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Copolymerization of Vinylidene Fluoride with Hexafluoropropylene in Supercritical Carbon Dioxide

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Introduction. Supercritical carbon dioxide ($scCO_2$) has been used as a medium for a wide range of chain-growth polymerizations. This research is the subject of several reviews.[1−6] The startup of a commercial facility to produce various grades of Teflon in $scCO_2$ underscores the potential industrial importance of this technology.[7,8]

The vast majority of the polymerizations that have been studied in $scCO_2$ are heterogeneous.[1] Only a few homogeneous polymerizations have been reported.[9−11] Nevertheless, the behavior of polymerizations in $scCO_2$, and the differences between heterogeneous and homogeneous polymerization, remain poorly understood. In this communication, we report the behavior of a copolymerization that can be tuned to proceed either homogeneously or heterogeneously, depending on total monomer concentration, monomer ratio, and pressure.

Copolymers of vinylidene fluoride (VF2) with hexafluoropropylene (HFP) are important commercial fluoropolymers.[12] When the HFP content is lower than 19−20 mol %, the copolymers are thermoplastic and semicrystalline, while for higher HFP contents, the copolymers are amorphous and elastomeric.[13,14] Most commercial poly(VF2-*co*-HFP) elastomers contain around 22 mol % HFP,[15] a composition that represents the best compromise between a low T_g and a fully amorphous polymer.

Copolymers of VF2 with HFP are produced commercially by suspension and emulsion polymerization in water.[16] Both processes generate large quantities of wastewater and require large quantities of energy to isolate the polymer in dry form. In addition, some processes may involve the use of ammonium perfluorooctanoate surfactants, which are environmentally suspect.[17] Polymerization in supercritical carbon dioxide ($scCO_2$) offers a green alternative for these challenges.

The solubility of poly(VF2-*co*-HFP) copolymers in $scCO_2$ changes with copolymer composition.[18,19] Low-HFP-content copolymers are not soluble at reasonable pressures and must be synthesized in $scCO_2$ via precipitation polymerization. High-HFP-content copolymers are soluble in CO_2 and can be synthesized using solution polymerization. For intermediate compositions, the copolymer can be synthesized by either technique. The synthesis of poly(VF2-*co*-HFP) copolymers in $scCO_2$ by both precipitation and solution polymerization is reported herein.

Experimental Section. Copolymerizations were done in a batch reactor, using perfluorobutyryl peroxide initiator ($[C_3F_7COO]_2$, PBP) at 35 °C, pressures of 310−415 bar, and a reaction time of 2 h.

a. Materials. Both VF2 (98% min) and HFP (99% min) were obtained from SynQuest Laboratories while SFC grade CO_2 (99.998%) was obtained from National Specialty Gases. All other chemicals were obtained from Fisher Scientific Co. and used as received.

b. PBP Initiator Synthesis. The PBP initiator was synthesized in Freon 113 as previously reported.[20] All manipulations of the initiator were performed in a NaCl/ice bath, and the final product was stored under dry ice. The iodine titration technique, ASTM Method E 298-91, was utilized to determine the concentration of the initiator in the solution. The half-life decomposition temperature of PBP at 35 °C in Freon 113 was reported to be 1.1 h.[20]

c. Experimental Apparatus. Polymerizations were conducted in an 80 mL cell equipped with a magnetically driven stirrer, thermocouple, rupture disk, and a sapphire window that permitted visual observation of the reaction mixture.

d. Polymerization Procedure. In a typical experiment, the reactor was purged three times with $scCO_2$ to remove oxygen. The monomers were charged in the desired ratio (HFP first, then VF2) using an Isco 260D syringe pump. Enough liquid CO_2 to form a homogeneous solution then was added. The reactor was heated to the desired temperature, and the initiator solution was transferred to a small tube connected to the CO_2 line under argon purge. Finally, the reactor was pressurized to the final pressure with additional CO_2, while simultaneously introducing the initiator to the reactor. A 260D Isco dual-cylinder syringe pump was used to maintain the pressure constant by continuously feeding $scCO_2$ to make up for the monomer that was consumed. Temperature control was ±0.2 °C, while pressure control was ±1 bar. After the reaction, pressure was released slowly through a glass flask with its mouth covered with double layers of filter paper to retain any copolymer carried in the released stream. Finally, the residual monomers and initiator were extracted three times from the copolymer using $scCO_2$.

