

Radical Copolymerization of Novel Trifluorovinyl Ethers with Ethyl Vinyl Ether and Vinyl Acetate: Estimating Reactivity Ratios and Understanding Reactivity Behavior of the Propagating Radical

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ABSTRACT: Two novel trifluorovinyl ether (TFVE) monomers were copolymerized with either ethyl vinyl ether (EVE) or vinyl acetate (VAc) in a redox-initiated aqueous emulsion: 1-(2-phenoxyethoxy)-1,2,2-trifluoroethene (Ph-TFVE) and 1-[2-(2-ethoxyethoxy)ethoxy]-1,2,2-trifluoroethene (Et-TFVE). Previous studies demonstrated a propensity for radical hydrogen abstraction from the oligoether pendant group during the homopolymerization of Et-TFVE with continued propagation of the resulting radical, thereby providing the rationale to investigate the copolymerization of our new TFVEs with EVE or VAc. Reactivity ratios were estimated using the error-in-variables model from a series of bulk free radical copolymerizations of Ph-TFVE with EVE or VAc. The reactivity ratios were $r_{\text{Ph-TFVE}} = 0.25 \pm 0.07$, $r_{\text{EVE}} = 0.016 \pm 0.04$; $r_{\text{Ph-TFVE}} = 0.034 \pm 0.04$, $r_{\text{VAc}} = 0.89 \pm 0.08$. Partial hydrolysis of polymers containing VAc to vinyl alcohol (VA) resulted in two terpolymers: poly(Ph-TFVE-co-VAc-co-VA) and poly(Et-TFVE-co-VAc-co-VA), respectively. We investigated the possibility of hydrogen abstraction from VAc during polymerization by comparing the molar mass before and after hydrolysis. Abstraction from VAc was not apparent during polymerization; however, abstraction from the oligoether pendant group of Et-TFVE was again evident and was more significant for those copolymers having a greater fraction of Et-TFVE in the monomer feed. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 1344–1354, 2000

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INTRODUCTION

Relative to hydrocarbon polymers, fluoropolymers offer unique advantages of chemical resistance and thermal stability, yet the former enjoy a greater breadth of applications. By copolymerizing fluorinated and hydrocarbon monomers, copolymers with properties intermediate to the two can be prepared

and used in diverse applications. Relative to hydrocarbon polymers, these copolymers generally have improved weatherability, thermal stability, and chemical resistance. Relative to fluoropolymers, these copolymers have increased solubility in organic solvents and facilitated processing.¹ By incorporating a reactive functional group into the backbone of the copolymer, further modification is facilitated, thereby obviating the use of the highly reactive species required for modification of perfluorinated polymers such as poly(tetrafluorethylene-co-hexafluoropropylene).^{2,3}

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We recently described the synthesis⁴ and polymerization⁵ of a series of new trifluorovinyl ethers (TFVEs) that combine hydrocarbon oligoether pendant groups with fluorocarbon backbones: 1-(2-alkoxyethoxy)-1,2,2-trifluoroethenes. Our poly(TFVE)s are thermally stable, soluble in most organic solvents and have a hydroxyl group available for further modification.⁶ Our TFVEs have a complicated polymerization mechanism that involves both hydrogen abstraction and β -scission by the propagating radical, the latter of which is also observed for fluoro/perfluorocarbon TFVEs. When we compared the molar mass data obtained by GPC with those obtained by ¹H NMR end group analysis, there appeared to be multiple hydride end groups per polymer chain, indicating that the resulting radical on the oligoether pendant group was capable of re-initiating polymerization across the fluorocarbon double bond. This led us to believe that copolymers of vinyl monomers and our TFVEs may be prepared by the same redox-initiated emulsion polymerization.

We chose to study the copolymerization of two of our TFVE monomers with ethyl vinyl ether (EVE) and vinyl acetate (VAc): 1-[2-(2-ethoxyethoxy)ethoxy]-1,2,2-trifluoroethene (Et-TFVE) and 1-(2-phenoxyethoxy)-1,2,2-trifluoroethene (Ph-TFVE), as shown in Figure 1.

Et-TFVE and Ph-TFVE were used because they demonstrate different mechanisms of homopolymerization; while both undergo β -scission, only Et-TFVE undergoes radical hydrogen ab-

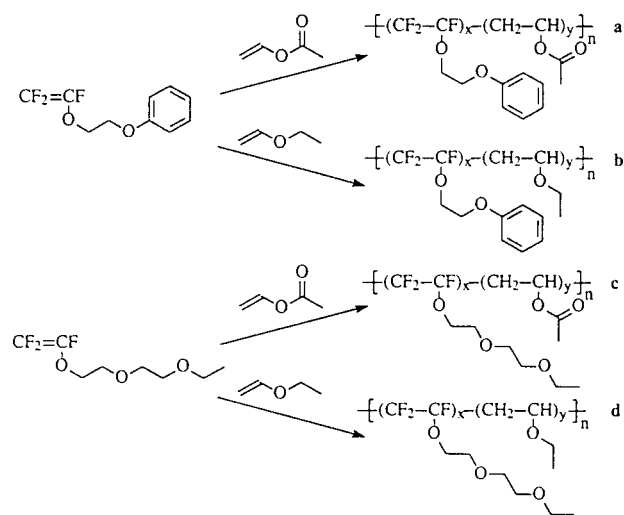


Figure 1. Copolymerization of Ph-TFVE or Et-TFVE with VAc or EVE to prepare: (a) poly(Ph-TFVE-co-VAc), (b) poly(Ph-TFVE-co-EVE), (c) poly(Et-TFVE-co-VAc), and (d) poly(Et-TFVE-co-EVE).

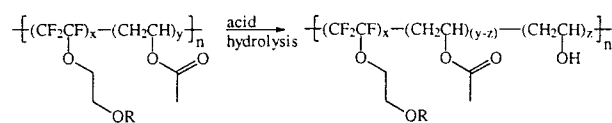


Figure 2. Partial hydrolysis of poly(TFVE-co-VAc) yields terpolymers, poly(TFVE-co-VAc-co-VA), where R is aryl or ethoxyethyl.

straction. Ethyl vinyl ether was studied because it does not homopolymerize readily under free radical conditions;⁷ thus any copolymer formed would likely have an alternating structure. Vinyl acetate was studied because it is a precursor to vinyl alcohol (VA), which incorporates a reactive functional group into the repeat unit.

