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# Capture and Utilization of Carbon Dioxide with Polyethylene Glycol

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## Green Chemistry for Sustainability

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# Foreword by Michele Aresta

Carbon dioxide is produced in several anthropogenic activities at a rate of *ca.* 35 Gt/y. The main sources are: (1) the combustion of fossil carbon (production of electric energy, transport, heating, industry), (2) the utilization of biomass (combustion to obtain energy, fermentation), and (3) the decomposition of natural carbonates (mainly in the steel and cement industry). Due to the fact that the natural system is not able to buffer such release by dissolving $CO_2$ into oceans (or water basins in general) or by fixing it into biomass or inert carbonates, $CO_2$ is accumulating in the atmosphere with serious worries about its influence on climate change. This has pushed toward finding solutions that may avoid that its atmospheric concentration may increase well beyond the actual 391 ppm (the preindustrial era value was 275 ppm). The growth of the energy demand by humanity makes the solution not simple as, according to most scenarios, at least 80 % of the total energy will still be produced from fossil carbon in the coming 30 years or so. This adds urgency to implementing technologies that may reduce both the amount of $CO_2$ released to the atmosphere and the utilization of fossil carbon. Therefore, besides efficiency technologies (in the production and use of energy) other routes must be discovered that may reduce either the production of $CO_2$ or its emission into the atmosphere. Among the former, perennial energy sources (such as: sun, wind, hydro, geothermal) are under exploitation. The reduction of the release of $CO_2$ to the atmosphere is based on its capture from continuous point sources (power-, industrial-, fermentation-, cement-plants) by using liquid or solid sorbents or membranes, a high-cost technology, today.

Such captured $CO_2$ can be either disposed in geologic cavities and aquifers or recycled. The former option corresponds to the $CO_2$ Capture and Storage (CCS) technology, the latter to the $CO_2$ Capture and Utilization (CCU) technology. CCS is believed to be able to manage in general larger amounts of $CO_2$ than CCU. The latter, on the other side, is able to recycle carbon, reducing the extraction of fossil carbon. CCS is energy demanding and economically unfavorable, CCU may or may not require energy (depending on the nature of the species derived from $CO_2$) and is economically viable, as all compounds derived from $CO_2$ or any use of $CO_2$ will have an added value. A concern about the utilization of $CO_2$ lays in the

amount of energy eventually necessary that cannot be derived from fossil carbon. This has prevented so far a large utilization of $CO_2$. But in a changing paradigm of deployment of primary energy sources, if the use of perennial sources will be more and more implemented, the conversion of $CO_2$ into chemicals and fuels may become economically convenient and energetically feasible. The deployment of wind and sun will play a key role in this direction. The former can be coupled with electricity generation and subsequent use of such form of energy in the conversion of $CO_2$, the latter can be used in a direct (photochemical, thermal) or indirect (photoelectrochemical) conversion of $CO_2$. The products obtainable from $CO_2$ are of various nature: fine chemicals, intermediates, fuels.

The $CO_2$ utilization option is a hot topic today and attracts the attention of several research groups all around the world. Dedicated reviews in peer reviewed journals and books make an analysis of possibilities. This book is a comprehensive and timely review of the use of PEG as solvent for $CO_2$ capture or for $CO_2$ conversion. The solvent plays a key role in the conversion of $CO_2$ as the decrease of entropy (gaseous $CO_2$ is converted into a liquid or solid) is against the reaction equilibrium which is shifted to the left. The use of good solvents for $CO_2$ or the use of supercritical $CO_2$ itself as solvent and reagent can help to push the reaction to the right. After an analysis of the phase behavior of the PEG/$CO_2$ system, the author describes the PEG/sc $CO_2$ biphasic solvent system and the role of functionalized-PEG as catalysts for $CO_2$ conversion. The use of PEG in the $CO_2$ capture and subsequent conversion closes the list of topics in the book. All together, the analysis of the PEG/$CO_2$ system presented by the author is complete, and very useful as it is accompanied by a quite exhaustive literature search.

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# Foreword by Chang-jun Liu

A great effort has been made worldwide toward $CO_2$ capture and utilization. There are some good progresses in the capture technologies. The question is: how can we handle the captured $CO_2$? Obviously, storage is not a good option. There are many potential problems with the storage in addition to the expensive cost with the capture and storage. The utilization could finally become the only solution with the serious $CO_2$ issue. Indeed, we have several processes with $CO_2$ as feedstock. However, compared to the huge amount of $CO_2$ generated, we need much more economically feasible processes to use $CO_2$. One has to face the challenges in energy and many others. Especially, any utilization technologies should not lead to more $CO_2$ emission. Unfortunately, we do not see a significant progress in $CO_2$ utilization. We need to work hard to develop such utilization technologies. To do so, more fundamental studies should be conducted. We have to acknowledge that not much fundamental studies are available with $CO_2$ utilization. For example, alumina is the most used catalyst support for $CO_2$ reforming and others. However, no information was available for how $CO_2$ adsorb and convert on it when we started to investigate it in 2009.

$CO_2$ utilization needs further intense fundamental studies, which will lead to novel utilization technologies and finally solve the problem of $CO_2$ emission. In this regard, I am very glad to see that Prof. Liang-Nian He in Nankai University has conducted excellent works in the development of polyethylene glycol-promoted $CO_2$ utilization technology. His group successfully studied the phase behavior of PEG/$CO_2$ system and reaction mechanism at molecular level. The materials they applied are cheap, green, and easy to be processed. And, a significant advantage of

the process Prof. He developed is that it combines the capture and utilization of $CO_2$. It has a great potential for a practical application. I believe that one will be very happy to read the book 'Capture and Utilization of $CO_2$ with Polyethylene Glycol' and find it very useful for future development. This book will be also an excellent reference for textbooks of green chemistry, catalysis, chemical engineering, and others.

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# Acknowledgments

# Contents

# Abbreviations

| | |
|---|---|
| [BMIm]BF$_4$ | 1-butyl-3-methyl-imidazolium tetrafluoroborate |
| BMImCl | 1-butyl-3-methyl-imidazolium chloride |
| [BMIm]PF$_6$ | 1-butyl-3-methyl-imidazolium hexafluorophosphate |
| CCS | $CO_2$ capture and storage/sequestration |
| CCU | $CO_2$ capture and utilization |
| [Choline][Pro] | (2-hydroxyethyl)-trimethyl-ammonium (*S*)-2-pyrrolidine-carboxylic acid salt |
| DBU | Diazabicyclo[5.4.0]-undec-7-ene |
| DMC | Dimethylcarbonate |
| DMF | Dimethylformamide |
| EC | Ethylene carbonate |
| EO | Ethylene oxide, oxyethylene |
| EOS | Equation of state |
| GSS | Gas-saturated solution |
| ILs | Ionic liquids |
| MBMTBP | 2,2′-methylene-bis(4-methyl-6-tert-butylphenol) |
| MEA | Monoethanolamine |
| MW | Molecular weight |
| PC | Propylene carbonate |
| PDMS | Polydimethylsiloxane |
| PEG | Polyethylene glycol |
| PEGda | Poly(ethylene glycol) diacrylate |
| PEO | Polyethylene oxide |
| PMPS | Poly(methylphenylsiloxane) |
| PO | Propylene oxide |
| PPG | Poly(propylene glycol) |
| PPGda | Poly(propylene glycol) diacrylate |
| PTC | Phase-transfer catalyst |
| PTHF | Poly(tetrahydrofuran) |
| PTMO | Polytetramethylene oxide |
| PVP | Polyvinyl pyrrolidone |

| RTILs | Room-temperature ionic liquids |
|-------|--------------------------------|
| scCO2 | Supercritical carbon dioxide |
| SCFs | Supercritical fluids |
| S–L–V | Solid–liquid–vapor |
| TEM | Transmission electron microscopy |
| TEMPO | 2,2,6,6-tetramethylpiperidine-1-oxyl |
| TEPA | Tetraethylenepentamine |
| THF | Tetrahydrofuran |
| TON | Total turnover number |
| TOF | Turnover frequency |
| TSILs | Task-specific ionic liquids |
| VOCs | Volatile organic compounds |

# Chapter 1
# Introduction

## 1.1 Introduction to Carbon Dioxide

The ever-increasing consumption of fossil fuels (oil, coal, petroleum, and natural gas), deforestation, and hydrogen production from hydrocarbons (steam conversion and partial oxidation) by humankind results in an accumulation of $CO_2$ in the atmosphere, from a concentration of 270 ppm at the beginning of the industrial revolution to more than 385 ppm today [1, 2]. It is now widely accepted that $CO_2$, with a growth rate of ca. 2 ppm/year in the atmosphere from the early 2000s, is one of the major greenhouse gases responsible for global warming. Thus, $CO_2$ chemistry (in particular, capture and/or utilization) has attracted much attention from the scientific community and is still a challenging issue in our century [3–6]. $CO_2$ capture and storage/sequestration (CCS) from fossil fuel combustion, e.g., coal-fired power plants, represents a critical component of efforts aimed at stabilizing $CO_2$ levels in the atmosphere adopting liquids, solids and membranes as adsorbents [7–10]. On the other hand, as an abundant, non-toxic, non-flammable, easily available, and renewable carbon resource, chemical utilization of $CO_2$ as green carbonyl source for making value-added chemicals or fuels has great significance [11–19]. Although $CO_2$ utilization is unlikely to consume significant quantities of $CO_2$, development of catalytic processes for chemical transformation of $CO_2$ into useful compounds would be of paramount importance from a standpoint of green and sustainable chemistry. However, few industrial processes utilize $CO_2$ as a raw material, because $CO_2$ is the most oxidized state of carbon, namely $CO_2$ could be thermodynamic stable molecule. The biggest obstacle to establishing industrial processes for $CO_2$ conversion would be due to its low energy level [12]. In short, its inherent thermodynamic stability and kinetic inertness hinder the development of efficient catalysts that achieve activation of $CO_2$ and its subsequent functionalization. Accordingly, only if we understand the underlying principles of $CO_2$ activation, can the goal of using $CO_2$ as an environmentally friendly and economically feasible source of carbon be achieved.

## 1.2 Supercritical $CO_2$/Poly(Ethylene Glycol) in Biphasic Catalysis

$CO_2$ is very attractive as reaction media in biphasic catalysis such as supercritical $CO_2$ (sc$CO_2$) [20–22], sc$CO_2$/$H_2O$ [23], sc$CO_2$/ionic liquids (ILs) [24–26], sc$CO_2$/ PEG [27, 28]. Sc$CO_2$/$H_2O$ biphasic system is found to be effective for water-soluble catalysts [23, 29, 30] but inefficient for reactions in which the reaction components are water-insoluble or sensitive to low pH of the aqueous phase [31]. Combination of ILs and sc$CO_2$ could solve such problem to a certain extent, especially by adopting task-specific ionic liquids (TSILs), allowing the use of hydrophobic homogeneous catalysis with catalyst recycling [24, 25, 32–34]. However, currently available ILs could be enormously expensive, and complicated synthetic and purification procedures are generally needed. In addition, knowledge about impact of ILs on the environment is still limited. Therefore, special attention should be paid to the toxicity issue related to ILs, for example, being harmful to aquatic organisms [35–38].

PEGs are a family of water-soluble linear polymers formed by interaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers. Interest in PEGs stems from its distinctive properties, such as inexpensive, thermally stable, almost negligible vapor pressure, toxicologically innocuous, and environmentally benign characterization [28]. Therefore, PEG could be regarded as an inexpensive, non-volatile, and environmentally benign solvent, which represents an interesting reaction medium for conventional solvent replacement [28, 39–42].

On the other hand, sc$CO_2$ has been touted as a suitable solvent for organic synthesis offering economical and environmental benefits due to its favorable physical and chemical properties, and readily tunable solvent parameters. Recyclability, ease of solvent removal, readily tunable solvent parameters, and moderate critical conditions ($Tc = 31.1$ °C, $Pc = 7.4$ MPa) make sc$CO_2$ a desirable alternative over conventional solvents [43–45]. In particular, dense $CO_2$ appears to be an ideal solvent for use in oxidation. Unlike almost any organic solvent, $CO_2$ will not be oxidized further, and hence the use of $CO_2$ as a reaction medium eliminates by-products originating from solvents. At the same time, dense $CO_2$ provides a safe reaction environment with excellent mass and heat transfer for aerobic oxidations. As a consequence, novel chemistry relevant to enhancing selectivity toward desired products, improving reactivity, and ease of product separation could be created when utilizing dense $CO_2$ as a reaction medium.

In particular, PEGs are able to dissolve common organic solids and metal complexes, which just have very limited solubility in sc$CO_2$. Therefore, the biphasic catalytic system using sc$CO_2$ as the continuous phase (extracting $CO_2$-soluble products) and PEG as the stationary phase to immobilize the PEG-philic catalyst could offer the possibility of recovering the expensive metal catalyst and running the metal-mediated chemical reactions under continuous flow conditions [27, 46].

More importantly, PEG could be regarded as a CO$_2$-philic material through interaction of CO$_2$ with the oxygen atoms of the ether linkages of PEG. In other words, "CO$_2$-expansion" effect could lead to changes in the physical properties of the liquid phase mixture including lowered viscosity and increased gas/liquid diffusion rates [28].

In summary, as an abundant, non-toxic, non-flammable, easily available, and renewable carbon resource, CO$_2$ is very attractive as an environmentally friendly feedstock for making commodity chemicals, fuels, and materials. Therefore, CO$_2$ chemistry has attracted much attention worldwide. On the other hand, polyethylene glycol (PEG) could act as a green replacement for organic solvents, phase-transfer catalyst, surfactant, support, and radical initiator in various reaction systems, significantly promoting catalytic activity and recovering the expensive metal catalyst. In particular, PEG could be regarded as a CO$_2$-philic material and thus has found wide applications in CO$_2$ capture and utilization. In this context, the PEG-functionalized catalysts have been developed for efficient transformation of CO$_2$ into fuel additives and value-added chemicals including cyclic carbonates, dimethylcarbonate, oxazolidinones, organic carbamates, and urea derivatives. In addition, the PEG-functionalized absorbents have been utilized for efficient capture of CO$_2$. We have proposed a carbon capture and subsequent utilization to address energy penalty problem in CO$_2$ capture and storage.

In this book, PEG-promoted CO$_2$ chemistry is summarized based on understanding about phase behavior of PEG/CO$_2$ system and reaction mechanism at molecular level. Those findings presented herein could pave the way for wide applications of PEG in the field of CO$_2$ absorption, activation, and conversion. In detail, we would like to discuss and update advances in capture and utilization of CO$_2$ with PEG, including phase behavior of PEG/CO$_2$ system (Chap. 2); PEG/scCO$_2$ as biphasic solvent system (Chap. 3) in which PEG as a green replacement for organic solvents (Sect. 3.1), as phase-transfer catalyst (PTC) (Sect. 3.2), as surfactant (Sect. 3.3), as support (Sect. 3.4), or as radical initiator (Sect. 3.5); utilization of PEG for physical and chemical absorption of CO$_2$ (Chap. 4); PEG-functionalized catalysts for transformation of CO$_2$ (Chap. 5) into cyclic carbonates (Sects. 5.1, 5.2), dimethylcarbonate (DMC) (Sect. 5.3), oxazolidinones (Sect. 5.4), organic carbamates (Sect. 5.5), or urea derivatives (Sect. 5.6). Finally, we will give one representative example for the utilization of PEG in CO$_2$ capture and utilization (CCU) (Chap. 6).

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# Chapter 2
# Phase Behavior of PEG/CO$_2$ System

**Abstract** High-pressure processes are widely applied in the polymer industry. Near-critical and supercritical fluids (SCFs) (e.g. scCO$_2$) are used owing to their easily tunable density, which enhances control of polymer solubility and good separability from polymer. On the other hand, for homogeneously catalytic reaction using polyethylene glycol (PEG) as a solvent, CO$_2$ can act as a miscibility switch to shift the system from homogeneous at atmospheric conditions to heterogeneous under CO$_2$ pressure. This allows for extraction of the products into the organic solvent phase and immobilization of the homogeneous catalyst in the PEG phase. Understanding of phase behavior in a biphasic solvent system such as PEG/CO$_2$, where a chemical reaction takes place in one phase and the products can be extracted to another phase, would be critical for the design of efficient and environmentally friendly reaction and separation process. In this chapter, phase behavior of different PEG/CO$_2$ systems from 1.13–29.00 MPa CO$_2$ pressure at 313.15–348.15 K with PEG molecular weights (MWs) in the range of 200–35000 is discussed. Ternary systems such as CO$_2$/PEG/ethanol, CO$_2$/PEG/1-pentanol, CO$_2$/PEG/1-octanol, CO$_2$/PEG/1, 4-dioxane, CO$_2$/PEG/acetonitrile and CO$_2$/PEG/1-octene are also investigated. Phase equilibrium data, solid–liquid–vapor (S–L–V) curve, influence of CO$_2$ addition on viscosity of PEG, solubility data of CO$_2$ in PEG or PEG in combination with an organic solvent and so on are explored.

**Keywords** Carbon dioxide · Polyethylene glycol · Phase behavior · Biphasic solvent system · Supercritical fluids · Phase equilibrium

High-pressure processes have been widely applied in the polymer industry. Near-critical and supercritical fluids (SCFs) are in particular used owing to their easily tunable density, which enhances the control of polymer solubility and their good separability from polymer material [1]. SCF solvents (e.g. scCO$_2$) offer a potential advantage for separation process. The solubility of different polymeric material in SCFs can be systematically varied by changing operating conditions. Several

authors have studied the solubility of polymers in SCFs, which is relevant to the fractionation of polymers and is influenced by pressure, temperature, and the molar mass of the polymer. Fundamental knowledge about phase behavior like equilibrium data under high-pressure conditions is needed to design and develop supercritical separation processes [2].

PEGs are water-soluble polymers which, due to their physiological acceptance, are used in large quantities in the pharmaceutical, cosmetics and food industries. Hence, recent research has focused on using PEG as a recyclable solvent for numerous homogeneously catalyzed reactions, such as the Heck, Suzuki–Miyaura, and Sonogashira coupling [3–6]. However, these reactions generally use organic solvents during the separation steps, allowing for extraction of the products and immobilization of the catalysts in the PEG phase. Unfortunately, this eliminates the environmentally benign nature of these solvent systems. Therefore, alternative separation methods, such as SCF extraction with benign solvents e. g. scCO$_2$ have been explored. CO$_2$ can act as a miscibility switch to shift the system from homogeneous at atmospheric conditions to heterogeneous under CO$_2$ pressure. This allows for extraction of the products into the organic solvent phase and immobilization of the homogeneous catalyst in the PEG phase [7].

During the past decade, scCO$_2$ has attracted a great deal of attention as "environmentally benign, inexpensive, and nonflammable alternative" solvent for organic reactions. The low viscosity, near-zero surface tension, relative chemical inertness and high diffusivity of scCO$_2$ results in negligible competitive adsorption with guest molecules on the host substrate and therefore facilitates solute transfer relative to normal solvents. Furthermore, since CO$_2$ is a gas at ambient conditions, the tedious drying procedure associated with conventional liquid solvents is circumvented and the product is free of residual solvent upon depressurization [8]. It also has relatively mild critical conditions (critical temperature, $Tc = 304$ K, critical pressure $Pc = 7.38$ MPa) and hence allows processing at moderate temperatures at which thermal degradation does not occur [9]. Understanding of phase behavior in biphasic solvent system such as PEG/CO$_2$, where a chemical reaction performs in one phase while the products can be extracted to another phase, would be critical for the design of efficient, environmentally friendly reaction and separation process.

## 2.1  Phase Behavior of Different PEG/CO$_2$ System

High-pressure phase equilibria of PEG/CO$_2$ systems was investigated by Gulari et al. [10] for the first time , in which the equilibrium phase compositions of different average molecular weight (MW) PEG/CO$_2$ systems are modeled by using an equation of state (EOS) based on a lattice model. The experimental data cover a range of pressures from 1.13 up to 29.00 MPa at 313 and 323 K. The solubility of PEG in scCO$_2$ is a strong function of MW. At a fixed temperature and pressure, the solubility of PEGs in CO$_2$ drops with MW and the threshold pressure above which

the solubility of PEG is detectable increases with MW, for example, 10 MPa for PEG400 and 15 MPa for PEG600. The solubility of $CO_2$ in PEG varies linearly with pressure, while at pressures above the threshold pressure, it remains relatively constant. The solubility of $CO_2$ in the liquid polymer phase drops with temperature for both PEG400 and PEG600 because $CO_2$, which is a volatile component, evaporates out of the liquid phase very effectively with an increase in temperature. In the SCF phase, the solubility of PEG in $CO_2$ highlights the effect of two competing factors: polymer vapor pressure and SCF density. For example, temperature increasing from 313 to 323 K does not affect the solubility of PEG400 in $CO_2$, which indicates that increase of vapor pressure of the solute and decrease of the $CO_2$ density are compensating each other. On the other hand, the solubility of PEG600 in $CO_2$ falls with temperature, which is governed by decrease in the $CO_2$ density or its solvation power, because PEG600 with higher MW has a lower vapor pressure.

The experimental phase equilibrium data for three systems PEG200/$CO_2$, PEG400/$CO_2$ and PEG600/$CO_2$ are measured at 313.15, 333.15 and 348.15 K in the range of 3.87–24.87 MPa $CO_2$ pressure [11]. A trend is shown by the PEG400/$CO_2$ and PEG600/$CO_2$ systems: at constant temperature, the respective solubilities increase with pressure; and at constant pressure, the respective solubilities decrease with temperature. In the $CO_2$-rich phase, the solubility of PEGs increases slightly with pressure, but it is always very low in a pressure range of 0–26 MPa. An increase in temperature or in PEG molar mass reduces the solubility. Qualitatively, the solubility of a polymer in SCFs decreases with the degree of polymerization. In the PEG-rich phase, the $CO_2$ solubility increases significantly with pressure, especially at low temperature.

