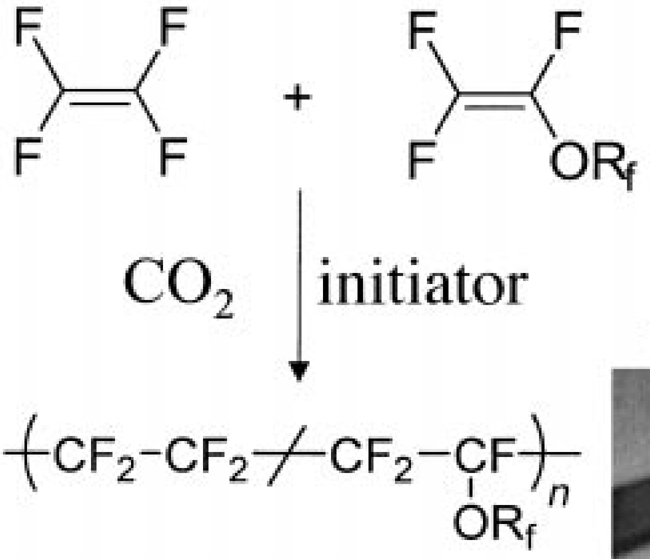
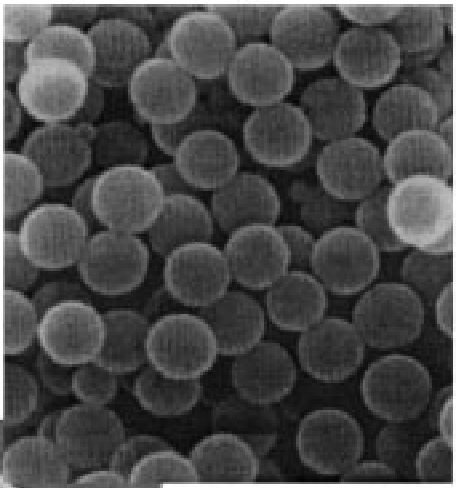
CO_2 Technology

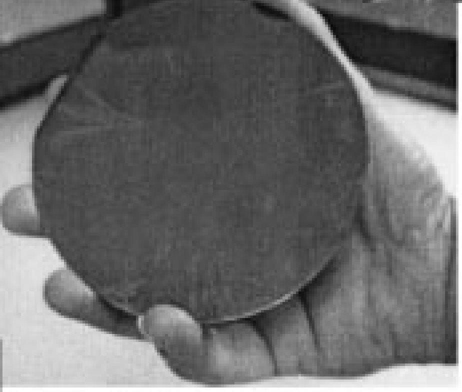
synthesis of fluoropolymers in $scCO_2$



dispersion polymerization

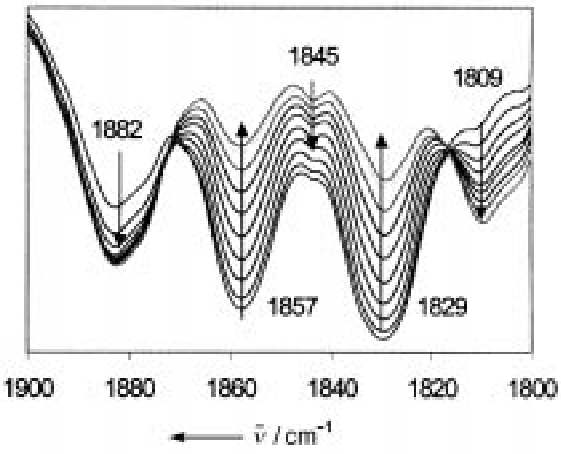


spin-coating from liquid CO_2



crystallization of polycarbonates with $scCO_2$

the decomposition kinetics of perfluoralkyl diacyl peroxides in $scCO_2$



Sustainable Pollution Prevention

ANGEWANDTE CHEMIE

CO_2 Technology Platform: An Important Tool for Environmental Problem Solving**

Sharon L. Wells and Joseph DeSimone*

CO_2 is a good solvent for many substances when compressed into its liquid or supercritical fluid state. Above the critical temperature and critical pressure ($T_c = 31\,^\circ C$, $P_c = 73.8$ bar, see Figure 1 for the phase diagram for CO_2), CO_2 has both gaslike viscosities and liquidlike densities. These moderate critical conditions allow CO_2 to be used within safe commercial and laboratory operating conditions. Small changes in temperature and pressure cause dramatic changes in the density, viscosity, and dielectric properties of CO_2, making it a tunable solvent that can be tailored for various applications. Combined, these unique properties make CO_2 a "solvent of choice" for the new millennium.

Keywords: carbon dioxide · micelles · polymers · supercritical fluids · surfactants

1. Introduction

Rapid technological advances have presented many complex ecological issues. As a result, pollution prevention and waste management represent two of the most profound challenges of the 21st century. The proliferation of the use of organic solvents, halogenated solvents, and precious water in manufacturing and processing industries, such as electronics, pharmaceuticals, dyes, and coatings, has created the right atmosphere for the creation and development of environmentally responsible and energy efficient processes. In the past decade, in an effort to meet these challenges, research groups have focused on making liquid and supercritical carbon dioxide ($scCO_2$) a viable solvent alternative. This pollution-prevention approach is much more sustainable and appropriate than the "end-of-pipe" approach embodied in many waste-management methods.

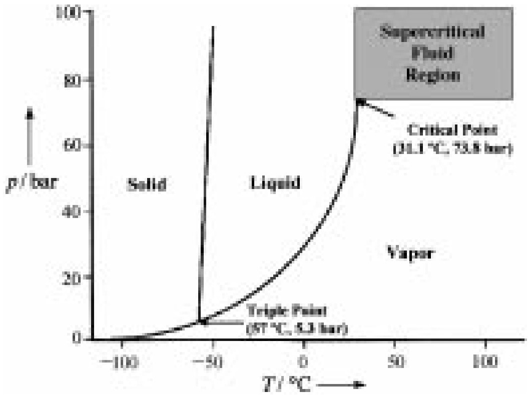


Figure 1. One-component phase diagram for CO_2.

Carbon dioxide is a natural solvent (phase diagram in Figure 1) that could replace water and many other solvents in many applications. CO_2 is advantageous because it is inexpensive, nonflammable, environmentally benign, and can be completely and easily removed from products.[1] CO_2 is also naturally occurring and readily available; it can be found in natural reservoirs and is a by-product from the production of ammonia, ethanol, hydrogen, and natural gases.[2, 3] CO_2 is routinely handled on a commercial scale using pressurized and refrigerated tanks for storage and processing liquid CO_2 and cylinders for compressed CO_2 gas. When released to the atmosphere, liquid CO_2 leaves no residue to contaminate either the environment or personnel.[2]

Processes that use CO_2 do not add directly to the greenhouse effect (global warming caused by the entrapment of heat into the atmosphere by gases that are emitted into the environment) but rather aid in the reduction of emitted CO_2. Most of the CO_2 sold today (82 %) is a by-product from other industries.[4] In addition to environmental benefits, CO_2-based processes can also be more energy efficient than those based on water or conventional solvents. The low heat of vapor-

---

[*] Prof. J. DeSimone,[+] S. L. Wells
Department of Chemistry
CB 3290, Venable and Kenan Laboratories
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599 (USA)
Fax: (+1) 919-962-5467
E-mail: desimone@unc.edu

[+] Department of Chemical Engineering, North Carolina State University
P.O. Box 7905, Raleigh, NC, 27695-7905 (USA)

[**] A list of abbreviations can be found at the end of the article.