Given the alternating structure observed for copolymers of electron-rich and electron-poor monomers,⁸ we suspected that our TFVEs would copolymerize azeotropically with EVE or VAc. In order to determine relative reactivity ratios, we prepared a series of Ph-TFVE copolymers under bulk conditions, thereby avoiding any differences related to monomer partitioning in the aqueous emulsion.⁹ Copolymer composition of bulk polymerized Ph-TFVE with EVE or VAc was determined at low monomer conversion using ¹H and ¹⁹F NMR for a series of feed compositions. Reactivity ratios were then determined using the error-in-variables model (EVM).¹⁰

Copolymers of poly(TFVE-co-VAc) served as precursors to two new terpolymers as a result of partial hydrolysis of the acetate: poly(Ph-TFVE-co-VAc-co-VA) and poly(Et-TFVE-co-VAc-co-VA), as shown in Figure 2. FTIR was used to quantitatively estimate the extent of hydrolysis while GPC was used to determine relative molar mass before and after hydrolysis, thereby providing some insight into the mechanism of polymerization.

EXPERIMENTAL

Et-TFVE and Ph-TFVE were synthesized as previously described⁴ and according to published methods¹¹ and purified by vacuum fractional distillation to greater than 97% purity as determined by GC, ¹H and ¹⁹F NMR. EVE and VAc were purchased from Aldrich (Ontario, Canada) and purified by short path distillation prior to use. Methanol, ammonium hydroxide, chloroform, and acetone were purchased from Fisher Scientific (Ontario, Canada). All other reagents were pur-

chased from Aldrich and used as received. All water was deionized and distilled from Millipore Milli-RO 10 Plus and Milli-Q UF Plus (Bedford, MA) systems and used at 18 M Ω resistance.

Characterization

Copolymers were characterized for molar mass by GPC (Waters 2690, Bedford, MA) equipped with a refractive index detector (Waters 410) and a series of Styragel[®] columns (Waters 10⁶, 10⁴ and 500 Å). Using a THF mobile phase, polymer molar mass was calculated relative to polystyrene standards (Aldrich). ¹H and ¹⁹F NMR spectra were obtained in CDCl₃ on a Varian Gemini spectrometer at 300.75 and 282.33 MHz, respectively, using TMS and CFCl₃ as external references. FTIR spectra (16 scans, 4 cm⁻¹ resolution) were obtained from thin polymer films or solutions using a Galaxy Series 5000 spectrometer. Thin films were prepared from ~2 % w/v polymer solutions (in CHCl₃ or THF) that were cast onto NaCl disks. Solution FTIR spectra were obtained from CHCl₃ or THF polymer solutions using a solution cell with a 0.10 mm path length and NaCl windows.

Emulsion Copolymerization of TFVEs with EVE or VAc

To a 100 mL round-bottom flask equipped with a magnetic stir bar and nitrogen purge, 29 mL of deionized water and 1 mL of a 3.1 × 10⁻⁵ M aqueous Fe(II) (as FeSO₄ · 7H₂O) solution were added for a total volume of 30 mL. The flask was placed in a temperature controlled reaction beaker and dissolved oxygen was removed using a nitrogen purge (1 h). Sodium hydrogen phosphate (0.15 g), sodium dodecylsulfate (0.3 g), and sodium hydrogensulfite (50 to 200 mg, 1 weight equivalent relative to the initiator) were added to the flask. With magnetic stirring, the temperature of the flask was adjusted to the desired polymerization temperature (typically 20 °C) using a Haake K15 water bath with a DC3 temperature controller. Ammonium persulfate (or potassium persulfate) (50 to 200 mg) was added to the flask prior to the addition of 4.0 g of a monomer mixture: (1) Et-TFVE + EVE; (2) Et-TFVE + VAc; (3) Ph-TFVE + EVE; (4) Ph-TFVE + VAc. The monomers were polymerized for 1 to 2 days after which they were isolated and purified.

Isolation and Purification of Et-TFVE Copolymers: Poly(Et-TFVE-co-EVE); Poly(Et-TFVE-co-VAc)

After adding 0.5 mL of conc. HCl to the copolymer latex, it was centrifuged to collect the precipitate.

The copolymer was dissolved in ethanol and then precipitated into water (twice) before drying under vacuum (P ~ 0.1 mmHg, 40 °C) to constant weight.

Isolation and Purification of Ph-TFVE Copolymers: Poly(Ph-TFVE-co-EVE); Poly(Ph-TFVE-co-VAc)

The polymer latex was added to ~300 mL of acidified (with ~0.5 mL conc. HCl) methanol to precipitate the polymer. The polymer was then vacuum filtered on a coarse frit funnel and washed twice with ~50 mL methanol, twice with ~50 mL deionized water, and finally with ~50 mL of methanol before drying under vacuum (P ~ 0.1 mmHg, 40 °C) to constant weight.

Bulk Copolymerization of Ph-TFVE with EVE or VAc

To a 2 mL glass vial was added 2,2'-azobisisobutyronitrile (AIBN, 0.019 g). The vial was sealed with a septum screw cap and purged with nitrogen for 5 min. Into the vial were injected 1.75 g of a mixture of Ph-TFVE and EVE or Ph-TFVE and VAc. The vial was placed in a 55–57 °C oven until a change in solution viscosity was visually observed (0.5–6 h). At that point, the contents of the vial were poured into ~40 mL of methanol to precipitate the polymer. The polymer was washed several times with methanol before drying under vacuum (P ~ 0.1 mmHg, 40 °C) to constant weight.