The solubilities of $CO_2$ in PEG400 and PEG600 are very similar at each temperature and pressure, while they are higher than the solubility in PEG200. This low solubility of $CO_2$ in PEG200 can be attributed to negative end-group effects. Indeed, the properties of low molar mass PEG in solution depend to a large extent on the presence of hydroxyl end groups, which are responsible for attractive interactions such as aggregation and auto-association in the presence of aqueous and organic solvents [12, 13]. However, for PEG/$CO_2$ systems the influence of hydroxyl end groups becomes negligible when the polymer mass is higher than 400 g mol$^{-1}$ [14].

PEGs with up to a molar mass of 600 g mol$^{-1}$ are liquid, while those with higher molar masses are solid. S–L–V transitions for PEG (with MW of 1,500, 4,000, 8,000 and 35,000 g mol$^{-1}$) are investigated [15]. Generally, applying static pressure to a substance in most cases results in an increase in the melting temperature (S–L transition under pressure). However, for PEG1500, PEG4000 and PEG35000, the liquefaction temperature increases as $CO_2$ pressure rises to about 10 bar as compared to the melting point at 1 bar; while at pressures greater than 10 bar, the transition temperature of the PEGs investigated decreases (for PEG1500, from 46.2 °C at 1 bar to 30 °C at 70 bar) due to the effect of $CO_2$ molar volume under different hydrostatic pressure. For V–L transition, the solubility of
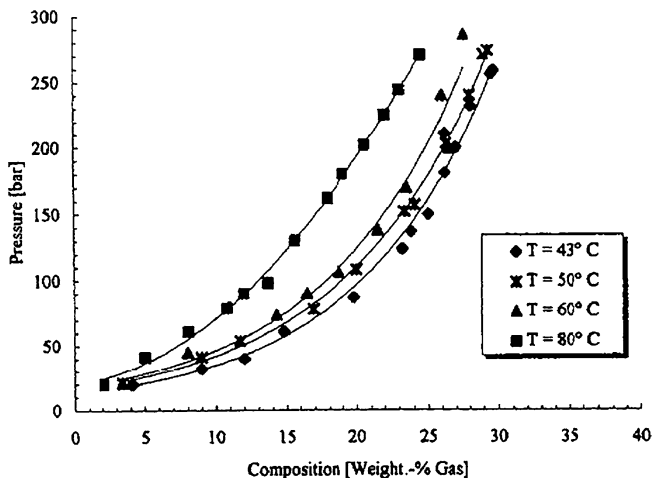
**Fig. 2.1** Solubility of CO$_2$ in PEG1500 at various temperatures and pressures. (Reprinted from Ref. [15], with permission from Elsevier)

CO$_2$ in PEG1500 decreases with increasing temperature, and increases with increasing pressure (Fig. 2.1).

Influence of SCF addition on polymer properties (density and viscosity) is measured in a range of temperatures from 313 to 348 K and at pressures up to 25 MPa [16]. For the CO$_2$-saturated PEG400 at 313.25, 332.89 and 347.77 K, a minimum viscosity of about 5 MPa s at 25 MPa is obtained at 313.25 K, corresponding to 89 % viscosity reduction. At 332.89 K this viscosity reduction is about 83 %, and at 347.77 K it is only 76 %. This phenomenon can be related to a decrease of the CO$_2$ solubility in the PEG400 when temperature increases. For densities of PEG400, it increases rapidly with CO$_2$ pressure in the low-pressure region ($P < 3$ MPa).

Phase equilibria in the binary polymer/gas systems such as PEG/propane, PEG/N$_2$ and PEG/CO$_2$ have been investigated, with PEG MW of 200, 1,500, 4,000 and 8,000 g mol$^{-1}$, in a temperature range of 50–120 °C and a pressure range from 5 to 300 bar using a static-analytical method [17]. It is found that CO$_2$ dissolves much better in PEG than does propane or N$_2$. With rising temperature, the PEG/CO$_2$ miscibility gap increases, whereas the miscibility gaps of the PEG/propane and the PEG/N$_2$ systems decrease. The influence of the polymer MW on the gas solubility is almost negligible for PEG1500–PEG8000, while the behaviour of the small PEG200 deviates significantly due to strong endgroup influence.

Understanding of phase behavior in biphasic systems such as PEG/CO$_2$ is critical for the design of an efficient and environmentally friendly reaction and separation process. Jessop et al. developed the first PEG/scCO$_2$ scheme in the rhodium catalyzed hydrogenation of styrene to ethyl benzene, in which the reaction is conducted at 40 °C and then swept with scCO$_2$ to remove the products, and the catalyst is immobilized in the PEG phase and recycled five times with no loss

in activity [18]. As previously reported, the solubility of PEG in scCO$_2$ can be dramatically reduced by increasing the temperature and by increasing the MW of PEG. Increasing the temperature of scCO$_2$ decreases in the solubility of PEG, while raises the solubility of typical organic small molecule products [19]. Commercially available PEG1500 is found to be a waxy solid at room temperature, melting at 48–51 °C, but a liquid at 40 °C if it is under a CO$_2$ pressure of greater than 90 bar. Thus, PEG1500 is chosen as solvent for scCO$_2$ extraction of ethylbenzene, with less co-extracted PEG (0.2 mg, 0.1 %), than the case with PEG900. Commercially available PEG fractions with average MWs of 300 and 600 are viscous liquids at room temperature but are readily extracted by scCO$_2$.

## 2.2 Phase Behavior of PEG/CO$_2$/Organic Solvent

In the polymer industry involving SCFs, a co-solvent is commonly needed because the solubility of a polymer in high-pressure is very low. In order to consider an effective method for the production of polymeric materials using scCO$_2$, it is essential to understand the liquid–liquid (L–L) phase behavior of CO$_2$ + polymer + co-solvent systems at constant pressure and temperature [9, 20].

A mixture of CO$_2$ + PEG + ethanol splits into two liquid phases at 15 MPa and 313.2 K: a polymer-rich phase and a polymer-lean phase [9]. The solubility of PEG in the polymer-lean (CO$_2$-rich) phase is very low (less than 1 wt. %) because CO$_2$ behaves as a non-solvent for PEGs. On the other hand, in the polymer-lean phase, the solubility of PEG increases with an increase in ethanol concentration because ethanol is a relatively good solvent for PEG at 313.2 K. In the L–L phase boundary of the PEG + CO$_2$ + ethanol system, the size of the two-phase region increases with an increase in the PEG MW from 1000 to 20000 at 313.2 K and 15 MPa (Fig. 2.2a). The effect of pressure (from 10 to 20 MPa) on the cloud point (cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance) of the CO$_2$ + PEG6000 + ethanol system at 313.2 K shows that the L–L boundary region decreases with increasing pressure (Fig. 2.2b), due to the increase of solvent density, resulting in the enlargement of the one phase region. When the ethanol to PEG6000 weight ratio is 95:5, the L–L boundary pressure increases with temperature (Fig. 2.2c), owing to the relatively rapid expansion of the solvent with increasing temperature, which makes it a less good solvent at higher temperatures [21]. The cloud point pressure increases with increasing in CO$_2$ concentration, and CO$_2$ enlarges the two-phase region. The addition of CO$_2$ to ethanol causes a lowering of the dissolving power of the mixed solvent.

The solubility of CO$_2$ in 1-pentanol, 1-octanol, PEG200, PEG200 + 1-pentanol and PEG200 + 1-octanol mixtures at 303.15, 313.15 and 323.15 K at pressures up to 8 MPa are measured, and the mass ratios of PEG200 to the alcohols are 1:0, 3:1, 1:1, 1:3 and 0:1, respectively [22]. The solubility of CO$_2$ in the neat solvents and the mixed solvents with different compositions increases with increasing pressure

**Fig. 2.2 a** Effect of the MW of PEG on the cloud point compositions of the CO$_2$ (1) + PEG (2) + ethanol (3) system at 313.2 K and 15 MPa. **b** Effect of pressure on the cloud point compositions of the CO$_2$ (1) + PEG (2) + ethanol (3) system at 313.2 K. **c** Cloud point pressures of the CO$_2$ (1) + PEG (2) + ethanol (3) system. The ethanol to PEG6000 weight ratio is 95:5. Symbols are experimental cloud point compositions. Solid lines are determined using the Sanchez-Lacombe EOS. (Reprinted with permission from Ref. [9], with permission from Elsevier)
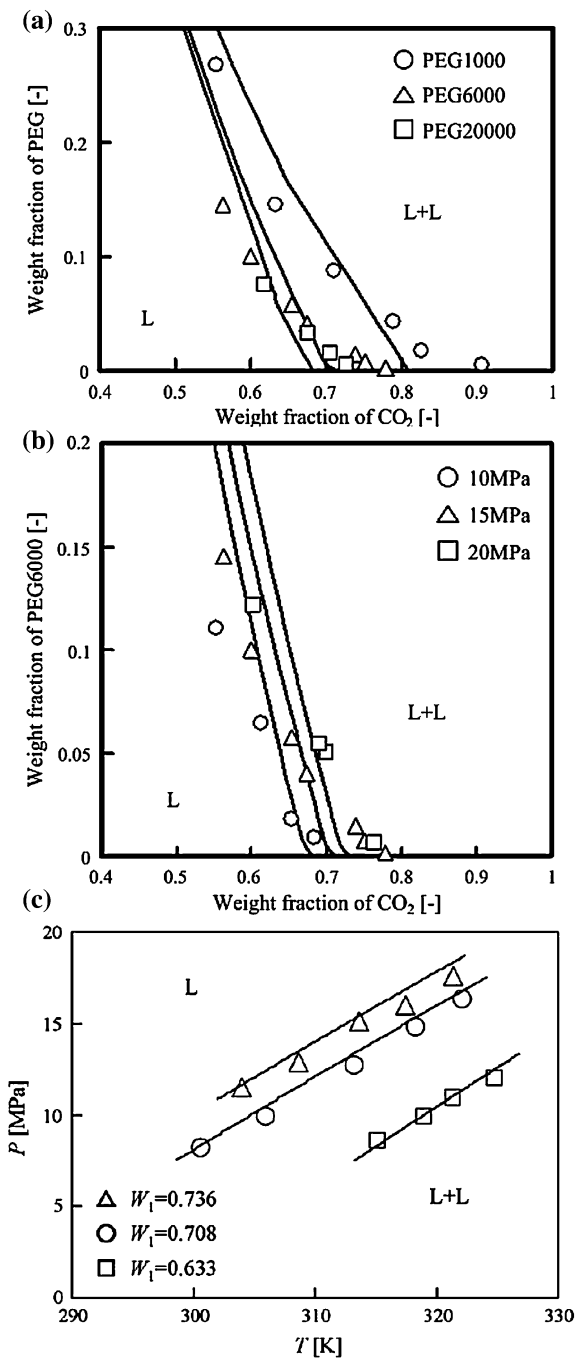
of CO$_2$. The solubility of CO$_2$ in 1-pentanol and 1-octanol is larger than that in PEG200, and the solubility of CO$_2$ in the mixed solvents increases with increasing weight percent of 1-pentanol or 1-octanol. The solubility of CO$_2$ in PEG200 + 1-pentanol is larger than that in PEG200 + 1-octanol, because CO$_2$ is more soluble in 1-pentanol than that in 1-octanol. In addition, an increase in temperature results in decrease in the solubility of CO$_2$.

Phase behavior for PEG400 and CO$_2$ with 1,4-dioxane and acetonitrile at 25 and 40 °C is explored, in which two liquid phases, a PEG-rich lower and an organic-rich upper, as well as a CO$_2$-rich vapor phase are showing [7]. For the PEG400/1,4-dioxane/CO$_2$ system at 25 °C, with CO$_2$ pressure increasing from 5.2 to 6.0 MPa, the compositions in the PEG-rich phase show increasing PEG content with decreasing amounts of both CO$_2$ and dioxane. The dioxane-rich phase shows a modest decrease in PEG content and significant increase in CO$_2$. The increase in CO$_2$ causes the dioxane content to decrease, which allows CO$_2$ to enhance its lead as the primary component of the second liquid phase at >90 wt %. For the EPG400/acetonitrile/CO$_2$ system at 25 °C with CO$_2$ pressure increasing from 5.5 to 6.2 MPa, the compositions in the PEG-rich phase show a minimal change in the PEG content, with increasing CO$_2$ and decreasing acetonitrile. The acetonitrile-rich phase shows decreasing PEG and acetonitrile with increasing CO$_2$.

For vapor–liquid equilibria for CO$_2$ + 1-octene + PEG at 308.15, 318.15 and 328.15 K at pressures up to 10 MPa, with PEG MWs of 200, 400 and 600, three-phase region of the ternary systems exists: a CO$_2$-rich phase, a 1-octene-rich phase and a PEG-rich phase [23]. The solubility of PEGs in 1-octene and in CO$_2$ is extremely low. Mass fraction of 1-octene increases with increasing pressure in the low-pressure range and decreases with an increase in pressure in the high-pressure region, because pressure affects the mass fraction in two opposite ways: first, the increase of pressure should enhance the dissolution of 1-octene because CO$_2$ reduces the PEG polarity, and the concentration of CO$_2$ in the PEG-rich phase increases with increasing pressure; second, an increase in pressure results in an increase in the solvent power of CO$_2$ in the vapor phase, which is unfavorable to the dissolution of 1-octene in the PEGs. The competition of the two factors results in the maxima in the curves. So the solubility of 1-octene in PEGs can be enhanced considerably by CO$_2$ at suitable pressures. For reactions involving olefins, the low solubility of the olefin in PEGs may lower reaction rates, reduce product yields and cause the reaction to be mass-transfer limited. This disadvantage can be overcome to a certain degree by adding CO$_2$. In addition, dissolution of CO$_2$ may reduce the viscosity because dissolution of CO$_2$ can reduce the viscosity of other liquids significantly, which may also enhance the reaction rate [24]. The mass fraction of 1-octene in the PEG-rich phase increases with increasing PEG MW. This is understandable that the polarity of a PEG with larger MW is lower, while 1-octene is non-polar. An increase in temperature results in an increase in mass fraction of 1-octene in the PEG-rich phase, originating from the higher solubility of 1-octene in the PEGs at higher temperature. The mass fraction of CO$_2$ in the PEG-rich phase increases continuously with increasing pressure, or increasing temperature at all the pressures and also with the increase of PEG MW.

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# Chapter 3
# PEG/scCO$_2$ Biphasic Solvent System

**Abstract** PEG is an inexpensive, non-volatile and environmentally benign solvent, which represents an interesting reaction medium for conventional solvent replacement. More importantly, PEG could be regarded as a CO$_2$-philic material through interaction of CO$_2$ with the oxygen atoms of the ether linkages of PEG. In other words, "CO$_2$-expansion" effect could lead to changes in the physical properties of the liquid phase mixture including lowered viscosity and increased gas/liquid diffusion rates. This chapter describes various functions of PEGs in catalytic reactions involving PEG/scCO$_2$ biphasic solvent system, including PEG as a green replacement for organic solvents for the RhCl(PPh$_3$)$_3$-catalyzed hydrogenation of styrene to ethyl benzene, lipase-catalyzed acylation of alcohols, aerobic oxidation of alcohols and olefins, hydrogenation of $\alpha$, $\beta$-unsaturated aldehydes (Sect. 3.1); PEG as PTC for catalytic reduction reactions (Sect. 3.2); PEG as surfactant for Aldol- and Mannich-type reactions (Sect. 3.3); PEG as support for oxidation of alcohols, hydroformylation of olefins (Sect. 3.4); and PEG as radical initiator for formylation of alcohols benzylic C=C cleavage reactions (Sect. 3.5).

**Keywords** Carbon dioxide · Polyethylene glycol · Biphasic solvent system · Phase-transfer catalyst · Surfactant · Radical initiator

## 3.1 PEG as a Green Replacement for Organic Solvents

ScCO$_2$ can serve as a particularly attractive mobile phase for organic reactions for several reasons [1]: (1) it has a good solvent power for gas molecules (e.g., oxidation reaction involving oxygen), (2) its fluid properties simplify mass transport and separation from the product (no residues), and (3) as an inert gas, its

presence reduces the risk of explosions drastically which makes the system inherently safe. On the other hand, PEG is cheap, chemically stable, and toxicologically absolutely inoffensive, and by choosing the right molecular weight, it is not extractable and especially in a compressed CO$_2$ (which can lower the melting point and the viscosity of PEG), while being a good solvent for many metal catalysts and organic compounds.

Homogeneous catalysis is generally preferable to heterogeneous catalysis in terms of enhancing activity and selectivity, but homogeneous catalysts suffer from being difficult to separate from the product. Biphasic catalysis, an important immobilization technology for rendering homogeneous catalysts recyclable, involves one solvent, generally polar, that dissolves and retains the catalyst, and another solvent, generally nonpolar, that dissolves the products. The success of such schemes requires that two liquids can be sufficiently different in properties, usually polarity, that partitioning of the catalyst will be almost exclusively to one phase. The first system of non-volatile organic compounds (non-VOCs) solvents for biphasic catalysis is H$_2$O/scCO$_2$ which is effective for water-soluble catalysts [2–4] but not effective for reactions where the reactant and catalyst are water-insoluble or sensitive to low pH of the aqueous phase [5]. The recently discovered ILs/scCO$_2$ system [6, 7] could be one candidate to address these problems, allowing the use of hydrophobic homogeneous catalysis with catalyst recycling [8–11] but ILs are moderately to enormously expensive, and knowledge of their environmental impact is still limited. Therefore, it is appealing to develop a new high efficient non-VOC solvent system. Fortunately, a new biphasic solvent system consisting of scCO$_2$ and PEG has been found suitable for homogeneous catalysis with catalyst recycling without the use of volatile or halogenated solvents [12].

PEG is inexpensive, nonvolatile, and benign reaction medium for the catalyst-bearing phase in biphasic catalysis with scCO$_2$ [13]. Non-volatile, catalyst-bearing phase in a biphasic solvent system is preferred because this eliminates evaporative losses and allows extraction of products from the liquid with scCO$_2$ without concomitant extraction of the solvent. PEG and CO$_2$ are so benign that they are approved for use in food and beverages, respectively. PEG/CO$_2$ biphasic system is an excellent combinative reaction medium for running the reactions in continuous mode, and thus the products can be easily separated by extraction with scCO$_2$.

The utility of the methodology for biphasic catalysis has been demonstrated with the RhCl (PPh$_3$)$_3$-catalyzed hydrogenation of styrene to ethyl benzene in PEG (MW = 900) (reaction conditions: 30 bar H$_2$, 50 bar CO$_2$, 40 °C and 19 h) [12]. A total of five cycles are performed with one batch of catalyst/PEG solution, without replenishing either the catalyst or the PEG. The catalyst keeping active as >99 % conversion is found for all five cycles.

The biphasic solvent system composed of PEG and scCO$_2$ is ideally suited for the lipase-catalyzed acylation of alcohols, both batch and continuous-flow acylations are possible (Scheme 3.1) [14].

The kinetic resolution of *rac*-1-phenylethanol has been carried out using the biphasic system PEG1500/scCO$_2$. In a batch reaction an ideal conversion of 50.4 % can be achieved, affording (R)- (ee $\sim$ 98.1 %) and (S)- (ee $\sim$ 99.7 %)

**Scheme 3.1** General scheme for biphasic lipase catalysis [14]
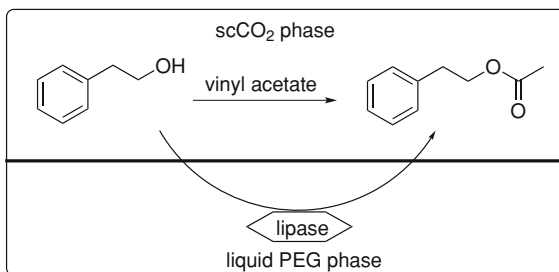


**Scheme 3.2** Aerobic oxidation of alcohols based on dispersed Pd nanoparticles in a PEG matrix with $scCO_2$ [13]
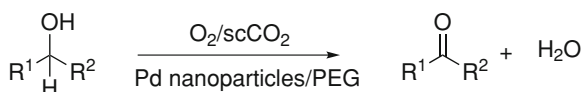


products. The reaction can be repeated over 11 times using the lipase-containing PEG after $scCO_2$ extraction (55 °C/140 bar) of the products, resulting in the steady performance of the system with conversion: 47.9–51.6 %.

The aerobic oxidation of alcohols to aldehydes and ketones is a fundamental chemical transformation for the production of a large variety of important intermediates and fine-chemical products. Catalytic processes for this reaction are being investigated intensively to replace stoichiometric oxidation processes that generate large amounts of heavy metal and solvent waste [15–17]. Among the transition metals, palladium nanoparticles show very promising catalytic performance [18–20]. However, there are two of the major limitations related to rapid catalyst deactivation by aggregation and formation of Pd-black [21], and the need for large amounts of organic solvents in batchwise solution-phase processes involving molecular oxygen [22, 23].

In this context, Leitner et al. have developed a novel catalytic system for selective aerobic oxidation of alcohols based on highly dispersed Pd nanoparticles in a PEG matrix with $scCO_2$ as the substrate and product phase (Scheme 3.2) [13].

Catalytically active particles can be formed from various palladium sources under supercritical reaction condition, which could be helpful for the particle dispersion. Therefore, those materials show high catalytic activity, selectivity, and stability for a broad range of substrates. Additionally, the PEG matrix effectively stabilizes and immobilizes the catalytically active particles, whereas the unique solubility and mass transfer properties of $scCO_2$ allow continuous processing at mild conditions, even with low-volatility substrates.

