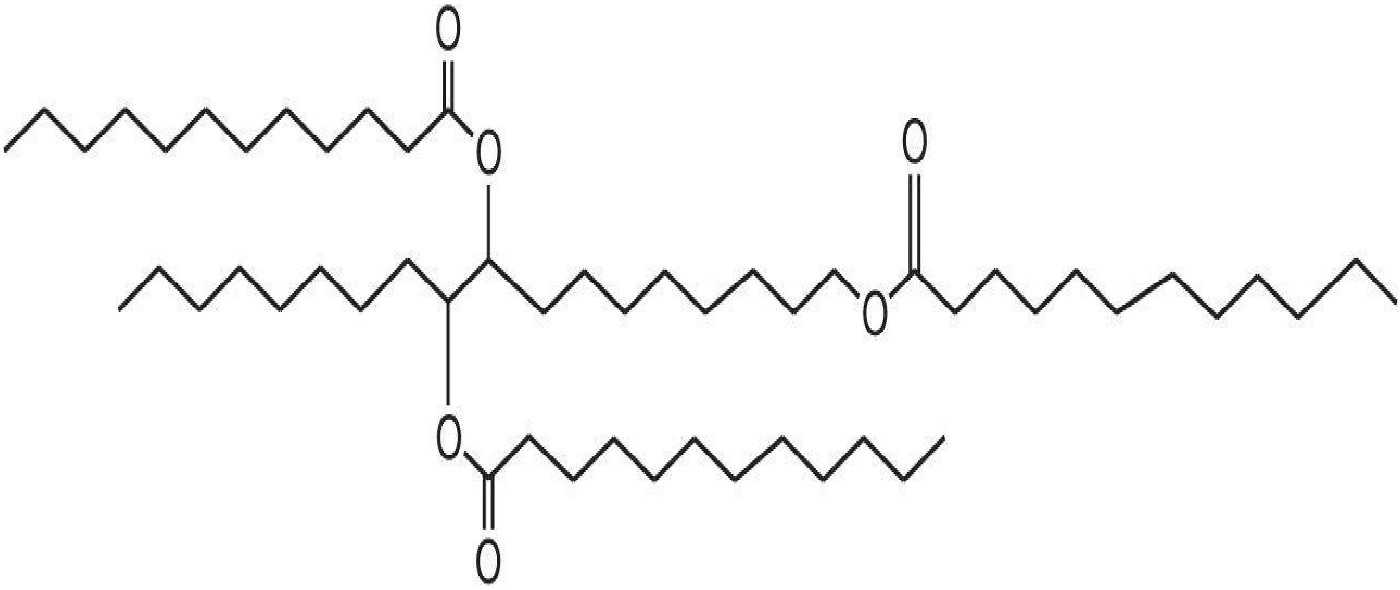


Figure 15.4

3. Miller[3] used biomass-derived unsaturated triglycerides from vegetable oils to prepare

diester bio-lubricants, (III). The process for isolating the biolubricant required hydrolysis and hydrogenation of the biomass triglycerides to prepare a biolubricant containing two saturated fatty acid esters. (See Fig. 15.5.)

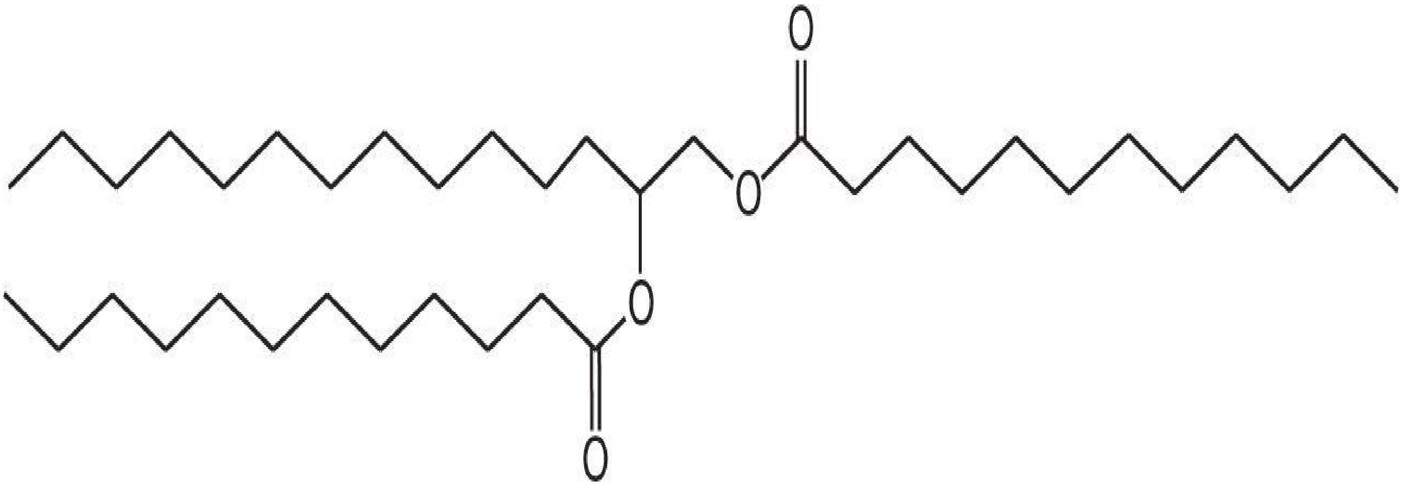


Figure 15.5

4. Beginning with renewable oleic acid, Miller[4] devised a method for preparing triester biolubricants as illustrated in Eq. 2. (See Fig. 15.6.)

Eq. 2

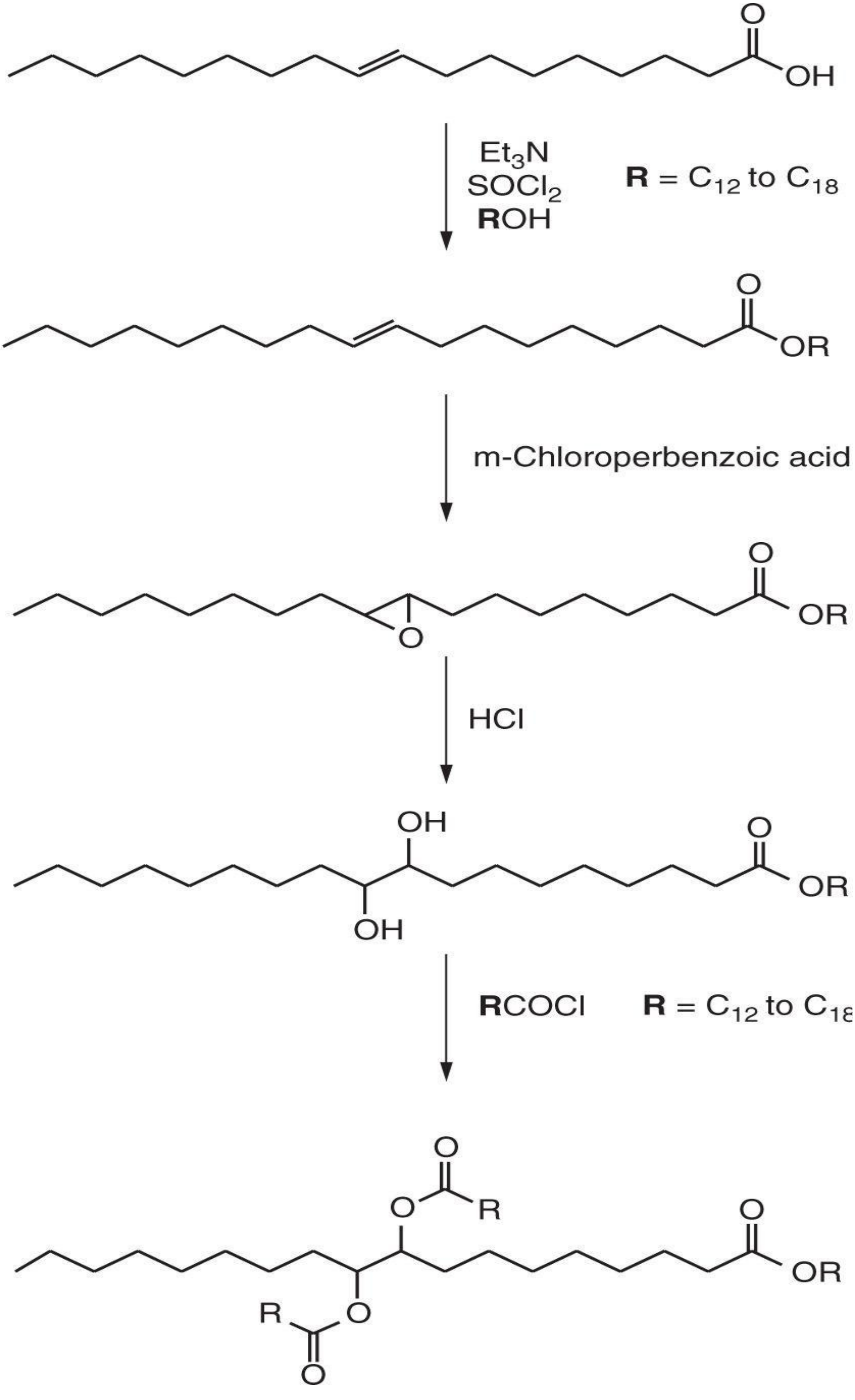

O
OH
Et3N
SOCl2
ROH
R = C12 to C18
O
OR
m-Chloroperbenzoic acid
O
O
OR
HCl
OH
O
OR
OH
RCOCl
R = C12 to C1
O
O
R
O
OR
R
O
O

Figure 15.6

References

1. Stephen J. Miller et al., *Diester-based lubricants and methods of making same*, U.S. Patent 8,324,423 (December 4, 2012)

2. Saleh A. Elomari et al., *Biolubricant esters from the alcohols of unsaturated fatty acids*, U.S. Patent 8,304,574 (November 6, 2012)

3. Stephen J. Miller, *Isolation and subsequent utilization of saturated fatty acids and α-olefins in the production of ester-based biolubricants*, U.S. Patent 8,097,740 (January 17, 2012)

4. Stephen J. Miller et al., *Triester-based lubricants and methods of making same*, U.S. Patent 7,544,645 (January 9, 2009)

Estolide Pour Point Depressants

Author	Jakob Bredsguard et al.
Patent Title	***Lubricant compositions comprising estolide base oils,*** U.S. Patent 8,287,754 (October 16, 2012)

Relevant Prior Patents by Author or Coauthors

High- and low-viscosity estolide base oils and lubricants, U.S. Patent Application 20120178660 (July 12, 2012)

Catalytic processes for preparing estolide base oils, U.S. Patent Application 20120172609 (July 5, 2012)

Estolide compositions having excellent low temperature properties, U.S. Patent Application 20120172269 (July 5, 2012)

Acetic acid-capped estolide base oils and methods of making the same, U.S. Patent Application 20120083435 (April 5, 2012)

Estolide compositions exhibiting high oxidative stability, U.S. Patent 8,372,301 (February 13, 2013)

Epoxidized estolides and methods of making and using the same, U.S. Patent 8,258,326 (September 4, 2012)

Product Application

Estolide oil compositions are useful as pour point depressants in both base oils and fuels.

Significance of Current Application

Pour point depressants are designed to inhibit lateral crystal growth of wax present in all base oils and fuels. Traditionally this concern has been addressed using two non-renewable co-polymers. Although petroleum-derived polyalkylacrylates and styrene-maleic acid block co-polymers have consistently been shown to be particularly effective, other oil viscosity modifiers based on petroleum-derived ethylene-propylene copolymers are also used. In this investigation, however, it was determined that base oils and fuels additized with renewable estolides are extremely effective in inhibiting lateral crystal growth. Estolides that were used as lubricant pour point depressants in this investigation are readily prepared from animal, vegetation or from combinations. It was also determined that base fuels additized with renewable estolides required significantly lower treatment levels than when additizing the identical base stock with either polyalkylacrylates, styrene-maleic acid block co-polymers, or ethylene-propylene copolymers.

Product Formation

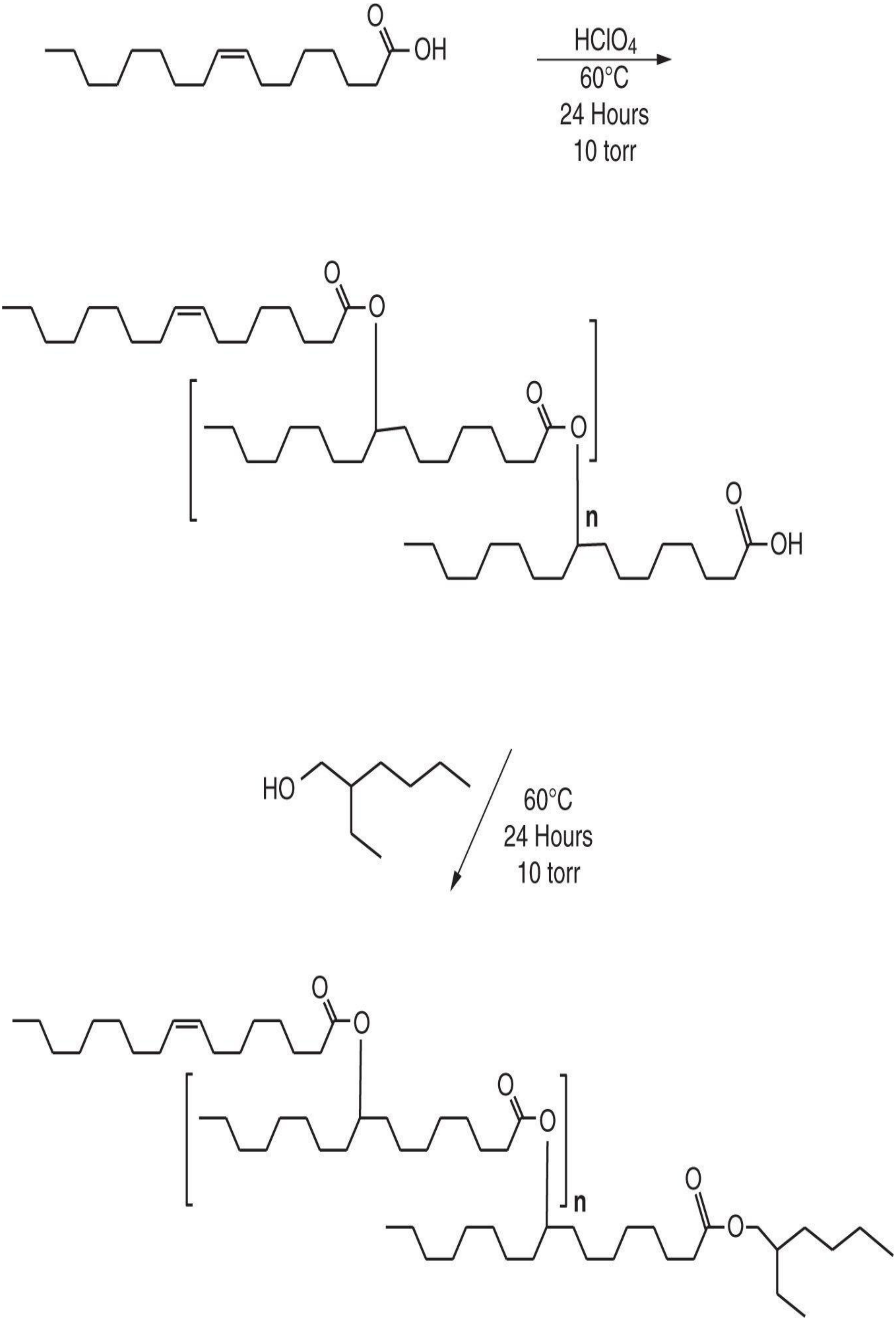
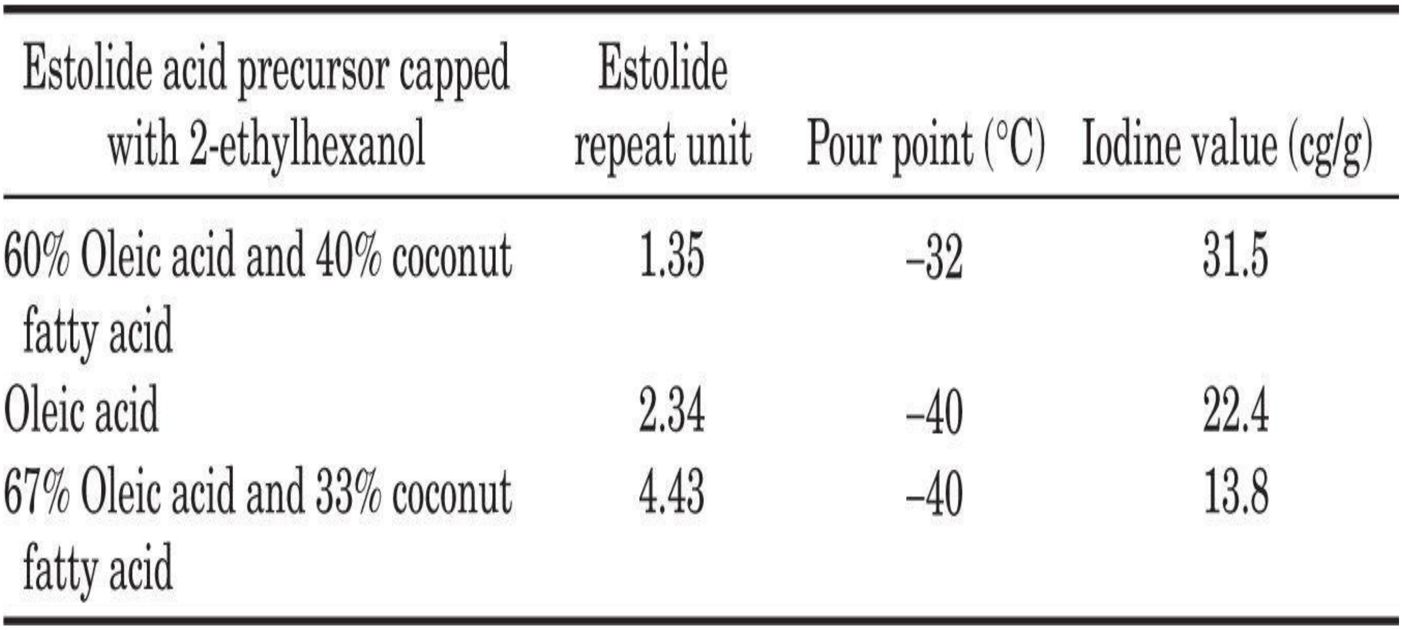

O
OH
HClO$_4$
60°C
24 Hours
10 torr
O
O
O
O
n
O
OH
HO
60°C
24 Hours
10 torr
O
O
O
O
n
O
O

Figure 15.7

Experimental

1. Preparation of estolide capped with 2-ethylhexanol. A 50-gallon glass-lined reactor was charged with 65 kg of oleic acid and 992.3 mL of 70% perchloric acid then heated to 60°C at 10 torr for 24 hours. The mixture was then treated with 29.97 kg of 2-ethylhexanol and further heated to 60°C at 10 torr for an additional 4 hours. The reaction mixture was then treated with 645.58 g of potassium hydroxide dissolved in 5,000 mL of 90% ethanol and 10% water to neutralized the acid. After cooling the solution to ambient temperature it was pumped through a 1 micron filter to remove salts. The reaction product was then washed with water. The two phase mixture was then separated and the organic phase re-filtered. Water, ethanol, and unreacted 2-ethylhexanol were removed from the reaction product by heating the mixture to 100°C at 2 torr until no further distillate emerged from the kettle. The final purification process for the reaction product entailed distilling the reaction mixture through a Myers 15 Centrifugal Distillation still at 200°C at 0.012 torr and the product isolated as a yellowish viscous oil. The purified reaction product was subsequently evaluated for pour point depression and iodine number. Testing results are provided in Table 15.3.

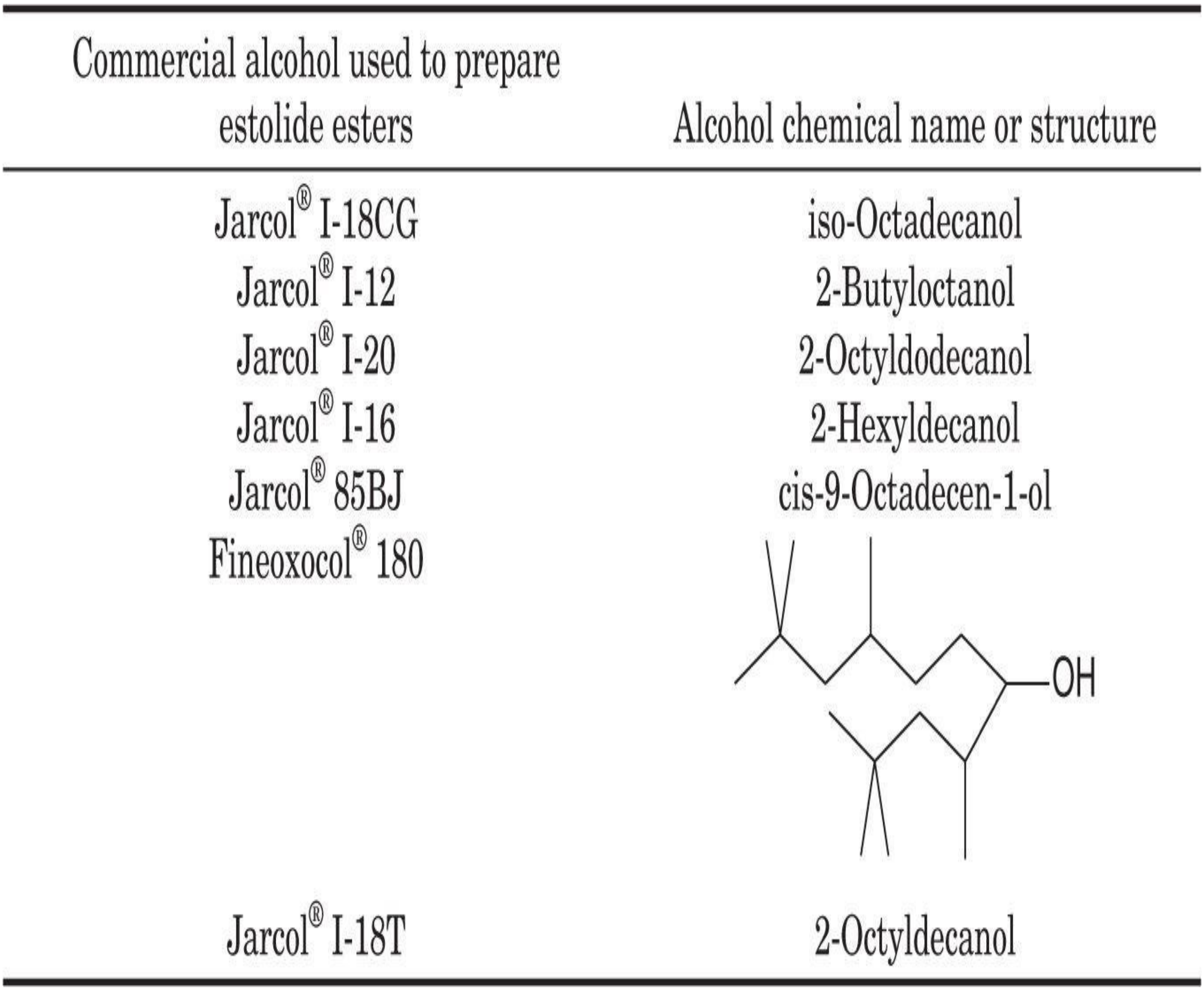
TABLE 15.3 Pour points of lubricating oils additized with estolide/fatty acid esters. In all cases, 2-ethylhexanol was used as the estolide capping agent.



Estolide acid precursor capped with 2-ethylhexanol	Estolide repeat unit	Pour point (°C)	Iodine value (cg/g)
60% Oleic acid and 40% coconut fatty acid	1.35	–32	31.5
Oleic acid	2.34	–40	22.4
67% Oleic acid and 33% coconut fatty acid	4.43	–40	13.8

2. Preparation of esterolide ester analogues. Additional esterolide esters were prepared using the Step 1 procedure. Replacement alcohols used as ester capping agents provided in Table 15.4.

TABLE 15.4 Replacement alcohols for 2-ethylhexanol used to cap estolides. In all cases estolide esters were effective when used as oil pour point depressants in base oil formulations.



Commercial alcohol used to prepare estolide esters	Alcohol chemical name or structure
Jarcol® I-18CG	iso-Octadecanol
Jarcol® I-12	2-Butyloctanol
Jarcol® I-20	2-Octyldodecanol
Jarcol® I-16	2-Hexyldecanol
Jarcol® 85BJ	cis-9-Octadecen-1-ol
Fineoxocol® 180	OH
Jarcol® I-18T	2-Octyldecanol

3. Lubricating oil formulation. Although neither the base oil formulation for the 4-stroke engine nor engine wear test results were provided by the author, polyisobutylene was used as a co-component in formulations. The most preferred polyisobutylene physical property was one having an Mn ~950 daltons and where it constituted from 5 wt% to 15 wt% of the lubrication package.

Testing Results

Notes and Observations

1. Salimon[1] used renewable ricinoleic acid, (I), to prepare estolides which were then converted into the estolide ethyl ester, (II), using ethyl alcohol with sulfuric acid as the reaction catalyst as illustrated in Eq. 1. When the estolide methyl ester was blended into basestocks, the additized basestock had low-temperature flow properties as low as approximately −52°C ± 0.08°C. In addition, basestocks additized with ricinoleic acid–based estolide ethyl ester had flash points >300°C. (See Fig. 15.8.)

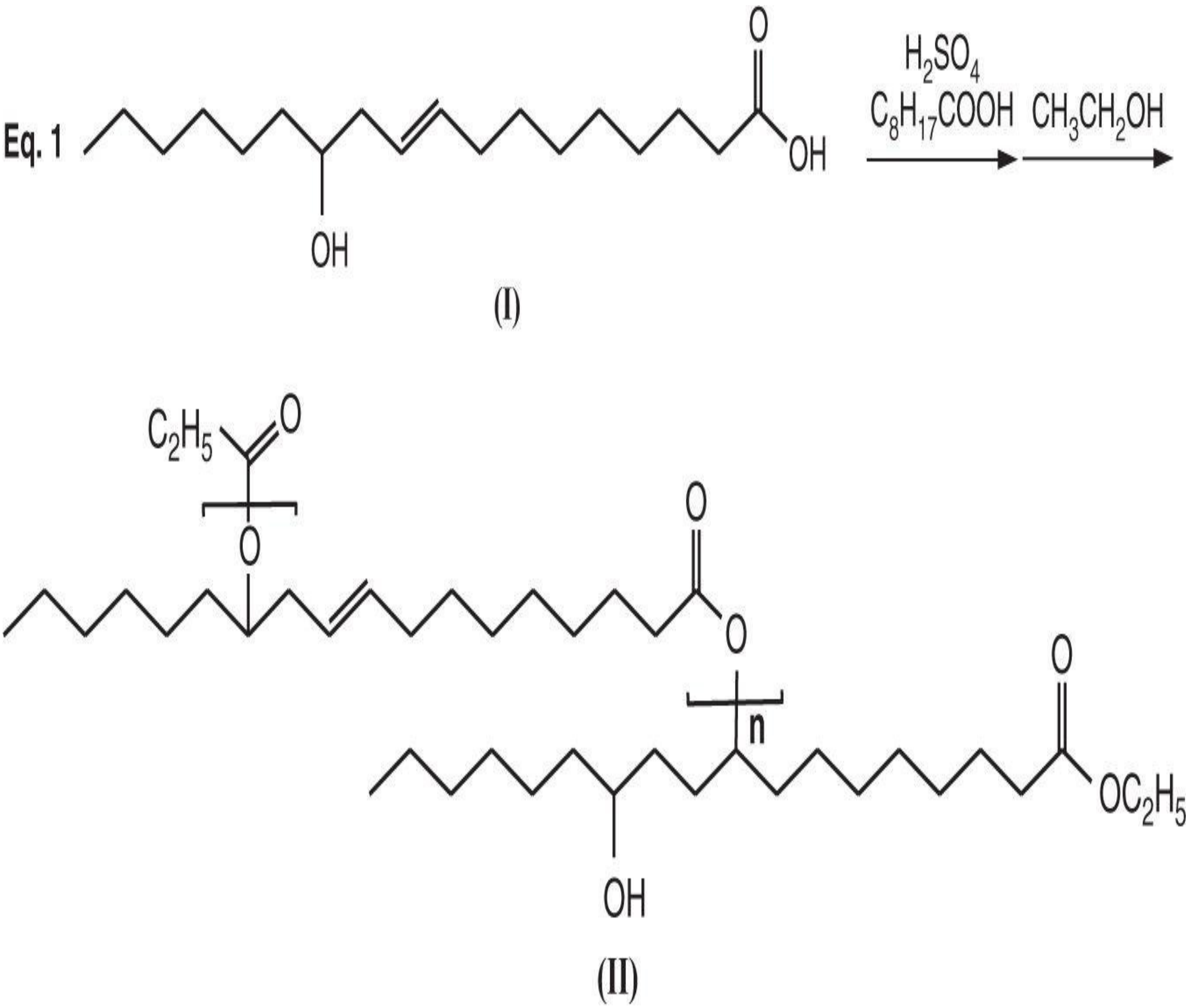
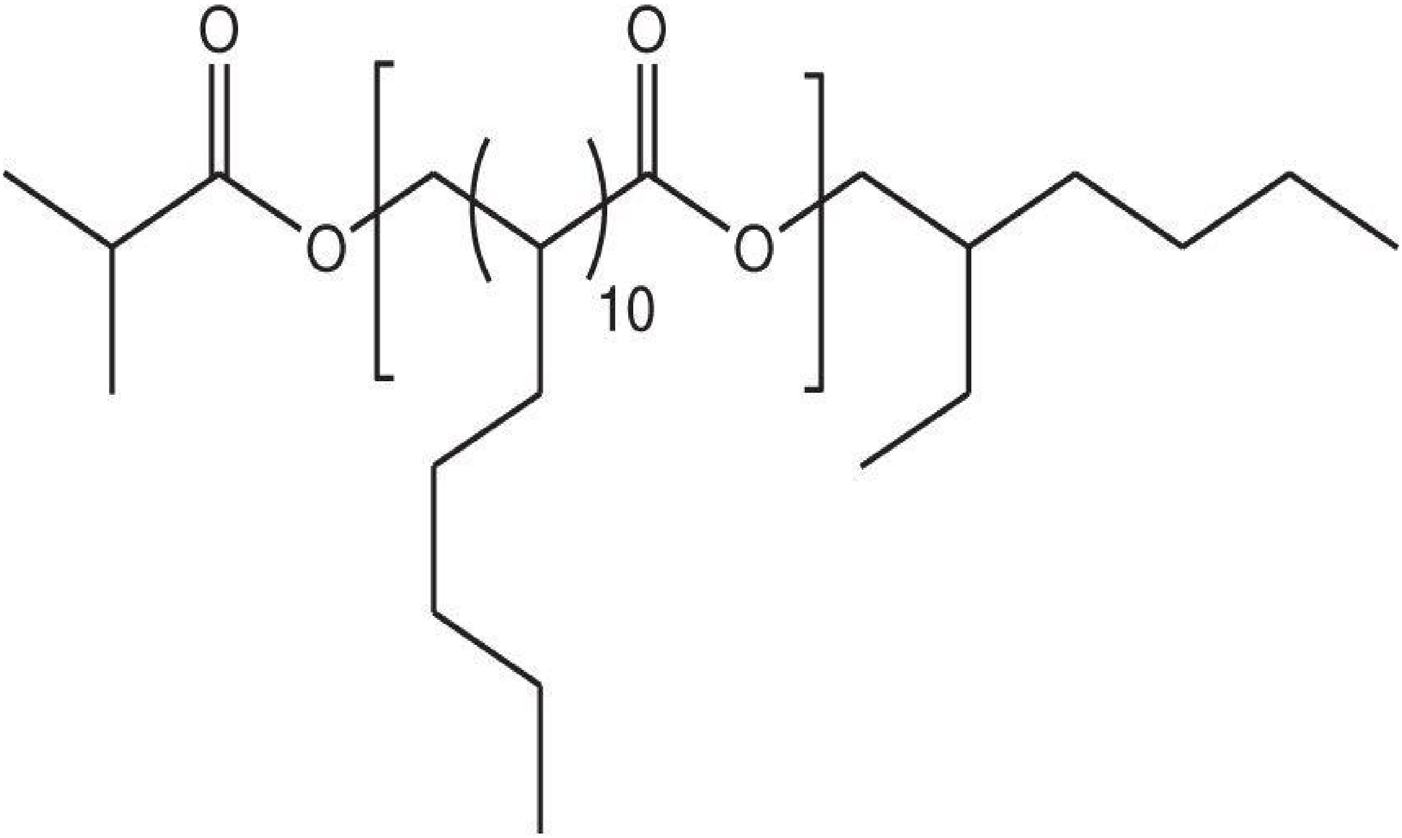


Figure 15.8

2. Greaves[2] prepared the renewable estolide ester, (III), which was designed to be used in crankcase oil formulations. Lubricating oils additized with this renewable estolide ester had a pour point of at least –33°C. A comparison of pour point depressant properties of estolide esters when blended in fully formulated lubricating oil packages is provided in Table 15.5. (See also Fig. 15.9.)

TABLE 15.5 The effectiveness of the estolide ester, (III), as a pour point depressant when used in fully formulated crankcase oil lubricating oil packages. Pour point depressions were determined according to ASTM D-97.

Component	Treat level (g)	Treat level (g)	Treat level (g)
Capped estolide, (III)	79	79	79
SYNATIVE DEHA (ester) **(Consumer product)**	10	10	0
SYNFLUID PAO-4 **(Consumer product)**	10	0	10
DURASYN 164 **(Consumer product)**	0	10	0
SYNALOX 100-30B **(Consumer product)**	0	0	10
LUBRIZOL 7671A **(Consumer product)**	1	1	1
Pour point (°C)	–40	–37	–31

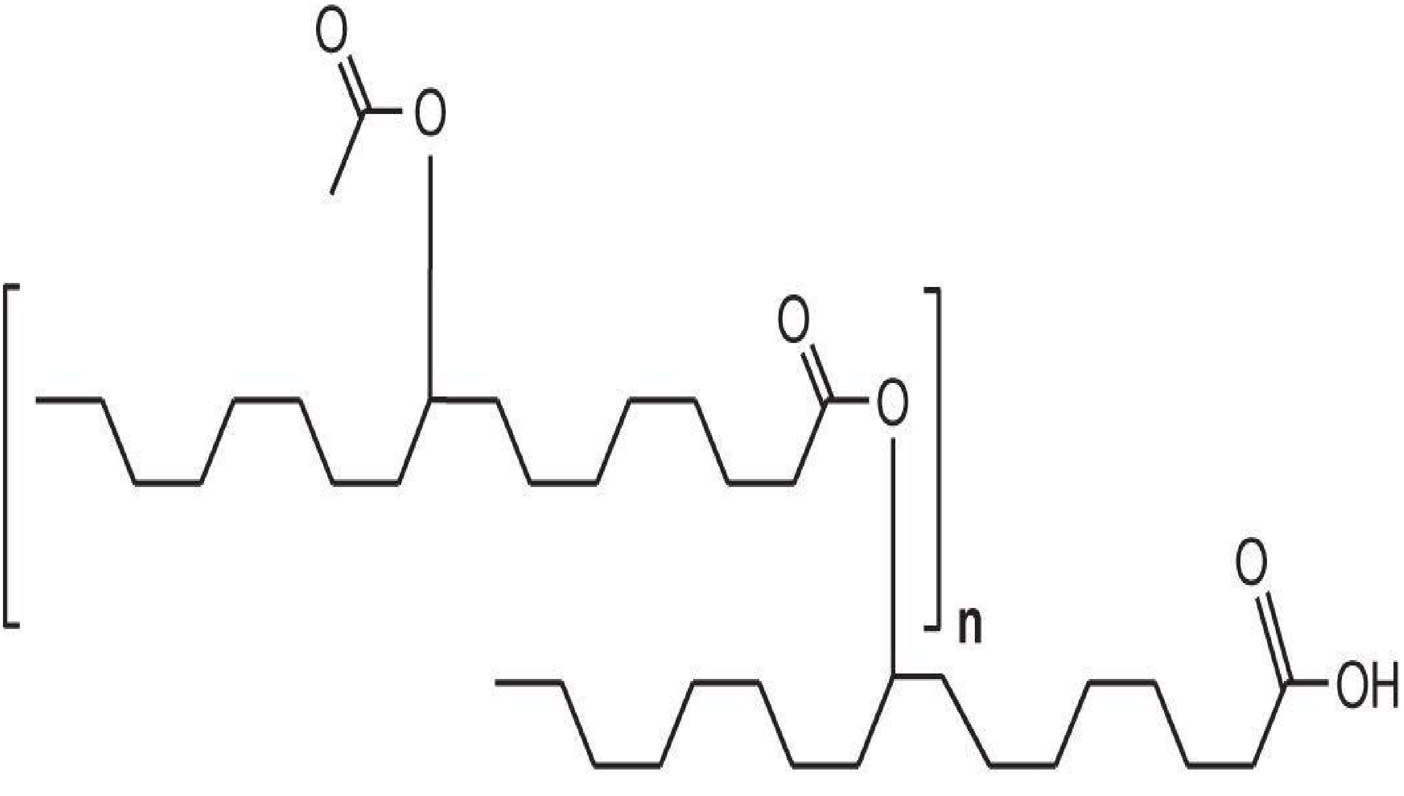


(III)

Figure 15.9

3. Bredsguard[3] additized base oils with oleic acid-based estolide esters using acetic acid, (IV). Acetate-capped estolides had low degradation rates and no aquatic toxicity in the range of 5,000 to 50,000 mgL. (See Fig. 15.10.)

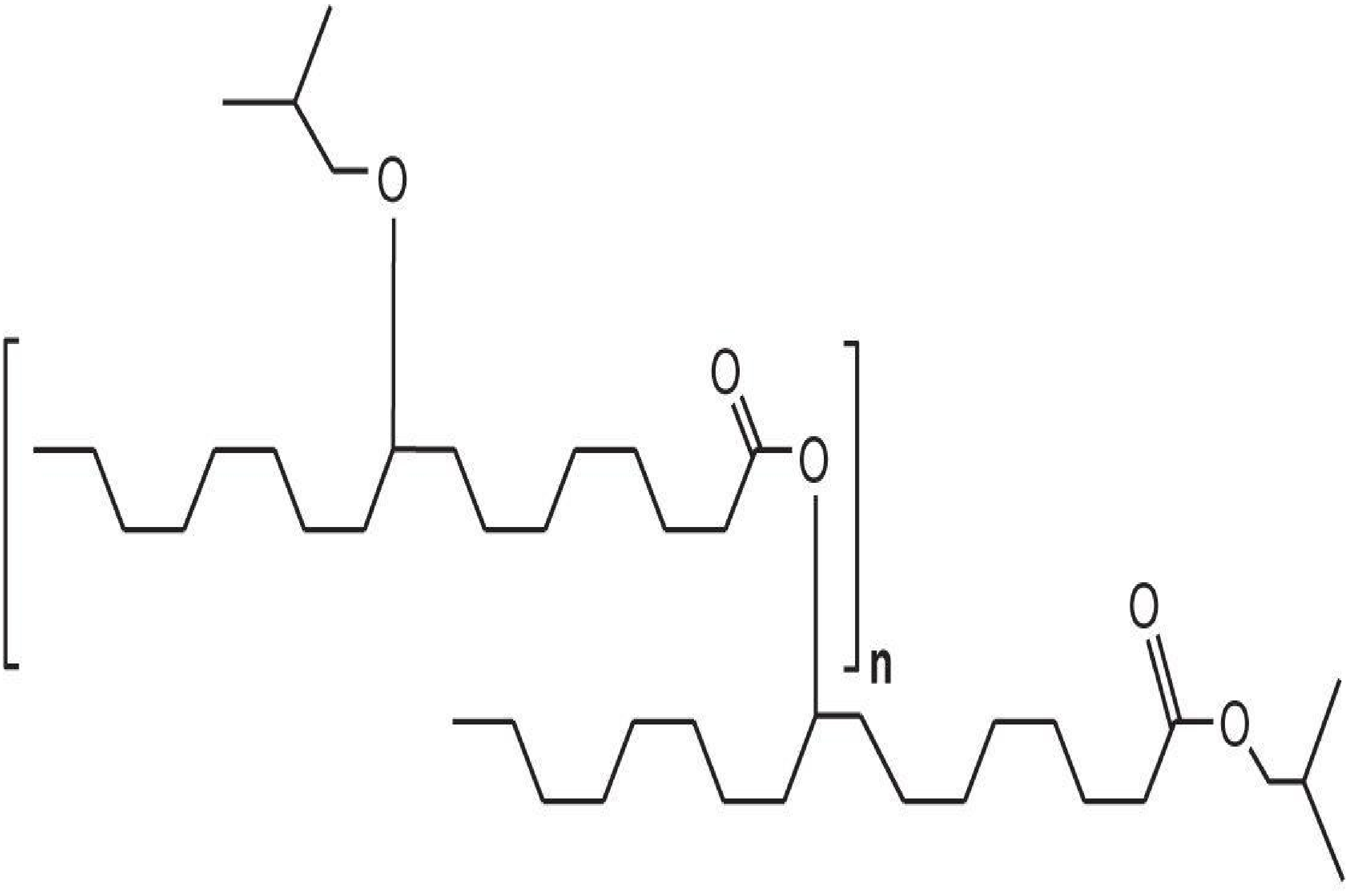
(See Fig. 15.10.)



(IV)

Figure 15.10

4. Bredsguard[4] determined that the optimum thermal stability for an oleic acid-derived estolide could be obtained by capping with isobutanol, (V). (See Fig. 15.11.)



(V)

Figure 15.11

References

1. Jumat Salimon et al., *Synthesis and physical properties of estolide esters using saturated fatty acids and ricinoleic acid*, School of Chemical Sciences and Food Technology, Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 Bangi, Malaysia (2009)

2. Martin R. Greaves et al., *Estolide compositions having excellent low temperature properties*, U.S. Patent Application 20120172269 (July 5, 2012)

3. Jakob Bredsguard et al., *Acetic acid-capped estolide base oils and methods of making the same*, U.S. Patent Application 20120083435 (April 5, 2012)

4. Jakob Bredsguard et al., *Estolide compositions exhibiting high oxidative stability*, U.S. Patent 8,372,301 (February 13, 2013)

Chapter

16

Nanoparticles

Degradable β-Amino Ester Nanoparticles

Author Robert S. Langer et al.

Patent Title ***Biodegradable poly (β-amino esters) and uses thereof***, U.S. Patent 8,287,849 (October 16, 2012)

Relevant Prior Patents by Author or Coauthors

Biodegradable shape memory polymeric sutures, U.S. Patent 8,303,625 (November 6, 2012)

*Biodegradable poly(*β*-amino esters) and uses thereof*, U.S. Patent RE43,612 (August 28, 2012)

Biodegradable elastomers, U.S. Patent 8,143,042 (March 27, 2012)

*End-modified poly(*β*-amino esters) and uses thereof*, U.S. Patent 8,071,082 (December 6, 2011)

N-Substituted monomers and polymers, U.S. Patent 8,034,365 (October 11, 2011)

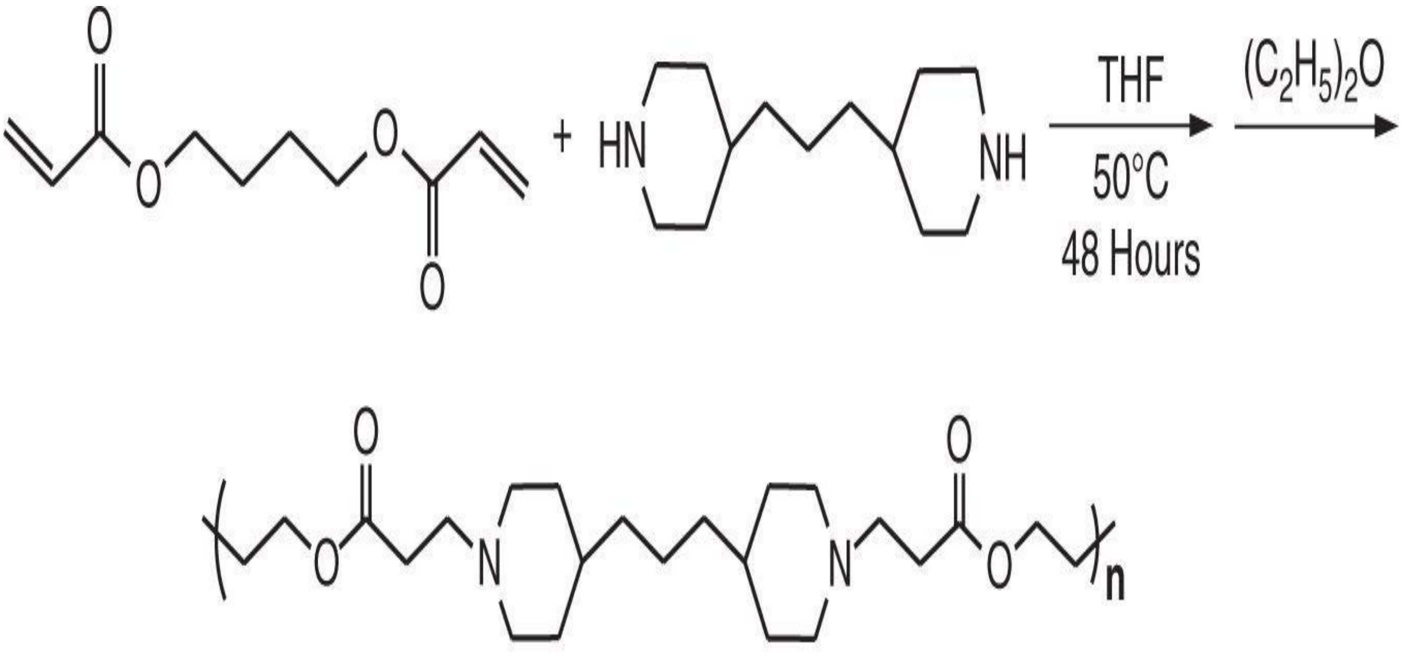
Product Application

Biodegradable and resorbable poly(β-amino esters) nanoparticles have been successfully used as polynucleotide delivery agents for RNA and DNA in the treatment of selected malignancy disorders in humans.

Significance of Current Application

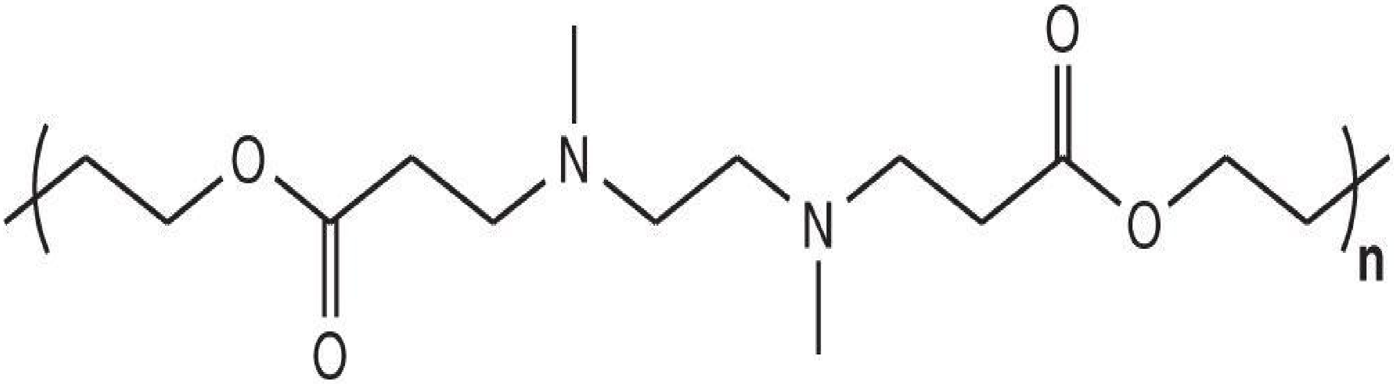
This investigation describes a novel and commercially viable method for delivering nucleotide-based drugs containing DNA or RNA in the treatment of selected malignancy disorders in humans. The method entailed preparing a piperazine-containing poly(β-amino ester) in a single-step synthesis by condensing piperazine with selected bis(acrylate esters). The method is very general and was used to prepare a wide variety of poly(β-amino esters) having varying molecular weights and relatively high yields. Once poly(β-amino esters) were prepared, they were used to encapsulate nucleotide-based drugs containing either DNA or RNA. They were then converted into nanoparticles. Preliminary studies of these nanoparticles nucleotide delivery agents indicate that they had very favorable hydrolysis decomposition kinetics in aqueous solutions as well as being cytotoxic to the NIH 3T3 cell line.

Product Formation

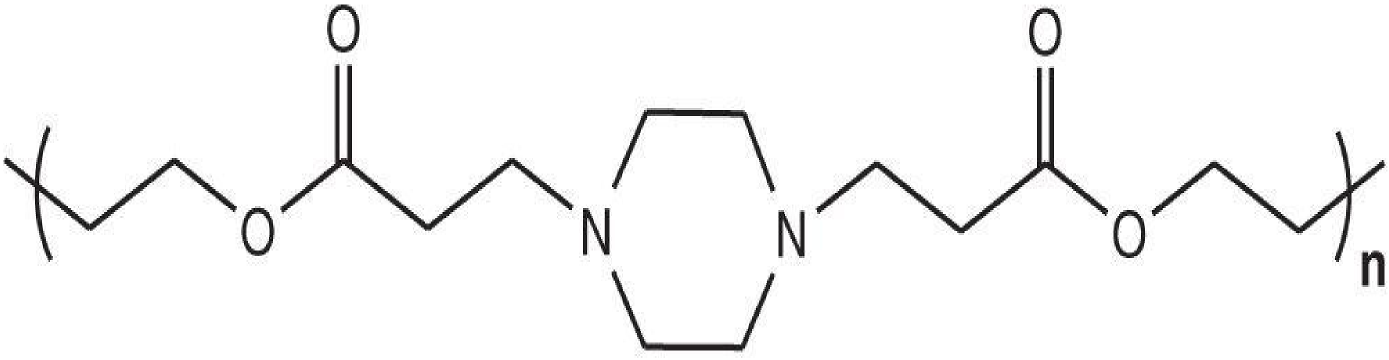


(I)

Poly(β-Amino Ester) Analogues



(II)



(III)

Figure 16.1

Experimental

1. Preparation of poly(piperizine-co-1,4-butanediol diacrylate), (I). In a typical reaction, 0.750 g of 1,4-butanediol diacrylate and 3.78 mmol of an aliphatic di-piperazine were weighed into two separate reaction vials and each dissolved in 5 mL of THF. The vial containing the dissolved aliphatic dipiperazine was then added to the vial containing renewable 1,4-butanediol diacrylate using a pipette and the mixture stirred at 50°C for 48 hours. The reaction solution was then cooled to ambient temperature and then slowly dripped into vigorously stirring diethyl ether. After collecting the precipitate by filtration, the product was dried under vacuum and isolated as a white solid. Analytical properties of the product are provided below.

^{1}**H-NMR** ($CDCl_3$ at 300 MHz) δ 4.11 (br t, 4H), 2.75 (br t, J=7.05 Hz, 4H), 2.53 (br s, 4H),

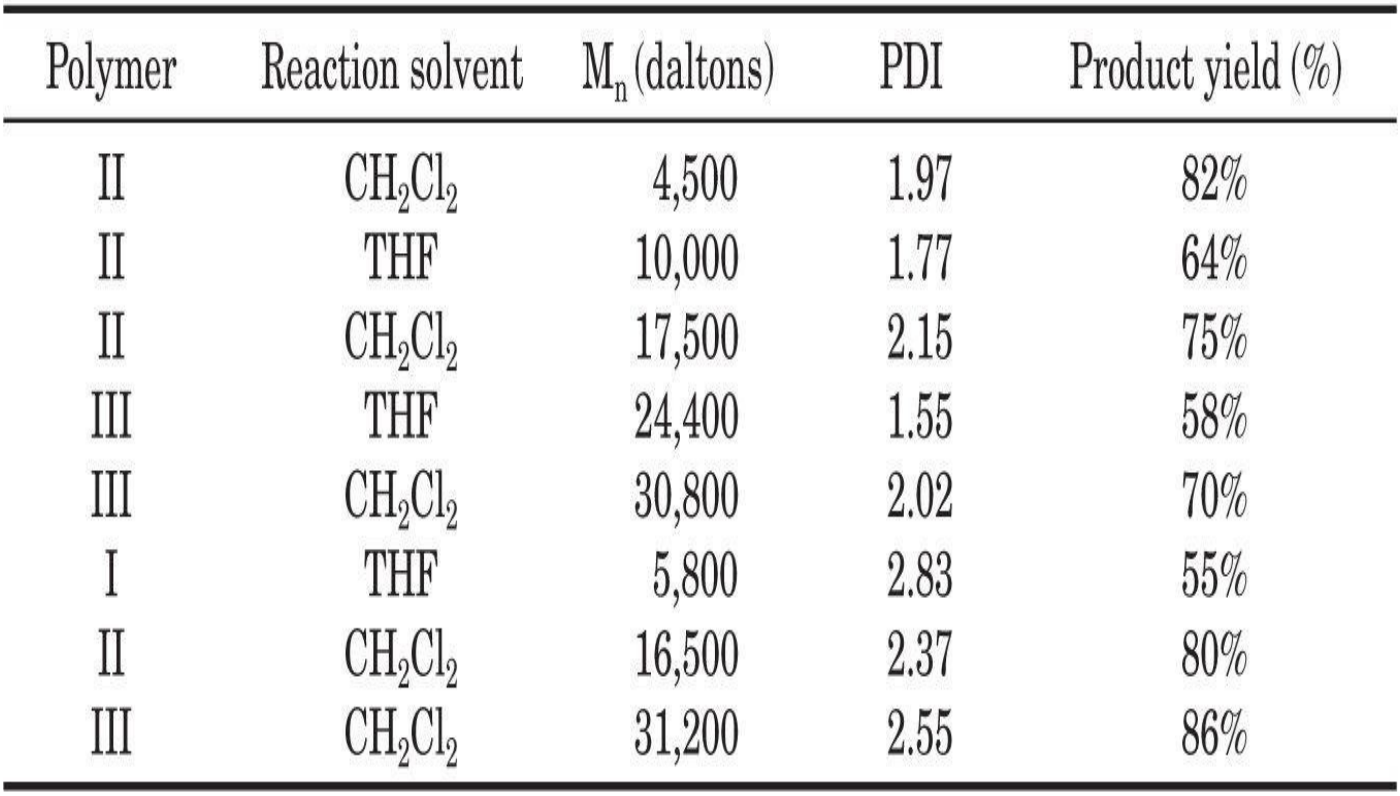
2.50 (br t, (obsc), J=7.20 Hz, 4H), 2.28 (br s, 6H), 1.71, (br m, 4H)

^{13}**C-NMR**($CDCl_3$ at 75.47 MHz) δ 172.55, 64.14, 55.31, 53.39, 42.47, 32.54, 25.53

Testing

A. Molecular weights. Molecular weight profiles for poly(β-amino esters) (I) through (III) are provided in Table 16.1.

TABLE 16.1 Representative molecular weights for poly(a-amino-esters) (I) through (III).



Polymer	Reaction solvent	M_n (daltons)	PDI	Product yield (%)
II	CH_2Cl_2	4,500	1.97	82%
II	THF	10,000	1.77	64%
II	CH_2Cl_2	17,500	2.15	75%
III	THF	24,400	1.55	58%
III	CH_2Cl_2	30,800	2.02	70%
I	THF	5,800	2.83	55%
II	CH_2Cl_2	16,500	2.37	80%
III	CH_2Cl_2	31,200	2.55	86%

B. Polymer degradation studies. Degradation studies were undertaken using the hydrochloride acid salts of poly(β-amino esters) (I) through (III). Initially, samples were dissolved in water to form solutions containing 5 mg/mL. Each solution was then added to either an acetate buffer at a pH of 5.1 or to an HEPES buffer having a pH of 7. Buffered samples were then incubated at 37°C on a mechanical rotator and 1 mL aliquots periodically removed. Samples were then frozen in liquid nitrogen, lyophilized, and then analyzed.

C. Cytotoxicity. Toxicity profiles of poly(β-amino esters) hydrochloride salts (I) through (III) were performed using the MTT/thiazolyl blue-dye-reduction assay using the NIH 3T3 cell line. In a typical analysis, cells were incubated with a selected poly(β-amino esters) hydrochloride salts (I) through (III) where they remained 100% viable relative to controls of polymer concentrations up to 100 mg/mL. Testing results indicate that poly(β-amino esters) hydrochloride salts (I) through (III) had an excellent cytotoxicity profile against the NIH 3T3 cell line.

Testing Results

A. Molecular weights of poly(β-amino esters) (I) through (III).

B. Polymer degradation studies. Experimental poly(β-amino esters) (I) through (III) were specifically designed to degrade through the hydrolysis of the ester bonds in the polymer backbone. An additional concern surrounding the overall stability and biocompatibility of poly(β-amino esters), however, was the potential for degradation occurring through a retro-Michael addition reaction pathway under physiological conditions. The basis for this concern was that these polymers had been prepared using the Michael addition reaction so that it was plausible they could undergo retro-Michael addition pathway under acidic conditions. This was of particular concern since poly(β-amino esters) prepared in this investigation would be subjected to a lower pH medium when within the endosome vesicles of cells during transfection. It was, however, empirically determined that when poly(β-amino esters) (I) through (III) were exposed to aqueous solutions having pH<3 or pH>12, degradation did not occur through a retro-Michael addition pathway. Moreover, no spectroscopic evidence for a retro-Michael addition reaction in aqueous solutions having a pH <3 or pH >12 was detected.

Notes and Observations

1. Zugates[1] end-modified a poly(β-amino ester), (IV), to prepare the aminated analogue, (V), to extend the usefulness of the polymers to both medical and non-medical applications, as illustrated in Eq. 1. (See Fig. 16.2.)

2. Anderson[2] prepared acrylate-terminated β-amino-esters and poly(β-amino esters) that were both heat and ultraviolet cross-linkable as well as being biodegradable under physiological conditions. β-Amino-ester monomers and polymers prepared from this process were useful as DNA and RNA delivery agents, plastics, coatings, and adhesives. Cross-linked poly(β-amino esters) exhibited a wide range of degradation times, mass loss profiles, and an elastic modulus ranging from 4 MPa to 350 MPa.

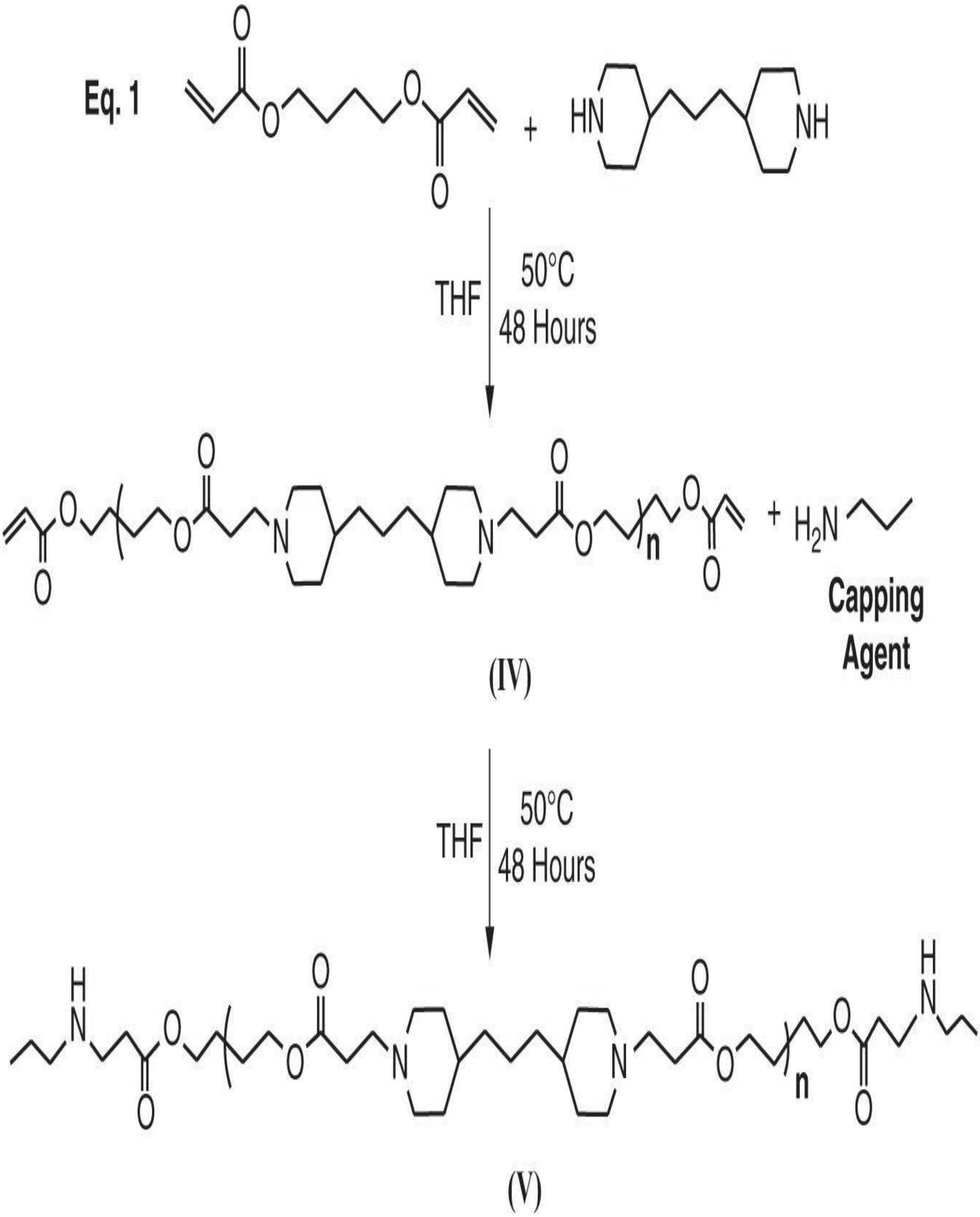
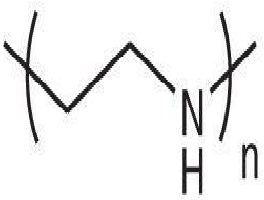


Figure 16.2

3. Zhao[3] prepared cationic polymers containing polyethylenimine, (VI), having an M_n of 600 daltons and containing the relatively hydrophobic group, (VII), which was effective as a delivery agent of bioactive agents such as DNA, RNA, oligonucleotides, proteins, and peptides to cells. (See Fig. 16.3.)



(VI)

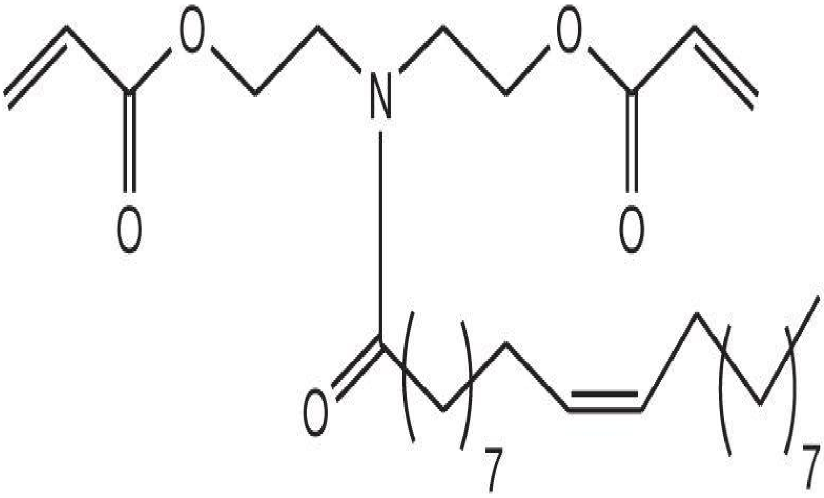
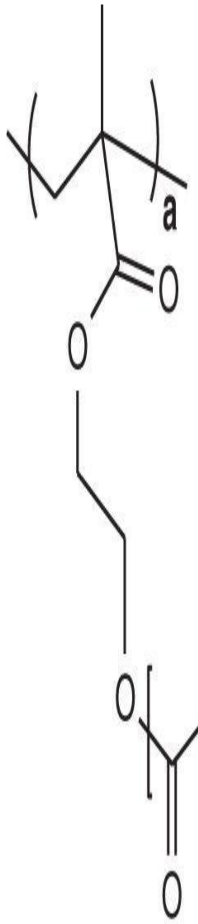
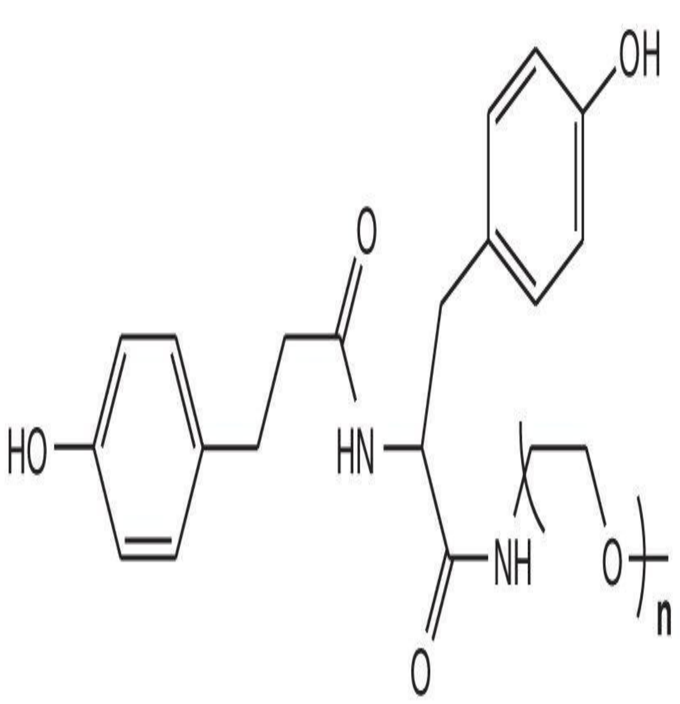


Figure 16.3



(VIII)



(IX)

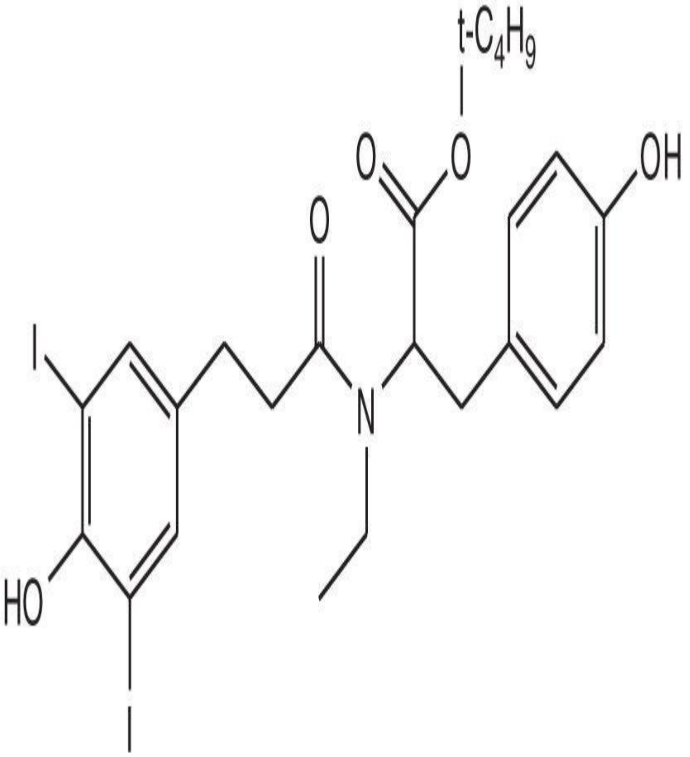


Figure 16.4

4. Baluca[4] prepared a series of both N-substituted and unsubstituted monomers and polymers for use in medical applications as stents. In the first instance, poly[(hydroxyethylmethacrylate)-g-caprolactone], (VIII), was prepared, but its high crystallinity limited its use. When it was modified with aromatic amines, (IX), or, (X), however, flexible polyurethanes stents were prepared. (See Fig. 16.4.)

References

1. Gregory T. Zugates et al., *End-modified poly(β-amino esters) and uses thereof*, U.S. Patent 8,071,082 (December 6, 2011)

2. Daniel Griffith Anderson et al., *Cross-linked, degradable polymers and uses thereof*, U.S. Patent Application 20080145338 (June 19, 2008)

3. Gang Zhao et al., *Biodegradable cationic polymers*, U.S. Patent 8,258,235 (September 4, 2012)

4. Ernest G. Baluca, *N-substituted monomers and polymers*, U.S. Patent 8,034,365 (October 11, 2011)

Chapter

17

Paint

Acetoacetylated Bio-Resins

Author Ekaterini Korovessi et al.

Patent Title ***Novel acetoacetoxy and enamine compounds and coatings therefrom***, U.S. Patent Application 20130036939 (February 14, 2013)

Relevant Prior Patents by Author or Coauthors

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,348,623 (February 19, 2002)

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,228,949 (May 8, 2001)

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,160,057 (December 12, 2000)

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,121,400 (September 19, 2000)

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,121,399 (September 19, 2000)

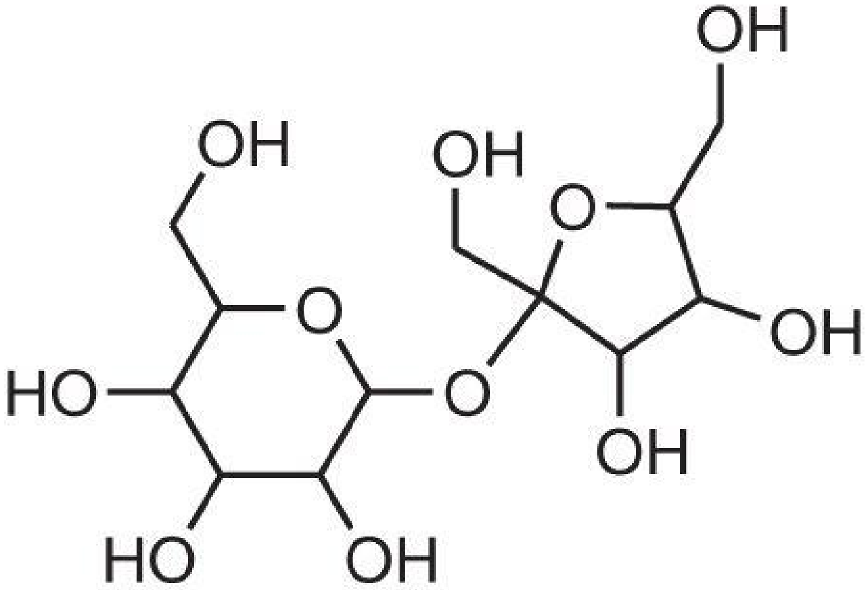
Product Application

Acetoacetylated and enamine bio-resins derived from sucrose were used in painting formulations where film strength and durability were required.

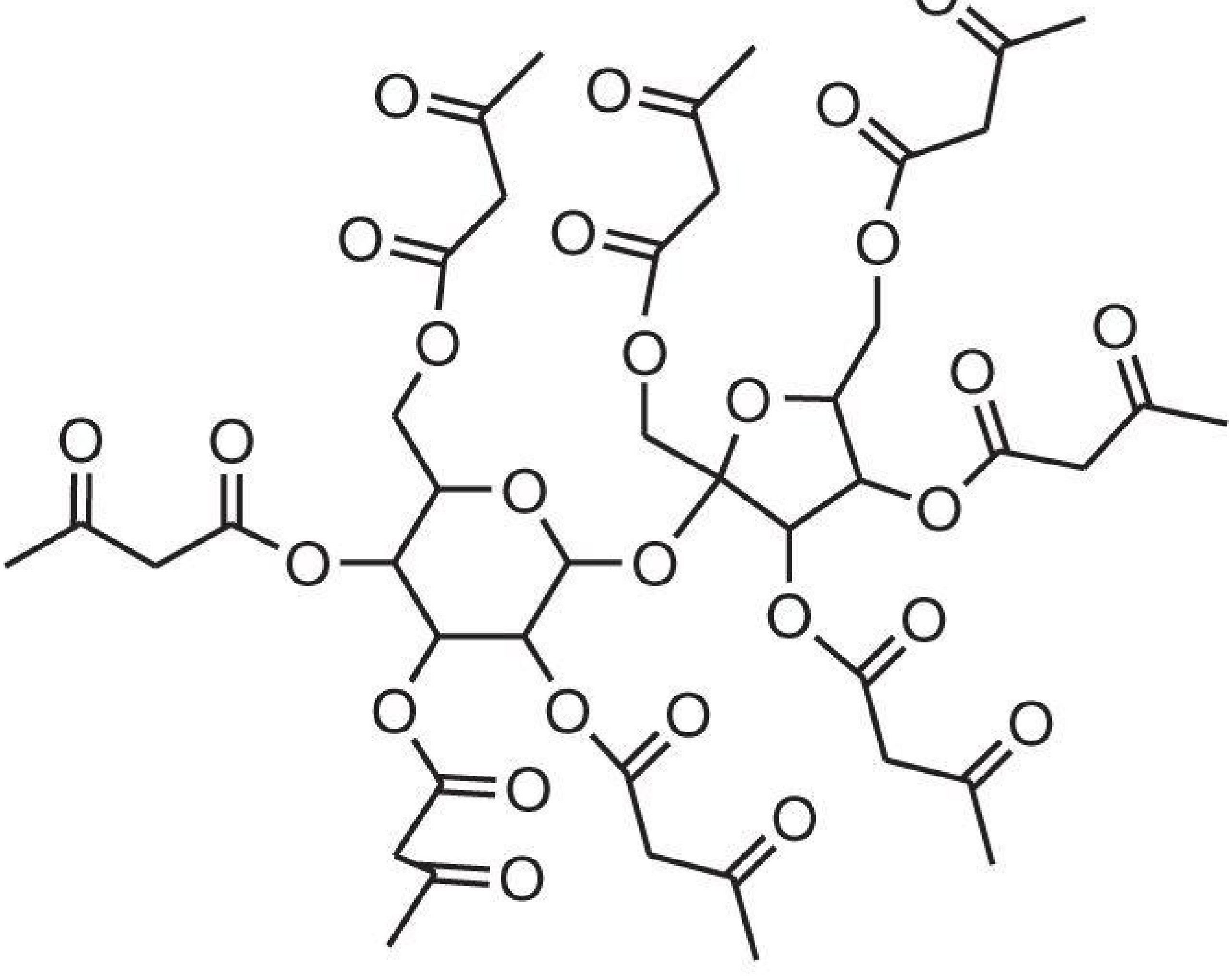
Significance of Current Application

The objective of this investigation was to develop paint additives utilizing renewable raw materials. Sucrose was selected as the renewable raw material since it has eight reactive hydroxyl groups which are easily esterified into non-toxic additives or intermediates. In addition, it was observed that when acetoacetylated or enamine resins derived from sucrose were used in paint formulations, uniform resin distribution resulted which had low viscosities and rapid air-drying. Furthermore, films derived containing these additives had excellent coating properties, strength, and durability. Finally, because of the ease and cost effectiveness in preparing these additives it is anticipated that these additives will be used in new and existing paint formulations.

Renewable Agents

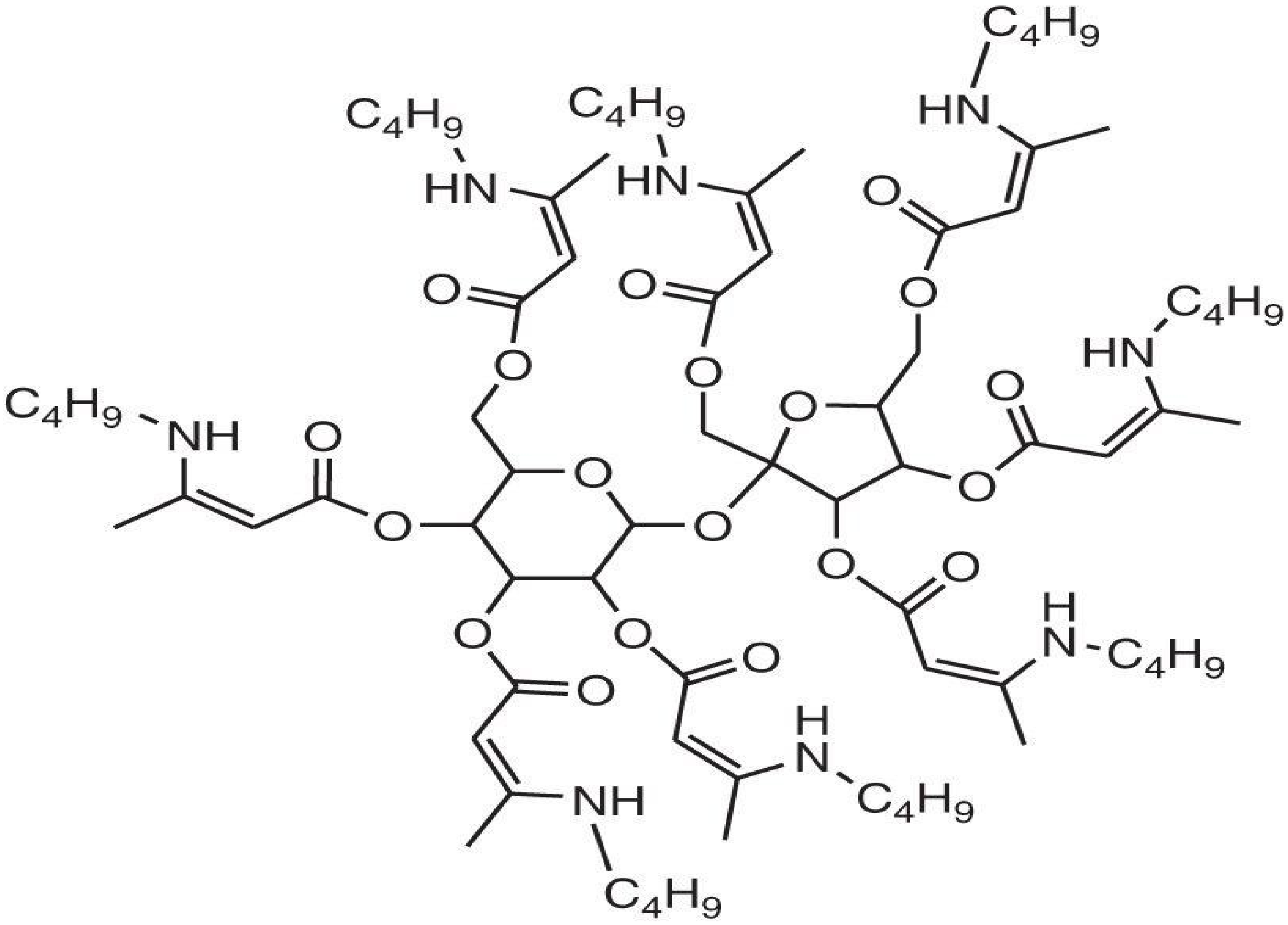


Sucrose



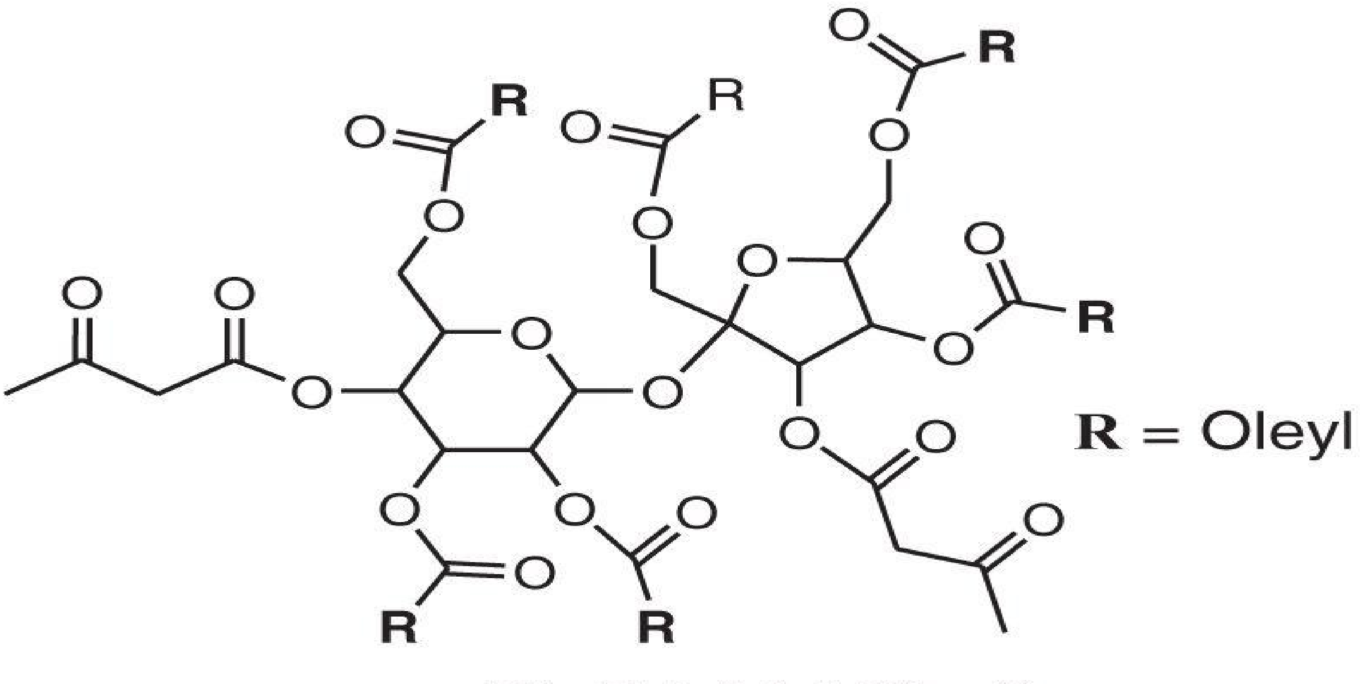
Bio-Paint Additive 1

(I)



Bio-Paint Additive 2

(II)



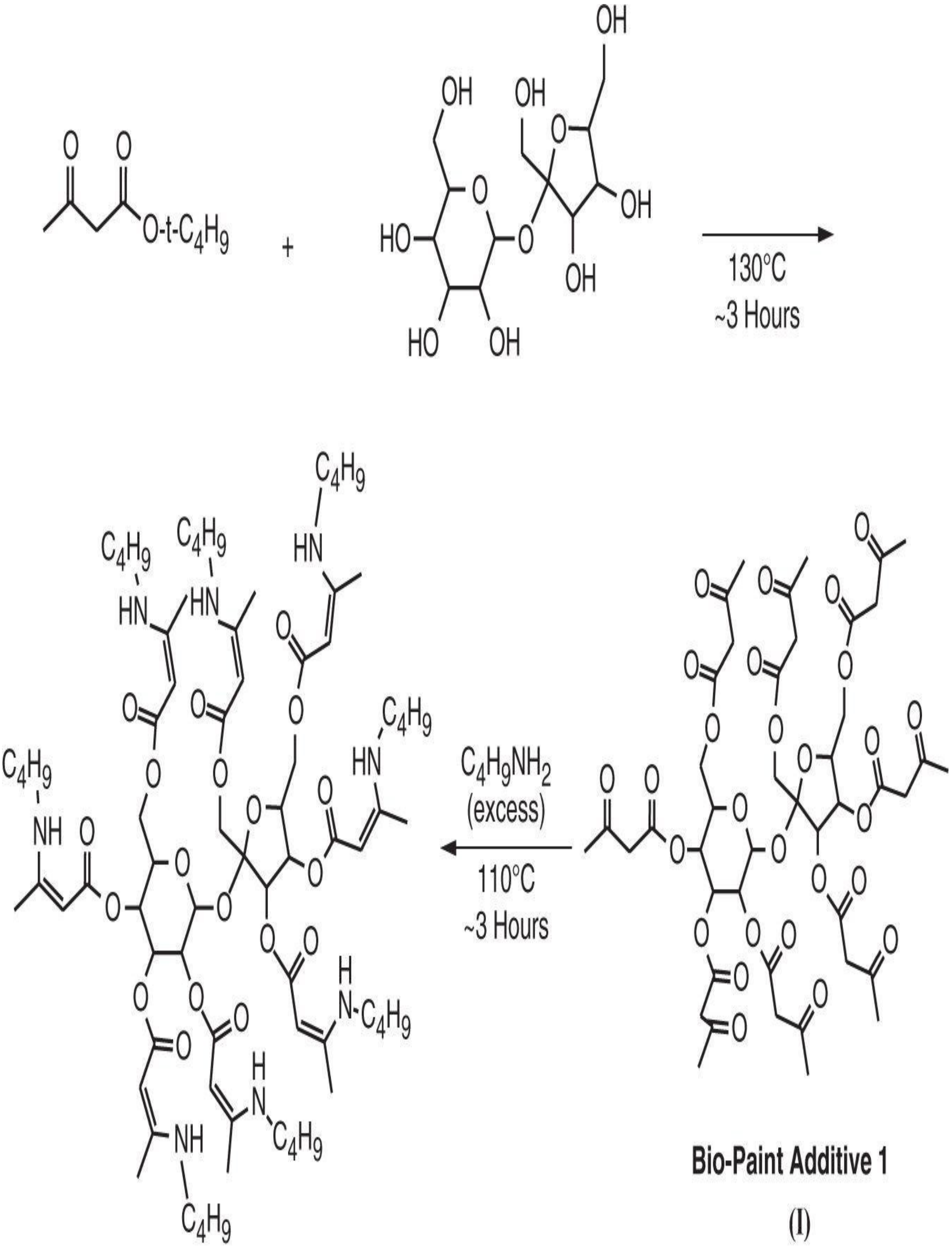
R = Oleyl

Bio-Paint Additive 3

(III)

Figure 17.1

Product Formation of Bio-Paint Additives 1 and 2



Bio-Paint Additive 1

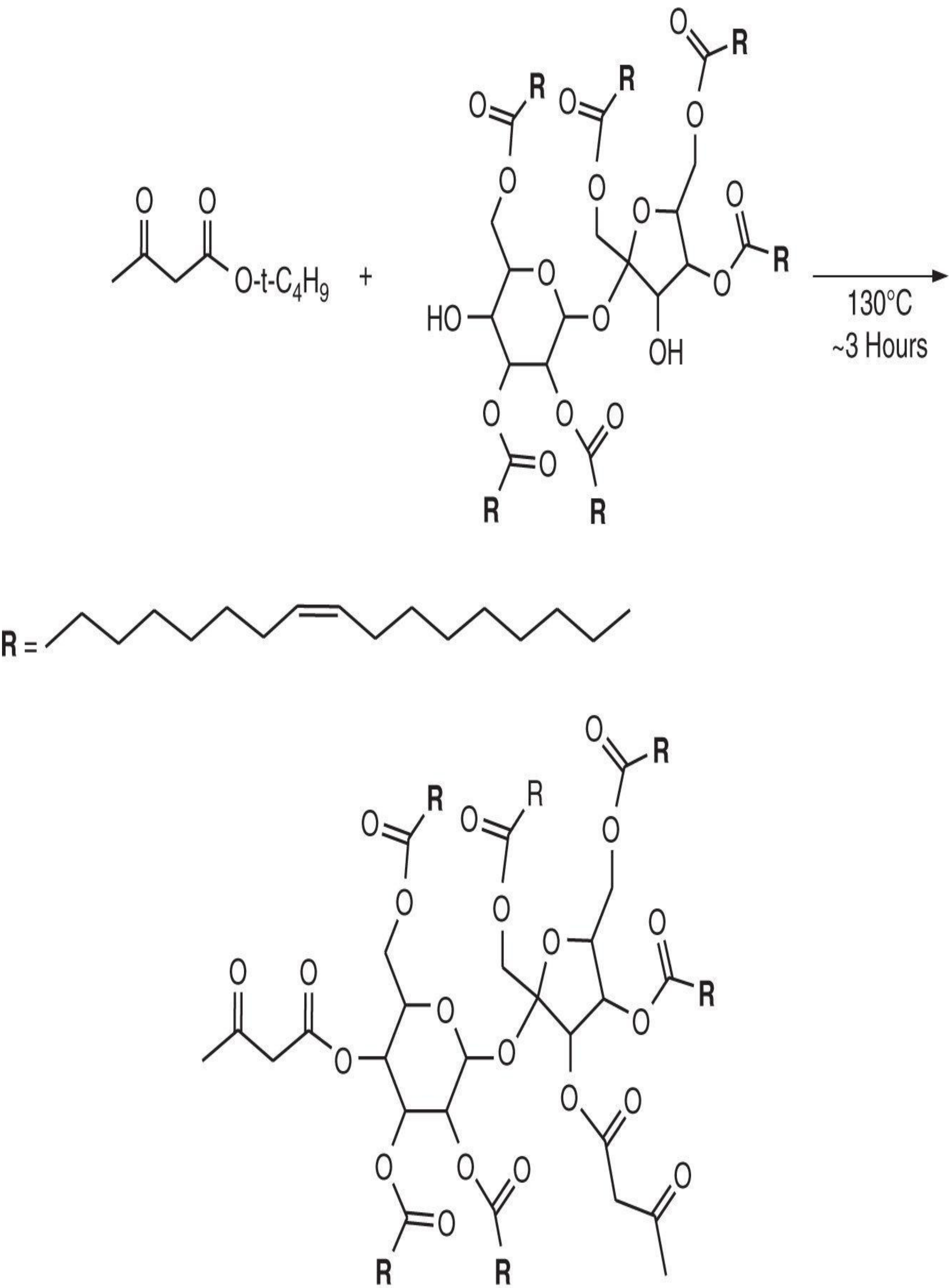
(I)

Bio-Paint Additive 2

(II)

Figure 17.2

Product Formation of Bio-Paint Additive 3



Bio-Paint Additive 3

(III)

Figure 17.3

Experimental

1. Preparation of bio-paint additive 1. A 500-mL four-neck flask containing a mechanical stirrer, nitrogen inlet, thermocouple, reflux condenser, and Dean-Stark trap was charged with 50.0 g of sucrose and 184.9 g of t-butyl-acetoacetate and then heated to 130°C for approximately 3 hours. During the reaction 84.8 g of t-butanol were collected in a Dean-Stark trap as the reaction by-product. After additional t-butanol stopped distilling over, the reaction was stopped and the product isolated as a viscous, yellow liquid. Infrared analysis spectroscopy was then used to confirm the absence of the broad hydroxyl stretching band at 3000 to 3600 cm^{-1} and the appearance of two carbonyl stretching bands at 1735 and 1780 cm^{-1}. Finally, ^{1}H-NMR spectroscopy did not detect hydroxyl sucrose protons at 1 to 5.7 ppm but did detect methylene protons associated with acetoacetates at both 2.1 to 2.3 ppm, and 3.4 to 3.7 ppm.

2. Preparation of bio-paint additive 2. A reactor was charged with 30 g of the Step 1 product and a five-molar excess of butyl amine and then heated to 110°C while water was collected in a Dean-Stark trap as the reaction by-product. After additional water stopped distilling over, the reaction was stopped and the enamine isolated as a viscous, reddish-yellow product. ^{1}H-NMR spectrum of the reaction product detected methylene protons at 0.8 and 3.2 ppm and a secondary amine proton at 8.4 to 8.5 ppm.

3. Preparation of bio-paint additive 3. A 500-mL four-neck flask containing a mechanical stirrer, nitrogen inlet, thermocouple, reflux condenser and Dean-Stark trap was charged with100 g of hexa(octadecaolenyl)-dihydroxy-sucrose (SEFOSE 1618U B6®) and 17.2 g of t-butyl-acetoacetate and then heated to 130°C for approximately 3 hours. During this heating period 9.1 g of t-butanol was distilled over and collected in Dean-Stark trap. After additional t-butyl alcohol stopped distilling over, the reaction was stopped and the product isolated as a light-yellow liquid.

4. Preparation of paint formulations containing bio-resins. Coating formulations containing one or more of the experimental products were then prepared. In the most preferred formulation, equivalent amounts of the Step 3 product were blended with the Step 2 product and then treated with a poly-functional amine having two or more primary amine groups. The blending solvent used was cyclohexane containing an aliphatic epoxyamine as the crosslinking agent.

Testing

A. Physical testing. The strength, durability, and associated physical properties of dried paint coatings containing blends of experimental additives derived from renewable sucrose were determined using mechanical testing.

B. Physical testing. The thickness of the cured coating was measured prior to testing.

C. Konig hardness. Konig pendulum hardness and gouged pencil hardness was determined according to ASTM D 4366-95 and ASTM D 3363-00, respectively.

D. Adhesion. The adhesion of cured coatings was evaluated using ASTM D 3359-97.

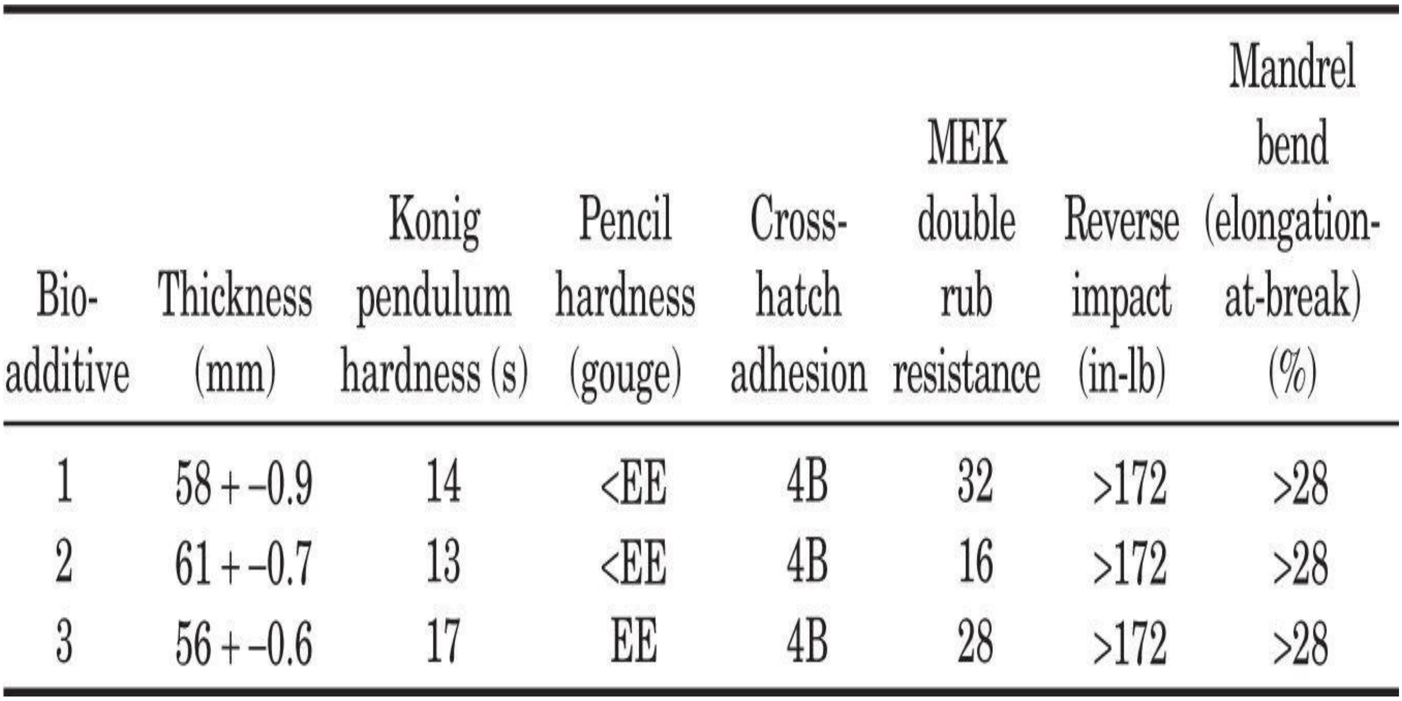
Methyl ethyl ketone was used during the double rub test, which was conducted according to ASTM D 5402-93.

E. Impact resistance. Impact resistance was evaluated according to ASTM D 2794-93 where the results were obtained using a four-pound metal cylinder while multiplying the maximum height in inches.

F. Mandrel bending. Mandrel bending was performed using the testing protocol provided in ASTM D 522-93a and where the results are presented as the elongation range of the coating at cracking. Testing results are provided in Table 17.1.

Testing Results

TABLE 17.1 Coating properties for three air-dried experimental coatings containing bio-paint additives 1 through 3. In all cases, coatings were soft and flexible although solvent resistance in all cured coated samples was marginal.



Bio-additive	Thickness (mm)	Konig pendulum hardness (s)	Pencil hardness (gouge)	Cross-hatch adhesion	MEK double rub resistance	Reverse impact (in-lb)	Mandrel bend (elongation-at-break) (%)
1	58 + -0.9	14	<EE	4B	32	>172	>28
2	61 + -0.7	13	<EE	4B	16	>172	>28
3	56 + -0.6	17	EE	4B	28	>172	>28

Notes and Observations

1. Selifonov[1] prepared a series of monomeric, (IV), and polymeric, (V), ketal derivatives using glycerine derived from renewable biomass-derived feedstocks that were then used as additives in paint formulations. Dried painted surfaces were very durable, flexible, and resistant to solvents.

2. Kuo[2] prepared two paint additive blends having virtually no volatile organic compound emissions. The first additive pair consisted of mixed esters of levulinic acid, (VI). The second additive pair was P&G CO-1214®, which consisted of 1-tetradecanol (myristyl alcohol), (VII), and dodecyl alcohol (lauryl alcohol), (VIII). All components in both additive mixtures were derived from renewable sources. (See Fig. 17.4.)

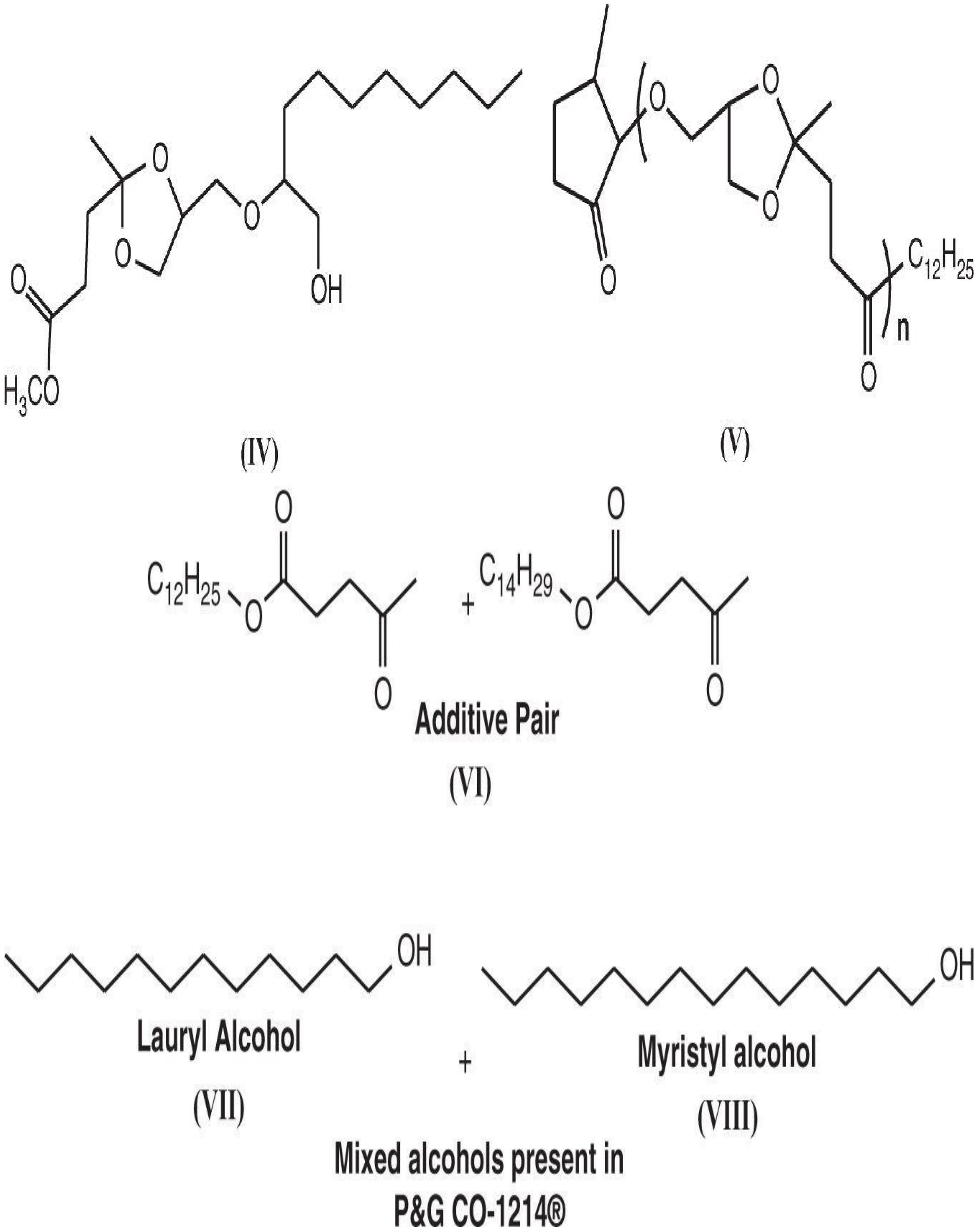
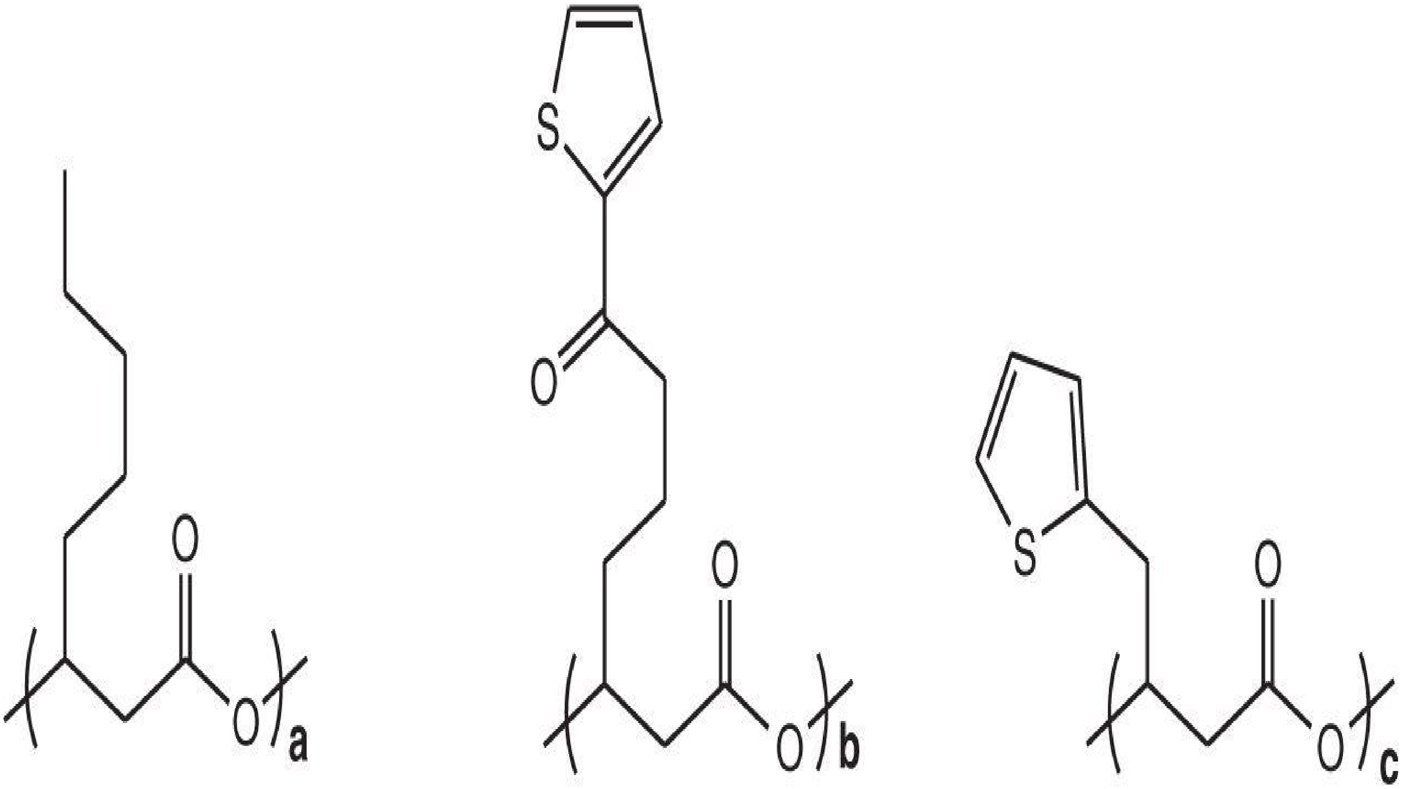


Figure 17.4

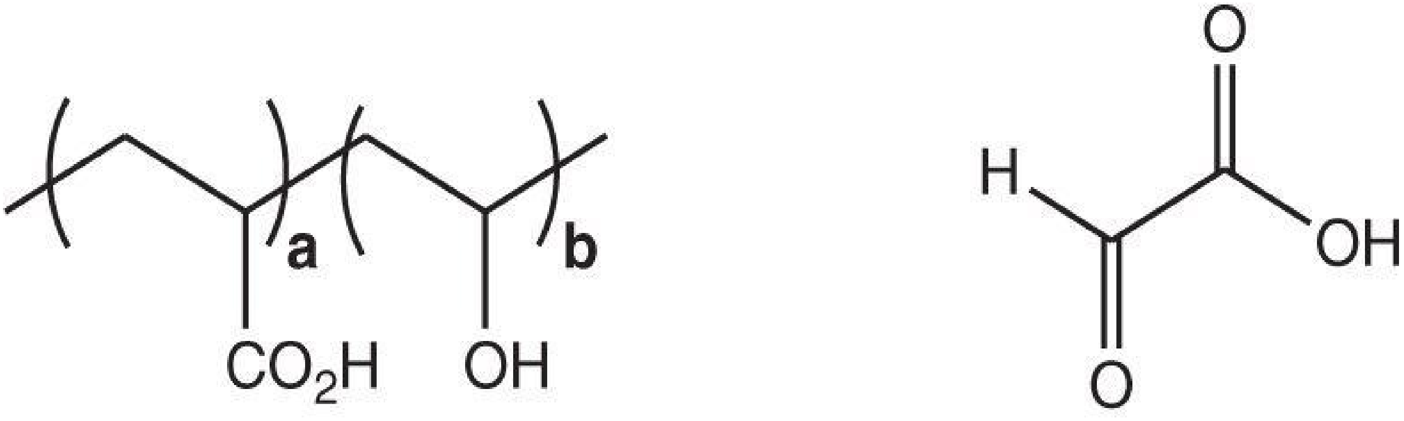
3. Yano[3] used microorganisms to prepare a series of polyhydroxyalkanoates, (IX) to (XI), which were intended as drug delivery agents. When these polymers were converted into microcapsules, however, they were also used as paint, dye, and pigment agents in paint formulations. (See Fig. 17.5.)



(IX) (X) (XI)

Figure 17.5

4. Tanaka[4] prepared a renewable paint additive that improved the film resistance to water, resisted color change due to oxidation, and had excellent stability in aqueous solutions. The additive was prepared by crosslinking poly(acrylic acid-co-vinyl alcohol), (XII), with glyoxylic acid, (XIII), then forming an emulsion composition with the polymer product. (See Fig. 17.6.)



(XII) (XIII)

Figure 17.6

References

1. Sergey Selifonov, *Glycerol levulinate ketals and their use*, U.S. Patent 8,178,701 (May 15, 2012)

2. Thauming Kuo et al., *Waterborne coating compositions containing low-VOC*

coalescents, U.S. Patent 8,383,710 (February 26, 2013)

3. Tetsuya Yano et al., *Particulate construct comprising polyhydroxyalkanoate and method for producing it*, U.S. Patent 7,615,233 (November 10, 2009)

4. Shinichi Tanaka et al., *Crosslinking agent, crosslinked polymer, and uses thereof*, U.S. Patent 8,426,632 (April 23, 2013)

Itaconic Acid Ester Bio-Resins

Author	Yvon Durant
Patent Title	***Emulsion polymerization of esters of itaconic acid,*** U.S. Patent 8,410,232 (April 2, 2013)

Relevant Prior Patents by Author

Regulated and continuous polymerization of polycarboxylic acid polymers, U.S. Patent 8,420,758 (April 16, 2013)

Polycarboxylic acid polymers, U.S. Patent 8,227,560 (July 24, 2012)

Coatings comprising itaconate latex particles and methods for using the same, U.S. Patent Application 20110037013 (February 17, 2011)

Absorbing materials containing polycarboxylic acid polymers, U.S. Patent 7,915,365 (March 28, 2011)

Detergents containing polycarboxylic acid polymers, U.S. Patent 7,910,677 (March 22, 2011)

Polycarboxylic acid polymers, U.S. Patent 7,910,676 (March 22, 2011)

Method for the production of aqueous polymer dispersions, U.S. Patent Application 20080009563 (January 8, 2010)

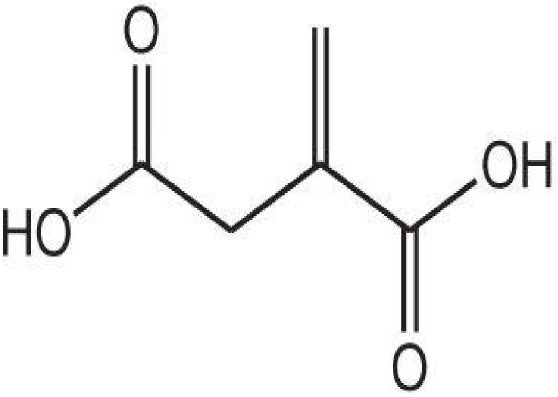
Product Application

Polyitaconic acid and polyitaconic acid esters are renewable materials that are used in adhesive, paint, and paper formulations.

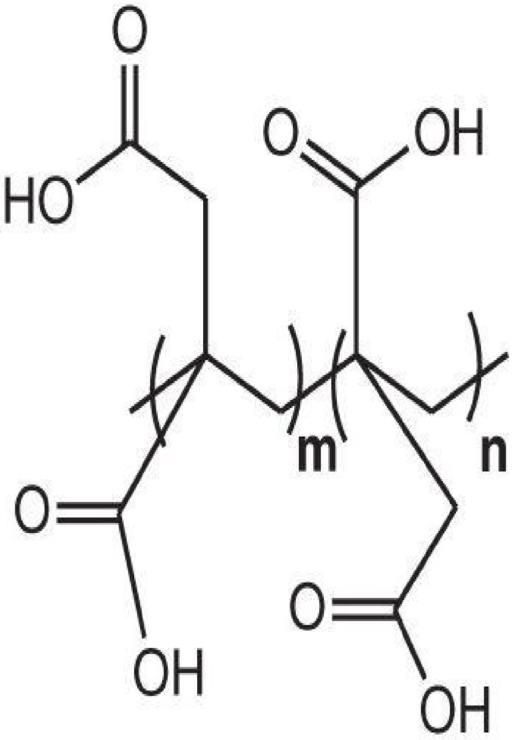
Significance of Current Application

Polyitaconic acid and polyitaconic acid esters were prepared using renewable itaconic acid in emulsion polymerizations to generate two renewable, sustainable, and biobased polymers. The two glass-transition temperatures of each biopolymer were from –40.0°C to 20.0°C and from –35.0°C to 110.0°C, which allows these materials to be used in a variety of adhesive, paint, and paper formulations. Finally, this investigation also discovered that when consistent volume average particle sizes of 95 to 200 nm of seed particles were generated, a moderate level of predictability of polymer number and average molecular weights could be determined.

