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Inverse Emulsion Polymerization of Acrylamide in Supercritical Carbon Dioxide

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Introduction. Supercritical fluids, that is, materials at temperatures and pressures above their critical values, possess intriguing physical properties which make them interesting media in which to conduct polymerization. For example, supercritical fluids exhibit "liquidlike" densities, and thus liquidlike solvent power, while also displaying "gaslike" viscosities under the same conditions.[1] Consequently, it is, in principle, possible to conduct an emulsion polymerization in a supercritical environment with a mixture viscosity that is 1–2 orders of magnitude lower than that in an analogous liquid system.

Despite the potential advantages for conducting polymerization in supercritical fluids, it must be noted that, as either the molecular weight or the polarity of the solvent increases, the critical temperature (T_c) of the solvent also rises precipitously. Thus, while the T_c's of CO_2, ethane, and fluoroform are all between 25 and 35 °C, the critical temperature of methanol is 240.0 °C, of toluene 320.6 °C, and of water 374.15 °C. Thus, conducting polymerization of a hydrophilic or highly polar monomer in a supercritical solvent, while also maintaining a process temperature less than 100 °C, will require use of an emulsion. Present work[2,3] has shown that the inverse emulsion polymerization of acrylamide, for example, can be carried out in supercritical ethane/propane mixtures at 65 °C, producing high molecular weight material at rapid rates. Further, the density of the continuous phase in that system exhibited significant influence on both the rate of reaction and the ultimate molecular weight of the polymer.

Although these previous results in supercritical alkanes are interesting, ideally one would prefer to conduct an emulsion polymerization of a water-soluble polymer in supercritical CO_2. Carbon dioxide is nonflammable, inexpensive, and relatively nontoxic and exhibits a critical temperature of only 31 °C. However, as shown by work by Consani and Smith,[4] most conventional alkyl-functional ionic surfactants exhibit very poor solubility in carbon dioxide. Further, while nonionic ethoxylated alcohol (C_iE_j-type) surfactants do dissolve in CO_2 in appreciable quantities, water uptake was found to be relatively low[5] and their ability to support emulsion polymerization of acrylamide poor.[3] Consequently, to extend the use of CO_2 to the inverse emulsion polymerization of water-soluble monomers, exploration of the rational design and synthesis of highly CO_2-soluble amphiphiles has been undertaken.[6] Like their conventional analogs, these molecules possess a polar head group designed to accomplish micelle formation, yet, unlike conventional compounds where an alkane tail (or tails) is covalently bonded to the head group, the target molecules possess a hydrophobic tail comprised of functional groups designed to interact favorably (in a thermodynamic sense) with carbon dioxide.

To identify potential CO_2-philic functional groups, the extensive literature data base covering solute structure–CO_2 solubility relationships has been consulted.[7-10] Although the calculated solubility parameter of supercritical carbon dioxide approaches that of hexane above 4350 psi at 40 °C,[11] Johnston and colleagues have shown that the quadrupole moment of carbon dioxide serves to inflate the calculated value of CO_2's solubility parameter to a point which is significantly above a number which actually reflects its solvating power.[5] We have determined that the inclusion of functional groups such as fluoroethers and dimethylsiloxane in a solute molecule will contribute to high solubility in CO_2. For example, whereas 13 000 MW fluoroether and silicone polymers exhibit solubilities greater than 5 wt % at pressures less than 4350 psi,[11] previous research has shown that polyolefin waxes of comparable molecular weight exhibit solubilities which are orders of magnitude lower at the pressures examined.[12,13] Desimone and colleagues[14] have recently shown that replacing alkyl groups with fluoroalkyl groups leads to dramatic increases in the solubility of polyacrylates in carbon dioxide. It appears that CO_2-philicity derives from several structure factors, including low solubility parameter, electron-donating capability, and low polarizability. Regarding surfactant solubility, preliminary results with model fluoroalkyl sulfonates, ionic-functional silicones, and fluoroethers[15,16] support the proposed hypothesis in that solubility in carbon dioxide rises significantly upon replacement of $-CH_2-$ with $-CF_2-$, $-Si(CH_3)_2O-$, or $-CF_2-CF(CF_3)O-$ in these compounds. This allows for the creation of a CO_2-soluble surfactant which is capable of creating inverse emulsions or microemulsions, due to the higher weight percents that are soluble.

