Polymerizations in Supercritical Carbon Dioxide

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Contents
I. Introduction 543
II. Chain-Growth Polymerizations in CO2 546
  A. Free-Radical Polymerizations 546
    1. Homogeneous Polymerizations 547
    2. Precipitation Polymerizations 547
    3. Dispersion and Emulsion Polymerizations 548
    4. Polymer Blend Synthesis 553
  B. Cationic Polymerizations 553
  C. Transition Metal-Catalyzed Polymerizations 556
  D. Thermal Ring-Opening Polymerization 557
III. Step-Growth Polymerizations 557
  A. Melt-Phase Condensation Polymerizations 557
  B. Sol–Gel Polymerizations 559
  C. Oxidative Coupling 559
IV. Conclusions 561
V. References 561

I. Introduction

In the search for new polymerization solvents, scientists have turned to supercritical fluids. Supercritical carbon dioxide possesses many properties that have allowed it to emerge as the most extensively studied supercritical fluid for polymerization reactions. The work presented in this review shows that supercritical CO2 is a viable and promising alternative to traditional solvents used in polymer synthesis. Much of this promise results from its fluid properties, effects on polymers, and environmental advantages.

Supercritical fluids have the best of two worlds: they can have gaslike diffusivities (which have important implications for reaction kinetics) while having liquidlike densities that allow for solvation of many compounds. They exhibit changes in solvent density with small changes in temperature or pressure without altering solvent composition.1 Because of these advantages, chemists have explored reaction mechanisms and solvent cage effects in supercritical fluids.2,3 Changing solvent quality also has substantial effects on reaction workup: it can affect the separation of the polymer from starting materials and catalysts and the polymer molecular weight fractionation. In addition, the low viscosity of supercritical fluids and their ability to plasticize glassy polymers have implications on polymer processing and kinetics. For example, conditions that give a low viscosity supercritical fluid result in diminished solvent cage effects in free-radical initiator decompositions.4

When carbon dioxide is used as the supercritical solvent, additional advantages can be realized. The chemical industry has become increasingly aware of environmental concerns over the use of volatile organic solvents and chlorofluorocarbons in the manufacture and processing of commercial polymer products. The use of water alleviates these problems somewhat, but still results in large amounts of hazardous aqueous waste that require treatment. As a result of these environmental concerns, supercritical CO2 represents a more environmentally friendly alternative to traditional solvents. CO2 is naturally occurring and abundant: it exists in natural reservoirs of high purity located throughout the world. In addition, it is generated in large quantities as a byproduct in ammonia, hydrogen, and ethanol plants and in electrical power generation stations that burn fossil fuels.5 CO2 has an easily accessible critical point with a Tc of 31.1 °C and a Pc of 73.8 bar.6 Because it is an ambient gas, CO2 can be easily recycled after use as a solvent to avoid any contribution to greenhouse effects. Finally, it is inexpensive, nonflammable, and nontoxic, making it an attractive solvent for large-scale synthesis.

There are several important issues, such as drying, solubility, and polymer plasticization, that are involved when supercritical CO2 is used as a polymerization solvent. Because CO2 is an ambient gas, the polymers can be isolated from the reaction media by simple depressurization, resulting in a dry polymer product. This feature eliminates energy-intensive drying procedures required in polymer manufacturing to remove solvent and represents potential cost and energy savings for CO2-based systems.

Solubility plays a very important role in the synthesis of polymers in supercritical CO2. While CO2 is a good solvent for most nonpolar and some polar molecules of low molar mass,7 it is a poor solvent for most high molar mass polymers under mild conditions (<100 °C, 350 bar). For example, poly(methyl acrylate) requires 2000 bar CO2 and 100 °C for a 105 g/mol polymer to dissolve in CO2.8 Such high pressures are not practical and are too costly for their widespread implementation in polymer manufacturing. The only polymers that show good solubility in CO2 under mild conditions are amorphous fluoropolymers and silicones.1,4,9–12

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While the parameters that govern solubility of polymers in CO₂ are not fully understood, several studies have been performed to probe the nature of solute–solvent interactions between polymers and CO₂. CO₂ has a low dielectric constant compared to alkanes, and its polarizability and polarizability/volume are lower than ethane and propane. Although CO₂ lacks a dipole moment, a substantial contribution to its solubility parameter is due to a large quadrupole moment. The quadrupole moment coupled with its Lewis acidity allow CO₂ to participate in interactions absent in hydrocarbons. Early work in this area suggested that weak interactions exist between CO₂ and functional groups on the polymer chains such as sulfones and carbonyls. Later, systematic studies implied that the interactions between CO₂ and the silicone portion of the polymer backbone govern the high solubility of these types of polymers. Work involving the use of Fourier transform infrared spectroscopy reveals that CO₂ exhibits Lewis acid–base type interactions with electron-donating functional groups of polymer chains such as the carbonyl group of poly(methyl methacrylate) (PMMA). McHugh found that in copolymers of ethylene and methyl acrylate, increasing the methyl acrylate content increased polymer solubility.
concluded that dipole–quadrupole interactions between CO2 and the acrylate unit contributed to the polymer solubility. Increasing the free volume of the polymer also increased solubility at temperatures above 100 °C, where the polar interactions are decreased.

The solubility of fluorine-containing polymers has been investigated. McHugh noted that while polyethylene is insoluble in CO2, even up to 270 °C and 2750 bar, perfluorinated ethylene-propylene copolymer has greatly improved solubility (200 °C, 1000 bar). Other work revealed that the interactions between CO2 and poly(trifluoropropyl methyl siloxane) are anomalously high, and the authors attributed this finding to specific interactions between CO2 and the polar fluorine containing group. More recently high-pressure 19F NMR studies have indicated specific interactions between CO2 and fluorocarbons.

These solubility requirements dictate the types of polymerization techniques employed in polymer synthesis. For example, amorphous fluoropolymers have been synthesized homogeneously in supercritical CO2. In contrast, many polymerization reactions in CO2 are conducted under heterogeneous processes, either as precipitation, dispersion, or emulsion polymerizations, due to the inherent insolubility of most polymers in CO2. Thus, important research in this field involves the synthesis of surfactants, which are a critical component of dispersion and emulsion polymerizations, for use as stabilizers in CO2. These stabilizers have been successfully employed in the heterogeneous polymerizations of CO2-insoluble polymers. The nature of the surfactant controls polymer properties and morphology, and these factors need to be considered in surfactant design.

The fractionation of polymers is another important area affected by polymer solubility in supercritical CO2. Careful and controlled lowering of the density of a polymer solution allows precipitation of the highest molecular weight polymer fraction. For example, CO2-soluble synthetic oils such as perfluoroalkyl polyethers, chlorotrifluoroethylene oligomers, and poly(dimethylsiloxane) (PDMS) were fractionated with supercritical CO2. In the case of PDMS, the starting sample with a number average molecular weight (Mn) of 4 x 10^5 g/mol was separated into six fractions with Mn ranging from 4 x 10^2 g/mol to 1 x 10^3 g/mol.

Another important feature of supercritical CO2 in polymerization is plasticization, which results in the lowering of the polymer’s glass transition temperature (Tg). Polymers have been shown to become highly plasticized by CO2. This plasticization allows important effects such as the removal of residual monomer from the polymer, incorporation of additives, and formation of foams. Table 1 summarizes some of the studies on the effect of CO2 plasticization on polymers. The effects of high-pressure CO2 on the glass transition temperature and mechanical properties of polystyrene (PS) have been measured by Young’s modulus and creep compliance. This work demonstrated the severe plasticization of PS as a function of CO2 pressure. In work by Choiu, differential scanning calorimetry (DSC) was used to study the plasticization of polymers by CO2 at pressures up to 25 bar. Even at such modest pressures as 25 bar, reductions in the glass transition temperatures of up to 50 °C were observed. Other studies included measurements of polymer swelling and creep compliance as a function of time to determine Tg of polycarbonate (PC), PS, and PMMA in CO2. Beckman examined the plasticization of PMMA by CO2 as a function of pressure using dielectric measurements. Johnston performed an in-depth study of the solubility of CO2 in the polymer and its effect on the Tg vs CO2 partial pressure behavior for PMMA, PS, and a random copolymer of methyl methacrylate and styrene. Johnston has also used in situ measurements of creep compliance to determine the Tg depression of PMMA and poly(ethyl methacrylate) in CO2. As evidenced by the above table, the effects of high-pressure CO2 on polymers are significant and can be exploited for various applications.

Table 1. Summary of Literature Studies on the Swelling and Plasticization of Homopolymers, Copolymers, and Polymer Blends by CO2

<table>
<thead>
<tr>
<th>Homopolymers</th>
<th>Copolymers</th>
<th>Polymer Blends</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(aryl ether ketone) (PEEK) DSC 9</td>
<td>poly(methyl methacrylate) (PMMA) creep compliance 27</td>
<td>PMMA/PVF2 DSC 22</td>
</tr>
<tr>
<td>polycarbonate (PC) DSC, swelling/sorption 23</td>
<td>poly(propylene) (PP) creep compliance 33</td>
<td>PS/PC DSC 174</td>
</tr>
<tr>
<td>substituted polycarbonates DSC 171</td>
<td>poly(styrene) (PS) swelling/sorption 33</td>
<td>PS/poly(ethyl methyl ether) sorption 175</td>
</tr>
<tr>
<td>poly(2,6-dimethylphenylene oxide) (PPO) DSC 30,32</td>
<td>poly(dimethylsiloxane) sorption 16,19,38</td>
<td></td>
</tr>
<tr>
<td>poly(dimethylsiloxane) (PDMS)</td>
<td>poly(ethylene terephthalate) (PET)</td>
<td></td>
</tr>
<tr>
<td>poly(ether imide) DSC 32</td>
<td>poly(ethylene) terephthalate) (PET)</td>
<td></td>
</tr>
<tr>
<td>polyethylene (PE) DSC 33</td>
<td>poly(ethyl methacrylate) (PEMA) sorptive dilation 29</td>
<td></td>
</tr>
<tr>
<td>poly(ethylene terephthalate) (PET) DSC 22,32,33</td>
<td>poly(methacrylate) (PMA) swelling/sorption 172</td>
<td></td>
</tr>
<tr>
<td>poly(ethyl methacrylate) (PEMA) sorptive dilation 29</td>
<td>poly(vinylpyrrolidone) (PVP) swelling/sorption 172</td>
<td></td>
</tr>
<tr>
<td>poly(isoprene)</td>
<td>poly(vinylidene fluoride) (PVF2)</td>
<td></td>
</tr>
<tr>
<td>poly(methyl methacrylate) (PMMA)</td>
<td>poly(vinylidene fluoride) (PVDF) DSC 32</td>
<td></td>
</tr>
<tr>
<td>swelling/sorption 172</td>
<td>poly(ethyl acrylate-co-styrene)</td>
<td></td>
</tr>
<tr>
<td>poly(vinyl acetate)</td>
<td>acrylonitrile butadiene styrene (ABS) DSC 32</td>
<td></td>
</tr>
<tr>
<td>poly(vinyl butyral)</td>
<td>high impact polystyrene DSC 32</td>
<td></td>
</tr>
<tr>
<td>poly(vinyl chloride) (PVC)</td>
<td>PMMA/PVF2 DSC 22</td>
<td></td>
</tr>
<tr>
<td>poly(vinylidene fluoride) (PVDF)</td>
<td>PS/PC DSC 174</td>
<td></td>
</tr>
<tr>
<td>poly(vinylpyrrolidone)</td>
<td>PS/poly(ethyl methyl ether) sorption 175</td>
<td></td>
</tr>
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</table>

a DSC = differential scanning calorimetry.
and other work, the plasticization of polymers by CO2 is well-established. 