Han's group has also developed the ZnO-supported Co(II) in PEG600/$scCO_2$ biphasic system for the oxidation of secondary alcohols into ketones using $O_2$ as terminal oxidant [24]. In the case of benzhydrol as the substrate (Scheme 3.3, $R^1=R^2=Ph$), 98, 91, and 89 % yield of the corresponding ketone can be obtained
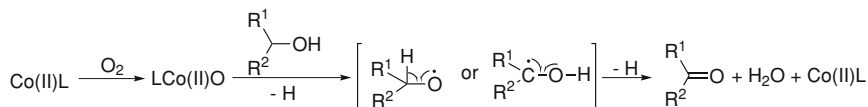
**Scheme 3.3** The possible oxidation mechanism of secondary alcohols catalyzed by Co(II) in PEG (Reprinted from Ref. [24], with permission from Elsevier)

under 1.5 MPa O$_2$, 10 MPa total pressure after adding CO$_2$ at 70 °C for 9 h catalyzed by CoCl$_2$·6H$_2$O, and its supported catalysts such as Co(II)/Al$_2$O$_3$, Co(II)/ZnO, respectively. However, the catalytic activities of the unsupported CoCl$_2$·6H$_2$O and Co(II)/Al$_2$O$_3$ decrease greatly when the recovered catalytic system is reused for further catalytic reactions. Whereas Co(II)/ZnO gives good stability in the four recycling experiments, indicating that ZnO can stabilize the catalyst in PEG/scCO$_2$ system for the oxidation reaction.

CO$_2$ affects the reaction rate presumably in two opposite ways. First, addition of CO$_2$ reduces the viscosity of PEG [25], which is favorable to enhance the reaction rate. On the other hand, CO$_2$ can expand the liquid and too much CO$_2$ can dilute the reaction species, which reduces the reaction rate. As a result, the maximum yield appears at 6 MPa total pressure including 1.5 MPa O$_2$ at 70 °C.

The reaction does not occur obviously in three commonly used ILs {1-butyl-3-methyl-imidazolium chloride ([BMIm]Cl), 1-butyl-3-methyl-imidazolium tetra-fluoroborate ([BMIm]BF$_4$), 1-butyl-3-methyl-imidazolium hexafluorophosphate ([BMIm]PF$_6$)}. Only 3 % yield can be obtained in water, indicating PEG is the best solvent for the oxidation of secondary alcohols when using Co(II)/ZnO as catalyst. This is because PEG can form Co(II) complex (Co(II)L), which can activate O$_2$ molecule and thereby promote the oxidation of organic compounds (Scheme 3.3) [26].

Processes involving the oxidation of olefins using air or oxygen could be of great importance to industrialized economies because of their role in converting petroleum hydrocarbon feedstocks into industrial organic chemicals. Unlike almost any organic solvent, CO$_2$ will not be oxidized further and hence appears to be an ideal solvent for oxidative reactions, eliminating by-products originating from the solvent. Moreover, high miscibility of the gaseous oxidant such as O$_2$ in scCO$_2$ could eliminate interphase transport limitations [27–29].

Palladium-catalyzed Wacker process using CuCl$_2$ or CuCl as co-catalyst in acidic aqueous medium under an oxygen atmosphere is an efficient process for the oxidation of alkenes to methyl ketones [30–35]. However, Wacker oxidation reaction generally suffers from Pd deactivation owing to aggregation and formation of less active Pd-black, high catalyst loading, and a limited substrate scope. In order to circumvent these problems, we introduce a biphasic PEG300 (MW = 300)/scCO$_2$ system on the Wacker oxidation of styrene into acetophenone and minor benzaldehyde catalyzed by PdCl$_2$/CuCl using molecular oxygen (Scheme 3.4) [36]. In pure CO$_2$, the conversion of styrene could reach 100 % with

**Scheme 3.4** PdCl$_2$/CuCl-catalyzed Wacker oxidation of alkenes to methyl ketones [36]
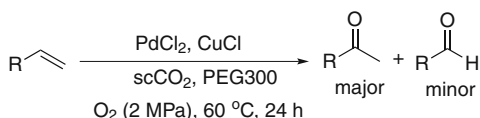
| R | Yield/% | Selectivity/% |
|---|---|---|
| Ph | 90 | 90 |
| p-Me-C$_6$H$_4$ | 87 | 87 |
| p-Cl-C$_6$H$_4$ | 72 | 90 |
| p-MeO-C$_6$H$_4$ | 85 | 85 |
| n-hexyl | 58 | 95 |
| n-butyl | 99 | 99 |

74 % yield of acetophenone and 22 % yield of benzaldehyde. The reaction also runs quiet well even in pure PEG300 (83 % yield and 83 % selectivity of acetophenone), possibly owing to its unique properties. Notably, utilization of biphasic PEG/scCO$_2$ system noticeably enhances the yield (92 %) and selectivity of acetophenone (92 %). Furthermore, the oxidation of styrene proceeds smoothly even in a low catalytic amount of 0.6 % relative to styrene (compared with 10 % catalyst loading as previously reported [37]), with 88 % yield and 92 % selectivity of acetophenone. Notably, the presence of PEG can stabilize the Pd(0) generated from the catalytic approach, allowing the catalyst to participate in more catalytic cycles [13], so the catalyst loading could be reduced.

It is well known that the properties of supercritical fluids are sensitive to pressure, and thus pressure may drastically influence the catalytic activity or the product selectivity when a reaction takes place in supercritical conditions. The favorable pressure for the Wacker oxidation of styrene is around 16 MPa of total pressure including 3 MPa O$_2$, at which the selectivity toward acetophenone reaches 92 %, while under a total pressure of 9 MPa, the selectivity for acetophenone is lower (86 %). However, CO$_2$ with a higher pressure of over 20 MPa might retard the interaction between the substrate and the catalyst, and might cause a low concentration of substrate in the vicinity of the catalyst, thus resulting in a relatively low yield [38].

Four common aromatic olefins as well as two aliphatic counterparts could be converted to the desired methyl ketones in good to excellent yields and selectivity through Wacker oxidation reaction as shown in Scheme 3.4.

It is noteworthy that benzaldehyde can be obtained as a main product with up to 85 % yield with concomitant of 10 % acetophenone and a small amount of benzoic acid if the co-catalyst CuCl is absent by using a biphasic scCO$_2$/PEG system, as shown in Scheme 3.5. The presence of CO$_2$ could suppress the generation of acetophenone. In addition, the oxidized products could be extracted with scCO$_2$, or with diethyl ether, and the PEG phase which immobilized the catalyst is readily reused without further purification or activation. PdCl$_2$ can be recycled for at least five times and the yield of benzaldehyde still reaches over 80 %. Pd leaching is found to be at the level of 0.5 ppm measured by Atomic Absorption Spectroscopy.
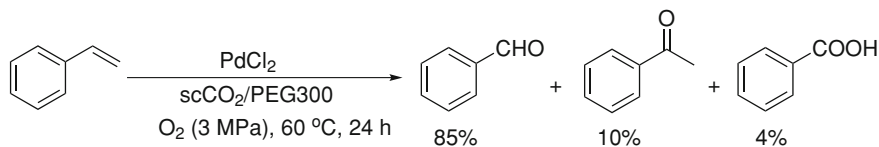
**Scheme 3.5** PdCl$_2$-catalyzed aerobic oxidation of styrene in scCO$_2$/PEG (Reproduced from Ref. [36] with permission from The Royal Society of Chemistry)

Biphasic system of PEG and compressed carbon dioxide being effective for selective hydrogenation of α, β-unsaturated aldehydes using PEG-soluble tetrakis (triphenylphosphine) ruthenium dihydride (H$_2$Ru(TPP)$_4$) catalyst has also been reported (Scheme 3.6) [39]. The reaction can proceed smoothly in the CO$_2$-dissolved expanded liquid PEG phase and the mass transfer rate is also larger as compared with the viscous neat PEG phase. When the biphasic reaction mixture is pressurized by 8 MPa CO$_2$, the conversion can be enhanced to >95 % and the selectivity to unsaturated alcohols is almost perfect (99 %) compared with the previous low conversion (51 %) without CO$_2$. The pressurization with CO$_2$ promotes the dissolution of H$_2$ into the liquid phases and the mass transfer in the liquid reaction phases, which may explain the rate enhancement observed. In addition, the liquid phases dissolving CO$_2$ molecules are also effective media for the H$_2$Ru(TPP)$_4$ complex catalyst to show its specific activity for selective hydrogenation of the C=O bond. PEG solvent with different molecular weights has been tested for citral hydrogenation under biphasic conditions with 8 MPa CO$_2$. Results indicate that the PEGs with various molecular weights (MW) of 600–6,000 show no difference in the conversion and selectivity. However, when the MW is increased to 10, 000 and 12, 000, the conversion decreases to 79 and 52 %, respectively, but the selectivity to unsaturated alcohols remains unchanged which may be explained by negative effects on the dissolution of H$_2$ and the mass transfer in the liquid reaction phase. The common feature is that the organic products are separable from the PEG phase by extraction with high pressure CO$_2$ stream. Another advantage is no leaching of Ru species from the PEG phase when the product separation performs by using CO$_2$ extraction. The catalyst-containing PEG phase is recyclable without any post-treatment but the catalyst activity gradually decreases during the repeated reaction runs, probably due to its structural alteration.

Particle design is presently a major development of supercritical fluids applications, mainly in the paint, cosmetic, pharmaceutical, and specialty chemical industries [40–42]. The particle formation of functional pigments with biodegradable polymer has been successfully performed by gas-saturated solution (GSS) process using scCO$_2$ and PEG in a thermostatted stirred vessel [43]. The average diameter of the particles obtained by GSS at different conditions (40 and 50 °C, 10–30 MPa) is about 0.78–1.472 μm.
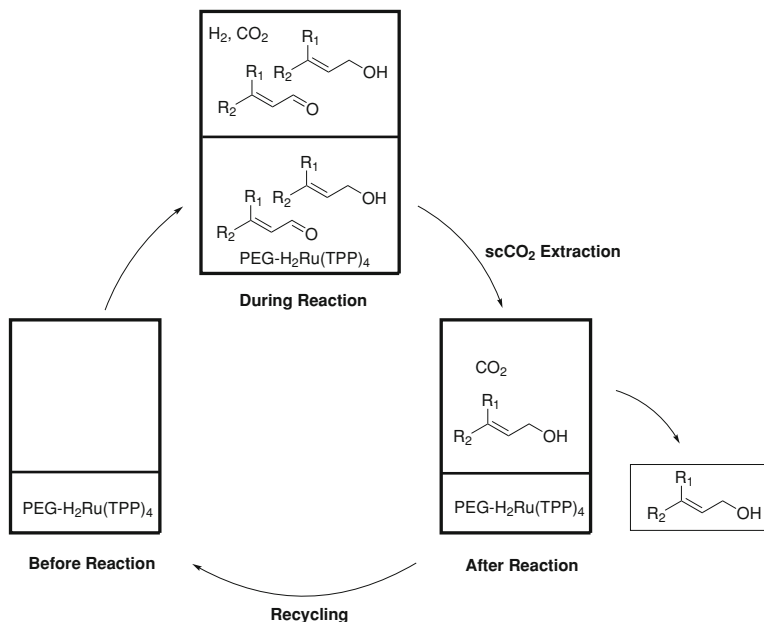
**Scheme 3.6** Reaction, separation, and recycling processes in hydrogenation of $\alpha$, $\beta$ -unsaturated aldehydes with Ru complex catalyst under gas ($H_2$, $CO_2$)-liquid (PEG) biphasic conditions (Reproduced from Ref. [39] with permission from The Royal Society of Chemistry)

## 3.2 PEG as Phase-Transfer Catalyst

Phase-transfer catalysis could be a powerful and widely used technique for conducting heterogeneous reactions between two or more reactants in two or more immiscible phases, by employing a PTC to transfer one of the reacting species from one phase into a second phase where the reaction can take place [44, 45].

PEGs have been extensively investigated as PTCs in many commercial processes to replace expensive and environmentally harmful PTCs [46, 47]. Compared with the commonly used PTCs, linear PEGs are much cheaper than analogous macrocyclic crown ethers and cryptands [48]. PEGs are also more stable at high temperatures, up to 150–200 °C, and show higher stability to acidic and basic conditions than quaternary onium salts [49].

Generally, PTC involves the transfer of an ionic reactant from an aqueous or solid phase into an organic phase across an interfacial area, where it reacts with a non-transferred reactant. Once reaction is complete, the catalyst must transport the ionic product back to the aqueous or solid phase to run a new catalytic cycle. The classical description of the PTC cycle between an aqueous or solid phase and an organic phase is illustrated in Scheme 3.7.

Traditional polar organic solvents are used in PTC to obtain a high rate of ion transfer and to increase reaction rates but less environmentally compatible.

**Scheme 3.7** PTC cycle
between an aqueous or solid
phase and an organic phase
[50]

Organic Phase

$$R-X \; + \; \overset{\oplus}{Q} \; \overset{\ominus}{Y} \; \longrightarrow \; R-Y \; + \; \overset{\oplus}{Q} \; \overset{\ominus}{X}$$

Interface $\left[ \; \overset{\oplus}{Q} \; \overset{\ominus}{Y} \; \rightleftharpoons \; \overset{\oplus}{Q} \; \overset{\ominus}{X} \; \right]$

$$\overset{\ominus}{Y} \qquad\qquad \overset{\ominus}{X}$$

Aqueous/Solid Phase
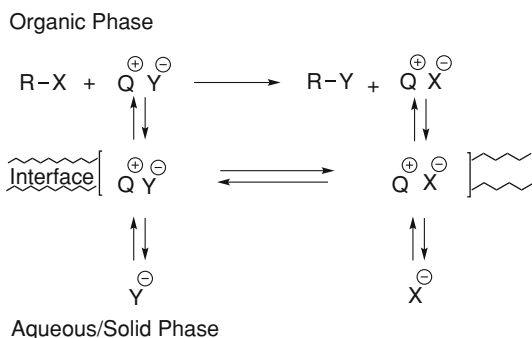
**Scheme 3.8** Three-phase
PTC system with a catalyst-
rich surface phase under
dynamic conditions [50]
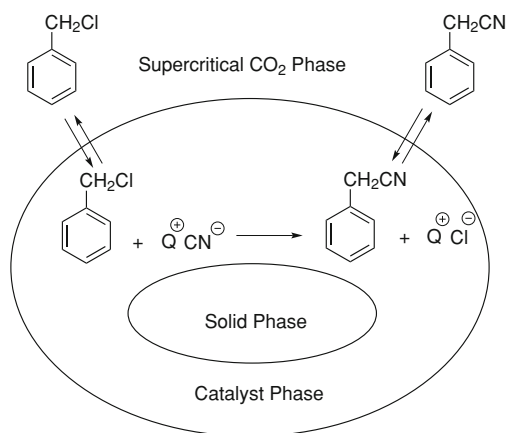
Delightedly, scCO$_2$ could give inexpensive, non-flammable, and environmentally benign advantages. Since scCO$_2$ is highly compressible in the near-critical region, small changes in temperature and pressure result in large density changes and considerable solubility variations [50]. Consequently, it is feasible that even non-polar scCO$_2$ might be acceptable solvents for many PTC reactions.

The mechanism for the nucleophilic displacement reaction of benzyl chloride with potassium cyanide has also been studied under multiphasic conditions, i.e., an scCO$_2$ phase and a solid salt phase with a tetraheptylammonium salt as the phase-transfer catalyst (PTC) (Scheme 3.8). The kinetic data and catalyst solubility measurements indicate that the reaction pathway involves a catalyst-rich third phase on the surface of solid salt phase.

Non-volatile solvents eliminate the health and environmental risks associated with the use of volatile solvents, but may pose their own risks and separation problems. Several liquid polymers, such as PEG, poly(propylene glycol) (PPG), poly(tetrahydrofuran) (PTHF), Polydimethylsiloxane (PDMS), poly(methylphenyl siloxane) (PMPS), and variations of those with ether or ester end-capping groups, are compared in terms of environmental risk, solvent polarity, and performance as
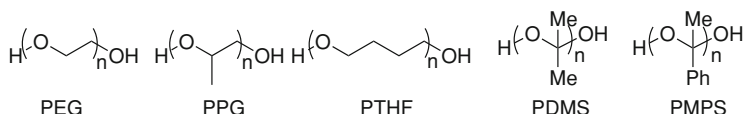
**Scheme 3.9** The structure of selected liquid polymers (Reproduced from Ref. [51], by permission of The Royal Society of Chemistry)

**Scheme 3.10** Liquid polymers as solvents for catalytic reduction reactions [51]
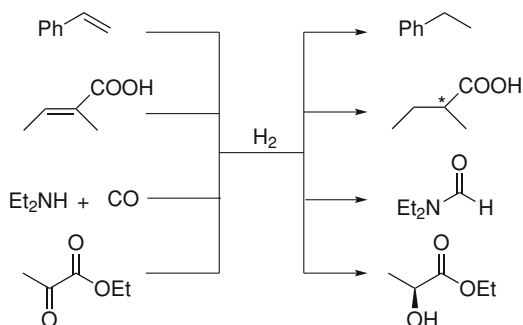


solvents for homogeneously catalyzed and whole-cell-catalyzed reductions (Scheme 3.9) [51].

The evidence currently available suggests that those polymers (except PTHF in emulsion form) have low or negligible toxicity to humans and various marine life and some of them (PEG, PTHF, and to a lesser extent PDMS and PPG) are biodegradable. In this aspect, PEG has a reasonable claim to the label ''green solvent'' because it is nonvolatile, nonflammable, nontoxic to humans, animals, and aquatic life, and biodegradable by bacteria in soil and sewage. Four different reduction reactions, such as hydrogenation of styrene, asymmetric hydrogenation of tiglic acid, hydrogenation of $CO_2$ in the presence of diethylamine to give diethylformamide, and the yeast-catalyzed reduction of ethyl pyruvate (Scheme 3.10), have been successfully performed in liquid polymer solvents, showing that these solvents have the potential to be more widely used as media for reactions and catalysis.

## 3.3 PEG as Surfactant

Although $scCO_2$ is an attractive alternative to conventional solvents, a drawback is that $CO_2$ behaves like a hydrocarbon solvent and that reactants and/or catalysts often have low solubility in $CO_2$. Several attempts are tested to improve the solubility in $scCO_2$, such as addition of small quantities of co-solvents, introduction of perfluorinated side chains in reactants and/or ligands [52–56], and addition of surfactant molecules creating colloidal particles with organic

| R$^1$ | R$^2$ | R$^3$ | R$^4$ | R$^5$ | SiR$^6$R$^7$R$^8$ | Yield/% |
|---|---|---|---|---|---|---|
| Ph | Bn | Me | Me | OMe | SiMe$_3$ | 72 |
| Ph | Ph | Me | Me | OMe | SiMe$_3$ | 85 |
| Ph | Ph | Me | Me | OMe | Si$^t$BuMe$_2$ | 97 |
| PhCH=CH- | Ph | Me | Me | OMe | Si$^t$BuMe$_2$ | 74 |
| 2-furyl | Ph | Me | Me | OMe | SiMe$_3$ | 75 |
| Ph | o-MeOC$_6$H$_4$ | H | H | SEt | SiMe$_3$ | 91 |
| Ph | o-MeOC$_6$H$_4$ | H | Me | SEt | SiMe$_3$ | 95 |
| Ph | o-MeOC$_6$H$_4$ | Me | Me | SEt | SiMe$_3$ | 39 |
| Ph | o-MeOC$_6$H$_4$ | H | Me | OMe | Si$^t$BuMe$_2$ | 68 |
| Ph | o-MeOC$_6$H$_4$ | Me | H | OMe | Si$^t$BuMe$_2$ | 63 |
| cyclohexyl | Ph | H | H | SEt | SiMe$_3$ | 89 |
| cyclohexyl | Ph | H | H | OEt | Si$^t$BuMe$_2$ | 67 |
| cyclohexyl | Ph | Me | Me | OMe | Si$^t$BuMe$_2$ | 44 |
| Ph | Ph | H | H | Ph | SiMe$_3$ | 78 (8 MPa) |

**Scheme 3.11** Mannich-type reactions in the CO$_2$-PEG system [57]

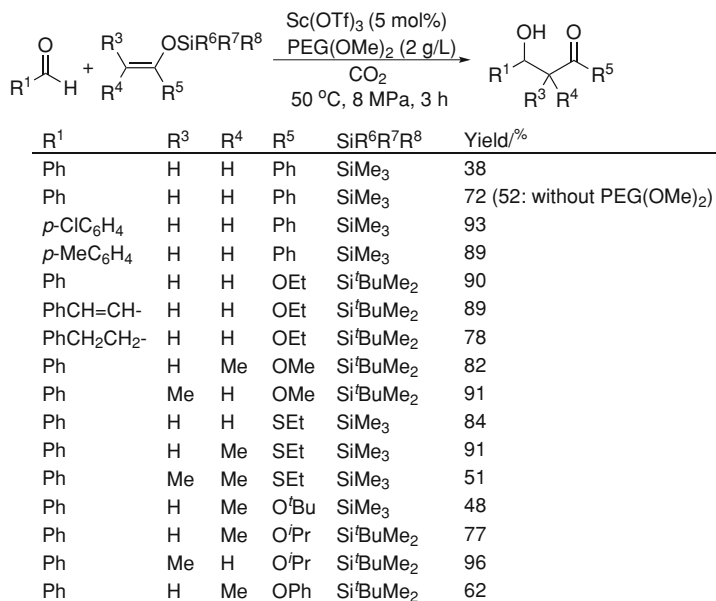compounds, in order to accelerate the reactions by concentrating substrates and catalysts inside the particles.

In 2004, Kobayashi reported for the first time Lewis acid-catalyzed organic reactions such as Aldol- and Mannich-type reactions proceeded smoothly in scCO$_2$ using PEG derivatives as surfactants. This could be the first attempt to use PEG as surfactant, facilitating the formation of emulsions in a single scCO$_2$ phase to synthesize small organic molecules [57].

In Yb(OTf)$_3$-catalyzed Mannich-type reaction of the imine with silicon enolate conducted in scCO$_2$, the desired product is obtained in only 10 % yield after 3 h due to the low solubility of reactants in scCO$_2$ (Scheme 3.11, R$^1$, R$^2$, R$^3$, R$^4$, R$^5$=Ph, Bn, Me, Me, OMe) [57]. Addition of PEG is found to improve the yield to 72 %. The formation of emulsions can be observed in the presence of PEG. The highest yield (72 %) can be reached at 15 MPa CO$_2$ pressure using PEG400 (MW = 400). This system has been applicable to various substrates including imines derived from aromatic and heterocyclic as well as aliphatic aldehydes and silicon enolates derived from esters, thioesters, and a ketone as depicted in Scheme 3.11.

