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Insights into the Properties of Novel Trifluorovinyl Ether Copolymers[1]

Yumin Yuan† and Molly S. Shoichet*,†,‡

Departments of Chemical Engineering and Applied Chemistry and Chemistry, University of Toronto, 200 College Street, Toronto, Ontario M5S 3E5, Canada

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ABSTRACT: We have prepared new trifluorovinyl ether (TFVE) polymers and copolymers that have oligoether hydrocarbon pendant groups, providing facilitated processability and increased solubility in common organic solvents than commercially available fluoropolymers. In particular, we synthesized homo- and copolymers by a redox-initiated emulsion polymerization with 1-[2-(2-ethoxy-ethoxy)-ethoxy]-1,2,2-trifluoroethene (Et-TFVE) and 1-[2-(2-*tertiary*-butoxy-ethoxy)-ethoxy]-1,2,2-trifluoroethene (*t*-Bu-TFVE). The *tert*-butyl group is a protected alcohol, which, upon removal, provides a reactive handle for further modification after polymerization. The monomers, which appeared to have similar reactivity, controlled the copolymer composition. Polymers were prepared with M_w's as high as 40 000 and polydispersities from approximately 2 to 3. Poly(Et-TFVE) was more thermally stable than poly(*t*-Bu-TFVE) as determined by thermogravimetric analysis. The polymers had similar glass-transition temperatures (T_g's) of approximately −60 °C; however, T_g increased with hydroxyl (i.e., TFVE-OH) content to +9 °C, as a result of hydrogen-bonding interactions. The hydroxyl functional groups of a TFVE-OH copolymer were modified with 1,6-hexamethylene diisocyanate to form a cross-linked polymer film, thereby demonstrating the potential utility of these functionalized polymers in coatings applications.

Introduction

Fluoropolymers are chemically inert, thermally stable, and biologically acceptable. Consequently, they have been used in numerous applications, from chemical erosion-resistant devices to coatings to vascular grafts.[2,3] Fluorochemicals are hydrophobic and oleophobic and have extremely low surface energies, making them useful blooming agents in processing applications.[2] However, perfluorinated polymers have limited processability and poor interactions with other polymers, curtailing their broader applicability.

Fluorinated trifluorovinyl ether (TFVE) polymers were prepared to overcome the limited processability of commercial fluoropolymers.[4] To further enhance interactions with other polymers in processing or blends applications, we have prepared TFVEs with hydrocarbon oligoether pendant groups. Unlike the perfluorinated backbone, the pendant group is hydrophilic and can interact with other polymers via hydrogen bonding. Although sacrificing on chemical inertness, the greater solubility of these new TFVE polymers in common organic solvents broadens the number of potential applications.

We recently reported the synthesis[5] and polymerization mechanism[6] of two novel TFVEs, namely, 1-[2-(2-ethoxy-ethoxy)-ethoxy]-1,2,2-trifluoroethene (Et-TFVE) and 1-[2-(2-*tertiary*-butoxy-ethoxy)-ethoxy]-1,2,2-trifluoroethene (*t*-Bu-TFVE). As shown in Figure 1, the polymers predominantly have a fluorocarbon backbone and a hydrocarbon, oligoether pendant group, with a structure similar to that of poly(ethylene glycol) (PEG). Because oligoether-[7] and PEG-modified[8,9] surfaces have been shown to resist protein adsorption, we anticipate that these new fluoropolymers will be protein-resistant. In addition, poly(*t*-Bu-TFVE) is a protected alcohol, which, upon deprotection, provides a reactive handle for further modification or cross-linking. Unlike traditional perfluorinated polymers, such as poly(tetrafluoroethylene) or poly(tetrafluoroethylene-*co*-hexafluoropropylene) which require corrosive reagents for modification,[10,11] the hydroxyl functionality incorporated into the pendant group of our backbone polymer facilitates modification.

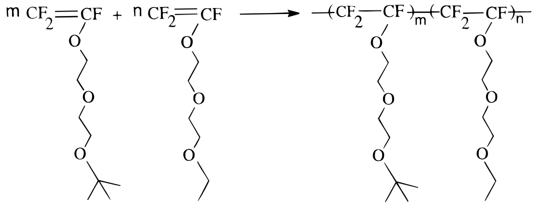

Figure 1. Synthesis of poly(Et-TFVE-*co*-*t*-Bu-TFVE) from 1-[2-(2-ethoxy-ethoxy)-ethoxy]-1,2,2-trifluoroethene (Et-TFVE) and 1-[2-(2-*tertiary*-butoxy-ethoxy)-ethoxy]-1,2,2-trifluoroethene (*t*-Bu-TFVE).

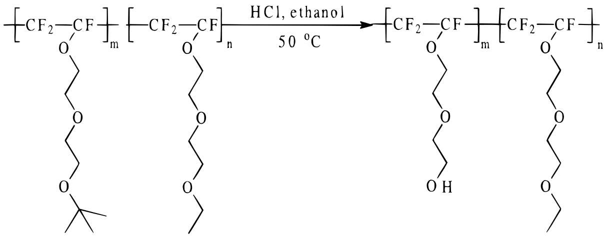

Figure 2. Hydrolysis of poly(Et-TFVE-*co*-*t*-Bu-TFVE) to poly(Et-TFVE-*co*-TFVE-OH).