The highly plasticized state of the polymer can result in increased polymerization rates by the enhanced diffusion of monomer into the polymer.\(^{34-36}\) The effects of this plasticization can be studied by controlling the reaction pressure and temperature. The plasticization of polymers with SCFs can also be used to lower the melt and solution viscosities\(^{37-39}\) and affect polymer morphology with supercritical drying\(^{40}\) or foaming.\(^{41-43}\)

Polymer plasticization by supercritical CO2 can also be used in the removal of residual monomer.\(^{1}\) The high transport properties of supercritical CO2 such as high diffusivity and low viscosity coupled with the propensity of CO2 to plasticize polymers were employed to remove N-vinylcarbazole from poly(N-vinylcarbazole).\(^{10}\) Supercritical CO2 treatment of polymer resulted in lowering monomer levels from 3.66% to 0.1%. In this system, traditional solvents were unsuitable for removal of residual monomer.

Supercritical fluid CO2 has indeed been shown to be a promising solvent in which to perform polymerization reactions. Chain-growth routes such as free-radical polymerization of styrenics, acrylates, and methacrylates, cationic polymerization of isobutylene, vinyl ethers, and styrene, and transition metal-catalyzed polymerization of norbornene and copolymerization of epoxides and CO2 have been reported. Step-growth reactions in CO2 have produced poly-carbonates, polyamides, polyesters, polypyrrole, polyphenoxides, and silica gels. In addition, the numerous supercritical CO2 processing techniques for polymers that are being developed become simplified when the synthesis of the polymer is performed in supercritical CO2. These examples illustrate the versatility and importance of supercritical CO2 as a solvent for polymerization reactions.

**II. Chain-Growth Polymerizations in CO2**

The major types of chain-growth polymerization routes include free-radical, cationic, anionic, and metal-catalyzed reactions. Most chain-growth polymerizations in CO2 have focused on free-radical polymerizations, but there are a number of reports in the areas of cationic and metal-catalyzed reactions. We are unaware of any reports of anionic polymerizations in CO2: reactive anions would attack the Lewis acid CO2, and thus anionic polymerizations in CO2 are unlikely unless extremely weak nucleophiles are involved, such as siloxanlates.

Initial breakthroughs in the 1960s in the use of compressed CO2 as a continuous phase for polymerizations, especially in cationic and free-radical precipitation polymerizations, were followed by very little activity in the 1970s and 1980s. The 1990s, however, have seen an explosion of research in this area. The next breakthrough in the use of CO2 as a polymerization medium was realized when siloxanes and amorphous fluoropolymers were identified as polymeric materials which had high solubilities in CO2 at easily attainable temperatures (T < 100 °C) and pressures (P < 350 bar).\(^{1}\) This realization opened up new areas of research in CO2, mainly homogeneous polymerizations as well as dispersion and emulsion polymerizations.

**A. Free-Radical Polymerizations**

Free-radical polymerizations can be classified as either homogeneous or heterogeneous reactions. In a homogeneous polymerization all components, including monomer, initiator, and polymer, are soluble throughout the duration of the reaction; a heterogeneous polymerization contains at least one insoluble component at some point during the reaction. Because the terminology to describe heterogeneous polymerization processes has been used inconsistently in the literature,\(^{44}\) a brief treatment of this subject is necessary to avoid confusion. The four most widely studied heterogeneous processes (precipitation, suspension, dispersion, and emulsion) can be clearly distinguished on the basis of the initial state of the polymerization mixture, the kinetics of polymerization, the mechanism of particle formation, and the shape and size of the final polymer particles.\(^{45}\) Other heterogeneous processes which are not presently of industrial importance and which will not be discussed here in detail include miniemulsion\(^{46,47}\) polymerization and microemulsion\(^{48,49}\) polymerization. In a precipitation polymerization, an initially homogeneous mixture of monomer, initiator, and solvent becomes heterogeneous during the reaction as insoluble polymer chains aggregate to form a separate polymer phase. In a suspension polymerization, on the other hand, neither the monomer nor the initiator are soluble in the continuous phase. The resulting polymer is also insoluble in the continuous phase, which simply acts as a dispersant and heat-dissipation agent during the polymerization. As a result of the high solubility of many common monomers and organic initiators in compressed CO2, suspension polymerizations in CO2 are not common and will not be presented herein. Dispersion and emulsion polymerizations constitute the colloid-forming polymerization methods that have been recently explored using CO2. A brief discussion of the traditional definitions of these colloid-forming processes follows.

A dispersion polymerization begins as a homogeneous mixture because of the solubility of both the monomer and the initiator in the continuous phase. Once the growing oligomeric radicals reach a critical molecular weight, the chains are no longer soluble in the reaction medium and phase separation occurs. At this point the surface active stabilizing molecule adsorbs to or becomes chemically attached to the polymer colloid and prevents coagulation or agglomeration of the particles. In this respect, a dispersion polymerization is often considered to be a "modified precipitation polymerization".\(^{49}\) Polymerization persists both in the continuous phase and in the growing polymer particles. Since the initiator and monomer are not segregated or compartmentalized, dispersion polymerizations do not follow Smith–Ewart kinetics. However, enhanced rates of polymerization are often observed due to the autocatalysis (Gel or Trommsdorf) effect within a growing polymer particle. The product from a dispersion polymerization exists as spherical polymer particles,
typically ranging in size from 100 nm to 10 μm. The history and theory of dispersion polymerization in organic media have been summarized in a book by Barrett\textsuperscript{44} and a recent review by Sudd.\textsuperscript{59} Due to the good solubility of many small organic molecules in CO\textsubscript{2}, dispersion polymerization constitutes the best heterogeneous method that has been developed thus far for producing high molecular weight, CO\textsubscript{2}-insoluble, industrially important hydrocarbon polymers.

In contrast to dispersion polymerization, the reaction mixture in an emulsion polymerization is initially heterogeneous due to the low solubility of the monomer in the continuous phase. Emulsion polymerization is a very active area of research, and the reader is referred to several recent books and reviews.\textsuperscript{20,49,51–53} For a reaction to take advantage of the desirable Smith–Ewart/Harkins kinetics,\textsuperscript{54} the monomer and initiator must be segregated with the initiator preferentially dissolved in the continuous phase and in the monomer phase. Traditionally, emulsion polymerizations employ oil-soluble monomers such as acrylics or styrenics dispersed in an aqueous medium containing a water-soluble initiator such as sodium persulfate, while “inverse” emulsion polymerizations employ water-soluble monomers, such as acrylamide, dispersed in an organic medium containing an oil-soluble initiator such as an organic azo or peroxide species. In either case, the insoluble polymer is stabilized as colloidal particles. The repulsive forces, which result from the surface charges imparted by an ionic initiating species, an added small molecule ionic surfactant, an added amphiphilic macromolecular stabilizer, or a combination of these to provide a charged surface, prevent the coagulation of the growing particles and lead to a stabilized colloid. As a result of the kinetics of an emulsion polymerization, high molecular weight polymer can be produced at high rates, with the rate of polymerization dependent upon the number of polymer particles. The polymer which results from an emulsion polymerization exists as spherical particles typically smaller than 1 μm in diameter. Due to the high solubility of most vinyl monomers in CO\textsubscript{2}, emulsion polymerization in CO\textsubscript{2} probably will not be a very useful process for the majority of commercially important monomers, although there are exceptions. For example, inverse emulsion polymerization of acrylamide in a water/CO\textsubscript{2} system has been reported.\textsuperscript{56}

1. Homogeneous Polymerizations

Amorphous or low-melting fluoropolymers can be synthesized homogeneously in CO\textsubscript{2} by either free-radical or cationic methods. Poor solubility in most common organic solvents represents an inherent problem in the synthesis and processing of many high molar mass amorphous fluoropolymers. In fact, chlorofluorocarbons (CFCs) and CO\textsubscript{2} are the best solvents for these types of polymers.\textsuperscript{4} However, due to the environmental problems associated with CFCs, they are no longer a viable solvent option. Carbon dioxide presents an ideal inert solvent for the polymerization of these types of highly fluorinated monomers without the environmental concerns.

