Chem. Rev. **1999,** *99,* 543–563

Polymerizations in Supercritical Carbon Dioxide

Jonathan L. Kendall,[†] Dorian A. Canelas,[†] Jennifer L. Young, and Joseph M. DeSimone*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

Received June 30, 1998 (Revised Manuscript Received November 23, 1998)

Contents

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 CO_2 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 CO_2 represents a more environmentally friendly alternative to traditional solvents. CO_2 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] CO_2 has an easily accessible critical point with a T_c of 31.1 °C and a P_c of 73.8 bar.[6] Because it is an ambient gas, CO_2 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 CO_2 is used as a polymerization solvent. Because CO_2 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 CO_2-based systems.

Solubility plays a very important role in the synthesis of polymers in supercritical CO_2. While CO_2 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 CO_2 and 100 °C for a 10^5 g/mol polymer to dissolve in CO_2.[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 CO_2 under mild conditions are amorphous fluoropolymers and silicones.[1,4,9–12]

[†] Present address: Lord Corp., Thomas Lord Research Center, P.O. Box 8012, Cary, NC 27512-8012.

10.1021/cr9700336 CCC: $35.00

Jonathan Kendall was born in Charlotte, NC, in 1969. He received his B.S. in chemistry from the University of North Carolina at Chapel Hill in 1991. He received his Ph.D. in chemistry from Stanford University in 1997, under the direction of Professor James P. Collman. During graduate school, he synthesized bis(porphyrin) sandwich complexes for three materials applications: nonlinear optics, liquid crystals, and semiconducting charge-transfer materials. He then returned to Chapel Hill for postdoctoral research in Professor Joseph DeSimone's lab. His work on polymer synthesis in liquid and supercritical carbon dioxide has been performed while serving as the Technical Coordinator for the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing, a CO_2-based research center sponsored by UNC—CH and North Carolina State University.

Dorian Canelas was born in 1970 in Honolulu, HI and raised in Wheat Ridge, CO. She received a B.S. in chemistry from Northeastern University in 1993. As an undergraduate, she worked on step-growth polymerizations and membrane modification under the direction of L. F. Hancock at W.R. Grace. She earned a Ph.D. from the University of North Carolina at Chapel Hill in 1997 under the direction of J. M. DeSimone. Her graduate work focused on dispersion polymerizations of vinyl monomers in surfactant-modified supercritical carbon dioxide. She is currently working on new thermoset chemistry at Lord Corporation in Cary, NC.

Jennifer Young was born and raised in Timonium, MD. She earned her B.S. degree in chemistry from the University of Richmond in 1995. She is currently working toward her Ph.D. under the direction of Professor M. DeSimone at the University of North Carolina at Chapel Hill. Her studies are focused on dispersion polymerizations in liquid and supercritical carbon dioxide.

Joseph DeSimone is Mary Ann Smith Professor of Chemistry at the University of North Carolina at Chapel Hill and of Chemical Engineering at North Carolina State University. He received his B.S. degree in chemistry in 1986 from Ursinus College in Collegeville, PA, and his Ph.D. in 1990 from the Department of Chemistry at Virginia Polytechnic Institute and State University. At VPI he worked with Professor James McGrath in the area of living polymerizations to synthesize novel block and graft copolymers. At UNC—CH, his research efforts are focused on developing synthetic pathways for polymer synthesis and processing in liquid and supercritical carbon dioxide. His accomplishments include homogeneous and heterogeneous polymerizations in CO_2. Recently, he has investigated the design and synthesis of surfactants for use in CO_2 as stabilizers in dispersion polymerizations, delivery of materials, and extractions. In 1996, he cofounded MICELL Technologies, which has developed environmentally friendly CO_2-based dry-cleaning and metal degreasing systems. In 1997, he and Professor Ruben Carbonell at NCSU started the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing (at UNC—CH and NCSU) to facilitate research on CO_2-based polymer synthesis and processing. Professor DeSimone was a 1993 Presidential Faculty Fellow and winner of the 1997 Presidential Green Chemistry Challenge Award. He is also the 1999 winner of the Carl S. Marvel Creative Polymer Chemistry Award.

While the parameters that govern solubility of polymers in CO_2 are not fully understood, several studies have been performed to probe the nature of solute–solvent interactions between polymers and CO_2. CO_2 has a low dielectric constant compared to alkanes, and its polarizability and polarizability/volume are lower than ethane and propane.[13] Although CO_2 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 CO_2 to participate in interactions absent in hydrocarbons. Early work in this area suggested that weak interactions exist between CO_2 and functional groups on the polymer chains such as sulfones[14] and carbonyls.[15] Later, systematic studies implied that the interactions between CO_2 and the silicone portion of the polymer backbone govern the high solubility of these types of polymers.[16] Work involving the use of Fourier transform infrared spectroscopy reveals that CO_2 exhibits Lewis acid–base type interactions with electron-donating functional groups of polymer chains such as the carbonyl group of poly(methyl methacrylate) (PMMA).[17] McHugh found that in copolymers of ethylene and methyl acrylate, increasing the methyl acrylate content increased polymer solubility.[18] It was concluded that dipole−quadrupole interactions between CO_2 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 CO_2, even up to 270 °C and 2750 bar, perfluorinated ethylene−propylene copolymer has greatly improved solubility (200 °C, 1000 bar).[18] Other work revealed that the interactions between CO_2 and poly(trifluoropropyl methyl siloxane) are anomalously high, and the authors attributed this finding to specific interactions between CO_2 and the polar fluorine containing group.[16,19] More recently high-pressure ^{19}F NMR studies have indicated specific interactions between CO_2 and fluorocarbons.[20]

These solubility requirements dictate the types of polymerization techniques employed in polymer synthesis. For example, amorphous fluoropolymers have been synthesized homogeneously in supercritical CO_2. In contrast, many polymerization reactions in CO_2 are conducted under heterogeneous processes, either as precipitation, dispersion, or emulsion polymerizations, due to the inherent insolubility of most polymers in CO_2. 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 CO_2. These stabilizers have been successfully employed in the heterogeneous polymerizations of CO_2-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 CO_2. Careful and controlled lowering of the density of a polymer solution allows precipitation of the highest molecular weight polymer fraction.[1] For example, CO_2-soluble synthetic oils such as perfluoroalkyl polyethers, chlorotrifluoroethylene oligomers, and poly(dimethylsiloxane) (PDMS) were fractionated with supercritical CO_2.[10] In the case of PDMS, the starting sample with a number average molecular weight (M_n) of 4×10^5 g/mol was separated into six fractions with M_n ranging from 4×10^2 g/mol to 1×10^6 g/mol.

Table 1. Summary of Literature Studies on the Swelling and Plasticization of Homopolymers, Copolymers, and Polymer Blends by CO_2

polymeric material	technique	ref(s)
Homopolymers		
poly(aryl ether ether ketone) (PEEK)	DSC[a]	170
polycarbonate (PC)	DSC	22,32
	swelling/sorption	23
substituted polycarbonates	DSC	171
poly(2,6-dimethylphenylene oxide) (PPO)	DSC	30,32
poly(dimethylsiloxane) (PDMS)	sorption	16,19,38
poly(ether imide)	DSC	32
polyethylene (PE)	DSC	33
poly(ethylene terephthalate) (PET)	DSC	22,32,33
poly(ethyl methacrylate)	sorptive dilation	29
(PEMA)	creep compliance	27
poly(iminoadipoylimino-hexamethylene) (nylon-6,6)		33
polyisoprene	swelling/sorption	172
poly(methyl methacrylate)	DSC	22,32
(PMMA)	creep compliance	24,26,27
	swelling/sorption	23,172,173
	dielectric measurements	25
poly(oxymethylene)	DSC	33
poly(propylene) (PP)	DSC	33
polystyrene (PS)	creep compliance	21,24,26
	DSC	22
	swelling/sorption	23,172
polysulfone	DSC	32
polyurethane	infrared spectroscopy	31
	DSC	32
poly(vinyl benzoate)	sorptive dilation	28
poly(vinyl butyral)	sorptive dilation	28
poly(vinyl chloride) (PVC)	DSC	22,32
poly(vinylidene fluoride) (PVF_2)	DSC	33
poly(vinylpyridine)	swelling/sorption	172
Copolymers		
poly(methyl methacrylate-*co*-styrene)	creep compliance	26,172
acrylonitrile butadiene styrene (ABS)	DSC	32
high impact polystyrene	DSC	32
Polymer Blends		
PMMA/PVF_2	DSC	22
PS/PC	DSC	174
PS/poly(vinylmethyl ether)	sorption	175

[a] DSC = differential scanning calorimetry.