We describe herein the synthesis and characterization of Et-TFVE and *t*-Bu-TFVE copolymers. We demonstrate that these new trifluorovinyl ether copolymers have interesting and unique properties, some of which can be predicted from the homopolymers. The copolymer composition, controlled by that of the monomers, affected thermal stability but not glass-transition temperature (T_g). As shown in Figure 2, the *t*-Bu-TFVE content in the copolymer dictates that of the hydroxyl groups and thus the consequent properties of the copolymer. The hydroxyl group content affects T_g and

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* To whom correspondence should be directed.

† Department of Chemical Engineering and Applied Chemistry.

‡ Department of Chemistry.

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provides a reactive handle, which when modified with a diisocyanate yields a cross-linked polymer film. The combination of a reactive handle in a processable fluoropolymeric material overcomes some of the current limitations of commercially available fluoropolymers.

Experimental Section

Reagents. The TFVE monomers, Et-TFVE and *t*-Bu-TFVE, were prepared as previously described[5] and according to published methods.[12] The monomers were purified by fractional distillation to greater than 99% purity, as determined by gas chromatography and ^{1}H and ^{19}F NMR. All 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. All materials and reagents were purchased from Aldrich (Ontario, Canada) and used as received unless otherwise specified.

Characterization. Polymers were characterized for molecular weight using a gel permeation chromatograph (GPC; Waters 2690; Bedford, MA), equipped with a refractive index detector (Waters 410) and a series of Styragel columns (Waters 10^5, 10^4, and 500 Å). By using a THF mobile phase, polymer molecular weight was calculated relative to polystyrene standards. ^{1}H and ^{19}F NMR spectra were obtained on a Varian Gemini 300 MHz spectrometer in $CDCl_3$ [or deuterated DMSO for poly(TFVE-OH)] using TMS and $CFCl_3$ as external references, respectively. FTIR spectra were obtained of thin films cast from chloroform on NaCl plates using a Galaxy Series 5000 spectrometer. Thin films were cast and cross-linked on disposable IR cards with PTFE windows. Glass-transition temperatures (T_g) were measured using a Perkin-Elmer 7 series differential scanning calorimeter (DSC), under an inert nitrogen atmosphere, with a heating rate of 10 °C/min and scanning range of either -120 to 0 °C for homo- and copolymers or -100 to $+20$ °C for hydrolyzed polymers. Thermal stability was measured by thermogravimetric analysis (TGA) using a Perkin-Elmer 7 series, under an inert nitrogen atmosphere, with a heating rate of 10 °C/min and a temperature range from 30 to 800 °C. Mass spectra were obtained on a Micromass 70-250S (double-focusing) mass spectrometer, arrayed with a HP5890 gas chromatograph (capillary column: J&W Scientific, DB-5ms, 30 m, 0.25 mm). High-resolution data were obtained at 10 000 (10% valley) resolution.

Emulsion Polymerization of Et-TFVE and *t*-Bu-TFVE. The monomers were homo- and copolymerized according to methodology previously described for the homopolymers using a redox-initiated aqueous emulsion polymerization.[6] Briefly, to a 100 mL round-bottom flask equipped with a magnetic stirrer and nitrogen purge was dissolved 2.6×10^{-4} g of Fe(II) (as $FeSO_4 \cdot 7H_2O$) in 30 mL of deionized water. Dissolved oxygen was removed using a nitrogen purge (45 min). Sodium hydrogen phosphate (0.15 g), sodium dodecyl sulfate (0.20 g), and sodium hydrogen sulfite (50 mg) were added to the flask. The temperature of the flask was adjusted to the desired polymerization temperature (20 °C) using a Haake K15 water bath with a DC3 temperature controller. Potassium persulfate (50 mg) was added to the flask prior to the addition of monomer (4.35−4.55 g). The monomer was polymerized for 2 days after which ~0.5 mL of concentrated HCl was added followed by centrifugation. The polymer was dissolved in ethanol and then precipitated in water (twice) before drying under vacuum ($P \approx 0.1$ mmHg at room temperature, RT). The yield was maintained between 15 and 30% to minimize copolymer compositional drift. *For Poly(Et-TFVE).* ^{1}H NMR: $\delta = 5.7$ (broad d, CF_2CFH), 4.15 (broad s, 2H, $CFOCH_2$), 3.8−3.4 (broad m, 8H, OCH_2), 1.2 (t, 3H, CH_3). *For Poly(t-Bu-TFVE).* ^{1}H NMR: $\delta = 5.7$ (broad d, CF_2CFH), 4.15 (broad s, 2H, $CFOCH_2$), 3.8−3.4 (broad m, 6H, OCH_2), 1.2 [s, 9H, $C(CH_3)_3$]. *For Poly(Et-TFVE-co-t-Bu-TFVE).* ^{1}H NMR: $\delta = 5.7$ (broad d, CF_2CFH), 4.15 (broad s, 4H, $CFOCH_2$), 3.8−3.4 (broad m, 14H, OCH_2), 1.2 [m, 12H, $C(CH_3)_3$ and CH_3].