Using supercritical CO\textsubscript{2} as the solvent, DeSimone used free-radical initiators to effect the synthesis of high molar mass amorphous fluoropolymers.\textsuperscript{4,11,57–59} Due to the high solubility of the polymers in the CO\textsubscript{2} continuous phase, the polymerizations remained homogeneous throughout the course of the reactions. Several fluorinated acrylate monomers, such as 1,1-dihydroperfluorooctyl acrylate (FOA), have been polymerized using this methodology to give high yields of high molecular weight polymer. Styrenes with a perfluoroalkyl side chain in the para position, such as p-perfluoroethylmethoxymethylstereene, constitute a second type of monomer polymerized via homogeneous solution polymerization in supercritical CO\textsubscript{2}. The product obtained from this polymerization in CO\textsubscript{2} was identical to the product of a solution polymerization in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), indicating that CO\textsubscript{2} does indeed represent an exceptionally good replacement solvent for this type of reaction. Moreover, this technique has proven to be valuable in the synthesis of statistical copolymers of the appropriate fluorinated monomers and other hydrocarbon monomers such as methyl methacrylate (MMA), butyl acrylate, ethylene, and styrene. Homogeneous solution polymerization has also been employed by DeSimone to prepare CO\textsubscript{2}-soluble polymeric amines by copolymerizing FOA with 2-(dimethylamino)ethylacrylate or 4-vinylpyridine.\textsuperscript{60}

The initiation and propagation kinetics of free-radical polymerizations in supercritical CO\textsubscript{2} have been studied. The earliest work in this area used ultraviolet spectroscopy to explore the thermal decomposition rate and initiator efficiency of 2,2'-azobisisobutyronitrile (AIBN) in CO\textsubscript{2}.\textsuperscript{11} By comparing the decomposition rate, k\textsubscript{D}, and the initiator efficiency, f, in CO\textsubscript{2} to that reported in the literature for other solvents, the authors observed higher initiator efficiencies, relative to higher viscosity solvents, as a result of the decreased solvent cage effect in the supercritical phase. More recent work has evaluated the free-radical propagation kinetics of styrene and methyl methacrylate in CO\textsubscript{2} using the pulsed laser polymerization (PLP) technique.\textsuperscript{62} Since the conversions were kept very low (<5%), the polymer chains remained in solution during these experiments as styrene monomer is a good (co)solvent for PS. The propagation rate, k\textsubscript{p}, was found to be very close to the bulk values for both monomers, indicating that the presence of CO\textsubscript{2} does not interfere with the chain-growth process. Another study compared the kinetics of the homogeneous polymerization of 1H,1H,5H-perfluoropentyl acrylate in supercritical CO\textsubscript{2} to those in conventional, liquid solvents such as Freon-113.\textsuperscript{62} Indeed, these kinetic studies have verified that CO\textsubscript{2} is an excellent medium in which to conduct free-radical reactions.

2. Precipitation Polymerizations

A topic of many early studies in CO\textsubscript{2} was the free-radical polymerization of industrially important vinyl monomers.\textsuperscript{53} Although many common vinyl monomers exhibit high solubility in CO\textsubscript{2}, most of the corresponding polymers exhibit exceedingly poor
solubilities in CO₂. As a result, all of the early studies in this area focused on precipitation polymerizations.

In 1968, Hagiwara and co-workers explored the free-radical polymerization of ethylene in CO₂ using either γ radiation or AIBN initiation.64-66 In this work, the infrared spectra of the polymers revealed that the presence of the CO₂ continuous phase had little effect on the polymer structure. They noted that while the ethylene monomer was initially soluble in the liquid CO₂, the polyethylene produced existed in a powder form which could easily be removed from the reactor. Powder products typically result from precipitation polymerizations; the advantage of using CO₂ stemmed from the dryness of the resulting polymer. Also in 1968, a French Patent issued to the Sumitomo Chemical Company disclosed the polymerization of several vinyl monomers in CO₂.67 The United States version of this patent was issued in 1970, when Fukui and co-workers published results for the free-radical precipitation polymerization of several hydrocarbon monomers in liquid and supercritical CO₂.68 As examples of this methodology, they demonstrated the preparation of the various homopolymers including poly(vinyl chloride) (PVC), PS, poly(acrylonitrile), poly(acrylic acid), and poly(vinyl acetate) (PVAc). In addition, they prepared the random copolymers poly(styrene-co-methyl methacrylate) and poly(vinyl chloride-co-vinyl acetate). Depending upon the monomer and the reaction conditions employed, these reactions resulted in gravimetric yields which varied from 15% to 97% and viscosity average molecular weights (Mₙ) ranging from 1.2 × 10⁴ to 1.6 × 10⁶ g/mol.

More recently, precipitation polymerizations of semicrystalline fluoropolymers in CO₂ have been studied by DeSimone. In particular, tetrafluoroethylene is a monomer of interest since it was determined that tetrafluoroethylene may be handled more safely as a mixture with CO₂.69 Tetrafluoroethylene copolymerizations70,71 with perfluoropropyl vinyl ether) and with hexafluoropropylene or homopolymerizations72 have been performed in CO₂, resulting in high yields of high molecular weight (>10⁶ g/mol) polymer. The two major advantages of this process, lack of chain transfer to solvent and absence of undesirable endgroups, have been recently reviewed.63

3. Dispersion and Emulsion Polymerizations

As was alluded to earlier, one key to a successful dispersion or emulsion polymerization is the surfactant. Its role is to adsorb or chemically attach to the surface of the growing polymeric particle and prevent the particles from aggregating by electrostatic, electrosteric, or steric stabilization. Consani and Smith have studied the solubility of over 130 surfactants in CO₂ at 50 °C and 100–500 bar.73 They concluded that microemulsions of commercial surfactants form much more readily in other low polarity supercritical fluids such as alkanes and xenon than in CO₂. Since traditional surfactants for emulsion and dispersion polymerizations were designed for use in an aqueous or organic continuous phase and are completely insoluble in CO₂, an exciting area of research is the design and synthesis of novel surfactants specifically for CO₂. Polymeric surfactants for steric stabilization are effective in solvents with low dielectric constants. This is one reason steric stabilization, rather than electrostatic stabilization, provides the stabilization mechanism of choice for CO₂-based systems. The polymeric stabilizer is a macromolecule that preferentially exists at the polymer–solvent interface and prevents aggregation of particles by coating the surface of each particle and imparting long-range repulsions between them. These long-range repulsions must be great enough to compensate for the long-range van der Waals attractions of the particles.44 This complex phenomenon depends not only on the amount and molecular weight of adsorbed stabilizer, but also on its conformation, which is affected by the nature of the solvent. When steric stabilization acts effectively in a heterogeneous system, the stabilizing molecule attaches to the surface of the polymer particle by either chemical grafting or physical adsorption. Amphiphilic materials such as block and graft copolymers, which have one component that is soluble in the continuous phase and another component, the anchor, that prefers to reside in the polymer phase, offer the highest probability for physical adsorption. The other route to stabilization includes the chemical grafting of the stabilizer to the particle surface, either through chain transfer to stabilizer or by using a functional stabilizer that can serve as an initiator, monomer, or terminating agent. In this case, the chemically grafted stabilizer cannot physically desorb from the particle surface, and as a result, grafted stabilizers impart better colloidal stability than physically adsorbed stabilizers. In CO₂-based systems, the types of surfactants that have been used for steric stabilization include CO₂-philic (CO₂-soluble) homopolymers, copolymers (statistical, block, or graft) containing a CO₂-philic component and a CO₂-phobic (CO₂-insoluble) anchoring component, and CO₂-philic reactive macromonomomers. Stuctures of the polymeric surfactants for CO₂ described in this paper are numbered and located in Figures 1 and 2.

Recently, the traditional Napper theory for steric stabilization in colloidal systems has been evaluated for applicability in highly compressible supercritical media. Peck and Johnston have developed a lattice fluid self-consistent field theory to describe a surfactant chain at an interface in a compressible fluid, allowing traditional colloidal stabilization theory74 to be extended to supercritical fluid continuous phases.75,76 In their theory, “holes” have been introduced into the lattice to account for the decreased concentration of molecules in the less dense supercritical phase. In this way, they are able to account for the compressibility of the continuous phase. The mechanism of steric stabilization was further studied by the Johnston group experimentally by turbidity and tensionmetry measurements of emulsion stability, critical flocculation density, and reversibility of flocculation.77 The system studied was an emulsion of poly(2-ethylhexyl acrylate) (PEHA) in CO₂ in the presence of a surfactant, either poly(1,1-dihydropolymer.
fluorooctyl acrylate) (PFOA) (1) homopolymer, PS-b-PFOA (2), or PFOA-b-poly(vinyl acetate)-b-PFOA. A distinct change in the emulsion stability was observed at the critical flocculation density (CFD), which corresponded with the $\theta$ point (where the second virial coefficient equals zero) for PFOA in bulk CO$_2$. The CFD is the density at which particles flocculate due to collapse of the soluble portion of the surfactant. While PFOA resulted in bridging flocculation of PEHA particles below the CFD, PS-b-PFOA was more strongly adsorbed and flocculation below the CFD was slower. In the companion study, dynamic light scattering confirmed the correlation between the CFD and the $\theta$ point density of PFOA in CO$_2$ by monitoring the PEHA droplet size as a function of time and CO$_2$ density in the presence of surfactant. Further theoretical developments have more recently been made by Meredith and Johnston for homopolymer stabilizers and copolymer and end-graft stabilizers in a supercritical fluid. The adsorption of surfactant at a planar surface and the free energies of interaction between two such surfaces were modeled. The effects of solvent density on the adsorbed amount of stabilizer and layer thickness, both of which would influence colloid stability, were examined. General design criteria was provided for copolymer and end-graft stabilizers. It is clear from these studies on steric stabilization in CO$_2$ that for effective stabilization, the surfactant must anchor to
the particle surface and must not be in a collapsed state at the reaction density.

The majority of the work in dispersion polymerizations in supercritical CO$_2$ has focused on methyl methacrylate (MMA). However, several other monomers have also been investigated as shown in Table 2. In 1994, DeSimone reported the dispersion polymerization of MMA in supercritical CO$_2$. This work represents the first successful dispersion polymerization of a lipophilic monomer in a supercritical fluid continuous phase. In these experiments, the authors took advantage of the amphiphilic nature of the homopolymer PFOA ($M_n = 1.1 \times 10^4$ or $2.0 \times 10^5$ g/mol) to effect the polymerization of MMA to high conversions (>90%) and high degrees of polymerization (>3000) in supercritical CO$_2$. These polymerizations were conducted in CO$_2$ at 65 °C and 207 bar, and AIBN or a fluorinated derivative of AIBN was employed as the initiator. The spherical polymer particles that resulted from these dispersion polymerizations were isolated following venting of CO$_2$ from the reaction mixture. Scanning electron microscopy showed that the product consisted of spheres in the 1–3 μm size range with a narrow particle size distribution (see Figure 3). In contrast, reactions that were performed in the absence of PFOA resulted in relatively low conversion (<40%). Moreover, the polymer that resulted from these precipitation polymerizations were isolated following venting of CO$_2$ from the reaction mixture. Scanning electron microscopy showed that the product consisted of spheres in the 1–3 μm size range with a narrow particle size distribution (see Figure 3). Without a doubt, the amphiphilic PFOA macromolecule played a vital role in the stabilization of the growing PMMA colloidal particles.