Another important feature of supercritical CO_2 in polymerization is plasticization, which results in the lowering of the polymer's glass transition temperature (T_g). Polymers have been shown to become highly plasticized by CO_2. 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 CO_2 plasticization on polymers. The effects of high-pressure CO_2 on the glass transition temperature and mechanical properties of polystyrene (PS) have been measured by Young's modulus and creep compliance.[21] This work demonstrated the severe plasticization of PS as a function of CO_2 pressure. In work by Choiu, differential scanning calorimetry (DSC) was used to study the plasticization of polymers by CO_2 at pressures up to 25 bar.[22] 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 T_gs of polycarbonate (PC), PS, and PMMA in CO_2.[23,24] Beckman examined the plasticization of PMMA by CO_2 as a function of pressure using dielectric measurements.[25] Johnston performed an in-depth study of the solubility of CO_2 in the polymer and its effect on the T_g vs CO_2 partial pressure behavior for PMMA, PS, and a random copolymer of methyl methacrylate and styrene.[26] Johnston has also used in situ measurements of creep compliance to determine the T_g depression of PMMA and poly(ethyl methacrylate) in CO_2.[27] As evidenced by the above and other[28−33] work, the plasticization of polymers by CO_2 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 CO_2 can also be used in the removal of residual monomer.[1] The high transport properties of supercritical CO_2 such as high diffusivity and low viscosity coupled with the propensity of CO_2 to plasticize polymers were employed to remove *N*-vinylcarbazole from poly(*N*-vinylcarbazole).[10] Supercritical CO_2 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 CO_2 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 CO_2 have been reported. Step-growth reactions in CO_2 have produced polycarbonates, polyamides, polyesters, polypyrrole, polyphenoxides, and silica gels. In addition, the numerous supercritical CO_2 processing techniques for polymers that are being developed become simplified when the synthesis of the polymer is performed in supercritical CO_2. These examples illustrate the versatility and importance of supercritical CO_2 as a solvent for polymerization reactions.

II. Chain-Growth Polymerizations in CO_2

The major types of chain-growth polymerization routes include free-radical, cationic, anionic, and metal-catalyzed reactions. Most chain-growth polymerizations in CO_2 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 CO_2: reactive anions would attack the Lewis acid CO_2, and thus anionic polymerizations in CO_2 are unlikely unless extremely weak nucleophiles are involved, such as siloxanolates.

Initial breakthroughs in the 1960s in the use of compressed CO_2 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 CO_2 as a polymerization medium was realized when siloxanes and amorphous fluoropolymers were identified as polymeric materials which had high solubilities in CO_2 at easily attainable temperatures ($T < 100$ °C) and pressures ($P < 350$ bar).[1] This realization opened up new areas of research in CO_2, 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] 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 CO_2, suspension polymerizations in CO_2 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 CO_2. 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 autoacceleration (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[44] and a recent review by Sudol.[50] Due to the good solubility of many small organic molecules in CO_2, dispersion polymerization constitutes the best heterogeneous method that has been developed thus far for producing high molecular weight, CO_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.[20,49,51−53] For a reaction to take advantage of the desirable Smith−Ewart/Harkins kinetics,[54] the monomer and initiator must be segregated with the initiator preferentially dissolved in the continuous phase and not 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_2, emulsion polymerization in CO_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_2 system has been reported.[56]

1. Homogeneous Polymerizations

Amorphous or low-melting fluoropolymers can be synthesized homogeneously in CO_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_2 are the best solvents for these types of polymers.[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_2 as the solvent, DeSimone used free-radical initiators to effect the synthesis of high molar mass amorphous fluoropolymers.[4,11,57−59] Due to the high solubility of the polymers in the CO_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*-perfluoroethyleneoxymethylstyrene, constitute a second type of monomer polymerized via homogeneous solution polymerization in supercritical CO_2. The product obtained from this polymerization in CO_2 was identical to the product of a solution polymerization in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), indicating that CO_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_2-soluble polymeric amines by copolymerizing FOA with 2-(dimethylamino)ethylacrylate or 4-vinylpyridine.[60]

The initiation and propagation kinetics of free-radical polymerizations in supercritical CO_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′-azobis-(isobutyronitrile) (AIBN) in CO_2.[11] By comparing the decomposition rate, k_d, and the initiator efficiency, f, in CO_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_2 using the pulsed laser polymerization (PLP) technique.[61] 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_p, was found to be very close to the bulk values for both monomers, indicating that the presence of CO_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_2 to those in conventional, liquid solvents such as Freon-113.[62] Indeed, these kinetic studies have verified that CO_2 is an excellent medium in which to conduct free-radical reactions.

2. Precipitation Polymerizations

A topic of many early studies in CO_2 was the free-radical polymerization of industrially important vinyl monomers.[63] Although many common vinyl monomers exhibit high solubility in CO_2,[7] most of the corresponding polymers exhibit exceedingly poor solubilities in CO_2. 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 CO_2 using either γ radiation or AIBN initiation.[64−66] In this work, the infrared spectra of the polymers revealed that the presence of the CO_2 continuous phase had little effect on the polymer structure. They noted that while the ethylene monomer was initially soluble in the liquid CO_2, 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 CO_2 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 CO_2.[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 CO_2.[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 (M_v) ranging from 1.2×10^4 to 1.6×10^6 g/mol.

More recently, precipitation polymerizations of semicrystalline fluoropolymers in CO_2 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 CO_2.[69] Tetrafluoroethylene copolymerizations[70,71] with perfluoro(propyl vinyl ether) and with hexafluoropropylene or homopolymerizations[72] have been performed in CO_2, resulting in high yields of high molecular weight ($>10^6$ 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 CO_2 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 CO_2. Since traditional surfactants for emulsion and dispersion polymerizations were designed for use in an aqueous or organic continuous phase and are completely insoluble in CO_2, an exciting area of research is the design and synthesis of novel surfactants specifically for CO_2. 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 CO_2-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 CO_2-based systems, the types of surfactants that have been used for steric stabilization include CO_2-philic (CO_2-soluble) homopolymers, copolymers (statistical, block, or graft) containing a CO_2-philic component and a CO_2-phobic (CO_2-insoluble) anchoring component, and CO_2-philic reactive macromonomers. Stuctures of the polymeric surfactants for CO_2 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 theory[74] 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 CO_2 in the presence of a surfactant, either poly(1,1-dihydroper-

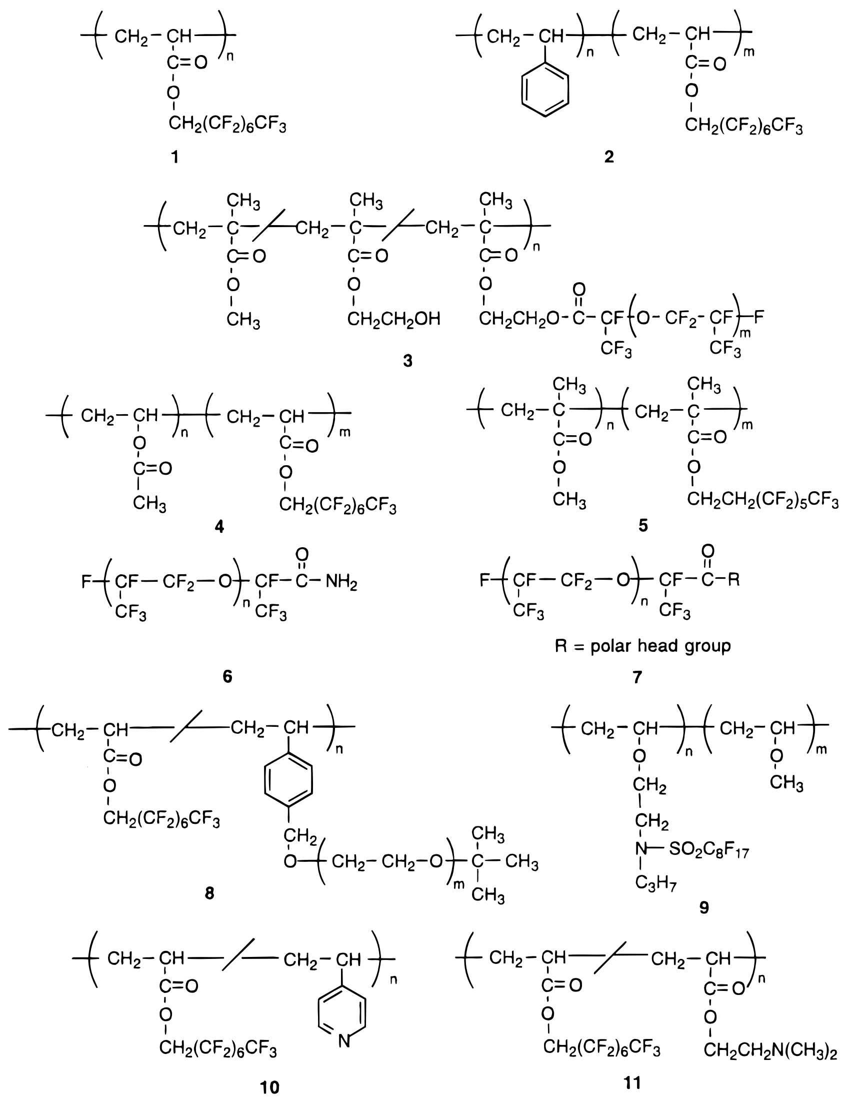


Figure 1. Stuctures of fluorinated polymeric surfactants for CO_2.

