

OPPORTUNITIES FOR POLLUTION PREVENTION AND ENERGY EFFICIENCY ENABLED BY THE CARBON DIOXIDE TECHNOLOGY PLATFORM

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■ **Abstract** Various applications using carbon dioxide (CO₂) have developed within the last decade and, if current trends continue, the CO₂ technology platform could emerge as the most commonly used solvent in the twenty-first century. An environmentally friendly platform that is wrapped in a successful business format with apparent implications for people and their communities is most likely to endure. Does the CO₂ technology platform meet the criteria for becoming a sustainable enterprise? Utilizing CO₂ as an alternative solvent in conventional processes has the potential to favorably impact the environment and our communities. There are, however, several barriers to adopting CO₂-based applications. Several concepts as well as obstacles to adopting the carbon dioxide technology platform are highlighted in this chapter.

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1. INTRODUCTION

Imagine an alternative for the automotive industry that would eliminate the use of toxic chlorinated solvents during metal degreasing processes. What if the electronics industry deposited specially designed photoresists by a spin coating process that was independent of organic solvents? Imagine a hydrogenation reaction that proceeds in an environmentally friendly solvent and yet achieves 100% conversion and selectivity. What if a nontoxic alternative to perchloroethylene could be offered to the dry cleaning industry—improving the quality of life for employees as well as customers? What if manufacturing industries didn't need to spend billions of dollars on environmental compliance issues to control the level of organic solvents emitted to the environment (Figure 1)?

Furthermore, what if the demands on municipal water and waste water systems could be dramatically reduced by changes in manufacturing technology (Figure 2)? Imagine an electronics industry that doesn't have to use hundreds of millions of gallons of water per day to remove sub-micron particles during the manufacture of integrated circuits and flat panel displays. Imagine a polymer industry that avoids using trillions of BTUs annually to dry commercial polymers manufactured in aqueous reaction media. Imagine a textile industry that doesn't need to use 100 pounds of water for every pound of yarn dyed.

A more sobering viewpoint would be to imagine the next century without this technology. What if we continue to deplete our world's natural resources, fill our skies with a seemingly unending array of pollutants, and muddy our waters with harmful toxins (Figure 3)? What if the industrial sector continues to consume a significant amount (20%–30%) of the world's freshwater supply (1)? How long will our current water supplies last? How long will our children and grandchildren remain in good health?

Environmental concerns over the extensive use of volatile organic solvents, halogenated solvents, and inordinate amounts of water by industries throughout the world have led to an extensive search for environmentally responsible solvents. The use of a particular solvent as a process aid, cleaning agent, or dispersant

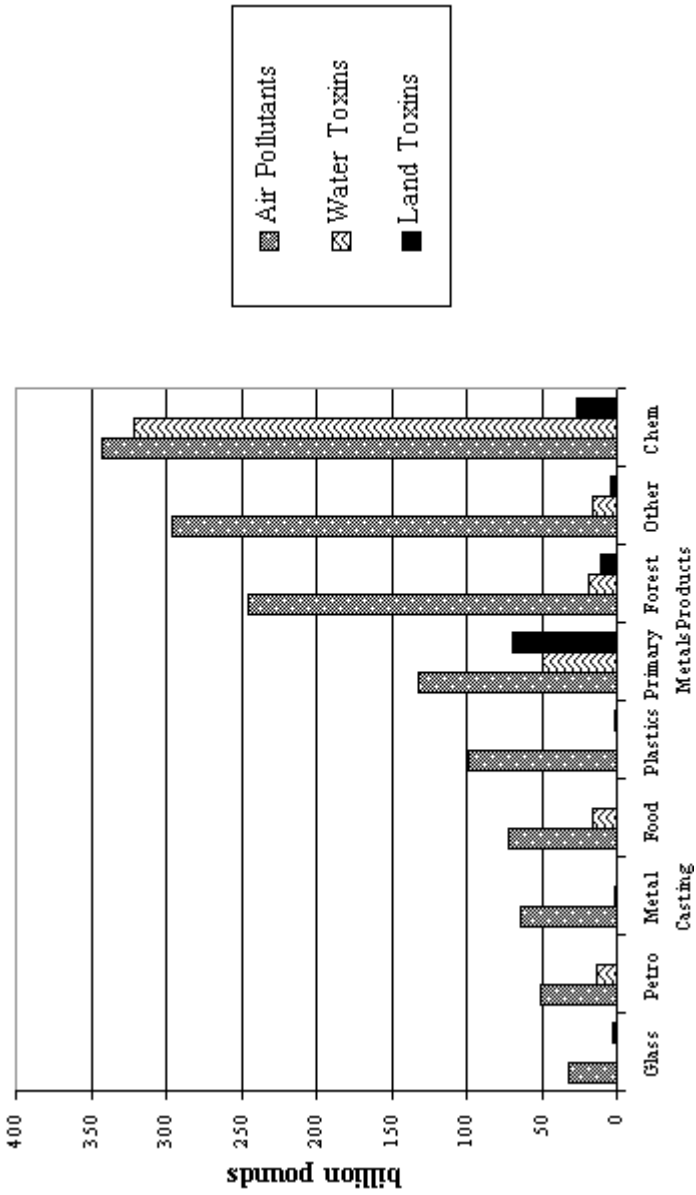


Figure 1 Toxic release inventory (TRI) of chemical releases to the environment in 1997 by industry sector. (From reference 111.)

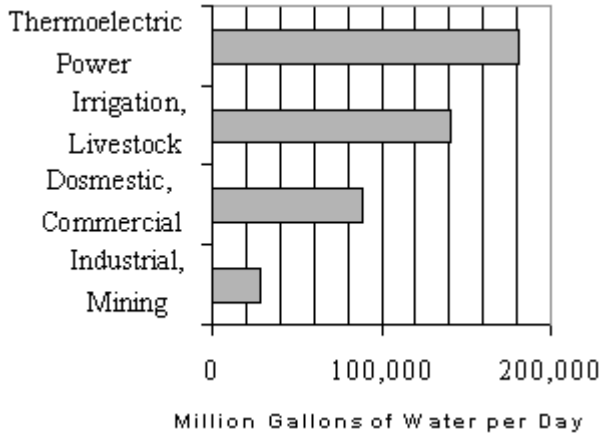


Figure 2 Consumption of freshwater by water-use category in 1995. (From reference 112.)

is a critical issue in light of the increasing demand for environmentally friendly chemistry and processes. Frequently, the solvent of choice for these processes is organic or halogenated, accounting worldwide for more than 30 billion pounds of solvent usage each year. Many industries rely heavily on our local communities' water/waste treatment facilities. The most significant users include the electronics, textile, pulp and paper, chemical, and mining industries. Whereas the inherently benign nature of water makes it desirable as a solvent, the commercial industries that rely on its usage encounter supply restrictions as well as problems associated with the corrosive nature of water (for example, rusting associated with metal

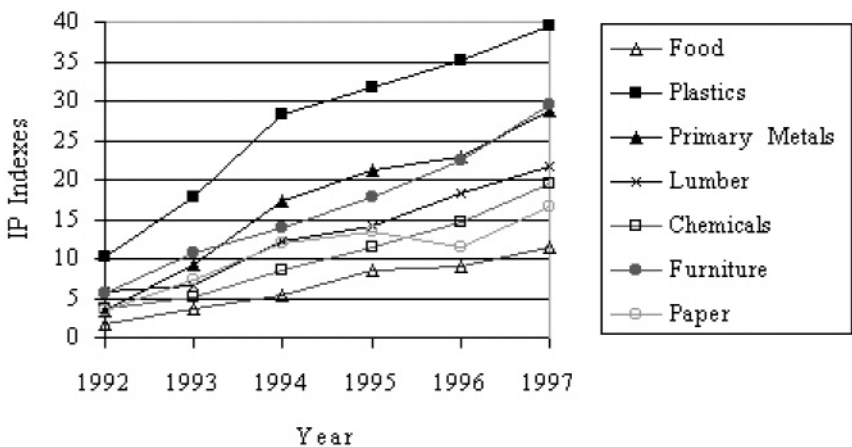


Figure 3 Growth by industrial sector according to industrial production indexes from 1991–1997. (From reference 111:4–23.)

degreasing) and its tendency to support microbial growth. Furthermore, the isolation of impurities and the necessity for additives to increase the solvating efficiency of water are concerns that must be addressed. Water also has a high heat of vaporization, incurring the use of trillions of BTUs yearly to dry commercial polymers made in aqueous reaction media. In addition, copious amounts of aqueous waste leads to the potential for contaminating drinking water.