Recent work in this area has revealed that very low amounts (0.24 wt % based on MMA) of PFOA ($M_w = 1.0 \times 10^6$ g/mol) are needed to prepare a stable dispersion of PMMA latex particles. Again, the PMMA particles were in the 1–3 μm size range. In addition, a large percentage (up to 83%) of the stabilizer could be subsequently removed from the PMMA product by extraction with CO$_2$. As a result of the relatively high cost of the stabilizer and the possible effects that residual stabilizer may have on product performance, the ability to remove and recycle the PFOA constitutes an important aspect of this system. The effects of the reaction time and pressure on the resulting conversion, molar masses, and particle size of the polymer products were investigated. A gel effect occurs within the PMMA particles between 1 and 2 h of reaction time. This result parallels the gel effect within the polymer particles which is normally observed between 20 and 80% conversion in a typical dispersion polymerization in liquid organic media. More importantly, the ability of CO$_2$ to plasticize PMMA facilitates the diffusion of monomer into the growing polymer particles, allowing the reaction to proceed to high conversion. To complement the use of fluorinated acrylates as stabilizers, the phase behavior of PFOA in CO$_2$ was thoroughly investigated. These cloud point experiments indicated lower critical solution temperature (LCST) phase behavior.

Further study on MMA dispersion polymerizations with PFOA stabilization investigated the influence of helium concentration in CO$_2$ on the resulting PMMA particle sizes and distribution. This study was important since many tanks of CO$_2$ are sold with a helium head pressure. It was found that the presence of 2.4 mol % helium in CO$_2$ increased the PMMA average particle diameters from 1.9 to 2.7 μm,
while decreasing particle size distribution from 1.29 to 1.03. Furthermore, the small percentage of helium in the reaction mixture decreases the solvent strength of the medium, as determined by solvatochromic investigations. Other scientists have noted the increase in retention times in SCF chromatography\textsuperscript{45-47} and the reduced extraction rate in SCF extractions\textsuperscript{88} when helium is present in CO\textsubscript{2}. An acoustic technique, used by Kordikowski and co-workers, measured the composition of helium in CO\textsubscript{2} tanks and showed the content to be unpredictable, presumably due to common lack of equilibration in the cylinder.\textsuperscript{89} Therefore, these diverse experiments illustrate that even seemingly “benign” components such as an inert gas can effect the solvent quality of CO\textsubscript{2}, and the CO\textsubscript{2} purity needs to be taken into consideration for process development and scale-up issues if the process, such as dispersion polymerization, is to be commercialized.

Another approach to preparing monodisperse PMMA particles in CO\textsubscript{2} has been the use of graft copolymers as stabilizers. While PFOA is an effective steric stabilizer for PMMA, fluoropolymers in general are expensive. The other class of CO\textsubscript{2}-soluble polymers includes PDMS (12). PDMS-based surfactants are cheaper, but are less soluble than PFOA at comparable molecular weights in CO\textsubscript{2}. The first work in this area by DeSimone involved the use of a monomethacrylate-terminated PDMS macromonomer (13), which reacts to form the stabilizer in situ.\textsuperscript{90} However, these studies showed that only a small portion of the added macromonomer actually copolymerized; the majority of the unreacted macromonomer could be removed from the surface of the particles by extraction with hexane or CO\textsubscript{2}. Polymerizations were conducted at both liquid and supercritical conditions, and by varying the reaction conditions, particles with a narrow particle size distribution were obtained in sizes ranging from 1.1 to 5.8 \textmu m. In contrast, PDMS homopolymer gave low yield and unstable latexes, presumably due to its inability to anchor and its lack of affinity for the PMMA particles. The dispersion polymerization of MMA stabilized by PDMS—monomethacrylate has recently been investigated in detail by O’Neill and co-workers, who studied the particle formation\textsuperscript{91} and growth\textsuperscript{92} for this system using turbidimetry. In the particle formation regime, mechanisms of coagulative nucleation and controlled coagulation were identified. To prevent uncontrolled coagulation (precipitation), a threshold pressure (207 bar) and stabilizer concentration (2 wt % on monomer) were required. Latex stability was limited by the low solubility of surfactant in the absence of monomer in CO\textsubscript{2}. The chronology of yield, particle size, morphology, particle number density, and molecular weight was studied. The results agreed with the experiments by Shaffer\textsuperscript{90} and with predictions from the model of Paine\textsuperscript{93} for conventional dispersion polymerizations.

A study by Lepilleur and Beckman employed a preformed graft copolymer dispersant which had an anchoring backbone of poly(MMA-co-hydroxyethyl methacrylate) and CO\textsubscript{2}-soluble poly(perfluoroprolylene oxide) side chains (3).\textsuperscript{94} Variations in the molecular weight and architecture of the stabilizer were explored by examining the effect of factors such as graft chain length and graft density on the resulting PMMA polymer colloid. At a given backbone length, as the graft chain length was changed, the trends in results varied, depending on the length of the backbone. For a given graft chain length, increasing the graft density (number of grafts on the backbone) resulted in better stabilization. At a constant backbone length, increasing the graft density resulted in reduced particle size and distribution, as did more, shorter grafts compared to fewer, longer grafts. As the backbone length was increased, the particle size and distribution decreased. It was shown that the backbone length must be long enough to anchor to the particles, but there must be enough soluble component to maintain the overall solubility of the surfactant in CO\textsubscript{2} for a successful dispersion polymerization.

Indeed, the dispersion polymerization of MMA in compressed CO\textsubscript{2} has been investigated in detail. Homopolymers, random copolymers, macromonomers, and graft copolymers have all been effectively employed as stabilizers to prevent coagulation in the PMMA/CO\textsubscript{2} system.

The dispersion polymerization of styrene in supercritical CO\textsubscript{2} using amphiphilic diblock copolymers has also been studied in detail. The surfactants which were investigated contained a PS anchoring block and either a PFOA\textsuperscript{95} or PDMS (14) soluble block. These reactions yield spherical PS particles which were isolated in the form of a dry, free-flowing powder. The resulting high yield (~90%) of PS was obtained in the form of a stable polymer colloid comprised of submicron-sized particles. For the block copolymeric stabilizers, the anchor-to-soluble balance (ASB), or ratio of the two block lengths, of the stabilizer was found to be a crucial factor affecting both the stability of the resulting latex in CO\textsubscript{2} and the particle morphology. The affinity of these amphiphilic diblock copolymers for the PS particle surface was confirmed by interfacial tension measurements in a CO\textsubscript{2} continuous phase.\textsuperscript{97}

In the studies of PFOA-based surfactants, the effects of surfactant block chain lengths, stabilizer concentration, and anchor block length on PS product were studied.\textsuperscript{95} A series of PS-b-PFOA copolymers were studied in which the length of both blocks was increased. Increasing the anchor and soluble block lengths resulted in decreased particle size (from 0.40 \textmu m to 0.24 \textmu m) and particle size distribution (from 8.3 to 1.1), presumably due to more effective stabilization of PS particles. With a constant anchor length of 3.7 \times 10\textsuperscript{3} g/mol PS, varying the PFOA block from 1.4 \times 10\textsuperscript{4} to 2.5 \times 10\textsuperscript{4} g/mol did not produce any trends in PS molecular weight or particle size. In this series, the anchor block may have been too short for strong adsorption to the particles, reducing the efficiency of stabilization. The effect of varying the anchor length at constant soluble block length was not studied with PS-b-PFOA. The PFOA homopolymer was not an efficient stabilizer for PS, resulting in low polymer yields of 44%. In contrast, PFOA homopolymer was an efficient stabilizer for PMMA,
as already illustrated. The specific affinity that PFOA has for PMMA is not extended to PS. However, PFOA homopolymer with unstable thiuram endgroups was shown to stabilize micron-sized PS particles via chemical grafting.50

PS-b-PDMS polymeric stabilizers were studied to determine the effects of anchor block length and soluble block length, CO2 pressure, and concentrations of surfactant, monomer, and initiator.96 In comparing two stabilizers with a PDMS block length of 2.5 × 10^4 g/mol, the longer PS anchor block length yielded particles with a larger diameter (0.22 vs 0.46 μm) with a narrower particle size distribution (1.31 vs 1.08). The stabilizers with a longer PDMS of 6.5 × 10^4 g/mol resulted in collapsed latexes and coagulated particles. The authors speculate that this may be due to the lower ratio of anchor-to-soluble block or due to lower solubility of the surfactant in CO2. A kinetic study of the dispersion polymerization showed that the molecular weight and the conversion increase as a function of time. As expected, both the concentration of monomer and the concentration of stabilizer affected the morphology of the resulting PS particles. Additionally, the temperature and pressure of the reaction mixture were found to effect results, such as average particle diameter and molecular weight, of the PS product. The importance of polymer collection procedures was shown by the aggregation of PS particles collected from the reactor after complete depressurization. In contrast, the polymer particles released from the reactor during the depressurization did not show any signs of flocculation in the SEM images. It was noted that none of the PS-b-PDMS copolymers were soluble in CO2 in the absence of monomer. PDMS homopolymer was not capable of stabilizing styrene dispersion polymerizations in CO2 as yield and molecular weights of PS were comparable to reactions in which no surfactant was used.

The preparation of stable dispersions of poly(vinyl acetate) (PVAc) and ethylene-vinyl acetate copolymers in liquid and supercritical CO2 has recently been investigated.99,100 Both fluorinated and siloxane-based stabilizers including homopolymers, block copolymers, and reactive macromonomers were employed. The influence of the concentration of stabilizer, stabilizer anchor-soluble balance, and pressure on the resulting colloidal product was explored. In addition, turbidimetry was used successfully to monitor dispersed phase volume fractions, particle sizes, and number densities during the polymerization. The vinyl acetate polymerizations stabilized by PDMS homopolymer, vinyl-terminated PDMS macromonomer (15), or PVAc-b-PDMS (16) all produced collapsed latexes of high yield and high molecular weight polymer, whereas the polymerizations stabilized by PVAc-b-PFOA (4) remained stable latexes. Turbidity showed that PFOA and PVAc-b-PFOA with a short anchoring group (PVAc M_n = 4 × 10^3 g/mol) had inefficient anchoring to the PVAc particles. The PVAc-b-PFOA with the longest blocks (PVAc M_n = 3.1 × 10^4 g/mol; PFOA M_n = 5.4 × 10^4 g/mol) produced the smallest diameter polymer particles.