e. Copolymer Characterization. The copolymer composition was determined by both fluorine elemental analysis and by ^{19}F NMR. The NMR spectra were recorded on a Bruker Avance spectrometer operating at 470.6 MHz using acetone-d_6 (99.9%) as the solvent and against trichlorofluoroethane ($CFCl_3$) as the internal reference. NMR parameters were 5 s pulse delay, 0.164 s acquisition time, and 32K data points. The shift assignments used are those reported in the literature.[21,22] The copolymer composition from NMR was calculated using eq 1.

$$\text{mol \% HFP} = \frac{I_{CF_3}/3}{I_{CF_2}/2} \qquad (1)$$

I_{CF_3} is the area of the integral corresponding to the fluorine of the CF_3 group in the HFP (corresponding to peaks located at ca. −70.4, −75.0, and −75.3 ppm); I_{CF_2} is the area of the integral corresponding to the fluorine of the CF_2 in both HFP and VF2 (corresponding to peaks from ca. −91.4 to −119 ppm).

The molecular weight was determined through both size exclusion chromatography (SEC) and end-group analysis using NMR. The SEC analyses were performed in tetrahydrofuran at

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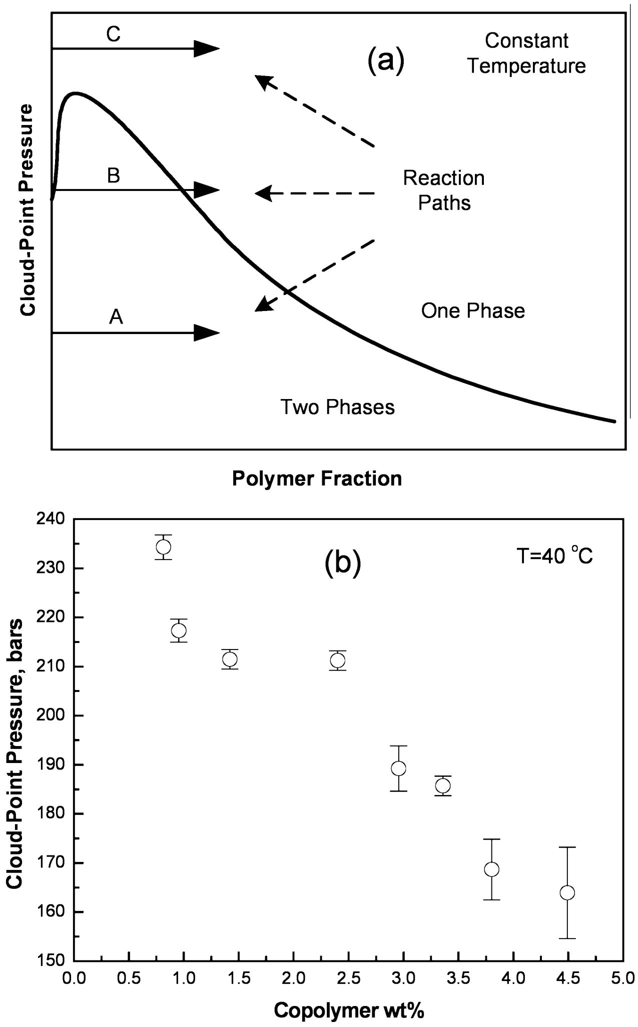

Figure 1. (a) Qualitative cloud-point pressure diagram of a polymer-supercritical fluid.[1] The horizontal lines represent the reaction paths with respect to the corresponding polymer cloud-point pressure curve. (b) Cloud-point pressure curve of Tecnoflon N215 in $scCO_2$.[19]

30 °C against polystyrene standards with a refractive index detector. Number-average molecular weight (M_n) was calculated via eq 2 from the NMR end-group analyses.

$$M_{n-NMR} = \frac{I_{CF_2}/2}{(I_{-80\ ppm}/3)/2}[150F_{HFP} + 64(1 - F_{HFP})] \quad (2)$$

Here, $I_{-80\ ppm}$ is the area of the integral corresponding to the fluorine of the CF_3 group in the C_3F_7 of the initiator; F_{HFP} is the mole fraction of HFP in the copolymer.

