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Synthesis of Fluorocarbon−Vinyl Acetate Copolymers in Supercritical Carbon Dioxide: Insight into Bulk Properties

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ABSTRACT: Tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), and vinylidene fluoride (VDF) were copolymerized with vinyl acetate (VAc) in supercritical fluid CO_2 by a free radical mechanism and without the use of a surfactant. A series of copolymers were synthesized with yields as high as 83% for TFE−VAc, 91% for CTFE−VAc, and 70% for VDF−VAc copolymers. Their weight-average molar masses, relative to polystyrene, were between 120 and 290 kg mol^{-1}, and polydispersity was between 1.6 and 2.4. A range of compositions was prepared with the amount of fluorocarbon in the copolymer varying from 13 to 84 mol %, as determined by elemental analysis. Monomer reactivity ratios were estimated using the error-in-variable method to be $r_{\mathrm{CTFE}} = 0.014 \pm 0.05$, $r_{\mathrm{VAc}} = 0.44 \pm 0.03$; $r_{\mathrm{TFE}} = -0.009 \pm 0.06$, $r_{\mathrm{VAc}} = 0.95 \pm 0.08$; and $r_{\mathrm{VDF}} = -0.4 \pm 0.04$, $r_{\mathrm{VAc}} = 1.67 \pm 0.6$. Proton NMR was used to estimate copolymer composition, based on triad sequences. These data, together with the reactivity ratio data, indicate that the fluorocarbons cross-propagate with VAc and that VAc propagates randomly. All samples were characterized by DSC for T_g with P(CTFE-*co*-VAc) having a T_g between 42 and 53 °C, P(TFE-*co*-VAc) between 34 and 41 °C, and P(VDF-*co*-VAc) between 20 and 33 °C. Hydrolysis of vinyl acetate to vinyl alcohol (VA) in P(TFE-*co*-VAc) yielded terpolymers, P(TFE-*co*-VAc-*co*-VA), with >80% of VAc hydrolyzed to VA, thereby providing a reactive functional group for further modification. Interestingly, only a small decrease in molar mass was observed after the hydrolysis of vinyl acetate to vinyl alcohol, reflecting the loss of acetic acid and suggesting that these polymers are linear. The results presented herein are particularly interesting because no surfactant (or dispersion agent) was required for apparent solubility in CO_2. The fluoropolymers prepared herein may find utility in coatings or paint applications.

Introduction

Carbon dioxide has been recognized as the supercritical fluid (SCF) solvent of choice for many industrial applications because it is both economically and environmentally attractive relative to traditional solvents used in separations,[1] extractions,[2] and polymerizations.[3−10] In addition to its low cost, the use of CO_2 in fluorinated olefin polymerizations provides other benefits. For example, when stored and handled in the presence of CO_2, TFE forms a pseudo-azoetrope which is less likely to deflagrate from oxygen initiation,[11] thereby making it much safer to use.

While many small molecules are soluble in CO_2, most polymers are insoluble. However, some fluoropolymers,[12] poly(siloxanes),[13] and poly(ether−carbonate) copolymers[14] are soluble in CO_2. For a fluoropolymer having a hydrocarbon backbone and a fluorocarbon pendant group, CO_2 solubility depends on both the number of fluorinated side groups and the molar mass of the side groups relative to that of the hydrocarbon main chain. It has been suggested that CO_2 either forms a weak complex with, or clusters near, the fluorine atom of the C−F bond (because C−F is more polar than C−H), thereby enhancing the fluoropolymer's solubility severalfold in CO_2.[15−18]

We previously reported the synthesis of a series of linear P(TFE-*co*-VAc)s in supercritical CO_2 using a fluorinated surfactant or dispersion agent.[3] Unlike similar copolymers prepared by emulsion which were highly branched,[19] our CO_2-synthesized polymers were linear. Hydrolysis of emulsion-polymerized P(TFE-*co*-VAc) resulted in a molar mass decrease of at least 10 orders of magnitude[19] whereas hydrolysis of our CO_2-polymerized P(TFE-*co*-VAc) resulted in the predicted molar mass decrease due to the loss of acetic acid.[3] We suggested that a branched polymer structure was formed during the aqueous emulsion polymerization due to radical abstraction of the VAc methyl hydrogens, which is a bimolecular process. Continued propagation of the resulting macroradical leads to branching and ester groups in the backbone.[19] The limited (or lack of) branching observed for CO_2-synthesized P(TFE-*co*-VAc) suggested that propagation competed more effectively with chain transfer processes in CO_2 than it did in water.[20] Since CO_2 can transport small molecules into even highly crystalline fluoropolymers,[21] it can facilitate diffusion of fluoromonomers into the precipitated polymer phase, thereby increasing the effective bimolecular rate for cross-propagation.

For P(TFE-*co*-VAc) synthesized with a dispersion agent, diffusion of TFE, VAc, and their polymeric radical chains in CO_2 seemed to be facilitated by the dispersion agent iteself. This in turn enhanced the yield and production of high molar mass polymers. However, the surfactant was difficult to remove after polymerization, and this limited the utility of these copolymers. For example, copolymer films were enriched with fluorine, yet it was unclear whether this resulted from the fluorocarbon surfactant or the fluorocarbon in the copolymer. This limited the potential use of these copolymers in coatings or paint applications.[22] Our goal was thus to synthesize linear P(TFE-*co*-VAc) without surfactant and to determine whether we could extend

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this methodology to other fluorocarbon−VAc copolymers, such as chlorotrifluoroethylene (CTFE) and vinylidene fluoride (VDF). To achieve this goal, we pursued the synthesis in supercritical CO_2. In an accompanying paper we describe the surface properties of these copolymers.