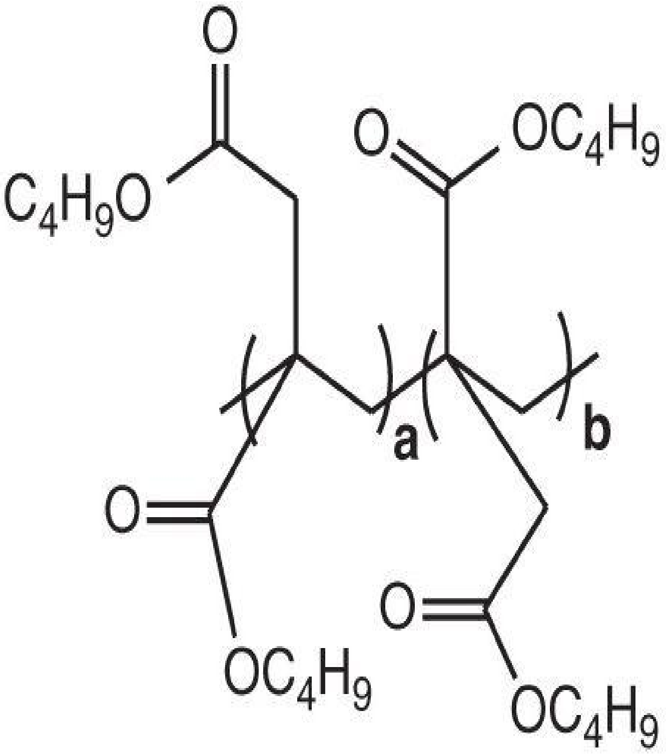
Renewable Agents



Itaconic acid



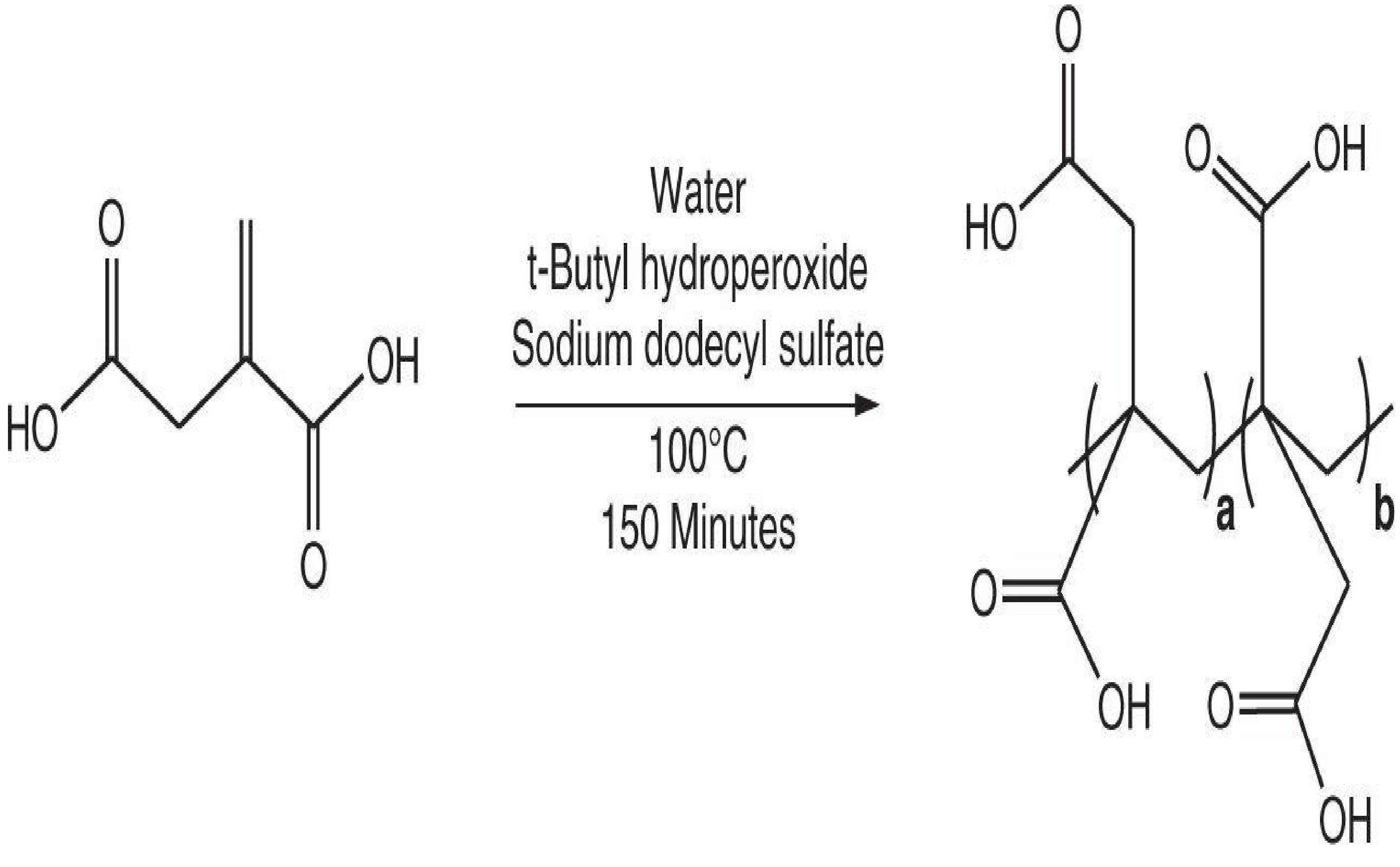
Polyitaconic acid



Polyitaconic acid butyl ester

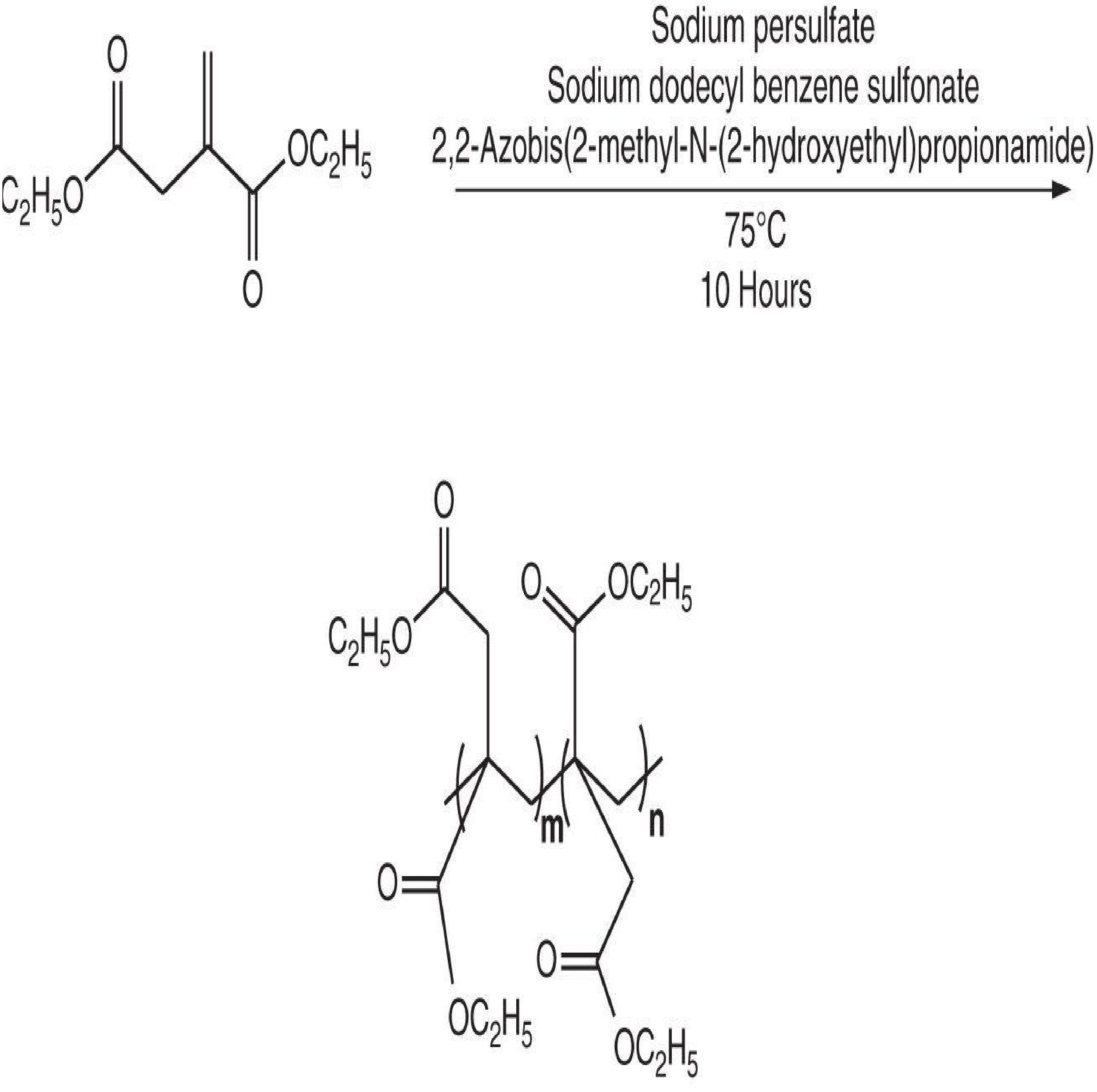
Figure 17.7

A. Product Formation 1



Polyitaconic acid

B. Polymerization Seed Formation



Polyitaconic Ethyl Ester Seed

C. Product Formation 2

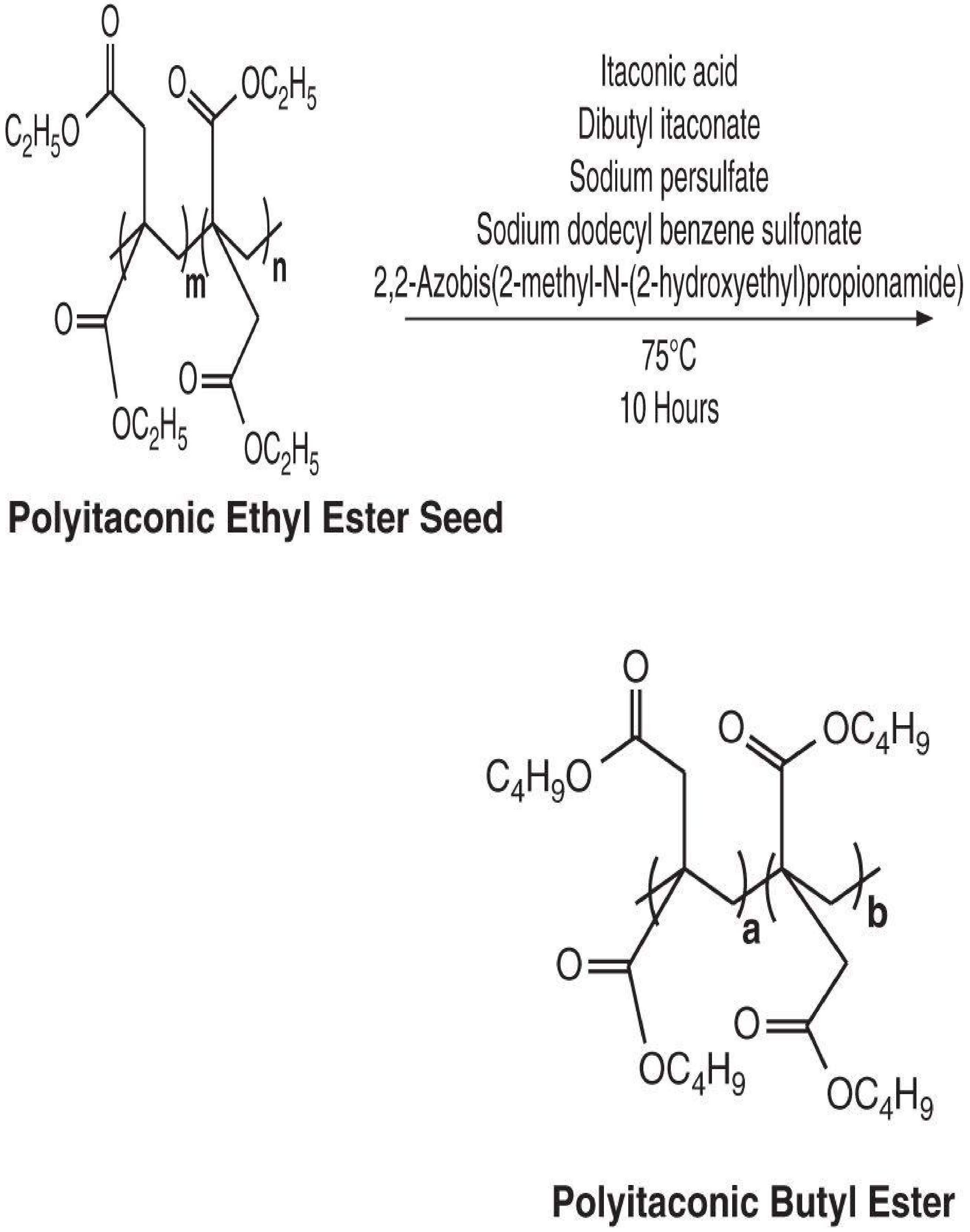


Figure 17.8

Experimental

1. Preparation of polyitaconic acid. A clean 500-mL beaker was charged with 100 g of itaconic acid, 0.3 g of sodium dodecyl sulfate, and 50 g of deionized water while the mixture was being manually stirred. The beaker was then placed into an ice water bath and then slowly treated with 30.8 g of sodium hydroxide. Once the addition was completed, the reaction mixture was further stirred with a large glass paddle while immersed in the ice water bath until the temperature stabilized between 2°C and 4°C. The solution was then poured into a 250-mL 3-neck round-bottom flask equipped with a mechanical stirrer, nitrogen feed line, condenser, and thermometer. The reaction mixture was then heated to 100°C and treated with 1 mL of aqueous 70% t-butyl hydroperoxide and then further heated to 100°C for 150 minutes. The mixture was then cooled to ambient temperature, concentrated, and the polymer isolated as a white solid. Analytical testing by ^{1}H-NMR indicated that the reaction had a 97.7% conversion while GPC of the reaction product using a polyacrylic acid standard indicated that polyitaconic acid had an Mn of 3,920 daltons.

2. Preparation of polyitaconic ethyl ester seed. A 5-L reactor was mechanically agitated to 100 rpm and then treated with 2,700 g of water and 1.4 g of sodium dodecyl benzene sulfonate and then purged with nitrogen while heating to 75°C. The mixture was then treated with 745 g of diethyl itaconate, 5.22 g of sodium persulfate, and 2.24 g of 2,2-azobis(2-methyl-N-(2-hydroxyethyl)propionamide) and heated to 75°C for 10 hours while under constant mechanical agitation. The emulsion was then cooled and determined to have a solids content of 18.9 wt% with a reaction conversion of 81%. The number and average molecular weight of the seed was 12,578 daltons with a weight average molecular weight of 66,783 daltons. The polyitaconic ethyl ester seed had an volume average particle size between 96.8 and 133.3 nm with glass-transition temperatures of 11.36°C and 79.15°C.

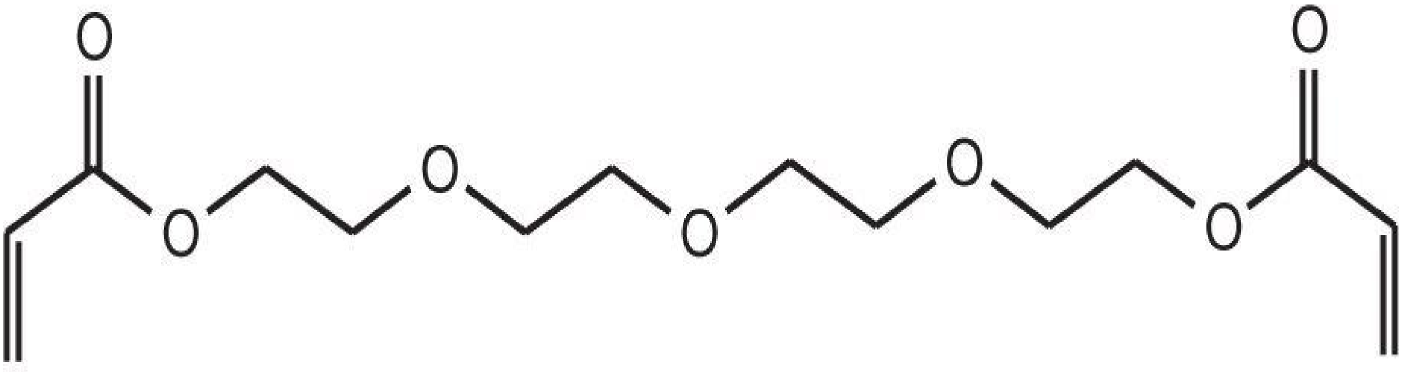
3. Preparation of polyitaconic butyl ester. A 5-L reactor was mechanically agitated at 100 rpm then treated with 634 g of polydiethyl itaconate seed containing 17.0 wt% solids, 8 g of sodium dodecyl benzene sulfonate, and 11 g of itaconic acid. After purging with nitrogen at 80°C, the solution was treated with 76 g of dibutyl itaconate and 1.4 g of sodium persulfate. After one hour the mixture was incrementally treated with 203 g of dibutyl itaconate and 4.2 g of 33.3 wt% sodium persulfate in an aqueous solution over a period of 6 hours. The reaction mixture was then cooled and the latex determined to contain a solids content of 36.0 wt% with a reaction conversion of 96%. The number average molecular weight of the product was 17,700 daltons with a weight average molecular weight of 276,120 daltons. The product had a volume average particle size distribution between 108.7 and 237.8 nm with three glass-transition temperatures of 26.06°C, 17.9°C, and 50.94°C.

Testing Results

Although the author provided paint formulations containing experimental additives alone or in mixtures, paint coating properties were not provided.

Notes and Observations

1. Durant[1] prepared a crosslinked polymer of itaconic acid with tetraethylene glycol diacrylate, (I), using a 10 L kneader-reactor at 70°C which was then used as a sizing agent in fibers. (See Fig. 17.9.)

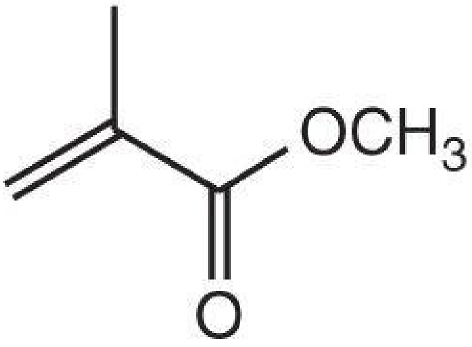


(I)

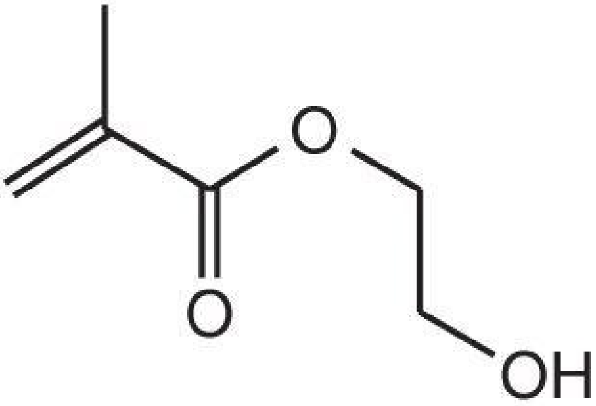
Figure 17.9

2. High molecular weight polyitaconic acid was prepared by Durant[2] and used as an absorbing agent in the treatment of incontinence. High molecular weight polyitaconic acid was prepared by the free-radical polymerization of di-sodium or di-potassium itaconicate. Polyitaconic acid was then regenerated by treating each polymer with dilute hydrochloric acid.

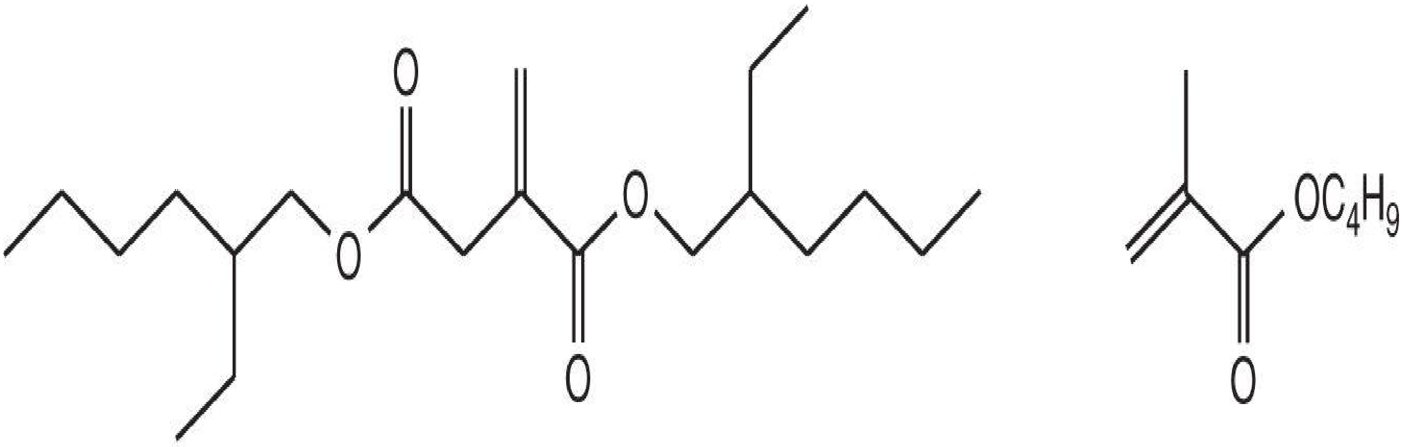
3. Ragunathan[3] prepared coatings consisting of latex particles that were designed to inhibit sound and vibration transmission through a substrate. The four-component latex consisted of methyl methacrylate, (II), hydroxyethyl methacrylate, (III), itaconic acid di(2-ethyl hexyl) ester, (IV), and butyl methacrylate, (V). The monomeric mixture was then free-radically initiated using ammonium persulfate and the latex isolated in quantitative yield. (See Fig. 17.10.)



(II)



(III)



(IV) (V)

Figure 17.10

4. Durant[4] prepared a biorenewable detergent by free-radically polymerizing itaconic acid in an aqueous medium containing sodium hydroxide and t-butyl hydroperoxide. The homopolymer had an average molecular weight of 10,180 daltons and a number average molecular weight of 3,920 daltons.

References

1. Yvon Durant et al., *Regulated and continuous polymerization of polycarboxylic acid polymers*, U.S. Patent 8,420,758 (April 16, 2013)

2. Yvon Durant et al., *Absorbing materials containing polycarboxylic acid polymers*, U.S. Patent 7,915,365 (March 28, 2011)

3. Kaliappa G. Ragunathan et al., *Coatings comprising itaconate latex particles and methods for using the same*, U.S. Patent Application 20110037013 (February 17, 2011)

4. Yvon Durant et al., *Detergents containing polycarboxylic acid polymers*, U.S. Patent 7,910,677 (March 22, 2011)

Chapter

18

Photosensitive Additives

Porphyrin Sensitizers for Solar Panels

Author	Chen-Yu Yeh et al.
Patent Title	***Green zinc porphyrin sensitizers and their applications,*** U.S. Patent Application 20130090469 (April 11, 2013)

Relevant Prior Patents by Author or Coauthors

Systems and methods for customizing photo presentations, U.S. Patent Application 20110231766 (September 22, 2011)

Solar panel assembly with heat dissipation improvement, U.S. Patent Application 20110155212 (June 30, 2011)

Porphyrin-based photosensitizer dyes for dye-sensitized solar cells, U.S. Patent 8,148,519 (April 3, 2012)

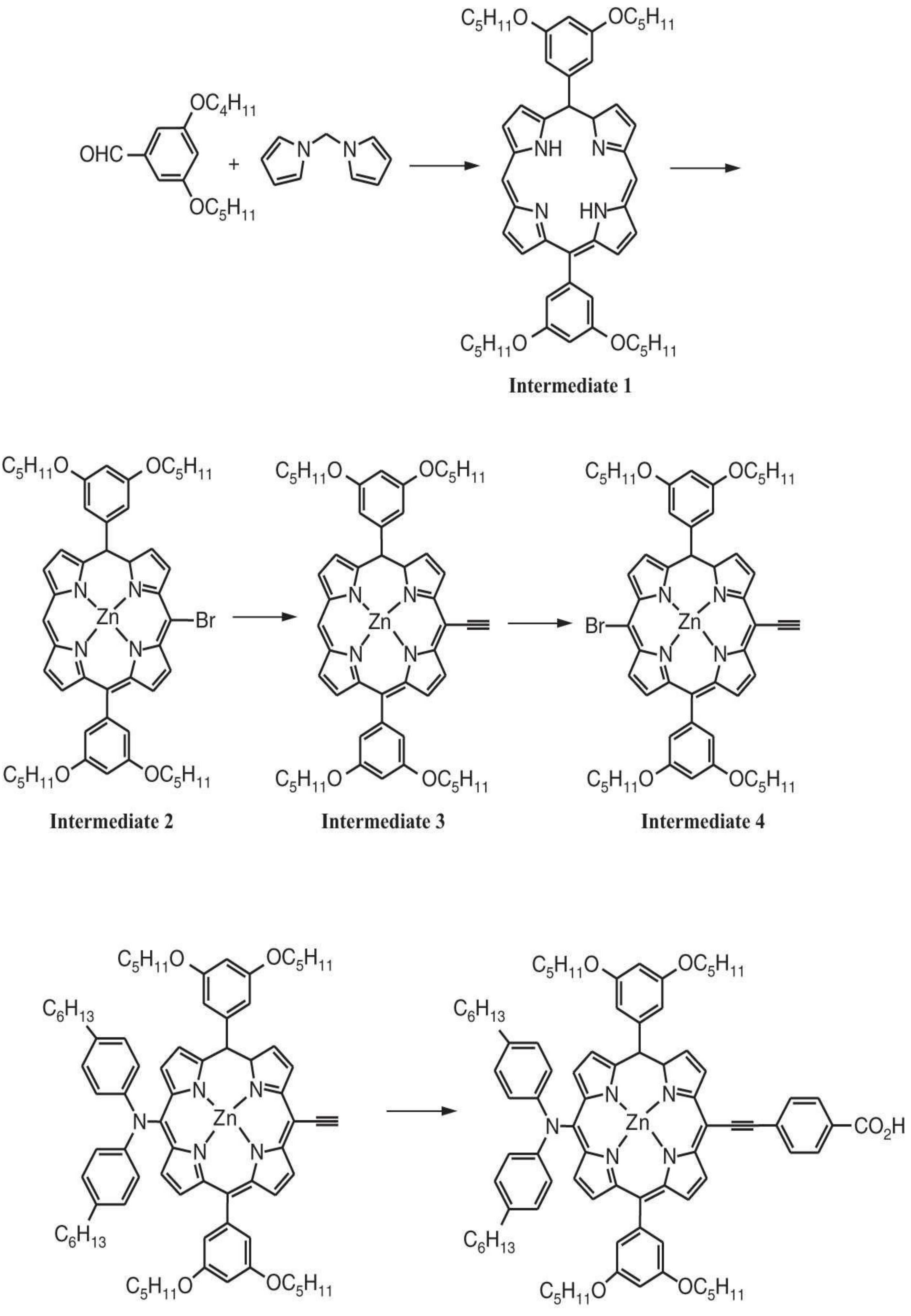
Product Application

Renewable zinc porphyrin sensitizers prepared in this investigation are designed to be used in the manufacture of high-efficiency dye-sensitive solar cells.

Significance of Current Application

There is a general and urgent need for producing sustainable and renewable energy resources, particularly in those areas using photovoltaic devices. Moreover, there is a further need for preparing these agents as cost-effectively as possible. While polypyridine/ruthenium-based dye-sensitized solar cells have achieved a conversion efficiency of more than 11%, the process has been plagued with serious environmental concerns. The current investigation has developed a method for readily and inexpensively synthesizing dye-sensitized solar cells in any standard chemistry laboratory. In addition to being environmentally non-toxic, zinc porphyrin sensitizers can be easily modified to obtain other unique and usable photovoltaic properties.

Product Formation



Intermediate 1

Intermediate 2

Intermediate 3

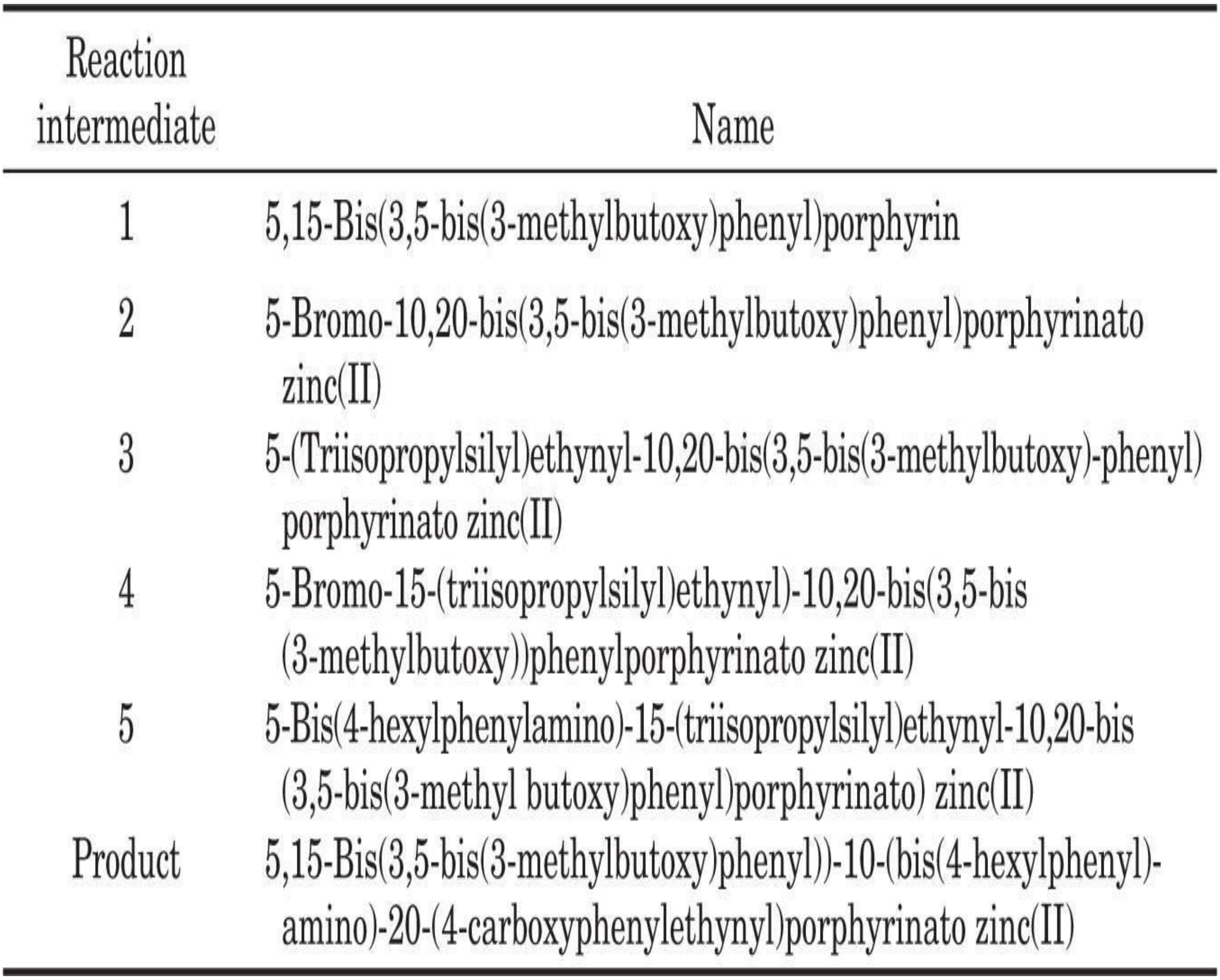
Intermediate 4

Intermediate 5

Product

Figure 18.1

Intermediate/Product Chemical Nomenclature



Reaction intermediate	Name
1	5,15-Bis(3,5-bis(3-methylbutoxy)phenyl)porphyrin
2	5-Bromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato zinc(II)
3	5-(Triisopropylsilyl)ethynyl-10,20-bis(3,5-bis(3-methylbutoxy)-phenyl) porphyrinato zinc(II)
4	5-Bromo-15-(triisopropylsilyl)ethynyl)-10,20-bis(3,5-bis (3-methylbutoxy))phenylporphyrinato zinc(II)
5	5-Bis(4-hexylphenylamino)-15-(triisopropylsilyl)ethynyl-10,20-bis (3,5-bis(3-methyl butoxy)phenyl)porphyrinato) zinc(II)
Product	5,15-Bis(3,5-bis(3-methylbutoxy)phenyl))-10-(bis(4-hexylphenyl)-amino)-20-(4-carboxyphenylethynyl)porphyrinato zinc(II)

Experimental

1. **Preparation of Intermediate 1.** A suspension of 6.00 g of dipyrromethane and 11.4 g of 3,5-di(isopentyloxy)-benzaldehyde was added to 5,400 mL of dichloromethane and stirred under a nitrogen atmosphere and deoxidized with nitrogen for 30 minutes. The reaction mixture was then treated with 2.75 mL of trifluoroacetic acid and stirred for 3.5 hours before treating it with 13.99 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. After the reaction had stirred for an additional hour it was concentrated and a residue was isolated. The residue was purified by silica-gel column chromatography using 1:1 dichloromethane/n-hexane. The residue was then re-crystallized from methanol/dichloromethane and the product was isolated in 30% yield.

2. **Preparation of Intermediate 2.** A reactor was charged with 1 g of the Step 1 product and then dissolved in 638 mL of dichloromethane and stirred under nitrogen atmosphere. The solution was then placed in an ice bath for 20 minutes and treated with 198 mg of N-bromosuccinimide dissolved in 80 mL of dichloromethane. The reaction was then monitored using thin-layer chromatography. When the reaction was completed, the mixture was quenched with acetone and a crude product was isolated. The residue was

purified by silica-gel column chromatography using 1:2 dichloromethane/n-hexane and a purple-red solid was isolated in 53% yield. The intermediate was then dissolved in 275 mL of dichloromethane and treated with zinc acetate dihydrate dissolved in 54 mL of methanol. The solution was stirred for 3 hours and the product was extracted with 200 mL of water. The organic layer was then dried over anhydrous magnesium sulfate and the product was isolated in 92% yield.

3. Preparation of Intermediate 3. A reactor was charged with 1.05 mmol of the Step 2 product, 1.26 mmol of triisopropyl-acetylene, 0.11 mmol of $Pd(PPh_3)_2Cl_2$, 0.11 mmol of copper(I) iodide, 32.8 mL of THF, and 6.5 mL of triethylamine then refluxed for 4 hours. The solvent was then removed by vacuum distillation and the residue purified by silica gel column chromatography using 1:2 dichloromethane/n-hexane and the product was isolated as a purple solid in 88% yield.

4. Preparation of Intermediate 4. To a stirred solution of 0.48 mmol of the Step 3 product dissolved in 265 mL of dichloromethane containing 26.5 mL of pyridine, 127.0 mg of N-bromo-succinimide were added and the mixture stirred for 30 minutes at ambient temperature. The solvent was then removed under reduced pressure and the residue purified by silica-gel column chromatography using 1:1 dichloromethane/n-hexane. After drying, the product was isolated in 90% yield.

5. Preparation of Intermediate 5. A reactor was charged with 1.77 mmol of bis(4-hexylphenyl)amine, 1.77 mmol of 60% NaH, 0.44 mmol of the Step 4 product, 0.177 mmol of DPEphos, and 0.11 mmol of $Pd(OAc)_2$ dissolved in 100 mL of dry THF. The mixture was then gently refluxed under a nitrogen atmosphere for 4 hours and then concentrated. The residue was purified by silica-gel column chromatography using 1:1 dichloromethane/n-hexane and the product was isolated in 57% yield.

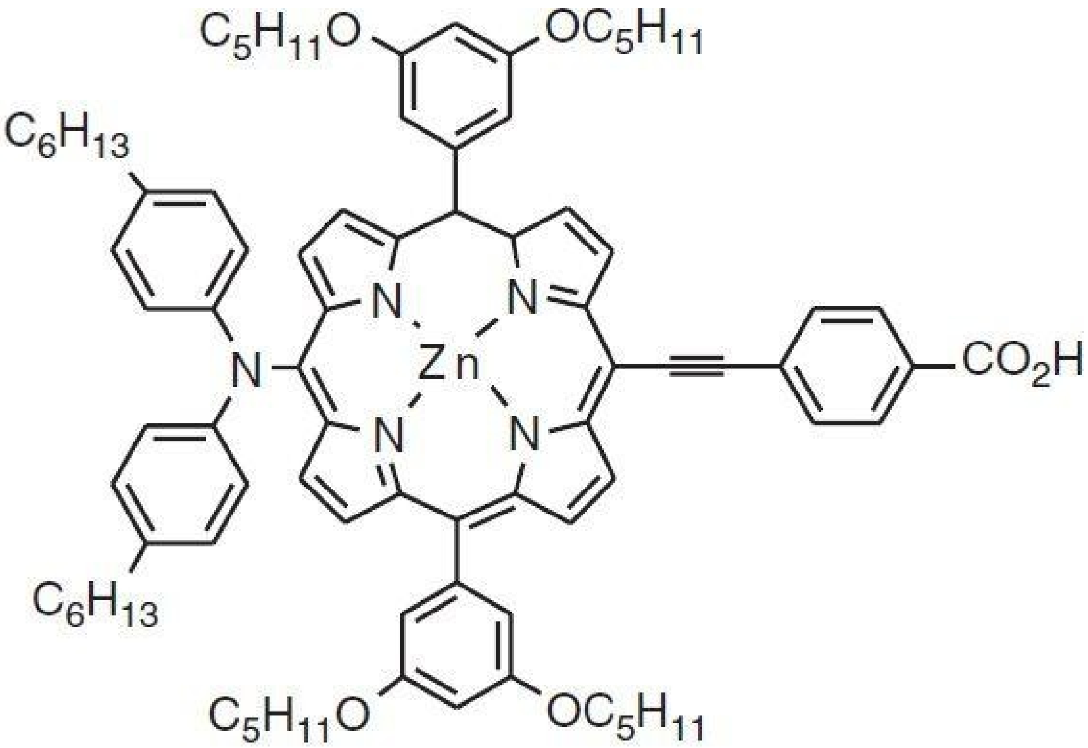
6. Preparation of product. A small glass reactor was charged with a solution consisting of 0.072 mmol of the Step 5 product dissolved in 10 mL of THF and then treated with 0.72 mL of 1M tetrabutyl-ammonium bromide. The solution was then stirred at ambient temperature for 30 minutes then quenched with water and extracted with dichloromethane. After drying over magnesium sulfate it was concentrated and the residue treated with 0.29 mmol of 4-iodobenzoic acid dissolved in a mixture of 35.5 mL of THF and 7.1 mL of triethylamine. The solution was then degassed with nitrogen for 10 minutes and further treated with 0.014 mmol of tris(dibenzylidene-acetone)dipalladium(0) and 0.14 mmol of triphenyl arsenic (III) refluxed for 4 hours and then concentrated. The residue was purified by silica-gel column chromatography using 20:1 dichloromethane/methanol. After being re-crystallized in 1:1 n-hexane/ethanol the product was isolated as a green solid in 90% yield.

Testing

Testing results for photoelectric conversion efficiencies of selected zinc porphyrin-based photosensitive porphyrins, (I), (II), (III), and a Reference, (IV), are provided in Table 18.1. (See also Fig. 18.2.)

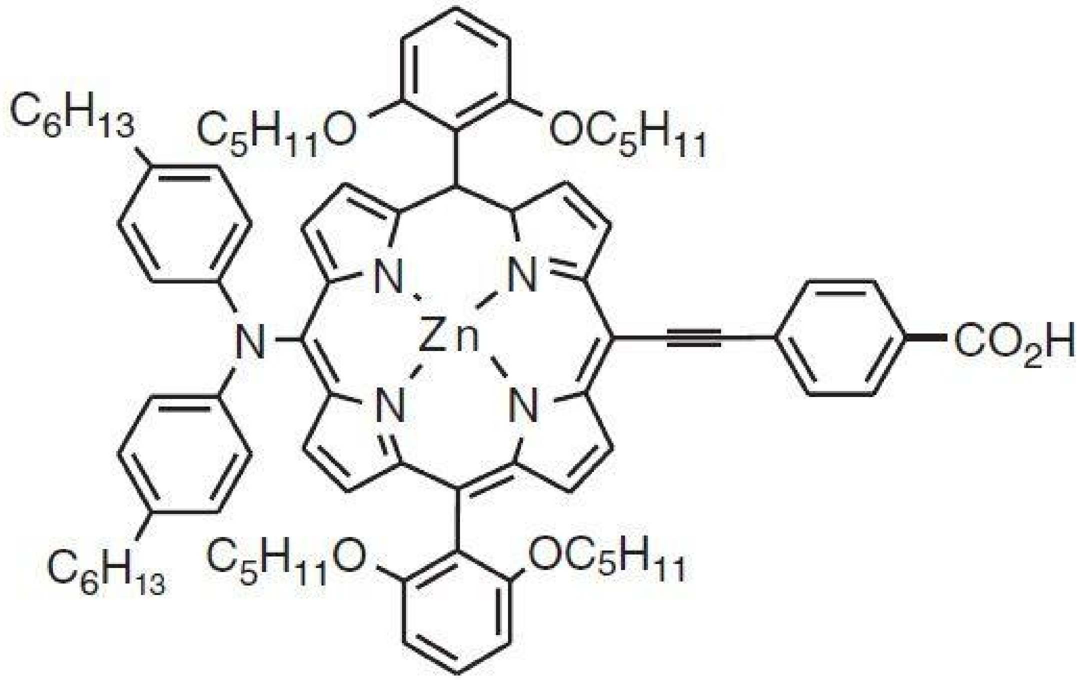
TABLE 18.1 Testing results indicate that green zinc porphyrin-based photosensitive product analogues, (I), (II), (III), exhibited more efficient push-pull performance when compared to the non-green Reference, (IV).

Experimental porphyrin analogue	Voc (V)	Isc (mA)	FF (–)	η (%)
I	0.720	14.720	0.67	7.100
II	0.716	14.860	0.672	7.155
III	0.618	12.498	0.623	4.811
Reference	01.71	4.149	0.656	6.593



Green zinc porphyrin-based photosensitive analogue

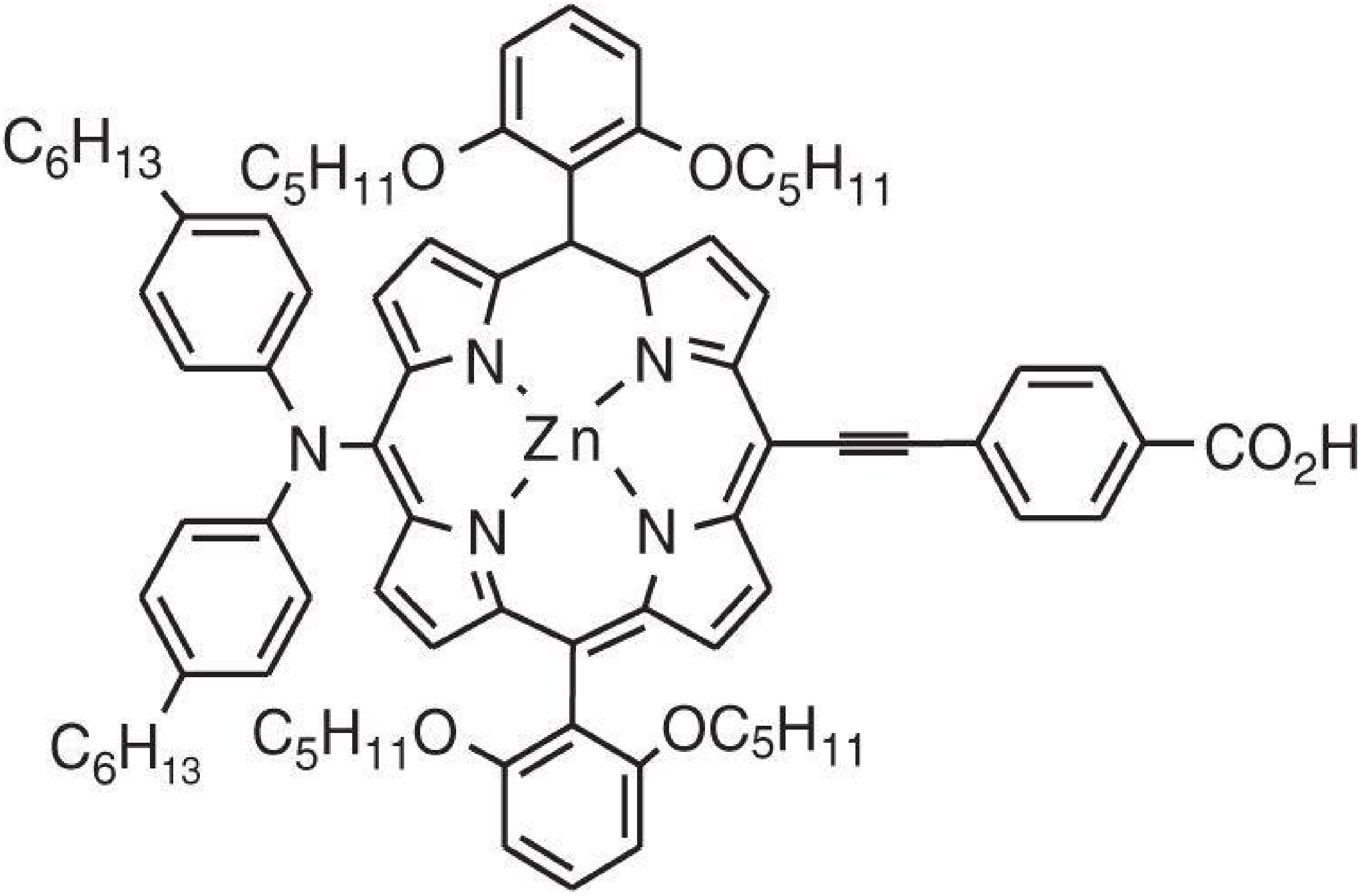
(I)



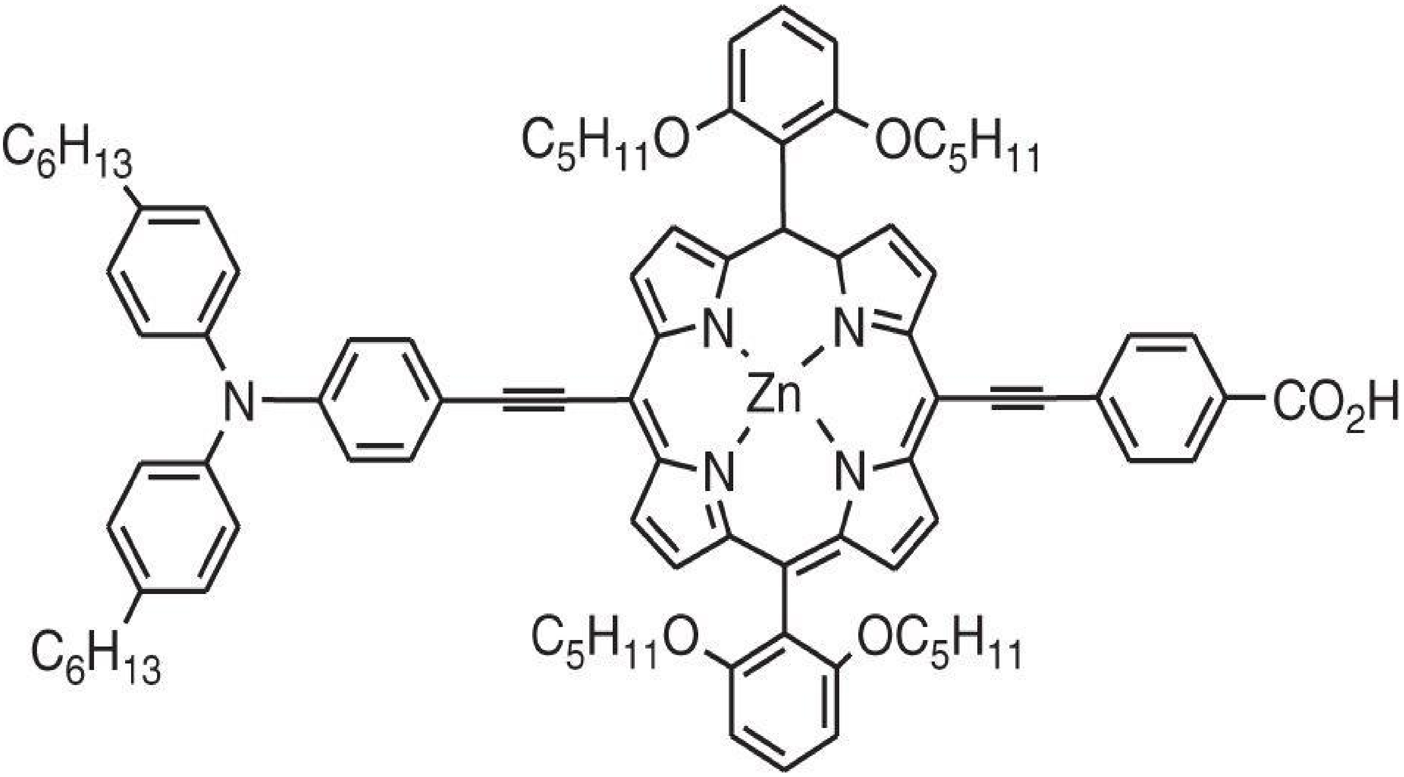
Green zinc porphyrin-based photosensitive analogue

(II)

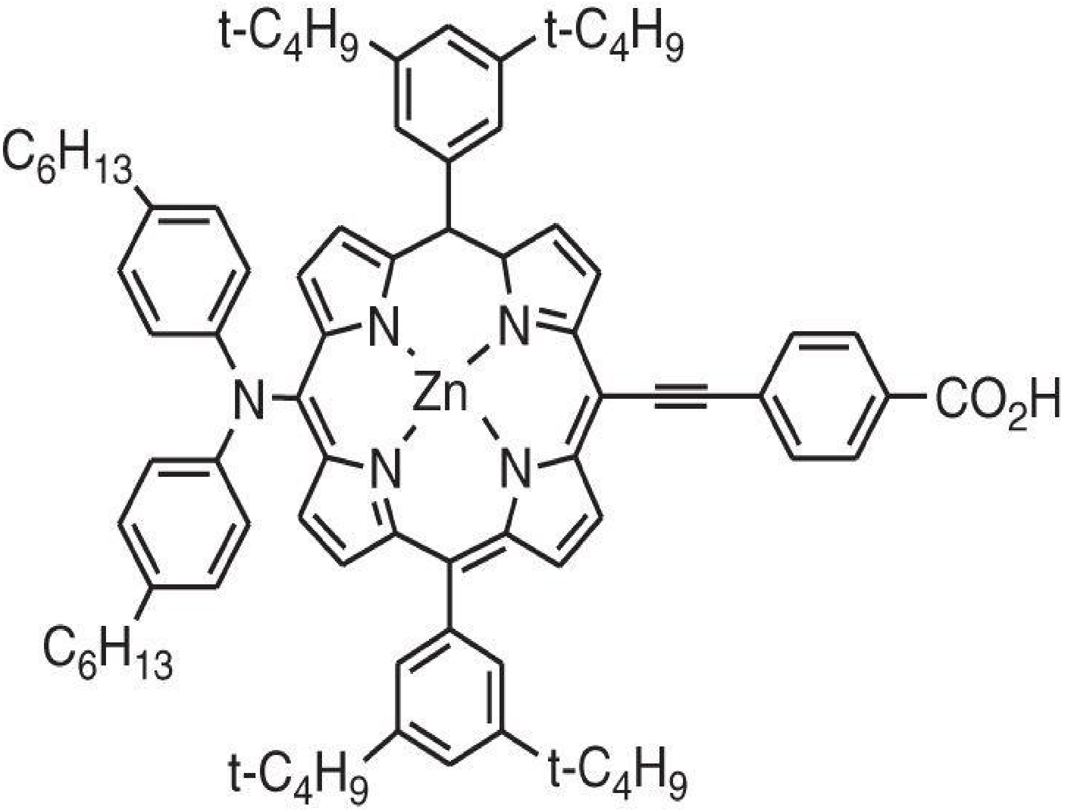
Green zinc porphyrin-based photosensitive analogue (I)



Green zinc porphyrin-based photosensitive analogue (II)


Green zinc porphyrin-based photosensitive analogue

(III)

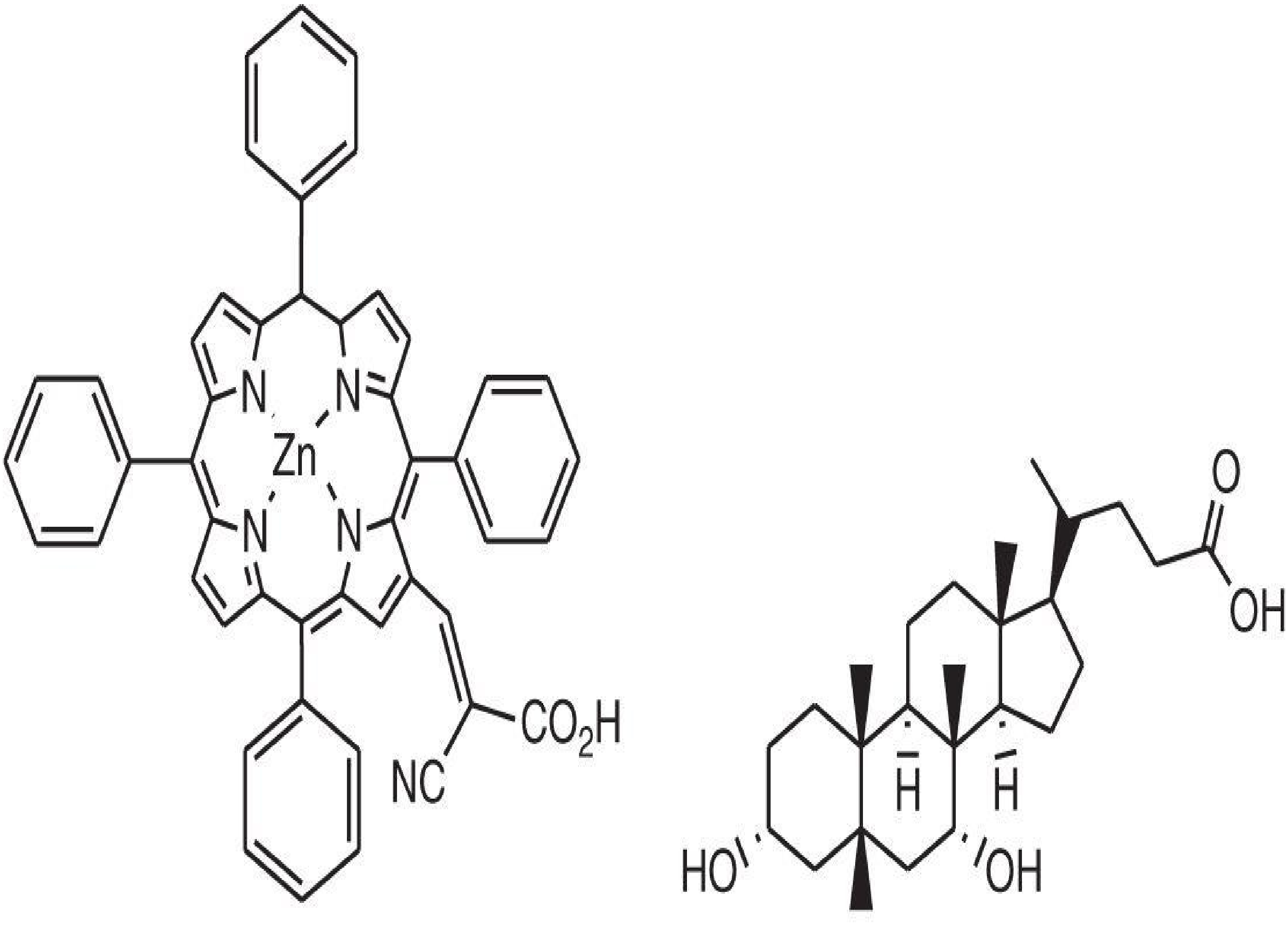

Reference

(IV)

Figure 18.2

Notes and Observations

1. In an earlier investigation by Yeh,[1] the effectiveness of a porphyrin sensitizer, (V), was improved by blending it with chenodeoxycholic acid, (VI). (See Fig. 18.3.)



(V) (VI)

Figure 18.3

2. Lindsey[2] devised a simple and high-yielding method for preparing ABCD-substituted porphyrins useful as photosensitizers, as illustrated in Eq. 1. (See Fig. 18.4.)

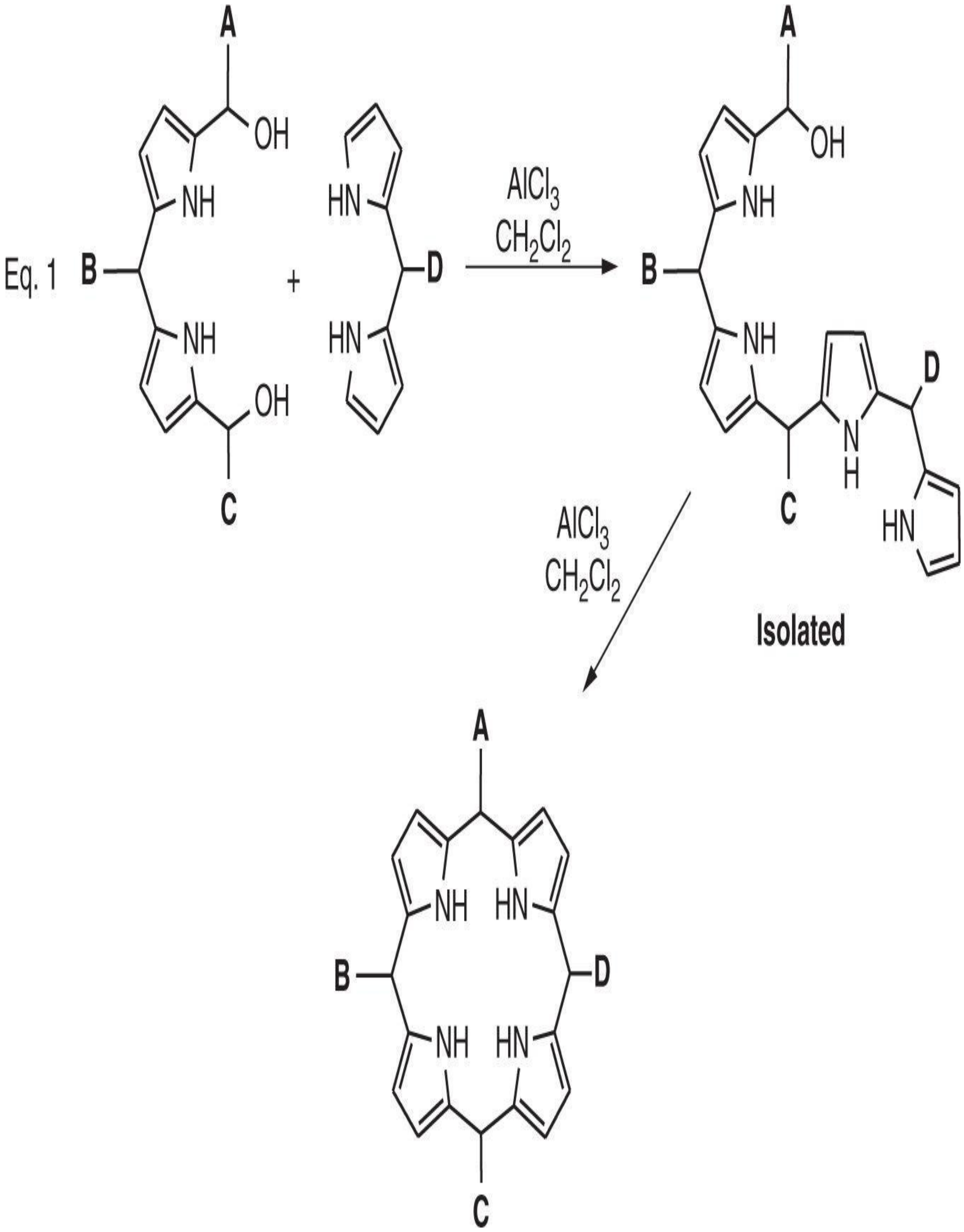
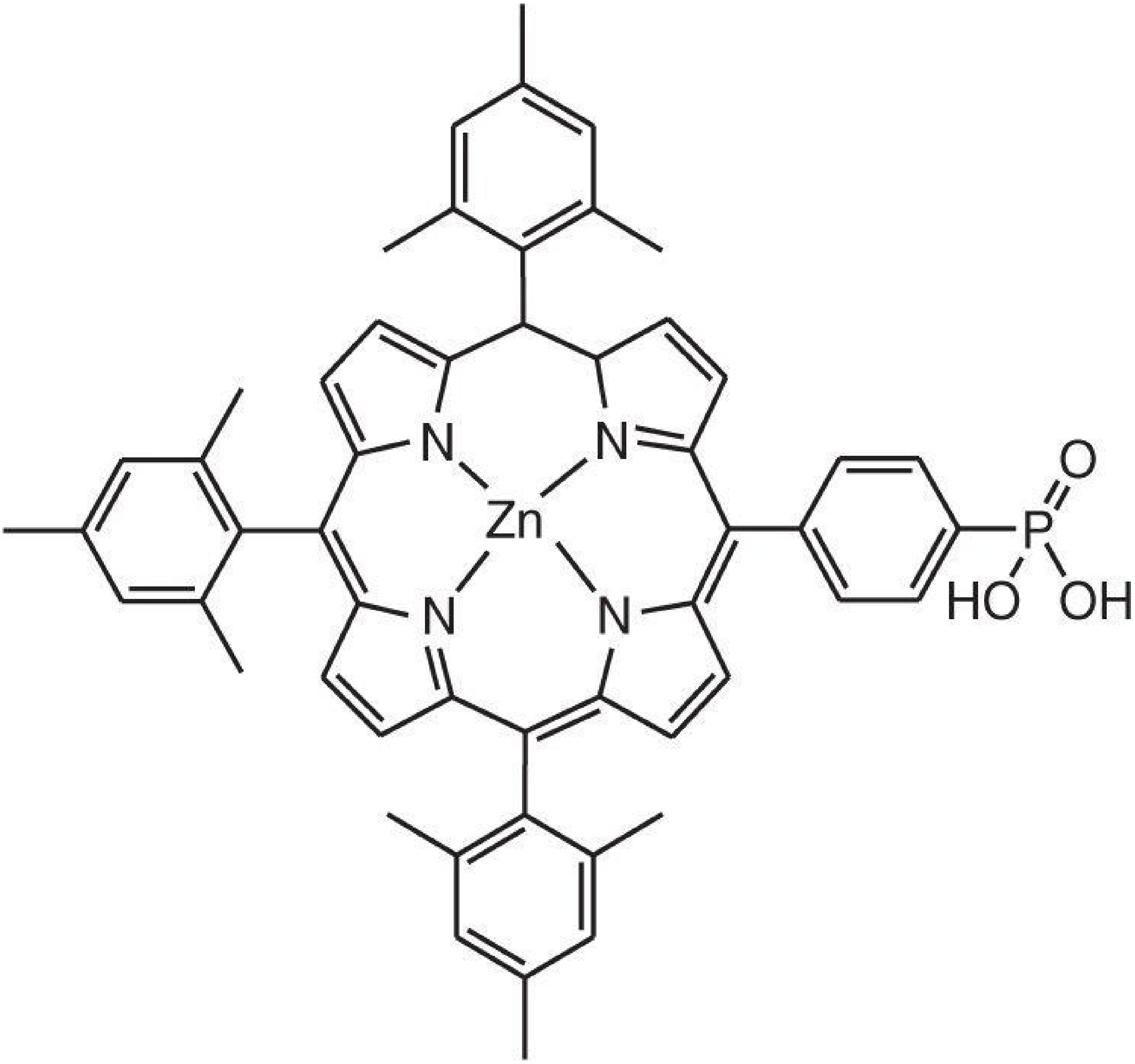


Figure 18.4

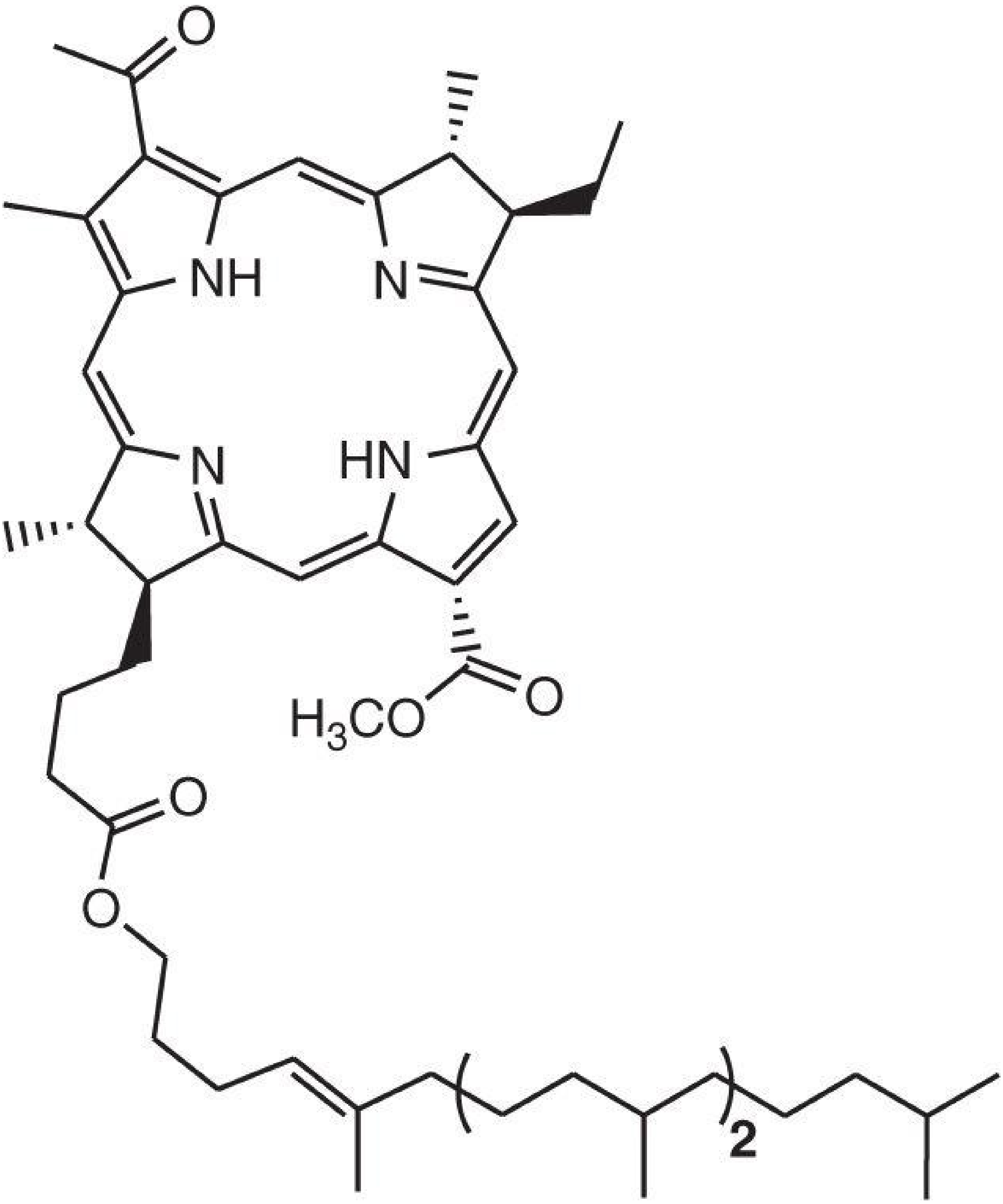
3. Lindsey[3] prepared phosphono-substituted porphyrins, (VII), that were designed to attach to metal-oxide surfaces for the production of solar cells and molecular memory devices. (See Fig. 18.5.)



(VII)

Figure 18.5

4. Kim[4] prepared bacteriochlorins, (VIII), that were useful in photodynamic therapy, luminescent compounds in flow cytometry, solar cells, light harvesting arrays, and molecular memory devices. (See Fig. 18.6.)



(VIII)

Figure 18.6

References

1. Chen-Yu Yeh et al., *Porphyrin-based photosensitizer dyes for dye-sensitized solar cells*, U.S. Patent 8,148,519 (April 3, 2012)

2. Jonathan S. Lindsey et al., *Synthetic route to ABCD-porphyrins*, U.S. Patent 8,304,561 (November 6, 2012)

3. Jonathan S. Lindsey et al., *Synthesis of phosphono-substituted porphyrin compounds for attachment to metal-oxide surfaces*, U.S. Patent 8,304,561 (November 6, 2012)

4. Han-Je Kim et al., *De novo synthesis of bacteriochlorins*, U.S. Patent 8,173,692 (May 8, 2012)

Chapter

19

Plasticizers

Diisoamyl Carbonate

Author	Matthieu Bandres et al.
Patent Title	***Plasticizer of natural origin for nail polish,*** U.S. Patent 8,187,576 (May 29, 2012)

Relevant Prior Patents by Author or Coauthors

Multiphase nail polish, U.S. Patent 7,645,444 (January 12, 2010)

Cosmetic composition for nails, free of phthalates, camphor and aromatic solvent, U.S. Patent Application 20030152535 (August 14, 2003)

Product Application

Non-irritating carbonate-based plasticizers are especially useful in cosmetic nail formulations since they form homogeneous, glossy, and fast-drying films when blended in nitrocellulose films.

Significance of Current Application

Phosgene has traditionally been used to prepare carbonates, but serious concerns about both personal safety in handling this reagent, as well as environmental toxicity, has provided the impetus to identify an alternative reagent. The current investigation has addressed these concerns by identifying phosgene replacement for synthesizing dialkyl carbonates in high yields. In this investigation, dimethyl carbonate was identified as a phosgene replacement reagent. In addition to being a considerably safer and non-toxic, the phosgene replacement reagent, dimethyl carbonate is inexpensively prepared and is readily available. Using this novel method, the required dialkyl carbonates were generated faster and in higher yields than when using phosgene. Furthermore, the formation of toxic organic-reaction waste products generated when using dimethylcarbonate to prepare dialkyl carbonates is limited to methyl alcohol, which can be recycled.

Product Formation

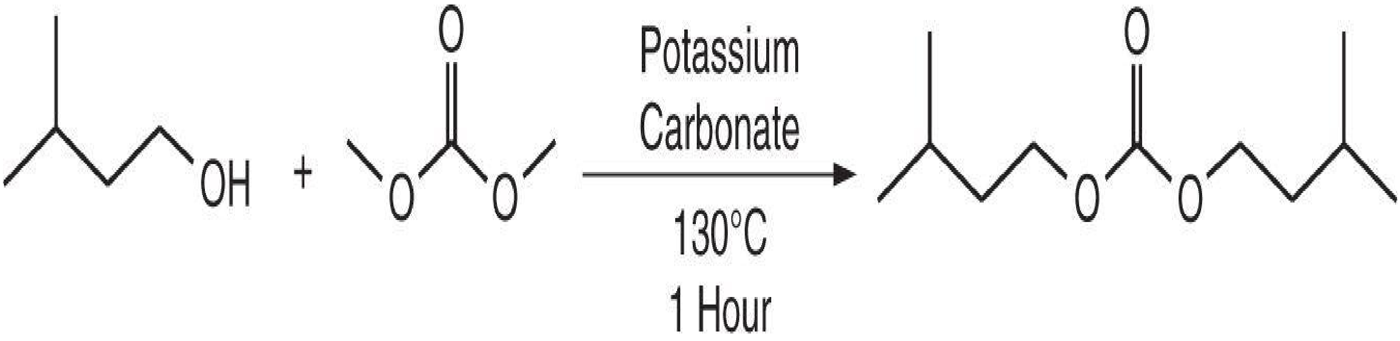


Figure 19.1

Experimental

1. Preparation of diisoamyl carbonate. A round-bottom flask was charged with isoamyl alcohol containing less than 1% water and dimethyl carbonate in a 5:1 stoichiometric ratio, respectively, then treated with a 1% catalytic amount of potassium carbonate. While vigorously stirring, the mixture was then heated to 130°C for 60 minutes with continuous removal of methanol. When methyl alcohol stopped distilling over, the reaction mixture was cooled, filtered, and the product was isolated in 75% yield.

Derivatives

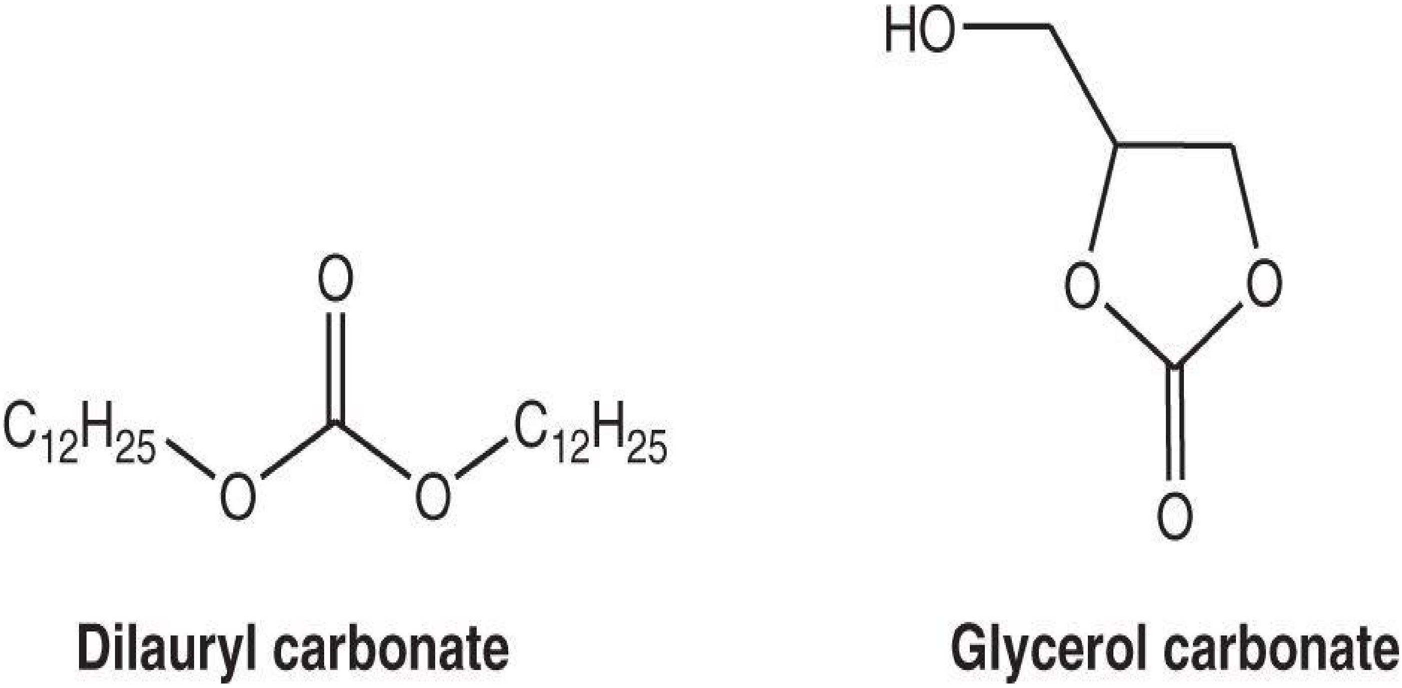
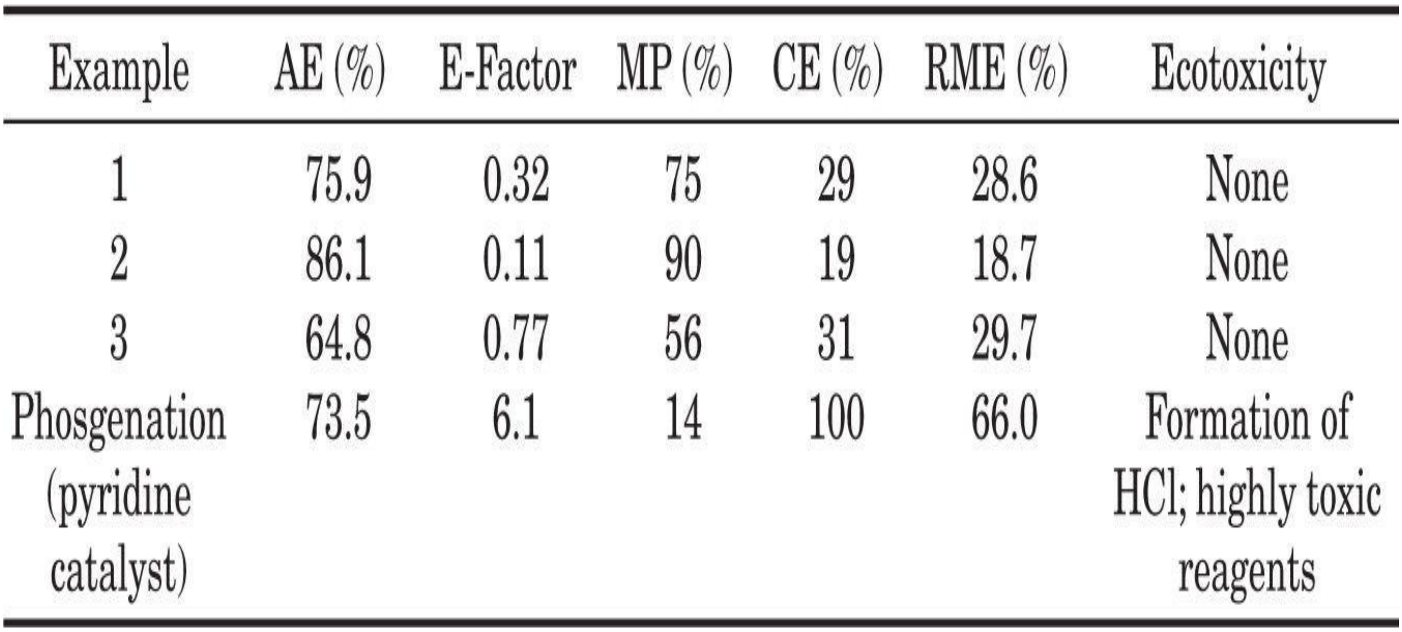


Figure 19.2

Testing

A. Evaluation of Carbonate Cleanliness When Using Diisoamylcarbonate Ecotoxicity factors were used to evaluate the safety for synthesizing diisoamylcarbonate using dimethyl carbonate and then compared to carbonylation methods using phosgene as a reagent. Testing results are provided in Table 19.1.

TABLE 19.1 Ecotoxicity factors associated with preparing dialkylcarbonates using dimethylcarbonate as the phosgene replacement reagent. In all categories, dialkylcarbonates prepared using dimethylcarbonate were preferred.



Example	AE (%)	E-Factor	MP (%)	CE (%)	RME (%)	Ecotoxicity
1	75.9	0.32	75	29	28.6	None
2	86.1	0.11	90	19	18.7	None
3	64.8	0.77	56	31	29.7	None
Phosgenation (pyridine catalyst)	73.5	6.1	14	100	66.0	Formation of HCl; highly toxic reagents

AE = atom economy

E-Factor = environmental factor

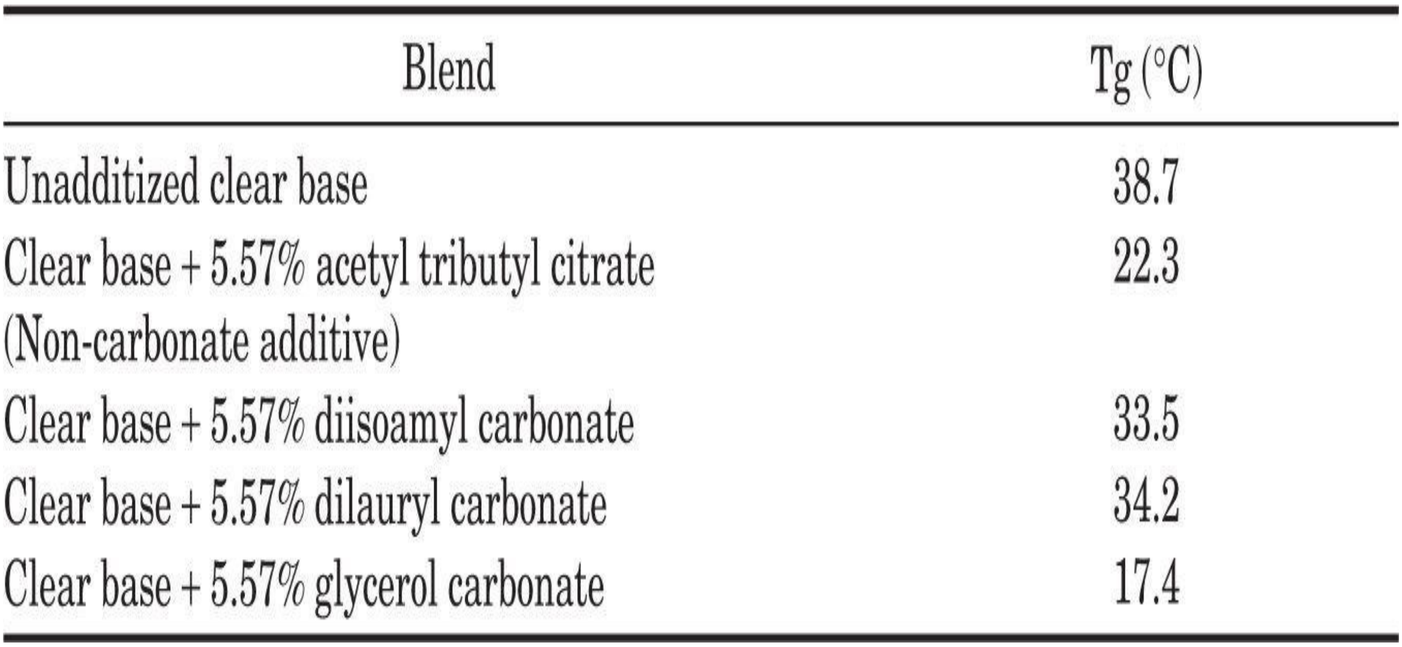
PM = mass productivity

CE = carbon efficiency

RME = reaction mass efficiency

B. Characterization of Plasticizing Capacity The glass-transition temperature of films using nitrocellulose as the clear base were measured by dynamic mechanical analysis, DMA. In this process, the glass-transition temperature, Tg, was used to characterize the mobility of polymer chains. Chains that moved efficiently provided polymers with a low glass-transition temperature, whereas chains with reduced or very limited mobility provided polymers with higher Tg values. The addition of selected dialkylcarbonate plasticizers was designed to lower Tg blends or polymers having a high Tg by separating polymer chains from one another, which resulted in an increase in the overall free volume. Testing results of the plasticizing effects of dialkyl carbonates prepared using dimethylcarbonate and then used to additize nitrocellulose are provided in Table 19.2.

TABLE 19.2 Effectiveness of dialkyl carbonate plasticizers prepared using dimethylcarbonate as a phosgene replacement reagent on the Tg of nitrocellulose clear base nail polish.

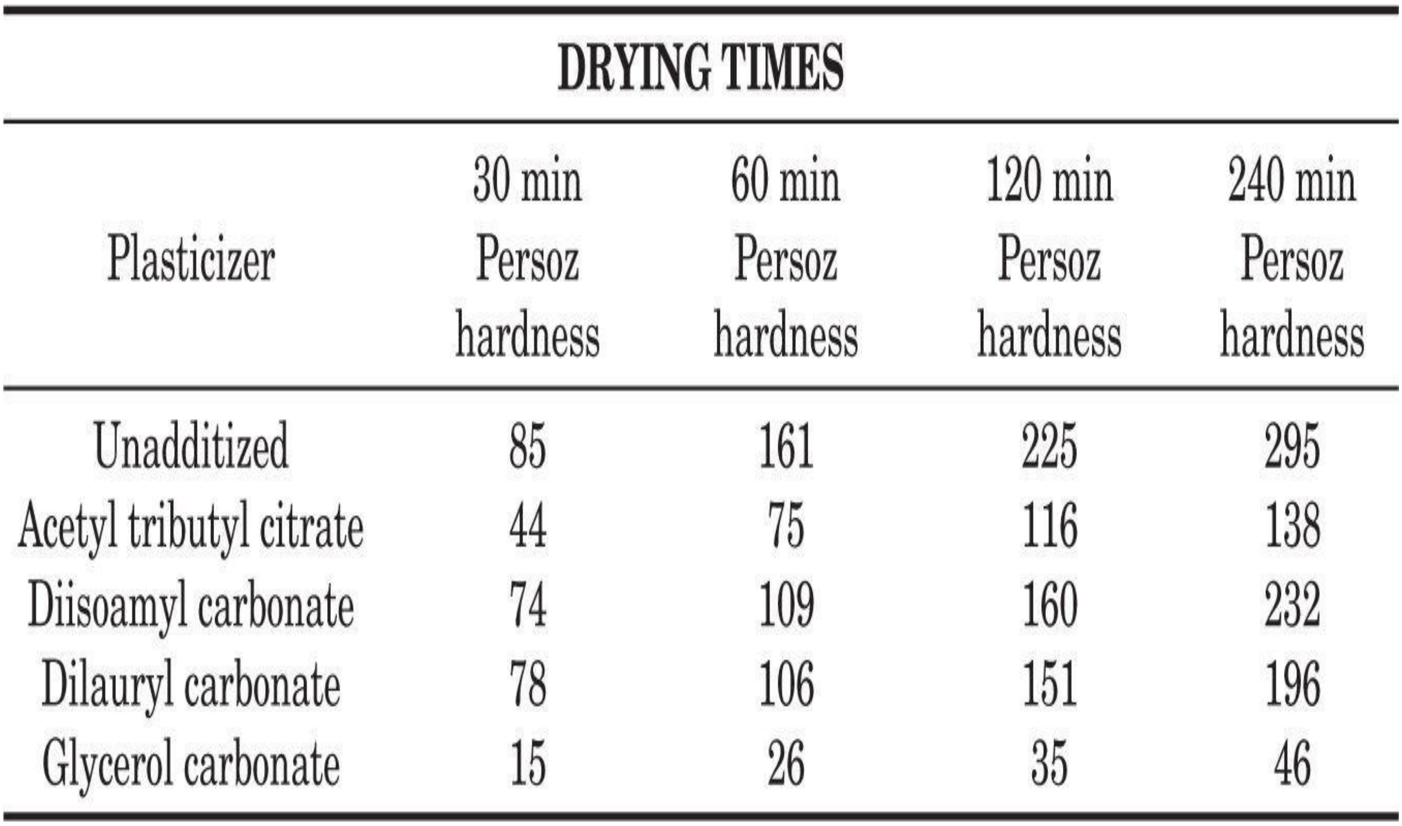


Blend	Tg (°C)
Unadditized clear base	38.7
Clear base + 5.57% acetyl tributyl citrate (Non-carbonate additive)	22.3
Clear base + 5.57% diisoamyl carbonate	33.5
Clear base + 5.57% dilauryl carbonate	34.2
Clear base + 5.57% glycerol carbonate	17.4

Persoz Hardness

Persoz hardness is designed to measure the softness or hardness of a film by measuring the number of oscillations required to stop a swinging pendulum. The damping time is directly proportional to the hardness of the film surface and was measured according the testing protocol described in ASTM D 4366 and EN ISO 1522 standards. Testing results for nitrocellulose films additized with dialkyl carbonates prepared using dimethylcarbonate as the phosgene replacement reagent and a non-carbonate citrate reference are provided in Table 19.3.

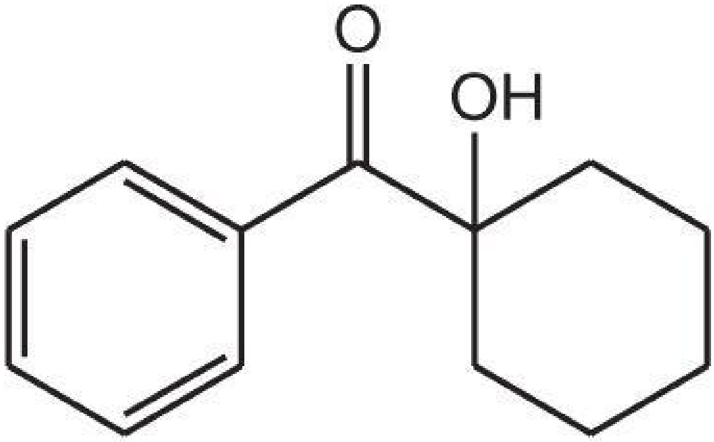
TABLE 19.3 Persoz hardness testing over time for selected dialkyl carbonates used as nitrocellulose plasticizers. Dialkyl carbonates were prepared using dimethyl carbonate as the phosgene replacement reagent. Lower values are preferred.



	DRYING TIMES			
Plasticizer	30 min Persoz hardness	60 min Persoz hardness	120 min Persoz hardness	240 min Persoz hardness
Unadditized	85	161	225	295
Acetyl tributyl citrate	44	75	116	138
Diisoamyl carbonate	74	109	160	232
Dilauryl carbonate	78	106	151	196
Glycerol carbonate	15	26	35	46

Notes and Observations

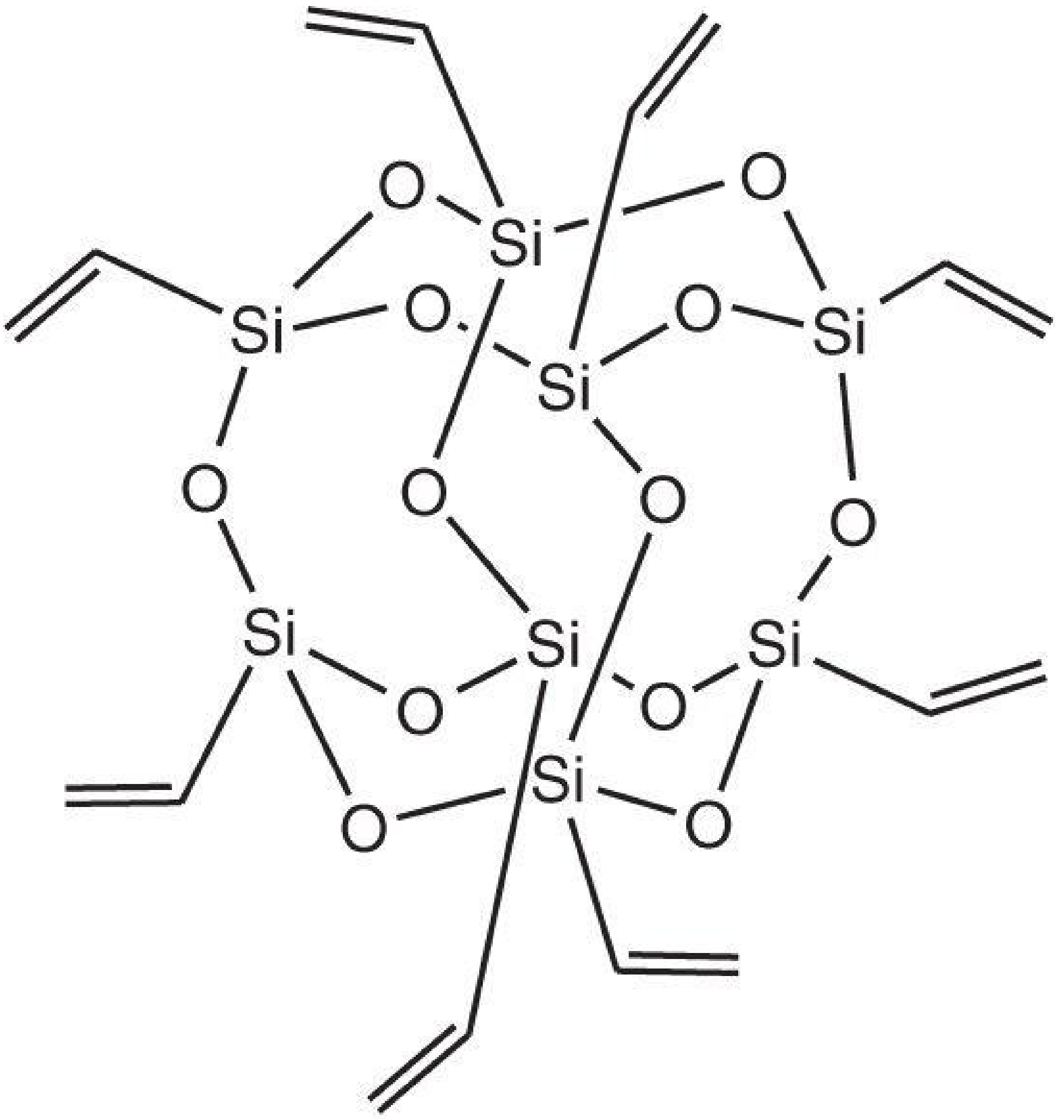
1. Kojima[1] used renewable oligomeric ethylene glycol having an Mn ~ 1,500 Daltons as the plasticizer for nitrocellulose-containing nail polishes. Di(trimethylolpropane) tetraacrylate was also included in the formulation as a self-cross-linkable photocuring agent.
2. Nail-coating compositions prepared by Haile[2] containing nitrocellulose as the gel base were plasticized with renewable sucrose acetate or camphor. Radiation-curable formulations were also prepared using 2-hydroxylethyl methacrylate containing the photosensitizer 1-hydroxycyclo-hexyl phenyl ketone, (I). (See Fig. 19.3.)



(I)

Figure 19.3

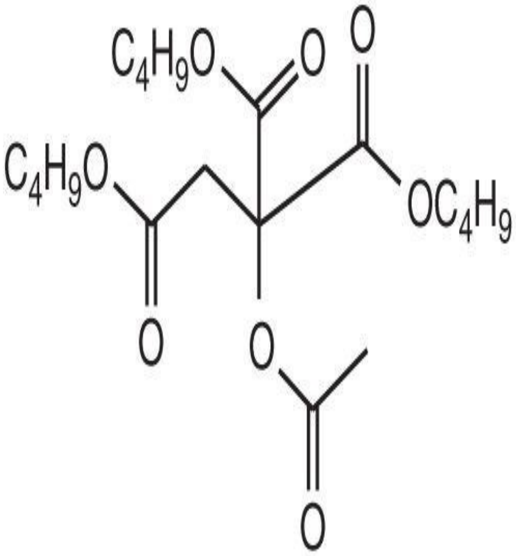
3. Maitra[3] prepared non-irritating lip gloss formulations consisting of renewable mammalian keratinous tissue and cross-linkable polyhedral oligosilsequioxanes, (II). Unspecified organic-inorganic hybrid nanocomposites were also added to the formulation to increase lip gloss. (See Fig. 19.4.)



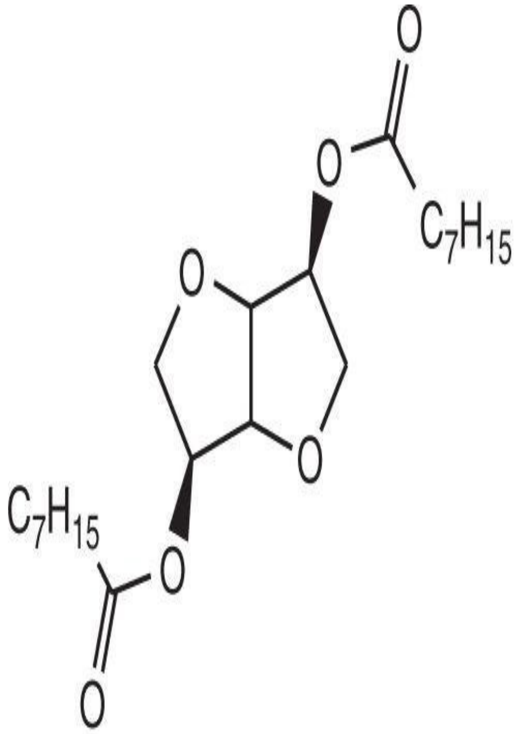
(II)

Figure 19.4

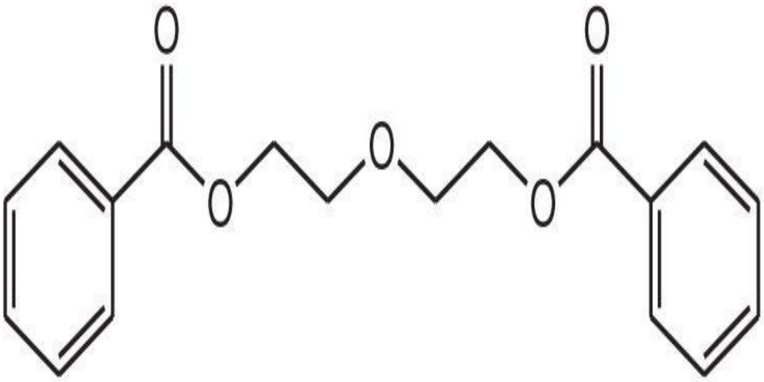
4. Nouguerede[4] prepared nail formulations containing nitrocellulose as the gel base that were additized with renewable acetyl tributyl citrate, (III), or isosorbide dioctanoate, (IV). Both renewable plasticizers were considerably less toxic and less volatile than formulations containing either diethylene glycol dibenzoate, (V), or glyceryl tribenzoate, (VI). (See Fig. 19.5.)



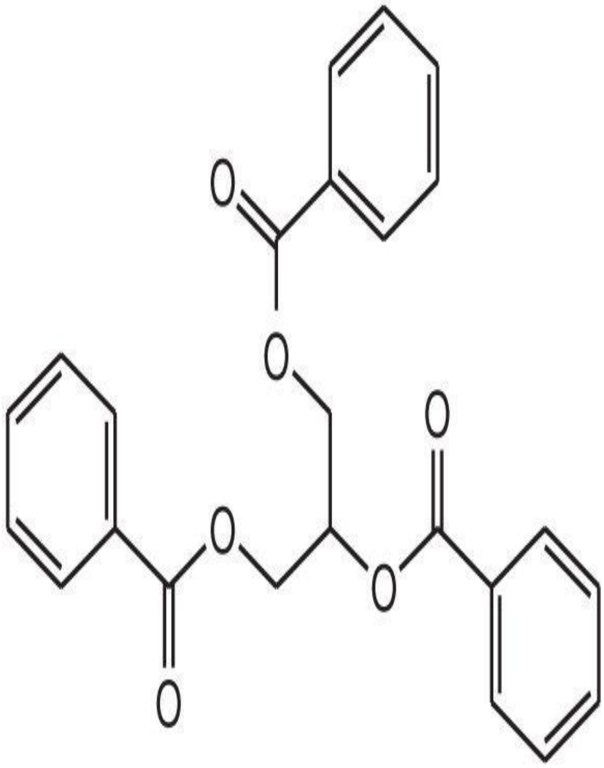
(III)



(IV)



(V)



(VI)

Figure 19.5

References

1. Kazuhiro Kojima et al., *Curable resin composition for covering a fingernail or artificial fingernail*, U.S. Patent Application 20120276028 (November 1, 2012)

2. Danny Lee Haile et al., *Compositions for removable gel applications for nails and*

methods of their use, U.S. Patent Application 20120199151 (August 9, 2012)

3. Prithwiraj Maitra et al., *Cosmetic nanocompositions based on in situ cross-linked POSS materials*, U.S. Patent Application 20120128746 (May 24, 2012)

4. Olivier Nouguerede et al., *Cosmetic composition for nails and the use of an isosorbide derivative*, U.S. Patent Application 20120003166 (January 5, 2012)

Chapter

20

Polymers

Biodegradable Poly(β-Amino Esters)

Author Robert S. Langer et al.

Patent Title ***Biodegradable poly(β-amino esters) and uses thereof,*** U.S. Patent 8,287,849 (October 16, 2012)

Relevant Prior Patents by Author or Coauthors

Biodegradable shape-memory polymeric sutures, U.S. Patent 8,303,625 (November 6, 2012)

*Biodegradable poly(*β*-amino esters) and uses thereof*, U.S. Patent RE43,612 (August 28, 2012)

Biodegradable elastomers, U.S. Patent 8,143,042 (March 27, 2012)

*End-modified poly(*β*-amino esters) and uses thereof*, U.S. Patent 8,071,082 (December 6, 2011)

N-substituted monomers and polymers, U.S. Patent 8,034,365 (October 11, 2011)

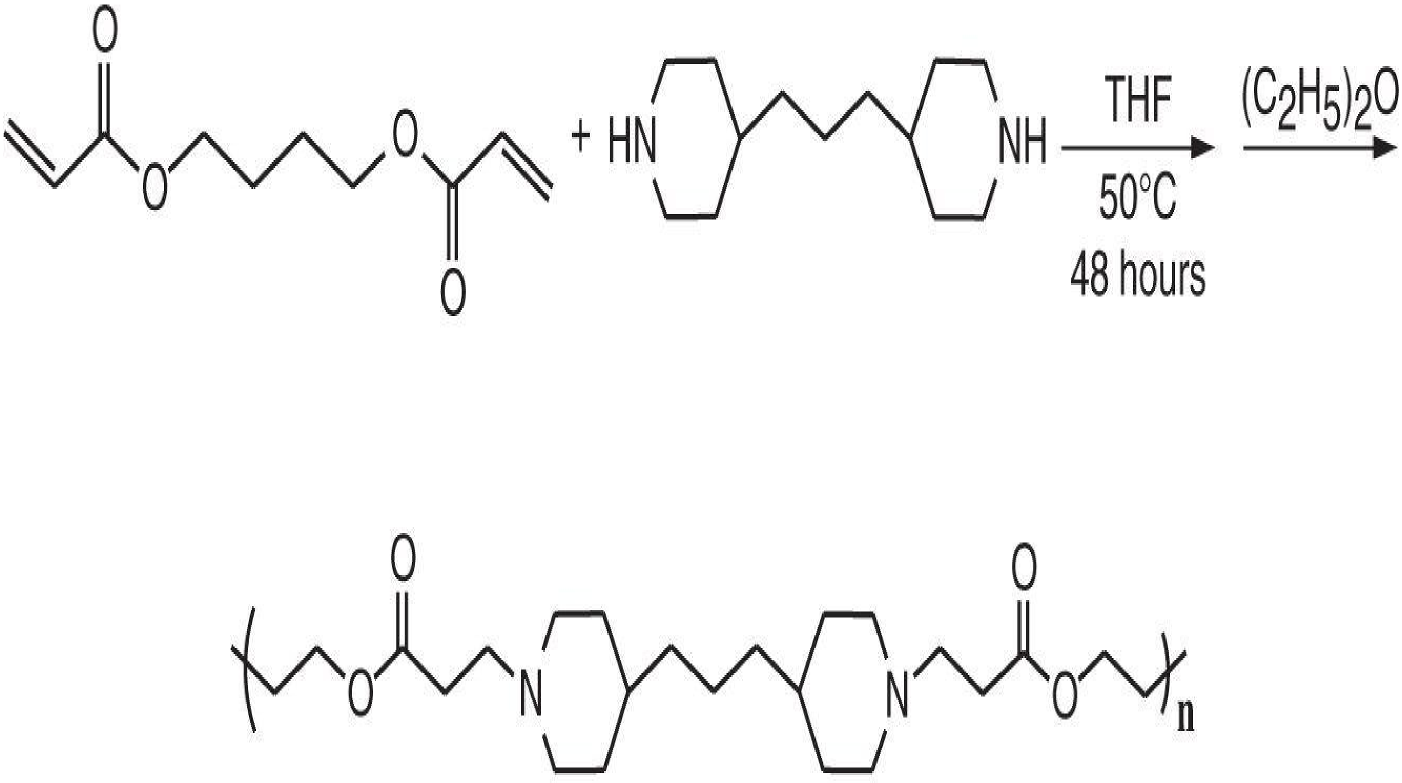
Product Application

Three non-cytotoxic biodegradable poly(β-amino esters) were prepared and then converted into nanoparticles. Poly(β-amino esters) nanoparticles were then used to both encapsulate and act as drug delivery agents for RNA and DNA polynucleotides. This drug delivery method was determined to be effective in the treatment of malignant tumors present in humans.

Significance of Current Application

This investigation describes a method for delivering nucleotide-based drugs containing DNA and RNA by encapsulating them into poly (β-amino ester) nanoparticles. The method for preparing these drug delivery agents entails a single-step preparation of poly(β-amino esters) reacting piperazine foaming bis(acrylate esters). This process can be used to generate a wide variety of poly(β-amino esters) of varying molecular weights in high yields. All poly(β-amino esters) prepared were completely biodegradable at physiological pH and did not present health hazards when used over extended time periods. Moreover, the cytotoxicity profiles of encapsulated poly-nucleotides contained in a poly(β-amino ester) matrix were effective against the NIH 3T3 cell line. Clinical studies indicated that experimental poly(β-amino esters) containing encapsulated DNA and RNA polynucleotides also were effective in treating fast-growing malignant tumors present in human beings. Finally, aqueous decomposition kinetic studies of poly(β-amino esters) under either physiological or highly acidic or basic conditions indicate that non-toxic metabolites were consistently generated.

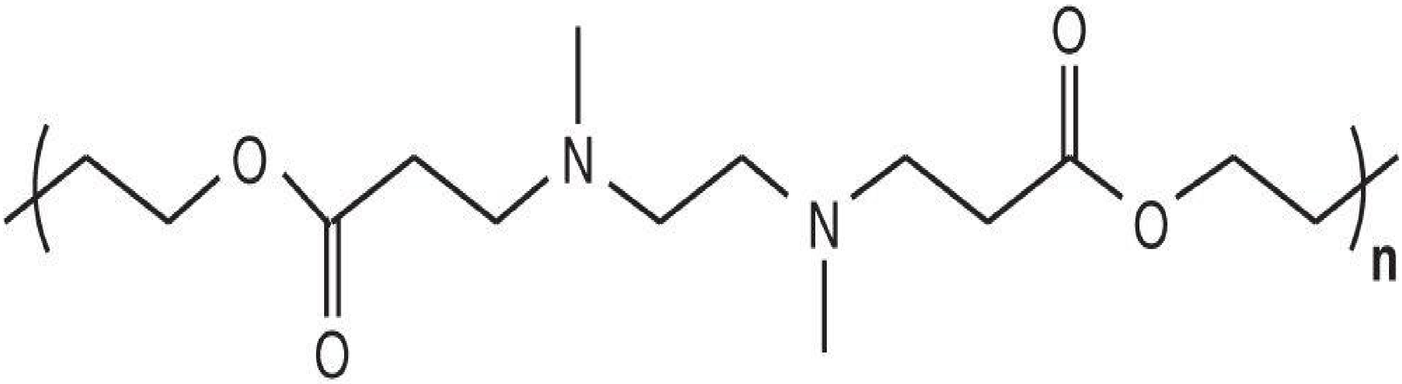
Product Formulation



(I)

Figure 20.1

Poly(β-amino esters) Derivatives



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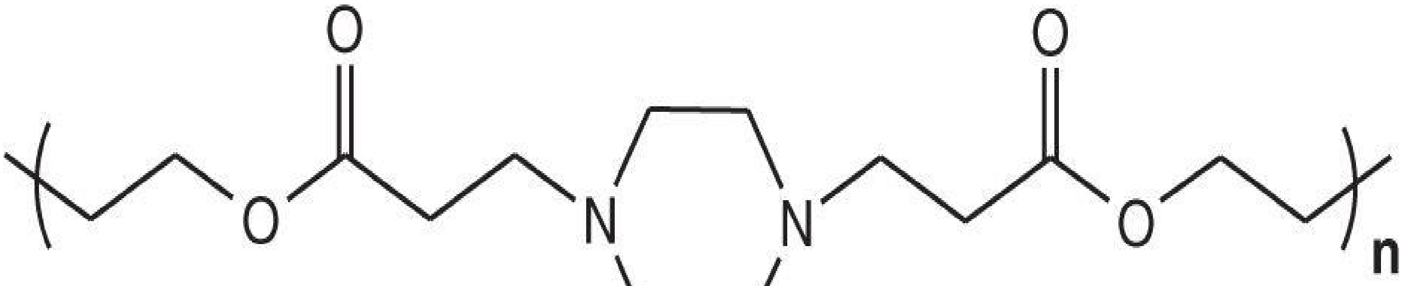


(III)

Figure 20.2

Experimental

1. Preparation of poly(piperizine-co-1,4-butanediol diacrylate), (I). In a typical experiment, 0.750 g of 1,4-butanediol diacrylate and 3.78 mmol of 1,3-di (4-piperazinyl) propane were weighed into two separate glass vials and dissolved in 5 mL of THF. The solution containing 1,3-di(4-piperazinyl) propane was then added to the 1,4-butanediol diacrylate vial using a pipette, and the mixture was stirred at 50°C for 48 hours. The reaction solution was cooled to ambient temperature and then slowly dripped into vigorously stirring diethyl ether. After collecting the product by filtration and drying the polymer under vacuum, the polymer was isolated. Structural characterization is provided below.

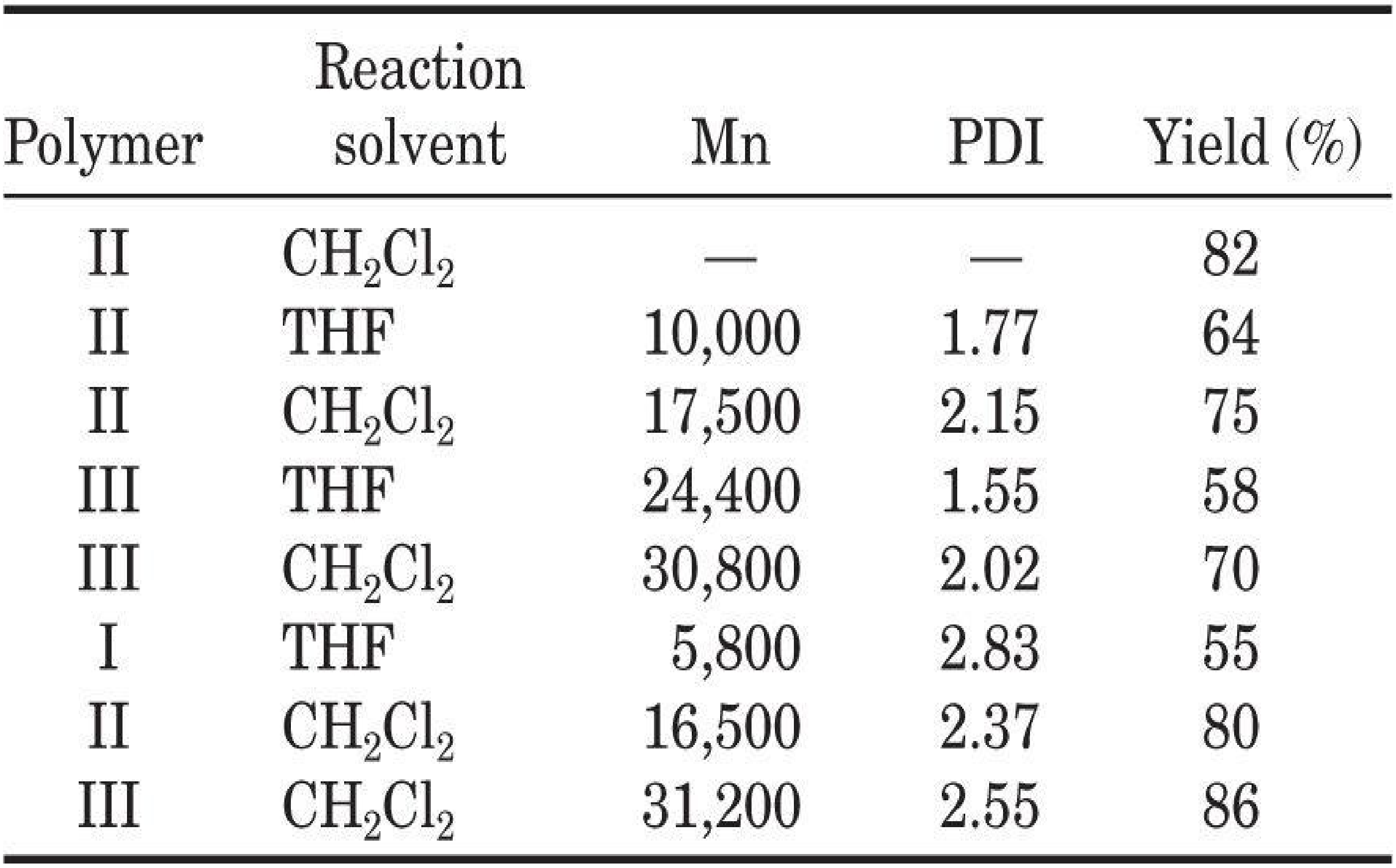
^{1}**H-NMR** ($CDCl_3$ at 300 MHz) δ 4.11 (br t, 4H), 2.75 (br t, J = 7.05 Hz, 4H), 2.53 (br s, 4H), 2.50 (br t, (obsc), J = 7.20 Hz, 4H), 2.28 (br s, 6H), 1.71, (br m, 4H)

^{13} **C-NMR** ($CDCl_3$ at 75.47 MHz) δ 172.55, 64.14, 55.31, 53.39, 42.47, 32.54, 25.53

Testing

A. Molecular Weights Molecular weight profiles for poly(β-amino esters) (I) through (III) were determined by GPC and are provided in Table 20.1.

TABLE 20.1 Molecular weight profiles for poly (β-amino esters) (I) through (III).



Polymer	Reaction solvent	Mn	PDI	Yield (%)
II	CH_2Cl_2	—	—	82
II	THF	10,000	1.77	64
II	CH_2Cl_2	17,500	2.15	75
III	THF	24,400	1.55	58
III	CH_2Cl_2	30,800	2.02	70
I	THF	5,800	2.83	55
II	CH_2Cl_2	16,500	2.37	80
III	CH_2Cl_2	31,200	2.55	86

B. Polymer Degradation Studies Degradation studies were conducted using the hydrochloride salts of poly(β-amino esters) (I) through (III). Initially the salts were dissolved in water to obtain a concentration of 5 mg/mL. Aqueous degradation studies of each salt was then conducted in water buffered at either pH 5.1 using acetate buffer or at pH 7 using a HEPES buffer. Samples were then incubated at 37°C on a mechanical rotator and 1-mL aliquots periodically removed. Samples' aliquots removed were immediately frozen in liquid nitrogen, lyophilized, and then analyzed by GPC.

C. Cytotoxicity Assays Cytotoxicity profiles of poly(β-amino esters) hydrochloride salts (I) through (III) containing encapsulated polynucleotides were conducted using the MTT/thiazolyl blue-dye reduction with the NIH 3T3 cell line. In a typical analysis, cells were incubated with a selected poly(β-amino esters) hydrogen chloride salt. It was observed that poly(β-amino esters) hydrogen chloride salts remained completely viable relative to control the polymer concentrations of up to 100 mg/mL. These results indicate excellent cytotoxicity profiles against the NIH 3T3 cell line for the experimental polymers.

Testing Results

A. Molecular Weights of poly(β-amino esters) (I) through (III)

B. Polymer Degradation Studies Experimental poly(β-amino esters) (I) through (III) were specifically designed to degrade by hydrolytic cleavage of the ester bonds in the polymer backbones. A concern surrounding the overall stability and biocompatibility of these materials, however, was the potential for a degradation route through a retro-Michael reaction pathway under physiological conditions. The basis for this concern was that since these copolymers had been prepared using the Michael reaction it was conceivable that a retro-Michael reaction degradation pathway could potentially occur under acidic conditions. This concern was further prompted by the observation that poly(β-amino esters) prepared in this investigation would be subjected to a physiological pH of between 5.0 and 5.5 once they were within the endosomal vesicles of cells during transfection. To address this concern it was determined that exposing poly(β-amino esters) salts (I) through (III) to pH conditions of pH < 3 or pH > 12 did not result in a retro-Michael degradation pathway. No spectroscopic evidence for a retro-Michael reaction under these harsh conditions was observed for poly(β-amino esters) salts (I) through (III).

C. Cytotoxicity Assays The cytotoxicity profiles of poly(β-amino-esters) (I) through (III) containing encapsulated polynucleotides was particularly effective against the NIH 3T3 cell line.

Notes and Observations

1. Zugates[1] end-modified a selected poly(β-amino-ester), (IV), to extend its usefulness in both medical and non-medical applications. The preparation of the end-modified poly(β-amino-ester), (V), using propylamine is illustrated in Eq. 1. (See Fig. 20.3.)

Eq. 1

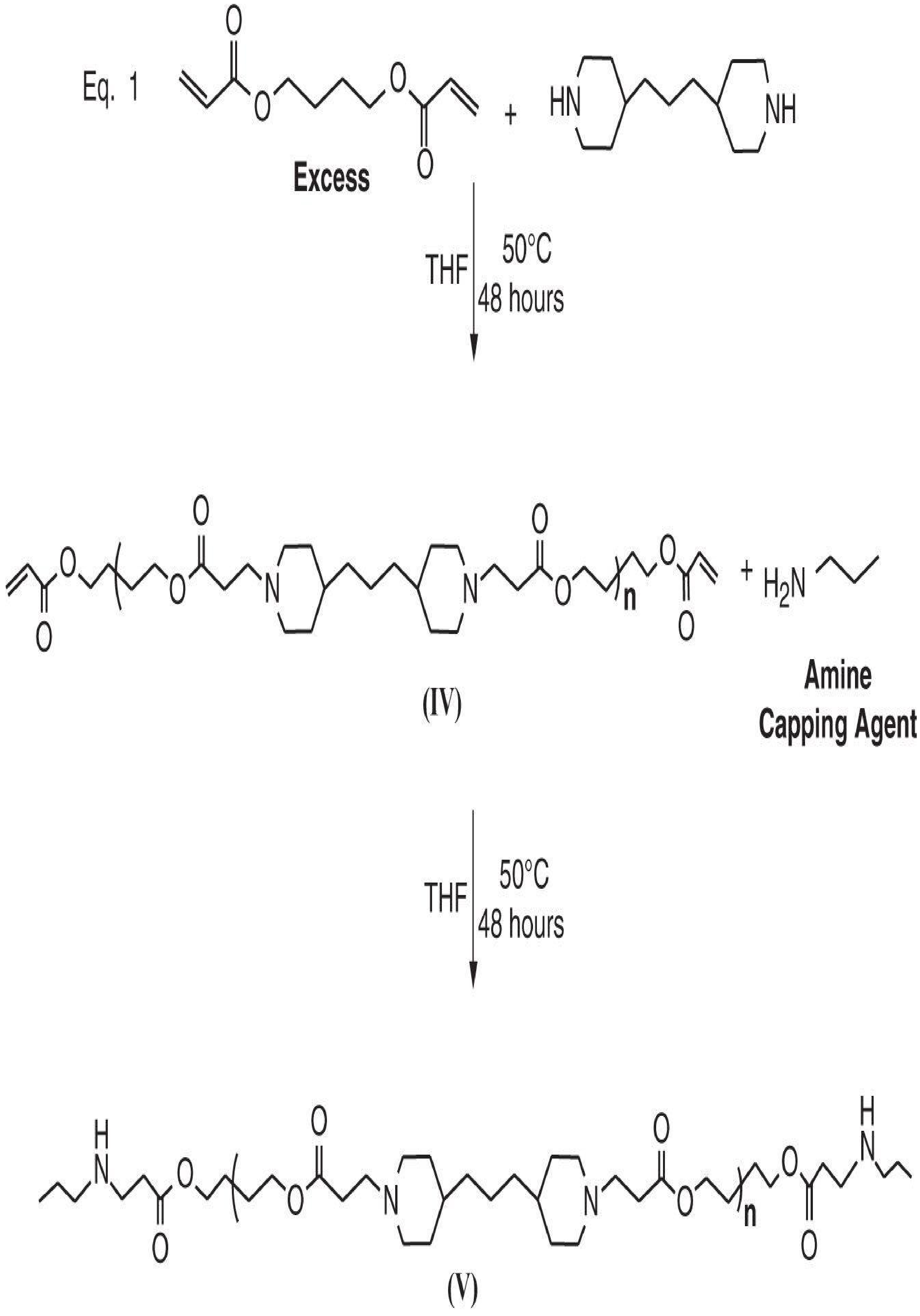
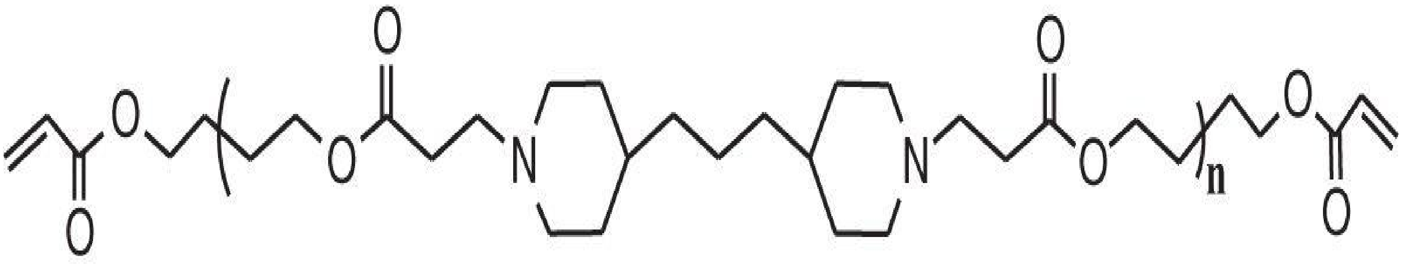
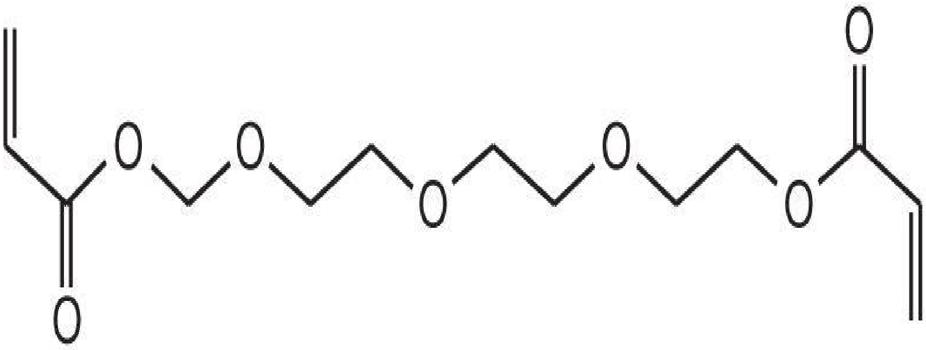

Excess
HN
NH
+
THF
50°C
48 hours
O
N
n
H_2N
Amine
Capping Agent
(IV)
H
(V)

Figure 20.3

2. Anderson[2] prepared blends of acrylate-terminated poly(β-amino ester), (IV), and oligomeric ethylene glycol diacrylate, (VI), which were both heat and ultraviolet crosslinkable as well as being biodegradable under physiological conditions. Polymers prepared from this investigation were extremely versatile and were used as DNA and RNA delivery agents, plastics, coatings, and adhesives. Crosslinked poly(β-amino-esters) exhibited a wide range of degradation times, mass-loss profiles, and an elastic modulus in the range of 4 MPa and 350 MPa. (See Fig. 20.4.)



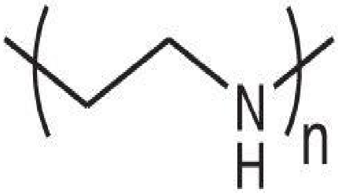
(IV)



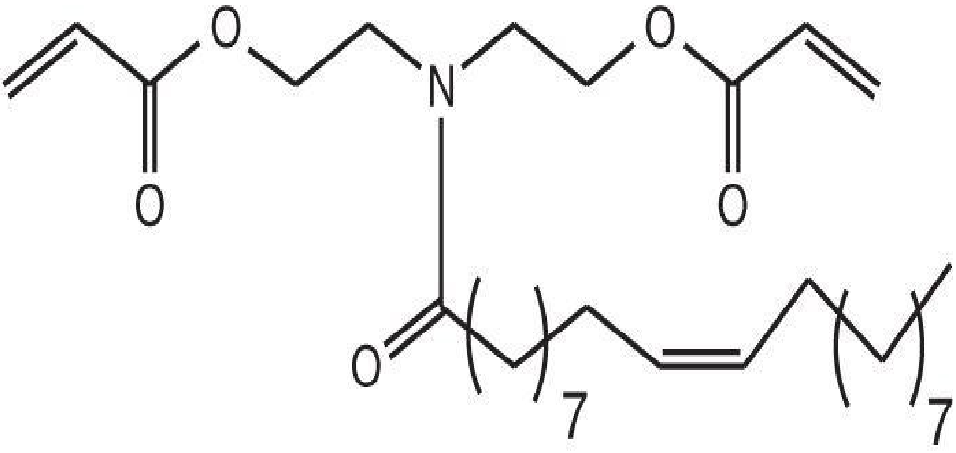
(VI)

Figure 20.4

3. Zhao[3] prepared cationic copolymers containing polyethylenimine, (VII), having an Mn of approximately 600 daltons with a relatively hydrophobic group, (VIII), which was effective as a drug delivery agent for bioactive agents such as DNA, RNA, oligonucleotides, proteins, and peptides to cells. (See Fig. 20.5.)