CO$_2$-PEG system is also effective for the scandium-catalyzed aldol reactions, and poly(ethylene glycol) dimethyl ether (PEG(OMe)$_2$, MW = 500) is more effective than PEG (Scheme 3.12) [57]. Emulsions in CO$_2$-PEG(OMe)$_2$ medium are observed when the concentration of the additive is 1 g/L. Not only benzaldehyde but also substituted aromatics, aliphatic, and α, β-unsaturated aldehydes react smoothly, and various silicon enolates derived from a ketones, esters, and thioesters also react well to afford the corresponding aldol adducts in high yields.

$$R^1-CHO + \underset{R^4}{\overset{R^3}{|}}C=C\underset{R^5}{\overset{OSiR^6R^7R^8}{|}} \xrightarrow[\substack{CO_2 \\ 50\ ^\circ C,\ 8\ MPa,\ 3\ h}]{\substack{Sc(OTf)_3\ (5\ mol\%) \\ PEG(OMe)_2\ (2\ g/L)}} R^1-\underset{R^3\ R^4}{\overset{OH\quad O}{|}}-R^5$$

| $R^1$ | $R^3$ | $R^4$ | $R^5$ | $SiR^6R^7R^8$ | Yield/% |
|---|---|---|---|---|---|
| Ph | H | H | Ph | $SiMe_3$ | 38 |
| Ph | H | H | Ph | $SiMe_3$ | 72 (52: without $PEG(OMe)_2$) |
| $p$-ClC$_6$H$_4$ | H | H | Ph | $SiMe_3$ | 93 |
| $p$-MeC$_6$H$_4$ | H | H | Ph | $SiMe_3$ | 89 |
| Ph | H | H | OEt | Si$^t$BuMe$_2$ | 90 |
| PhCH=CH- | H | H | OEt | Si$^t$BuMe$_2$ | 89 |
| PhCH$_2$CH$_2$- | H | H | OEt | Si$^t$BuMe$_2$ | 78 |
| Ph | H | Me | OMe | Si$^t$BuMe$_2$ | 82 |
| Ph | Me | H | OMe | Si$^t$BuMe$_2$ | 91 |
| Ph | H | H | SEt | $SiMe_3$ | 84 |
| Ph | H | Me | SEt | $SiMe_3$ | 91 |
| Ph | Me | Me | SEt | $SiMe_3$ | 51 |
| Ph | H | Me | O$^t$Bu | $SiMe_3$ | 48 |
| Ph | H | Me | O$^i$Pr | Si$^t$BuMe$_2$ | 77 |
| Ph | Me | H | O$^i$Pr | Si$^t$BuMe$_2$ | 96 |
| Ph | H | Me | OPh | Si$^t$BuMe$_2$ | 62 |

**Scheme 3.12**  Aldol reactions in the $CO_2$-PEG system [57]

## 3.4  PEG as Support

Commercially available PEG derivatives with either two or one CH$_2$OH end group make it easy to prepare a variety of PEG-supported ligands and/or catalysts, which could precipitate quantitatively after reaction upon adjusting certain parameters, such as temperature, solvent, polarity, and pH value of the solution. At present, PEG-supported catalysts have been widely used in many reactions for recycling homogeneous catalyst [58, 59].

The selective oxidation of alcohols into the corresponding aldehydes or ketones is a class of transformation for production of a large variety of important intermediates and fine-chemical products, and numerous approaches have been explored successfully [60, 61].

Our group have developed 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-functionalized PEG for biomimetic oxidation of alcohols together with CuCl in compressed $CO_2$, through a so-called 'mono-phase reaction, two-phase separation' process to recover the catalyst, thus leading to conducting a homogeneous catalysis in a continuous mode [62].

CuCl, PEG6000-(TEMPO)$_2$, and oxygen are essential for the oxidation of benzyl alcohol into benzaldehyde. The presence of $CO_2$ improves the reaction, presumably being ascribed to high miscibility of $O_2$ into compressed $CO_2$, thus eliminating interphase transport limitation, and 'expandable effect' of PEG in compressed $CO_2$ [63, 64].

**Table 3.1** The aerobic oxidation of alcohol catalyzed by PEG6000-(TEMPO)$_2$/CuCl in compressed CO$_2^a$ (Reprint from ref [62]., with permission of Thieme Medical Publishers, Inc)
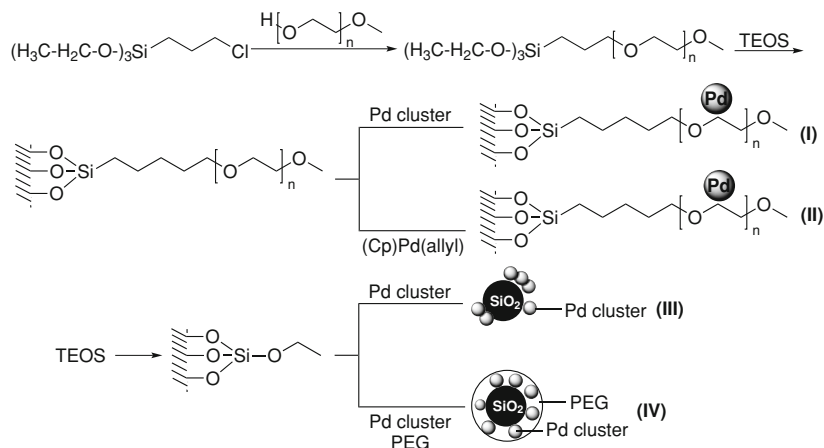
PEG6000-(TEMPO)$_2$ (2.5 mol%), CuCl (5 mol%), 1-methylimidazole (5 mol%), O$_2$ (1 MPa), CO$_2$ (6 MPa)

PEG6000-(TEMPO)$_2$, MW = 6000

| Entry | Substrate | Product | T/°C | t/h | Conv./%[b] | Yield/%[b] |
|---|---|---|---|---|---|---|
| 1[c] | (benzyl alcohol) | CHO | 60 | 2 | 86 | 86 |
| 2 | O$_2$N—(benzyl alcohol) | O$_2$N—CHO | 100 | 2 | 99 | 94 |
| 3 | (2-nitrobenzyl alcohol) NO$_2$ | CHO NO$_2$ | 100 | 3 | 85 | 82 |
| 4 | MeO—(benzyl alcohol) | MeO—CHO | 60 | 3 | 78 | 76 |
|  |  |  | 100 | 3 | 99 | 92 |
| 5 | (3-methoxybenzyl alcohol) OMe | CHO OMe | 60 | 3 | 83 | 82 |
| 6 | (2-methoxybenzyl alcohol) OMe | CHO OMe | 60 | 3 | 63 | 62 |
| 7[c] | (furfuryl alcohol) | CHO | 60 | 3 | 19 | 16 |
|  |  |  | 60 | 10 | 95 | 91 |
| 8 | Ph—CH(OH)—Ph | Ph—CO—Ph | 100 | 24 | 30 | 26 |
| 9 | (1-phenylethanol) | (acetophenone) | 100 | 24 | 42 | 38 |
| 10 | (2-phenylethanol) OH | CHO | 60 | 24 | 30 | 26 |
| 11[c] | (allyl alcohol) OH | CHO | 60 | 3 | 98 | 95 |

[a] Reaction conditions: alcohol (1.93 mmol), PEG6000-(TEMPO)$_2$ (0.3045 g), 2.5 mol% catalyst loading with respect to the initial amount of benzyl alcohol, CuCl (9.6 mg), 1-methylimidazole (7.7 uL), P$_{O2}$ = 1 MPa, P$_{total}$ = 7 MPa; [b] Isolated yield; [c] Determined by GC

For catalyst recyclability, PEG6000-(TEMPO)$_2$/CuCl is solidified by cooling the resultants, followed by addition of diethyl ether, and thus recovers by simple filtration, and the catalytic system retains excellent catalytic performance after three runs. The presence of base (1-methylimidazole) is crucial for the oxidation of alcohols, which could deprotonate the alcohol and coordinate to Cu [65–67].

**Scheme 3.13** Preparation of catalyst materials based on Pd-nanoparticles on different silica supports. Pd cluster: $[Pd_{561}phen_{60}(OAc)_{180}]$, (Cp)Pd(allyl): $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$, TEOS: tetraethoxysilane (Reproduced from Ref. [68] by permission of The Royal Society of Chemistry)

Under the conditions of alcohol (1.93 mmol), PEG6000-(TEMPO)$_2$ (2.5 mol %), CuCl (5 mol %), 1-methylimidazole (5 mol%), O$_2$ (1 MPa), CO$_2$ (6 MPa), benzylic (yield: 62–94 %), allylic (yield: 95 %), heterocyclic (yield: 91 %), and aliphatic alcohols (yield: 26 %) are selectively converted into their corresponding aldehydes or ketones, and the over oxidized products are rarely detected (Table 3.1).

Leitner et al. have synthesized the PEG-modified silica stabilized and immobilized palladium nanoparticles for aerobic alcohol oxidation in combination with scCO$_2$ as reaction medium under mild conditions, which show high activity and excellent stability under continuous-flow operation [68]. ScCO$_2$ could diffuse the substrates and products from the active nanoparticles in a gas-like manner. This allows rapid chemical transformation at the active center, ensures efficient removal of the products from the surface, and minimizes the mobility of solid-supported catalytically active species [69]. In this way, catalysts based on palladium nanoparticles together with PEG as stabilizing matrix could avoid aggregating and forming less active and selective Pd-black [20, 60, 70].

Four kinds of supported Pd complexes are prepared (Scheme 3.13): catalyst **I** is the PEG-modified silica-supported Pd cluster; catalyst **II** is the PEG-modified silica-supported (Cp)Pd(allyl) complex; catalyst **III** is the silica-supported Pd cluster; catalyst **IV** is the silica embedded in a thin PEG film-supported Pd cluster.

The performance of the different catalysts for aerobic oxidation of cinnamyl alcohol is compared under batchwise conditions. The non-covalently modified supports (**III**, **IV**) show longer induction periods, implying that the covalently PEG-modified surface (**I**) provides the best environment for the catalysts formed on basis of the Pd$_{561}$ cluster. The results of batchwise aerobic alcohol oxidation in

**Table 3.2** Results of batchwise aerobic alcohol oxidation in scCO$_2$ using catalyst **I**[a] (Reproduced from Ref. [68] with permission from The Royal Society of Chemistry)

| Entry | Substrate | Product | t/h | Conv./% | Sel./% | TON[b] |
|-------|-----------|---------|-----|---------|--------|--------|
| 1 |  |  | 4 | 98.0 | 98.5 | 45 |
| 2 |  |  | 5 | 96.8 | 98.5 | 47 |
| 3 |  |  | 12 | 58.8 | 99.5 | 29 |
| 4 |  |  | 16 | 96.5 | 98.8 | 45 |
| 5 |  |  | 18 | 46.4 | 98.2 | 22 |
| 6 |  |  | 8 | 12.3 | 47.8 | 3[c] |

[a] Reaction conditions: T = 80 $^{\circ}$C; V(reactor) = 36 mL; catalyst **I** = 90 mg, substrate = 1.95 mmol; d(CO$_2$/O$_2$) = 0.55 g mL$^{-1}$, molar ratio CO$_2$ : O$_2$ = 92 : 8; [b] Total turnover number (TON) = mol product/mol Pd; [c] Acid butyl ester is formed as a second product, together with small amounts of butanal

scCO$_2$ using catalyst **I** is listed in Table 3.2. Benzylic, allylic and secondary alcohols can be rapidly and selectively converted into the corresponding carbonyl compounds in scCO$_2$. The primary alkyl alcohol butanol gives poor conversion yielding mainly the acid and corresponding ester.

Significant differences for these catalysts are observed for continuous-flow fixed-bed oxidation of benzyl alcohol under supercritical conditions. Catalyst **III**, which contains only adsorbed Pd clusters without any stabilizing matrix, shows the lowest initial activity and a continuous and fairly rapid deactivation. The non-covalently bound PEG film (**IV**) leads to a slightly higher activity, but deactivation is still significant. In contrast, the covalently bound PEG chains (**I, II**) show an excellent activity and stabilization of the Pd cluster. After 30 h, catalyst **I** gives a total TON of 1,750 corresponding to an average turnover frequency (TOF) of 58 h$^{-1}$, based on the total Pd-loading as the most conservative basis. Transmission electron microscopy (TEM) micrographs taken before and after the reaction confirm that the covalently bound PEG-chains effectively prevent agglomeration of the Pd nanoparticles on the surface during the catalytic process.

Bidentate nitrogen ligand (2, 2′-dipyridylamine) tethered covalently to the tip of PEG has been synthesized for the stabilization of palladium nanoparticles during alcohol oxidation in scCO$_2$/PEG biphasic media [71].
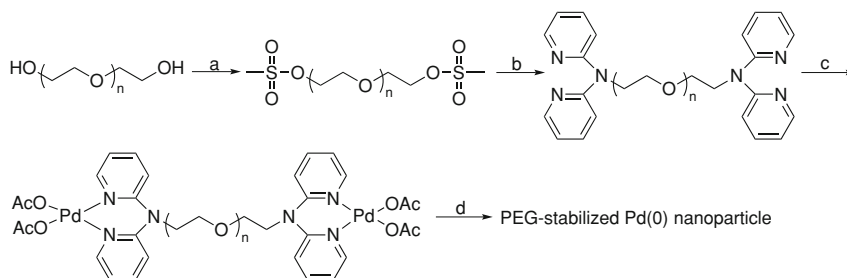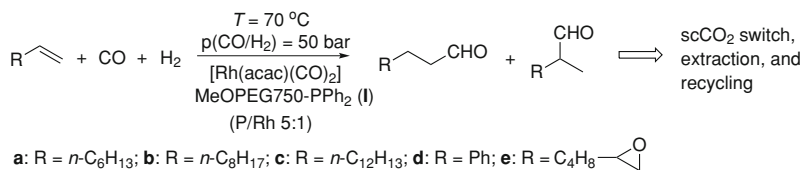
**Scheme 3.14** Typical preparation procedure of the palladium catalysts. Reagents and conditions: (*a*) MeSO$_2$Cl, pyridinium, CH$_2$Cl$_2$, 0 °C, 24 h. (*b*) 2, 2′-Dipyridylamine, NaH, DMF, 90 °C, 4 h. (*c*) Pd(OAc)$_2$, acetic acid, 2 h. (*d*) H$_2$, room temperature, 20 min [71]

The preparation of the functionalized PEG is shown in Scheme 3.14. For the oxidation of benzyl alcohol to benzaldehyde, the functionalized PEG-stabilized Pd(0) nanoparticle is demonstrated to be more active and selective in comparison with the commercially available Pd/C catalyst, polyvinyl pyrrolidone (PVP)-stabilized Pd nanocatalyst and Pd(0) catalyst without stabilization. In addition, the PEG-stabilized catalyst shows good stability and activity in four runs, with a slight decrease in the selectivity to benzaldehyde, which might be caused by accumulation of water in catalytic cycles, leading to the hydration of benzaldehyde, followed by dehydrogenation of the corresponding geminal diol to benzoic acid [72]. TEM analysis of the catalysts before and after reaction shows that the incorporation of the functionalized ligand (2, 2′-dipyridylamine functionalized PEG) in the PEG/scCO$_2$ could result in enhancing the activity with preventing the aggregation of Pd nanoparticles.

One of the ideal goals for synthetic chemistry is to find a regulated system in which a defined substitution pattern in the periphery of the metal's coordination sphere affects the catalyst's solubility, making it possible to switch between two states: the catalyst is homogeneously dissolved during the reaction and precipitates quantitatively in the separation stage [73].

Ideally, in a regulated system all reaction components are removed from the precipitated catalyst quantitatively under mild conditions to ensure that the catalyst remains available for repeated application in homogenous form after re-dissolving. In particular, it would be attractive to devise a "catalyst cartridge" with a single catalyst batch for a range of transition metal-catalyzed conversions utilizing different substrates or even different reaction types in the same apparatus with an integrated separation technique [74, 75].

Several limitations hamper the development of efficient systems for cartridge catalysts based on the more conventional regulated systems: (1) Thermal and/ or chemical stress can lead to deactivation of the organometallic catalyst; (2) Additives used to induce precipitation may accumulate in the catalyst
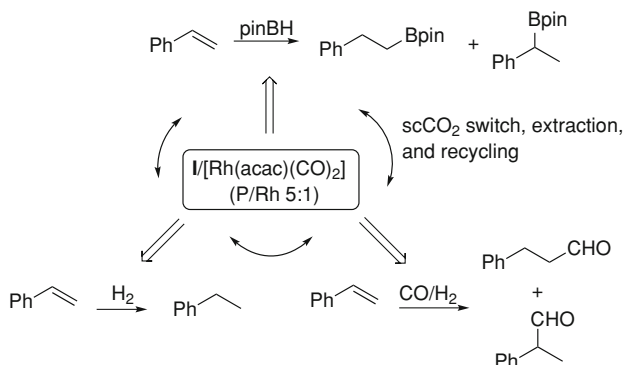
$$R \diagdown\diagup + CO + H_2 \xrightarrow[\substack{[Rh(acac)(CO)_2] \\ MeOPEG750\text{-}PPh_2 \textbf{(I)} \\ (P/Rh\ 5:1)}]{\substack{T = 70\ ^\circ C \\ p(CO/H_2) = 50\ bar}} R\diagdown\diagup\diagdown CHO + \substack{CHO \\ R\diagdown\diagup} \Longrightarrow \substack{scCO_2\ switch, \\ extraction,\ and \\ recycling}$$

**a**: R = $n$-C$_6$H$_{13}$; **b**: R = $n$-C$_8$H$_{17}$; **c**: R = $n$-C$_{12}$H$_{13}$; **d**: R = Ph; **e**: R = C$_4$H$_8$—$\triangleleft^O$

**Scheme 3.15** Hydroformylation as a benchmark reaction to validate the cartridge catalyst system MeOPEG750-PPh$_2$/[Rh(acac)(CO)$_2$]/scCO$_2$ (Reproduced from Ref. [76], with the permission of John Wiley and Sons)

compartment or require additional operations for purification of the product stream; (3) Reaction and separation are difficult to integrate if pressurized gases are used as reagents; (4) As the catalyst must be soluble in a broad range of reaction mixtures of different polarities, it can be difficult or even impossible to find a suitable solvent for separation without cross-contamination and catalyst leaching.

The design and application of a system approaching the cartridge catalyst ideal based on the use of a PEG-modified phosphine ligand in a CO$_2$-regulated reaction/ separation sequence has been reported by Leitner et al. [76]. A PEG chain of moderate length (MW = 750, $n = 16$) is used having a medium polarity compatible with a broad range of chemical environments and an almost negligible vapor pressure considerably below that of typical reaction products in fine-chemical applications. This substitution pattern makes the catalysts based on ligand MeOPEG750-PPh$_2$ (**I**) (Scheme 3.15) soluble in a variety of organic substrates without the need for additional solvents, whereas those catalysts can be completely insoluble in scCO$_2$ even at high density. The hydroformylation of 1-octene is initially chosen as the benchmark reaction to validate these considerations (Scheme 3.15).

A catalyst cartridge based on compound **I**/[Rh(acac)(CO)$_2$] (P/Rh = 5:1) has been successfully implemented for the hydroformylation of a set of structurally diverse olefins (Scheme 3.15) using scCO$_2$ to induce a phase switch and mass separation [74, 75]. However, the standard solvent extraction could be impossible to achieve such comparable efficient separation owing to the similarities in polarity between catalyst and some of the substrates.

Based on the promising performance of the cartridge system **I**/[Rh(acac)(CO)$_2$]/ scCO$_2$ for hydroformylation, a series of different reaction types are extended. The hydrogenation, hydroformylation, and hydroboration of styrene are chosen as test reactions for the catalyst cartridge, as illustrated in Scheme 3.16. All three reactions involve phosphine rhodium hydride fragments as part of the active intermediates, providing a reasonable chance of linking the different catalytic cycles. As a result, the reaction sequence can indeed be realized with the cartridge system **I**/[Rh(acac)(CO)$_2$]/scCO$_2$. Excellent results (conversion and selectivity $\geq 80$ %) are obtained over extended periods of time independent of the starting point and the order of the subsequent reactions.
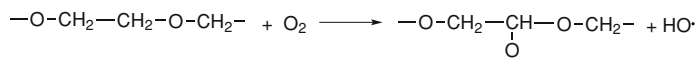
Ph ⟶ (pinBH) ⟶ Ph—Bpin  +  Ph—Bpin

scCO₂ switch, extraction, and recycling

**I**/[Rh(acac)(CO)₂] (P/Rh 5:1)

Ph ⟶ (H₂) ⟶ Ph

Ph ⟶ (CO/H₂) ⟶ Ph—CHO  +  Ph—CHO

**Scheme 3.16** A series of different catalytic reactions carried out sequentially with the cartridge catalyst system **I**/[Rh(acac)(CO)₂]/scCO₂; pinBH = pinacolborane (Reproduced from Ref. [76], with the permission of John Wiley and Sons)

1. PEG reacts with oxygen to form α -hydroperoxide

—O–CH₂—CH₂–O–CH₂–  +  O₂  ⟶  —O–CH₂—CH—O–CH₂—
with O–OH substituent
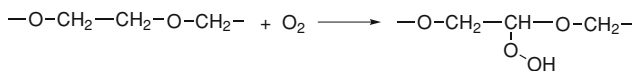
2. The peroxide decomposes according to a radical mechanism

—O–CH₂—CH₂–O–CH₂–  +  O₂  ⟶  —O–CH₂—CH—O–CH₂—  + HO•

3. Formic esters are produced as the thermal degradation products in air

—O–CH₂—CH—O–CH₂–  ⟶  —O–CH₂—CHO  + •O–CH₂—

**Scheme 3.17** The mechanism for thermal oxidative degradation of PEG [80]

## 3.5  PEG as Radical Initiator: PEG Radical Chemistry in Dense $CO_2$

PEG is susceptible to oxidative attack by free radicals and goes through thermal degradation in the presence of oxygen at elevated temperatures (over 70 °C). In this context, PEG and oxygen can react to form PEG peroxide in excess air through a random chain scission process, leading to the formation of many low-molecular-weight oxygenated products of great complexity [77–80].