Cooper and coauthors recently reported the first synthesis of well-defined cross-linked polymer microspheres in supercritical CO2.55 Divinylbenzene and ethylvinylbenzene were copolymerized at 65 °C and 310 ± 15 bar using AIBN as an initiator. The reaction was performed both in the presence and in the absence of a surfactant. Without surfactant, 1.5–5 μm particles were isolated. When the polymerization employed a 3 wt % (based on monomer) of a block copolymer surfactant containing PMMA and a fluorinated methacrylate (5), much smaller particles (∼0.41 μm) with a relatively narrow particle size distribution were observed. Yields greater than 90% were obtained both with and without surfactant. This study demonstrated the formation of various sizes of cross-linked microspheres in supercritical CO2.

Adamsky and Beckman have explored the possibility of carrying out an inverse emulsion polymerization of acrylamide in supercritical CO2.56,101 In these reactions, acrylamide was polymerized in the presence of water, a cosolvent for the monomer, in a CO2 continuous phase at 345 bar and 60 °C with AIBN initiation. Reactions were conducted both with and without the stabilizer, an amide end-capped poly(hexafluoropropylene oxide) (6). In the absence of the stabilizer, the precipitation polymerization of acrylamide resulted in a high conversion of high molecular weight polymer which formed a single solid mass in the bottom of the reaction vessel. In the presence of stabilizer, the reaction solution was reported to have a milky-white appearance that was indicative of latex formation; however, the conversion and molecular weights were comparable to those obtained in the unstabilized reactions.

More studies in the field of inverse emulsion polymerizations in CO2 are expected with the recent discoveries of surfactants which have the ability to form microemulsions of water and water soluble molecules in CO2. In 1993, DeSimone reported the use of the macromonomer technique to synthesize and characterize an amphiphilic graft copolymer with a CO2-philic PFOA backbone and hydrophilic poly(ethylene oxide) (PEO) grafts (8).102 In this study, solvatochromic characterization was employed to demonstrate that the PEO grafts enabled the solubility of the hydrophilic, CO2-insoluble dye methyl orange in supercritical CO2. This graft copolymer was further characterized by small-angle X-ray scattering (SAXS) and shown to form spherical micelles in the presence of water in a CO2 continuous phase.103 This work represented the first direct confirmation that micelles can form in a CO2 continuous phase. Beckman and co-workers have studied the phase behavior of both silicone-based and fluoro ether-functional amphiphiles in supercritical CO2.12,154 A fluoro ether-functional amphiphile (7) was shown to permit the extraction of thymol blue from aqueous solution into CO2. The effect of pressure on the emulsion behavior of fluoro ethers terminated with sorbitol esters, sulfates, and sulfonates in mixtures of CO2 and water were investigated.105 Another advance in this area was made when Johnston and co-workers demonstrated the formation of a one-phase microemulsion consisting of the hybrid fluorocarbon/hydrocarbon
insoluble polymer substrate and to infuse CO$_2$- carbonate, and to infuse styrene monomer and a free-radical initiator into the swollen polymer. The plasticization of polymers by supercritical CO$_2$ has been exploited for the synthesis of polymer blends. In general, CO$_2$ is used to swell a CO$_2$- insoluble polymer substrate and to infuse a CO$_2$- soluble monomer and initiator into the substrate. Subsequent polymerization of the monomer generates the polymer blend. Watson and McCarthy used supercritical CO$_2$ to swell solid polymer substrates, including poly(chlorotrifluoroethylene), poly(4-methyl-1-pentene), high-density polyethylene (HDPE), nylon-6,6, poly(oxyethylene), and bisphenol A carbonate, and to infuse styrene monomer and a free-radical initiator into the swollen polymer. The polymerization reaction was run either before decompression of the CO$_2$ or after decompression and recompression with N$_2$. Mass uptakes of up to 118% based on the original polymer were reported. As expected, diffusion rates in CO$_2$-swollen polymers were dramatically increased over nonswollen polymers. Using ethylbenzene as a model for styrene, the equilibrium for monomer uptake was 25 times faster with CO$_2$ under the conditions studied than with out CO$_2$. X-ray analysis showed that the polystyrene existed in phase-segregated regions throughout the matrix polymer, and thermal analysis showed that radical grafting reactions were not significant.

In a related study, styrene (with and without cross-linker) was infused into three fluoropolymer substrates, polymerized, and subsequently sulfonated in order to provide surface modification to the polymeric substrates. Polystyrene was shown to be present throughout the blends and semi-interpenetrating networks of each of the three polymer substrates, PTFE, poly(TFE-co-hexafluoropropylene), and poly-(chlorotrifluoroethylene). The modified surfaces were characterized by X-ray photoelectron spectroscopy and by water contact angle measurements. The wettability of all modified fluoropolymer substrates was increased by the surface modification.

In a separate study, the morphology and mechanical performance of PS/HDPE composites were identified. As in the previous experiments, the polymer substrate, HDPE, was swollen with CO$_2$ in the presence of styrene and initiator. The subsequent polymerization produced the blend, with PS located in the amorphous interlamellar regions of the polyethylene spherulite and in the spherulite centers. The PS/HDPE blends exhibited a modulus enhancement, strength improvement with increasing PS content, loss in fracture toughness, and increase in brittleness.

B. Cationic Polymerizations

Cationic polymerizations represent a challenging field in polymer science, and their extension to supercritical fluids has been equally difficult. The high reactivity of carbocation results in fast polymerization reactions, but also leads to unwanted side reactions such as chain transfer and termination. These side reactions limit the usefulness of cationic polymerizations. The inherent basicity of monomers that are capable of being polymerized cationically and the acidity of the protons $\beta$ to the carbocation on the polymer make proton abstraction by the monomer a built-in side reaction that is difficult to suppress. These side reactions are often reduced by lowering the reaction temperature. Upon cooling, because side reactions typically have higher activation energies, the propagation rate decreases less relative to the secondary reactions, and a higher degree of polymerization is achieved.

Living cationic polymerization methods have been developed to produce well-defined polymers. These living methods allow for control of molecular weight, molecular weight distribution, end group functionality, polymer microstructure, and reactivity. They also permit the synthesis of block copolymers of precise block length and compositions. Polymerization control is gained in living cationic systems by stabilization of the active carbocation through nucleophilic interactions. This stabilization is generally achieved by association with a suitable nucleophilic counterion or, if the counterion is only weakly nucleophilic, by association with an added Lewis base. Both methods reduce the positive charge on the carbocation and the acidity of the $\beta$-hydrogens, which results in essentially no chain transfer to monomer. The nucleophilic interaction between the counterion and the carbocation is key in stabilizing the polymerization and preventing side reactions. Winston developed an ion pair spectrum to describe the active site in cationic polymerizations. Classical nonliving car-
bocationic polymerization is found to have solvent-separated ion pairs, while living systems have contact ion pairs. Solvent choice plays an important role in cationic polymerizations because it affects the equilibrium between contact pairs and solvent-separated ion pairs and the activation energy of transfer and termination reactions. Nonpolar solvents are generally desirable for cationic polymerizations because they suppress ion separation.

Because of the tunability of the solvent properties such as dielectric constant, supercritical CO2 should make for an interesting medium for studying cationic reactions. One disadvantage is the critical temperature of CO2 (31.1 °C). Since cationic polymerizations are usually performed at low temperatures (often −70 to −30 °C) to diminish side reactions, cationic polymerizations in supercritical CO2 are inherently problematic. In fact, much of the early experiments using CO2 as a solvent for cationic reactions were performed in liquid CO2 at low temperatures. However, it has been shown that good results can be obtained in liquid and supercritical CO2. Further, CO2 has been shown to be inert to cationic polymerization conditions.

The earliest work in cationic polymerizations in CO2 was aimed at preparing industrially important hydrocarbon polymers in CO2. These initial experiments utilized chain-growth polymerization mechanisms to produce polymers which were relatively insoluble in the CO2 continuous phase at the reaction conditions employed. While these early experiments often resulted in a low yield of low molecular weight products, this work was fundamental in demonstrating the compatibility of cationic chain-growth mechanisms with CO2.

A 1960 report by Biddulph and Plesch explored the heterogeneous polymerization of isobutylene in liquid CO2 at −50 °C.116 Two catalyst systems were shown to be effective: AlBr3 and TiCl4 (using ethyl bromide and isopropyl chloride, respectively, as cosolvents). The AlBr3-catalyzed reactions proceeded very fast, but were incomplete and gave molecular weights of about 5 × 103 g/mol. The low conversion was attributed to catalyst becoming embedded in the white polymer precipitate. The TiCl4 reaction was slower, but proceeded to completion and gave molecular weights of about 3 × 104 g/mol.

A 1970 patent covering the precipitation polymerization of vinyl compounds in liquid CO2 included the polymerization of ethyl vinyl ether at room temperature.68 This heterogeneous reaction was catalyzed by either SnCl4 or BF3·OEt2. A yield of 57% was reported, but no other characterization was given.

The first systematic study of cationic polymerizations in compressed liquid was a series of papers in the late 1960s, reporting the precipitation polymerization of formaldehyde in liquid and supercritical CO2. A carboxylic acid, such as acetic or trifluoroacetic acid, was added to catalyze the polymerization.117-119 The polymerizations were performed at 20–50 °C and gave conversions of 50–60%. By infrared spectroscopy, it was shown that CO2 was not being incorporated into the polymer backbone. This spectroscopic measurement confirmed that CO2 is inert to the propagating cationic species. It was also noted that some polymer was produced in the absence of added catalyst. The authors speculated that an impurity was causing the polymerization in the absence of added catalyst because the degree of polymerization increased linearly with conversion. In 1969, the authors elucidated their impurity as formic acid (formed from the reaction of formaldehyde with water) by careful control of monomer synthesis to either repress or increase acid formation.120

Kennedy, building on earlier work by Plesch,116 reported the polymerization of isobutylene (IB) in supercritical CO2 using 2-(2,4,4-trimethylpentyl) chloride (TMPCl) as an initiator and a Lewis acid catalyst such as BCl3, TiCl4, or SnCl4 as the co-initiator.121 Polymerizations were conducted at 32.5–36 °C and 75–135 bar. Methyl chloride was added as a cosolvent (3%) (presumably to solubilize the ionic species), and its presence gave higher conversions and narrower polydispersity indices (PDI = Mw/Mn). Conversions of up to 30–35% and polymers with Mn of 1 × 103 to 2.5 × 103 g/mol and PDIs of 1.5–3.1 were produced. Because 1H NMR results showed significant amounts of unsaturated end groups, chain transfer to monomer likely limited molecular weights, as expected from such a high reaction temperature. The mixed initiating system of TMPCl/(TiCl4/BCl3) was used to form well-defined polyisobutylene with terminal chloride (−Cl) end groups (see Scheme 1).122 Reaction conditions similar to those used previously were employed: 32.5 °C, 140 bar CO2, and 5–10% MeCl. After 3 h, conversions of 40–45%, molecular weights of 1.8 × 103 to 2.4 × 103 g/mol, and relatively low PDIs of 1.3–1.5 were obtained. The same experiments performed in hexane gave essentially no polymer and a conversion of about only 0.5%. Thus, although low molecular weight material was produced in CO2, the molecular weights were higher than in hexane. 1H NMR spectra showed no evidence of olefinic end groups (in contrast to the TiCl4 or SnCl4 initiated polymers). Dehydrochlorination followed by 1H NMR spectroscopy determined each polymer chain was terminated by a chloride, indicating an absence of chain-transfer side reactions.