1433-7851/01/4003-0519 $ 17.50+.50/0

ization of CO_2 significantly reduces the energy costs that are associated with water-intensive processing industries and also eliminates the inevitable contamination problems associated with the pollution of water effluent streams.

The highly versatile nature of CO_2 has been exploited in numerous industries and applications. CO_2 has been used for decades for food freezing and for pH control in the textile and pulp-and-paper industries.[2] Commercialized in the 1970s as a "natural" extractant in decaffeination processes, coffee, tea, and spice industries have used $scCO_2$ to replace dichloromethane and ethylene dichloride.[5] In 1997, Ford Motor Company switched some of their bumper-coating processes from hazardous solvent-based paints and primers to utilize CO_2 technology.[6] More recently, Micell Technologies has commercialized an innovative process wherein molecular-engineered surfactant molecules, combined with CO_2, provide an environmentally friendly alternative to the traditionally hazardous solvents used today, such as perchloroethylene (PERC).[7]

A steady stream of emerging technologies has brought CO_2 all the way from a potential alternative solvent in the early 1970s, to its ever growing present day use in many industries and applications. The most recent example is DuPont's announcement to build a $275 million dollar manufacturing plant that will employ carbon dioxide technology to produce Teflon and other fluoropolymers.[8]

This review will discuss the technology platform that allows CO_2 to be an environmental problem-solving tool for sustainable economic growth.

2. From Polymer Synthesis to Molecular-Engineered Surfactants

Although CO_2 is a good solvent for many small molecules, most polymeric materials have a very low solubility in CO_2.[9] This presents major limitations for the applicability of CO_2 in many processes. These limitations lead researchers to the design and synthesis of molecules that would bring CO_2 into a new application areas.

2.1. Homogeneous Fluoropolymer Synthesis

Only two classes of polymers are significantly soluble in CO_2 at practical operating conditions; these are amorphous (and low melting) fluoropolymers and polysiloxanes[1, 10, 11] (for other in-depth studies on polymer solubility in CO_2, see refs. [12] and[13]). DeSimone et al. were the first to report a homogeneous free radical polymerization using a semi-fluorinated acrylate monomer in $scCO_2$.[11] This milestone led to the homogeneous synthesis of many other fluorinated polymers including poly(2-(*N*-ethylperfluorooctanesulfonamido) ethyl acrylate), poly(1,1-dihydroperfluorooctyl acrylate), and poly(perfluoroethyleneoxymethylstyrene).[14–17]

The polymerization of tetrafluoroethylene to PTFE in CO_2 is of particular importance because it emphasizes a safe new route to fluorolefin polymers. Conventional routes to fluoropolymers typically employ aqueous or chlorofluorocarbon (CFC) based solvent systems that do not have readily abstractable hydrogen atoms, which leads to premature chain termination. Aqueous based processes also generally produce carboxylic acid and acid fluoride end groups that can only be removed by expensive steps, such as high-temperature hydrolysis or fluorination. The Montreal Protocol banned the use of CFCs because of their deteriorating effect on the earth's ozone layer.[18] CO_2 provides several advantages; no production of unstable end groups, elimination of expensive energy-intensive heating and fluorination steps, and easy separation of the polymer from solution. (For a more detailed review of the synthesis of fluoropolymers in CO_2 see refs. [16–18].)

Joseph M. DeSimone was born in 1964 in Norristown, Pennsylvania. He received his B.S. degree in chemistry in 1986 from Ursinus College in Collegeville, Pennsylvania and his Ph.D. degree in 1990 from the Department of Chemistry at Virginia Polytechnic Institute and State University where he worked with Professor James E. McGrath. He joined the Department of Chemistry at the University of North Carolina at Chapel Hill (UNC-CH) in July 1990, as an Assistant Professor. The University named Dr. DeSimone as the Mary Ann Smith Professor of Chemistry in 1995. In 1995, he was also appointed as a Professor in the Department of Chemical Engineering at North Carolina State University (NCSU). On July 1, 1999, Professor DeSimone was named the William R. Kenan, Jr. Distinguished Professor of Chemistry at UNC-CH and Chemical Engineering at NCSU. His research efforts are focused on developing synthetic pathways for polymer synthesis and processing in liquid and supercritical carbon dioxide. In 1992, he was a recipient of a National Science Foundation Young Investigator Award and in 1993 he was honored by the White House with his naming as a Presidential Faculty Fellow, one of the only thirty given nationally to young faculty members in science and engineering. In 1996, Professor DeSimone co-founded MICELL Technologies, INC, a start-up company focused on using detergent-modified carbon dioxide as an environmentally responsible replacement for organic and halogenated solvents used in a variety of applications ranging from precision cleaning of microelectronics to garment dry cleaning. In 1997, the White Housed honored Professor DeSimone again with his selection to receive the 1997 Presidential Green Chemistry Award. In 1999, Professor DeSimone was awarded the American Chemical Society's Carl S. Marvel Creative Polymer Chemistry Award. Joe, his wife Suzanne, their son Phillip and daughter Emily, reside in Chapel Hill, North Carolina.

2.2. Molecular-Engineered Surfactants

Fluoropolymers and siloxanes represent a very small fraction of the industrially important polymers; therefore, surfactants are needed to broaden the efficacy of liquid and supercritical CO_2 to include the synthesis of other polymers using heterogeneous polymerization methods. Just as surfactants are important to aqueous technologies, surfactants are also the key to extractions, coatings, cleaning, drug delivery, and heterogeneous polymerizations in CO_2. The lack of commercially available CO_2 surfactants led researchers to develop CO_2 soluble amphiphilic block-copolymer surfactants that incorporated "CO_2 philic" fluorinated or siloxane components and "CO_2 phobic" hydrophilic or lipophilic components.

2.2.1. Fluoroacrylate-Based Polymeric Surfactants

As a result of the inherent incompatibility of the fluorocarbon monomers with other synthetic methods, controlled free radical polymerization techniques were the first to be employed for the synthesis of the amphiphilic block copolymers for use in CO_2-based systems. Because of the insolubility of most fluoropolymers in common organic solvents and the presence of some special features in several fluorinated monomers (e.g. two acidic hydrogens on the methylene adjacent to the ester group in 1,1,2,2-tetrahydroperfluorooctyl acrylate (TAN)), controlled free radical polymerization methods appeared to be the most versatile available. Specifically iniferter polymerization[19] and atom-transfer radical polymerization (ATRP)[20] techniques were implemented for the synthesis of the block copolymers.

