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Synthesis of Fluoropolymers in Supercritical Carbon Dioxide

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Fluoropolymers are used in many technologically demanding applications because of their balance of high-performance properties. A significant impediment to the synthesis of variants of commercially available amorphous fluoropolymers is their general insolubility in most solvents except chlorofluorocarbons (CFCs). The environmental concerns about CFCs can be circumvented by preparing these technologically important materials in supercritical fluids. The homogeneous solution polymerization of highly fluorinated acrylic monomers can be achieved in supercritical carbon dioxide by using free radical methods. In addition, detailed decomposition rates and efficiency factors were measured for azobisisobutyronitrile in supercritical carbon dioxide and were compared to those obtained with conventional liquid solvents.

The dissemination of CFCs into the atmosphere has been identified as one of the main causes of the depletion of the ozone layer (*1*). As a result, extensive research efforts have focused on alternatives to CFCs in applications such as refrigerants and aerosols. Additionally, CFCs are used as solvents for a variety of standard commercial processes. An important example of this is the solubilization of highly fluorinated polymers—known generally as fluoropolymers—in CFCs to form homogeneous solutions for polymer processing and synthesis. These fluoropolymers, used extensively as lubricants in computer disk drives, protective coatings, aircraft fuel sealants, and so forth, are generally insoluble in many traditional organic solvents (*2*) and therefore both their synthesis (using solution polymerization methods) and their processing depend on CFC solvents. We have found a way to circumvent the environmental concerns about CFCs by preparing these technologically important materials in supercritical fluids (SCFs). We report here the successful synthesis of high molar mass fluoropolymers by using homogeneous free radical polymerization methods in supercritical carbon dioxide (CO_2).

In addition to offering an environmentally sound alternative to CFCs, SCFs can provide insight into the general role that solvents play in polymerization reactions. Heretofore, research into the role of solvent strength in chemical reactions has been limited by the need to use multicomponent solvents in order to manipulate the bulk solvent strength, that is, the solubility parameter δ. The mean δ-value in mixed solvents is often masked by specific solute-solvent interactions. Because of their large compressibilities, researchers can use SCFs to produce a wide range of solvent strengths by varying the pressure rather than the composition of the solvent. The resulting significant and controllable changes in density readily allows investigations into solvent effects without changing the solvent composition (*3*, *4*). We illustrate the generality of polymerizations in SCFs with the determination of the decomposition kinetics and efficiency factor for the initiator, azobisisobutyronitrile (AIBN), followed by homopolymerization studies of 1,1-dihydroperfluorooctyl acrylate (FOA) and the synthesis of statistical copolymers of FOA with ethylene, styrene, butyl acrylate, and methyl methacrylate in supercritical CO_2.

The insolubility of most amorphous fluoropolymers in common organic solvents necessitates the use of CFC solvents when homogeneous solution polymerizations of fluoromonomers are desired. Although it has been known for some time that oligomeric perfluoropolyethers and poly(chlorotrifluoroethylene) are soluble in CO_2 (*3*), we have discovered that many other fluoropolymers are very soluble in both liquid and supercritical CO_2. In general, the only other solvents known for these highly fluorinated polymers are CFCs. Specifically, high molar mass (>250,000 g/mol) homopolymers of a variety of fluorinated acrylic monomers are soluble in CO_2 up to 25% (w/v) in some cases depending on pressures and temperatures (*5*). These are exceedingly high solubility values for a polymer in CO_2. For comparison, the hydrocarbon analogs of these polymers, such as poly(methyl methacrylate), are essentially insoluble in CO_2. We believe the high solubility of these fluoropolymers in CO_2 is indicative of a specific solute-solvent interaction between fluorine and CO_2.