Deprotection of the *t*-Butyl Group of *t*-Bu-TFVE Polymers. To a 25 mL round-bottom flask equipped with a magnetic stir bar was added ~5 mL of ethanol in which 0.2−0.3 g of poly(*t*-Bu-TFVE) or poly(Et-TFVE-*co*-*t*-Bu-TFVE) was dissolved. To this solution was added 1−2 mL of concentrated HCl. The solution was heated at 50 °C for 2−4 h, with longer times being used to hydrolyze samples with greater *t*-Bu-TFVE contents. The hydrolyzed polymers were recovered by drying under vacuum ($P = 0.1$ mmHg at 50 °C) for at least 10 h. *For Poly(Et-TFVE-co-TFVE-OH).* ^{1}H NMR: $\delta = 5.7$ (broad d, CF_2-CFH), 4.15 (broad s, 4H, $CFOCH_2$), 3.8−3.4 (broad m, 14H, OCH_2), 2.5 (s, 1H, OH), 1.2 (t, 3H, CH_3).

Reprotection of the Hydroxyl Group of TFVE-OH Polymers. To a 250 mL three-neck flask equipped with a condenser cooled to −78 °C by dry ice/acetone were added 0.50 g of poly(Et-TFVE-*co*-TFVE-OH) − having 46 mol % TFVE-OH content, 50 mL of CH_2Cl_2, and 2.5 g of Amberlyst resin with stirring at room temperature. Isobutene gas was bubbled into the solution for 8 h, after which the Amberlyst resin was removed by filtration, the CH_2Cl_2 was removed by rotary evaporation, and the copolymer was dried under vacuum ($P = 0.1$ mmHg at RT). *For Poly(Et-TFVE-co-t-Bu-TFVE).* ^{1}H NMR: $\delta = 5.7$ (broad d, CF_2CFH), 4.15 (broad s, 4H, $CFOCH_2$), 3.8−3.4 (broad m, 14H, OCH_2), 1.2 [m, 12H, $C(CH_3)_3$ and CH_3]. A small broad peak at 1.9 ppm may be attributed to the hydroxyl proton of TFVE-OH, reflecting incomplete reprotection.

Modification of Hydroxyl-Functionalized Polymers. In a 10 mL beaker, 60 mg of poly(Et-TFVE-*co*-TFVE-OH), with 30 mol % hydroxyl content, and 94 mg of 1,6-hexamethylene diisocyanate (HDI) were dissolved in 4 mL of chloroform, after which a trace amount of dibutyltin dilaurate catalyst was added. Approximately 3−4 drops of solution were placed on the PTFE window of a disposable IR card and heated at 60 °C for up to 30 min. The modification reaction was monitored by FTIR by the disappearance of the isocyanate and hydroxyl peaks at 2275 and 3453 cm^{-1}, respectively. The remaining solution was cast in a disposable aluminum pan and heated at 60 °C for 1 h. The extent of modification/cross-linking was determined by comparing the dry mass of cross-linked films before and after immersion in 5 mL of ethanol for 24 h. Uncross-linked polymer readily dissolved in ethanol.

Calculation of Copolymer Composition. The ^{1}H NMR data was used to calculate both the composition of poly(Et-TFVE-*co*-*t*-Bu-TFVE) and the extent of hydrolysis of the *t*-Bu-TFVE polymers, by use of eqs 1 and 2, respectively. The

$$\frac{A_{CH2}}{8x + 10y} = \frac{A_{CH3}}{9x + 3y} \qquad (1)$$

$$\frac{A_{CH2}}{8x + 8z + 10y} = \frac{A_{CH3}}{9x + 3y} \qquad (2)$$

normalized ratio of the integrated areas of the methylene and methyl groups was used to calculate the composition of poly(Et-TFVE-*co*-*t*-Bu-TFVE). Specifically, if we let x represent the mole fraction of *t*-Bu-TFVE and y represent that of Et-TFVE, then we can normalize the integrated areas under the methylene (A_{CH2}) and methyl (A_{CH3}) ^{1}H NMR peaks as described in eq 1. Given that $x + y = 1$, the copolymer composition was calculated.

By using a similar equation, the extent of hydrolysis of *t*-Bu-TFVE polymers was calculated with z representing the mole fraction of TFVE-OH in the polymer. Given the mole fraction of Et-TFVE (y) as determined in eq 1 and that $x + z = 1 - y$, the mole fractions of *t*-Bu-TFVE (x) and TFVE-OH (z) were calculated according to eq 2. For fully deprotected *t*-Bu-TFVE samples, $x = 0$.