The iniferter technique has been used to synthesize a wide range of hydrophilic, lipophilic, and fluorocarbon polymers including poly(2-dimethylaminoethyl methacrylate) (PDMAEMA), polystyrene (PS), poly(vinyl acetate) (PVAc), poly(1,1-dihydroperfluorooctyl acrylate) (PFOA), and 1*H*,1*H*-perfluorooctyl methacrylate (PFOMA).[21, 22] While ATRP is not as widely applicable to as many monomers as the iniferter technique, ATRP does give much more controlled and well-defined polymers. ATRP has been shown to be effective in synthesizing polymers derived from acrylates, methacrylates, and styrenics as well as fluorocarbon monomers such as FOMA, FOSEA, FOSEMA, and TAN.[22] Additionally, Xia et al. recently demonstrated the synthesis of PFOA using ATRP in $scCO_2$.[23] Several hydrocarbon–fluorocarbon diblock copolymers synthesized by these techniques are listed in Table 1.

Table 1. Hydrocarbon–fluorocarbon diblock copolymers.

Hydrocarbon block	M_n [kg mol^{-1}]	PDI[a]	Fluorocarbon block	M_n [kg mol^{-1}]	Techniques
PS	3.7	1.7	PFOA	39.8	Iniferter
PS	6.6	1.8	PFOMA	42.3	Iniferter
PVAc	4.4	1.6	PFOA	43.1	Iniferter
PMMA	8.1	1.3	PFOMA	55.9	ATRP
P(*t*BuAc)	5.0	1.6	PFOMA	52.6	ATRP
PHEMA	4.0	1.5	PFOMA	40.0	ATRP

[a] PDI = polydispersity index.

2.2.2. Characterization of Fluoroacrylate Polymeric Surfactants

When amphiphilic copolymers are placed in a solvent that is selectively good for one block and a non-solvent for the other, they tend to self-assemble to form micelles in solution. Extending this concept to CO_2 systems, the formation of micelles should occur in a CO_2 medium, where the micellular core is CO_2-phobic, and the CO_2-philic corona extends into the solvent. The limited solubility of fluorinated polymers in ordinary organic solvents prevents the use of conventional methods for polymer characterization; therefore high-pressure scattering and NMR spectroscopic techniques are employed to study copolymer micelles in solution.[24–32] Small angle neutron (SANS) and X-ray (SAXS) scattering methods have provided valuable information on the conformational properties of polymeric surfactants in CO_2. In particular, extensive SANS and SAXS measurements were performed on poly(ethylene oxide)-*g*-PFOA, and PS-*b*-PFOA samples in CO_2 over a range of temperatures and pressures.[24]

Experiments were performed on a PEO-*g*-PFOA sample at 60 °C and three different pressures (470, 300, and 255 bar) in CO_2 in the presence of water, with a water/surfactant ratio of 0.32/1. The oscillatory nature of the scattering curves indicated the formation of spherical core–shell micelles. A depiction of a spherical micelle of PFOA-*g*-PEO with the collapsed PEO chains and water molecules within the core is shown in Figure 2. From core–shell-model fits to the scattering curves, the outer radii of the aggregates were found to be approximately 125 Å and the polydispersities were relatively low. Measurements were also performed on the polymer in CO_2 in the absence of water which showed that the micelle dimensions were smaller. The radius of gyration taken from a core–shell fit increased from ~56 Å (no added water) to 86 Å (H_2O swollen) and 136 Å (D_2O swollen).

The scattering curves from PS-*b*-PFOA in CO_2 also confirmed that core–shell spherical micelles are formed. SANS characterization of micelles with added hydrogenated and deuterated PS oligomer showed >99 % of the added oligomer was stabilized in the core of the micelle.[27] The micellar core volume increased with added oligomer as a function of oligomer concentration (Figure 3). There was approximately an eight-fold increase in the volume of the micelle core with the addition of up to 20 % (w/w) oligomer.

Chu and Zhou[25] and Buhler et al.[30] were the first to use high-pressure light-scattering methods to study the micellization and critical micelle density (CMD, a reversible unimer-to-micelle transition upon a decrease in CO_2 solvent density). Aided by high-power lasers, static and dynamic light scattering (DLS) methods have also proven to be powerful, reliable, and readily assessable techniques to study the characteristics of polymers in CO_2. Very detailed studies of PVAc-*b*-PFOA and PVAc-*b*-PTAN copolymers, both of which exhibited the CMD transition, were recently reported in the literature.[30]

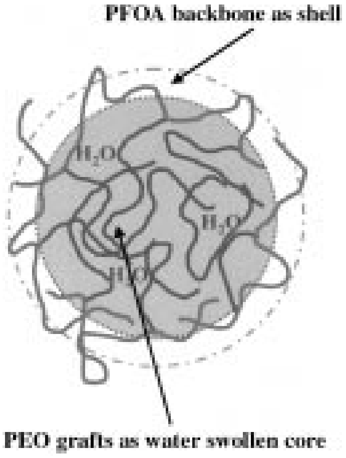


Figure 2. Proposed Structure of a PFOA-*g*-PEO graft copolymer micelle in supercritical CO_2.

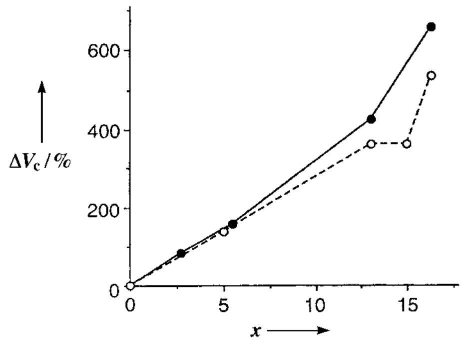


Figure 3. Swelling of 3.7^k-*b*-39.8^k surfactant micelles in CO_2 (65 °C, 340 bar) with PS oligomers. Surfactant concentration = 4% (w/v). ΔV_c = change in core volume, x = PS oligomer concentration; ● = H-Oligomer, ○ = D-Oligomer.

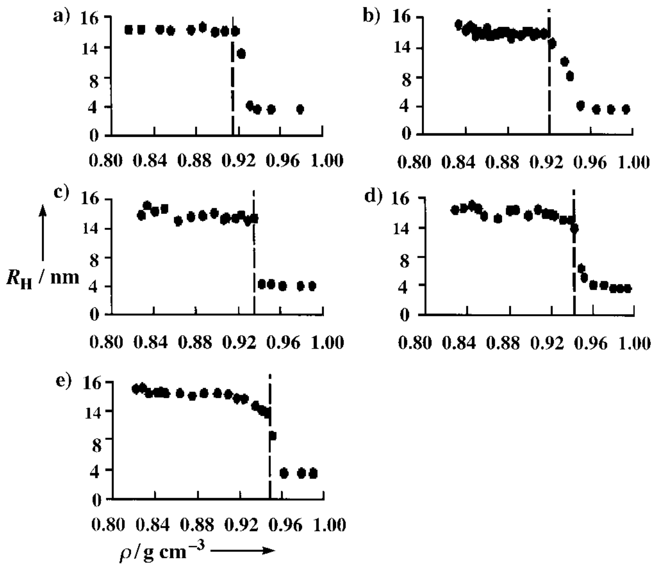


Figure 4. Effect of the CO_2 density (ρ) on the hydrodynamic radius for a copolymer concentration c: a) 1.88×10^{-3} g cm^{-3}, b) 3×10^{-3} g cm^{-3}, c) 6×10^{-3} g cm^{-3}, d) 1.125×10^{-2} g cm^{-3}, e) 2×10^{-2} g cm^{-3} at temperature T = 45 °C. Dashed lines indicate the onset of the micelles → unimers transition.