Acid Hydrolysis of Poly(Ph-TFVE-co-VAc)

To a 50 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser were added 0.50 g of polymer, 10 mL of CHCl₃, 10 mL of methanol, up to 0.5 mL of water, and 0.25 mL of concentrated sulfuric acid. The mixture was stirred and refluxed for either 1 or 4 d. At that point, a colorless translucent mixture had formed. The volume of the mixture was reduced to approximately half by solvent evaporation. The mixture was then diluted to 25 mL with CHCl₃. Sodium bicarbonate was added to the polymer solution with stirring until neutral to pH paper. The solution was decanted and the solvent removed by rotary evaporation. The crude polymer was dissolved in 10 mL of acetone and precipitated in 100 mL of water. The polymer was further purified by centrifuging, decanting the supernatant solution, washing with water, and centrifuging again to

collect the polymer. The polymer was dried to constant mass under vacuum ($P \sim 0.1$ mmHg, 40°C).

Acid Hydrolysis of Poly(Et-TFVE-co-VAc)

To a 50 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser were added 0.50 g of polymer, 15 mL of methanol, up to 0.5 mL of water, and 0.25 mL of concentrated sulfuric acid. The mixture was refluxed for 1 d. At that point, a colorless transparent solution had formed. The mixture volume was halved by solvent evaporation. The polymer solution was then diluted to approximately 25 mL with methanol. Sodium bicarbonate was added to the polymer solution and stirred until neutral to pH paper. The solution was decanted and the solvent removed by rotary evaporation. The crude polymer was dissolved in 10 mL of acetone and filtered on a fine frit funnel or centrifuged to remove residual salts. The acetone was removed by rotary evaporation and the polymer was dried to constant mass under vacuum ($P \sim 0.1$ mmHg, 40°C).

Base Hydrolysis of Poly(Et-TFVE-co-VAc)

Two methods were attempted: (1) To a 50 mL round-bottom flask equipped with a magnetic stir bar were added 0.50 g of polymer, 15 mL of methanol, and 1 mL of concentrated ammonium hydroxide. The mixture was stirred at room temperature for up to 4 d after which the solvent was removed by rotary evaporation. The polymer was dried to constant mass under vacuum ($P \sim 0.1$ mmHg, 40°C). (2) To a 50 mL round-bottom flask equipped with a magnetic stir bar were added 0.50 g of polymer, 15 mL of methanol, and 1 mL of 10% aqueous sodium hydroxide in methanol. The mixture was stirred at room temperature for up to 1 d after which a discoloration was observed. The solvent was removed by rotary evaporation and the polymer purified by repeated precipitation/centrifugation in water. The polymer was dried to constant mass under vacuum ($P \sim 0.1$ mmHg, 40°C).

RESULTS

Aqueous Emulsion Copolymerization

A series of copolymers of Ph-TFVE or Et-TFVE with either EVE or VAc were prepared by aqueous

emulsion polymerization, as was shown in Figure 1. Poly(Et-TFVE-co-EVE) was a transparent, colorless, highly viscous material at room temperature while poly(Et-TFVE-co-VAc) was a transparent, colorless material with a rubbery texture at room temperature. The latter would cold flow if left undisturbed over a period of days. Both Ph-TFVE-containing copolymers, poly(Ph-TFVE-co-EVE) and poly(Ph-TFVE-co-VAc), were white solid materials at room temperature, which formed transparent colorless films when cast from solution. As summarized in Table I for representative samples, the polymers generally had high molar mass, were prepared in yields as high as 80%, yet were polydisperse. Copolymers of Et-TFVE and Ph-TFVE with EVE (entries 1–4) were enriched with the TFVE relative to the monomer feed composition whereas copolymers of Et-TFVE and Ph-TFVE with VAc (entries 5–9) were generally slightly enriched with VAc. Polymerization of Ph-TFVE with VAc (entries 5 and 6) generally resulted in lower yields than that of Et-TFVE with VAc (entries 7–9).

Measurement of Copolymer Composition of Emulsion Polymers

Copolymer composition was determined using ^1H and ^{19}F NMR (cf. Table I). We accounted for any residual monomer using the ^{19}F NMR data and then calculated the mole fraction of monomers using the ^1H NMR data. Typical ^1H NMR spectra of the copolymers are shown in Figure 3.

Copolymer composition was calculated from ^1H NMR spectra by equating the integrated ratios with the associated number of protons expected based on copolymer structure. For example, copolymer composition for poly(Et-TFVE-co-EVE) was calculated according to eq 1 where x and y are the total number of protons associated with Et-TFVE and EVE in the copolymer, respectively; and $A_{\text{CH}_2/\text{CH}}$ and A_{CH_3} are the integrated ratios under the methylene/methyne and methyl ^1H NMR peaks, respectively. A similar equation was used to calculate the composition of poly(Et-TFVE-co-VAc), with modifications made to eq 1 to account for the different chemical structure. For all polymers, we assumed that $x + y = 1$.

$$\frac{A_{\text{CH}_2/\text{CH}}}{10x + 5y} = \frac{A_{\text{CH}_3}}{3x + 3y} \quad (1)$$

The compositions of poly(Ph-TFVE-co-VAc) and poly(Ph-TFVE-co-EVE) were determined

Table I. Representative Data for the Aqueous Emulsion Copolymerization of TFVEs with Either EVE or VAc

Polymer #	Copolymer	TFVE in Monomer Feed (mol %)	M_w/M_n (kg/mol)	PDI	Yield ^a (%)	TFVE in Copolymer (mol %)
1 ^b	Poly(Ph-TFVE-co-EVE)	40	283/85.3	3.32	76	46
2 ^c	"	50	198/65.5	3.02	75	53
3 ^c	Poly(Et-TFVE-co-EVE)	44	180/36.8	4.89	80	51
4 ^c	"	50	92.7/25.4	3.65	62	62
5 ^d	Poly(Ph-TFVE-co-VAc)	44	378/141	2.69	50	46
6 ^d	"	50	179/72.4	2.47	27	43
7 ^e	Poly(Et-TFVE-co-VAc)	44	168/43.5	3.86	70	42
8 ^e	"	50	226/39.5	5.73	79	44
9 ^f	"	60	137/24.4	5.61	45	48

^a Yields were determined as a weight fraction based on a total monomer weight of 4 g.