We anticipated that copolymers of VAc with fluorocarbon monomers could be synthesized in high yields and to high molar masses, without using a surfactant, because PVAc and fluorocarbon polymers are often soluble in CO_2 and a fluorocarbon−VAc copolymer would have decreased crystallinity relative to their respective homopolymers. For example, PTFE can be dissolved in CO_2 at high pressure and temperature,[23] and PVAc is more soluble in CO_2 than either polystyrene (PS) or poly(methyl methacrylate) (PMMA).[24,25] We report the first surfactant-free synthesis of fluorocarbon−VAc copolymers in CO_2.

Experimental Section

Reagents. All chemicals were purchased from Aldrich (Ontario, Canada) and used as received unless otherwise specified. TFE was prepared by vacuum pyrolysis of PTFE[26] and stored at room temperature over d-limonene in a 300 mL stainless steel sample cylinder fitted with an 1800 psi safety rupture disk. [*Caution: Tetrafluoroethylene is inherently dangerous. Anyone contemplating handling TFE under high pressure should familiarize oneself with safe handling procedures. TFE can explode with the force of TNT.*] The d-limonene inhibitor was removed by inline filtration through chromatographic silica gel (200−425 mesh, Fisher Scientific, Ontario, Canada) prior to use.

The diethyl peroxydicarbonate initiator was prepared in Freon 113, according to a published procedure,[27] and stored at −20 °C. The initiator was standardized by iodometry and was typically 7.5% (w/w). SFC purity CO_2 was obtained from Matheson (Ontario, Canada). Water was deionized and distilled from Millipore Milli-RO 10 Plus and Milli-Q UF Plus (Bedford, MA) systems and used at 18 MΩ resistance.

Synthesis of Fluorocarbon−Vinyl Acetate Copolymers: P(TFE-*co*-VAc), P(CTFE-*co*-VAc), and P(VDF-*co*-VAc). Polymerizations were conducted in CO_2 in a custom-built, 50 mL, stainless steel, high-pressure reactor. The head of the reactor was fitted with a Parr (Moline, IL) A1120HC magnetic drive, and the base of the reactor was heated by a removable stainless steel water jacket connected to a temperature-controlled water bath (model 1160A, VWR, Ontario, Canada). The reactor was sealed and evacuated ($P \leq 0.01$ mmHg). The base of the reactor was then chilled to approximately −50 °C using a liquid nitrogen bath. Meanwhile, the desired amount of chilled VAc ($T \sim 0$ °C) was added to a test tube and then transferred by cannula to the evacuated reactor. Diethyl peroxydicarbonate (0.5% w/w) initiator was then added to a test tube and transferred by cannula to the evacuated reactor.

With stirring, the desired amount of TFE was added to the reactor for a total monomer weight of 20 g. CO_2 was then added and maintained at a pressure of 30−40 bar while warming the reactor to approximately 10 °C. At that temperature, CO_2 was condensed into the reactor at a pressure of 56 ± 5 bar over 1−2 min. The preheated water jacket was placed around the base of the reactor. The reactor was heated to the desired polymerization temperature (45 ± 1 °C) over a period of 10−15 min. Pressures were initially between 200 and 230 bar.

Polymerizations were stopped after 24 h by cooling the reactor to room temperature. Stirring was stopped, and the reactor was slowly vented. At a pressure of less than 60 bar, the reactor was fully vented to atmospheric pressure and then opened. The white and tacky solid, which had formed in the reactor, was dissolved in acetone, quantitatively removed and precipitated into water. The polymer was further purified by blending in 400 mL of an ice cold water/ethanol bath (1:1, v/v). The polymer was collected by vacuum filtration and washed several times with water before drying (40 °C, $P < 0.1$ mmHg). Identical methods were followed for P(CTFE-*co*-VAc) and P(VDF-*co*-VAc), with CTFE and VDF (Caledon Laboratories, Ontario) used in the place of TFE.

Table 1. Bulk Analysis of Copolymers

fluorocarbon	fluoromonomer in feed (mol %)	yield (wt %)	fluoromonomer in copolymer (mol %)		T_g (°C)	M_w/M_n/PDI (kg mol^{-1})
			NMR[a]	elemental analysis[b]		
TFE	13.1	76	3.9	7.0	34	210/ 98/2.14
	34.5	79	21.2	26.0	39	226/119/1.90
	50.0	70	30.1	35.0	41	262/137/1.91
	67.7	79	42.1	63.3	38	290/157/1.84
	83.3	83	52.0	85.6	38	254/156/1.62
CTFE	14.5	84	10.1	16.6	43	265/110/2.41
	21.4	91	20.5	25.6	48	282/119/2.37
	42.5	88	29.8	41.6	49	271/122/2.22
	67.7	60	44.5	55.1	49	255/109/2.35
	83.8	37	52.0	68.5	53	218/102/2.13
VDF	23.3	69	1.7	13.7	33	172/86/2.00
	44.6	59	5.8	16.5	25	158/88/1.79
	62.1	44	12.3	23.0	20	117/73/1.60

[a] Based on the integral area of VAc ^{1}H NMR methine peaks and all TFE ^{19}F NMR peaks using α,α,α-trifluorotoluene as an integral reference. [b] Determined from % C analysis.

Acid Hydrolysis of P(TFE-*co*-VAc) to P(TFE-*co*-VAc-*co*-VA). To a 250 mL round-bottom flask equipped with a condenser and a magnetic stir bar were added 2 g of polymer, 75 mL of ethanol, 1 mL of distilled water, and 0.5 mL of concentrated sulfuric acid. The mixture was stirred and refluxed for 4 days. A clear polymer solution resulted and was then cooled to room temperature and neutralized by the slow addition of sodium bicarbonate, with vigorous stirring. The polymer solution was centrifuged to remove the sodium sulfate salt and the supernatant removed. The polymer was collected after removing the ethanol by rotary evaporation and then further dried under vacuum (40 °C, $P < 0.1$ mmHg).

