Polymerization of Tetrafluoroethylene in a Hybrid Carbon Dioxide/Aqueous Medium

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Poly(tetrafluoroethylene) (PTFE) is primarily manufactured by free-radical polymerization methods in aqueous media using heterogeneous processes.[1] In general, two types of aqueous processes, referred to as suspension and dispersion polymerization, are employed. Suspension polymerization of TFE involves the use of little or no dispersing agent coupled with vigorous agitation and yields a coagulated granular resin. Dispersion polymerization of TFE involves the use of an emulsifying agent, such as ammonium perfluorooctanoate, in conjunction with mild agitation and typically yields a stable colloidal dispersion of PTFE particles.

Carbon dioxide has recently been employed as an inert medium for a variety of free-radical reactions (a recent review focusing on polymerizations is available).[2] CO_2 has even proved inert to the highly electrophilic fluorocarbon radicals based on TFE.[3,4] We have recently reported dispersion polymerizations in a carbon dioxide continuous phase resulting in spherical colloidal particles of poly(methyl methacrylate) using CO_2-soluble amphiphiles.[5] Previous reports by us have also detailed solution[6] and precipitation[7] polymerizations in carbon dioxide. In addition, others have reported precipitation polymerizations[8−10] and attempts at emulsion polymerization for the synthesis of water-soluble polymers in CO_2.[11,12]

Because carbon dioxide and water exhibit low mutual solubilities, the combination of carbon dioxide based processes and conventional aqueous heterogeneous polymerization processes is similar to the biphasic fluorocarbon/hydrocarbon system for olefin hydroformylation recently reported by Horvath[13] and provides a substantial departure from current technologies allowing for the compartmentalization of monomer, polymer, and initiator based on their solubility characteristics. Furthermore, the tunability inherent to supercritical fluids allows one to vary the density, viscosity, and solvent strength of the carbon dioxide phase with simple changes in pressure or temperature. It is well known that carbon dioxide significantly plasticizes many polymers,[14] allowing one to tune not only the solvent environment but potentially the glass transition temperature, melting temperature, and viscosity of the polymer being formed. In addition, the diffusion rate of small molecules into and out of plasticized polymer particles during the reaction should be influenced by the partition coefficient of CO_2 for the system. These biphasic systems are ideally suited for handling highly reactive monomers such as chloroprene or tetrafluoroethylene, where diluting the monomers with inert carbon dioxide can serve to moderate reactivity. Also, water's high heat capacity can be advantageous in controlling exothermic polymerizations. It was recently discovered that tetrafluoroethylene (TFE), a potentially dangerous material to handle,[15] may possibly be handled more safely as a mixture with CO_2.[3,16] As such, it would be ideal if TFE could be handled and polymerized directly as a mixture with carbon dioxide, which would mitigate the potential hazards associated with handling the neat monomer. Herein we report the polymerization of tetrafluoroethylene in a hybrid CO_2/aqueous reaction mixture using water-soluble persulfate initiator with and without surfactants (shown below).

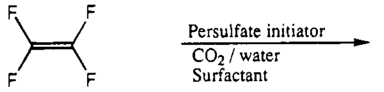

Table 1. Reagent Quantities Charged, Yields, and Molar Masses Obtained for Tetrafluoroethylene Polymerizations in the 25-mL Reactor

TFE (g)	$S_2O_8^{2-}$ (mol)	surfactant [$C_7F_{15}COO^-$]	yield (%)	M_n (kg/mol)
4.9	9.2×10^{-5}	5.5×10^{-3}	82	20
5.5	9.2×10^{-5}	5.2×10^{-3}	72	20
4.8	1.8×10^{-6}		43	260
5.3	3.9×10^{-6}		13	900