^b 50 mg $K_2S_2O_8$, polymerized at 30 °C for 2 d.

^c 50 mg $(NH_4)_2S_2O_8$, polymerized at 20 °C for 2 d.

^d 200 mg $(NH_4)_2S_2O_8$, polymerized at 20 °C for 1 d.

^e 50 mg $(NH_4)_2S_2O_8$, polymerized at 20 °C for 1 d.

^f 200 mg $(NH_4)_2S_2O_8$, polymerized at 20 °C for 2 d.

similarly using the integrated ratios under the ¹H NMR peaks associated with the phenyl protons of Ph-TFVE ($A_{C_6H_5}$) and the methyl/methylene/methyne protons ($A_{CH_3/CH_2/CH}$). For example, eq 2 was used to determine the composition for poly(Ph-TFVE-co-EVE), where x and y are the total number of protons associated with Ph-TFVE and EVE, respectively.

$$\frac{A_{CH_3/CH_2/CH}}{4x + 8y} = \frac{A_{C_6H_5}}{5x} \quad (2)$$

We tried to use ¹H NMR to determine whether hydrogen abstraction had occurred during propagation of either TFVE with VAc or EVE; however, the abstracted hydrogen could not be identified by ¹H NMR for any polymer sample. This may be rationalized by the high molar mass of the polymers relative to the number of hydrides formed, and, in some cases, to overlapping NMR signals.

Measurement of Reactivity Ratios of Bulk Polymers

Ph-TFVE was copolymerized with EVE or VAc in bulk, with AIBN initiation, to determine relative reactivity ratios (r_1 , r_2). The reactivity ratios of only Ph-TFVE-containing copolymers were studied because their synthesis, yield and purification were more easily controlled than copolymers with Et-TFVE. For example, Ph-TFVE homopolymerizes without radical hydrogen abstraction.⁵

The reactivity ratios of Ph-TFVE-containing copolymers were calculated using the Mayo-Lewis model, as described in eq 3:¹²

$$F_1 = \frac{r_1 f_1^2 + f_1(1 - f_1)}{r_1 f_1^2 + 2f_1(1 - f_1) + r_2(1 - f_1)^2} \quad (3)$$

The terms, F_1 and f_1 , represent the mole fraction of monomer 1 in the copolymer and in the feed, respectively. The error-in-variables model (EVM)¹⁰ was used to determine reactivity ratios because it is statistically valid and takes the error in the independent variable into account, that is, the monomer feed composition. In using EVM, we assumed that: (1) the polymerization was chemically controlled, (2) there were no diffusional limitations, and (3) compositional drift was negligible. We were able to satisfy the latter two assumptions by synthesizing the polymers in bulk and to low conversions ($\leq 10\%$) and yields. The polymerization results for poly(Ph-TFVE-co-EVE) and poly(Ph-TFVE-co-VAc) are summarized in Table II.

In order to use the EVM¹⁰ method to estimate reactivity ratios, error estimates were required for both the monomer feed composition and the copolymer composition. An error estimate of 0.7% was used for monomer feed compositions, reflecting the precision of gravimetric analysis and estimated monomer purity. An error estimate of 6% was used for copolymer compositions, reflecting

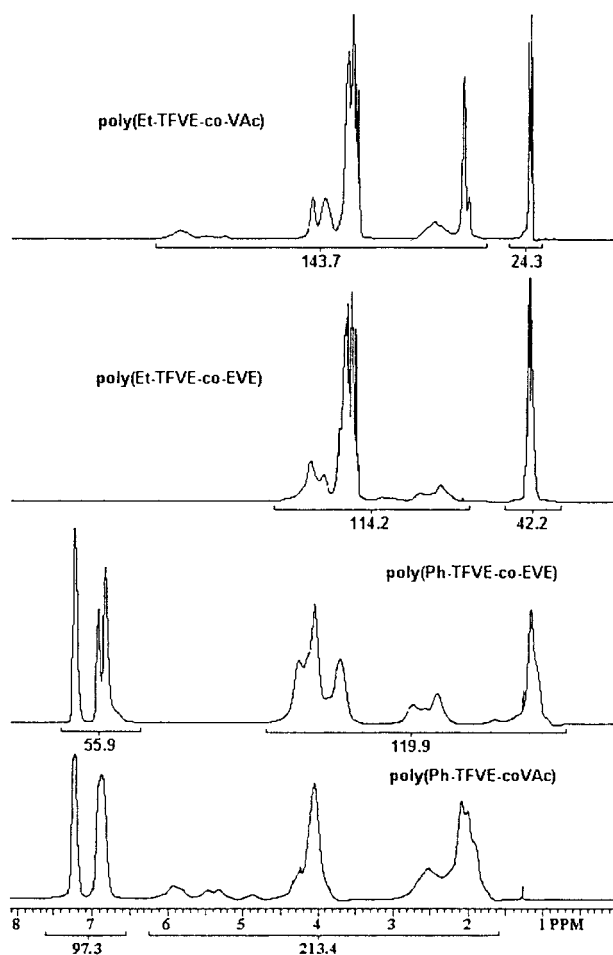


Figure 3. Representative ^1H NMR spectra of each copolymer: (a) poly(Ph-TFVE-co-VAc), (b) poly(Et-TFVE-co-EVE), (c) poly(Ph-TFVE-co-EVE), and (d) poly(Et-TFVE-co-VAc).