Kennedy studied the temperature effects of IB polymerization in CO2.123 Over the range of 32–48 °C, conversion dropped from 40% to 4% and the molecular weights dropped from 2 × 104 to 7 × 102 g/mol. In addition, although polymers synthesized at 32 °C had greater than 99% terminal chloride groups, that value fell to 60% for 38 °C and 44% for 48 °C, consistent with a higher probability of chain transfer to monomer at the higher temperatures. For this reaction, a ceiling temperature of 88–90 °C was noted that some polymer was produced in the absence of added catalyst. The authors speculated that an impurity was causing the polymerization in the absence of added catalyst because the degree of polymerization increased linearly with conversion. In 1969, the authors elucidated their impurity as formic acid (formed from the reaction of formaldehyde with water) by careful control of monomer synthesis to either repress or increase acid formation.

Scheme 1. Synthesis of −Cl-Terminated PIB

\[
\begin{align*}
\text{Cl} & \quad \text{TiCl}_4/\text{BCl}_3 \\
\text{Cl} \quad \text{TiCl}_4/\text{BCl}_3 \\
\end{align*}
\]
was consistent with those determined for conventional solvent systems.124-128

An isobutylene–styrene copolymer was also synthesized in CO2 using MeCl as a cosolvent and the TMPCl/TiCl4 initiating system.129 A conversion of 15% was produced, but molecular weights and PDIs were not reported. The authors only noted that longer reaction times produced higher molecular weights.

In the synthesis of phenol-terminated polyisobutylene, the first example of electrophilic aromatic alkylation in supercritical CO2 was reported.130 TMPCl and polyisobutylene–Cl (Mn = 2000 g/mol) were alkylated by phenol at 32.5 °C and 140 bar in the presence of BF3·OEt2 for 24 h. Yields of 75% and 60% were observed.

The isomerization polymerization of 3-methyl-1-butene and 4-methyl-1-pentene has also been studied in supercritical CO2.131,132 The reactions were performed at 140 bar CO2 and 32.5 °C with residual water and AlCl3 as the catalyst system. As with IB polymerization, a cosolvent (5% methyl chloride or 10% ethyl chloride) was used to obtain good results. For 3-methyl-1-butene, a 40% conversion, a molecular weight of 1000 g/mol, and a PDI of 1.41 were observed; for 4-methyl-1-pentene the results were 70%, 1700 g/mol, and 2.16.

DeSimone reported a study of cationic polymerization of vinyl ethers in supercritical CO2.133,134 Both precipitation and homogeneous polymerizations were reported. The initiation system was based on Higashimura’s living cationic polymerization method developed for hydrocarbon solvents. This method uses the Lewis acid ethyl aluminum dichloride and the acetic acid adduct of isobutyl vinyl ether (IBVE) as the initiator in the presence of a Lewis base deactivator such as ethyl acetate (see Scheme 2).133 The polymerization of IBVE began homogeneously, but became heterogeneous as the polymer precipitated. Yields of polymer synthesized in CO2 were similar to results obtained in cyclohexane, but with broader PDIs (for example, 1.2 for cyclohexane and 1.8 for CO2 at 40 °C, 345 bar). At 60 °C, the polydispersity of polymers produced in CO2 increased to greater than 9, indicating no molecular weight control, perhaps due to increased chain transfer to monomer and lower CO2 density, which would allow for faster precipitation of polymer.

The homogeneous polymerization of 2-(N-propyl-N-perfluoroctylsulfonamido)ethyl vinyl ether (FVE) was also performed (see Scheme 3).133,134 The polymerizations were homogeneous throughout the reaction and gave molecular weights of, for example, 4 × 10^3 g/mol with a PDI of 1.6. The narrow PDIs achieved with the CO2-soluble fluorinated polymer compared to the broad PDIs obtained with the CO2-insoluble poly(IBVE) suggest that solubility of the resulting polymer plays an important role in determining polydispersity in these cationic polymerizations in supercritical CO2.

Ring-opening polymerization of cyclic ethers were initiated by BF3 in liquid CO2 and compared to reactions performed in methylene chloride (see Scheme 4).134 Bis(ethoxyethyl)oxetane (BEMO) was polymerized at −10 °C in CO2 (290 bar). As expected from insolubility of the resulting polymer, the CO2 reaction was heterogeneous, but the same reaction performed in methylene chloride was homogeneous. The yields were comparable (about 70%), but the PDI was 1.9 for CH2Cl2 and 2.7 for CO2. A fluorinated cyclic eather, 3-methyl-3′-[(1,1-dihydroheptafluorobutoxy)methyl]-oxetane (F0x-7) was polymerized homogeneously in both CO2 (0 °C and 289 bar) and Freon-113 (−10 °C). The polymer synthesized in Freon-113 had a molecular weight of 3.9 × 10^4 g/mol, a PDI of 1.7 and a yield of 70%; the results for the polymer synthesized in CO2 were 2.0 × 10^4 g/mol, 2.0 and 77% yield. Thus, when homogeneous conditions were used, similar results were obtained for the BEMO polymerized in methylene chloride and the F0x-7 polymerized in either CO2 or Freon-113.

Initial attempts to perform the first cationic dispersion polymerization in CO2 were with BEMO and IB.134 The polymerizations were catalyzed by BF3·THF (for BEMO) or SnCl4 (for IB) and were conducted in the presence of CO2-soluble surfactants such as poly(F0x-7), poly(FOA), and poly(styrene)-b-PDMS. In the absence of surfactant, the polymer precipitated. Yields and molecular weights were not improved by the presence of surfactants, but the polymer products were stable dispersed colloids in CO2 which could be redispersed in Freon-113 after removal of CO2. Scanning electron microscopy (SEM), which examined polymer following removal of CO2, detected slight particle formation despite the semi-
crystalline nature of poly(BEMO) and low $T_g$ of poly(IB). However, since an in situ technique was not used to measure the particles, the absence of well-defined particles in SEM images does not mean the particles were not stable and dispersed in the CO$_2$.

To overcome the problems associated with SEM analysis of poly(BEMO) and poly(IB), a more conclusive example of cationic dispersion polymerizations in CO$_2$ was reported with styrene. First, a suitable surfactant for polystyrene was synthesized in CO$_2$, using the vinyl ether system previously reported. A block copolymer was synthesized from FVE and methyl vinyl ether (MVE) (9) using the EtAlCl$_2$/FVE acetic acid adduct/EtOAc initiating system. The poly-(FVE) block serves as the soluble block for steric stabilization, and the poly(MVE) block serves as the anchoring unit due to its miscibility with PS. The surfactants were employed in the cationic polymerization of styrene initiated by TiCl$_4$ at 330 bar CO$_2$ in the temperature range of 0 to 25 °C. The results of these reactions were quite sensitive to temperature effects. No improvement in yields or molecular weights and no stable colloids were observed for reactions performed at 0 °C. At 15 °C, the presence of 4 wt % stabilizer leads to increased yields (from about 50% to 95–97%), increased molecular weights, and decreased PDIs. The reaction had a milky-white appearance, indicative of a stable polymer colloid. SEM analysis showed well-defined PS particles with a broad distribution of sizes that ranged from several hundred nanometers to one micrometer in diameter. At 25 °C, yields for the reaction in the presence or absence of surfactant are lower than at 15 °C, and particles appear coagulated by SEM for reactions performed in the presence of surfactant. The lower yields are probably due to higher rate of chain transfer at the higher temperature.

C. Transition Metal-Catalyzed Polymerizations

Metal-catalyzed polymerizations have been performed in supercritical CO$_2$. The ring-opening metathesis polymerization (ROMP) of bicyclo[2.2.1]-hept-2-ene (norbornene) in CO$_2$ was catalyzed by [Ru(H$_2$O)$_6$(tos)$_2$] (see Scheme 5). The reaction was performed at 65 °C with pressures ranging from 60 to 345 bar. The insoluble polymer precipitated, and there was no obvious correlation between pressure and molecular weight (which ranged between 10$^4$ and 10$^6$ g/mol), yield (30–76%), or PDI (2.0–3.6).

The [Ru(H$_2$O)$_6$(tos)$_2$] catalyst is insoluble in CO$_2$, but can be solubilized by the addition of methanol. When the polymerization was performed with up to 16 wt % methanol as a cosolvent, the $M_n$ and PDI were in the same range as the polymernorbomene produced in the absence of methanol, but the yields increased with increasing methanol content. For example, the reaction with 16 wt % methanol gave a similar yield in 5 h as the reaction without methanol gave in 16 h. Therefore the reaction was much faster in the presence of methanol. A profound effect on polymer microstructure was found with increasing methanol content. The presence of methanol decreased the cis-vinylene content in the resulting polymer (83% cis for no methanol and 33% cis for 16 wt % methanol). Presumably the addition of a polar cosolvent favors the trans-propagating species at the metal center and allows for control of polymer microstructure by control of cosolvent content. This hypothesis could be confirmed by observing the effect of other polar cosolvents on the polymer trans content. However, these experiments have not been conducted by the authors.

Higher activities for the ROMP of norbornene were observed with ruthenium and molybdenum carbene catalysts reported by Grubbs and Schrock respectively (see Figure 4). While the Ru catalyst appeared insoluble in CO$_2$, the Mo catalyst was partially soluble. These catalysts gave up to 94% yield of precipitated polynorbornene in CO$_2$ (97% using toluene as a cosolvent) and molecular weights in the range 10$^5$–10$^6$ g/mol at much milder reaction conditions of 25–45 °C and about 100 bar. The Ru catalyst gave about 25% cis content with no apparent dependence on density while the Mo catalyst gave 66% cis content at a reaction density of 0.57 g/mL and 82% cis at 0.72 g/mL. The ruthenium carbene catalyst was also used to polymerize cis-cyclooctene in 50% yield and a molecular weight of 10$^3$ g/mol. The polymers produced in CO$_2$ were similar in molecular weight and microstructure to those produced by conventional means in dichloromethane.