As the manufacturing and service industries attempt to avoid the production, use, and subsequent release of contaminated water, volatile organic solvents, chlorofluorocarbons (CFCs), and other noxious solvents and contaminants into our environment, there is a need for innovative approaches to the traditional processes. The chemicals industry is the second largest energy-user, with the majority of its energy consumed during the manufacture of products (Figure 4). Petroleum refining is one of the most energy-intensive manufacturing industries in the United States, accounting for almost 23% of the energy consumed in 1994 by the manufacturing industries cited in Figure 4. The need to develop a more environmentally responsible and energy-efficient solvent technology platform is paramount; the leading candidate is liquid and supercritical carbon dioxide (CO₂).

Carbon dioxide, in both the supercritical and liquid forms, is an excellent alternative solvent, having both gas-like diffusivities (an important property with

Total = 34.1 quadrillion Btu

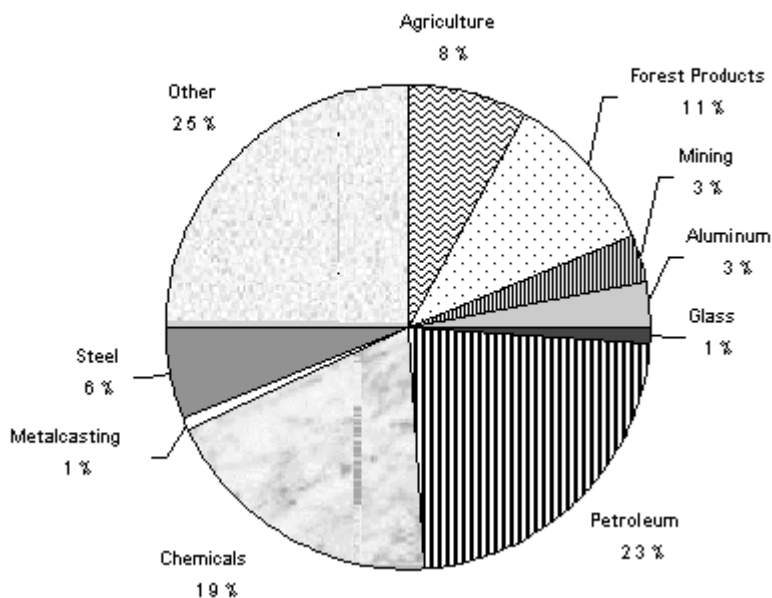


Figure 4 Industrial energy use. (From reference 112.)

implications for reaction kinetics) and liquidlike densities that allow for solvation of many compounds. Small changes in temperature or pressure enable CO₂ to exhibit changes in solvent density without altering solvent composition (2). In addition, the low viscosity of supercritical CO₂ and its ability to plasticize glassy polymers have implications for polymer processing and kinetics. CO₂ has an easily accessible critical point with a T_c of 31.1°C and a P_c of 73.8 bar. Furthermore, CO₂ is nontoxic and inexpensive (\$0.05/lb). The dissolving power of CO₂ is tunable over a broad range of solvent quality because of its compressibility, especially in the supercritical region (2–5) (Figure 5).

As a naturally occurring gas, CO₂ exists in natural reservoirs of high purity located throughout the world, including the Four Corners region where Utah, Colorado, New Mexico, and Arizona intersect (6). CO₂ is also abundantly present in natural reservoirs in the Mississippi, where it is transported by pipeline to many west Texas oil fields for use in enhanced oil recovery processes (6). In addition, it is generated in large quantities as a byproduct in ammonia, hydrogen, and ethanol plants. Indeed, CO₂ is as ubiquitous as water, yet it is much less precious. Electrical power generation stations that burn fossil fuels supply ~90% of the world's commercial energy and generate copious amounts of CO₂ (7). In fact, since the industrial revolution, there has been a significant increase in the amount of CO₂ (a green house gas) emissions. It is estimated that less than 1% of the CO₂ that is generated is captured for use, hence the demand for CO₂ will always be far less than what is generated as a by-product.

2. ENABLING EARLY DEVELOPMENTS

Technological breakthroughs in the last decade indicate that dense carbon dioxide could be the most commonly used solvent in the twenty-first century (8). A major incentive for using CO₂ as a solvent for commercial polymerizations is the elimination of environmentally harmful organic solvents and reduction of waste streams generated during polymerizations. There is also the potential to lower residual monomer levels by online supercritical fluid extractions. Polymers can be produced in dry form with no solvent or water-drying step. This affords significant energy savings by the elimination of the heat of vaporization of water needed to dry polymers produced by traditional aqueous emulsion, suspension, and solution polymerizations. Polymer processing energy requirements are also reduced by utilizing downstream CO₂-based operations (i.e. polymer extrusion).

It is clear from all of the reasons outlined above that CO₂ would be an ideal emerging technology platform to mitigate or even eliminate many of the problems associated with conventional solvents. However, two significant barriers inhibit this vision: the poor solvency of CO₂ (hence the need to design surfactants for CO₂) and the lack of understanding regarding the usefulness of CO₂ as a reaction medium. Two recent developments—the synthesis of fluoropolymers in CO₂ (including the discovery of the high solubility of many fluoropolymers in CO₂)

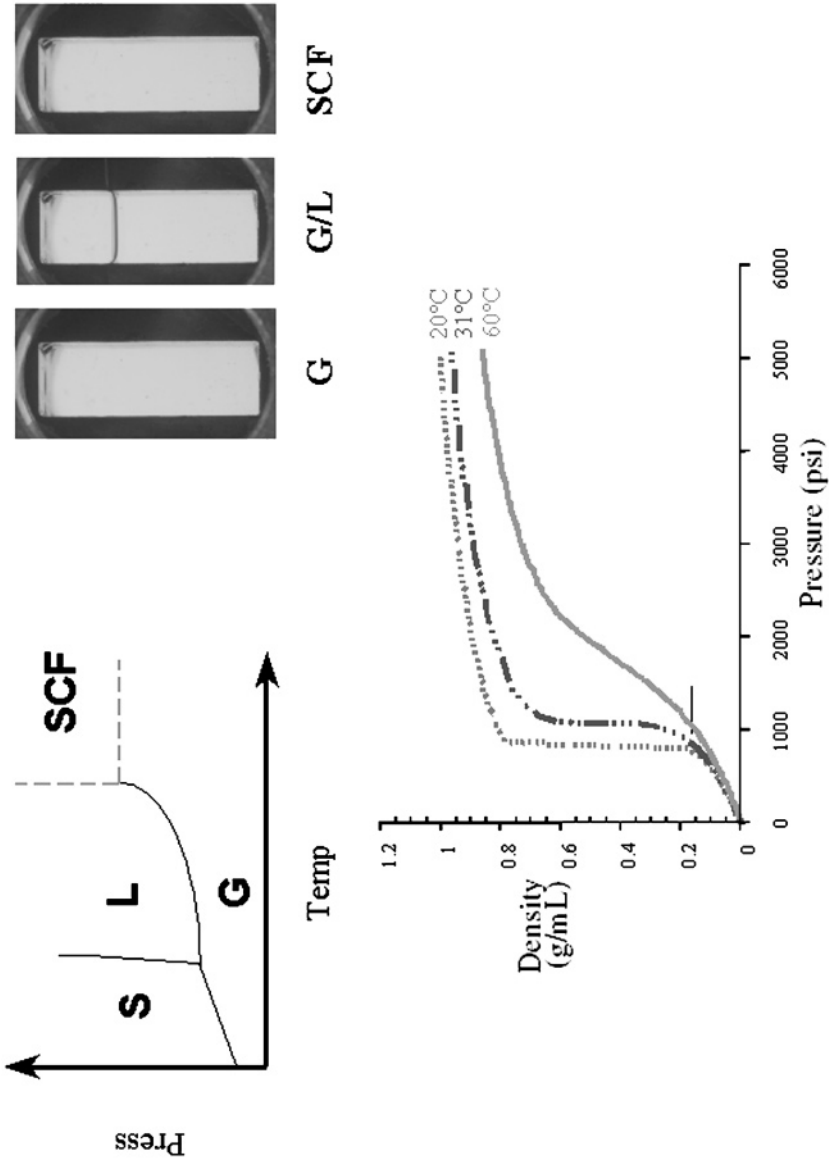


Figure 5 Phase diagram for carbon dioxide and visual representation of transition from gas to liquid to supercritical fluid. The properties of carbon dioxide are tunable with changes in pressure and temperature.

and the rational design of surfactants for CO₂—are the enabling key discoveries that will allow the emerging CO₂ technology platform to be sustainable and hence have a positive impact on society.