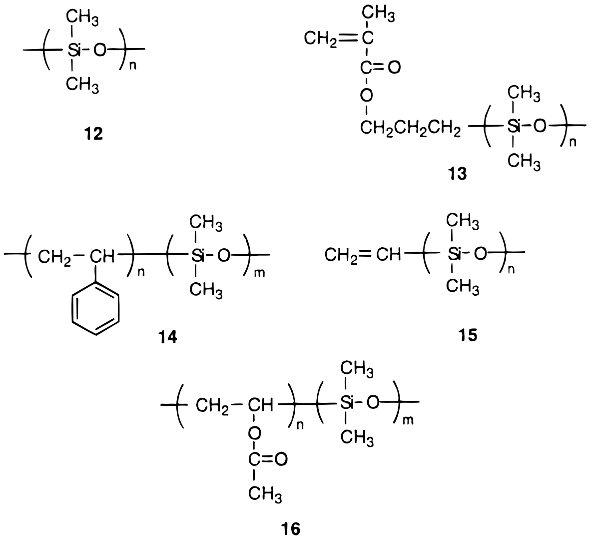


Figure 2. Stuctures of PDMS-based polymeric surfactants for CO_2.

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 θ 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,[78] dynamic light scattering confirmed the correlation between the CFD and the θ 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[79] and copolymer and end-graft stabilizers[80] 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

Table 2. Summary of Dispersion and Emulsion Polymerization Studies in Liquid and Supercritical Carbon Dioxide

monomer(s)	stabilizers	ref(s)
acrylamide	amide end-capped poly(hexafluoropropylene oxide)	56
2,6-dimethylphenylene oxide	PFOA homopolymer, PFOA-based random copolymers, and PS−PFOA block copolymer	60
divinylbenzene and ethylvinylbenzene	fluorinated methacrylate-PMMA block copolymer	55
methyl methacrylate	PFOA homopolymer	34,81,84
	PDMS-based macromonomer	90−92
	fluorinated graft or block copolymers	94,176
styrene	PFOA homopolymer; PS−PFOA block copolymers	95
	PDMS homopolymer; PS−PDMS block copolymers	96,177
	FVE-MVE block copolymer	135
vinyl acetate	PFOA and PDMS homopolymers, PDMS macromonomer, PVAc−PDMS and PVAc−PFOA block copolymers	99,100
vinyl acetate and ethylene	PDMS homopolymer; PVAc−PFOA block copolymer	100

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.[81] 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 2.0×10^5 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 had an unstructured, nonspherical morphology that contrasted sharply with the spherical polymer particles produced in the dispersion polymerizations. 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.[34,82] 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.[44] 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.

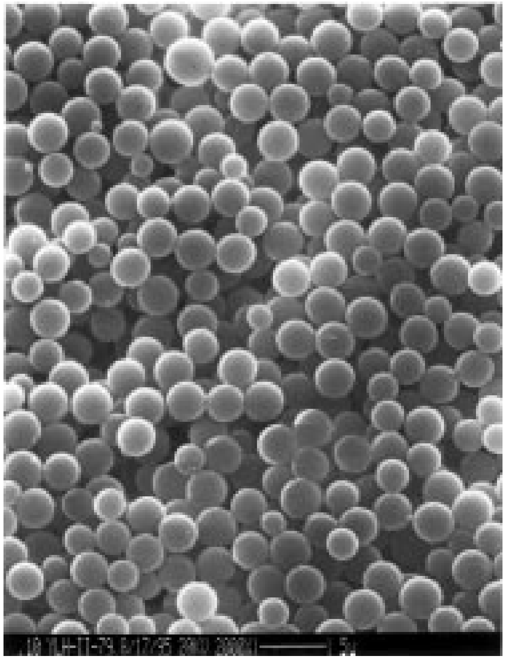


Figure 3. Scanning electron micrograph of PMMA particles produced by dispersion polymerization in CO_2 using PFOA as the stabilizer.

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.[83,84] 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[85−87] and the reduced extraction rate in SCF extractions[88] when helium is present in the CO_2. An acoustic technique, used by Kordikowski and co-workers, measured the composition of helium in CO_2 tanks and showed the content to be unpredictable, presumably due to common lack of equilibration in the cylinder.[89] Therefore, these diverse experiments illustrate that even seemingly "benign" components such as an inert gas can effect the solvent quality of CO_2, and the CO_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_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_2-soluble polymers includes PDMS (**12**). PDMS-based surfactants are cheaper, but are less soluble than PFOA at comparable molecular weights in CO_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.[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_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 μm. 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[91] and growth[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 % based on monomer) were required. Latex stability was limited by the low solubility of surfactant in the absence of monomer in CO_2. The chronology of yield, particle size, morphology, particle number density, and molecular weight was studied. The results agreed with the experiments by Shaffer[90] and with predictions from the model of Paine[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_2-soluble poly(perfluoropropylene oxide) side chains (**3**).[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_2 for a successful dispersion polymerization.

Indeed, the dispersion polymerization of MMA in compressed CO_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_2 system.

The dispersion polymerization of styrene in supercritical CO_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[95] or PDMS (**14**)[96] 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_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_2 continuous phase.[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.[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 μm to 0.24 μm) 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 3.7×10^3 g/mol PS, varying the PFOA block from 1.4×10^4 to 2.5×10^4 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.[98]

PS-*b*-PDMS polymeric stabilizers were studied to determine the effects of anchor block length and soluble block length, CO_2 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 $\times 10^4$ 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 CO_2. 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 CO_2 in the absence of monomer. PDMS homopolymer was not capable of stabilizing styrene dispersion polymerizations in CO_2, 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 CO_2 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 $M_n = 4 \times 10^3$ g/mol) had inefficient anchoring to the PVAc particles. The PVAc-*b*-PFOA with the longest blocks (PVAc $M_n = 3.1 \times 10^4$ g/mol; PFOA $M_n = 5.4 \times 10^4$ 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 CO_2.[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 ($\leq$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 CO_2.

Adamsky and Beckman have explored the possibility of carrying out an inverse emulsion polymerization of acrylamide in supercritical CO_2.[56,101] In these reactions, acrylamide was polymerized in the presence of water, a cosolvent for the monomer, in a CO_2 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 CO_2 are expected with the recent discoveries of surfactants which have the ability to form microemulsions of water and water soluble molecules in CO_2. In 1993, DeSimone reported the use of the macromonomer technique to synthesize and characterize an amphiphilic graft copolymer with a CO_2-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, CO_2-insoluble dye methyl orange in supercritical CO_2. 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 CO_2 continuous phase.[103] This work represented the first direct confirmation that micelles can form in a CO_2 continuous phase. Beckman and co-workers have studied the phase behavior of both silicone-based and fluoro ether-functional amphiphiles in supercritical CO_2.[12,104] A fluoro ether-functional amphiphile (**7**) was shown to permit the extraction of thymol blue from aqueous solution into CO_2. The effect of pressure on the emulsion behavior of fluoro ethers terminated with sorbitol esters, sulfates, and sulfonates in mixtures of CO_2 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 surfactant $C_7F_{15}CH(OSO_3^-Na^+)C_7H_{15}$ and water in CO_2.[106] In this work, the water-to-surfactant ratio in a single-phase microemulsion was as high as 32 at 25 °C and 231 bar. It was shown that with 1.9 wt % surfactant, 2 wt % water was solubilized in CO_2, which is 10 times the amount of water soluble in pure CO_2. In more recent work, Johnston demonstrated the formation of aqueous microemulsion droplets in a CO_2 continuous phase using an ammonium carboxylate perfluoropolyether surfactant, $[(OCF_2CF(CF_3))_n(OCF_2)_m]OCF_2COO^-NH_4^+$.[107] Several spectroscopic techniques were employed to investigate the properties of these aqueous microemulsions. These approaches to the formation of microemulsions in nonpolar supercritical fluids has been the focus of two recent reviews.[108,109] Since evidence was shown in the studies by DeSimone, Beckman, and Johnston that their surfactants form microemulsions of water and, in some cases water soluble molecules, in CO_2, these surfactants could potentially be used to form microemulsions of water and a water soluble monomer in CO_2 for inverse emulsion polymerizations.

The fields of dispersion and emulsion polymerizations have been developed over the past 30 years to become convenient methods for the preparation of spherical polymer particles. Advances in the design and synthesis of amphiphilic block and graft copolymers for use as stabilizers in supercritical fluids has allowed tremendous latitude in the composition of the polymeric microspheres. Breakthroughs in the design and synthesis of nonionic surfactants that are interfacially active in a CO_2 medium have been pivotal to the development of the dispersion and emulsion polymerizations technique in this fluid.

4. Polymer Blend Synthesis

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(oxymethylene), and bisphenol A carbonate, and to infuse styrene monomer and a free-radical initiator into the swollen polymer.[35,36,110] 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.[111] 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.[112] 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 carbocations 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 β 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.[113] 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.[114] 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 β-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. Winstein developed an ion pair spectrum to describe the active site in cationic polymerizations.[115] Classical nonliving carbocationic 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 CO_2 should make for an interesting medium for studying cationic reactions. One disadvantage is the critical temperature of CO_2 (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 CO_2 are inherently problematic. In fact, much of the early experiments using CO_2 as a solvent for cationic reactions were performed in liquid CO_2 at low temperatures. However, it has been shown that good results can be obtained in liquid and supercritical CO_2. Further, CO_2 has been shown to be inert to cationic polymerization conditions.