Results and Discussion

Synthesis of Poly(Et-TFVE), Poly(*t*-Bu-TFVE) and Poly(Et-TFVE-*co*-*t*-Bu-TFVE). The polymers were prepared by a redox-initiated aqueous emulsion polymerization using potassium persulfate, ferrous ion, and sodium bisulfite. We took advantage of previous experi-

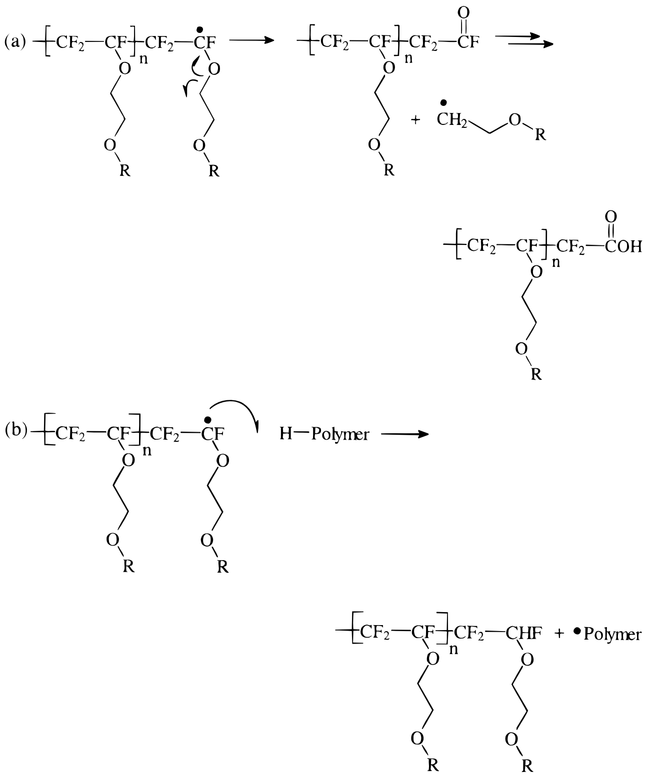

Figure 3. Possible polymerization mechanisms of termination/chain transfer: (a) β-scission and (b) hydrogen abstraction (inter- or intramolecular).

mental data that suggested the polymerization conditions: 20 °C, 5 wt % surfactant (relative to monomer) and 3×10^{-5} M iron(II) concentration.[6] All reactions proceeded for 2 days, after which the emulsion was broken and the polymer purified. Yields were observed as high as 60%.

The homo- and copolymerizations of Et-TFVE and *t*-Bu-TFVE seemed to follow similar mechanisms, as determined by FTIR and ^{1}H NMR. The polymerization mechanisms of poly(Et-TFVE) and poly(*t*-Bu-TFVE) were similar, involving both β-scission (cf. Figure 3a) and hydrogen-abstraction (cf. Figure 3b) termination/chain-transfer reactions.[6] Evidence for β-scission was provided by FTIR data with the presence of a carbonyl peak at 1775 cm^{-1} ascribed to a carboxylic acid by comparison to a small molecule analogue (ClF_2CCO_2H) and previous experimental results.[13] Although the initiator may also lead to carboxylic acid end groups, this is unlikely at the low temperatures used. Evidence for hydrogen abstraction was provided by ^{1}H NMR data with the presence of a peak at 5.7 ppm ascribed to a hydride by comparison to a small molecule analogue ($CH_3OCF\mathbf{H}CF_3$) and experimental data.[6] The copolymer, poly(Et-TFVE-*co*-*t*-Bu-TFVE), showed similar evidence of both β-scission, with a FTIR carbonyl peak at 1775 cm^{-1}, and hydrogen abstraction, with a ^{1}H NMR hydride peak at 5.7 ppm.

Copolymer Composition. A series of copolymers were prepared by varying the composition of Et-TFVE and *t*-Bu-TFVE monomers in the feed. The ^{1}H NMR data were used to calculate copolymer composition, according to eq 1; however, ^{1}H NMR could not be used to determine molecular weight because of the possibility of multiple hydride ends per polymer chain.[6] As shown in Table 1, seven polymers were prepared with *t*-Bu-TFVE compositions ranging from 0 to 100 mol %. The yield for all polymers was limited to between 15% and 32% to minimize copolymer compositional drift. The M_w and polydispersity index (PDI) varied from 10 300 to 39 300 and 1.6 to 3.2, respectively. Greater polydispersity was observed for higher contents of *t*-Bu-TFVE in the polymer. As shown in Figure 4, the copolymer composition was readily controlled by the monomer feed ratio; Et-TFVE and *t*-Bu-TFVE appeared to have similar reactivity, demonstrating near ideal copolymerization behavior.

Table 1. Copolymer Composition,[a] Molecular Weight and Polydispersity,[b] and T_g of Poly(Et-TFVE-*co*-*t*-Bu-TFVE)

monomer feed: *t*-Bu-TFVE (mol %)	copolymer composition: *t*-Bu-TFVE (mol %)	yield (%)	M_w (g/mol)	M_n (g/mol)	PDI	T_g (°C)
0	0	32	18 400	8 650	2.12	−61
10	11	27	12 200	6 700	1.82	
20	20	29	14 100	7 340	1.92	
30	24	15	10 300	6 335	1.63	
50	46	18	19 900	9 100	2.18	−63
70	68	23	21 100	9 400	2.24	
100	100	28	39 300	12 400	3.21	−60

[a] Calculated from ^{1}H NMR data. [b] Calculated from GPC data. [c] Measured by DSC.