2.1 Fluoropolymers and CO₂

Fluoropolymers are used in many technologically demanding applications because of their balance of high-performance properties. Several significant impediments to the synthesis of commercially important fluoropolymers exist, including their general insolubility in most solvents, the undesirable effect of chain transfer of fluoroolefin radicals to most hydrogen containing solvents (hence the extensive use of chlorofluorocarbon solvents), and their high hydrophobicity (which necessitates the use of specially fluorinated surfactants when synthesized in water). Preparing these technologically important materials in supercritical CO₂ can circumvent the environmental concerns for CFCs and can avoid the ensemble of problems associated with their synthesis in water. The feasibility of utilizing liquid or supercritical CO₂ as a reaction medium has been demonstrated by DeSimone et al for the homogenous solution polymerization of poly(1,1-dihydroperfluorooctyl acrylate) [poly(FOA)] (9) and for the heterogeneous precipitation polymerization of fluoroolefins such as tetrafluoroethylene (10) (Figure 6). Using 60 w/v% solids in a homogeneous phase with supercritical CO₂, high molar mass homo- and copolymers (~106 g/mol) of fluorinated acrylate monomers were obtained at high conversion (>95%) (9).

Copolymers of tetrafluoroethylene and perfluoro(propyl vinyl ether) were synthesized in high yields employing bis(perfluoro-2-propoxypropionyl) peroxide as a free radical initiator in supercritical CO₂ (11). Melt viscosities of the isolated polymer were too high to measure by conventional methods, indicating that molecular weights were in excess of 1×10^6 g/mol. Recent efforts by Charpentier et al have demonstrated the feasibility of performing a continuous, once-through system for precipitation polymerization of vinylidene fluoride (VF2) in supercritical CO₂ (12). The polymerization was initiated by diethyl peroxydicarbonate at 75°C and 275 bar. The conversion of VF2 in these polymerizations ranged from 7% to 24%—an acceptable range because the unreacted monomer is continuously recycled.

Polymerization of fluoropolymers in CO₂ opens the door of possibility for the commercialization of CO₂-based fluoropolymer polymerizations. DuPont has led

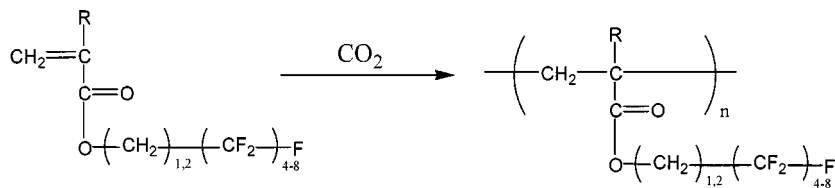


Figure 6 Synthesis of poly(FOA) in carbon dioxide.

the way for transferring this technology to full-scale plant operations (13). Construction has begun on a new DuPont facility to test production of fluoropolymers in carbon dioxide. The \$40 million plant will be located in Bladen County, North Carolina and is scheduled to be completed by 2006. If the test facility is successful, DuPont is scheduled to expand the Bladen County facility, investing up to \$275 million over the next 7 years.

2.2 CO₂-Philic/Hydrophilic Surfactants

In addition to amorphous low-melting fluoropolymers and siloxane-based polymers, carbon dioxide is a good solvent for high vapor pressure fluids. Although it readily dissolves many of these small molecules, CO₂, in both the liquid and supercritical states, is a very poor solvent for many compounds, including most high molecular weight polymers and polar compounds such as water, ionic species, proteins, etc. In order for CO₂ to be an effective continuous phase for applications such as separations, extractions, coatings, and polymerizations, surfactants must be developed analogous to classical surfactant systems in conventional continuous phases (i.e. water or inverse systems).

However, unlike conventional organic solvents that are often capable of dissolving high molar mass oleophilic compounds [e.g. the ability to readily dissolve poly(propylene oxide), polyisoprene, polybutadiene, and polystyrene in solvents such as toluene, cyclohexane, and tetrahydrofuran], CO₂ is a poor solvent for most of these compounds at readily accessible conditions (<300°C and <350 bar). Indeed, CO₂ is more akin to a fluorinated solvent (fluorous phase) than it is to hydrocarbon solvents. As such, we can classify (14) the solubility characteristics from a CO₂-centric viewpoint whereby we can have compounds that can be classified as "CO₂-philic" and "CO₂-phobic." CO₂-phobic compounds can be further subdivided into hydrophilic and lipophilic or oleophilic (Figure 7). With this being understood, one can now molecularly engineer interfacially active compounds through the judicious catenation of CO₂-philic segments with CO₂-phobic segments.

DeSimone (9, 14–17), Fulton (17, 18), Johnston (19, 20), and Beckman (21, 22) have established the design criteria for molecularly engineered surfactants that can stabilize and disperse otherwise insoluble matter into a CO₂ continuous phase. Through their research efforts, an ideal model surfactant for CO₂ contains a CO₂-philic segment that is comprised of either a fluorinated segment or a siloxane segment attached to a CO₂-phobic segment of oleophilic or hydrophilic character (22a,b). By altering the molecular weight, morphology, topology, composition, temperature, and pressure, amphilies of this nature enhance the efficacy of liquid and supercritical CO₂ to dissolve or emulsify highly polar and highly lipophilic, oligomeric, and polymeric compounds.

2.2.1 Graft Copolymer Surfactants for CO₂ Applications A copolymer of poly(ethylene oxide) (PEO) grafted onto a backbone of poly(1,1-dihydroperfluorocyl

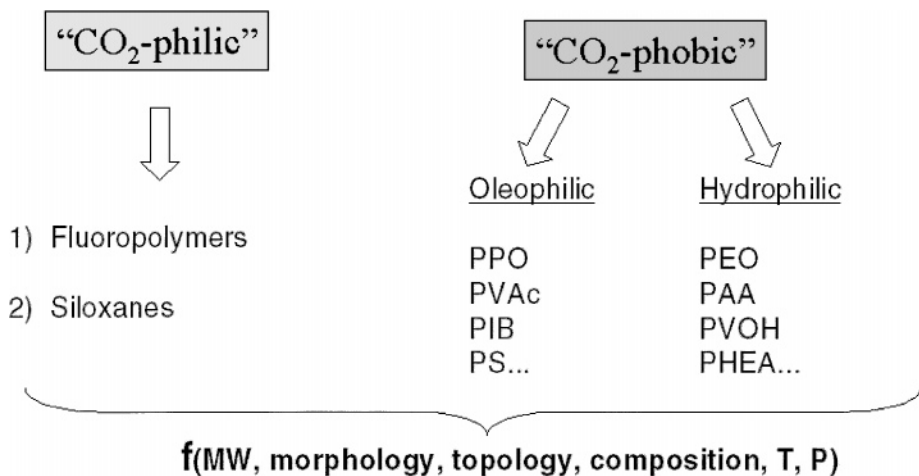


Figure 7 Solubility of polymers in carbon dioxide.

acrylate) (PFOA) or PFOA-g-PEO has been synthesized by Maury et al (14). The PEO macromonomer was analyzed prior to grafting into the copolymer and determined by gel permeation chromatography to have a molecular weight of 5000 g/mol. The copolymer was characterized in Freon-113 by proton nuclear magnetic resonance spectroscopy to determine the percent PEO incorporation. The final graft copolymer was found to contain 15% ethylene oxide based on the total weight of the polymer. The graft copolymer was reported to have a low solubility in conventional solvents, making characterization difficult, yet interesting results were obtained when solution properties in CO₂ were studied with the aid of small angle X-ray scattering measurements (17). The scattering measurements were observed in CO₂ at 60°C in the presence of water (water-to-surfactant ratio of 0.32). A 5000 PEO segment is completely insoluble in CO₂, and this fact, coupled with the scattering data, led the authors to a model in which the PEO grafts exist in the center of a core-shelled structure (17). The PFOA-based shell limits the CO₂-PEO interaction, thus facilitating the stabilization of a micellar structure. The radius of the PEO core was determined to be 105 Å, a diameter much larger than a single, collapsed 5 K PEO chain. This led to the conclusion that the PEO chains attached to a single PFOA backbone as well as those from other graft copolymer chains aggregate in the core region of the micelle. Approximately 600 PEO segments occupy the core, based on the measured volume of the micelle core and the bulk density of PEO. The micellelike structure of the graft copolymer solution greatly enhanced the solubility of water in the CO₂ solvent. Up to 10 wt% of the copolymer was soluble in CO₂ at 220 bar and 60°C.