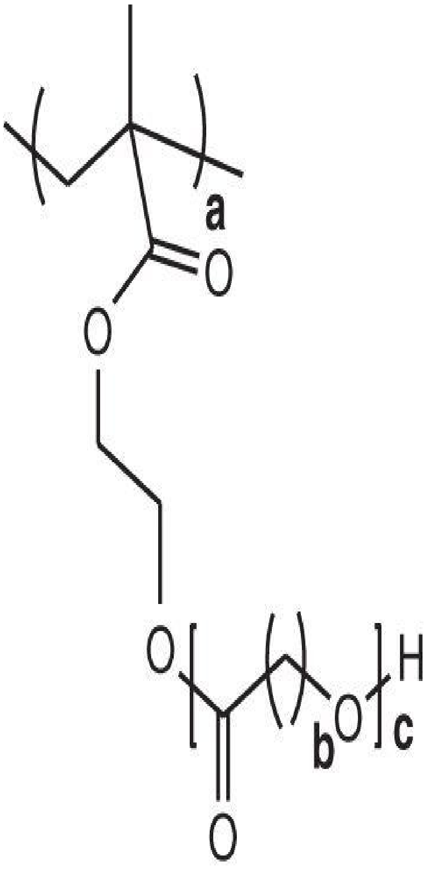
(VII)



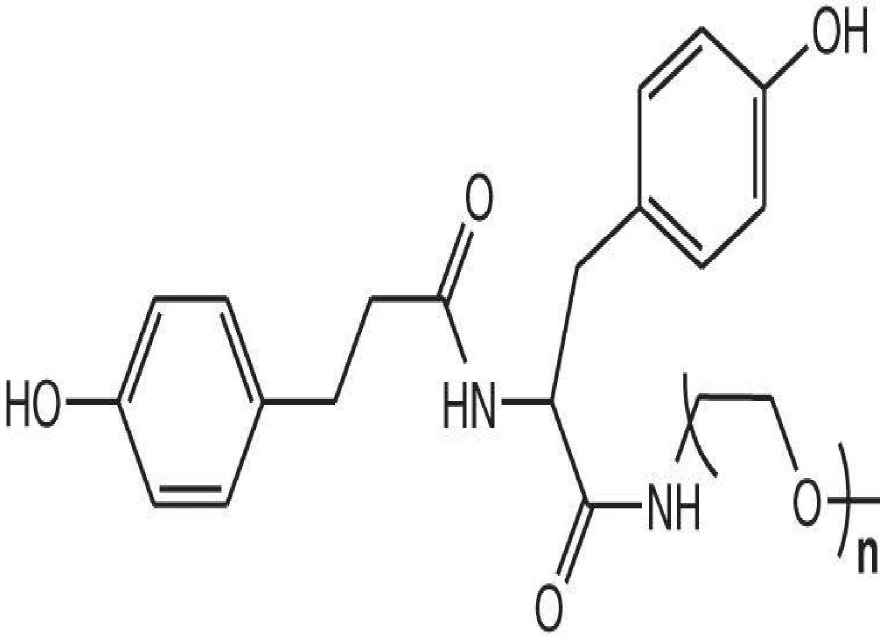
(VIII)

Figure 20.5

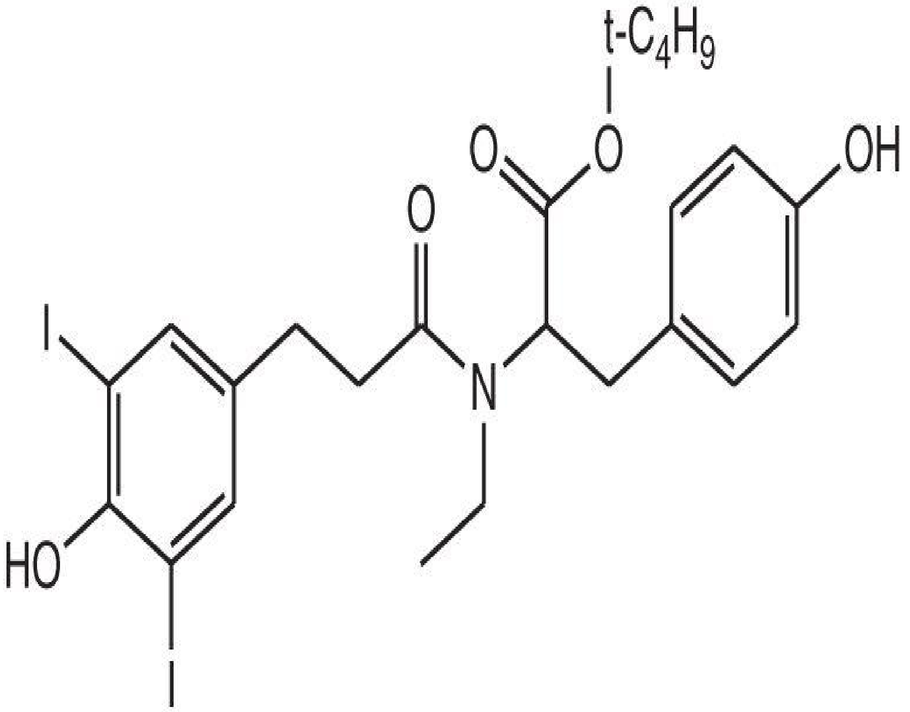
4. Baluca[4] prepared a series of both N-substituted and unsubstituted monomers and polymers that were used in medical applications as stents. In the first instance, poly[(hydroxyethylmethacrylate)-g-caprolactone], (IX), was prepared, but its high crystallinity limited its use. When it was modified by transesterification to introduce bulky aromatic amide substituents, (X) and (XI), however, the crystallinity was substantially diminished. The low-crystal content polymer was then converted into polyurethane stents by condensing it with aliphatic diisocyanates. (See Fig. 20.6.)



(IX)



(X)



(XI)

Figure 20.6

References

1. Gregory T. Zugates et al., *End-modified poly(*β*-amino esters) and uses thereof*, U.S.

Patent 8,071,082 (December 6, 2011)

2. Daniel Griffith Anderson et al., *Crosslinked, degradable polymers and uses thereof,* U.S. Patent Application 20080145338 (June 19, 2008)

3. Gang Zhao et al., *Biodegradable cationic polymers*, U.S. Patent 8,258,235 (September 4, 2012)

4. Ernest G. Baluca, *N-Substituted monomers and polymers*, U.S. Patent 8,034,365 (October 11, 2011)

Biodegradable Polyesters

Author	Kazuhiko Inoue et al.
Patent Title	***Biodegradable resin, biodegradable resin composition, biodegradable molded object, and process for producing biodegradable resin,*** U.S. Patent 8,258,254 (September 4, 2012)

Relevant Prior Patents by Author or Coauthors

Nonvolatile memory element, manufacturing method thereof, and nonvolatile semiconductor apparatus using the nonvolatile memory element, U.S. Patent 8,022,502 (September 20, 2011)

Product Application

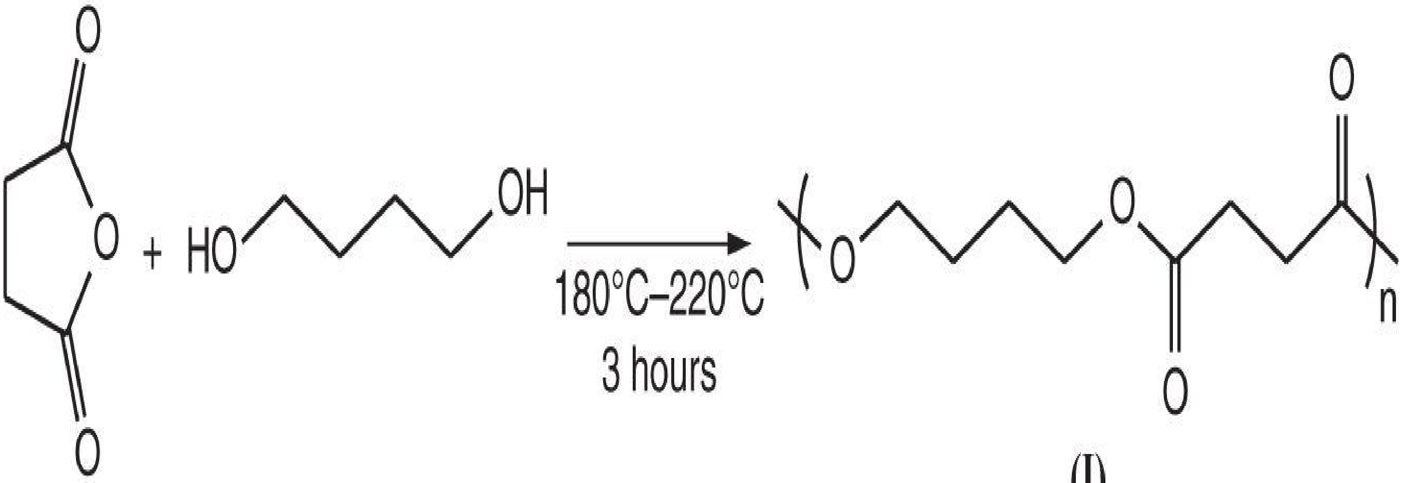
A polyester resin or plastic composition was prepared that can be efficiently recycled and that has excellent heat resistance needed for mold processing into beverage containers.

Significance of Current Application

In order to increase the applications of plastics used in industrial applications, it is essential that plastics can be easily shaped, are lightweight, inexpensive, durable, and have good heat resistance. To achieve all of these requirements, however, plastics contain some degree of crosslinking. Once crosslinked, however, plastics or polymers become less biodegradable and less bio-decomposable. Moreover, these materials become extremely difficult to recycle since they are usually thermosets and cannot be efficiently dry-blended with other recycled plastics, even at elevated temperatures. As a result, they are typically relegated for use as fuel in combustion furnaces or placed into landfills. Combustion of crosslinked plastics is especially undesirable since they create serious air pollution concerns. The current investigation addresses this problem of recycling thermosets by synthesizing plastic materials that behave as thermosets on the one hand but remain both biodegradable and bio-decomposable.

Product Formation

1. Preparation of poly(succinic acid-co-1,4-butanediol) ***(Composition A1)***.The unadditized polyester, poly(succinic acid-co-1,4-butanediol), (I) was prepared having an Mn ~ 3,000 daltons. (See Fig. 20.7.)

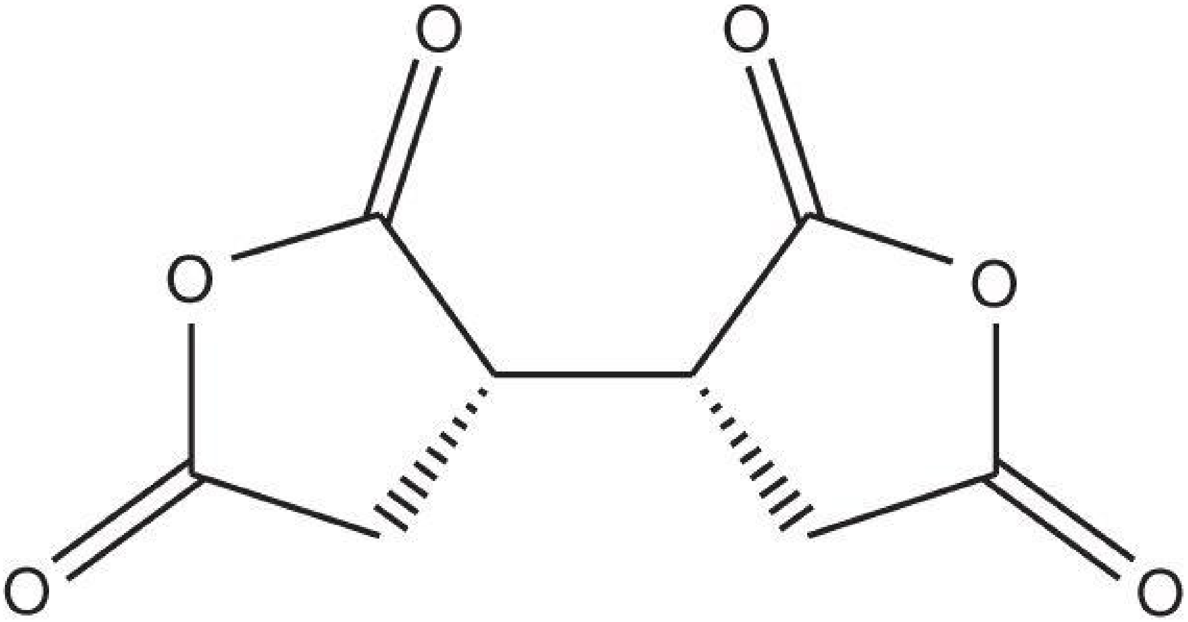


(I)

Poly(succinic acid-co-1,4-butanediol)

Figure 20.7

2. Preparation of poly(succinic acid-co-1,4-butanediol) melt-kneaded with butanetetracarboxylic dianhydride *(Composition 1)*. A blend consisting of 100 g of Composition A1 and 6.6 g of 1,2,3,4-butanetetra-carboxylic dianhydride was melt-kneaded at 200°C as indicated in (II). (See Fig. 20.8.)

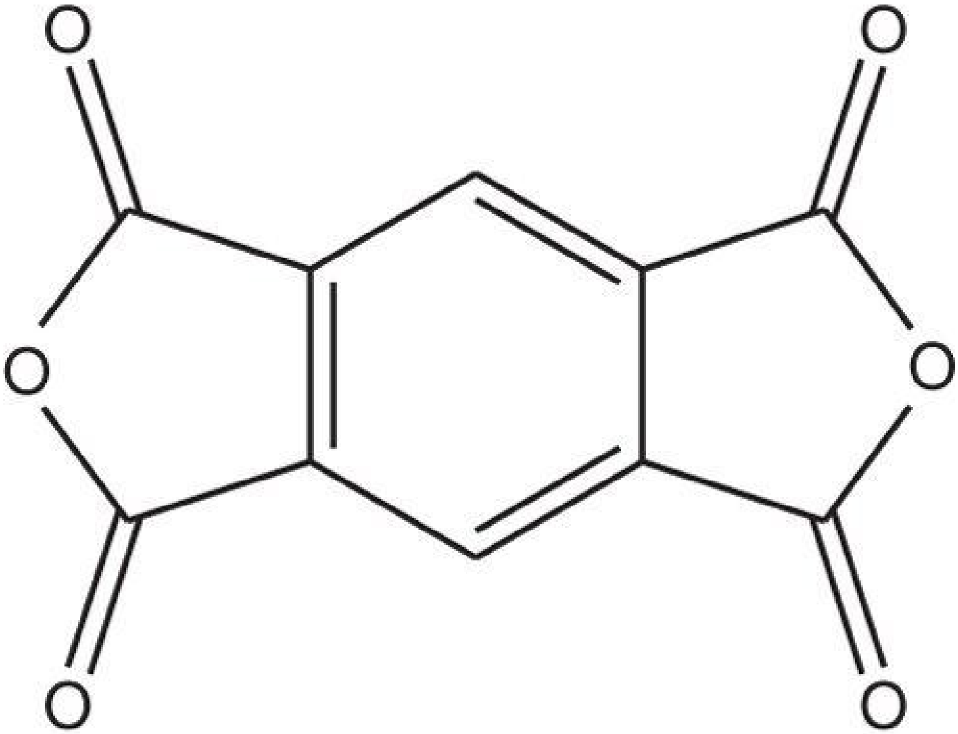


(II)

Figure 20.8

3. Preparation of poly(succinic acid-co-1,4-butanediol) melt-kneaded with butanetetra carboxylic dianhydride then melt-kneaded with pyromellitic anhydride *(Composition 2)*.

A blend consisting of 100 wt% of Composition A1 and 7.3 wt% of pyromellitic anhydride was melt-kneaded at 200°C as indicated in (III). (See Fig. 20.9.)

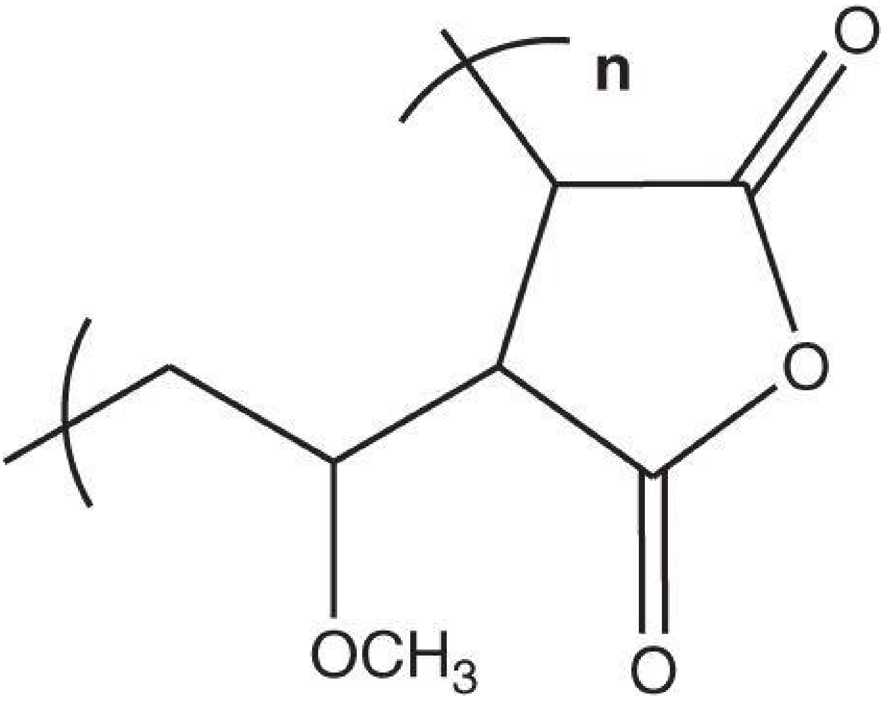


(III)

Pyromellitic anhydride

Figure 20.9

4. Preparation of poly(succinic acid-co-1,4-butanediol) melt-kneaded with poly(methyl vinyl ether)-co-maleic anhydride *(Composition 3)*. A blend consisting of 100 wt% of Composition A1 poly(succinic acid-co-1,4-butanediol) and 0.4 wt% of methyl vinyl ether-maleic anhydride copolymer having an Mn ~ 900,000 daltons melt-kneaded at 200°C as indicated in (IV). (See Fig. 20.10.)



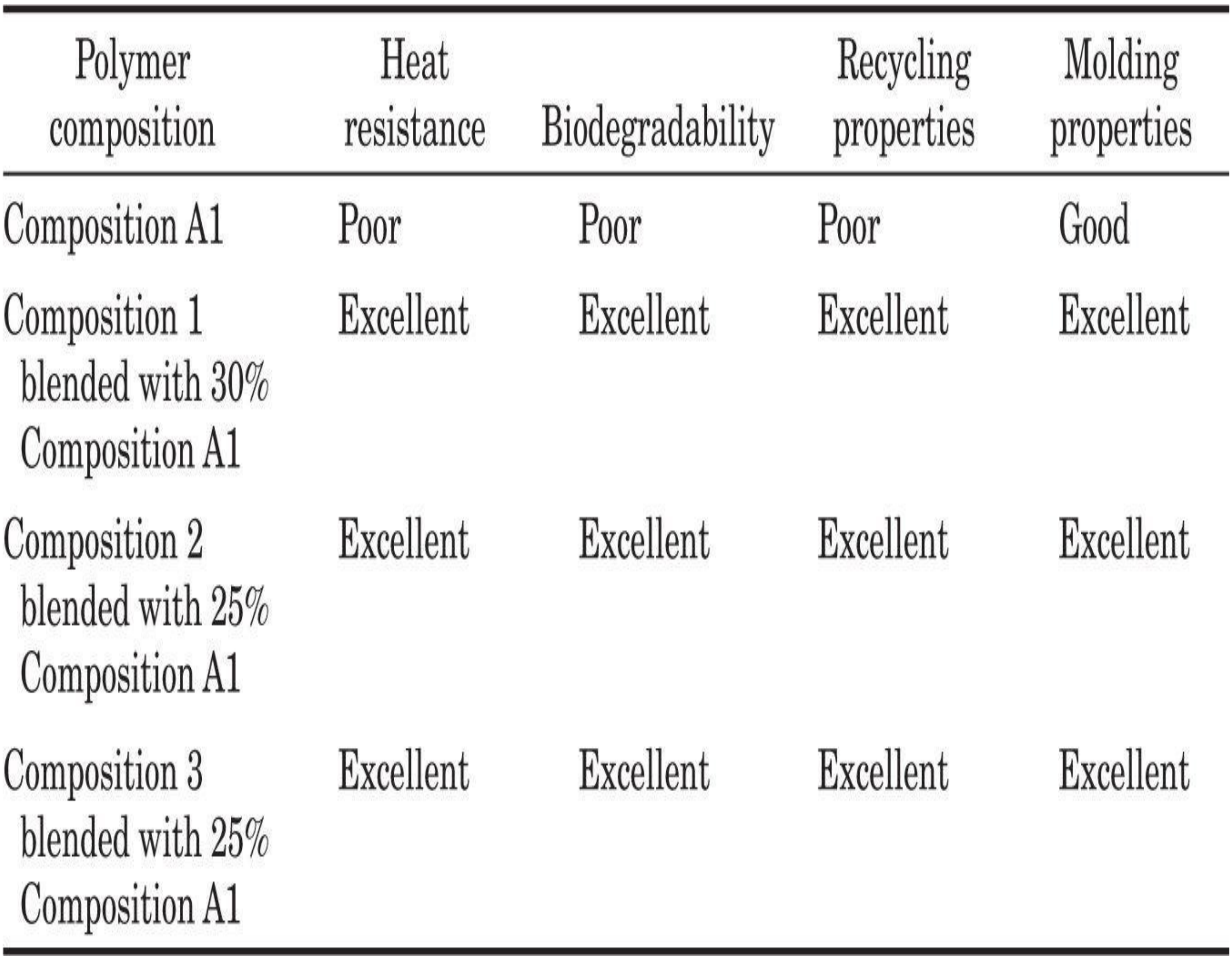
(IV)

Figure 20.10

Experimental

1. Preparation of Composition A1. A large reaction kettle equipped with a stirrer, fractional condenser, thermometer, and nitrogen-introducing-tube was charged with 716 g of succinic acid and 613 g of 1,4-butanediol and heated to 180°C–220°C for 3 hours. The reaction mixture was then further heated to 180°C–220°C under reduced pressure for 3 hours to remove unreacted monomers. After cooling, the polyester was isolated and had a number average molecular weight of 3,000 daltons and was then used in blends without further purification. Biodegradable properties of Compositions 1 through 3 blended with Composition A1 are provided in Table 20.2.

TABLE 20.2 Biodegradable properties of neat Composition A1 and blends comprising Compositions 1 through 3. In addition to being biodegradable, Compositions 1 through 3 blended with Composition A1 had excellent molding properties.



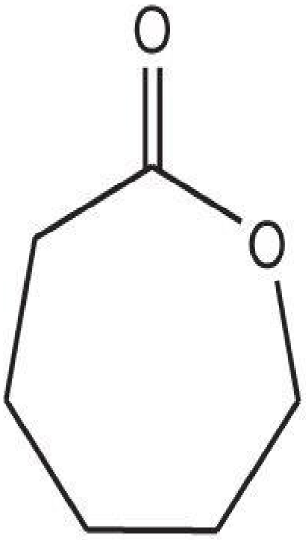
Polymer composition	Heat resistance	Biodegradability	Recycling properties	Molding properties
Composition A1	Poor	Poor	Poor	Good
Composition 1 blended with 30% Composition A1	Excellent	Excellent	Excellent	Excellent
Composition 2 blended with 25% Composition A1	Excellent	Excellent	Excellent	Excellent
Composition 3 blended with 25% Composition A1	Excellent	Excellent	Excellent	Excellent

Testing

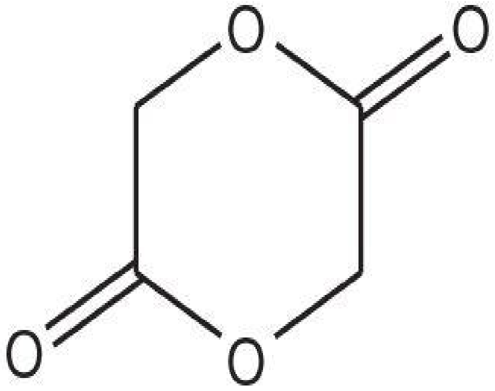
Biodegradable Testing of Thermosets Containing Composition A1

Notes and Observations

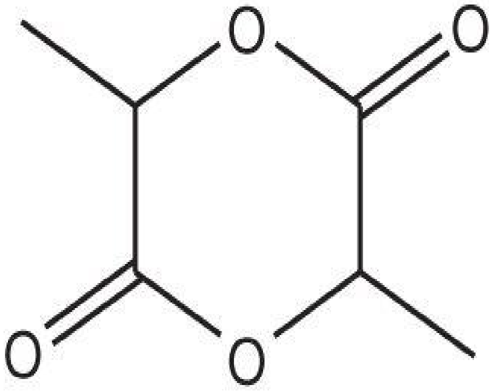
1. Guelcher[1] prepared biodegradable polyurethane foams. In this process, a polyester diol intermediate was prepared by condensing ε-caprolactone, (IV), glycolide, (V), and d,l-lactide, (VI). Once the polyurethane resin was prepared it was blended with lysine methylester diisocyanate, (VII), water, turkey red oil as the stabilizer, and calcium stearatepolyurethane. Weight loss after 4 weeks was then determined by incubating the polymer in phosphate-buffered saline at 37°C and exceeded 70%. (See Fig. 20.11.)



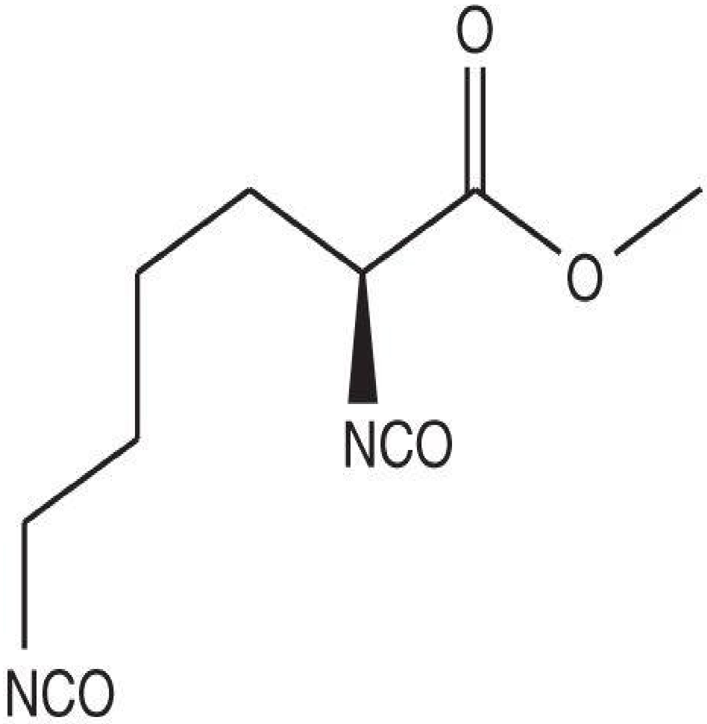
(IV)



(V)



(VI)



(VII)

Figure 20.11

2. Hoshino[2] prepared a series of aliphatic polyester resins that had excellent moldability as well as excellent melt tension at the time of molding, so that they could be used as a general-purpose plasticmolding agent in injection molding, hollow molding, or in extrusion molding. The highly biodegradable aliphatic polyester resin containing carboxylic acid termini was prepared by condensing 100.3 g of succinic acid, (VIII), 99.5 g of 1,4-butanediol, (IX), and 0.37 g of malic acid, (X). (See Fig. 20.12.)

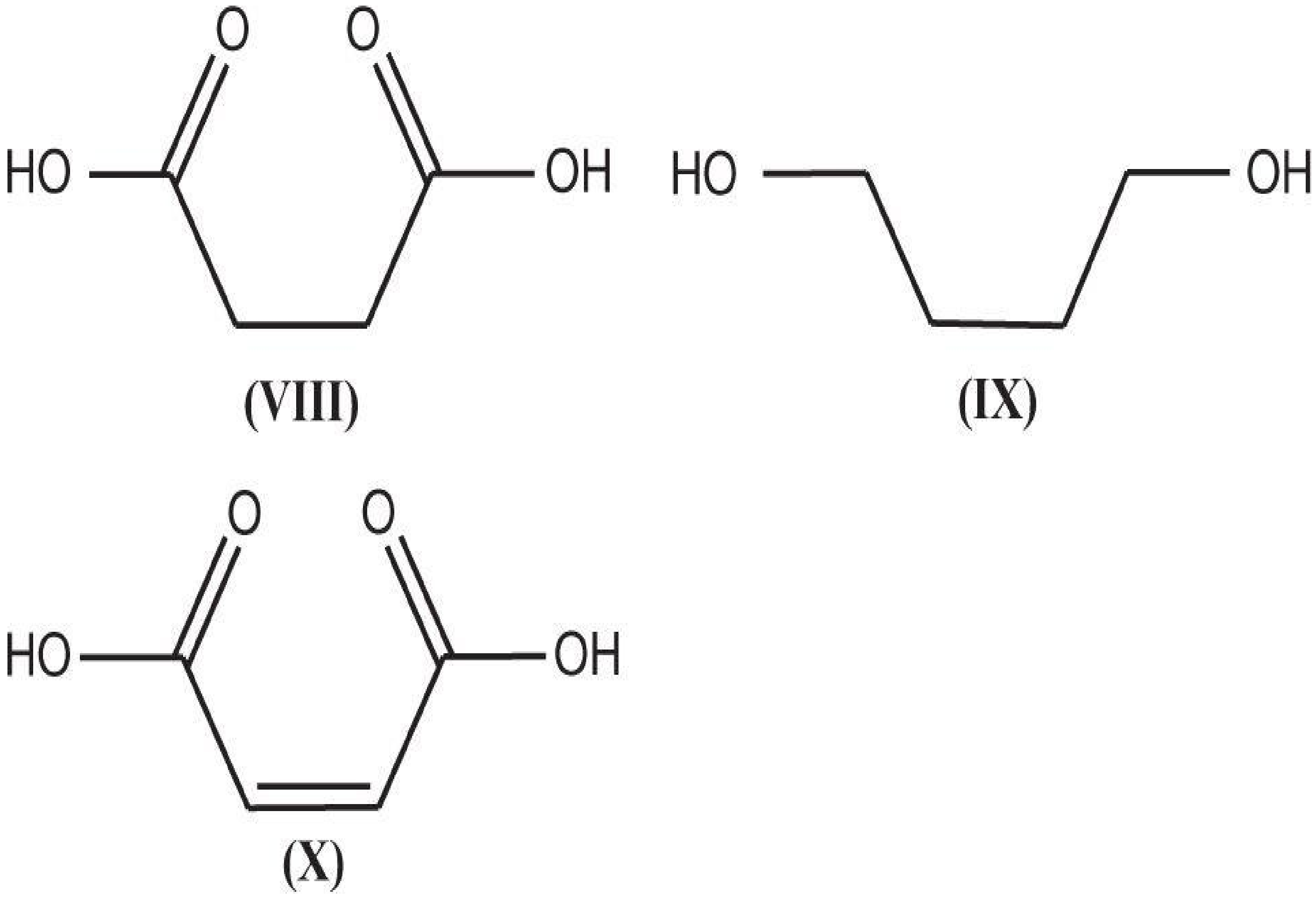
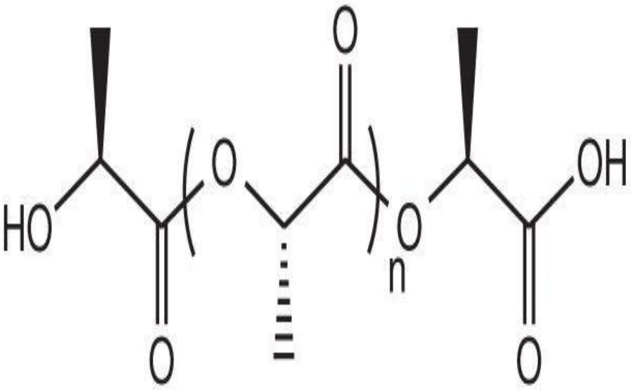
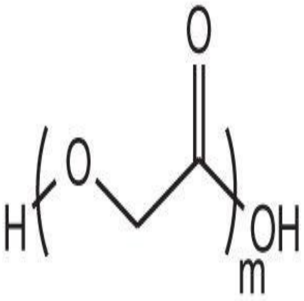


Figure 20.12

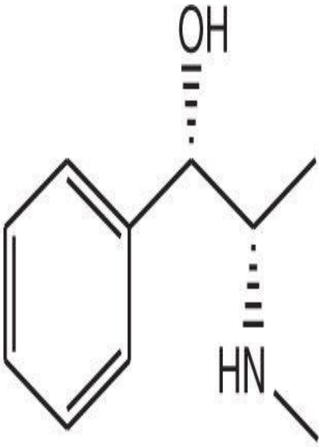
3. Tengler[3] prepared biodegradable spheres consisting of (S)-poly(lactic acid), (XI), and poly(glycolic acid), (XII), which was then used as a drug delivery agent for pseudoephedrine, (XIII); chlorpheniramine, (XIV); and dextromethorphan, (XV). (See Fig. 20.13.)



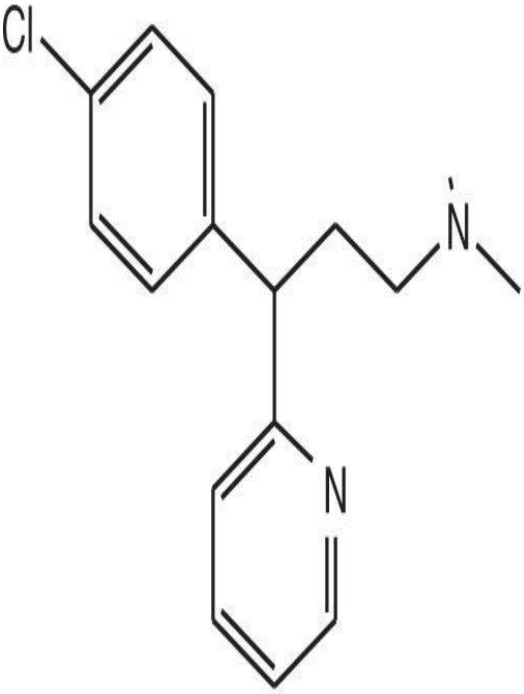
(XI)



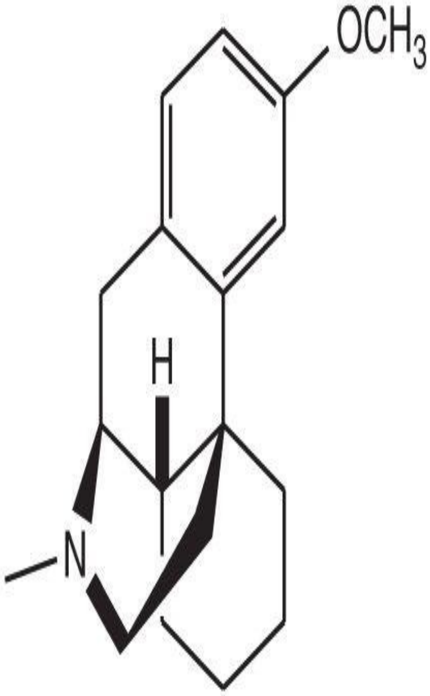
(XII)



(XIII)



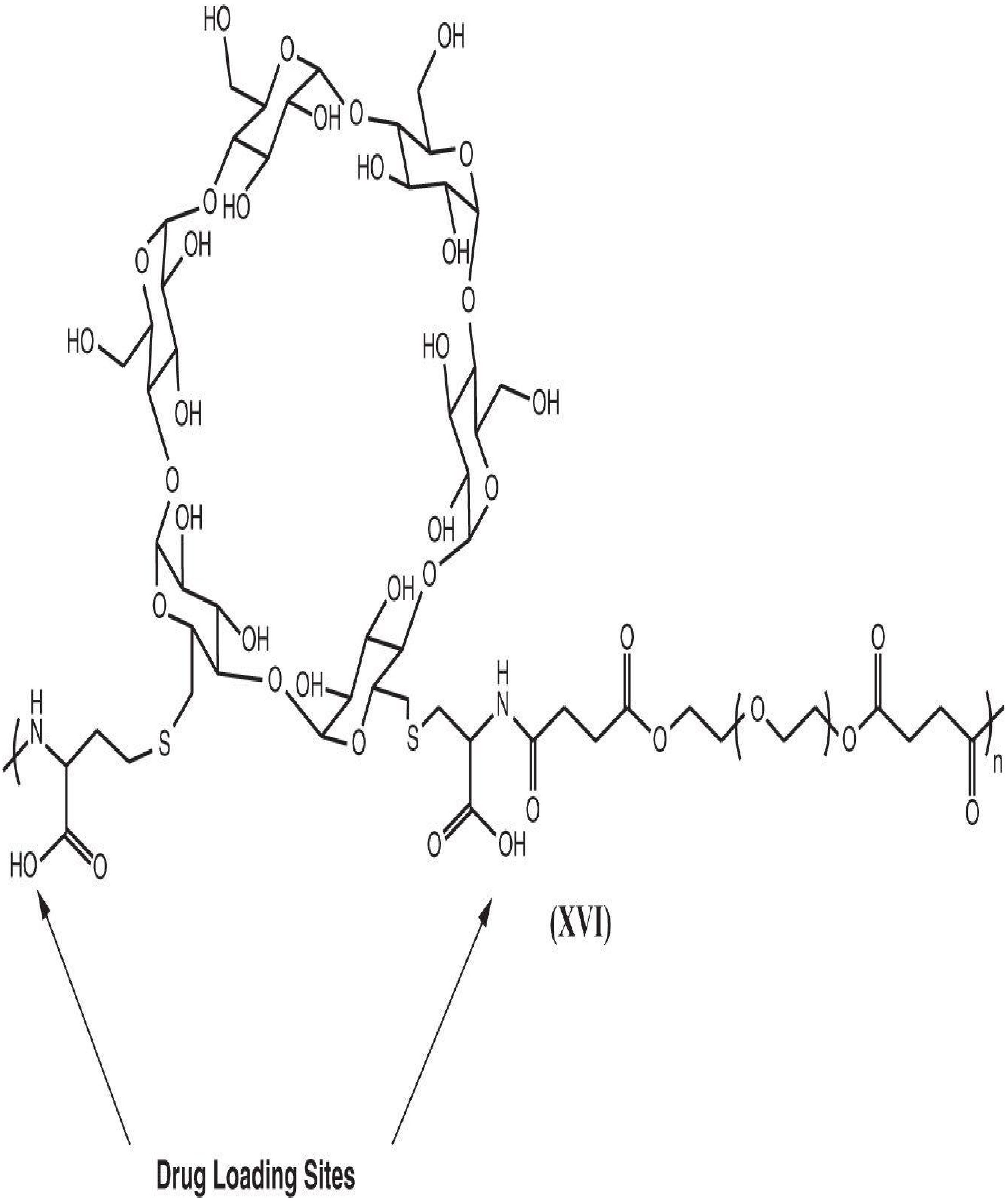
(XIV)



(XV)

Figure 20.13

4. Cheng[4] prepared a non-toxic biodegradable cyclodextrin resin, (XVI), which was used as a slow-release drug delivery agent for antineoplastic agents. (See Fig. 20.14.)



(XVI)

Drug Loading Sites

Figure 20.14

References

1. Scott A. Guelcher et al., *Degradable polyurethane foams*, U.S. Patent 8,318,820 (November 27, 2012)

2. Toyomasa Hoshino et al., *Aliphatic polyester resin and its production method*, U.S. Patent 8,318,893 (November 27, 2012)

3. Mark Tengler et al., *Compositions and methods of making sustained release liquid formulations*, U.S. Patent 8,318,210 (November 27, 2012)

4. Jianjun Cheng et al., *Cyclodextrin-based polymers for therapeutics delivery*, U.S. Patent 8,314,230 (November 20, 2012)

Biodegradable Poly(1,3-Trimethylene Carbonate)

Author Dirk Wybe Grijpma et al.

Patent Title ***Method for preparing a degradable polymer network,*** U.S. Patent Application 20130123384 (May 16, 2003)

Relevant Prior Patents by Author or Coauthors

Degradable therapeutic delivery device, U.S. Patent 8,399,012 (March 19, 2013)

Biocompatible crosslinked polymers with visualization agents, U.S. Patent 7,592,418 (September 22, 2009)

Method for providing shaped biodegradable and elastomeric structures of (co) polymers of 1,3-trimethylene carbonate (TMC), shaped biodegradable and elastomeric structures, and the use of these structures, U.S. Patent 7,572,838 (August 11, 2009)

Biocompatible crosslinked polymers, U.S. Patent 7,009,034 (March 7, 2006)

Biodegradable elastomer and method of preparing same, U.S. Patent 6,984,393 (January 10, 2006)

Methods of making functional biodegradable polymers, U.S. Patent Application 20030232929 (December 18, 2003)

Crosslinking agents and methods of use, U.S. Patent Application 20020114775 (August 22, 2002)

Bioresorbable copolymers, U.S. Patent 6,093,792 (July 24, 2000)

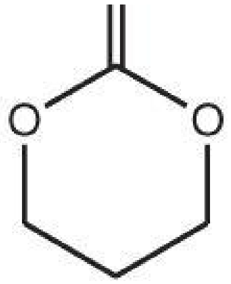
Product Application

Poly(1,3-trimethylene carbonate) is an effective biodegradable scaffold that, when incorporated into tissue, is used to grow human mesenchymal stem cells.

Significance of Current Application

There is a persistent need for tissue engineering to provide or design methods for tissue replacement using biodegradable scaffolds. Poly (1,3-trimethylene carbonate) was selected as a tissue scaffold because of its ease in preparation, excellent biocompatible, and biodegradable properties. Poly(1,3-trimethylene carbonate) has a glass-transition temperature of –17°C, which means the polymer remains amorphous and flexible after photocrosslinking, which is necessary to form a stable network. While poly(1,3-trimethylene carbonate) is inherently biodegradable, the erosion rate of poly(1,3-trimethylene carbonate) can be modified by copolymerizing it with varying amounts of 1,6-hexanediol. In this investigation, a copolymeric scaffold was prepared using trimethylene carbonate and 1,6-hexanediol that successfully grew human mesenchymal stem cells, and the copolymer completely biodegraded in four weeks. Finally, the remarkable biocompatibility and non-toxicity of both poly(1,3-trimethylene carbonate) and copolymers of 1,3-trimethylene carbonate and 1,6-hexanediol suggests they can potentially be used as scaffolding networks in other biological applications.

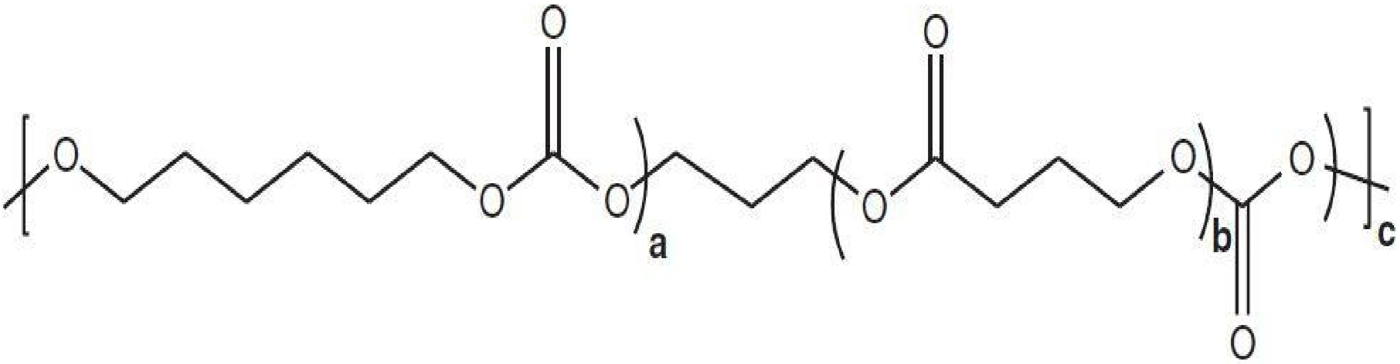
Renewable Agent



1,3-Trimethylcarbonate

Figure 20.15

Biodegradable Scaffolding Agent



Poly(1,3-trimethylene carbonate-co-1,6-hexanediol)
Scaffold

Figure 20.16

Product Formation

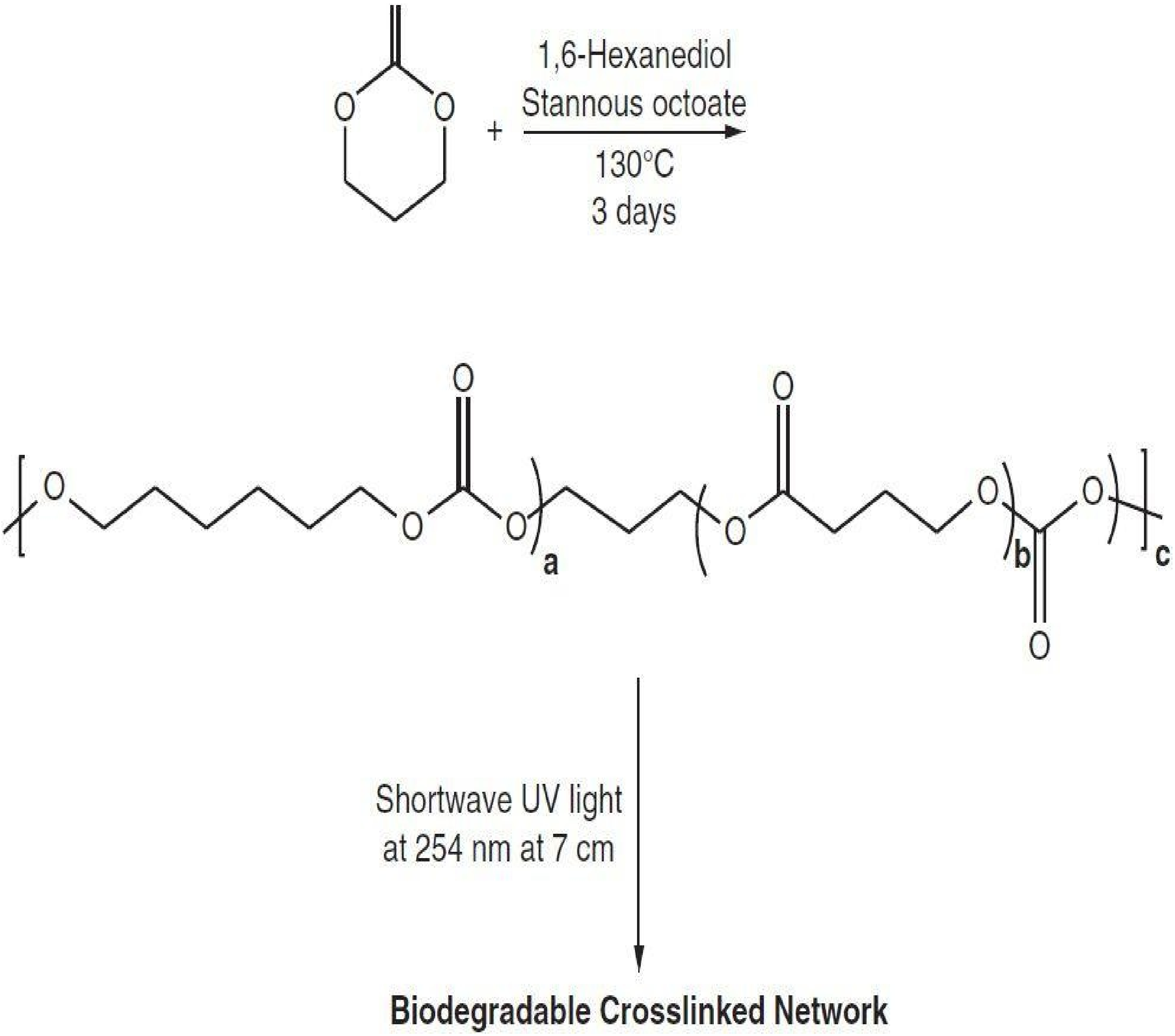
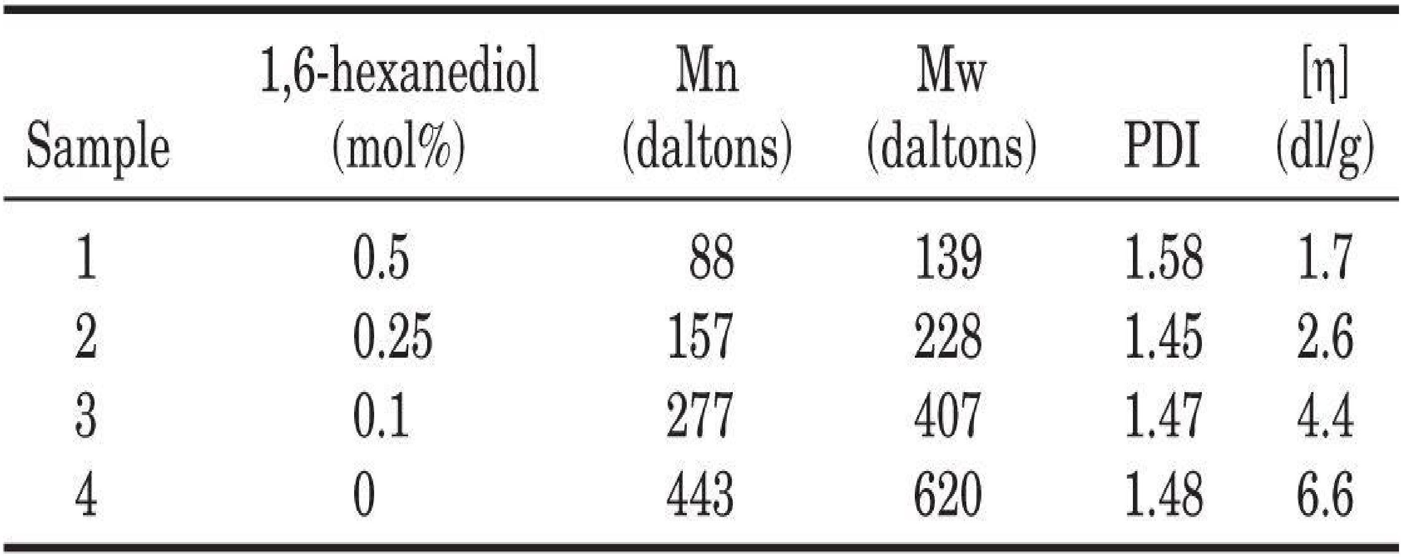


Figure 20.17

Experimental

1. Preparation of the biodegradable scaffold. A polymer reaction was charged with one equivalent of 1,3-trimethylene carbonate, up to 1-molar equivalent of 1,6-hexanediol, and a catalytic amount of stannous octoate. The mixture was heated to 130°C for 3 days while thoroughly mixing. The solution was then cooled to ambient temperature and purified by dissolution in chloroform followed by precipitation into ethanol. Finally, the precipitate was isolated and then dried at ambient temperature under vacuum. A summary of physical properties of poly(1,3-trimethylene carbonate-co-hexanediol) is provided in Table 20.3.

TABLE 20.3 Physical properties of the biodegradable scaffold prepared using 1,3-trimethylene carbonate and 1,6-hexanediol.



Sample	1,6-hexanediol (mol%)	Mn (daltons)	Mw (daltons)	PDI	[η] (dl/g)
1	0.5	88	139	1.58	1.7
2	0.25	157	228	1.45	2.6
3	0.1	277	407	1.47	4.4
4	0	443	620	1.48	6.6

2. Preparation of biodegradable scaffold films. The copolymer was initially additized with antioxidants PETA and Irgacure® 369. The mixture was then compression molded at 140°C using 500-µm-thick stainless steel molds at approximately 25 kg/cm^2 and then quenched in cold water. Films prepared by this method were clear and flexible.

3. Preparation of biodegradable photo-crosslinked scaffold films. Compression-molded Step 2 product films were vacuum sealed in laminated polyethylene/polyamide bags and then exposed to shortwave UV light at 254 nm at a distance of 7 cm. Both sides of the film were illuminated at ambient temperature for different time periods. The light intensity at this distance was approximately 10–14 mW/cm^2 but was reduced to 5–7 mW/cm^2 because of the damage incurred to the polyethylene/ester bags.

4. Preparation of biodegradable tissue scaffolds. A solution was prepared by dissolving 20 wt% of the Step 1 product containing PETA and the photoinitiator, 1-[4[(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one [Irgacure® 2959] dissolved in dichloromethane. The solution was then treated with 80 wt% of ethylene carbonate. The solution was then evaporated and the mixture extruded between 100°C and 120°C at 4 bars of nitrogen pressure. Three dimensional scaffolds containing 20 layers of fibers were then extruded having a thickness of 130 µm. The scaffolds were then crosslinked by UV irradiation for 300 minutes while maintaining the temperature at 20°C. Finally, the scaffolds were isolated and stored under nitrogen at 4°C until needed.

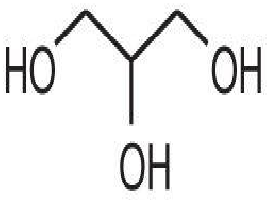
5. Incorporation of human mesenchymal stem cells into biodegradable tissue scaffolds. Human mesenchymal stem cells were cultured on disk-shaped, photo-crosslinked containing the Step 4 product. The sterilized Step 4 product films were 15 mm in diameter and 200 µm thick. The cells were cultured at an initial seeding density of $5 \cdot 10^4$ cells/cm^2 and the growing medium refreshed twice a week. After four weeks of culturing cells, the films were fixed by treating with 3.7% paraformaldehyde. The surface was then analyzed by scanning with electron microscopy, and the results indicated that the cell population had dramatically increased. In addition, there was no present evidence of the copolymer scaffold in the tissue samples.

Testing

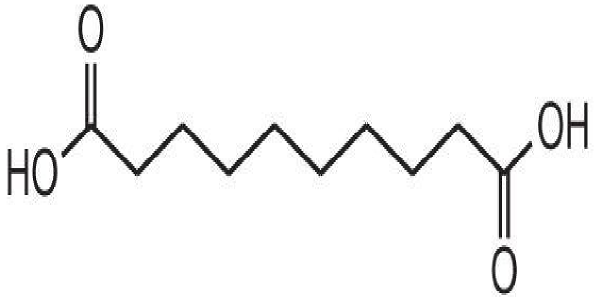
Testing was limited to polymer characterization as provided in Step 1 and Table 20.3.

Notes and Observations

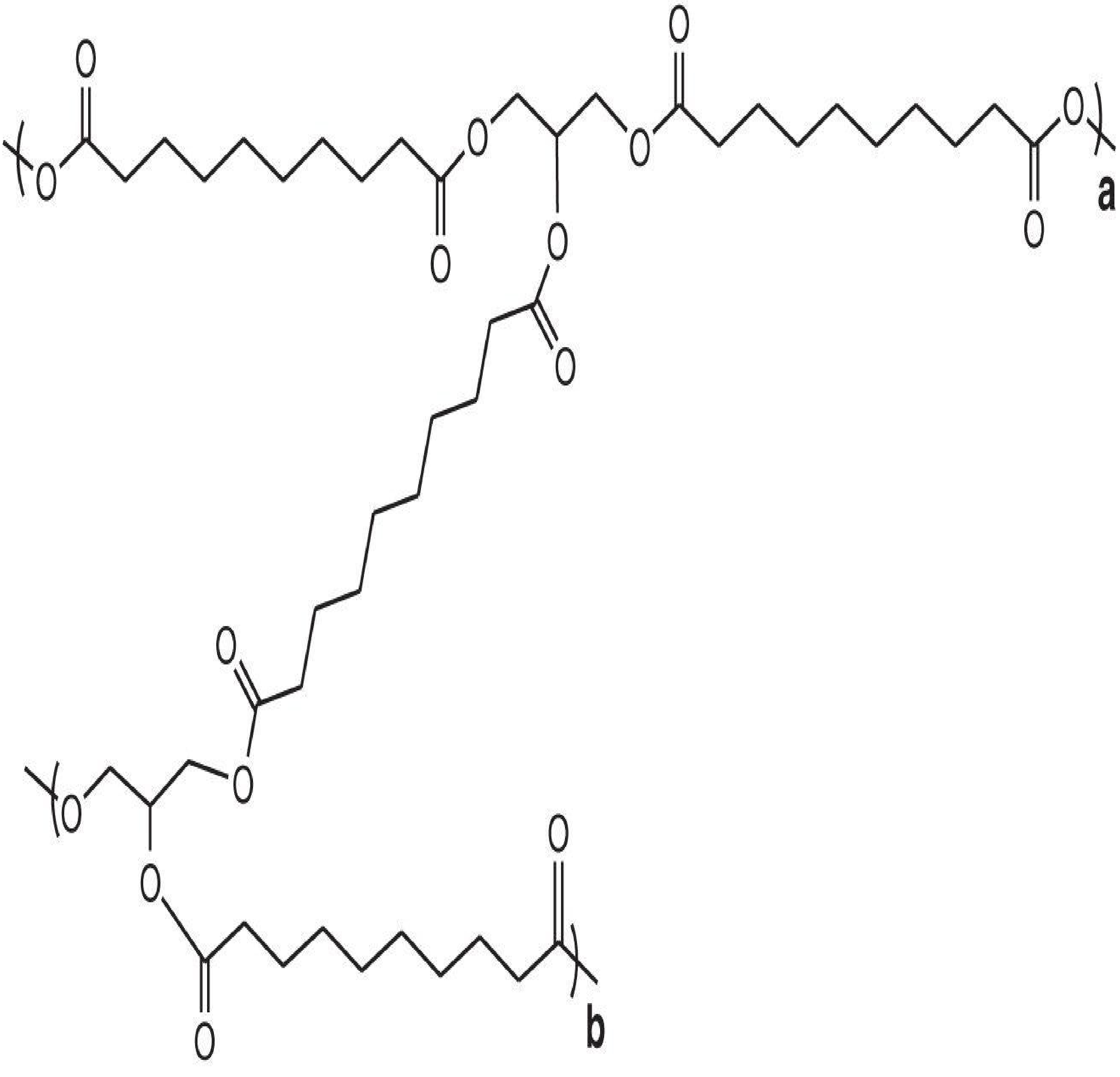
1. Smith[1] prepared a vaginal insert consisting of the reaction product of glycerol, (I), and sebacic acid, (II), to form a crosslinked biodegradable elastomeric polyester, (III). The biodegradable polymer was then used as a delivery agent for estrogen, testosterone, and progesterone. (See Fig. 20.18.)



(I)



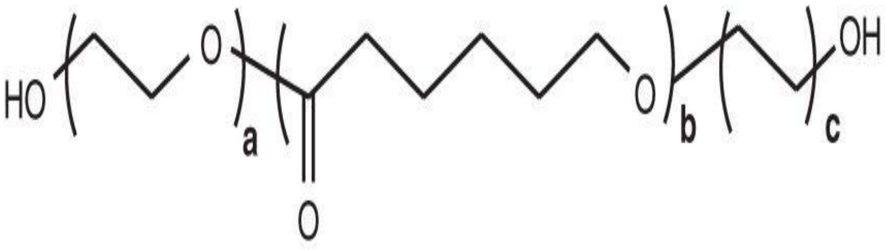
(II)



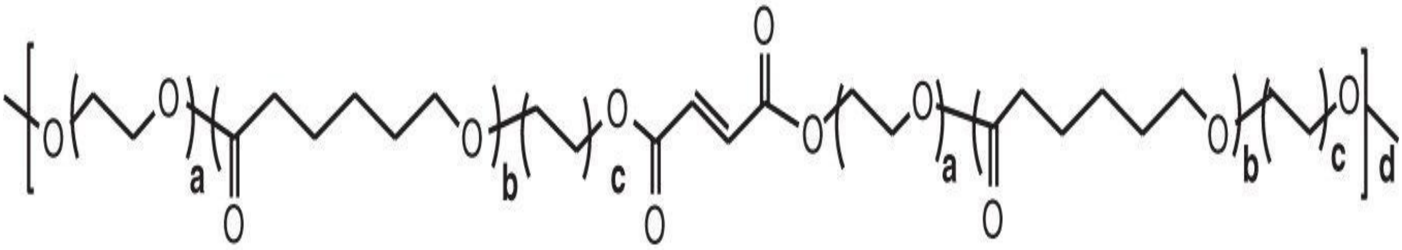
(III)

Figure 20.18

2. Pathak[2] devised a multi-step process for preparing biocompatible and biodegradable crosslinked polymers. Initially, poly(ethylene glycolb-caprolactone polyol), (IV), was prepared by reacting polycaprolactone with polyethylene glycol [PLURONIC® F68]. This intermediate was then post-reacted with succinic anhydride to form the diblock copolymer, (V). The diblock copolymer was then converted into a crosslinked network by reacting it with both N-hydroxysuccinimide and N-hydroxysulfosuccinimide. The product was then used in drug delivery formulations. (See Fig. 20.19.)



(IV)

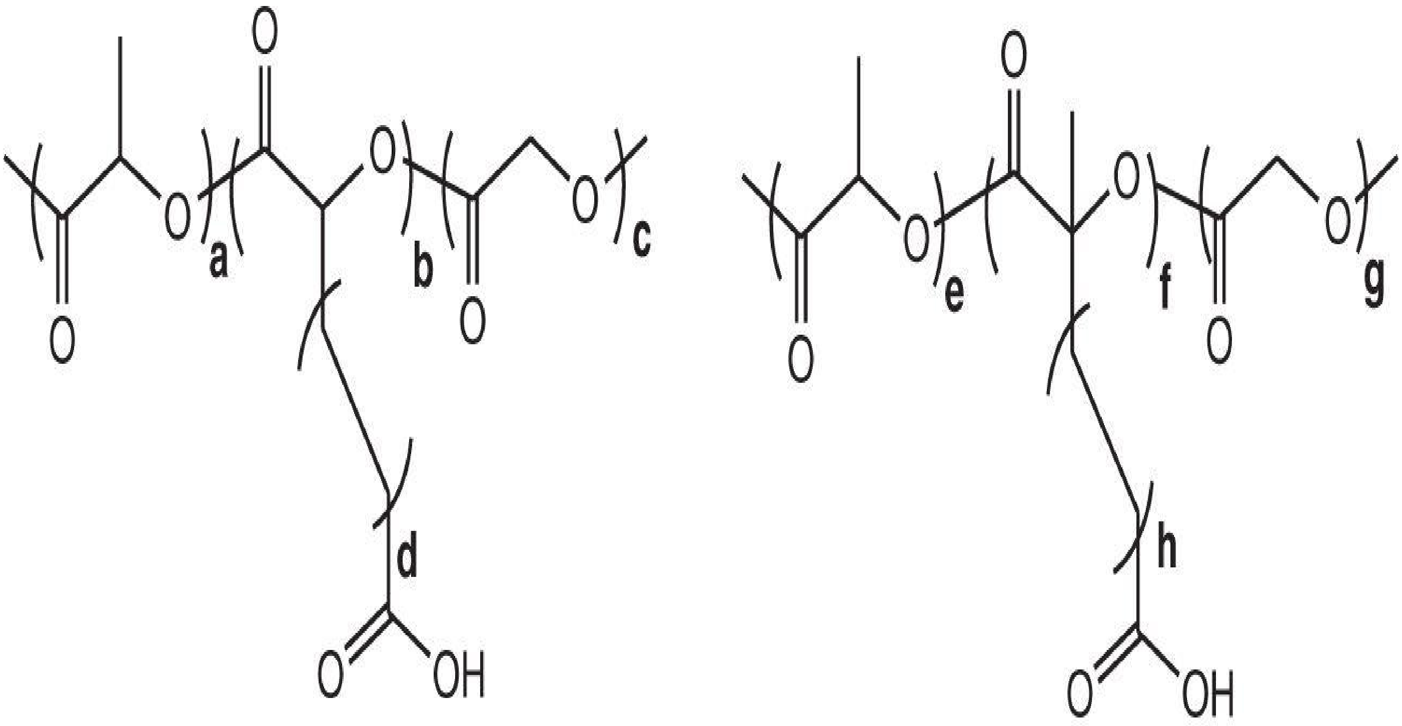


(V)

Figure 20.19

3. In an earlier investigation by Grijpma,[3] it was determined that random copolymers of 1,3-trimethylene carbonate and ε-caprolactone degraded less when exposed to gamma radiation than block copolymers of 1,3-trimethylene carbonate and ε-caprolactone.

4. Huang[4] prepared a mixture of drug delivery agents using renewable poly(lactic-co-glycolic acid) by free radically-grafting acrylic acid onto selected biodegradable polymer backbones, (VI) and (VII). Once prepared, both modified polymers were used as drug delivery agents. (See Fig. 20.20.)



(VI) (VII)

Figure 20.20

References

1. Molly K. Smith et al., *Degradable therapeutic delivery device*, U.S. Patent 8,399,012 (March 19, 2013)

2. Chandrashekhar P. Pathak et al., *Biocompatible crosslinked polymers*, U.S. Patent 7,009,034 (March 7, 2006)

3. Dirk Wybe Grijpma et al., *Method for providing shaped-biodegradable and elastomeric structures, and the use of these structures*, U.S. Patent 7,572,838 (August 11, 2009)

4. Yanbin Huang et al., *Methods of making functional biodegradable polymers*, U.S. Patent 7,037,983 (May 2, 2006)

Biomass Preparation of Polyethylene Terephthalate

Author	Seiko Sato
Patent Title	***Biomass plastic alternative to polyethylene terephthalate and method for producing the biomass plastic,*** U.S. Patent Application 20130066039 (March 14, 2013)

Relevant Prior Patents by Author

Resin Composition, U.S. Patent Application 20130030104 (January 31, 2013)

Product Application

Polyethylene terephthalate is a plastic that can be used in forming molded products for use in either beverage or food containers as well as in preparing clothing fibers.

Significance of Current Application

The biomass synthesis of polyethylene terephthalate is unprecedented. Polyethylene terephthalate is ordinarily prepared by the chemical reaction of petroleum-derived terephthalic acid with ethylene glycol at elevated temperatures and under high vacuum. This method generates tremendous amounts of organic toxic waste products, is energy intensive, and uses petrochemicals derived from the limited amounts of existing petroleum reserves. The current investigation has identified a method for producing polyethylene terephthalate using Bacillus subtilis, Bacillus pumilus, Bacillus thuringiensis, and Corynebacterium glutamicum microorganisms in a process that does not generate toxic organic waste products, requires a minimum of energy input, and is completely renewable.

Microorganism-Generated Polyethylene Terephthalate

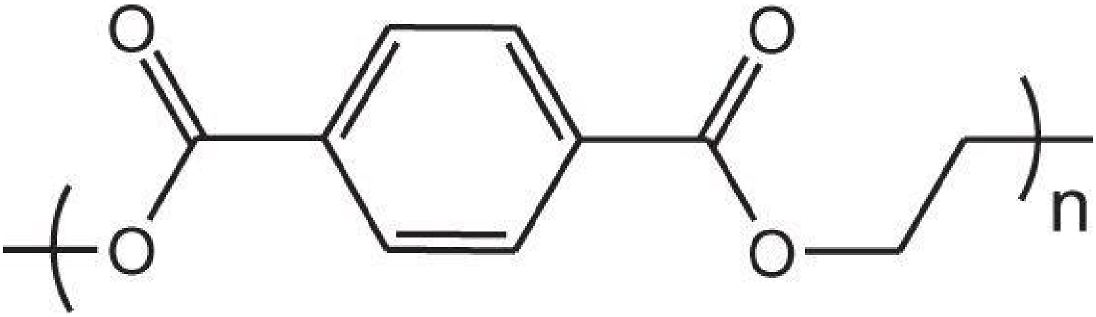


Figure 20.21

Experimental Process Overview

1. A microorganism mixture consisting of Bacillus subtilis, Bacillus pumilus, and Bacillus thuringiensis was cultured at approximately 45°C for up to 3 days in a starch and silicic acid medium.
2. The growing microorganism mixture from Step 1 was then treated with Corynebacterium glutamicum and the mixture was cultured for an additional 3 days at

approximately 40°C.

3. The microorganism mixture from Step 2 was then used to prepare polyethylene terephthalate, which was then isolated from the reaction mixture.

Experimental

1. Preparation of a three-component microorganism mixture and starch. A biomass was prepared consisting of 1 kg of Kaoliang starch, ground fruit pulp of jujube, and approximately 100 g of magnesium silicate derived from coral fossil powder, or shell powder, and containing between 10 wt% and 15 wt% of water. The biomass was then treated with a 3:5:2 weight ratio of Bacillus subtilis, Bacillus pumilus, and Bacillus thuringiensis, respectively, to make a total volume of about 10 wt%. It was then cultured for several days at approximately 45°C.

2. Preparation of a four-component microorganism mixture with starch. The biomass containing Bacillus subtilis, Bacillus pumilus, and Bacillus thuringiensis was treated with Corynebacterium glutamicum and the mixture was further cultured for up to 3 days at 40°C.

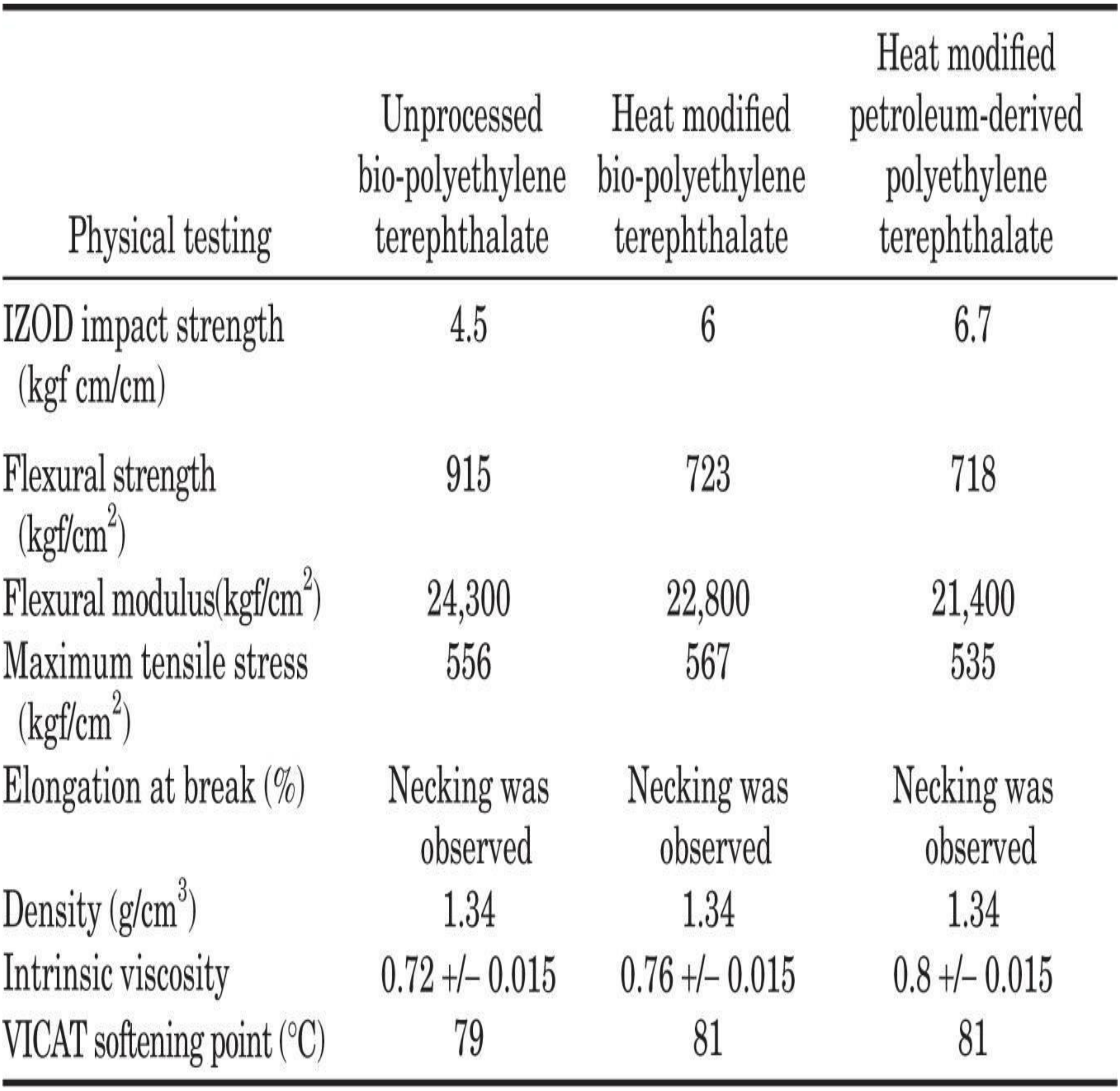
3. Preparation of polyethylene terephthalate from a four-component microorganism mixture. After the Step 2 mixture reacted for approximately 36 hours, polyethylene terephthalate formed and was identified as a gel-like precipitate. Polyethylene terephthalate biopolymer was isolated by gently and repeatedly vibrating the culture container, which subsequently caused the biopolymer to fall from floating cellular residue and debris. After isolating the biopolymer, it was then dried and ground to a powder.

Testing

A. Polymer identification. The biomass plastic was identified by infrared spectroscopy. Infrared spectra of bio-derived and petroleum-derived polyethylene terephthalate samples were identical.

B. Physical testing

TABLE 20.4 Physical test results of two bio-derived polyethylene terephthalate samples compared to a commercial petroleum-derived PET sample. Physical properties of the three copolymer samples were essentially identical.



Physical testing	Unprocessed bio-polyethylene terephthalate	Heat modified bio-polyethylene terephthalate	Heat modified petroleum-derived polyethylene terephthalate
IZOD impact strength (kgf cm/cm)	4.5	6	6.7
Flexural strength (kgf/cm^2)	915	723	718
Flexural modulus(kgf/cm^2)	24,300	22,800	21,400
Maximum tensile stress (kgf/cm^2)	556	567	535
Elongation at break (%)	Necking was observed	Necking was observed	Necking was observed
Density (g/cm^3)	1.34	1.34	1.34
Intrinsic viscosity	0.72 +/– 0.015	0.76 +/– 0.015	0.8 +/– 0.015
VICAT softening point (°C)	79	81	81

Notes and Observations

1. Singh[1] biosynthesized eicosapentaenoic acid, (I), docosapentaenoic acid, (II), and docosahexaenoic acid, (III), in good yields using Pavlova salina CS-4 plasmids incorporated into yeast cells by heat shock methods. (See Fig. 20.22.)

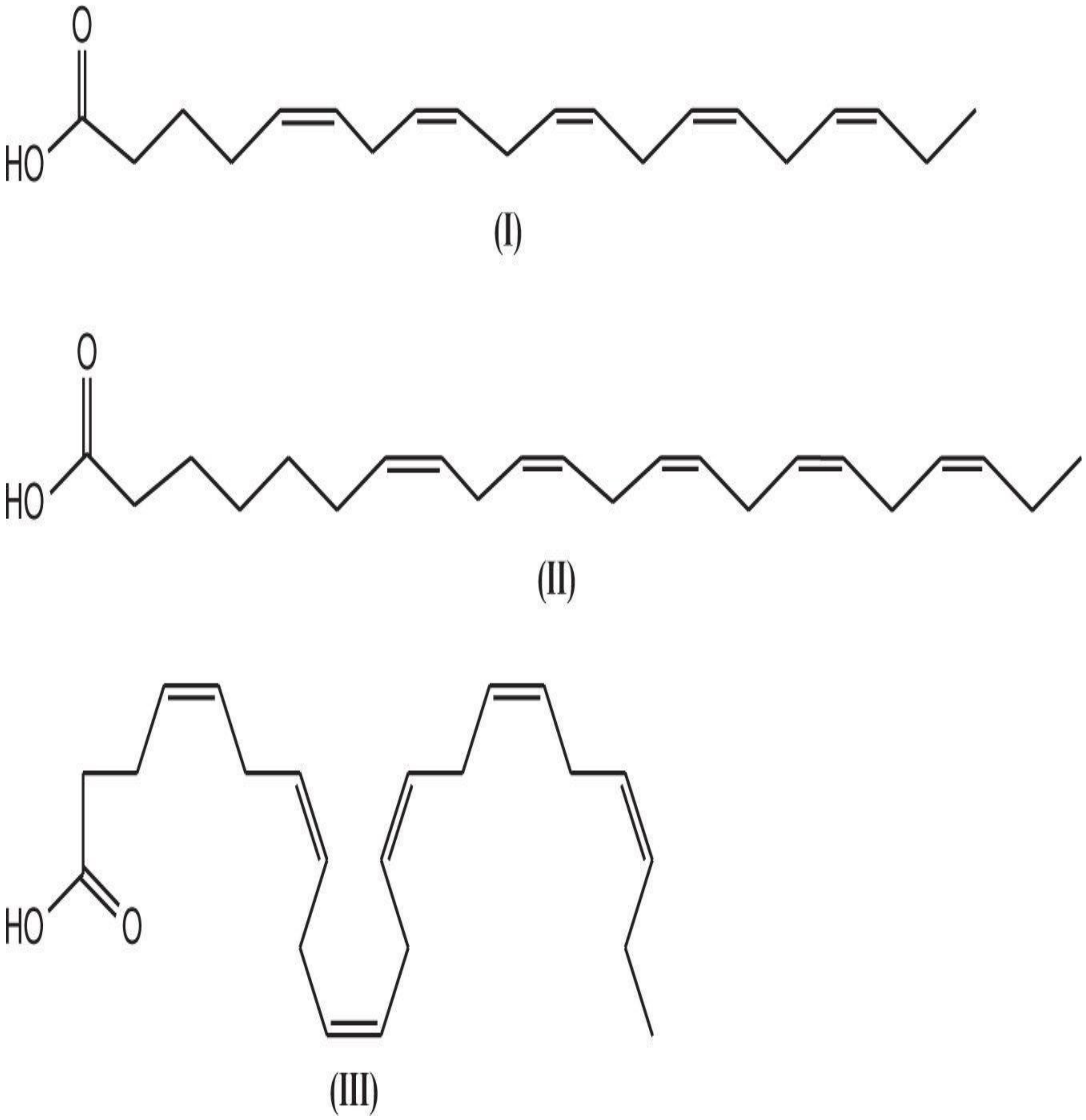
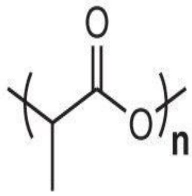


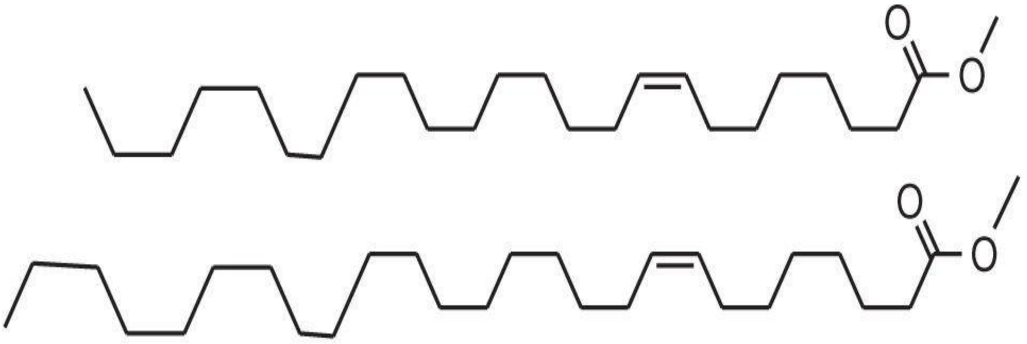
Figure 20.22

2. Riebel[2] formed biolaminates and bioadhesives using biologically derived polylactic acid, (IV), and soybean, (V). The blends were then used in wood paneling applications. In this process, bio-plasticizers were added to polylactic/soybean blends and the panel mixture was then heated to at least 150°C and then pressed for 2.5 minutes with 50 PSI to ensure a strong contact with the bio-adhesive. Bio-adhesive components prepared from this process, (VI) through (IX), are illustrated in Fig. 20.23.



Polylactic Acid

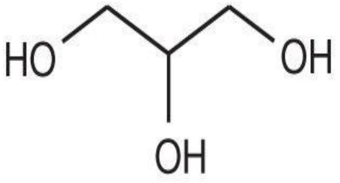
(IV)



Two Components of Soybean oil

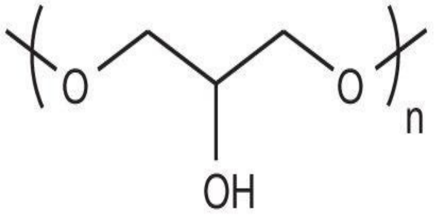
(V)

Renewable Plasticizers



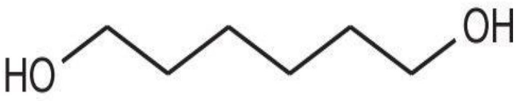
Glycerine

(VI)



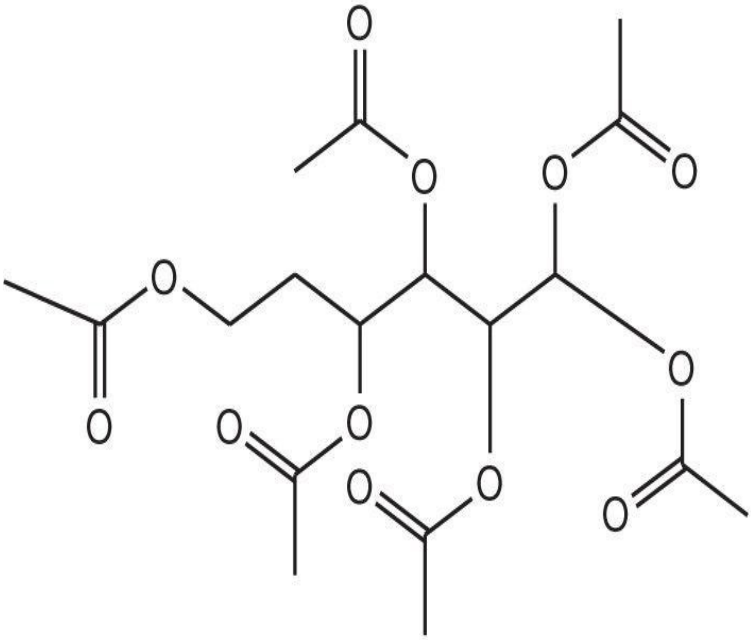
Polyglycerine

(VII)



1.6-Hexanediol

(VIII)



Sorbitol Hexaactate

(IX)

Figure 20.23

3. Shearer[3] pyrolysized biomasses derived from cellulosic materials, ligni-containing materials, animal by-products, organic wastes, landfill matter, marine waste, agricultural waste (animal or human) to 450°C and 525°C in the absence of air to form a semi-brittle biochar. The biochar was then used exclusively as a bioremediation agent, particularly in addressing chemical and oil spills.

4. Foo[4] dramatically increased the amount of levulinic acid and levulinic acid derivatives from inexpensive renewable biomass feedstock by treating the feedstock with 5-methyl-pyrrolidin-2-one ionic liquid derivatives, (X) to (XI), and then heating the mixture to approximately 100°C for several hours. (See Fig. 20.24.)

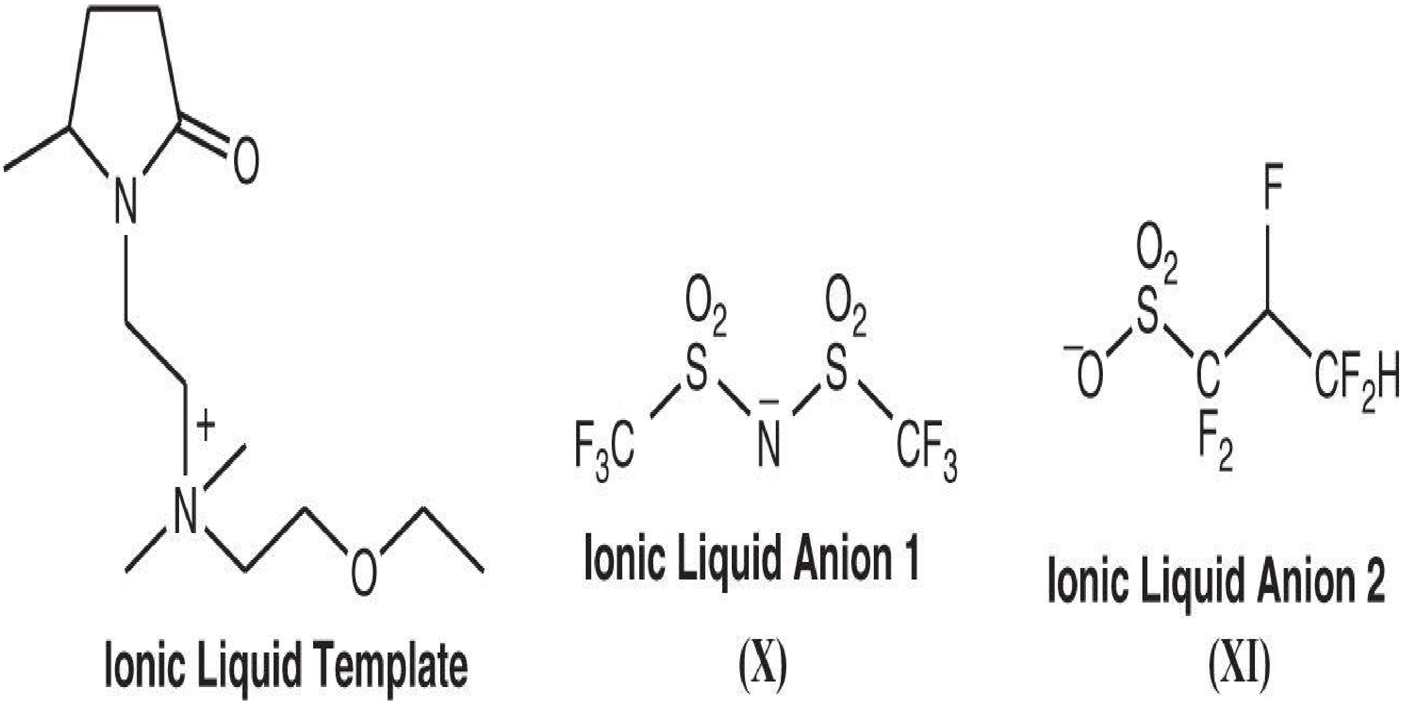


Figure 20.24

References

1. Surinder Pal Singh et al., *Synthesis of long-chain polyunsaturated fatty acids by recombinant cell*, U.S. Patent Application 20130060053 (March 7, 2013)

2. Michael J. Riebel et al., *Cellulosic biolaminate composite assembly and related methods*, U.S. Patent 8,389,107 (March 15, 2013)

3. David Shearer et al., *Biochar*, U.S. Patent 8,361,186 (January 29, 2013)

4. Thomas Foo, *Functionalized N-substituted pyrrolidonium ionic liquid*, U.S. Patent 8,350,056 (January 8, 2013)

Bisphenol-A Replacement Monomers

Author	William B. Carlson et al.
Patent Title	***Bisphenol-A replacement monomers,*** U.S. Patent 8,329,846 (December 11, 2012)

Relevant Prior Patents by Author or Coauthors

Bisphenol-A replacement materials, U.S. Patent Application 20120283359 (November 8, 2012)

Biocompatible polymerizable acrylate products and methods, U.S. Patent Application 20120264214 (October 18, 2012)

Partially hydrogenated bisphenol-A-based polymers as substitutes for bisphenol-A-based polymers, U.S. Patent Application 20120070593 (March 22, 2012)

Environmentally benign plasticizers based on derivatives of acetone, U.S. Patent Application 20110318292 (December 29, 2011)

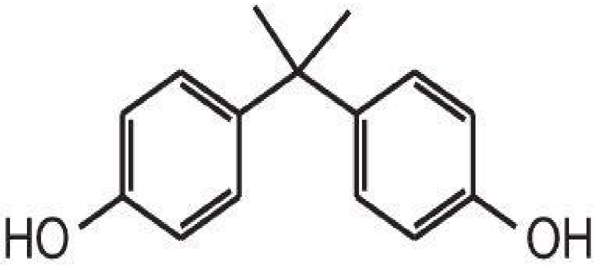
Product Application

Polycarbonates, polyurethanes, and polyacrylates containing tetradeca-hydroanthracene-9,9'diol as a repeating unit were determined to be effective as bisphenol-A replacement monomers. Tetradeca-hydroanthracene-9,9'diol-containing polymers are non-toxic and can be used in food and beverage containers, medical devices, or in coating applications.

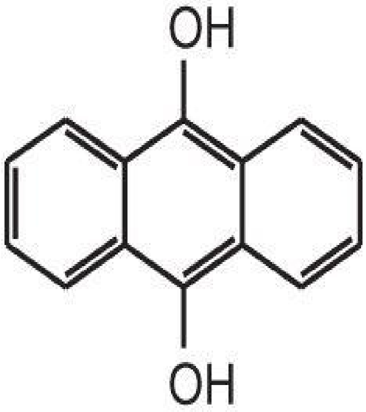
Significance of Current Application

Bisphenol-A-containing polymers have great mechanical strength and high glass-transition temperatures. Many of these copolymers, however, are susceptible to degradation and yellowing upon exposure to light, heat, and moisture, which may potentially release monomeric bisphenol-A. Since trace amounts of bisphenol-A are considered to act as an endocrine disruptor, birth defects, miscarriages, and neurological disorders have been attributed to its release by ingestion or consumption; hence, the replacement of bisphenol-A as a comonomer is considered essential. To address this problem, non-toxic alternatives to monomeric bisphenol-A in this investigation were identified, prepared, and then used to prepare copolymers. Copolymers using bisphenol-A-replacement monomers had excellent physical properties, which are required for commercialization of a variety of plastics.

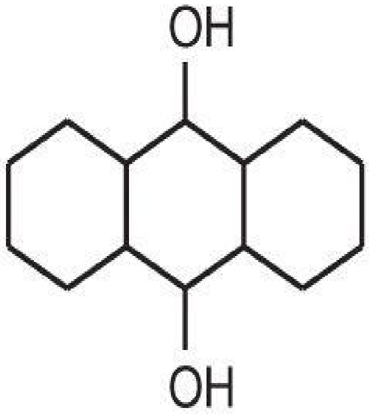
Bisphenol-A Replacement Monomers



Bisphenol A



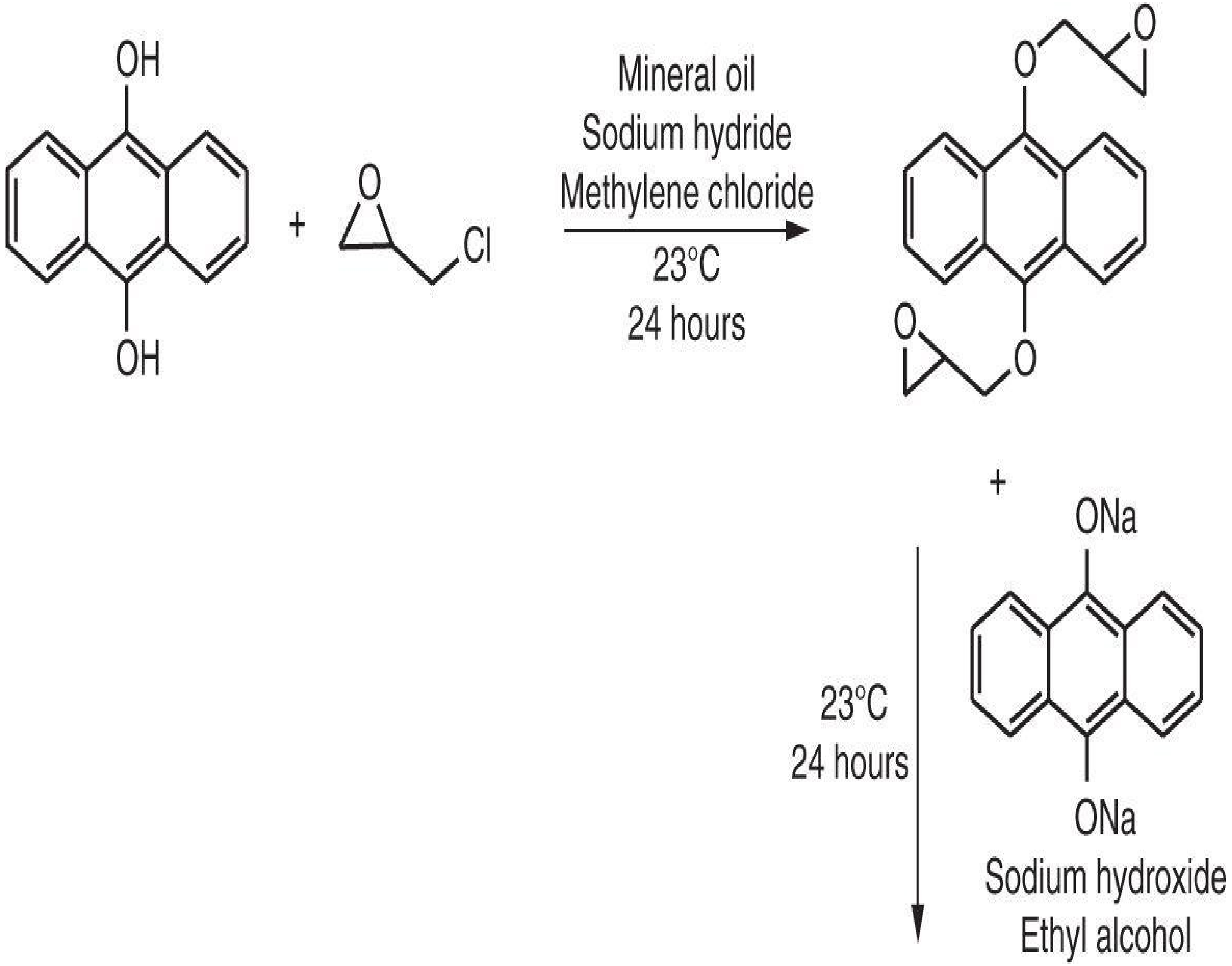
Bisphenol A
Replacement Monomer 1



Bisphenol A
Replacement Monomer 2

Figure 20.25

Product Formation


OH
OH
+
O
Cl
Mineral oil
Sodium hydride
Methylene chloride
23°C
24 hours
O
O
O
O
+
ONa
ONa
23°C
24 hours
Sodium hydroxide
Ethyl alcohol

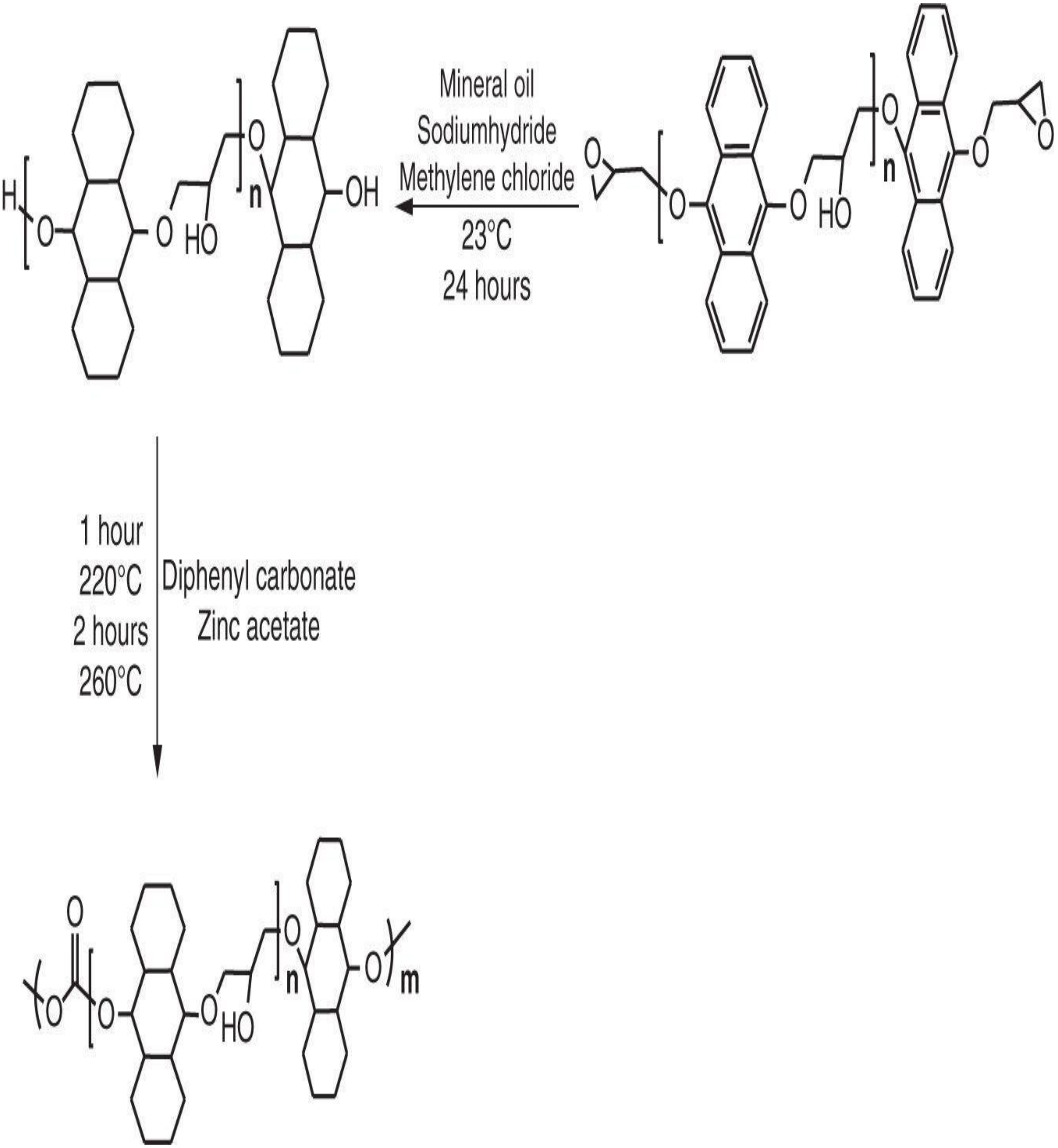


Figure 20.26

Experimental

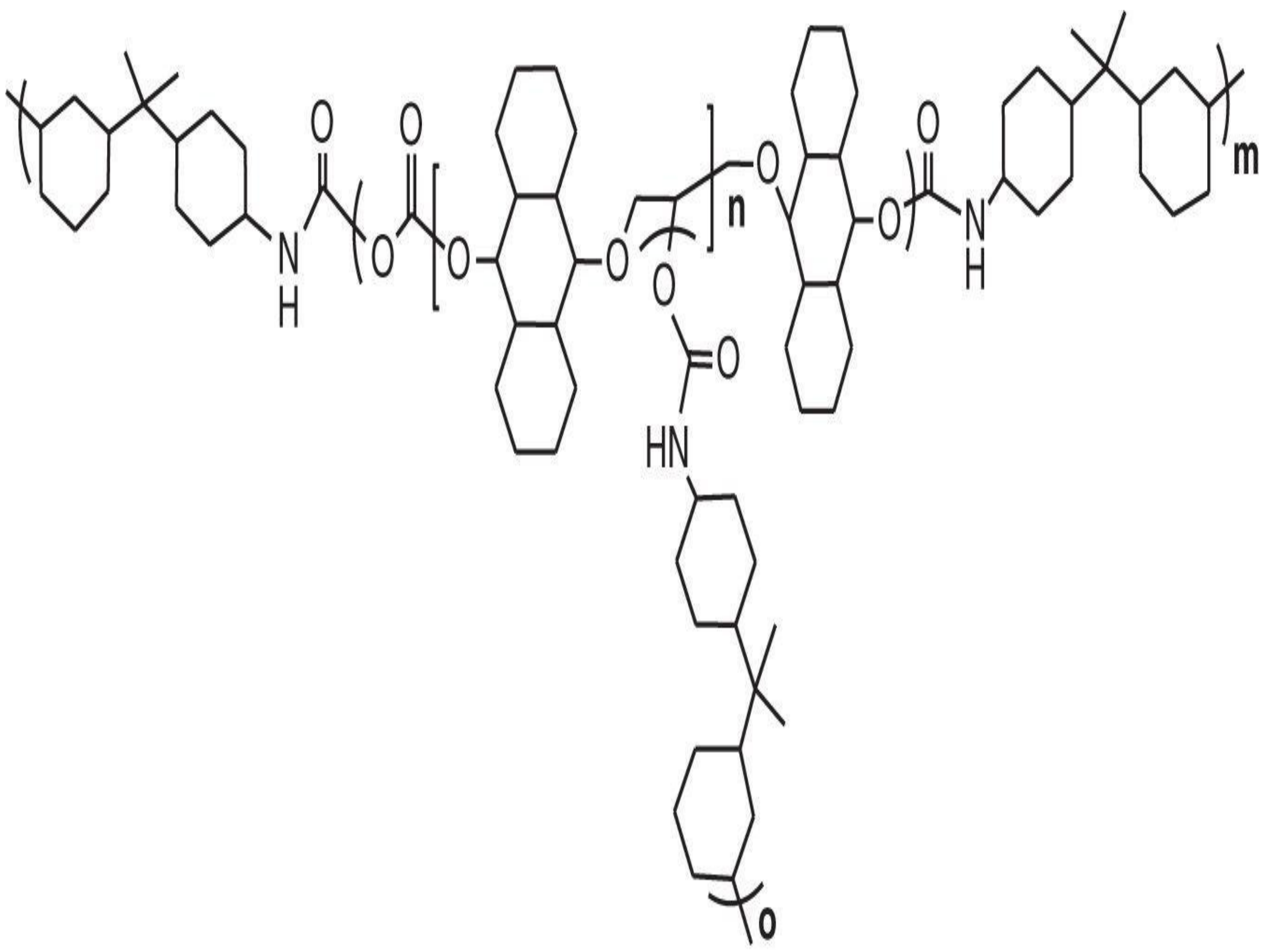
1. Preparation of anthracene-9,10-diglycidyl ether. A reactor was charged with one equivalent of anthracene-9,10-diol dissolved in anhydrous THF and under a protective argon atmosphere and then slowly treated with an excess of 60 wt% of sodium hydride dispersed in xylenes. Once the bubbling ceased, the sodium alkoxide was cannulated in a solution of epichlorohydrin, dissolved in dry THF, and stirred for 24 hours at ambient temperature. The mixture was then treated with water and the product was isolated by extraction with methylene chloride. The mixture was concentrated, purified by silica chromatography, and the product mixture was isolated in yields greater than 90%.

2. Formation of oligomeric anthracene-9,10-diglycidyl ether. A round-bottom flask containing anthracene-9,10-diol dissolved in ethyl alcohol was treated with two equivalents of sodium hydroxide and heated to reflux; water was removed by collecting in a Dean-Stark trap. The mixture was then treated with the Step 1 product and heated to reflux for about 3 hours and then slowly cooled to ambient temperature. The mixture was then treated with dilute hydrochloric acid until a pH of 6.5 was obtained and the reaction product mixture concentrated by distillation. The oily residue that remained was extracted with methylene chloride, dried using magnesium sulfate, filtered, and the product was isolated in over 95% yield as a white semisolid.

3. Hydrogenation of oligomeric tetradecahydroanthracene-9,9'diol. The Step 2 product was hydrogenated at 150°C under 2 atmospheres of hydrogen using palladium on carbon as the reaction catalyst and then isolated in quantitative yield as a white solid after workup.

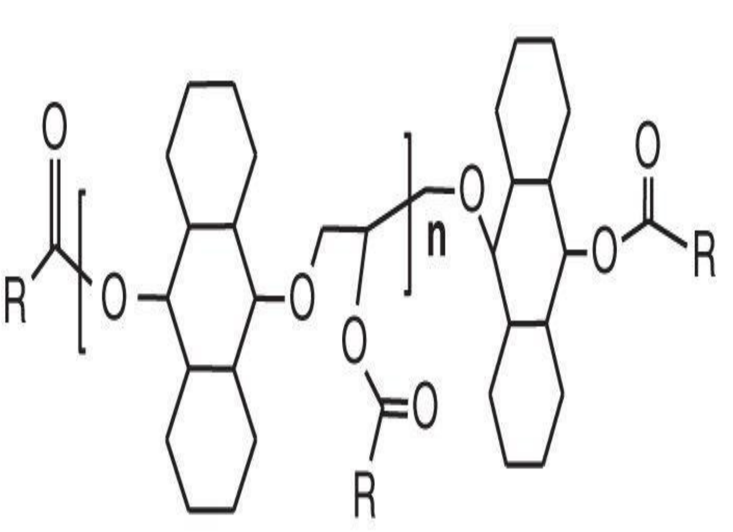
4. Preparation of poly(tetradecahydroanthracene-9,9'polycarbonate). A three-necked glass reactor equipped with a mechanical stirrer, nitrogen inlet, and a distillation unit was charged with the Step 3 product along with a slight excess of diphenylcarbonate and then heated to 200°C and treated with zinc acetate dihydrate. After the reaction was heated for 45 minutes the pressure was reduced to 20 mm Hg. The temperature was then increased to 260°C for 1 hour and the reaction pressure further reduced to 1 mm Hg. The mixture was then heated for an additional 2 hours at 260°C at full vacuum and then cooled to ambient temperature. The reaction product was isolated, dissolved in chloroform, and (I) precipitated dropwise into methanol. The polycarbonate was isolated by filtration and then dried under reduced pressure at 100°C overnight. A polyster of linoleic acid, II, was also prepared.

Polyurethane and Polyester Derivatives Using Bisphenol-A-Replacement Monomer



(I)

Polyurethane of 2,2-propylene-bis(4-cyclohexylisocyanate)

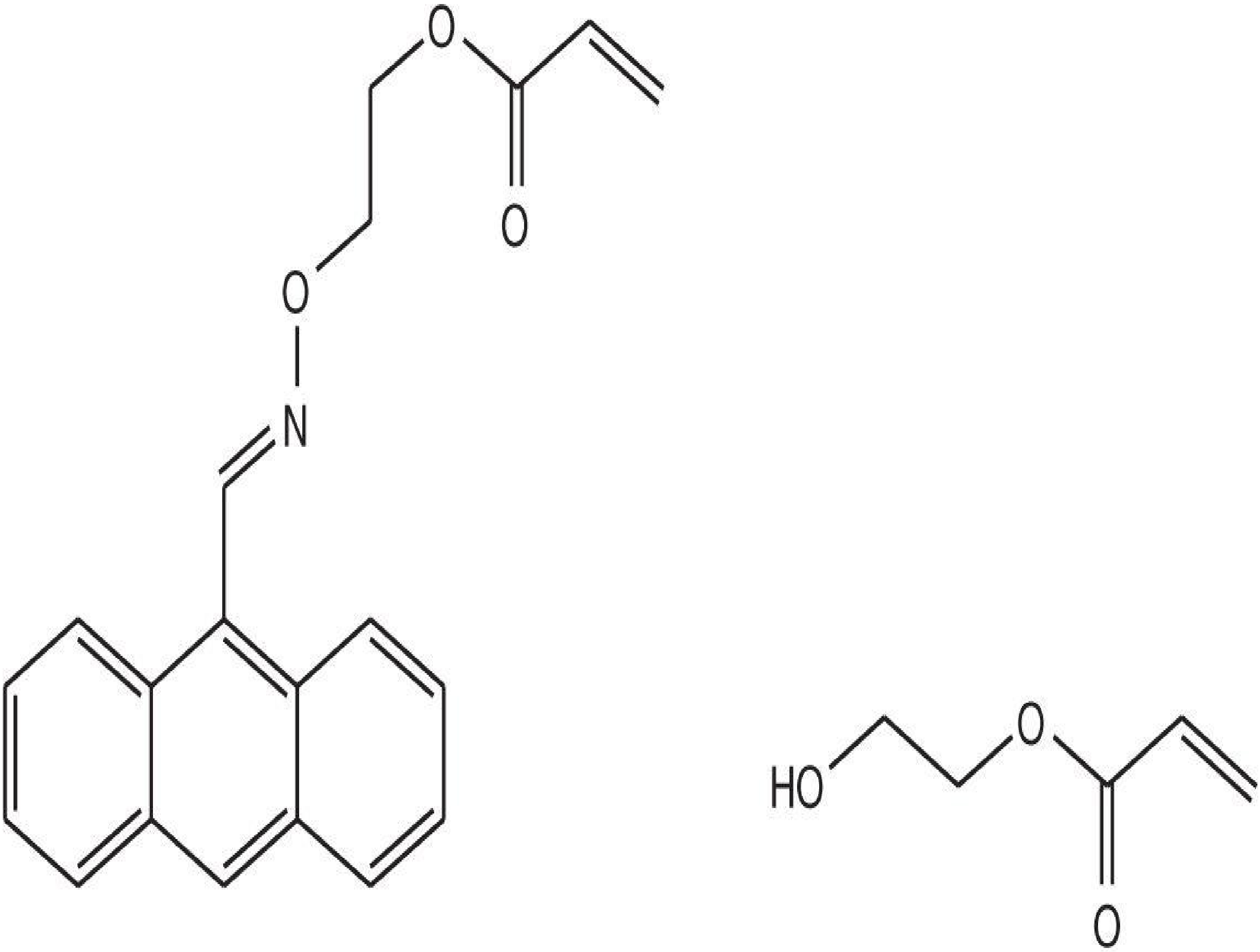


(II)

Figure 20.27

Notes and Observations

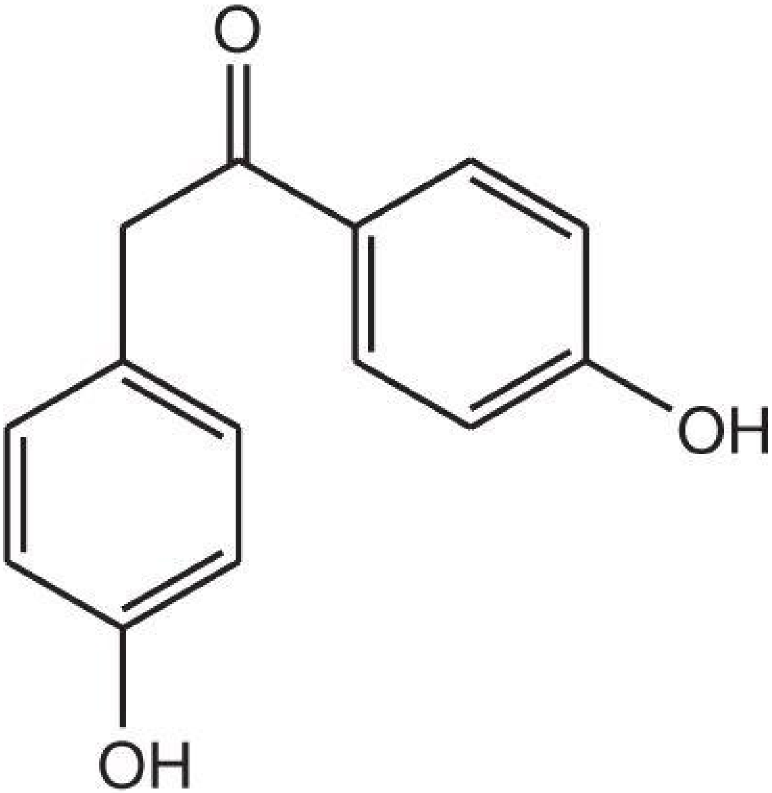
1. Hong[1] prepared relatively low-toxic organic anti-reflective polymers using 9-anthracenemethylimineethylacrylate, (III), and then copolymerized them with 2-hydroxyethylacrylate, (IV), to enhance the material strength and broaden the product versatility. (See Fig. 20.28.)



(III) (IV)

Figure 20.28

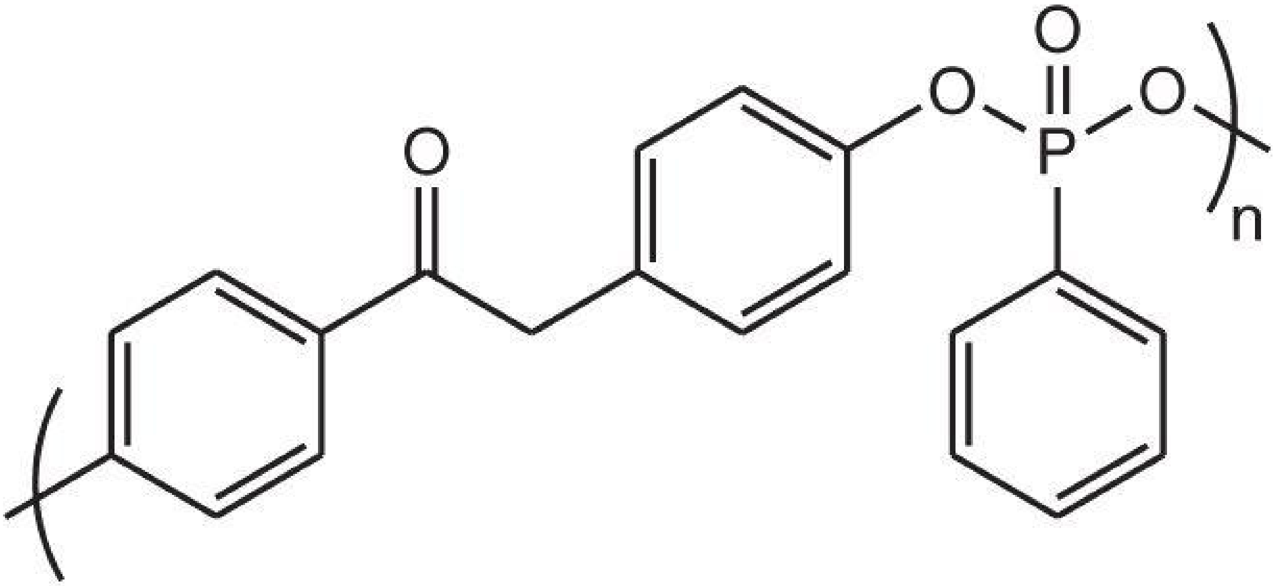
2. Emrick[2] used 4,4’-bishydroxydeoxybenzoin, (VI), as a replacement comonomer for bisphenol-A in preparing engineered plastics. At elevated temperatures, 4,4’-bishydroxydeoxybenzoin-containing copolymers demonstrated improved anti-flammable properties with lower toxic emissions. (See Fig. 20.29.)



(V)

Figure 20.29

3. Emrick[3] replaced bisphenol-A with 4,4’-bishydroxydeoxybenzoin to prepare polyphosphonates, (VII), with reduced flammability properties. Deoxybenzoin-based polyphosphonates exhibited reduced flammability properties with no toxic emissions at decomposition temperatures typically associated with bisphenol-A. (See Fig. 20.30.)

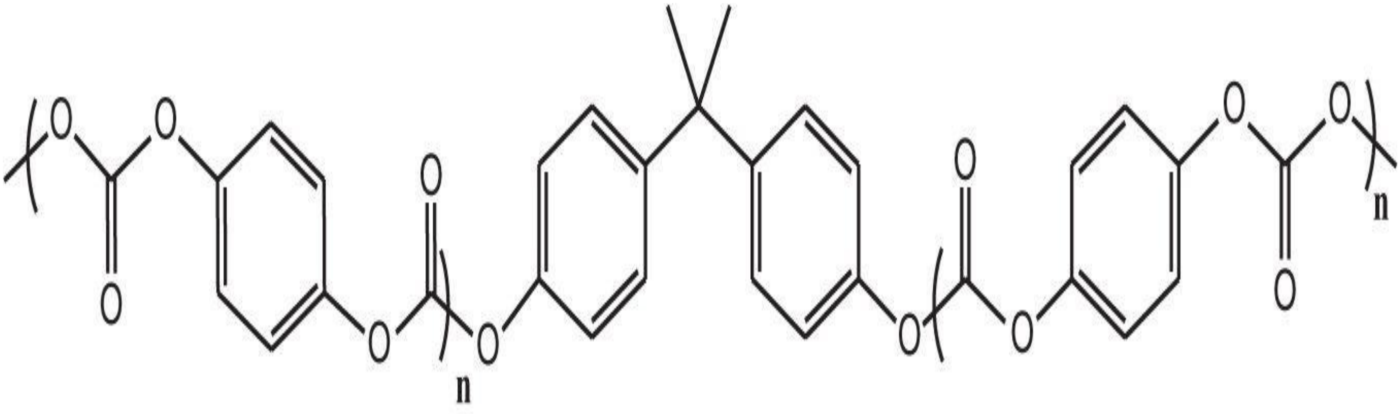


(VII)

Figure 20.30

4. Shinohata[4] prepared engineered materials consisting of polycarbonates having an Mn ~50,000 daltons linked together using bisphenol-A, (VIII). The low bisphenol-A incorporation level was designed to limit and address toxicity concerns. (See Fig.

20.31.)



(VIII)

Figure 20.31

References

1. Sung-eun Hong et al., *Organic anti-reflective coating polymer, anti-reflective coating composition comprising the same and methods of preparation thereof*, U.S. Patent Application 20030003397 (January 2, 2003)

2. Todd Emrick et al., *Deoxybenzoin-derived anti-flammable polymers*, U.S. Patent 8,314,202 (November 20, 2012)

3. Todd Emrick et al., *Deoxybenzoin-based anti-flammable polyphosphonate and poly(arylate-phosphonate) copolymer compounds, compositions, and related methods of use*, U.S. Patent 7,863,400 (January 4, 2011)

4. Masaaki Shinohata et al., *Isocyanates and aromatic hydroxy compounds*, U.S. Patent 8,293,934 (October 23, 2012)

Catalysts for Recycling Polyethylene Terephthalate

Author	James Lupton Hedrick et al.
Patent Title	***Catalytic depolymerization of polymers containing electrophilic linkages using nucleophilic reagents,*** U.S. Patent Application 20120302781 (November 19, 2012)

Relevant Prior Patents by Author or Coauthors

Methods of depolymerizing terephthalate polyesters, U.S. Patent Application 20120223270 (September 6, 2012)

Catalytic depolymerization of polymers containing electrophilic linkages using nucleophilic reagents, U.S. Patent Application 20110004014 (January 6, 2011)

Catalytic polymerization of polymers containing electrophilic linkages using nucleophilic reagents, U.S. Patent Application 20110003949 (January 6, 2011)

Catalytic depolymerization of polymers containing electrophilic linkages using nucleophilic reagents, U.S. Patent 8,309,618 (November 13, 2012)

Thermally reversible cross-linked poly (aryl ether ketone) media and method for high density data storage, U.S. Patent 8,337,954 (December 25, 2012)

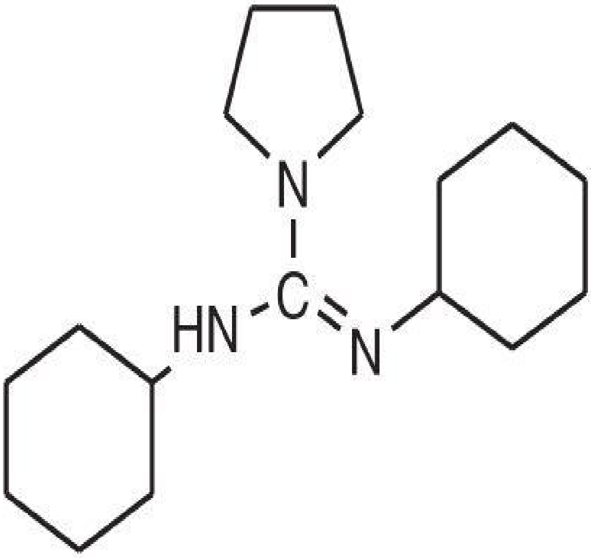
Product Application

Guanidine derivatives have been found effective as catalysts in recycling the engineering thermoplastic polyethylene terephthalate by depolymerizating the polyester. Valuable commodity chemicals were produced from this depolymerization process that can be used for carpeting, clothing, tire cords, beverage containers, film, automotive applications, and electronics.