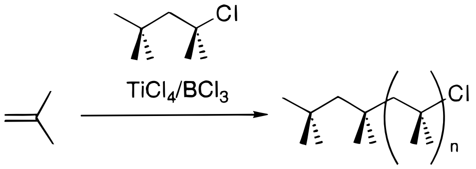
The earliest work in cationic polymerizations in CO_2 was aimed at preparing industrially important hydrocarbon polymers in CO_2. These initial experiments utilized chain-growth polymerization mechanisms to produce polymers which were relatively insoluble in the CO_2 continuous phase at the reaction 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 CO_2.

A 1960 report by Biddulph and Plesch explored the heterogeneous polymerization of isobutylene in liquid CO_2 at −50 °C.[116] Two catalyst systems were shown to be effective: $AlBr_3$ and $TiCl_4$ (using ethyl bromide and isopropyl chloride, respectively, as cosolvents). The $AlBr_3$-catalyzed reactions proceeded very fast, but were incomplete and gave molecular weights of about 5×10^5 g/mol. The low conversion was attributed to catalyst becoming embedded in the white polymer precipitate. The $TiCl_4$ reaction was slower, but proceeded to completion and gave molecular weights of about 3×10^4 g/mol.

A 1970 patent covering the precipitation polymerization of vinyl compounds in liquid CO_2 included the polymerization of ethyl vinyl ether at room temperature.[68] This heterogeneous reaction was catalyzed by either $SnCl_4$ or $BF_3{\cdot}OEt_2$. 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 CO_2. 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 CO_2 was not being incorporated into the polymer backbone. This spectroscopic measurement confirmed that CO_2 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]

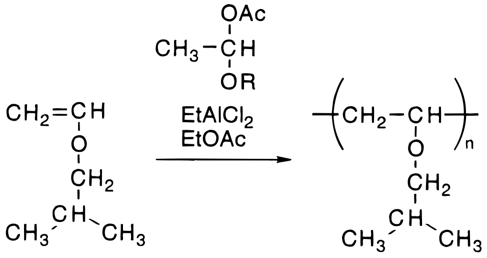
Scheme 1. Synthesis of −Cl-Terminated PIB



Kennedy, building on earlier work by Plesch,[116] reported the polymerization of isobutylene (IB) in supercritical CO_2 using 2-(2,4,4-trimethylpentyl) chloride (TMPCl) as an initiator and a Lewis acid catalyst such as BCl_3, $TiCl_4$, or $SnCl_4$ 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 ($PDI = M_w/M_n$). Conversions of up to 30−35% and polymers with M_n of 1×10^3 to 2.5×10^3 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/($TiCl_4$/BCl_3) was used to form well-defined polyisobutylene with terminal chloride ($-Cl^t$) end groups (see Scheme 1).[122] Reaction conditions similar to those used previously were employed: 32.5 °C, 140 bar CO_2, and 5−10% MeCl. After 3 h, conversions of 40−45%, molecular weights of 1.8×10^3 to 2.4×10^3 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 only about 0.5%. Thus, although low molecular weight material was produced in CO_2, the molecular weights were higher than in hexane. ^1H NMR spectra showed no evidence of olefinic end groups (in contrast to the $TiCl_4$ or $SnCl_4$ 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 CO_2.[123] Over the range of 32−48 °C, conversion dropped from 40% to 4% and the molecular weights dropped from 2×10^3 to 7×10^2 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 ± 9 °C, calculated by linear extrapolation of molecular weight to 56 g/mol (mass of IB) as a function of temperature,

Scheme 2. Cationic Synthesis of P(IBVE) in Supercritical CO_2



was consistent with those determined for conventional solvent systems.[124−128]

An isobutylene−styrene copolymer was also synthesized in CO_2 using MeCl as a cosolvent and the TMPCl/$TiCl_4$ 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.

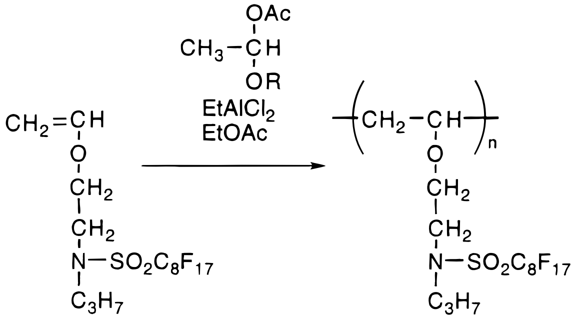
In the synthesis of phenol-terminated polyisobutylene, the first example of electrophilic aromatic alkylation in supercritical CO_2 was reported.[130] TMPCl and polyisobutylene−Cl^t (M_n = 2000 g/mol) were alkylated by phenol at 32.5 °C and 140 bar in the presence of $BF_3 \cdot OEt_2$ for 24 h. Yields of 75% and 60% respectively were observed.

The isomerization polymerization of 3-methyl-1-butene and 4-methyl-1-pentene has also been studied in supercritical CO_2.[131,132] The reactions were performed at 140 bar CO_2 and 32.5 °C with residual water and $AlCl_3$ as the catalyst system. As with the 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.

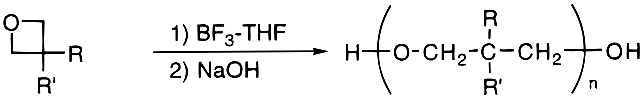
DeSimone reported a study of cationic polymerization of vinyl ethers in supercritical CO_2.[133,134] Both precipitation and homogeneous polymerizations were reported. The initiation system was based on Higashimura's living cationic polymerization method developed for hydrocarbon solvents. This method 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).[113] The polymerization of IBVE began homogeneously, but became heterogeneous as the polymer precipitated. Yields of polymer synthesized in CO_2 were similar to results obtained in cyclohexane, but with broader PDIs (for example, 1.2 for cyclohexane and 1.8 for CO_2 at 40 °C, 345 bar). At 60 °C, the polydispersity of polymers produced in CO_2 increased to greater than 9, indicating no molecular weight control, perhaps due to increased chain transfer to monomer and lower CO_2 density, which would allow for faster precipitation of polymer.

The homogeneous polymerization of 2-(*N*-propyl-*N*-perfluorooctylsulfonamido)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 CO_2-soluble fluorinated polymer compared to the broad PDIs obtained with the CO_2-insoluble poly(IBVE) suggest that solubility of the resulting polymer plays an important role in determining polydispersity in these cationic polymerizations in supercritical CO_2.

Scheme 3. Synthesis of Poly(FVE)



Scheme 4. Ring-Opening Polymerization of Oxetanes in CO_2



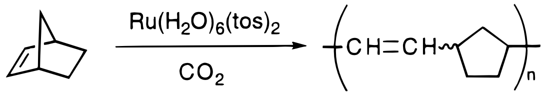
R=R'= $-CH_2OCH_2CH_3$ for BEMO

R= $-CH_3$; R'= $-CH_2OCH_2CF_2CF_2CF_3$ for FOx-7

Ring-opening polymerization of cyclic ethers were initiated by BF_3 in liquid CO_2 and compared to reactions performed in methylene chloride (see Scheme 4).[134] Bis(ethoxymethyl)oxetane (BEMO) was polymerized at −10 °C in CO_2 (290 bar). As expected from insolubility of the resulting polymer, the CO_2 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 CH_2Cl_2 and 2.7 for CO_2. A fluorinated cyclic ether, 3-methyl-3′-[(1,1-dihydroheptafluorobutoxy)methyl]-oxetane (FOx-7) was polymerized homogeneously in both CO_2 (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 CO_2 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 FOx-7 polymerized in either CO_2 or Freon-113.

Initial attempts to perform the first cationic dispersion polymerization in CO_2 were with BEMO and IB.[134] The polymerizations were catalyzed by $BF_3 \cdot$THF (for BEMO) or $SnCl_4$ (for IB) and were conducted in the presence of CO_2-soluble surfactants such as poly(FOx-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 CO_2 which could be redispersed in Freon-113 after removal of CO_2. Scanning electron microscopy (SEM), which examined polymer following removal of CO_2, detected slight particle formation despite the semi-

Scheme 5. ROMP of Norbornene in Supercritical CO_2



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.[135] First, a suitable surfactant for polystyrene was synthesized in CO_2, using the vinyl ether system previously reported.[134] 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 [$Ru(H_2O)_6(tos)_2$] (tos = *p*-toluenesulfonate) (see Scheme 5).[136,137] 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 10^5 g/mol), yield (30−76%), or PDI (2.0−3.6).

The [$Ru(H_2O)_6(tos)_2$] 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 polynorbornene 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.

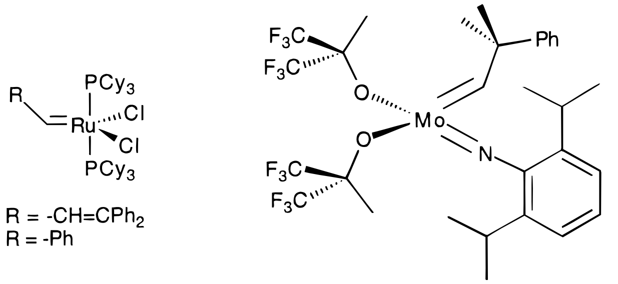
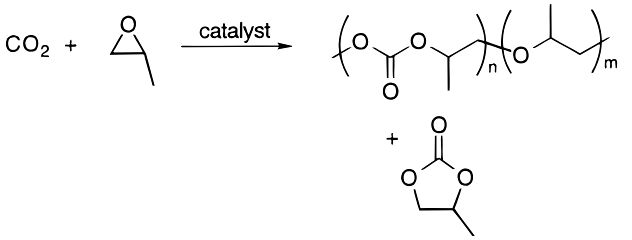


Figure 4. Catalysts for ROMP of norbornene in supercritical CO_2.