As a result of the very high solubilities of these materials in supercritical CO_2, we set out to investigate the synthesis of fluoropolymers with the use of homogeneous solution free radical polymerization methods in CO_2 as an inert solvent. The rate of radical generation through the thermal decomposition of an initiator will influence both the overall rate of polymerization and the molar mass of the resulting polymer. Specifically, the rate of polymerization, R_P, is dependent on the square root of the initiator concentration [I]:

$$R_P = k_P[M]\left(\frac{fk_d[I]}{k_t}\right)^{1/2}$$

and the kinetic chain length, υ (the average

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number of monomer molecules polymerized by each primary radical) is inversely dependent on the square root of the initiator concentration:

$$v = \frac{k_p[M]}{2(fk_dk_t[I])^{1/2}}$$

where k_p, k_d, k_t are the rate constants for propagation, initiator decomposition, and termination, respectively, [M] denotes the monomer concentration, and f is the initiator efficiency. The initiator efficiency is defined as the fraction of radicals formed in the primary step of initiator decomposition that diffuse out of the solvent "cage" and are subsequently successful in initiating the polymerization of monomer. Values of f lower than unity are common and very often result from side reactions of the radicals produced during the primary step of initiator decomposition such as recombination of the germinate free radical pairs (6).

The rate of decomposition of AIBN (absorption maximum at 347 nm) in supercritical CO_2 was measured by using ultraviolet spectroscopy (*7*) with a high-pressure spectroscopic cell fitted with sapphire windows (8). The spectra obtained every 30 min at 59.4° ± 0.1°C in supercritical CO_2 at 207 (± 0.5) bar are shown in Fig. 1. The decreasing absorption maximum at 347 nm corresponds to the loss of AIBN, and the increasing maximum at 290 nm corresponds to $(CH_3)_2(CN)C{-}N{=}C{=}C(CH_3)_2$, which is formed from the recombination of primary radicals (9). The absorbance of AIBN as a function of time is plotted in Fig. 2 according to first-order kinetics and is shown along with the data obtained for neat benzene at ambient pressure and also for a mixture of CO_2 and tetrahydrofuran (THF). The rate of AIBN decomposition in supercritical CO_2 ($k_d = 3.4 \times 10^{-6}$ s^{-1}) is ~2.5 times lower than that observed in benzene ($k_d = 8.4 \times 10^{-6}$ s^{-1}) at ambient pressures (*10*). The higher decomposition rate in benzene is presumably due to the higher dielectric strength of benzene (*11*), which stabilizes the transition state of the primary scission reaction to a greater degree than does supercritical CO_2. This idea is further supported by the enhanced decomposition rate measured for CO_2 upon the addition of a polar cosolvent (Fig. 2).

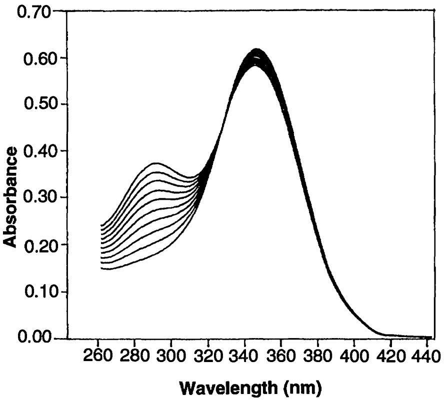


Fig. 1. Thermal decomposition of AIBN in CO_2 at 59.4° ± 0.1°C and 207 (± 0.5) bar; [AIBN] = 1.22×10^{-2} M. Ultraviolet spectra were collected once every 30 min.

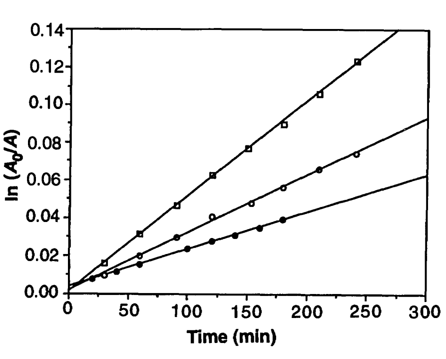


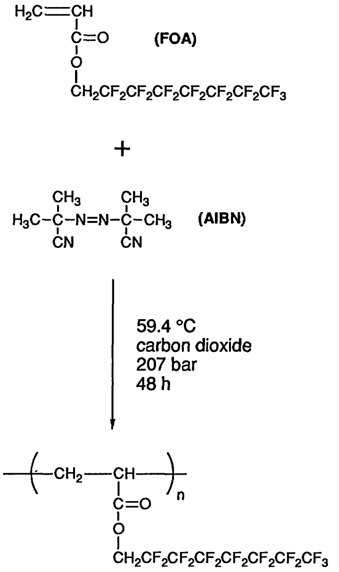
Fig. 2. Plot of ln(A_0/A) (absorbance at 347 nm) versus time for AIBN thermal decomposition at 59.4° ± 0.1°C in different solvents: (□) benzene; (○) CO_2 with 5 v/v % THF as cosolvent at 207 (± 0.5) bar; (●) pure CO_2 at 207 (± 0.5) bar.