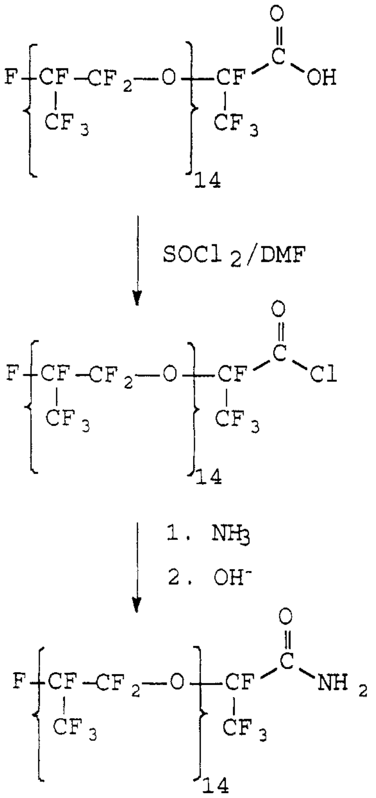

Figure 1. Surfactant synthesis.

Previously, Candeau and colleagues have shown that amide-functional nonionic amphiphiles are effective in supporting the inverse microemulsion polymerization of acrylamide in conventional liquids.[17] In the present work, a hexafluoropropylene oxide oligomer end-capped with an amide group is used to conduct what we believe to be the first emulsion polymerization of a water-soluble monomer (acrylamide) in carbon dioxide. AIBN was used as the initiator in all of the polymerizations presented. Its efficiency in supercritical CO_2 has recently been evaluated.[18]

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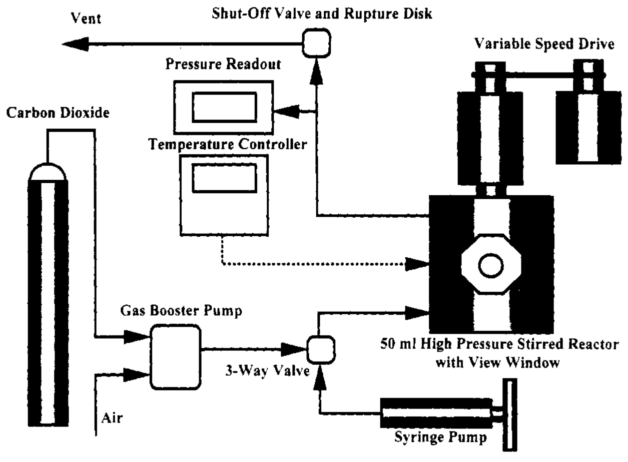

Figure 2. Experimental apparatus.

Experimental Section. Materials. Krytox carboxylic acid 157FSL (poly(hexafluoropropylene oxide), carboxylic acid capped, molecular weight = 2500) was used as received from DuPont, Inc. Perfluoromethylcyclohexane (technical grade, 90%), thionyl chloride (99+%), *N,N*-dimethylformamide (99+% HPLC grade), 112 Freon (99+% spectrophotometric grade) and acrylamide (99+% electrophoresis grade) were used as received from Aldrich. Ammonia (99+% anhydrous) from Liquid Carbonic Gasses was used as received. 2,2′-Azobis(isobutyronitrile) (AIBN; Polysciences, Inc.) was recrystallized twice from methanol. Carbon dioxide (Bone Dry grade from Linde Specialty Gasses) was purified by passing through a high-pressure gas purifier (Liquid Carbonic) to remove water and trace organics.