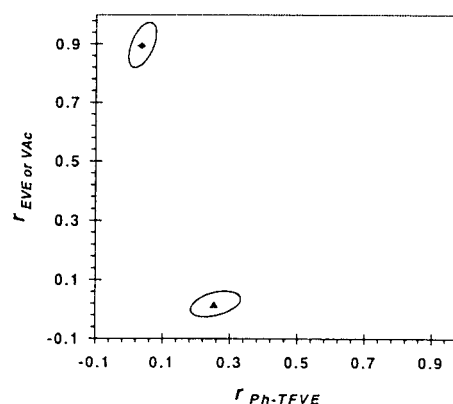


Figure 4. Estimated reactivity ratios and 95% confidence intervals for bulk copolymerized Ph-TFVE with EVE or VAc. For Ph-TFVE copolymerized with EVE (▲): $r_{\text{Ph-TFVE}} = 0.25 \pm 0.07$, $r_{\text{EVE}} = 0.016 \pm 0.04$. For Ph-TFVE copolymerized with VAc (◆): $r_{\text{Ph-TFVE}} = 0.034 \pm 0.04$, $r_{\text{VAc}} = 0.89 \pm 0.08$.

the standard deviation calculated for three separate measurements of the composition of poly(Ph-TFVE-co-EVE) (cf. last three entries in Table II for $f_{\text{Ph-TFVE}} = 0.691$). Figure 4 is a graphical representation of the estimated reactivity ratios for both copolymer series and their respective 95% confidence ellipses. Under bulk copolymerization conditions, $r_{\text{Ph-TFVE}}$ is 0.25 ± 0.07 and r_{EVE} is 0.016 ± 0.04 , indicating that the radical on EVE cross-propagated with Ph-TFVE whereas that on Ph-TFVE showed a tendency to homopropagate. Given that both the confidence interval for r_{EVE} overlaps zero and EVE does not readily homopolymerize under free radical conditions, r_{EVE} is near zero. Under similar bulk copolymerization conditions, $r_{\text{Ph-TFVE}}$ is 0.034 ± 0.04 and r_{VAc} is

Table II. Bulk Copolymerization of Ph-TFVE with Either EVE or VAc

Ph-TFVE + EVE					Ph-TFVE + VAc				
$f_{\text{Ph-TFVE}}$	Yield ^a (%)	$F_{\text{Ph-TFVE}}$	M_w/M_n (kg/mol)	PDI	$f_{\text{Ph-TFVE}}$	Yield ^a (%)	$F_{\text{Ph-TFVE}}$	M_w/M_n (kg/mol)	PDI
0.205	6.7	0.503	52.5/30.1	1.74	0.244	5.0	0.209	151/91.2	1.66
0.338	9.3	0.517	46.6/26.4	1.77	0.294	5.2	0.241	119/68.9	1.73
0.495	11.8	0.549	42.4/26.7	1.59	0.364	5.0	0.283	89.4/49.7	1.80
0.583	10.6	0.585	42.9/26.4	1.63	0.490	6.7	0.369	71.3/41.3	1.73
0.649	8.3	0.570	41.4/25.0	1.66	0.726	12.2	0.461	33.1/18.8	1.76
0.691	2	0.575	19.8/11.9	1.66	"	"	0.429	"	"
"	"	0.644	"	"					
"	"	0.622	"	"					

^a Yields are corrected to account for residual TFVE monomer in the copolymer sample.

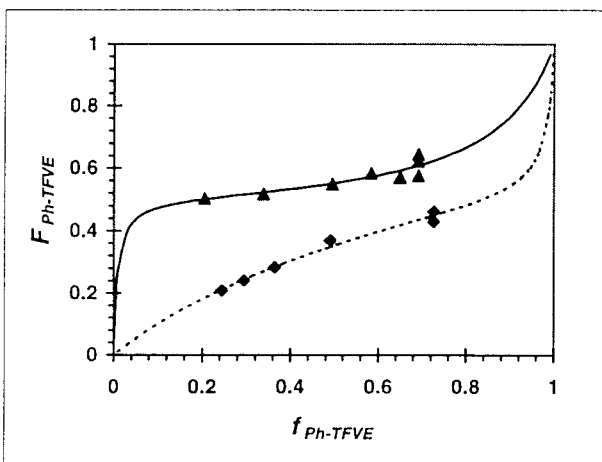


Figure 5. For each copolymerization series, $F_{\text{Ph-TFVE}}$ versus $f_{\text{Ph-TFVE}}$ was plotted using the reactivity ratio data: the experimental data were compared to the predicted curves for Ph-TFVE and EVE (—▲—) and Ph-TFVE and VAc (—◆—).

0.89 ± 0.08 , indicating that the radical on Ph-TFVE cross-propagated with VAc, whereas that on VAc propagated randomly. Given that the confidence interval of $r_{\text{Ph-TFVE}}$ overlaps zero yet Ph-TFVE can homopolymerize, $r_{\text{Ph-TFVE}}$ is likely nonzero.

The experimental $F_{\text{Ph-TFVE}}$ versus $f_{\text{Ph-TFVE}}$ data (cf. Table II) and the predicted curve based on estimated reactivity ratios and eq 3 for each copolymerization series are plotted in Figure 5. Copolymers of Ph-TFVE and EVE are enriched with Ph-TFVE for lower $f_{\text{Ph-TFVE}}$ yet reach a plateau at higher contents. Copolymers of Ph-TFVE and VAc are enriched with VAc, with a practical limitation of less than 50% Ph-TFVE incorporated.

Hydrolysis of Poly(TFVE-co-VAc)

Vinyl acetate copolymers were partially hydrolyzed to vinyl alcohol (VA) to both demonstrate the availability of the hydroxyl functional group for further modification and as a means to determine whether hydrogen was abstracted from the vinyl acetate pendant group during polymerization. In the event that hydrogen was abstracted from VAc during polymerization, the resulting copolymer would have an ester group within the backbone, which, in turn, would result in a substantial decrease in polymer molar mass upon hydrolysis. Given the susceptibility of ether

groups to acid, base hydrolysis was the preferred method.

We reacted poly(Et-TFVE-co-VAc) with concentrated ammonium hydroxide in methanol, yet VAc was not hydrolyzed to VA, as determined by FTIR. We also reacted poly(Et-TFVE-co-VAc) with 10% aqueous sodium hydroxide in methanol. Despite limited hydrolysis, the polymer solution discolored from clear to orange-red, likely as a result of elimination reactions, as evidenced by an FTIR carbon-carbon double bond peak at $\sim 1675 \text{ cm}^{-1}$.