2.2.2 Block Copolymer Surfactants for CO₂ Applications A small diblock molecule consisting of a perfluoroalkane chain has been covalently linked to a

PEO segment and characterized by small angle X-ray scattering in CO₂ (17). The perfluoroalkane chain was reported to have a number average molecular weight of 384 g/mol, whereas the PEO segment was reported to be 340 g/mol. The poly(tetrafluoroethylene)-block-PEO sample contained a range of molecular weights, and the corresponding scattering curve showed two distinct regions. The model proposed by the authors involved small premicellar surfactant aggregates consisting of fewer than 10 surfactant molecules and a second group of larger surfactant molecules containing 6 to 8 PEO units (17). The large aggregates could be classified as conventional reverse micelles.

2.2.3 Perfluoropolyether Chelating Agents KrytoxTM Fluorosurfactants, also known as perfluoropolyether (PFPE) carboxylic acids, have been converted to chelating agents and subsequently evaluated for solubility in CO₂ (22). The chelating agents were designed to possess a head group of either bis(picoyl amine) or dithiol and a tail of PFPE. The phase behavior of the chelating agents was shown to vary with molecular weight of the PFPE-tail component. As the molecular weight of the PFPE-tail increased, the total molecular weight of the compound increased, thereby decreasing its solubility in CO₂. On the other hand, increasing the ratio of the PFPE-tail segment to the polar head group segment enhanced the solubility of the chelating agent.

2.3 CO₂-Philic/Lipophilic Surfactants

A semifluorinated diblock F(CF₂)₁₀(CH₂)₁₀H has been characterized by small angle X-ray scattering using 5–6 wt% surfactant concentrations in CO₂ at 65°C (17). The scattering data provided radius of gyration measurements that were compared to theoretical calculations for the individual molecules. For the conditions of this experiment, a model was developed that depicted no more than three to four unimers (individual copolymer chains) per aggregate for the diblock.

Utilizing small-angle neutron scattering measurements in CO₂ at 65°C, a diblock of polystyrene and poly(FOA), polystyrene-block-PFOA, provided quite different results (16). Relying on calibrated small-angle neutron scattering curves, a model was developed that depicted the block copolymers as a spherical core-shell structure. By systematically increasing the PFOA block length, the radius of the total particle increased with a simultaneous decrease in the swelling of the corona. The solvent strength of CO₂ is easily tuned so that by increasing the density of CO₂ the aggregation number was observed to decrease, creating more dynamic micelles. It was proposed that a critical micelle density exists analogous to a critical micelle concentration to describe the phenomenon of unimer-to-aggregate transitions for amphiphilic materials in CO₂.

2.4 Reversible Self-Assembly

The phenomena of a critical micelle concentration suggested by previous scattering measurements of block copolymers (16) was confirmed in a study of polyvinyl

acetate (PVAC)-*b*-poly(1,1,2,2-tetrahydroperfluorooctyl acrylate) (PTAN) (23). Three regions were observed on the phase diagram of the copolymer: (*a*) a two-phase region at low CO₂ density, (*b*) solutions of spherical micelles at intermediate CO₂ densities, and (*c*) solutions of unimers at high CO₂ densities. The aggregation number (the number of copolymer chains in a micelle) decreased with an increasing density of supercritical CO₂ in region (*a*). An increase of the CO₂ density corresponds to the improvement of solvent quality for both blocks of the copolymer (PVAC and PTAN). The hydrodynamic radii of micelles and unimers were measured using dynamic light scattering in regions (*b*) and (*c*), respectively. This light-scattering study is the first one reporting a solvent density-induced transition, a critical micelle density, between spherical micelles at lower supercritical CO₂ density and unimers at higher CO₂ density. The light-scattering technique appears to be a very powerful tool for the analysis of carbon dioxide density-induced micellization transition (Figure 8, see color insert). This phenomenon is unique to supercritical fluids and demonstrates a convenient control over the polymer solubility.

3. APPLICATION OPPORTUNITIES ENABLED BY THE DESIGN OF CO₂-SOLUBLE POLYMERS

3.1 A New Coatings Technology Based on Liquid CO₂

Hundreds of millions of pounds of solvents are manufactured each year for use in coatings applications. A wide range of coating materials and processes can utilize environmentally friendly CO₂ as a potential replacement for traditional solvents used as delivery media. PFPE-based coating materials are viewed with particular interest for a number of reasons including their exceptional performance in aggressive environments (as compared to other fluoropolymer coatings) and their solubility in dense carbon dioxide. The applications currently envisioned include coatings for buildings/bridges, fouling-release coatings, spin coating for microlithography, and lubricants for magnetic drives. A few of these applications will be discussed in more detail below.

3.1.1 New Environmentally Friendly Lithographic Processes The properties of fluoroacrylate polymers can be controlled in CO₂ to provide polymers with a range of glass transition temperatures, functionalities, molecular weights, and architectures (9). The synthetic control of fluoropolymer synthesis in CO₂ provides the opportunity to develop new coatings and polymerization technologies. Spin coating photoresists from liquid CO₂ is a novel idea that could have a great impact on the electronics industry. This industry currently uses one million gallons of solvent each year on a single fabrication line. The use of these solvents requires extensive safety and waste processing equipment. To impact this industry with the benefits of CO₂ technology, photoresists need to be identified and synthesized for

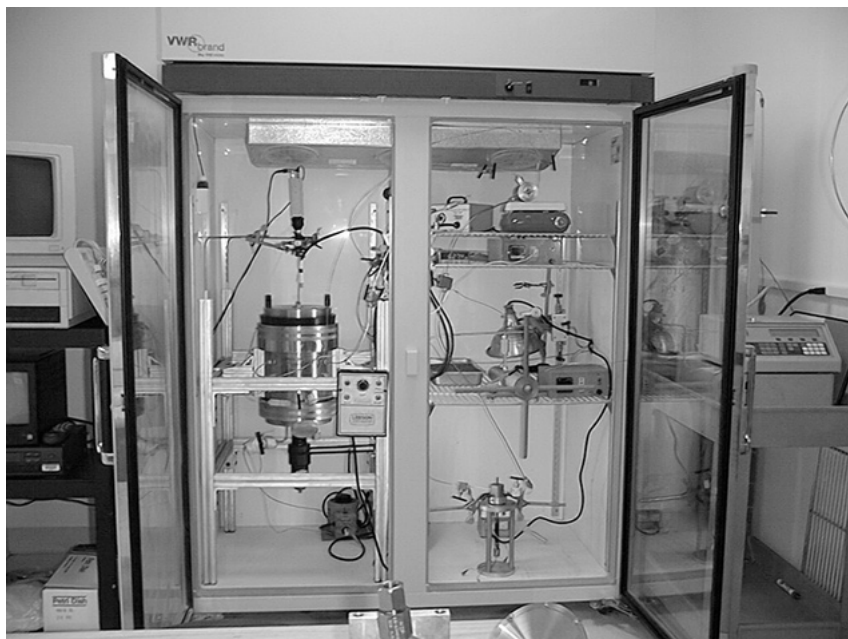


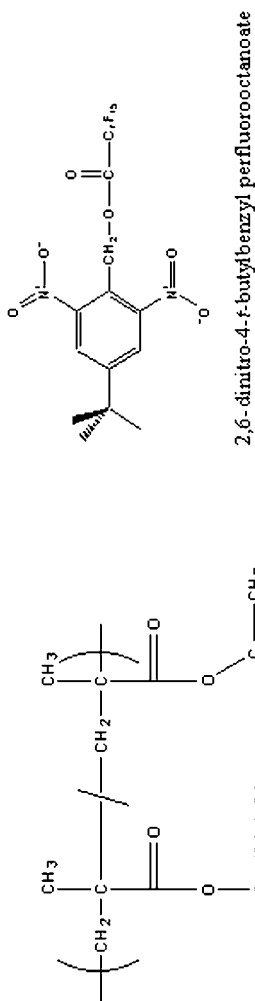
Figure 9 Liquid CO₂ spin coating apparatus.

the unique purpose of deposition from a novel liquid CO₂ spin-coating device. Such a device has been constructed, as shown in Figure 9. The high pressure spin coating apparatus consists of a top-loading high pressure vessel with a magnetic drive unit extending through the bottom of the chamber. The drive shaft is connected to a rotating chuck upon which the substrates are placed. The chuck may be rotated at speeds up to 2500 rpm. CO₂ is pumped into the vessel until the overall pressure is just below the vapor pressure of CO₂. The photoresist polymer is added to a second pump, where it is dissolved in liquid carbon dioxide. Uniform film thickness will result if CO₂ is evaporated at a rate that allows moderate changes in the liquid viscosity.