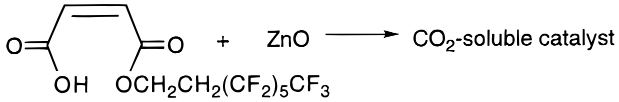
Higher activities for the ROMP of norbornene were observed with ruthenium and molybdenum carbene catalysts reported by Grubbs[138−140] and Schrock,[141] respectively (see Figure 4).[142] While the Ru catalyst appeared insoluble in CO_2, the Mo catalyst was partially soluble. These catalysts gave up to 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 10^5 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[143] (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

Scheme 6. Scheme for Copolymerization of Propylene Oxide and CO_2



Scheme 7. Synthesis of CO_2-Soluble Zinc Catalyst for Cyclohexene Oxide/CO_2 Copolymerization



decreased the polymer yield while increasing the fraction of carbonate linkages relative to ether linkages. In contrast, dichloromethane increases carbonate linkages without significantly decreasing yield.

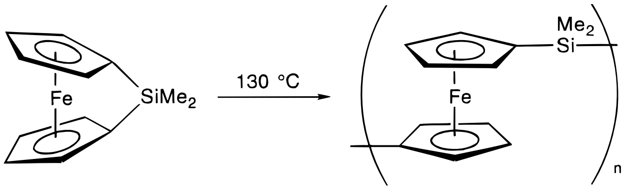
A phenoxide zinc catalyst, [(2,6-diphenylphenoxide)$_2$-Zn(Et_2O)$_2$], produced polycarbonate from CO_2 and cyclohexene oxide in CO_2.[144] The reaction was performed at 80 °C and 55 bar to yield a polymer with a molecular weight of 3.8 × 10^5 g/mol and only 9% ether linkages. The terpolymerization of propylene oxide, cyclohexene oxide, and CO_2 gave a good yield of polymer with about 20% propylene carbonate linkages.

A CO_2-soluble Zn catalyst was developed for copolymerization of cyclohexene oxide and CO_2 (see Scheme 7).[145] The catalyst was synthesized from ZnO and the mono(1H,1H,2H,2H-perfluorooctyl) ester of maleic acid and was soluble in CO_2 over a wide pressure range and up to 90 °C. Above 90 °C, an irreversible phase separation occurred. The turnover numbers of up to 400 g of polymer/g of Zn obtained for this catalyst are among the highest reported for the copolymerization of epoxides and CO_2.

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]ferrocenophane in the melt.[146,147] This melt-phase route produced high molecular weight polymer (M_w = 5.2 × 10^5 g/mol). Other synthetic methods, such as condensation polymerization,[148] do not produce the polymer in sufficiently high molecular weight for commercial applications. Extending their work, the authors investigated this reaction in supercritical CO_2.[149] 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_2 avoids this problem. The thermal ring-opening polymerization of a [1]silaferroceneophane was performed in the presence of supercritical CO_2 at 207 bar and at three different temperatures: 75 °C, 100 °C, and 130 °C (see Scheme 8). The molecular weights obtained in CO_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_w of 2.87 × 10^5 g/mol, was produced at 130 °C. In addition to the lower molecular weights, the PDIs of the CO_2 samples were broader (3.0−5.1 vs 1.5). However, when the concentration of monomer was increased from 500 mg/60 mL CO_2 to 2 g/60 mL for the 130 °C reaction, the molecular weight increased to 5.9 × 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_2.

Scheme 8. Ring-Opening Polymerization of Silicon-Bridged [1]Ferroceneophane in Supercritical CO_2



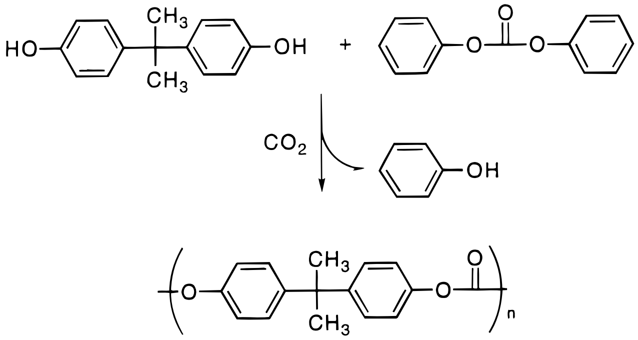
III. Step-Growth Polymerizations

A. Melt-Phase Condensation Polymerizations

There are two features that make melt-phase condensation reactions performed in the presence of supercritical CO_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_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_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_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,[150] but this method requires high capital costs and necessitates maintenance to remain operational for long periods of time on a commercial scale. Because CO_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.

Scheme 9. Synthesis of Polycarbonate from Bisphenol A and Diphenyl Carbonate in the Presence of Supercritical CO_2



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.[151] The latter avoids the use of phosgene and methylene chloride,[152] but the high viscosity of the melt limits the molecular weight attained.[151] In fact, the chain stiffness, which adds to the commercial value of polycarbonates, causes the high viscosity.[153] The utility of supercritical CO_2 in producing high molecular weight polycarbonates by melt polymerization is 2-fold: CO_2 solubilizes the phenol (about 12 wt % at 272 bar and 100 °C)[154] to extract the byproduct, driving the reaction to higher conversion, and plasticizes the polycarbonate[155] to lower its viscosity, facilitating the processing.[151]

Odell studied the melt polymerization of bisphenols (such as bisphenol A, bisphenol P, bisphenol AF, and bisphenol Z) with diphenyl carbonate in CO_2 (see Scheme 9).[151,156] The reactor was first heated to 70 °C to melt the reactants. The system was then filled with CO_2 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 2.2×10^3 to 1.1×10^4 g/mol ($M_w = 4.5 \times 10^3$ to 2.7×10^4 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 CO_2 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 CO_2 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.[151] (Polycarbonate A)-*b*-poly(dimethylsiloxane) was used to produce a microcellular foam in the synthesis of polycarbonate A in CO_2. The authors speculated that a dispersed polymer may allow for more effective removal of phenol because of higher polymer surface area.

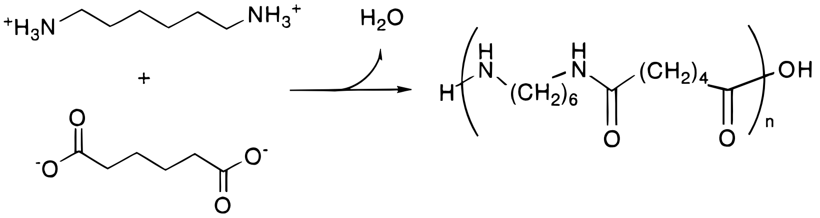
Polycarbonate synthesis from bisphenol A and diphenyl carbonate catalyzed by tetraphenylphosphonium tetraphenyl borate was performed in the presence of supercritical CO_2 by DeSimone.[157,158] The authors noted that although diphenyl carbonate is soluble in CO_2, only a slight excess (1.005 equiv) was 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 CO_2 and heating to 270 °C for 1 h. High molecular weight polymer (up to 1.3×10^4 g/mol) was achieved at 270 °C and 296 bar CO_2. The high solubility of phenol in CO_2 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 CO_2 at 50 °C to 87 °C and up to 600 bar for 12 h, resulted in crystalline polymer.[155] 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 CO_2-induced crystallization results on amorphous polycarbonate chips[157] and demonstrated that the CO_2-crystallized chips could be chain extended to high molecular weight using solid-state polymerization methods. The use of CO_2 could potentially allow the molecular weight of polycarbonate to be increased by solid-state polymerization in supercritical CO_2.

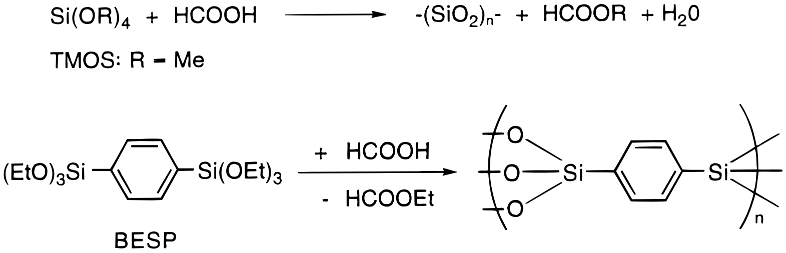
Melt-phase polycondensation reactions are commonly used to prepare poly(ethylene terephthalate) (PET). PET is an important plastic that sees widespread use in fiber, film, and food packaging applications for materials. Bis(hydroxyethyl) terephthalate (BHET) was converted to poly(ethylene terephthalate) (PET) using an Sb_2O_3 catalyst and temperatures of 250−280 °C under a variable flow (2−10 mL/min) of CO_2 at 207 bar.[157,159] Molecular weights produced under these conditions varied from 3×10^3 to 6.3×10^3 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 2×10^4 g/mol).[160] Because the ethylene glycol condensate is soluble in CO_2 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 CO_2 solubility of ethylene glycol is lower than that of phenol (vide supra) and may partially account for the lower effectiveness of supercritical CO_2 in PET synthesis compared to polycarbonate synthesis.