Two series of reactions are presented. The first was conducted in a 25-mL high-pressure cell which has been previously described.[3] The cell was fitted with a horizontal paddle stirrer in place of the sapphire window to provide improved mixing. A second series of reactions was conducted in an 800-mL Autoclave Engineers high-pressure reactor modified and fitted with an insert to reduce the total volume to approximately 500 mL. For reactions in the small cell, the reactor was purged thoroughly with argon prior to use. An aqueous solution (12 mL) of ammonium persulfate (Aldrich, used as received) was then charged before the cell was cooled to well below 0 °C, and a 50/50 wt/wt % mixture of tetrafluoroethylene and carbon dioxide (polymer-grade TFE supplied as a mixture with CO_2 courtesy of DuPont) was condensed into the cell under pressure. For reactions employing surfactant, the sodium or ammonium salt of perfluorooctanoic acid (PCR or courtesy of DuPont, used as received) was added as a component of the initiator solution. The reactor was then heated to the desired reaction temperature for the allotted time. Stirring was initiated when the aqueous solution present melted, allowing the stirrer to rotate freely. Reactions in the 500-mL autoclave were conducted in a similar fashion, except 250 mL of water was employed and the stirring rate was maintained at 1000+ rpm once the aqueous phase had melted. Prior to each reaction the reactors were treated with a persulfate solution at 80−100 °C for several hours. After the allotted reaction time of 4−24 h, the cell was cooled and the upper gas phase vented. The white spongy product was collected, washed and dried, and then analyzed by thermal analysis and electron microscopy. Product number-average molecular weights were estimated based on heats of crystallization.[17]

The amounts of monomer, initiator, and surfactant charged as well as yields and molecular weights for products from reactions conducted in the 25-mL cell are summarized in Table 1. At relatively high initiator concentrations, yields were greater than 70%, but molar masses were relatively low (20 kg/mol). As initiator concentration was decreased, the molar mass of the products increased, but yields decreased precipitously. This indicates that yield and molecular weight are limited by monomer transport from the supercritical or

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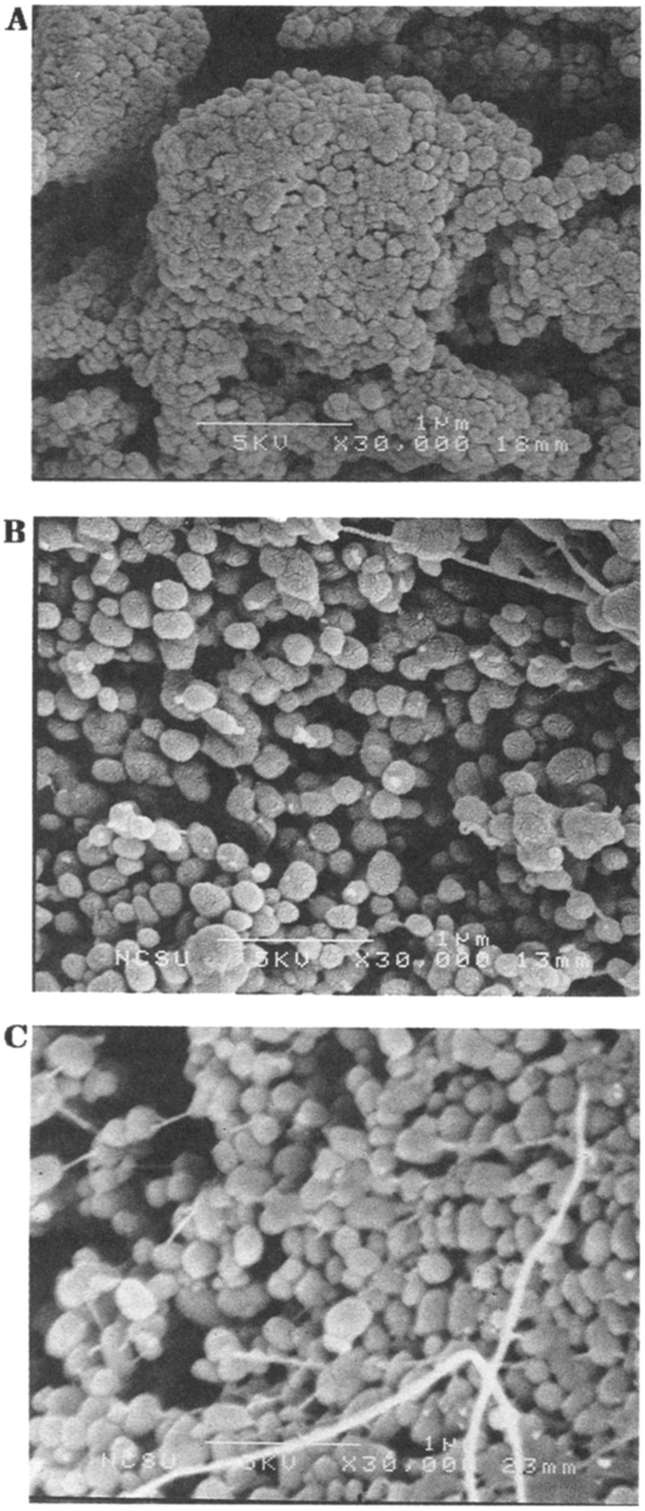