Potential candidates for 193-nm negative resist and positive e-beam resist systems are shown in Figure 10. The photoresists are based on copolymers of fluoroalkyl methacrylates, which yield glassy polymers that are soluble in CO₂ between 0–20°C at vapor pressure (9). Tert-butyl methacrylate is a common component in photoresists, as the t-butyl group is readily removed by photoacid generators to produce the methacrylic acid (MAA).

3.1.2 Free Meniscus Coatings Free meniscus coating (FMC) is yet another area that could be impacted by a more environmentally responsible solvent such as CO₂.

New 193 nm Negative Resist System



Adapted from Reichmanis et. al. *Macromolecules* **1990**, *23*, 145.

New Positive e-Beam Resist System

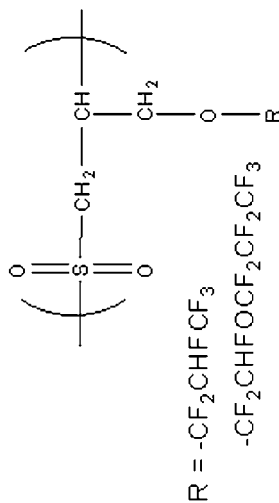


Figure 10 Potential positive and negative photoresists for liquid CO₂ spin-coating.

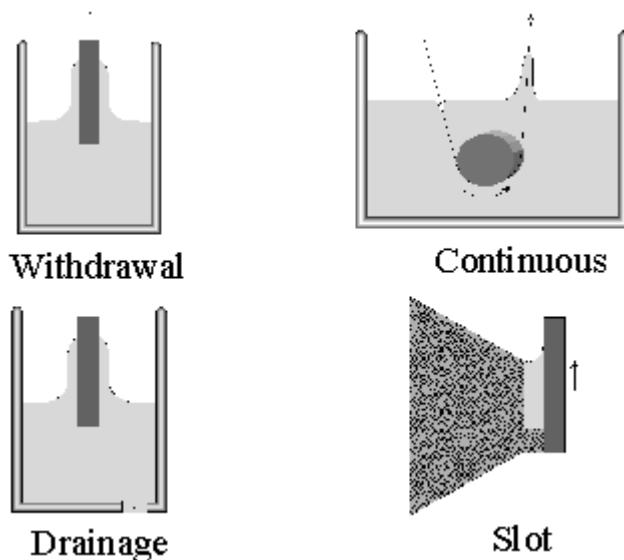


Figure 11 Methods utilized during free meniscus coating.

By definition, any coating technique that utilizes gravity and a meniscus to form a coating is considered free meniscus coating. The meniscus is used to determine properties including withdrawal, drainage, slot, and continuous coating (24) (Figure 11). Various substrates, such as discrete objects—like plates, spheres, and manufactured parts—and filaments and biers, are typically coated by this technique. Almost all the solvents employed are organic and regulated by the Environmental Protection Agency. As one can imagine, nonuniform films often result from this coating technique, as concentration gradients provide a limited control of solvent evaporation. In addition, thin films are difficult to create because withdrawal velocities limit production capacity, and the physical property modifiers decrease control of the film quality.

Liquid CO_2 should be a good FMC solvent. Thin liquid films are possible using CO_2 , and low viscosity and shear stress reduce gradients and rough surface effects. In addition, density manipulations aid in controlling film thickness. Evaporation is regulated using pressure gradients where the main driving force is the difference between the vaporization pressure and the system pressure (Figure 12, see color insert). One potential application for free meniscus coating from liquid CO_2 arises in the electronics industry. Hard disks are the primary storage device in most computers. PFPE lubricant is currently applied by dip coating in a fluorocarbon solvent. PFPEs are soluble in liquid and supercritical CO_2 , opening the door to new opportunities for FMC.

3.2 Metal Extractions

The interest in using CO₂ for metal extractions has been to capitalize on enhanced diffusivity (mass transfer) and pressure tunability—characteristics that should allow for facile separations (16). The polymer-ligand-metal complexes that form can be readily precipitated from solution by altering the CO₂ pressure. Most of the work in CO₂ metal extractions has employed common extracting ligands, such as β -diketones, dithiocarbamates, and organophosphorus reagents (25a–h, 26–28). When fluorine-containing moieties are incorporated into the chelating ligands, the metal complexes show enhanced solubility in CO₂ (25c,e,g; 27; 28g; 29). Yazdi and Beckman attached CO₂-philic oligomer or polymer moieties—consisting of either highly fluorinated or polysiloxane groups—to ligands, improving both the solubility of the metal-ligand complex as well as the ligand extraction efficiency (30a–d). For example, perfluoropolyether-based extractants with dithiocarbamate, dithiol, and picolylamine head groups require only 1.5 eq of chelate for efficient CO₂-extractions of mercury (57%–87%), lead (20%–75%), and arsenic (31%–58%) in CO₂ at 2000 psi and room temperature. Powell et al have taken a different approach to incorporate multiple ligand sites onto the backbone of a single CO₂-soluble fluorinated acrylate polymer chain, allowing for up to 30 wt % polymer in CO₂ (31) (see Figure 8, see color insert). Preliminary extraction efficiencies of 59% were obtained using ligand to metal ratios of 2.7 to 1.

3.3 CO₂-Swellable Supports

Environmentally benign cleaning and extraction processes are in high demand, with the search focusing on a solvent and detergents capable of removing a broad range of contaminants from solid and liquid substrates. A combination of physico-chemical processes contributes to the overall contaminant removal rate, including adsorption and penetration of surfactants into the contaminant film, reduction in viscosity as a result of solvent penetration, shear, and secondary solubilization and diffusion into the bulk phase. The development of novel surfactants for CO₂ has greatly increased the interest in this solvent for cleaning and extraction processes (52).

Cross-linked fluoropolymer beads of 30 μ m to 2 mm can be obtained during the controlled agitation of a well-designed suspension polymerization. Cretté & DeSimone have prepared beads of this type that swell more than 200% in CO₂ (S Cretté & JMD DeSimone, unpublished results). Several potential applications for these beads exist, including separation of gas mixtures containing CO₂. More specifically, CO₂/methane separations can be performed through a high-pressure column filled with fluorinated beads. The gas mixture will be impoverished in carbon dioxide, which will plasticize the fluorinated part of the beads (Figure 13, see color insert). Transition metal and enzymatic catalysis are two other fields of application. Fluorinated copolymers are designed and synthesized either with ligand sites for metal coordination or enzyme attachment sites.

4. APPLICATION OPPORTUNITIES ENABLED BY THE DESIGN OF SURFACTANTS FOR CO₂

4.1 Dispersion Polymerizations

The relative insolubility of many industrially important polymers in supercritical CO₂ necessitates the use of heterogeneous polymerization techniques. Conventional heterogeneous dispersion polymerizations of unsaturated monomers are performed in either aqueous or organic dispersing media with the addition of interfacially active agents to stabilize the colloidal dispersion that forms. Successful stabilization of the polymer colloid during polymerization results in the formation of high molar mass polymers with high rates of polymerization. A similar analogy applies to dispersion polymerization in CO₂ where stabilization has been accomplished with the aide of nonionic-homopolymers (15, 34–40), block copolymers (34, 37–43), and reactive macromonomer surfactants (22a,b; 39; 40; 45). Supercritical CO₂—in conjunction with free radical initiators and specifically designed, interfacially active, stabilizers—is an environmentally responsible alternative to aqueous and organic dispersing media for heterogeneous dispersion polymerizations.