Polyamides have also been synthesized in the melt phase in the presence of supercritical CO_2.[157,158] Because primary amines react with CO_2 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

Scheme 10. Melt-Phase Synthesis of Nylon 6,6



Scheme 11. "Water-Free" Sol−Gel Polymerization Technique Used in Supercritical CO_2



280 °C for 3 h in the presence of 207 bar CO_2, producing a molecular weight of up to 2.45×10^4 g/mol of nylon 6,6. Interestingly, the melting point of the salt in the presence of CO_2 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 CO_2 was investigated.[161] Sol−gel polymerization of tetraalkoxylsilanes and 1,4-bis(triethoxysilyl) benzene (BESP) to give silica aerogels and polysilsesquioxane aerogels, respectively, was performed in supercritical CO_2 (see Scheme 11).

Because CO_2 is a nonpolar medium, sol−gel polymerization in supercritical CO_2 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 $NR_4OH{\cdot}xH_2O$, to form microemulsions of water, catalyst, alkoxysilane, and surfactant in supercritical CO_2 gave only low yields (<10%) of silica or polysilsesquioxanes in the form of precipitates with low surface areas.[161]

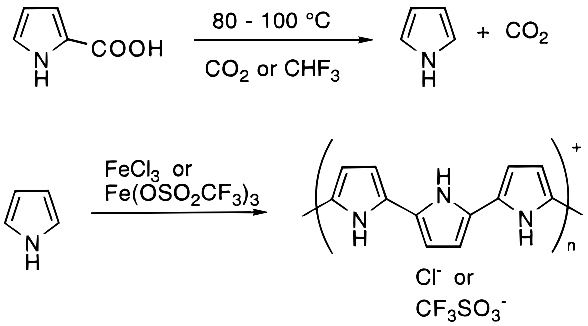
The low miscibility of water and CO_2 was avoided by using the "water free" sol−gel polymerization technique.[164] Alkoxysilanes react with anhydrous formic acid to give silanols that condense to give siloxane bonds necessary for creating a network polymer that will form a gel. The alcohol produced is converted to the formate ester. Supercritical CO_2 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 CO_2 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 CO_2 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 CO_2. 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 m^2/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 m^2/g vs 1000−1600 m^2/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

Scheme 12. Polypyrrole Synthesis by in Situ Monomer Generation



ether. The synthesis of polypyrrole has been extended to SCFs to take advantage of their processing benefits. Polypyrrole was synthesized in supercritical fluoroform and in supercritical CO_2 with in situ pyrrole generation by decarboxylation of 2-carboxypyrrole, which allows control of polymerization onset because elevated temperatures are required (see Scheme 12).[166] The pressure cell was charged with 2-carboxypyrrole 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 CO_2, 2-carboxypyrrole and the chemical oxidant $FeCl_3$ had limited solubility. In contrast, pyrrole and the oxidant $Fe(OTf)_3$ (OTf = $CF_3SO_3^-$) were soluble. Not surprisingly, $Fe(OTf)_3$ gave better results: the $FeCl_3$ catalyst gave yields of 50−60%, where the more soluble $Fe(OTf)_3$ catalyst gave higher yields (87%).

Although it may seem counterintuitive to perform a decarboxylation reaction in high-pressure CO_2, any deleterious effects by CO_2 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 CO_2, higher yields were obtained with higher pressure, indicating that any effects of CO_2 on the decarboxylation are not obvious and that the lower yields are not limited by the decarboxylation step.

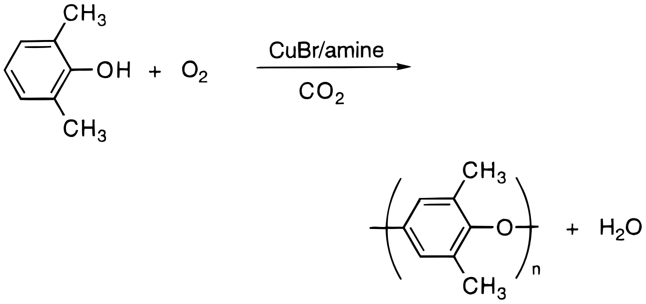
Four-point probe, pressed pellet conductivity measurements were as high as 5×10^{-2} S/cm, a value that is 2−3 orders of magnitude lower than polypyrrole prepared in traditional organic solvents.[167,168] The authors suggest that the lower conductivity is perhaps due to over-oxidation of the conjugated 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 are 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 CO_2. 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.[169] 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 CO_2 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.[169] 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 CO_2 at 45 °C and 241 bar.[169] The solubility of $Fe(OTf)_3$ in CO_2 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 CO_2 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 CO_2 was less effective than organic solvents at removing the reaction byproducts, probably because of their lower solubility in CO_2 compared to methanol. The authors proposed the synthesis of more CO_2-soluble oxidants for use in this process.

Another example of oxidative coupling reactions in supercritical CO_2 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 CO_2 was investigated as a solvent replacement for the synthesis of poly(2,6-dimethylphenylene oxide) (see Scheme 13).[60] Oxygen, which was used as the oxidant in these polymerizations, was miscible with CO_2 under the reaction conditions (25−40 °C, 345 bar). The high-pressure reactor was filled with CO_2, O_2, 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

Scheme 13. Oxidative Coupling of 2,6-Dimethylphenol



acrylate (DMAEA)] and CO_2-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 CO_2-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.[60] 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 1.7×10^4 g/mol). Thus, block copolymers of FOA and styrene were effective stabilizers for the dispersion polymerization of 2,6-dimethylphenol in supercritical CO_2.

IV. Conclusions

The numerous examples presented here demonstrate that supercritical CO_2 is rapidly becoming a viable alternative solvent for polymerizations. Supercritical CO_2 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 CO_2, 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 CO_2 has opened the door for the preparation of a wide range of polymeric materials in this unique solvent.

V. References

(1) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth-Heineman: Stoneham, 1993.
(2) Jessop, P. G.; Ikariya, T.; Noyori, R. *Organometallics* **1995**, *14*, 1510.
(3) Kaupp, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1452.
(4) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945−947.
(5) Barer, S. J.; Stern, K. M. In *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; American Chemical Society: Washington, DC, 1988; p 1.
(6) Quinn, E. L.; Jones, C. L. *Carbon Dioxide*; Reinhold: New York, 1936.
(7) Hyatt, J. A. *J. Org. Chem.* **1984**, *49*, 5097−5101.
(8) Rindfleisch, F.; DiNoia, T.; McHugh, M. A. *Polym. Mater. Sci. Eng.* **1996**, *74*, 178.
(9) Yilgor, I.; McGrath, J. E.; Krukonis, V. J. *Polym. Bull.* **1984**, *12*, 499.
(10) Krukonis, V. *Polym. News* **1985**, *11*, 7−16.
(11) Guan, Z.; Combes, J. R.; Menceloglu, Y. Z.; DeSimone, J. M. *Macromolecules* **1993**, *26*, 2663−2669.
(12) Hoefling, T. A.; Newman, D. A.; Enick, R. M.; Beckman, E. J. *J. Supercrit. Fluids* **1993**, *6*, 165−171.
(13) McFann, G. J.; Johnston, K. P.; Howdle, S. M. *AIChE J.* **1994**, *40*, 543−555.
(14) Pilato, L. A.; Litz, L. M.; Hargitay, B.; Osborne, R. C.; Farnham, A. G.; Kawakami, J. H.; Fritze, P. E.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1975**, *16*, 41.
(15) Fried, J. R.; Li, W. *J. Appl. Polym. Sci.* **1990**, *41*, 1123.
(16) Shah, V. M.; Hardy, B. J.; Stern, S. A. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 313−317.
(17) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 1729.
(18) Rindfleisch, F.; DiNoia, T. P.; McHugh, M. A. *J. Phys. Chem.* **1996**, *100*, 15581−15587.
(19) Shah, V. M.; Hardy, B. J.; Stern, S. A. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 2033−2047.
(20) Dardin, A.; DeSimone, J. M.; Samulski, E. T. *J. Phys. Chem. B* **1998**, *102*, 1775−1780.
(21) Wang, W.-C. V.; Kramer, E. J.; Sachse, W. H. *J. Polym. Sci.: Polym. Phys. Ed.* **1982**, *20*, 1371−1384.
(22) Chiou, J. S.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1985**, *30*, 2633−2642.
(23) Wissinger, R. G.; Paulaitis, M. E. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 2497−2510.
(24) Wissinger, R. G.; Paulaitis, M. E. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 631−633.
(25) Goel, S. K.; Beckman, E. J. *Polymer* **1993**, *34*, 1410−1417.
(26) Condo, P. D.; Paul, D. R.; Johnston, K. P. *Macromolecules* **1994**, *27*, 365−371.
(27) Condo, P. D.; Johnston, K. P. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 523−533.
(28) Kamiya, Y.; Hirose, T.; Mizoguchi, K.; Terada, K. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 1409−1424.
(29) Kamiya, Y.; Mizoguchi, K.; Hirose, T.; Naito, Y. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 879−892.
(30) Handa, Y. P.; Lampron, S.; O'Neill, M. L. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 2549−2553.
(31) Briscoe, B. J.; Kelly, C. T. *Polymer* **1995**, *36*, 3099−3102.
(32) Shieh, Y.-T.; Su, J.-H.; Manivannan, G.; Lee, P. H. C.; Sawan, S. P.; Spall, W. D. *J. Appl. Polym. Sci.* **1996**, *59*, 707−717.
(33) Shieh, Y.-T.; Su, J.-H.; Manivannan, G.; Lee, P. H. C.; Sawan, S. P.; Spall, W. D. *J. Appl. Polym. Sci.* **1996**, *59*, 695−705.
(34) Hsiao, Y.-L.; Maury, E. E.; DeSimone, J. M.; Mawson, S. M.; Johnston, K. P. *Macromolecules* **1995**, *28*, 8159−8166.
(35) Watkins, J. J.; McCarthy, T. J. *Macromolecules* **1994**, *27*, 4845−4847.
(36) Watkins, J. J.; McCarthy, T. J. *Macromolecules* **1995**, *28*, 4067−4074.
(37) Kwag, C.; Gerhardt, L. J.; Khan, V.; Gulari, E.; Manke, C. W. *Polym. Mater. Sci. Eng.* **1996**, *74*, 183.
(38) Garg, A.; Gulari, E.; Manke, C. W. *Macromolecules* **1994**, *27*, 5643.
(39) Mertsch, R.; Wolf, B. A. *Macromolecules* **1994**, *27*, 3289−3294.
(40) Elliott, J. R.; Srinivasan, G.; Dhanuka, M.; Akhaury, R. United States Patent 5,128,382, 1992.
(41) Srinivasan, G.; Elliot, J. R. *Ind. Eng. Chem. Res.* **1992**, *31*, 1414−1417.
(42) Wessling, M.; Borneman, Z.; Van Den Boomgaard, T.; Smolders, C. A. *J. Appl. Polym. Sci.* **1994**, *53*, 1497−1512.
(43) Goel, S. K.; Beckman, E. J. *AIChE J.* **1995**, *41*, 357−367.
(44) Barrett, K. E. J. *Dispersion Polymerization in Organic Media*; John Wiley and Sons: New York, 1975.
(45) Arshady, R. *Colloid Polym. Sci.* **1992**, *270*, 717.
(46) Miller, C. M.; Blythe, P. J.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J. Polym. Sci.: Part A: Polym. Chem.* **1994**, *32*, 2365−2376.
(47) El-Aasser, M. S.; Miller, C. M. In *Polymeric Dispersions: Principles and Applications*; Asua, J. M., Ed.; Kluwer Academic Press: Boston, 1997; Vol. 335, p 109−126.