PEG can be severely degraded in air. Its melting point and heat of fusion are reduced by as much as 13 °C and 32 kJ kg$^{-1}$, respectively [81]. The thermal degradation of PEG in air follows a random chain scission oxidation mechanism, and could be suppressed by addition of an antioxidant, 2, 2′-methylene-bis (4-methyl-6-tert-butylphenol) (MBMTBP), due to the reaction of MBMTBP with ROO radicals formed in the propagation step [79]. Low-molecular-weight esters including formic esters are produced as the main products of the thermal degradation of PEG (Scheme 3.17) [80].

For the first time, we have found that PEG radicals, generated by thermal oxidative degradation of PEG, can be utilized to initiate free-radical reactions in an efficient, viable, and environmentally benign manner in conjunction with the use of dense CO$_2$ [82]. Our initial work started with investigating the formylation of alcohols in the PEG/O$_2$/CO$_2$ system acting as initiator, oxidant, and solvent, using hexadecanol as a model compound (Scheme 3.18(**a**), R$^1$, R$^2$ = $n$-C$_{15}$H$_{31}$, H). Reaction of hexadecanol with PEG1000 (MW = 1000) in the presence of O$_2$ (2.5 MPa) and CO$_2$ (13.5 MPa) at 100 °C for 12 h give the formylated product hexadecyl formate in 68 % isolated yield produced via formylation of alcohol with formic acid generated in situ during the degradation of PEG [77, 78], along with 15 % yield of palmitic acid through a PEG radical mechanism [80]. Temperature >100 °C is required to induce thermal oxidative degradation of PEG. An appropriate CO$_2$ pressure (14 MPa) significantly enhances the reaction rate, probably due to the "CO$_2$ expansion of a liquid" effect [12], and apparently improves the selectivity toward formate. The conversion dramatically decreases when the molecular mass of PEG is increased from 300 to 6,000 (from 77 to 21 %); specifically in the case of PEG20000, the reaction does not occur at all because of increased limitations on the mass transport of gaseous oxygen in the highly viscous, long-chain PEG [83]. In the case of isobutyl alcohol (Scheme 3.18(**a**), R$^1$, R$^2$ = $i$ – Pr, H), PEG could be recycled for at least five times with retention of reaction activity, with the products being extracted by either scCO$_2$ or ether. A series of primary and secondary aliphatic alcohols were selectively converted to the corresponding formates with yield of 66–72 %, whereas the tertiary aliphatic alcohol remained unchanged owing to steric hindrance. On the other hand, benzylic alcohol is preferentially oxidized to benzoic acid (89 %) and benzaldehyde (1 %) alongside with 4 % of the formylated product (Scheme 3.18(**b**)). Oxygenation of benzyl alcohol in the presence of PEG1000 and 2.5 MPa O$_2$, 13.5 MPa CO$_2$ at 120 °C for 12 h furnishes the benzoic acid (89 %) concomitant with benzaldehyde and benzyl formate (Scheme 3.18(**c**)) [84]. For the substrate scope, primary and secondary alcohols can be oxygenized into the corresponding carbonyl compounds in fair to high yields (53–93 %). In general, substrates with an electron donating group (Ar = 4-MeO-Ph) generally show higher activity than those having an electron withdrawing group (Ar = 4-NO$_2$-Ph). With regard to selectivity, secondary benzylic alcohols show higher selectivity toward ketone, while primary ones afford carboxylic acid as a dominant product.

PEG/O$_2$/CO$_2$ system can also be utilized in benzylic C=C cleavage reactions. Styrene gives almost full conversion, furnishing the benzylic C=C cleaved products composed of benzaldehyde (34 %) and benzoic acid (46 %) (Scheme 3.18(**e**), R$^5$ = H). Prolonging reaction time or higher oxygen concentrations favors deeper oxidation, resulting in significant increase in the yield of benzoic acid. Interestingly, allylic sp$^3$ C–H oxidation can also be realized in PEG/O$_2$/CO$_2$ system; cyclohexene as the substrate gives rise to cyclohex-2-enone (9 %) and cyclohex-2-enol (28 %) as main products (Scheme 3.18(**f**)).

A proposed mechanistic scheme is outlined in Scheme 3.18. The reaction of PEG with oxygen is prone to generating PEG radicals [80], which are supposed to
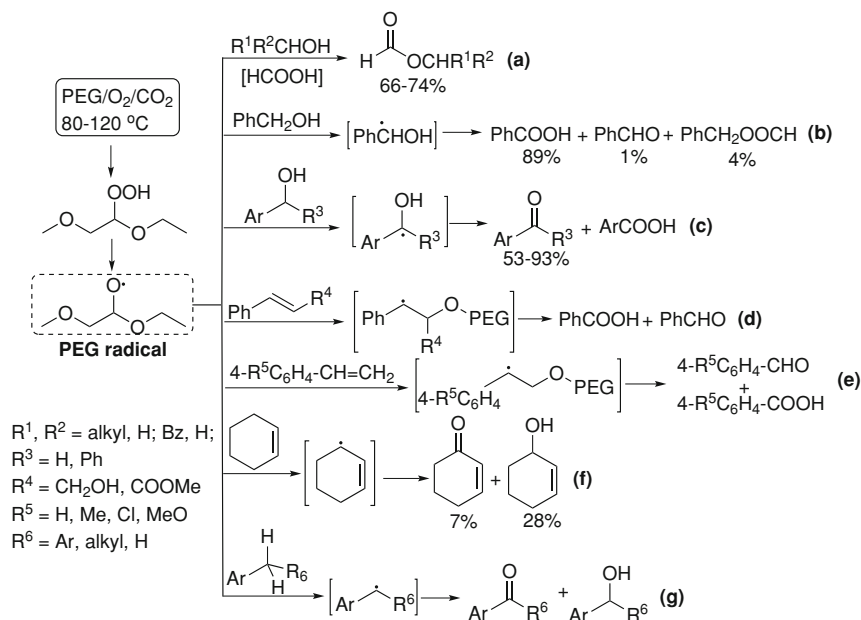
**Scheme 3.18** The proposed pathways of organic reactions initiated by PEG radicals generated by thermal oxidative degradation [82]

further form acetic acid or initiate substrates to generate relatively stable radicals. Benzylic or allylic substrates could be favorable for forming benzylic or allylic radicals, whereas aliphatic alcohols could preferentially go through the formylating pathway. The free-radical mechanism is also supported by the radical species detected by electron paramagnetic resonance experiments, a broadening distribution of the molecular weight of PEG, generation of a peroxide intermediate as detected by KI/starch test, and the suppressing effect of TEMPO on the reactions.

   In summary, the utility of this concept of practically utilizable free-radical chemistry of PEG induced by molecule oxygen in dense carbon dioxide is demonstrated to be successfully applied to important and fundamental organic reactions with enormous synthetic potentials. Current applications include selective formylation of primary and secondary aliphatic alcohols, and oxidation of benzylic alcohols, and benzylic C=C cleavage reactions and benzylic $sp^3$ C–H oxidation. We find that both PEG and molecule oxygen are prerequisite to performing those reactions smoothly. Given that dense $CO_2$ is immune to free-radical chemistry; it is an ideal solvent for such free-radical reactions. As a result, dense $CO_2$ in this elegant study allows such reactions initiated by PEG radical able to be tuned by subtly adjusting reaction parameter like $CO_2$ pressure, thus leading to enhancing the product selectivity. Attaining high selectivity toward the desired product makes this methodology more practical in organic synthesis. These scrutinous

findings inspired with a serendipity in the course of continuing effort devoted to developing efficient sustainable process for the oxidation of organic substrates such as alcohols and olefins in PEG/dense CO$_2$ biphasic system lead to creating a novel concept of utilizable free-radical chemistry of PEG, and would thereby offer an environmentally friendly, metal-free, cost-efficient, and viable access to a diverse set of synthetic useful transformations without any additional free-radical initiator or a catalyst. Further applications of the present protocol to other reactions are in progress. Given more time for in-depth investigation, free-radical chemistry of PEG thermal degradation will surely become an even more powerful tool for organic synthesis and find its place in many more industrial applications to establish sustainable and economically competitive process.

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# Chapter 4
# CO$_2$ Capture with PEG

**Abstract** The capture of CO$_2$ from fossil fuel combustion, e.g., coal-fired power plants, represents a critical component of efforts aimed at stabilizing greenhouse gas levels in the atmosphere. In addition, removal of CO$_2$ from natural gas is of vital importance to maintain and expand the availability of these clean-burning, efficient fuel sources. In recent years, worldwide efforts have been devoted to developing various technologies/processes for CCS, including adopting liquids, solids, and membranes as adsorbents. Interest in PEGs stems from its distinctive properties, such as inexpensive, thermally stable, almost negligible vapor pressure, toxicologically innocuous, and environmentally benign characterization. The functionalized-PEGs have been developed for both physical and chemical capture of CO$_2$, including PEGs (Sect. 4.1), PEG-modified solid absorbents (Sect. 4.2), PEG-functionalized gas-separation membranes (Sect. 4.3) and PEG-functionalized liquid absorbents (Sect. 4.4). Indeed, PEG could increase the solubility of CO$_2$ in the absorbent through chemical interactions, which is detected by in situ FT-IR under pressure.

Carbon capture and sequestration is a technology that is being explored to curb the anthropogenic emission of CO$_2$ into the atmosphere. With the environmental issues and energy crisis problem associated with "greenhouse gas effect" being more and more prominent, CO$_2$ capture–fixation–conversion has been a worldwide hot topic for sustainable development [1–12].

Many criteria must be considered when choosing or developing absorbents for CO$_2$ removal, including selectivity, cost, and stability. There are mainly two CO$_2$ separation issues: (1) For post combustion capture from flue gas (e.g., coal-fired power station), a major obstacle is the low pressure of the flue gas (1 atm), with just 15 % CO$_2$ concentration together with other component gasses, predominantly N$_2$.

However, the energy penalty problem using traditional aqueous monoethanolamine (MEA) for this purpose has been estimated as 25–40 % [13, 14]. (2) Natural gas reserves (mainly CH$_4$) are typically contaminated with over 40 % CO$_2$ and N$_2$, and CO$_2$ separation occurs under high-pressure conditions and at high temperatures (250–450 °C) in this process [1, 15]. A number of excellent reviews have summarized advances in the field of CO$_2$ capture and storage adopting different absorbents including liquid absorbents such as conventional aqueous amine solutions, chilled ammonia, and TSILs; solid absorbents such as zeolites, activated carbons, metal-based adsorbents, hydrotalcite-like compounds, organic and organic–inorganic hybrid adsorbents; membranes such as polymers, solubility-controlled membranes, carbon-based membranes, mixed-matrix membranes, and zeolite membranes [1, 11, 15–27].

## 4.1 Physical Solubility of CO$_2$ in PEGs

Influence of various parameters on the solubility of CO$_2$ in PEG has been investigated by gravimetric measurement [28]. (1) CO$_2$ pressure: the solubility of CO$_2$ in polymer increases with increasing pressure by plasticization effect of CO$_2$ [29–31]. By raising the pressure, the gaseous molecules are forced to enter polymer chains, resulting in more gas molecules to be adsorbed. (2) Chain mobility of PEG: a higher mobility of the molecules in the liquid form of the polymer accounts for the significantly higher solubility values. Lower solubility of CO$_2$ in the solid polymer refers to the presence of the crystalline phase, where the packed configuration of the chains does not allow the penetration of gas molecules, the solubility in these regions being close to zero. (3) Molecular weight (MW) of PEG: the difference in solubility is negligible for lower pressures at near the critical point of CO$_2$ [29, 31], but PEG with a higher MW at higher pressure could offer a reduced free volume to be occupied by the gas molecules. At the same time, the number of interactions between the end groups of the polymer chains and CO$_2$ molecules is higher for the polymer with lower MW, which account for the good solubility of CO$_2$ in PEG.

The solubilities of CO$_2$ in solvent PEGs with MW of 150, 200, 300, and 400 are measured over the range of pressure from 100 to 1200 kPa and temperature from 303.15 to 333.15 K [32]. Henry's constant being obtained by linear fitting of the experimental data, based on molar fraction and the molality of CO$_2$ in PEG400 vary from 4.78 to 7.09 MPa and 1.56 to 2.48 MPa·kg·mol$^{-1}$ from 303.15 to 333.15 K, respectively.

**Table 4.1** $CO_2$ adsorption half-times and capture capacities of TEPA/$SiO_2$ and PEG/TEPA/$SiO_2$ during the 1st and 30th cycles

| Sorbent | $T_{0.5}$/s | | $CO_2$ capture capacity/mmol $CO_2$ $g^{-1}$ sorbent | | | |
|---|---|---|---|---|---|---|
| | 1st cycle | 30th cycle | 1st cycle | | 30th cycle | |
| | | | Weakly adsorbed | Strongly adsorbed | Weakly adsorbed | Strongly adsorbed |
| TEPA/$SiO_2$ | 16.8 | 20.4 | 445.80 | 2,087.46 | 234.73 | 871.85 |
| PEG/TEPA/ $SiO_2$ | 12.6 | 19.2 | 45.05 | 1,110.46 | 99.22 | 445.14 |

Reproduced from Ref. [40], with the permission of John Wiley and Sons

## 4.2 PEG-Modified Solid Absorbents

For $CO_2$ capture applications from flue gas using aqueous amine solutions, a large energy cost is paid to heat $H_2O$ in the aqueous amine solution during the amine-regenerating and $CO_2$ stripping step. A portion of this process cost can be avoided by immobilization of aqueous amines onto solid supports. In addition, unlike amine solutions, degradation due to evaporation and vessel corrosion is less problematic because solid–solid contact between solid support particles could be scarce [16]. Unlike zeolites and activated carbon, amino-functionalized sorbents have been proved to be tolerant and even positive to moisture during $CO_2$ capture, thus eliminating the need for strict humidity control prior to $CO_2$ capture [33, 34].

Solid sorbents should possess a minimum $CO_2$ capture capacity of 2,000 μmol $CO_2$ $g^{-1}$ sorbent to provide a performance comparable to those of large-scale liquid amine solution processes with significant energy [35] and cost reductions [16, 36–39]. In addition, sorbent stability under multiple $CO_2$ capture cycles has to be considered for further development of solid amine processes.

PEG is used for stabilizing the silica-supported tetraethylenepentamine (TEPA) (TEPA/$SiO_2$), abbreviated as PEG/TEPA/$SiO_2$ being prepared by wet impregnation, for $CO_2$ capture. PEG200 can be particularly selected because of its potential to disperse TEPA via interaction of its −OH groups with the -$NH_2$ groups of TEPA [40]. The adsorbed $CO_2$ species from $CO_2$ capture at 55 °C can be classified as weakly adsorbed $CO_2$ and strongly adsorbed $CO_2$. The former is related to a hydrogen-bonding species (i.e. $NH_2$—O) which exhibits IR absorption at 2,627 $cm^{-1}$; the latter is associated with carbamate at 1,520 $cm^{-1}$ and carboxylate species at 1,430 $cm^{-1}$. PEG is found to decrease the overall $CO_2$ capture capacity, the degradation rate of TEPA/$SiO_2$, and the adsorption half-time; and to increase the fraction of weakly adsorbed $CO_2$ species as summarized in Table 4.1. The stabilizing role of PEG on TEPA/$SiO_2$ can be attributed to hydrogen bonding between the $NH_2$/NH groups of TEPA and the OH groups of PEG. This hydrogen-bonding interaction slows down the formation of carbamate and its conversion to carboxylate, the species that blocks amine sites for $CO_2$ capture.
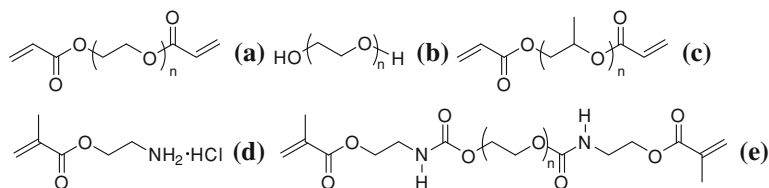
**Scheme 4.1** Chemical structures of the principal membrane. **a** poly(ethylene glycol)diacrylate (PEGda). **b** poly(ethylene oxide) (PEO). **c** poly(propylene glycol)diacrylate (PPGda). **d** 2-aminoethylmethacrylate (AEMA) hydrochloride. **e** poly(ethylene glycol)urethane dimethacrylate (PEGudm) [53]

## 4.3 PEG-Functionalized Gas-Separation Membranes

The increasing interest in $H_2$ as the next-generation fuel, expected to replace dwindling petroleum reserves continues to drive the development of purification strategies by which to separate $H_2$ from other light gasses [41–43]. Since most of the worldwide $H_2$ supply derives directly from synthetic gas ("syngas") via the two-stage water–gas shift reaction, removal of $CO_2$ from $H_2$ is of paramount importance [44–46]. Such separation can be achieved by exposing a high-pressure $CO_2/H_2$ gas stream to a polymer membrane [44] or subjecting to liquid amine-based membranes [45] or zeolitic adsorbents [46], thereby yielding a purified, high-pressure $H_2$ retentate [47].

Initial gas-transport studies have established that those microphase separated materials exhibit high $CO_2/H_2$ selectivity due to high $CO_2$ solubility in relatively low molecular weight (rubbery) PEG microdomains [48–51], which is attributed to specific interactions between the penetrant $CO_2$ molecules, each possessing a quadripolar moment due to the difference in electronegativity between the C and O atoms, and the ether linkages located along the PEG backbone [52].

Gas-separation membranes composed of polyethers such as poly(ethylene glycol) diacrylate (PEGda) or poly(propylene glycol) diacrylate (PPGda) exhibit high selectivity in $CO_2$ solubility, which makes them attractive for use in $H_2$ and air purification. Patel et al. [53] have investigated the factors governing $CO_2$ and $H_2$ transport in mixed polyether matrices (Scheme 4.1). Blending PEO homopolymers varying in molecular weight into the PEGda matrix prior to cross-linking reduces both $CO_2$ permeability and $CO_2/H_2$ selectivity due solely to the formation of PEG crystals. Addition of PPGda into the PEGda matrix increases the permeability of $CO_2$ and $H_2$ according to the rule of mixtures. Chemical incorporation of amine functionalities into the PEGda matrix, or the synthesis of the urethane methacrylate-terminated PEG oligomer, results in membranes that exhibit marginally lower $CO_2/H_2$ selectivity, but occasionally higher $CO_2$ permeability.

Pebax$^{®}$ is a thermoplastic elastomer: PA is an aliphatic polyamide "hard" block (e.g., nylon-6, nylon-12) and PEG is an amorphous polyether (polyethylene oxide (PEO) or polytetramethylene oxide (PTMO)) "soft" block (Scheme 4.2).

$$HO \left[ \underset{\underset{O}{\|}}{C} - PA - \underset{\underset{O}{\|}}{C} - O - PE - O \right]_n H$$
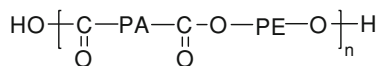
**Scheme 4.2** Chemical structure of Pebax®. Reprinted from Ref. [56], with permission from Elsevier

The PA blocks provide the mechanical strength and gas transport occurs through the PEO phase [49]. The mechanical, chemical, and physical properties can be conventionally modeled by varying the segment and MW of polyamide and polyether as well as the content of each block, [54]. Different grade of Pebax® membranes have high $CO_2/N_2$ and $CO_2/H_2$ selectivity, due to the strong affinity of the polar ether linkages for $CO_2$ [50]. High permeability and high selectivity for $CO_2$ over $N_2$ as well as $SO_2$ over $N_2$ are attributed to polarizability of gasses due to PEO segments [55].

Peinemann's group has prepared Pebax®/PEG blend membranes (50 wt % of PEG) using ethanol/water as solvent [56]. Use of PEG200 can improve the performance of Pebax® membrane. In addition, $CO_2$ permeability can be increased twofold and the $CO_2/H_2$ selectivity is enhanced from 9 to almost 11, owing to morphological and structural changes in the copolymer system. Higher PEG content leads to lower crystallinity in the membranes and high interaction between oxyethylene (EO) units and $CO_2$, resulting in increase of diffusivity and permeability coefficient. Moreover, addition of PEG into the Pebax block copolymer could increase free volume, being correlated with increased diffusion coefficients and gas permeabilities. Morphology analyzed by SEM and AFM shows that the lamellar structure is deteriorated with adding PEG200 into Pebax®, and the amorphous phase is thus increased. Therefore, the permeability is enhanced for all gasses, especially for $CO_2$ due to the presence of EO units.

Aminosilane-modified PEG, PEG-block-PPG-block-PEG (PEPEG), and PPG-block-PEG-block-PPG (PPEPG) diacrylate prepolymers are synthesized as alternative membrane materials for gas separation (Scheme 4.3) [57]. By combining the in situ sol–gel process and cross-linking process together, the silane-modified prepolymers form flexible nanocomposite membranes with a maximum $CO_2$ permeability of 274 barrer and $CO_2/N_2$ selectivity of about 30. The $CO_2$ permeabilities of silane cross-linked PEPEG and PPEPG membranes are higher than those of silane cross-linked PEG membranes, whereas the $CO_2/N_2$ and $CO_2/H_2$ selectivities increase as the PEG content increases in the membrane.