Characterization. Polymer molar mass was characterized by a GPC (Waters U6K injector, 510 pump) equipped with a refractive index detector (Waters 2410) and a series of Ultrastyragel columns (Waters 10^6, 10^4, and 500 Å). Using an ethyl acetate mobile phase at a flow rate of 1 mL min^{-1}, polymer molar masses were calculated relative to polystyrene standards. FTIR absorbance spectra (Galaxy series 5000 spectrometer, 16 scans, 4 cm^{-1} resolution) were taken of thin polymer films. Thin films were prepared from ~2% (w/v) solution in THF (for parent copolymers) and in ethanol (for hydrolyzed copolymers) cast onto ZnSe disks. ^{1}H and ^{19}F NMR spectra (Varian Gemini spectrometer) were obtained in CD_6CO and $CDCl_3$ at 300.75 and 282.33 MHz, respectively, and using TMS and α,α,α-trifluorotoluene as external and internal references, respectively. Elemental analysis was conducted by Canadian Microanalytical Service (British Columbia, Canada). Glass transition temperature (T_g) was measured using a differential scanning calorimeter (DSC, TA 2010), under an inert nitrogen atmosphere, with a heating rate of 10 °C/min and scanning range of −20 to 70 °C.

Results and Discussion

A series of fluorocarbon−VAc copolymers were synthesized in supercritical CO_2 and characterized for bulk composition, molar mass, and T_g, the results of which are summarized in Table 1.

All of the copolymers were soluble in ethyl acetate, and most were soluble in common organic solvents, such as acetone and chloroform; the exceptions were P(TFE-*co*-VAc) with TFE contents ≥63% and P(CTFE-*co*-VAc) with CTFE ≥55%. Two methods were used to estimate copolymer composition: NMR and elemental analysis. The compositions calculated by NMR were consistently lower than those calculated by elemental analysis, and longer ^{19}F NMR transient acquisition/pulse delay times were inconsequential to composition. We[3] and others[28] have observed similar discrepancies in copolymer composition calculated by NMR and elemental analysis for fluoropolymers yet cannot provide a suitable explanation. Given the inadequacy of NMR for these calculations, elemental analysis was determined to be the best estimate of composition.

The yields of P(TFE-*co*-VAc) copolymers range from 70 to 83% and are independent of the TFE mass fraction in the monomer feed. Molar mass generally increases with increasing TFE in the copolymer while PDI decreases. This suggests that P(TFE-*co*-VAc) macroradical chains and TFE and VAc monomers interact with CO_2, which enhances their solubility in a continuous polymerization phase. The mole fraction of TFE in P(TFE-*co*-VAc) reflects the mole fraction in the feed for higher TFE contents, which suggests that TFE helps to solubilize P(TFE-*co*-VAc). Both TFE and VAc monomers likely diffuse easily into a continuous polymer−CO_2 phase, which favors a high yield and molar mass for the TFE−VAc copolymers. The PDI of all TFE−VAc copolymers is ≤ 2.1, indicating that growing radical chains can diffuse easily in CO_2. The solubility of P(TFE-*co*-VAc) in CO_2 may be related to T_g, which is similar to that of PVAc of 38 °C, which in turn has been shown to be soluble in CO_2.[24,25]

The mole fraction of CTFE in P(CTFE-*co*-VAc) reflects the composition in the feed given an error of ~2% in the feed and elemental analysis measurements; however, the mole fraction of CTFE in P(CTFE-*co*-VAc) decreased with higher CTFE feed compositions. The CTFE−VAc copolymers were formed with high yields, up to 91%, for CTFE mole fractions up to 42 mol %. However, at higher CTFE mole fractions (i.e., ≥ 55 mol %), the yield decreased considerably to as low as 37%. These data suggest that VAc enhances the solubility of CTFE and CTFE−VAc macroradical chains in the continuous CO_2 phase until the VAc is consumed. The yield and molar mass of P(CTFE-*co*-VAc) decrease because CTFE does not homopolymerize under these reaction conditions; CTFE has been shown to form oligomers in supercritical fluids.[29] PCTFE swells in CO_2 at pressures ≥ 240 atm and temperatures of 80 °C[21] while absorption of CO_2 has been shown to depress the glass transition temperature of polymers.[25] Since the T_g of P(CTFE-*co*-VAc) increases gradually with the increasing CTFE mole fraction, the rigidity of the polymer chains increases and the mobility of CO_2 molecules dissolved in the polymer likely decreases. This may limit the solubility and yield of P(CTFE-*co*-VAc) at higher CTFE contents in CO_2.

For VDF−VAc copolymers, yield and molar mass decreased with increasing mass fractions of VDF. There appeared to be an upper limit of 23 mol % of VDF in the VAc copolymer. In fact, the mole fraction of VDF incorporated in VDF−VAc copolymers was the lowest among the three fluoromonomers studied. The PDI was low and decreased from 2.0 to 1.6 with increased VDF content, indicating facile diffusion of macroradicals in CO_2. The decrease in T_g of VDF−VAc copolymers with increased VDF mole fraction supports the VDF−VAc macroradical diffusion hypothesis as a larger free volume favors the interactions of CO_2 with the copolymer chains. For example, it has been suggested that CO_2 forms a weak complex with the fluorine atoms in the VDF repeat units;[15,30] however, VDF copolymers, such as VDF−hexafluoropropylene (HFP), are more soluble in CO_2 than PVDF itself because P(VDF-*co*-HFP) has a larger free volume than PVDF.[30]

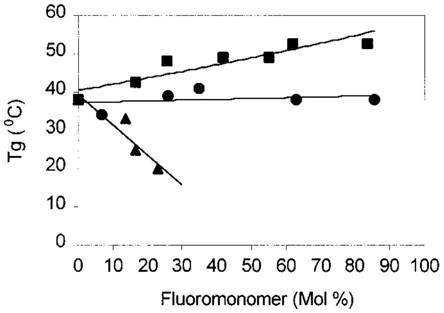

Figure 1. T_g of fluorocarbon−vinyl acetate copolymers as a function of fluoromonomer (mol %) in the copolymer: (■) P(CTFE-*co*-VAc); (●) P(TFE-*co*-VAc); (▲) P(VDF-*co*-VAc).