There have also been a number of reports of polycarbonate synthesis from the copolymerization of CO$_2$ and epoxides. The precipitation copolymerization of CO$_2$ and propylene oxide in supercritical CO$_2$ has been reported using zinc(II) glutarate as a heterogeneous catalyst (Scheme 6). The polycarbonate, with a molecular weight of about 10$^4$ g/mol, was formed at 60 or 85 °C with both sub- and supercritical pressures (21–83 bar). Polymerizations performed in CO$_2$ above the critical pressure had an increased percentage of carbonate linkages relative to the ether linkages (over 90% vs less than 75%). Propylene carbonate was formed as a byproduct, and its production was increased with increasing temperature. Yields were generally around 10–20%, but the addition of acetonitrile or hexane as a cosolvent

![Figure 4. Catalysts for ROMP of norbornene in supercritical CO$_2$.]
The catalyst was synthesized from ZnO and the cyclohexene oxide in CO\textsubscript{2}. The reaction was performed in supercritical CO\textsubscript{2} at 207 bar and at three different temperatures: 75 °C, 100 °C, and 130 °C (see Scheme 5).

Thermal Ring-Opening Polymerization

D. Thermal Ring-Opening Polymerization

Ring-opening polymerizations represent an accessible route to organometallic polymers from highly strained precursors. Manners obtained a high molecular weight poly(ferrocenylsilane) by the thermal ring-opening polymerization of a silicon-bridged [1]ferroceneophane in the melt. This melt-phase route produced high molecular weight polymer (M\textsubscript{w} = 5.2 \times 10^5 g/mol). Other synthetic methods, such as condensation polymerization, do not produce the polymer in sufficiently high molecular weight for commercial applications. Extending their work, the authors investigated this reaction in supercritical CO\textsubscript{2}. Performing a thermal ring-opening polymerization reaction in a solvent would normally require high boiling compounds that are difficult to remove. However, using supercritical CO\textsubscript{2} avoids this problem. The thermal ring-opening polymerization of a [1]silaferrroceneophane was performed in the presence of supercritical CO\textsubscript{2} at 207 bar and at three different temperatures: 75 °C, 100 °C, and 130 °C (see Scheme 6).

Scheme 6. Scheme for Copolymerization of Propylene Oxide and CO\textsubscript{2}

\[
\text{CO}_2 + \overset{\text{catalyst}}{\text{O}} + \overset{\text{O}}{\text{O}} + \overset{\text{N}}{\text{ZnO}} \rightarrow \text{CO}_2\text{-soluble catalyst}
\]

The molecular weights obtained in CO\textsubscript{2} were the same order of magnitude as the solvent-free method, but the values were uniformly lower. The highest molecular weight sample, with M\textsubscript{w} of 2.87 \times 10^5 g/mol, was produced at 130 °C. In addition to the lower molecular weights, the PDIs of the CO\textsubscript{2} samples were broader (3.0–5.1 vs 1.5). However, when the concentration of monomer is increased from 500 mg/60 mL CO\textsubscript{2} to 2 g/60 mL for the 130 °C reaction, the molecular weight increased to 5.9 \times 10^5 g/mol and the PDI decreased to 2.0. Further experiments are required to determine the efficacy of performing this reaction in supercritical CO\textsubscript{2}.

III. Step-Growth Polymerizations

A. Melt-Phase Condensation Polymerizations

There are two features that make melt-phase condensation reactions performed in the presence of supercritical CO\textsubscript{2} advantageous: easier processing and high molecular weight materials. Many condensation polymerizations are performed in the melt phase to produce high molecular weight material without the need for organic solvents. A disadvantage to this route is the high viscosity of the high molecular weight polymer produced. Because CO\textsubscript{2} is capable of plasticizing the polymer melt phase, it increases the free volume of the melt and lowers the melt viscosity, which translates into a more easily processed material. Because CO\textsubscript{2} is a swelling agent that is a nontoxic ambient gas, it is a particularly attractive swelling agent for polymers, such as polyesters and polycarbonates, whose end use includes packaging for food or beverage applications.

In addition to greater processability, polymers synthesized in supercritical CO\textsubscript{2} can achieve higher molecular weights. In condensation polymerizations, the reaction is driven by the removal of a small molecule condensate. Enhancement of the condensate removal results in higher reaction rates and higher molecular weights. Conventional methods use high vacuum to remove the condensate, but this method requires high capital costs and necessitates maintenance to remain operational for long periods of time on a commercial scale. Because CO\textsubscript{2} can highly plasticize the polymer and solubilize the small molecule condensate, it can serve to assist in the removal of condensate by carrying it out of the reactor. The increase in free volume as a result of the plasticization should provide more polymer surface area for condensate removal and also result in greater mobility of chain ends to allow better reaction kinetics.
This strategy has been employed in the synthesis of polycarbonates, polyesters, and polyamides. There are two industrially important routes to polycarbonates: interfacial reactions in methylene chloride using phosgene, and melt transesterification of bisphenol and diphenyl carbonate. The latter avoids the use of phosgene and methylene chloride, but the high viscosity of the melt limits the molecular weight attained. In fact, the chain stiffness, which adds to the commercial value of polycarbonates, causes the high viscosity. The utility of supercritical CO₂ in producing high molecular weight polycarbonates by melt polymerization is 2-fold: CO₂ solubilizes the phenol (about 12 wt % at 272 bar and 100 °C) to extract the byproduct, driving the reaction to higher conversion, and plasticizes the carbonate to lower its viscosity, facilitating the processing.

Odell studied the melt polymerization of bisphenols (such as bisphenol A, bisphenol P, bisphenol AF, and bisphenol Z) with diphenyl carbonate in CO₂ (see Scheme 9). The reactor was first heated to 70 °C to melt the reactants. The system was then filled with CO₂ and heated to the target temperature. Temperatures between 180 and 250 °C and pressures of 207–241 bar were used to obtain number average molecular weights ranging from 2.2 \times 10^2 to 1.1 \times 10^4 g/mol (M_w = 4.5 \times 10^3 to 2.7 \times 10^4 g/mol). While molecular weight increased with increasing temperature, the temperature and pressure parameters were selected to provide sufficient extraction of phenol condensate while minimizing removal of diphenyl carbonate starting material. The plasticization of the polymer by CO₂ allows for much easier stirring versus the vacuum system. Like in the vacuum system, the rate did not depend on the choice of bisphenol used. In the vacuum system, temperature is used to lower melt viscosity and drive the reaction, but in the CO₂ case the high temperature is used to increase solubility of byproducts without extracting the reactants and drive the reaction. In addition, to improve polymer molecular weight, a dispersant was employed. (Polycarbonate A)-b-poly(dimethylsiloxane) was used to produce a microcellular foam in the synthesis of polycarbonate A in CO₂. The authors speculated that a dispersed polymer may allow for more effective removal of phenol because of higher polymer surface area.

Polycarbonate synthesis from bisphenol A and diphenyl carbonate catalyzed by tetr phenyl phosphonium tetr phenyl borate was performed in the presence of supercritical CO₂ by DeSimone. The authors noted that although diphenyl carbonate is soluble in CO₂, only a slight excess (1.005 equiv) was required for the reaction because, once a degree of polymerization of two is achieved, removal of diphenyl carbonate is not significant. The system was heated to 150 °C to melt the reactants and then heated at 160 °C under a slow flow of argon, followed by pressurization with CO₂ and heating to 270 °C for 1 h. High molecular weight polymer (up to 1.3 \times 10^4 g/mol) was achieved at 270 °C and 296 bar CO₂. The high solubility of phenol in CO₂ allows for its efficient removal, and its recovery was used to monitor the reaction progress.

Beckman showed that exposure of thin films of bisphenol A polycarbonate to CO₂ at 50 °C to 87 °C and up to 600 bar for 12 h, resulted in crystalline polymer. The crystallinity was observed as an endotherm at about 210–230 °C in the heating cycle of the differential scanning calorimetry (DSC) of the sample. Usually the crystallization of polycarbonate is induced by organic solvents. DeSimone obtained similar CO₂-induced crystallization results on amorphous polycarbonate chips and demonstrated that the CO₂-crystallized chips could be chain extended to high molecular weight using solid-state polymerization methods. The use of CO₂ could potentially allow the molecular weight of polycarbonate to be increased by solid-state polymerization in supercritical CO₂.

Melt-phase polycondensation reactions are commonly used to prepare poly(ethylene terephthalate) (PET). PET is an important plastic that sees widespread use in fiber, film, and food packaging applications for materials. Bis(hydroxyethyl) terephthalate (BHET) was converted to poly(ethylene terephthalate) (PET) using an Sb₂O₃ catalyst and temperatures of 250–280 °C under a variable flow (2–10 mL/min) of CO₂ at 207 bar. Molecular weights produced under these conditions varied from 3 \times 10^3 to 6.3 \times 10^3 g/mol. Polymer molecular weight, determined from intrinsic viscosity measurements, increased significantly with flow rate and/or reaction time. However, the molecular weights reported here are less than those normally produced by vacuum melt-phase polymerization (about 2 \times 10^4 g/mol). Because the ethylene glycol condensate is soluble in CO₂ up to 2–3 wt %, it is expected that the condensate could be effectively removed from the swollen polymer product to result in a higher molecular weight. However, the CO₂ solubility of ethylene glycol is lower than that of phenol (vide supra) and may partially account for the lower effectiveness of supercritical CO₂ in PET synthesis compared to polycarbonate synthesis.

Polyamides have also been synthesized in the melt phase in the presence of supercritical CO₂. Because primary amines react with CO₂ to form carbamates, the nylon salt route was used (see Scheme 10). A 1:1 salt of hexamethylenediamine and adipic acid was heated at 220 °C for 2 h and then at
280 °C for 3 h in the presence of 207 bar CO₂, producing a molecular weight of up to $2.45 \times 10^4$ g/mol of nylon 6,6. Interestingly, the melting point of the salt in the presence of CO₂ was depressed from 190 to 150 °C. This melting point depression is beneficial because the polymerizations can be run at lower temperatures, which translates to lower energy costs.