Typically, a free radical dispersion polymerization in supercritical CO₂ starts as a one-phase, homogeneous system such that both the monomer and the polymerization initiator are soluble in the polymerization medium. As the reaction progresses, the resulting growing polymer phase separates into primary particles. Amphipathic molecules—mediators that prevent particle flocculation and aggregation—present in the system stabilize these primary particles. Polymer colloids produced by dispersion polymerizations are usually stabilized by a steric mechanism rather than an electrostatic mechanism that is common to colloidal stabilization in aqueous environments (15). Steric stabilization of a colloidal dispersion is usually imparted by amphipathic macromolecules that become adsorbed onto the surface of the dispersed phase. These amphipathic macromolecules contain an anchoring segment that attaches to the particle (usually by physical adsorption), and stabilizing moieties that are soluble in the continuous phase. The stabilizing moieties project into the continuous phase (which needs to be a good solvent for the stabilizing moieties) and prevent flocculation by mutual excluded volume repulsions during a Brownian collision, thereby imparting stability to the colloid.

Conventional lipophilic monomers, exemplified by methyl methacrylate, can be quantitatively (>90%) polymerized heterogeneously to very high conversion in supercritical CO₂. This polymerization proceeds in the presence of poly(FOA) resulting in kinetically stable dispersions of micrometer-sized particles with a narrow size distribution (15). The amphiphilic activity exhibited by poly(FOA) suggests that environmentally responsible CO₂ is a viable replacement for the solvent traditionally used in heterogeneous polymerizations and lays the foundation for surfactant-modified, CO₂-based separations processes.

4.2 Microemulsions

Over the past six years a lot of attention has been given to surfactant-stabilized water dispersed into a continuous CO₂ phase (19, 46, 46a–i). Spectroscopic evidence has been presented for the formation of these microemulsions (47). Surfactants reported to stabilize water-in-CO₂ microemulsion include ammonium carboxylate perfluoroether (PFPE-COO⁻NH₄⁺) (46, 48, 49), the hybrid hydrocarbon-fluorocarbon C₇F₁₅CH(OSO₃⁻Na⁺)C₇H₁₅ (46a), a di-chain hybrid surfactant (C₇H₁₅)-(C₇F₁₅)-CHSO₄⁻Na⁺ (46b), and di(1*H*,1*H*,5*H*-octafluoro-*n*-pentyl) sodium sulfosuccinate (di-HCF₄) (46c–e). The safe and tunable environment afforded by w/c microemulsion has recently been exploited as a host for a wide variety of hydrophiles (46e) and a protein bovine serum albumin (46f), as well as a reaction vessel for small organic molecules (46g) and cadmium sulfide semiconductor nanoparticles (46h). The low pH range of the w/c microemulsion has been varied to values of 5–7 with the addition of a buffer, lending these types of systems to enzymatic reactions that exhibit optimum catalytic turnover of substrate at higher pH values (46i).

4.3 Dry Cleaning and Degreasing Industries

Throughout the world there is an increasing concern regarding the contamination of ground water as a result of the negligence of industrial manufacturers and service industries that were not, and some that are still not, good stewards of our environment. Unfortunately, the levels of stewardship suggested by solvent manufacturers to solvent users over the past 50 years may have been inadequate to fully protect our environment. Many communities in the United States face the threat of their drinking water supplies being contaminated with trichlorethylene, perchloroethylene (perc), and petroleum as a result of cleaning and degreasing operations such as dry cleaning and metal finishing. These alarming situations are exemplified by the now well-known incidences such as the Cuyahoga River fire in Ohio and the linkage between ground water contamination and illness portrayed in the book and movie “A Civil Action.” Most recently, studies reported (60) by researchers at the London School of Hygiene and Tropical Medical found that pregnant women who work in dry cleaners where perc is used had a miscarriage rate of about 20%, nearly double the rate for those not working in the industry. In addition, researchers at the Silent Spring Institute (61) found a possible linkage between the high rate of cancer among wealthy women and their frequent use of dry cleaning. Clearly, communities around the nation are concerned about contamination of their drinking water by dry cleaning solvents (62, 63). CO₂ offers an important and economically viable pollution prevention solution for many of the problems now facing the cleaning industries.

4.3.1 Dry Cleaning of Garments The dry cleaning industry is an \$8 billion service industry in the United States and a \$24 billion industry globally. There are an estimated 100,000 dry cleaning machines distributed around the world

and 80%–90% of them utilize perc as the primary cleaning solvent. The U.S. Environmental Protection Agency has identified perc as a groundwater contaminant and a probable human carcinogen. In recent years, government regulations and greater consumer awareness of environmental and health issues has led the dry cleaning industry to search for a safer alternative to perc. Petroleum-based solvents were considered, but the associated disadvantages are numerous including their potential to ignite, zoning restrictions, taxation for use, and governmental regulations. Furthermore, the potential for ground water contamination is similar to the problem encountered with underground storage tanks for gas stations.

Liquid CO₂ is an environmentally safe alternative solvent for the dry cleaning and other cleaning industries to consider. MICELL™ Technologies (www.micell.com), a company cofounded by DeSimone, introduced a novel liquid CO₂ cleaning process (Micare™) that has been developed and favorably recognized by the Environmental Protection Agency and the garment and textile care industry. The Micare™ process is a CO₂-based cleaning system that poses no environmental or human health risk, lowers energy consumption, saves money, improves cleaning performance, and reduces environmental regulatory burdens. MICELL™ Technologies has introduced a liquid CO₂ dry cleaning machine that is fully automated and equipped with an ultrafine (5–10 micron lint filter) filtration system. More than 98% of the CO₂ used during the cleaning cycle is recycled. In addition, the nonhazardous detergent system is also recycled. The machine uses a large conventional rotating basket and has a 60 lb cleaning capacity with a 40 minute cleaning cycle (Figure 14). With an overwhelmingly favorable response from dry cleaners, sixty machines are expected to be in place by the end of 2000. This introduction by MICELL™ Technologies is now encouraging others such as Global Technologies (www.globaltechnol.com) to enter the market.

4.3.2 Metal Degreasing Industries Manufacturing industries have traditionally used CFCs and other halogenated solvents for the precision cleaning of metal surfaces. Approximately 170 million pounds of CFC-113 and methyl chloroform were used in 1993 in the United States alone for vapor degreasing operations (64). The search for an alternative solvent intensifies as regulations restrict the use of CFCs. Many are looking for a solvent that matches the degreasing power of CFCs without the environmental problems. Replacements such as perfluorocarbons and hydrochlorofluorocarbons are only short-term solutions with many problems including toxicity issues, financial burdens, and environmental concerns of their own. Aqueous cleaning replacements are being considered, but there are still several disadvantages including poor performance in comparison to halogenated solvents, copious amounts of waste that require special handling procedures, extensive drying steps to remove residual water, and flash rusting. Hoggan et al (65) have developed a process that uses CO₂ and specially designed detergents to remove cutting oils, drawing oils, and other metal contaminates. The process utilizes liquid CO₂ (with a density similar to water but a viscosity like that of a gas) and

Figure 14 Liquid CO₂ dry cleaning machine.



thus can reach places water and organic solvents miss. A unique separation system allows the CO₂ and detergents to be recycled for reuse so the resulting waste stream is minimized to that of the contaminant oil and a small amount of the nontoxic detergent.

5. BUILDING ON EXPERIENCE TO INTRODUCE NOVEL CO₂-BASED APPLICATIONS

The experience associated with using CO₂ in such processes as (a) homogeneous solution polymerization; (b) heterogeneous precipitation and dispersion polymerization; (c) spin coating and free meniscus coatings; (d) cleaning, separations, and extractions; (e) microcellular foaming and polymer impregnation; (f) phase transfer reactions and small molecule reactions; (g) heterogeneous and homogeneous catalysis; and (h) enzymatic catalysis has inevitably led to a lot of industrial interest. New applications for CO₂ are popping up with a level of creativity that has not tapered off from the original fundamental developments in the field. Two such applications include CO₂-swollen melt phase step growth polymerization and solid-state polymerization.