The main assumption in this procedure is that the polymeric radicals terminate by combination. This accounts for the factor of 2 in the denominator of eq 2. This assumption is consistent with PDI values around 1.5 observed in this work and previously for the homopolymerization of VF2 in CO_2.[23] Another assumption is that chain transfer reactions are unimportant. The chain transfer reactions that can occur in CO_2 are to either monomer, polymer, or initiator. There is no evidence from the literature that chain transfer to monomer can occur to VF2. (Chain transfer to HFP is unlikely since it contains only C−F bonds.) However, chain transfer to polymer may be important at high monomer concentrations.[23]

Results and Discussion. Figure 1a shows a typical cloud-point pressure curve for a polymer in a supercritical fluid,[1] while Figure 1b shows the cloud-point pressure curve for Tecnoflon N215 copolymer (Solvay-Solexis) in $scCO_2$ (23.1 mol % HFP by NMR (21.3 ± 1.28 mol % HFP by elemental fluorine analysis), M_n = 54 kDa, and PDI = 2.62).

In a batch polymerization experiment, the pressure and temperature are constant while polymer fraction increases with time. Therefore, a horizontal line in Figure 1a represents the reaction path of a typical experiment. A path far below the cloud-point curve will give rise to a completely heterogeneous reaction. Such a path is shown as line A. If the reaction path is above the highest point in the curve, as shown by line C, the reaction will be homogeneous. Finally, as shown by line B, a reaction path can begin below the cloud-point pressure curve and cross it as the reaction proceeds. In this case, the copolymer will precipitate from the solution initially but will redissolve when the cloud-point curve is crossed. The polymerization begins as a precipitation polymerization but finishes as a homogeneous polymerization.

Table 1 shows the reaction conditions and the results of the copolymerization of VF2 with HFP at 35 °C with either 310 or 415 bar total pressure. Three comonomer feed compositions were used (30, 50, and 64.5 mol % HFP), using the same initial total monomer concentration (1.52 mol/L) and two different initial initiator concentrations (1.52×10^{-3} and 3.16×10^{-3} mol/L). The reaction time was 2 h. The yield (mass of copolymer produced/total mass of monomers fed) ranged from about 6.5 to 16.1%. This low yield was deliberate, to limit copolymer composition drift, and is the result of both the short reaction time and the low temperature. With one exception, the copolymer composition obtained via fluorine elemental analysis is higher than the NMR result. Nevertheless, the two compositions are close enough to lend confidence to the results. The values of M_n from NMR end-group analysis and SEC agree reasonably well. This may be somewhat fortuitous since the SEC results are relative to polystyrene standards and in view of the assumptions in the NMR end-group calculation.

For the experiments with 30 mol % HFP comonomer feed composition, the HFP content of the copolymer was about 8.0−9.4 mol % by NMR analysis. This copolymer is essentially insoluble in $scCO_2$ at the pressures of these experiments; i.e., the cloud-point pressure curve is much higher than the reaction path. The copolymer precipitated at the start of the reaction, and the reaction medium remained visually heterogeneous throughout the reaction. This behavior is consistent with the reaction path shown as line A in Figure 1a.

For the 64.5 mol % HFP comonomer feed composition, the copolymer contained about 23.8−25.4 mol % HFP by NMR analysis. The cloud-point pressure curve for this copolymer composition is substantially lower than the curve shown in Figure 1b. The copolymer remained in solution throughout the reaction, consistent with the reaction path shown as line C.

Finally, the experiments with 50 mol % HFP comonomer feed composition produced a copolymer containing about 15.8−18.1 mol % HFP by NMR analysis. At both pressures, the reaction was heterogeneous initially but became homogeneous as the reaction proceeded, consistent with line B in Figure 1.