(48) Candau, F. In *Polymeric Dispersions: Principles and Applications*; Asua, J. M., Ed.; Academic Press: Boston, 1997; Vol. 335, p 127.

(49) Kumar, D.; Butler, G. B. *J.M.S. − Rev. Macromol. Chem. Phys.* **1997**, *C37*, 303−333.

(50) Sudol, E. D. In *Polymeric Dispersions: Principles and Applications*; Asua, J. M., Ed.; Kluwer Academic Press: Boston, 1997; Vol. 335, p 141−153.

(51) Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic Press: London, 1995.

(52) Dardin, A.; Cain, J. B.; DeSimone, J. M.; Johnson, J., C. S.; Samulski, E. T. *Macromolecules* **1997**, *30*, 3593−3599.

(53) Fitch, R. M. *Macromol. Symp.* **1995**, *92*, 1−11.

(54) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592−599.

(55) Cooper, A. I.; Hems, W. P.; Holmes, A. B. *Macromol. Rapid Commun.* **1998**, *19*, 353−357.

(56) Adamsky, F. A.; Beckman, E. J. *Macromolecules* **1994**, *27*, 312.

(57) DeSimone, J. M. International Patent Application PCT/US93/01626, 1993.

(58) Guan, Z.; Combes, J. R.; Elsbernd, C. S.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 446−447.

(59) Ehrlich, P. *Chemtracts: Org. Chem.* **1993**, *6*, 92−94.

(60) Kapellen, K. K.; Mistele, C. D.; DeSimone, J. M. *Macromolecules* **1996**, *29*, 495−496.

(61) van Herk, A. M.; Manders, B. G.; Canelas, D. A.; Quadir, M.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 4780−4782.

(62) Ryan, J.; Erkey, C.; Shaw, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38*, 428−429.

(63) Canelas, D. A.; DeSimone, J. M. *Adv. Polym. Sci.* **1997**, *133*, 103−140.

(64) Hagiwara, M.; Mitsui, H.; Machi, S.; Kagiya, T. *J. Polym. Sci: Part A-1* **1968**, *6*, 603−608.

(65) Hagiwara, M.; Mitsui, H.; Machi, S.; Kagiya, T. *J. Polym. Sci.: Part A-1* **1968**, *6*, 609−621.

(66) Kagiya, T.; Machi, S.; Hagiwara, M.; Kise, S. United States Patent 3,471,463, 1969.

(67) Company, S. C. French Patent 1,524,533, 1968.

(68) Fukui, K.; Kagiya, T.; Yokota, H.; Toriuchi, Y.; Kuniyoshi, F. United States Patent 3,522,228, 1970.

(69) Van Bramer, D. J.; Shiflett, M. B.; Yokozeki, A. United States Patent 5,345,013, 1994.

(70) Romack, T. J.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 8429−8431.

(71) DeYoung, J. P.; Romack, T. J.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38*, 424−425.

(72) Romack, T. J.; Kipp, B. E.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 8432−8434.

(73) Consani, K. A.; Smith, R. D. *J. Supercrit. Fluids* **1990**, *3*, 51−65.

(74) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: New York, 1983.

(75) Peck, D. G.; Johnston, K. P. *J. Phys. Chem.* **1993**, *97*, 5661−5667.

(76) Peck, D. G.; Johnston, K. P. *Macromolecules* **1993**, *26*, 1537−1545.

(77) O'Neill, M. L.; Yates, M. Z.; Harrison, K. L.; Johnston, K. P.; Canelas, D. A.; Betts, D. E.; DeSimone, J. M.; Wilkinson, S. P. *Macromolecules* **1997**, *30*, 5050−5059.

(78) Yates, M. Z.; O'Neill, M. L.; Johnston, K. P.; Webber, S.; Canelas, D. A.; Betts, D. E.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 5060−5067.

(79) Meredith, J. C.; Johnston, K. P. *Macromolecules* **1998**, *31*, 5507−5517.

(80) Meredith, J. C.; Johnston, K. P. *Macromolecules* **1998**, *31*, 5518−5528.

(81) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. R.; Combes, J. R. *Science* **1994**, *265*, 356−359.

(82) Hsiao, Y.-L.; Maury, E. E.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 190−191.

(83) Hsiao, Y.-L.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)* **1996**, *74*, 260.

(84) Hsiao, Y.-L.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2009.

(85) Gorner, T.; Dellacherif, J.; Perut, M. *J. Chromatogr.* **1990**, *514*, 309−316.

(86) Rosselli, A. C.; Boyer, D. S.; Houck, R. K. *J. Chromatogr.* **1989**, *465*, 11−15.

(87) Leichter, E.; Strode, J. T. B., III; Taylor, L. T.; Schweighardt, F. K. *Anal. Chem.* **1996**, *68*, 894−898.

(88) Raynie, D. E.; Delaney, T. *J. Chromatogr. Sci.* **1994**, *32*, 298−300.

(89) Kordikowski, A.; Robertson, D. G.; Poliakoff, M. *Anal. Chem.* **1996**, *68*, 4436−4440.

(90) Shaffer, K. A.; Jones, T. A.; Canelas, D. A.; DeSimone, J. M.; Wilkinson, S. P. *Macromolecules* **1996**, *29*, 2704.

(91) O'Neill, M. L.; Yates, M. Z.; Johnston, K. P.; Smith, C. D.; Wilkinson, S. P. *Macromolecules* **1998**, *31*, 2848−2856.

(92) O'Neill, M. L.; Yates, M. Z.; Johnston, K. P.; Smith, C. D.; Wilkinson, S. P. *Macromolecules* **1998**, *31*, 2838−2847.

(93) Paine, A. J. *Macromolecules* **1990**, *23*, 3109−3117.

(94) Lepilleur, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 745−756.

(95) Canelas, D. A.; Betts, D. E.; DeSimone, J. M. *Macromolecules* **1996**, *29*, 2818.

(96) Canelas, D. A.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 5673−5682.

(97) Harrison, K. L.; da Rocha, S. R. P.; Yates, M. Z.; Johnston, K. P.; Canelas, D. A.; DeSimone, J. M. *Langmuir* **1998**, *14*, 6855−6863.

(98) Canelas, D. A. Ph.D. Thesis, University of North Carolina at Chapel Hill, 1997.

(99) Canelas, D. A.; Betts, D. E.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38*, 628−629.