The efficiency of radical generation was measured by using a radical scavenger method (*12*). Specifically, galvinoxyl was used to measure the fraction of the primary radicals that diffuse out of the solvent cage and into the bulk solvent. The decreasing concentration of galvinoxyl (762 nm) was followed with time and the results were plotted according to

$$A_t = A_0 - (2fk_d[I]_0\varepsilon l)t$$

where t = time, A_0 and A_t are the absorbance of galvinoxyl at time = 0 and time = t, respectively, ϵ is the extinction coefficient of galvinoxyl, and l is the path length of the high-pressure cell. As shown in Fig. 3, a straight line is obtained for CO_2 at 59.4° ± 0.1°C and 207 (± 0.5) bar, and from the slope the efficiency factor, f = 0.83 (± 0.02) was obtained. This high value can be contrasted with the efficiency factor of AIBN measured in benzene, which is only f = 0.53 (± 0.02) at 59.4° ± 0.1°C. The high radical efficiencies measured in supercritical CO_2 are the result of the low viscosity of CO_2 at these conditions (*13*) relative to benzene. In other words, there is no significant cage effects that promote the recombination of the newly formed primary radical pairs and radical diffusion into the bulk solvent is facile.

The homogeneous polymerization of FOA in supercritical CO_2 is described in Scheme 1. The high-pressure polymerizations were conducted in a view cell (8) in order to verify the homogeneous nature of the reactions. In a typical polymerization reaction, the fluorinated monomer FOA (5.0 g, purified by column chromatography) and recrystallized AIBN (50 mg) were put into a 10-ml high-pressure reaction view cell containing a micromagnetic stir bar. The cell was purged with argon for ~10 min and then filled with CO_2 to less than 70 bar. During an 1-hour period, the cell



Scheme 1. Homopolymerization of FOA in CO_2.

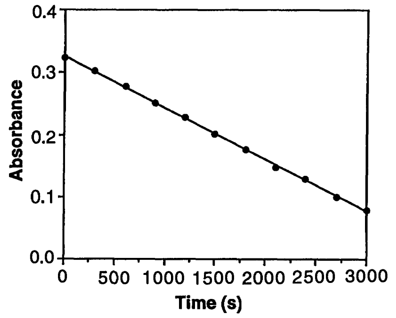


Fig. 3. The variation in absorbance at 762 nm with time for the galvinoxyl in AIBN/CO_2 solution; T = 59.4° ± 0.1°C, P = 207 (± 0.5) bar, [AIBN] = 6.1×10^{-3} M, [galvinoxyl] = 4.74×10^{-4} M.

Table 1. Statistical copolymers of FOA with methyl methacrylate (MMA), styrene, butyl acrylate (BA), and ethylene. Polymerizations were conducted at 59.4 (± 0.1)°C and 345 (± 0.5) bar for 48 hours in CO_2. Intrinsic viscosities (in deciliters per gram) were determined in 1,1,2-trifluorotrichloroethane (Freon-113) at 30°C.

Copolymer	Feed ratio (f_1)	Incorporated (F_1)	Intrinsic viscosity (dl/g)
Poly(FOA-*co*-MMA)	0.47	0.57	0.10
Poly(FOA-*co*-styrene)	0.48	0.58	0.15
Poly(FOA-*co*-BA)	0.53	0.57	0.45
Poly(FOA-*co*-ethylene)	0.35		0.14