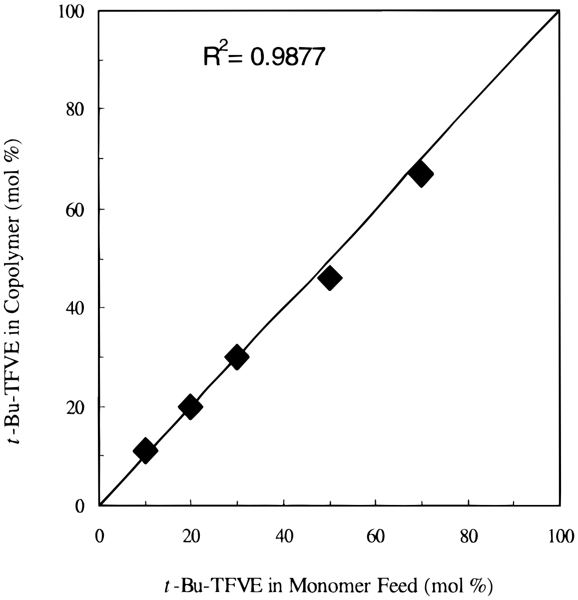

Figure 4. Copolymer composition, calculated from ^{1}H NMR data, as determined by the monomer composition in the feed. The solid line (—) represents ideal copolymerization behavior and the dots (◆) the experimental data.

Deprotection of the *tertiary*-Butoxy Group of Poly(*t*-Bu-TFVE) to Poly(TFVE-OH). Copolymers of Et-TFVE and *t*-Bu-TFVE were prepared with a range of *t*-Bu-TFVE contents in order to prepare polymers with a range of hydroxyl contents. As shown in Figure 2, the *tertiary*-butoxy group was removed under acidic conditions, yielding hydroxyl reactive handles. We confirmed that the polymers were hydrolyzed by both ^{1}H NMR and FTIR. The ^{1}H NMR data indicated a decrease in the integrated ratio of methyl to methylene groups and the appearance of a hydroxyl peak at 2.4–3.5 ppm after hydrolysis; some methyl peaks were expected from the terminal ethyl group of Et-TFVE. By using the ^{1}H NMR data and eq 2, all polymers were fully hydrolyzed to ≥99%. As shown in Figure 5, the FTIR spectra of hydrolyzed polymers showed both a broadening of the hydroxyl stretch at 3480 cm^{-1} and its shift to

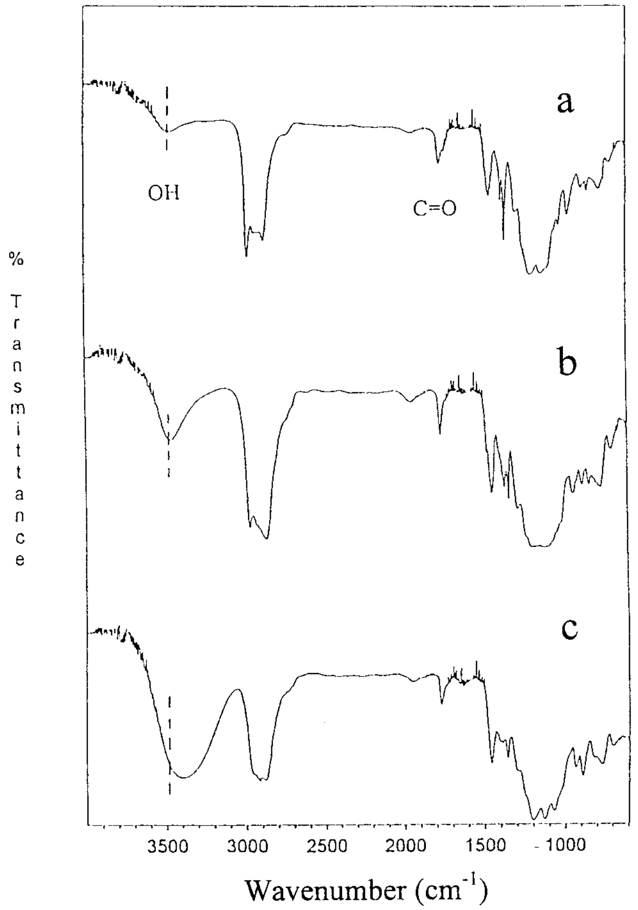

Figure 5. FTIR spectra showing a broadening and shift to lower wavenumbers of the hydroxyl stretch with increased TFVE-OH content in the copolymer: (a) poly(Et-TFVE-*co-t*-Bu-TFVE) with 20 mol % t-Bu-TFVE; (b) poly(Et-TFVE-*co*-TFVE-OH) with 20 mol % TFVE-OH content; and (c) poly(Et-TFVE-*co*-TFVE-OH) with 70 mol % TFVE-OH content.

lower wavenumbers with increased TFVE-OH content. This is indicative of increased hydrogen-bonding interactions.[14]

As shown in Table 2, three copolymers with 10, 30, and 46 mol % *t*-Bu-TFVE were prepared in 40−60% yield and characterized by GPC before and after hydrolysis. After hydrolysis, M_n was essentially constant for all polymers but M_w increased for the 30 mol % and 46 mol % polymers only. Consequently, the polydispersity increased for these copolymers after hydrolysis. Because we had anticipated that M_n and M_w would simply decrease upon hydrolysis, these results were somewhat puzzling.

