Synthesis of Linear Poly(tetrafluoroethylene-*co*-vinyl acetate) in Carbon Dioxide

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ABSTRACT: Tetrafluoroethylene (TFE) and vinyl acetate (VAc) were copolymerized in carbon dioxide by a free radical mechanism to yield a series of poly(TFE-*co*-VAc)s with weight-average molar masses, relative to polystyrene, between 110 and 209 kg mol^{-1}. The copolymer composition was controlled by the monomer feed concentration to have between 40 and 71 mol % TFE. Hydrolysis of the copolymer's vinyl acetate groups to vinyl alcohol (VA) yielded terpolymers, poly(TFE-*co*-VAc-*co*-VA), thereby providing a reactive functional group for further modification. Previous syntheses of poly(TFE-*co*-VAc) in aqueous media resulted in a branched structure due to radical hydrogen abstraction from VAc followed by continued propagation during polymerization. Consequently, a 10-fold or greater decrease in molar mass was observed following hydrolysis. Interestingly, after synthesizing poly(TFE-*co*-VAc) in supercritical carbon dioxide, only a small decrease in molar mass was observed after hydrolysis. This suggests that, in carbon dioxide, abstraction is suppressed relative to polymer propagation, thereby yielding predominantly linear poly(TFE-*co*-VAc).

Introduction

Fluoropolymers have been used in a wide array of applications, including those in coatings,[1] optical,[2] and biomedical fields.[3] However, the inherent thermal stability of commercially available fluoropolymers limits their processability while the inherent chemical stability limits their solubility in organic solvents. To overcome some of these limitations, we,[4,5] and others,[6] have synthesized trifluorovinyl ether (TFVE) polymers. Our poly(TFVE)s have a hydrocarbon oligoether pendant group and a perfluorinated backbone, thereby incorporating some hydrocarbon properties into a fluorinated system. By combining hydrocarbon and fluorocarbon properties, the resulting polymers are easier to process and more soluble in organic solvents. By using a functionalized monomer, a reactive group is incorporated into the polymer, thereby facilitating further modification and circumventing the need to use highly reactive species that are required for fluoropolymer surface modification.[7,8]

An alternate approach to prepare a processable, organic solvent-soluble, functionalized fluoropolymer is to copolymerize tetrafluoroethylene (TFE) with vinyl acetate (VAc). TFE and VAc copolymers have been previously synthesized in aqueous and organic media;[1,9] yet the solvents used limit the polymer formed to either a narrow range of compositions or a highly branched structure. For example, when poly(TFE-*co*-VAc) was prepared by aqueous emulsion, the propagating radical abstracted a methyl hydrogen from VAc, which continued to propagate, thereby forming copolymer branches. Upon hydrolysis of poly(TFE-*co*-VAc), VAc ester groups were converted to the corresponding vinyl alcohol (VA) concomitant with a 10−100-fold decrease in the weight-average molar mass (M_w).[1] It was proposed that esters were incorporated into the polymer backbone, thus accounting for the substantial decrease in M_w upon hydrolysis.

Herein, we report the copolymerization of TFE and VAc in supercritical carbon dioxide, which is an environmentally friendly and convenient solvent for fluoropolymer synthesis.[10,11] It has also been used for the dispersion homo- and copolymerization of VAc with other hydrocarbon monomers.[12] In addition, by using CO_2, we obviate the need to remove organic solvents postpolymerization, which limited the utility of previous copolymers of TFE and VAc.[13] We observed a slight decrease in molar mass upon hydrolysis of VAc to VA, indicating that our polymers, unlike those previously synthesized in water emulsions, are essentially linear.

Experimental Section

Materials. Vinyl acetate (Aldrich, Ontario, Canada) was used as received. TFE was prepared by vacuum pyrolysis of poly(tetrafluoroethylene)[14] (Aldrich, Ontario, Canada) 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 pressures should familiarize himself or herself with safe handling procedures. TFE can explode with the force of TNT.*] The 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 THF, using a published procedure,[15] and stored in THF at −20 °C. The initiator was standardized by iodometry and was typically 7.5% (w/w). FC-171 Fluorad was kindly provided by 3M (St. Paul, Minnesota) and used as received. SFC purity CO_2 was obtained from Matheson (Ontario, Canada). Acetone, ethyl acetate, ethanol, THF, and concentrated sulfuric acid were obtained from Fisher Scientific (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.