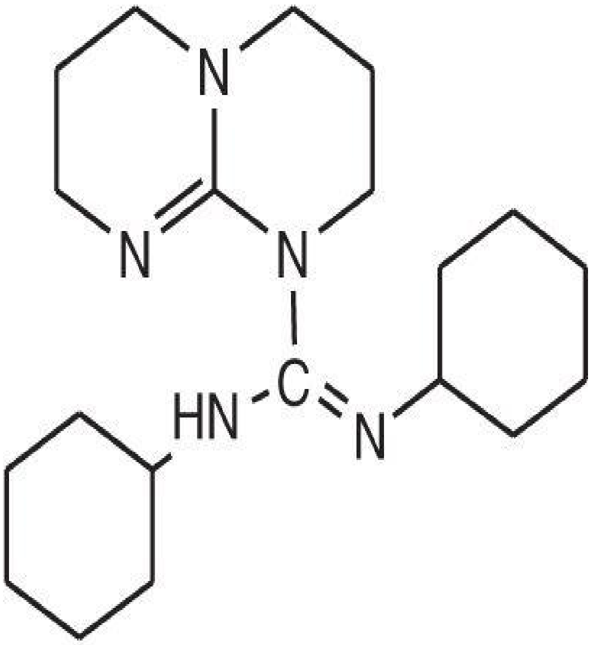
Significance of Current Application

The current method describes a simple method of waste reclamation and plastic recycling of the engineering thermoplastic, polyethylene terephthalate. The recycling process entails mixing polyethylene terephthalate with a guanidinium depolymerization catalyst then post-reacting this intermediate with a nucleophile such as an alcohol or amine. The depolymerization process produces monomeric diesters and diamide mixtures. This may be the first viable process of diverting polyesters targeted for landfills into commercially valuable and sustainable chemical intermediates through an ambient-temperature depolymerization reaction process.

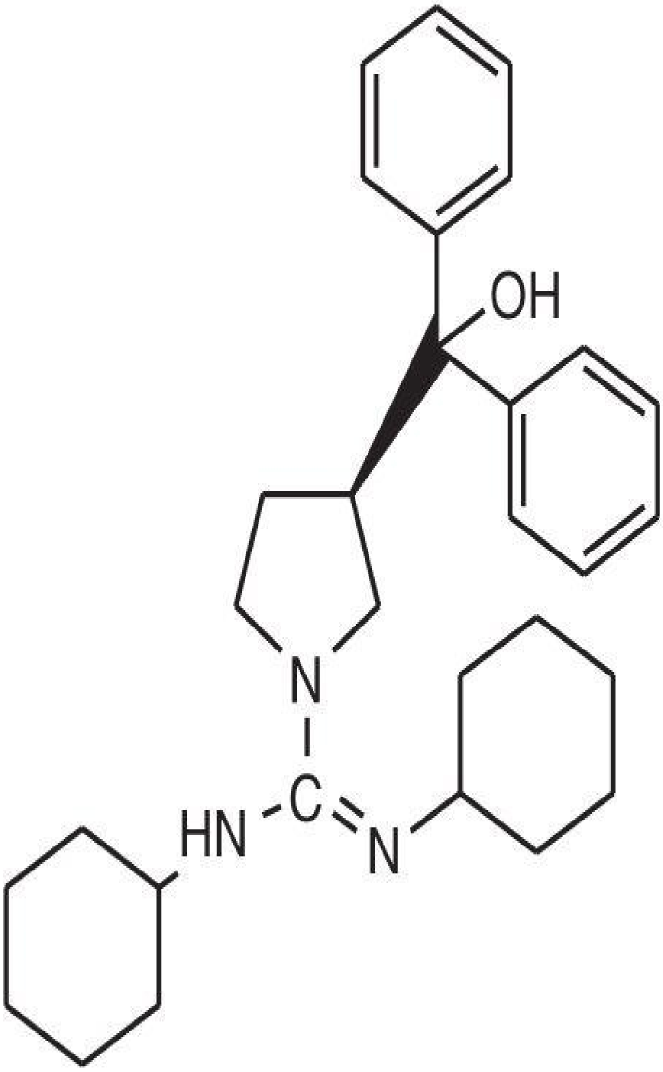
Depolymerization Catalysts



(I)



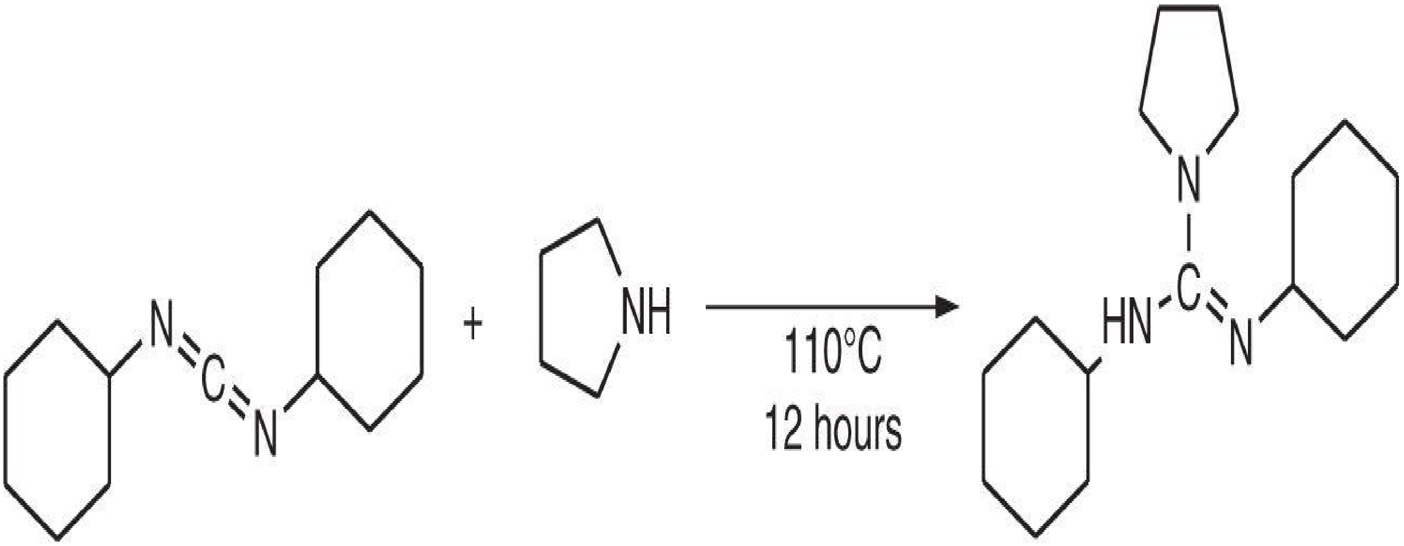
(II)



(III)

Figure 20.32

Catalyst Formation



(I)

Figure 20.33

Depolymerization Route

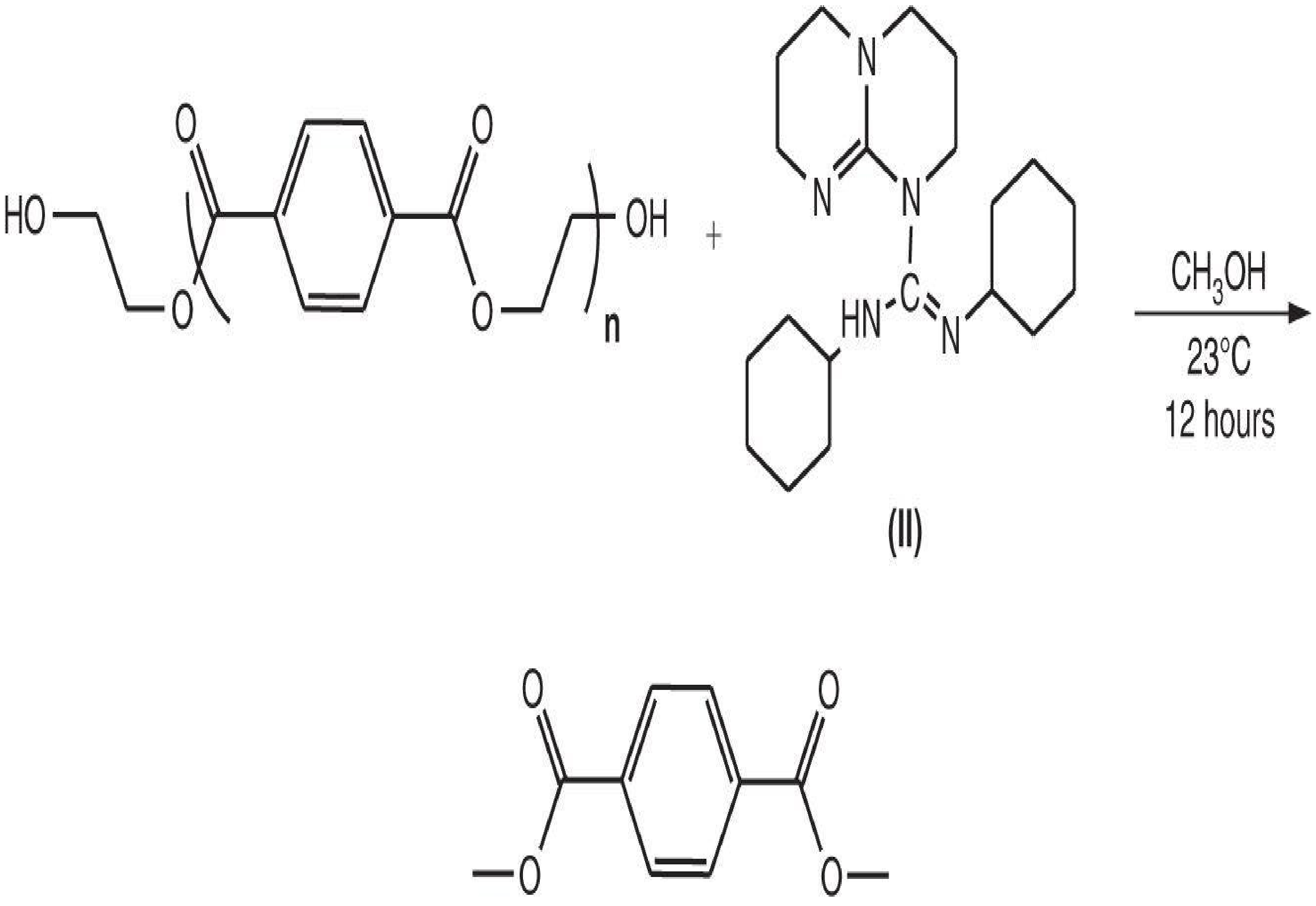


Figure 20.34

Experimental

1. Preparation of guanidinium Depolymerization Catalyst 2. A reactor was charged with 3 g of dicyclohexylcarbodiimide and 10 mL of pyrrolidine and then refluxed overnight under dry nitrogen. Excess pyrrolidine was then distilled off and the product was purified by Kugelroh distillation at 265°C. The product was isolated as a colorless oil in 48% yield and used without further purification. Product characterization is provided below.

^{1} **H-NMR** (400 MHz, $CDCl_3$) ε (ppm) 6.02, [br s, ^{1}N, N–H]; 3.79 [t, 2H, backbone CH_2, J = 7.0 Hz]; 3.05 [t, 2H, backbone CH_2, J = 7.0 Hz]

^{13} **C-NMR** (100.6 MHz, $CDCl_3$) ε (ppm) 171.18 [central sp^2 C]; 52.62 [backbone CH_2] 49.38 [backbone CH_2].

LRMS (m/z): 112.1 (positive ion, M+H).

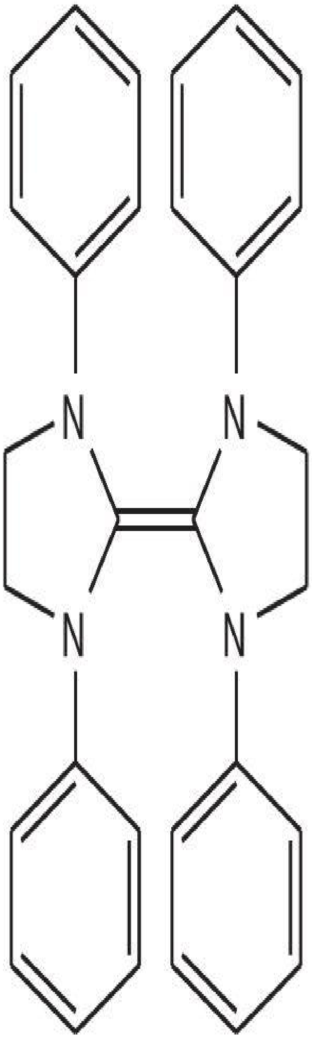
2. Depolymerization of polyethylene terephthalate. A small reaction kettle containing a 250-mg square piece of polyethylene terephthalate was immersed in 1 mL toluene then treated with 20 drops of methanol and 25 mg of the Step 1 depolymerization catalyst. After standing overnight at ambient temperature, the polyester square disintegrated. The reactor was then diluted with methylene chloride, extracted with water, concentrated, and then analyzed. ^{1}H-NMR indicated that the only reaction product was dimethylteraphthalate, identified by its two definitive peaks.

Testing

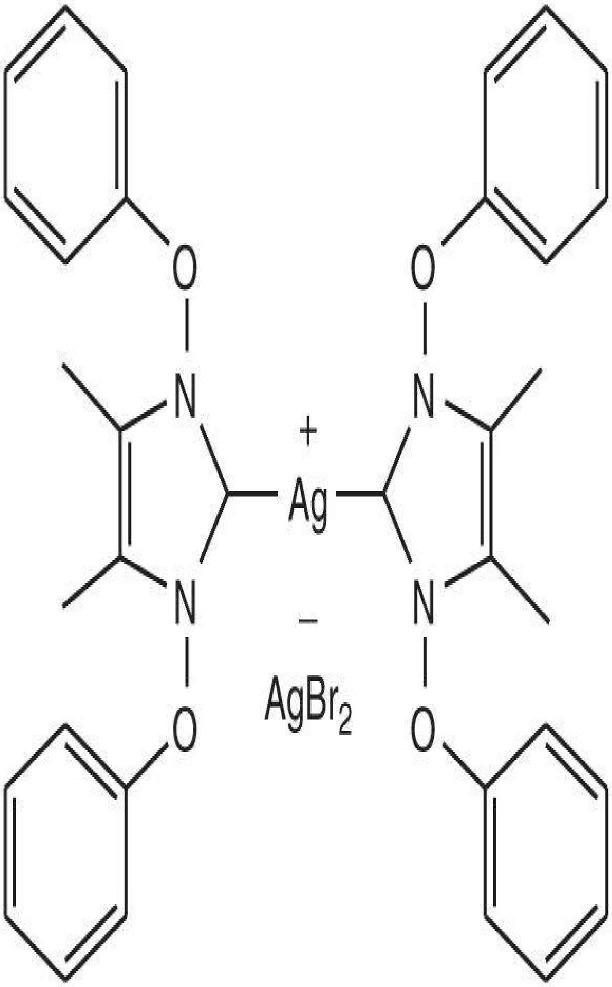
Depolymerization testing results provided by the author indicated the process was quantitative. Polyethylene terephthalate squares immersed in solutions containing depolymerization catalysts (I) through (III) were all effective in converting polyethylene terephthalate squares into either dimethyl teraphthalate or N,N-dimethyl teraphthalamide.

Notes and Observations

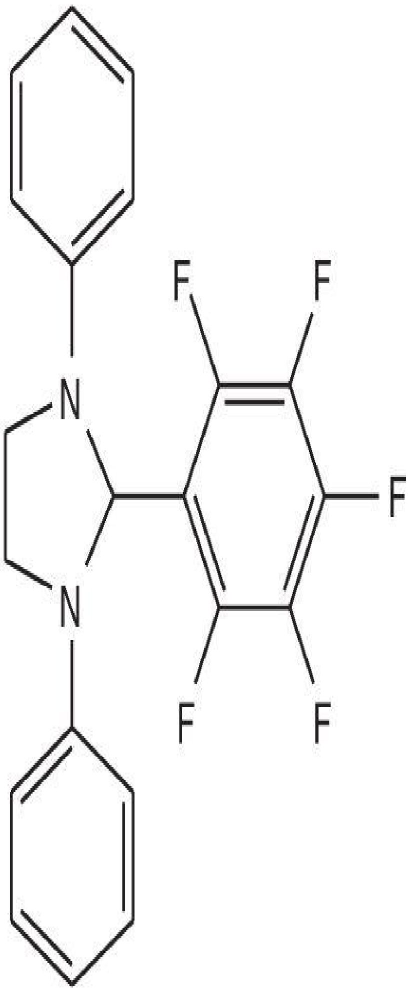
1. Imidazole derivatives, (IV) through (VI), that generated N-heterocyclic carbenes upon thermolysis at 80°C were previously prepared by the author[1] and used to depolymerize polypropylene carbonate, poly(bisphenol-A carbonate), and poly(1,4-butylene adipate). In this process, the formation of undesirable by-products resulting from polymer degradation was minimal. (See Fig. 20.35.)



(IV)



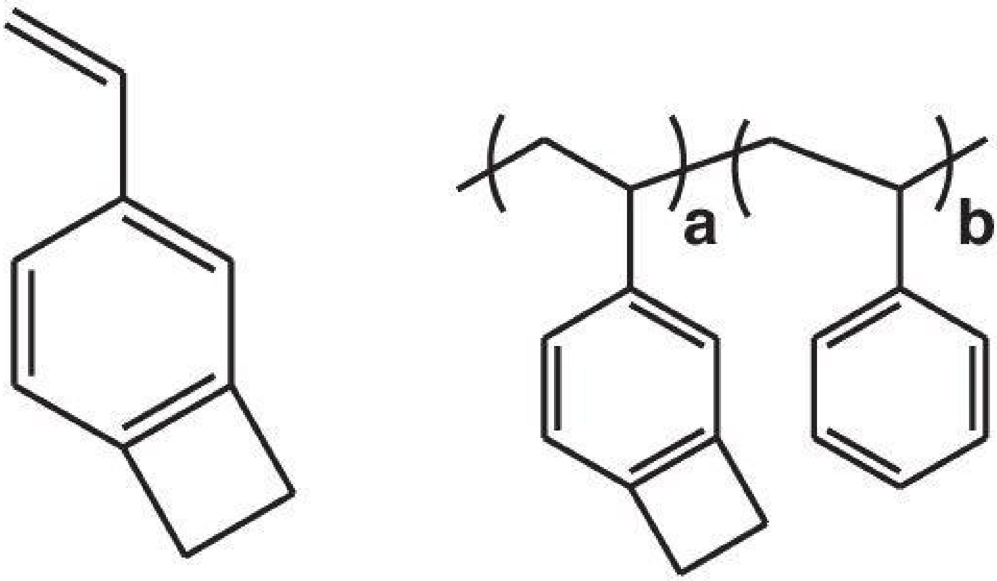
(V)



(VI)

Figure 20.35

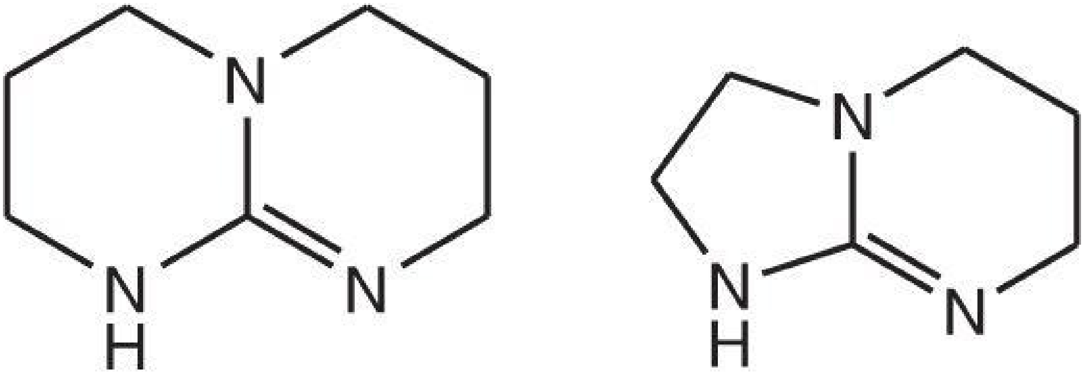
2. Hawker[2] converted recycled styrene into 4-vinyl-benzocyclobutene, (VII), then copolymerized it with additional recycled styrene to form a polymer, (VIII), that underwent irreversible crosslinking when heated to 125°C for 3 hours. Crosslinked particles formed from this process were used in the manufacture of dielectric materials in electronic devices. (See Fig. 20.36.)



(VII) (VIII)

Figure 20.36

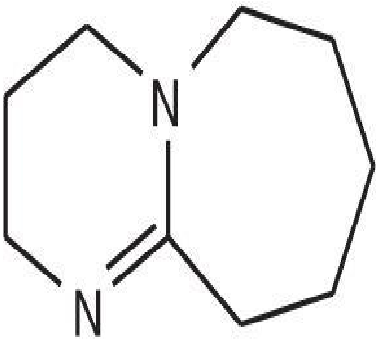
3. Two additional bicyclic polyethylene terephthalate depolymerization catalysts, (IX) and (X), were recently reported by Hedrick[3] and are illustrated in Fig. 20.37.



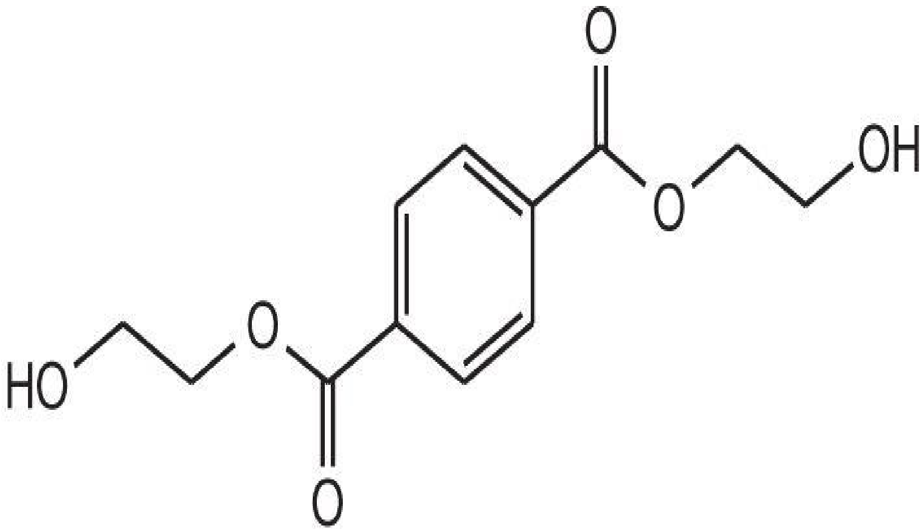
(IX) (X)

Figure 20.37

4. Alabdulrahman[4] used 1,8-diazabicycloundec-7-ene, (XI), to depolymerize post-consumer polyethylene terephthalate at 190°C in the presence of ethylene glycol to prepare monomeric 2-hydroxyl ethyl diesters, (XII). (See Fig. 20.38.)



(XI)



(XII)

Figure 20.38

References

1. James Lupton Hedrick et al., *Catalytic depolymerization of polymers containing electrophilic linkages using nucleophilic reagents*, U.S. Patent 7,544,800 (January 9, 2009)

2. Craig Jon Hawker et al., *Preparation of cross-linked particles from polymers having activatible crosslinking groups*, U.S. Patent 6,992,115 (January 31, 2006)

3. James Lupton Hedrick et al., *Catalytic depolymerization of polymers containing electrophilic linkages using nucleophilic reagents*, U.S. Patent 8,309,618 (November 13, 2011)

4. Abdullah M. Alabdulrahman et al., *Methods of depolymerizing terephthalate polyesters*, U.S. Patent Application 20120223270 (September 6, 2012)

Dextrose-Derived Polyfarnesenes

Author Derek James McPhee

Patent Title ***Farnesene interpolymers,*** U.S. Patent 8,217,128 (July 10, 2012)

Relevant Prior Patents by Author

Polyfarnesenes, U.S. Patent 8,273,181 (November 20, 2012)

Polyfarnesenes, U.S. Patent 8,048,976 (November 1, 2011)

Farnesene interpolymer, U.S. Patent 7,868,115 (January 11, 2011)

Compositions comprising a farnesene interpolymer, U.S. Patent 7,868,114 (January 11, 2011)

Fuel compositions comprising farnesane and farnesane derivatives and method of making and using same, U.S. Patent 7,399,323 (July 15, 2008)

Product Application

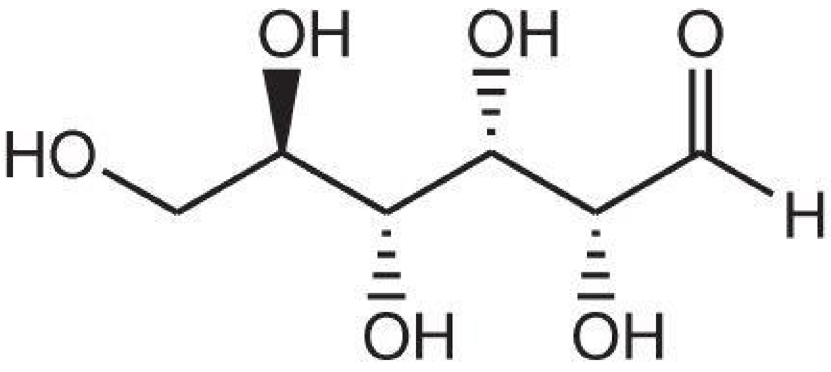
Dextrose-derived α-farnesene and β-farnesene copolymers can be used in preparing molded articles such as toys, grips, soft touch handles, bumper rub strips, floorings, and auto floor mats.

Significance of Current Application

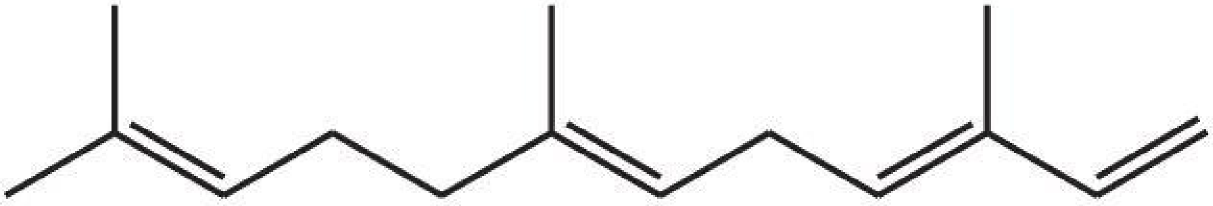
This investigation has developed an efficient method for preparing renewable α-farnesene or β-farnesene by reacting them with dextrose in the presence of bioengineered microorganisms isolated from Saccharomyces cerevisiae.

In many commercial applications, there is an urgent need for preparing renewable copolymers as replacement monomers for vinyl halides, vinyl ether, acrylonitrile, acrylic ester, methacrylic ester, acrylamide or methacrylamide. The current investigation addresses two concerns associated with preparing renewable and commercially viable renewable copolymers. First, an inexpensive and high-yielding method was identified for preparing both renewable α-farnesene and β-farnesene using dextrose and bioengineered microorganisms isolated from Saccharomyces cerevisiae. The second concern focused on methods to prepare renewable high-molecular weight-block copolymers containing selected α-olefin monomers and either α-farnesene or β-farnesene. α-Olefins were selected as the comonomer with either α-farnesene or β-farnesene to thermally enhance their physical properties and to ensure their commercial success when they are processed at elevated temperatures to prepare molded articles.

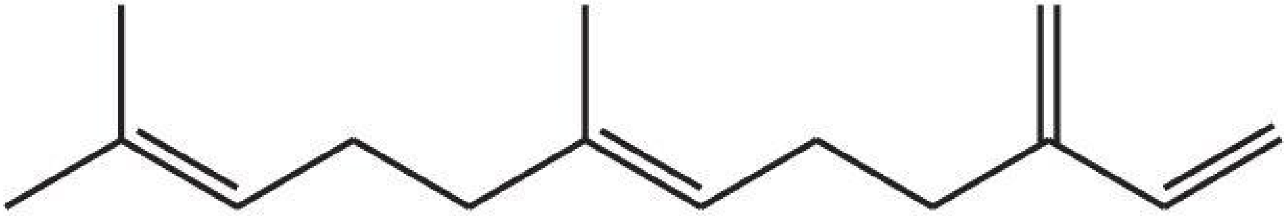
Renewable Reagent and Monomers



Dextrose



α-Farnesene



β-Farnesene

Figure 20.39

Product Formulation

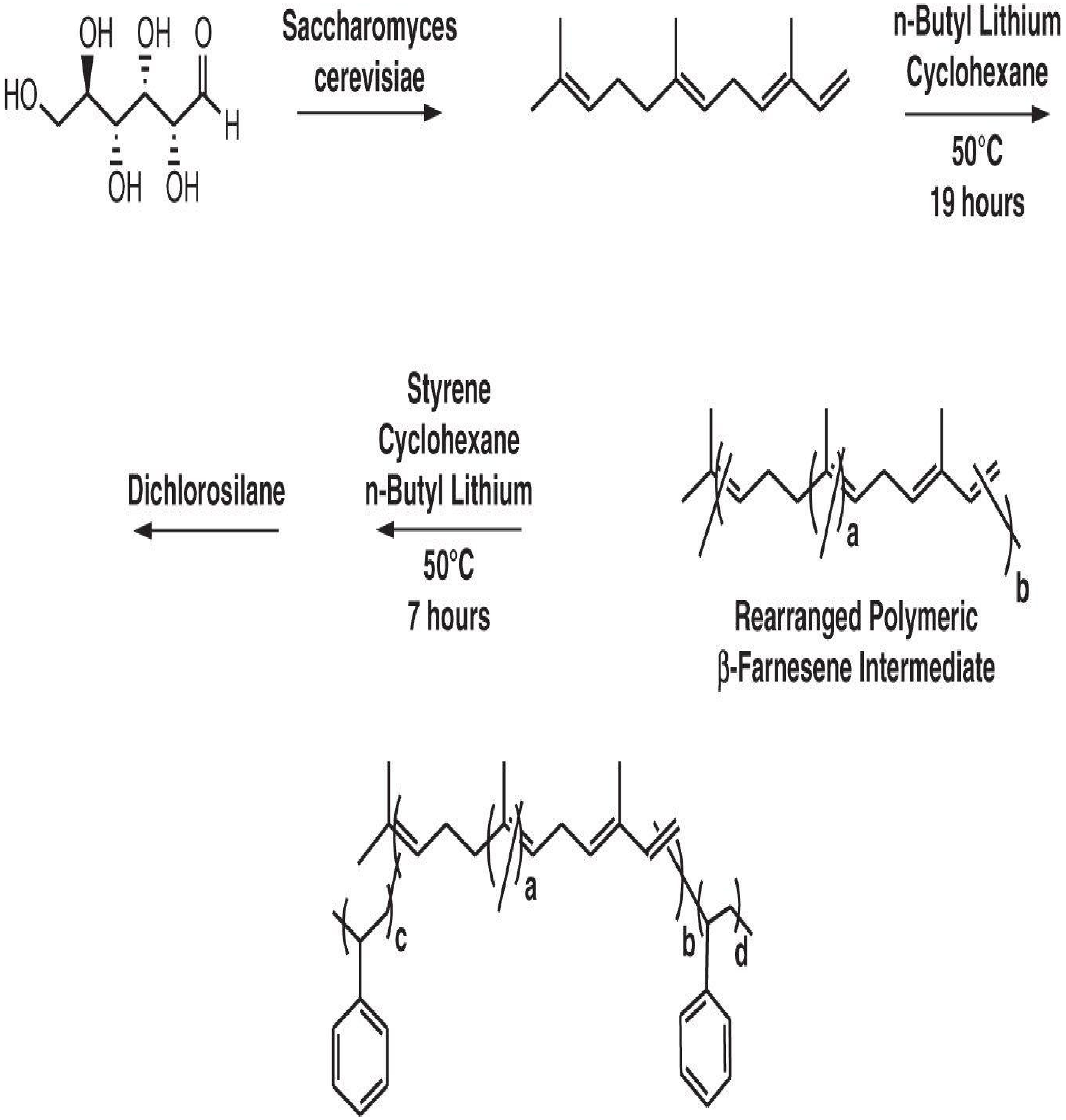


Figure 20.40

Experimental

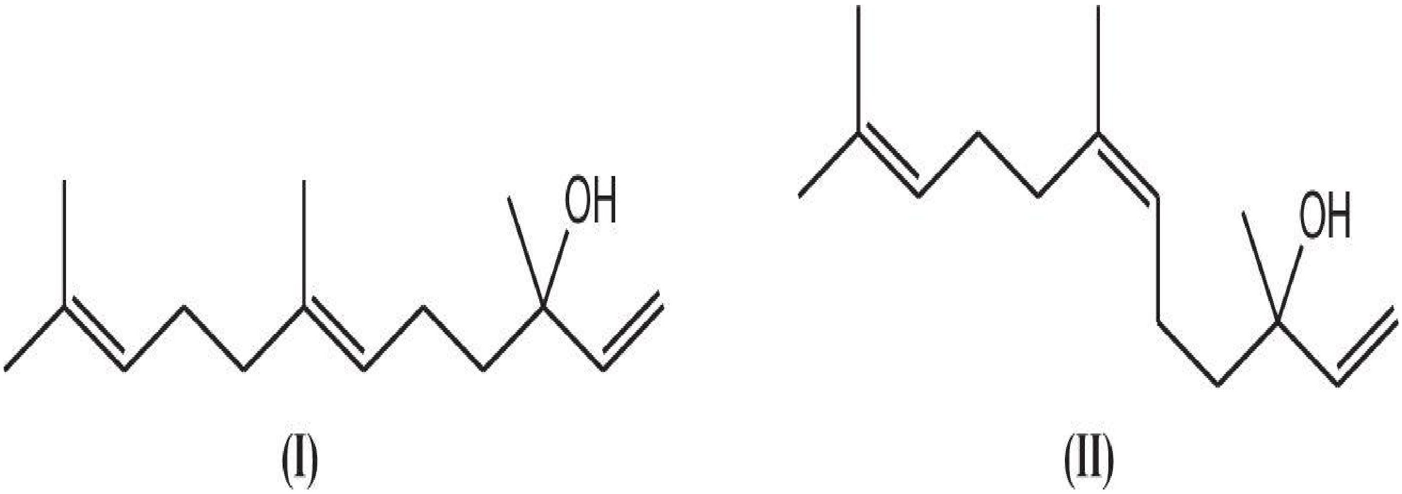
1. Preparation of β-farnesene from dextrose. Genomic DNA was isolated from Saccharomyces cerevisiae that consisted of strain mixtures Y002 (CEN.PK2 background; MATA; ura3-52; trp1-289; leu2-3,112; his3.DELTA.1; MAL2-8C; SUC2), Y007 (S288C background MATA trp1.DELTA.63), Y051 (S288C background; MAT αhis3 Δ1 leu2.Δ 0 lys2.Δ0 ura3. Δ0 P.sub.GAL1-HMG1$^{1586\text{-}3323}$ $P_{GAL1\text{-}upc2\text{-}1}$ erg9:$P_{MET3\text{-}ERG9}$::HIS3 $P_{GAL1\text{-}ERG20}$ $P_{GAL1\text{-}HMG1}^{1586\text{-}3323}$), and EG123 (MATA ura3; trp1; leu2; his4 can1). These strains were then grown overnight in a liquid medium containing 1% yeast extract, 2% bacto-peptone, and 2% dextrose. Cells were then isolated from 10 mL of liquid cultures by centrifugation at 3,100 rpm and cell pellets were then washed in 10 mL of purified water and re-centrifuged. The cell-free solution was then concentrated by distillation and β-farnesene was isolated in quantitative yield.

2. Preparation of 1,4-polyfarnesene. A dried three-neck reactor under argon atmosphere was charged with a solution of 92.29 g of the Step 1 product dissolved in 13.7% of cyclohexane and then treated with $1.85 \cdot 10^{-3}$ mol of n-butyl lithium. Once the initiator was added, the reactor mixture was heated to 50°C for approximately 19 hours or until cyclohexane was consumed, as monitored by UV-Vis spectroscopy. Thereafter, the reaction product was precipitated from the reaction mixture using ethanol containing 1% t-butyl catachol. The polymer was then dried in a vacuum oven for 2 hours at 60°C and the product was isolated in 97% yield having an Mn of 105,000 daltons.

3. Preparation of poly(styrene-b-1,4-farnesene-b-polystyrene). Flask 1 was dried and kept under argon atmosphere and then charged with the Step 2 product to form a 12% solution of β-farnesene dissolved in cyclohexane. A second dried flask stored under argon was then charged with a 20.65-g solution of 10% styrene dissolved in cyclohexane and then treated with $6.88 \cdot 10^{-4}$ mol of n-butyl lithium. The mixture was heated for about 16 hours at 50°C until all styrene had been consumed, as monitored by GPC. Thereafter, the second flask was treated with 19.61 g of β-farnesene from Flask 1 and the reaction continued for approximately 7 hours, as monitored by GPC. The second flask was then further treated with three equal aliquots of $3.44 \cdot 10–^{4}$ mol of the coupling agent dichlorosilane so that the molar ratio of Li-to-Cl of the reaction mixture was 1:2. This reaction mixture continued to react until a color change from yellow to clear was observed. The reaction product was then precipitated in ethanol containing 1% t-butyl catachol and dried in a vacuum oven at 60°C for two hours. After the solvent was removed by distillation, the product was isolated as a white, fluffy solid in 97% yield.

Notes and Observations

1. Anet[1] previously prepared α- and β-farnesenes by dehydrating trans-, (I), and cis-nerolidol, (II), with phosphoryl chloride in pyridine. (See Fig. 20.41.)



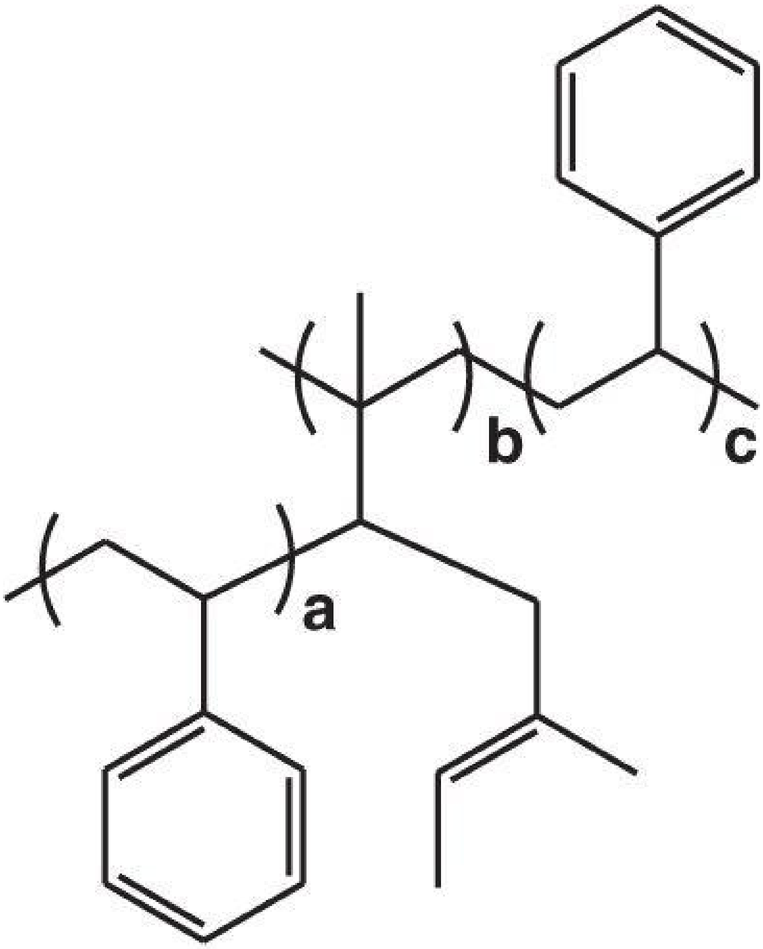
(I) (II)

Figure 20.41

2. Isoprenoid-modifying enzymes were recently prepared by Ro[2] and consisted of synthase mRNA (AY640154; Cucumis sativus). Purified enzymes were then used to prepare isoprenes, particularly α-farnesene, from galactose and glucose.

3. Meadows[3] prepared 3-hydroxy-3-methylglutaryl-CoA from acetyl-CoA that was effective in preparing both α- and β-farnesene from monosaccharides including glucose, galactose, mannose, fructose, and ribose.

4. In a subsequent investigation by the author,[4] β-farnesene was prepared from dextrose using Saccharomyces cerevisiae that was then converted into poly(styrene-β-3,4-farnesene-b-polystyrene), (III), by initiating the reaction of styrene and poly(β-farnescene) with n-butyl lithium in the presence of N,N,N′,N′-tetramethylethylenediamine. (See Fig. 20.42.)



(III)

Figure 20.42

References

1. E. F. L. J. Anet, *Synthesis of (E,Z)*-α, *(Z,Z)*-α, *and (Z)*-β-*farnesene*, *Aust. J. Chem.*, 23 (10), 2101–2108 (1970)

2. Dae-Kyun Ro, *Polynucleotides encoding isoprenoid modifying enzymes and methods of use thereof*, U.S. Patent Application 20120288905 (November 15, 2012)

3. Adam Meadows, *Production of acetyl-coenzyme A-derived compounds*, U.S. Patent Application 20120288891 (November 15, 2012)

4. Derek James McPhee, *Farnesene interpolymers*, U.S. Patent Application 20120244304 (September 27, 2012)

Films from Poly(Ester/Starch/Protein) Biopolymers

Author	Bo Shi et al.
Patent Title	***Biodegradable and renewable film,*** U.S. Patent 8,329,601 (December 11, 2012)

Relevant Prior Patents by Author or Coauthors

Water-sensitive film containing an olefinic elastomer, U.S. Patent 8,338,508 (December 25, 2012)

Biodegradable water-sensitive films, U.S. Patent 8,329,977 (December 11, 2012)

Film formed from a blend of biodegradable aliphatic-aromatic copolyesters, U.S. Patent 8,227,658 (July 24, 2012)

Water-sensitive film containing thermoplastic polyurethane, U.S. Patent 8,147,965 (April 3, 2012)

Thermoplastic starch for use in melt-extruded substrates, U.S. Patent 7,998,888 (August 16, 2011)

Product Application

A method for preparing a renewable biopolymer was converted into films and then used to prepare disposable absorbent articles such as feminine hygiene products and incontinence products.

Significance of Current Application

The majority of films and film coatings are prepared from non-renewable sources, particularly non-biodegradable low-density polyethylene. Initially, replacing non-renewable and non-biodegradable low-density polyethylene with biodegradable aliphatic-aromatic copolyesters resulted in consumer products that had limited flexibility and other physical properties that made processing of these materials extremely difficult. To address these problems, this investigation has identified renewable and biodegradable thermoplastic–polymeric mixtures that are effective as surface coating agents for consumer applications with dramatically improved processing properties and processing times at reduced temperatures.

Component Mixture 1

A) Wheat Gluten A protein composite found in wheat and related grains. It is a composite of gluten and gladin cojoined with starch in the endosperm.

B) Glucosol ™ 800 Modified starch having a weight average molecular weight of approximately 2,900,000 daltons with a polydispersity of approximately 28.

C) Excel P-40S Mixtures of oleate and stearate mono-and di-glycerides that are used as emulsifiers, lubricants, and anti-static agents in plastic mixtures.

Component Mixture 2

ECOFLEX® Resins, (I). ECOFLEX Resins are biodegradable aromatic-aliphatic copolyester mixture derived from the condensation of 1,4-butanediol or adipic acid with either terephthalic acid or dimethylterephthalate. (See Fig. 20.43.)

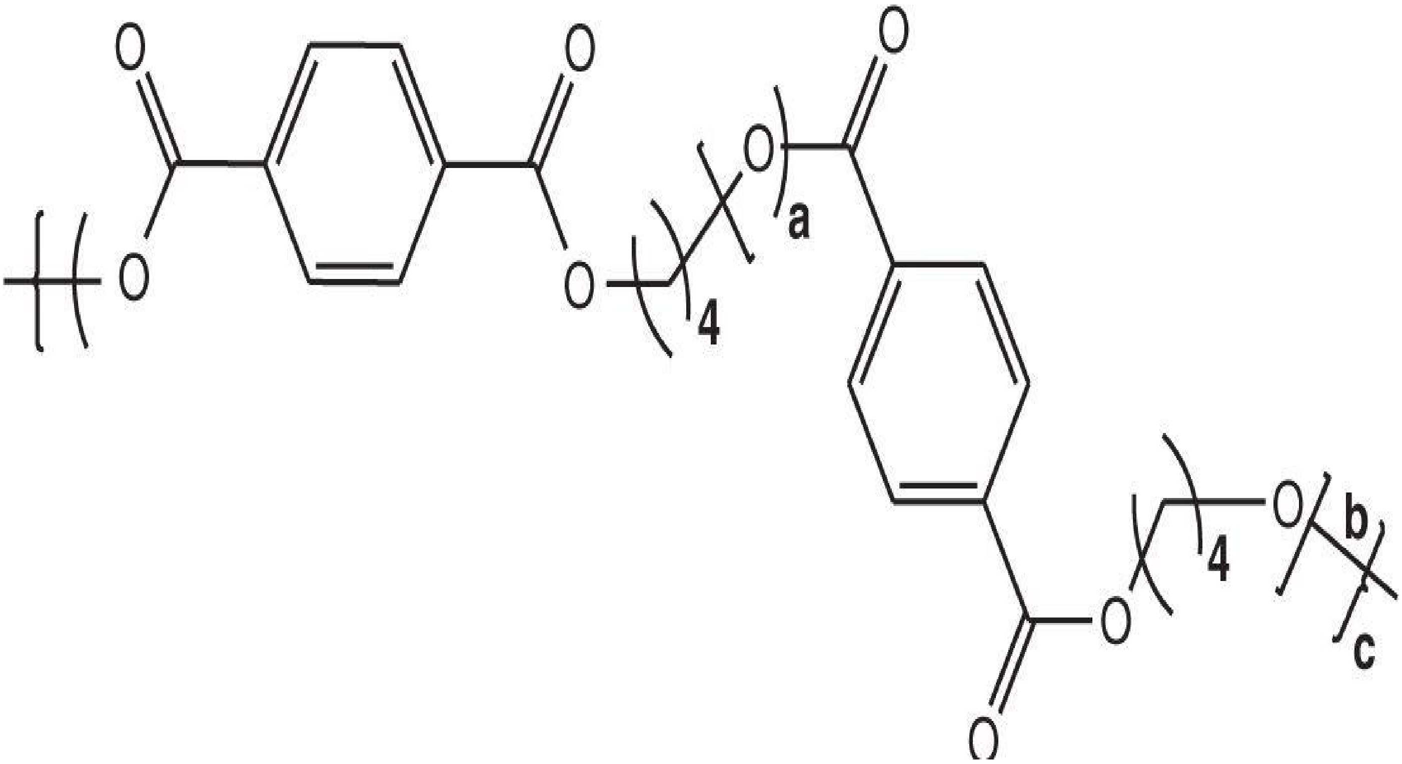
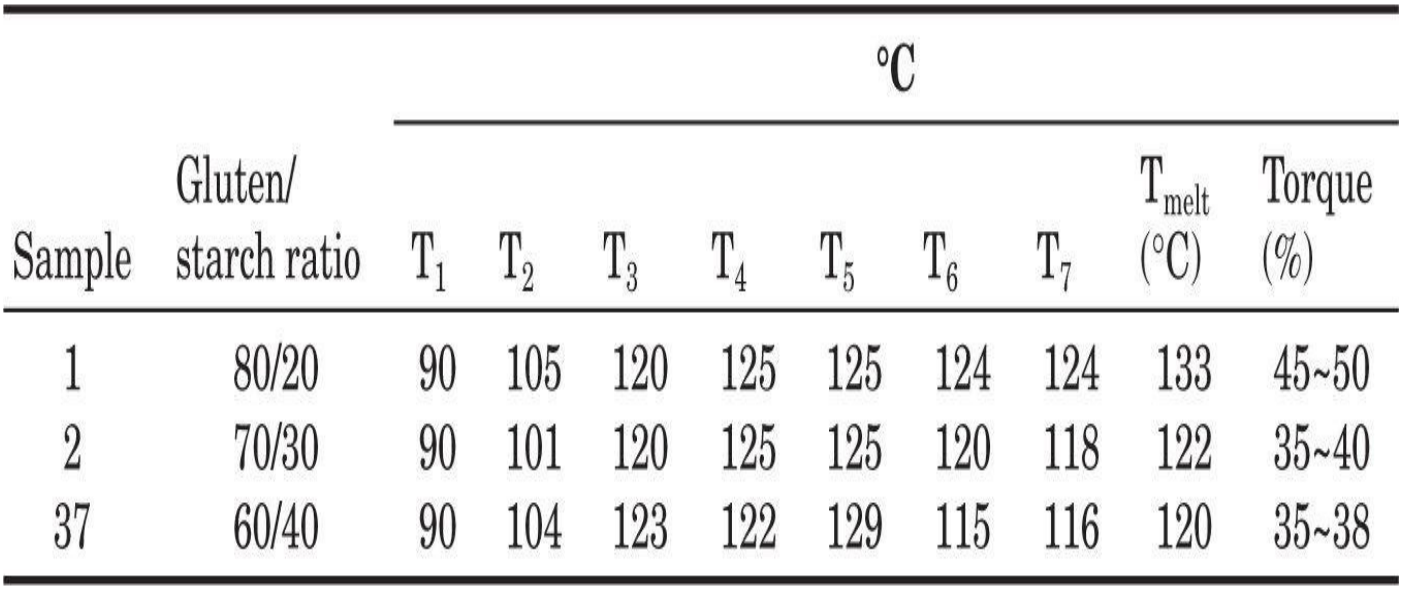


Figure 20.43

Experimental

1. Preparation of mixture 1. Mixtures consisting of Glucosol® 800, wheat gluten, and 2 wt% Excel P-40S were blended in a Hobart® mixer (according to ratios indicated in Table 20.5) for approximately 5 minutes and then added to a K-Tron® feeder. The mixture was then fed into a ZSK-30 extruder where the first barrel received the mixture at 10 lbs/h and where the extruder was heated according to barrel temperature profiles (also provided in Table 20.5). Glycerine was then pumped into barrel 5 with a pressurized injector rate of 2.5 lbs/h so that a 20 wt% concentration was formed. A die was then used to convert the blended mixture into strands having diameter openings between 2 mm and 7 mm with a length of 13 mm. Once the strands were cooled on a conveyer belt, they were pelletized.

TABLE 20.5 Gluten and starch ratios used in preparing Mixture 1. Extruderbarrel-processing temperatures used for preparing starch-gluten strands are also provided.



		°C								
Sample	Gluten/ starch ratio	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_{melt} (°C)	Torque (%)
1	80/20	90	105	120	125	125	124	124	133	45~50
2	70/30	90	101	120	125	125	120	118	122	35~40
37	60/40	90	104	123	122	129	115	116	120	35~38

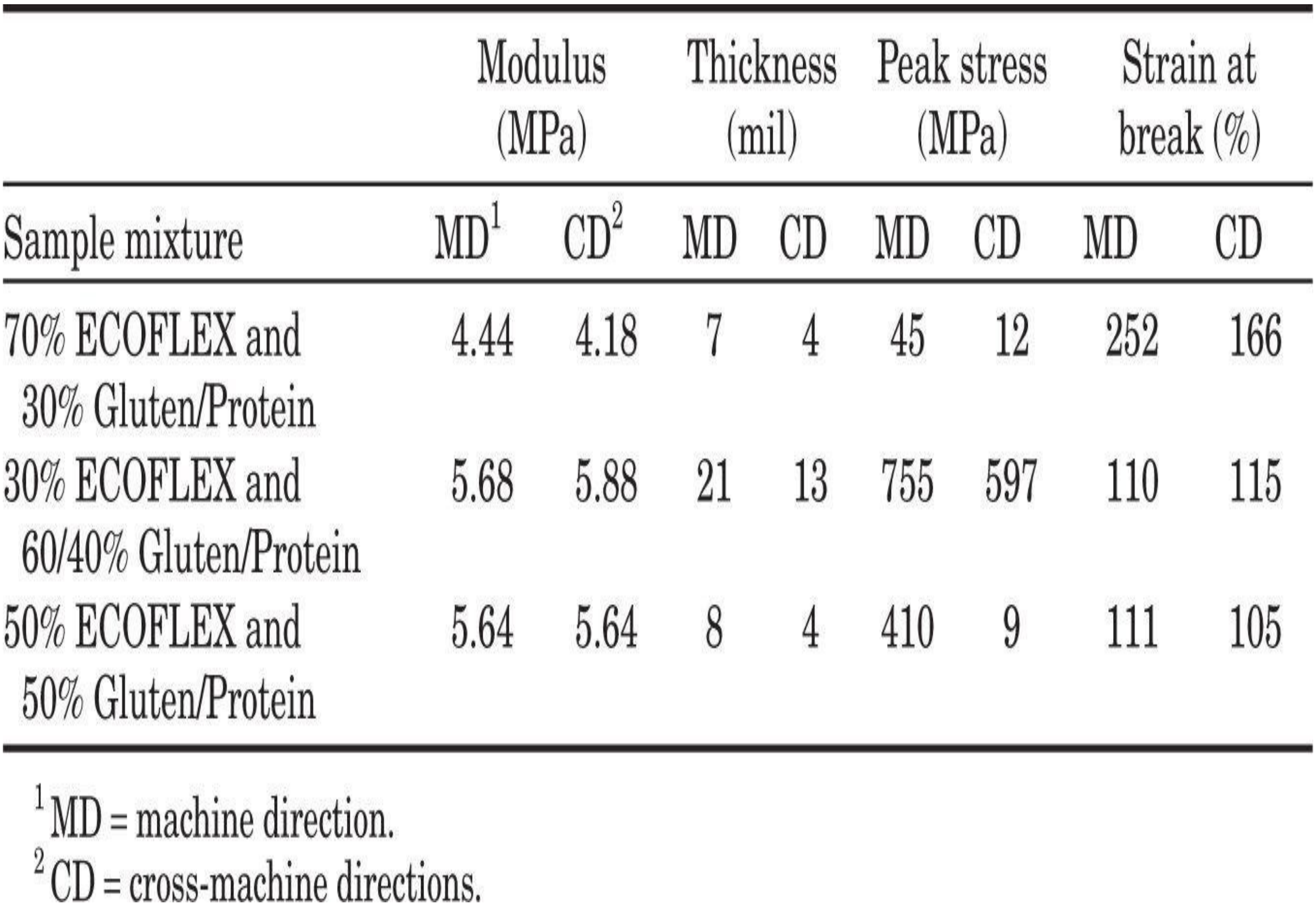
Extruder Temperature Profile

2. Preparation of biodegradable film. A mixture consisting of 70 wt% ECOFLEX resin was dry blended with 30 wt% of the Step 1 thermoplastic mixture using a Rheomex® 252 single screw extruder and then cast into a film. The processing temperatures in the three barrel zones was 135°C, 140°C, 140°C, respectively; 140°C for the pump, and 140°C for the die. The melt temperature for the dry blend was 157°C. The pellet-feeding rate was set at 60 rpm with the torque fluctuating within 2400 nm to 2500 nm. Finally, the pressure at the die was approximately 2400 psi, which generated films having a thickness between 2 mil and 5 mil. Once the extruded films were isolated and cooled, the film surfaces was observed to be extremely soft and flexible.

Testing

A. Film tensile strength. The tensile strength of films was determined in accordance with ASTM Standard D638-99. In this process, a constant rate of extension tensile tester was used. The tensile testing unit used was the Sintech® 1/D equipped with TESTWORKS® 4.08B software. Film samples were initially cut into dog-bone shapes having a center width of 3.0 mm. These samples were held between grips having a front and back face measuring 25.4 mm × 76 mm. During testing, samples were stretched at a crosshead speed of 127 millimeters per minute until breakage occurred. The modulus, peak stress, and strain at break (peak elongation) were then measured in the machine direction (“MD”) and cross-machine directions (“CD”). Physical properties of the films are provided in Table 20.6.

TABLE 20.6 Mechanical properties of ECOFLEX and wheat-gluten-p performed using mechanically held 3.0-mm-thick bone-shaped samples.



	Modulus (MPa)		Thickness (mil)		Peak stress (MPa)		Strain at break (%)	
Sample mixture	MD[1]	CD[2]	MD	CD	MD	CD	MD	CD
70% ECOFLEX and 30% Gluten/Protein	4.44	4.18	7	4	45	12	252	166
30% ECOFLEX and 60/40% Gluten/Protein	5.68	5.88	21	13	755	597	110	115
50% ECOFLEX and 50% Gluten/Protein	5.64	5.64	8	4	410	9	111	105

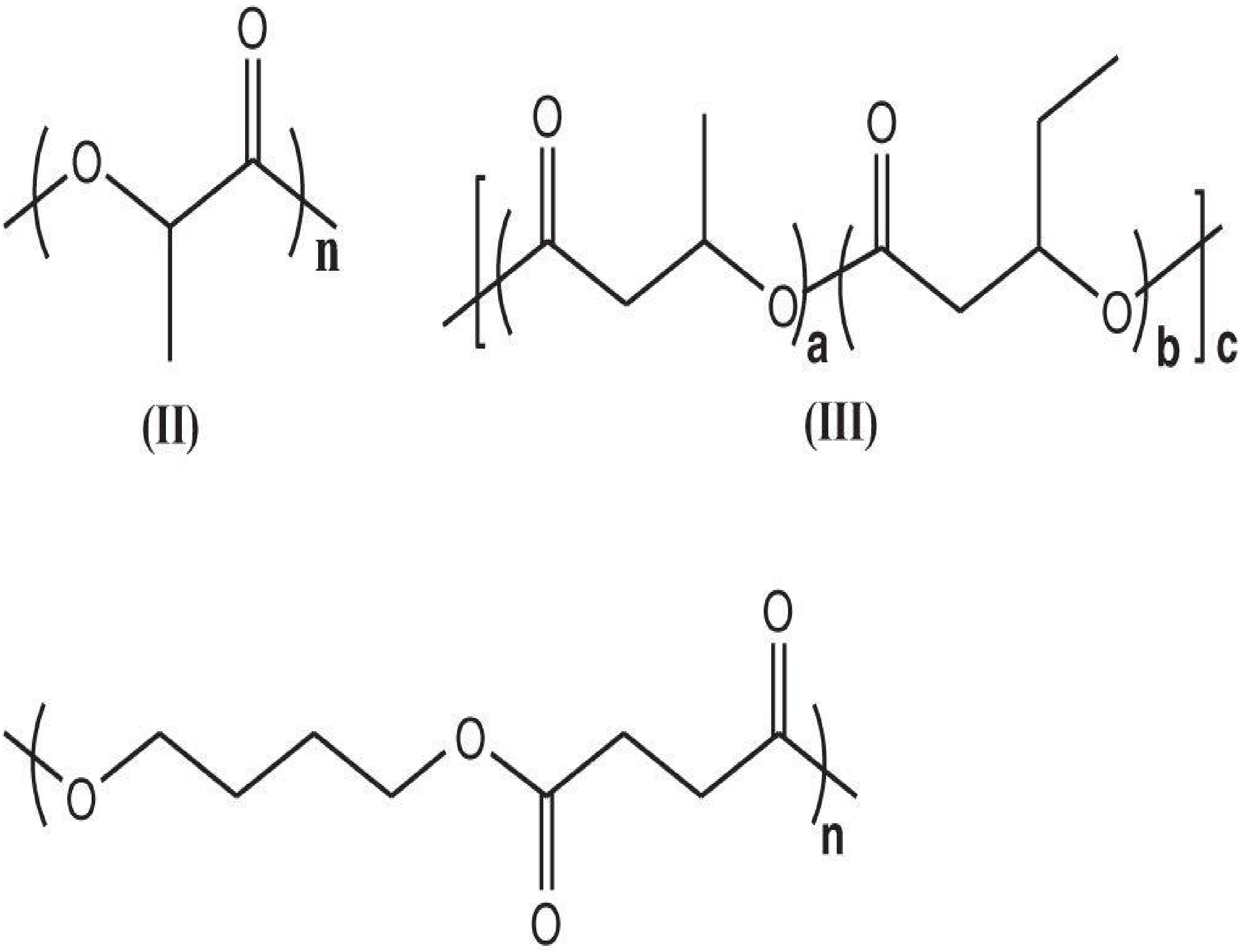
[1] MD = machine direction.

[2] CD = cross-machine directions.

Testing Results

Notes and Observations

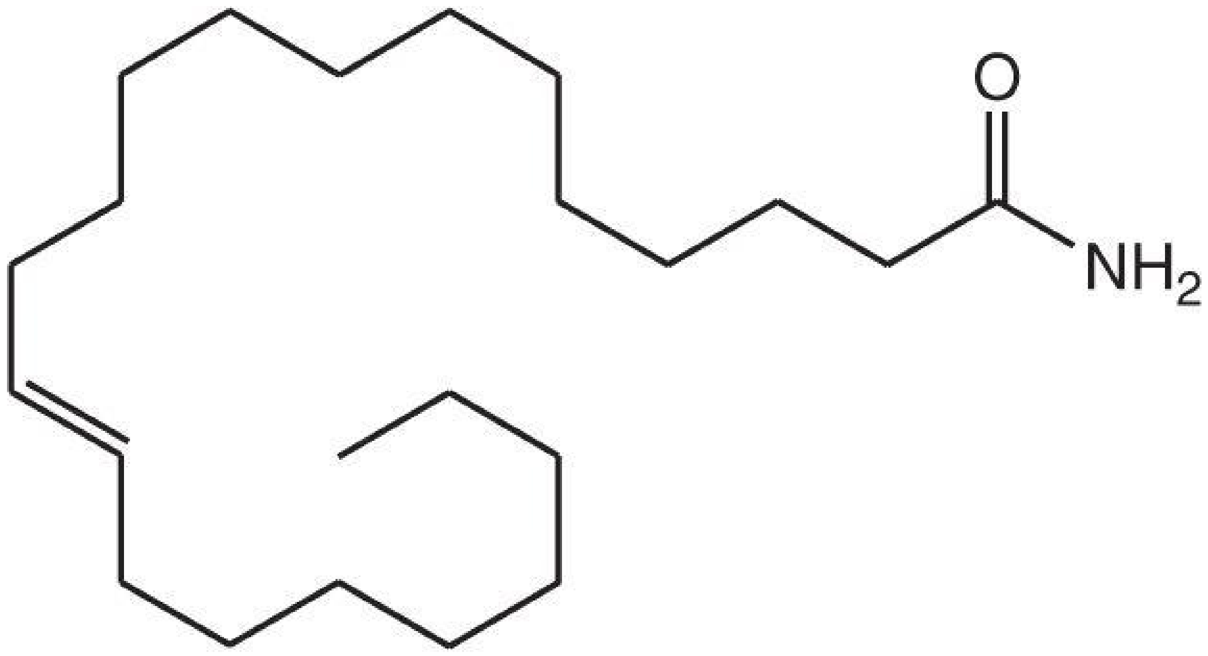
1. Wang[1] prepared a biodegradable water-sensitive film consisting of a mixture of 87.0 mol%:89.0 mol% hydrolyzed polyvinyl acetate and the remaining portion consisting of equivalent amounts of hydroxylpropyl starch and polyvinyl alcohol using sorbitol as the plasticizer. Films prepared from this blend were then used in consumer disposable goods such as sanitary napkins and adult incontinence garments.
2. Biodegradable films that were used for personal care products, such as sanitary napkins and adult incontinence garments, were prepared by Wang[2] using films consisting of blends of polylactide, (II), grafted with poly(β-hydroxybutyrate-co-β-poly(butylenes-hydroxyvalerate), (III), and polybutylsuccinate, (IV). (See Fig. 20.44.)



(II) (III) (IV)

Figure 20.44

3. Bastioli[3] prepared disposable-bag films using a biodegradable film that was characterized as having a high level of air permeability (“breathability”) that was suitable for use in industrial composting. The film composition consisted of approximately 36.4% starch, 50% Ecoflex, 13.6% glycerol, and 0.2 parts of erucamide, (V). (See Fig. 20.45.)



(V)

Figure 20.45

4. Goino[4] prepared biodegradable polylactic acid resins having antistatic and anti-fogging properties by incorporating surfactants, such as tetraalkylammonium succinyl sulfates, in the blending composition.

References

1. James H. Wang et al., *Biodegradable water-sensitive films*, U.S. Patent 8,329,977 (December 11, 2012)

2. James H. Wang et al., *Grafted biodegradable polymer blend compositions*, U.S. Patent 7,053,151 (May 30, 2006)

3. Catia Bastioli et al., *Highly breathable biodegradable film bag*, U.S. Patent Application 20080038496 (February 14, 2008)

4. Masaya Goino et al., *Biodegradable resin composition*, U.S. Patent Application 20070298237 (December 27, 2007)

Flame Retardants Using Sucrose-Based Polyurethanes

Author Joseph Mooney et al.

Patent Title ***Sugar-based polyurethanes, methods for their preparation, methods of use thereof,*** U.S. Patent Application 20130030067 (January 31, 2013)

Relevant Prior Patents by Author or Coauthors

Room temperature curable polymers and precursors thereof, U.S. Patent 8,178,645 (May 15, 2012)

Polyurethane foams made from hydroxymethyl-containing polyester polyols, U.S. Patent 8,133,930 (March 13, 2012)

Polyester polyols containing secondary alcohol groups and their use in making polyurethanes such as flexible polyurethane foams, U.S. Patent 7,750,108 (June 6, 2010)

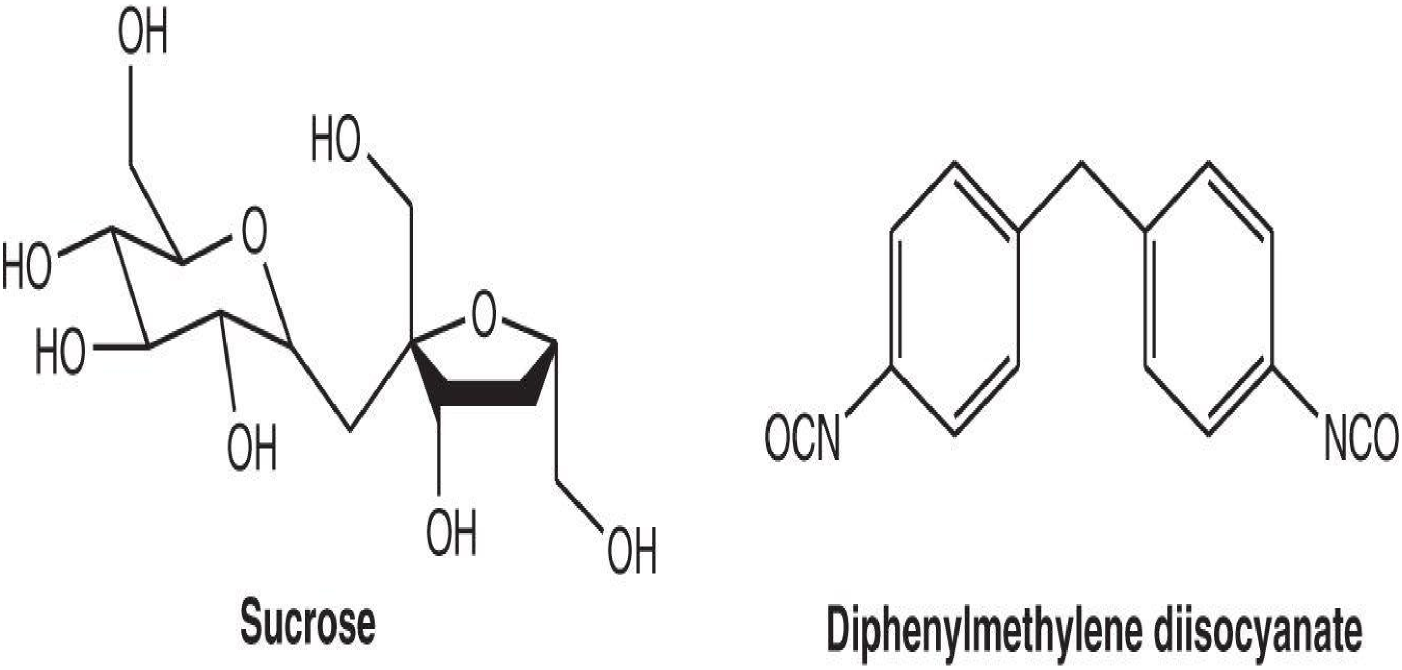
Product Application

Flame-resistant crosslinked polyurethane foams were prepared by reacting biorenewable sucrose with diphenylmethylene diisocyanate containing the flame retardant, tris(chloroisopropyl)phosphate. These materials are suitable as either flame-retardant resins or as heat and noise insulation panels.

Significance of Current Application

Flame-resistant polyurethane foam articles and resin composites used in commercial or industrial applications are prepared by reacting a non-renewable polyol with a selected diisocyanate. In the current investigation, polyurethane foams were prepared by reacting varying ratios of biorenewable sucrose as the polyol with a selected diisocyanate. Polyurethane foams prepared using sucrose as the polyol produced either soft or rigid, or open or closed foams that were then converted into commercial articles. These mixtures were then chemically modified with flame retardants that could be used as either non-combustible foams or to produce inexpensive heat and noise insulation panels.

Components



Sucrose

Diphenylmethylene diisocyanate

Figure 20.46

Component 1 Mixture

A solution consisting of 89 wt% of sucrose dissolved in water was treated with 1.7 wt% of silicone glycol copolymer as a surfactant and then thoroughly stirred and treated with 3 wt% of the reaction catalysts, bis(2-dimethylaminoethyl)ether and 4 wt% of bis(dimethylaminoethyl). While stirring, the mixture was further treated with the emulsifier, nonylphenol ethoxylate, and the chain linker, diethanolamine.

Component 2 Mixture

A blend consisting of 70 parts of diphenylmethylene diisocyanate and 30 parts of the flame retardant, tris(chloroisopropyl)phosphate, was thoroughly mixed together before use.

Product Formation

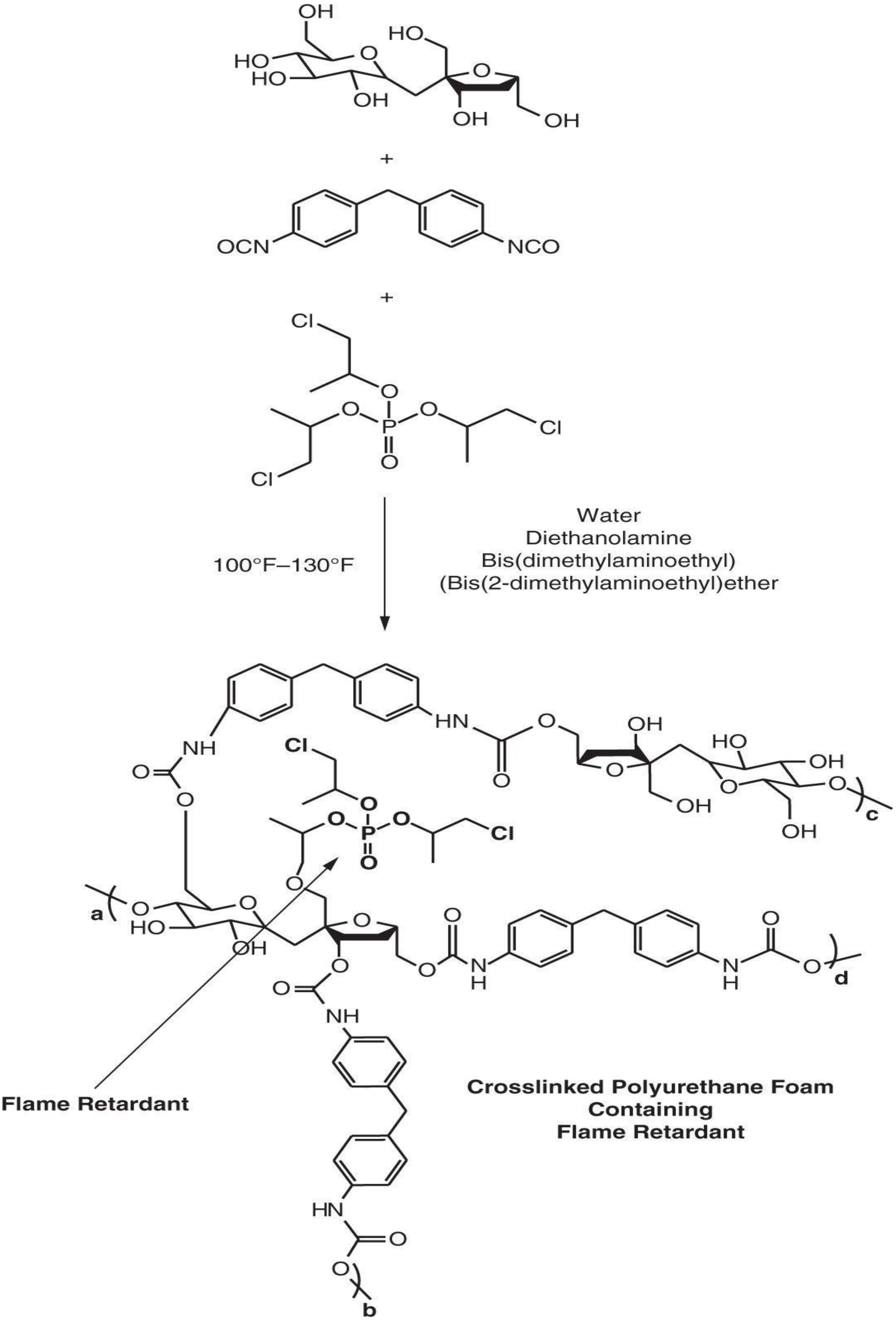
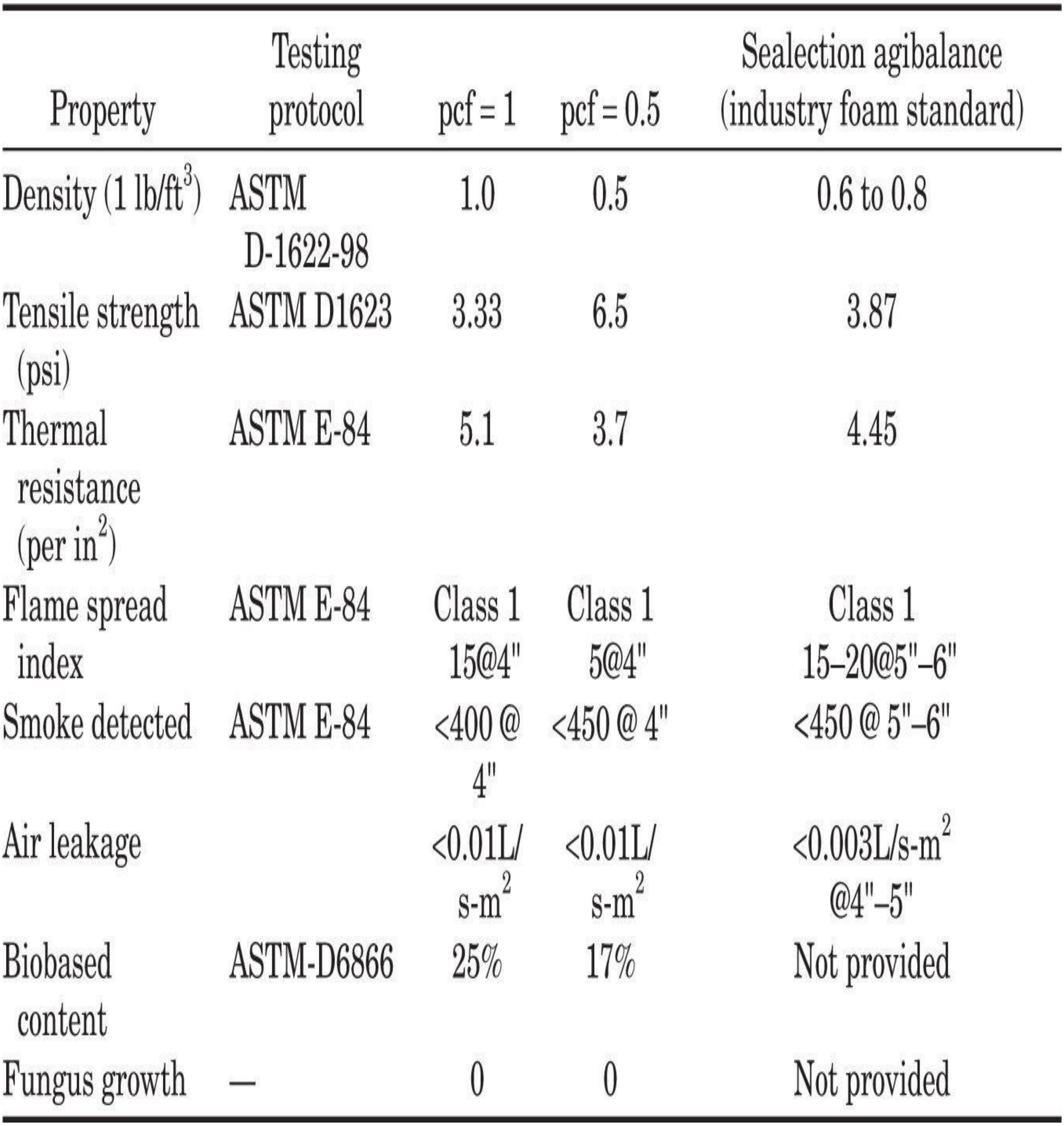

Water
Diethanolamine
Bis(dimethylaminoethyl)
(Bis(2-dimethylaminoethyl)ether
100°F–130°F
OCN
NCO
Cl
Flame Retardant
Crosslinked Polyurethane Foam
Containing
Flame Retardant
a
b
c
d

Figure 20.47

Experimental

1. Preparation of polyurethane spray foam. A spray-foam mixture consisting of a 1:1 blend of Component Mixture 1 and Component Mixture 2 was heated between 100°F and 130°F and then sprayed onto wooden panels. The polyurethane foam spray adhered to the surface evenly and without pealing. The foam appeared rigid and contained closed foam fells suitable for use as a noise or thermal insulation agent since it produced a foam surface having a pcf of approximately 1.0 lb/ft^3. Physical properties of the reaction product are provided in Table 20.7.

TABLE 20.7 Physical testing of polyurethane foams additized with the flame retardant tris(chloroisopropyl)phosphate. The recognized industry foam insulation standard, Sealection Agibalance®, is provided as a reference.

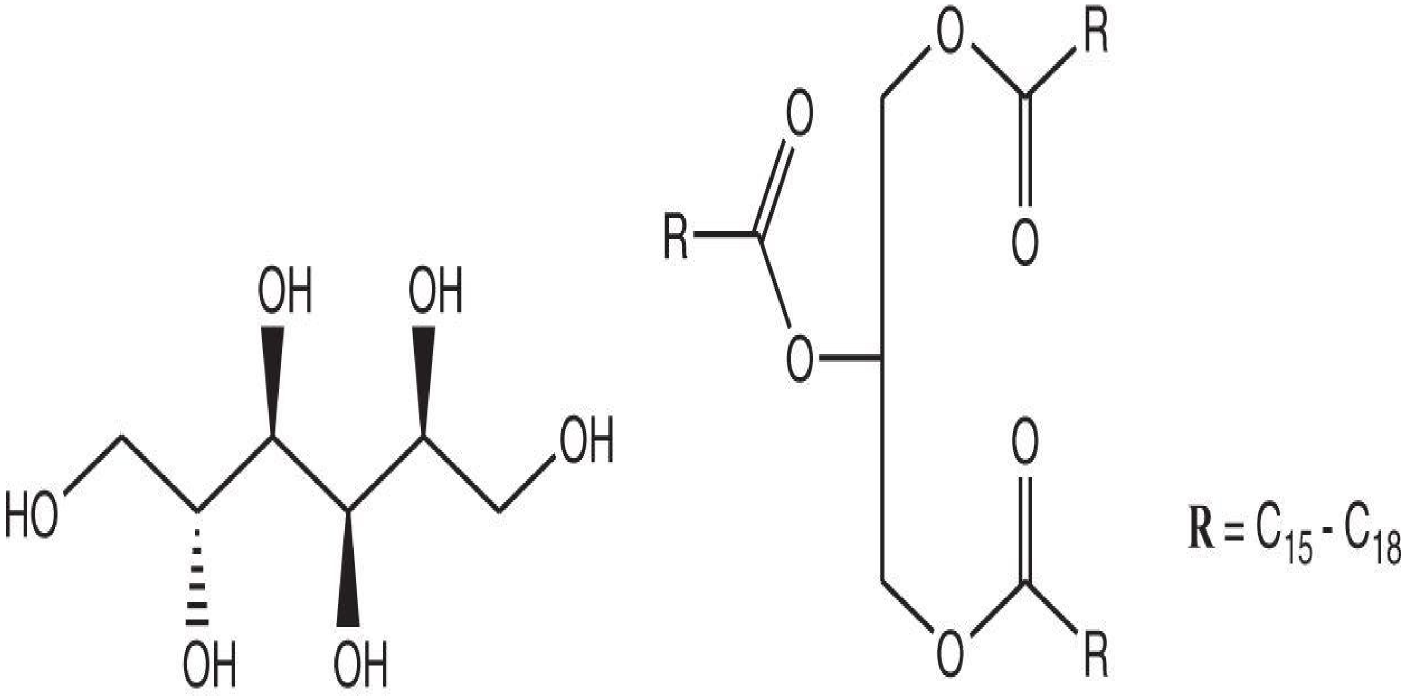


Property	Testing protocol	pcf = 1	pcf = 0.5	Sealection agibalance (industry foam standard)
Density (1 lb/ft^3)	ASTM D-1622-98	1.0	0.5	0.6 to 0.8
Tensile strength (psi)	ASTM D1623	3.33	6.5	3.87
Thermal resistance (per in^2)	ASTM E-84	5.1	3.7	4.45
Flame spread index	ASTM E-84	Class 1 15@4"	Class 1 5@4"	Class 1 15–20@5"–6"
Smoke detected	ASTM E-84	<400 @ 4"	<450 @ 4"	<450 @ 5"–6"
Air leakage		<0.01L/s-m^2	<0.01L/s-m^2	<0.003L/s-m^2 @4"–5"
Biobased content	ASTM-D6866	25%	17%	Not provided
Fungus growth	—	0	0	Not provided

Testing Results

Notes and Observations

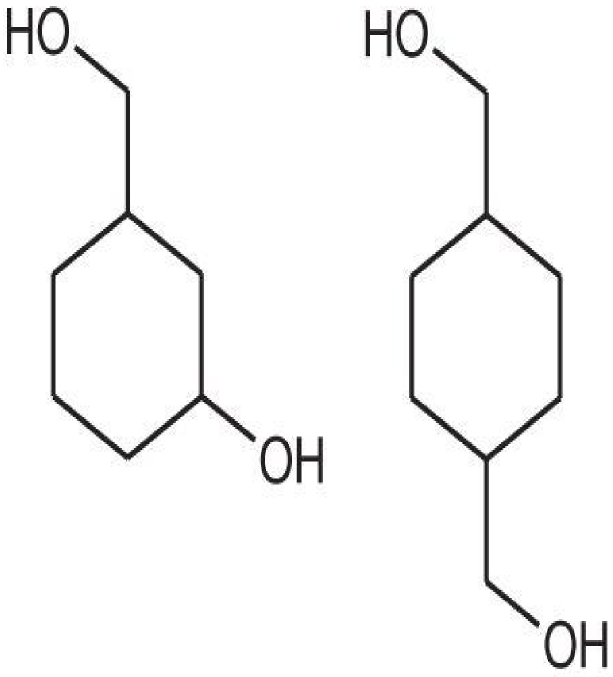
1. Kurth[1] formed polyurethane insulation panels in a two-step process. Initially, a transesterified polyol was prepared by reacting sorbitol, (I), with rapeseed oil, (II). Optimum transesterification was observed when tetra-2-ethylhexyl titonate was used as the reaction catalyst. The polyol mixture was then post-reacted with diphenylmethylene diisocyanate and polyurethane panels were isolated. (See Fig. 20.48.)



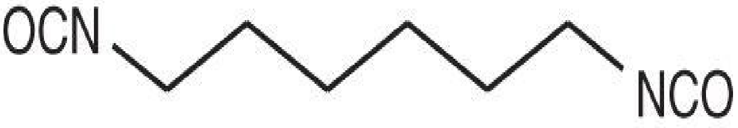
(I) (II)

Figure 20.48

2. Stollmaier[2] prepared polyurethanes by reacting sorbitol, sucrose, glycerol, or 1,3-/1,4-cyclohexane dimethanol, (III), with either 1,6-hexamethylene diisocyanate, (IV), or isophorone diisocyanate, (V). Polyurethanes generated from these reactions were then used in paint formulations since very low volatile-organic-solvent emissions were observed when painted surfaces were drying. (See Fig. 20.49.)



(III)



(IV)

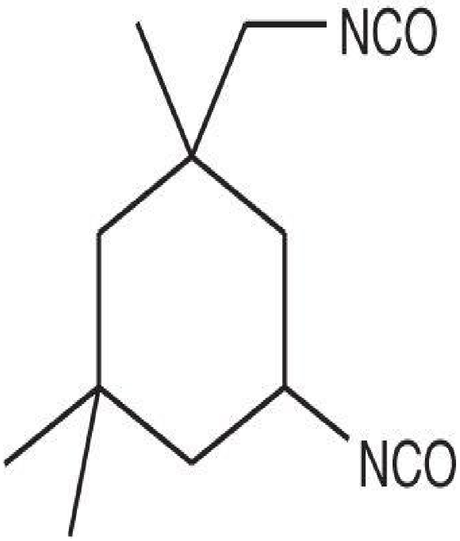
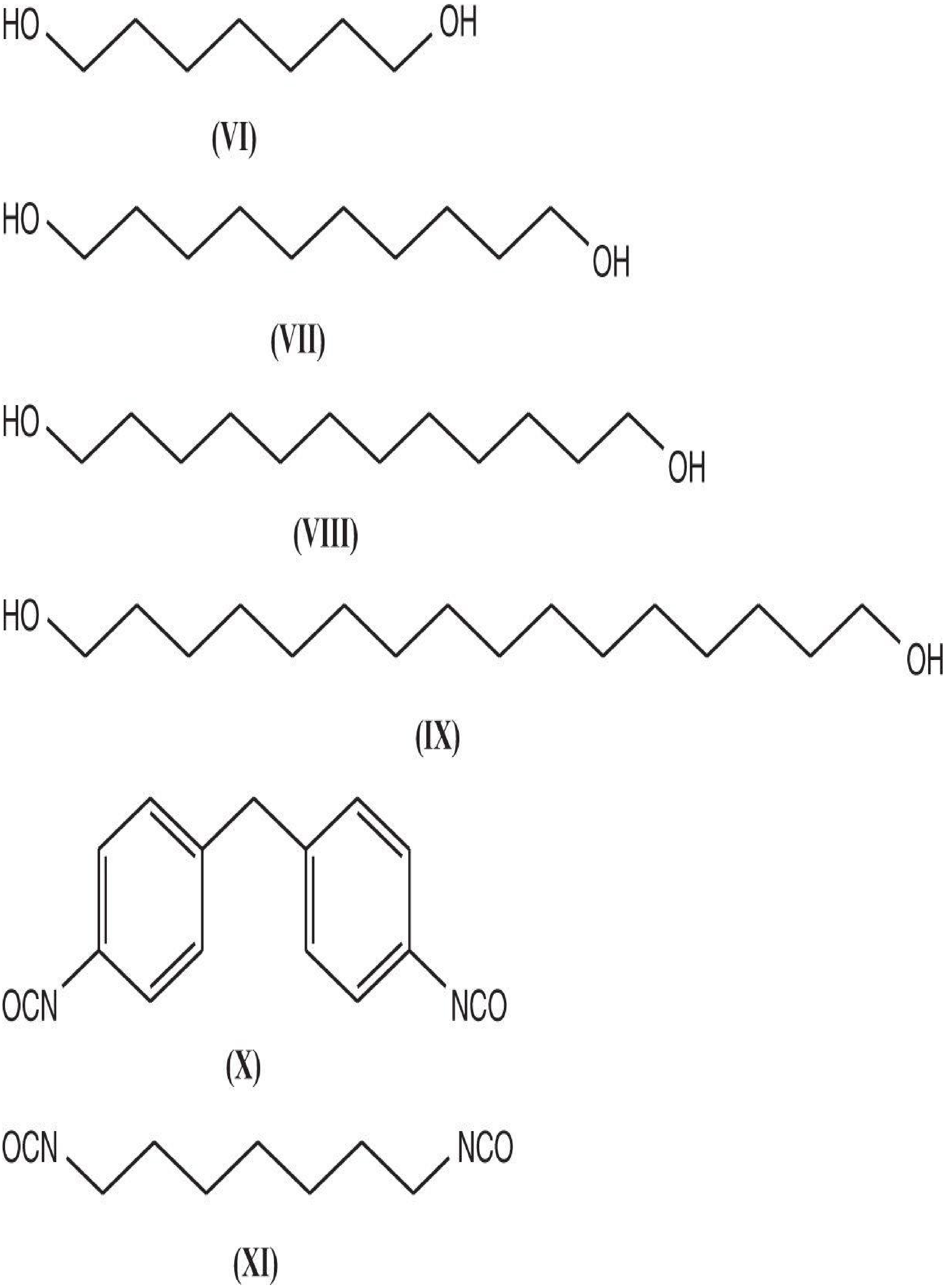


Figure 20.49

3. Tuominen[3] prepared non-toxic and bioabsorbable water-swellable polyurethanes that were used in medical applications as suppository or pessary agents when treating vaginal disorders. Polyurethanes used in this application were prepared by condensing either 1,6-hexanediol, (VI), 1,10-decanediol, (VII), 1,12-dodecanediol, (VIII), or 1,16-hexadecanediol, (IX), with either diphenylmethylene diisocyanate, (X), or 1,6-hexamethylene diisocyanate, (XI). (See Fig. 20.50.)



(VI)

(VII)

(VIII)

(IX)

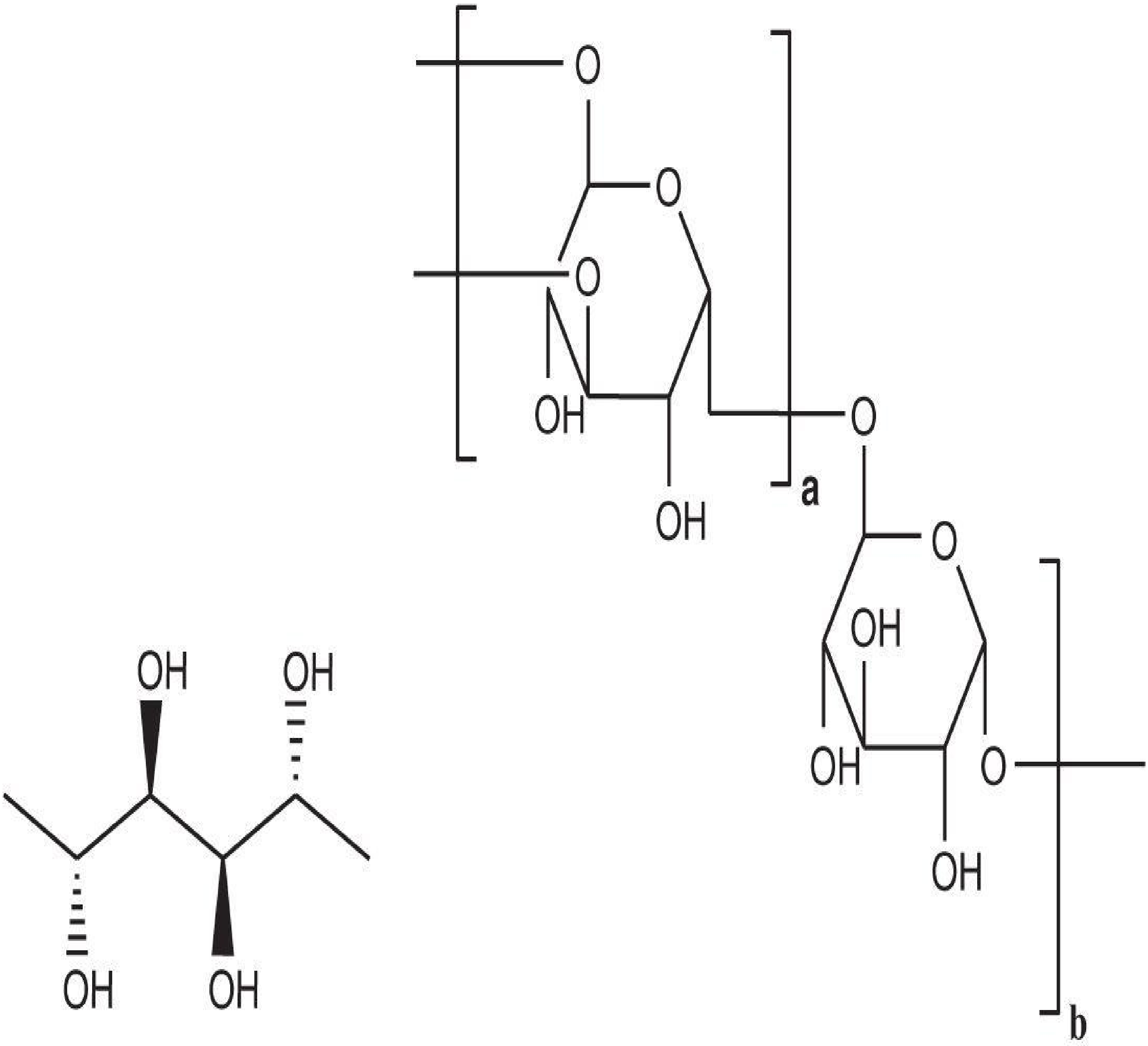
(X)

(XI)

Figure 20.50

4. Bioabsorbable polyurethanes which were used as adhesives or sealants in medical and

surgical applications were prepared by Hadba.[4] Polyurethane resins were prepared by reacting renewable polyols such as sorbitol, mannitol, (XII), sucrose, dextran, (XIII), or cyclodextrin with either toluene diisocyanate or diphenylmethylene diisocyanate. (See Fig. 20.51.)



(XII) (XIII)

Figure 20.51

References

1. Thomas M. Kurth et al., *Transesterified polyol having selectable and increased functionality and urethane material products formed using the polyol*, U.S. Patent 8,333,905 (December 18, 2012)

2. Friederike Stollmaier et al., *Polyurethane dispersions and coatings produced therefrom*, U.S. Patent 8,362,142 (January 29, 2013)

3. Jukka Tuominen et al., *Polyurethane elastomers*, U.S. Patent 8,361,273 (January 29, 2013)

4. Ahmad R. Hadba et al., *Bioabsorbable surgical composition*, U.S. Patent 8,357,361 (January 22, 2013)

Paint Containing Acetoacetylated Sugar Resins

Author Sergey Selifonov et al.

Patent Title ***Novel acetoacetoxy and enamine compounds and coatings therefrom,*** U.S. Patent Application 20130036939 (February 14, 2013)

Relevant Prior Patents by Author or Coauthors

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,348,623 (February 19, 2002)

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,228,949 (May 8, 2001)

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,160,057 (December 12, 2000)

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,121,400 (September 19, 2000)

Polymers of 3-butene esters, their preparation and use, U.S. Patent 6,121,399 (September 19, 2000)

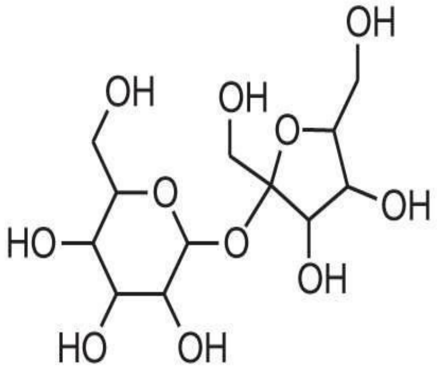
Product Application

Acetoacetylated and enamine resins derived from sucrose are useful in painting formulations where film strength and durability are required.

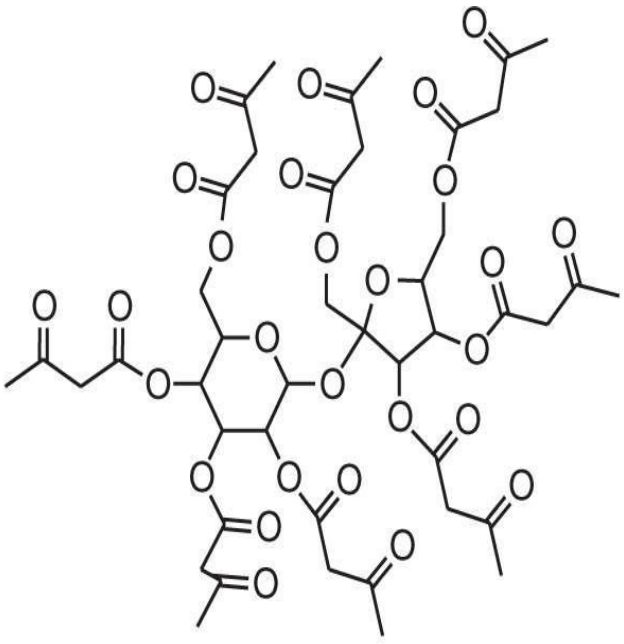
Significance of Current Application

The objective of this investigation was to develop paint additives utilizing renewable raw materials. Sucrose was selected as the renewable raw material because it has eight reactive hydroxyl groups that are easily esterified into non-toxic additives or intermediates. In addition, it was observed that when acetoacetylated and enamine resins derived from sucrose were used in paint formulations, films had uniform resin distribution with low viscosities and rapid air-drying. In addition, films derived from these additives had excellent coating properties such as strength and durability.

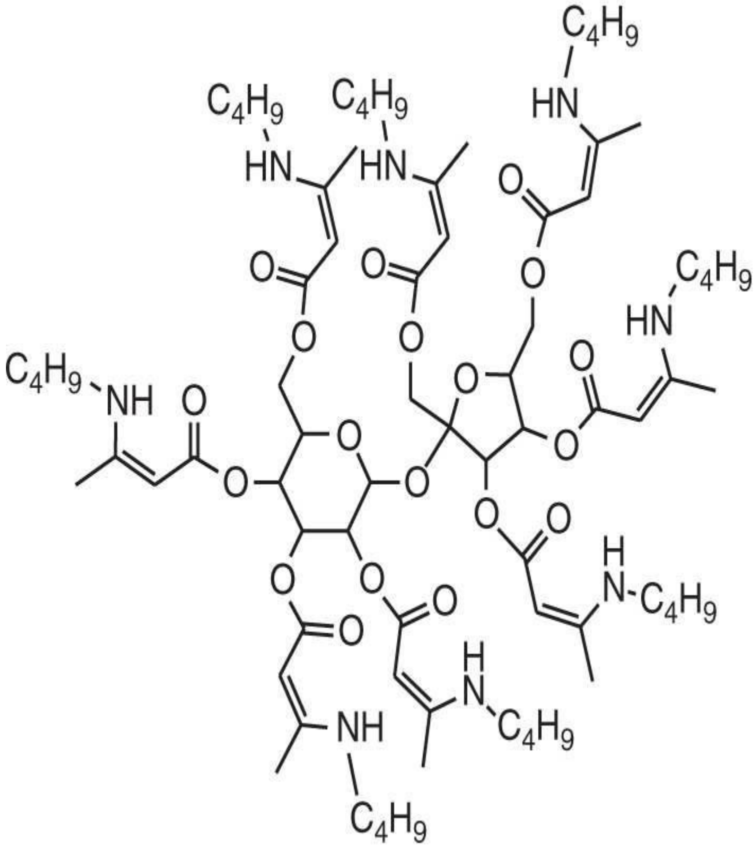
Renewable Agents



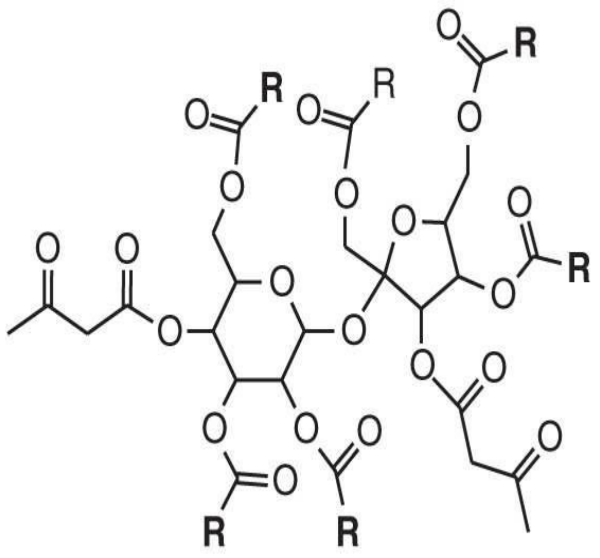
Sucrose



**Acetoacetoxylated
Sucrose
Biocoating 1**



**Acetoacetoxylated
and Enaminated
Sucrose
Biocoating 2**



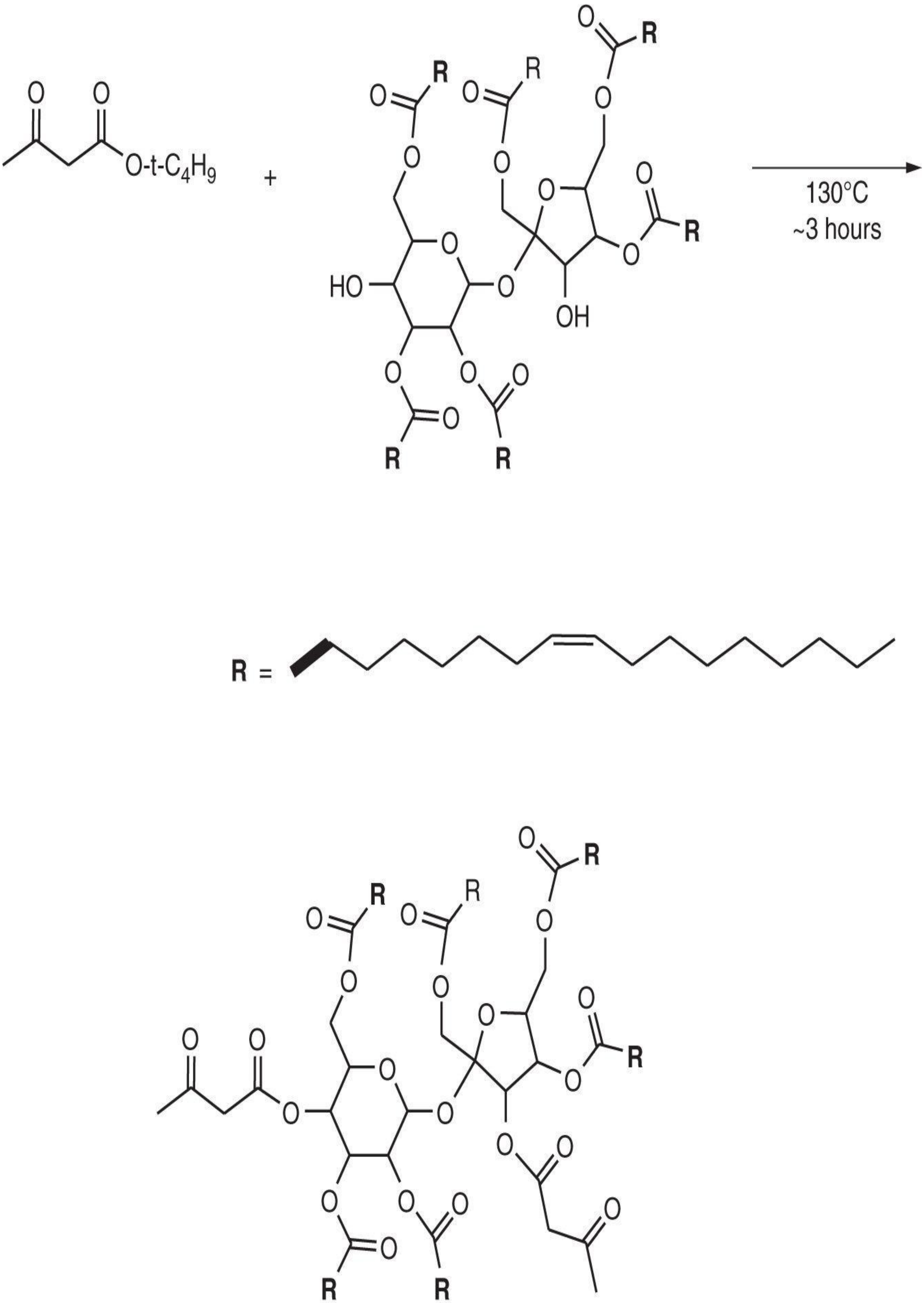
**Acetylated Sucrose soyate
Biocoating 3**

R = Oleyl

Figure 20.52

Product Formation

A. Biocoatings 1 and 2



Biocoating 3

Figure 20.53

Experimental

1. Preparation of acetoacetoxylated sucrose (Biocoating 1). A 500-mL four-neck flask containing a mechanical stirrer, nitrogen inlet, thermocouple, reflux condenser, and a Dean-Stark trap was charged with 50.0 g of sucrose and 184.9 g of t-butyl-acetoacetate. The reaction mixture was then heated to 130°C for approximately 3 hours. During the heating phase, 84.8 g of t-butanol was collected in a Dean-Stark trap as the reaction by-product. After additional t-butanol stopped distilling over, the reaction was stopped and the product was isolated as a viscous, yellow oil. Infrared analysis spectroscopy was used to confirm the absence of the broad sucrose-hydroxyl stretching band at 3000 cm^{-1} to 3600 cm–^{1} and the appearance of two carbonyl stretching bands at 1735 cm–^{1} and 1780 cm–^{1}. Finally, ^{1}H-NMR spectroscopy did not detect sucrose hydroxyl protons at 4.1 ppm to 5.7 ppm but did detect methylene protons associated with acetoacetates at 2.1 ppm to 2.3 ppm and 3.4 ppm to 3.7 ppm.

2. Preparation of acetoacetoxylated enaminated sucrose (Biocoating 2). A reactor was charged with 30 g of the Step 1 product and a 5-molar excess of butyl amine and then heated to 110°C while collecting water in a Dean-Stark trap as the reaction by-product. After additional water stopped distilling over, the reaction was stopped and the enamine was isolated as a viscous, reddish-yellow oil. ^{1}H-NMR spectrum of the reaction product detected methylene protons at 0.8 ppm and 3.2 ppm and a secondary amine proton at 8.4 ppm to 8.5 ppm.

3. Preparation of acetylated sucrose soyate (Biocoating 3). A 500-mL four-neck flask containing a mechanical stirrer, nitrogen inlet, thermocouple, reflux condenser, and a Dean-Stark trap was charged with 100 g of hexa(octadecaolenyl)-dihydroxy-sucrose (SEFOSE 1618U B6®) and 17.2 g of t-butyl-acetoacetate and then heated to 130°C for approximately 3 hours. During that period, 9.1 g of t-butanol was distilled over and collected in the Dean-Stark trap. After additional t-butyl alcohol stopped distilling over, the reaction was stopped and the product was isolated as a light-yellow liquid.

Testing

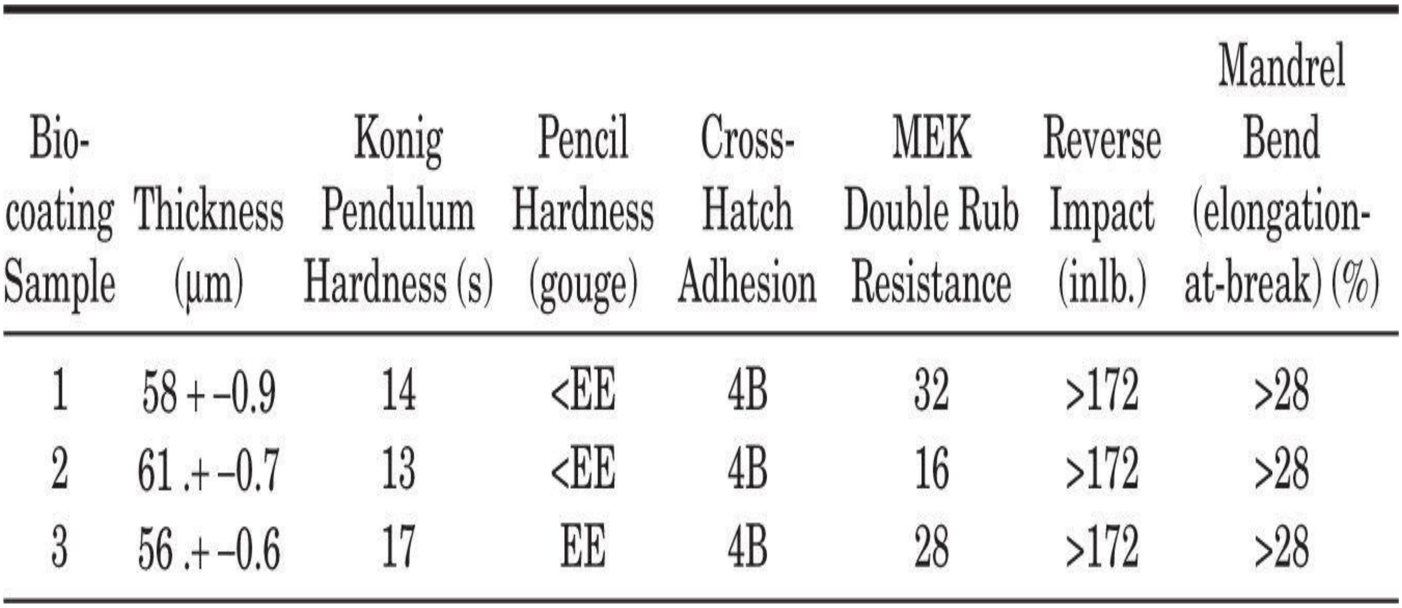
A. Paint formulations containing resins. Coating compositions contained one or more of the experimental samples. An acetoxylated polyol ester of a fatty acid was blended with Biocoating 2 and a poly-functional amine having two or more primary amine groups. The blending solvent was cyclohexane containing an aliphatic epoxyamine as the crosslinking agent.

B. Physical testing. The strength, durability, and associated physical properties of dried paint coatings containing experimental examples derived from this investigation were determined using mechanical testing. The thickness of the cured coating was measured prior to any test, while both the Konig pendulum hardness and gouged-pencil hardness were determined according to ASTM D 4366-95 and ASTM D 3363-00, respectively, testing protocols.

The adhesion of cured coatings was determined according to ASTM D 3359-97. Methyl

ethyl ketone solvent-resistance testing was used during the double-rub test according to ASTM D 5402-93. Impact-resistance testing was performed according to ASTM D 2794-93 using a 4-lb metal cylinder while multiplying the maximum height in inches. Finally, Mandrel bend testing was performed using the test protocol provided in ASTM D 522-93a and where the results are presented as the elongation range of the coating at cracking. All testing results are provided in Table 20.8.

TABLE 20.8 Coating properties for three air-dried coating samples. In all cases, coatings were soft and flexible. Cured biocoating solvent resistance to methylethyl ketone, however, was poor.

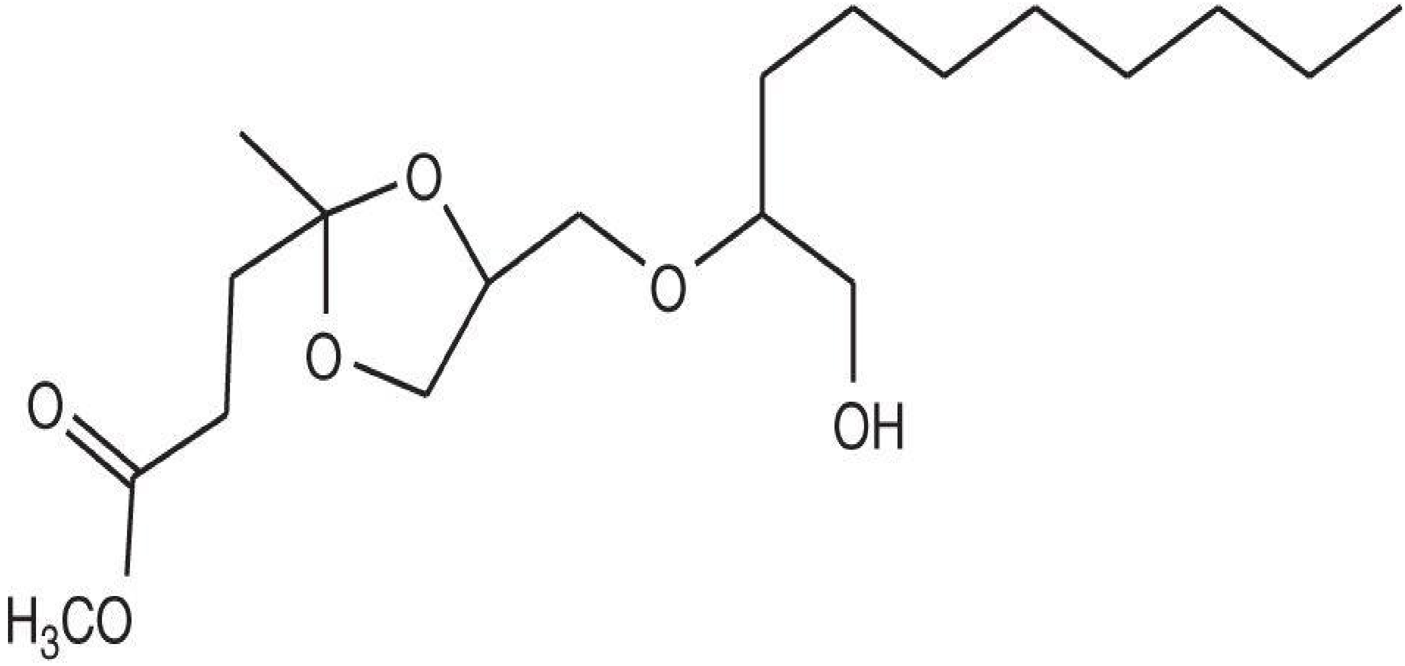


Bio-coating Sample	Thickness (µm)	Konig Pendulum Hardness (s)	Pencil Hardness (gouge)	Cross-Hatch Adhesion	MEK Double Rub Resistance	Reverse Impact (inlb.)	Mandrel Bend (elongation-at-break) (%)
1	58 + -0.9	14	<EE	4B	32	>172	>28
2	61 .+-0.7	13	<EE	4B	16	>172	>28
3	56 .+-0.6	17	EE	4B	28	>172	>28

Testing Results

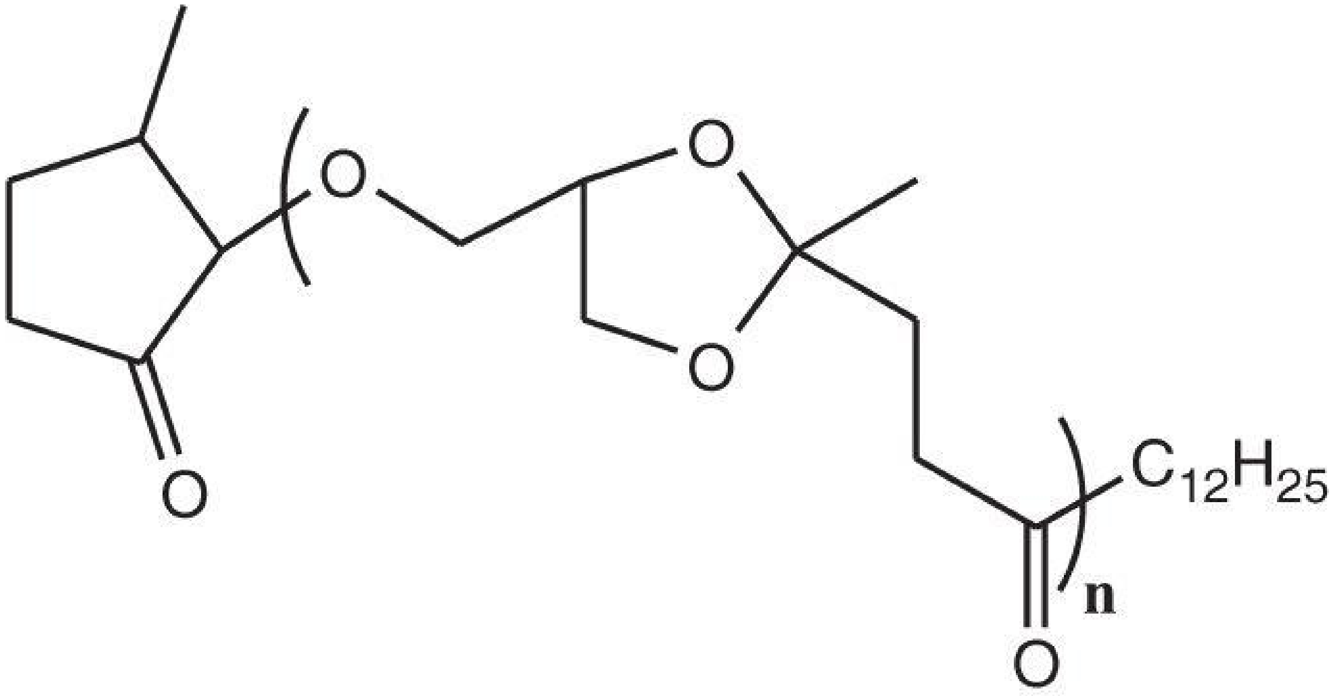
Notes and Observations

1. Selifonov[1] prepared a series of monomeric, (I), and polymeric, (II), ketal derivatives using glycerine derived from renewable biomass-derived feedstocks which were then used as additives in paint formulations. Dried painted surfaces were very durable, flexible, and resistant to solvents. (See Fig. 20.54.)