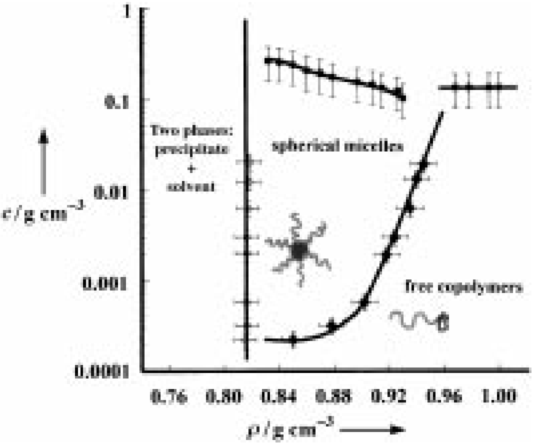


Figure 5. Phase diagram in the copolymer concentration (c) and the CO_2 density (ρ) plane at a fixed temperature T = 45 °C. (○) cloud line (solubility line), (◆) spherical micelles → unimers transition, and (●) overlap concentration c^*.

Figure 4 shows the hydrodynamic size plotted against CO_2 density for 10.3 ^{k}PVAc-*b*- 60.4 ^{k}PTAN solution (where the numbers refer to the molar mass of the particular block in 10^3 g mol^{-1} units). In the low-density range 15 nm spherical micelles are found, as the density increases, the CMD transition region is reached leading into the 3–4 nm unimer region. In addition to showing the CMD, the DLS data was used to show the coexistence of unimers and micelles in the transition region. This coexistence prompted the construction of a copolymer–surfactant/CO_2 binary phase diagram (Figure 5). Three regions on the phase diagram can be identified a) a two phase region at CO_2 densities below 0.82 g cm^{-3} where the polymer was insoluble, resulting in phase separation into polymer rich and solvent rich phases, b) a region of spherical micelles at intermediate CO_2 densities, c) a unimer region at high densities. The coexistence line connecting the micelle and unimer phases not only indicates the CMD at constant copolymer concentrations, but also the CMC at a particular CO_2 density.

2.2.3. Polysiloxane-Based Surfactants

The use of silicone-based surfactants for applications in CO_2 technology is more attractive than the use of fluorinated materials for a number of reasons. The synthesis of siloxane-based stabilizing systems is cheaper and they are more soluble in conventional solvents which facilitates characterization. Additionally, these surfactants can be synthesized by anionic polymerization methods leading to narrow molecular-weight distributions. Several groups have studied polysiloxanes in CO_2 and reported the high solubility of these materials.[33, 34] Hoefling et al. have designed and synthesized silicone-based amphiphiles and explored the relationship between structure and solubility by phase-behavior experiments.[35] More recently, the design and synthesis of silicone containing "ambidextrous" surfactants was reported by Yates and coworkers.[36] The surfactants synthesized were a poly(dimethylsilozane)-*b*-poly(methacrylic acid) and a poly(dimethylsiloxane)-*g*-pyrrolidonecarboxylic acid. These surfactants (as discussed in section 3.2) demonstrated the ability to stabilize an organic latex in either a nonpolar medium, dense liquid CO_2 (CO_2 with a density of $>1.0\,g\,cm^{-3}$), or water.

2.2.4. *Perfluoropolyether Surfactants*

In 1985 Krukonis reported the solubility of perfluorinated polyethers in carbon dioxide, an observation made while conducting fractionation studies on a commercially available high molecular weight perfluoropolyether oil.[1] This polymer was fractionated at 80 °C over a pressure range from 82 bar to 275 bar. Since then, a considerable amount of research has focused on the design and synthesis of fluoroether functional surfactants. Hoefling and colleagues demonstrated the high CO_2 solubility of two nonionic perfluoropolyether surfactants, hydroxyaluminum bis(poly(hexafluoropropylene oxide)carboxylate) and poly(hexafluoropropylene oxide)carboxylic acid, and an anionic surfactant, sodium poly(hexafluoropropylene oxide)carboxylate.[37] The twin-tail surfactant was selected for its potential usefulness as a CO_2-thickener, but no appreciable increase in the solution viscosity was observed.

Fluorinated polyether surfactants have been prepared for CO_2-based applications such as heavy-metal extraction, dispersion polymerizations, and protein extraction.[38] In the case of heavy-metal extraction, a perfluoropolyether containing a dithiol end group has been synthesized and found to extract as much as 98% of mercury from contaminated soil in laboratory-scale CO_2 extractions. It was determined that over 90% of the total extraction occurred during the first hour. Other functionalities have been incorporated in the polymer chains for use as chelating agents and a review of these materials can be found elsewhere.[39] (For more details on surfactants, surfactant synthesis and characterization in CO_2 see the review by Carson et al.[40])

3. Surfactant-Aided Polymerizations

Without the aid of surfactants or stabilizing agents, at a critical chain length, CO_2-phobic polymers will precipitate from a CO_2 solution during synthesis. Many precipitation polymerizations are carried out in this fashion, producing commercially important, melt-processible polymers;[41, 42] however, for amorphous polymers this method typically results in both undefined morphologies and low degrees of polymerization.[43] As an alternative approach amphiphilic copolymers of the nature described above (Section 2.2) have been employed in the heterogeneous polymerization of many monomers in CO_2.

3.1. Dispersion Polymerizations

For surface-coating applications, dispersion polymerizations are used to produce uniform polymer particles with diameters ranging from 100 nm to 10 µm. Briefly, a dispersion polymerization is a heterogeneous polymerization process by which latex particles are formed in the presence of a suitable stabilizer from an initially homogeneous reaction mixture.[44] High degrees of polymerization are observed because the insoluble polymer is stabilized sterically as a colloid and does not precipitate. In 1994, DeSimone and co-workers performed the first successful dispersion polymerizations in $scCO_2$ by employing CO_2 soluble amphiphilic stabilizers.[45, 46] The free radical initiated polymerization of methyl methacrylate (MMA) was the first of a series of dispersion polymerizations of lipophilic monomers using PFOA as the stabilizer.[47, 48] PFOA behaves very similarly to amphiphilic block copolymers, in that it contains an acrylic-like backbone (CO_2-phobic) which functions as an anchoring unit that can either physically adsorb or chemically graft onto the growing particles, while the fluorinated side groups (CO_2-philic) extend the chain into the continuous phase, preventing flocculation of particles through steric stabilization (Figure 6).