5.1 CO₂-Swollen Melt Phase Step Growth Polymerization

Polycarbonates are an important class of polymers due primarily to their toughness and optical clarity. Produced at a rate of 2.7 billion pounds per year and expected to increase to 4 billion pounds per year, the polycarbonate market is growing as digital versatile discs and polycarbonate windows become common place (66). Poly(bisphenol A carbonate) is commercially synthesized by two different methods: (a) the interfacial reaction between phosgene dissolved in an organic solvent and bisphenol A dissolved in an aqueous alkali solution and (b) the bulk reaction between diphenyl carbonate and bisphenol A. Copious amounts of aqueous and organic waste are generated in the former synthetic route. Whereas the bulk reaction reduces the generation of waste, this type of reaction is limited to intermediate molecular weights as a result of side reactions and high viscosities. High viscosity hinders mixing and removal of condensate from the melt phase polymerization. The combined effect is slower reaction rates.

CO₂ is a viable aide in polymer processing where it swells a polymer melt and effectively lowers the processing temperature. In a closed system, the polymer swelling correlates to CO₂ mass uptake by the polymer. Swelling measurements allow for the determination of the diffusion coefficient of CO₂ in the polymer (Figure 15). It has been demonstrated that CO₂ is able to swell polycarbonate in the melt phase producing both a reduction in melt viscosity and an increase in free volume of the melt (67).

The increase in free volume as a result of the plasticization should provide more polymer surface area for condensate removal and greater mobility of chain ends.

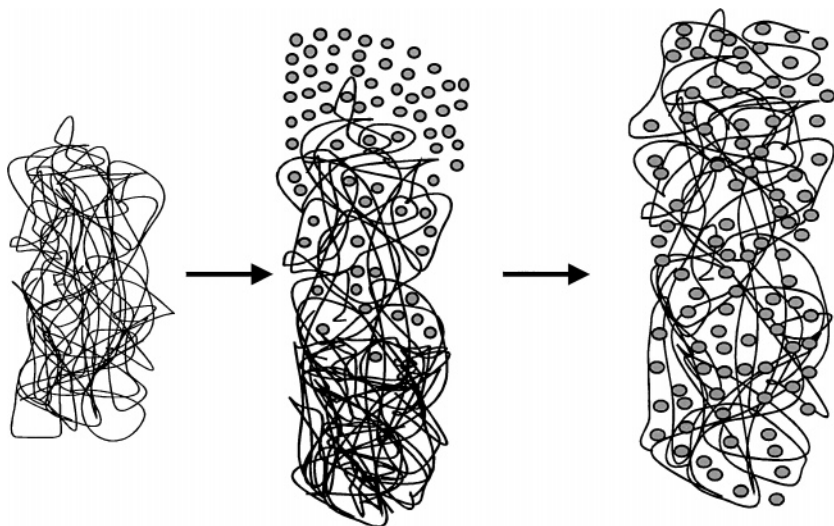


Figure 15 Swelling and plasticization of a polymer melt by CO₂.

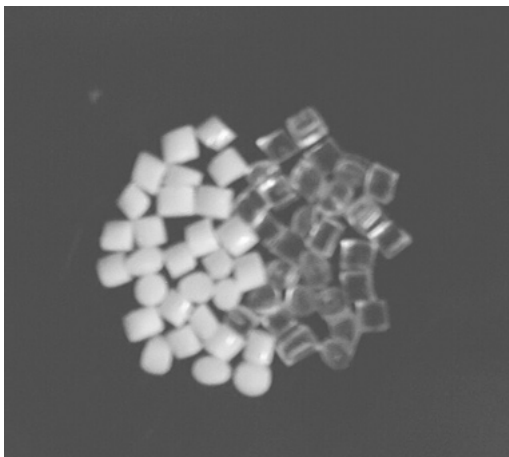
Furthermore, CO₂ is compatible with the mechanism associated with the synthesis of poly(bisphenol A carbonate) from bisphenol A and diphenyl carbonate. New opportunities in reducing the production/processing costs and improved materials (e.g. optical clarity) could result from the reduction in viscosity of the melt-phase swollen with CO₂.

5.2 Solid State Polymerizations

Another approach to avoiding the high temperature and high viscosity encountered in the bulk reaction is to perform solid-state polymerization on low molecular weight polycarbonate oligomers. Polycarbonate does not crystallize by thermal annealing to any appreciable extent; however, it undergoes solvent-induced crystallization by organic solvents (68)—which are difficult to handle in a wide-scale commercial plant and undesirable in that they raise potential environmental risks—and by the addition of nucleating agents (69). Additionally, pulling a vacuum for 24 hours at temperatures above 150°C does not rid the polymer of residual solvent (68, 70). Polycarbonate films have been shown to undergo crystallization upon exposure to CO₂ at elevated pressures and temperatures (71). At the end of the crystallization process, CO₂ was found to rapidly degas from the polymer after venting.

The solid-state polymerization process is efficient when the polymer is in the form of small pellets. As the pellet size increases, a molecular weight gradient and morphological changes develop between the center and the surface of the pellet. The gradient is caused by the condensate molecule diffusing out of the interior particle. The solid-state polymerization progresses by inducing crystallization in the polycarbonate pellet (Figure 16). CO₂ cannot only aide in the crystallization of polycarbonate, but also in the removal of the condensate. By utilizing supercritical CO₂ as the sweep fluid, the solid-state polymerization of polycarbonate

Figure 16 Amorphous polycarbonate pellets (*top*) shown to crystallize (*bottom*) by carbon dioxide.



can be viewed as a supercritical fluid extraction of condensate from the polymer particle. In addition, CO₂ plasticizes the amorphous regions of the polycarbonate sample, providing increased mobility for chain extension reactions. Lower reaction temperatures should be feasible because the presence of CO₂ depresses the glass transition temperature of the polymer. This is just one example of the benefits of using supercritical CO₂ as a processing aide. Other examples could be envisioned if the mechanism of polymerization is compatible with the use of CO₂.

5.3 Microcellular Foams

Supercritical fluids (SCFs) in general and carbon dioxide in particular, provide a suitable medium for impregnating polymer matrices with metal nanoparticles. The impregnation of polymers and related porous solids has been monitored by Fourier transform infrared and UV-vis spectroscopy (72–77). In some cases, a metal-containing precursor has been incorporated into the polymer matrix and subsequently decomposed. The decomposed material is removed by venting CO₂ and if necessary subsequently flushing with scCO₂. These materials are being considered for electronic and optoelectronic devices and novel biomaterials for prosthetic replacements. (COD)-PtMe₂ has been infused into polymer PMP and PTFE, respectively, to provide a composite material with <50 nm-sized Pt particles (78, 79). By venting scCO₂ in the preparation of composite material prior to hydrogenating the infused (COD)PtMe₂ precursor, smaller particles were obtained (79). This work has been extended to include deposition of metal films on substrate and impregnation of catalyst supports (79). Infusion techniques in the pharmaceutical field has lead to controlled-release drug materials (80). Another area of interest has been SCF-assisted dyeing of textiles with mordant dyes (81). Spray coatings have also received interest; the UNICARB system (commercialized by Union Carbide) claims a 30%–70% reduction in VOCs by replacing the conventional organic solvents of the process with 10–50 wt% scCO₂ (82). Powder coatings have been revolutionized by the VAMP process, which involves swelling a polymer with scCO₂ and subsequently expanding the mixture through a valve. The foam breaks up as it is expanded, resulting in a fine powder that is at least 50% cheaper to manufacture than by conventional processing. The VAMP approach has been used to produce synthetic bone material for medical use (83).

5.4 Catalysis in Supercritical Fluids

Several traditional chemical reactions are candidates for supercritical CO₂. Catalytic reactions are important, and the field is rapidly expanding, with the opportunity for using scCO₂ existing for both homogeneous and heterogeneous catalysis. Using SCFs avoids the potential hazards associated with volatile organic solvents and reduces the waste materials associated with isolating the hydrogenation product. In addition, reaction efficiency is improved because hydrogen is completely miscible with SCFs.

Homogeneous catalysis in SCFs provides rates or selectivities that can be significantly higher than in conventional solvents. Hydrogenation of scCO_2 into formic acid is a classic reaction (84–88). A number of reports have been published that demonstrate continuous hydrogenation using fixed-bed catalysts (89, 90). Epoxidation of tBUOOH in CO_2 has been reported (91). Alkylation reactions have also been reported (92, 93).