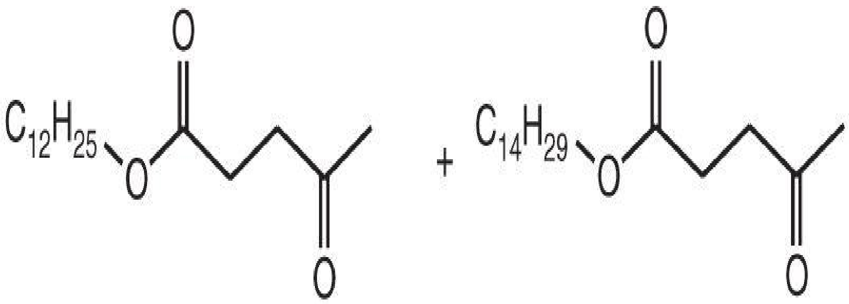
(I)

Figure 20.54



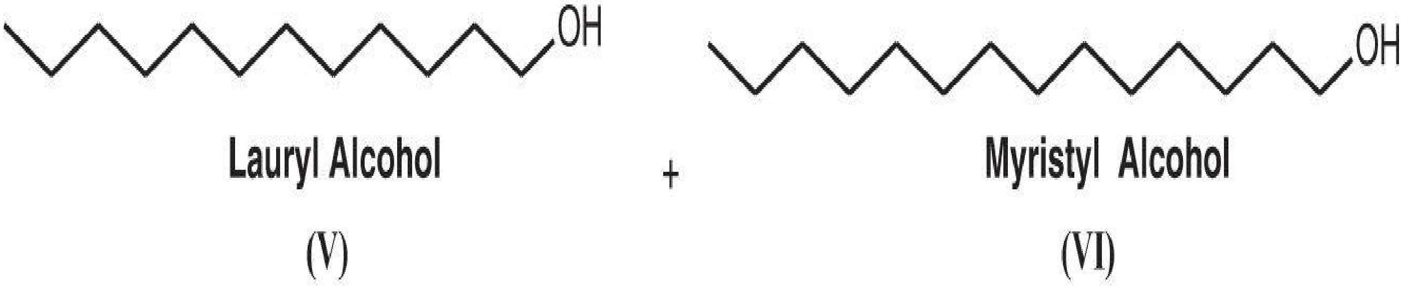
(II)

2. Kuo[2] prepared paint additives having virtually no volatile organic compound emissions consisting of the Additive Pair esters of levulinic acid, (III), or the Additive Pair comprising P&G CO-1214®, (IV), which consisted of equal molar amounts of 1-tetradecanol (V), and dodecyl alcohol, (VI). All four components in both Additive Pairs were derived from renewable sources. (See Fig. 20.55.)



Additive Pair-1

(III)

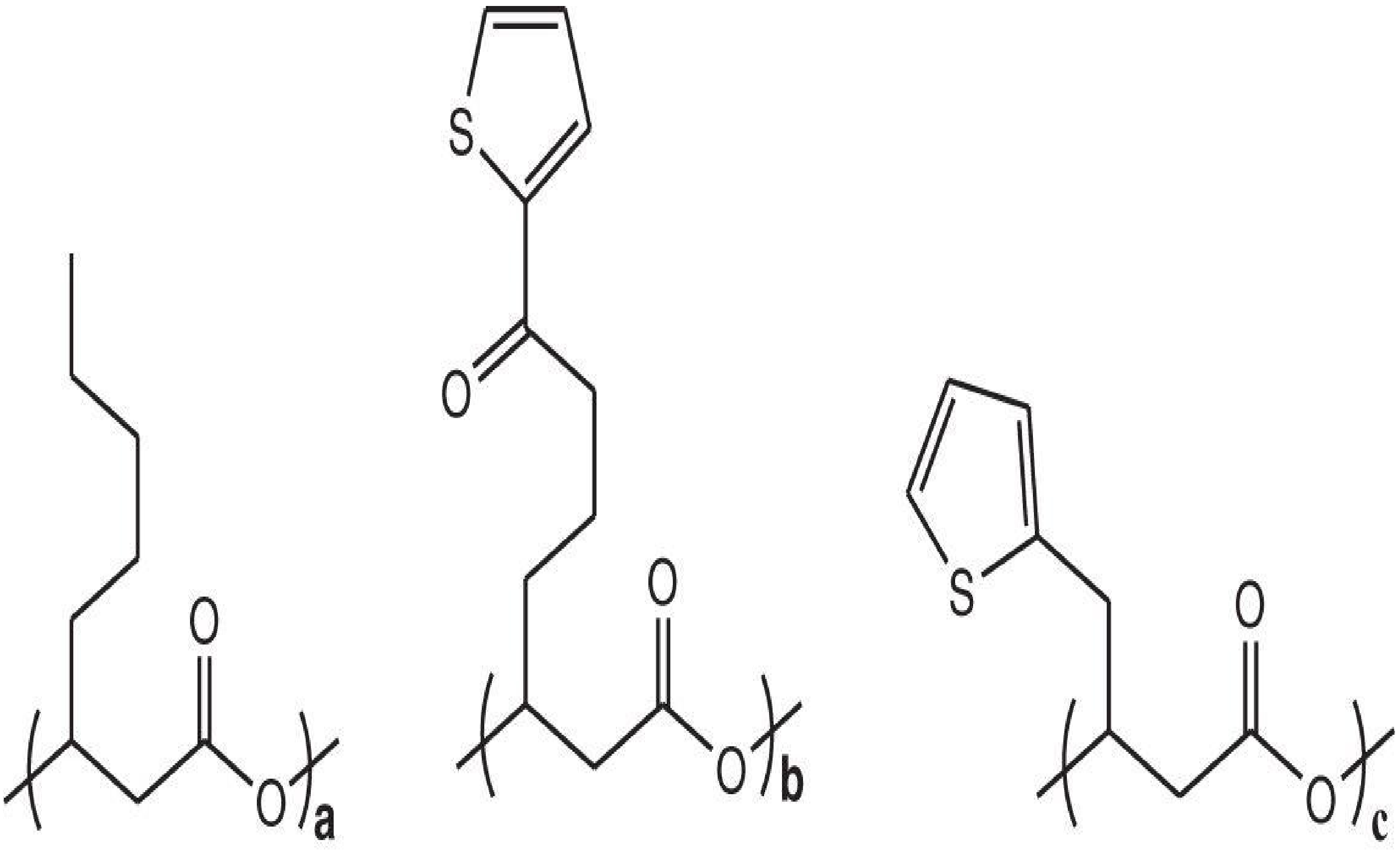


Additive Pair-2
(P&G CO-1214)®

(IV)

Figure 20.55

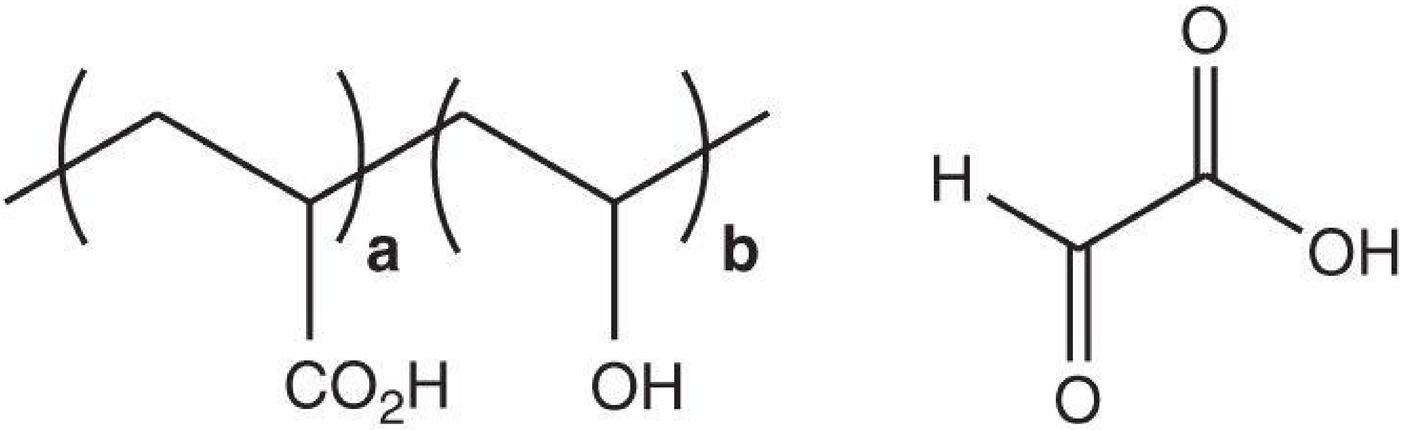
3. Yano[3] used microorganisms to prepare a series of polyhydroxyalkanoates, (VII) through (IX), which were intended as drug delivery agents. When these polymers were converted into microcapsules, however, they were also used as paint, dye, and pigment agents in paint formulations. (See Fig. 20.56.)



(VII) (VIII) (IX)

Figure 20.56

4. Tanaka[4] prepared a renewable paint additive that when used in painting formulations improved the film resistance to water, resisted color change due to oxidation, and had excellent stability in aqueous solutions. The additive was prepared by crosslinking poly(acrylic acid-co-vinyl alcohol), (X), with glyoxylic acid, (XI), then forming an emulsion composition with the product. (See Fig. 20.57.)



(X) (XI)

Figure 20.57

References

1. Sergey Selifonov, *Glycerol levulinate ketals and their use*, U.S. Patent 8,178,701 (May 15, 2012)

2. Thauming Kuo et al., *Waterborne coating compositions containing low-VOC coalescents*, U.S. Patent 8,383,710 (February 26, 2013)

3. Tetsuya Yano et al., *Particulate construct comprising polyhydroxyalkanoate and method for producing it*, U.S. Patent 7,615,233 (November 10, 2009)

4. Shinichi Tanaka et al., *Crosslinking agent, crosslinked polymer, and uses thereof*, U.S. Patent 8,426,632 (April 23, 2013)

Photochemically Stable Poly(Ester/Amide/Urethanes)

Author	Franziska Freese et al.
Patent Title	***Biodegradable polyester film,*** U.S. Patent Application 20120288650 (November 15, 2012)

Relevant Prior Patents by Author or Coauthors

Process for film production, U.S. Patent Application 20110237750 (September 29, 2011)

Biosynthesis of polyisoprenoids, U.S. Patent Application 20110201771 (August 18, 2011)

Glyoxal and methylglyoxal as additive for polymer blends, U.S. Patent Application 20110124807 (May 26, 2011)

Product Application

Photochemically stable and biodegradable mixed poly(ester/amide/urethane) films having improved elongation film properties are useful in exterior coatings, polymer blends, and in thermosensitive materials.

Significance of Current Application

There is a continuing need to both identify monomers that can be used to prepare biodegradable polymers and to identify Ultraviolet A stabilizers to limit photodegradation to these polymers. Limiting photodegradation from Ultraviolet A is particularly desirable. This investigation has determined that biodegradable poly (ester/amide/urethane) can be easily photostabilized using the Ultraviolet A stabilizer, CGX UVA 006®. It was further determined that the degree of photo-stabilization was directly proportional to the amount of CGX UVA 006 contained in the blend. It was further determined that CGX UVA 006 VI outperformed nine of the most significant commercially available Ultraviolet A stabilizers.

Components

Component 1 V monomers used to prepare biodegradable poly(ester/amide/urethane)s are provided in Fig. 20.58.

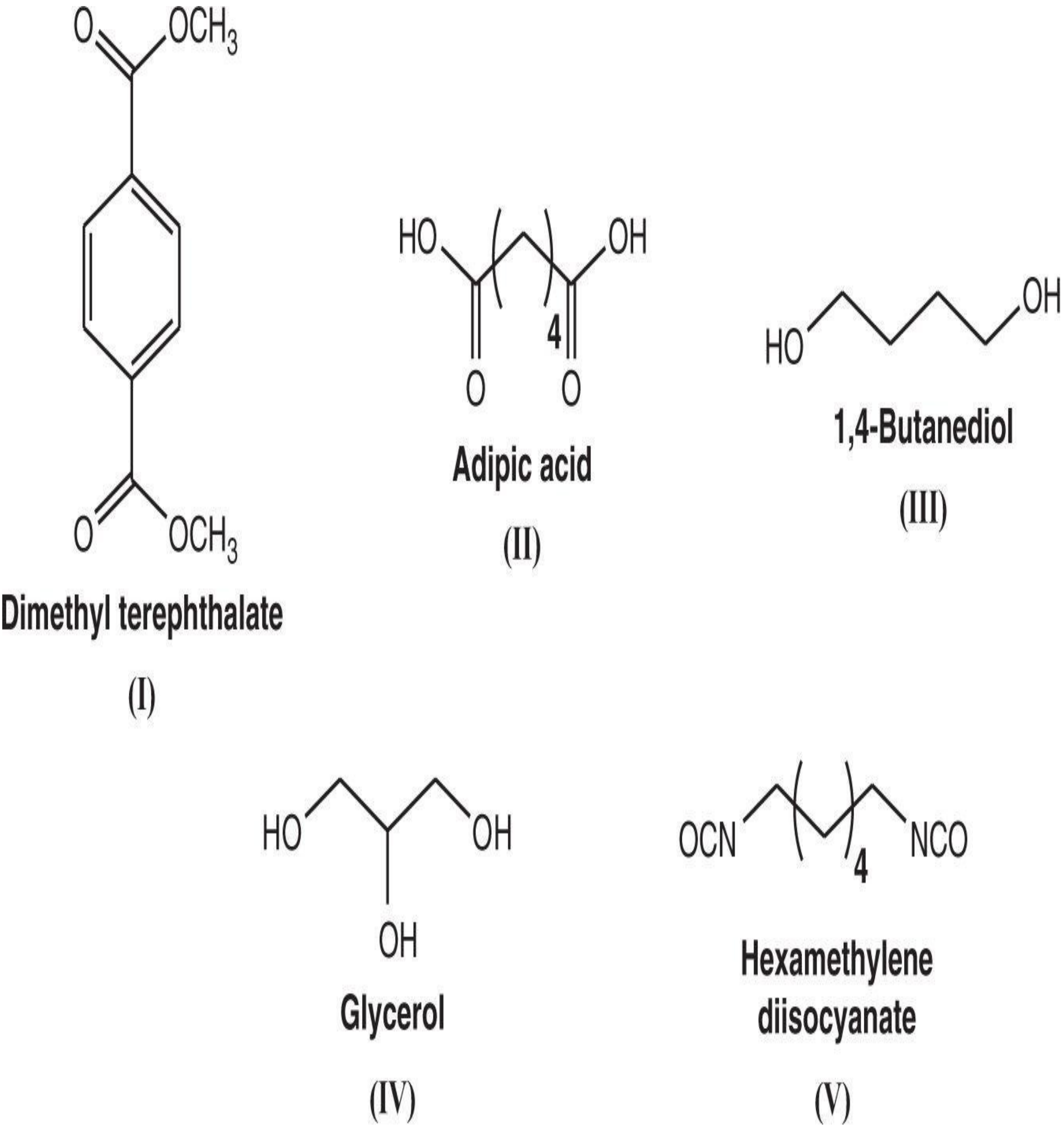
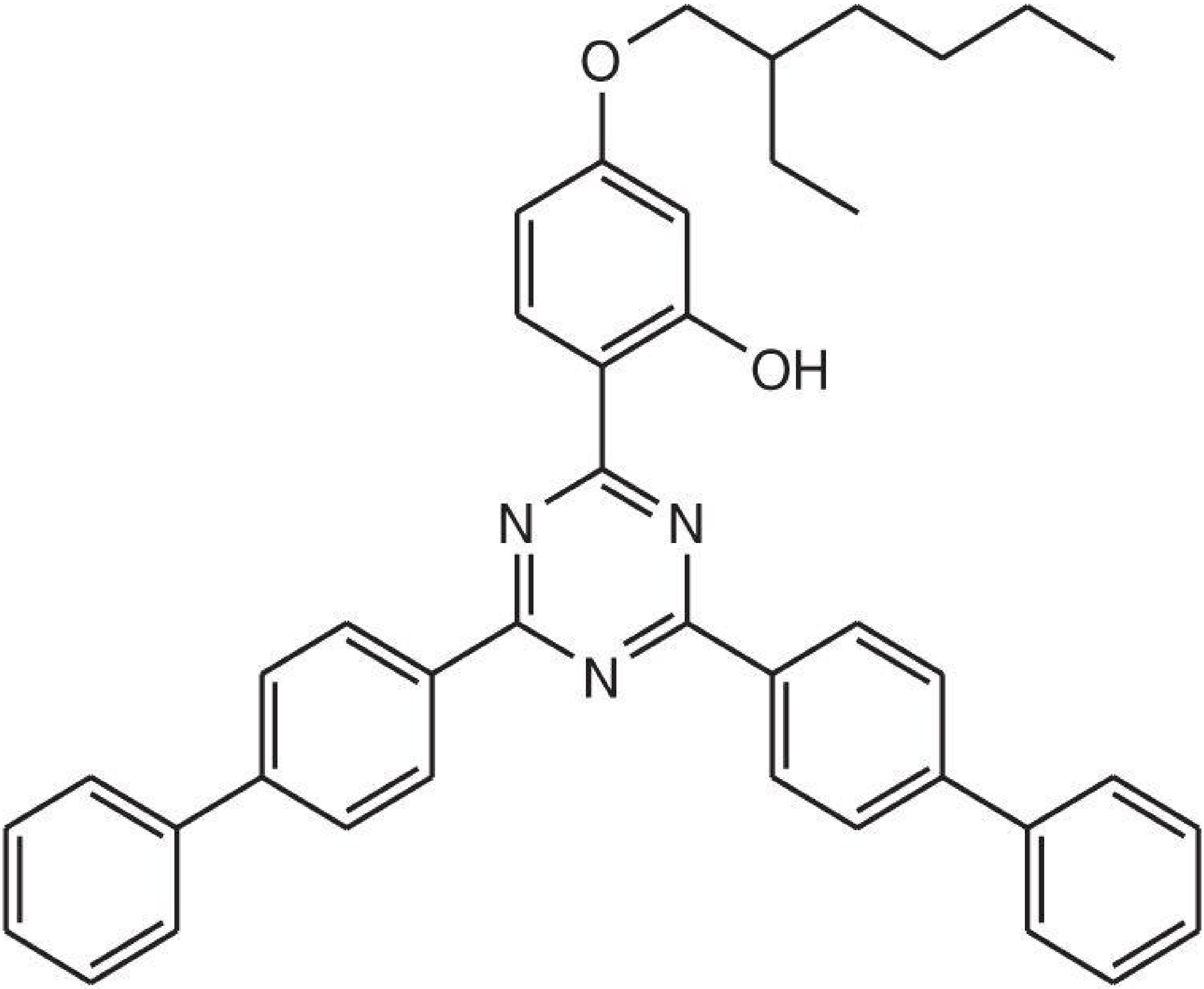


Figure 20.58

Component 2: Ultraviolet A absorber CGX UVA 006. 4,6-(Bisbiphenyl-4-yl-1,3,5-triazin-2-yl)-5-(2-ethyl-n-hexyloxy)phenol, (I), was selected as the preferred Ultraviolet A stabilizer because it has an extremely high Ultraviolet A absorption coefficient, low volatility, and excellent heat stability. (See Fig. 20.59.)



CGX UVA 006

(VI)

Figure 20.59

Product Formation

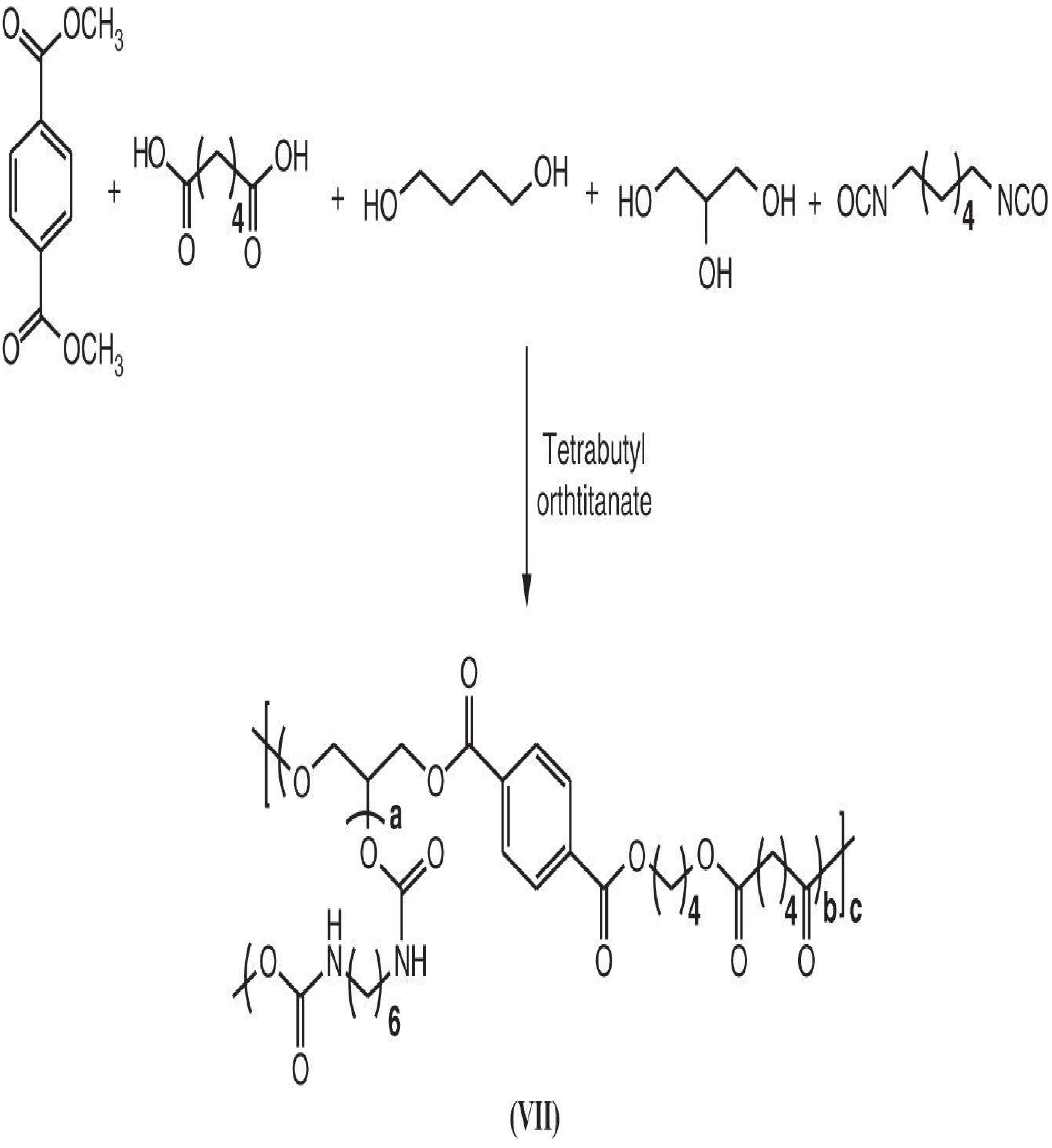


Figure 20.60

Experimental

1. Preparation of biodegradable poly(ester/amide/urethane) resin. A reactor was charged with 87.3 kg of dimethyl terephthalate, 80.3 kg of adipic acid, 117 kg of 1,4-butanediol, and 0.2 kg of glycerol in an amount so that the ratio of alcohol components to acid components was 1:30:l, respectively. When the mixture was fully blended it was treated with 0.028 kg of the catalyst tetrabutyl orthotitanate, then initially heated to 180°C for 6 hours, and then further heated to 240°C for 3 hours to distill off unreacted dihydroxy compounds. The reaction mixture was then treated with the slow addition of 0.9 kg of hexamethylene diisocyanate while continuing to heat the reaction mixture to 240°C for an additional hour. After cooling to ambient temperature, the mixed poly(ester/amide/urethane) resin VII was isolated and had a melting point of 119°C and an Mn of 23,000 daltons.

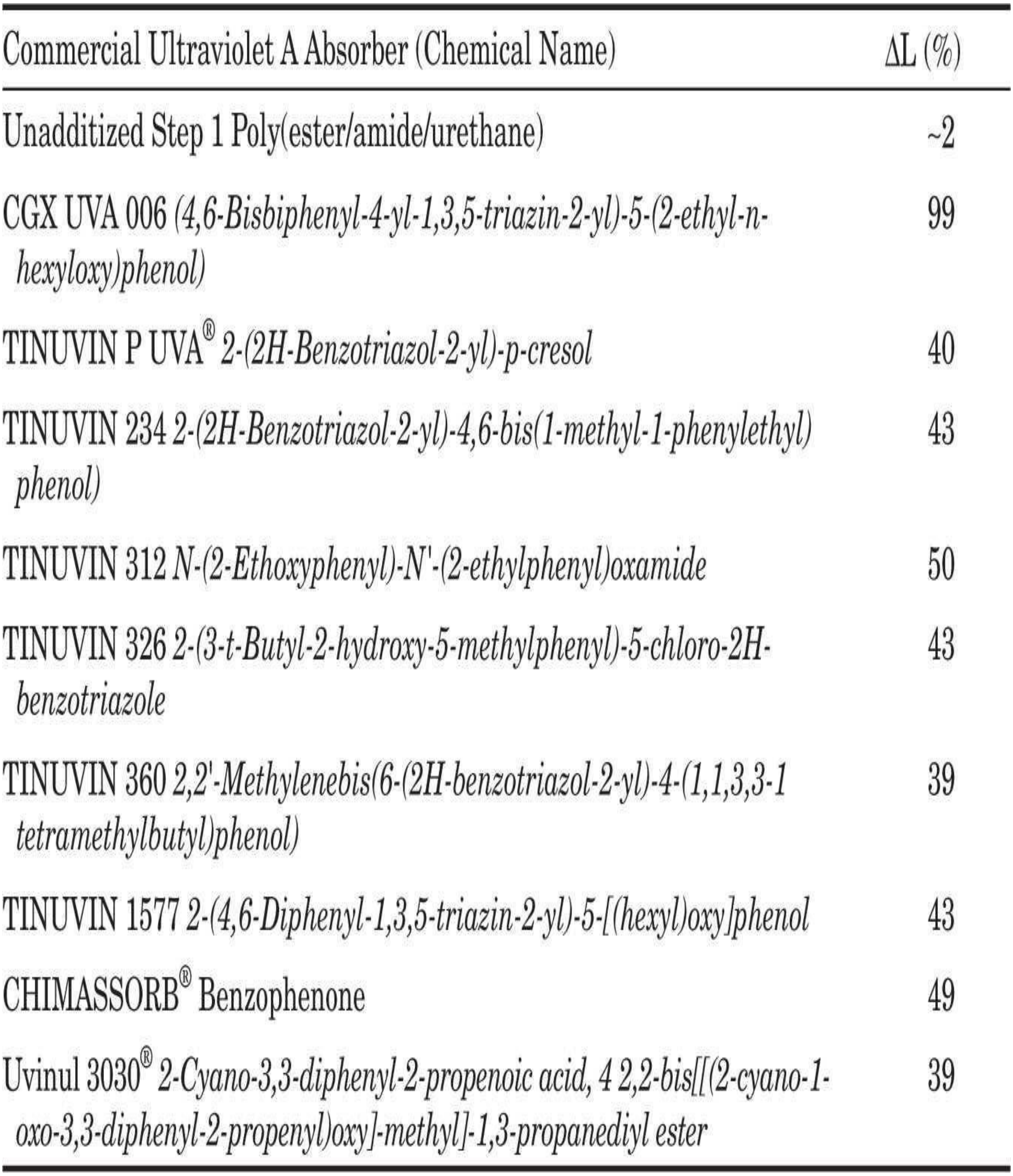
2. Preparation of blend of poly(ester/amide/urethane) containing CGX UVA 006. A cold-feed extruder charged with the Step 1 product and up to 10,000 ppms of the Ultraviolet A stabilizer, CGX UVA 006, was used to prepare films having a thickness of approximately 12 µm.

Testing

A. Tensile strength. Film samples prepared using the Step 1 product were subjected to artificial weathering using an xenon arc lamp (according to DIN EN ISO 4892-2) for a period of 250 hours, which roughly corresponds to three months of outdoor weathering in the south-European climatic zone. In this testing, the Step 1 product was additized with nine different commercially available Ultraviolet A absorbers at equivalent treatment levels. Thereafter, the tensile strength of weathered films was compared to unweathered and unadditized poly(ester/amide/urethane) reference films (according to ISO 527-3) to assess film mechanical properties. Finally, weathered films were also evaluated to determine the 50% decrease point in tensile strain at break. Physical testing results for the Step 1 product additized with nine different Ultraviolet absorbers are provided in Table 20.9.

Testing Results

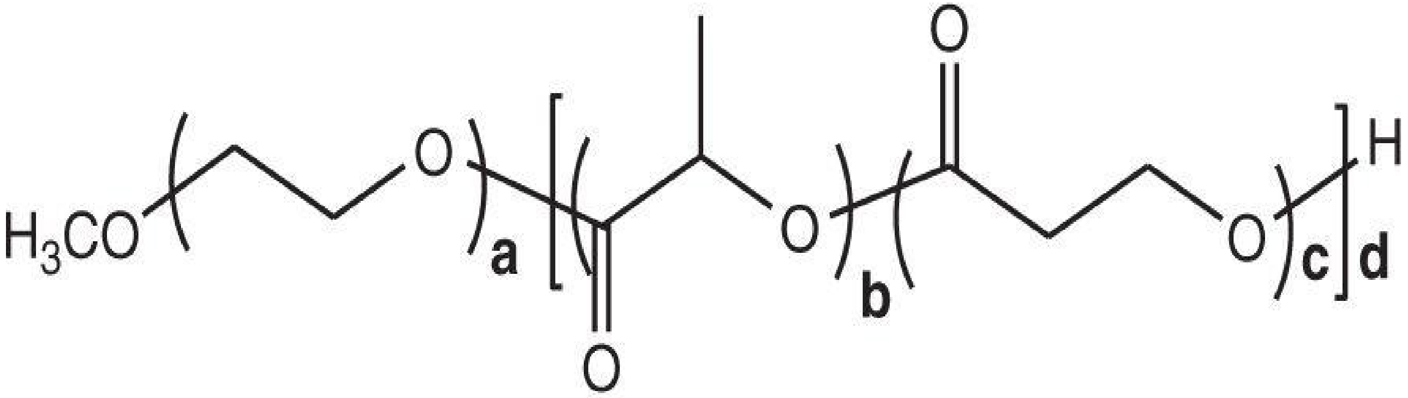
TABLE 20.9 Effect of selected Ultraviolet A absorbers on the elongation of the Step 1 poly(ester/amide/urethane) product after exposure to a xenon arc lamp for 250 hours. Higher elongation values are preferred.



Commercial Ultraviolet A Absorber (Chemical Name)	ΔL (%)
Unadditized Step 1 Poly(ester/amide/urethane)	~2
CGX UVA 006 *(4,6-Bisbiphenyl-4-yl-1,3,5-triazin-2-yl)-5-(2-ethyl-n-hexyloxy)phenol)*	99
TINUVIN P UVA® *2-(2H-Benzotriazol-2-yl)-p-cresol*	40
TINUVIN 234 *2-(2H-Benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl) phenol)*	43
TINUVIN 312 *N-(2-Ethoxyphenyl)-N'-(2-ethylphenyl)oxamide*	50
TINUVIN 326 *2-(3-t-Butyl-2-hydroxy-5-methylphenyl)-5-chloro-2H-benzotriazole*	43
TINUVIN 360 *2,2'-Methylenebis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-1 tetramethylbutyl)phenol)*	39
TINUVIN 1577 *2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]phenol*	43
CHIMASSORB® Benzophenone	49
Uvinul 3030® *2-Cyano-3,3-diphenyl-2-propenoic acid, 4 2,2-bis[[(2-cyano-1-oxo-3,3-diphenyl-2-propenyl)oxy]-methyl]-1,3-propanediyl ester*	39

Notes and Observations

1. Yu[1] prepared a biodegradable diblock copolymer consisting of polyethyleneglycol having an Mn ~ 500 daltons and a random copolymer of lactide and β-propiolactone, (VIII). Once prepared, the biodegradable copolymer was dissolved in water and formed a thermosensitive material having a phase transfer temperature between 25°C and 50°C. (See Fig. 20.61.)



(VIII)

Figure 20.61

2. Uradnisheck[2] improved the elongation properties of renewable polylactic acid, behenamide, and poly(ethylene-ter-n-butyl acrylate-ter-glycidyl methacrylate) by over 80% by plasterizing it with poly(trimethylene ether) glycol.

3. Films prepared by Kaufman[3] consisting of the biodegradable terpolymer, ECOFLEX, a polyester composed of 1,4-butanediol, adipic acid, and terphthalic acid were mixed with calcium carbonate having a particle size of 1 μm. When the mixture was converted into films, they remained biodegradable but had an improved water vapor transmission rate of over 2000 g/m.

4. Wang[4] prepared a three-component polymer blend consisting of 15 mol% hydroxypropylated starch, 80 mol% of poly(vinyl alcohol), and 5 mol% glycerol dihydroxy stearate. Films produced from this blend exhibited a dry ultimate tensile strength from about 10 to about 80 MPa and an elongation of about 50%.

References

1. Ya-Jen Yu et al., *Biodegradable copolymer and thermosensitive material*, U.S. Patent 8,309,623 (November 13, 2012)

2. Julius Uradnisheck, *Poly(hydroxyalkanoic acid) plasticized with poly(trimethylene ether) glycol*, U.S. Patent 8,349,955 (January 8, 2013)

3. Ross T. Kaufman et al., *Highly breathable biodegradable films*, U.S. Patent 8,334,327 (December 18, 2012)

4. James H. Wang, *Biodegradable water-sensitive films*, U.S. Patent 8,329,977 (December 11, 2012)

Renewable cis-Isoprene

Author	Frank J. Feher et al.
Patent Title	***Polymers of isoprene from renewable resources,*** U.S. Patent 8,420,759 (April 16, 2013)

Relevant Prior Patents by Author or Coauthors

Compositions and methods for producing isoprene, U.S. Patent 8,288,148 (October 16, 2012)

Isoprene synthase variants for improved microbial production of isoprene, U.S. Patent 8,173,410 (May 8, 2012)

Increased isoprene production using mevalonate kinase and isoprene synthase, U.S. Patent Application 20100184178 (July 22, 2010)

Reduction of carbon dioxide emission during isoprene production by fermentation, U.S. Patent Application 20100167370 (July 1, 2010)

Conversion of prenyl derivatives to isoprene, U.S. Patent Application 20100113846 (May 6, 2010)

Increased isoprene production using the archael lower mevalonate pathway, U.S. Patent Application 20100086978 (April 8, 2010)

Product Application

Cis-isoprene is an extremely important monomer used in the synthesis of styrene-isoprene-butadiene rubbers, styrene-isoprene-styrene block copolymers, and styrene-isoprene block copolymers. These copolymers are used in preparing automotive tires and engineered materials.

Significance of Current Application

Isoprene is a non-renewable monomer. Isoprene used in industry is isolated predominately as a by-product of thermal cracking petroleum or naphtha. To a lesser extent, it is extracted from petrochemical streams. In either case, fossil fuel sources are involved, which results in producing equivalent amounts of both cis- and trans-isomers. Each fossil fuel method used to obtain isoprene is an energy-intensive process which generates large amounts of toxic by-products. To address these concerns the current investigation has identified a simple and inexpensive method for preparing renewable cis-isoprene. The method uses renewable glucose and modified yeast to generate the more important cis-isoprene isomer. This is economically important since cis-isoprene can be readily converted into the stereo-regular cis-1,4-polybutadiene, which is more structurally and chemically similar to naturally occurring rubber. In addition, block co- and ter-polymer rubbers containing cis-isoprene were also prepared since they have high industrial utilization, especially in preparing automotive tires and engineered plastics. Of particular interest are poly(butadiene-co-isoprene) rubbers, poly(styrene-co-isoprene) rubbers, and poly(styrene-ter-isoprene-ter-butadiene) rubbers.

Product Formation

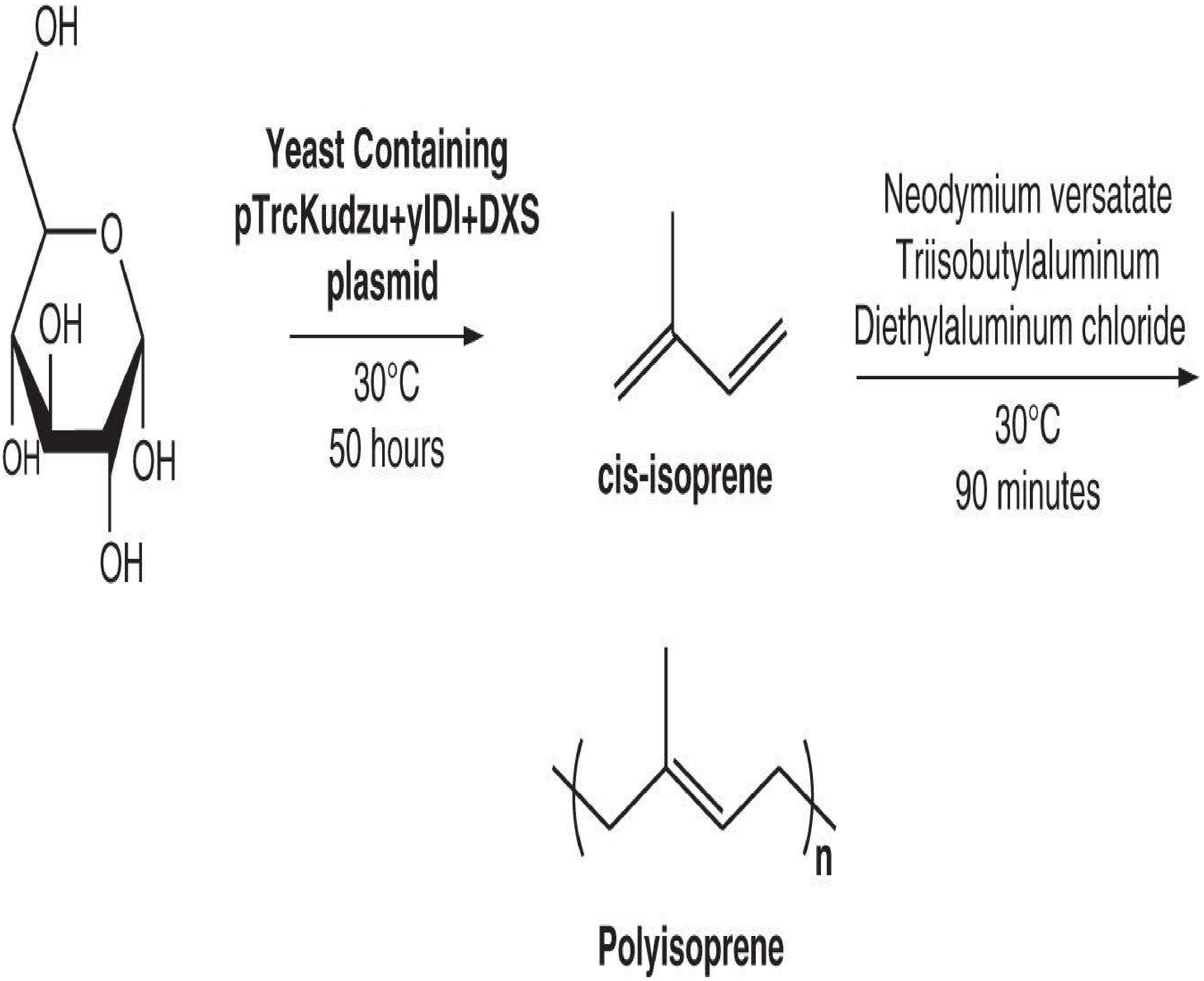


Figure 20.62

Experimental

1. Preparation of cis-isoprene from glucose and yeast extract using modified E. coli. Isoprene was prepared from glucose and yeast extract at a pH of 7.0 and at 30°C in a 500-L bioreactor using E. coli cells containing the pTrcKudzu+yIDI+DXS plasmid. A 2.5-L bioreactor was charged with 20 mL of frozen inoculum of E. coli stored in a mixed medium consisting of soytone/yeast extract/glucose growth medium having an optical density of 0.15 at 550 nm that contained 2.5 L of tryptone/yeast extract medium. After the yeast growth medium has an optical density of 1.0 at 30°C, 2.0 L of the mixture was transferred to the 500-L bioreactor where yeast extract and glucose were incrementally added. The total amount of glucose and yeast extract delivered to the bioreactor during the 50-hour fermentation period was 181.2 kg and 17.6 kg, respectively. The cis-isoprene titer gradually increased over the 50-hour fermentation period, and a total of 55.1 g of product was isolated.

2. Isolation of cis-isoprene using activated charcoal desorption. Throughout the 50-hour fermentation period a total of 130 g of activated charcoal was added to the reactor and to the gas-egress tube to adsorb a stream of fermentor off-gas. When the reaction was complete the reaction mixture was treated with 563 mL of cyclohexane to activated charcoal present in the gas-egress tube. After the slurry had been agitated for 2 hours, a vacuum at 100 mbar was attached and cis-isoprene gas was collected in a 30-mL cryogenic trap immersed in liquid nitrogen. The remaining cis-isoprene adsorbed on the activated charcoal present in the slurry in the reaction-product solution was isolated and then collected by vacuum distillation at 100 mbar over a period of several hours. Cis-Isoprene samples were then combined and dried over 3-Â molecular sieves. Gas chromatography indicated the sample was 99.1% pure and a total 58.9 g of cis-isoprene were isolated.

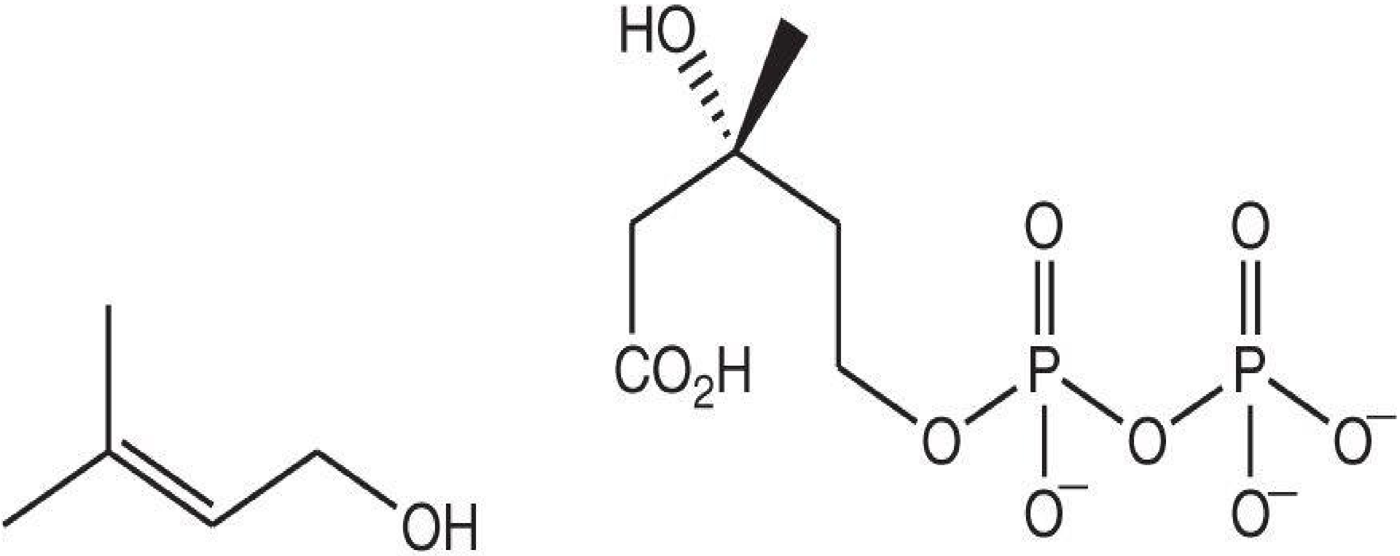
3. Preparation of neodymium catalyst for cis-isoprene polymerization. A catalytic mixture was prepared consisting of 2.68 mL of 0.51 M neodymium versatate dissolved in hexane, 54 mL of 1.0 M triisobutylaluminum dissolved in hexane, and 3.40 mL of 1.0 M diethylaluminum chloride dissolved in hexane. To assess the concentration and activity of neodymium in the sample, an aliquot was removed using a plastic syringe fitted with steel cannula and added to a solution containing 22.4 mL of 15 wt% 1,3-butadiene dissolved in hexane. The aliquot was placed into a 100-mL glass vessel with a septum top and agitated for 30 minutes at ambient temperature. A second aliquot was then added to the same solution and the mixture was heated to 65°C for 30 minutes. After workup, polybutadiene was isolated and the concentration of the catalyst assayed based on neodymium was determined to be 0.0164 M.

4. Solution polymerization of cis-isoprene with neodymium catalyst. A 4-mL screw-top glass vial containing a Teflon-coated stir bar was annealed at 150°C for 3 hours and then charged with 1.5 g of 7.7 wt% of cis-isoprene dissolved in cyclohexane. The vial was then treated with 60 µl of the Step 3 catalyst and the mixture was heated to 65°C while stirring at 500 rpm. After approximately 15 minutes, the solution became viscous. After a reaction had continued for an additional 90 minutes, the reaction mixture was quenched with 30 µl of a mixture of 90% isopropanol containing 10% of butylated hydroxytoluene. A sample of the cement was removed and GPC indicated that it had an Mw of 935,000 daltons with a cismicrostructure content of >90% as determined by ^{13}C-NMR.

Notes and Observations

1. Cervin[1] converted glucose into cis-isoprene using E. coli expressed in the Bacillus subtilis aprEnprE Pxyl-comK strain, BG3594comK, using the replicating plasmid, pBS19 with achloramphenicol resistance cassette, under control of the aprE promoter.
2. Bott[2] prepared and polymerized cis-isoprene prepared from glucose using the modified isoprene synthase, IspS, present in E. coli. The protein sequence for the isoprene synthase had a SEQ ID NO:6 with a restrictive endonuclease digestion using BspLU11I/PstI ligated into pTrcHis2B that had been digested with NcoI/PstI.
3. McAuliffe[3] used cells derived from E. coli, P. citrea, B. subtilis, T. reesei, Y. lipolytica, and S. cerevisiae to convert prenyl alcohol, (I), into mevalonate diphosphate, (II). The intermediate was then treated with a concentrated inorganic acid to decarboxylate prenyl

alcohol to generate cis-isoprene. (See Fig. 20.63.)



(I) (II)

Figure 20.63

4. Beck[4] increased the overall yields of biogenerated cis-isoprene from cultured cells using the archaeal mevalonate kinase polypeptide M. mazei mevalonate kinase. The method also entailed using the feedback-resistant archaeal mevalonate kinase. After a 55-hour fermentation period, the yield of cis-isoprene was 15.9%.

References

1. Marguerite A. Cervin et al., *Compositions and methods for producing isoprene*, U.S. Patent 8,288,148 (October 16, 2012)

2. Richard R. Bott et al., *Isoprene synthase variants for improved microbial production*, U.S. Patent 8,173,410 (May 8, 2012)

3. Joseph C. McAuliffe et al., *Conversion of prenyl derivatives to isoprene*, U.S. Patent Application 20100113846 (May 6, 2010)

4. Zachary Q. Beck et al., *Increased isoprene production using the archael lower mevalonate pathway*, U.S. Patent Application 20100086978 (April 8, 2010)

Renewable α-Olefin Copolymers

Author Guillaume Le et al.

Patent Title ***Polyolefin derived from renewable resources, and method for producing same,*** U.S. Patent 8,338,549 (December 25, 2012)

Relevant Prior Patents by Author or Coauthors

Block copolymer derived from renewable materials and method for making such block copolymer, U.S. Patent 8,231,950 (July 31, 2012)

Composition containing polypropylene and/or a propylene copolymer obtained from renewable materials, and uses thereof, U.S. Patent Application 20110305900 (December 15, 2011)

Production of grafted polyethylene from renewable materials, the obtained polyethylene and uses thereof, U.S. Patent Application 20110152454 (June 23, 2011)

Product Application

The current investigation has developed a method for producing low-molecular-weight copolymers of ethylene and renewable α-olefins from unsaturated fatty acid glycerol triesters that can be used as lubricants in automotive engines.

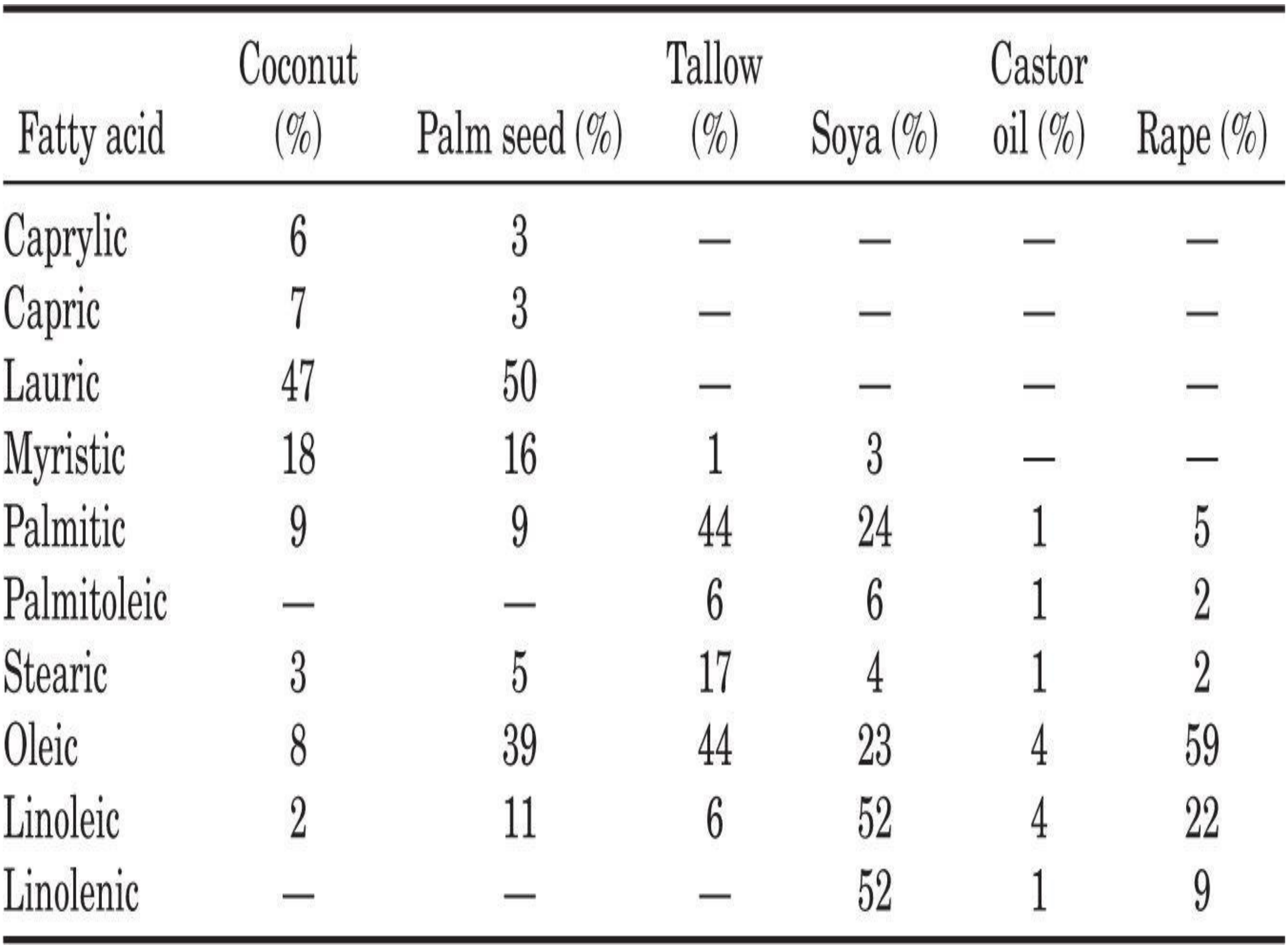
Significance of Current Application

Low-molecular-weight poly(ethylene-copropylene) copolymers are routinely used in lubricants in motor vehicles. To obtain propylene, for example, cracking of non-renewable crude oil is required to produce propane followed by a steam-cracking of propane to prepare propene. Both processes are energy intensive, generate toxic side products, and consume non-renewable resources. The current investigation has developed a method for generating these automotive engine lubricants using α-olefin comonomers produced from renewable unsaturated fatty acid glycerol triesters, (I). The process does not generate toxic organic-waste products and requires only moderate energy input to produce the polymer.

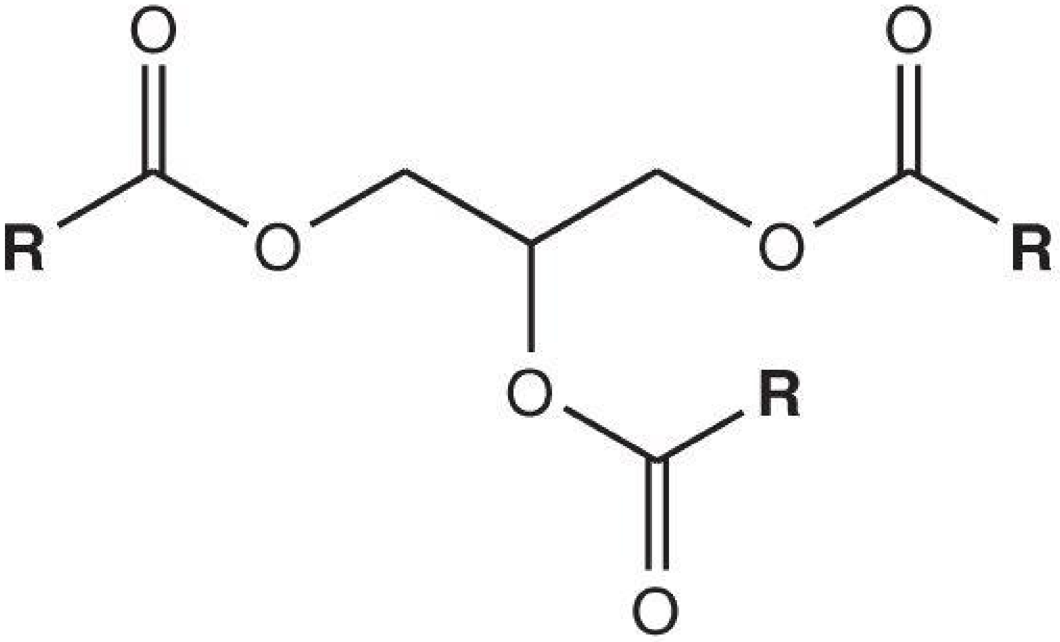
Sources of Unsaturated Fatty Acid Glycerol Triesters

An overview of unsaturated fatty acid glycerol triesters, (I), from renewable feedstocks is provided in Table 20.10. (See also Fig. 20.64.)

TABLE 20.10 Fatty acid composition of selected glycerol triesters



Fatty acid	Coconut (%)	Palm seed (%)	Tallow (%)	Soya (%)	Castor oil (%)	Rape (%)
Caprylic	6	3	—	—	—	—
Capric	7	3	—	—	—	—
Lauric	47	50	—	—	—	—
Myristic	18	16	1	3	—	—
Palmitic	9	9	44	24	1	5
Palmitoleic	—	—	6	6	1	2
Stearic	3	5	17	4	1	2
Oleic	8	39	44	23	4	59
Linoleic	2	11	6	52	4	22
Linolenic	—	—	—	52	1	9



Unsaturated Fatty Acid Triesters

(I)

Figure 20.64

Product Formation

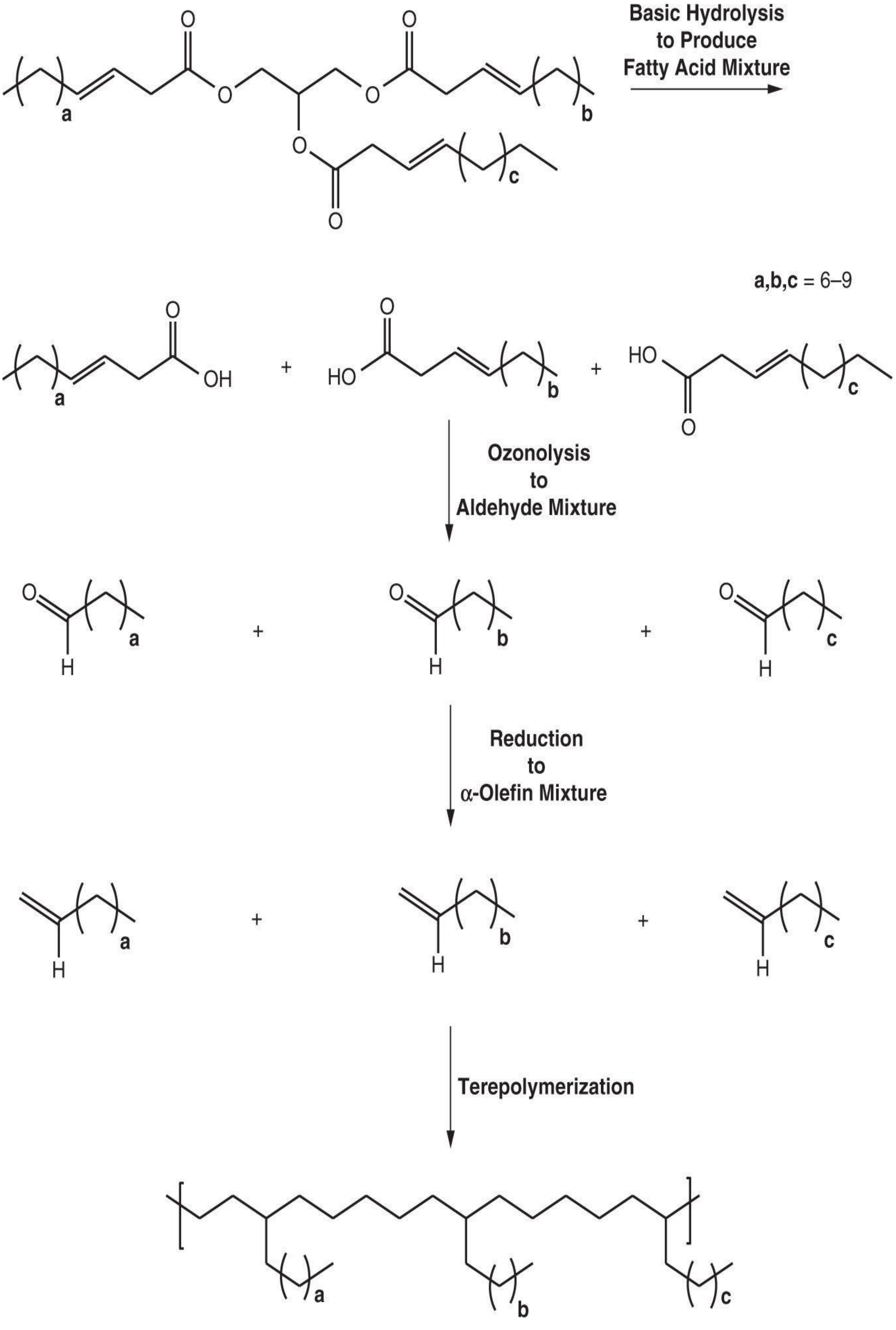

Basic Hydrolysis
to Produce
Fatty Acid Mixture
a,b,c = 6–9
Ozonolysis
to
Aldehyde Mixture
Reduction
to
α-Olefin Mixture
Terepolymerization
O
OH
HO
H
a
b
c

Figure 20.65

Experimental

1. Preparation of poly(ethylene-co-fatty acid alkenes). A metallic reactor was charged with 90 mol% of ethylene and 10 mol% of a mixture of fatty acid alkenes under a reaction pressure of 25 bar at 90°C. The reaction was performed at a gas speed of 0.6 m/s containing a 15-m fluidized bed with a reactor inlet set at 40°C. Under these reaction conditions the reaction product yield was 120 m^3/h.

Testing

The density for terpolymer samples was determined according to ASTM D 1505, while melt-flow-index properties were determined according to ASTM D 1238. Testing results are provided in Table 20.11.

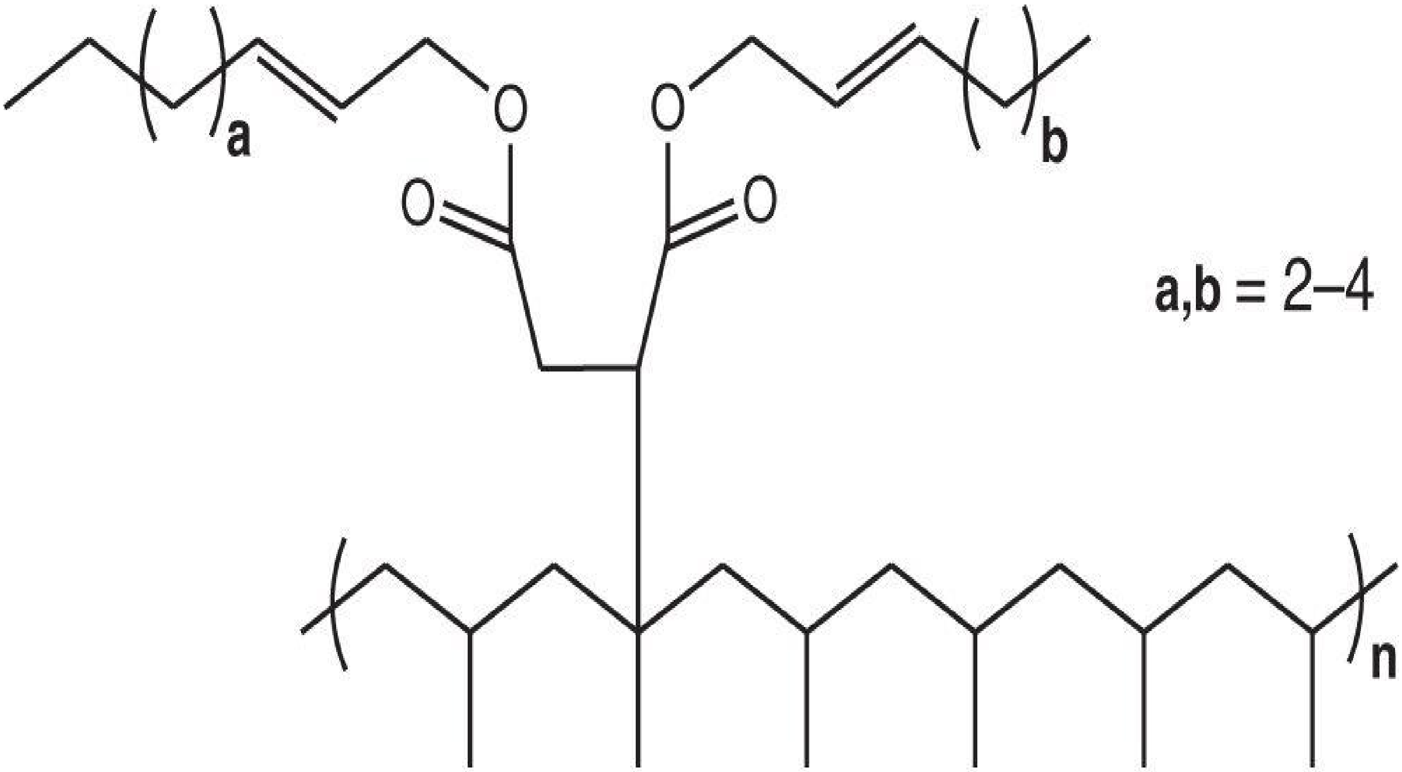
TABLE 20.11 Physical properties of ethylene copolymerized with fatty acid alkenes derived from unsaturated fatty acid glycerol triesters.

Test	Terepolymer 1	Terepolymer 2	Terepolymer 3
Melt index (g/10 minutes)	1.0	3.4	0.1
Density (g/cm^3)	0.9154	0.9164	0.9115
Melt flow index @ 190°C (kg)	2.16	—	—

Testing Results

Notes and Observations

1. Devisme[1] prepared n-butanol from a fermentation reaction using either Clostridium aurantibutyricum or Clostridium butylicum with renewable plant matter and then converted the product into maleic anhydride. A graft copolymer, (II), was then prepared by reacting maleic anhydride with C_1 to C_8 unsaturated alcohols and the product was used to prepare textiles, garden furniture additives, and flexible motor-vehicle components. (See Fig. 20.66.)



(II)

Figure 20.66

2. Malet[2] prepared both homo- and block copolymers using plant-derived furfural, as illustrated in Eq. 1. Once furfural was isolated it was then converted into tetrahydrofuran, as illustrated in Eq. 2. Tetrahydrofuran was then used to prepare flexible homo- or copolyethers, as illustrated in Eq. 3. (See Fig. 20.67.)

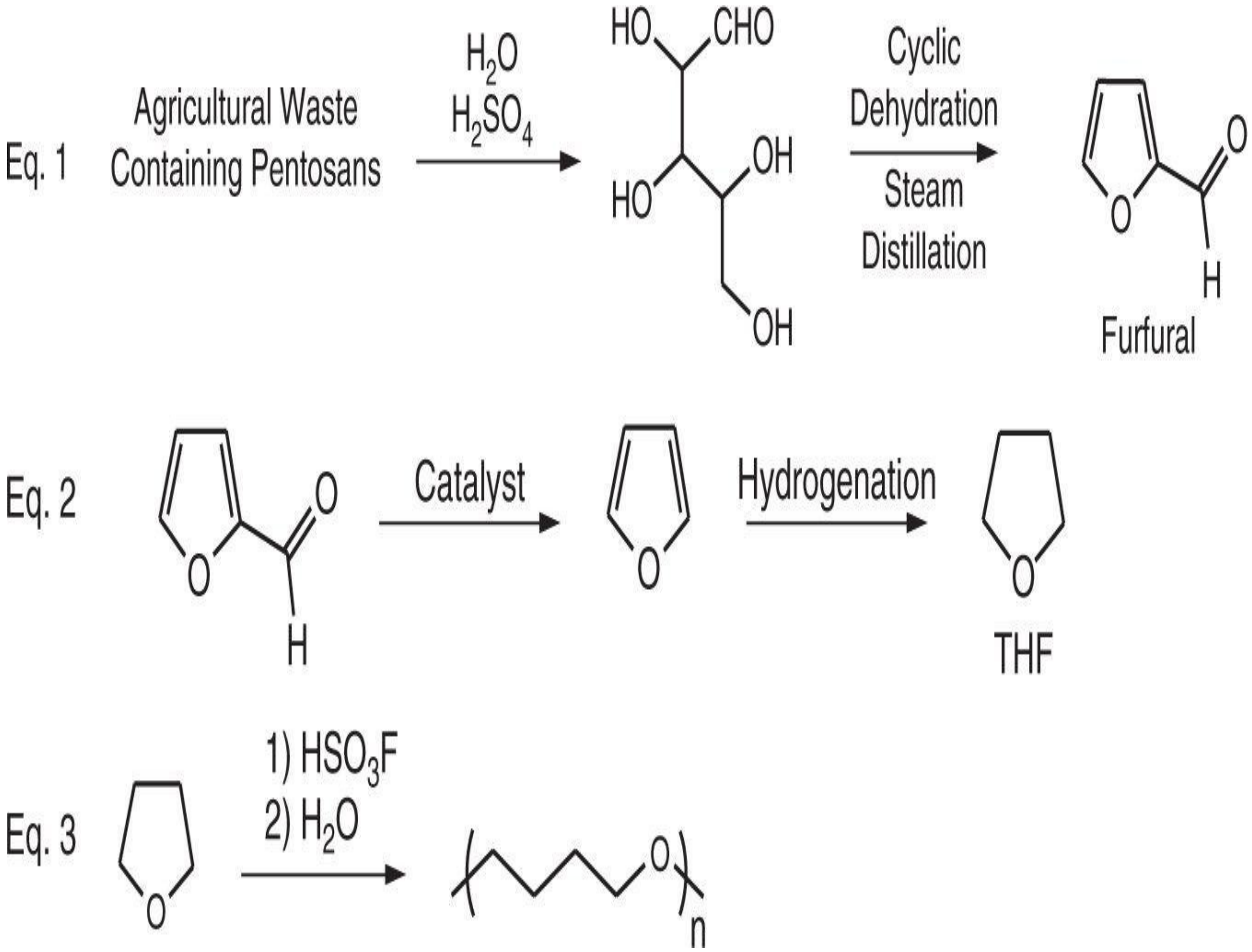


Figure 20.67

3. Elastomeric polyethylene surfaces modified with renewable maleic anhydride were prepared by Devisme[3] by passing a mixture of polyethylene and maleic anhydride containing t-butyl peroxyacetate through a twin screw extruder. Polyethylene was also surface modified using the same grafting method and 1-hexene. In both cases, elastomers were used as lubricant additives.

4. Devisme[4] prepared oligomeric copolymers of ethylene and vinyl acetate where both monomers were obtained from renewable sources. Low-molecular-weight copolymers were then used in automotive lubricant formulations as friction modifiers.

References

1. Samuel Devisme et al., *Compositions containing polypropylene and/or a polypropylene copolymer obtained from renewable materials, and uses thereof*, U.S. Patent Application 20110305900 (December 15, 2012)

2. Frederic Malet et al., *Block copolymer derived from renewable materials and methods for making such block copolymer*, U.S. Patent 8,231,950 (July 31, 2012)

3. Samuel Devisme et al., *Production of grafted polyethylene from renewable materials and uses thereof*, U.S. Patent Application 20110152454 (June 23, 2011)

4. Samuel Devisme et al., *Manufacture of ethylene/carboxylic vinyl ester copolymers from*

renewable materials, copolymers obtained and uses, U.S. Patent Application 20110287204 (November 24, 2011)

Solventless Preparation of Engineered Plastics

Author Chun-Hua Chuang

Patent Title ***Solvent-free low-melt viscosity imide oligomers and thermosetting polymide composites,*** U.S. Patent RE43,880 (December 25, 2012)

Relevant Prior Patents by Author

Polyimides derived from novel asymmetric dianhydrides, U.S. Patent 8,093,348 (January 10, 2012)

Synthesis of asymmetric tetracarboxylic acids and corresponding dianhydrides, U.S. Patent 7,425,650 (September 16, 2008)

Synthesis of asymmetric tetracarboxylic acids and dianhydrides, U.S. Patent 7,381,849 (June 3, 2008)

Solvent-free low-melt viscosity imide oligomers and thermosetting polyimide composites, U.S. Patent 7,015,304 (March 21, 2006)

High-solids polyimide precursor solutions, U.S. Patent 6,784,276 (August 31, 2004)

Product Application

Engineered thermoset plastics containing imide oligomers have excellent thermal stability, solvent resistance, high strength and a high glass-transition temperature, which makes them suitable for use in aerospace systems component, airframes, missiles, and rockets.

Significance of Current Application

The current investigation has devised a single-step solventless method for preparing low-melt-viscosity imide oligomers. Oligomers from this process contain reactive multi-unsaturated end groups that formed thermosets by melt processing. The absence of high-boiling solvents such as N,N-dimethylformamide or N-methyl-2-pyrrolidinone, reduces energy expenditures and dramatically lowers imide manufacturing costs, particularly those associated with solvent removal and imide purification.

Product Formation

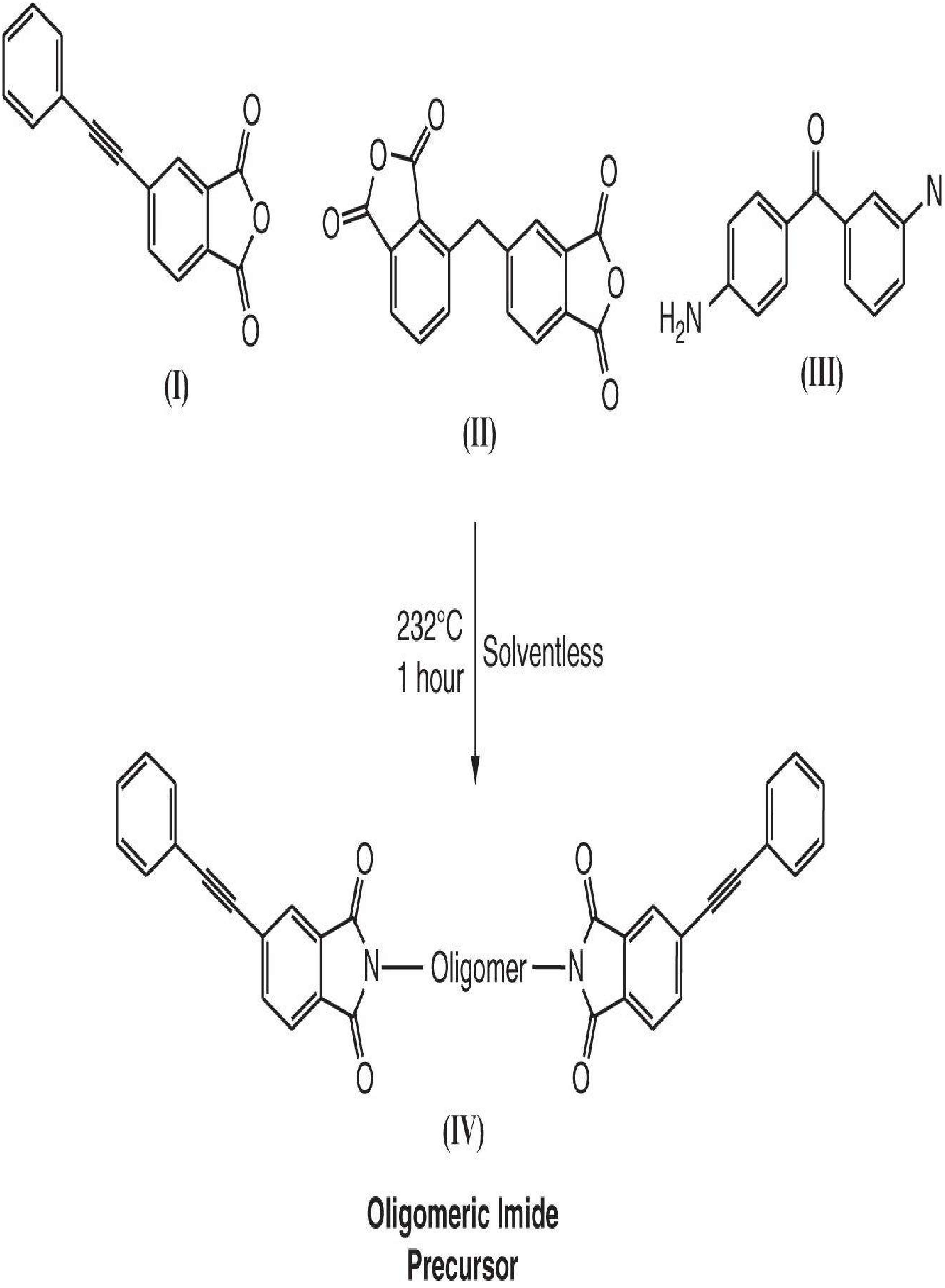


Figure 20.68

Oligomeric Imide Derivatives

Oligomeric imide analogues were also prepared by replacing 2,3, 3′,4′-diphenyl tetracarboxylic dianhydride, (II), with dianhydrides, (V) and (VI), as illustrated in Fig. 20.69.

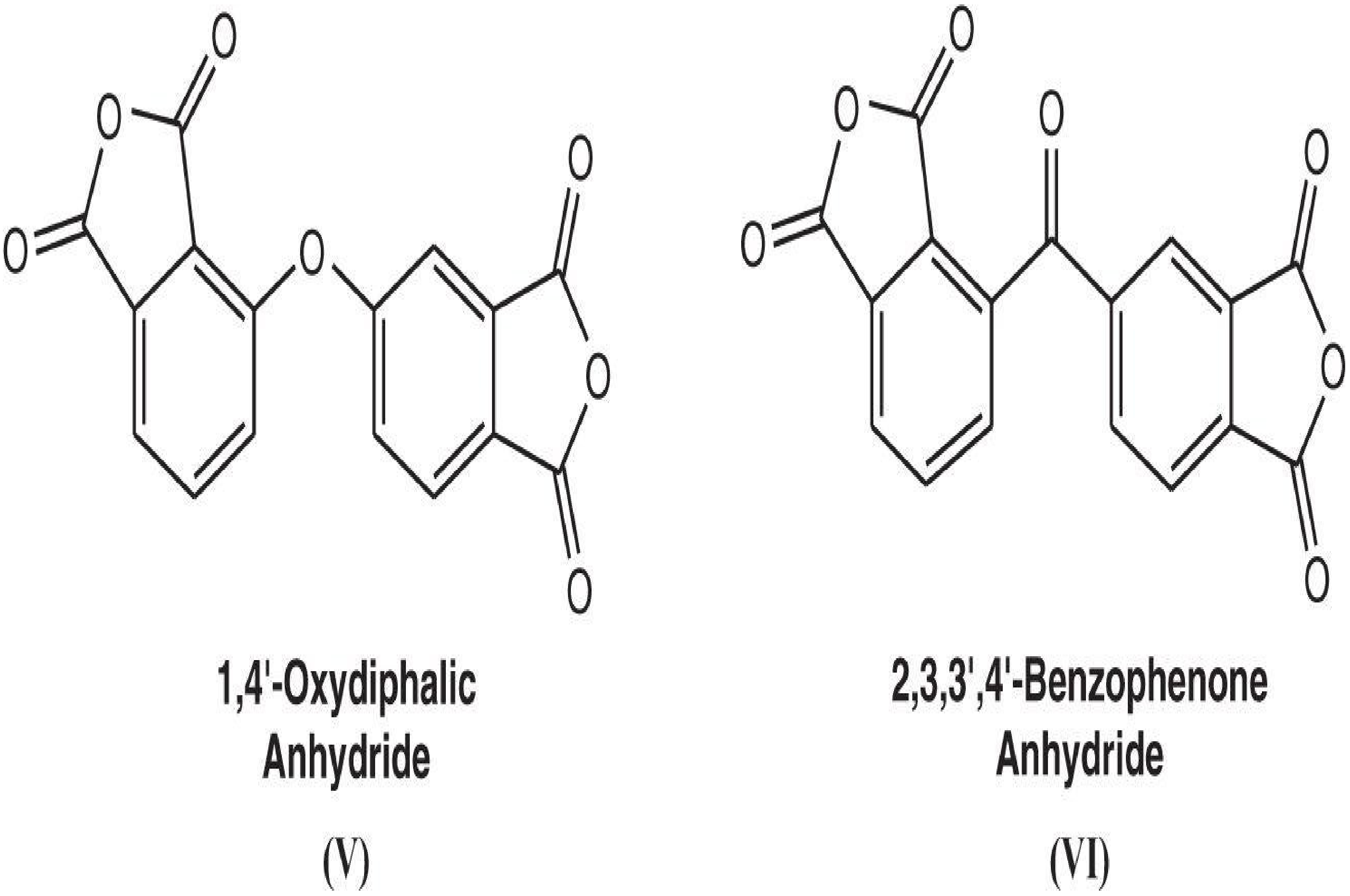


Figure 20.69

Experimental

1. Preparation of oligomer imide precursor. A small resin kettle containing an efficient mechanical stirrer was charged with 6.206 g of 4-phenylethynylphthalic anhydride, (I), 3.678 g of 2,3,3′,4′-diphenyl tetracarboxylic dianhydride, (II), and 35.5 g of 3,4′-diamino-benzophenone, (III). These three components were then thoroughly mixed until completely blended. The solid powder mixture was then heated to melt at 232°C for 1 hour to form the oligomeric imide precursor, (IV).

2. Curing the oligomeric imide precursor. After grinding the oligomeric imide precursor prepared in Step 1 into a solid powder, it had a melt viscosity between 5 and 10 poise, which was determined using a Brookfield viscometer. The low-melt-viscosity resin was then processed using both resin transfer molding and resin film infusion techniques where it was cured at 371°C for 2 hours. The thermoset polyimide was then isolated as a slightly yellow solid and had a T_g of 350°C.

Notes and Observations

1. Asymmetric dianhydrides used in the current investigation were previously prepared by Chuang,[1] as illustrated for 2,3,3′,4-benzophenone dianhydride in Eq. 1. (See Fig. 20.70.)

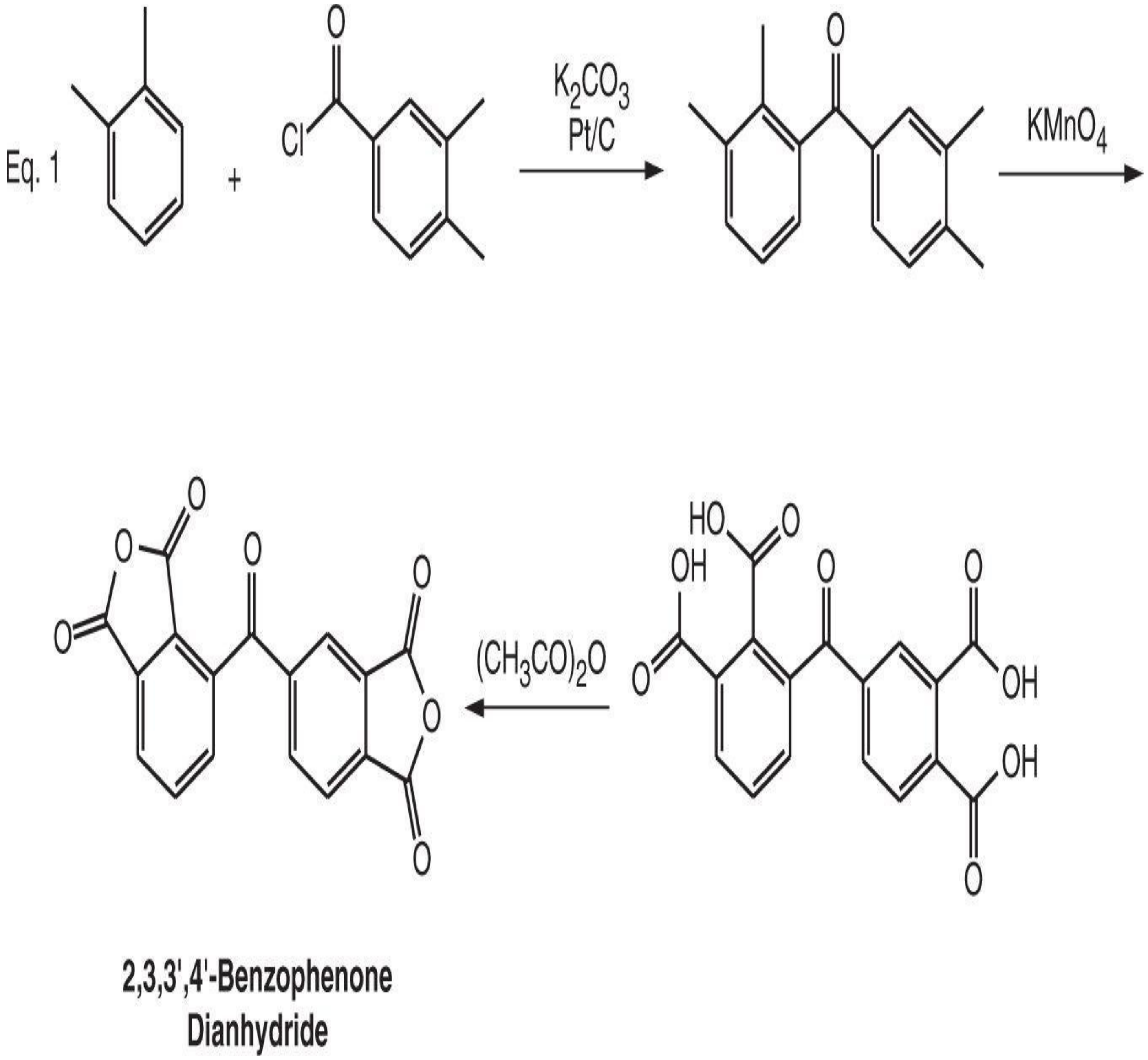


Figure 20.70

2. Diakoumakos[2] prepared solventless flame-retardant-polymer compositions by terepolymerizing a mixture of oligomeric polyorganosiloxanes methacrylic with acrylic acid and aromatic epoxides. The blend was terepolymerized with nanoclays Cloisite® 25A and Nanofil® 32 by initially heating the mixture between 250°C and 260°C for 6 hours at 3500 rpm. The cured flame-retardant composition was then isolated as a paste.

3. Nelson[3] developed a solventless process for modifying polymeric materials for subsequent use in grafting reactions or as transesterification reagents. In this process, poly(styrene-t-butyl methacrylate), (VII), was initially demethylated by heating with p-toluenesulfonic acid to generate the reaction product intermediate, (VIII), which was in equilibrium with an anhydride, as illustrated in Eq. 2. Once the anhydride was generated, it was post-reacted with amines to produce polyamides at low cost. (See Fig. 20.71.)

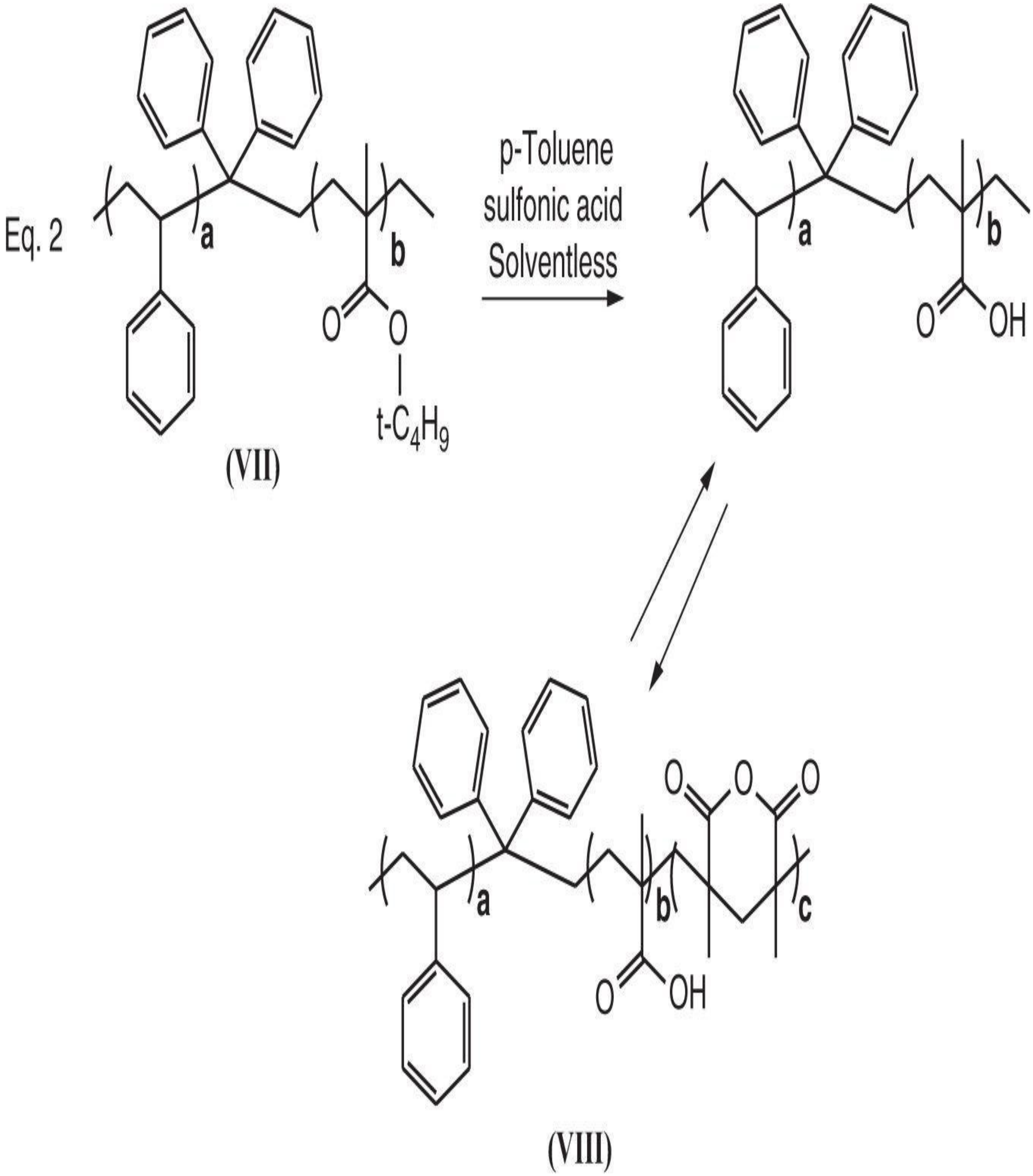
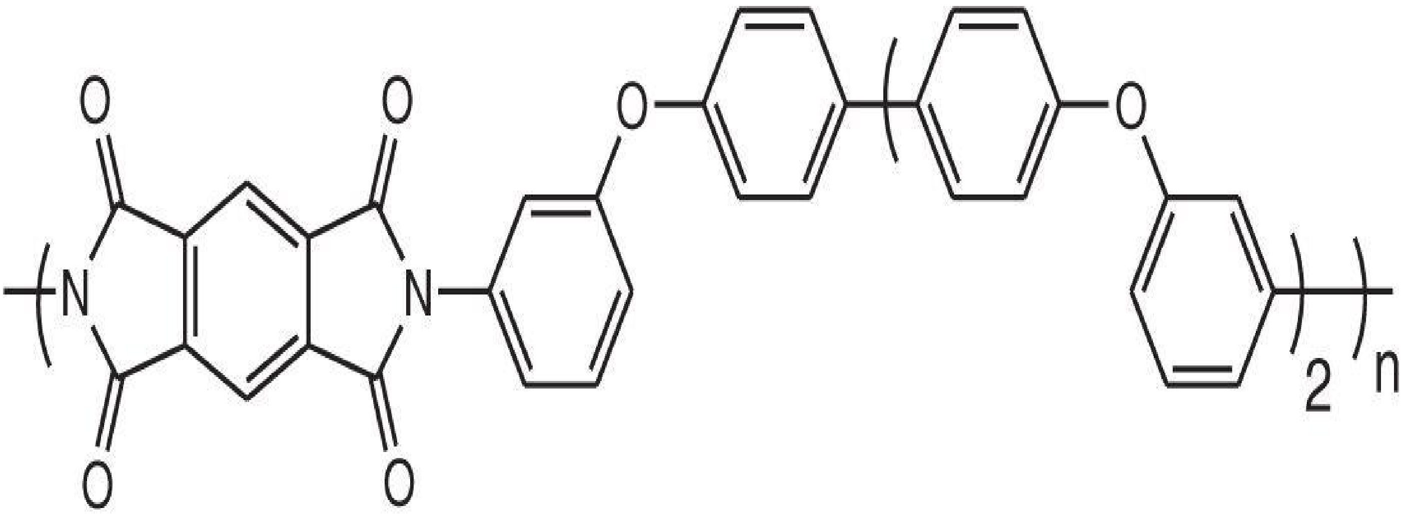


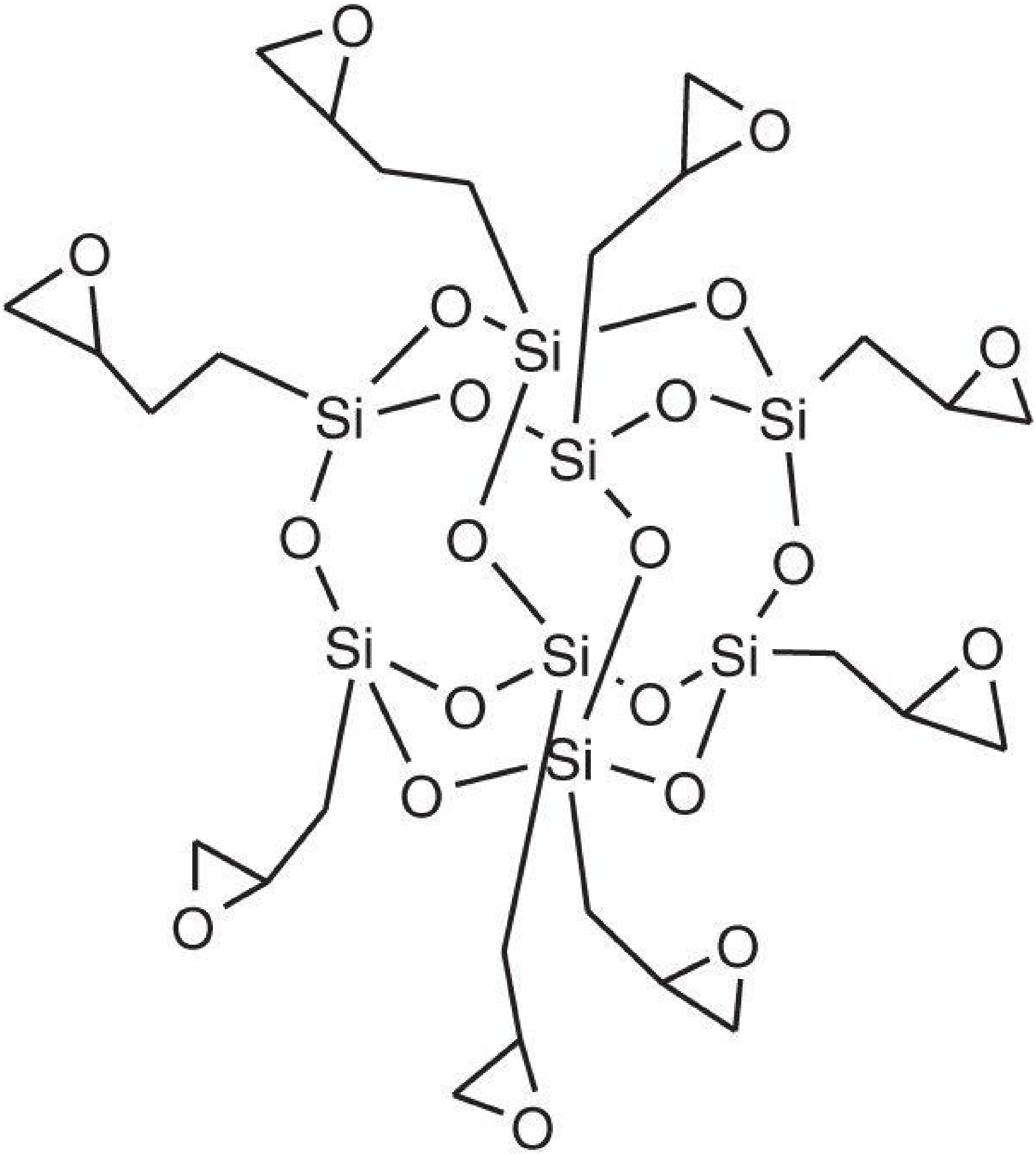
Figure 20.71

4. Wu[4] devised a solventless method for preparing oligosilsequioxane polyimide surfaces. The process entailed treating a polyimide surface, (IX), with oligosilsequioxane epoxides, (X), and then heating the coating at 260°C for 20 minutes. (See Fig. 20.72.)



(IX)

Figure 20.72



(X)

References

1. Chun-Hua Chuang, *Polyimides derived from novel asymmetric dianhydrides*, U.S. Patent 8,093,348 (January 10, 2012)

2. Constantinos D. Diakoumakos et al., *Flame retardant polymer compositions*, U.S. Patent 7,635,728 (December 22, 2009)

3. James M. Nelson et al., *Process to modify polymeric materials and resulting compositions*, U.S. Patent 7,632,916 (December 15, 2009)

4. Jin Wu et al., *Polyhedral silsesquioxane modified polyimide containing intermediate transfer members*, U.S. Patent 8,283,398 (October 9, 2012)

Thermosets from Polylactides

Author Feng Jing et al.

Patent Title ***Bifunctional lactide monomer derivative and polymers and materials prepared using the same,*** U.S. Patent 8,203,007 (July 19, 2012)

Relevant Prior Patents by Author or Coauthors

Bioabsorbable polymer compositions exhibiting enhanced crystallization and hydrolysis rates, U.S. Patent 8,236,904 (April 7, 2012)

Block copolymer modified vegetable oil and polymer blends and methods of making same, U.S. Patent 7,888,418 (February 15, 2011)

Polylactide composites and methods of producing the same, U.S. Patent 7,939,603 (May 10, 2011)

Polymer synthesis from macrocycles, U.S. Patent 7,714,097 (May 11, 2010)

Product Application

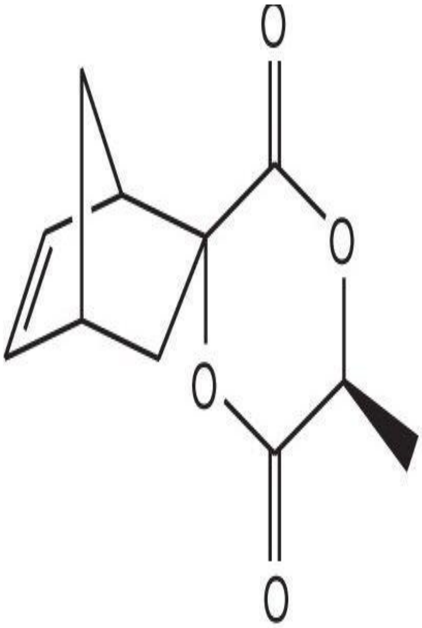
Strength-enhanced biorenewable polylactide fibers and bulk plastics prepared from this investigation are targeted for use in upholstery, microwavable trays, clothing materials and fabrics, engineering plastics, and medical devices.

Significance of Current Application

There is a continuous need to prepare polylactide polymers with improved thermal properties to expand their use in industrial applications. Of particular interest is using polylactide polymers in thermo-formable applications. This application, however, would require that polylactides withstand elevated processing temperatures while remaining rigid and tough. Polylactides with improved durability and water transport control properties would also enable them to be used in hot/cold containment packaging. The current investigation has developed a method for enhancing the thermal properties of biorenewable polylactic acid by graft polymerizing them onto the non-renewable 1,5-cyclooctadiene substrate after ring-opening polymerization.

Components

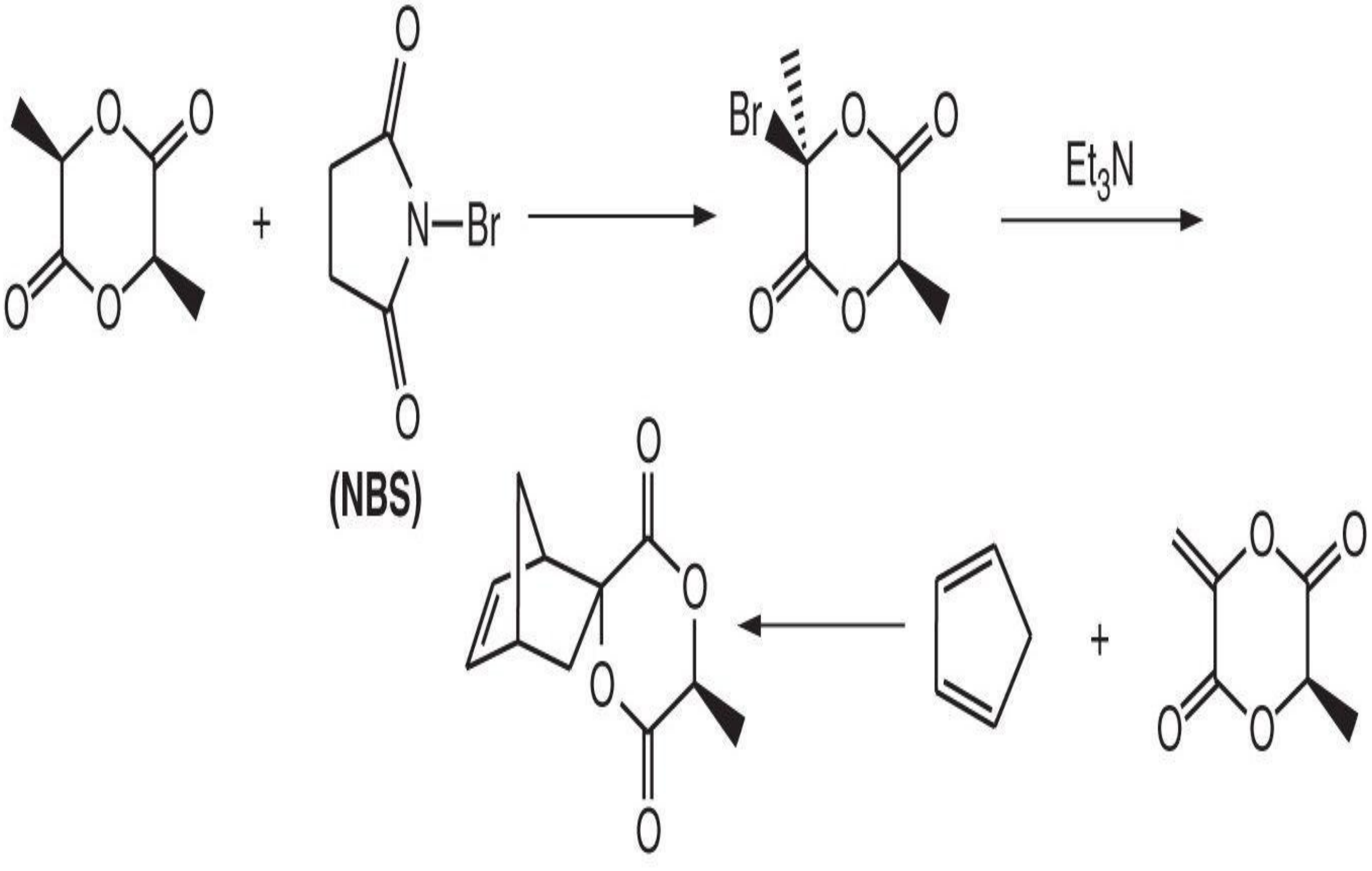
Component 1: Monomer 1 Spiro[6-methyl-1,4-dioxane-2,5-dione-3,2′ -bicyclo[2.2.1]hept[5]ene], (I) Monomer 1 Preparation



Monomer 1

(I)

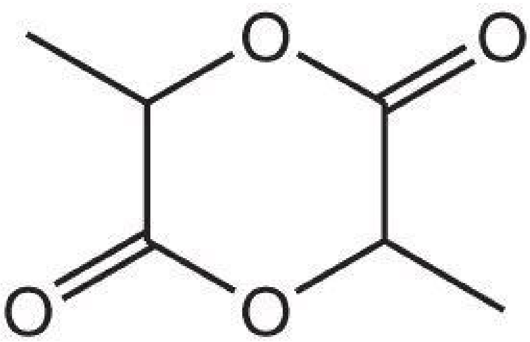
Monomer 1 Preparation



Monomer 1

Figure 20.73

Component 2: Monomer 2

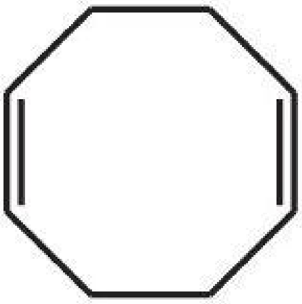


Monomer 2

(II)

Figure 20.74

Component 3: Monomer 3



Monomer 3

(III)

Figure 20.75

Production Formation

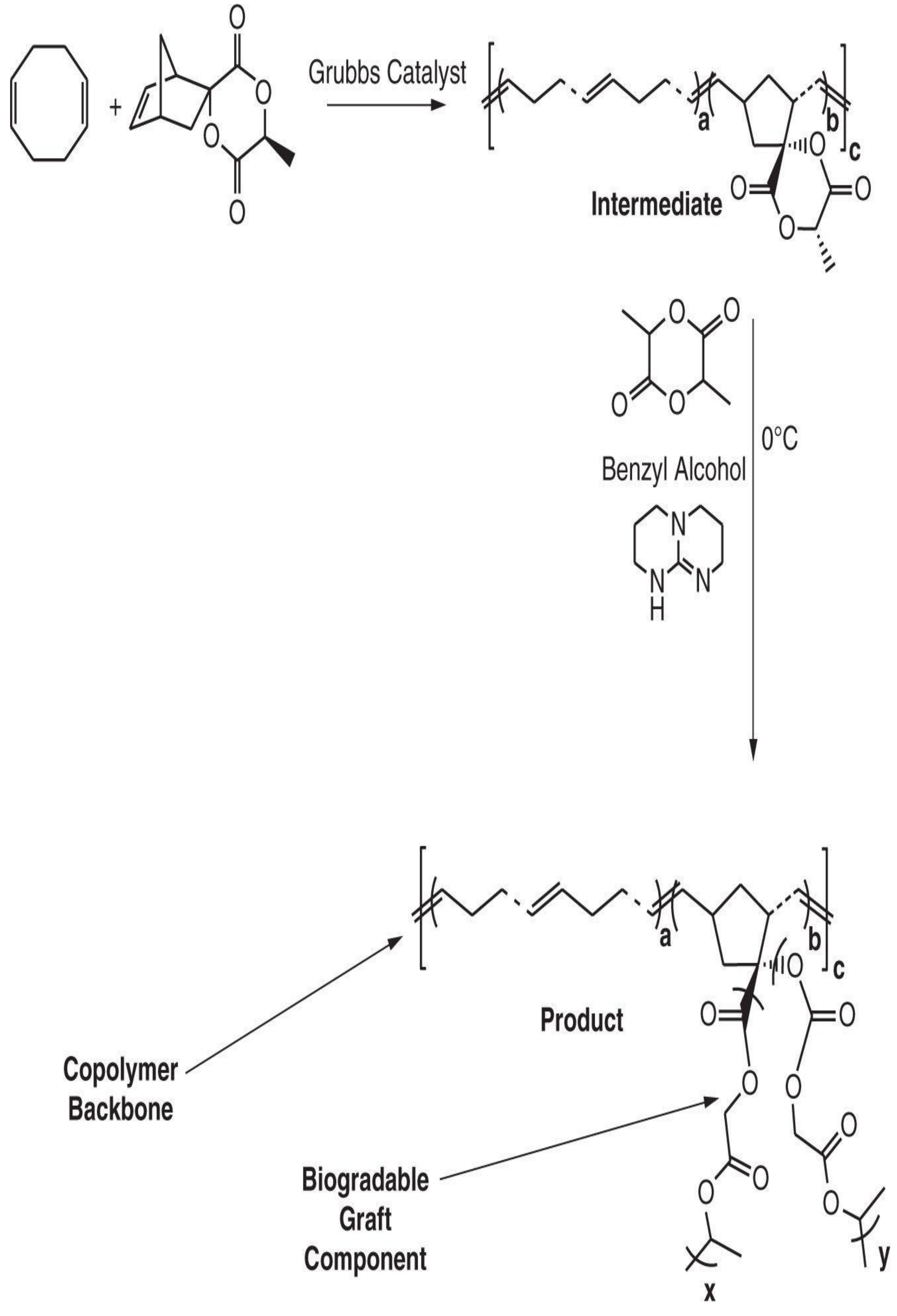

Grubbs Catalyst
Intermediate
a
b
c
0°C
Benzyl Alcohol
Product
a
b
c
Copolymer Backbone
Biogradable Graft Component
x
y

Figure 20.76

Experimental

1. Preparation of 3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione. A 2-L reactor was charged with 200.0 g of l-lactide, 1 L of benzene, and 272.0 g of N-bromosuccimide, and then refluxed and treated with the dropwise addition of 6.72 g of benzoyl peroxide dissolved in 100 mL of benzene over 20 minutes. The mixture was then cooled to ambient temperature and filtered. The filtrate was evaporated to dryness and a pale yellow solid was isolated that was then dissolved in 1.5 L of methylene chloride. The solution was washed three times with saturated sodium bisulfite solution and once with saturated brine and then dried over magnesium sulfate. Thereafter, the solution was evaporated and re-treated with saturated brine. After drying over magnesium sulfate, the solution was evaporated to dryness, re-crystallized with a 1:1 mixture of ethyl acetate and hexanes, and 137.9 g of a white crystal were isolated.

2. Preparation of 3-methyl-6-methylene-1,4-dioxane-2,5-dione. A 500-mL reaction flask was charged with 31.2 g of the Step 1 product and 200 mL of methylene chloride and then cooled in an ice bath and treated with the dropwise addition of 21.5 mL of triethylamine. After approximately 1 hour in the ice bath, the reaction mixture was brought to ambient temperature and stirred for an additional hour. The mixture was then transferred to a separatory funnel and washed three times with 1 M HCl and once with saturated brine. The organic layer was dried over magnesium sulfate and then concentrated. A pale-yellow solid was isolated and purified by silica-gel column chromatography using methylene chloride and an isolated white solid. The solid was further purified by sublimation at 45°C and 11.88 g of white crystals were isolated.

3. Preparation of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2’-bicyclo[2.2.1]-hept[5]ene].

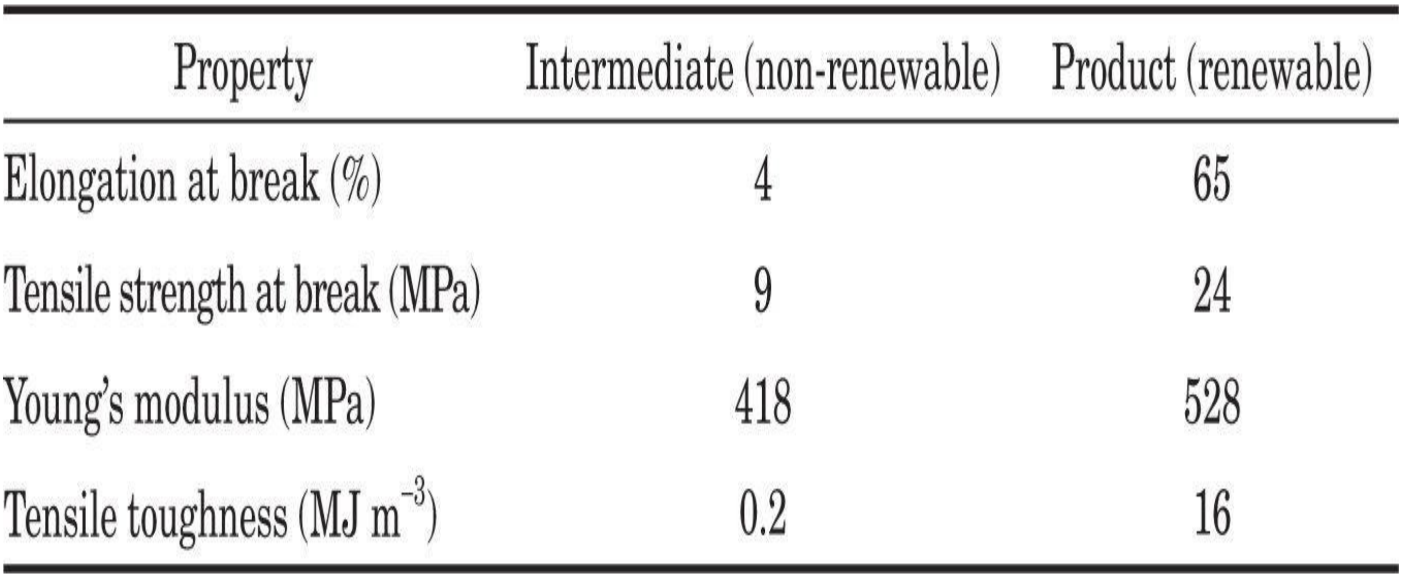
A 250 mL round bottom beaker was charged with 15.0 g of the Step 2 product and 14.0 g cyclooctadiene dissolved in 100 mL of benzene, and the mixture refluxed overnight under argon. The reaction mixture was then cooled to ambient temperature, and benzene and unreacted cyclooctadiene were removed by rotary evaporation. The crude product was purified by silica-gel column chromatography first using hexanes to remove dicyclooctadiene and methylene chloride, and a yellowish solid was isolated. The solid was then purified by sublimation at 50°C, and 20.74 g of product were isolated as a white crystal.

4. Preparation of grafted spiro[6-methyl-1,4-dioxane-2,5-dione-3,2′-bicyclo[2.2.1]-hept[5]ene] intermediate. A vial was charged with 30.1 µl of cis-2-butene-1,4-diol diacetate, 32.4 mg of a second-generation Grubbs’ catalyst,[1] and 40 mL of methylene chloride. The vial was then treated with the Step 3 product and then placed into a 150-mL pressure vessel containing 10.0 g of 0.595 g of 1,5-cyclooctadiene dissolved in 30 mL of methylene chloride, and then stirred. Thereafter, the reaction catalyst was added to initiate polymerization at ambient temperature. After 20 hours, the reaction mixture was quenched by adding excess ethyl vinyl ether to the reaction vessel. The polymer solution was then precipitated twice in methanol to remove both the catalyst and ethyl vinyl ether and a solid polymer was isolated.

5. Preparation of poly(d,l-lactide) graft copolomer. A 150-mL vial was charged with 1.0 g of the Step 4 product, 4.0 g of d,l-lactide, 28.7 mL of benzyl alcohol, 40 mL of methylene chloride, and a stir bar and then treated with 3.9 mg of 1,5,7-triazabicyclo[4.4.0]dec-5-ene dissolved in 1 mL of methylene chloride. Once the lactide ring-opening metathesis polymerization reaction was initiated, the mixture was placed into an ice bath for 1 hour and then quenched using excess benzoic acid. The solution was then evacuated to dryness and the graft copolymer was isolated as a white solid.

Testing Results

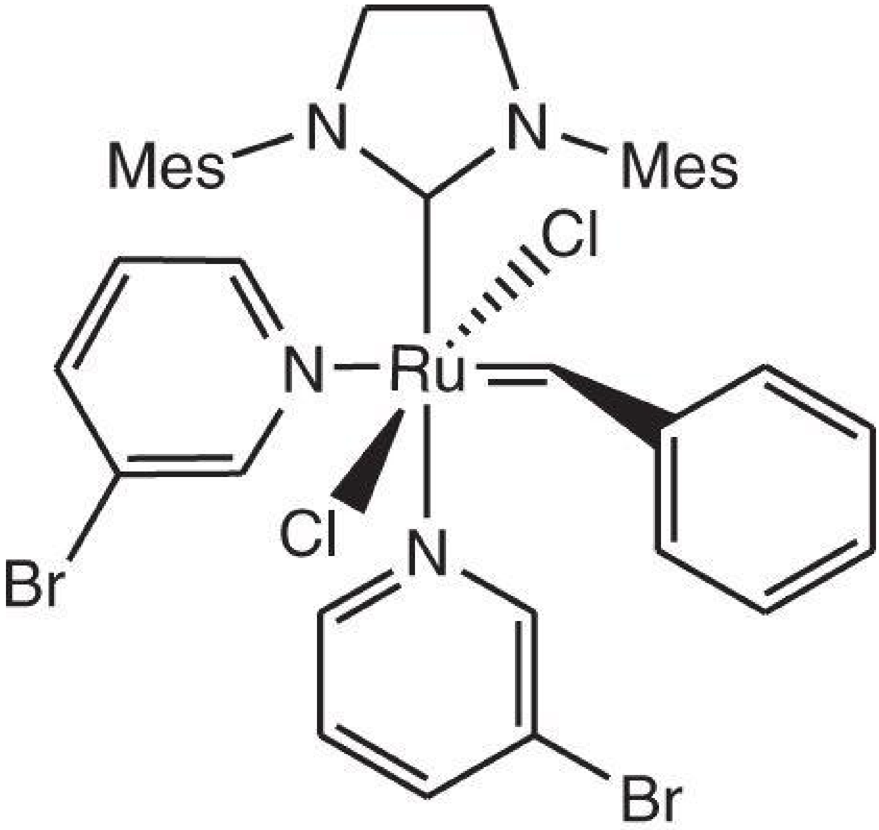
Table. 20.12 Mechanical strength comparison of the non-renewable intermediate and renewable product containing graft poly(D,L-lactide).



Property	Intermediate (non-renewable)	Product (renewable)
Elongation at break (%)	4	65
Tensile strength at break (MPa)	9	24
Young's modulus (MPa)	418	528
Tensile toughness (MJ m^{-3})	0.2	16

Notes and Observations

1. The second-generation Grubbs[1] catalyst ring-opening metathesis polymerization catalyst, (IV), used in Step 4 is illustrated in Fig. 20.77.

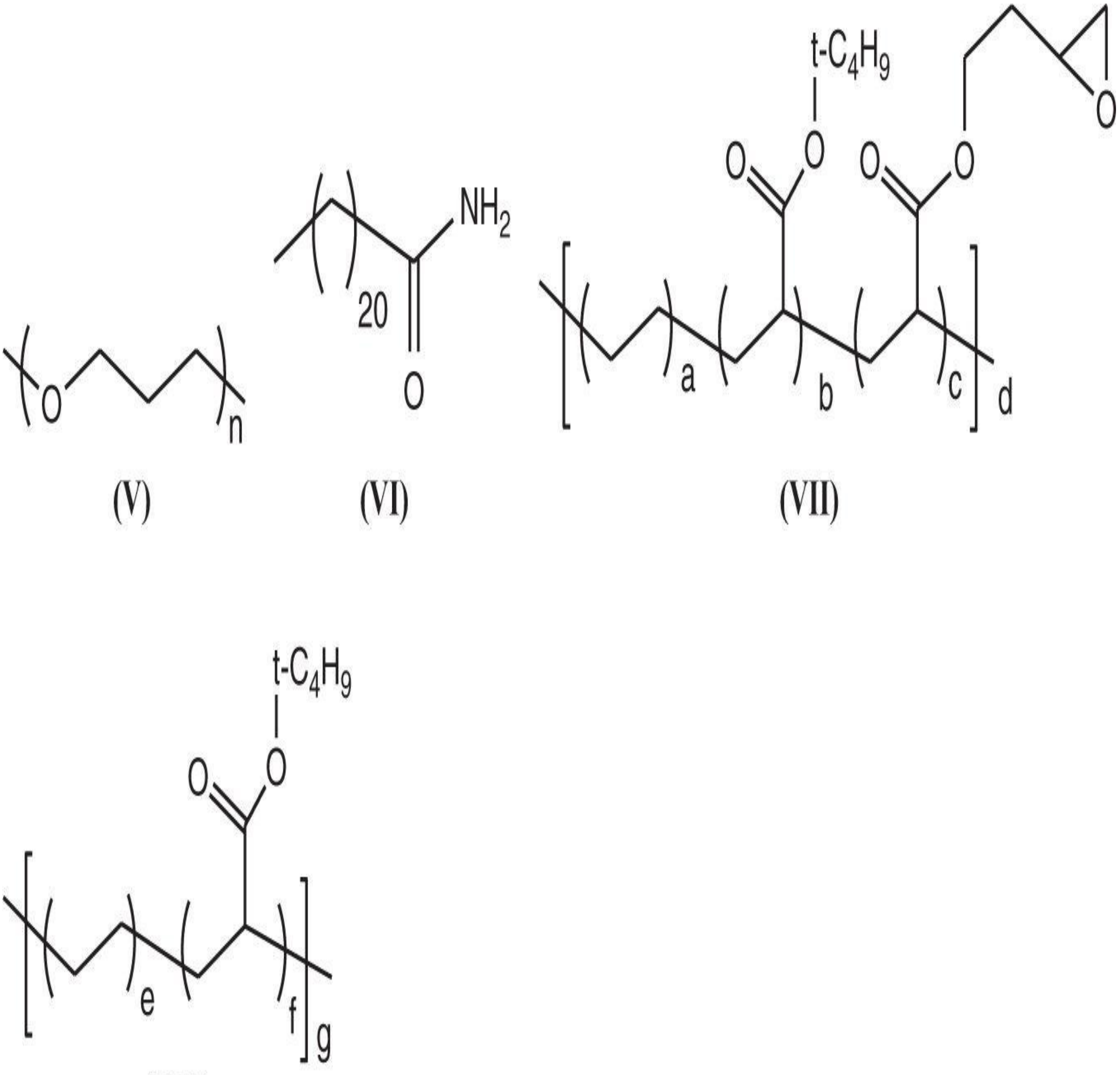


Second Generation Grubbs ROMP Polymerization Catalyst

(IV)

Figure 20.77

2. Uradnisheck[2] improved the thermal properties of polylactic acid for use in thermal storage applications by blending it between 2 wt% and 15 wt% of poly(trimethylene oxide) glycol, (V), behenamide, (VI), poly(ethylene-ter-butyl acrylate-ter-glycidyl methacrylate), (VII), and poly(ethylene-b-butyl acrylate), (VIII). (See Fig. 20.78.)