Characterization. Polymer molar mass distributions were characterized by GPC (Waters U6K injector, 510 pump) equipped with a refractive index detector (Waters 2410) and a series of Ultrastyrogel columns (Waters 10^6, 10^4, and 500 Å). Using an ethyl acetate mobile phase (1 mL min^{-1}), polymer molar masses were calculated relative to polystyrene standards (Aldrich, Ontario, Canada). FTIR absorbance spectra (16 scans, 4 cm^{-1} resolution) were obtained from thin polymer

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Table 1. Copolymers of TFE and VAc

				TFE in copolymer (mol %)			
sample no.	TFE in feed (mol %)	initiator (wt %)[a]	yield (wt %)[a]	NMR[b]	mass balance	elemental analysis[c]	M_w/M_n/PDI (kg mol^{-1})
1	48	0.38	78	13	34	40	209/116/1.80
2	67	0.38	70	31	53	58	164/99.0/1.66
3	67	1.5	71	38	54	59	112/76.7/1.46
4	80	0.38	60	36	67	71	110/77.3/1.42

[a] Based on an initial monomer weight of 20 g. [b] 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 internal reference. [c] Determined from % C analysis.

films using a Galaxy series 5000 spectrometer. Thin films were prepared from ~2% (w/v) THF solutions cast onto NaCl disks. ^{1}H and ^{19}F NMR spectra were obtained in acetone-d_6 on a Varian Gemini spectrometer at 300.75 and 282.33 MHz, respectively, using TMS and α,α,α-trifluorotoluene (Aldrich, Ontario, Canada) as external and internal references, respectively. Elemental analysis was done by Canadian Microanalytical Service Ltd. (British Columbia, Canada).

Polymerizations in Carbon Dioxide. Polymerizations were carried out 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. 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 initiator in THF was added to a cold 25 mL test tube. The test tube was evacuated ($P \sim 0.1-1$ mmHg) to remove most of the THF. Then the desired amount of chilled VAc ($T \sim 0$ °C) and 1.00 g of Fluorad FC-171 surfactant were added. The test tube contents were mixed by shaking and then transferred by cannula to the evacuated reactor. With stirring, the desired amount of TFE was added to the reaction for a total monomer weight of 20 g. CO_2 was then added and maintained at a pressure of 20−40 bar while warming the reactor to approximately 5 °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 30−40 min. Pressures were initially between 230 and 260 bar.

Polymerizations were stopped after 24 h by first cooling the reactor to room temperature and slowing the rate of stirring. The reactor was then slowly vented to atmospheric pressure. At a pressure of less than 60 bar, stirring was stopped as the polymer coagulated and started to bind the stir shaft. The reactor was then fully vented to atmospheric pressure and 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 and ethanol mixture (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). Four copolymer compositions were prepared:

Poly(TFE-*co*-VAc) [1]. Yield 15.6 g (78%). ^{1}H NMR: δ = 6.05 (broad peak, 0.28H, −TFE−CH$_2$−C*H*(OAc)−TFE−), 5.65 (broad peak, 0.28H, −VAc−CH$_2$−C*H*(OAc)−TFE−), 5.4 (broad peak, 0.26H, −TFE−CH$_2$−C*H*(OAc)−VAc−), 5.0 (broad peak, 0.17H, −VAc−CH$_2$−C*H*(OAc)−VAc−), 2.2−2.9 (broad peaks, 2H, CH$_2$), 1.9−2.2 (sharp peaks, 3H, CH$_3$). ^{19}F NMR: δ = −47 to −53 (broad peaks, CF$_2$), −55 to −64 (broad peaks, CF$_2$). Anal. Found: C, 42.02; H, 3.99; F, 20.58.

Poly(TFE-*co*-VAc) [2]. Yield 14.0 g (70%). ^{1}H NMR: δ = 6.05 (broad peak, 0.52H, −TFE−CH$_2$−C*H*(OAc)−TFE−), 5.65 (broad peak, 0.22H, −VAc−CH$_2$−C*H*(OAc)−TFE−), 5.4 (broad peak, 0.20H, −TFE−CH$_2$−C*H*(OAc)−VAc−), 5.0 (broad peak, 0.06H, −VAc−CH$_2$−C*H*(OAc)−VAc−), 2.2−2.9 (broad peaks, 2H, CH$_2$), 1.9−2.2 (sharp peaks, 3H, CH$_3$). ^{19}F NMR: δ = −48 to −53 (broad peaks, CF$_2$), −55 to −64 (broad peaks, CF$_2$). Anal. Found: C, 36.35; H, 2.90; F, 36.13.