Heterogeneous catalysis in scCO_2 is also an active area of research, and a recent publication has reviewed the field (94). Alkylation (95), esterification (96, 97), hydrogenation (89, 90, 98, 99), and oxidation (100) are some of the reactions that have been reported in scCO_2 . Isomerization of 1-hexene has been accomplished using CO_2 and cosolvent of *n*-pentane and *n*-hexane (101, 102).

The use of SCFs as nonaqueous solvents for enzyme-catalyzed reactions provides all the advantages typically associated with this type of media as well as the ability to control biocatalytic reactions. The focal point of interest in this field employs carbon dioxide as the reaction medium. A variety of lipase enzymes have been studied in acidolysis (103–105), oxidation (106), esterification (107, 108), and racemic (109) reactions [see the recent review by Mesiano et al (110)].

6. CONCLUSIONS

The uses of liquid and supercritical CO_2 have developed substantially over the last few years, with viable applications now existing in polymer synthesis, coatings, heterogeneous and homogeneous catalysis, solid supports, and the dry cleaning industry. This emerging technology platform has the potential to improve energy efficiency, reduce/eliminate emissions, eliminate health and safety hazards related to handling and shipping noxious chemicals, and enhance the manufacturing throughput.

A number of concepts have already been demonstrated, but there are still several barriers to adopting the CO_2 -based applications presented in this review. There is a large capital cost associated with the current engineering approach to high-pressure reactor designs. Furthermore, there are currently few investment incentives for adopting pollution prevention policies. It is clear that new chemistry is needed to improve current processes and promote the development of new materials properties.

Creative new chemistry would enable new processes while avoiding the need for solvents or water, enable a deeper understanding of current processes through model compounds, and enable integration of the reaction and separation processes. The fundamental ground work in the field of CO_2 research has been laid, but in addition to the barriers outlined above, two problems remain: (a) effectively communicating what should be targeted in this vast field and (b) making the scientific community adequately informed so they can communicate across disciplines and across industrial, governmental, and academic barriers. Overcoming these obstacles to adopting a carbon dioxide technology platform is a pivotal point in

converting traditionally hazardous processes to the more environmentally responsible processes of the future.

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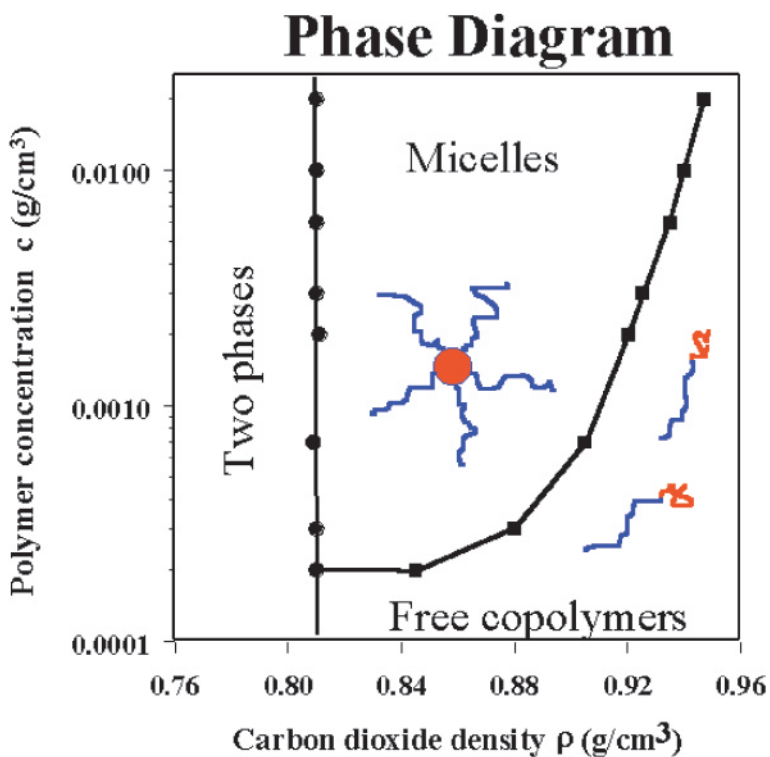


Figure 8 Phase diagram showing reversible micellization of copolymer.

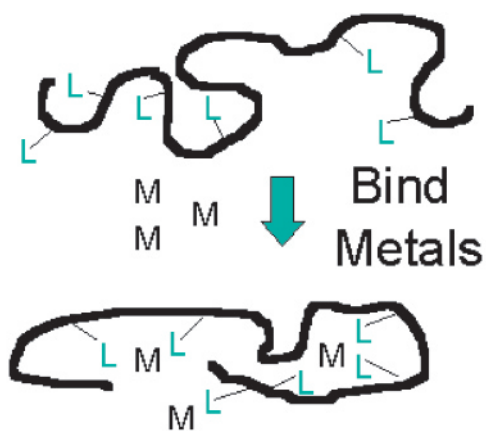


Figure 12 Design of CO₂-philic polymers with ligand sites for metal extractions.

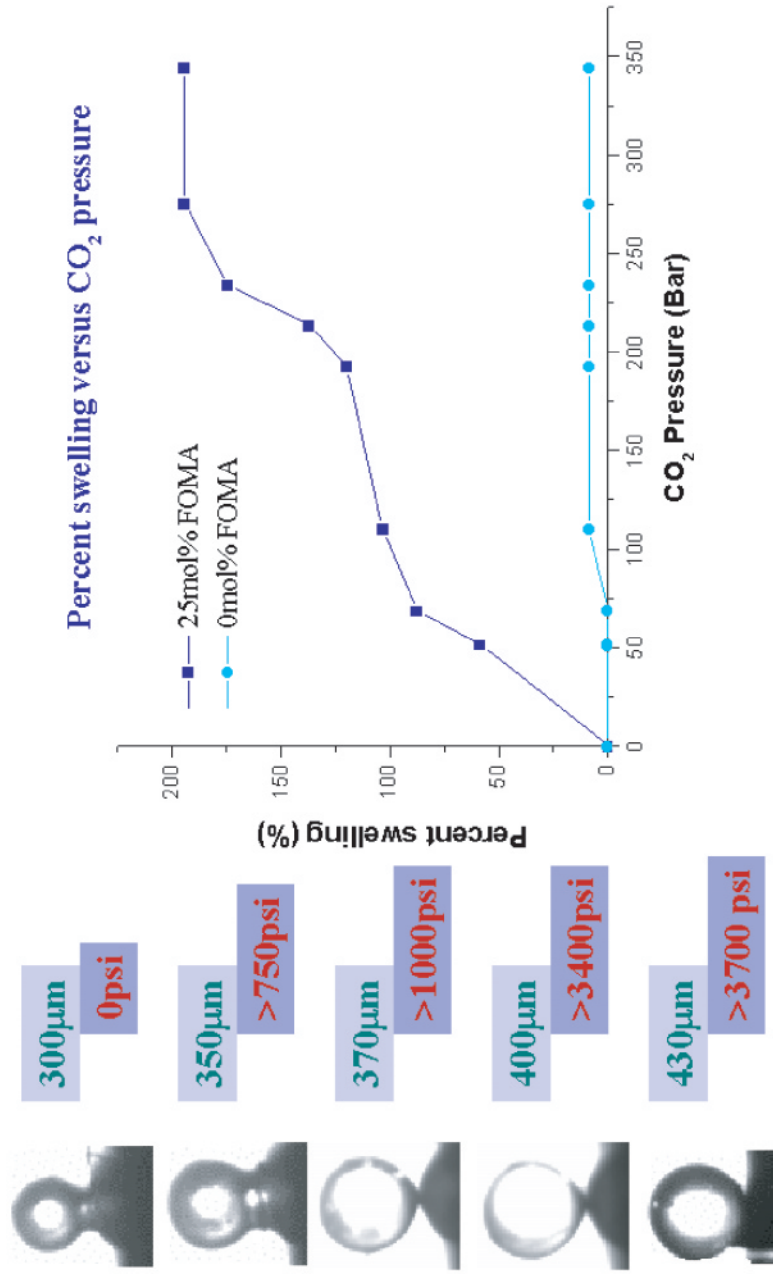


Figure 13 CO₂-induced swelling of cross linked beads.