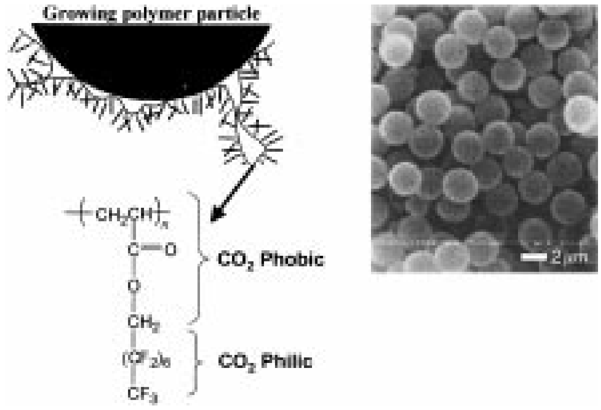


Figure 6. Left: Mechanism of dispersion polymerization and particle formation in $scCO_2$. Right: Scanning electron micrograph of particles isolated from polymerization run in CO_2.

Until recently there have been few examples demonstrating the synthesis of hydrophilic polymers in CO_2 by dispersion polymerization. Carson et al. recently reported the first dispersion polymerization of a hydrophilic monomer, 1-vinyl-2-pyrrolidone, in $scCO_2$ also by using PFOA as a stabilizer.[49] Spherical and relatively uniform particles with diameters ranging from 0.56 and 2.89 µm were produced.

Commercially available and less expensive siloxane-based macromonomers were also found to be effective stabilizers in the dispersion of MMA.[50] Macromonomers are not amphiphilic in nature, but they contain polymerizable terminal functional groups that are chemically grafted onto the growing polymer, thus providing steric stabilization. By using this method, high molecular weight, well-defined spherical particles of PMMA were obtained with diameters ranging from 1.1 – 5.8 µm depending on reaction conditions.

The surfactants developed by Yates and co-workers were also reported to stabilize PMMA particles produced by dispersion polymerizations in CO_2; their transfer to water results in an aqueous latex.[36] Two surfactants were investigated, a block copolymer containing PDMS ($M_w = 5500\,g\,mol^{-1}$) and methacrylic acid ($M_w = 900\,g\,mol^{-1}$) and a graft copolymer of PDMS and pyrrolidonecarboxylic acid ($M_{w,\,total} = 8500\,g\,mol^{-1}$). While use of the graft copolymer produced smaller and more uniform PMMA particles (ca. 3 µm), they rapidly flocculated in a dispersed aqueous buffer solution. However, the particles produced using the block copolymer resulted in an electrostatically stabilized latex in water at concentrations at least up to 10 wt% in buffered solutions of pH 8 and 11.

Amphiphilic diblock copolymers containing fluorinated or siloxane segments have also been employed in the dispersion polymerization of styrene, vinyl acetate, vinyl acetate-*co*-ethylene, and 2,6-dimethylphenol to make poly(2,6-dimethylphenylene oxide).[47, 48, 51] Diblock copolymers offer steric stabilization, the CO_2-phobic block anchors onto the growing polymer chain while the CO_2-philic block extends out into the solvent medium. These type of stabilizers offer the added ability to control the diameters and size distributions of particles by variations in the ratio of the anchoring (CO_2-phobic) block to the stabilizing (CO_2-philic) block.

3.2. Emulsion Polymerization

Adamsky and Beckman have employed an amide end-capped poly(hexafluoropropylene oxide) surfactant in the inverse emulsion polymerization of acrylamide in CO_2.[37, 38] These polymerizations were conducted in the presence of water, a co-solvent for the monomer, at a CO_2 pressure of 345 bar and 60 °C using AIBN as the initiator. When surfactant was added to the polymerizations, the CO_2 solution had a milky-white appearance similar to that of conventional inverse emulsion polymerizations. Additionally, intrinsic viscosity measurements of the resultant polymer revealed significantly higher molecular weights than conventional emulsion polyacrylamide. However, in the absence of any surfactant the solution appeared similar to a simple dispersion polymerization of an aqueous solution in CO_2. Phase separation occurred immediately when agitation ceased and a large mass of precipitated polymer was collected.

4. Solving Environmental Problems with CO_2

4.1. Polycarbonate Synthesis

Toughness and optical clarity makes polycarbonates an important class of polymers that are useful in many applications including compact (CD) and digital video disks (DVD), military shields and bullet proof windows. Traditionally two routes have been employed to synthesize high molecular weight polycarbonates: an interfacial route that involves the reaction between phosgene and 2,2-bis(*p*-hydroxyphenyl)propane (bisphenol A) in a biphasic reaction system of methylene chloride and alkaline water; and the melt-phase transesterfication between bisphenol and diaryl carbonate.[52] While the interfacial route requires large volumes of environmentally harmful solvents, it is the predominant method for polycarbonate synthesis. The more environmentally friendly melt-phase process has significant disadvantages including low product molecular weights incurred as a result of high viscosities, and the formation of color bodies which are a result of the high reaction temperatures. The color bodies significantly reduce the optical properties of the material, making it unsuitable for data storage applications. Recently two new routes have been demonstrated to synthesize polycarbonates: melt-phase transesterfication in the presence of $scCO_2$ and solid-state polymerization (SSP) with $scCO_2$ as a crystallization agent.

4.1.1. Melt Phase Synthesis

Burke et al. have shown reaction condensates in a melt-phase step-growth polymerization can be effectively removed by swelling or plasticizing the polymer melt.[53] Plasticizing agents reduce the viscosity, increase chain mobility and free volume, and increase the diffusivity of the small molecule condensate, thus driving the polymerization to higher conversions and higher molecular weights. However, conventional agents are typically expensive, toxic, and difficult to separate from the end product, thus making their usage minimal. In contrast, nontoxic $scCO_2$ was found to be an excellent easily removable plasticizing agent.[54, 55] Gross et al. have taken advantage of these properties of CO_2 to swell and melt-phase polymerize bisphenol A poly(carbonate).[56] Swelling results of two low molecular weight polycarbonates samples indicated that the polymer could be swollen to greater than 50% of its original volume (Figure 7).

In addition to CO_2 swelling the polymer, it was also used in melt-phase reactions to extract the phenol by-product and thus drive the reaction to higher conversions. The swollen melt-phase polymer system displayed enhanced reaction rates compared to a non-$scCO_2$ system, as evidenced by higher molecular weights produced in the same reaction time. This is expected since in melt-phase step-growth polymerizations the poor diffusivity of the condensate in viscous polymer melts often limits the reaction rate.

4.1.2. Solid-State Polymerization (SSP)

High reaction temperatures and tedious vacuum techniques are necessary for the operation of melt-phase polymerizations on an industrial scale. Despite solid-state polymerization (SSP) being the method of choice for the preparation of step-growth polymers such as poly(ethylene terephthalate) (PET) in large volume polycarbonate SSP is commercially impractical. In an SSP process, the reaction temperature of precrystallized polymer particles needs to be above the polymer glass transition temperature (T_g) to ensure chain mobility but below the melting temperature (T_m) to prevent sticking and coalescence of particles.