Figure 1. Scanning electron micrographs of poly(tetrafluoroethylene) prepared using a hybrid CO_2/aqueous system without added surfactant (A), using a hybrid CO_2/aqueous system with added surfactant (B), and using conventional TFE dispersion polymerization methods (C).

gaseous CO_2/TFE phase into the aqueous phase where the initiator is partitioned (this is not unexpected based on previous reports).[18] Pressures for these reactions were between 50 and 120 bar (700–1800 psig) and as expected were strongly dependent on reaction temperature and the amount of carbon dioxide present in the system.

Figure 1 shows scanning electron micrographs (SEMs) depicting the morphology obtained for a polymerization reaction conducted in a CO_2/aqueous system with and without added surfactant (1B and 1A, respectively) and the morphology of a sample obtained from a commercial coagulated dispersion-grade poly(tetrafluoroethylene) (1C). The electron micrograph for the sample prepared in the absence of surfactant shows large agglomerations (ca. 0.5–3 μm) of small polydisperse primary particles, similar to what is expected for conventional granular PTFE. Although the molar masses differ by orders of magnitude, the particle morphology resemblance is striking for the samples prepared with added surfactant. Each micrograph shows spherical particles with diameters of 100–200 nm with intermittent fibrils. Based on previous reports detailing PTFE morphology as a function of molar mass[19] and surfactant concentration,[20] spherical partical morphologies were not expected for our samples made with surfactant. Investigation of this apparent anomaly will be addressed in a future publication.

Table 2. Reagent Quantities Charged, Yields, and Molar Masses Obtained for Tetrafluoroethylene Polymerizations in the 500-mL Autoclave Reactor

TFE (g)	$S_2O_8^{2-}$ (mol)	surfactant [$C_7F_{15}COO^-$]	yield (%)	M_n (kg/mol)
25.5	3.5×10^{-6}	9.2×10^{-5}	85	350
25.5	1.3×10^{-5}	9.2×10^{-5}	82	260
24.7	3.8×10^{-6}		90	900
25.1	1.5×10^{-5}		90	230

Results from larger scale polymerizations (given in Table 2) employing dramatically increased agitation rates and little or no added surfactant were designed to mimic conventional granular type processes and gave high reproducible yields and relatively high molar masses. Because higher agitation rates were available for these systems, lower initiator concentrations could be employed, allowing the formation of relatively high molar mass polymer in high yield. Some commercial products exhibit higher molar masses (up to ca. 20 million g/mol), but those produced in our laboratory are quite respectable for reactions run under batch conditions at the relatively low monomer concentrations employed. Pressures for these reactions ranged from 50 to 65 bar (700–950 psig). SEMs displaying nonuniform agglomerates with diameters of ca. 0.5–3 μm compared well with those of commercial granular materials.

In conclusion, tetrafluoroethylene has been successfully polymerized in a hybrid carbon dioxide/aqueous medium with and without added surfactant. Product morphologies appear similar to those encountered in traditional dispersion and granular poly(tetrafluoroethylene) prepared in the absence of carbon dioxide, but some anomalies may exist. In light of the potential for safer handling of TFE monomer as a mixture with carbon dioxide, and the many other potential advantages offered by these hybrid systems, polymerizations of TFE in water/carbon dioxide mixtures may well provide a viable route to the manufacture of tetrafluoroethylene-based fluoropolymers and open doors to new materials and processing methodologies for water-insoluble materials in general.

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