The copolymer of the 46 mol % hydrolyzed *t*-Bu-TFVE (TFVE-OH) was reprotected with a *tert*-butyl group in an attempt to better understand the changes observed for M_w and PDI. After reprotecting the hydroxyl group, the copolymer was characterized by ^{1}H NMR which, according to eq 2, indicated that ~80 mol % of all hydroxyl groups were reprotected with the *t*-butoxy group. After reprotection of the TFVE-OH groups, the GPC data indicated that M_n was 9200 (from 8900), M_w was 43 200 (from 42 700) and PDI was 4.70 (from 4.80). Compared to the original, protected poly(Et-TFVE-*co*-*t*-Bu-TFVE), the reprotected copolymer had a similar M_n (9200 vs 9220) but a higher M_w (43 200 vs 36 500) and a higher PDI (4.70 vs 3.96). Because the effect of deprotection/reprotection is more pronounced on M_w than on M_n, a small fraction of high-molecular-weight polymers may have resulted from the hydrolysis reaction.

Given that the FTIR and ^{1}H NMR data of poly(Et-TFVE-*co*-TFVE-OH) indicated the presence of carboxylic acid end groups and hydroxyl groups, additional high-molecular-weight species may have formed as a result of esterification between the pendant hydroxyl groups and the terminal carboxylic acid groups. Alternatively, under the acidic conditions used, two hydroxyl groups may have reacted to form a new ether bond. For either scenario, a branched polymer may have formed resulting in the observed increase in M_w. The reprotection reaction, where a *tert*-butyl group was added to the hydroxyl pendant group, resulted in an increase in M_n (to the original deprotected molecular weight) yet little change in M_w and PDI. Because it is unlikely that the conditions used in the reprotection reaction would have broken any newly formed ester or ether bonds, a branched polymer may have formed. However, because neither esterification nor new ether bond formation were evident by FTIR and the ^{1}H NMR data indicated that 80% of the available hydroxyl groups were reprotected, it is likely that less than 20% of the copolymers were branched.

Thermal Properties of Poly(Et-TFVE), Poly(*t*-Bu-TFVE), Poly(Et-TFVE-*co*-*t*-Bu-TFVE), and Poly(Et-TFVE-*co*-TFVE-OH). The polymers were characterized by both DSC (for T_g) and TGA (for thermal stability) to correlate chemical composition with thermal properties. Poly(Et-TFVE) samples with M_n's of 4000 and 13 000 had T_g's of −62 °C and −60 °C, respectively, indicating that molar mass had little effect on T_g. In addition, both poly(Et-TFVE) and poly(*t*-Bu-TFVE) had similar T_g's of −61 °C and −60 °C, respectively. As was expected from the Fox equation, the T_g of poly(Et-TFVE-*co*-*t*-Bu-TFVE), having 50 mol % Et-TFVE, was similar to that of the homopolymers, with a T_g of −63 °C. The hydrolyzed polymers with TFVE-OH had distinctly different T_g's from the protected polymers. As shown in Figure 6, the T_g of poly(Et-TFVE-*co*-TFVE-OH) was measured for different copolymer compositions, from 0% to 100% TFVE-OH, as determined from *t*-Bu-TFVE compositions and assuming 100% deprotection. The T_g increased with hydroxyl content, from −61 °C for poly(*t*-Bu-TFVE) to +9 °C for poly(TFVE-OH). The increase in T_g likely reflected increased hydrogen-bonding interactions that are either intra- or intermolecular in nature.[14] The physical nature of the polymers changed with hydroxyl content, from a viscous liquid for poly(*t*-Bu-TFVE) to a white tacky solid for poly(TFVE-OH).

The thermal stability of all polymers was measured by TGA. The data are summarized in Figure 7a, b, c for poly(Et-TFVE), poly(Et-TFVE-*co*-*t*-Bu-TFVE), and poly(*t*-Bu-TFVE), respectively. As shown in Figure 7a, poly(Et-TFVE) decomposed in one stage, with an onset temperature at 300 °C, 10% mass loss at 327 °C, and 85% mass loss at 400 °C. The polymer likely degraded by an unzipping reaction with a carbonaceous residue left at 400 °C. Mass spectra of poly(Et-TFVE) at 315 °C and 400 °C had predominantly the same peaks, indicating the likelihood of the unzipping mechanism. Although no peaks could be ascribed to the monomer, this may reflect the instability of the molecular ion. As shown in Figure 7c, poly(*t*-Bu-TFVE) decomposed in two stages, with an onset temperature in the first stage at 115 °C and 10% mass loss at 140 °C, likely due to