(V) (VI) (VII)

(VIII)

Figure 20.78

3. Shimizu[3] determined that the physical properties of both Nylon 11 and poly(vinylidene fluoride) could be dramatically improved by melt blending them together at 210°C. The physical properties of the blend included improvements in low- and high-shearing times as well as dynamic storage and loss moduli. In addition, the viscosity ratio between Nylon 11 and poly(vinylidene fluoride) was estimated to be about 1.61 at 230°C, which would allow for a wider variety of mechanical processing.

4. Ohashi[4] prepared phosphorus-free flame retardants by treating films of polylactic acid with up to 0.1 wt% sodium hydroxide. The flame-retardant film was completely biodegradable and had excellent flame retardancy and good mechanical strength.

5. Narita[5] prepared molding sheets using a eutectic mixture of 25 wt% poly-L-lactic acid and 75 wt% poly-D-lactic acid. At temperatures exceeding 250°C, the blend remained

stable for up to 10 minutes.

References

1. Robert H. Grubbs et al., Angew. Chem. Int. Ed. 41, pp. 4035–4037 (2002)
2. Julius Uradnisheck, “Poly(hydroxyalkanoic acid) plasticized with poly(trimethylene ether) glycol,” U.S. Patent 8,349,955 (January 8, 2013)
3. Hiroshi Shimizu et al., “Resin melting and shearing method, resin molding processing method and resin products,” U.S. Patent 8,349,953 (January 8, 2013)
4. Akihiro Ohashi et al., “Polylactic acid resin article comprising grains of metal-hydroxide particles,” U.S. Patent 8,349,935 (January 8, 2013)
5. Junichi Narita et al., “Moldings comprising a polylactic acid composition,” U.S. Patent 8,337,991 (December 25, 2012)

Thermosets from Renewable Polyesters

Author	Guillaume Cledat et al.
Patent Title	***Unsaturated polyester resins modified by substitution with lactic acid or an acid and alcohol component of the polyester,*** U.S. Patent Application 20130123421 (May 16, 2013)

Relevant Prior Patents by Author or Coauthors

Biodegradable starch-containing composition with improved tear Strength, U.S. Patent 8,415,021 (April 9, 2013)

Methods of making functional biodegradable polymers, U.S. Patent Application 20030232929 (December 18, 2003)

Bio-based amorphous polyester resins for emulsion aggregation toners, U.S. Patent 8,163,459 (April 24, 2012)

Wet strength resins derived from renewable resources, U.S. Patent 8,241,461 (August 14, 2012)

Copolymers with enhanced tear strength, U.S. Patent Application 20110213056 (September 1, 2011)

Unsaturated polyester-urethane prepolymer and its applications, U.S. Patent Application 20090312451 (December 17, 2009)

Product Application

Unsaturated resins are designed to be used in thermosetting compositions. These polyester resins are useful for preparing molded parts, laminates, fibers, and sheet-molding products.

Significance of Current Application

This investigation has developed a single-step method for preparing unsaturated polyester resins that are effective as thermosets and are completely renewable with properties that can be selectively altered. Industrially prepared thermosets use non-renewable materials, and the synthesized product requires extensive energy input. In this study, essentially all chemical precursors were derived from renewable and sustainable resources. Moreover, energy requirements for both the synthesis and processing of these renewable resins required very low energy input. Moreover, reagents needed to prepare the thermoset did not pose toxicity hazards to humans, and temperatures required to process the thermoset did not produce volatile organic emissions. Finally, the experimental design used to prepare thermosets using renewable unsaturated materials and intermediates is sufficiently generic that existing methods using petroleum-derived monomers can be easily replaced with biomonomers described in this study.

Renewable Thermoset Monomers

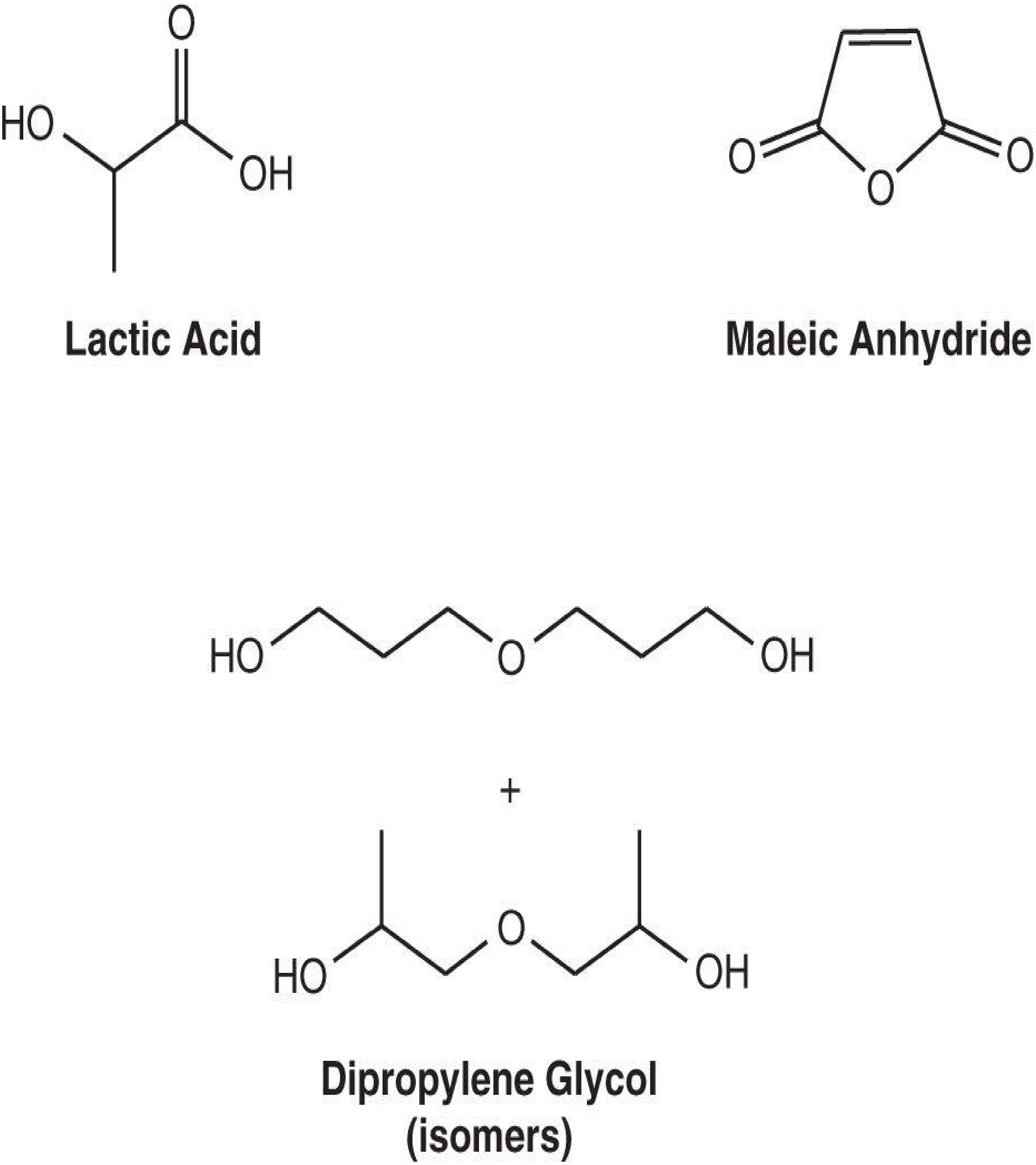


Figure 20.79

Non-Renewable Monomer

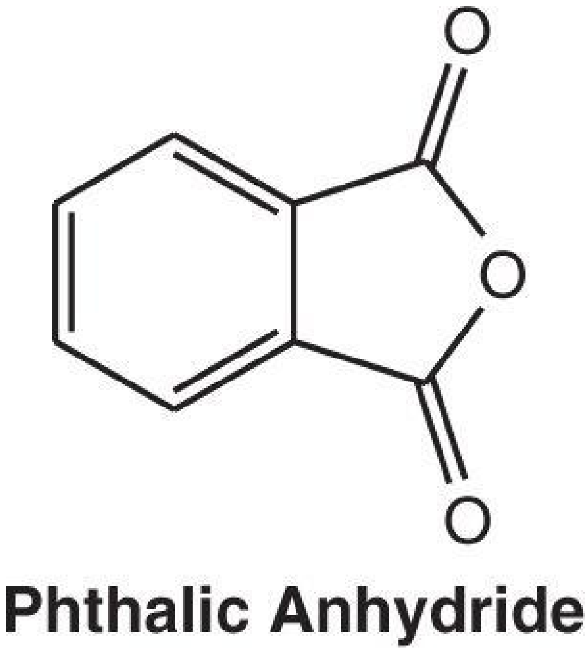


Figure 20.80

Product Formation

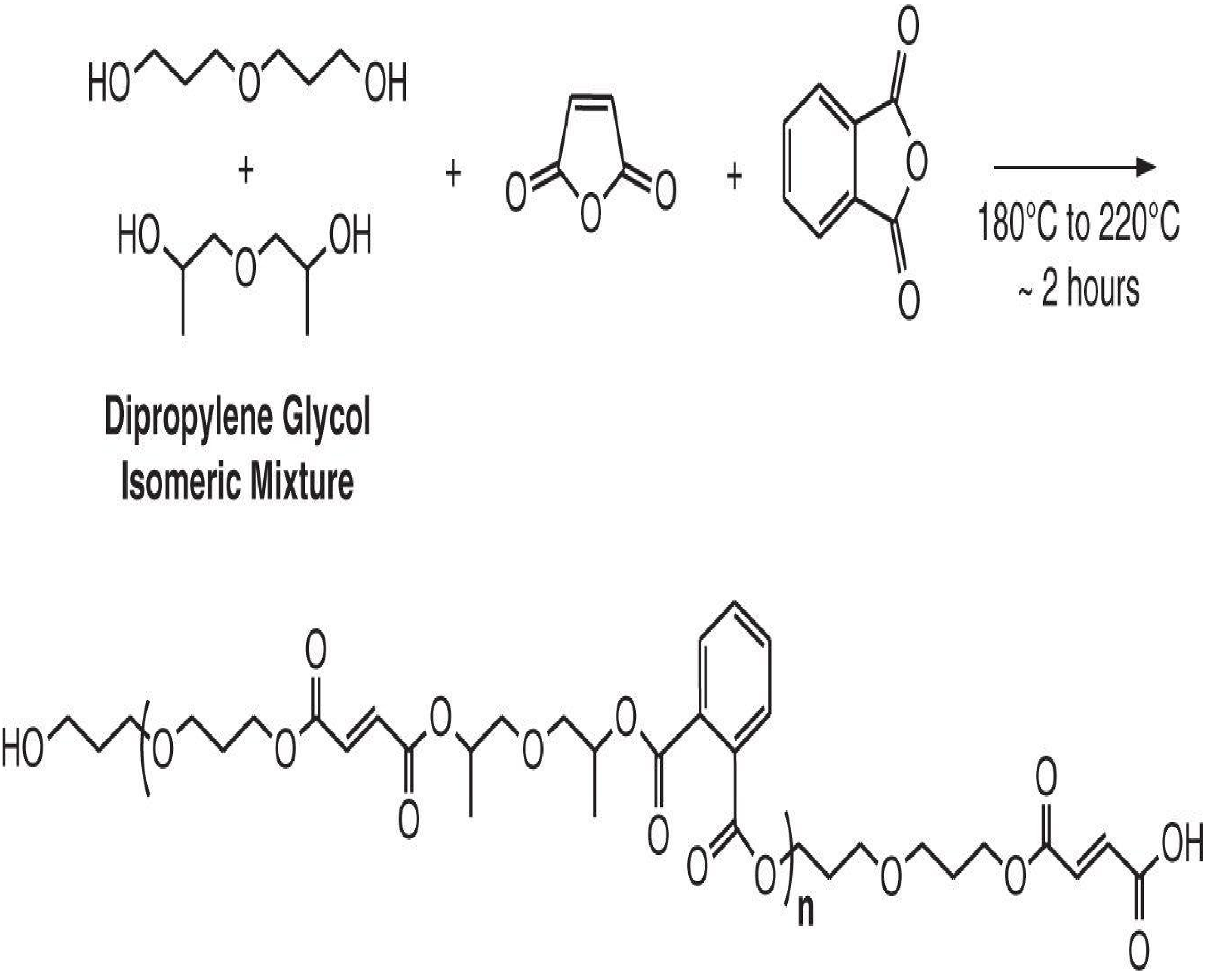
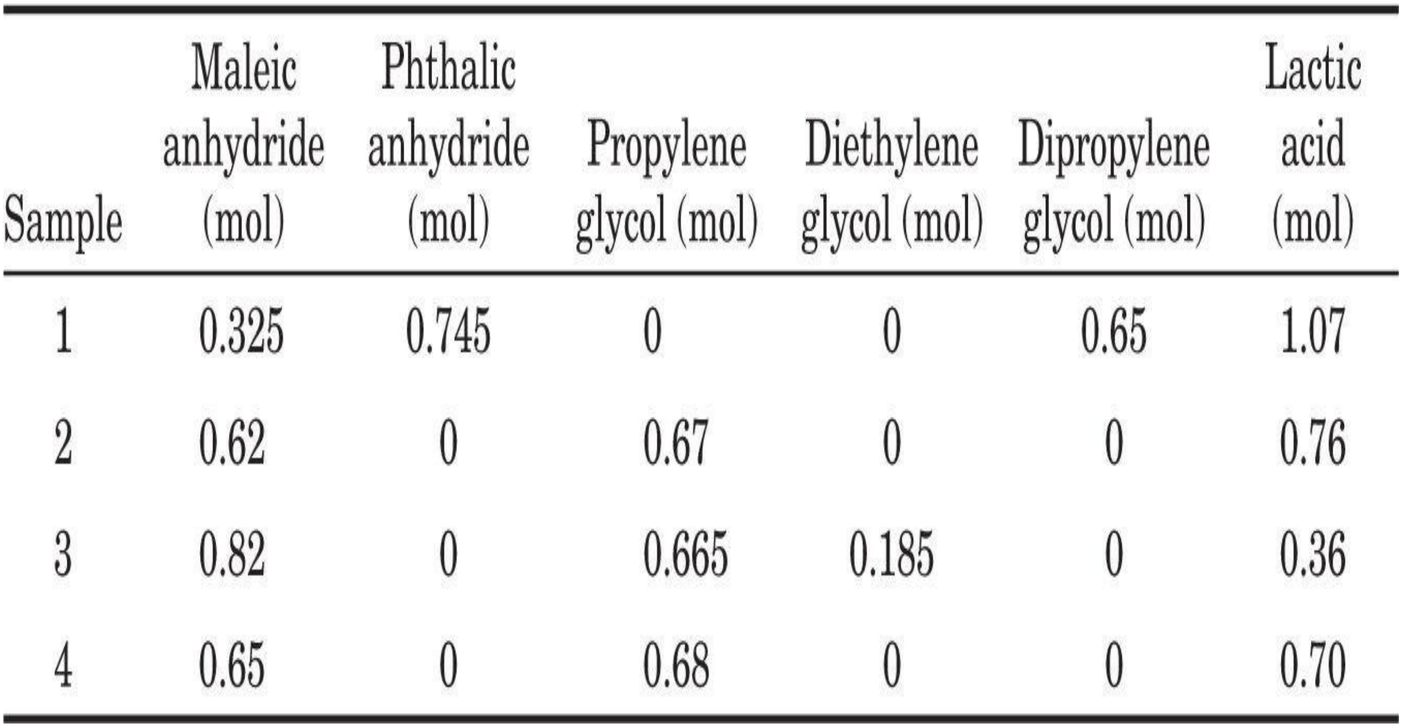


Figure 20.81

Experimental

1. Preparation of renewable thermoset. A polymerization reaction kettle equipped with a mechanical stirrer and a Dean-Stark trap was charged with 0.325 moles of maleic anhydride, 0.745 moles of phthalic anhydride, and 0.65 moles of dipropylene glycol. While stirring, the reaction mixture was heated between 180°C and 220°C under a blanket of nitrogen. Water formed during the condensation reaction was collected in the Dean-Stark trap, and the volume was used to gauge the degree of conversion. Throughout the reaction, aliquots were removed and the viscosity of the resin was monitored according to the Ball Drop Method. When a minimum viscosity of 4.8 dPa sec was reached, the reaction was stopped and the resin collected was used as a pre-crosslinked thermoset component without purification. Other reaction stoichiometries used to prepare other pre-crosslinked unsaturated-polyester thermoset resins are provided in Table 20.13.

TABLE 20.13 Reaction stoichiometries used in preparing other pre-crosslinked renewable unsaturated polyester thermoset resins.



Sample	Maleic anhydride (mol)	Phthalic anhydride (mol)	Propylene glycol (mol)	Diethylene glycol (mol)	Dipropylene glycol (mol)	Lactic acid (mol)
1	0.325	0.745	0	0	0.65	1.07
2	0.62	0	0.67	0	0	0.76
3	0.82	0	0.665	0.185	0	0.36
4	0.65	0	0.68	0	0	0.70

Testing

A. Wetting of fibers. In this test, powdered glass fibers were used. A square of approximately 20 cm^2 was cut out and 20 g of the Step 1 product were placed at the center. The spreading behavior of the resin was then measured after 24 hours. It was determined that the more the resin spread, the less the resin penetrated the glass fiber. Testing results of fiber wetability are provided in Table 20.14.

B. Tensile properties. In this test, Step 1 samples were cut from a molded resin and then crosslinked between two glass plates using 1.5 wt% of the accelerator Akzo® NL49P and 1.2 wt% of the free radical polymerization initiator, Akzo Butanox® M50. Plates were then cured for 16 hours at 80°C and then for an additional 2 hours at 120°C. Samples were then evaluated for tensile stress properties according to standard ISO 527-1:1993. Testing results are provided in Table 20.14.

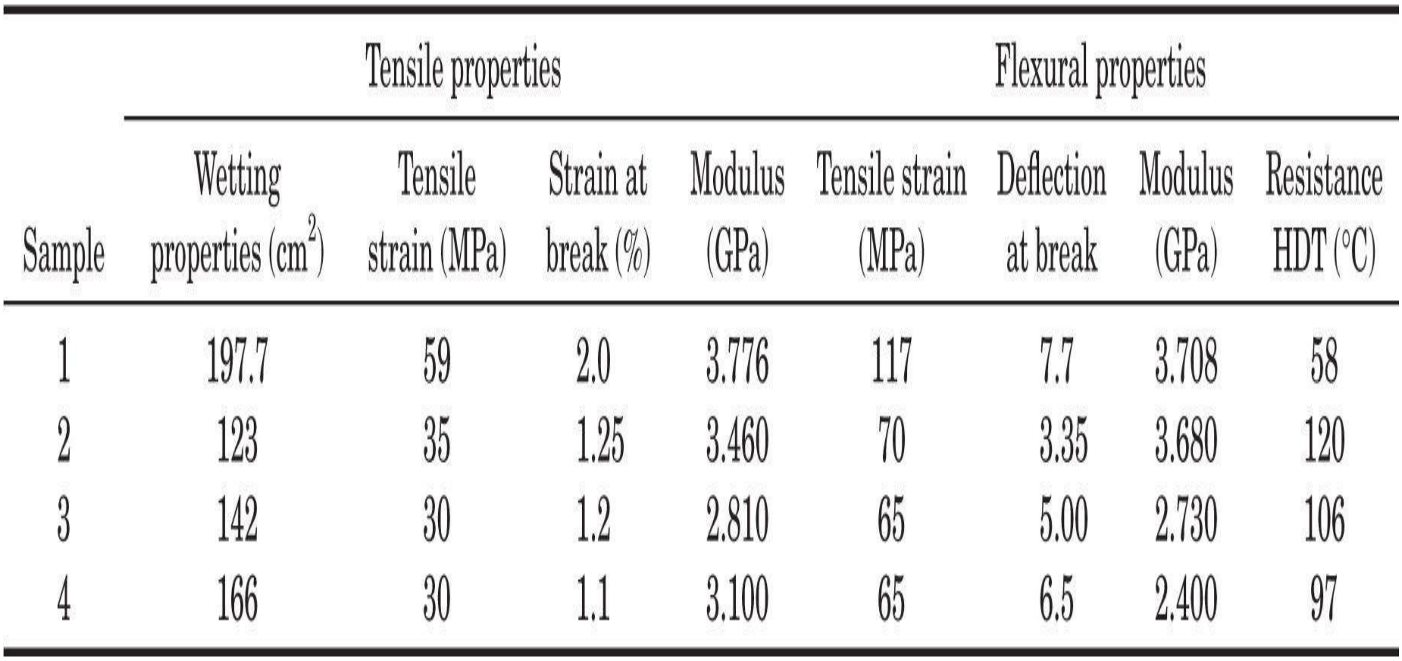
C. Flexural Properties Flexural properties were determined under flexural stress according to standard ISO 178:2003.

D. HDT HDT properties of experimental polyesters were determined according to the ISO 75-2:1999 testing method.

Testing Results

Testing results for experimental samples are provided in Table 20.14.

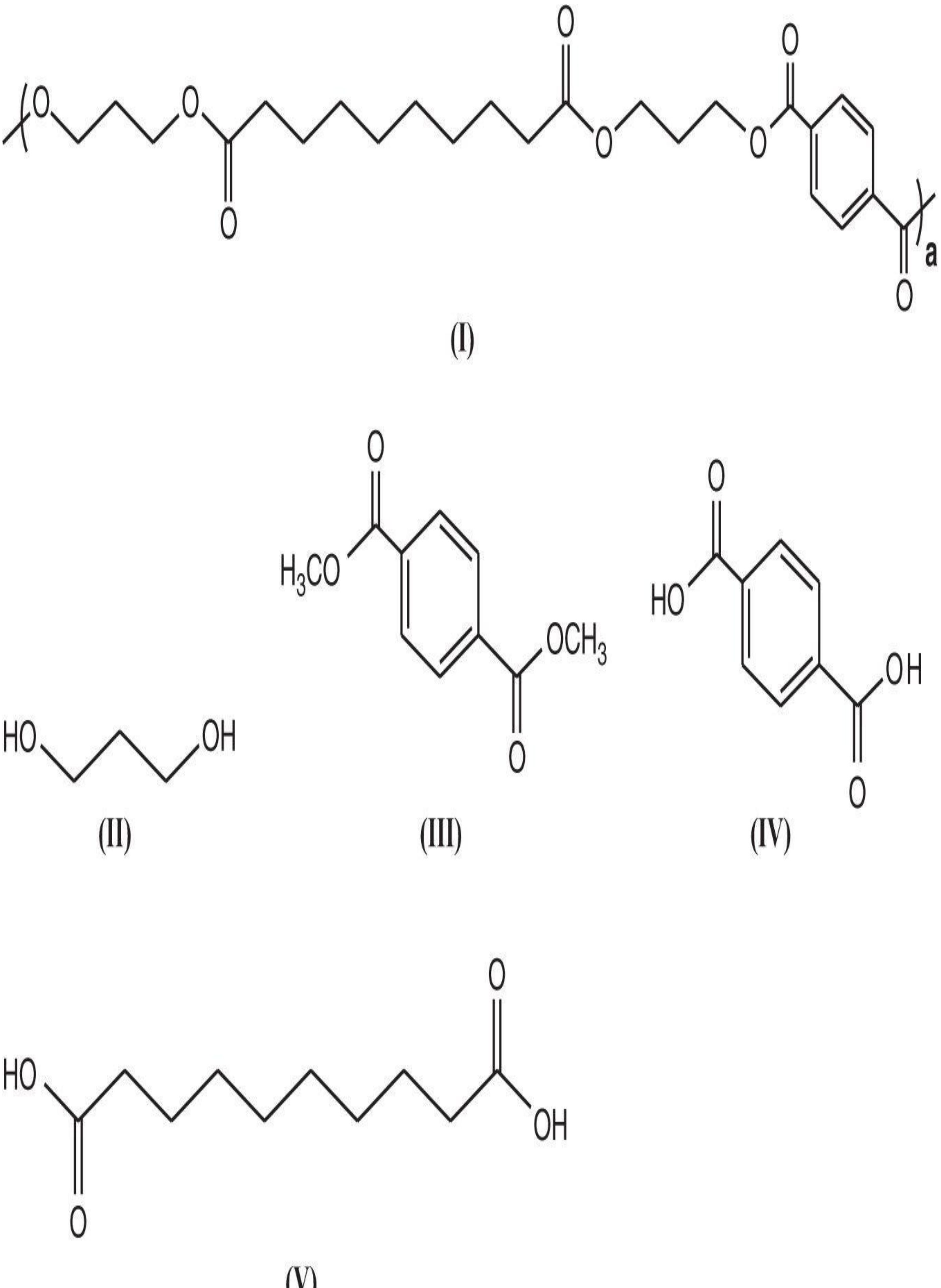
TABLE 20.14 Physical properties of renewable polyester resins.



	Tensile properties				Flexural properties			
Sample	Wetting properties (cm^2)	Tensile strain (MPa)	Strain at break (%)	Modulus (GPa)	Tensile strain (MPa)	Deflection at break	Modulus (GPa)	Resistance HDT (°C)
1	197.7	59	2.0	3.776	117	7.7	3.708	58
2	123	35	1.25	3.460	70	3.35	3.680	120
3	142	30	1.2	2.810	65	5.00	2.730	106
4	166	30	1.1	3.100	65	6.5	2.400	97

Notes and Observations

1. Hasty[1] prepared a series of mixed copolyester resins, (I), by the condensation polymerization of 1,3-propanediol, (II), dimethyl terephthalate, (III), or terephthalic acid, (IV), with sebacic acid, (V). Although these materials are used in engineering plastic applications, it was also determined that the terephthalic acid content in these renewable polyester resins had only a modest impact on tear strength. (See Fig. 20.82.)


(I)

(II)

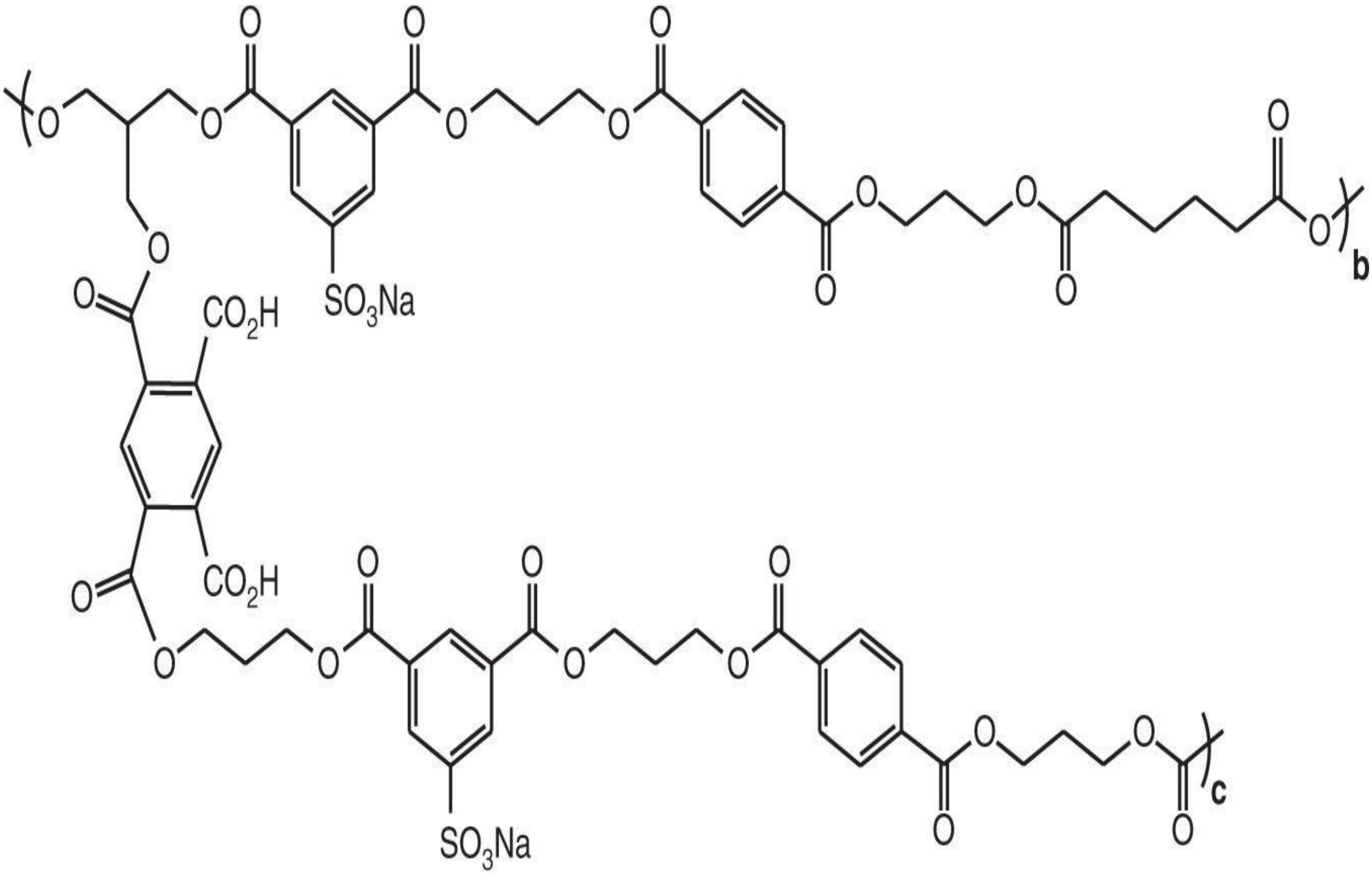
(III)

(IV)

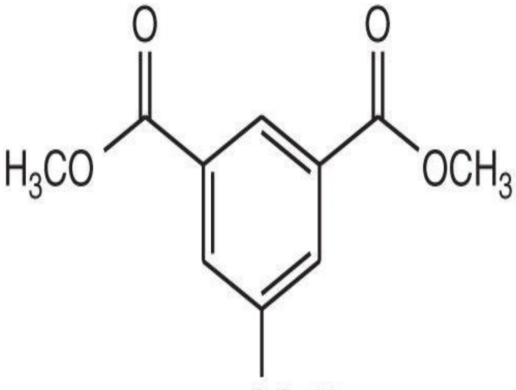
(V)

Figure 20.82

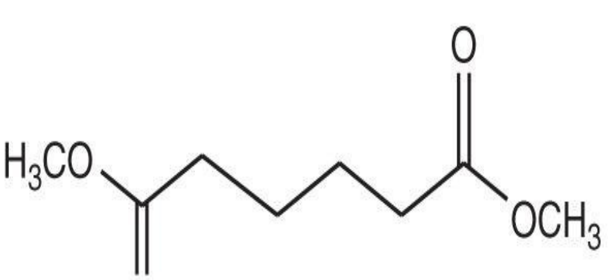
2. Gohil[2] prepared biodegradable aliphatic-aromatic polyester film resins, (VI), by condensing dimethyl terephthalate, 1,3-propanediol, (II), dimethyl-isophthalate-5-sodium sulfonate, (VII), dimethyl adipate, (VIII), and 1,2,4,5-benzenetetracarboxylic dianhydride, (IX). Polyester resins prepared from this process had thermal stabilities far in excess of most biodegradable polyester resins used in preparing films and coatings. (See Fig. 20.83.)



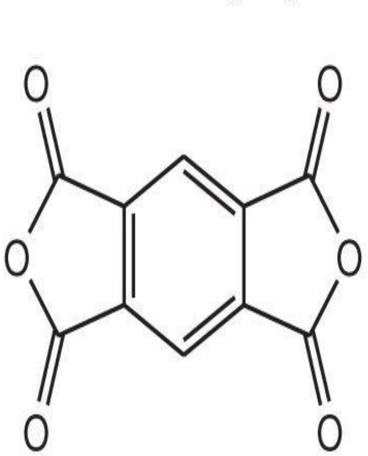
(VI)



(VII)



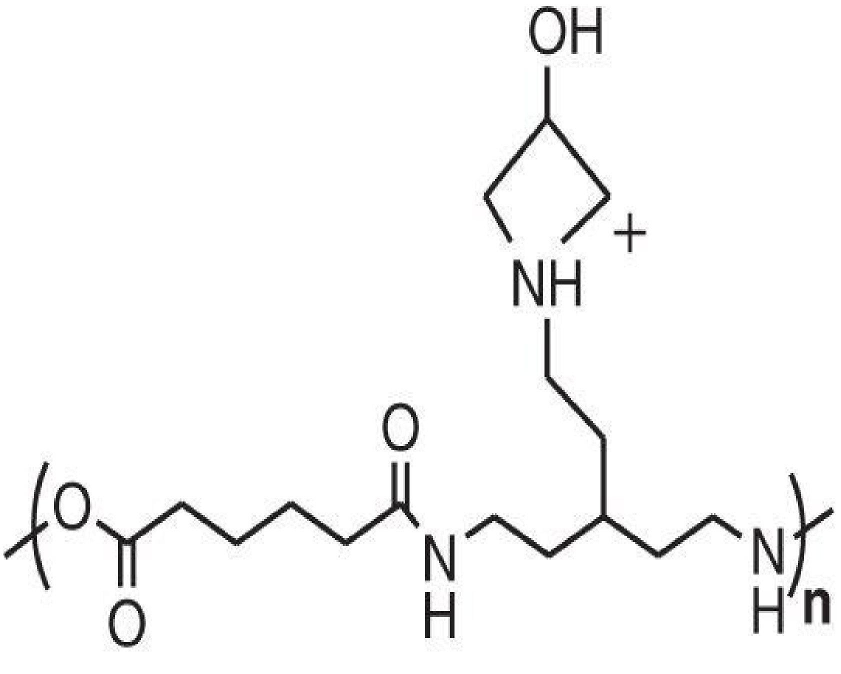
(VIII)



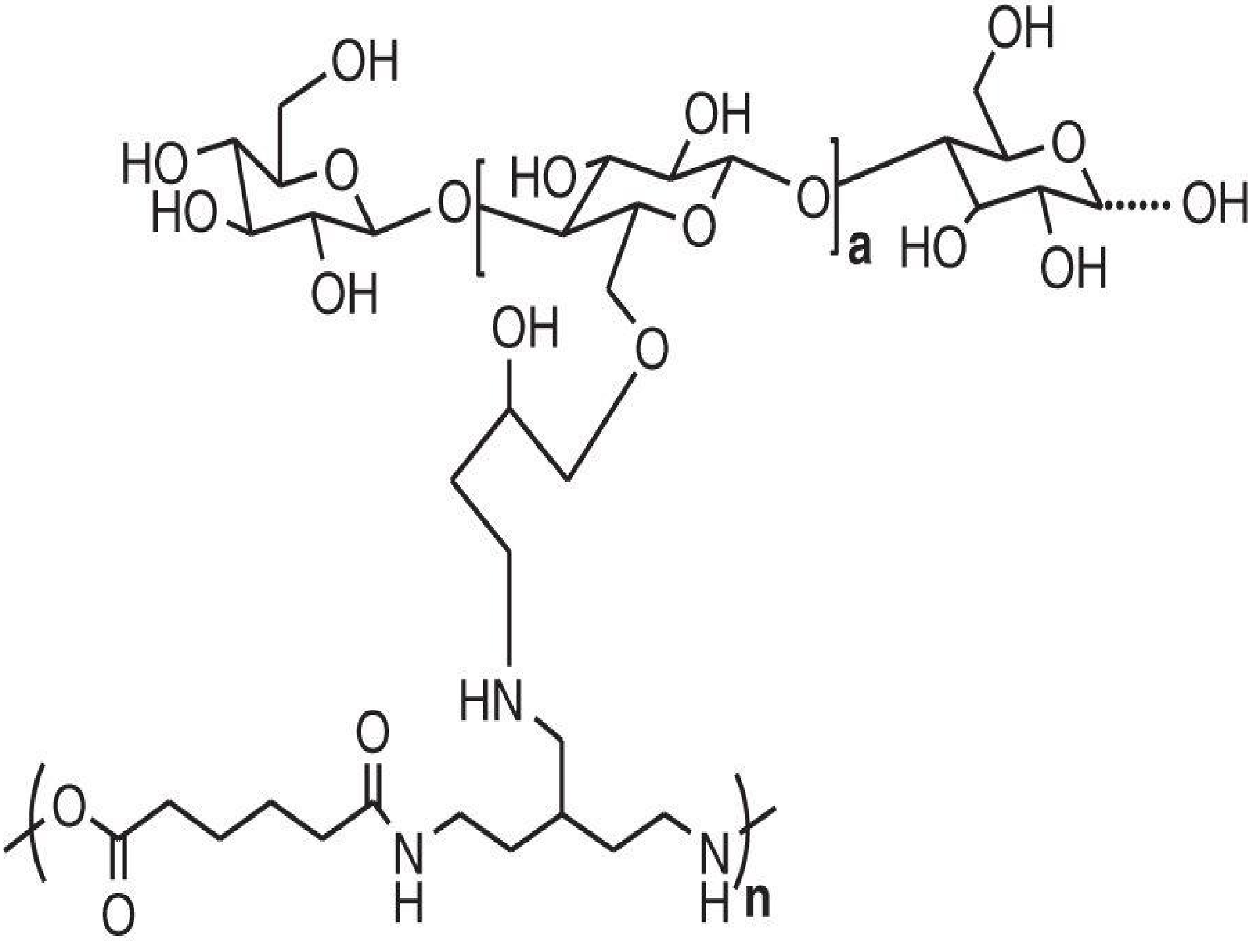
(IX)

Figure 20.83

3. Dyer[3] prepared biodegradable cellulose tissue by initially reacting the bioderived monomers diethylenetriamine, adipic acid, and epichlorohydrin to form a polyamino-amide epichlorohydrin intermediate, (X). The intermediate was then reacted with cellulose to form a high-absorbing and biodegradable tissue, (XI), and was used in treatment of incontinence disorders. (See Fig. 20.84.)



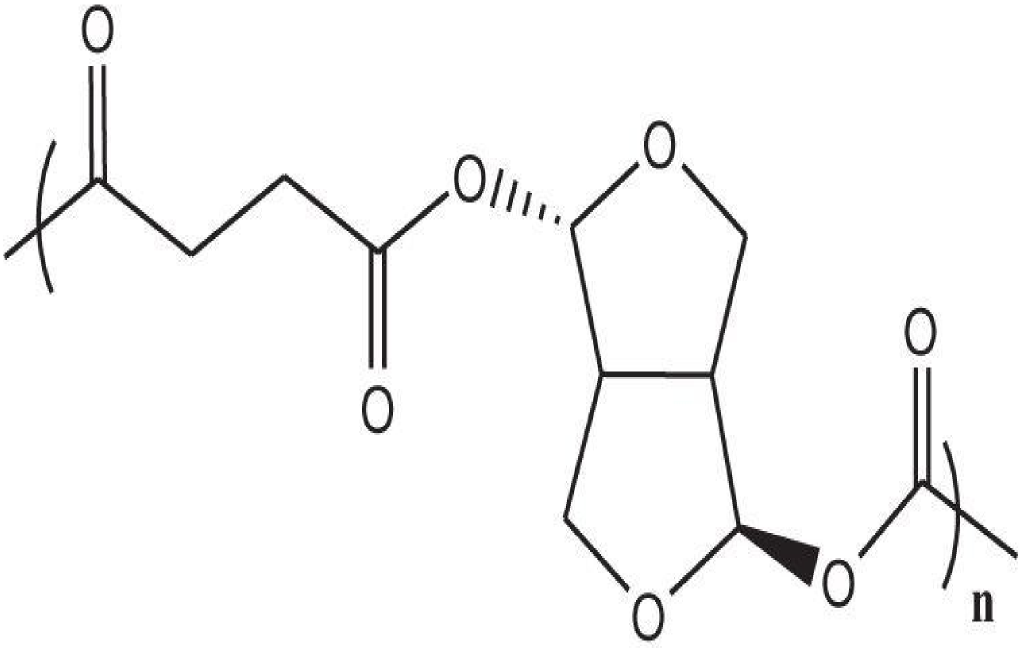
(X)



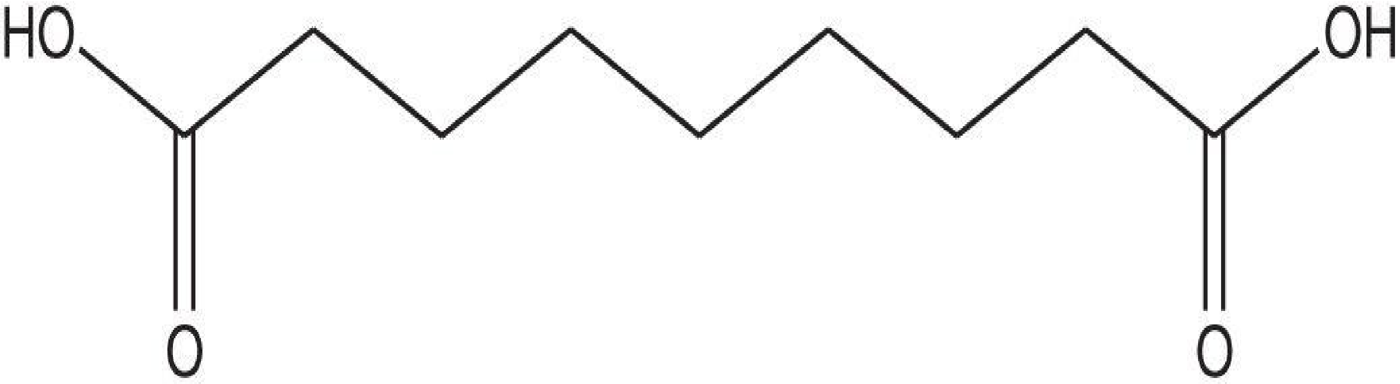
(XI)

Figure 20.84

4. Farrugia[4] prepared a biobased amorphous polyester resin, (XII), by the reaction of isosorbide with either nonanedioic acid, (XIII), or succinic acid, (XIV). Renewable polyester resins prepared from this reaction were used as emulsion aggregation toners in xerographic machines for forming print and images. (See Fig. 20.85.)

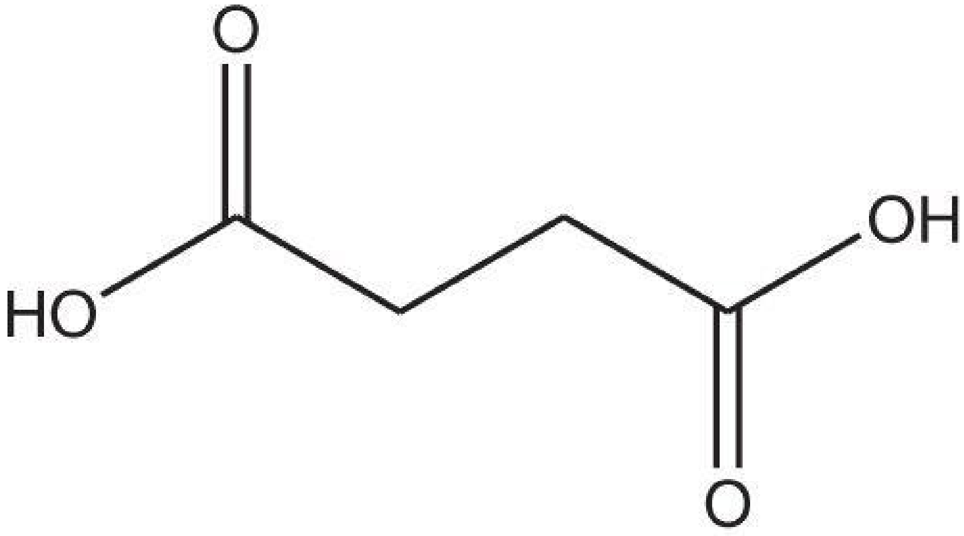


(XII)



(XIII)

Figure 20.85



(XIV)

References

1. Noel M. Hasty et al., *Copolymers with enhanced tear strength*, U.S. Patent Application 20110213056 (September 1, 2011)

2. Rameschandra M. Gohil et al., *Aliphatic-aromatic polyesters, and articles made therefrom*, U.S. Patent Application 20090123767 (May 14, 2009)

3. John Collins Dyer et al., *Wet strength resins derived from renewable resources*, U.S. Patent 8,241,461 (August 14, 2012)

4. Valerie M. Farrugia et al., *Biobased amorphous polyester resins for emulsion aggregation toners*, U.S. Patent 8,163,459 (April 24, 2012)

Thermosets from Epoxidized Soybean and Vulcanized Vegetable Oils

Author Guoqiang Qian et al.

Patent Title ***Biorenewable copolymer thermoplastic elastomers,*** U.S. Patent Application 20130005901 (January 3, 2013)

Relevant Prior Patents by Author or Coauthors

Thermosetting shape memory polymers with ability to perform repeated molecular scale healing, U.S. Patent Application 20120303056 (November 29, 2012)

Thermoplastic elastomers exhibiting superior food contact Compliance, U.S. Patent Application 20120070601 (March 22, 2012)

Biorenewable thermoplastic elastomers, U.S. Patent Application 20110306711 (December 15, 2011)

Thermoplastic elastomers exhibiting superior abrasion resistance properties, U.S. Patent Application 20110082225 (April 7, 2011)

Thermoplastic elastomers exhibiting superior barrier properties, U.S. Patent Application 20120309062 (December 6, 2012)

Product Application

Copolyesters derived from the condensation and esterification of epoxized soybean with vulcanized vegetable oils are used to make plastic articles requiring a Shore A Hardness value of about 40 to about 70.

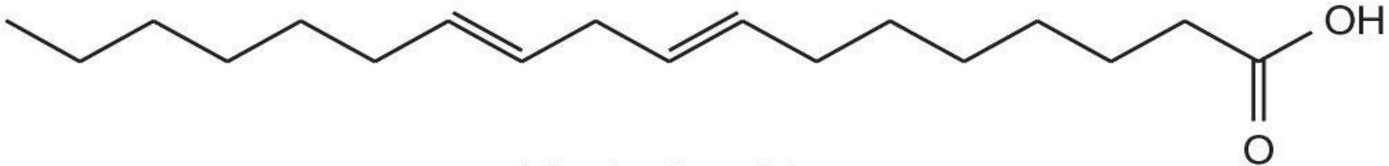
Significance of Current Application

Although there is a pressing need to prepare thermoplastic elastomers using only biorenewable components, it is extremely difficult, however, to identify renewable reagents needed to prepare elastomers having similar physical properties to those of thermoplastic elastomers derived from fossil fuels. The present investigation has developed a relatively simple method that can be used to prepare renewable thermoplastic elastomers comparable to fossil fuel-derived analogues. The method is simple, versatile, and entails modifying new or existing bio-renewable elastomers. This investigation further determined that by altering the reaction stoichiometries of epoxized soybean oil with vulcanized vegetable oils, an entire range of commercially viable renewable thermoplastic elastomers can be effectively generated. Finally, the experimental simplicity of this method suggests that potentially limitless modifications can be utilized to generate other commercially viable renewable thermoplastic elastomers.

Components

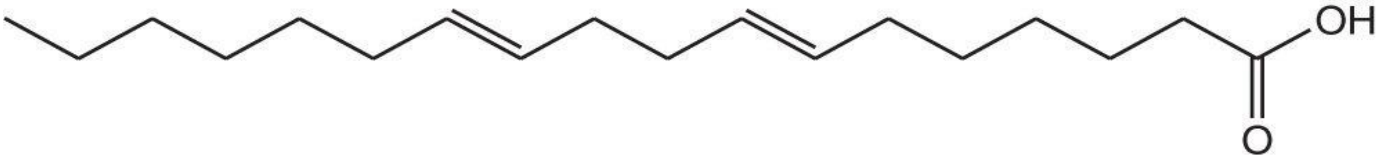
Component 1: Epoxized soybean oil mixture. Soybean oil consists predominately of linolenic acid, (I), linoleic acid, (II), and oleic acid, (III). Epoxidized analogues of each of these unsaturated fatty acids are provided below in (IV) through (VI), respectively, comprising Component 1. (See Fig. 20.86.)

Renewable Three
Fatty Acid
Epoxide Precursors



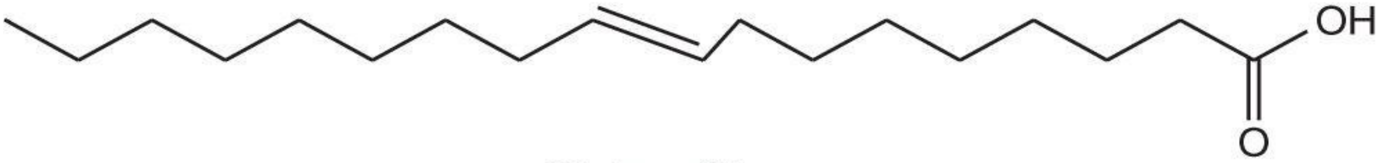
Linolenic acid

(I)



Linoleic acid

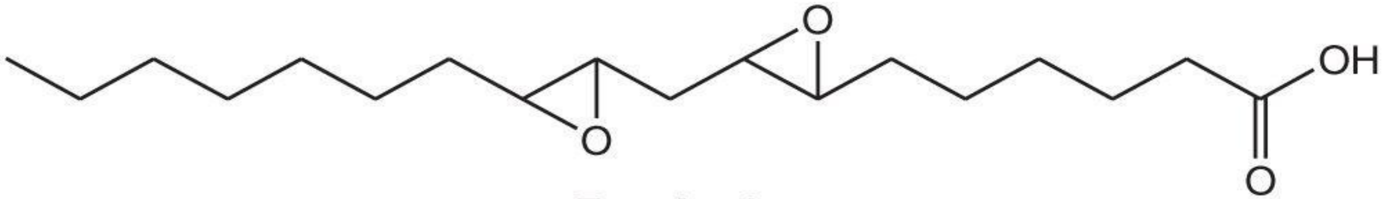
(II)



Oleic acid

(III)

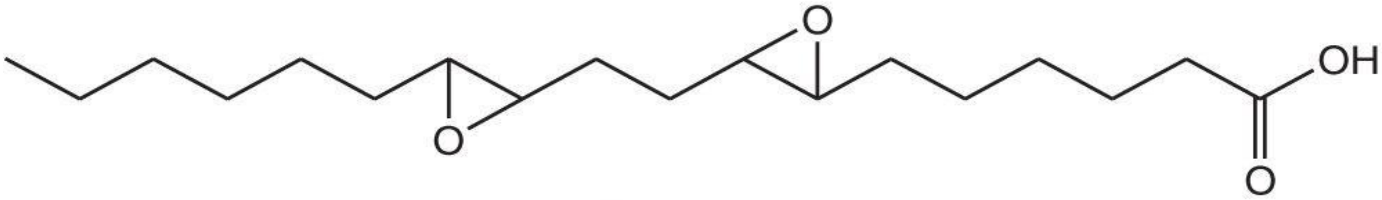
Reagent Co-Component 1



Epoxized
Linolenic acid

(IV)

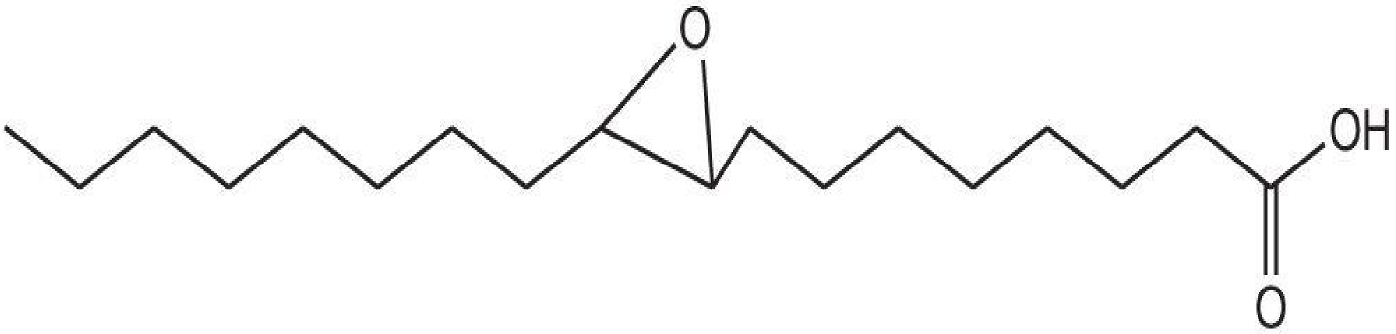
Reagent Co-Component 2



Epoxized
Linoleic acid

(V)

Reagent Co-Component 3



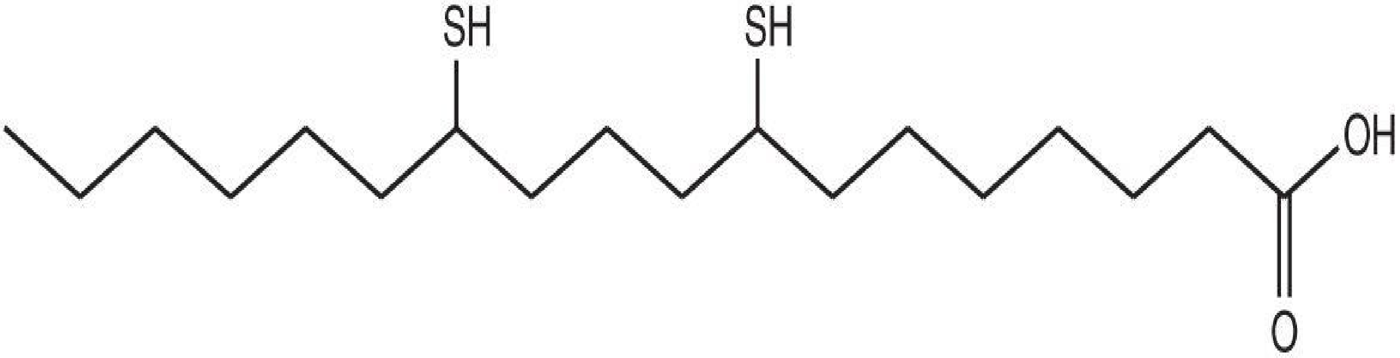
Epoxized
Oleic acid

(VI)

Figure 20.86

Component 2: Vulcanized vegetable oil mixture. Vulcanized analogues of linolenic acid, (I), linoleic acid, (II), and oleic acid (III) were also used as co-reagents. Vulcanated linolenic acid, linoleic acid, and oleic acid are provided below in (VII) through (IX), respectively, comprising Component 2. (See Fig. 20.87.)

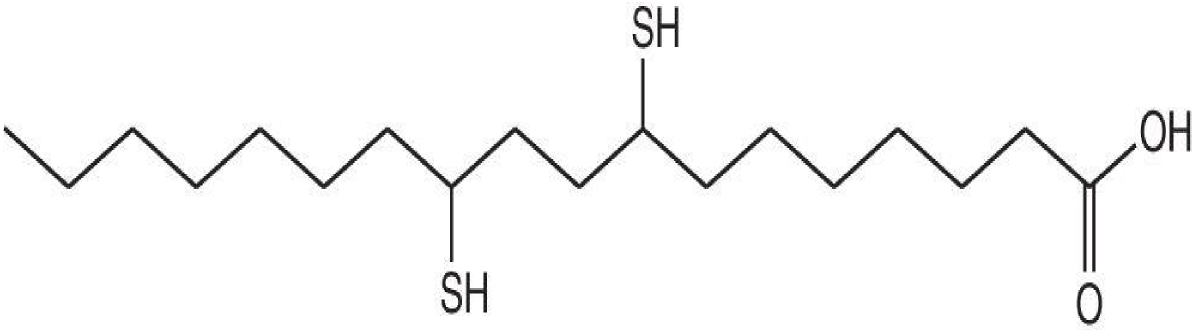
Reagent Co-Component 4



Vulcanized Linolenic acid

(VII)

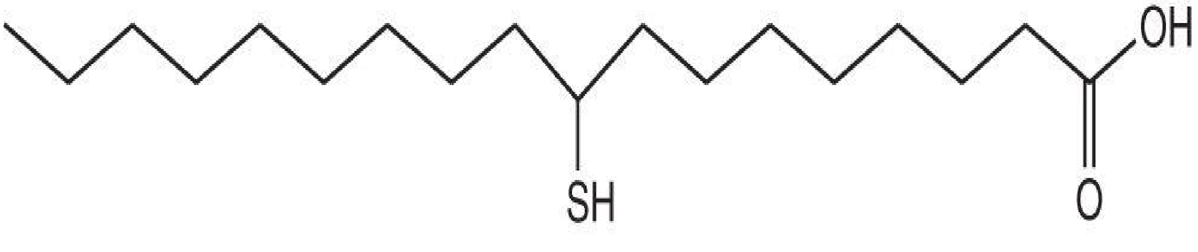
Reagent Co-Component 5



Vulcanized Linoleic acid

(VIII)

Reagent Co-Component 6



Vulcanized Oleic acid

(IX)

Figure 20.87

Product Formation

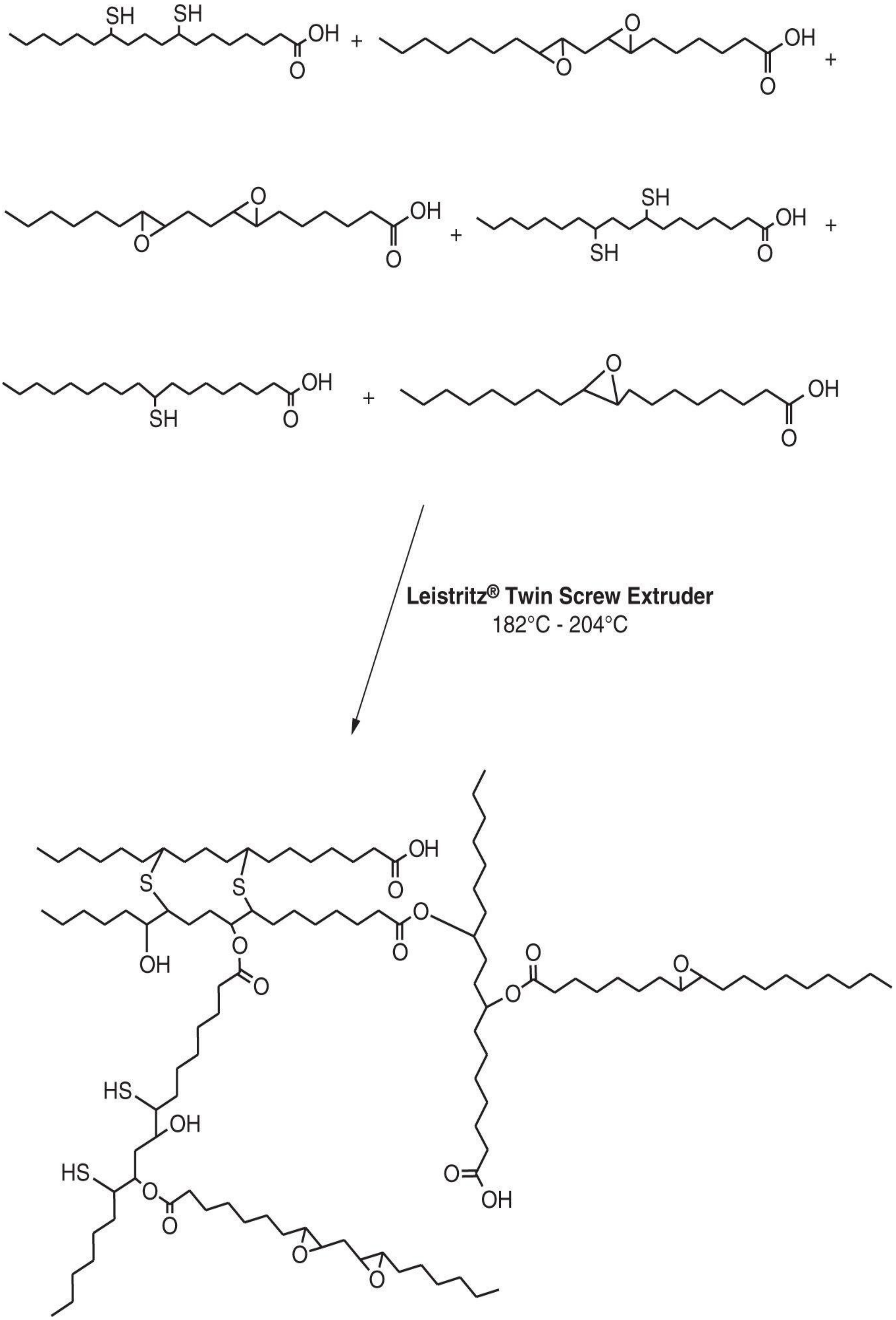
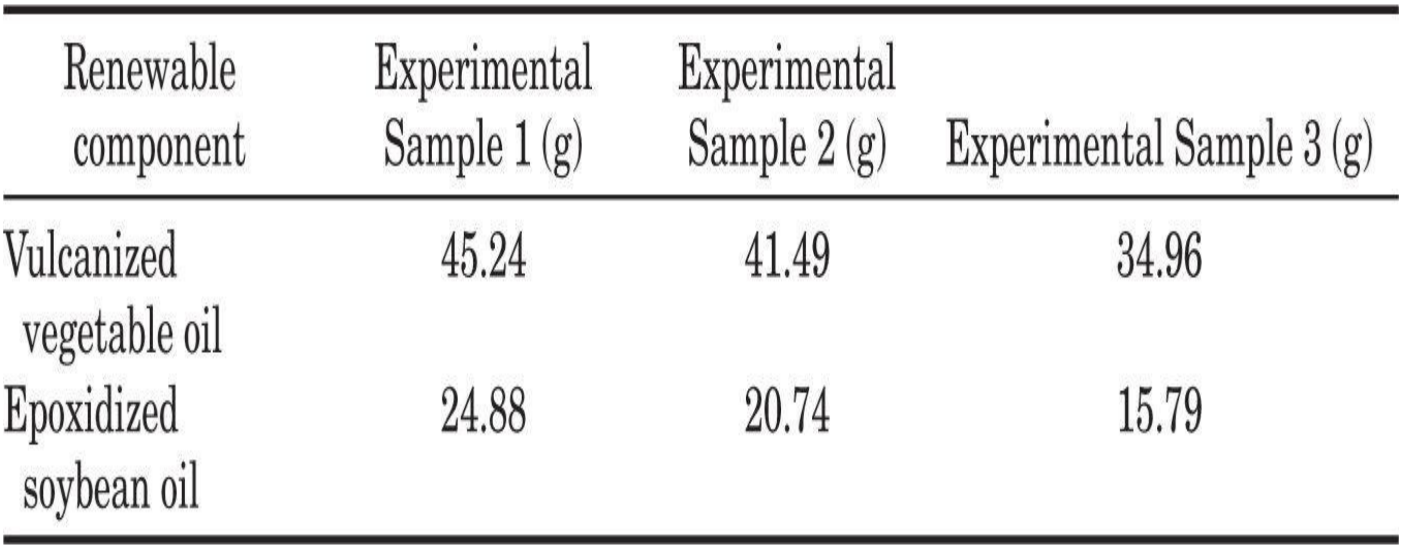

SH
OH
O
+
Leistritz® Twin Screw Extruder
182°C - 204°C
S
HS

Figure 20.88

Experimental

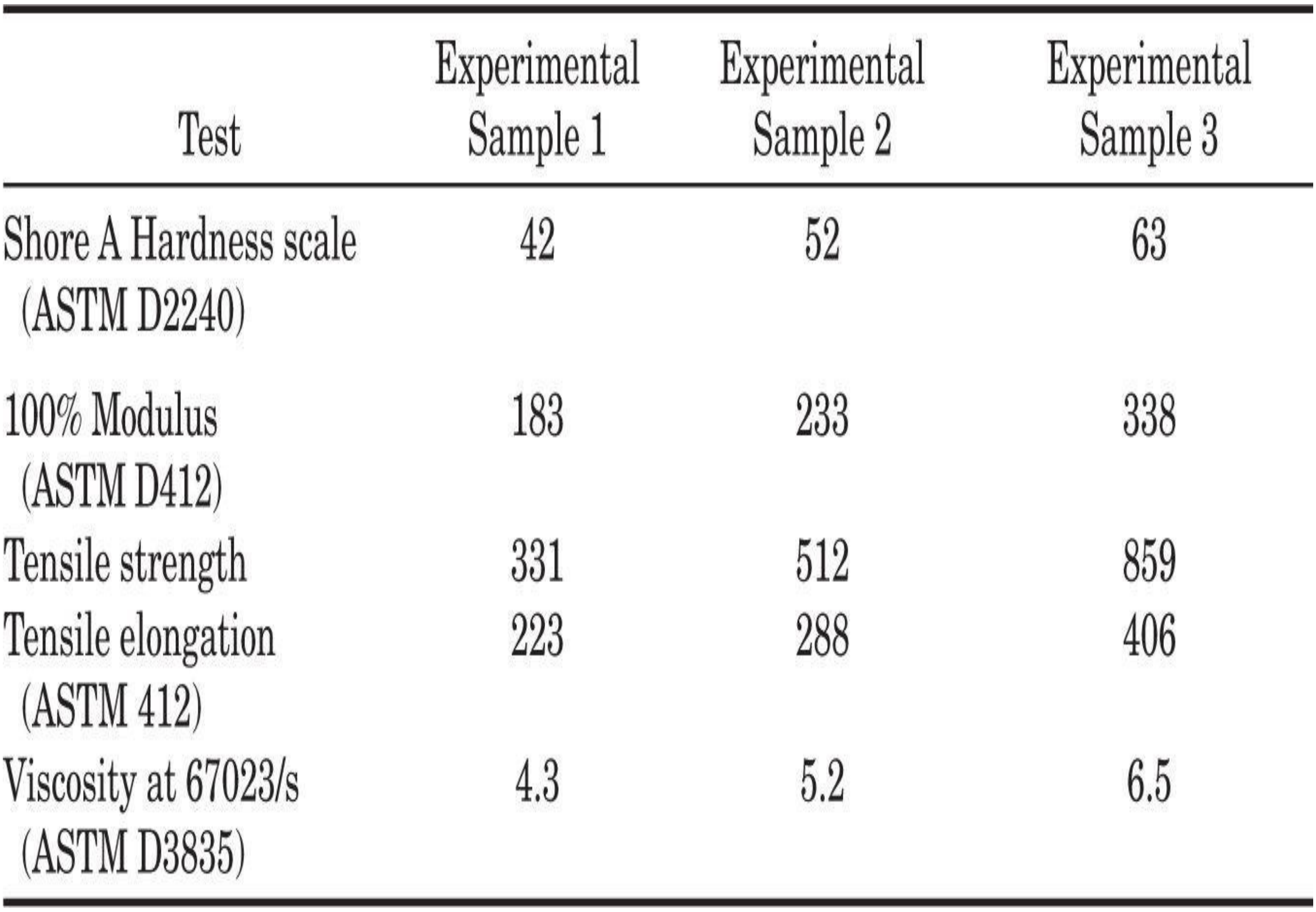
1. Preparation of renewable thermoplastic elastomer. Equivalent amounts of epoxidized soybean oil and vulcanized vegetable oils were added into a Leistritz twin screw extruder having a mixing speed of 500 rpm. The temperature zone profile of the extruder barrels was 182°C in Zone 1, 193°C in Zone 2, 204°C in Zone 3, 204°C in Zone 4, 204°C in Zone 5, 204°C in Zone 6, 204°C in Zone 7, 204°C in Zone 8, and 193°C in the die. After compounding the pellets obtained from the extruder, they were then molded into 5″ × .6″ × 0.125″ plaques for Shore A Hardness and performance testing. Other stoichiometries used in preparing the biorenewable thermoset resins are provided in Table 20.15, while physical testing of these materials is summarized in Table 20.16.

TABLE 20.15 Reagent charges of epoxidized soybean oil and vulcanized vegetable oils used in preparing renewable oligomeric thermosets.



Renewable component	Experimental Sample 1 (g)	Experimental Sample 2 (g)	Experimental Sample 3 (g)
Vulcanized vegetable oil	45.24	41.49	34.96
Epoxidized soybean oil	24.88	20.74	15.79

TABLE 20.16 Selected physical properties of renewable thermoset oligomers. Each renewable thermoset oligomers were using a Leistritz Twin-Screw Extruder having seven temperature zones.

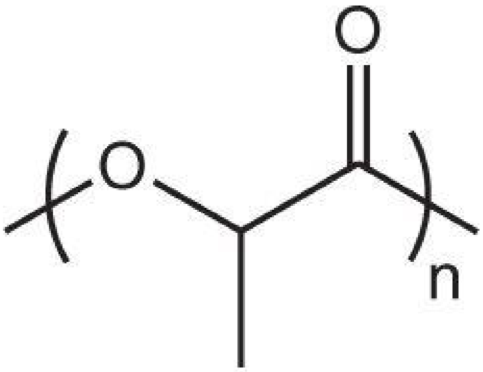


Test	Experimental Sample 1	Experimental Sample 2	Experimental Sample 3
Shore A Hardness scale (ASTM D2240)	42	52	63
100% Modulus (ASTM D412)	183	233	338
Tensile strength	331	512	859
Tensile elongation (ASTM 412)	223	288	406
Viscosity at 67023/s (ASTM D3835)	4.3	5.2	6.5

Testing Results

Notes and Observations

1. Riebel[1] prepared fire-retardant composite sheets consisting of a mixture of ammonium phosphate, agrifiber substrate wheat straw, and biorenewable polylactic acid, (X). In addition, a flexible composite bio-copolymer consisting of polylactic acid and soybean oil, 95:5, respectively, was also prepared and used in biolaminate formulations. (See Fig. 20.89.)

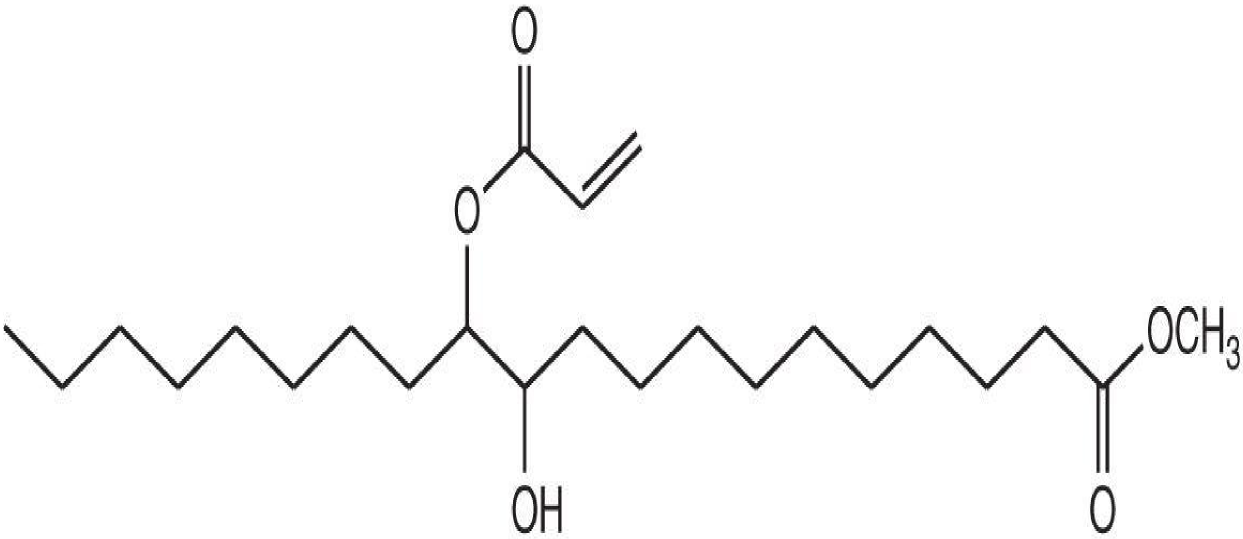


(X)

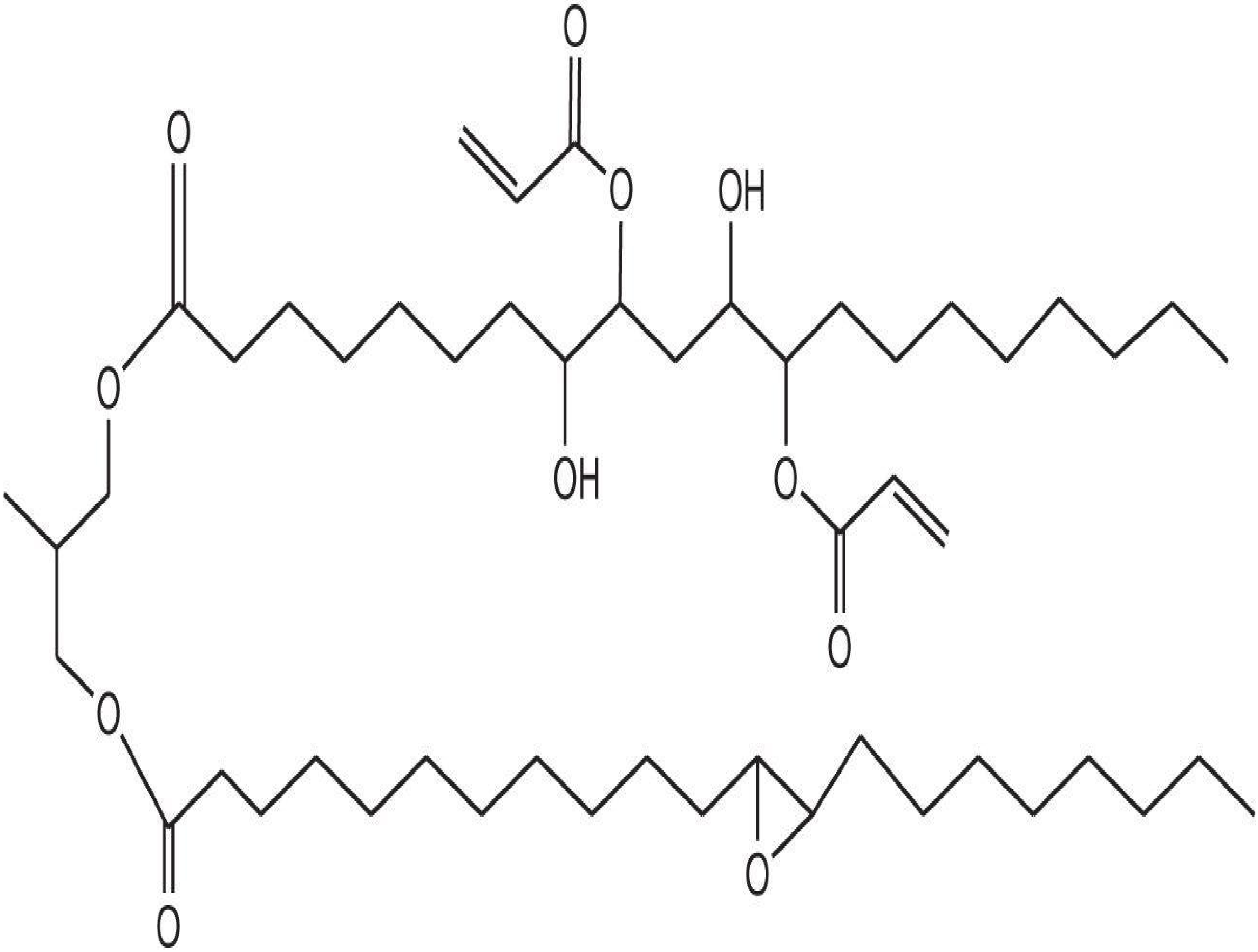
Figure 20.89

2. Chen[2] prepared biorenewable coatings consisting of acrylated soybean oil, (XI) and (XII), that were effective as adhesion promoters when used in acrylated-paint

formulations. All bioadhesion promoters were UV-curable when the photoinitiator Irgacure-2022 consisted of a 1:4 blend of phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide) and 2-hydroxy-2-methyl-1-phenyl-1-propanone. (See Fig. 20.90.)



(XI)

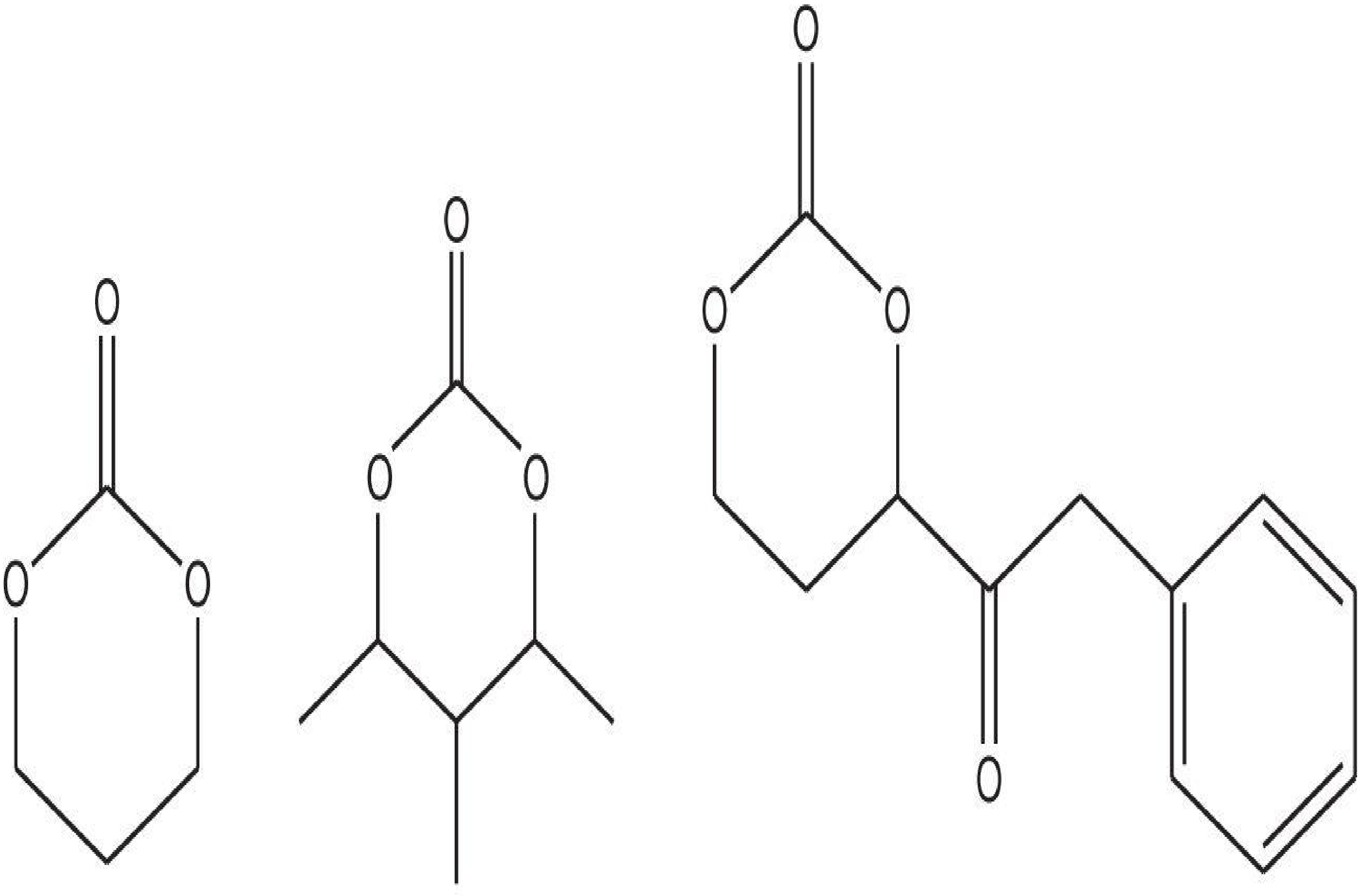


(XII)

Figure 20.90

3. Van Horn[3] used biodegradable and biorenewable resin compositions such as polylactide, poly(lactic-co-glycolic acid), polycaprolactone, starch, polyvinyl alcohol, and ethylene vinyl alcohol that, when treated with a blowing agent mixture consisting of carbon dioxide gas and a selected hydrofluoromethane derivative, formed a low-density foam. These expanded biorenewable foams had excellent dimensional stability, closed-cell structures, and were resistant to chemical breakdown over time.

4. Navarro[4] prepared trimethylene carbonate, (XIII), trimethyltrimethylene carbonate, (XIV), and 2-methyl-2-carboxybenzyl trimethylene carbonate, (XV), by reacting bio-resourced or biogenerated 1,3-propanediol with carbon dioxide. These materials were subsequently converted into bio-polycarbonates at 30°C using methanesulfonic acid as the reaction catalyst. (See Fig. 20.91.)



(XIII) (XIV) (XV)

Figure 20.91

References

1. Michael Riebel et al., *Fire retardant biolaminate composite and related assembly*, U.S. Patent Application 20120291377 (November 22, 2012)

2. Zhigang Chen, *Plant oil-based UV-curable coating*, U.S. Patent Application 20120202909 (August 9, 2012)

3. Brett L. Van Horn, *Biodegradable foams with improved dimensional stability*, U.S. Patent Application 20120225961 (September 6, 2012)

4. Christophe Navarro et al., *Organic systems for the ring-opening polymerization of cyclic carbonates in order to obtain (bio)-polycarbonates*, U.S. Patent Application 20120108786 (May 3, 2012)

Waterproofing Using Phase-Separated Polycitrate Coesters

Author Kevin A. O'Lenick et al.

Patent Title ***Naturally derived citrate polyesters having liquid and solid domains,*** U.S. Patent 8,192,726 (June 5, 2012)

Relevant Prior Patents by Author or Coauthors

Guerbet citrate polyesters, U.S. Patent 8,367,861 (February 5, 2013)

Alkoxylated guerbet citrate polyesters, U.S. Patent 8,277,787 (October 2, 2011)

Citrate silicone polyesters, U.S. Patent 8,273,841 (September 25, 2012)

Sorbitol polyesters having liquid and solid domains, U.S. Patent 8,192,727 (June 5, 2012)

Naturally derived citrate polyesters having liquid and solid domains, U.S. Patent 8,182,796 (May 22, 2012)

Citric acid esters, U.S. Patent 8,168,817 (May 1, 2012)

Guerbet citrate polyesters, U.S. Patent 8,148,569 (April 3, 2012)

Product Application

Polymeric citrate esters prepared in this investigation are primarily targeted as waterproofing agents in cosmetic formulations containing sunscreens, which are effective against UVA and UVB light. In addition, because citrate graft polyesters have a smooth and unique texture and are also used in skin care formulation products. Finally, polymeric citrate esters are also used as wood, plastic, or concrete waterproofing agents.

Significance of Current Application

Sunscreens are designed to protect the user from harmful exposure to UVA and UVB light. However, a serious concern is that sunscreens are not sweat- and waterproof. The current investigation has developed a simple and inexpensive method for waterproofing cosmetic formulations containing sunscreens using renewable chemical agents. In this method, citrate polyesters were initially prepared containing renewable liquid and solid-fatty groups. Once these intermediate biopolyesters were crosslinked, however, the citric-acid ester component contained in the cosmetic formulation remained liquid, while the fatty acid component was converted into a solid at ambient temperature. In either case, the modified crosslinked citric-acid ester remained affixed to the user's skin. In addition, once the citrate polyester was blended in cosmetic formulations containing a sunscreen, the product mixture could be efficiently applied to the user's skin to provide waterproofing protection. Finally, the effectiveness of citrate polyesters as waterproofing agents suggests they can be used in other industrial waterproofing applications for protecting wood, plastics, or concrete surfaces.

Renewable Reagents

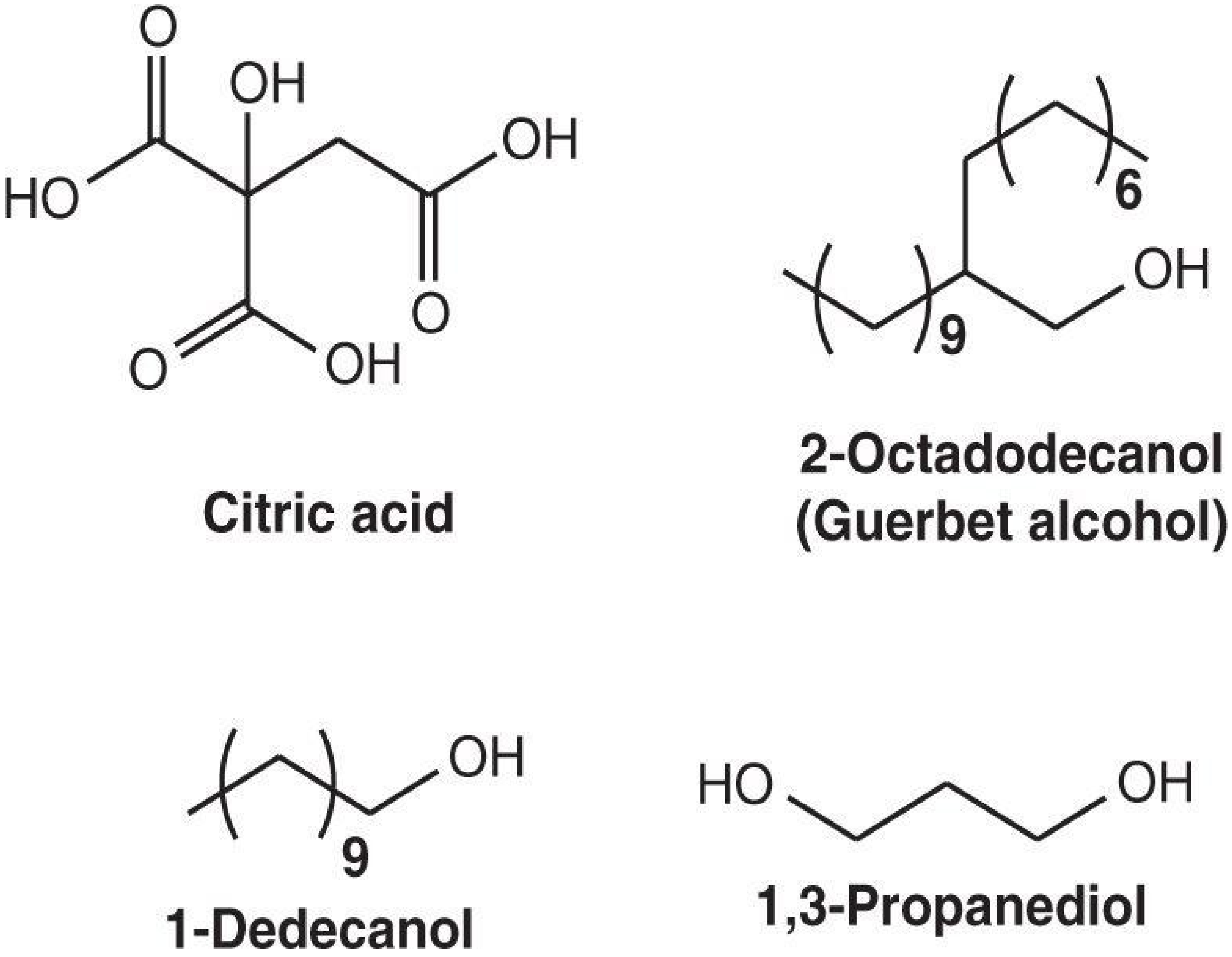


Figure 20.92

Product Formation

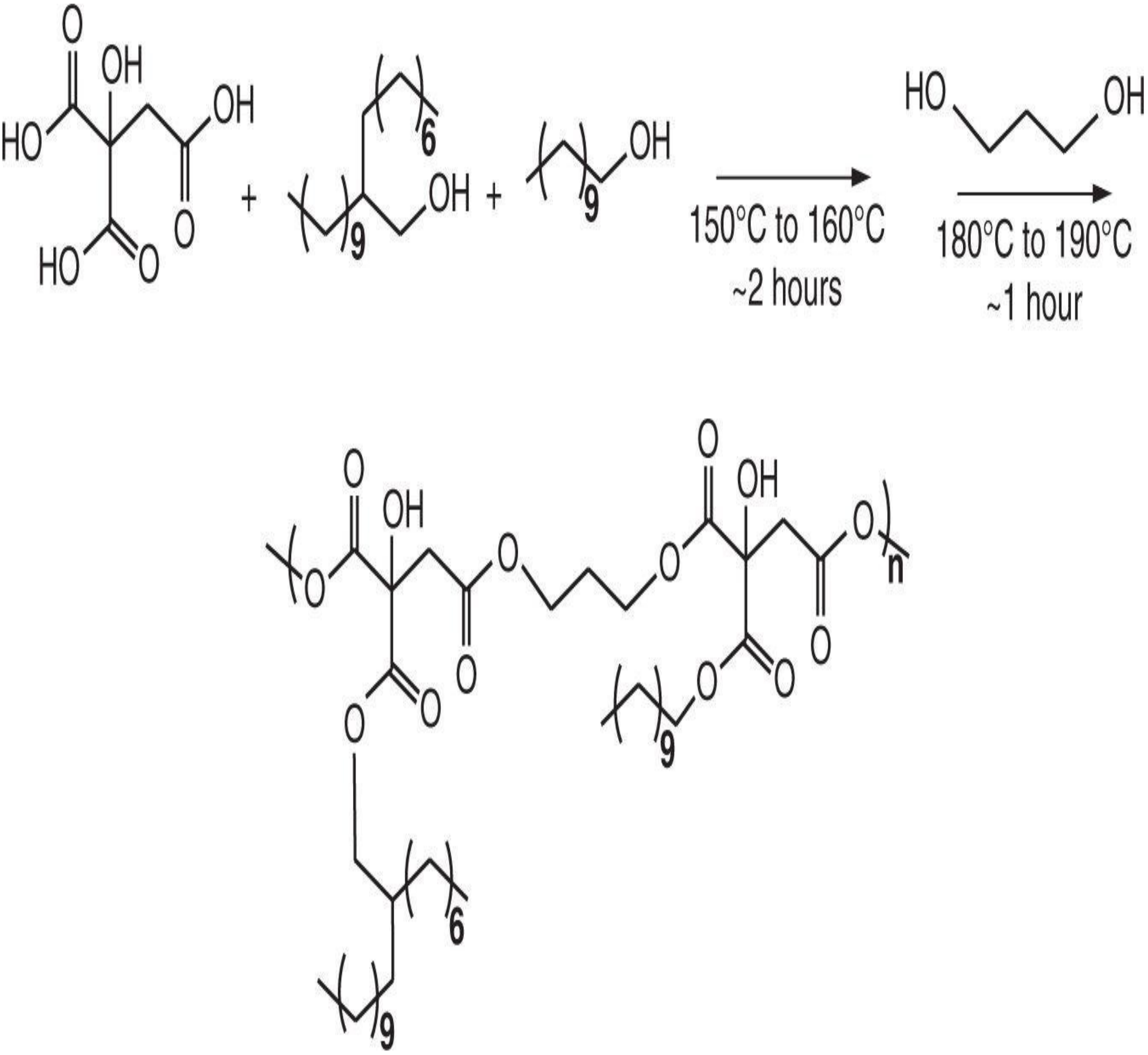


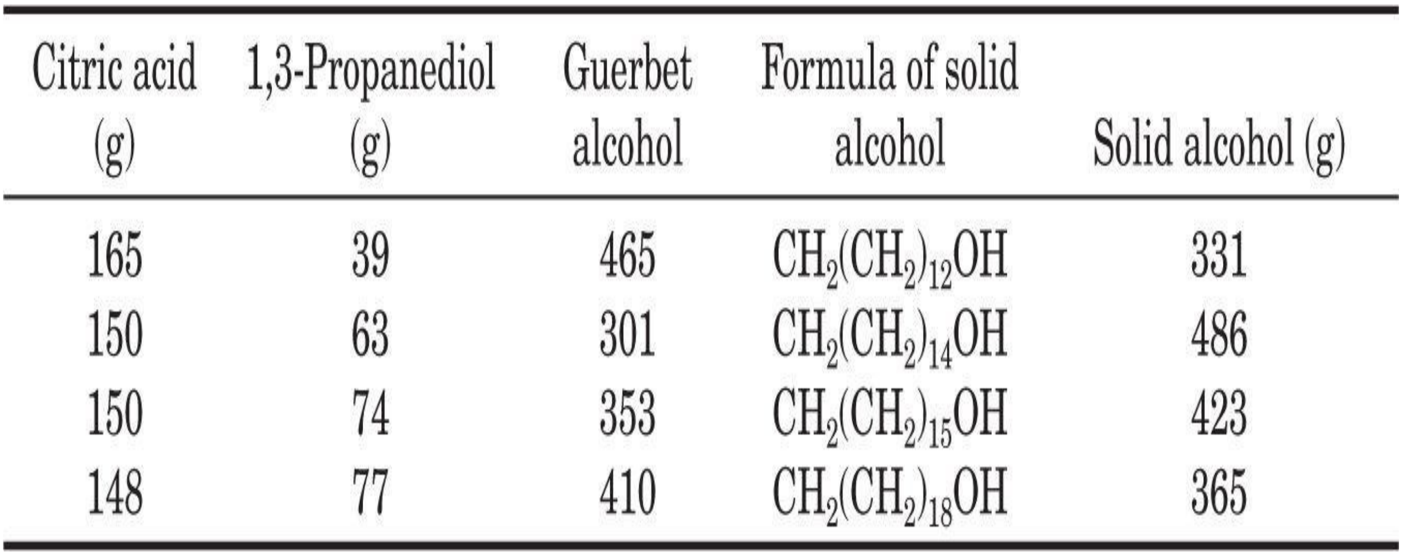
Figure 20.93

Experimental

1. Preparation of renewable waterproofing agent. A glass reactor equipped with a heating mantle and distillation unit designed to remove water generated during the course of the reaction was charged with 138 g of citrate acid, 433 g of the Guerbet alcohol, 2-octyldodecanol, and 402 g of the solid fatty alcohol, 1-dodecanol. The reaction mixture was then heated between 150°C and 160°C and remained in this temperature range until the acid value became low. The reaction mixture was then treated with 28 g of 1,3-propanediol and further heated between 180°C and 190°C while collecting water distilled from the reaction pot. After the reaction vessel was cooled to ambient temperature, a semi-solid was isolated and used without purification in waterproof sunscreen formulations. Other reaction stoichiometries used to prepare analogues of the Step 1 product using the identical reaction conditions are provided in Table 20.17.

TABLE 20.17 Various stoichiometries used to prepare waterproofing analogues that were subsequently used in sunscreen formulations. In all preparations, the Guerbet

alcohol consisted of 2-octyldodecanol.

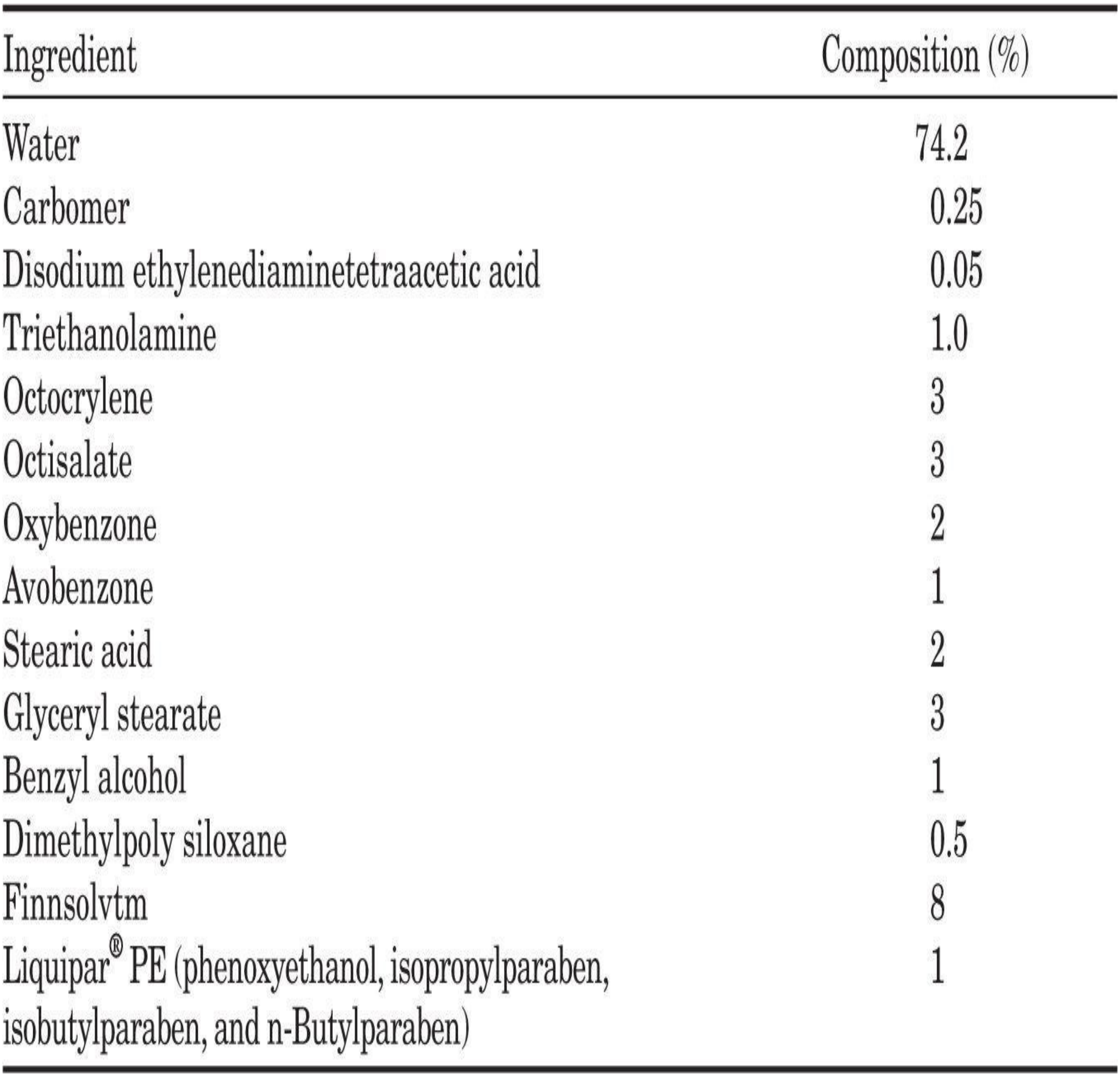


Citric acid (g)	1,3-Propanediol (g)	Guerbet alcohol	Formula of solid alcohol	Solid alcohol (g)
165	39	465	$CH_2(CH_2)_{12}OH$	331
150	63	301	$CH_2(CH_2)_{14}OH$	486
150	74	353	$CH_2(CH_2)_{15}OH$	423
148	77	410	$CH_2(CH_2)_{18}OH$	365

Testing

A. Sunscreen formulations. To evaluate the Step 1 product effectiveness as a waterproofing agent in sunscreen formulation, 8.5 wt% of the experimental material was blended in the cosmetic formulation, as illustrated in Table 20.18.

TABLE 20.18 Sunscreen formulation used to evaluate the effectiveness of the Step 1 Product as a waterproofing agent. Optimum treatment level of the waterproofing agent in formulation blends was 8.5 wt%.

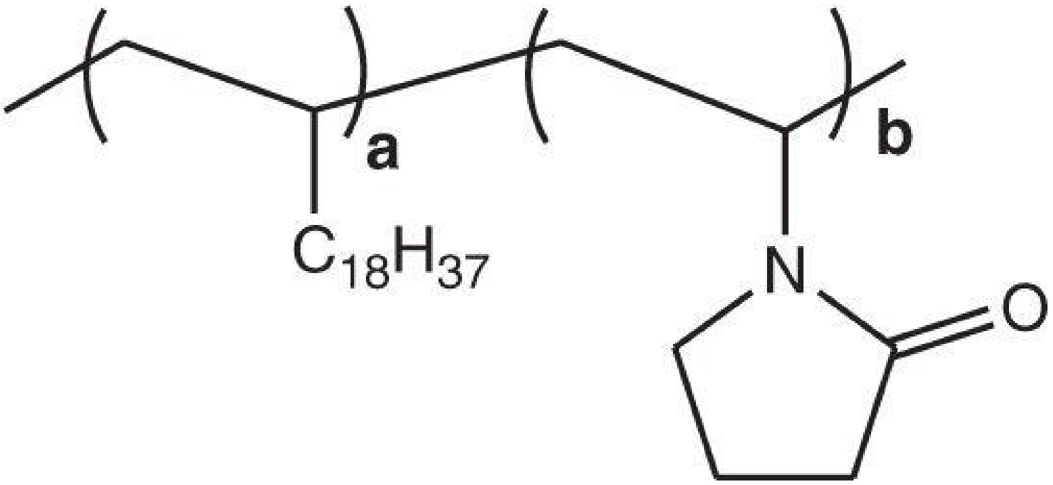


Ingredient	Composition (%)
Water	74.2
Carbomer	0.25
Disodium ethylenediaminetetraacetic acid	0.05
Triethanolamine	1.0
Octocrylene	3
Octisalate	3
Oxybenzone	2
Avobenzone	1
Stearic acid	2
Glyceryl stearate	3
Benzyl alcohol	1
Dimethylpoly siloxane	0.5
Finnsolvtm	8
Liquipar® PE (phenoxyethanol, isopropylparaben, isobutylparaben, and n-Butylparaben)	1

B. Sunscreen effectiveness against UVA and UVB. The effectiveness of the waterproofing agent in sunscreen formulations against UVA and UVB was determined by using a single port Solar Light® Model 15S Xenon Arc (a Solar Simulator lamp having a continuous light spectrum in the UVA and UVB range).

Testing Results

Based on the waterproofing effectiveness of the Step 1 product in sunscreen formulations, a significantly higher UVA and UVB protection for the user was observed when compared to an identical sunscreen formulation not containing this waterproofing barrier. Based on the results of this study, the experimental sunscreen formulation containing 8.5 wt% of the Step 1 product was as effective as the commercially available but non-renewable waterproofing agent, VP/Eicosene Copolymer, (I), illustrated in Fig. 20.94.



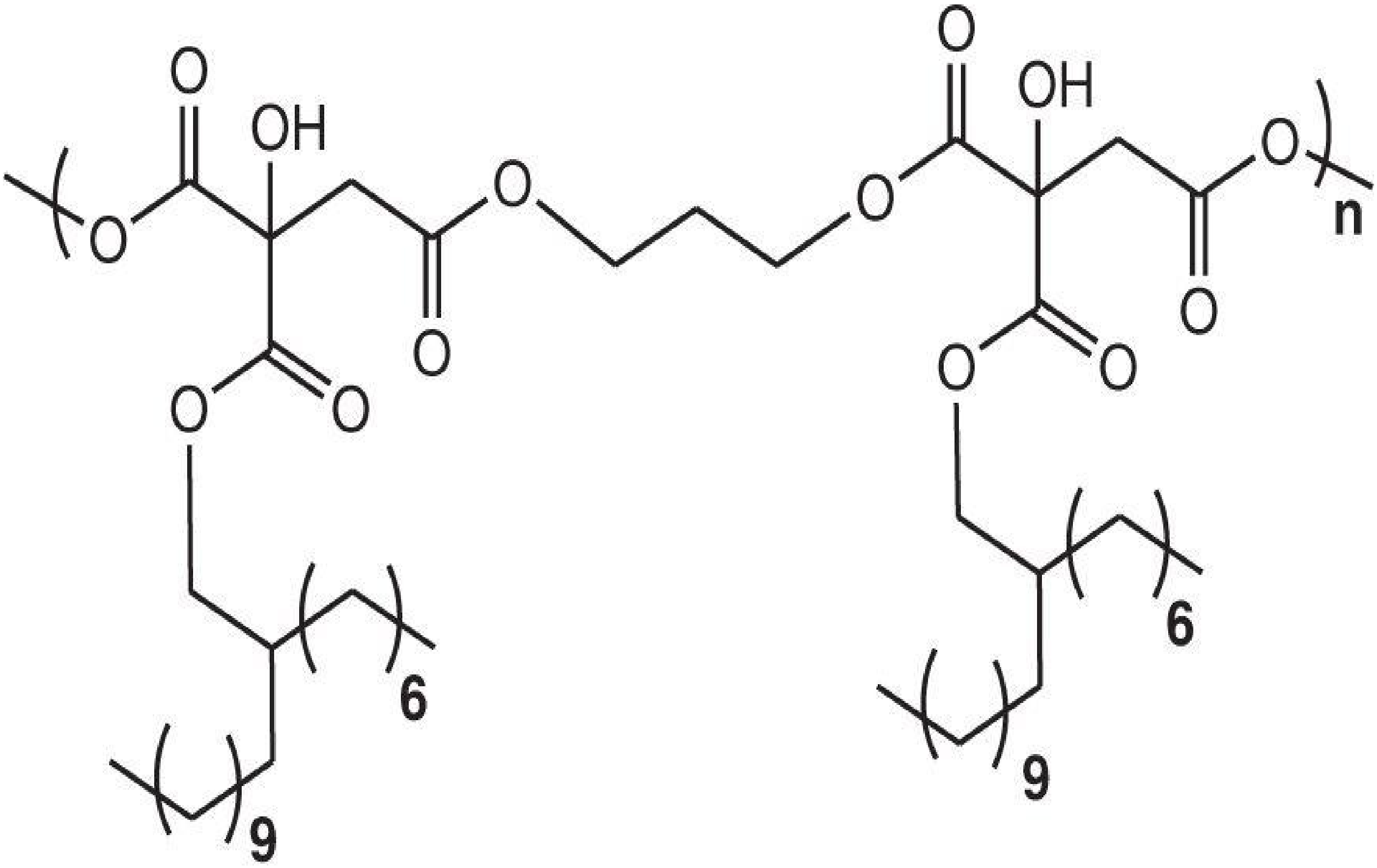
Ganex V-220
Poly(eicosene-co-vinylpyrrolidone)

(I)

Figure 20.94

Notes and Observations

1. In a subsequent investigation by O'Lenick,[1] citric acid polyesters were prepared again using the renewable Guerbet alcohol, 2-octyldodecanol.Depending upon the reaction stoichiometry, Guerbet alcohol citrate polyesters, (II), were low-order liquids that ranged from very dry and easily spread, to medium viscosity, to viscous liquids displaying good cushion and play tome properties. The good cushion and play tome properties of the materials made were ideally suitable for use in personal skin care product formulations. (See Fig. 20.95.)



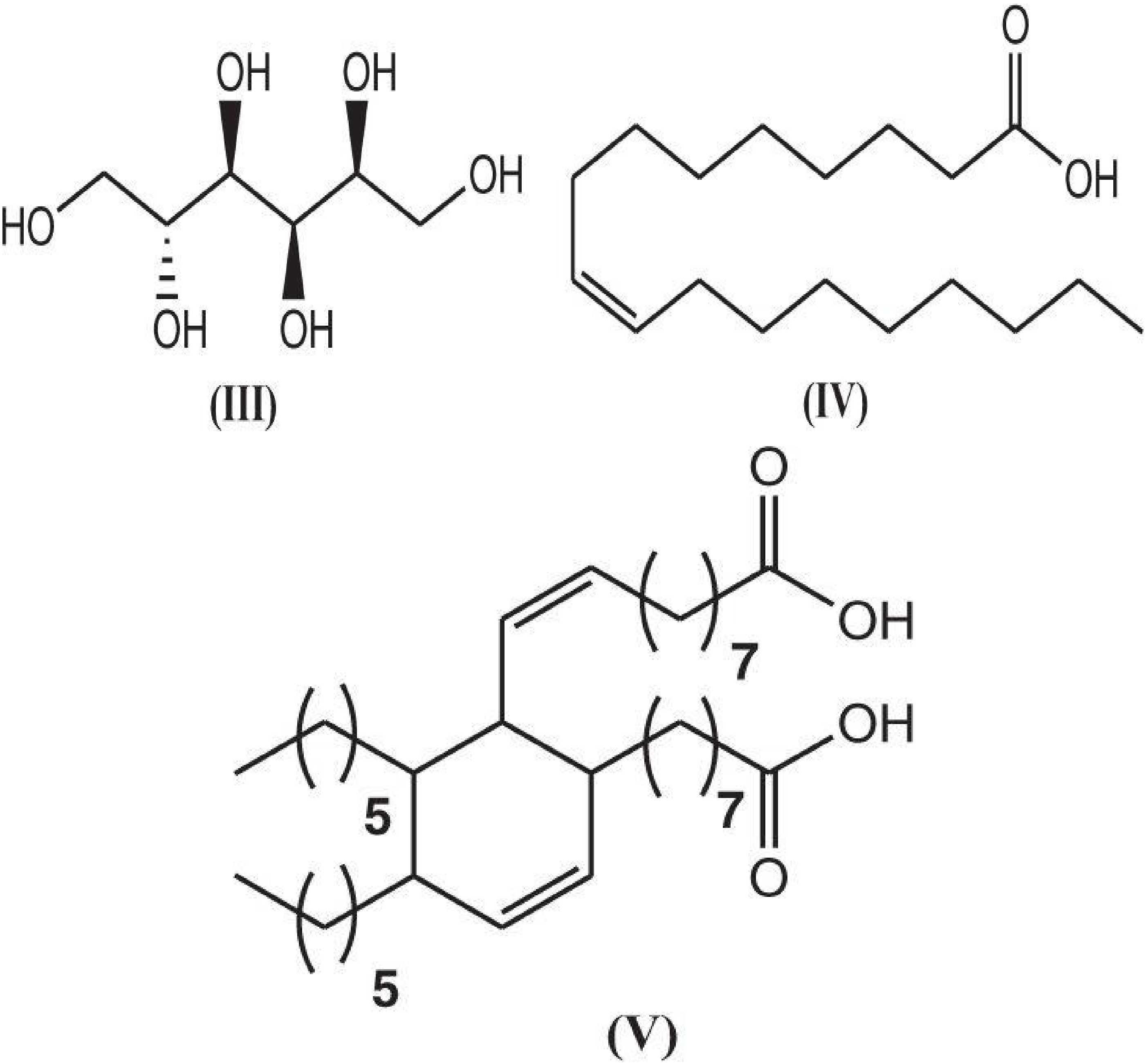
Guerbet alcohol citrate polyester

(II)

Figure 20.95

2. Naturally occurring and renewable citrate polyesters having liquid and solid domains consisting of citric acid, 2-octyldecanol, 1,3-propanediol, and 1-undecanol were previously prepared by O'Lenick.[2] At the end of the reaction, however, the product was purified by removing unreacted or partially esterified citric acid or other low molecular-weight citric acid esters removed under very high vacuum and elevated temperature. The renewable product generated from this process was used exclusively in cosmetic formulations because of its outstanding skin-smoothing characteristics and waterproofing properties.

3. O'Lenick[3] prepared renewable polyesters by reacting sorbitol, (III), with oleic acid, (IV), to generate an ester intermediate that was then crosslinked with an unsaturated aliphatic diacid, (V). The reaction product generated by this process was effective as a waterproofing agent in cosmetic formulations. (See Fig. 20.96.)



(III) (IV) (V)

Figure 20.96

4. O’Lenick[4] prepared renewable esters consisting of C_{30}-C_{50} Guerbet alcohols with oleic acid. When used in cosmetic shampoo formulations, the ester mixture was effective in repairing damaged hair. In addition, these fatty acid esters provided a smooth texture and lubricated the surface of the hair while repairing damage caused by harsh shampoos.

References

1. Kevin A. O’Lenick et al., *Guerbet citrate polyesters*, U.S. Patent 8,367,861 (February 5, 2013)

2. Kevin A. O’Lenick et al., *Naturally derived citrate polyesters having liquid and solid domains*, U.S. Patent 8,182,796 (May 22, 2012)

3. Kevin A. O’Lenick et al., *Sorbitol polyesters having liquid and solid domains*, U.S. Patent 8,192,727 (June 5, 2012)

4. Kevin A. O’Lenick et al., *Citric acid esters*, U.S. Patent 8,168,817 (May 1, 2012)

Chapter

21

Remediation Processes

Elimination of Polyaromatics from Contaminated Soil

Author P. K. Andy Hong

Patent Title ***Degradation of polycyclic aromatic hydrocarbons,*** U.S. Patent 8,298,814 (October 30, 2012)

Relevant Prior Patents by Author

Fragmentation of heavy hydrocarbons using an ozone-containing fragmentation fluid, U.S. Patent 7,909,985 (May 22, 2011)

Pressurizing depressurizing cycles for removal of contaminants in environmental samples, U.S. Patent Application 20090159536 (June 25, 2009)

Fragmentation of heavy hydrocarbons using an ozone-containing fragmentation fluid, U.S. Patent Application 20060163117 (July 27, 2006)

Remediation with ozone of sediments containing organic contaminants, U.S. Patent 7,115,203 (October 3, 2006)

Product Application

Treatment of soil contaminated with mutagenic polyaromatics using both gaseous ozone dissolved in water under high pressure followed by degradation of these intermediates by naturally occurring E. coli was determined to be effective in remediating soil contaminated with toxic aromatics organic agents. Contamination-free soil was then used in either agricultural or recreational applications.

Significance of Current Application

Polycyclic aromatic hydrocarbons are a group of aromatic compounds containing two or more fused benzenoid rings in either a linear, angular, or cluster structure. Although they occur naturally in soils generated by pyrolysis of wood in forests or agricultural fires, industrial processes involving crude oil, coal, and oil shale spills have significantly contributed to the problem. What makes the elimination of polycyclic aromatic hydrocarbons from soils urgent is that they are hydrophobic, recalcitrant, and bioaccumulating. In addition, their tendency to adsorb to or be suspended on particulates and biota further contributes to their presence and accumulation in soil and sediment. These physical properties result in a pervasive soil-contamination problem. The current investigation addresses these concerns using a two-step soil remediation process. Initially, ozone dissolved in water and under high pressure is injected into the soil to oxidize pyrenes to mix non-toxic intermediates. Once mixed, non-toxic pyrans contained in the soil are exposed to naturally occurring E. coli. Over time, these non-toxic intermediates become chemically degraded into mixed oxidation products and then ultimately into carbon dioxide. This soil remediation method is simple, relatively inexpensive, versatile, and extremely effective in eliminating pyrenes and related polyaromatics.

Remediation Process

A. Ozonolysis of benzo[a]pyrene into non-aromatics. The oxidation method to eliminate polyaromatics from contaminated soil consists of Four Phases provided in Figs. 21.1 to 21.4.