Reaction of poly(Et-TFVE-co-VAc) with sulfuric acid in methanol successfully hydrolyzed VAc to VA, as demonstrated by FTIR. The fraction of hydrolyzed VAc was calculated from the FTIR data by comparing the absorbance of the carbonyl peak before and after hydrolysis. Assuming similar extinction coefficients for the parent and hydrolyzed polymer and correlating absorbance with weight fraction of residual VAc, the extent of hydrolysis was calculated. As shown in Figure 6 for poly(Et-TFVE-co-VAc) (entry 7, Table I), the VAc carbonyl peak at 1760 cm^{-1} decreased while the VA hydroxyl peak at $\sim 3400 \text{ cm}^{-1}$ increased and broadened with increased hydrolysis.

Poly(Ph-TFVE-co-VAc), (entry 6, Table I) was hydrolyzed in methanol/ CHCl_3 to poly(Ph-TFVE-co-VAc-co-VA). Approximately 5% of the VAc were hydrolyzed after 1 day and 30% after 4 days, as calculated from FTIR as described above. Interestingly, as shown in Figure 7, the hydroxyl peak maximum shifted to $\sim 3500 \text{ cm}^{-1}$ from the $\sim 3400 \text{ cm}^{-1}$ observed for poly(Et-TFVE-co-VAc-co-VA) that was shown in Figure 6. The peak maximum and breadth reflect a difference in hydrogen bonding interactions. Intra- and intermolecular hydrogen bonding was likely superior in poly(Et-TFVE-co-VAc-co-VA) where there are more hydroxyl groups, longer oligoether groups, and less steric hindrance of the pendant group relative to poly(Ph-TFVE-co-VAc-co-VA).

While the FTIR data demonstrated the availability of hydroxyl functional groups for further modification, the GPC data was used to determine whether hydrogen abstraction occurred during the synthesis of VAc-containing polymers. We anticipated that the simple conversion of vinyl acetate to vinyl alcohol would result in a modest decrease in molar mass. The GPC-determined molar mass changed unexpectedly after hydrolysis as summarized in Table III. For poly(Ph-TFVE-co-VAc), an apparent increase in both M_w and M_n were observed following hydrolysis with a

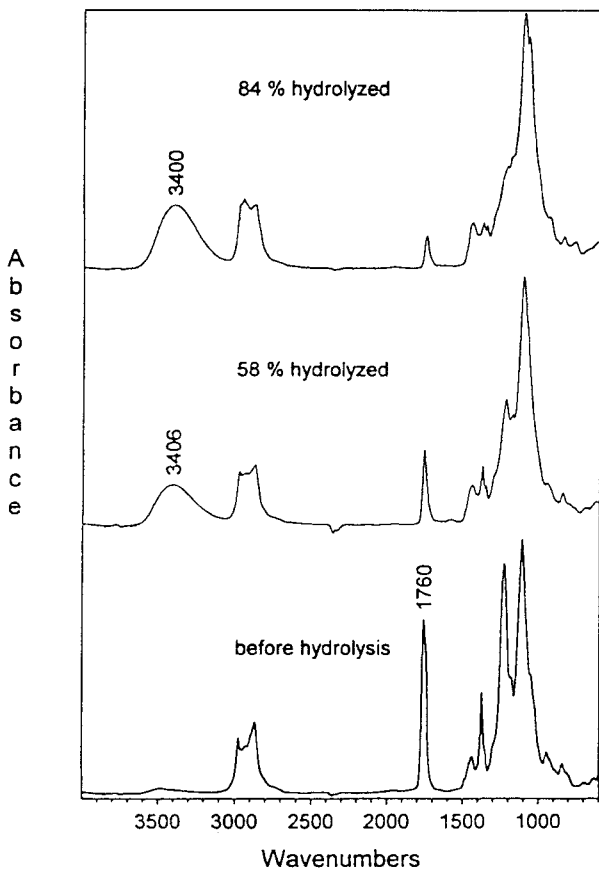


Figure 6. FTIR spectra of poly(Et-TFVE-co-VAc), **7**, before and after hydrolysis.

greater increase observed for greater amounts of VAc hydrolyzed. For poly(Et-TFVE-co-VAc), the change in molar mass was a function of both extent of hydrolysis and the fraction of Et-TFVE in the monomer feed. As shown for entry **7** (Table III, 42 mol % TFVE), at 58% hydrolysis, both M_w and M_n increased whereas at 84% hydrolysis M_w and M_n decreased. As shown for entry **9** (Table III, 48 mol % TFVE), at 45% hydrolysis, both M_w and M_n appeared to decrease. Thus as Et-TFVE content increased (entry **9** vs. **7**), molar mass decreased upon hydrolysis.

The GPC molar mass distributions provide a more complete picture of the changes in molar mass that were summarized in Table III. The distributions are shown in Figures 8 and 9 for poly(Ph-TFVE-co-VAc) (entry **6**, Table III) and poly(Et-TFVE-co-VAc) (entries **7** and **9**, Table III), respectively, before and after hydrolysis. For poly(Ph-TFVE-co-VAc) (Fig. 8), molar mass appeared to increase with extent of hydrolysis while the distribution shape was mostly unchanged.

This change in apparent molar mass reflects the increase in polymer hydrodynamic volume (V_H) with conversion of VAc to VA.

For poly(Et-TFVE-co-VAc) [Fig. 9(a)], molar mass apparently increased at 58% hydrolysis, likely reflecting increased V_H ; however, molar mass apparently decreased substantially at 84% hydrolysis, likely reflecting the relative impact of VAc hydrolysis and backbone cleavage over any V_H increase, as described in more detail below. In Figure 9(b), molar mass decreased after hydrolysis of only 45% of the VAc groups, which likely reflected backbone cleavage and its greater Et-TFVE content, as further discussed below. With 36% more Et-TFVE in the feed, the propensity for hydrogen abstraction during polymerization increased and thus the susceptibility of the polymer to acidic conditions also increased.