Poly(TFE-*co*-VAc) [3]. Yield 14.2 g (71%). ^{1}H NMR: δ = 6.05 (broad peak, 0.53H, −TFE−CH$_2$−C*H*(OAc)−TFE−), 5.65 (broad peak, 0.22H, −VAc−CH$_2$−C*H*(OAc)−TFE−), 5.4 (broad peak, 0.20H, −TFE−CH$_2$−C*H*(OAc)−VAc−), 5.0 (broad peak, 0.05H, −VAc−CH$_2$−C*H*(OAc)−VAc−), 2.2−2.9 (broad peaks, 2H, CH$_2$), 1.9−2.2 (sharp peaks, 3H, CH$_3$). ^{19}F NMR: δ = −48 to −53 (broad peaks, CF$_2$), −55 to −64 (broad peaks, CF$_2$). Anal. Found: C, 36.02; H, 2.77; F, 33.81.

Poly(TFE-*co*-VAc) [4]. Yield 12.0 g (60%). ^{1}H NMR: δ = 6.05 (broad peak, 0.66H, −TFE−CH$_2$−C*H*(OAc)−TFE−), 5.65 (broad peak, 0.17H, −VAc−CH$_2$−C*H*(OAc)−TFE−), 5.4 (broad peak, 0.15H, −TFE−CH$_2$−C*H*(OAc)−VAc−), 5.0 (broad peak, 0.02H, −VAc−CH$_2$−C*H*(OAc)−VAc−), 2.2−2.9 (broad peaks, 2H, CH$_2$), 1.9−2.2 (sharp peaks, 3H, CH$_3$). ^{19}F NMR: δ = −49 to −53 (broad peaks, CF$_2$), −55 to −64 (broad peaks, CF$_2$). Anal. Found: C, 32.24; H, 2.08; F, 49.19.

Acid Hydrolysis. To a 125 mL round-bottom flask equipped with a condenser and a magnetic stir bar were added 3 g of polymer, 75 mL of ethanol, 1 mL of water, and 0.5 mL of concentrated sulfuric acid. The flask was heated, and the contents were stirred and refluxed for 3 days. A nearly colorless, transparent solution resulted. The solution was then cooled to room temperature. Sodium bicarbonate was slowly added, with vigorous stirring, until the solution was neutral to pH paper. The polymer solution was precipitated into water with vigorous stirring, collected by vacuum filtration, and repeatedly washed with water prior to drying (40 °C, $P <$ 0.1 mmHg).

Base Hydrolysis. To a 125 mL round-bottom flask equipped with a magnetic stir bar were added 3 g of polymer, 75 mL of ethanol, and 5 mL of 30% aqueous NaOH. The contents of the flask were stirred overnight, resulting in an orange to dark red solution. The polymer solution was precipitated into water with vigorous stirring, collected by vacuum filtration, and repeatedly washed with water prior to drying (40 °C, $P <$ 0.1 mmHg).

Results

Poly(TFE-*co*-VAc) was synthesized in supercritical carbon dioxide at three TFE and two initiator concentrations, the results of which are summarized in Table 1. The copolymer compositions were estimated by three techniques: NMR, mass balance, and elemental analysis. Mass balance was used to estimate a lower limit of TFE incorporated into the copolymer by assuming that (1) all of the VAc monomer was incorporated into the copolymer and (2) the polymer had been quantitatively isolated from the reactor. Using these assumptions, the mass of TFE in the copolymer was calculated as the difference between the polymer yield and the mass of VAc monomer used. As shown in Table 1, the composition calculated by NMR was consistently lower than that calculated by mass balance; longer ^{19}F NMR transient acquisition/pulse delay times were inconsequential to composition. Since mass balance provides a lower limit for TFE incorporation, NMR did not accurately reflect the composition of our samples. Interestingly, Feiring observed similar discrepancies between NMR and elemental analysis for his fluoropolymers.[2]