Since the copolymer composition drift was small in these experiments, an estimate of the "effective" reactivity ratios of both comonomers in $scCO_2$ at 35 °C could be obtained. The values of the effective reactivity ratios with the 95% confidence limits are

$$r_{HFP} = 0 \pm 0.08 \quad \text{and} \quad r_{VF2} = 3.61 \pm 0.71 \text{ at 310 bar}$$

$$r_{HFP} = 0.09 \pm 0.09 \quad \text{and} \quad r_{VF2} = 4.67 \pm 0.77 \text{ at 415 bar}$$

Table 1. Copolymerization of VF2 with HFP at 35 °C, 2 h Reaction Time, and 1.52 mol/L Total Initial Monomer Concentration[a]

run no.	P (bar)	comonomer feed composition (mol % HFP)	I_0, 10^{-3} (mol/L)	yield (wt %)	copolymer composition from NMR (mol % HFP)	copolymer composition from fluorine analysis (mol % HFP)	$M_{\text{n}-\text{SEC}}$ (kDa)	$M_{\text{n}-\text{NMR}}$ (kDa)	PDI	reaction medium
1	310	30.0	1.52	10.0	9.2	10.48 ± 1.00	21.1	18.2	1.56	completely heterogeneous
2	310	30.0	3.16	14.6	9.4	10.86 ± 1.01	16.6	14.2	1.56	completely heterogeneous
3	415	30.1	1.52	10.7	8.0	9.23 ± 0.97	24.2	19.7	1.53	completely heterogeneous
4	415	30.1	3.16	16.1	8.5	9.60 ± 0.98	19.3	15.8	1.50	completely heterogeneous
5	310	50.0	1.52	9.8	17.6	20.69 ± 1.26	20.0	20.6	1.68	completely heterogeneous
6	310	50.0	3.16	13.7	18.1	19.95 ± 1.24	14.0	15.5	1.63	heterogeneous initially but became more homogeneous with time
7	415	50.0	1.52	11.5	17.3	19.23 ± 1.22	27.2	26.0	1.58	heterogeneous initially but became more homogeneous with time
8	415	50.0	3.16	15.6	15.8	19.21 ± 1.22	15.8	14.7	1.61	heterogeneous initially, homogeneous finally
9	310	64.4	1.52	6.5	25.3	24.26 ± 1.36	15.9	16.1	1.63	completely homogeneous
10	310	64.6	3.16	10.5	25.1	28.86 ± 1.48	11.1	11.1	1.45	completely homogeneous
11	415	64.6	1.52	7.3	23.8	26.46 ± 1.42	17.9	15.5	1.60	completely homogeneous
12	415	64.4	3.16	9.3	25.4	28.25 ± 1.47	12.2	10.4	1.58	completely homogeneous

[a] P = pressure; I_0 = initial initiator concentration; initiator solution concentration in Freon 113 = 0.06−0.08 M.

These reactivity ratios were calculated using nonlinear regression of the copolymerization equation[24] using DataFit with the Levenberg−Marquardt algorithm.[25] The average comonomer mixture composition during reaction and the final copolymer composition, obtained by averaging the NMR and fluorine elemental analysis results, were used in the calculation. In performing these calculations, it was assumed that the polymerization took place in solution. No attempt was made to account for any polymerization that might have taken place in the polymer particles, as this would have required knowledge of the concentrations of the monomers in the polymer phase. The same approach was used in the literature to calculate the reactivity ratios from emulsion polymerization data.[26,27] In view of this approximation, the reactivity ratios calculated can be considered as "effective" reactivity ratios. The calculated ratios lie within the range of published values: 2.45[26] to 6.7[27] for VF2 and 0[21,28,29] to 0.12[30] for HFP.

The SEC results in Table 1 show that the molecular weight increases with pressure and decreases as the HFP/VF2 feed ratio increases. Since HFP cannot homopolymerize at these reaction conditions, only VF2 units can add to growing chains ending with an HFP. Consequently, as the HFP/VF2 feed ratio increases, the probability of termination relative to propagation increases, which leads to a decrease in the molecular weight.

Current research involves continuous copolymerization of VF2 with HFP using a stirred tank reactor (CSTR). For certain copolymer compositions, it will be possible to carry out the copolymerization either homogeneously or heterogeneously. This will allow a quantitative evaluation of the effect of precipitation on copolymer properties and reaction kinetics.

Conclusions. The copolymerization of VF2 with HFP in $scCO_2$ was carried out using PBP initiator over a range of pressures and monomer ratios. Depending on the initial monomer ratio and reaction pressure, the reaction can proceed heterogeneously, homogeneously, or heterogeneously initially, becoming homogeneous with increasing reaction time. Reaction pressure impacts both the copolymer molecular weights and copolymer composition.

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Supporting Information Available: A representative ^{19}F NMR spectrum and the experimental details of the cloud-point measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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