Crystallization is usually induced in polycarbonates by treatment with organic solvents and nucleating agents since the polymer does not crystallize on its own thermally.[57] The solvents known to induce crystallinity (e.g. acetone and methylene chloride) not only pose potential environmental hazards but are also difficult to handle in an industrial scale plant. Prompted by the discovery by Beckman and Porter of the crystallization of thin films of polycarbonate by CO_2 at elevated temperatures and pressures,[58] Gross et al. extended the crystallization process to granules and beads of low

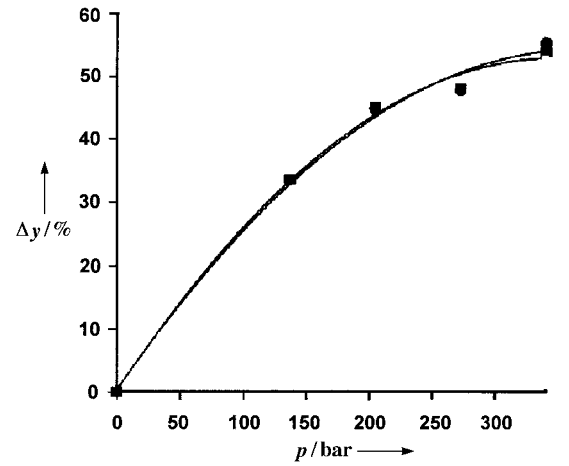


Figure 7. Percent swelling of polycarbonates (M_n of 2500 (■) and 5000 $g mol^{-1}$ (●)) at 235 °C at various CO_2 pressures.

molecular weight polycarbonates in an effort to create materials that could undergo SSP without using toxic organic solvents.[59] Low molecular weight polycarbonate samples were exposed to $scCO_2$ and were reported to be between 19 to 30% crystalline, depending on conditions. As a result of exposure to CO_2, the samples lost their transparency and became white and opaque (Figure 8).

The results from the SSP of the precrystallized samples indicated that there could be a seven-fold increase in the molecular weight of the final product, depending on reaction conditions. The observed increase in molecular weight demonstrated that the use of $scCO_2$ to induce crystallinity was effective for the SSP of polycarbonates.

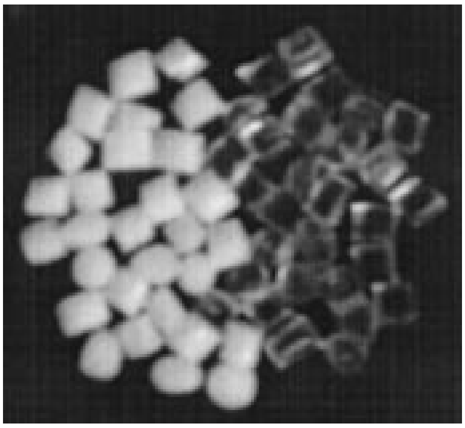


Figure 8. Crystallization of polycarbonate pellets aided by $scCO_2$. Right: amorphous, left: crystalline.

4.2. Coatings in CO_2

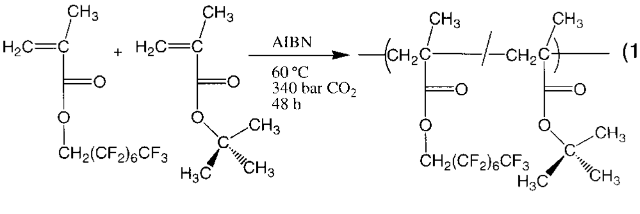
Perfluoropolyethers have unique properties that make them suitable for the coating and protection of historical buildings and monuments made of stone.[60, 61] These transparent, colorless polymers are highly water repellent and have been proven to reduce water absorption into stone by 80 to 90% for at least 30 months. They have low surface energies and are stable to corrosive acids, high temperatures, UV radiation, and oxidizing agents.[62] Results in the field of stone protection have shown that perfluoropolyethers offer very encouraging results, however, the only common solvents for these polymers are ozone-depleting CFCs. Hénon et al. have recently shown CO_2 offers several advantages over CFCs for polymeric stone-protective materials.[63] Aside from previously stated properties of CO_2 and its ability to readily dissolve perfluoropolyethers, its low critical pressure affords the opportunity to spray coat polymers onto the surface of stones. This method of application has the potential to be faster than brush applications and to produce a much more homogenous coating. The atomization of the coating product can be achieved through the rapid expansion of supercritical solution (RESS). In the RESS process, a dilute solution of a solute in the $scCO_2$ is expanded through a nozzle, from a high upstream pressure to a lower downstream pressure. The polymer then precipitates from the solution because of the lower solubility of the solute at gaslike solvent densities. The solubility properties of perfluoropolyethers in CO_2 are the key parameters in properly designing the RESS process.

Cloud-point and spray-coating measurements of various perfluorinated polymers from CO_2 demonstrate that $scCO_2$ is a viable solvent for the dissolution and spray application of fluorinated polymers onto stone surfaces and a good alternative to the currently used CFCs.[63, 64] (For more details about the RESS process and its application to stone protection see refs. [58–61, 65–68].

4.3. Spin Coating and Photolithography

The semiconductor industry has averaged an annual growth of 15% for the last 30 years. Sustained growth is dependent upon the industry's ability to increase microchip performance while decreasing the cost of each microchip. A typical semiconductor processing line producing 5000 wafers per day will generate 8000 liters of waste solvent and 8000 liters of contaminated rinse water per day. These contaminated organic and aqueous solvents are not only environmentally unfriendly, but are also expensive to recover and expensive to dispose. Carbon dioxide provides an excellent opportunity to eliminate hazardous waste produced while spin coating and developing integrated circuits. Several advantages offered by CO_2 include: the easy solvent removal, recovery and drying, the elimination of current ventilation equipment, and the low solvent viscosity makes it ideal for penetrating the increasingly smaller gaps. Despite all the advantages, there are several challenges incurred with the use of CO_2 for this application. Solubility limitations of current photoresist materials necessitate the development of new CO_2 compatible resists that must also be soluble in liquid CO_2 at vapor pressure, that is, CO_2 liquid in coexistance with its vapor. Furthermore, chambers to facilitate high-pressure spin coating must be built. In an attempt to meet and overcome these challenges, Hoggan et al. have reported the synthesis of a suitable resist material and the construction of a high-pressure spin coating apparatus.[69]

A series of random copolymers of FOMA and *tert*-butyl methacrylate (TBM) have been synthesized [Eq. (1)] as a negative resist for deep-UV lithography. In the presence of a photoacid generator, the acid sensitive *tert*-butyl groups are cleaved, significantly decreasing the solubility of the polymer in CO_2. This change in solubility is the mechanism by which a pattern can be developed to form an integrated circuit. These photoresist polymers where then spun into films at slightly sub-ambient temperatures and elevated pressures using the liquid CO_2 spin-coating apparatus shown in Figure 9. Initial results indicated that the films spun were between 1–10 μm with a high level of uniformity. These experiments demonstrated that CO_2 can be used in lithography processing.