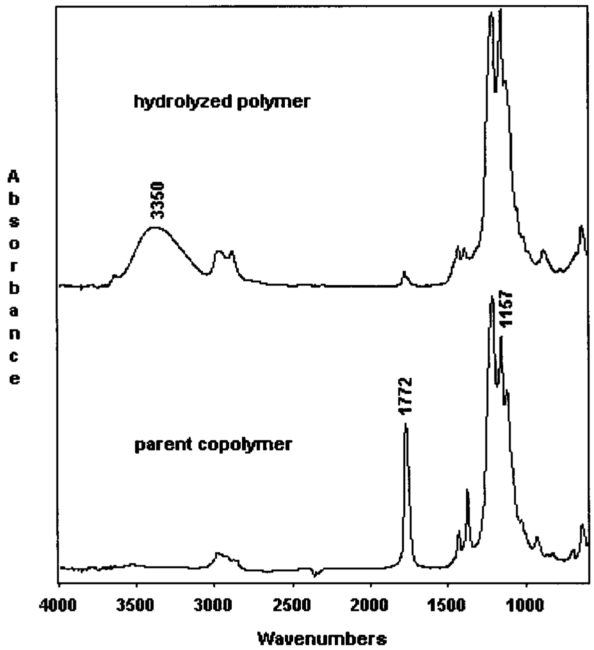

Figure 1. FTIR spectra of poly(TFE-*co*-VAc), **4**, before and after hydrolysis.

Table 2. Hydrolysis of Poly(TFE-*co*-VAc)

sample no.	M_w/M_n/PDI (kg mol^{-1}) before hydrolysis	after hydrolysis	% VAc hydrolyzed
1	209/116/1.80	194/69.9/2.77	98
2	164/99.0/1.66	152/77.8/1.95	96
3	112/76.7/1.46	116/61.9/1.87	92
4	110/77.3/1.42	100/64.4/1.55	92

Given the assumptions required to determine the composition by mass balance and the apparent inadequacy of NMR for these calculations, elemental analysis was determined to be the best estimate of composition.

As shown in Table 1, initiator concentration affected molar mass but was of little consequence to copolymer composition. All of the polymers had M_ws greater than 100 000 g/mol and PDIs lower than 2.

Poly(TFE-*co*-VAc) was hydrolyzed under acidic conditions to poly(TFE-*co*-VAc-*co*-VA) as determined from FTIR by both a large decrease in the VAc carbonyl absorption (1772 cm^{-1}) and the appearance of a hydroxyl absorption (ca. 3350 cm^{-1}). The extent of hydrolysis was calculated by the change in the carbonyl absorbance relative to a reference absorbance (ca. 1157 cm^{-1}) in which the intensity did not change significantly following hydrolysis. As indicated in Figure 1 and as shown in Table 2, most of the VAc groups were hydrolyzed to VA groups.

By comparing the molar mass data in Tables 1 and 2, molar mass typically decreased and polydispersity increased after hydrolysis. As shown in Figure 2, the molar mass distribution shifted to lower molar mass as a result of hydrolysis, yet a small high molar mass tail appeared. Some of the polymer chains likely condensed under the acidic hydrolysis conditions used. Although hydrolyses were carried out in dilute solutions in the presence of water, the high molar mass tail was evident in all distributions. While base hydrolysis[1] would have been the preferred method of hydrolysis, it was ineffective, resulting in discoloration and decomposition of the polymer, likely as a result of elimination reactions.

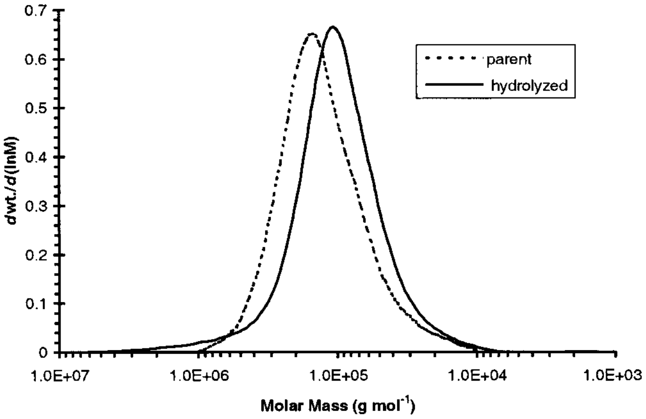

Figure 2. Molar mass distribution of poly(TFE-*co*-VAc), **2**, before and after hydrolysis.