DISCUSSION

Copolymers of Et-TFVE and Ph-TFVE with EVE or VAc (cf. Table I) were prepared by free radical

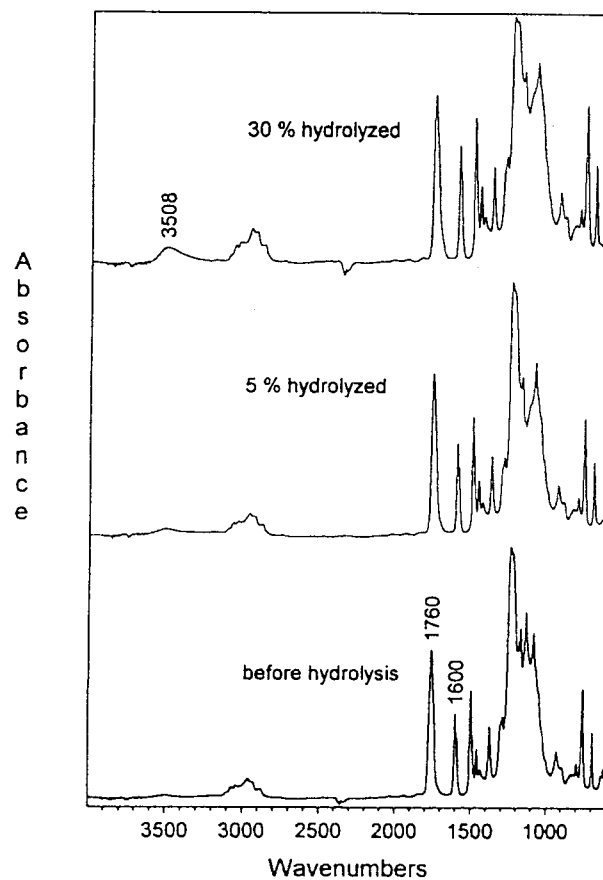


Figure 7. FTIR spectra of poly(Ph-TFVE-co-VAc), **6**, before and after hydrolysis.

Table III. Hydrolysis of Poly(TFVE-co-VAc)

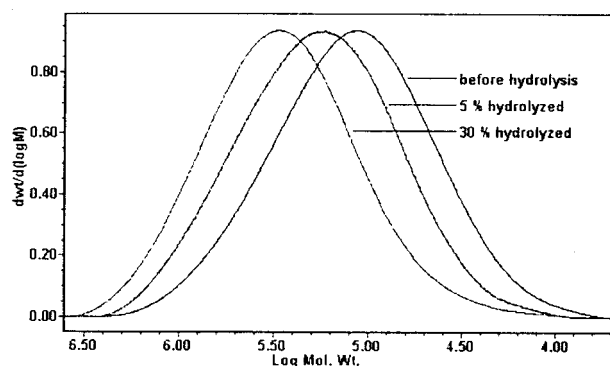
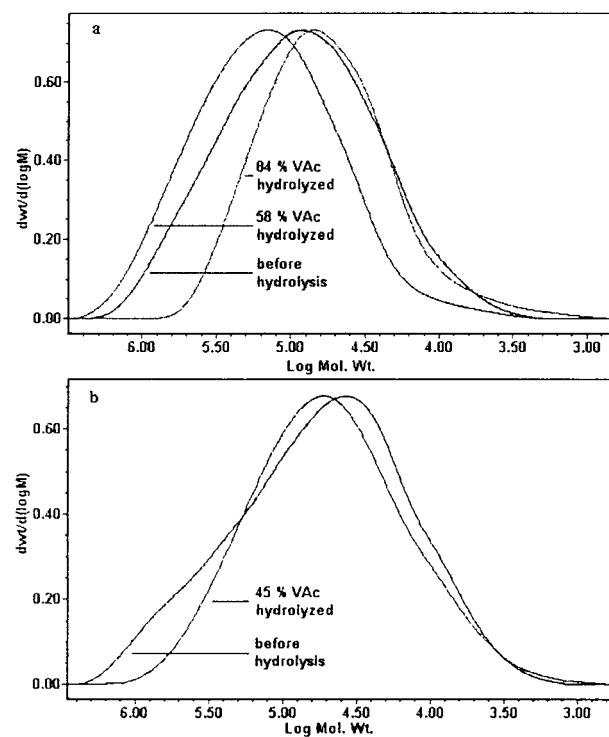
Polymer #	Polymer Type	VAc Hydrolyzed (mol %)	Before Hydrolysis		After Hydrolysis	
			M_w/M_n (kg/mol)	PDI	M_w/M_n (kg/mol)	PDI
6	Poly(Ph-TFVE-co-VAc)	~ 5	192/75.4	2.55	285/118	2.42
6 ^a	"	30	"	"	420/176	2.39
7	Poly(Et-TFVE-co-VAc)	58	168/43.5	3.86	255/74.7	3.41
7 ^b	"	84	"	"	90.1/30.2	2.98
9	"	45	137/24.4	5.61	92.0/22.2	4.14

^a Refluxed for 4 d.^b No water added to the hydrolysis reaction.

aqueous emulsion polymerization with compositions between 42 and 62% TFVE. Under bulk polymerization conditions, the reactivity ratios were calculated for Ph-TFVE with either EVE or VAc. Poly(Ph-TFVE-co-EVE) likely had EVE repeat units alternating with those of Ph-TFVE, but not vice versa (i.e., there may be some Ph-TFVE blocks). Poly(Ph-TFVE-co-VAc) likely had Ph-TFVE repeat units alternating with those of VAc, but not vice versa (i.e., there were very likely VAc blocks). Given that the structures of the propagating radicals of Ph-TFVE and Et-TFVE were similar, we assumed that the reactivity of Et-TFVE with either EVE or VAc was similar to that calculated for Ph-TFVE under similar reaction conditions, excluding the effects of radical hydrogen abstraction observed for Et-TFVE.

Intramolecular radical hydrogen abstraction was previously identified during the homopolymerization of Et-TFVE, but not of Ph-TFVE,⁵ due to the differences in pendant group structure adjacent to the propagating radical. Those mono-

mers with methylene or methyl groups six or more atoms away from the propagating end seemed most susceptible to hydrogen abstraction. We suspected that intramolecular abstraction from VAc or EVE may have also occurred during copolymerization, with continued propagation of the resulting radical. Previous synthesis of poly(tetrafluoroethylene-co-vinyl acetate) by free radical aqueous emulsion polymerization indicated

**Figure 8.** Molar mass distributions of poly(Ph-TFVE-co-VAc), **6**, before and after hydrolysis.**Figure 9.** Molar mass distributions of poly(Et-TFVE-co-VAc) before and after hydrolysis: (a) 44% Et-TFVE in the monomer feed (entry **7**, Table III), (b) 60% Et-TFVE in the monomer feed (entry **9**, Table III).