(1)

FOMA TBM Poly(FOMA-*r*-TBM)

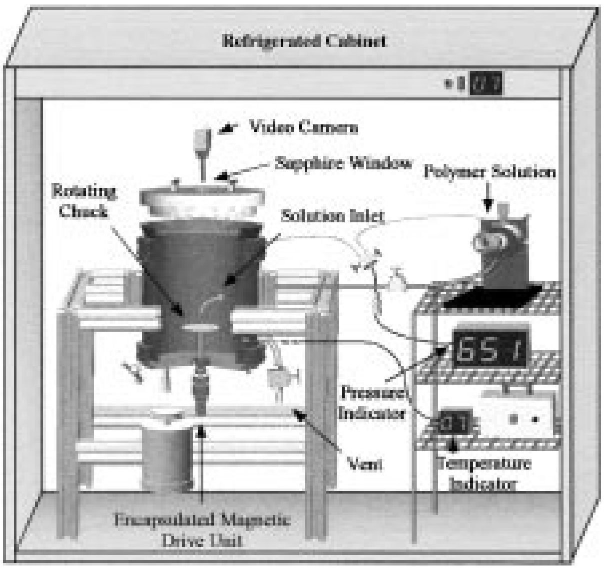


Figure 9. Liquid CO_2 spin-coating apparatus.

5. Barriers and Potential Solutions

While the utilization of CO_2 has significantly increased over the past few years, there are still barriers that hinder its use and acceptance in many industries and applications. The lack of innovative chemistry and fundamental science/theory are two of the major drawbacks. New chemistries are needed to synthesize new CO_2-soluble materials that enable processes that avoid conventional solvents and water, improve properties of current materials, and enable the integration of reaction and separation processes. A better understanding of interfacial phenomena in compressible media is needed especially as it relates to the solubilization and emulsification of substances in CO_2. An increase in the basic science associated with thermo–physical properties of CO_2 could greatly enhance the understanding of mass-transport phenomenon, multicomponent phase equilibria, reaction kinetics, and thermodynamics. Other barriers that limit the use of CO_2 include: high capital cost, the lack of pollution prevention investment incentives for industry, inadequate communication between industry and academia, and the lack of researchers with an adequate knowledge base. Many of these barriers can be overcome when researchers from various fields start to collaborate to tackle some of the present issues associated with CO_2. Furthermore, the continual and increased support of industry and government would also provide scientists and engineers with both the means and motivation to continue CO_2-based research.

6. Outlook and Summary

A significant amount of research has shown that carbon dioxide can and will have a major impact on many industries in the 21st century. It has been demonstrated for many applications that CO_2 is not only a viable environmentally friendly solvent, but that it also offers improvements over many of the current processes. Recent advances in areas such as dispersion polymerization, polycarbonates synthesis, protective stone coating, and spin coating are representative and predictive of the capabilities of CO_2. With increased collaboration, creative research, and a steady resource base, the possibilities for the broad utilization of carbon dioxide are numerous.

7. List of Abbreviations

AIBN	azobisisobutylrolnitrile
ATRP	atom transfer radical polymerization
CFC	chlorofluorocarbon
CMD	critical micelle density
DLS	dynamic light scattering
PDMAEMA	poly(2-dimethylaminoethyl acrylate)
PFOA	poly(1,1-dihydroperfluorooctyl acrylate)
FOMA	1,1,-dihydroperfluorooctyl methacrylate
FOSEA	2-(N-ethylperfluorooctanesulfonamido)ethyl acrylate
FOSEMA	2-(N-ethylperfluorooctanesulfonamido)ethyl methacrylate
PVAc	poly(vinyl acetate)
PS	polystyrene
MMA	methyl methacrylate
P_c	critical pressure
PDMS	polydimethylsiloxane
PEO	poly(ethylene oxide)
PERC	perchloroethylene
PET	polyethylene terephtalate
PHEMA	poly(hydroxyethylmethacrylate)
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering

sc	supercritical
SSP	solid-state polymerization
TAN	1,1,2,2,-tetrahydroperfluorooctyl acrylate
TFE	tetrafluoroethylene
TBM	*tert*-butyl methacrylate
T_c	critical temperature

We gratefully acknowledge financial support from the Kenan Center for the Utilization of Carbon in Manufacturing and the National Science Foundation through the NSF Science and Technology Center for Environmentally Responsible Solvents and Processes.

Received: June 25, 2000 [A390]

---

[1] M. McHugh, V. Krukonis, *Supercritical Fluid Extraction-Principles and Practice*, Butterworths, Boston, **1986**.

[2] R. Steiner, *Chem. Eng.* **1993**, *100*, 114.

[3] S. Barer, K. Stern, *Catalytic activation of Carbon Dioxide*, American Chemical Society, Washington, **1988**.

[4] *CO_2 Dry Cleaning: Minimizing Environmental Impact*, Company Bulletin, MICELL Technologies, **2000**.

[5] S. Moore, S. Samdani, G. Ondrey, G. Parkinson, *Chem. Eng.* **1994**, *101*, 32.

[6] D. Canelas, J. M. DeSimone, *Chem. Br.* **1998**, 38.

[7] Anonymous, *Chem. Eng.* **1997**, *104*, 66.

[8] G. Parkinson, *Chem. Eng.* **1999**, *106*, 17.

[9] J. Hyatt, *J. Org. Chem.* **1984**, *49*, 5097.

[10] W. Tuminello, G. Dee, M. McHugh, *Macromolecules* **1995**, *28*, 1506.

[11] J. M. DeSimone, Z. Guan, C. Eisbernd, *Science* **1992**, *257*, 945.

[12] F. Rindfleisch, T. DiNoia, M. McHugh, *J. Phys. Chem.* **1996**, *100*, 15581.

[13] M. O'Neill, Q. Fang, K. Johnston, *Ind. Eng. Chem. Res.* **1998**, *37*, 3067.

[14] J. M. DeSimone, US-A 5496901 **1993**.

[15] Z. Guan, J. Combes, C. Eisbernd, J. DeSimone, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1993**, *34*, 446.

[16] T. J. Romack, J. M. DeSimone, *Macromolecules* **1995**, *28*, 8429.

[17] T. J. Romack, B. E. Kipp, J. M. DeSimone, *Macromolecules* **1995**, *28*, 1724.

[18] S. A. Montzka, *Science* **1996**, *272*, 1318.

[19] T. Otsu, M. Yoshida, *Makromol. Chem. Rapid Commun.* **1982**, *3*, 127.

[20] T. Patten, J. Xia, T. Abernathy, K. Matyjaszewski, *Science* **1996**, *272*, 866.

[21] *High Pressure Chemical Engineering* (Eds.: D. Betts, J. B. McClain, J. M. DeSimone, C. Trepp), Elsevier, Amsterdam, **1996**.