## 4.4 PEG-Functionalized Liquid Absorbents

ILs are salts being composed of distinct cations and anions that are capable of facilely tuning, and whereby can be designed for task-specific applications through smart choice of the respective cation and/or anion. Nowadays, ILs have been extensively
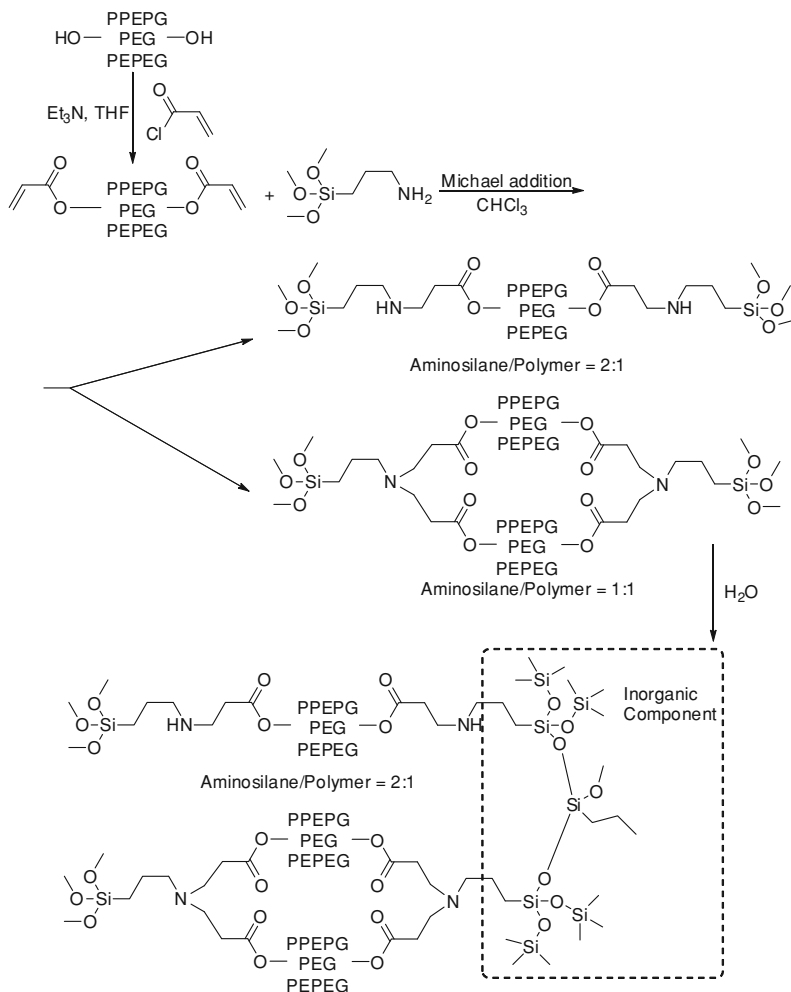
**Scheme 4.3** Reaction mechanism during the fabrication of aminosilane cross-linked PEG/PEPEG/PPEPG membranes. Reprinted with the permission from Ref. [57]. Copyright 2010 American Chemical Society

investigated with a wide range of interesting applications [58], because of their limitless attractive properties, such as wide liquid temperature ranges, good thermal stabilities, high ionic conductivity, and high solvation interactions with both polar and nonpolar compounds. In particular, ILs have attracted significant attention in the field of gas separation from the scientific community due to their great values for chemical research and potential applications in industry [59]. In the past decades, design and synthesis of functionalized ILs as green absorbents in gas separation offer a new opportunity for developing novel capture systems that are capable of reversibly capturing CO$_2$ with a high capacity and absorption rate [27, 60–62].
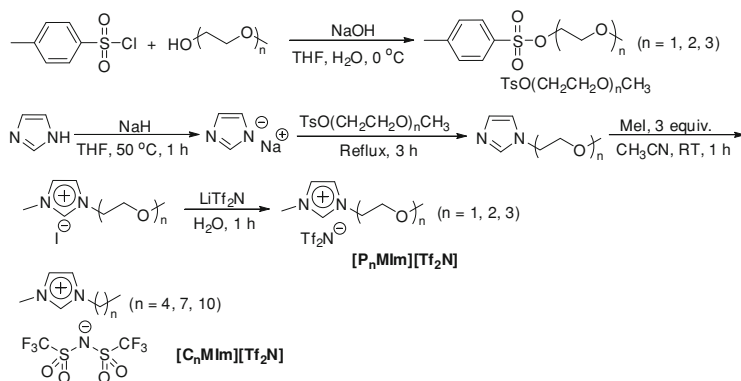
**Scheme 4.4** Synthesis of [P$_n$MIm][Tf$_2$N] and structures of [C$_n$MIm][Tf$_2$N]. Reprinted with the permission from Ref. [72]. Copyright 2007 American Chemical Society

Separation of $CO_2$ from $N_2$ or $CH_4$ comprises an area of critical industrial, social, and environmental importance where room-temperature ionic liquids (RTILs) are showing great potential [3, 63, 64]. The commonly used ILs for this purpose are 1-alkyl-3-methylimidazolium salts, represented by the formula [C$_n$MIm][X], where C$_n$ is an n-alkyl chain of varying length and X is typically a molecular anion with a delocalized negative charge, such as bis(trifluoromethane)sulfonimide, [Tf$_2$N$^-$] (Scheme 4.4) [65–71].

Bara et al. [72] has created the hybrid RTILs comprised of small PEG chains (one, two, or three oligo(ethylene glycol) units) tethered to an imidazolium cation to test the solubilities of $CO_2$, $N_2$, and $CH_4$ (Scheme 4.4). The solubility of $CO_2$ at 40 °C is found to be similar to those of the best performing [C$_n$MIm][Tf$_2$N] ($n = 4, 7, 10$) RTILs. However, $N_2$ and $CH_4$ solubilities are smaller in comparison with those of [C$_n$MIm][Tf$_2$N] RTILs. Consequently, ideal solubility selectivities of $CO_2/N_2$ and $CO_2/CH_4$ are 25–75 % larger in [P$_n$MIm][Tf$_2$N] systems when compared to analogous [C$_n$MIm][Tf$_2$N] RTILs.

Absorption of $CO_2$ at ambient pressure using basic ILs have attracted much attention in recent years, such as IL consisting of an imidazolium cation with a primary amine moiety and tetrafluoroborate anion [3], tetrabutylphosphonium amino acids [73]. Chitin and chitosan can be dissolved in [BMIm]Cl [74] and so on.

Some ILs have been proven to be toxic. However, toxicology of most ILs is unclear and needs to be evaluated [75–77]. Therefore, synthesis of the ILs using renewable raw materials is attractive [78–82]. Absorption/desorption of $CO_2$ by IL where both cation and anion are from renewable materials, (2-hydroxyethyl)-trimethyl-ammonium (S)-2-pyrrolidine-carboxylic acid salt [Choline][Pro] (Scheme 4.5), and [Choline][Pro]/PEG200 mixture, has been studied in the range of 35–50 °C at ambient pressure (Fig. 4.1) [6]. Both the neat IL and IL/PEG200 mixture could capture $CO_2$ effectively and could be easily regenerated under vacuum or by bubbling nitrogen through the solution. The molar ratio of $CO_2$ to
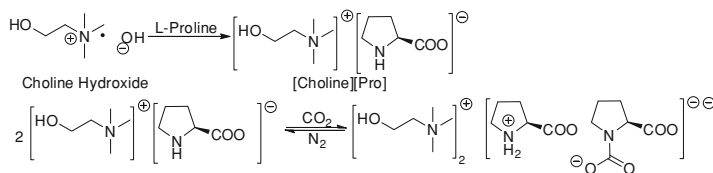
**Scheme 4.5** Schematic illustration to synthesize the ionic liquid [Choline][Pro] and its reaction with CO$_2$ Reproduced from Ref [6] by permission of The Royal Society of Chemistry
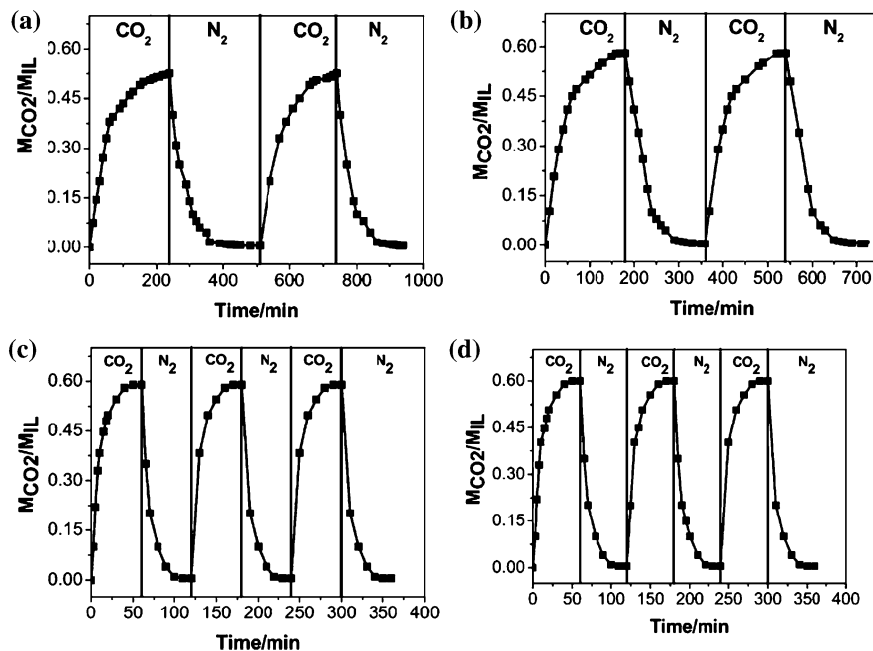


**Fig. 4.1** Cycles of CO$_2$ absorption by [Choline][Pro] and [Choline][Pro]/PEG200 mixtures. **a** $W_{[Choline][Pro]}/W_{PEG200} = 1{:}0$, 50 °C. **b** $W_{[Choline][Pro]}/W_{PEG200} = 2{:}1$, 35 °C. **c** $W_{[Choline][Pro]}/W_{PEG200} = 1{:}1$, 35 °C. **d** $W_{[Choline][Pro]}/W_{PEG200} = 1{:}3$, 35 °C. Reproduced from Ref. [6] by permission of The Royal Society of Chemistry

the IL could exceed 0.5 slightly, which is theoretical maximum for absorption of CO$_2$ chemically, indicating that both chemical and physical absorption exist. Addition of PEG200 in the IL could enhance the rates of absorption and desorption of CO$_2$ significantly by decreasing the viscosity of the absorption system.

Hydrocarbon surfactant liquids are promising candidates for CO$_2$ capture with the following advantages: (1) The hydrocarbon surfactants are cheap and nontoxic; (2) The solubility of CO$_2$ in surfactants can be readily tuned by tailoring the amphiphilic structure of polar head and nonpolar tail; (3) As the hydrocarbon surfactants are nonvolatile, CO$_2$ can be desorbed without loss of the surfactants
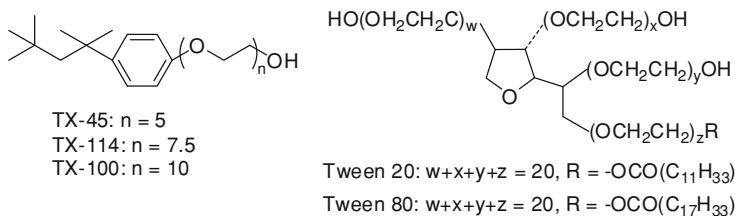
**Scheme 4.6**  Molecular structures of the Triton surfactants and Tween surfactants used for $CO_2$ absorption. Reproduced from Ref. [83] by permission of The Royal Society of Chemistry

**Fig. 4.2**  FTIR spectra of TX-100/$CO_2$ at different pressures at 25 °C, the inset presents the dependence of wavenumber (*WN*) of OH-stretching on pressure. Reprinted with permission from Ref. [83]. Copyright 2011 Royal Society of Chemistry
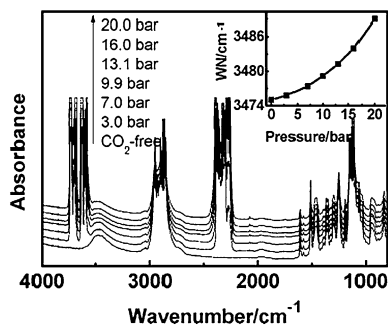


[83]. TX-45, TX-114, TX-100 have the same hydrophobic group (4-(1,1,3,3-tetramethylbutyl)phenyl), but have different lengths of hydrophilic polyethoxyl chain, i.e. $n = 5$, 7.5 and 10, respectively (Scheme 4.6); Tween 20 and Tween 80 have the same molecular structure and EO number, while differentiate in the hydrophobic alkyl chain length. It is well known that the smaller the Henry's constant, the larger the solubility. The Henry's constants of $CO_2$ (e.g., 25 °C) in the surfactants with more EO content are smaller (TX-45: $39.8 >$ TX-114: $28.7 >$ TX-100: 20.0), while the effect of alkyl chain length on the Henry's constant is very limited (Tween 20: 10.7 and Tween 80: 10.1). The absolute value of the enthalpy increases considerably with increasing EO content (TX-45: $-14.5 \pm 2.1$, TX-114: $-15.9 \pm 2.3$ and TX-100: $-20.4 \pm 1.6$) [83].

The OH-stretching vibration of TX-100, appearing at 3,475 cm$^{-1}$ in the absence of $CO_2$, gradually shifts to higher frequency with the dissolution of $CO_2$ (Fig. 4.2), indicating that the hydrogen bond interaction between the terminal hydroxyl of TX-100 with the oxygen atoms of EO groups or terminal hydroxyl groups of other TX-100 molecules is weakened [84, 85]. Since $CO_2$ is an electron acceptor and EO is an electron donor, the Lewis acid–base interaction between $CO_2$ and EO is responsible for the shift of the band, which enhances the dissolution of $CO_2$ in the surfactants [86–89].

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# Chapter 5
# Functionalized-PEG as Catalysts for $CO_2$ Conversion

**Abstract**   Chemical utilization of $CO_2$ as green carbonyl source has great significance as an alternative to conventional phosgene processes in organic synthesis, which pose drawbacks associated with using copious amounts of chloride based solvent and corrosion of reaction equipment as a result of commonly coproduced hydrochloric acid and alkali chloride salts. Although $CO_2$ utilization is unlikely to consume significant quantities of $CO_2$, development of catalytic processes for chemical transformation of $CO_2$ into useful compounds is of paramount importance from a standpoint of green and sustainable chemistry. Functionalized-PEG has been synthesized for efficient transformation of $CO_2$ into fuels or value-added chemicals, such as cyclic cabonates from $CO_2$ and epoxides (Sect. 5.1), dimethylcarbonate from $CO_2$, epoxides and methanol (Sect. 5.2), cyclic carbonates from $CO_2$ and halohydrin (Sect. 5.3), oxazolidinones from $CO_2$ and aziridines (Sect. 5.4), organic carbamates from amines, $CO_2$ and alkyl halides (Sect. 5.5) and urea derivatives from $CO_2$ and amines (Sect. 5.6).

As an abundant, nontoxic, non-flammable, easily available, and renewable carbon resource, $CO_2$ is very attractive as an environmentally friendly feedstock for making commodity chemicals, fuels, and materials [1–7]. In this respect, PEGs-functionalized catalysts have been developed for efficient transformation of $CO_2$ into value-added chemicals or fuels such as cyclic carbonates, dimethyl carbonate (DMC), oxazolidinones, organic carbamates and urea derivatives.
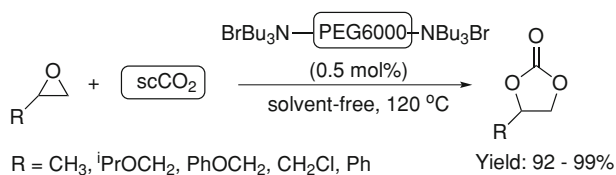
**Scheme 5.1**  Synthesis of carbonates from epoxides and $CO_2$ promoted by PEG6000(NBu$_3$Br)$_2$. Reprinted from Ref. [10], with permission from Elsevier

## 5.1 Synthesis of Cyclic Carbonates from $CO_2$ and Epoxides

Chemical fixation of $CO_2$ into useful organic compounds has attracted intense attention in view of resource utilization and pollution prevention [8]. One of the most promising methodologies in this area is the direct synthesis of carbonates via coupling of $CO_2$ with epoxides since one carbon atom and two oxygen atoms can be incorporated in one step without forming any co-products with high atom efficiency. Moreover, cyclic carbonates have been widely used as polar aprotic solvents, intermediates for organic and polymeric synthesis, and ingredients for pharmaceutical/fine chemicals in biomedical applications [9].

A polyethylene glycol (PEG)-supported quaternary ammonium salt is proved to be an efficient and recyclable homogeneous catalyst for solvent-free synthesis of cyclic carbonates from $CO_2$ and epoxides under supercritical conditions [10]. The PEG6000(NBu$_3$Br)$_2$ displays higher catalytic activity than the unsupported quaternary ammonium (Bu$_4$NBr) and the support (PEG6000) itself, even more effective than the simple physical mixture of Bu$_4$NBr and PEG6000 under the same conditions ($CO_2$ 8 MPa, 120 °C, 6 h, catalyst loading 0.5 mol %). Additionally, the PEG-supported catalyst, PEG6000(NBu$_3$Br)$_2$, is found to be applicable to a variety of terminal epoxides, providing the corresponding cyclic carbonates in 92–99 % yields and with excellent selectivities (Scheme 5.1).

A possible mechanism for the PEG6000(NBu$_3$Br)$_2$-catalyzed cycloaddition of $CO_2$ with epoxides is proposed as shown in Scheme 5.2. The proposed mechanism involves the activation of propylene oxide (PO) by the ammonium cation (step I), the ring opening of the epoxide via nucleophilic attack of bromine at the least-hindered carbon (step II), and the insertion of $CO_2$ into the N–O bond (step III). Subsequent cyclization via an intramolecular nucleophilic attack (step IV) leads to the propylene carbonate (PC) and the regeneration of the catalyst.

Guanidinium salt has special properties of high thermal and chemical stability, tunable groups attached on the three N atoms in the molecular structure, and excellent catalytic activity for cycloaddition of $CO_2$ and epoxides to produce cyclic carbonate [11, 12]. A functionalized-PEG, hexaalkylguanidinium bromide (Scheme 5.3) being covalently tethered to PEG (MW = 6000) is utilized as an active homogeneous catalyst, which includes the benefits of recyclability and high catalytic activity, for the synthesis of cyclic carbonates from $CO_2$ and epoxides with almost quantitative yield and excellent selectivity [13].
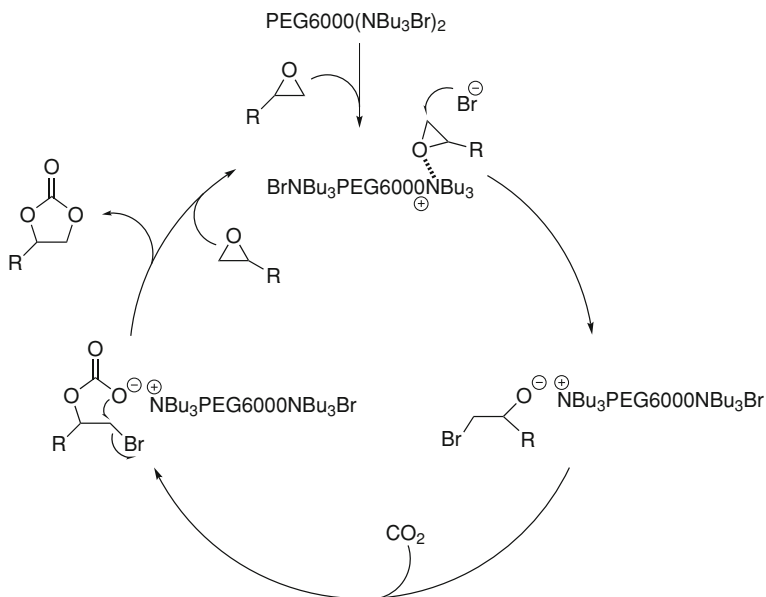
**Scheme 5.2** Proposed mechanism for PEG6000(NBu$_3$Br)$_2$−catalyzed cycloaddition of $CO_2$ with epoxides. Reprinted from Ref. [10], with permission from Elsevier

**Scheme 5.3** Synthesis of various carbonates catalyzed by PEG6000-supported hexaalkylguanidinium bromide [13]
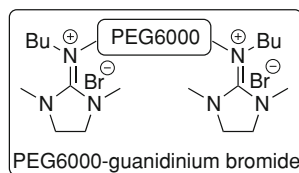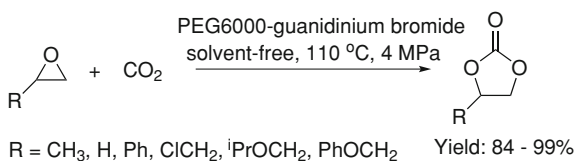


A series of epoxides are chosen to be tested for the synthesis of the corresponding carbonates in the presence of the catalyst (0.5 mol % relative to epoxide) under the optimal reaction conditions (110 °C, 4 MPa, 4 h), as shown in Scheme 5.3. Supporting guanidinium bromide on $CO_2$-philic polymer enhances the catalytic activity. Notably, the catalyst is able to be reused with retention of high catalytic activity and selectivity.

The cycloaddition of PO and $CO_2$ to form PC promotes by a phosphonium salt covalently bound to PEG6000 and gives excellent yield and selectivities (Reaction conditions: BrBu$_3$PPEG6000PBu$_3$Br, 1 mol %; reaction pressure, 1 MPa; reaction temperature, 120 °C; reaction time, 6 h) (Scheme 5.4) [14].