Table 3. A Comparison of the Expected and Observed Changes in Molar Mass Ratios of Hydrolyzed (H) to Parent (P) Polymers

sample no.	expected M_H/M_P	observed M_{nH}/M_{nP}	M_{wH}/M_{wP}
1	0.70	0.60	0.93
2	0.80	0.79	0.94
3	0.83	0.81	1.04
4	0.86	0.83	0.91

To determine whether the decrease in molar mass was simply due to pendant group hydrolysis or a result of hydrolyzed esters in the polymer backbone, the expected molar mass decrease was compared to that observed. The calculation of the expected decrease in molar mass of the average repeat unit of hydrolyzed to parent copolymers (M_H/M_P) was done using elemental analysis data. The extent of hydrolysis was factored into the calculation of M_H (cf. Tables 1 and 2). The observed changes in molar mass were calculated from the data presented in Tables 1 and 2 for number-average and weight-average molar mass ratios, M_{nH}/M_{nP} and M_{wH}/M_{wP}, respectively. As shown in Table 3, the expected ratios are similar to those observed for M_n yet lower than those observed for M_w. The high molar mass tail observed for the hydrolyzed samples likely accounts for the discrepancy between M_{wH}/M_{wP} data and M_H/M_P calculated.

Discussion

Unlike previous poly(TFE-*co*-VAc) syntheses in water emulsions where a branched structure was formed, in supercritical carbon dioxide we observed a predominantly linear polymer. It was hypothesized that a branched polymer was formed during the water emulsion polymerization due to radical hydrogen abstraction of a VAc methyl hydrogen. Continued propagation of the resulting radical resulted in ester groups at the branch points.[1] Consequently, M_w was observed to decrease significantly upon hydrolysis. We found that the molar mass averages did not change substantially upon hydrolysis of our CO_2-synthesized polymers. More importantly, the expected and observed molar mass ratios are similar, yet in all cases, M_{nH}/M_{nP} are consistently slightly lower than the respective M_H/M_P (cf. Table 3). Notwithstanding that GPC measures molar mass indirectly through hydrodynamic volume, this suggests that hydrogen abstraction is negligible and likely did not occur in most cases. If hydrogen abstraction did occur, the results suggest that it may be slightly more preva-

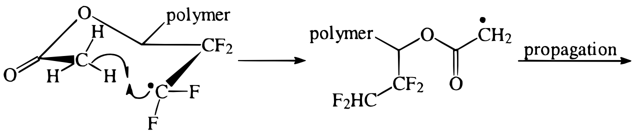

Figure 3. Proposed intramolecular mechanism for hydrogen abstraction during propagation of the copolymerization of VAc and TFE.

lent in cases where the fraction of VAc in the copolymer is equal to or greater than the fraction of TFE (i.e., sample 1).

The absence of radical hydrogen abstraction from VAc may indicate that propagation competes more effectively with chain-transfer processes in CO_2 [16] than it did in water. Since most polymeric materials swell considerably in CO_2 and CO_2 is able to transport small molecules into highly crystalline fluoropolymer matrices,[17] CO_2 may facilitate diffusion of TFE and VAc monomers into the polymer phase. Thus, the rate of propagation, a bimolecular process, may increase relative to chain transfer, if a significant amount of the latter is a unimolecular process.

Hydrogen abstraction may be considered a unimolecular process as a result of an intramolecular mechanism. For example, intramolecular hydrogen abstraction has been proposed in the aqueous emulsion homopolymerization 1-alkoxy-1,2,2-trifluoroethenes.[5] Therein, hydrogen was likely abstracted from the pendant group adjacent to the propagating radical, resulting in a new propagating radical. A similar mechanism may also be used to rationalize the aqueous emulsion copolymerization of TFE and VAc, as shown in Figure 3. This mechanism also accounts for branching and the significant decrease in M_w following hydrolysis. Changes in diffusion would have little effect on this mechanism. Thus, if hydrogen abstraction is unimolecular, as we have described, then the rate of propagation should increase relative to that of hydrogen abstraction. Clearly, propagation is favored over hydrogen abstraction in CO_2 to a greater extent than it is in an aqueous emulsion.

Conclusions

We have prepared a series of poly(TFE-*co*-VAc)s in supercritical CO_2 and found them to be essentially linear. Radical hydrogen abstraction chain-transfer reactions, which are characteristic of the copolymerization of many hydrocarbon monomers with TFE, were apparently suppressed relative to propagation as a consequence of using CO_2 as the continuous phase. As a result, predominantly linear copolymers were formed which are likely more robust than those formed by aqueous emulsion. Other hydrocarbon monomers might also copolymerize in CO_2 with TFE to form linear copolymers. Eventually, fluoropolymer properties may be tailored to specific applications instead of having the application fit the fluoropolymer.

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