(100) Canelas, D. A.; Betts, D. E.; DeSimone, J. M.; Yates, M. Z.; Johnston, K. P. *Macromolecules* **1998**, *31*, 6794−6805.

(101) Adamsky, F. A.; Beckman, E. J. *Macromolecules* **1994**, *27*, 5238.

(102) Maury, E. E.; Batten, H. J.; Killian, S. K.; Menceloglu, Y. Z.; Combes, J. R.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 664−665.

(103) Fulton, J. L.; Pfund, D. M.; McClain, J. B.; Romack, T. R.; Maury, E. E.; Combes, J. R.; Samulski, E. T.; DeSimone, J. M.; Capel, M. *Langmuir* **1995**, *11*, 4241−4249.

(104) Newman, D. A.; Hoefling, T. A.; Beitle, R. R.; Beckman, E. J.; Enick, R. M. *J. Supercrit. Fluids* **1993**, *6*, 205−210.

(105) Singley, E. J.; Liu, W.; Beckman, E. J. *Fluid Phase Equilib.* **1997**, *128*, 199−219.

(106) Harrison, K.; Goveas, J.; Johnston, K. P.; O'Rear, I., E. A. *Langmuir* **1994**, *10*, 3536−3541.

(107) Johnston, K. P.; Harrison, K. L.; Clarke, M. J.; Howdle, S. M.; Heitz, M. P.; Bright, F. V.; Carlier, C.; Randolph, T. W. *Science* **1996**, *271*, 624.

(108) Bartscherer, K. A.; Minier, M.; Renon, H. *Fluid Phase Equilib.* **1995**, *107*, 93.

(109) McFann, G. J.; Johnston, K. P. In *Microemulsions: Fundamental and Applied Aspects*; Kumar, P., Mittal, K. L., Eds.; Dekker: New York, 1999, in press.

(110) Watkins, J. J.; McCarthy, T. J. *Polym Mater Sci Eng* **1996**, *74*, 402.

(111) Rajagopalan, P.; McCarthy, T. J. *Macromolecules* **1998**, *31*, 4791−4797.

(112) Kung, E.; Lesser, A. J.; McCarthy, T. J. *Macromolecules* **1998**, *31*, 4160−4169.

(113) Higashimura, T.; Sawamoto, M.; Miyamoto, M. *Macromolecules* **1984**, *17*, 265.

(114) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111.

(115) Winstein, S.; Chippinger, B.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597.

(116) Biddulph, R.; Plesch, P. *J. Chem. Soc.* **1960**, 3913.

(117) Yokota, H.; Kondo, M.; Kagiya, T.; Fukui, K. *J. Polym. Sci.: Part A-1* **1968**, *6*, 425−434.

(118) Yokota, H.; Kondo, M.; Kagiya, T.; Fukui, K. *J. Polym. Sci.: Part A-1* **1968**, *6*, 435−446.

(119) Yokota, H.; Kondo, M.; Kagiya, T.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1412−1416.

(120) Kagiya, T.; Kondo, M.; Narita, K.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1688−1693.

(121) Pernecker, T.; Kennedy, J. P. *Polym. Bull. (Berlin)* **1994**, *32*, 537−543.

(122) Pernecker, T.; Kennedy, J. P. *Polym. Bull. (Berlin)* **1994**, *33*, 13−19.

(123) Deák, G.; Pernecker, T.; Kennedy, J. P. *Polym. Bull. (Berlin)* **1994**, *33*, 259−265.

(124) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991.

(125) Dainton, F. S.; Ivin, K. J. *Trans. Faraday Soc.* **1950**, *46*, 331.

(126) Wall, L. A. *SPE J.* **1960**, 810.

(127) Maslinka-Solich, J.; Chemir, M.; Marek, M. *Collect. Czech. Chem. Commun.* **1969**, *34*, 2611.

(128) Noro, Y.; Fueki, K.; Kuri, Z. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1894.

(129) Kennedy, J. P.; Pernecker, T. United States Patent 5,376,744, 1994.

(130) Deák, G.; Pernecker, T.; Kennedy, J. P. *Macromol. Rep.* **1995**, *A32*, 979−984.

(131) Pernecker, T.; Deak, G.; Kennedy, J. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 243−244.

(132) Pernecker, T.; Deak, G.; Kennedy, J. P. *Macromol. Rep.* **1995**, *A32*, 969−978.

(133) Clark, M. R.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 482−483.

(134) Clark, M. R.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 3002−3004.

(135) Clark, M. R.; Kendall, J. L.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 6011−6014.

(136) Mistele, C. D.; Thorp, H. H.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 507−508.

(137) Mistele, C. D.; Thorp, H. H.; DeSimone, J. M. *J. Macromol. Sci. A* **1996**, *33*, 953−960.

(138) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858.

(139) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.

(140) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(141) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(142) Fürstner, A.; Koch, D.; Langemann, K.; Leitner, W.; Six, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2466−2469.

(143) Darensbourg, D. J.; Stafford, N. W.; Katsurao, T. *J. Mol. Catal. A: Chem.* **1995**, *104*, L1−L4.

(144) Darensbourg, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)* **1996**, *74*, 431−432.

(145) Costello, C. A.; Berluche, E.; Han, S. J.; Sysyn, D. A.; Super, M. S.; Beckman, E. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)* **1996**, *74*, 430.

(146) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

(147) Pittman, C. U.; Yukihiko, S. *Chem. Lett.* **1975**, 383.

(148) Neuse, E. W.; Bednarik, L. *Macromolecules* **1979**, *12*, 187.

(149) Christian, P.; Howdle, S. M.; Gügel, A.; Manners, I.; Massey, J. *Polym. Prepr.* **1997**, *38*, 434−435.

(150) Canelas, D. A.; Burke, A. L.; DeSimone, J. M. *Plastics Engineering* **1997**, *53*, 37−40.

(151) Odell, P. G.; Hamer, G. K. *Polym. Prepr.* **1997**, *38*, 470−471.

(152) Romano, U.; Tesei, R.; Mauri, M. M.; Rebora, P. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 396−403.

(153) Sundararajan, P. R. *Macromolecules* **1989**, *22*, 2149−2154.

(154) Hedrick, J. L.; Mulcahey, L. J.; Taylor, L. T. *ACS Symp. Ser.* **1992**, *488*, 206−220.

(155) Beckman, E.; Porter, R. S. *J. Polym. Sci. B* **1987**, *25*, 1511−1517.

(156) Odell, P. G. United States Patent 5,698,665, 1997.

(157) Burke, A. L. C.; Givens, R. D.; Jikei, M.; DeSimone, J. M. *Polym. Prepr.* **1997**, *38*, 387−388.

(158) Givens, R. D.; Jikei, M.; DeSimone, J. M. *Polym. Prepr.* **1997**, *38*, 468−469.

(159) Burke, A. L. C.; Maier, G.; DeSimone, J. M. *Polym. Mater. Sci. Eng.* **1996**, *74*, 248−249.

(160) Tate, S. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 8, p 6106.

(161) Loy, D. A.; Russick, E. M.; Yamanaka, S. A.; Baugher, B. M.; Shea, K. J. *Chem. Mater.* **1997**, *9*, 2264−2268.

(162) Fricke, J. *Springer Proc. Phys.* **1986**, *6*, 2−19.

(163) Hrubesh, L. W. *Chem. Ind.* **1990**, 824−827.

(164) Sharp, K. G. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 35−41.

(165) Loy, D. A.; Shea, K. J.; Russick, E. M. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 699−704.

(166) Kerton, F. M.; Lawless, G. A.; Armes, S. P. *J. Mater. Chem.* **1997**, *7*, 1965−1966.

(167) Myers, R. E. *J. Electron. Mater.* **1986**, *2*, 61.

(168) Maeda, S.; Armes, S. P. *J. Mater. Chem.* **1994**, *4*, 935.

(169) Fu, Y.; Palo, D. R.; Erkey, C.; Weiss, R. A. *Macromolecules* **1997**, *30*, 7611−7613.

(170) Handa, Y. P.; Capowski, S.; O'Neill, M. *Thermochim. Acta* **1993**, *226*, 177−185.

(171) Banerjee, T.; Lipscomb, G. G. *J. Appl. Polym. Sci.* **1998**, *68*, 1441−1449.

(172) Zhang, Y.; Gangwani, K. K.; Lemert, R. M. *J. Supercrit. Fluids* **1997**, *11*, 115−134.

(173) Kamiya, Y.; Mizoguchi, K.; Terada, K.; Fujiwara, Y.; Wang, J.-S. *Macromolecules* **1998**, *31*, 472−478.

(174) Kato, S.; Tsujita, T.; Yoshimizu, H.; Kinoshita, T.; Higgins, J. S. *Polymer* **1997**, *38*, 2807−2811.

(175) Mokdad, A.; Dubault, A.; Monnerie. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 2723−2730.

(176) Yong, T.-M.; Hems, W. P.; van Nunen, J. L. M.; Holmes, A. B.; Steinke, J. H. G.; Taylor, P. L.; Segal, J. A.; Griffin, D. A. *Chem. Commun. (Cambridge)* **1997**, *18*, 1811−1812.

(177) Canelas, D. A.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37*, 542−543.

CR9700336