The DSC thermal traces of the copolymers showed a single T_g, which generally increased with both TFE and CTFE composition, yet decreased with VDF content. As shown in Figure 1, the T_g values of both P(CTFE-*co*-VAc) and P(VDF-*co*-VAc) are a linear function of the monomer mole fraction in the copolymer.

Measurement of Reactivity Ratios of CO_2-Synthesized Copolymers. TFE, CTFE, and VDF were copolymerized with VAc in CO_2 to low conversion (<10%) to determine relative reactivity ratios (r_1, fluoromonomer; r_2, VAc). The reactivity ratios were calculated using the differential form of the Mayo−Lewis equation, as described in eq 1:[31]

$$F_1 = \frac{r_1 f_1^{\,2} + f_1(1 - f_1)}{r_1 f_1^{\,2} + 2f_1(1 - f_1) + r_2(1 - f_1)^2} \tag{1}$$

The terms F_1 and f_1 represent the instantaneous mole fraction of monomer 1 in the copolymer and in the feed, respectively. The error-in-variable model (EVM)[32] was used to statistically fit data to the Mayo−Lewis equation. EVM has been shown to be statistically valid and takes the errors in the independent variable into account.[32] To use EVM, the following assumptions are made: polymerization is chemically controlled, diffusional limitations are minimal, and compositional drift is negligible, the latter two of which were satisfied. The polymerization results for P(TFE-*co*-VAc), P(CTFE-*co*-VAc), and P(VDF-*co*-VAc) are summarized in Table 2.

To estimate reactivity ratios by EVM,[32] error estimates were required for both the monomer feed and copolymer composition. An error estimate of 0.7% was used for monomer feed compositions, reflecting the precision of gravimetric measurements and estimated monomer purity. Error estimates of 1.2%, 4.7%, and 24.5% were used for copolymer compositions of P(TFE-*co*-VAc), P(CTFE-*co*-VAc), and P(VDF-*co*-VAc), respectively, reflecting the copolymer purity and the standard deviation for three separate elemental analysis measurements at the same composition (cf. the last three entries in Table 2 for $f_{\mathrm{TFE}} = 14.2$, $f_{\mathrm{CTFE}} = 37.7$, and $f_{\mathrm{VDF}} = 6.3$). Figure 2 is a graphical representation of the estimated reactivity ratios for all copolymer series and their respective 95% confidence ellipses.

Under CO_2 copolymerization conditions, $r_{\mathrm{VAc}} = 0.95 \pm 0.08$ and $r_{\mathrm{TFE}} = -0.009 \pm 0.06$, indicating that the radical on TFE primarily cross-propagates with VAc whereas the radical on VAc propagates randomly. Given

Table 2. CO_2 Copolymerization of VAc with TFE (f_{TFE}), VDF (f_{VDF}), or CTFE (f_{CTFE}) to Low Conversion To Determine Fluorocarbon Composition in the Copolymer (F)

f_{TFE} (mol %)	yield (wt %)	F_{TFE} (mol %)	M_w/M_n (kg mol^{-1})	PDI
		TFE + VAc		
15.0	5.2	15.8	280/187	1.49
34.7	2.8	26.8	141/111	1.27
50.4	4.2	35.7	224/150	1.49
66.7	1.9	39.3	182/118	1.54
14.3	9.8	14.2	300/200	1.50
14.3	9.8	13.9	300/200	1.50
14.3	9.8	13.9	300/200	1.50

f_{CTFE} (mol %)	yield (wt %)	F_{CTFE} (mol %)	M_w/M_n (kg mol^{-1})	PDI
		CTFE + VAc		
12.8	10.2	18.3	300/195	1.53
24.0	6.51	31.1	302/211	1.43
41.2	5.85	38.8	242/175	1.38
67.7	3.2	44.4	199/132	1.50
33.0	7.25	37.7	257/178	1.44
33.0	7.25	35.2	257/178	1.44
33.0	7.25	38.3	257/178	1.44

f_{VDF}	yield (wt %)	F_{VDF} (mol %)	M_w/M_n (kg mol^{-1})	PDI
		VDF + VAc		
28.7	5.0	13.7	191/132	1.46
44.3	7.0	18.3	151/106	1.42
66.6	3.3	9.1	100/76	1.31
66.2	8.0	10.9	97/72	1.34
28.7	14.5	6.3	169/108	1.56
28.7	14.5	8.0	169/108	1.56
28.7	14.5	10.3	169/108	1.56

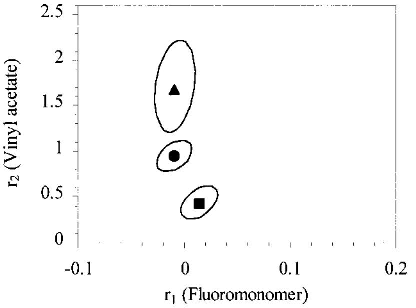

Figure 2. Estimated reactivity ratios and 95% confidence ellipses for the CO_2 copolymers: (■) P(CTFE-*co*-VAc); (●) P(TFE-*co*-VAc); (▲) P(VDF-*co*-VAc).

that the confidence interval for r_{TFE} overlaps zero, it is likely that TFE does not homopolymerize under these free radical conditions, in the presence of VAc. As is shown in Table 1, at high conversions and low VAc fractions (≤40%), TFE cross-propagates with VAc and VAc does not homopolymerize, whereas at high conversions and high VAc fractions (≥40%), TFE cross-propagates with VAc but VAc does homopolymerize. The difference observed in VAc behavior may reflect differences in CO_2 solubility of TFE−VAc macroradical chains, TFE, and/or VAc, depending upon the concentration of TFE itself.