**Scheme 5.4** Synthesis of various carbonates catalyzed by BrBu3PPEG6000PBu3Br. Reproduced from Ref. [14] by permission of The Royal Society of Chemistry



R = $CH_3$, $^iPrOCH_2$, Ph, $PhOCH_2$, $CH_2Cl$     Yield: 89 - 99%
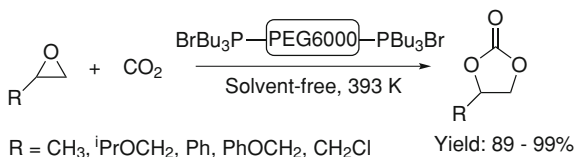
A series of catalytic cycles are examined to test the catalyst recycling. As a result, the catalyst (BrBu$_3$PPEG6000PBu$_3$Br) keeps high catalytic activity and selectivity after five cycles. Hence, immobilization of a phosphonium salt on a soluble polymer (e.g. PEG) could provide an alternative pathway for realizing homogeneous catalyst recycling.

Recently, PEG-functionalized basic ILs have been proved to be highly efficient and stable catalysts for the cycloaddition reaction of $CO_2$ to epoxides without utilization of any organic solvent or additive under modest reaction conditions as depicted in Scheme 5.5 [15].

The high efficiency is presumably due to activation of epoxide assisted by hydrogen bonding and activation of $CO_2$ by the oxygen atoms of the ether linkages of PEG [16, 17], or the presence of the secondary amino group in the cation, which has the potential to activate $CO_2$ molecule [18–24], on the basis of in situ FT-IR investigation under $CO_2$ pressure.

PC synthesis from $CO_2$ and PO is carried out in the presence of a series of the PEG-functionalized ILs (Scheme 5.5) under identical reaction conditions (catalyst loading, 1 mol %; $CO_2$ pressure, 1 MPa; 120 °C; 3 h). All the halide anions give good results with catalytic activity increasing in the order of $I^- < Cl^- < Br^-$, probably owing to good leaving ability and nucleophilicity. Both PC yield and selectivity decrease markedly with PEG chain length of the cation increasing from PEG150 to PEG400, probably due to the increased mass-transport limitation. Furthermore, catalytic efficiency of cations derived from various bases decreases in the order of TBDPEG150TBD$^{2+}$ > DMImPEG150DMIm$^{2+}$ > MImPEG150MIm$^{2+}$ > DBN-PEG150DBN$^{2+}$ > DBUPEG150DBU$^{2+}$. Notably, activation of $CO_2$ can be achieved by adopting BrTBDPEG150TBDBr with a secondary amino group in the cation as catalyst with formation of the carbamate species.

The scope of the substrates is further explored. A series of epoxides are chosen to be tested for the synthesis of the corresponding carbonates under the reaction conditions (BrTBDPEG150TBDBr 1 mol %, 120 °C, 0.1 and 1 MPa, 3–20 h). The catalyst can be applicable to a variety of terminal epoxides, providing the corresponding cyclic carbonates in high yields ($\geq$ 93 %) and excellent selectivities (> 99 %).

The proposed mechanism of cycloaddition reaction of $CO_2$ with epoxides catalyzed by BrTBDPEG150TBDBr is depicted in Scheme 5.6.

To gain a deeper insight into the reaction mechanism, in situ FT-IR spectroscopy under $CO_2$ pressure is employed to identify the possible intermediates during the reaction proceeding. The in situ FT-IR spectrum of BrTBDPEG150TBDBr before and after reaction with $CO_2$ (at 3 MPa, 120 °C) is shown in Fig. 5.1a. There
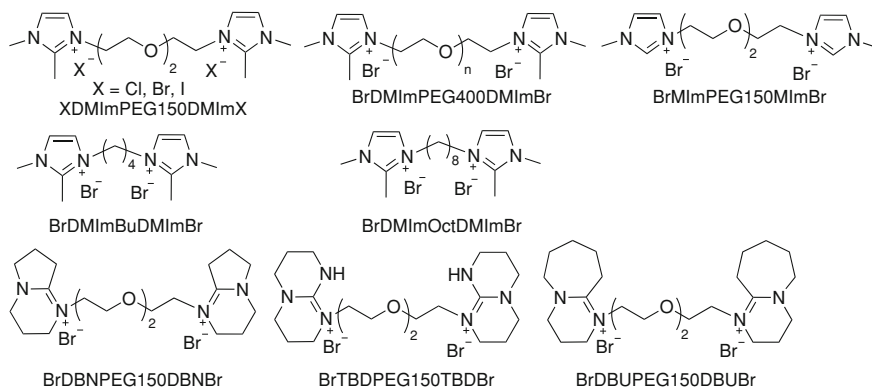
**Scheme 5.5** Structures of PEG-functionalized ionic liquids for the synthesis of cyclic carbonates. Reproduced from Ref. [15] by permission of The Royal Society of Chemistry
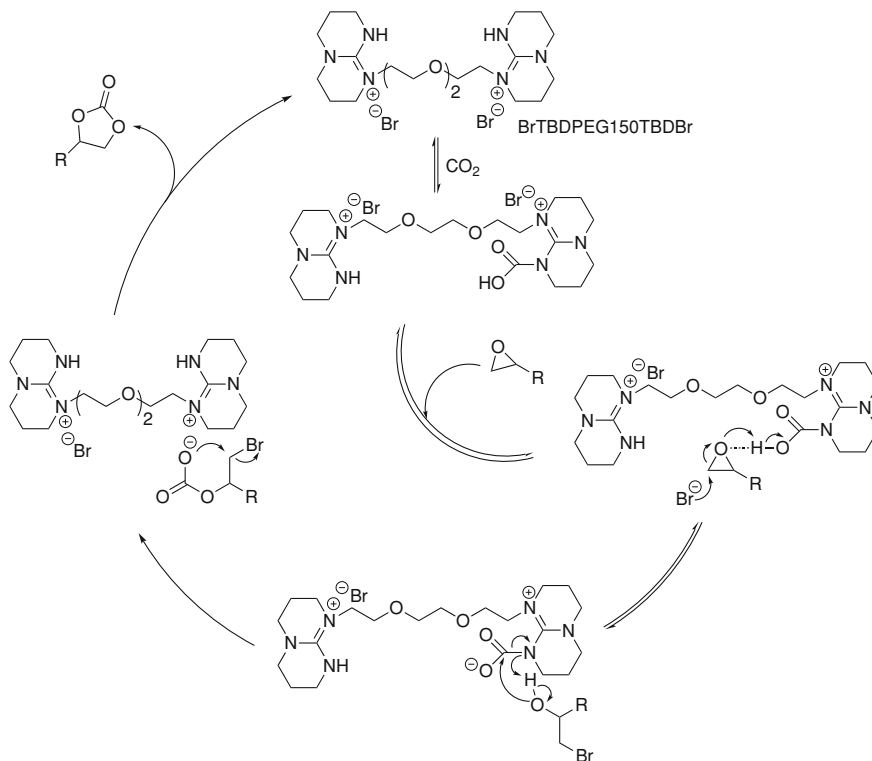
**Scheme 5.6** Proposed mechanism for the BrTBDPEG150TBDBr-catalyzed cycloaddition reaction of $CO_2$ with epoxides. Reproduced from Ref. [15] by permission of The Royal Society of Chemistry

are three important features in the spectrum. First, the N–H stretch observed at 3150 and 3208 $cm^{-1}$ decreases when $CO_2$ reacts with the IL. Secondly, the new peak at 2333 $cm^{-1}$ could correspond to physically dissolved $CO_2$. In addition, the bands originating from the carbamic ammonium salt between 2800–3000 $cm^{-1}$ and in the 2000–2800 $cm^{-1}$ region are not present along with addition of $CO_2$. Thirdly, there is a new band centered at 1749 $cm^{-1}$, which can correspond to the new COOH moiety formed from the reaction of $CO_2$ with the IL [25]. As shown in Fig. 5.1b, the absorption intensity of asymmetric (C=O) vibrations (1749 $cm^{-1}$) gradually increases in the course of the reaction between BrTBDPEG150TBDBr and $CO_2$, suggesting formation of carbamic acid (1545 $cm^{-1}$ is characteristic of a carbamate anion) [26]. Notably, absorption peaks of the carbonyl group at 1749 $cm^{-1}$ (BrTBDPEG150TBDBr-$CO_2$ carbamic acid) and 1790 $cm^{-1}$ (PC) increases gradually along with the reaction time (Fig. 5.1b), presumably implying the activation of $CO_2$ by the secondary amino group in the cation of IL BrTBD-PEG150TBDBr, which leads to significant promotion of the cycloaddition reaction of PO and $CO_2$.

Finally, the catalyst is readily recovered after separation from the reaction mixture and then used for the next run without further purification. The results indicate that the yield of PC is almost constant after five successive recycles (Fig. 5.2).

## 5.2  Synthesis of Dimethylcarbonate from $CO_2$, Epoxides and Methanol

DMC has been drawing much attention as a safe, non-corrosive, and environmentally friendly building block for the production of polycarbonate and other chemicals [27], an additive to fuel oil owing to a high octane number [28] and an electrolyte in lithium batteries due to its high dielectric constant [29]. From the viewpoint of green chemistry, the two-step transesterification process utilizing $CO_2$ as a raw material is much attractive [30–40]. However, the major disadvantages of this process are high energy consumption and investment, due to the need to separate the cyclic carbonate intermediate. Hence, it is very desirable to integrate the cycloaddition of $CO_2$ with epoxide and the transesterification of cyclic carbonate with methanol into a one-pot reaction [14, 41]. The TSIL BrTBDPEG150TBDBr bearing both secondary and tertiary nitrogen in the cation being capable of activating methanol, delightedly displays high activity for the transesterification of ethylene carbonate (EC) with methanol (Scheme 5.7), 85 % yield of DMC being obtained with 1:20 molar ratio of EC/methanol within 4 h (Table 5.1) [15]. In addition, integration of the cycloaddition and transesterification reaction in a one pot operation gives 83 % yield of DMC.

Previously, our group have reported cycloaddition of PO and $CO_2$ to form PC promotes by a phosphonium salt covalently bound to PEG6000 with excellent yield and selectivities [14]. Further studies show that inorganic base/phosphonium

**Fig. 5.1** Results of in situ IR spectroscopy under $CO_2$ pressure monitoring at various reaction time. Reaction conditions: (**a**) and (**b**) BrTBDPEG150TBDBr (1 mmol), $CO_2$ (3 MPa), 120 °C; **c** PO (10 mmol), BrTBDPEG150TBDBr (0.5 mmol), $CO_2$ (3 MPa), 120 °C, 1749 $cm^{-1}$ corresponds to peak for carbonyl group of carbamic acid formed between $CO_2$ and BrTBDPEG150TBDBr. 1790 $cm^{-1}$ was the carbonyl group absorption of the product PC. Reproduced from Ref. [15] by permission of The Royal Society of Chemistry
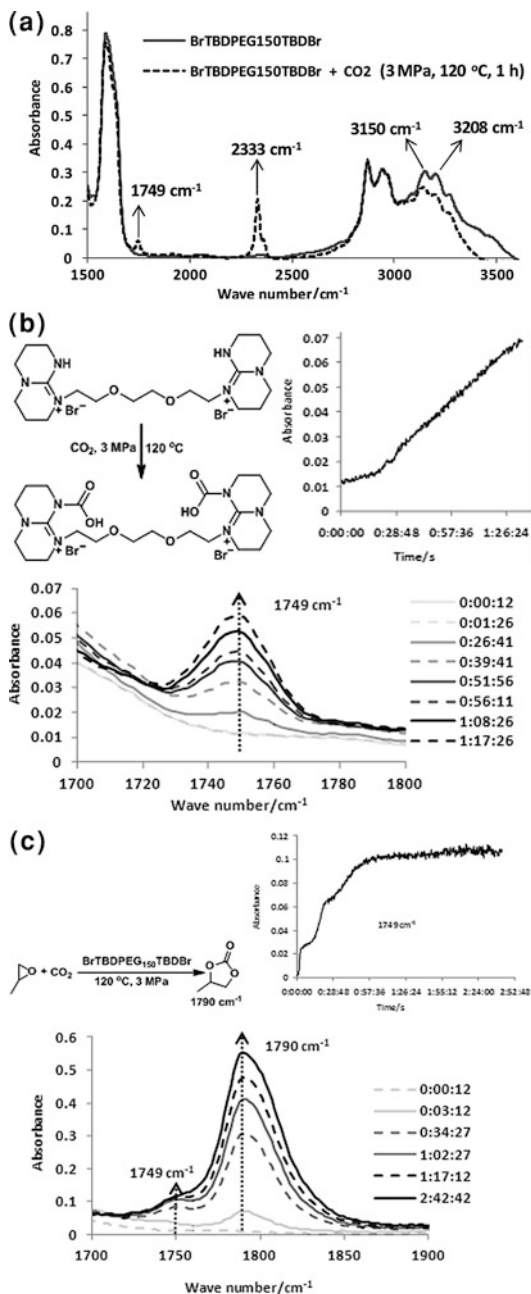


halide-functionalized PEG ($K_2CO_3$/BrBu$_3$PPEG6000PBu$_3$Br) are active for DMC synthesis from PO, $CO_2$ and alcohols (methanol, ethanol, isopropanol) under mild reaction conditions, even under low $CO_2$ pressure (2 bar) (Scheme 5.8).

**Fig. 5.2** Recyclability of the catalyst. Reaction conditions: PO, 10 mmol; BrTBDPEG$_{150}$TBDBr, 1 mol %; CO$_2$ pressure, 1 MPa; 120 °C; 3 h. PC yield is determined by GC. Reproduced from Ref. [15] by permission of The Royal Society of Chemistry
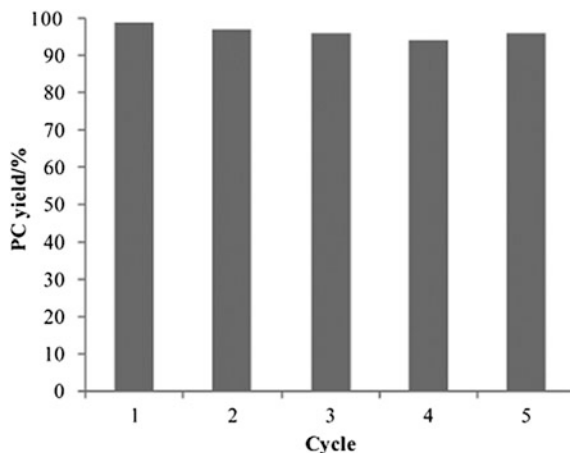


**Scheme 5.7** Two-step process for DMC production utilizing CO$_2$ as a raw material. Reproduced from Ref. [15] by permission of The Royal Society of Chemistry
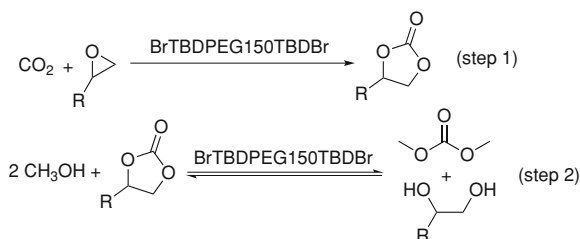


Notably, an almost quantitative yield of DMC and 1, 2-diols can be attained under the optimized reaction conditions. Additionally, the catalyst is easily reused in almost consistent in yield and selectivity. This process eliminates the requirement for toxic and wasteful feedstocks such as phosgene and carbon monoxide and has successfully been applied to synthesize the other symmetric dialkyl carbonates and 1, 2-diols.

## 5.3 Synthesis of Cyclic Carbonates from CO$_2$ and Halohydrin

PEG proves to be an efficient reaction medium for the reaction of vicinal halo-hydrin with carbon dioxide in the presence of a base to synthesize cyclic carbonates (Scheme 5.9) [42]. Notably, PEG400 (MW = 400) as an environmentally friendly solvent exhibits a unique influence on reactivity compared with conventional organic solvents. Various cyclic carbonates can be prepared in high yield employing this protocol. The process presented here has potential applications in the industrial production of cyclic carbonates because of its simplicity, cost benefits, ready availability of starting materials, and mild reaction conditions.

**Table 5.1** BrTBDPEG150TBDBr-catalyzed DMC synthesis through transesterification reaction[a]. Reproduced from Ref. [15] by permission of The Royal Society of Chemistry

| Entry | Molar ratio (EC: MeOH) | T/h | EC conv. (%)[b] | DMC yield (%)[b] |
|---|---|---|---|---|
| 1 | 1:10 | 4 | 87 | 64 |
| 2 | 1:20 | 4 | 96 | 85 |
| 3 | 1:30 | 4 | 95 | 86 |
| 4 | 1:20 | 2 | 89 | 45 |
| 5 | 1:20 | 5 | 90 | 87 |
| 6[c] | 1:20 | 4 | 90 | 83 |

[a] Reaction conditions: EC, 10 mmol; BrTBDPEG150 TBDBr, 1 mol % relative to EC; 70 °C
[b] Determined by GC using an internal standard technique
[c] EO:MeOH = 1:20. After the cycloaddition reaction of ethylene oxide (EO) with $CO_2$ under optimal reaction conditions of (EO, 10 mmol, 10.5808 g; BrTBDPEG150TBDBr, 1 mol %; $CO_2$ pressure, 1 MPa; 120 °C; 3 h), MeOH (200 mmol) is added, and then the mixture is transferred to a 25 mL flask, and refluxed for 4 h at 70 °C. The products are analyzed by GC using biphenyl as internal standard and further identified using GC–MS by comparing retention times and fragmentation patterns with authentic samples
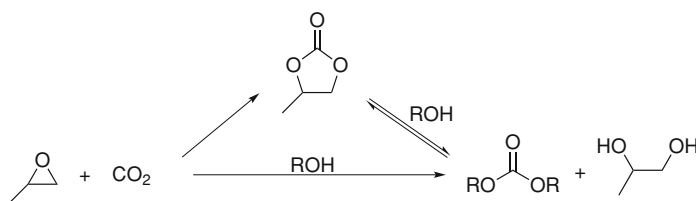


**Scheme 5.8** The one-pot process for dialkyl carbonate synthesis using different alcohols. Reproduced from Ref. [14] by permission of The Royal Society of Chemistry



**Scheme 5.9** Synthesis of cyclic carbonates from halohydrin with $CO_2$ catalyzed by PEG/$K_2CO_3$ system. Reprinted with the permission from Ref. [42]. Copyright 2009 CSIRO PUBLISHING
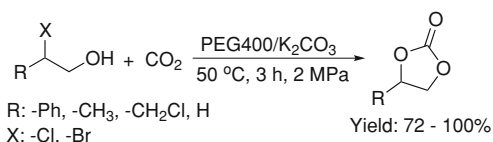
In the experiment study, solvent screening is carried out by using the reaction conditions of 3 h, 50 °C, $P_{CO2}$ 2 MPa. No conversion of vicinal bromohydrin is observed in the low polarity solvents such as dioxane, CHCl$_3$, tetrahydrofuran (THF) and $CH_2Cl_2$. With the increasing polarity of the solvents as $H_2O$ > N,N-dimethylformamide (DMF) > $CH_3CN$, the yield of styrene carbonate increases except for with water. Water shows poor performance probably owing to its poor solubility towards the reactants. PEG400 as the reaction media gives full conversion with excellent selectivity. It is distinct that the environmentally benign solvent PEG400 has a potential utility for the synthesis of styrene carbonate with
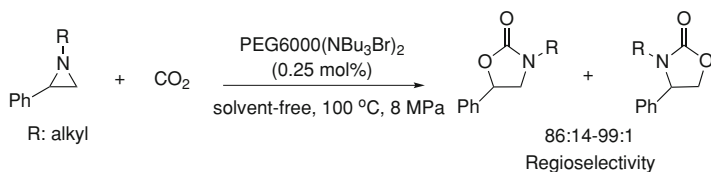
**Scheme 5.10** Chemical fixation $CO_2$ catalyzed by quaternary ammonium bromide functionalized PEG [46]

high yield under mild reaction conditions. Subsequently, the effects of the reaction temperature and the molecular weight of PEG are investigated. At 50 °C, a 99 % yield for styrene carbonate is attained, whereas room temperature shows low reaction rate. However, PEG1000 gives poor activity, being presumably ascribed to the increased mass transport limitation of gaseous $CO_2$ in the highly viscous PEG with a long chain.

This protocol is applicable to different types of vicinal halohydrins such as chlorohydrins, bromohydrins and phenyl and alkyl-substituted halohydrins, to produce the corresponding cyclic carbonates. The advantages of using PEG400 as the reaction medium can be outlined as follows. First, it is assumed that PEG400 can form complexes through coordinating the potassium cation such as crown ether does, which results in an increase in the basicity of $K_2CO_3$ [43]. Second, the 'CO$_2$−expansion of PEG' effect [44, 45] leads to changes in the physical properties of the reaction mixture, such as lowered viscosity, increased gas/liquid diffusion rates, and solubility of the reactants, thereby improving the synthetic process. Third, another merit of using PEG as a reaction media is the ease of product separation.

## 5.4 Synthesis of Oxazolidinones from $CO_2$ and Aziridines

As catalyst recycling is often a vital problem in homogeneous catalysis, efficient recycling concepts have been developed. To preserve the benefits of a homogeneous catalyst while co-opting the primary benefits of a heterogeneous catalyst, one strategy is to graft the active species onto an insoluble support, whereby the catalyst can be readily separated from the reaction mixture by filtration. Notably, an appealing methodology would employ a $CO_2$−philic support for the reaction such that the supported catalyst dissolves during the reaction and can precipitate quantitatively at the separation stage. Based on this consideration, we have reported the PEG6000-(NBu$_3$Br)$_2$, a quaternary ammonium bromide covalently bound to PEG6000, is an efficient and recyclable catalyst for the cycloaddition reaction of aziridines to $CO_2$ under mild conditions without utilization of additional organic solvents or co-catalysts (Scheme 5.10) [46]. The experimental results show that 5-aryl-2-oxazolidinone is obtained in high yield with excellent
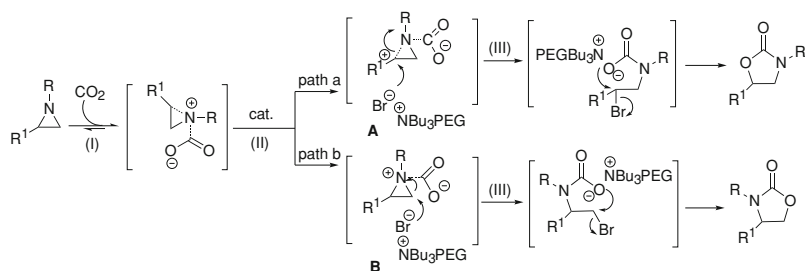
**Scheme 5.11** A putative mechanism for the PEG6000(NBu$_3$Br)$_2$– catalyzed cycloaddition of CO$_2$ with aziridine. Reprinted with the permission from Ref. [46]. Copyright 2008 American Chemical Society

regioselectivity as well as a wide variety of 1-alkyl-2-arylaziridines. Additionally, the catalyst can be recovered by centrifugation and reused without significant loss of catalytic activity and selectivity.