Phase 1

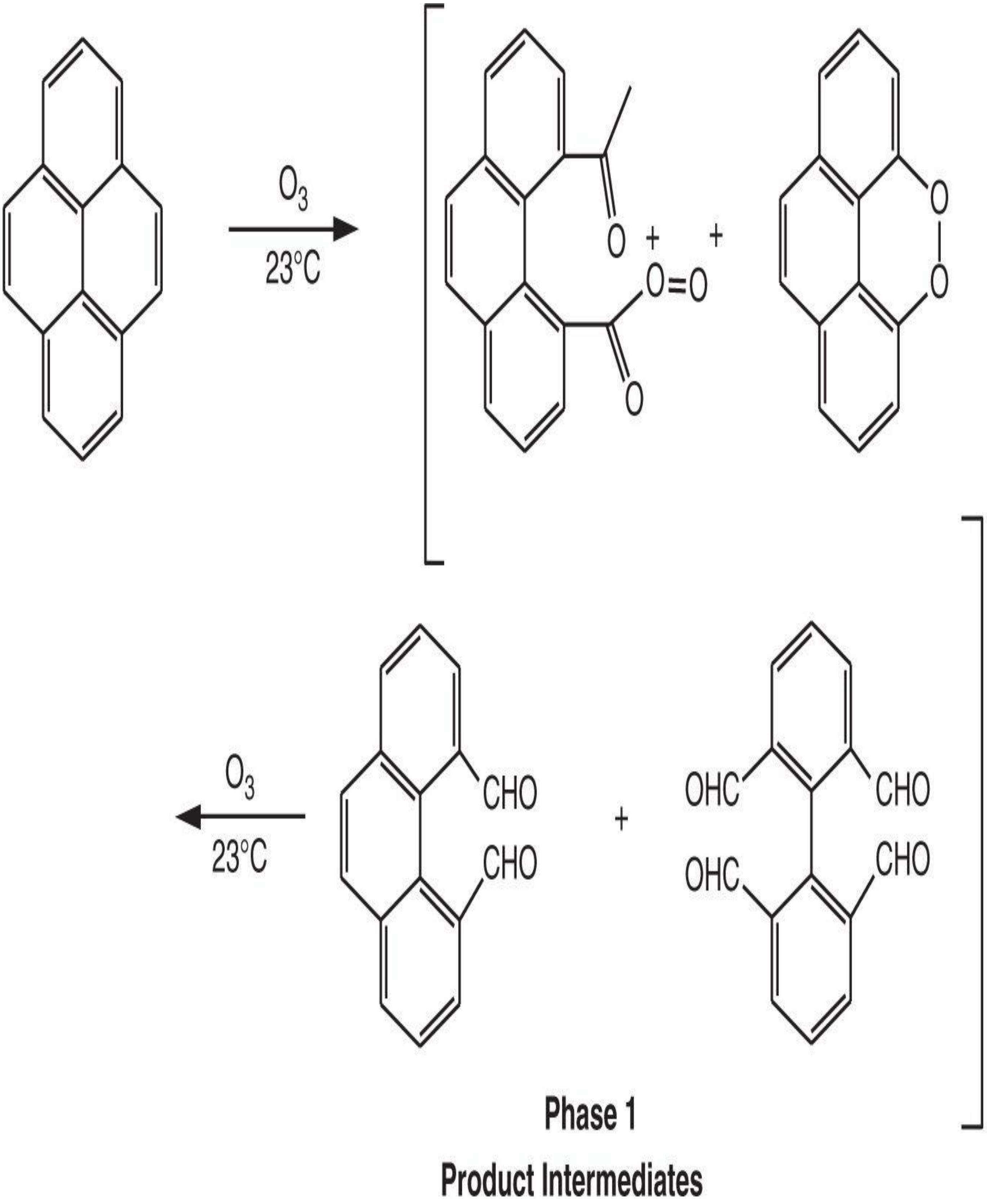


Figure 21.1

Phase 2

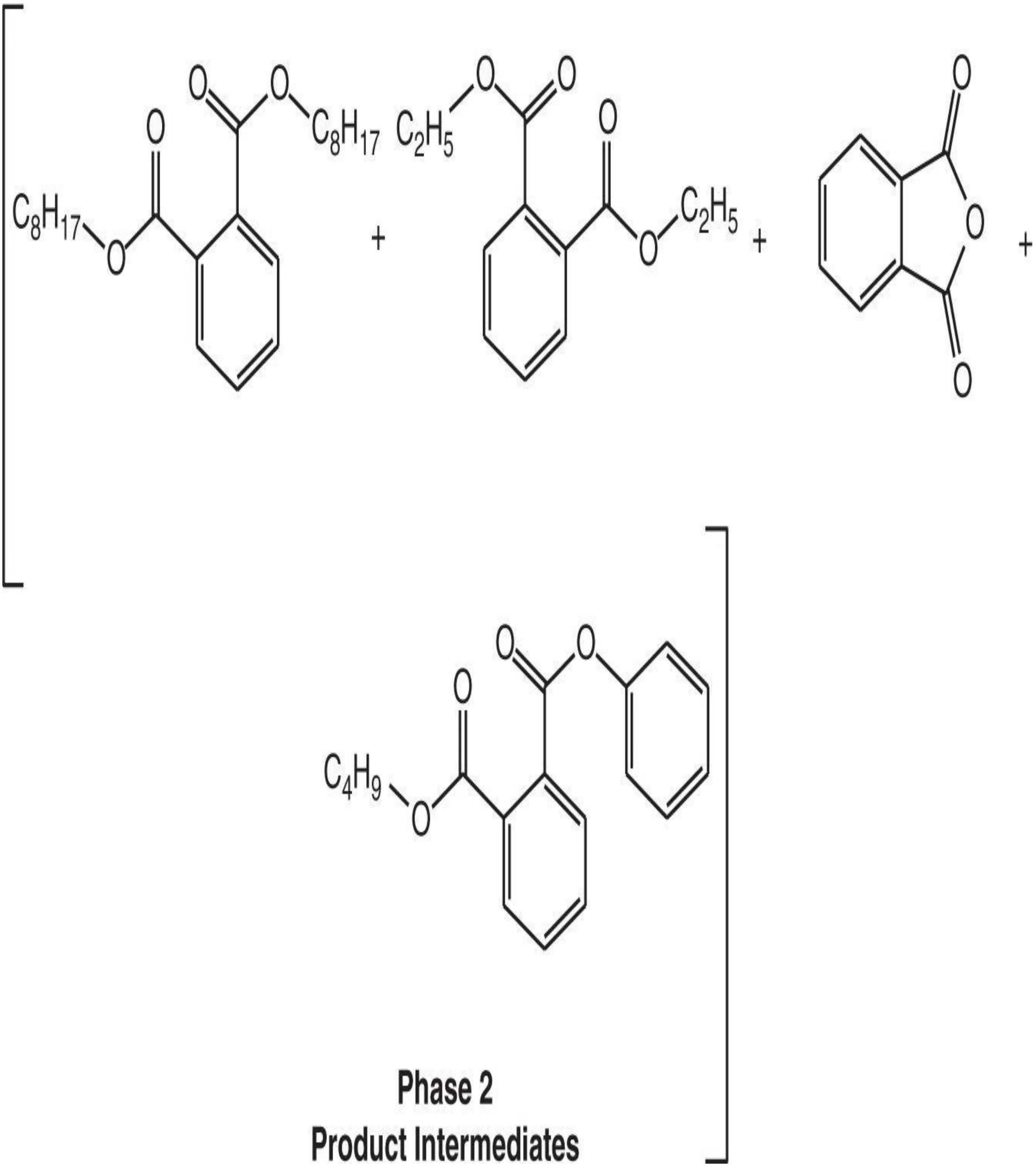


Figure 21.2

Phase 3

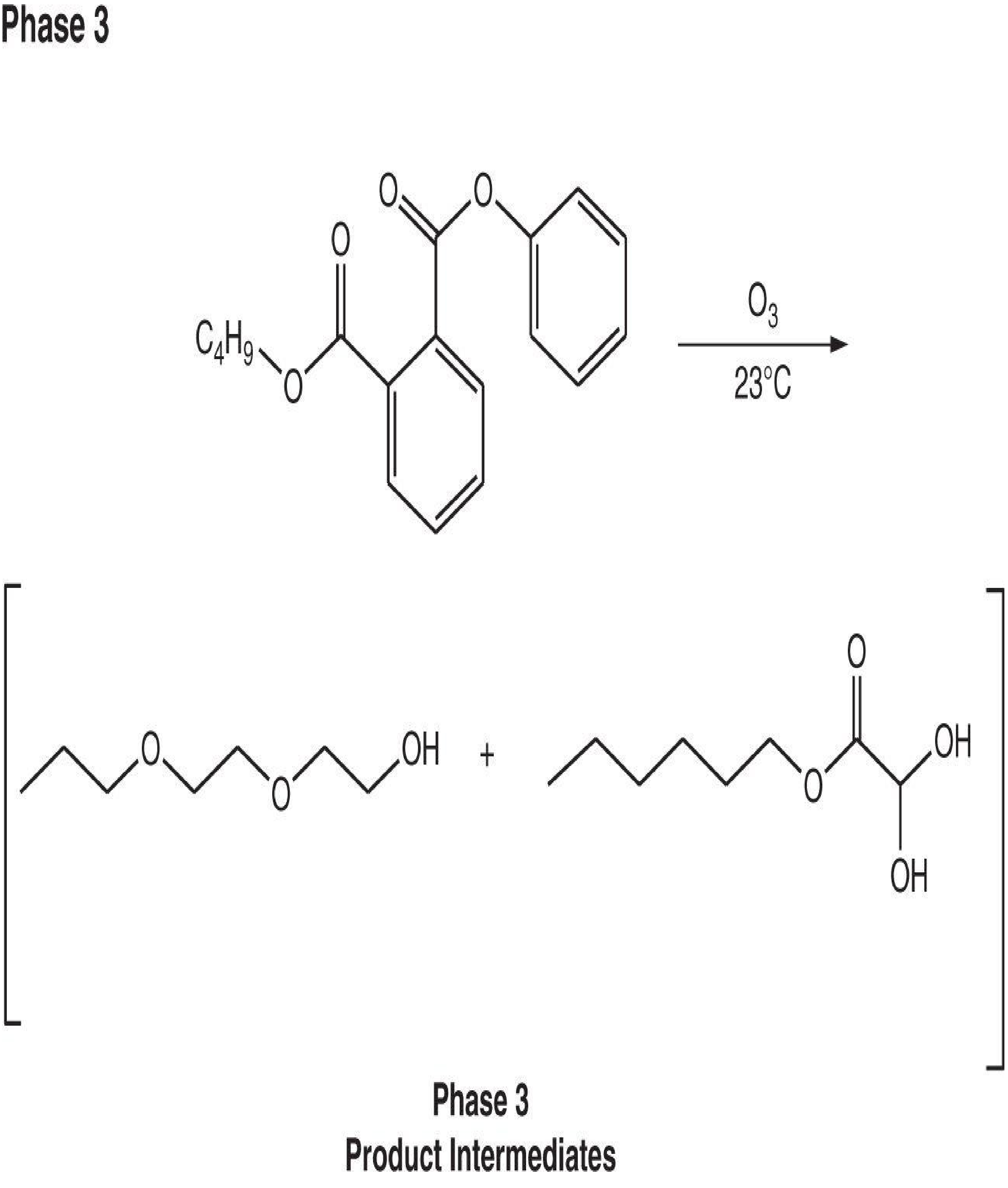


Figure 21.3

Phase 4

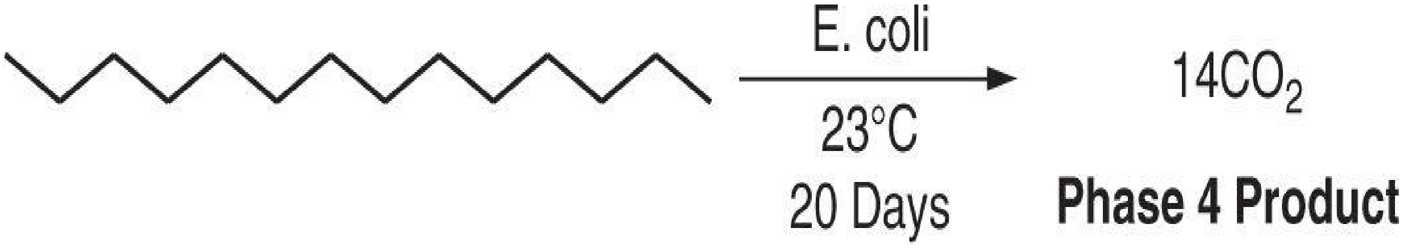


Figure 21.4

Experimental

1. Ozonolysis of benzo[a]pyrene. A saturated aqueous solution of benzo[a] pyrene dissolved in 150 mL of water was added to a clean, pressurized reaction kettle. The mixture was then treated with ozone for 50 minutes and was stirred overnight. The oxidized mixture was then filtered through 0.45-μm filter paper and the components were separated using column chromatography. A summary of benzo[a]pyrene ozonolysis products were then identified by gas chromatography using compound retention times and are provided in Table 21.1.

TABLE 21.1 Benzo[a]pyrene ozonolysis product intermediates identified by gas chromatography.

Retention time (min)	Compound name
9.89	1-Pentene, 2-isopropyl
9.99	1-Hexene, 4-methyl, 2-isopropyl
10.25	1-Pentene, 3,4-dimethyl, 2-propyl
10.93	1-Pentene, 3,4,4-trimethyl, 2-ethyl
11.01	1-Pentene, 3,4-methyl, 2-dimethyl
11.10	1-Hexene, 3,4-dimethyl, 2-ethyl
11.27	1-Hexene, 4,5-dimethyl, 2-ethyl
11.33	1-Hexene, 4,5-dimethyl, 2-ethyl
12.11	1-Pentene,3-methyl, 2-isobutyl
15.66	3-Decene, 9-methyl
37.60	Methylchrysene
38.42	7-Methyl-8-propanalpyrene
38.70	Phthalic anhydride
45.66	4-Methyl-5-methanal-chrysene
47.38	Pentadecane (C15)
47.51	Benzoic acid, ethyl ester
47.75	Benzoic acid, propyl ester
49.04	Tridecane
49.27	Bis (2-ethylhexyl) phthalate
51.82	1,2-Benzenedicarboxylic acid, diisononyl ester
52.21	1,2-Benzenedicarboxylic acid, diisononyl ester
52.28	1,2-Benzenedicarboxylic acid, diisononyl ester
52.48	1,2-Benzenedicarboxylic acid, diisononyl ester
52.57	1,2-Benzenedicarboxylic acid, diisononyl ester
52.68	1,2-Benzenedicarboxylic acid, diisononyl ester
52.78	1,2-Benzenedicarboxylic acid, diisononyl ester
52.92	1,2-Benzenedicarboxylic acid, diisononyl ester
53.02	1,2-Benzenedicarboxylic acid, diisononyl ester
53.20	1,2-Benzenedicarboxylic acid, diisononyl ester
53.25	1,2-Benzenedicarboxylic acid, diisononyl ester
53.51	1,2-Benzenedicarboxylic acid, diisononyl ester
53.89	1,2-Benzenedicarboxylic acid, diisononyl ester

2. Biodegradation of benzo[a]pyrene ozonolysis products using E. coli bacteria. An incubator was charged with all benzo[a]pyrene ozonolysis products and E. coli at ambient temperature and sample aliquots were removed at incubation periods of 0, 5, 10, 15, and 20 days. Analytical testing results are provided below:

> **A.** Gas chromatography indicated that benzo[a]pyrene ozonolysis products having retention times of ~15 minutes or less were completely biodegraded by E. coli.
>
> **B.** Gas chromatography testing also indicated that benzo[a]pyrene ozonolysis products having retention times of between ~15 minutes and ~48 minutes were biodegraded by at least 81% by E. coli.
>
> **C.** Benzo[a]pyrene ozonolysis products having retention times of 49 minutes or higher were biodegraded between 35% and 58% using E. coli.

Notes and Observations

1. Kerfoot[1] treated contaminants present in water at a deep-well site with ozone by introducing ozone into the well containing a laminar microporous diffuser. The diffuser generated ozone micro-bubbles that were more thoroughly dispersed in the well water. This method of groundwater remediation was effective in eliminating benzene, polyhalobenzene and derivatives, and polyhaloaliphatics. Following ozonolysis, oxidation products were then completely removed from the well water by naturally occurring microorganisms.

2. Kerfoot[2] eliminated groundwater and soil contamination by introducing ozone dissolved in water and by continuously adjusting the acidity and basicity during ozonolysis.

3. Miller[3] used fine-pore diffusers to saturate groundwater and soil with oxygen in a treatment system designed to lower the amounts of dissolved arsenic and iron.

4. Bowman[4] initially injected a compressed gas mixture consisting of ozone and air into contaminated soil and water. After this initial treatment phase was completed, the remediation area was then injected with 70% hydrogen peroxide into the aquifer in an effort to eliminate contaminants from soil adjacent to the surrounding area and water.

References

1. William B. Kerfoot, *Soil and water remediation system and method*, U.S. Patent 8,302,939 (November 2, 2012)

2. William B. Kerfoot, *Superoxidant poiser for groundwater and soil treatment with in-situ oxidation-reduction and acidity-basicity adjustment*, U.S. Patent Application 20090272697 (July 5, 2009)

3. Gregory P. Miller et al., *Apparatus, method and system of treatment of arsenic and other impurities in groundwater*, U.S. Patent Application 20060243668 (November 2, 2003)

4. Reid H. Bowman et al., *System and method for remediating contaminated soil and groundwater in situ*, U.S. Patent Application 20050067356 (March 31, 2005)

Remediation of Fabrics Contaminated with Food and Soil Using an Alkyl Polypentoside and Polyglucoside Mixture

Author	Charles Allen Hodge et al.
Patent Title	***Alkyl polypentosides and alkyl polyglucosides (C_8–C_{11}) used for enhanced food and soil removal,*** U.S. Patent Application 20120053111 (March 1, 2012)

Relevant Prior Patents by Author or Coauthors

Skin cleansing compositions with polyglycerol esters and hydrophobically modified polymers, U.S. Patent 8,338,348 (December 25, 2012)

Natural disinfecting cleaners, U.S. Patent 7,939,488 (May 10, 2011)

Natural cleaners, U.S. Patent 7,939,487 (May 10, 2011)

Natural cleaners, U.S. Patent 7,939,486 (May 10, 2011)

Antimicrobial foam hand soap comprising inulin or an inulin surfactant, U.S. Patent 7,803,746 (September 28, 2010)

Natural heavy duty cleaners, U.S. Patent 7,618,931 (November 17, 2009)

Surfactant composition, cleaning compositions containing same, and methods for using, U.S. Patent 7,503,332 (March 17, 2009)

Compositions comprising low-DP polymerized surfactants and methods of use thereof, U.S. Patent 7,446,088 (November 4, 2008)

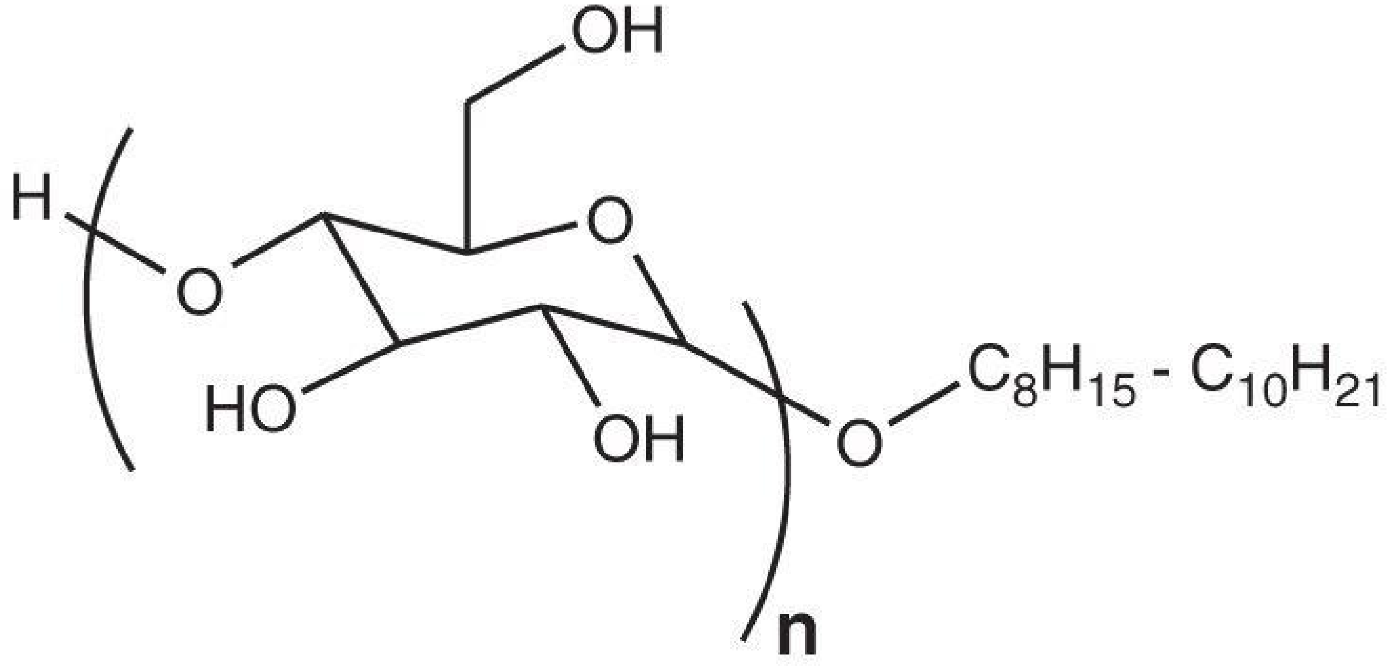
Product Application

The product mixture of the current investigation is designed to be used in cleaning and detergent formulations containing high-mineral-content water to clean fabrics.

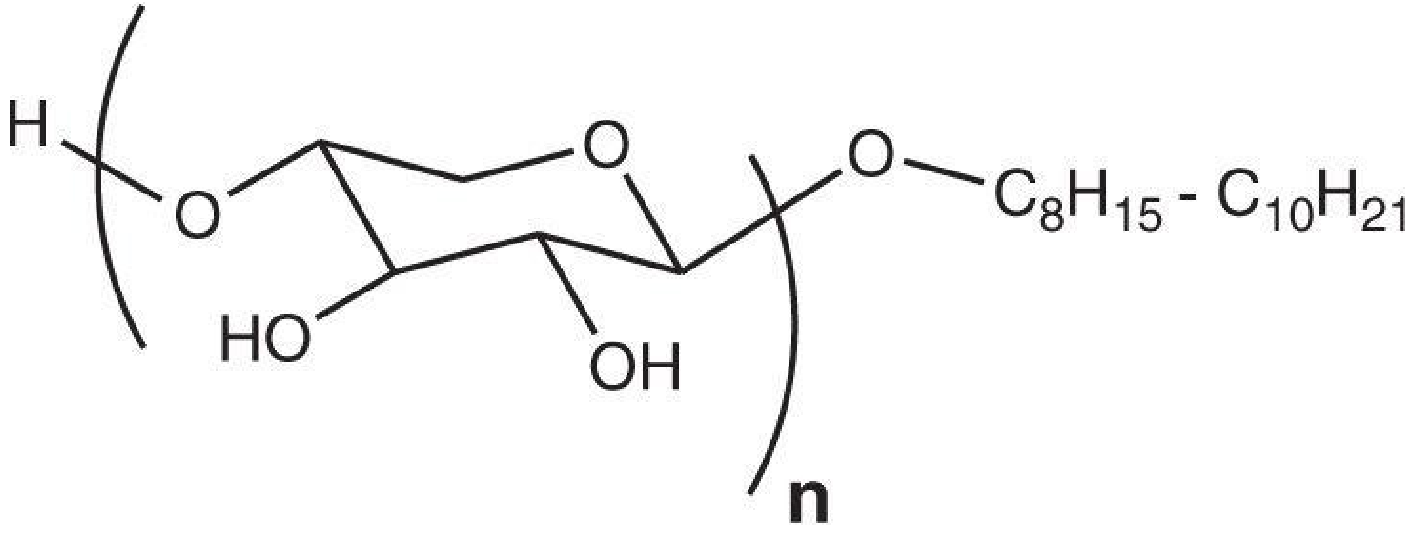
Significance of Current Application

Detergents that are used in either surface cleaning or laundering formulations are additized with petroleum-derived nonylphenol ethoxylates. Moreover, the effectiveness of nonylphenol ethoxylates as cleaning-agent components has resulted in these agents becoming an integral component in consumer detergent, surfactant, or degreaser formulations. Despite this, however, non-renewable nonylphenol ethoxylate surfactants and cleaners are of particular environmental concern. Nonylphenol ethoxylates are non-biodegradable and exhibit estrogen-like properties. There is also concern that these materials can potentially contaminate water, vegetation, and marine life. To address these concerns, the current investigation has determined that mixtures of C_8H_{15} to $C_{10}H_{21}$ polypentoside and polyglucoside can be used as nonylphenol ethoxylate replacement additives in cleaning and laundering formulations. First, both polypentoside and polyglucoside were obtained from wheat bran straw glycoside waste at very favorable market prices. Second, blends of polypentoside and polyglucoside are renewable, nontoxic, appear to have infinite shelf lives, and do not require product reformulation of either institutional cleaning or detergent packages when used as a nonylphenol ethoxylates replacement component. Finally, the use of polypentosides and polyglucosides as replacement additives for petroleum-derived nonylphenol ethoxylates is even more appealing because of its overall effectiveness, safety, and efficiency.

Renewable Agents



Polyglucoside



Polypentoside

Figure 21.5

Polypentoside and Polyglucoside Description

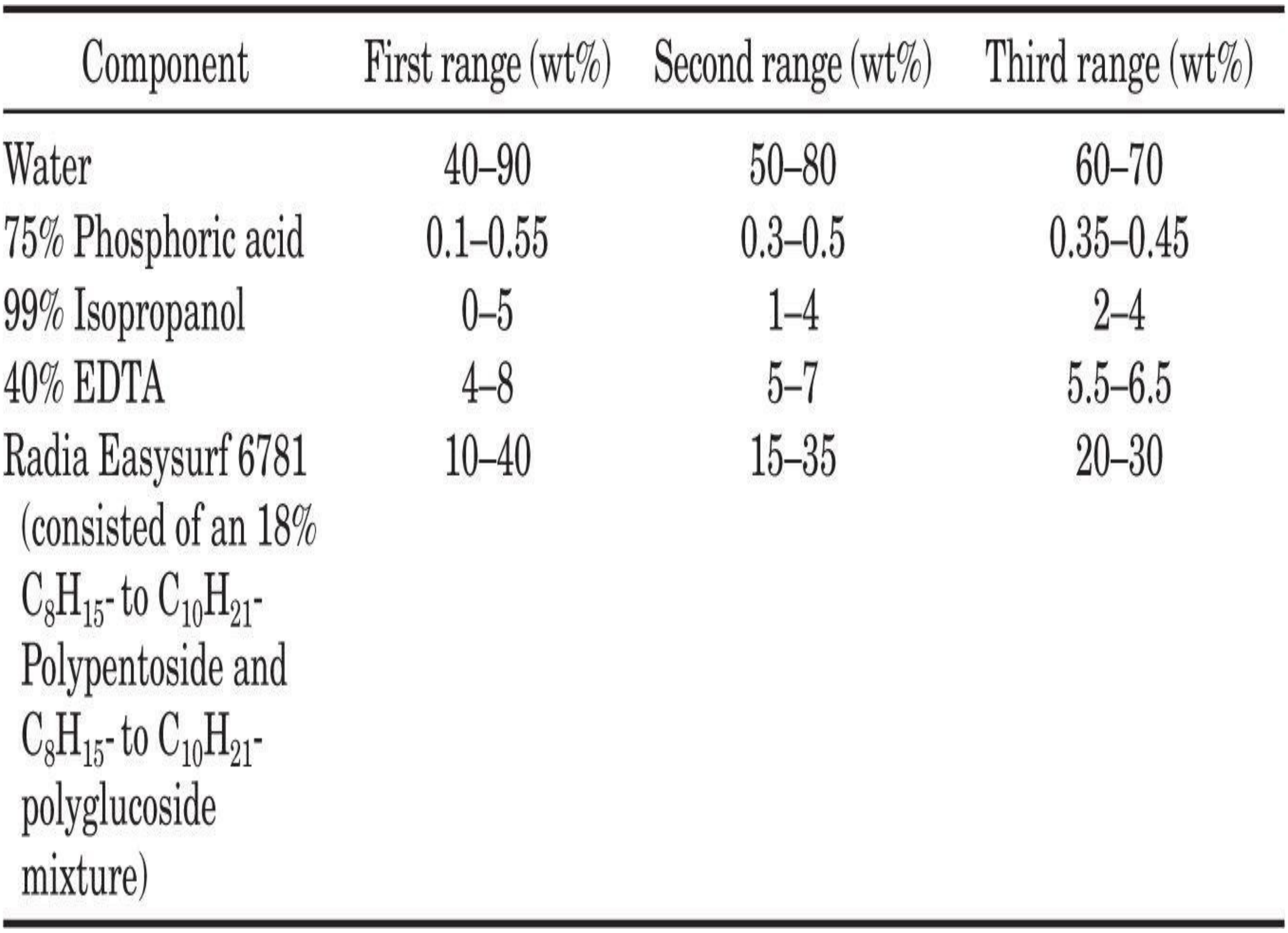
Radia® Easysurf 6781 is a mixture consisting of C_8H_{15}-to $C_{10}H_{21}$-polypentoside and C_8H_{15}- to $C_{10}H_{21}$-polyglucoside derived from wheat bran/straw glycosides and manufactured by Wheatco, Inc. The surfactant is ethoxy-free and completely renewable and degradable. The mixture is sold in 4-, 8-, and 16-oz gallon concentrations of approximately 18% activity. These and other alkyl-polypentoside and alkyl-polyglucoside mixtures are available from:

Wheatco Sales and Service
1801 9th St.
Wheatland, WY 82201
(307) 322-2333

Experimental

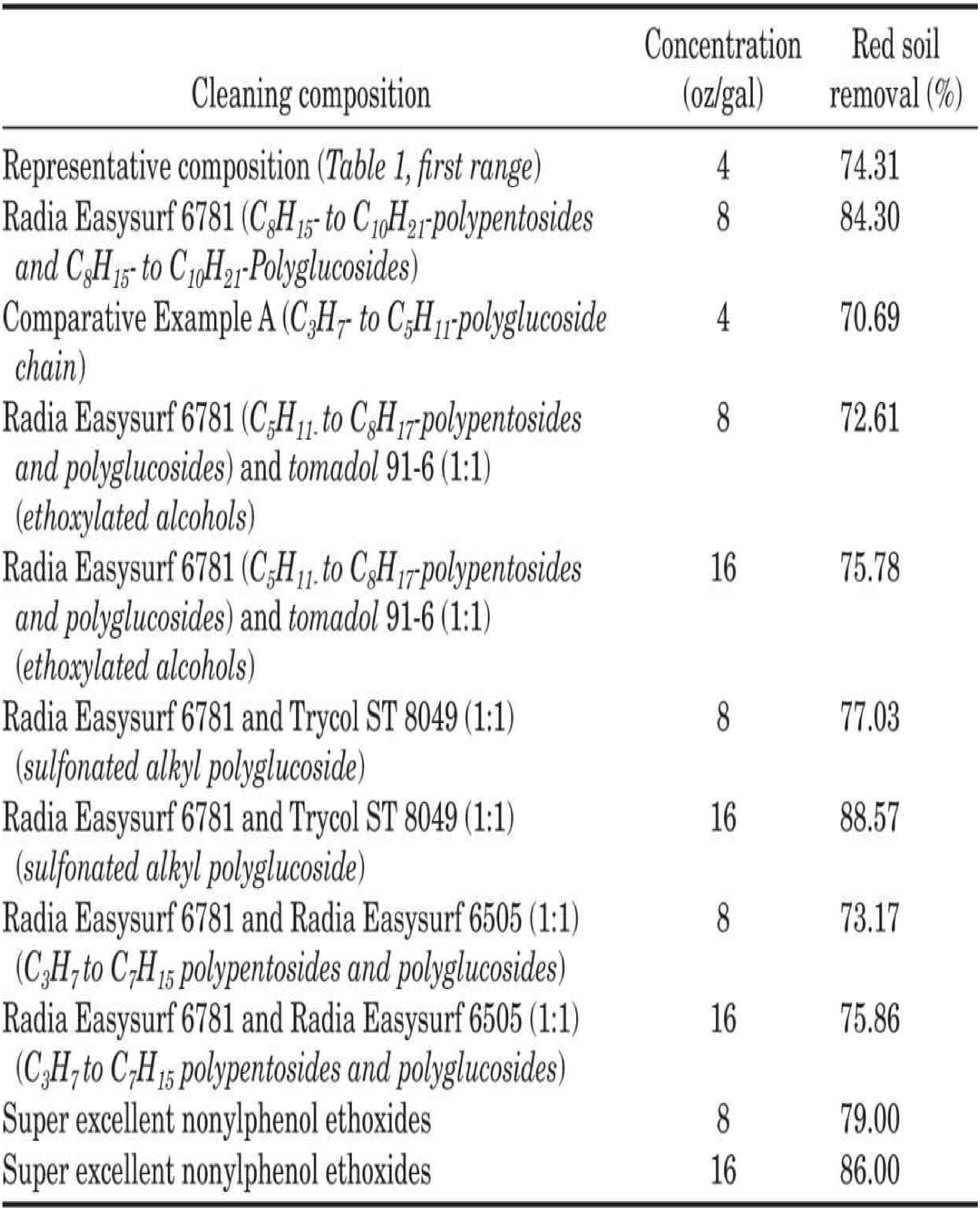
1. Preparation and testing of detergent additized with Radia Easysurf 6781. Cleaning grooved tiles of 3″ × 3″ were soiled with a mixture consisting of 50 g of red soil, 30 g of lard, 30 g of corn oil, 15 g of whole powdered egg, 1.5 g of red iron(III) oxide, as well as a mixture containing 20% protein. In the contamination process, vinyl sides were soiled with 0.75 g of the soiling mixture using a 3-in foam brush. The tiles were then dried at ambient temperature for 24 hours. Soil removal tests were then conducted using a Precision Force Applicator with a small synthetic sponge. The synthetic sponge was initially dampened with water and excess water squeezed out. The sponge was then saturated with about 50 g of the experimental cleaning composition containing Radia Easysurf 6781 (provided in Table 21.2). Tiles were initially scrubbed with about 2 lbs. of pressure with the moistened synthetic sponge for 16 cycles. The tiles were then rotated 90 degrees every 4 cycles until the tiles had been rotated 360 degrees. After this cleaning process, the tiles were then rinsed with tap water and dried at ambient temperature. Cleaning effectiveness of the experimental compositions are provided in Tables 21.3 and 21.4.

TABLE 21.2 Cleaning composition used to clean tile spattered with the soiling mixture. The cleaning blend formulation behaved as a C_8H_{15}- to $C_{10}H_{21}$-polypentoside and C_8H_{15}- to $C_{10}H_{21}$-polyglucoside replacement for non-renewable nonylphenol ethoxides.



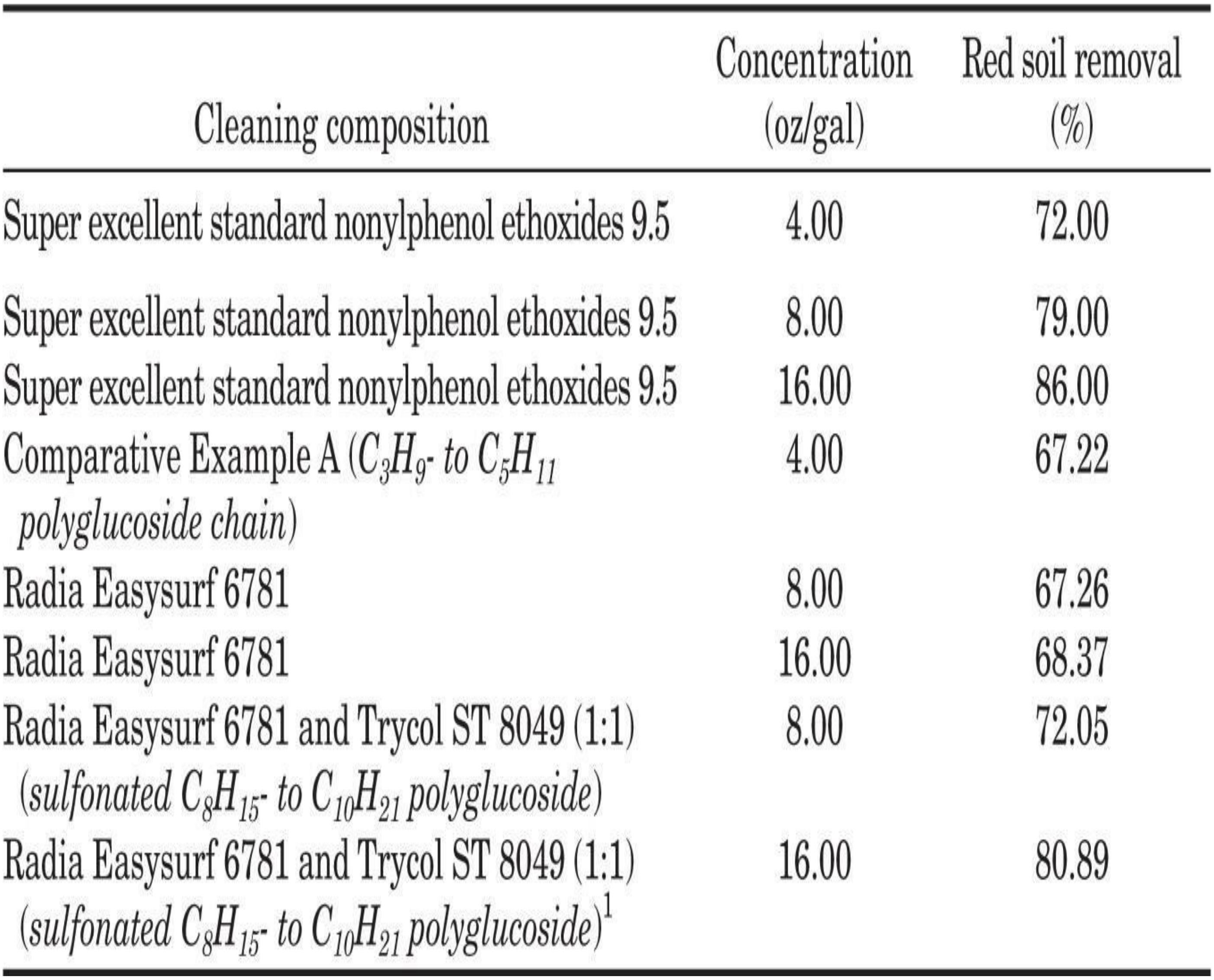
Component	First range (wt%)	Second range (wt%)	Third range (wt%)
Water	40–90	50–80	60–70
75% Phosphoric acid	0.1–0.55	0.3–0.5	0.35–0.45
99% Isopropanol	0–5	1–4	2–4
40% EDTA	4–8	5–7	5.5–6.5
Radia Easysurf 6781 (consisted of an 18% C_8H_{15}- to $C_{10}H_{21}$-Polypentoside and C_8H_{15}- to $C_{10}H_{21}$-polyglucoside mixture)	10–40	15–35	20–30

TABLE 21.3 Cleaning effectiveness of detergents containing polypentosides and polypentoside as replacements additives for non-renewable nonylphenol ethoxides.



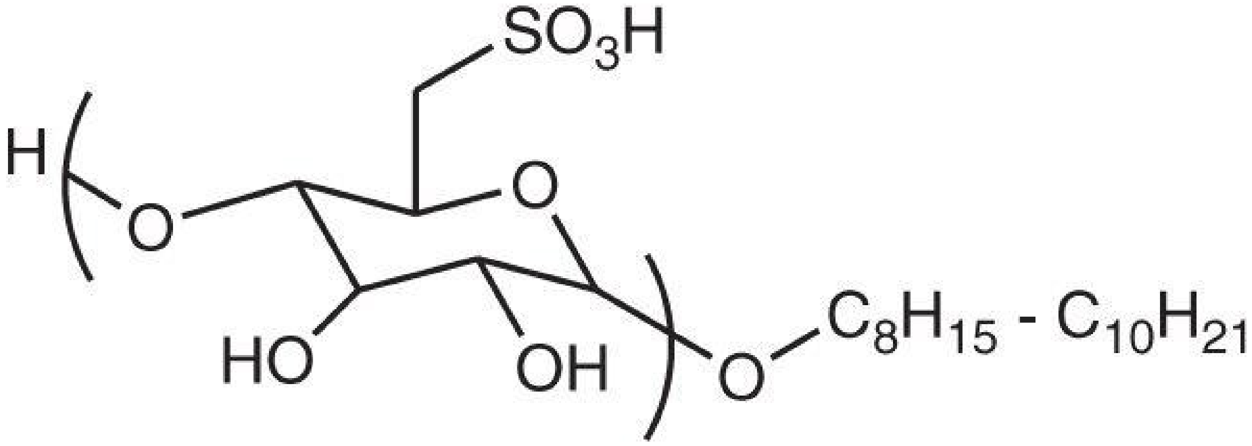
Cleaning composition	Concentration (oz/gal)	Red soil removal (%)
Representative composition (*Table 1, first range*)	4	74.31
Radia Easysurf 6781 (*C_8H_{15}- to $C_{10}H_{21}$-polypentosides and C_8H_{15}- to $C_{10}H_{21}$-Polyglucosides*)	8	84.30
Comparative Example A (*C_3H_7- to C_5H_{11}-polyglucoside chain*)	4	70.69
Radia Easysurf 6781 (*C_5H_{11}. to C_8H_{17}-polypentosides and polyglucosides*) and *tomadol* 91-6 (1:1) (*ethoxylated alcohols*)	8	72.61
Radia Easysurf 6781 (*C_5H_{11}. to C_8H_{17}-polypentosides and polyglucosides*) and *tomadol* 91-6 (1:1) (*ethoxylated alcohols*)	16	75.78
Radia Easysurf 6781 and Trycol ST 8049 (1:1) (*sulfonated alkyl polyglucoside*)	8	77.03
Radia Easysurf 6781 and Trycol ST 8049 (1:1) (*sulfonated alkyl polyglucoside*)	16	88.57
Radia Easysurf 6781 and Radia Easysurf 6505 (1:1) (*C_3H_7 to C_7H_{15} polypentosides and polyglucosides*)	8	73.17
Radia Easysurf 6781 and Radia Easysurf 6505 (1:1) (*C_3H_7 to C_7H_{15} polypentosides and polyglucosides*)	16	75.86
Super excellent nonylphenol ethoxides	8	79.00
Super excellent nonylphenol ethoxides	16	86.00

TABLE 21.4 Cleaning effectiveness of selected formulations of alkyl polypentosides and alkyl polyglucosides alone or in conjunction with the surfactant Trycol ST 8049, a sulfonated C_{8H15}- to $C_{10}H_{21}$-polyglucoside.



Cleaning composition	Concentration (oz/gal)	Red soil removal (%)
Super excellent standard nonylphenol ethoxides 9.5	4.00	72.00
Super excellent standard nonylphenol ethoxides 9.5	8.00	79.00
Super excellent standard nonylphenol ethoxides 9.5	16.00	86.00
Comparative Example A (*C_3H_9- to C_5H_{11} polyglucoside chain*)	4.00	67.22
Radia Easysurf 6781	8.00	67.26
Radia Easysurf 6781	16.00	68.37
Radia Easysurf 6781 and Trycol ST 8049 (1:1) (*sulfonated C_8H_{15}- to $C_{10}H_{21}$ polyglucoside*)	8.00	72.05
Radia Easysurf 6781 and Trycol ST 8049 (1:1) (*sulfonated C_8H_{15}- to $C_{10}H_{21}$ polyglucoside*)[1]	16.00	80.89

[1] Structure of Radia Easysurf 6781



Testing

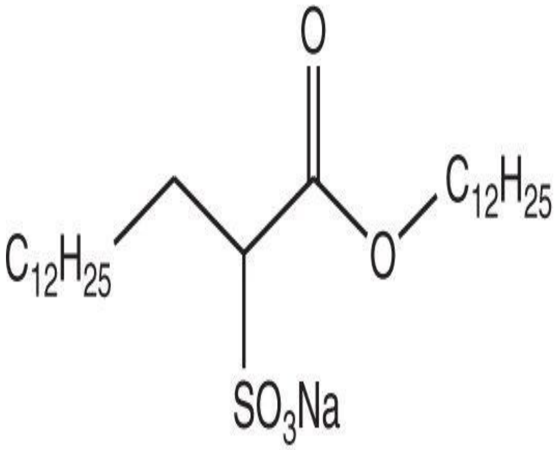
Cleaning formulations

Testing Results

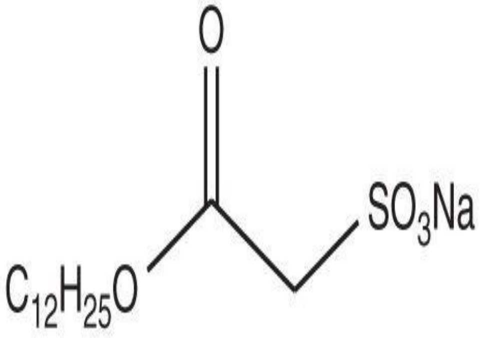
A. Cleaning effectiveness testing

Notes and Observations

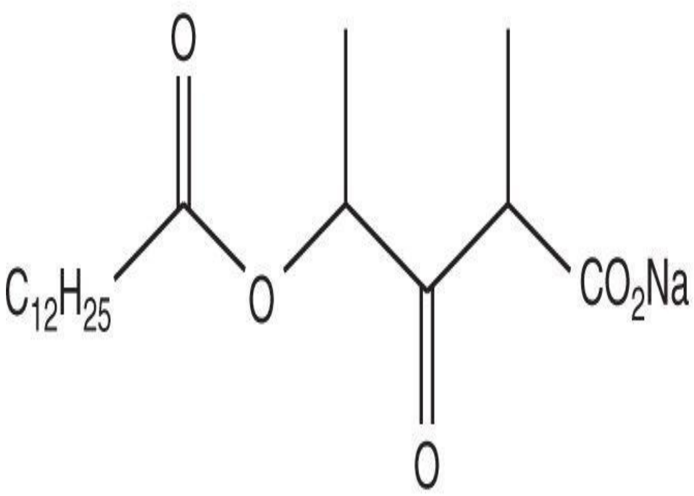
1. Anim-Danso[1] prepared a series of renewable detergent surfactants for use in personal care products. When used in cleaning formulations at higher treatment levels, however, these formulations were useful as detergents in cleaning hard surfaces. Components present in the detergent formulation include α-sulfo fatty acid esters, (I), alkyl sulfoacetates, (II), acyl lactylates, (III), acyl glycinates, (IV), and disodium lauroyl glutamates, (V). (See Fig. 21.6.)



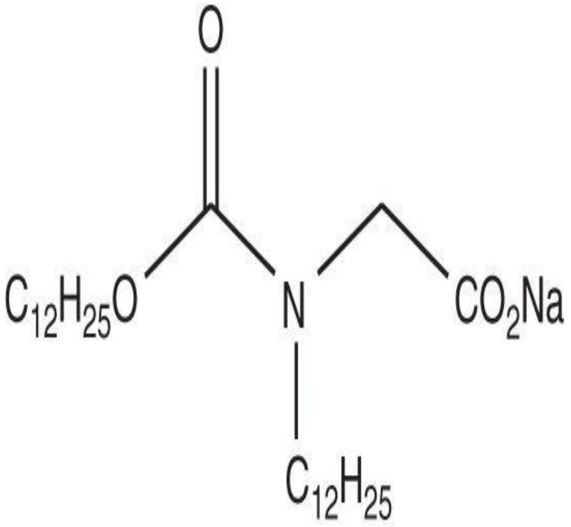
(I)



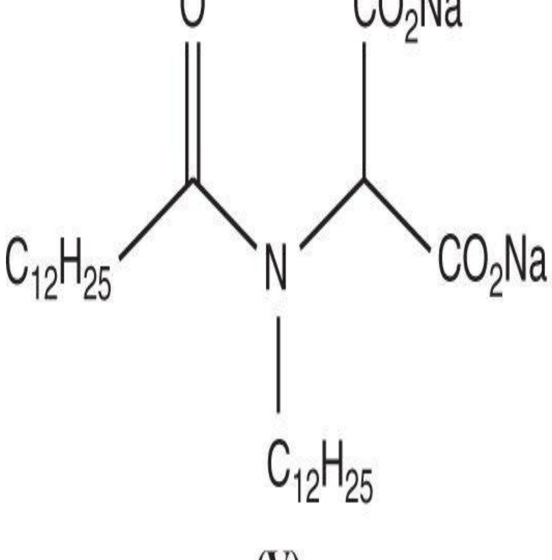
(II)



(III)



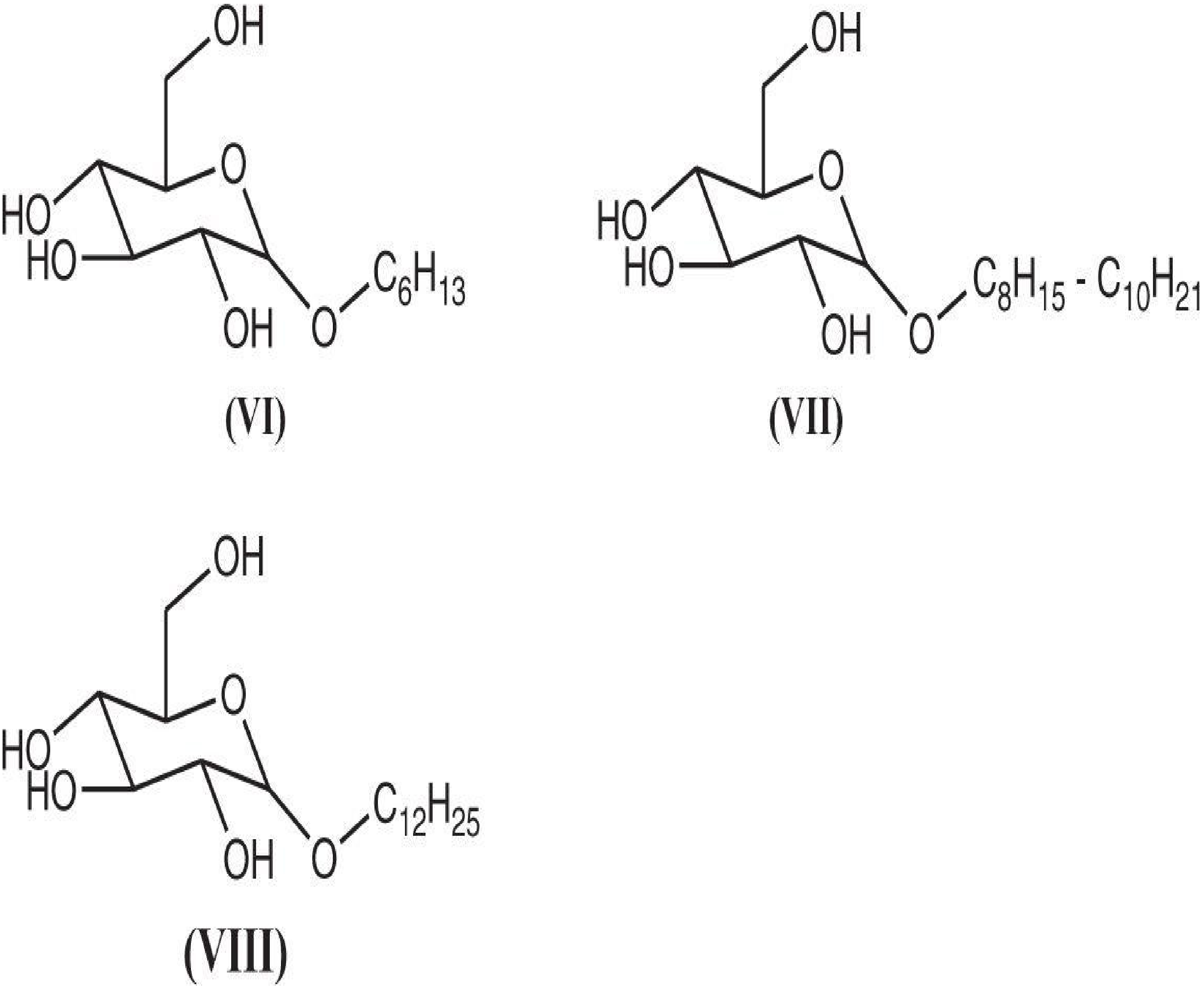
(IV)



(V)

Figure 21.6

2. In laundry formulations prepared by Scheuing[2] containing C_6H_{13}, (VI), C_8H_{17} to $C_{10}H_{21}$, (VII), and $C_{12}H_{25}$, (VIII), alkylpolyglucosides, optimum cleaning was observed using mixed polyglucoside alkyl chain lengths. (See Fig. 21.7.)



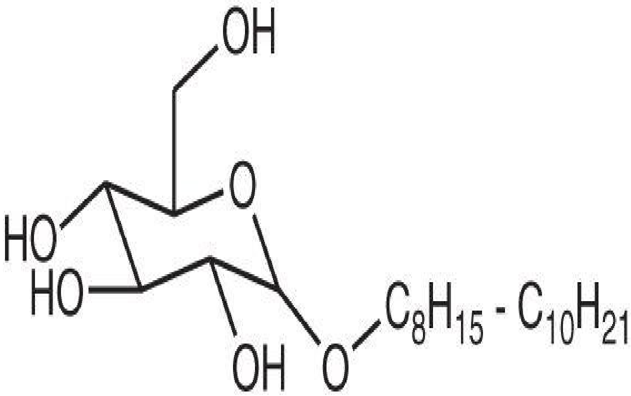
(VI) (VII)

(VIII)

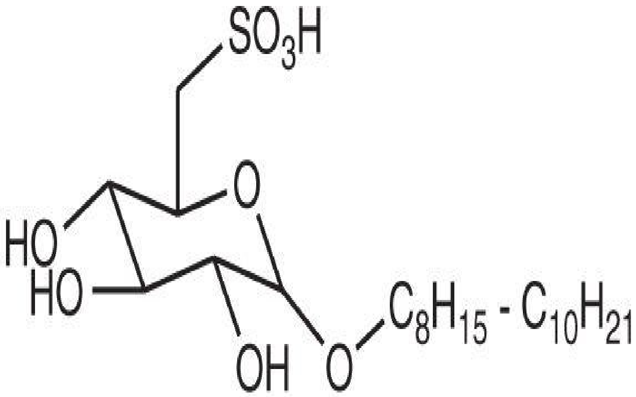
Figure 21.7

3. A renewable cleaning composition prepared by Scheuing[3] designed to clean laundry and either soft and hard surfaces performed better than commercial compositions containing non-renewable cleaning agents. The renewable cleaning agent consisted of an alkyl polyglucoside having average chain lengths greater than C_8H_{17}. It was subsequently determined in the investigation that the most desirable alkylglucosides could be obtained from coconuts since they contain a mixture of C_9H_{19} to $C_{11}H_{23}$ alkyl polyglucosides.

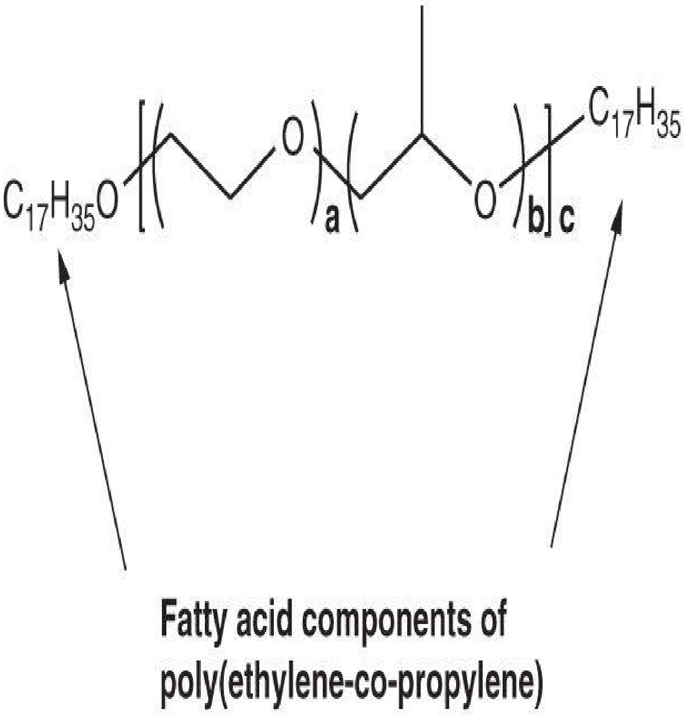
4. Gross[4] prepared a three-component cleaning formulation consisting of renewable C_9H_{19} to $C_{11}H_{23}$ polyglucosides [Glucopon° 215 CS UP], (IX), a sulfonated C_9H_{19} to $C_{11}H_{23}$ polyglucoside [Trycol® ST-8049], (X), and the fatty acid, ethylene-propylene copolymer [Dehypon° LS36], (XI). (See Fig. 21.8.)



(XI)



(X)



(XI)

Figure 21.8

References

1. Emmanuel Anim-Danso et al., *Skin cleansing compositions with polyglycerol esters and hydrophobically modified polymers*, U.S. Patent 8,338,348 (December 25, 2012)

2. David R. Scheuing et al., *Natural cleaners*, U.S. Patent 7,939,487 (May 10, 2011)

3. David R. Scheuing et al., *Natural heavy duty cleaners*, U.S. Patent 7,618,931 (November 17, 2009)

4. Stephen F. Gross et al., *Surfactant composition, cleaning compositions containing same, and methods for using*, U.S. Patent 7,503,332 (March 17, 2009)

Remediation of Fabrics Contaminated with Food and Soil Using Polyquaternary Functionalized Alkyl Polyglucosides

Author Charles Allen Hodge et al.

Patent Title ***Polyquaternary functionalized alkyl polyglucosides for enhanced food and soil removal,*** U.S. Patent Application 20130053297 (February 28, 2013)

Relevant Prior Patents by Author or Coauthors

Cleaning composition with surface modification polymer, U.S. Patent Application 20130072419 (March 21, 2013)

Quaternary functionalized alkyl polyglucosides for enhanced food and soil removal, U.S. Patent Application 20130040873 (February 14, 2013)

Betaine functionalized alkyl polyglucosides for enhanced food and soil removal, U.S. Patent Application 20130023458 (January 24, 2013)

Poly phosphate functionalized alkyl polyglucosides for enhanced food and soil removal, U.S. Patent Application 20120322710 (December 20, 2012)

Stearyl- and lauryldimoniumhydroxy alkyl polyglucosides for enhanced food and soil removal, U.S. Patent Application 20120094891 (April 19, 2012)

Poly sulfonated functionalized alkyl polyglucosides for enhanced food and soil removal, U.S. Patent Application 20120071388 (March 22, 2012)

Product Application

Polyquaternary functionalized alkyl polyglucosides prepared in this investigation are designed to be used as renewable replacement additives for nonylphenol ethoxylates currently present in laundering formulations. Laundering formulations containing polyquaternary functionalized alkyl polyglucosides are particularly needed in institutional settings for cleaning severely soiled clothing.

Significance of Current Application

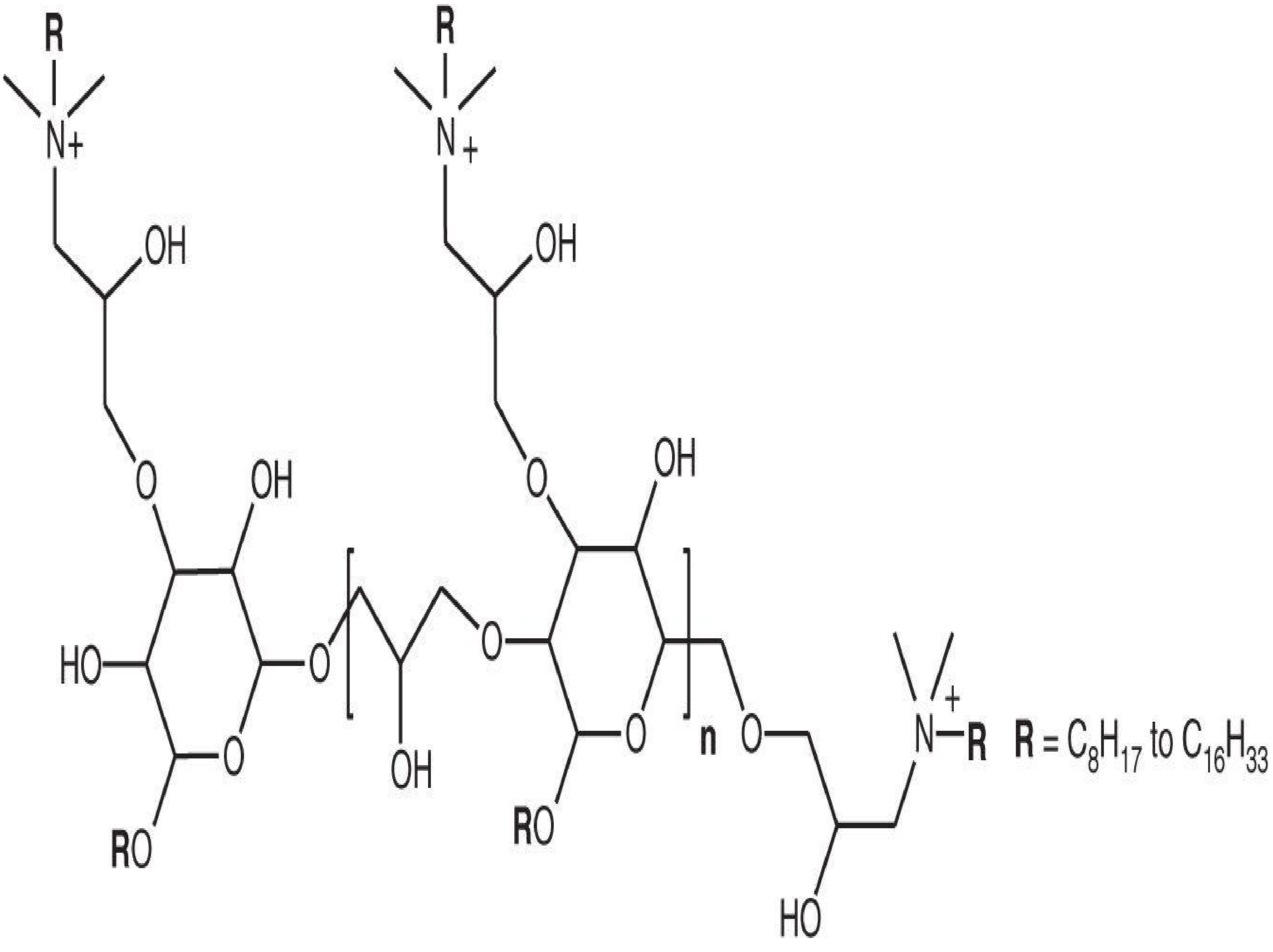
Alkyl phenol ethoxylates are very effective as cleaning additives when used in detergent and cleaning formulations. Despite its cleaning efficacy, however, alkyl phenol ethoxylates are toxic, corrosive, and are derived from non-renewable petrochemicals. The current investigation has determined that renewable, non-irritating, and non-toxic polyquaternary alkyl polyglucosides derived from wheat bran/straw glycoside can be used as replacement additives for alkyl phenol ethoxylates. Laundering formulations additized with polyquaternary alkyl polyglucosides were empirically determined to be more effective in removing severely soiled clothing and bedding materials. Fabrics washed with laundering materials additized with this renewable agent generated softer clothing that was more favorably received by the institutionalized population.

Polyquaternary alkyl polyglucosides are readily prepared, competitively priced with detergents containing alkyl phenol ethoxylates, and are completely non-toxic. In addition, this investigation further determined that polyquaternary alkyl polyglucosides could be used to directly replace alkyl phenol ethoxylates in existing laundry formulations since polyquaternary alkyl polyglucosides were completely compatible with coadditives such as:

A. Thickening Agents
F. Stabilizing Agents
B. Bleaching Agents
G. Dispersants
C. Detergent Fillers
H. Dyes and Fragrances
D. Defoaming Agents
I. Adjuvants
E. Antiredeposition Agents

Compatibility of polyquaternary alkyl polyglucosides with other components present in the detergent formulation is an attractive feature of this renewable additive since package reformulations and re-testing would be completely unnecessary.

Laundry Replacement Additive for Alkyl Phenol Ethoxylates



Alkyl Ammonium Polyglucoside

Figure 21.9

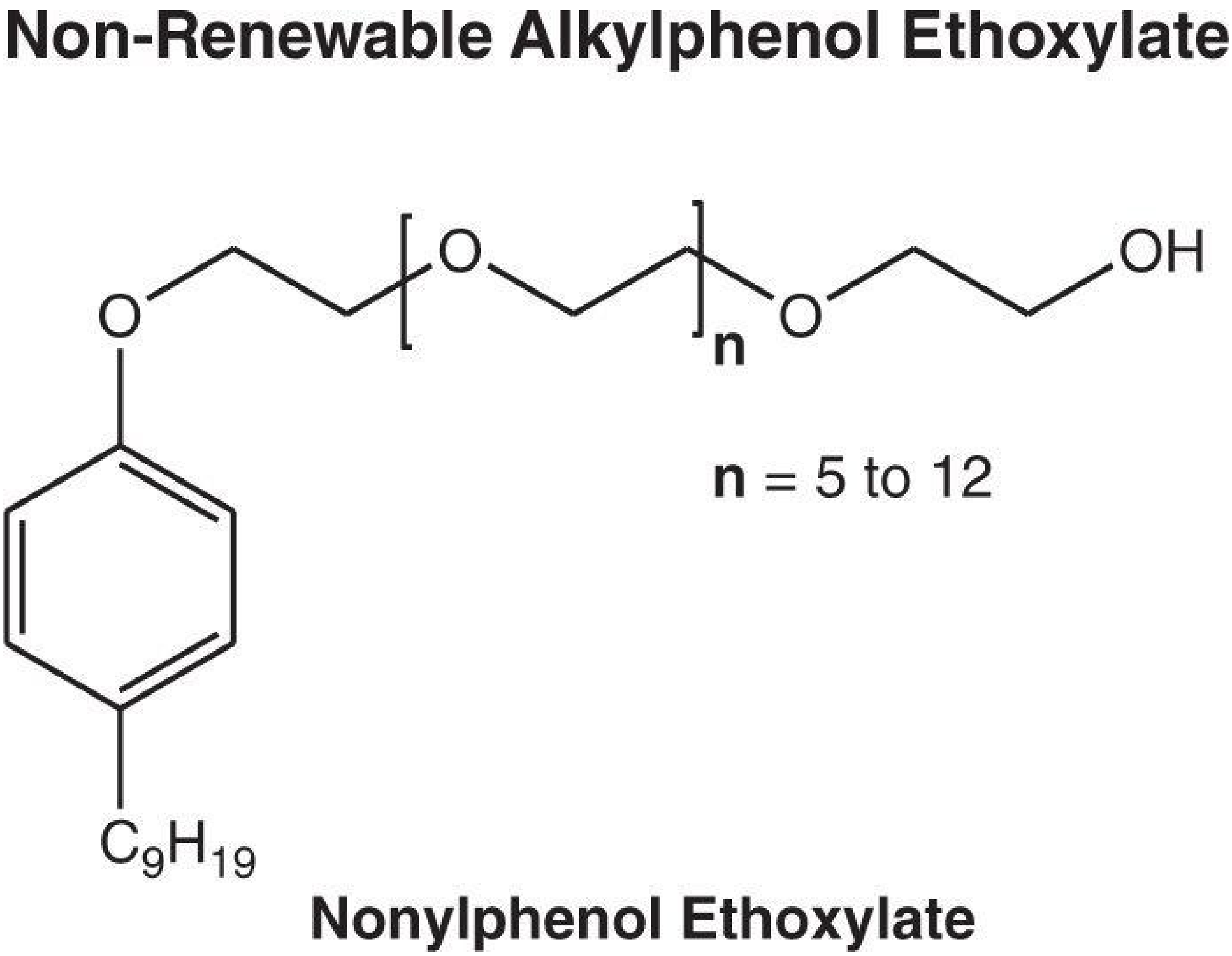


Figure 21.10

Product Resources

Additional alkyl ammonium polygucosides are available from Colonial Chemical, Inc., South Pittsburg, Tenn. including:

A. Poly(cocoglucosides hydroxypropyltrimonium chloride) where

R = **C_8 to C_{16}**

B. Poly Suga® Quat S1010P, Polyquaternium-79 Poly(stearyldimonium hydroxypropyl propyldecylglucosides chloride) where

R = **C_{10} to C_{14}**

C. Quat L1010P, Polyquaternium-78 Poly(lauryldimonium hydroxypropyl decylglucosides chloride) where

R = **C_{10} to C_{11}**

D. Poly Suga Quat L1210P, Polyquaternium-80 Poly(lauryldimonium hydroxypropyl laurylglucosides chloride) where

R = **C_{12} to C_{14}**

E. Poly Suga Quat 1218P, Polyquaternium-82 Poly(laurylglucosides hydroxypropyltrimonium chloride) where

$$\mathbf{R = C_{12}}$$

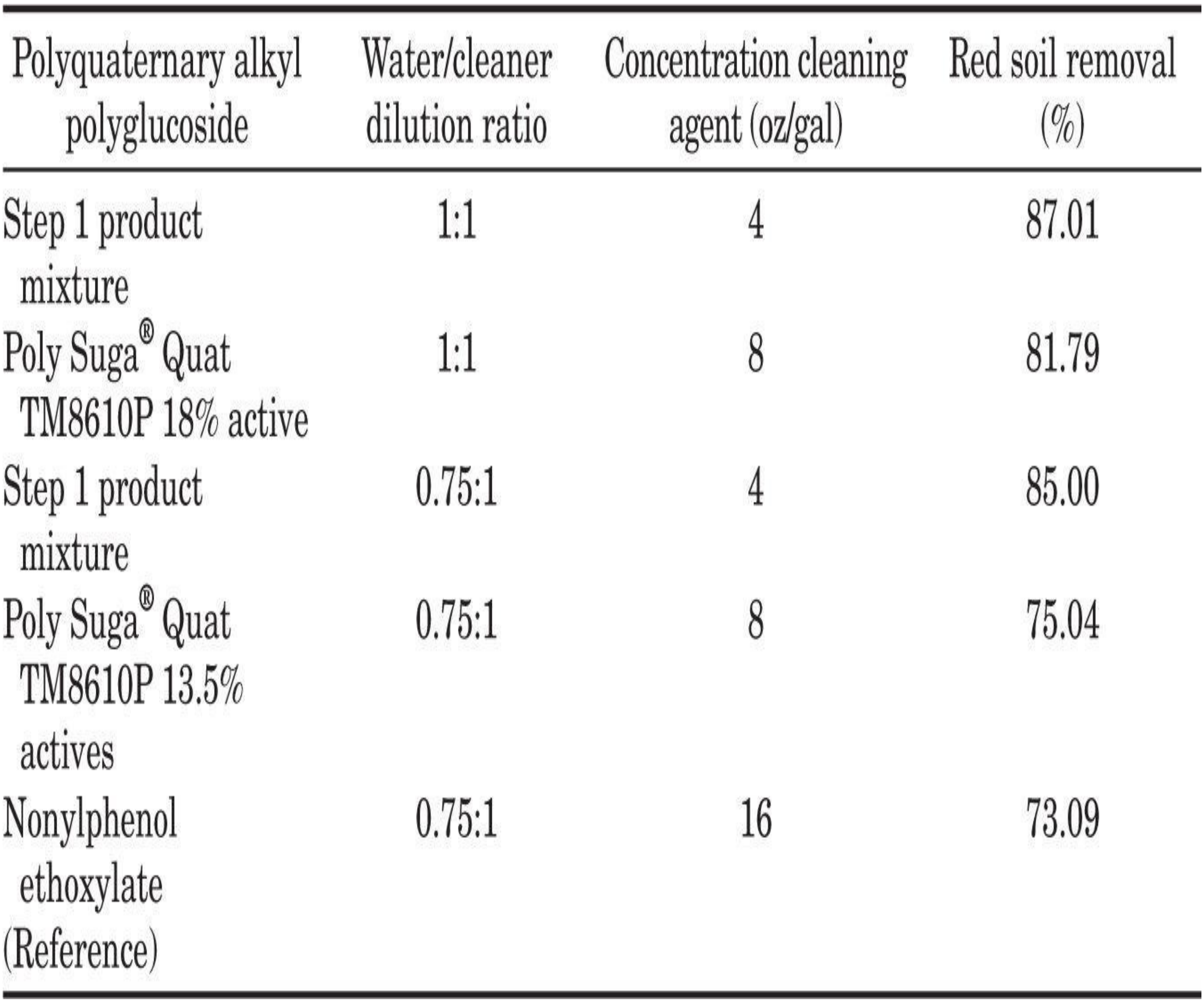
Experimental

1.Preparation of detergent containing poly Suga Quat L1210P. An aqueous solution was prepared by adding four fluid ounces of 18% active Suga® Quat L1210P to 1 gal of household water at ambient temperature. The mixture was then thoroughly stirred using a wooden paddle until a visual inspection of the solution indicated the absence of particles. Once prepared, the solution was used immediately.

Testing

A. Effectiveness of removing red soil using a detergent containing poly Suga Quat L1210P. A red soiling sample consisting of 30 g of lard, 30 g of corn oil, 15 g of whole powdered eggs, and 1.5 g of red iron(III) oxide was used as the soiling mixture in all testing. In this test, 3-in × 3-in white vinyl tiles were soiled with 0.75 g of the soiling mixture using a 3-in foam brush. After the soiled tiles dried overnight at ambient temperature, tiles were placed into a soaking tray containing approximately 200 g of Step 1 detergent mixture containing Suga Quat L1210P for approximately one minute. Cleaning results are provided in Table 21.5.

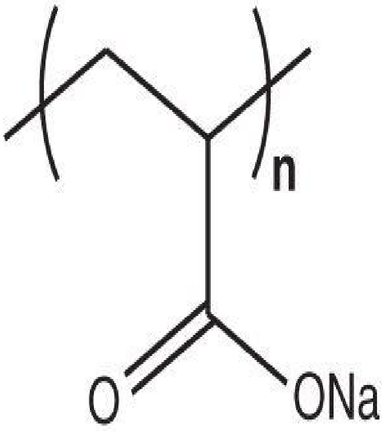
TABLE 21.5 Cleaning effectiveness of polyquaternary alkyl polyglucosides using tiles the soiling mixture composition. At equivalent or lower treatment rates renewable polyquaternary alkyl polyglucosides consistently outperformed nonylphenol ehoxylate.



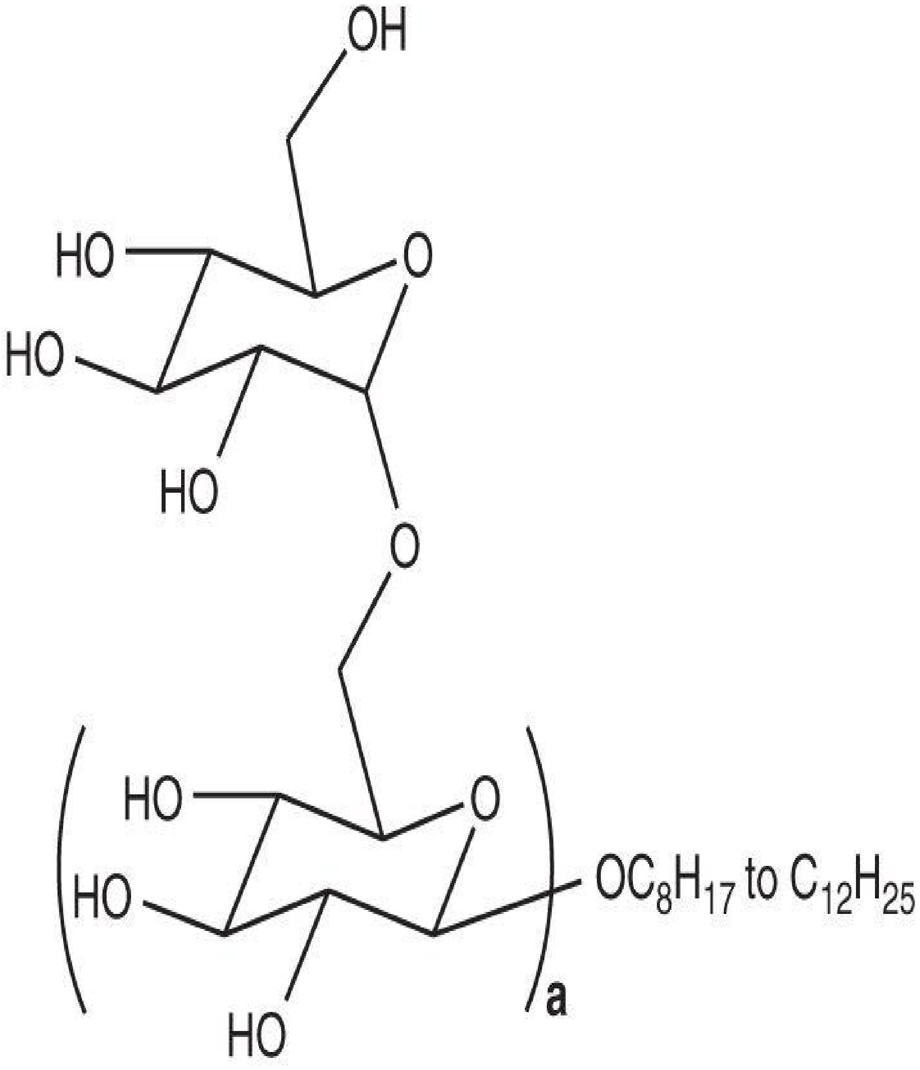
Polyquaternary alkyl polyglucoside	Water/cleaner dilution ratio	Concentration cleaning agent (oz/gal)	Red soil removal (%)
Step 1 product mixture	1:1	4	87.01
Poly Suga® Quat TM8610P 18% active	1:1	8	81.79
Step 1 product mixture	0.75:1	4	85.00
Poly Suga® Quat TM8610P 13.5% actives	0.75:1	8	75.04
Nonylphenol ethoxylate (Reference)	0.75:1	16	73.09

Notes and Observations

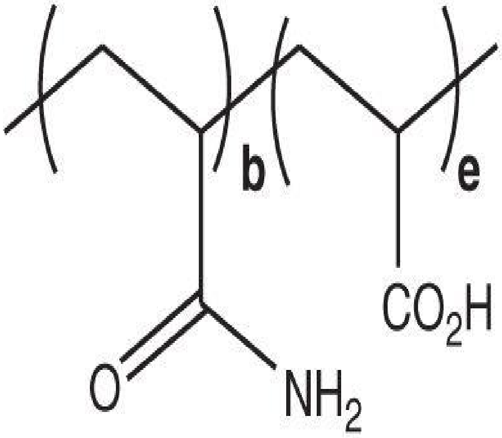
1. Blattner[1] prepared a surface detergent using three renewable and commercially available materials components. The first cleaning component consisted of Acusol® 460N, sodium polyacrylate, (I), while the second component consisted of Glucopon 215 UP, a C_6 to C_{12} alkyl polyglucoside, (II). Finally, the third consisted of Mirapol Surf-S 110A, a poly(acrylamide-coacrylic acid), (III), copolymer having an Mn ~ 35,000 daltons. When the three-component blend was used as a bathroom cleaning agent, no toxic-organic volatile emissions were detected. It was determined in the initial investigation that the original product formulation could be easily modified to accommodate a wide variety of consumer cleaning demands. (See Fig. 21.11.)



(I)



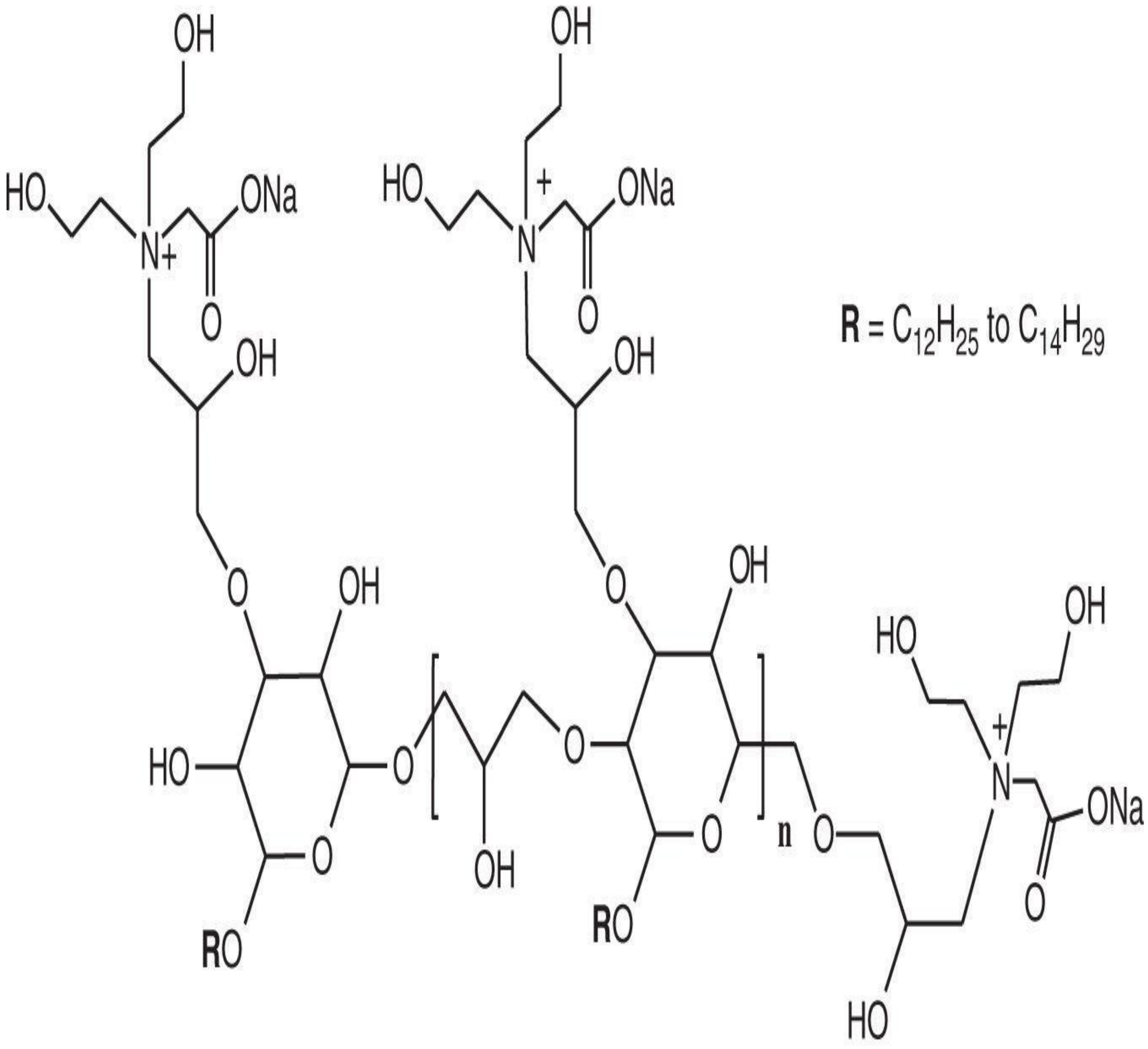
(II)



(III)

Figure 21.11

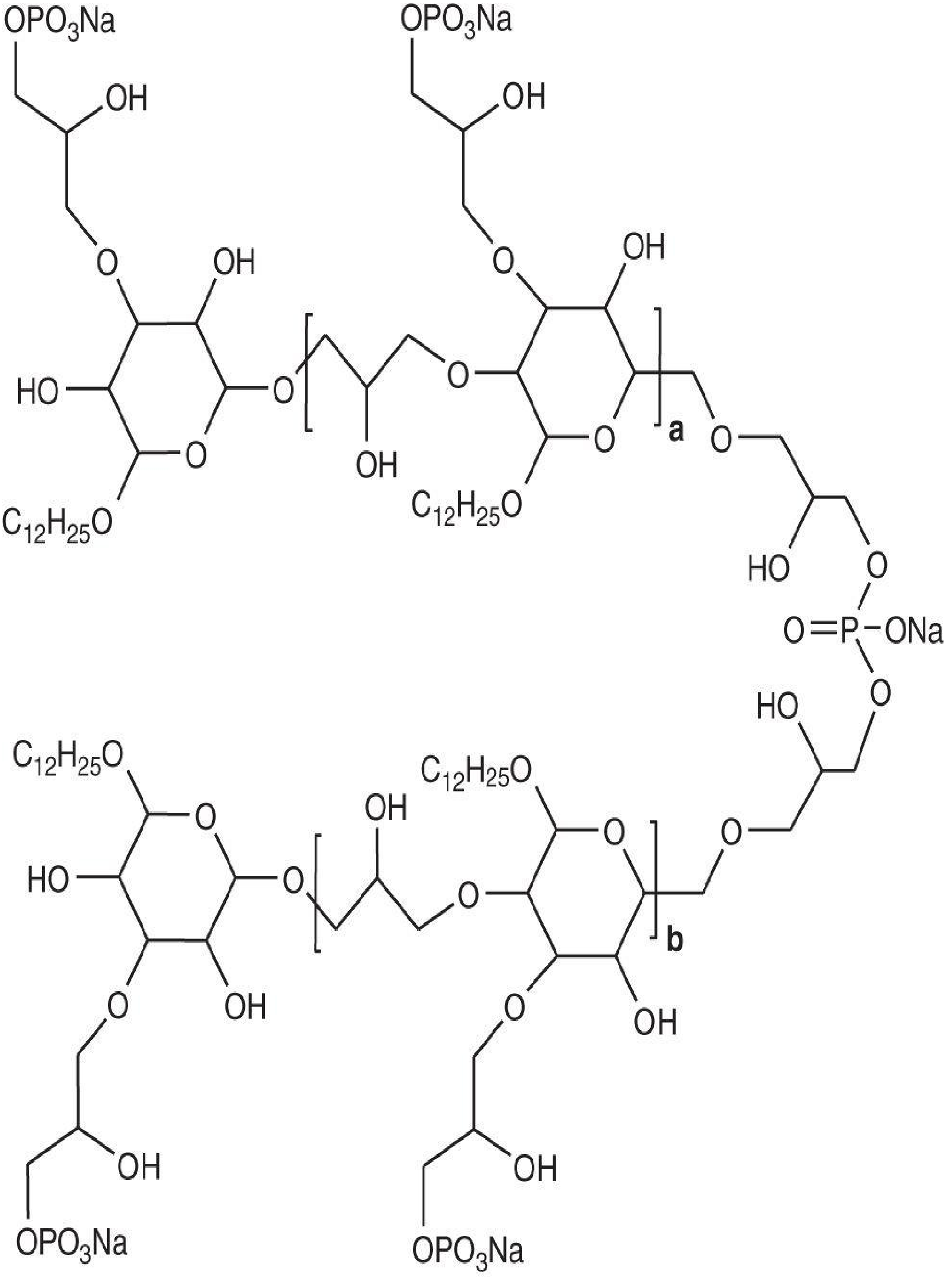
2. Renewable sodium bis-hydroxyethylglycinate laurylpolyglucosides, (IV), was used by Hodge[2] to prepare water-soluble cleaning agents that were considerably more effective than nonylphenol ethoxylate at twice the treatment dosage. (See Fig. 21.12.)



(IV)

Figure 21.12

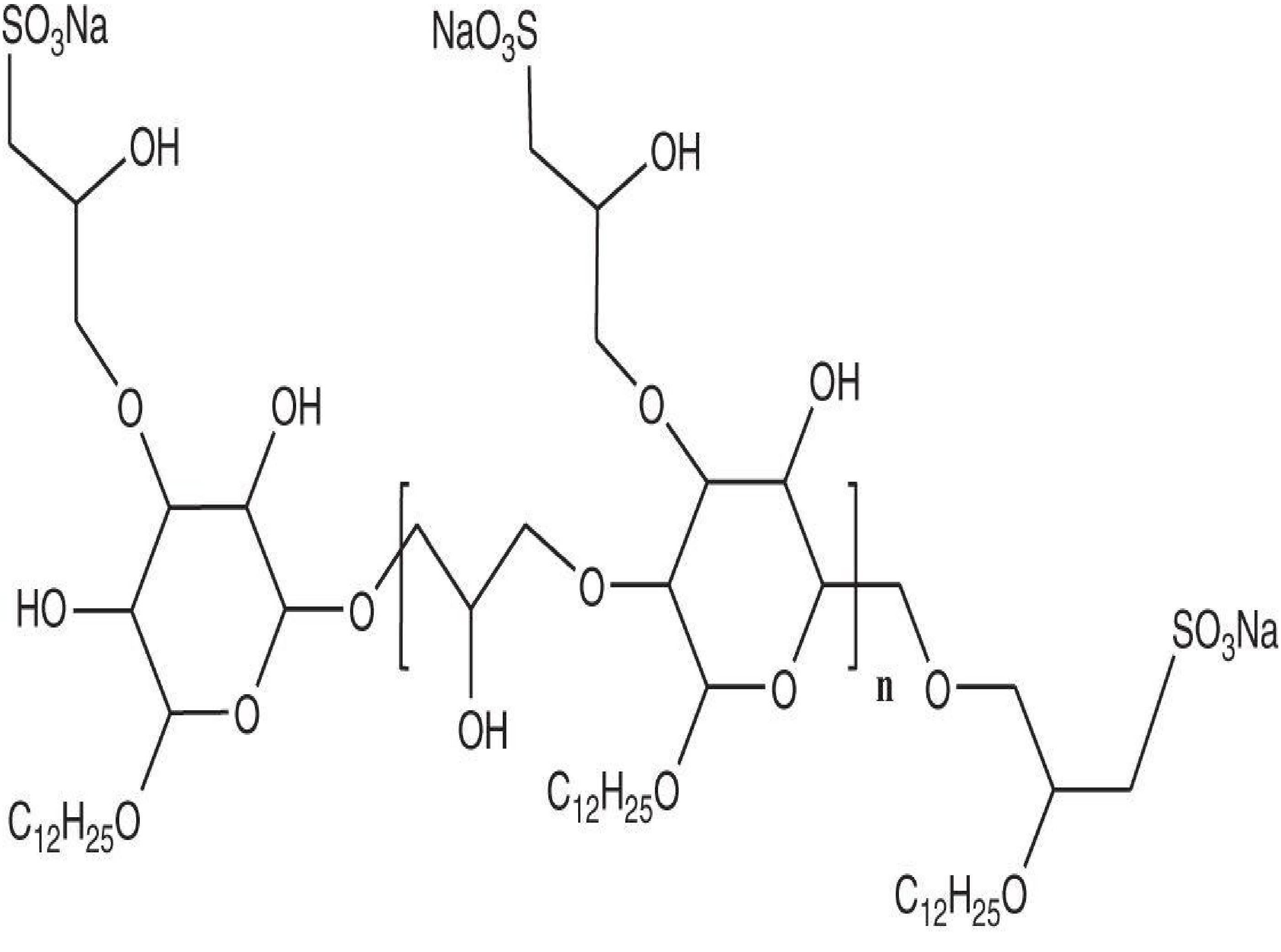
3. Biorenewable polyphosphate functionalized lauryl polyglucosides, (V), exhibiting excellent detergency were prepared by Hodge.[3] Functionalized lauryl polyglucosides were subsequently used as a nonylphenol ethoxylate replacement additive to prepare environmentally friendly and non-toxic detergent formulations. (See Fig. 21.13.)



(V)

Figure 21.13

4. Hodge[4] prepared a biorenewable and environmentally friendly laundering composition using polysulfonate functionalized lauryl polyglucosides, (VI), as a replacement additive for nonylphenol ethoxylates. Detergent packages containing polysulfonate functionalized lauryl polyglucosides were capable of cleaning fabrics containing both heavy soil and (up to) 20 percent dried proteins. (See Fig. 21.14.)



(VI)

Figure 21.14

References

1. Amanda Ruth Blattner et al., *Cleaning composition with surface modification polymer*, U.S. Patent Application 20130072419 (March 21, 2013)

2. Charles Allen Hodge et al., *Betaine functionalized alkyl polyglucosides for enhanced food and soil removal*, U.S. Patent Application 20130023458 (January 24, 2013)

3. Charles Allen Hodge et al., *Polyphosphate functionalized alkyl polyglucosides for enhanced food and soil removal*, U.S. Patent Application 20120322710 (December 20, 2012)

4. Charles Allen Hodge et al., *Polysulfonated functionalized alkyl polyglucosides for enhanced food and soil removal*, U.S. Patent Application 20120071388 (March 22,

2012)

Remediation of Municipal Waste Using Natural Non-Pathogenic Microbes

Author Michael T. Saul et al.

Patent Title ***Bioremediation methods,*** U.S. Patent 8,187,862 (May 29, 2012)

Relevant Prior Patents by Author or Coauthors

Bacterial parts washer, composition and method of use, U.S. Patent Application 20030235904 (December 23, 2003)

Remediation of contaminates including low bioavailability hydrocarbons, U.S. Patent 7,056,061 (July 6, 2006)

Biological cleaning system comprising microbes for digesting oils and/or greases, U.S. Patent 6,884,301 (April 26, 2006)

Bacterial parts washer, composition and method of use, U.S. Patent 6,762,047 (July 13, 2004)

Method for waste degradation, U.S. Patent 6,245,552 (July 12, 2001)

Bioremediation of petroleum pollutants with alkane-utilizing bacteria, U. S. Patent 6,110,372 (August 29, 2000)

Product Application

Municipal articles contaminated with petroleum or petroleum waste products were remediated using the natural non-pathogenic microbes, Pseudomonas putida strains B and –E. Decontaminated articles were then transferred to a non-toxic landfill to prepare mulch.

Significance of Current Application

Municipalities must continuously address costs associated with municipal waste. In the current investigation, a municipal-waste bioremediation method was developed to address the disposal and handling of petroleum-contaminated waste. The method developed to address this problem is simple, does not require the use of energy, and decontaminates petroleum-contaminated soil or other waste by treating them with Pseudomonas putida strains B and –E. The only necessary requirement to successfully remediate petroleum-contaminated soil or other waste is that moderate mixing is required for time periods ranging from one to three weeks. Once petroleum-contaminated soil or other waste has been successfully processed, the contamination-free soil is used to prepare garden mulch.

Remediation Components

A. Definition and effectiveness. Pseudomonas putida strains B and –E are gram-negative, rod-shaped saprotrophic soil bacterium. Both demonstrate a unique ability to metabolize and degrade organic compounds contained in oil. Blends containing these two biological strains are preferred to other Pseudomonas analogues since they are not opportunistic human pathogens when used in either degradation or remediation applications.

B. Organic compounds preferred by pseudomonas putida strains B and - E. Pseudomonas putida strains B and –E are highly effective in metabolizing the following toxic chemical agents contained in petroleum products, fuel oil, and oil.

A. Benzene
B. Toluene
C. Ethylbenzene
D. Xylenes
E. Petroleum constituents in gasoline-contaminated media
F. Fuel oils and heavier petroleum products
I. Trimethylbenzenes
J. Polycyclic aromatic hydrocarbons including:
Naphthalene, anthracene, acenaphthene, acenaphthylene, benzo(a) anthracene, benzo(a)pyrene, benzo(b) pyrene, fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, and pyrene
K. Halogenated aliphatic and aromatic compounds such as: Aldrin, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, carbon tetrachloride, chlorobenzene, chlorotoluenes, dichlorobenzene, dichloroethanes, dichloroethylene, dichlorotoluene, tetrachloroethane, trichloroethane, pentachlorophenol, and vinyl chloride.

Experimental

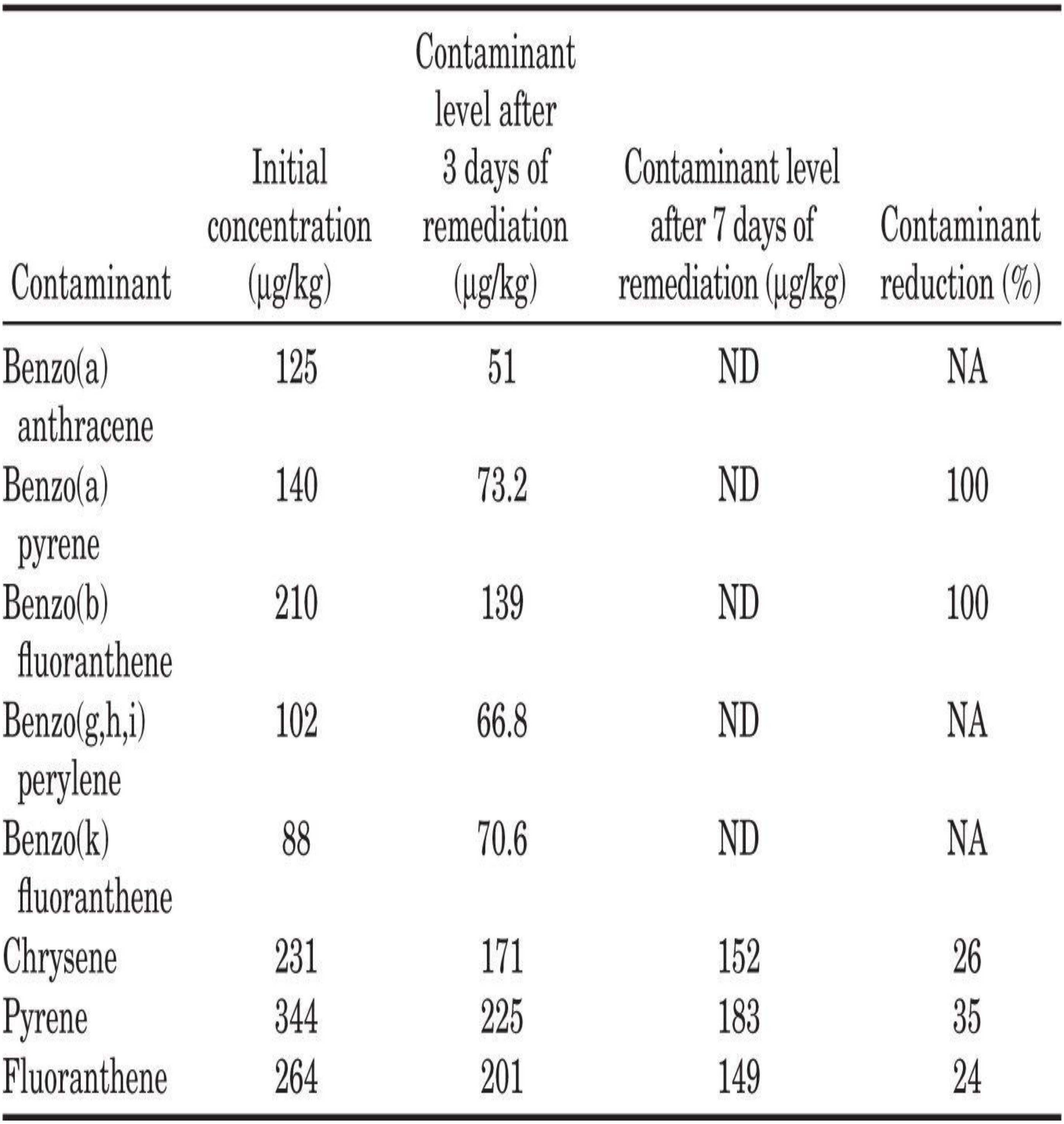
1. Remediation of municipal waste using Pseudomonas putida strains B and – E (PETROX 18 ®). Municipal debris from street-sweeping operations was collected then filtered to remove glass, metal, and other large pieces of refuse. Material containing petroleum-based contaminants was then moved to a test container consisting of a

100-ft × 8-ft × 2-ft

windrow. Once the container was filled with petroleum-contaminated materials, a SCAT® windrow turner aerated and homogenized the material by carrying it several feet above its initial level and dropping it back to the ground. An initial reference sample of untreated debris was removed and used as a control.

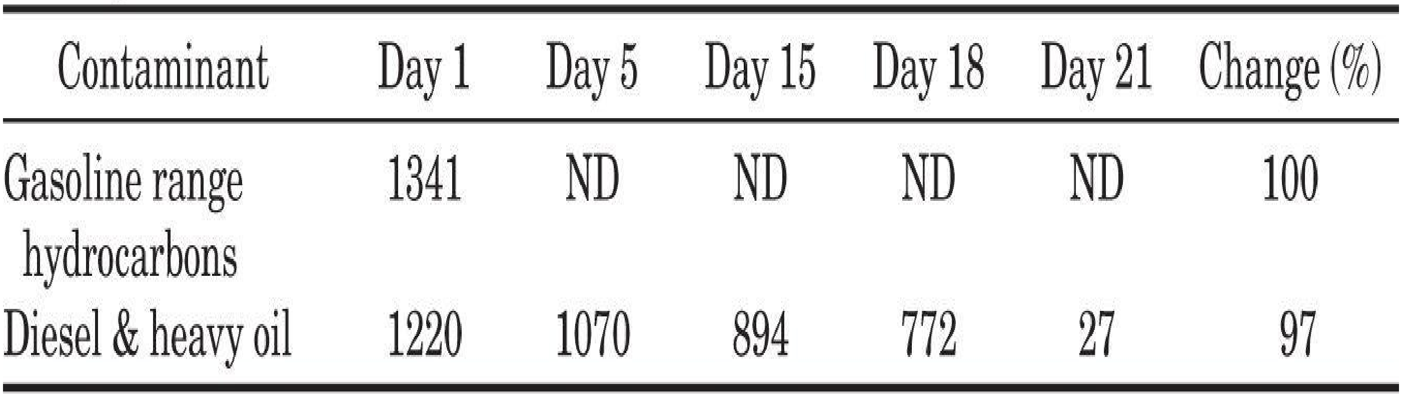
Four sealed drums containing freeze-dried lyophilized PETROX 18 were then delivered to the remediation site and then mixed with 500 gal of water. This mixture was then sprayed onto the municipal debris while turning and mixing the debris to ensure even exposure to PETROX 18. Solid sample aliquots were then collected after 3, 7, and 21 days of treatment. Since the temperature during the treatment period averaged 95°F, water was sprayed onto the treated mixture throughout the remediation period to maintain a temperature of ~90° **F**. Degradation products of selected petroleum, polycyclic aromatics, and other miscellaneous organic contaminants after 3 and 7 days were then evaluated using gas chromatography (analytical results are provided in Table 21.6). Additional degraded samples were also removed after 1, 5, 15, 18, and 21 days (analytical test results provided in Table 21.7).

TABLE 21.6 Effect of PETROX 18 in lowering chemical contaminants present in petroleum-contaminated municipal waste after 3 and 7 days.



Contaminant	Initial concentration (μg/kg)	Contaminant level after 3 days of remediation (μg/kg)	Contaminant level after 7 days of remediation (μg/kg)	Contaminant reduction (%)
Benzo(a) anthracene	125	51	ND	NA
Benzo(a) pyrene	140	73.2	ND	100
Benzo(b) fluoranthene	210	139	ND	100
Benzo(g,h,i) perylene	102	66.8	ND	NA
Benzo(k) fluoranthene	88	70.6	ND	NA
Chrysene	231	171	152	26
Pyrene	344	225	183	35
Fluoranthene	264	201	149	24

TABLE 21.7 Effect of PETROX 18 in lowering petroleum contaminants present in municipal waste after a total of 21 days.



Contaminant	Day 1	Day 5	Day 15	Day 18	Day 21	Change (%)
Gasoline range hydrocarbons	1341	ND	ND	ND	ND	100
Diesel & heavy oil	1220	1070	894	772	27	97

Notes and Observations

1. Meyer[1] used combinations of E. coli and pseudomonas putida strains B and –E to degrade selective nitroaromatics such as m-nitrotoluene, m-nitrobenzyl alcohol, m-nitrobenzaldehyde, and m-nitrobenzoic acid into non-toxic and innocous materials.

2. Seeger Pfeiffer[2] developed a bioremediation method for removing polychlorobiphenyls containing from one to three chlorine atoms. In this method, polychlorobiphenyls were successfully degraded using Cupriavidus necator strain JMS34. This bioremediation process completely degraded or minimized polychlorobiphenyl contaminants.

3. Baseeth[3] prepared a microemulsion composition consisting of 38 wt% soy soapstock, 45 wt% ethyl lactate, 12 wt% ethoxylated monoglyceride, and 5 wt% chemically modified lecithin. This blend was effective in decontaminating mixed cultures of halo-respiring bacteria present in contaminated well water.

4. Dong[4] prepared 0.5–2.36 mm granules containing a $FeOSi(OH)_3$ by reacting FeOOH and H_4SiO_4. Surface complexes of the granule were effective in absorbing arsenite and arsenate ions and other heavy metal ions in a pH range of 2 to 10.

References

1. Daniel Meyer et al., Suitability of recombinant Escherichia coli and Pseudomonas putida strains for selective biotransformation of m-nitrotoluene by xylene monooxygenase, *Appl. Environ. Microbiol.*, 71 (11), 6624–6632 (November, 2005)

2. Michael Seeger Pfeiffer et al., *PCB-degrading recombinant bacterium, product for the bioremediation and method of bioremediation*, U.S. Patent 7,989,194 (August 2, 2011)

3. Shireen Baseeth et al., *Microemulsion for bioremediation*, U.S. Patent 8,377,329 (February 19, 2013)

4. Liganjie Dong, *Methods and compositions for removal of arsenic and heavy metals from water*, U.S. Patent 8,361,920 (January 29, 2013)

Water Remediation Contaminated with Perchloroethene

Author	Shireen Baseeth et al.
Patent Title	***Microemulsion for bioremediation methods,*** U.S. Patent 8,377,329 (February 13, 2013)

Relevant Prior Patents by Author or Coauthors

Methods of bioremediation, U.S. Patent Application 20120056127 (March 8, 2012)

Water dispersible compositions and methods of using the water dispersible compositions, U.S. Patent 8,080,266 (December 20, 2011)

Methods of remediation of water, U.S. Patent 8,057,675 (November 15, 2011)

Compositions and uses thereof in bioremediation, U.S. Patent 7,785,468 (August 30, 2010)

Methods of bioremidation, U.S. Patent Application 20100314312 (December 16, 2010)

Product Application

Remediation of well water contaminated with perchloroethenes was efficiently accomplished by treating the water with a microemulsioncontaining soy soapstock, ethyl lactate, ethoxylated monoglyceride, and lecithin.

Significance of Current Application

Chlorinated solvents are the most common class of groundwater contaminants found at hazardous waste sites in the United States. For example, an EPA list of the top 25 most frequently detected contaminants at polluted well water sites indicated that the top ten were either chlorinated solvents or their degradation products. As a result of these observations there is a pressing need for water remediation on sites contaminated with chlorinated solvents or chlorinated solvent by-products. It is preferable that the water remediation process requires the use of inexpensive biorenewable reagents that quickly convert perchloroalkane derivatives into innocuous materials. The current investigation has identified a simple method that directly addresses these concerns.

Emulsion Requirements

The emulsion composition was designed to remove chlorinated solvents or chlorinated solvent by-products. The emulsion can consist of up to six renewable components. In addition, the emulsion itself can consist of as few as four renewable components or as many as six renewable components.

Emulsion Components

Component 1. Ethoxylated monoglyceride, (I).

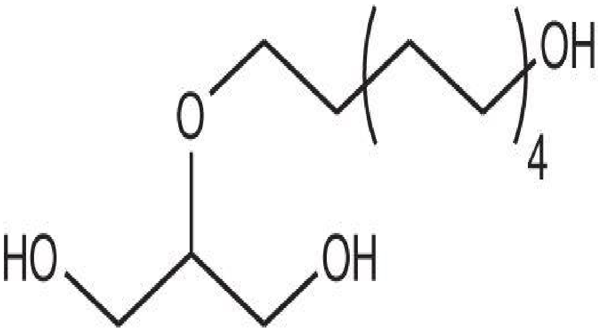
Component 2. Soybean soapstock composition can consist of as many as nine or more components; three of these components are illustrated, (II).

Component 3. Lecithin, (III).

Component 4. Sodium stearoyl lactate, (IV).

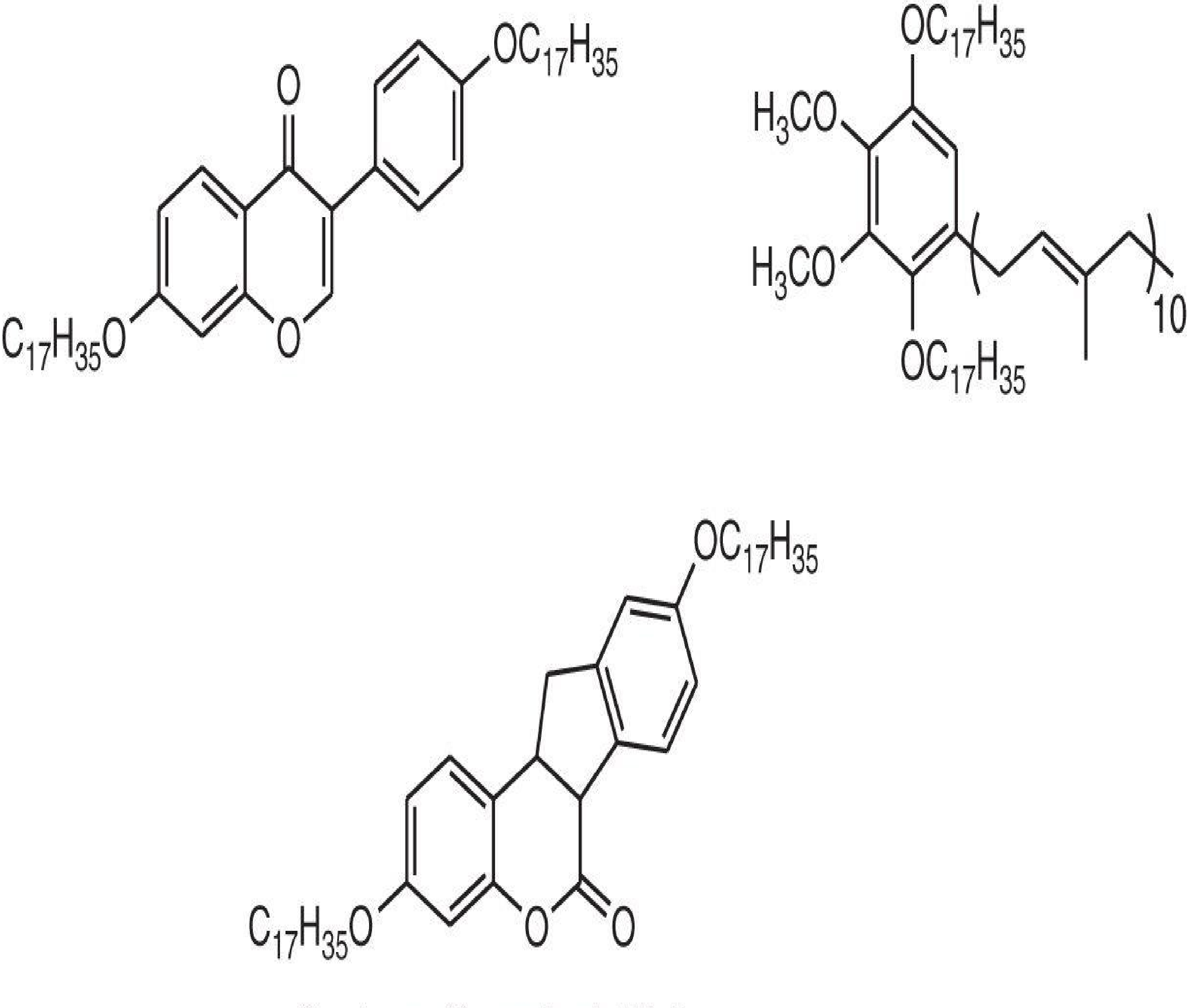
Component 5. Ethyl lactate, (V).

Component 6. Polylactate, (VI).



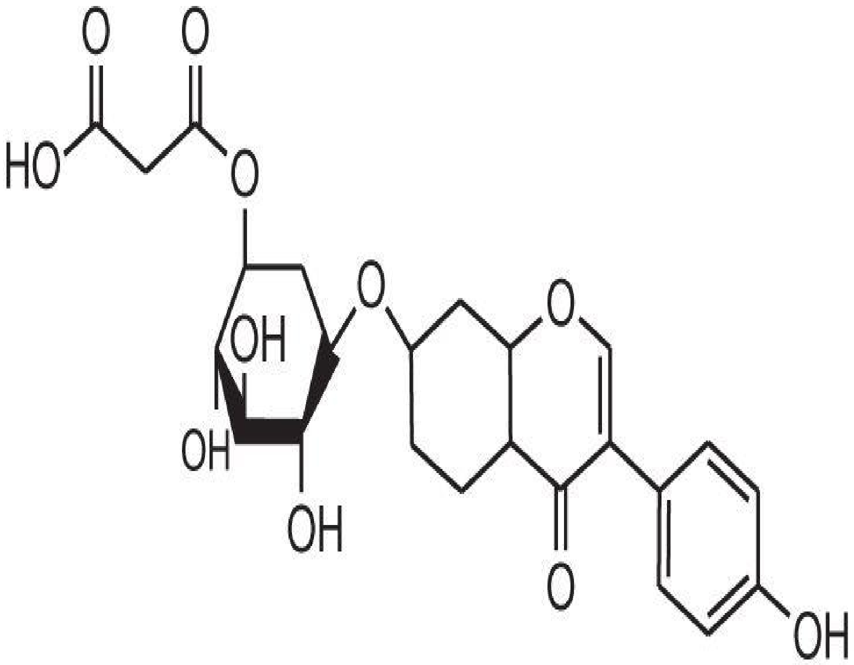
Ethoxylated Monoglyceride

(I)



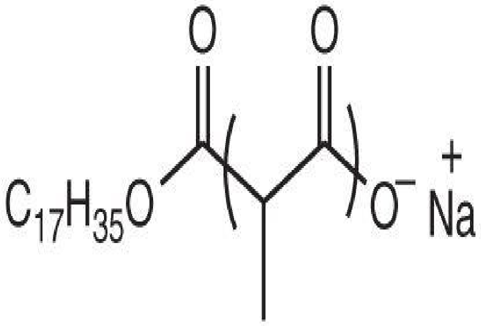
Soybean Soapstock Mixture

(II)



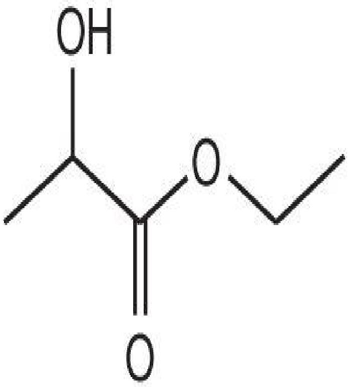
Lecithin

(III)



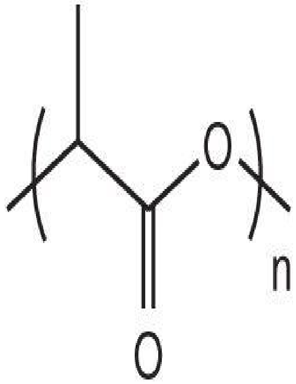
Sodium Stearoyl Lactylate

(IV)



Ethyl Lactate

(V)



Polylactate

(VI)

Figure 21.15

Emulsion Formation and Particle Size

Mixtures were prepared by blending four to six components in specified ratios. Components used in the blend could consist of ethoxylated monoglyceride, (I); soy soapstock, (II); lecithin, (III); sodium stearoyl lactylate, (IV); ethyl lactate, (V); or polylactate, (VI). Component mixtures were mechanically ground at ambient temperature until an average particle size of 100 nm or less was obtained.

Experimental

1. Preparation of a solid four-component blend. A four-component blend was prepared consisting of 38 wt% of soy soapstock, 45 wt% of ethyl lactate, 12 wt% of ethoxylated monoglyceride, and 5 wt% of lecithin. The four-blend mixture was then placed into a mortar and thoroughly ground together using a glass paddle.

2. Preparation of a four-component microemulsion. After mixing the Step1 blend, it was homogenized under high-shear mixing between 30 minutes and 60 minutes at ambient temperature. The homogenized blend was then poured into a 250-mL graduated cylinder containing 100 mL of water. After gently shaking the water and the four-component homogenized mixture, a microemulsion immediately formed. This microemulsion remained stable and unchanged for over 30 days, and photomicrographs indicated that the microemulsion had an average particle-size distribution of less than 100 nm.

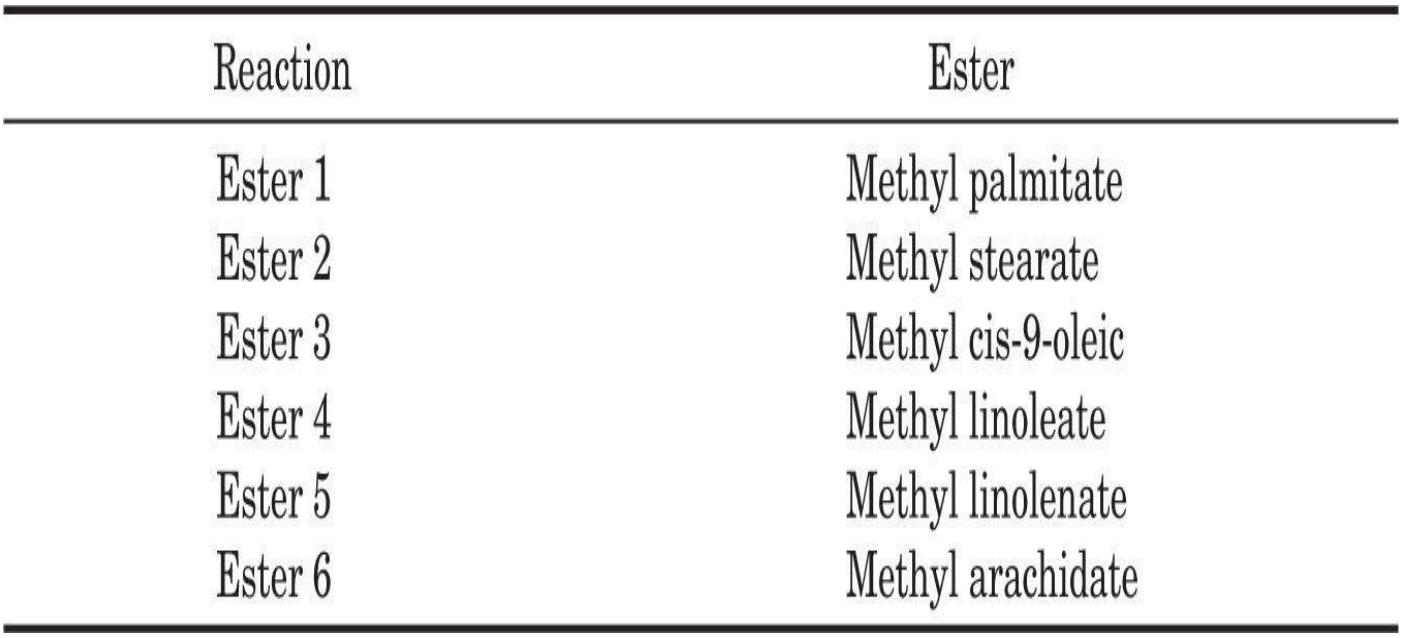
3. Preparation of perchloroethene-free water using the four-component microemulsion.

A control degradation system for bioremediating contaminated groundwater microcosms was constructed and consisted of 160-mL serum bottles, 100 mL of groundwater, 1 g of limestone, 19.54 mmol of perchloroethene, PCE, an excess of various electron donors, and 3 mL of inoculum containing dechlorinating bacteria known to convert PCE to ethane. The inoculum consisted of halo-respiring bacteria that had been enriched to obtain optimal cell density. Three serum bottles, however, were additized with the microemulsion produced in Step 2 of this investigation. Each serum bottle of the model bioremediation study began using a specified amount of PCE. Throughout the degradation process, trichloroethene (TCE), cis-dichloroethene (DCE), vinyl chloride (VC), and ethane were monitored using gas chromatography. Sampling of serum-glass containers was done three to four times daily over a 70-day period. The serum container, additized with the Step 2 microemulsion, degraded perchloroethene by over 75 percent within the first 24-hour period. The aqueous microemulsion remediation agent also degraded the remaining perchloroethene and the chlorinated intermediates including trichloroethene, cis-dichloroethene, and vinyl chloride. The remediation time period needed to remove the remaining perchloroethene, intermediates including trichloroethene, cis-dichloroethene, and vinyl chloride was 6 days.

Notes and Observations

1. Soy soapstock esters used as a remediation component in the treatment were previously prepared by McNeff [1] in high yields. The fatty esters were prepared using a slurry of the fatty acid precursor and then catalyzed using modified zirconia dioxide particles having a diameter between 0.5 μm and 15 μm. For example, the esterification of soybean oil with a butanol using modified zirconia dioxide was performed at 55°C using eqimolar amounts of acid-to-alcohol. The product was isolated in >95% yield. Other remediation esters are provided in Table 21.8.

TABLE 21.8 Fatty esters prepared by reacting eqimolar amounts of the fatty acid and alcohol. The reaction was catalyzed by zirconia dioxide. Yields typically were > 95%.



Reaction	Ester
Ester 1	Methyl palmitate
Ester 2	Methyl stearate
Ester 3	Methyl cis-9-oleic
Ester 4	Methyl linoleate
Ester 5	Methyl linolenate
Ester 6	Methyl arachidate

2. In an earlier investigation by the author,[2] a composition consisting of soapstock, ethoxylated monoglyceride, lecithin, sodium stearoyl lactylate, polylactate, and ethyl lactate was used to prepare emulsifiable oil formulations. The six-component mixture was then used to decompose a variety of percloroalkanes present in a contaminated ground-water site. Water-remediation treatment levels of 0.2 mL of the emulsion with 100 mL of perchloro-contaminated water were notably effective.

3. Kent[3] removed halogenated solvents from contaminated well water using a mixture of sodium lactic, ethyl lactate, and metallic iron powder. Water remediation time for this dehalogenation method typically required 9 to 12 months.