Surfactant Synthesis/Characterization. The amide end-capped poly(hexafluoropropylene oxide) surfactant was prepared via reduction of the Krytox acid to the acid chloride, followed by reaction with anhydrous ammonia (Figure 1). In a typical experiment, 100 g of Krytox FSL (40 mmol) was dissolved in 100 g of perfluoromethylcyclohexane in a three-necked flask equipped with a dry ice cold finger. Subsequently, 9.51 g of thionyl chloride (80 mmol) and 2.92 g of dimethylformamide (40 mmol) are added, and the mixture has been heated under reflux conditions (under an inert atmosphere) for several hours. The solvent and residual reactants were removed under vacuum. The acid chloride was then reacted with excess ammonia under pressure. Typically, 25 g of acid chloride in 50 g of dried Freon 112 ($C_2Cl_2F_4$) was added to a Parr 100-cm^3 stirred reactor. The reactor was then immersed in a dry ice/acetone bath and cooled to −35 °C, at which point a large excess of anhydrous ammonia was added. The reactor was then slowly warmed to room temperature while stirring. Following the removal of excess ammonia, the product was washed three times with 5% aqueous NaOH, followed by three washings with distilled water, and then vacuum drying for 48 h.

Characterization was by FT-IR (Mattson Polaris with MCT detector) and ^{1}H NMR (Bruker 300). Krytox-COOH: FT-IR, 1776 cm^{-1}; ^{1}H NMR, 9.63 ppm. Krytox-COCl: FT-IR, 1809 cm^{-1}. Krytox-$CONH_2$: FT-IR, 1753 cm^{-1}. –NH_2: FT-IR, 3300 cm^{-1}; ^{1}H NMR, 7.96 and 6.57 ppm.

Phase Behavior. The phase behavior of the amide-functional fluoroether oligomer in carbon dioxide was measured using a high-pressure, variable volume view cell (D. B. Robinson, Inc.), as previously described.[15]

Polymerization. High-pressure emulsion polymerizations were carried out in a 50-cm^3 reactor equipped with a blade stirrer and aligned sapphire windows (Figure 2), designed for operation at pressures to 7500 psi and temperatures to 150 °C. Typically, 10 g of acrylamide, 10 g of deionized water, 10 mg of AIBN, and various levels of surfactant are charged to the reactor, which is then sealed, purged with CO_2 for several minutes, and then heated and pressurized to the reaction conditions of 5000 psi and 60 °C while stirring at 600 rpm. Following 1 h, heating is discontinued and the CO_2 is slowly vented through a 3:1 chloroform/MeOH mixture. The contents of the reactor are then removed, and the resulting product dried. The emulsion formulation charged to the reactor was modeled after common commercial inverse emulsion systems.[19]

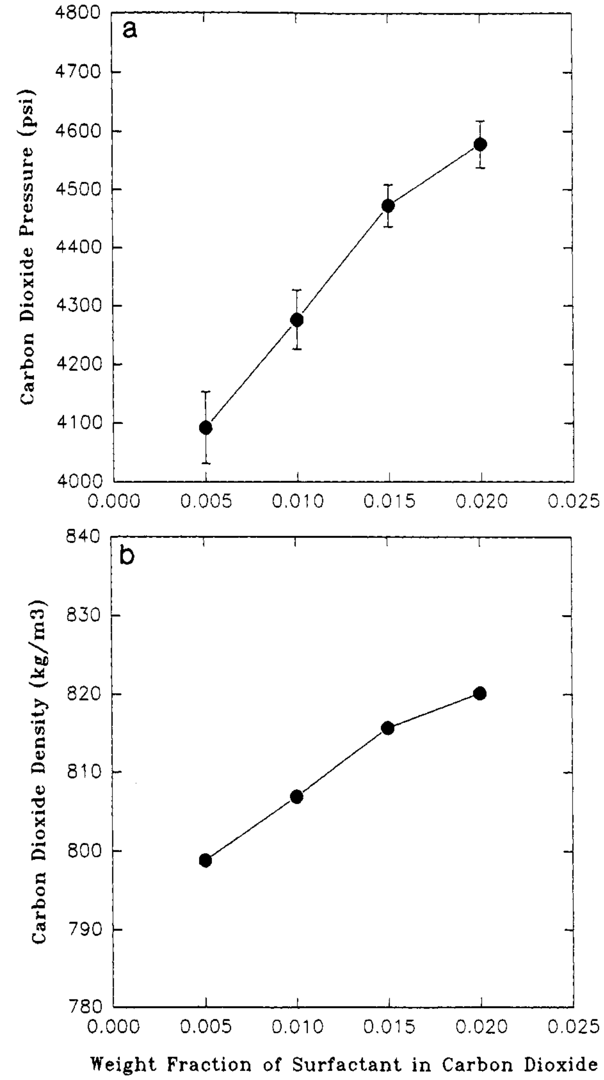

Figure 3. (a) Cloud points of surfactant at 60 °C. (b) Carbon dioxide density at the cloud point.