was heated to 59.4° ± 0.1°C and the pressure was increased to 207 (± 0.5) bar by the addition of more CO_2 (a total of ~6.6 g of CO_2 added). The polymerization was continued at these conditions for 48 hours, during which time the system remained homogeneous and optically clear. At the end of the polymerization, CO_2 was vented and the polymer, which is not soluble in CO_2 at lower pressures, precipitated. The polymer and any unreacted monomer were quantitatively removed from the reaction vessel by dissolution in 1,1,2-trifluorotrichloroethane (Freon-113). The polymer was precipitated into a large excess of methanol, washed several times with methanol, and dried in vacuo overnight to give 3.25 g of transparent viscous polymer (yield: 65%). Fourier transform infrared (FTIR) (*14*) and ^{1}H nuclear magnetic resonance (NMR) (*15*) spectra showed that the polymer synthesized in CO_2 was identical to the polymer made in CFCs. Gel permeation chromatography (GPC) indicated that the polymer made in CO_2 had a molar weight of ~270,000 g/mol (*16*). Similar results could be obtained for a variety of other highly fluorinated acrylic monomers whose corresponding homopolymers are essentially insoluble in all traditional solvents except CFCs.

Polymer synthesis in supercritical CO_2 was also extended to statistical copolymers of fluorinated monomers with conventional hydrocarbon-based monomers such as methyl methacrylate, butyl acrylate, styrene, and ethylene. The corresponding homopolymers of the conventional hydrocarbon monomers are essentially insoluble in CO_2 at these conditions (*3*). Copolymers of FOA were made under similar conditions as described above. The molar ratios of the monomers in the feed, f_1, and the molar ratios incorporated into the copolymer, F_1, are given in Table 1. Homogeneous copolymerizations could be maintained even with very high concentrations of comonomer as shown.

Supercritical CO_2 is an excellent alternative to CFCs for conducting homogeneous solution homo- and copolymerization of fluorinated monomers. Under the conditions used here, we found that AIBN decomposes at a rate 2.5 times slower in CO_2 than in benzene but with greater efficiency. We have demonstrated that it is possible to synthesize high molar mass homo- and copolymers of fluorinated monomers in a homogeneous fashion in supercritical CO_2. This new process for the synthesis of fluoropolymers and copolymers points to the potential for using supercritical CO_2 in other solution polymerizations such as group transfer polymerization, living cationic polymerizations, and perhaps even some anionic polymerizations whose active chain end could be stabilized in CO_2.

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15. ^{1}H NMR (1,1,2-trifluorotrichloroethane with $CDCl_3$ in sealed capillary in annulus, 200 MHz, 23°C): δ 2.12 and 1.81 (m, 2H); δ 2.47 (s, 1H); δ 4.59 (t, 2H).
16. Molar masses were measured with GPC with a 1,1,2-trifluorotrichloroethane mobile phase and fluoropolymer molecular weight standards.
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Internal Stark Effect Measurement of the Electric Field at the Amino Terminus of an α Helix

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The strengths of electrostatic interactions in biological molecules are difficult to calculate or predict because they occur in complicated, inhomogeneous environments. The electric field at the amino terminus of an α helix in water has been determined by measuring the shift in the absorption band for a covalently attached, neutral probe molecule with an electric dipole moment difference between the ground and excited electronic states (an internal Stark effect). The field at the interface between the helix and the solvent is found to be an order of magnitude stronger than expected from the dielectric properties of bulk water. Furthermore, although the total electric dipole moment of the helix increases with length, the electric field at the amino terminus does not.

Interactions involving charged and polar groups are important determinants of the properties of biological macromolecules. Theoretical assessment of these electrostatic interactions is difficult because they occur in complicated environments and frequently near solvated surfaces of irregular shape and composition. Determining the strength of electrostatic interactions is a difficult experimental problem as well. The standard methods involve: (i) measuring the change in the pK_a (K_a, acid dissociation constant) of an ionizable group; or (ii) mutating a charged or polar group and measuring the change in stability or function. Although these measurements depend on the electrostatic potential at a particular position in the folded state, the physical interpretation of the results is complicated by structural relaxation, differences in solvation of the mutated or charged groups, and changes in the unfolded state.

We have developed a method to measure the electric field (instead of the potential) that uses a relatively nonperturbing, uncharged probe molecule. The method is used to measure the electric field at the amino termini of short, stable, monomeric α helices in water. The results are straightforward to interpret because the field does not have to be inferred from the effects of

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