4. Mierswa[4] devised a method to reduce the amount of waterborne bacteria and viruses present in biologically polluted well water. The method used a converter electrically coupled with a microprocessor. This electronic remediation process produces two delayed-control signals in two connected transistors at a frequency between 2 kHz and 5 kHz by a controlled electric field.

References

1. Clayton V. McNeff et al., *Methods and apparatus for producing alkyl esters from lipid feed stocks and systems including same*, U.S. Patent 7,897,798 (March 1, 2011)

2. Shireen Baseeth et al., *Compositions and uses thereof in bioremediation*, U.S. Patent 7,785,468 (August 31, 2010)

3. Kent S. Sorenson, Jr., *Halogenated solvent remediation*, U.S. Patent Application 20050109696 (May 26, 2005)

4. Sven Mierswa, *Reducing waterborne bacteria and viruses by a controlled electric field*, U.S. Patent 8,382,992 (February 26, 2013)

Chapter

22

Roadway Repairs

Asphalt Recycling Using Fatty Acid/Esters

Author	Christine Deneuvillers et al.
Patent Title	***Vegetable-based products of the succative type for recycling and rejuvenating reclaimed asphalt pavements in situ or in a dedicated plant,*** U.S. Patent Application 20120315088 (December 13, 2012)

Relevant Prior Patents by Author or Coauthors

Resins of natural origin derived from vegetable oil and from hydroxyacids, U.S. Patent Application 20100010245 (January 14, 2010)

Use of biopolymer-based binder for roads, road-related and civil engineering applications, U.S. Patent 8,207,254 (January 26, 2012)

Use of solvents derived from renewable resources, paints and coating including them, method for preparing them, U.S. Patent 8,317,911 (November 27, 2012)

Method for preparing fatty acid esters of natural origin functionalized by oxidation for use as fluxing oils for bitumen, U.S. Patent Application 20080250975 (October 16, 2008)

Product Application

A two-component renewable solvent consisting of Vegeflux®, which consists of fatty acids, fatty esters, and Tall Oil, which is a very complex mixture of both high-molecular fatty acids and very high-molecular-weight alcohols, has been found to be effective in recycling bitumen and asphalt. Roads rejuvenated from these blends were determined to be durable, stable, and resistant to wear.

Significance of Current Application

The current investigation has identified a renewable additive mixture that can be used to recycle old or damaged asphalt pavement. Traditionally, impaired or discarded asphalt has been rejuvenated by extensive heating with non-renewable petrochemicals, notably polyaromatics, for roadway repair and maintenance. However, polyaromatics are suspected of being toxic and carcinogenic, and the extensive heating of petrochemicals causes them to flow and volatilize, which can lead to their persistence in the air, water, and soil.

Finally, the current method for recycling asphalt can be characterized as being energy intensive, inefficient, and dangerous.

It is anticipated that combinations of naphthalene derivatives and low-molecular-weight aromatics will be used as replacement agents for petrochemicals containing polyaromatics. The aquatic toxicity of this combination remains unclear.

The current investigation directly addresses all of these concerns while using renewable food-grade fatty acids and esters as asphalt binding agents. In the initial phase, all chemical agents are non-toxic, and once the asphalt blend using food-grade fatty acids and esters is formed, it can be used to repair any form of either loose or damaged asphalt.

Renewable Chemical Agents

1. Vegeflux® 20/30 PJ. A neutral fatty acid and ester mixture surfactant meeting the following technical requirements:

A. Water content NF T 60-113% < 0.5

B. Relative density at 25° C = 0.88 to 0.98 [ISO 3838 testing protocol]

C. Viscosity at 40° C mm^2/s = 7 to 11

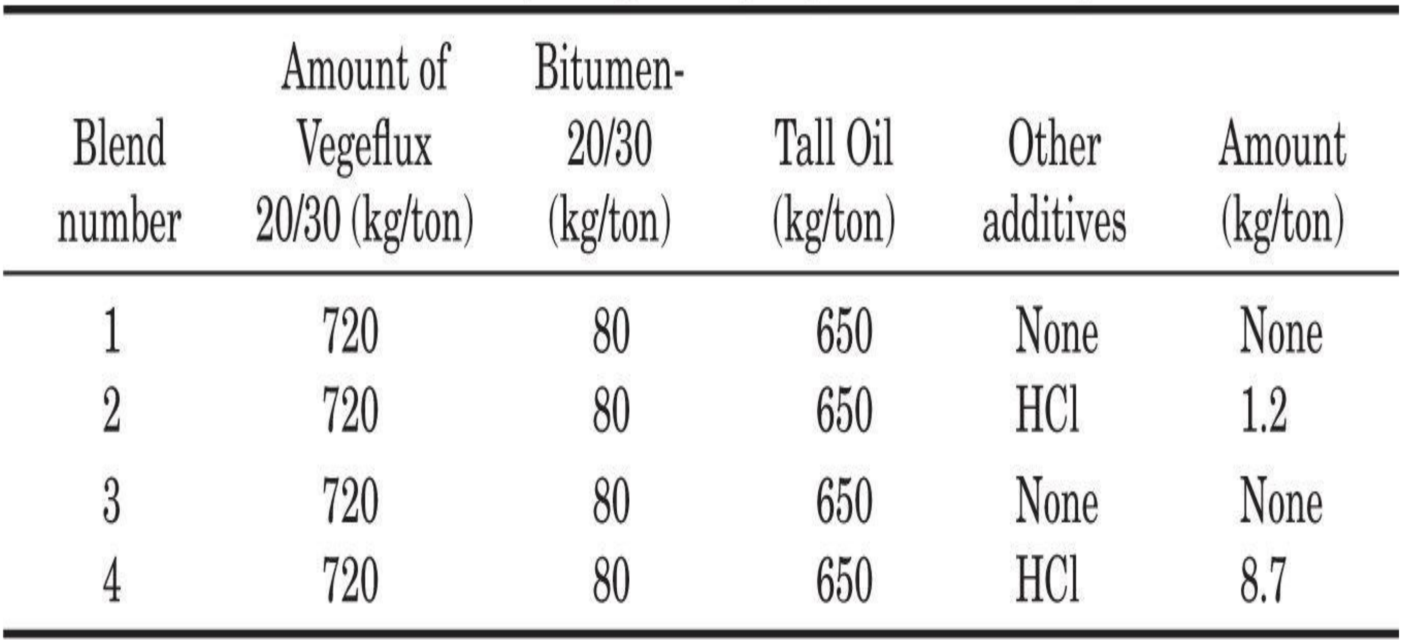
D. Cleveland flash point >160 ° C [EN ISO 2592 testing protocol]

2. Tall Oil. A high-molecular-weight acid and ester mixture consisting of rosins, 15% unsaponifiable eterols, resins acids, notably abietic acid and isomers, palmitic, oleic, and linoleic acids, fatty alcohols and stetols, as well as alkyl hydrocarbon derivatives.

Experimental

1. Formation of blends using reclaimed asphalt pavements. Blends were prepared using 20 mm to 0.063 mm of milled asphalt having a bitumen content of 5.2% to 3.8% and water content of 4.5% to 3.0%. Asphalt blending formulations are provided in Table 22.1.

TABLE 22.1 Asphalt rejuvenating compositions. All blends prepared in these formulations were effective in repairing damaged pavements or asphalt roads.

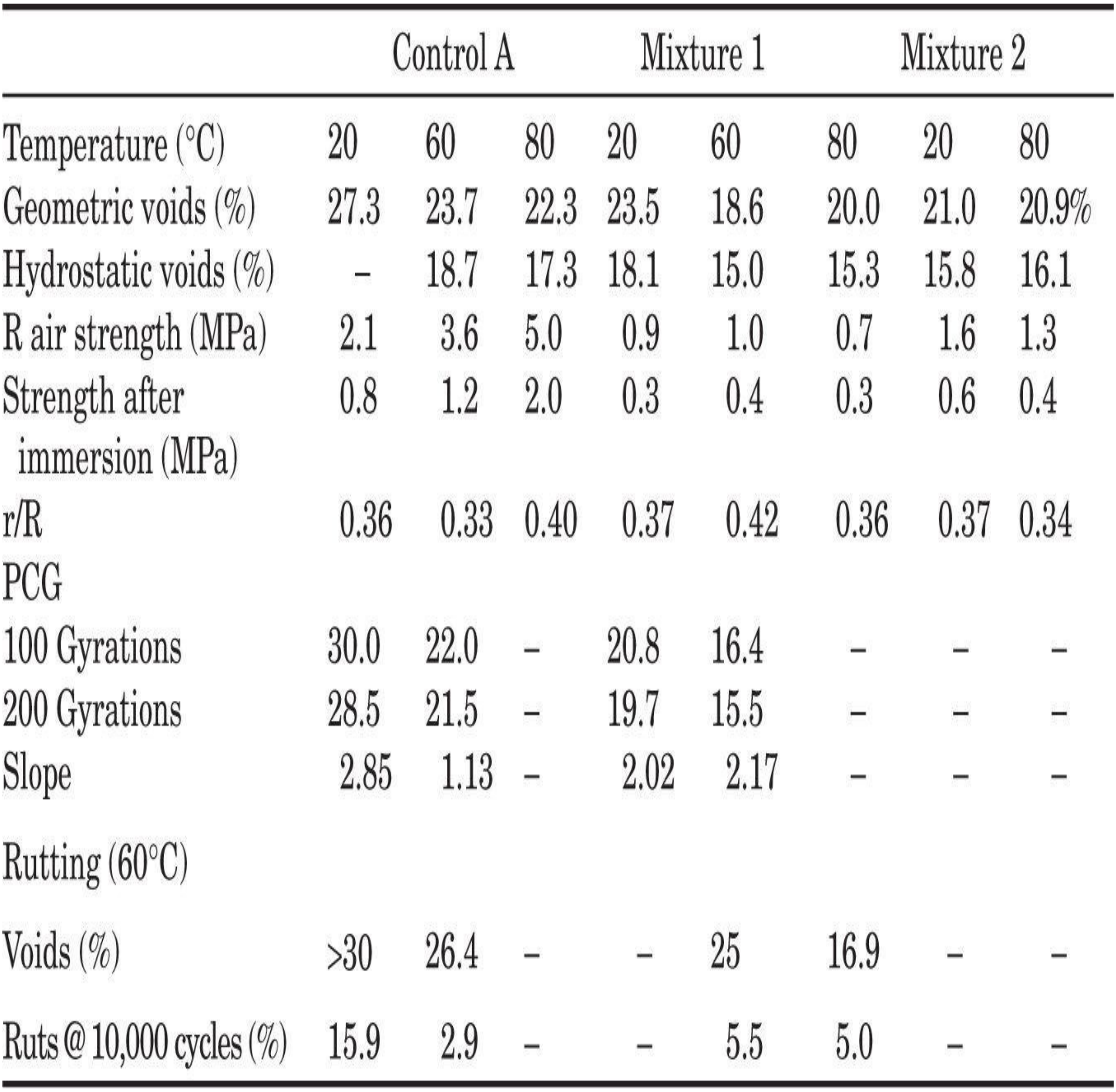


Blend number	Amount of Vegeflux 20/30 (kg/ton)	Bitumen-20/30 (kg/ton)	Tall Oil (kg/ton)	Other additives	Amount (kg/ton)
1	720	80	650	None	None
2	720	80	650	HCl	1.2
3	720	80	650	None	None
4	720	80	650	HCl	8.7

Testing

A. Rutting assay. Rutting assay of experimental blends was evaluated according to standard NF EN 12697-22. In this test the rutting resistance of asphalt blends under typical road conditions was duplicated and compared to the stresses prevailing on public roadways. The rut-depth evolution was measured as a function of the number of cycles, and the assays were performed on 5- and 10-cm-thick mix plates that had been conditioned by heating to 35°C for 14 to 15 days. Testing results are provided in Table 22.2.

TABLE 22.2 Rutting test results using recycled asphalt containing Vegeflux 20/30 PJ and Tall Oil. In all instances, blends demonstrated excellent workability and rutting resistance.



	Control A			Mixture 1			Mixture 2	
Temperature (°C)	20	60	80	20	60	80	20	80
Geometric voids (%)	27.3	23.7	22.3	23.5	18.6	20.0	21.0	20.9%
Hydrostatic voids (%)	–	18.7	17.3	18.1	15.0	15.3	15.8	16.1
R air strength (MPa)	2.1	3.6	5.0	0.9	1.0	0.7	1.6	1.3
Strength after immersion (MPa)	0.8	1.2	2.0	0.3	0.4	0.3	0.6	0.4
r/R	0.36	0.33	0.40	0.37	0.42	0.36	0.37	0.34
PCG								
100 Gyrations	30.0	22.0	–	20.8	16.4	–	–	–
200 Gyrations	28.5	21.5	–	19.7	15.5	–	–	–
Slope	2.85	1.13	–	2.02	2.17	–	–	–
Rutting (60°C)								
Voids (%)	>30	26.4	–	–	25	16.9	–	–
Ruts @ 10,000 cycles (%)	15.9	2.9	–	–	5.5	5.0	–	–

Testing Results

Notes and Observations

1. Bricout[1] prepared blends of used agriculturally derived biosolvents and the binder, Vegeflux, in paint formulations containing up to 17 wt% pigments and 44% calcium carbonate filler to reduce toxic organic-solvent emissions from drying paint.
2. Takamura[2] prepared a mixture consisting of an aqueous emulsion of polystyrene, ethylenediamine tetraacetic, sodium hydroxide, and n-butyl acrylate and then free radically polymerized the mixture using sodium persulfate. The resulting polymer latex was then blended with pulverized recycled asphalt to form a surface-wetting substrate that was subsequently reused in repairing pavement.
3. Reinke[3] eliminated the use of environmentally toxic petrochemical-based lubricants required for recycling warm asphalt by replacing petrochemical-based lubricants with environmentally friendly Sasobit®, (I), and Montan waxes, (II). (See Fig. 22.1.)

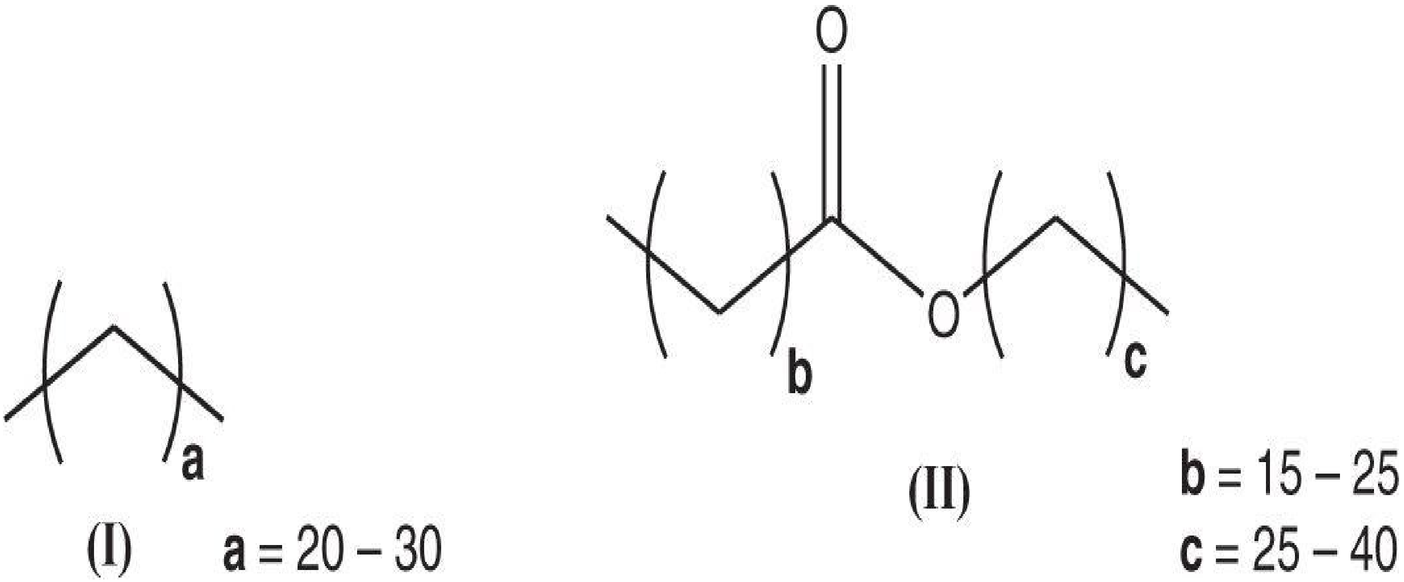


Figure 22.1

4. Luccarelli[4] used a mixture of renewable pine extract and biodiesel as an asphalt solvent replacement for petrochemical-based lubricants. Solutions prepared from renewable pine extract and biodiesel had a very low viscosity but were completely workable in repairing asphalt roads at ambient temperature.

References

1. Xavier Bricout et al., *Use of solvents derived from renewable resources, paints and coating including them, method for preparing them*, U.S. Patent Application 20090211486 (August 27, 2009)

2. Koichi Takamura et al., *Method and composition for enhancing the performance of an emulsion-based surface treatment*, U.S. Patent Application 20120322922 (December 20, 2012)

3. Gerald H. Reinke et al., *Warm mix asphalt binder compositions containing lubricating additives*, U.S. Patent 8,323,394 (December 4, 2012)

4. Charles J. Luccarelli et al., *Asphalt mix workable at ambient temperatures with only biodegradable solvents and method of manufacturing the same*, U.S. Patent 8,287,635 (October 16, 2012)

Glycerol, Triglycerides, and Lactic Acid Bitumen Binders

Author Christine Deneuvillers

Patent Title ***Use of a biopolymer-based binder for roads, road-related and civil engineering applications,*** U.S. Patent 8,207,254 (June 26, 2012)

Relevant Prior Patents by Author

Use of solvents derived from renewable resources, paints and coating including them, method for preparing them, U.S. Patent 8,317,911 (November 12, 2012)

Method for preparing fatty acid esters of natural origin functionalized by oxidation for use as fluxing oils for bitumen, U.S. Patent 7,951,238 (May 31, 2011)

Resins of natural origin derived from vegetable oil and from hydroxy acids, U.S. Patent Application 20100010245 (January 14, 2010)

Product Application

Engineering blends derived from bitumen and renewable biopolymer binders consisting of the reaction products of glycerol, triglycerides, and lactic acid were determined to be effective in repairing roads and in related civil engineering projects.

Significance of Current Application

Road works and related civil engineering projects utilizing bitumen currently use acrylic-type vinylic latexes as the binding agent. Although acrylic-type vinylic latexes are effective binders, they are derived from either fossil fuel sources or from petrochemicals. The current investigation has determined that the reaction product mixture of glycerol, triglycerides, and lactic acid can be used as vinylic-latex-replacement bitumen binders. Binder and bitumen replacement blends generated from this investigation can be used in other civil engineering projects such as building or repairing roads, formation of industrial and sport grounds or walkways, and related civil engineering applications. Finally, binder resins were all derived from renewable chemical agents. These agents include glycerol, triglycerides, and lactic acid. These three chemicals are non-toxic, non-hazardous, and are easily blended.

Product Formation

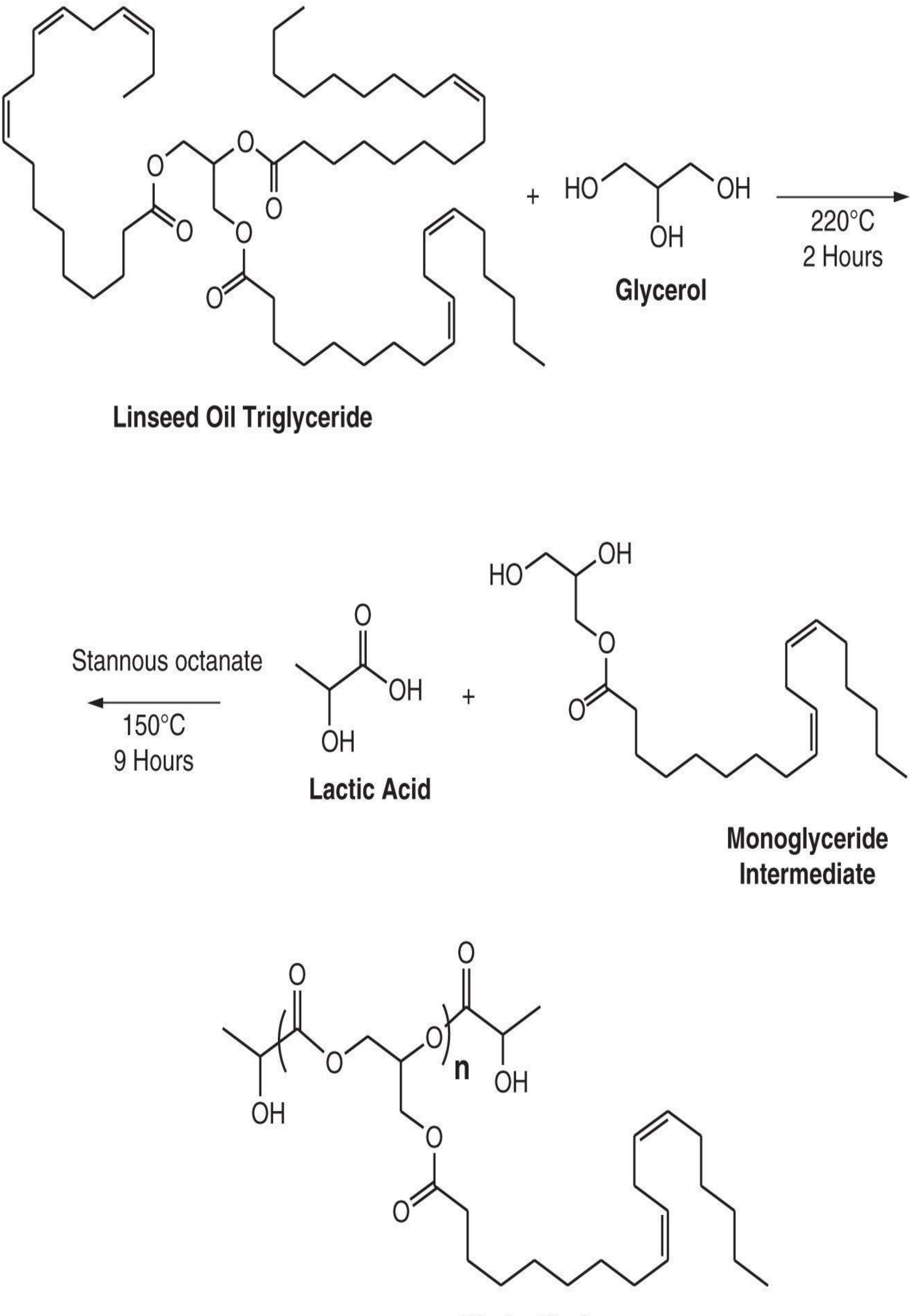

Linseed Oil Triglyceride
+
Glycerol
220°C
2 Hours
Monoglyceride Intermediate
+
Lactic Acid
Stannous octanate
150°C
9 Hours
n
Binder Resin

Figure 22.2

Experimental

1. Preparation of the monoglyceride intermediate. A glass reactor was charged with linseed triglyceride oil and glycerol in a [glycerol]/[oil] molar ratio of 2.0 and then heated to 220 °C for 2 hours. The reaction mixture was then treated with sodium hydroxide while measuring the reaction extend by HPLC. When HPLC indicated that the monoglyceride content exceeded 95% conversion, the mixture was cooled to ambient temperature and the product was isolated and used without any purification.

2. Preparation of the binder resin. A glass reactor was charged with the Step 1 product and lactic acid in a [lactic acid]/[mono glyceride] molar ratio of 12.0:5.0, respectively. The mixture was then heated for 9 hours at 150 °C and then cooled, and the reaction product was isolated as a white semi-solid.

3. Binder formulations. Three renewable resin binder formulations were prepared and then used in bitumen/binder blends. Resin binder formulations A1 through A3 are provided below.

A. Resin binder formulation A1. Resin binder formulation A1 consisted of 15% of the monoglyceride mixture derived from 80% linseed oil and 20% glycerol and 85% lactic acid.

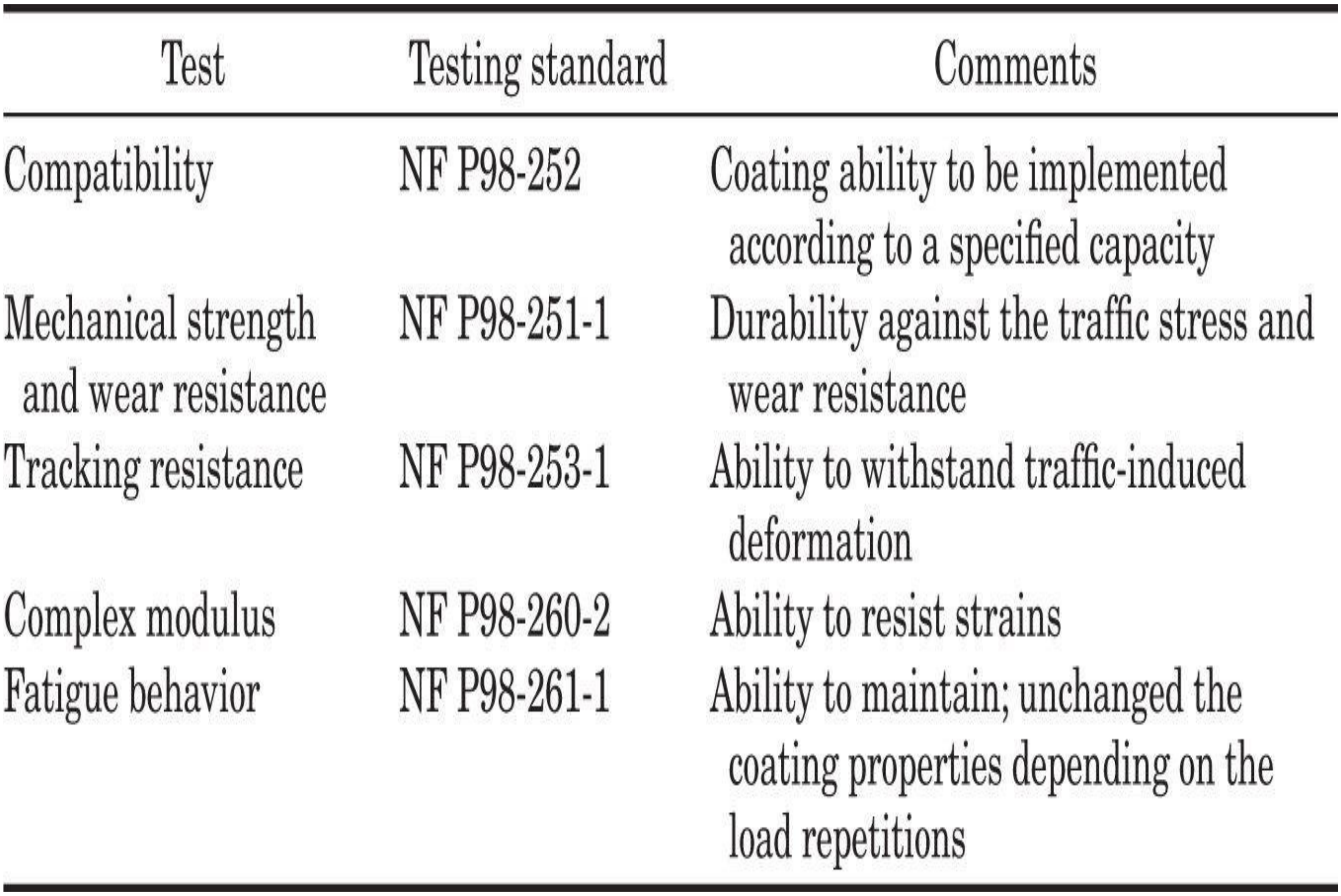
B. Resin binder formulation A2. Resin binder formulation A2 consisted of 15% of the monoglyceride mixture derived from 80% rapeseed oil and 20% glycerol and 85% of lactic acid.

C. Resin binder formulation A3. Resin binder formulation A3 consisted of a mixture of mono- and diglycerides obtained from castor oil and lactic acid where the molar ratio of mono- and diglyceride was 60:40, respectively, with a lactic acid to molar ratio of 25.0:1.0, respectively.

Testing

Testing was performed on bitumen blends containing resin binder formulations A1 through A3 using the testing protocols provided in Table 22.3.

TABLE 22.3 Testing protocols used to evaluate bitumen-resin binder formulation A1 through A3 blends when formulated in 85% to 97% aggregates containing 3–15% of the renewable resin.



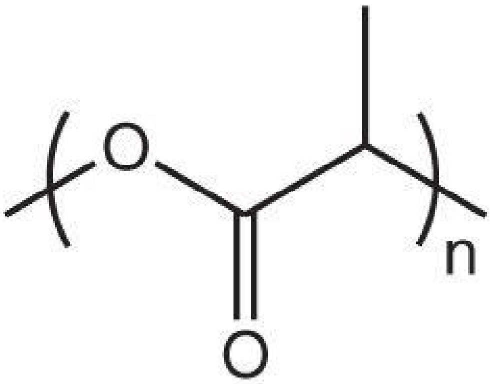
Test	Testing standard	Comments
Compatibility	NF P98-252	Coating ability to be implemented according to a specified capacity
Mechanical strength and wear resistance	NF P98-251-1	Durability against the traffic stress and wear resistance
Tracking resistance	NF P98-253-1	Ability to withstand traffic-induced deformation
Complex modulus	NF P98-260-2	Ability to resist strains
Fatigue behavior	NF P98-261-1	Ability to maintain; unchanged the coating properties depending on the load repetitions

Testing Results

Each bitumen and renewable binding resin performed satisfactorily and successfully passed all engineering testing.

Notes and Observations

1. Nelson[1] demonstrated that when blends of the biopolymer polylactic acid, (I), having a melt index of 5–6 and monomeric ethylene vinyl acetate were extruded at 170 °C very limited thermal degradation was observed. Engineered blends of polylactic acid and monomeric ethylene vinyl acetate with bitumen were subsequently prepared and used to repair surface damage on asphalt roadways. (See Fig. 22.3.)

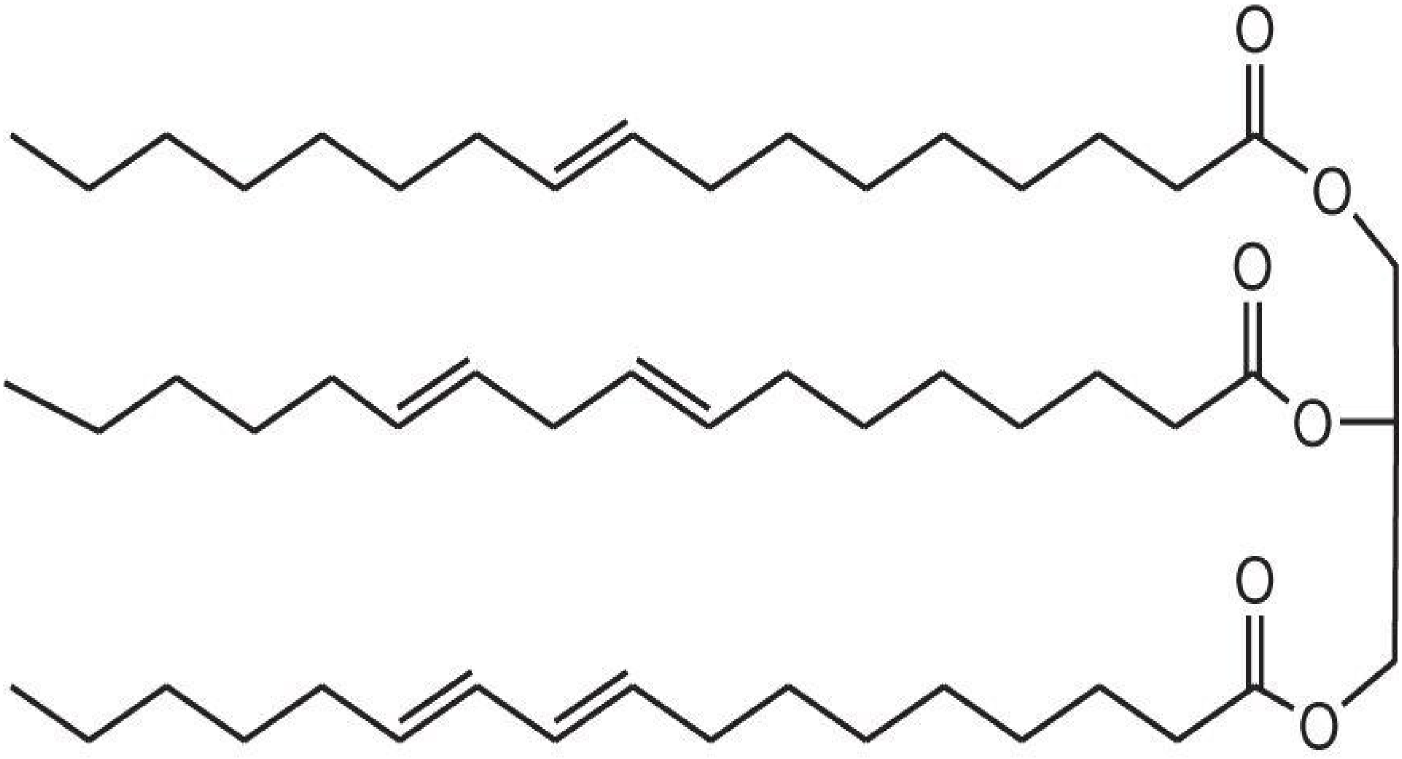


(I)

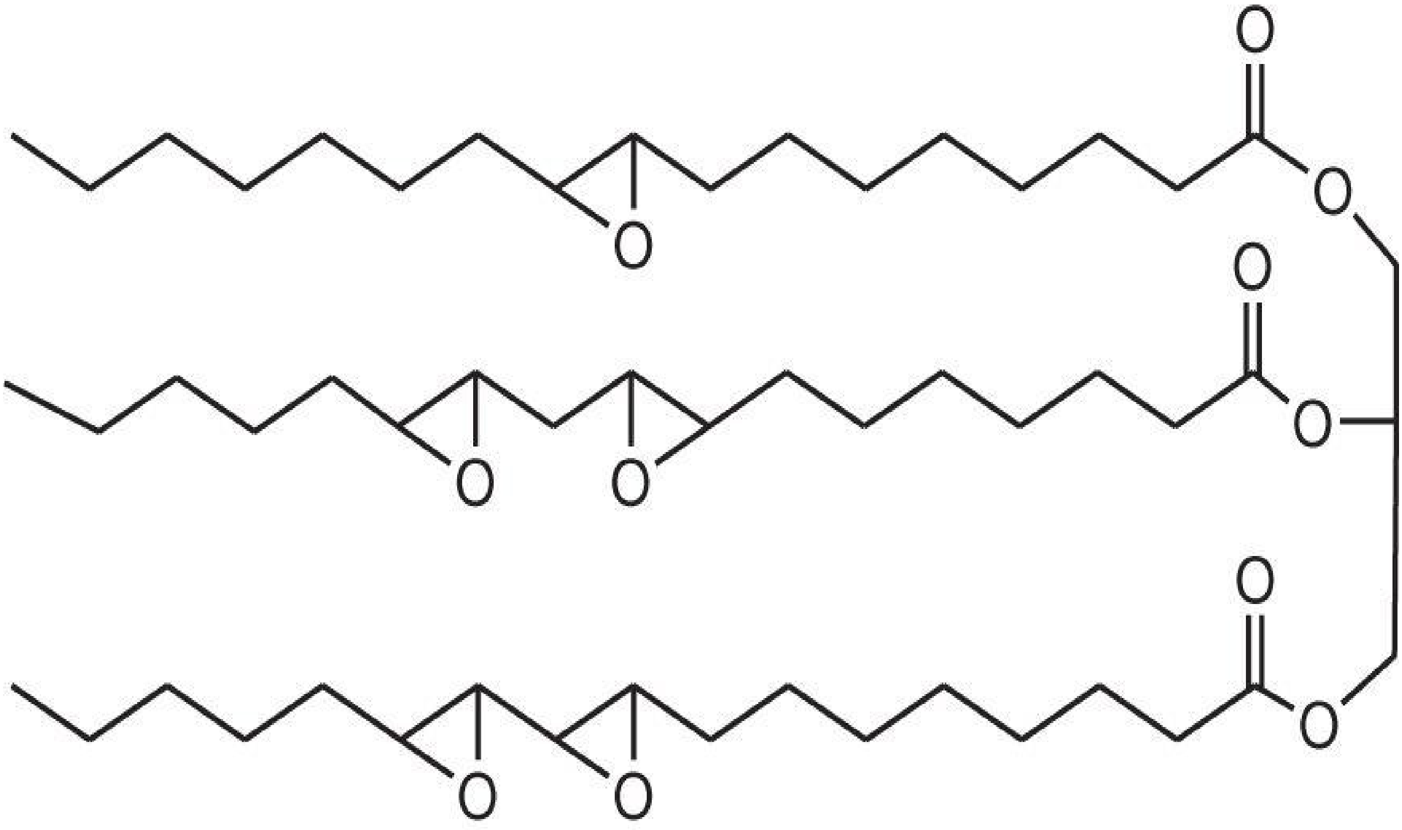
Figure 22.3

2. Kruper[2] brominated sunflower oil and then extruded it with polystyrene foams and resin to enhance the thermal stability and flame retardancy of polystyrene. Extruded blends containing polystyrene resins and brominated sunflower oil were superior to polystyrene foams additized with a mixture of organotincarboxylate and hexabromo-stearic acid.

3. Roh[3] epoxidized renewable soybean oil, (II), and then post-reacted this epoxide intermediate, (III), and with either 2-ethylhexanoic acid, oleic acid, or 2,2-dimethylol-propionic acid to form high-density crosslinked polyols. Polyol intermediates were then post-reacted with aliphatic diisocyanates to form crosslinked polyurethanes needed in medical applications. (See Fig. 22.4.)



(II)



(III)

Figure 22.4

4. Forth[4] blended partially cured vegetable oil with graded aggregates having a maximum aggregate particle size of approximately 15 mm. These two-component blends and shapes were successfully used as oxidation-resistant components or as foams to cover or overlay existing construction materials. Other partially cured vegetable oils successfully used in this process included linseed oil, castor oil, tung oil, grape-seed oil, and Tall Oil. All oils used in this process were industrial by-products of papermaking.

References

1. Michael A. Nelson, *Biological polymeric compositions and methods related thereto,* U.S. Patent Application 20080125532 (May 29, 2008)

2. William J. Kruper, Jr., et al., *Extruded polymer foams containing brominated fatty acid-based flame retardant additives,* U.S. Patent 8,324,288 (December 4, 2011)

3. Yeonsuk Roh et al., *Polyol formed from an epoxidized oil stocks*, U.S. Patent 8,308,975 (November 13, 2012)

4. John Paul Forth et al., *Vegetable oil based construction materials,* U.S. Patent 8,298,330 (October 30, 2012)

Chapter

23

Surfactants

Biomass-Derived Glycerol Ketal Surfactants

Author Sergey Selifonov

Patent Title ***Glyceryl ether compounds and their use,*** U.S. Patent 8,318,814 (November 27, 2012)

Relevant Prior Patents by Author or Coauthors

Glycerol levulinate ketals and their use, U.S. Patent 8,178,701 (May 15, 2012)

Glycerol ether compounds and their use, U.S. Patent 8,084,635 (December 22, 2011)

Glycerol levulinate ketals and their use, U.S. Patent 8,053,468 (November 8, 2011)

Preparation of lactic acid derivatives and their use, U.S. Patent 7,211,693 (November 1, 2007)

Product Application

Aliphatic ketal-protected glycerol derivatives prepared in this investigation were used as surfactants in cleaning, laundry, soap, and consumer personal care formulations.

Significance of Current Application

There is a continuing need to identify renewable surfactants for use in cleaning, laundry, soap, and personal care compound formulations. Of particular interest, however, is the identification of both non-ionic and ionic surfactant compounds that perform well in water containing elevated levels of alkali-earth metal salts. Surfactants that are currently used in cleaning formulations designed for use in hard-water applications are relatively expensive, and many of these chemical precursors are produced using hazardous non-renewable petrochemicals. The typical synthesis of these surfactants using petrochemicals may require as many as five separate steps. Moreover, all of these synthetic steps generate large amounts of toxic organic-waste products and are energy intensive.

In this investigation, surfactants were prepared using renewable and inexpensive reagents. Surfactants derived from this investigation had excellent solubilizing and emulsifying properties in water containing high amounts of calcium and magnesium ions. Finally, processes used to prepare surfactants from the renewable materials were high yielding and used considerably simpler chemical methods to prepare non-petrochemically derived surfactants.

Product Formation

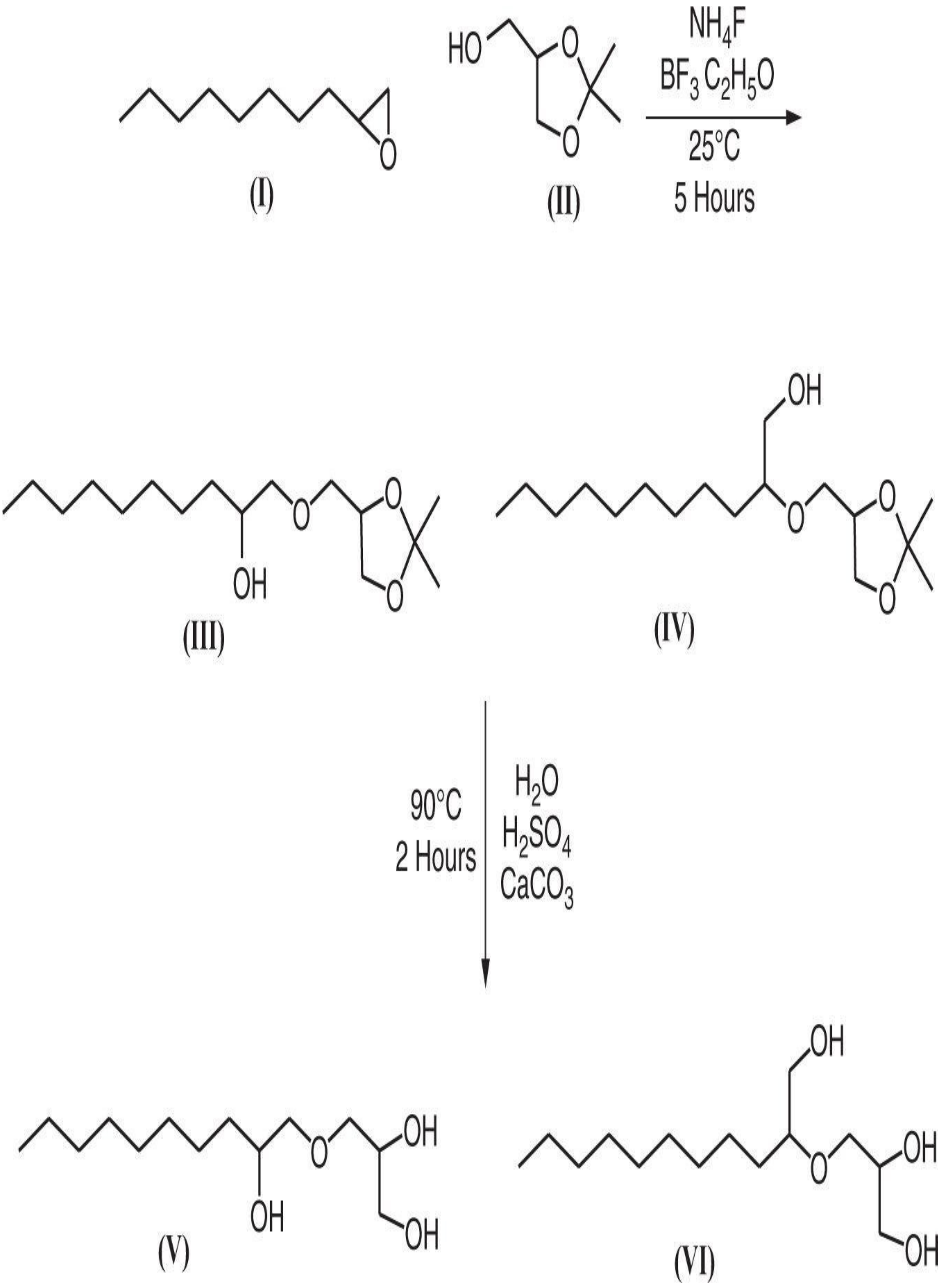


Figure 23.1

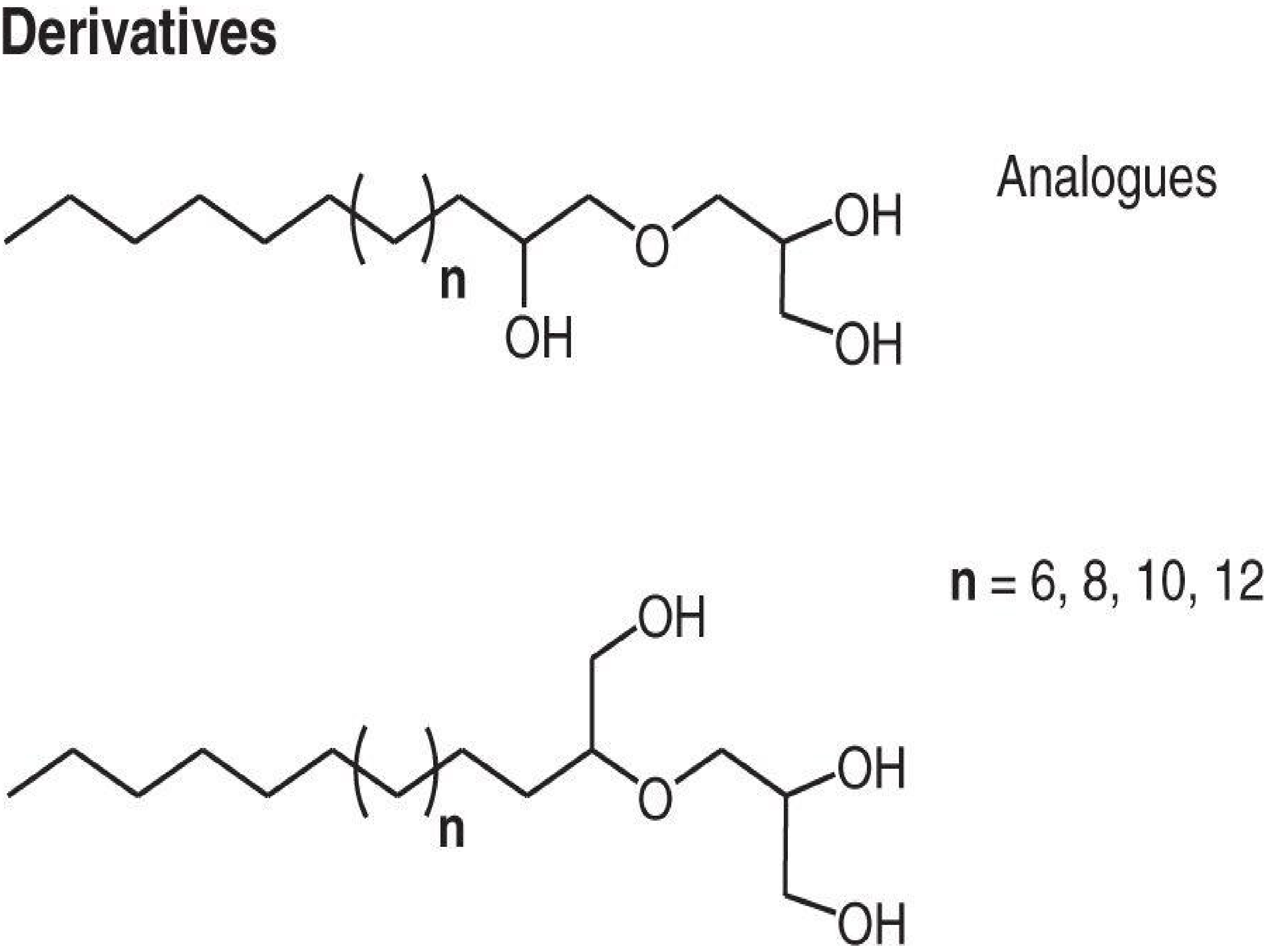


Figure 23.2

Experimental

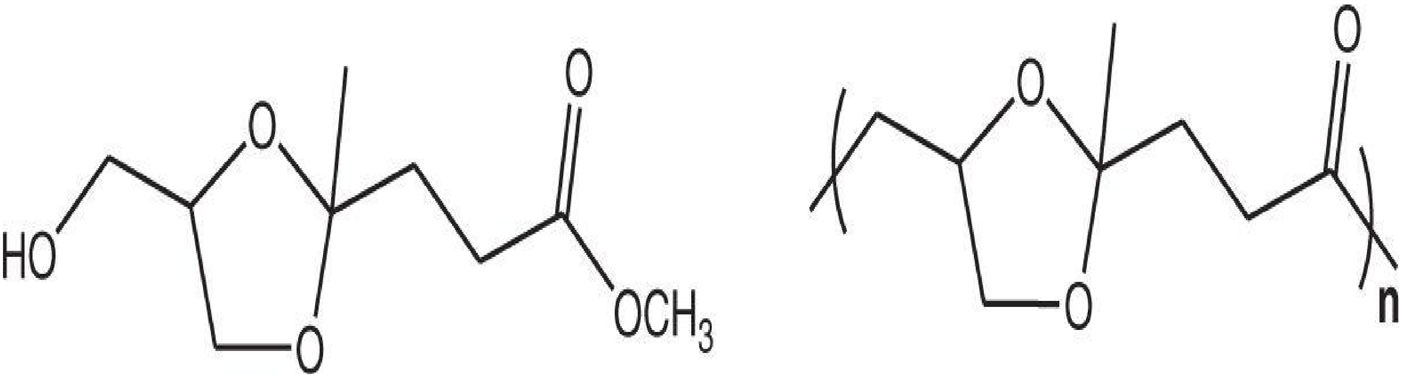
1. Preparation of ketal intermediates, (III) and (IV). A reactor was charged with 5 g of 94% pure decene-1,2-oxide, (I), dissolved in 15 mL of solketal,[1],[2] (II), stirred at 25°C, and then treated with 0.05 mL of boron trifluoride diethyl etherate. The mixture was then stirred for another 20 minutes whereupon an exotherm occurred causing the temperature to rise to 55°C. While at this elevated temperature the mixture was further treated with ammonium fluoride that produced a suspension formation. The mixture was then stirred for an additional 2 hours and then filtered. Excess solketal was removed from the ketal intermediate mixture by distillation under reduced pressure. After cooling the mixture to ambient temperature, 7.8 g of a colorless liquid were isolated.

Analysis of the mixture by gas chromatography-mass spectrometry determined it was a two-component mixture containing 85% stereoisomers of ketal compounds, (III) and (IV).

2. Preparation of biomass-derived surfactants, (V) and (VI). A reactor was charged with a mixture consisting of 1 g of the Step 1 product, 5 g of water, and 0.01 g of sulfuric acid and then heated for 2 hours between 90°C and 95°C. After cooling to ambient temperature, the reaction mixture was neutralized with 0.1 g of calcium carbonate and then filtered, the isolated and purified and the reaction mixture had an opalescent smectic appearance. The mixture was then purified by distillation under reduced pressure and 0.6 g of viscous product were isolated as an unctuous, opalescent semi-solid with a pearl-like appearance.

Notes and Observations

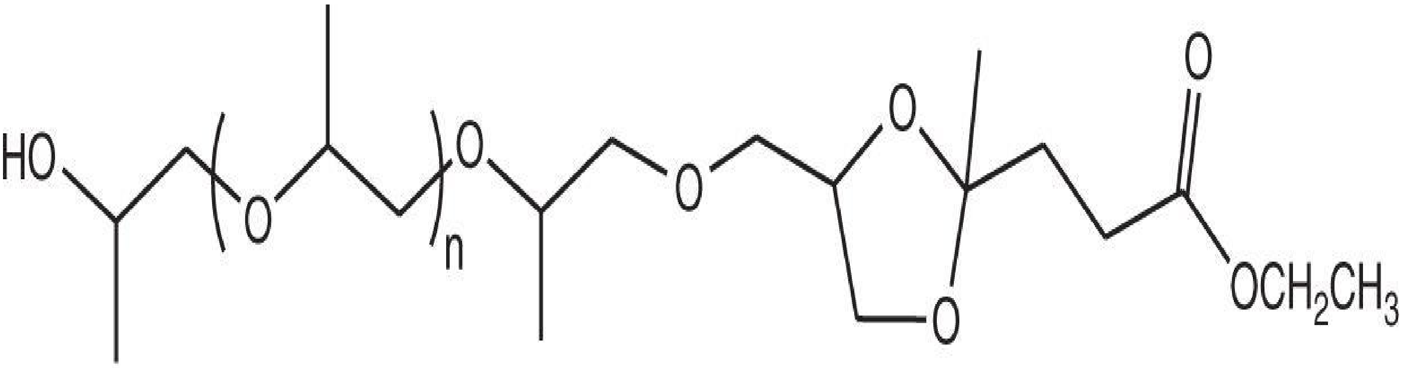
1. In an earlier investigation by the author,[3] bio-derived glycerol was converted into glycerol levulinate ketal, (VII), and used as a surfactant and plasticizer. Glycerol levulinate ketal was also prepared and then polymerized, (VII), and used in coating formulations. (See Fig. 23.3.)



(VII) (VIII)

Figure 23.3

2. Rieth[4] used biobase-derived glycerol to prepare polypropylene glycol of ethyl levulinate ketal, (IX), which was effective as a fabric softener in laundry formulations. (See Fig. 23.4.)



(IX)

Figure 23.4

3. Selifonov[5] prepared polyurethanes by condensing poly(glycerol leuvlinate ketals) with hexamethylene diisocyanate and the reaction product was used as a co-component in the manufacturing of flexible polyurethane composites.

4. Mullen[6] used crude leuvulinic acid, (X), derived from biomass containing between 10 wt% and 12 wt% biomass impurities to prepare diester, (XI), which was then used as a plasticizer for polymers as well as being an intermediate in synthesizing polyamides, polyurethanes, polyesters, and related condensation polymers. (See Fig. 23.5.)

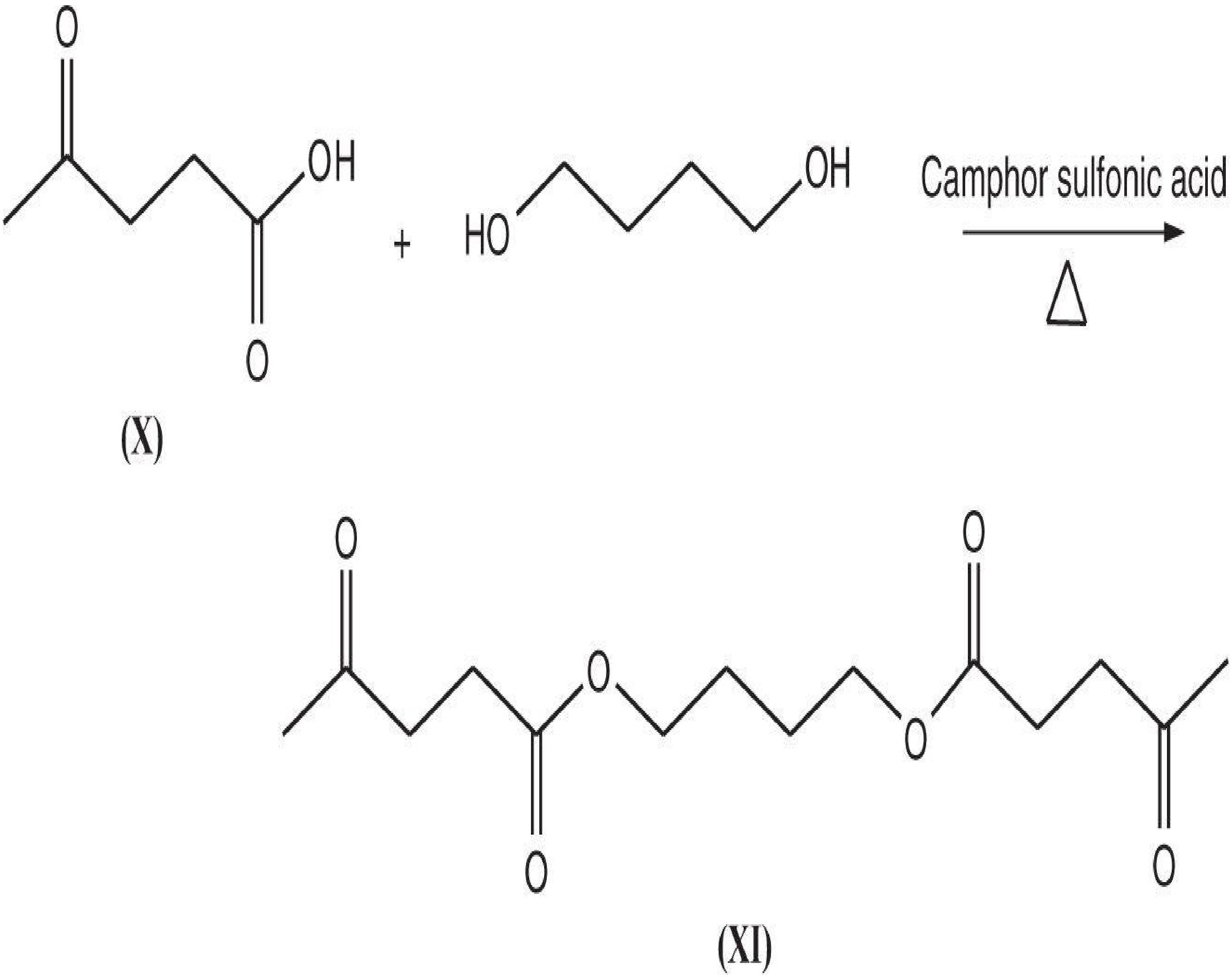


Figure 23.5

References

1. J. Hazimah et al., Recovery of glycerol and diglycerol from glycerol pitch, *Journal of Oil and Palm Research*, vol. 15(1), pp. 1321–1328 (2003)

2. P. Muturi et al., Epoxidized vegetable oils as reactive diluents. I. Comparison of vernonia, epoxidized soybean and epoxidized linseed oils, *Progress in Organic Coatings*, vol. 25, pp. 85–94 (1994)

3. Sergey Selifonov, *Glycerol levulinate ketals and their use*, U.S. Patent 8,178,701 (May 15, 2012)

4. Lee Richard Rieth et al., *Fabric softener compositions and methods of manufacture thereof*, U.S. Patent 8,188,030 (May 29, 2012)

5. Sergey Selifonov, *Glycerol levulinate ketals and their use in the manufacture of polyurethanes, and polyurethanes formed therefrom*, U.S. Patent Application 20120196947 (August 2, 2012)

6. Brian D. Mullen et al., *Ketocarboxylic acids, methods of manufacture and uses there of*, U.S. Patent Application 20120123147 (May 17, 2012)

Chapter

24

Thermoplastics

Thermoplastics Containing Renewable Components

Author Rene Saint-Loup et al.

Patent Title ***Method for preparing thermoplastic compositions of plasticized starch, and such compositions,*** U.S. Patent Application 20120289629 (November 15, 2012)

Relevant Prior Patents by Author or Coauthors

Process for preparing compositions based on a starchy component and on a synthetic polymer, U.S. Patent Application 20110118390 (May 19, 2011)

Starch-containing thermoplastic or elastomer compositions, and methods for preparing such compositions, U.S. Patent Application 20110086949 (April 14, 2011)

Method for preparing thermoplastic compositions based on plasticized starch and resulting compositions, U.S. Patent Application 20100311905 (December 9, 2010)

Thermoplastic compositions based on soluble starch and methods for preparing such compositions, U.S. Patent Application 20100305271 (December 2, 2010)

Thermoplastic polyurethanes containing a salt of zirconium phosphate, U.S. Patent Application 20080114093 (May 15, 2008)

Product Application

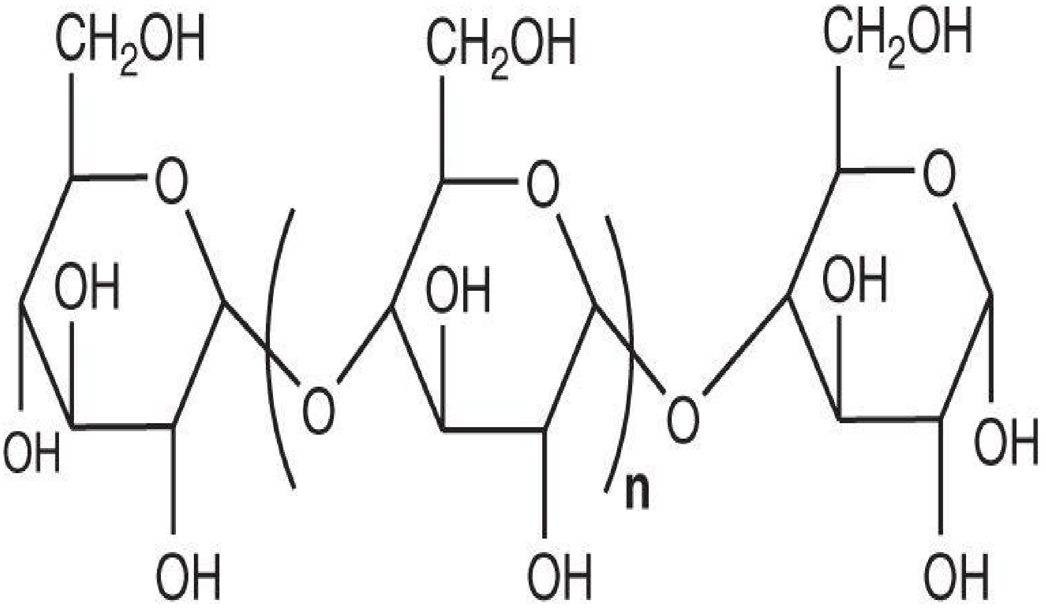
High-impact thermosets containing biopolymers were prepared and used in the production of light- and high-strength automotive and aircraft components. The use of these light- and high-strength materials is anticipated to be used in military applications.

Significance of Current Application

Crosslinked-biopolymeric thermoplastic compositions containing amylaceous components are renewable and form very stable thermosets. In order to ensure high-impact strength in these renewable thermosets, it is essential that at least one component of the composite completely blends with all other components. This component miscibility must also be observed when the blend is mixed or reacted with a solvent or co-reagent, respectively. In this investigation, polypropylene was used as the thermoset-blending or miscibility component in the product package. To enhance the miscibility of this non-polar component in a polar medium, polypropylene was converted into poly (propylene-g-maleic anhydride). To further enhance the strength of this mixture, wheat starch was then added and the mixture reacted with renewable glycerol and sorbitol. The desired high-impact thermoset strength was finally obtained by reacting diphenyl diisocyanate with poly (propylene-g-maleic anhydride) previously modified with excess glycerol and sorbitol to generate crosslinked polyurethanes. Crosslinked polyurethanes form composites with enhanced miscibility and improved strength. As a result of this crosslinking process using diphenyl diisocyanate, the thermoplastic composite had improved high-impact properties and improved strength properties.

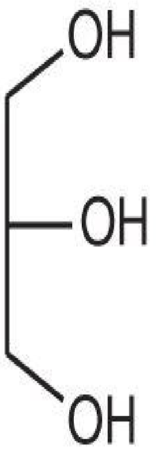
Composite Components

Eight reagents, (I) through (VIII), were used to form the high-strength renewable thermoset. (See Fig. 24.1.)



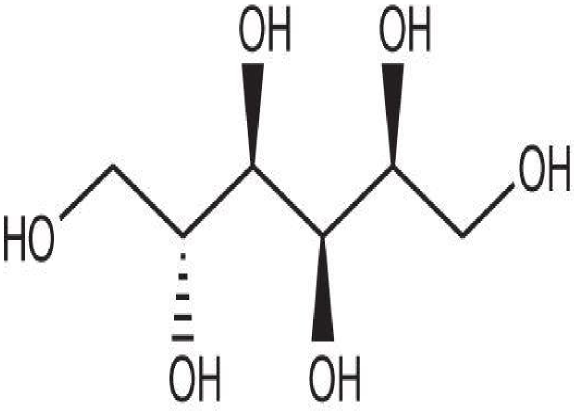
Wheat Starch

(I)



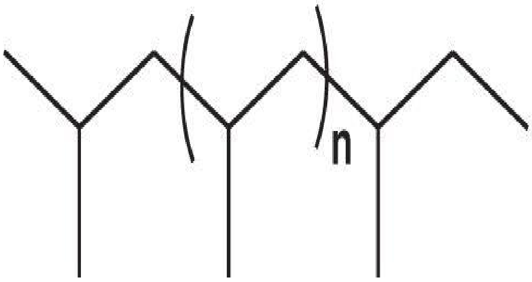
Glycerol

(II)



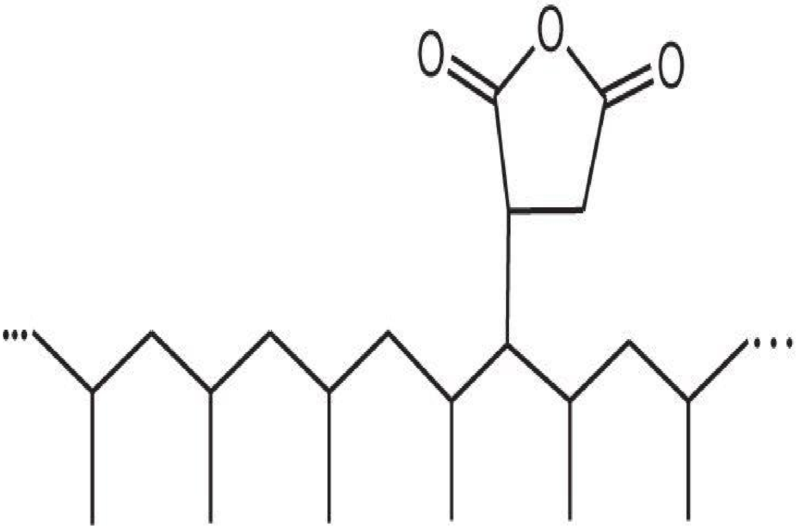
Sorbitol

(III)



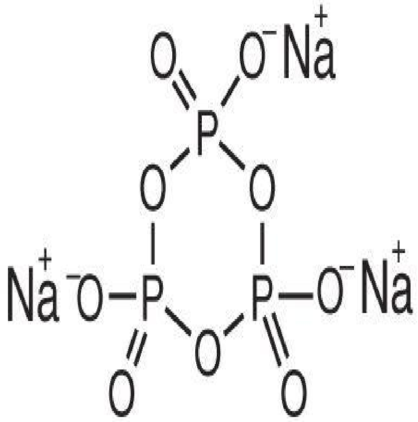
Polypropylene

(IV)



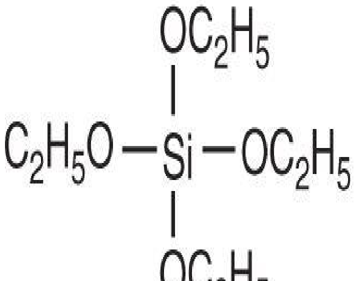
Poly(propylene-g-maleic anhydride)

(V)



Sodium Trimetaphosphate

(VII)



$$\begin{array}{c} OC_2H_5 \\ | \\ C_2H_5O-Si-OC_2H_5 \\ | \\ OC_2H_5 \end{array}$$

Tetraethoxysilane

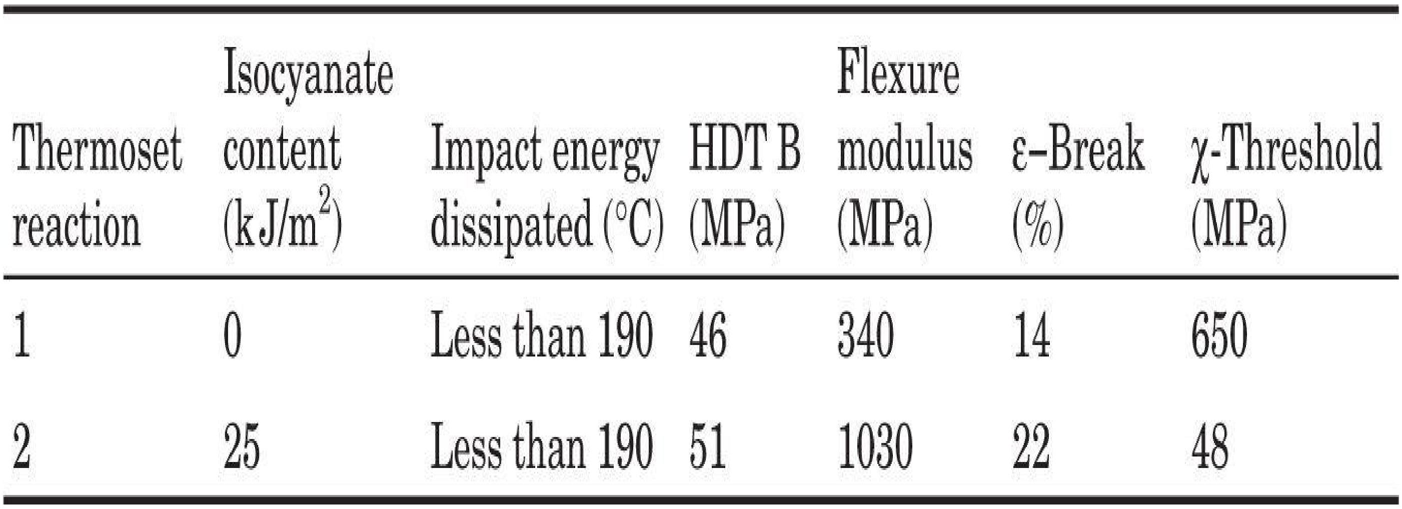
(VIII)

Figure 24.1

Experimental

1. Preparation of renewable thermoset. A glass reactor was charged with 35 wt% of wheat starch, (I), having a water content of approximately 12% and 16 wt%, an equivalent amount of glycerol, (II), and sorbitol, (III). After thoroughly mixing, the reactor was treated with 25 wt% of polypropylene, (IV), 25 wt% of poly(propylene-g-maleic anhydride), (V), and a 25 wt% mixture of methylene diphenyl diisocyanate, (VI), sodium trimetaphosphate, (VII), and tetraethoxysilane, (VIII). Toluene was then added and the mixture was heated to reflux for approximately 4 hours. After cooling the mixture to ambient temperature, a yellowish solid was isolated from the reaction container. Physical properties of this thermoset are provided in Table 24.1.

TABLE 24.1 Thermoset composite properties prepared using renewable glycerol and sorbitol. The thermoplastic had considerable strength while remaining elastic and pliable.



Thermoset reaction	Isocyanate content (kJ/m^2)	Impact energy dissipated (°C)	HDT B (MPa)	Flexure modulus (MPa)	ε-Break (%)	χ-Threshold (MPa)
1	0	Less than 190	46	340	14	650
2	25	Less than 190	51	1030	22	48

Testing Results

Notes and Observations

1. Thermoplastics containing starch were prepared by Morris[1] by melt-blending starch with two terpolymers. The first terpolymer was prepared by reacting 1,4-butanediol, terephthalic acid, and adipic acid. The second terpolymer was prepared using 1,3-propanediol, dimethyl terephthalate, and either sebacic acid or dipropylene glycol. A blend of these terpolymers containing starch was then extruded at 190°C where no evidence of decomposition was observed. Blown films were also prepared using this composite where it was noted that both Elmendorf tear resistance according to ASTM D1922 and enhanced tensile properties according to ASTM D882 were dramatically improved.
2. Tomka[2] prepared processable thermoplastics using blends containing modified starch and glycerin or sorbitol plasticizers with an unspecified sulfonated aliphatic-aromatic copolyester. The thermal conversion of the composite ranged from 145°C to 180°C, which was a direct reflection of the monomer ratios in the blend.
3. Morris[3] prepared two thermoset composites consisting of terpolymers blended with

starch. The first terpolymer consisted of 1,4-butanediol, terephthalic acid, and adipic acid. The second terpolymer consisted of 1,3-propanediol, dimethylterephthalate, and either sebacic acid or dipropylene glycol and 300 ppm of sodium acetate trihydrate. Starch was then added to each terpolymer and the mixture was extruded through a twin-screw extruder. The barrel had a temperature range from 180°C to 205°C. Shaped articles such as films were prepared from the terpolymer-starch composite, which exhibited a dramatic increase in expected tear strength.

4. Chen[4] prepared biodegradable polymers containing various ratios of a starch blend, an enzyme that hydrolyzes starch and with an activity ranging from 15,000 units to 40,000 units, and polybutylene succinate. The fourth component was described as analiphatic-aromatic copolyester. Articles produced from this four-component composite completely degraded in several months, as anticipated.

References

1. Barry Alan Morris et al., *Biodegradable starch-containing composition with improved tear strength*, U.S. Patent 8,415,021 (April 9, 2013)

2. Shigeo Otome, *Thermoplastically processable starch and a method of making it*, U.S. Patent 5,362,777 (November 8, 1994)

3. Barry Alan Morris et al., *Biodegradable starch-containing blend*, U.S. Patent 8,409,677 (April 2, 2013)

4. C. Will Chen et al., *Starch-based biodegradable material composition*, U.S. Patent Application 20090075346 (March 19, 2009)

Chapter

25

Toners

Renewable Terpolyester Toner

Author Guerino G. Sacripante et al.

Patent Title ***Rosin-based resin and toner containing same,*** U.S. Patent 8,431,303 (April 30, 2013)

Relevant Prior Patents by Author or Coauthors

Toner compositions, U.S. Patent 8,431,309 (April 30, 2013)

Synthesis and emulsification of resins, U.S. Patent 8,394,568 (March 12, 2013)

Toner compositions and processes, U.S. Patent 8,257,895 (September 4, 2012)

Toner process, U.S. Patent 8,247,157 (August 21, 2012)

Toner compositions and methods, U.S. Patent 8,221,951 (July 17, 2012)

Toner compositions and processes, U.S. Patent 8,221,948 (July 17, 2012)

Toner compositions, U.S. Patent 8,211,607 (July 3, 2012)

Toner compositions, U.S. Patent 8,197,998 (July 12, 2012)

Product Application

Polyester terpolymers derived from renewable monomers including sebacic acid, fumaric acid, and ethylene glycol were designed to be used in inexpensive toner compositions or formulations in photocopying machines.

Significance of Current Application

The current investigation has addressed the need to both identify and prepare renewable toner compositions that can be directly used in existing photocopying machines. Most toner formulations continue to use terpolyesters containing terpolymer-starch composite in the toner formulation despite the overwhelming evidence that bisphenol A is extremely toxic. The current investigation directly addresses bisphenol A toxicity by completely eliminating this agent when preparing terpolymers. These alternative terpolymers were effective when used in toner formulations as well as inexpensive to prepare. In addition, the replacement terpolymer was prepared using only renewable and sustainable reagents. These include sebacic acid, fumaric acid, and ethylene glycol. Terpolymers derived from renewable reagents and used in toner formulations did not negatively impact either image reproducibility or quality of the image during photocopying.

Renewable Agents

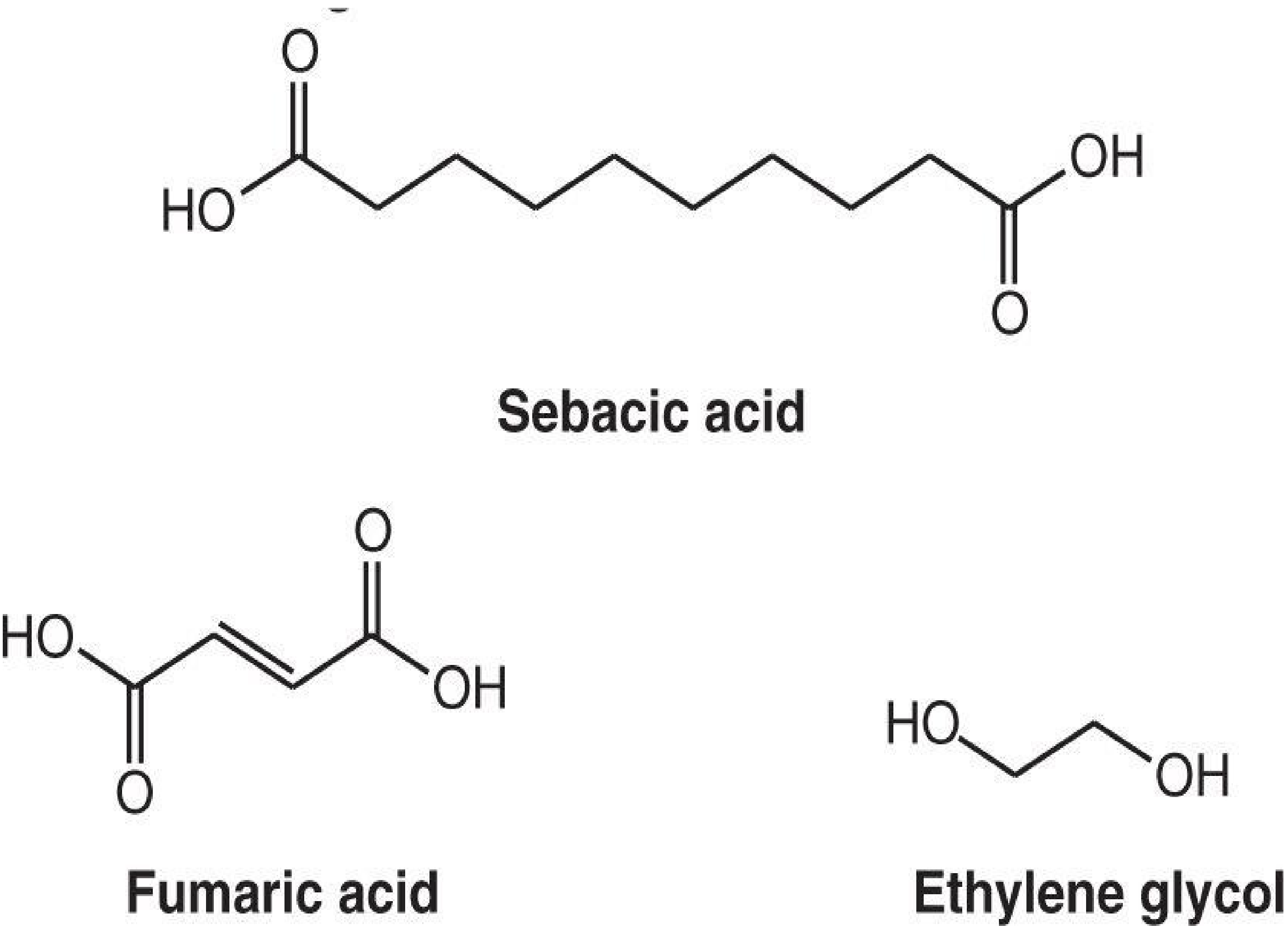
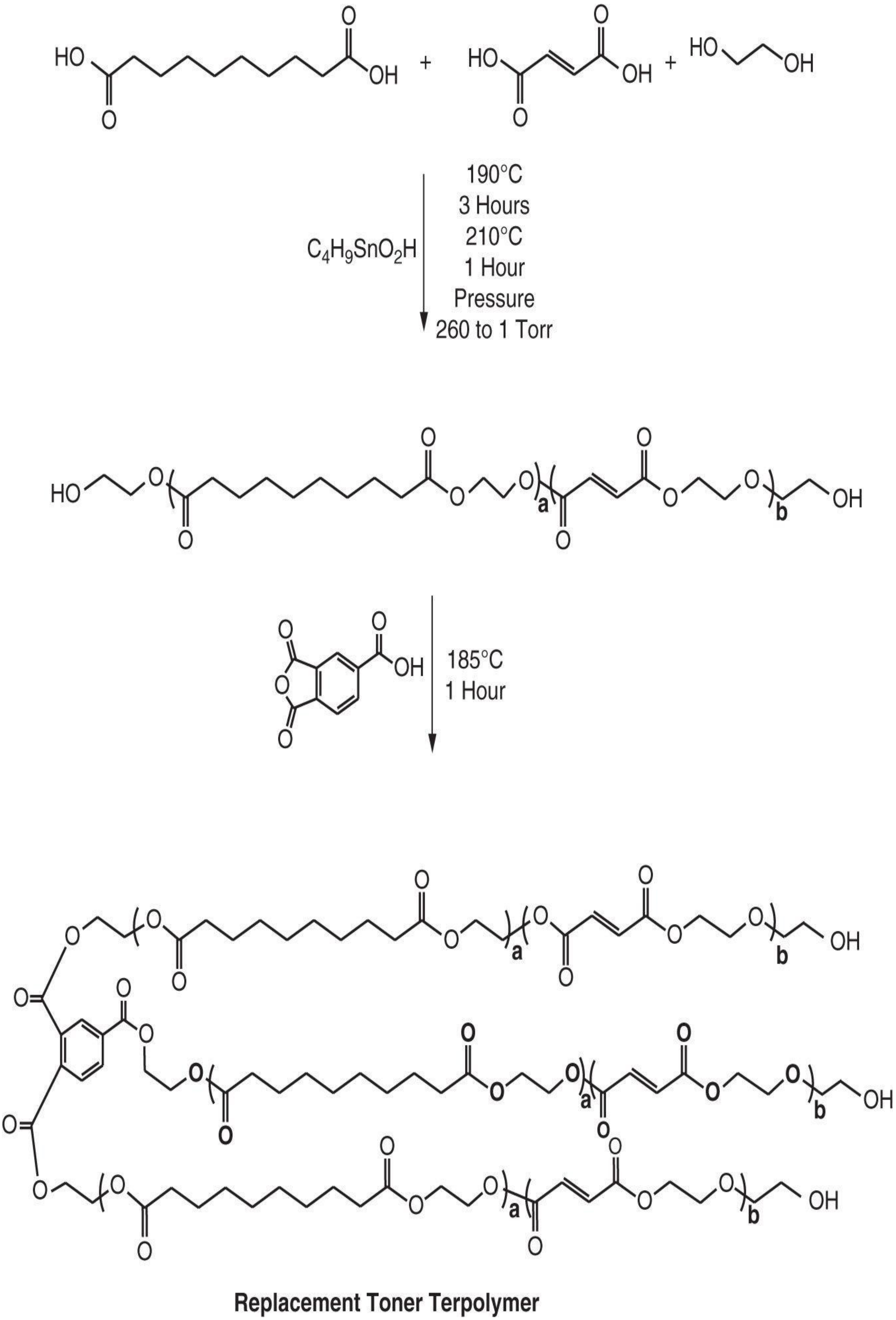


Figure 25.1

Product Formation



Replacement Toner Terpolymer

Figure 25.2

Experimental

1. Preparation of renewable replacement toner terpolyester. A 2-L Hoppes reactor equipped with a heated-bottom drain valve, high-viscosity double-turbine agitator, and distillation receiver containing a cold water condenser was charged with 900 g of sebacic acid, 84 g of fumaric acid, 655.2 g of ethylene glycol, and 1.5 g of butyltin hydroxide oxide as the reaction catalyst. The reactor was then heated to 190°C for 3 hours and then further heated to 210°C for 1 hour. At this point the reaction pressure was slowly reduced to approximately 260 Torr for 1 hour, then further reduced to 5 Torr for an additional hour, and finally reduced to 1 Torr for 30 minutes. The polyester intermediate was cooled to 185°C and then treated with 24 g of trimellitic anhydride and heated for an additional hour at 185°C. The resin was then isolated through the heated-bottom drain valve of the Hoppes reactor and analytical testing of the product was performed. Testing results of this terpolymer are provided below.

Softening point: 93°C

Viscosity: 29 poise @ 199°C

Melting point (DSC): 70°C to 80°C

Acid number: 10 meq/g

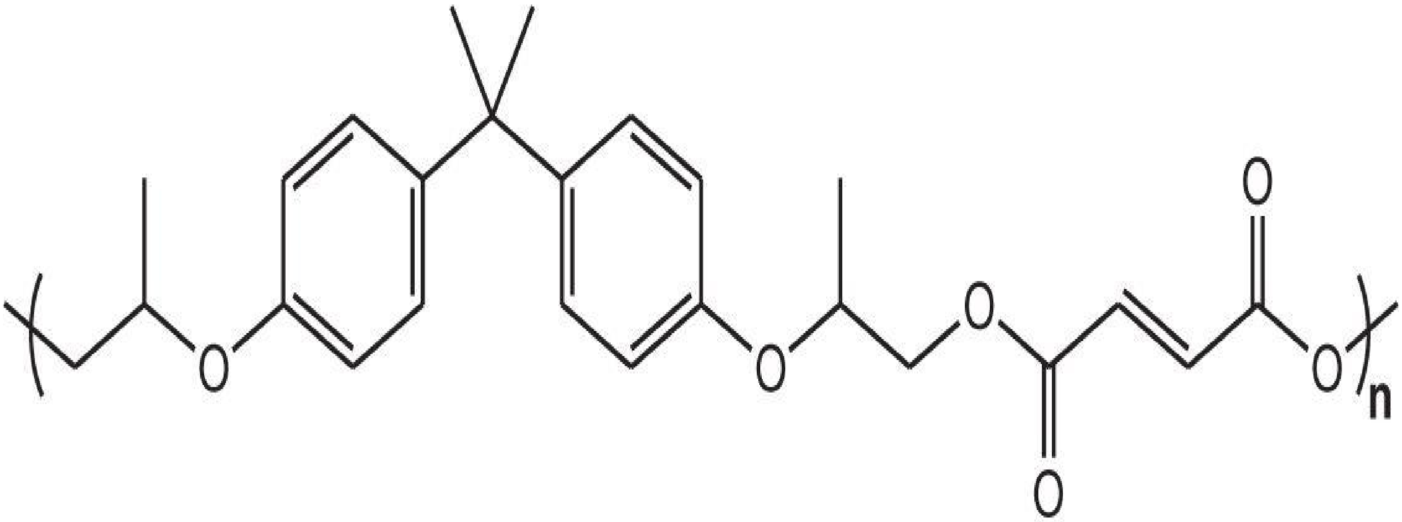
Particle size: 155 nm

Testing

Testing was limited to characterization of terpolymer analogues prepared according to the Step 1 procedure. Toner formulations were not provided by the author.

Notes and Observations

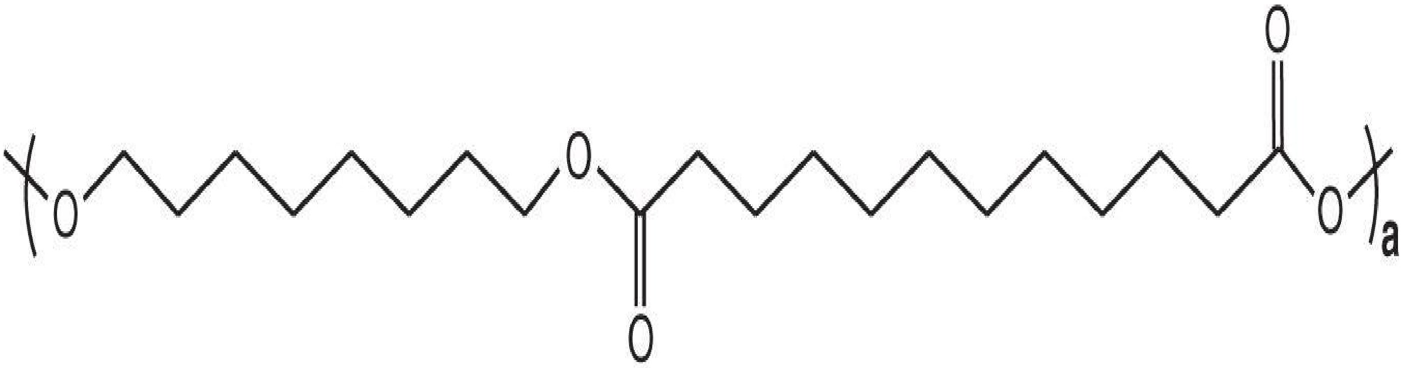
1. Zhou[1] prepared a renewable toner consisting of an amorphous and partially unsaturated polyester resin, poly(propoxylated bisphenol co-fumarate), (I), which had excellent coalescence properties after thermally crosslinking between 80°C and 140°C. (See Fig. 25.3.)



(I)

Figure 25.3

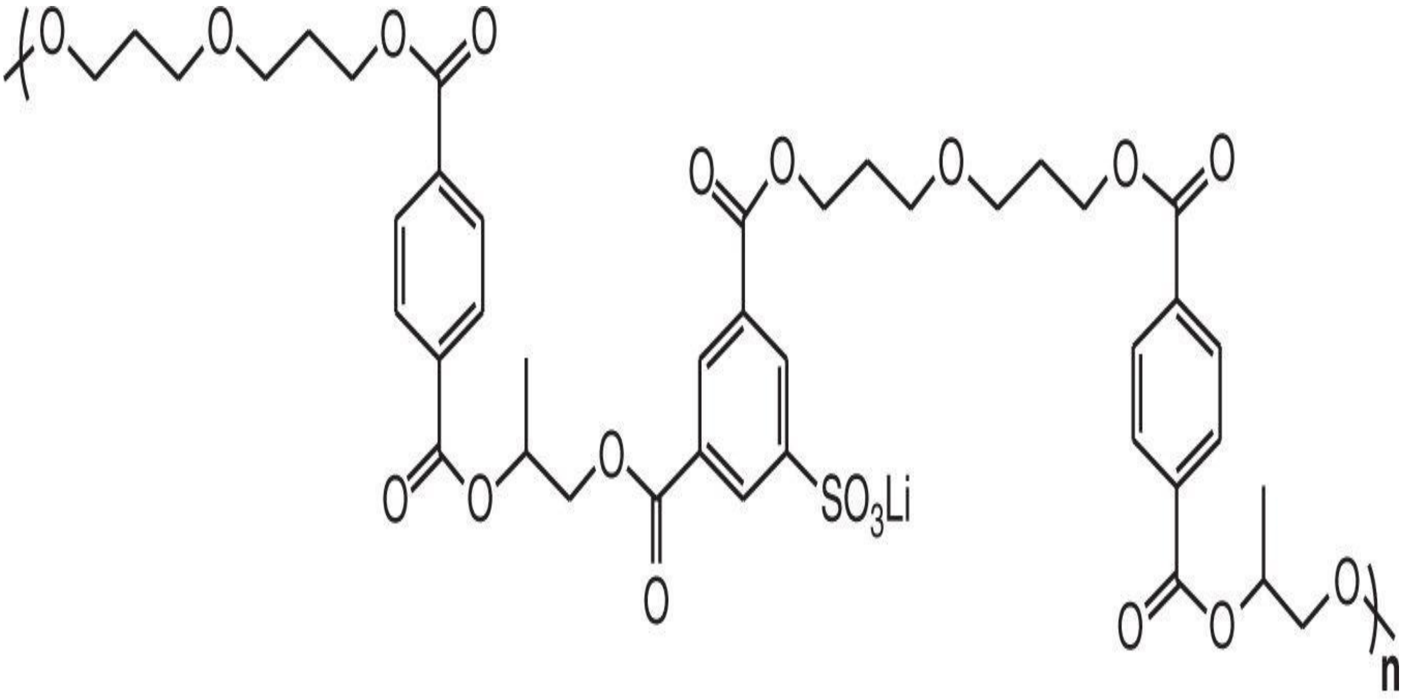
2. Qiu[2] condensed dodecanedioic acid with 1,9-nonanediol to form a crystalline polyester, (II), having an Mn = 3100 daltons. The polymer was subsequently emulsified by reacting with the anionic surfactant, TAYCA®, and sodium hydroxide, which formed polyester particles having an average size of 41.4 nm. The emulsified polyester was subsequently used in toner formulations. (See Fig. 25.4.)



(II)

Figure 25.4

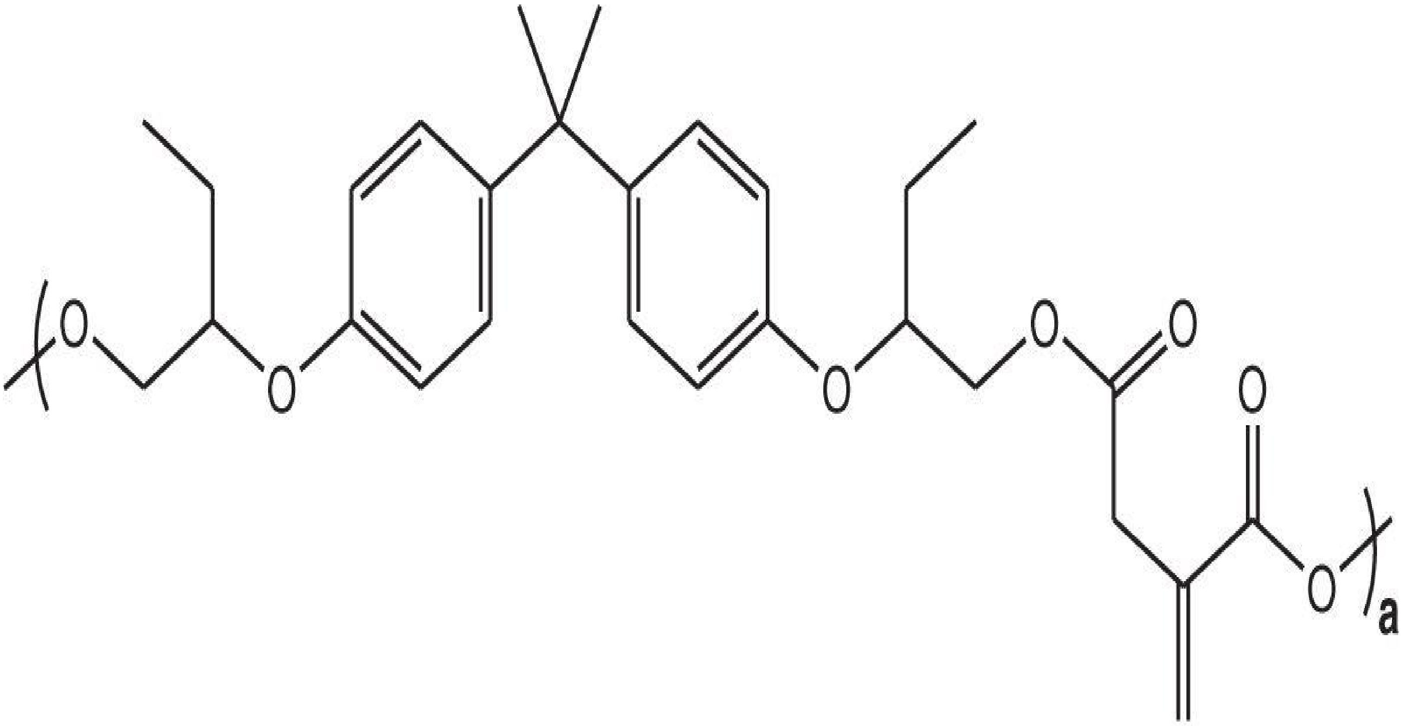
3. Nosella[3] prepared a toner composition consisting of emulsified copolyester containing dimethyl terephthalate, 5-lithium sulfoisophthalic acid, propylene glycol, and dipropylene glycol, (III). Aqueous solutions containing up to 3.3 wt% of the terpolymer resin had a volume average diameter of about 27 nm. (See Fig. 25.5.)



(III)

Figure 25.5

4. Zhou[4] prepared a series of bio-based, amorphous polyester toner resins, one of which consisted of poly(butyloxylated bisphenol co-itaconate), (IV). A 16.93 wt% of the emulsified polyester resin had a volume average diameter of about 151 nm. (See Fig. 25.6.)



(IV)

Figure 25.6

References

1. Ke Zhou et al., *Toner compositions*, U.S. Patent 8,431,309 (April 30, 2013)

2. Shigang Qiu et al., *Synthesis and emulsification of resins*, U.S. Patent 8,394,568 (March 12, 2013)

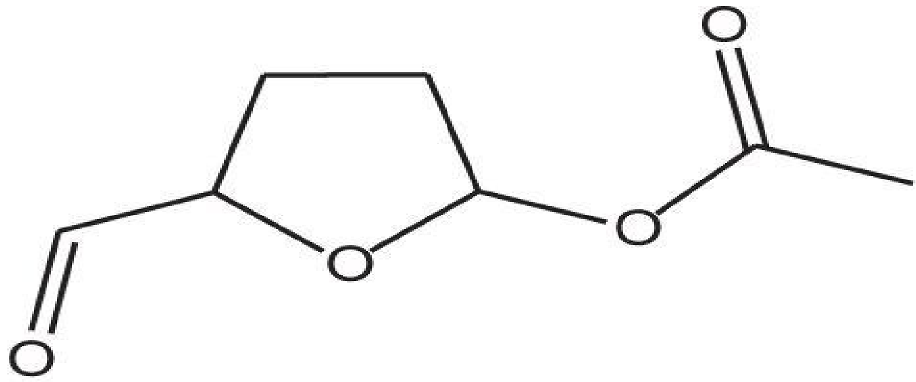
3. Kimberly D. Nosella et al., *Toner process*, U.S. Patent 8,247,157 (August 21, 2012)

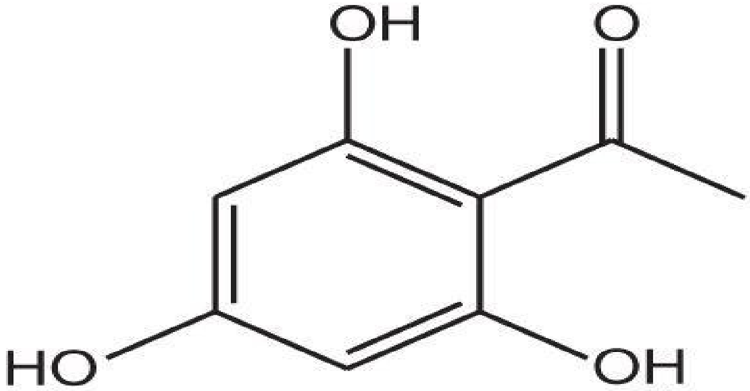
4. Ke Zhou et al., *Toner compositions and processes*, U.S. Patent 8,221,948 (July 17, 2012)

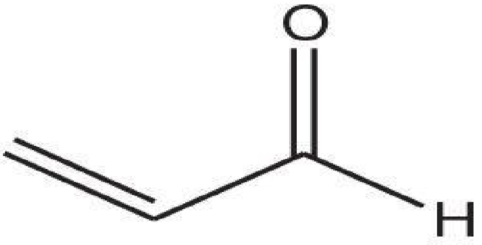
Appendix

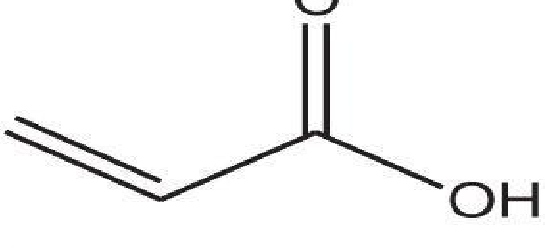
A

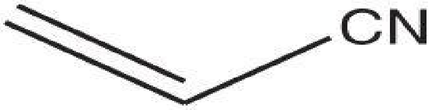
Renewable Compounds

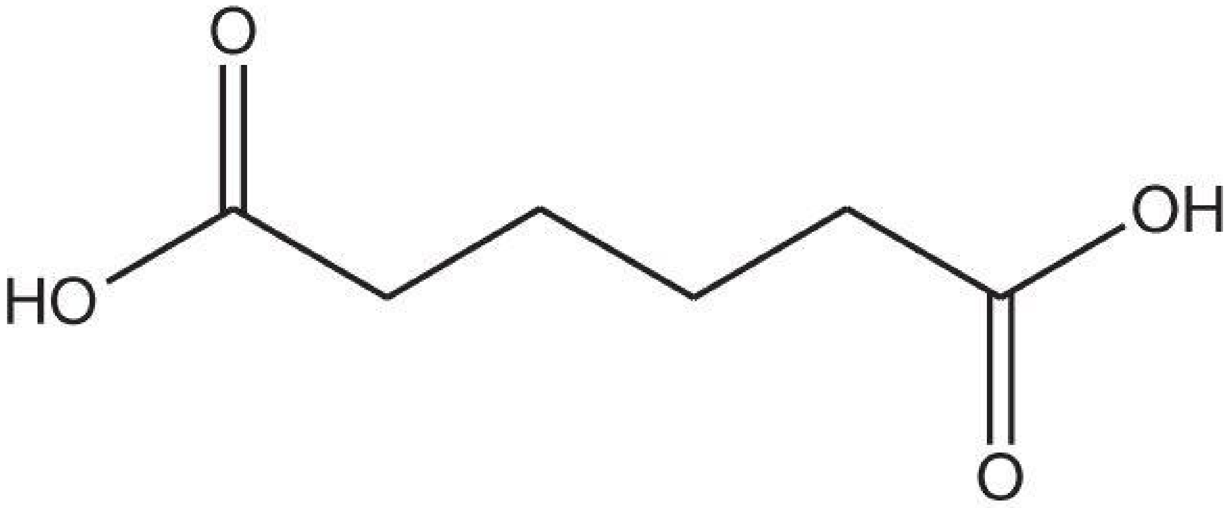

5-Acetoxymethylfurfural


2-Acetyl-1,3,5-trihydroxylbenzene

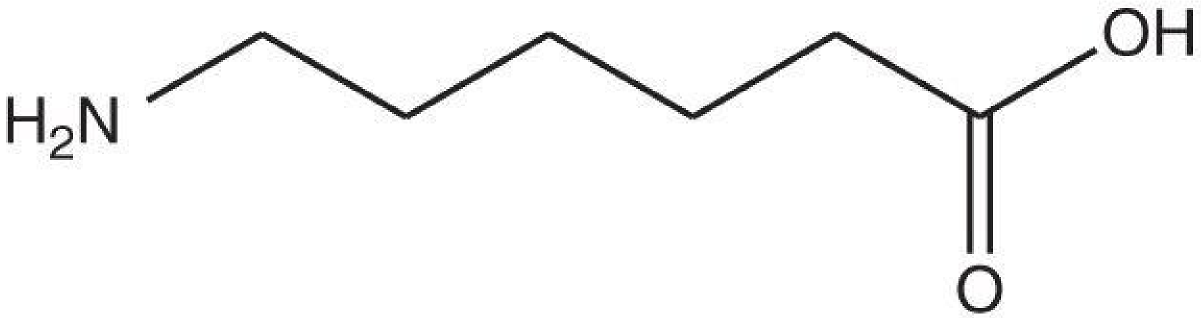

Acrolein


Acrylic acid


Acrylonitrile



Adipic acid



6-Aminocaproic acid

2-Amino-1-hydroxypropane

Arabinose

Arachidic acid

Behenic acid

Brominated sunflower oil

Bryostatin 1

1,4-Butanediol

1,4-Butanediol diacrylate

1,2,3,4-Butanetetraol

Butyl methacrylate

Butyric acid

ε-Caprolactone

Citric acid

Decanedioic acid

2,6-Diacetyl-1,3,5-trihydroxybenzene

Diammonium succinate

1-Decanol

Di(2-ethylhexyl) itaconate

Dimethyl adipate

Dipropylene glycol isomeric mixture

Docosahexaenoic acid

Docosapentaenoic acid

Dodecyl alcohol

Dodecyl levulinate

Eicosatetraeneoic acid

Estolides

Ethyl alcohol

Ethyl levulinate

Ethyl lactate

Ethylene glycol

Ethylene vinyl acetate

α-Farnesene

β-Farnesene

Formic acid

Furan

Furan dicarboxylic acid

Furfural

Furfurol

Galactose

Galacturonic acid

Glucose

Glucuronic acid

Glycerin

Glycidol

Glycolic acid

Hexane

Hexabromostearic acid

1,6-Hexanediol

Hexanoic acid

Hydrogen

Hydroxyacetone

3-Hydroxybutyric acid

4-Hydroxybutyric acid

(R),(S)-3-Hydroxyisobutyrate

Hydroxyethyl methacrylate

4-Hydroxyvaleric acid

5-Hydroxyvaleric acid

6-Hydroxycaproic acid

6-Hydroxylhexanoic acid

5-Hydroxymethylfurfural

2-Hydroxypropanone

Isobutanol

Isobutylene

cis-Isoprene

Isosorbide

Isosorbide dioctanoate

Isosorbide glyceryl lauryl ether

Isosorbide laurylmonoether

Itaconic acid

l-Lactic acid

l-Lactide

d,l-Lactide

Levulinic acid

γ-Linoleic acid

Maleic anhydride

Mannitol

Mannose

Methacrylic acid
Methionine
2-Methyl-2-carboxybenzyl trimethylene carbonate
Methyl methacrylate
cis- and trans-3-Methyl-1,4-dioxan-2-one
Monoammonium succinate
Myristic acid
Octadecane-1,9,10-triyl trioctanate
Octadecane-1,9,10-triyl trisdecanoate
2-Octyldodecanol (Guerbet alcohol)
Oleic acid
Palmitic acid
Pentaerythritol
Peracetic acid
1,2-Propanediol
1,3-Propanediol
1,3-Propanediol distearate
1,3-Propanediol monostearate
Propylene glycol
Ribose
Ricinoleic acid
Rosin
Sebacic acid
Sorbitol
Sorbitol hexaacetate
Starch nanocrystals
Stearidonic acid
Succinic acid
Sunflower oil
1-Tetradecanol
Tetradecanedioic acid
1-Tetradecanyl levulinate

Trimethyl trimethylene carbonate

1,3-Trimethylene carbonate

Trimethylene carbonate

Trimethylolpropane

γ-Valerolactone

Xylan

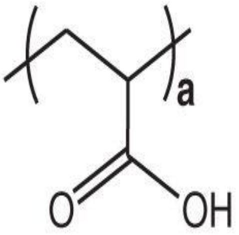
Xylose

Appendix

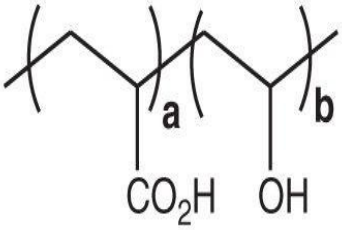
B

Renewable Polymers

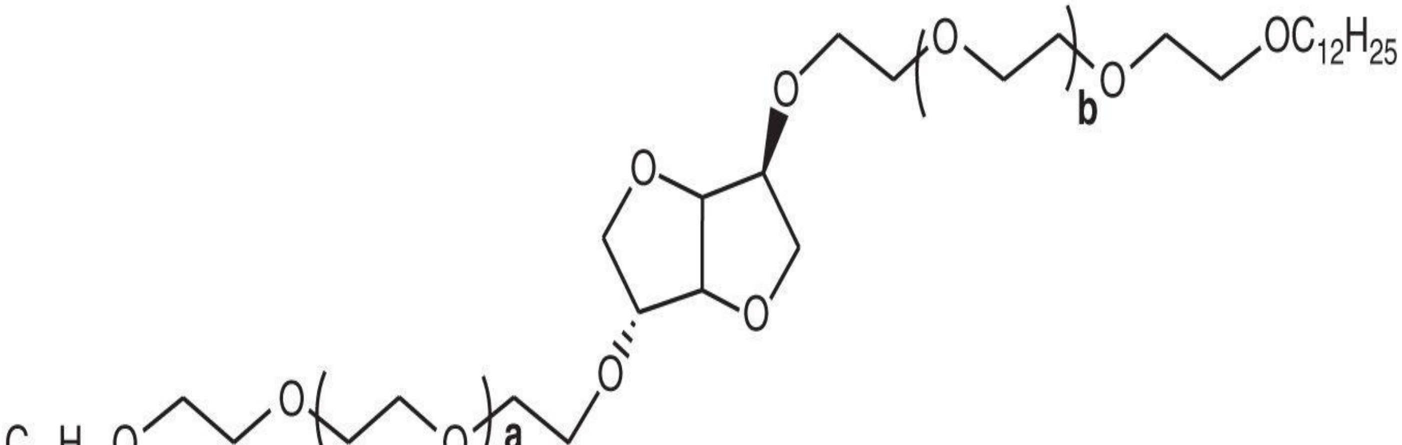
Polyacrylic acid



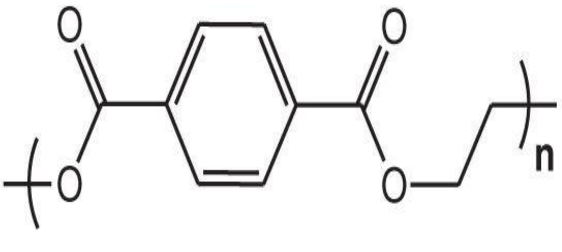
Poly(acrylic acid-co-vinyl alcohol)



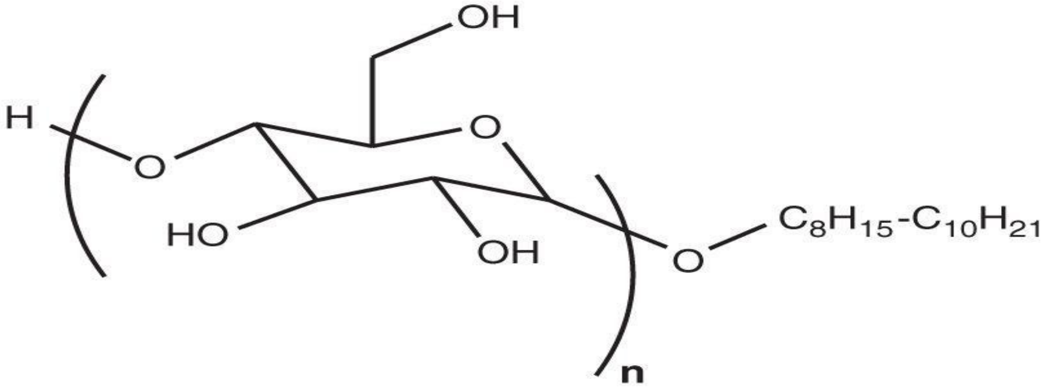
Poly(ethylene ether) isosorbide



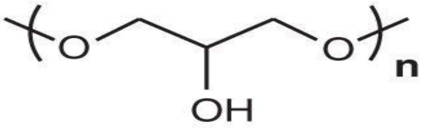
Polyethylene terephthalate



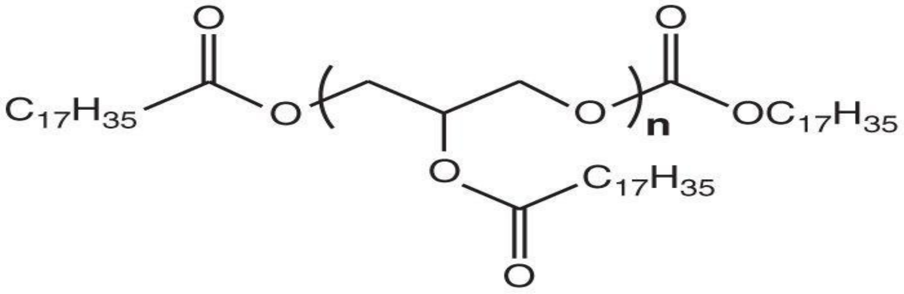
C_8H_{15} to $C_{10}H_{21}$-Polyglucoside



Polyglycerine

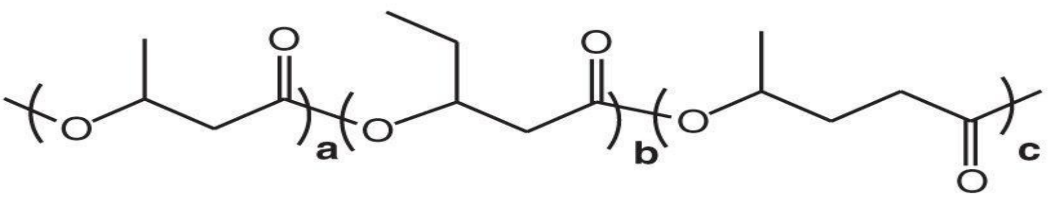


Polyglycerol stearate

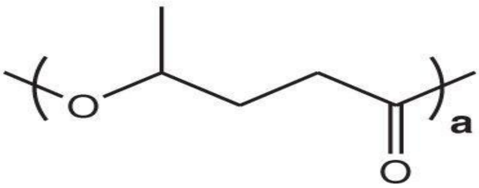


Poly(4-hydroxybutrate)

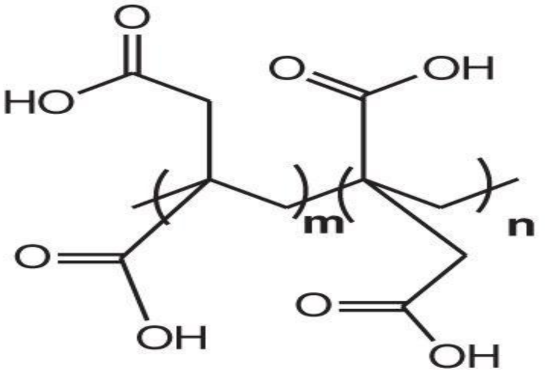
Poly(3-hydroxybutyrate-ter-3-hydroxyvalerate-ter-4-hydroxyvalerate)



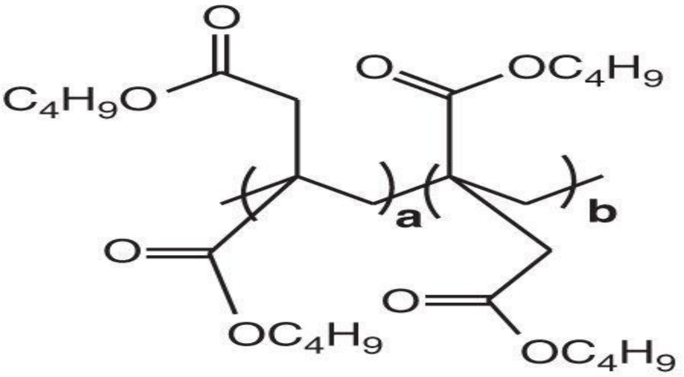
Poly(5-hydroxyvalerate)



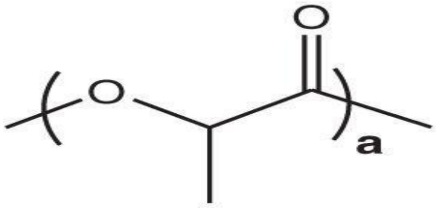
Polyitaconic acid



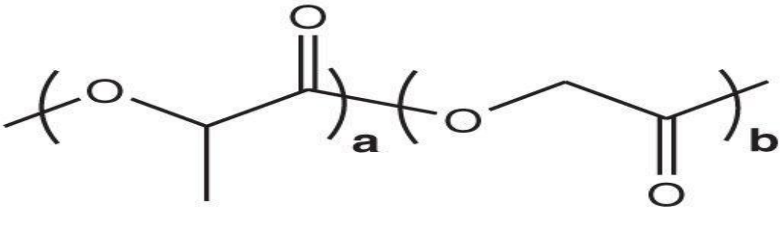
Polyitaconic butyl ester



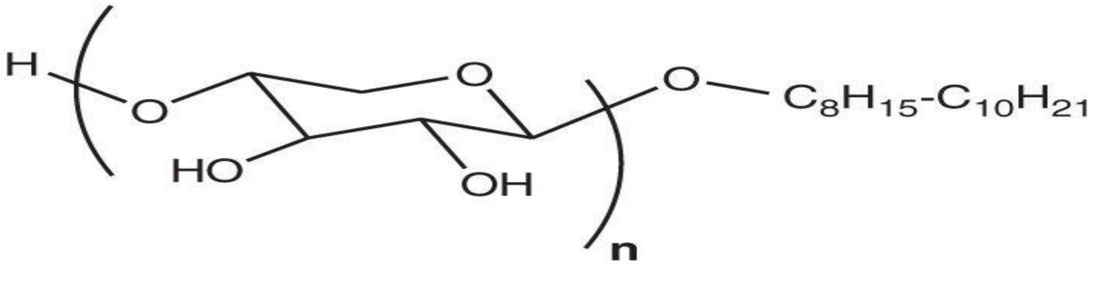
Poly(d,l-lactic acid)



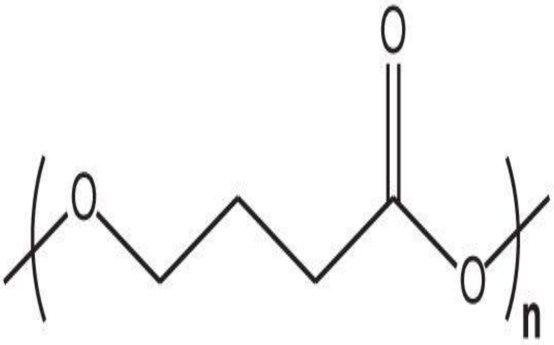
Poly(d,l-lactic-co-glycolic acid)



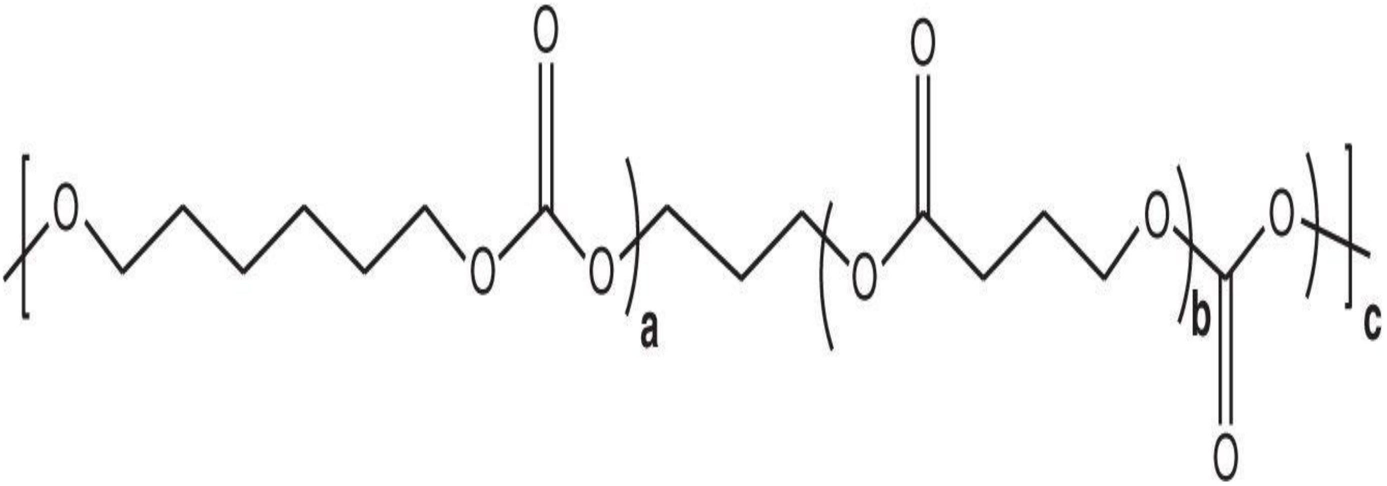
C_8H_{15} to $C_{10}H_{21}$-Polypentoside



Poly(1,3-trimethylene carbonate)



Poly(1,3-trimethylene carbonate-co-hexanediol)



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