**B. Sol–Gel Polymerizations**

Sol–gel processing is important for producing amorphous, porous silica and polysilsesquioxane gels.¹⁶¹ Shrinkage and cracking during the drying of monolithic sol–gels have limited their commercial applications. A promising processing route to avoid shrinkage and cracking is the avoidance of capillary forces associated with air-drying by drying above the critical temperature and critical pressure of the solvent,¹⁶²,¹⁶³ resulting in aerogels that retain more of the original volume of the wet gel. To avoid the high cost associated with elevated temperatures and pressures required for supercritical alcohols, the use of supercritical CO₂ was investigated.¹⁶¹ Sol–gel polymerization of tetraalkoxysilanes and 1,4-bis-(triethoxysilyl) benzene (BESP) to give silica aerogels and polysilsesquioxane aerogels, respectively, was performed in supercritical CO₂ (see Scheme 11).

Because CO₂ is a nonpolar medium, sol–gel polymerization in supercritical CO₂ cannot use standard formulations due to the large quantities of water needed for hydrolysis and condensation of the alkoxysilane monomers. Alcohols are generally used as sol–gel solvents to permit mixing of water and nonpolar alkoxysilane monomers. Attempts at using a phase-transfer catalyst, such as NR₄OH·xH₂O, to form microemulsions of water, catalyst, alkoxysilane, and surfactant in supercritical CO₂ gave only low yields (<10%) of silica or polysilsesquioxanes in the form of precipitates with low surface areas.¹⁶¹

The low miscibility of water and CO₂ was avoided by using the “water free” sol–gel polymerization technique.¹⁶⁴ Alkoxysilanes react with anhydrous formic acid to give silanols that condense to give siloxane bonds necessary for creating a network polymer that will form a gel. The alcohol produced is converted to the formate ester. Supercritical CO₂ and formic acid are completely miscible at the temperatures and pressures used in the experiments. About 2–6 equiv of tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), or BESP and formic acid were heated at 35–40 °C and 410 bar CO₂ until a homogeneous slightly amber solution was observed. Because the formic acid is present at 13–36 wt %, it should actually be considered a cosolvent. For TMOS and BESP, gelation occurred in less than 12 h. The gel was then aged for 12–18 h, and the pressure was released over an 8–18-h period. Opaque white silica aerogels in nearly quantitative yields were observed. The gels appeared identical to gels prepared by conventional sol–gel techniques. The gels prepared in supercritical CO₂ exhibited some signs of cracking and shrinkage during drying. No gels were obtained using TEOS, consistent with its lower reactivity. Even aqueous acid-catalyzed sol–gel polymerizations of TEOS can require months for gels to form, which is much longer than the 12-h experiments reported here.

SEM analysis showed that the silica gels were highly porous and contained interconnected particles. The particles were 100–200 nm in diameter and contained larger pores than gels prepared in ethanol or formic acid and then extracted by supercritical CO₂. By SEM and TEM, the polysilsequioxane aerogels appeared similar to those produced by traditional methods. Nitrogen sorption porosimetry revealed mesoporous materials (mean pore diameters 20–500 Å). Surface areas of silica gels (260–308 m²/g) were similar to gels formed in ethanol or formic acid. BESP aerogels had surface areas lower than those prepared by aqueous sol–gel polymerizations in organic solvents (471–586 m²/g vs 1000–1600 m²/g).¹⁶⁵

**C. Oxidative Coupling**

Polypyrrole has received much attention as an organic conducting polymer because of its high conductivity and good thermal stability. It is usually synthesized by chemical oxidative polymerization in water, ethyl acetate, acetonitrile, methanol, or diethyl
Either. The synthesis of polypyrrole has been extended to SCFs to take advantage of their processing benefits. Polypyrrole was synthesized in supercritical fluoriform and in supercritical CO2 with in situ pyrrole generation by decarboxylation of 2-carboxypyrrrole, which allows control of polymerization onset because elevated temperatures are required (see Scheme 12). The pressure cell was charged with 2-carboxypyrrrole and oxidant (in a 2.33:1 mole ratio) and then pressurized. The reactor was then heated to 80–110 °C to commence the decarboxylation and polymerization reactions. In CO2, 2-carboxypyrrrole and the chemical oxidant FeCl3 had limited solubility. In contrast, pyrrole and the oxidant Fe(OTf)3 (OTf = CF3SO3) were soluble. Not surprisingly, Fe(OTf)3 gave better results: the FeCl3 catalyst gave yields of 50–60%, whereas the more soluble Fe(OTf)3 catalyst gave higher yields (87%).

Although it may seem counterintuitive to perform a decarboxylation reaction in high-pressure CO2, any deleterious effects by CO2 on this reaction are not clear. The yields of the polymer based on starting material were lower than in the control reaction performed in toluene (92%). However, in CO2, higher yields were obtained with higher pressure, indicating that any effects of CO2 on the decarboxylation are not obvious and that the lower yields are not limited by the decarboxylation step.

Four-point probe, pressed pellet conductivity measurements were as high as 5 × 10−2 S/cm, a value that is 2–3 orders of magnitude lower than polypyrrole prepared in traditional organic solvents. The authors suggest that the lower conductivity is perhaps due to over-oxidation of the conjugated chains, which was caused by the elevated temperature required by the precursor monomer route used in this report (polypyrrole is normally prepared at room temperature). But since conductivity of organic materials is known to depend on multiple factors, such as structure and composition, more investigations are required to establish the origins of lower conductivity. An even lower conductivity (9 × 10−4 S/cm) was observed for the control polypyrrole prepared by the monomer precursor route in refluxing toluene. Further, the morphologies of the polymers prepared in supercritical fluids were different than polypyrrole prepared in traditional solvents. Usually a globular structure is found for materials prepared in aqueous or nonaqueous solvents. SEM showed fibrous morphologies of the materials prepared in supercritical CO2. The fibers were 100–200 nm in diameter and several micrometers long.

Although the high conductivities of polypyrrole make it a promising candidate for organic conductor applications, it has the processing drawback of being insoluble, hard, and brittle. These mechanical property problems can be overcome by blending polypyrrole with an insulating polymer, either by in situ polymerization or direct blending. For example, the host polymer can be impregnated with an oxidant and then exposed to pyrrole vapor. To facilitate the incorporation of the oxidant, the host polymer is usually swollen with water or an organic solvent. After the polymerization is complete, the polymer is washed to remove byproducts, which include metal salts. Because of its ability to highly plasticize polymers and its recovery advantages of solutes, supercritical CO2 was investigated as an alternative solvent for delivery of oxidants into a polyurethane foam, which was subsequently used in the in situ polymerization of pyrrole. The goal of this research was to exploit the high diffusivities of solutes in supercritical fluids to facilitate oxidant penetration into the polymer host and byproduct removal from the final polymer blend.

A polyurethane foam was soaked in a solution of Fe(OTf)3 in supercritical CO2 at 45 °C and 241 bar. The solubility of Fe(OTf)3 in CO2 under these conditions was determined to be 0.01 wt %. The oxidant uptake was linear with the square root of time, indicative of Fickian diffusion. After soaking, the foam was exposed to pyrrole vapor (1 Torr, 4 h), and the conductivity of the foam was measured by the four-point probe method. An increase in oxidant uptake correlated with an increase in conductivity; the conductivity increased linearly with soak time and reached 3 × 10−2 S/cm for 24 h. The polypyrrole content in the blend was estimated at 3 wt % for the most conductive sample. Supercritical CO2 was used to remove polymerization byproducts such as Fe(OTf)2 and unreacted Fe(OTf)3. Samples were extracted at 45 °C and 241 bar. The supercritical CO2 was less effective than organic solvents at removing the reaction byproducts, probably because of their lower solubility in CO2 compared to methanol. The authors proposed the synthesis of more CO2-soluble oxidants for use in this process.

Another example of oxidative coupling reactions in supercritical CO2 is the poly(2,6-dimethylphenylene oxide) synthesis. The oxidative coupling of 2,6- and 2,3,6-substituted phenols is usually performed in toluene, benzene, halogenated hydrocarbons, dimethyl sulfate, or organic solvent/water biphasic systems. Supercritical CO2 was investigated as a solvent replacement for the synthesis of poly(2,6-dimethylphenylene oxide) (see Scheme 13). Oxygen, which was used as the oxidant in these polymerizations, was miscible with CO2 under the reaction conditions (25–40 °C, 345 bar). The high-pressure reactor was filled with CO2, O2, 2,6-dimethylphenol, and CuBr catalyst. The reaction commenced with the addition of an amine. The insoluble polymer resulted in a precipitation polymerization. Small molecule amines [pyridine and 2-(N,N-dimethylamino)ethyl...
acrylate (DMAEA)) and CO₂-soluble polymeric amines [poly(FOA-co-vinylpyridine) (10) and poly(FOA-co-DMAEA) (11)] were used in the reaction. While the small molecule bases should produce a heterogeneous catalyst, the polymeric amines should increase the solubility of the catalyst, although the solubility characteristics of either system were not reported. It was hoped that the polymeric amines would result in a dispersion polymerization and give higher yields. Although the polymeric amines produced a stable latex, an increase in yields or molecular weights of polymer normally associated with dispersion polymerization was not observed.

Because polystyrene is miscible with poly(2,6-dimethylphenylene oxide), it was thought to be a good candidate as the CO₂-phobic component in surfactants for the dispersion polymerization of 2,6-dimethylphenol. Random and block copolymers of styrene and FOA were synthesized and were added to the dimethylphenol polymerizations. Presence of the random copolymer led to higher yields but not higher molecular weights. However, the reaction stabilized with the block copolymer gave higher yields (up to 86%) and higher molecular weights (up to 1.7 × 10⁴ g/mol). Thus, block copolymers of FOA and styrene were effective stabilizers for the dispersion polymerization of 2,6-dimethylphenol in supercritical CO₂.

IV. Conclusions

The numerous examples presented here demonstrate that supercritical CO₂ is rapidly becoming a viable alternative solvent for polymerizations. Supercritical CO₂ has been used as the continuous phase for all types of chain-growth and step-growth polymerization mechanisms, including metal-catalyzed, free-radical, and ionic processes. Several unique aspects of supercritical CO₂, including the ability to tailor the solvent quality by changing the pressure, have been exploited to prepare materials with various morphologies and properties. In addition, the design and synthesis of surfactants which are interfacially active in supercritical CO₂ has opened the door for the preparation of a wide range of polymeric materials in this unique solvent.

V. References