Under similar CO_2 copolymerization conditions, $r_{VAc} = 0.44 \pm 0.02$ and $r_{CTFE} = 0.014 \pm 0.05$, indicating that the radical on CTFE primarily cross-propagates with VAc whereas the radical on VAc propagates randomly. Given that the confidence interval of r_{CTFE} overlaps zero, CTFE does not homopolymerize under the reaction conditions. Since both reactivity ratios approach zero, both monomers tend to cross-propagate with the other, yielding a largely random copolymer with possibly some alternating regions. Murray et al.[33] measured the reactivity ratios of CTFE and VAc to be $r_{VAc} = 0.68$ and $r_{CTFE} = 0.04$ under emulsion conditions. The difference in reactivity ratios measured in CO_2 and emulsion likely reflects differences in solubility of VAc, CTFE, and macroradicals in the two mediums. As indicated by the data in Table 1, VAc likely solvates the propagating macroradical chain in CO_2, thereby accounting for the higher yields and molar masses attained at higher VAc concentrations. Polymerization in CO_2 is often considered as a precipitation polymerization because the monomers are soluble in CO_2, but the macroradical propagating chains are only weakly soluble. Precipitation affects copolymer composition and monomer sequence distribution when accessibility of the reaction site is different for each monomer.[34] This is likely the case in CO_2, where preferential solvation of one monomer is enhanced by differences in the polarity of the solvent and the monomers; the polar monomer is pushed by the nonpolar solvent from the solution phase to the polymer phase.

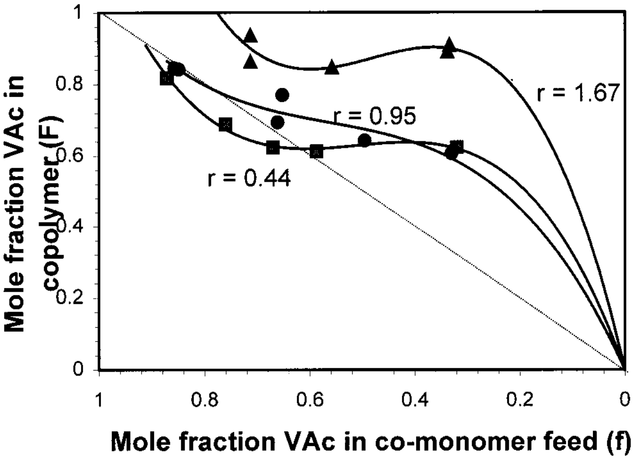

Figure 3. F_{VAc} vs f_{VAc} experimental data and the predicted curves calculated from reactivity ratio data, for each copolymerization series: (■) P(CTFE-*co*-VAc); (●) P(TFE-*co*-VAc); (▲) P(VDF-*co*-VAc).

Under CO_2 copolymerization conditions, $r_{VAc} = 1.67 \pm 0.6$ and $r_{VDF} = -0.4 \pm 0.04$, indicating that the radical on VDF primarily cross-propagates with VAc whereas the radical on VAc can homopolymerize more readily than it could in the presence of either TFE or CTFE. The r_{VDF} value is highly negative and does not overlap with zero, reflecting the inadequacy of the EVM software to accurately calculate r_{VDF}, and thus we consider the true value to be zero (and this is reflected in Figure 2).

Figure 3 summarizes the experimental F_{VAc} vs f_{VAc} data (cf. Table 2), and the predicted curve based on estimated reactivity ratios for each copolymerization series. Copolymers of CTFE with VAc were enriched with CTFE at lower monomer concentrations (i.e., $f_{CTFE} \leq 40\%$) yet reached a plateau at higher contents. At low conversion and low TFE monomer concentrations (i.e., $f_{TFE} \leq 15\%$), the copolymer composition reflected that of the monomer feed. At low conversion and higher TFE monomer concentrations, there was consistently lower TFE in the copolymer than in the monomer feed; however, at high conversion, the TFE content in the copolymer reflected that of the feed. The difference in copolymer composition with conversion reflects the

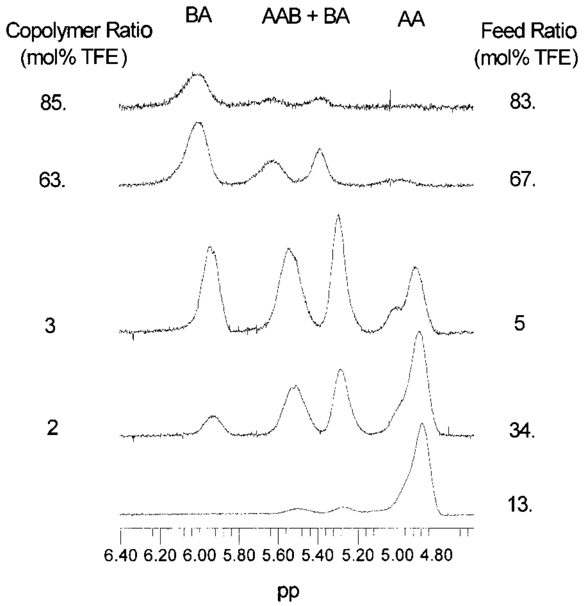

Figure 4. ^{1}H NMR spectra of the methine region of P(TFE-*co*-VAc) of different compositions.

differences in TFE vs VAc monomer reactivity ratios. Copolymers of VDF with VAc were always enriched with VAc regardless of VDF concentration in the monomer feed.