[22] D. Betts, T. Johnson, C. Anderson, J. M. DeSimone, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1997**, *38*, 760.

[23] J. Xia, T. Johnson, S. Gaynor, K. Matyjaszewski, J. M. DeSimone, *Macromolecules* **1999**, *32*, 4802.

[24] D. Chillura-Martino, R. Triolo, J. McClain, J. Combes, D. Betts, D. Canelas, J. M. DeSimone, E. Samulski, H. Cochran, J. Londono, G. Wignall, *J. Mol. Struct.* **1996**, *383*, 3.

[25] E. Buhler, A. V. Dobrynin, J. M. DeSimone, M. Rubinstein, *Macromolecules* **1998**, *31*, 7347.

[26] J. Londono, R. Dharmapurikar, H. Cachran, G. Wignall, J. McClain, D. Betts, D. Canelas, J. DeSimone, E. Samulski, D. Chillura-Martino, R. Triolo, *J. Appl. Crystallogr.* **1997**, *30*, 690.

[27] J. B. McClain, D. E. Betts, D. A. Canelas, E. T. Samulski, J. M. DeSimone, J. D. Londono, H. D. Cochran, G. D. Wignall, D. Chillura-Martino, R. Triolo, *Science* **1996**, *274*, 2049.

[28] J. McClain, D. Londono, J. Combes, T. Romack, D. Canelas, D. Betts, G. Wignall, E. Samulski, J. DeSimone, *J. Am. Chem. Soc.* **1996**, *118*, 917.

[29] R. Triolo, J. Londono, G. Wignall, D. Betts, S. Wells, E. Samulski, J. DeSimone, *Langmuir* **2000**, *16*, 416.

[30] S. Zhou, B. Chu, *Macromolecules* **1998**, *31*, 7746.

[31] A. Dardin, J. McClain, J. M. DeSimone, C. S. Johnson, E. Samulski, *Macromolecules* **1997**, *30*, 3593.

[32] A. Dardin, J. M. DeSimone, E. Samulski, *Phys. Chem. B* **1998**, *102*, 1775.

[33] X. Zhao, R. Watkins, S. Barton, *J. Appl. Polym. Sci.* **1995**, *55*, 773.

[34] R. Mertsch, B. Wolf, *Macromolecules* **1994**, *27*, 3289.

[35] T. Hoefling, D. Newman, R. Enick, E. Beckman, *J. Supercrit. Fluids* **1993**, *6*, 165.

[36] M. Yates, K. Lim, G. Li, J. Shim, S. Maniar, K. Johnston, S. Webber, *Macromolecules* **1999**, *32*, 1018.

[37] T. Hoefling, D. Stofesky, M. Reid, E. Beckman, *J. Supercrit. Fluids* **1992**, *6*, 237.

[38] A. Yazdi, C. Lepilleur, E. Singley, W. Lui, A. Adamsky, R. Enick, E. Beckman, *Fluid Phase Equilib.* **1996**, *117*, 297.

[39] A. Yazdi, E. Beckman, *J. Mater. Res.* **1995**, *10*, 530.

[40] T. Carson, S. Wells, J. M. DeSimone, *Reactions and Synthesis in Surfactant Systems*, Marcel Dekker, New York, **1999** submitted.

[41] T. Romack, E. Maury, J. DeSimone, *Macromolecules* **1995**, *28*, 912.

[42] P. Odell, G. Hamer, *Polym. Mater. Sci. Eng.* **1996**, *74*, 404.

[43] A. L. Cooper, J. M. DeSimone, *Polym. Mater. Sci. Eng.* **1996**, *74*, 262.

[44] K. E. Barrett, *Dispersion Polymerization in Organic Media*, Wiley, London **1975**.

[45] J. M. DeSimone, E. Maury, Y. Menceloglu, J. McClain, T. Romack, J. Combes, *Science* **1994**, *265*, 356.

[46] Y. Hsiao, E. Maury, J. DeSimone, *Macromolecules* **1995**, *28*, 8159.

[47] D. A. Canelas, D. E. Betts, J. M. DeSimone, *Macromolecules* **1996**, *29*, 2818.

[48] K. Kapellen, C. Mistele, J. DeSimone, *Macromolecules* **1996**, *29*, 495.

[49] T. Carson, J. Lizotte, J. M. DeSimone, *Macromolecules* **2000**, *33*, 1917.

[50] K. Shaffer, T. Jones, D. Canelas, J. DeSimone, *Macromolecules* **1996**, *29*, 2704.

[51] D. Canelas, D. Betts, J. M. DeSimone, *Macromolecules* **1998**, *31*, 6794.

[52] L. H. Tangle, F. R. Diaz, *Eur. Polym. J.* **1987**, *23*, 109.

[53] A. Burke, R. Givens, M. Jikei, J. M. DeSimone, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1997**, *38*, 387.

[54] A. Garg, E. Gulari, C. Manke, *Macromolecules* **1994**, *27*, 5643.

[55] P. Condo, D. R. Paul, K. P. Johnston, *Macromolecules* **1994**, *27*, 365.

[56] S. Gross, R. Givens, M. Jikei, J. Royer, S. Khan, J. M. DeSimone, *Macromolecules* **1998**, *31*, 9090.

[57] J. P. Mercier, *J. Polym. Sci. Polym. Symp.* **1967**, *16*, 2059.

[58] E. Beckman, R. Porter, *J. Polym. Sci. Part B* **1987**, *25*, 1511.

[59] S. Gross, D. Flowers, G. Roberts, D. Kiserow, J. M. DeSimone, *Macromolecules* **1999**, *32*, 3167.

[60] A. Pasetti, G. Moggi, R. Ingoglia, U. Matteoli, *L'Edilizia* **1990**, *5*, 329.

[61] F. Piacenti, F. Ciampelli, A. Pasetti, I-A1135597, 4499146, **1981**.

[62] L. Helmick, *Lubr. Eng.* **1994**, *50*, 449.

[63] F. Henon, M. Camaiti, A. Burke, R. Carbonell, J. DeSimone, F. Paicenti, *J. Supercrit. Fluids* **1999**, *15*, 173.

[64] F. E. Henon, Ph.D. thesis, *Department of Chemical Engineering*, North Carolina State University, Raleigh (USA) **1999**.

[65] R. Carbonell, J. M. DeSimone, F. Henon, US-A Patent filed October **1997**.

[66] D. Matson, J. Fulton, R. Petersen, R. Smith, *Ind. Eng. Chem. Res.* **1987**, *26*, 2298.

[67] S. Mawson, K. Johnston, J. Combes, J. DeSimone, *Macromolecules* **1995**, *28*, 3182.

[68] S. Mohamed, P. Debenendetti, R. Prud'homme, *AIChE J.* **1989**, *35*, 325.

[69] E. Hoggan, J. M. DeSimone, R. G. Carbonell, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Mater. Sci. Eng. Part 2 Aug 22*, **1999**, 218.