A possible reaction pathway for the PEG6000(NBu$_3$Br)$_2$-catalyzed cycloaddition of CO$_2$ with aziridine is shown in Scheme 5.11. This mechanism is analogous to that of the LiI-catalyzed version for the same reaction [47]. It involves three steps: coordination of CO$_2$ to aziridine (step I), then ring opening of the aziridine through two different pathways as represented by paths a and b mainly depending on the nature of the R$^1$ group with alkyl substitution at the N-position (step II), and subsequent cyclization via an intramolecular nucleophilic attack leading to oxazolidinones and regeneration of the catalyst (step III). The rate dependence on the steric effect of the R group on the nitrogen atom implies that the coordination of CO$_2$ to the aziridine (I) is a reversible step in the catalytic cycle and the substrates with less sterically hindered R would be favorable for the coordination with CO$_2$, thus resulting in higher reaction rate compared with those substrates with more sterically hindered R. The proposed mechanism could also account for the effect of the R$^1$ substituent on the selective formation of 4- (path a) or 5-oxazolidinone (path b). As deduced from, if R$^1$ is an aryl group, the intermediate **A** would be more stable than **B** and thus 5-oxazolidinone would be predominantly formed; in contrast, if R$^1$ is an alkyl group, **B** would be favored, which in turn results in dominantly producing 4-oxazolidinone.

## 5.5 Synthesis of Carbamates from Amines, CO$_2$ and Alkyl Halides

Organic carbamates hold extensive applications in pharmaceutical industry, agriculture and have been widely used as key intermediates or protecting groups in synthetic chemistry [48, 49]. The conventional synthesis of organic carbamates involves using highly toxic phosgene as a carbonylating agent, and organic

$$2\ R_2NH\ +\ CO_2\ \xrightleftharpoons{PEG400}\ [R_2NH_2 \cdot PEG]^{\oplus}{}^{\ominus}[O_2CNR_2]\ \xrightarrow{R^1X}\ R_2NCOOR^1$$

**Scheme 5.12** PEG-enhanced synthesis of organic carbamates from amines, $CO_2$ and alkyl halides [50]

solvents are required, whereby causing environmental problems. Therefore, much effort has been directed toward developing alternative routes to the synthesis of carbamates using $CO_2$ as a carbonyl reagent in place of phosgene. Fortunately, $CO_2$ is able to react with an amine to form an ammonium carbamate, and subsequently with an alkyl halide in conjunction with a base, forming an organic carbamate.

An efficient and environmentally benign method for the PEG400-enhanced synthesis of organic carbamates with high chemoselectivity from amines, $CO_2$ and alkyl halides under room temperature and atmospheric pressure utilizing $K_2CO_3$ as a base is reported (Scheme 5.12) [50]. PEG probably could serve as both a solvent and PTC, and also activate the carbamic anion so that PEG could depress the alkylation and enhance the selectivity toward the target product.

In this reaction, PEG400 mainly plays an irreplaceable role in three possible ways, including: (1) forming an adduct of $[R_2NH_2 \bullet PEG]^+$ $[O_2CNR_2]^-$ to increase the solubility of the ammonium carbamate salt; (2) lowering the interaction of $[R_2NH_2 \bullet PEG]^+$ with $[O_2CNR_2]^-$, and improving the reactivity of $[O_2CNR_2]^-$, and thus depressing N-alkylation of the amine; (3) weakening the electrostatic interactions between the ion pairs of $K_2CO_3$ to increase the reactivity of the carbonate anion. Moreover, the protocol worked well for various aliphatic and aromatic amines, and halides.

## 5.6 Synthesis of Urea Derivatives from $CO_2$ and Amines

Urea derivatives are an important class of carbonyl compounds and useful chemical intermediates in the synthesis of pharmaceuticals, agricultural chemicals, and dyes; and they are also used as antioxidants in gasoline and additives in plastics [51–54].

Conventionally preparative methodologies of urea derivatives are based on the use of dangerous reagents and the synthesis of ureas starting from $CO_2$ has drawn much attention because this chemical processes can be regarded one of the green routes. PEG and its derivatives are commonly known to be inexpensive, thermally stable, almost negligible vapor pressure, toxicologically innocuous, and environmentally benign media for chemical reactions, serves as PTC and coordinate with metal cations. In this context, KOH/PEG1000-catalyzed processes for the synthesis of urea derivatives from amines and $CO_2$ without using any dehydrating agent is reported (Scheme 5.13) [55].

**Scheme 5.13** KOH/PEG-catalyzed synthesis of symmetrical urea from amine and CO$_2$ [55]
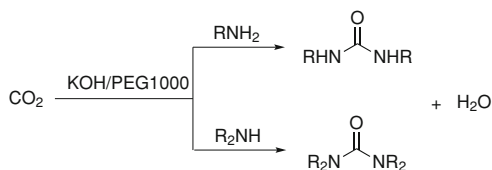


**Scheme 5.14** A possible reaction pathway for the formation of urea [55]
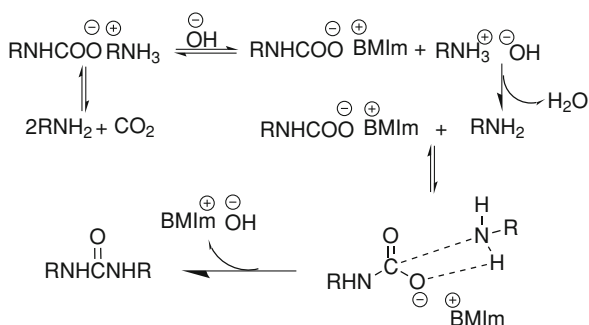


The reaction does not occur at all without catalyst and PEG1000 itself also gives no product. The catalytic performance seems to be strongly dependent on its basicity. Generally a stronger base can favor the formation of dibutyl urea, and KOH is found to show the best activity among the tested bases. PEG1000 as support is found to facilitate the reaction. On the other hand, the MW has a significant impact on the catalytic activity of KOH/PEG. Both low PEG molecular weight (MW < 200) and PEG with long chain (MW > 20000) show poor activity. Therefore, a minimum molecular weight of at least 200 for optimal activity is required; increased mass-transport limitation and the cage effect make a negative impact.

PEG as a support could enhance the reaction, which could be explained with the proposed mechanism as shown in Scheme 5.14. The reaction involves two steps, that is, formation of the ammonium carbamate and dehydration to the urea. In this reaction, PEG could form [R$_2$NH$_2$PEG]$^+$ [R$_2$NCO$_2$]$^-$, and thus could increase the thermodynamic stability of [R$_2$NH$_2$]$^+$. Increasing the basicity of the base with the help of PEG could also facilitate formation of the ammonium carbamate salt.

Using this protocol, primary aliphatic amines, secondary aliphatic amines, and diamines could be converted into the corresponding urea derivatives in moderate yields. Additionally, catalytic efficiency of cations derived from various bases decreases in the order of > diamines > primary amines > secondary amines > aniline, probably being due to the steric effect and basicity. The catalyst could also be recovered after a simple separation procedure, and reused over five times with retention of high activity. This process presented here could show much potential application in industry due to its simplicity and ease of catalyst recycling.

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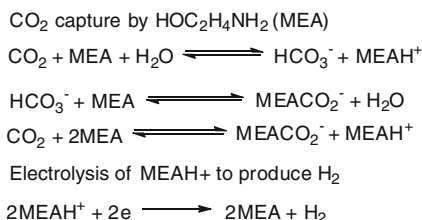
# Chapter 6
# CO$_2$ Capture, Activation, and Subsequent Conversion with PEG

**Abstract** Although significant advances have been made in the field of CCS, there are still inherent drawbacks. In particular, extensive energy input in desorption and compression process would be a crucial barrier to realize practical CCS. Hence, reducing huge energy requirement could be an essential prerequisite for a breakthrough in absorption techniques. Chemical reactions involving CO$_2$ are commonly carried out at high pressure and using pure CO$_2$, which may not be economically suitable and also pose safety concerns. The challenge is to develop efficient catalysts that are capable of activating CO$_2$ under low pressure (preferably at 1 atm), and thus incorporating CO$_2$ into organic molecules catalytically. In this regard, herein, we have proposed CO$_2$ capture and utilization (CCU) concept as one part of CO$_2$ chemistry. The essence of our strategy is to use the captured CO$_2$, also being considered as an activated form of CO$_2$, as a feedstock, which renders the reaction system suitable for accomplishing chemical transformation of CO$_2$ under low pressure (ideally at 1 atm), and simultaneously getting rid of desorption step in CCU process. Indeed, activation of CO$_2$ through carbamate/alkyl carbonate formation with amines has been reported and detected by in situ FT-IR under pressure.

In the past decades, numerous strategies have been proposed for chemical absorption of CO$_2$ [1–14]. Although significant advances have been made, there are still inherent drawbacks such as extensive energy consumption for CO$_2$ desorption, low capture efficiency, and slow sorption kinetics to be addressed. Most importantly, Jessop and his coworkers have developed mixtures of volatile organic alcohols (e.g. hexanol) and amidine/guanidine bases for highly efficient reversible CO$_2$ capture to produce liquid amidinium/guanidinium alkylcarbonates ILs [15–17]. Afterwards, Dai's group proposed several efficient strategies for

**Scheme 6.1** $CO_2$ capture by MEA and electrochemical reduction of $MEAH^+$ ion [18]

$CO_2$ capture by $HOC_2H_4NH_2$ (MEA)

$CO_2 + MEA + H_2O \rightleftharpoons HCO_3^- + MEAH^+$

$HCO_3^- + MEA \rightleftharpoons MEACO_2^- + H_2O$

$CO_2 + 2MEA \rightleftharpoons MEACO_2^- + MEAH^+$

Electrolysis of MEAH+ to produce $H_2$

$2MEAH^+ + 2e \longrightarrow 2MEA + H_2$

reversible chemisorption with equimolar $CO_2$ absorption that employs absorbents derived from superbases together with different non-volatile weak proton donors like hydroxyl-funtionalized ILs [5], imidazolium ILs [6], fluorinated alcohol, imidazole, and phenol [7, 8], which demonstrate superior sorption performance in comparison with those sorption systems based on conversional ILs. However, extensive energy input in desorption process would be a big problem for practical CCS. Hence, reducing energy requirement is an essential prerequisite for a breakthrough in absorption techniques. Moreover, the reactions involving $CO_2$ are commonly carried out at high pressure, which may not be economically suitable and also pose safety concerns. The challenge is to develop efficient catalysts that are capable of activating $CO_2$ under low pressure (preferably at 1 atm), and thus incorporating $CO_2$ into organic molecules catalytically.

Hence, an alternative concept CCU is proposed to address the energy penalty problem in the CCS process. The essence is to directly use the captured $CO_2$ i.e., activated one as a feedstock to synthesize value-added chemicals, getting rid of the desorption step. Very recently, Huang et al. described a strategy of capturing $CO_2$ by utilizing imidazolium IL/MEA system and then electrochemical reduction of $MEAH^+$ ion to $H_2$ simultaneously leading to carbamate salts formation (Scheme 6.1) [18].

Diazabicyclo[5.4.0]-undec-7-ene (DBU) has been successfully immobilized on methylhydrosiloxane support (HMS-DBU) for $CO_2$ capture with 100 % degree of functionalization (Scheme 6.2) [19]. Notably, HMS-DBU is found to be recyclable and shows retention of activity in five recycles. $CO_2$ is absorbed under ambient temperature and could be desorbed at 120 °C, which renders the material suitable for carrying out carboxylation reactions of ketones to $\beta$-keto esters at 25 °C with excellent yields.

Selective precipitation of ammonium carbamate can be achieved by reacting gaseous $CO_2$ and $NH_3$ in anhydrous ethanol, 1-propanol or DMF in a flow reactor that operates in continuous mode [20]. And then, the pure ammonium carbamate is used to produce urea with good yield (up to 54 % on carbamate basis) at 120–140 °C in the presence of inexpensive Cu (II) and Zn (II) catalysts. (Scheme 6.3)

We have also reported a CCU approach to solve the energy penalty problem in CCS process. The essence of our strategy is to use binary system consisting of PEG/superbase for $CO_2$ capture and whereby substantial activation, which renders
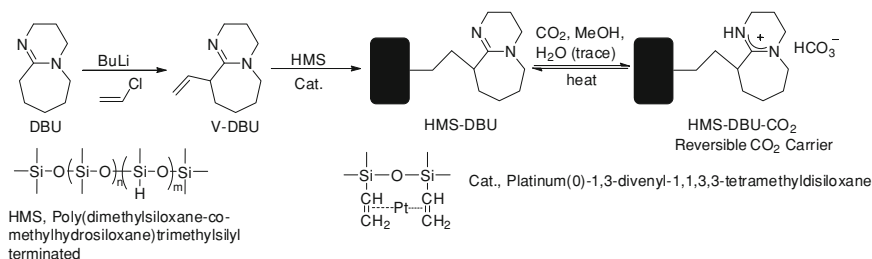
**Scheme 6.2** Preparation of reversible CO$_2$ carrier HMS-DBU. Reproduced from Ref. [19] by permission of The Royal Society of Chemistry
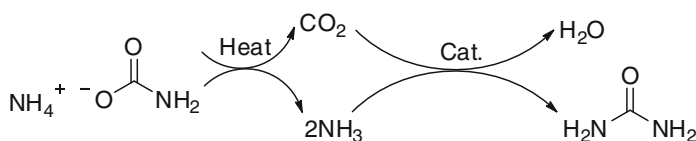

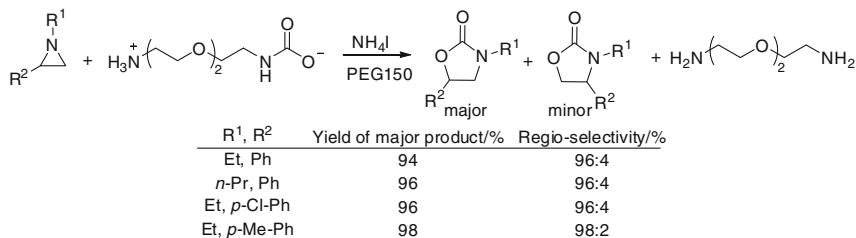
**Scheme 6.3** Synthesis of urea from ammonium carbamate [20]
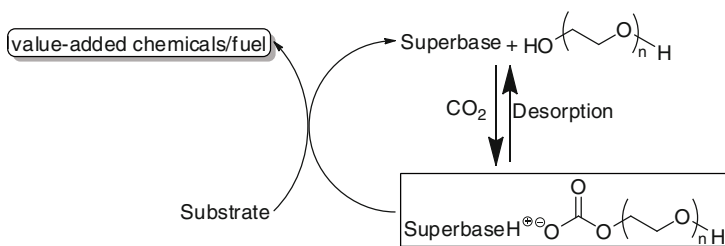


**Scheme 6.4** CCU protocol using PEG/superbase binary system [21]

this system suitable for accomplishing chemical transformation of CO$_2$ under low pressure (1 atm), getting rid of desorption step (Scheme 6.4) [21, 22].

CO$_2$ molecule can undergo a reaction with PEG150 and DBU under CO$_2$ atmosphere during the absorption reaction of CO$_2$ to form the liquid amidinium alkylcarbonate salt (Scheme 6.5(1)). The basicity of the superbase, as decreases in the order: TBD > DBU > DBN > TMG > DMICH > MIm ∼ DABCO, could play a key role in CO$_2$ sorption performance. The PEG/superbase system is capable of rapid capture of almost equimolar CO$_2$ per mole superbase. The release of CO$_2$ proceeds rapidly and essentially completes within 15 min at 120 °C. Notably, no significant drop in CO$_2$ absorption capacity is detected after five successive absorption–desorption cycles. In addition, an amine-functionalized PEG e.g., NH$_2$PEG150NH$_2$/PEG150 gives rise to CO$_2$ uptake of greater than one
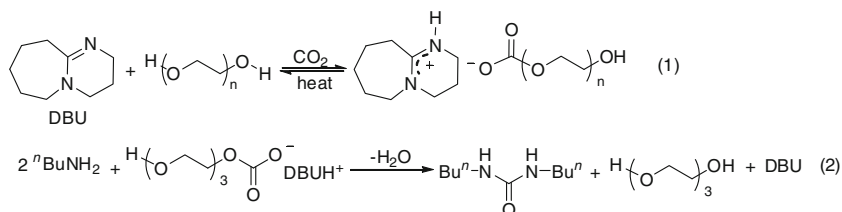
**Scheme 6.5** Urea formation upon $CO_2$ absorption/activation with DBU/PEG150 [21]



| $R^1$, $R^2$ | Yield of major product/% | Regio-selectivity/% |
|---|---|---|
| Et, Ph | 94 | 96:4 |
| n-Pr, Ph | 96 | 96:4 |
| Et, p-Cl-Ph | 96 | 96:4 |
| Et, p-Me-Ph | 98 | 98:2 |

**Scheme 6.6** Cycloaddition reaction of aziridines with the captured $CO_2$ by $NH_2PEG150NH_2$/PEG150 to produce 5-phenyloxazolidin-2-ones [21]

$CO_2$ per two bases with respect to the available functional groups and approaches the 1:2 stoichiometry expected from the hypothetical mechanism as reported [3]. Any uptake in excess of 0.5 mol $CO_2$ per mole of amino group (i.e. 1:2 stoichiometry) could be attributed to physical absorption.

Indeed, the ammonium alkylcarbonate salt formed upon $CO_2$ uptake could result in $CO_2$'s activation, which is confirmed by NMR, in situ FT-IR, and giving excellent reactivity in incorporating captured $CO_2$ into organic molecules catalytically under low pressure.

Based on the experimental results utilizing PEG/superbase binary system for $CO_2$ capture, we perform subsequent reaction to synthesize urea derivatives by using the captured $CO_2$ as a starting material, the absorbent as a catalyst and energy input being supplied to chemical reactions in order to validate our strategy. The liquid amidinium carbonate salt formed (Scheme 6.5(1)) upon $CO_2$ (gas, 1 atm) absorption with DBU/PEG150 directly reacts with n-butylamine at 110 °C (Scheme 6.5(2)), successfully affords the target product i.e., dibutylurea in almost quantitative yield (96 %) without the use of additives. Furthermore, the reaction of n-butylamine (0.25 mmol) with $CO_2$ (1 atm) in the presence of DBU (3 mmol)/PEG150 (3 mmol) gives 97 % yield of urea, much higher than that of the same reaction without PEG (31 % yield), also hinting that $CO_2$ molecule can presumably be activated by superbase/PEG, thus can render the reaction proceeding smoothly under mild conditions, which could probably go through the similar pathway as the organic base-catalyzed synthesis of urea as previously reported [23–25]. Using this protocol, primary aliphatic amines, secondary aliphatic

amines, and diamines could successfully be converted into the corresponding urea derivatives in high yields (77–99 %).

This strategy can also be applied to synthesize oxazolidinones from the captured CO$_2$ and aziridines. The cycloaddition reaction of 1-ethyl-2-phenylaziridine (R$^1$, R$^2$ = Et, Ph) with the captured CO$_2$ by NH$_2$PEG150NH$_2$/PEG150 gives rise to 5-phenyloxazolidin-2-one at 40 °C in >99 % of yield and selectivity, while CO$_2$ pressure as high as 3 MPa in the absence of absorbents is needed to attain comparable results. The generality of this protocol is also examined. Indeed, both electron-withdrawing and electron-donating group on the benzene ring give good results (yield: 94–98 %, Scheme 6.6).

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# Author Biography

Professor Liang-Nian He received his Ph.D. degree from Nankai University in 1996 under the guidance of academician Ru-Yu Chen. He worked then as a Chinese postdoctoral fellow with academician Ren-Xi Zhuo at Wuhan University. He had worked as a Postdoctoral Research Associate at National Institute of Advanced Science and Technology, Japan from 1999 to 2003 before joining Nankai University in April 2003. He has over 130 scientific publications and 6 patents. He also edited eight books and chapters, delivered more than 30 invited lectures at international/national conferences and universities and research organizations. Now He is a Fellow of the Royal Society of Chemistry (FRSC), an Editor-in-Chief for "Green and Sustainable Chemistry", an associate Editor of "Sustainable Development", and a member of Editorial Broad of "Current Organic Synthesis", "Current Chemical Research", "Reports in Organic Chemistry", "Current Catalysis", "Recent Patents on Catalysis", and a member of Chinese Fine Chemical Committee.

Current Research: His research involves $CO_2$ chemistry, green synthetic chemistry, catalysis in green solvent and biomass conversion (castor-based energy), particularly chemical transformation of $CO_2$ into fuels and value-added chemicals as well as $CO_2$ capture and utilization. Great efforts have been directed towards constructing C-C, C-O and C-N bond on the basis of $CO_2$ activation through molecular catalysis owing to its kinetic and thermodynamic stability. The aim of his research is to demonstrate the versatile use of $CO_2$ in organic synthesis, with the main focus on utilization of $CO_2$ as a building block for synthesis of industrial useful compounds and fuel additives such as cyclic carbonates, oxazolidinones, lactones, quinazolines $CO_2$ capture by using efficient chemical absorbents and the potential

use of dense $CO_2$ (supercritical $CO_2$) or green solvent like ionic liquid, polyethylene glycol as an alternative solvent and otherwise specific roles in organic synthesis are also involved.