Copolymer Composition. To gain a greater understanding of the molecular composition of our fluorocopolymers, ^{1}H NMR was used to determine the occurrence of trimer repeats. Specific attention was devoted to the VAc methine hydrogen because its peak position is sensitive to the repeat unit of either side. The resonance of the methine protons is observed at $\delta = 4.6-6.4$ ppm for P(TFE-*co*-VAc), at $\delta = 4.6-6.6$ ppm for P(CTFE-*co*-VAc), and at $\delta = 4.6-5.6$ ppm for P(VDF-*co*-VAc). The methine proton resonance patterns of a series of P(TFE-*co*-VAc), P(CTFE-*co*-VAc), and P(VDF-*co*-VAc) are shown in greater detail in Figures 4, 5, and 6, respectively. For P(TFE-*co*-VAc), the resonance peak at $\delta = 4.9$ corresponds to the methine resonance of VAc units (A) centered in AAA triads. The resonance peak occurring between $\delta = 5.8$ and 6.2 increases in relative intensity as the TFE content of the copolymers increases and is assigned to the VAc units having two TFE (B) neighbors, i.e., BAB triads. Finally, the resonance peaks between $\delta = 5.1$ and 5.8 are assigned to VAc units centered in BAA and AAB triads.

The methine proton resonance peaks for P(CTFE-*co*-VAc) are observed at $\delta = 4.6-6.8$ ppm and are similar to those of P(TFE-*co*-VAc). However, there are some notable differences in the resonance patterns. For example, the BAB triad resonance peaks ($\delta = 6.0-6.4$ ppm) for P(CTFE-*co*-VAc) appear as a doublet (Figure 5) instead of a broad singlet as was observed for P(TFE-*co*-VAc). Another difference is in the region of BAA and AAB triads where three peak areas having relative intensities of 2:1:1 are clearly distinguished. Murray et al.[33] have attributed theses areas to eight different BAA and AAB stereochemical structures, and this may also explain the differences observed in the BAB triad peaks for P(CTFE-*co*-VAc) vs P(TFE-*co*-VAc).

The resonance patterns of P(VDF-*co*-VAc), unlike those of P(TFE-*co*-VAc) and P(CTFE-*co*-VAc), did not have any BAB triads, even when 66 mol % of VDF was used in the feed (Figure 6). This further underscores the propensity for VDF to cross-propagate with VAc and for VAc to homopolymerize, as was supported by the reactivity ratio data.

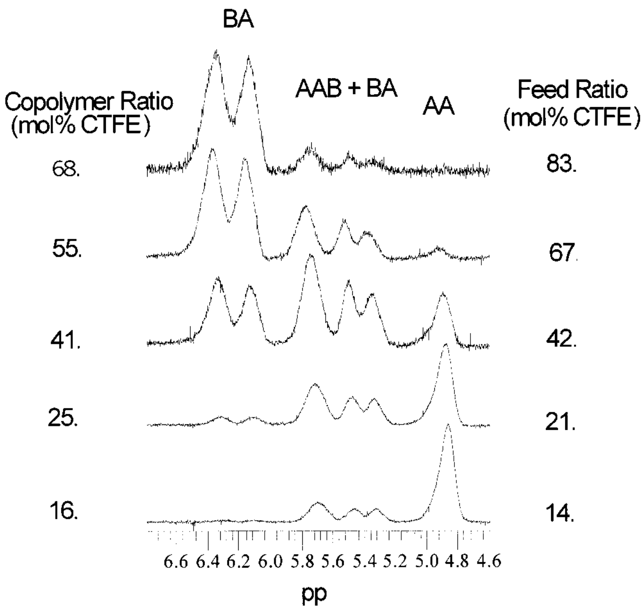

Figure 5. ^{1}H NMR spectra of the methine region of P(CTFE-*co*-VAc) of different compositions.

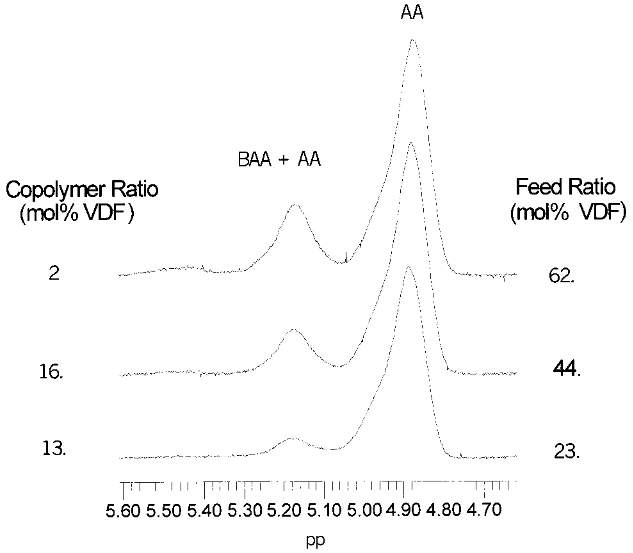

Figure 6. ^{1}H NMR spectra of the methine region of P(VDF-*co*-VAc) of different compositions.

Comparing the integrated areas under the peaks in the triad sequences, that is AAA vs BAB, AAB, and BAA, provides some insight into the propensity for VAc to homopolymerize in the presence of the different fluoromonomers. For P(TFE-*co*-VAc) and P(CTFE-*co*-VAc), AAA triads increase with VAc concentration and decrease with fluoromonomer concentration. Thus, the probability for cross-propagation increases with fluoromonomer concentration in the feed. For the same fluoromonomer mole fraction in the feed, the probability for CTFE to alternate with VAc is greater than that for TFE to alternate with VAc based on the triad sequence peak integrated areas. Unlike CTFE and TFE, VDF does not show any tendency to alternate with VAc.