Table 2. Change of Molecular Weight and Polydispersity of Copolymers before and after Hydrolysis of the *tertiary*-Butoxy Group of *t*-Bu-TFVE

copolymer composition: *t*-Bu-TFVE (mol %)	yield[a] (mass %)	GPC data poly(Et-TFVE-co-*t*-Bu-TFVE) M_w (g/mol)	M_n (g/mol)	PDI	GPC data poly(Et-TFVE-co-TFVE-OH) M_w (g/mol)	M_n (g/mol)	PDI
10	42	11 440	6 170	1.85	11 100	5 630	1.97
30	45	24 600	7 860	3.12	30 900	7 800	3.96
46	60	36 500	9 220	3.96	42 700	8 900	4.80
46[b]		43 230	9 200	4.70			

[a] Copolymerization without conversion control. [b] TFVE-OH hydroxyl groups were reprotected with *t*-butyl groups. ^{1}H NMR data indicated that $\sim$80 mol % of hydroxyl groups were reprotected.

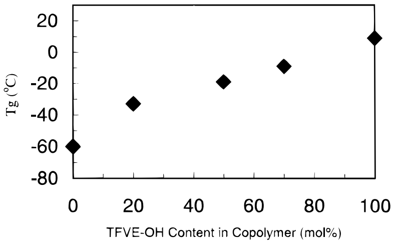

Figure 6. T_g of TFVE-OH polymers vs TFVE-OH content.

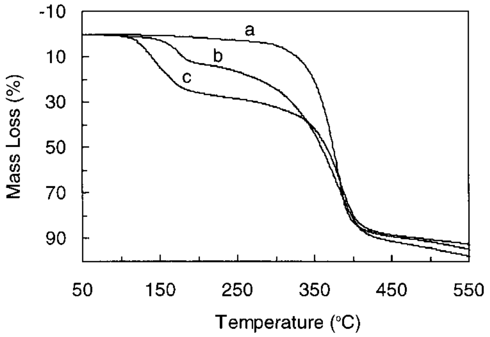

Figure 7. Polymer thermal stability (by TGA) as a function of composition: (a) poly(Et-TFVE); (b) poly(Et-TFVE-*co*-*t*-Bu-TFVE) with $^{50}/_{50}$ mol composition; and (c) poly(*t*-Bu-TFVE).

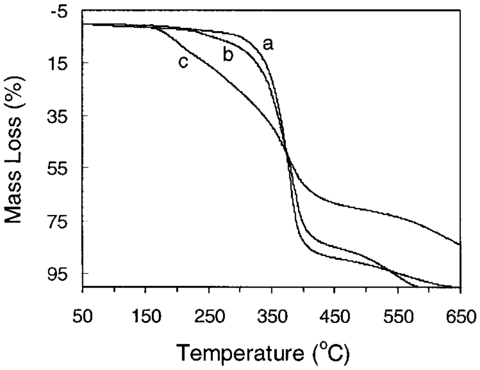

Figure 8. Polymer thermal stability (by TGA) as a function of composition: (a) poly(Et-TFVE); (b) poly(Et-TFVE-*co*-TFVE-OH) with $^{50}/_{50}$ mol composition; and (c) poly(TFVE-OH).

decomposition of the *tert*-butyl group. Approximately 26% mass loss was observed in the first stage of decomposition, reflecting the *tert*-butyl content of $\sim$24 wt %. In the second stage of decomposition, the onset temperature was observed at 280 °C, an additional 10% (i.e., 40% total) mass loss at 330 °C, and 90% mass loss at 400 °C. These results indicate that poly(Et-TFVE) is more thermally stable than poly(*t*-Bu-TFVE), reflecting the relative instability of the *tert*-butyl terminal group to that of the ethyl. As shown in Figure 7b, the $^{50}/_{50}$ copolymer of poly(Et-TFVE-*co*-*t*-Bu-TFVE) exhibited thermal behavior between the two homopolymers, having a two-stage thermal decomposition. In the first stage of decomposition (at 140 °C), the copolymer lost 13% of its mass relative to the 26% lost by the *t*-Bu-TFVE homopolymer, thereby reflecting the copolymer composition.

The thermal stability of hydrolyzed polymers is shown in Figure 8. Figure 8a shows the thermal profile for poly(Et-TFVE) for comparison purposes. Figure 8b is the profile for the $^{50}/_{50}$ copolymer of poly(Et-TFVE-*co*-TFVE-OH), and Figure 8c is that of poly(TFVE-OH). All of these polymers demonstrated one-stage decomposition profiles. Poly(TFVE-OH) had an onset temperature of 150 °C and 10% mass loss at 205 °C. Interestingly, at 400 °C poly(TFVE-OH) lost 60% of its mass, whereas other polymers lost over 85% of their mass. Poly(TFVE-OH) lost 85% of its mass at temperatures exceeding 650 °C. Poly(TFVE-OH) was more thermally stable than poly(*t*-Bu-TFVE) which had an onset temperature of 115 °C. The copolymer, poly(Et-TFVE-*co*-TFVE-OH), demonstrated a thermal behavior between the two homopolymers yet had a profile more similar to that of poly(Et-TFVE) than poly(TFVE-OH) (cf. Figure 8b).