Polyacrylamide Characterization. Intrinsic viscosities were determined for the products of the three reactions as per a standardized industrial procedure[19] which was developed from available literature.[20,21] In a typical experiment, the polymer samples were double diluted to arrive at a 0.15% mass concentration of polymer in distilled, deionized water. Next, 4 mL of this solution was mixed with 4.3 mL of 2 N NaCl, and 4 mL of the resulting solution was placed in a Cannon–Ubbelohde viscometer tube in a 30 °C water bath. Timed measurements were made at three concentrations, using 1 N NaCl for subsequent dilutions. Polymer yields were determined by washing 1% polymer solutions with a 3:1 chloroform/MeOH mixture to remove any residual monomer and then drying.

Table 1. Results of Acrylamide Polymerization in Carbon Dioxide at 60 °C

polymer property	surfactant concn 0%	 1%	 2%
intrinsic velocity (dL/g)	11.60	12.28	9.15
wt av mol wt[a] ($M_w \times 10^{-6}$)	6.61	7.09	4.92
Huggins constant	0.310	0.505	0.479
percent yield (wt %)	97.4	99.8	99.8

[a] Reference 21: estimated M_w from empirical relation eq 3.

Results and Discussion. Surfactant Characterization. Phase behavior results (cloud-point curve) for the krytox-amide/CO_2 mixture at 60 °C are shown in parts a and b of Figure 3. As can be seen, the surfactant is miscible with CO_2 under the polymerization conditions employed. In Figure 3b, the results from Figure 3a are transformed to a density basis, showing that there is relatively little fluctuation in CO_2 density in the range of conditions under study. The surfactant's ability to form micelles is implied,[16,17] and the micelle size was not determined.

Polymerization. Upon agitation, the reactor contents, regardless of the surfactant concentration, adopted a milky-white appearance similar to that of conventional inverse emulsion polymerizations. It is to be noted, however, that the 0% surfactant run (see Table 1) appeared to be a simple dispersion polymerization of an aqueous solution in CO_2, from which a large mass of polymer precipitated during the run. Unlike the krytox-amide runs, the 0% surfactant mixture immediately phase separated after agitation ceased.

Polyacrylamide Characterization. Although all reactions were allowed to proceed for 1 h, preliminary experiments showed that the polymerizations employing the krytox-amide go to completion in less than 15 min at 60 °C. Products formed in those reactions where krytox-amide had been added consisted of water- and CO_2-swollen beads of less than 1 mL in size. The agglomerated bead mass filled the entire volume of the reactor, whereas the 0% run was a single solid mass at the bottom of the vessel. Characterization by viscometry[19] (Table 1) revealed that, although all of the polymers formed were of high molecular weight (previous work has shown that suspension polymerization of acrylamide in carbon dioxide will produce high polymer[22]), the materials formed via the emulsion route exhibited a lower degree of branching, as evidenced by Huggins coefficients close to 0.5.[20,21] That the addition of 2% surfactant led to a lower molecular weight may be due to chain transfer to surfactant. In general, the molecular weights obtained via polymerization in carbon dioxide are comparable to those generated in a conventional polymerization in an alkane medium.[23,24]

Conclusion. A new, highly CO_2-soluble surfactant has been successfully used to create an inverse emulsion for carrying out the polymerization of acrylamide in supercritical CO_2. The polymer intrinsic viscosities demonstrate that the product is of significant molecular weight in comparison to conventional emulsion polyacrylamide. The Huggins constants identify the surfactant-containing polymerizations as yielding more linear products. The yields of these polymerizations were also significantly higher than the no-surfactant polymerization. These results strongly support the conclusion that successful inverse emulsion polymerizations have been carried out for the first time in supercritical CO_2.

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