Hydrolysis of P(TFE-*co*-VAc) to P(TFE-*co*-VAc-*co*-VA) Demonstrates Linearity of Copolymers. P(TFE-*co*-VAc) was hydrolyzed under acidic conditions to P(TFE-*co*-VAc-*co*-VA), as evidenced by FTIR by both a large decrease in the VAc carbonyl peak (1744 cm^{-1}) and the appearance of a hydroxyl peak (ca. 3337−3346 cm^{-1}). The extent of hydrolysis was calculated by the change in the carbonyl absorbance relative to a reference $-CF_2-$ absorbance peak (ca. 1157 cm^{-1}) in which the intensity did not change significantly following hydrolysis.[3] Copolymers with mole fractions of TFE ≤35 mol % were hydrolyzed but were then insoluble in ethyl acetate and THF, rendering molar mass determination by GPC difficult. To overcome this difficulty, a copolymer with a higher TFE content, P(TFE-*co*-VAc) with 63 mol % TFE, was partially hydrolyzed (to 83%), yielding terpolymers P(TFE-*co*-VAc-*co*-VA). The M_w, M_n, and PDI before hydrolysis, for P(TFE-*co*-VAc), was 289 kg mol^{-1}, 157 kg mol^{-1}, and 1.84 whereas after hydrolysis, for P(TFE-*co*-VAc-*co*-VA), it was 296 kg mol^{-1}, 127 kg mol^{-1}, and 2.33. Thus, M_n decreased after hydrolysis, but M_w and PDI increased. Overall, the molar mass distribution shifted to a lower molar mass as a result of hydrolysis, yet a small high molar mass tail appeared in the GPC chromatogram, thereby explaining the increase in M_w and PDI. We had previously observed a similar high molar mass tail in hydrolyzed, CO_2 synthesized fluoro-copolymers that were synthesized with a surfactant.[3] The high molar mass tail can be attributed to either condensation of polymeric chains under the acidic hydrolysis conditions used or the formation of hydrogen-bonding interactions between VA hydroxyl functional groups and VAc, thereby increasing the hydrodynamic volume of P(TFE-*co*-VAc-*co*-VA) relative to P(TFE-*co*-VAc). To confirm that the decrease in molar mass resulted from a pendant group hydrolysis and not from hydrolyzed esters in the polymer backbone, we compared the expected (or calculated) molar mass decrease to that observed. Specifically, we compared the hydrolyzed (H) to parent (P) molar mass ratios. The expected ratio was calculated from the molar mass of the average repeat unit of the hydrolyzed to parent copolymer (M_H/M_P). The expected (M_H/M_P) was calculated from NMR data, with the extent of hydrolysis being factored into M_H, as outlined in eq 2:[3]

$$M_H/M_P(\text{expected}) = \frac{\bar{F}_{TFE}MW_{TFE} + (1-\bar{F}_{TFE})[(1-H)MW_{VAc} + (H)MW_{VA}]}{\bar{F}_{TFE}MW_{TFE} + (1-\bar{F}_{TFE})MW_{VAc}} \tag{2}$$

F_{TFE} is the mole fraction of TFE in the copolymer. MW_{TFE}, MW_{VAc}, and MW_{VA} are the monomer molar masses of TFE, VAc, and VA, respectively. H is the mole fraction of VAc that was hydrolyzed. The observed changes in molar mass were calculated using the GPC determined number- and weight-average molar mass ratios, $M_{n,H}/M_{n,P}$ and $M_{w,H}/M_{w,P}$, respectively. The expected ratio M_H/M_P of 0.83 is only slightly higher than that for M_n, $M_{n,H}/M_{n,P}$, of 0.8 and lower than that of M_w, $M_{w,H}/M_{w,P}$, of 1.02. $M_{w,H}/M_{w,P}$ is greater than the expected M_H/M_P because of the high molar mass tail. This suggests that hydrogen abstraction during polymerization was negligible, and linear copolymers were formed in the surfactant-free CO_2 polymerization of P(TFE-*co*-VAc). Clarke et al.[35] demonstrated that hydrogen abstraction during VAc emulsion polymerization occurs at both acetoxy methyl and tertiary hydrogen positions; while we disproved the former in CO_2, if the latter occurred in CO_2, we would not detect it by GPC characterization of hydrolyzed polymers. However, NMR data were used to calculate the expected M_H/M_P, and this value closely approximates our observed results ($M_{n,H}/M_{n,P}$), confirming that branching is limited (or nonexistent) in CO_2. Jones proposed that "dendritic" or highly branched polymeric structures were formed as a result of radical hydrogen abstraction in aqueous emulsions.[19] Formation of these structures can be rationalized to have occurred through inter- or intramolecular mechanisms, which can be considered bimolecular processes. Herein, the significant reduction of radical hydrogen abstraction from VAc may indicate that propagation competes more effectively with chain transfer processes in CO_2.[20]

Table 3. Comparison of the ^1H NMR Peak Areas in the Methine Region of Fluorocarbon−VAc Copolymers

	integrated peak areas		
	A_{AAA}	$A_{AAB+BAA}$	A_{BAB}
TFE in feed (mol %)			
13.1	0.91	0.08	0.00
34.5	0.46	0.47	0.06
50	0.20	0.56	0.22
67.7	0.04	0.42	0.53
83.8	0.00	0.26	0.73
CTFE in feed (mol %)			
14.5	0.67	0.33	0.00
21.4	0.42	0.50	0.08
42.4	0.13	0.53	0.33
67.7	0.01	0.3	0.68
83.8	0.00	0.12	0.87
VDF in feed (mol %)			
23.3	0.95	0.04	0.00
44.6	0.82	0.17	0.00
62.1	0.77	0.22	0.00

Table 4. Comparison of P(TFE-*co*-VAc) Synthesized with and without Surfactant

TFE in feed (mol %)	M_w/M_n/PDI (with surfactant) (kg mol^{-1})	M_w/M_n/PDI (without surfactant) (kg mol^{-1})
48−50	230/137/1.67	262/137/1.91
67−68	206/122/1.68	290/157/1.84
80−83	172/113/1.52	254/156/1.62

P(TFE-*co*-VAc) is linear regardless of the presence of surfactant, yet the PDIs of all copolymers synthesized with a surfactant were lower than those synthesized without a surfactant. As shown in Table 4, PDIs were between 1.52 and 1.68 for P(TFE-*co*-VAc) with a surfactant[3] and between 1.62 and 1.91 without a surfactant. This suggests that the surfactant enhances the solubility of the macroradical chains, which then facilitates the formation of high molar mass polymers.