Modification of the Hydroxyl-Functionalized Poly(TFVE-OH). Hydroxyl-functionalized fluoropolymers were prepared to allow facile modification with, for example, cross-linking reagents for coatings applications. As a demonstration of its availability, the hydroxyl functionality in poly(Et-TFVE-*co*-TFVE-OH) was modified with the HDI cross-linking reagent using dibutyltin dilaurate catalysis at 60 °C. The reaction was monitored by FTIR in terms of both the disappearance and appearance of characteristic peaks for the reaction of a hydroxyl and an isocyanate to form a urethane. As shown in Figure 9 for poly(Et-TFVE-*co*-TFVE-OH) having 30 mol % TFVE-OH content, the polymer had the characteristic hydroxyl stretch at 3453 cm^{-1} (cf. Figure 9a). Upon addition of the cross-linking agent for 5 min at RT, the characteristic isocyanate peak ($\nu_{N=C=O}$) was observed at 2275 cm^{-1} as were two small peaks attributed to the urethane bonds at 1724 cm^{-1} for $\nu_{C=O}$ and 3345 cm^{-1} for ν_{N-H} (cf. Figure 9b). After 10 min at 60 °C, both hydroxyl and isocyanate peaks had diminished, and the two characteristic urethane peaks had strengthened (cf. Figure 9c). After an additional 20 min (30 min total) at 60 °C, the isocyanate peak at 2275 cm^{-1} was no longer visible, and the urethane peaks were predominant (cf. Figure 9d). The FTIR data indicated that cross-linking was complete within 30 min at 60 °C.

To confirm the modification reaction, an identical polymer film (prepared with HDI and catalyst) was cast and heated at 60 °C for 60 min. The film was immersed for 24 h at RT in ethanol, in which uncross-linked polymer readily dissolved. After ethanol extraction, the dry mass of the polymer film was 85% of that prior to

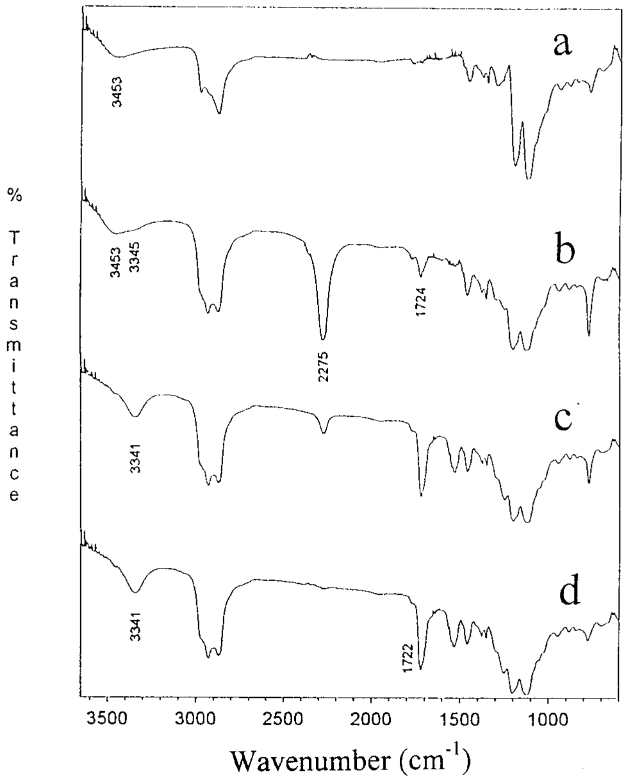

Figure 9. FTIR spectra of (a) poly(Et-TFVE-*co*-TFVE-OH) having 30 mol % TFVE-OH content and crosslinked with HDI for (b) 5 min, RT; (c) 10 min, 60 °C; and (d) 30 min, 60 °C.

extraction, indicating that most of the TFVE-OH groups were cross-linked.

Conclusions

The new trifluorovinyl ether polymers and copolymers offer thermal stability, solubility in common organic solvents, and facile derivatization. By controlling the monomer composition, the copolymer composition was manipulated, leading to a range of polymers and properties. The TFVE copolymers, having a protected hydroxyl group, were found to have properties analogous to their homopolymers in terms of synthetic mechanism and thermal properties. Copolymers had glass-transition temperatures and decomposition temperatures that were predicted by those of the homopolymers. However, the TFVE copolymers with deprotected hydroxyl groups (i.e., TFVE-OH copolymers) had properties different from their protected analogues. For example, poly(Et-TFVE-*co*-TFVE-OH) showed an increased T_g and a shift of the hydroxy FTIR peak to lower wavenumbers with increased TFVE-OH content, both of which can be attributed to increased hydrogen-bonding interactions (cf. Figures 5 and 6). The hydroxyl content, controlled by copolymer composition, broadened the range of potential applications to, for-example, solventless coatings that require in situ cross-linking. Future studies will investigate the hydroxyl groups as reactive handles for further modification and the use of these TFVE polymers as additives to control interfacial properties.

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