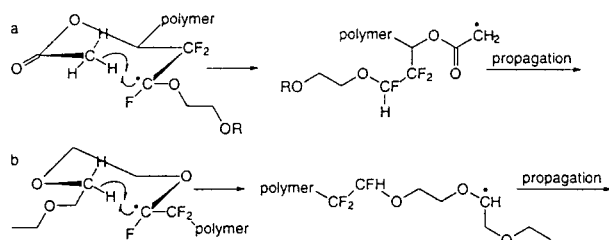


Figure 10. Examples of intramolecular radical hydrogen abstraction during TFVE copolymerization with continued propagation of the resulting radical: (a) abstraction from VAc results in esters in the backbone, where R is ethoxyethyl or aryl; (b) abstraction from Et-TFVE pendant group results in ethers in the backbone.

radical hydrogen abstraction, with continued propagation of the radical, during polymerization.¹³ The polymer likely had ester groups in the backbone, thereby accounting for the 10-fold decrease in molar mass observed by GPC following hydrolysis. As shown in Figure 10(a), abstraction of a VAc methyl hydrogen during copolymerization with either Ph-TFVE or Et-TFVE would also result in ester groups in the backbone. In addition, copolymers with Et-TFVE will result in ether groups in the backbone, as shown in Figure 10(b).

Since ¹HNMR was not useful in identifying the hydride formed as a result of abstraction, the simplest way to test whether hydrogen was abstracted during the copolymerization of TFVE and VAc was to study the effect of hydrolysis on molar mass of poly(Ph-TFVE-co-VAc). If hydrogen was abstracted, it would be from the VAc alone (and not Ph-TFVE), which would result in ester groups in the backbone that upon hydrolysis would cause a significant decrease in the weight average molar mass.

Unexpectedly, hydrolysis of poly(Ph-TFVE-co-VAc) to poly(Ph-TFVE-co-VAc-co-VA) (entry 6, Table III) resulted in a large distribution shift to higher molar mass (cf. Figure 9 and Table III): for only ~5 % VAc hydrolysis, M_w increased by 48% while for 30% VAc hydrolysis, M_w increased by 119%. The shapes of both distributions after hydrolysis appeared to be unchanged relative to the parent copolymer. Since by FTIR, VAc had been hydrolyzed to VA (cf. Fig. 7), the apparent increase in GPC-determined molar mass reflected an increase in V_H . Since molar mass appeared to increase after hydrolysis, it was likely that few or no esters were incorporated in the backbone due to hydrogen abstraction during polymerization of VAc with Ph-TFVE and, by analogy, with Et-TFVE.

Hydrolysis of poly(Et-TFVE-co-VAc) to poly(Et-TFVE-co-VAc-co-VA) (entry 7, Table III) resulted in a 52% increase in M_w after 58% VAc hydrolysis yet in a 46% decrease in M_w after 84% VAc hydrolysis. Given the FTIR evidence for VAc hydrolysis to VA (cf. Figure 6), the apparent increase in molar mass of the former may be rationalized in terms of increased V_H . Given that no evidence of VAc hydrogen abstraction was found for the copolymerization of Ph-TFVE and VAc, the significant decrease in M_w at 84% VAc hydrolysis must be rationalized differently. Since ethers are susceptible to strong acids and polymerization of Et-TFVE results in ether segments in the polymer backbone, the decrease in M_w can be attributed to hydrolysis of ether backbone segments. While there may have been some backbone ether cleavage for the 58% VAc hydrolyzed sample, its effect on molar mass was masked by the net increase in V_H . While the decrease in molar mass may also be rationalized by the hydrolysis of pendant oligoether groups, the methylene C—H absorption (2860 cm^{-1}) and the ether C—O absorption (1115 cm^{-1}) were unchanged (cf. Figure 6). Furthermore, the ratio of the VAc C=O absorption to the aryl C=C absorption (of Ph-TFVE) decreased in accordance with the extent of VAc hydrolysis. Thus, while there may have been some oligoether group cleavage, it likely did not account for the distribution shift observed.

Hydrolysis of poly(Et-TFVE-co-VAc) to poly(Et-TFVE-co-VAc-co-VA) (entry 9, Table III), resulted in a 30% decrease in M_w after only 45% hydrolysis of VAc. As was shown in Figure 9(b), the distribution of the hydrolyzed sample was narrower with a 47% higher peak molar mass. This suggested a significant amount of ether cleavage in the polymer backbone. If we assume from the Ph-TFVE reactivity ratio data, that Et-TFVE also alternates with VAc and given that this sample had the highest Et-TFVE content of those studied, then the lifetime of a radical on Et-TFVE was relatively long, resulting in a high probability of abstraction. Thus it is likely that many more ether groups were incorporated into the backbone and some of these were cleaved under milder acid conditions. The distribution shift was somewhat offset by an increase in the hydrodynamic volume resulting in a decreased polydispersity.

Interestingly, the distribution shifts observed for poly(Ph-TFVE-co-VAc-co-VA) were significantly larger than those observed for poly(Et-TFVE-co-VAc-co-VA) in view of the fraction of VAc hydrolyzed. Considering that radical hydrogen abstrac-

tion from the pendant group of Ph-TFVE did not occur,⁵ there were no ether bonds in the backbone of the polymer to be cleaved. Consequently, the increase in polymer hydrodynamic volume was not offset by the formation of smaller molecules.

Since no hydride peaks were evident by ¹H NMR for Ph-TFVE homopolymers or copolymers with EVE, it is unlikely that hydrogen was abstracted from EVE pendant groups during polymerization. Thus the only source of hydrogen abstraction in homo- and copolymers of EVE was the Et-TFVE pendant oligoether group.

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