Conclusions

We have prepared a series of fluorocarbon−VAc copolymers in supercritical CO_2, with a broad range of compositions, high yields, and high molar masses. We demonstrated, for the first time, that surfactant-free CO_2 polymerization of all three fluorocarbons with VAc was possible and that P(TFE-*co*-VAc) was linear. All TFE−VAc copolymers have high yields and high molar masses, suggesting good solubility in CO_2. CTFE−VAc copolymers are synthesized in high yield when <50 mol % of CTFE is in the feed. At higher concentrations of CTFE (≥50%), the gradual consumption of VAc results in lower polymer yields and molar masses, suggesting that CTFE is less soluble than TFE in CO_2. However, CTFE is more reactive than TFE with respect to VAc, indicating that the propensity for cross-propagation of monomers is greater for CTFE−VAc than TFE−VAc. VDF−VAc copolymers were synthesized with the lowest yields of the three fluorocarbons studied due to the decreased reactivity (and likely CO_2 solubility) of VDF relative to VAc. However, the relatively low PDIs of P(VDF-*co*-VAc) indicate that their macroradicals are soluble in CO_2.

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References and Notes

(1) Paulaitis, M. E.; Krukonis, V. J.; Reid, R. C. *Rev. Chem. Eng.* **1983**, *1*, 179.
(2) Hubert, P.; Vitzthum, O. G. *Angew. Chem., Int. Engl.* **1978**, *17*, 710−715.
(3) Lousenberg, R. D.; Shoichet, M. S. *Macromolecules* **2000**, *33*, 1682−1685.
(4) Guan, Z.; Elsbernd, C. S.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 329−330.
(5) Lepilleur, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 745−756.
(6) Combes, J. R.; Guan, Z.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 865−867.
(7) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356−359.
(8) Romack, T. J.; DeSimone, J. M.; Treat, T. A. *Macromolecules* **1995**, *28*, 8429−8431.
(9) Romack, T. J.; Maury, E. E.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 912−915.
(10) Canelas, D. A.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 5673−5682.
(11) Van Bramer, D. J.; Shiflett, M. B.; Yokozeki, A. United States Patent 5,345,013, 1994.
(12) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945−947.
(13) Hoefling, T. A.; Newman, D. A.; Enick, R. M.; Beckman, E. J. *J. Supercrit. Fluids* **1993**, *6*, 165−171.
(14) Sarbu, T.; Styranec, T.; Beckman, E. J. *Nature (London)* **2000**, *405*, 165−168.
(15) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 1729−1736.
(16) Shah, V. M.; Hardy, B. J.; Stern, S. A. *J. Polym. Sci., Polym. Phys.* **1993**, *31*, 313.
(17) Patterson, D. *Polym. Eng. Sci.* **1982**, *22*, 64.
(18) Mertdogan, C. A.; Byun, H. S.; McHugh, M. A.; Tuminello, W. H. *Macromolecules* **1996**, *29*, 6548.
(19) Jones, C. W. United State Patent 5,723,556, 1998.
(20) DeYoung, J. P.; Romack, T. J.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (2), 424−425.
(21) Watkins, J. J.; McCarthy, T. J. *Macromolecules* **1995**, *28*, 4067−4074.
(22) Takayanagi, T.; Yamabe, M. *Prog. Org. Coat.* **2000**, *40*, 185−190.
(23) Tuminello, W. H.; Dee, G. T.; McHugh, M. A. *Macromolecules* **1995**, *28*, 1506−1510.
(24) Canelas, D. A.; Betts, D. E.; DeSimone J. M.; Yates, M. Z.; Johnston, P. K. *Macromolecules* **1998**, *31*, 6794−6805.
(25) Rindfleisch, F.; DiNoia, T. P.; McHugh, M. A. *J. Phys. Chem.* **1996**, *100*, 15581−15587.
(26) Hunadi, R. J.; Baum, K. *Synthesis* **1982**, *39*, 454.
(27) Strain, F.; Bissinger, W. E.; Dial, W. R.; Rudoff, H.; DeWitt, B. J.; Stevens, H. C.; Langston, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 1254−1263.
(28) Feiring, A. E.; Wonchoba, E. R. *Macromolecules* **1998**, *31*, 7103−7104.
(29) McHugh, M.; Krukonis, V. In *Supercritical Fluid Extraction: Principles and Practices*; Butterworth Publishers: Stoneham, MA, 1986; pp 148−163.
(30) Dinoia, T. P.; Conway, S. E.; Lim, J. S.; Mchugh, M. A. *J. Polym. Sci., Polym. Phys.* **2000**, *38*, 2832−2840.
(31) Polic, A. L.; Duever, T. A.; Penlidis, A. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 813−822.
(32) Dube, M.; Sanayei, R. A.; Penlidis, A.; O'Driscoll, K. F.; Reilly, P. M. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 703−708.
(33) Murray, D. L.; Harwood: H. J.; Shendy, S. M. M.; Piirma, I. *Polymer* **1995**, *36*, 3841−3848.
(34) Polchocka, K. *J. Macromol. Sci., Rev. Macromol. Chem.* **1981**, *C20*, 67−148.
(35) Clarke, J. T.; Howard, R. O.; Stockmayer, W. H. *Makromol. Chem.* **1961**, *427*, 44−46

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