# Polymerization of Novel Trifluorovinyl Ethers: Insight into the Mechanisms of Termination and Chain Transfer[1]

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**ABSTRACT:** New trifluorovinyl ether polymers were synthesized with the view toward overcoming the high chemical and thermal stabilities commonly associated with fluoropolymers. Trifluorovinyl ether copolymers, with fluorinated pendant groups, have previously been prepared to overcome limitations in processibility. To further enhance solubility in common organic solvents and to improve processibility, we prepared three new trifluorovinyl ether monomers, having hydrocarbon ether pendant groups, for polymerization: 1-[2-(2-ethoxy ethoxy)ethoxy]-1,2,2-trifluoroethene (Et-TFVE), 1-[2-(2-*t*-butoxy ethoxy)ethoxy]-1,2,2-trifluoroethene (*t*-Bu-TFVE), and 1-(2-phenoxy ethoxy)-1,2,2-trifluoroethene (Ph-TFVE). Homopolymers of these three monomers were prepared by aqueous emulsion polymerization with the use of a redox initiator. Poly(Et-TFVE) and poly(Ph-TFVE) were prepared with a range of molar masses, the highest of which had weight average molar masses of 33,800 g $\text{mol}^{-1}$ and 59,000 g $\text{mol}^{-1}$, respectively. As a result of monomer reactivity and structure, the polymerization mechanism was complicated, resulting in $\beta$-scission termination/chain transfer for all three polymers and hydrogen abstraction chain transfer for poly(Et-TFVE) and poly(*t*-Bu-TFVE). To the best of our knowledge, this is the first example of hydrogen abstraction from the pendant group of the trifluorovinyl ether itself. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 3301–3308, 1999

**Keywords:** poly(trifluorovinyl ether); emulsion polymerization; hydrogen abstraction; $\beta$-scission

## INTRODUCTION

Fluoropolymers have unique properties, allowing them to be used in diverse applications, from lining chemical storage tanks to vascular grafts.[2] Many industrial applications, such as fuel cells,[3] take advantage of the high thermal and chemical stabilities of fluoropolymers. Yet, it is these very properties that limit their broader applicability. To facilitate processing, fluorinated trifluorovinyl ether (TFVE) copolymers have been prepared.[4] To further enhance processibility and solubility in common organic solvents while expanding the number of potential applications, we prepared a series of novel TFVEs,[5] having hydrocarbon ether pendant groups for polymerization.

As shown in Figure 1, three new monomers were prepared for polymerization: 1-[2-(2-ethoxy ethoxy)ethoxy]-1,2,2-trifluoroethene (Et-TFVE), 1-[2-(2-*t*-butoxy ethoxy)ethoxy]-1,2,2-trifluoroethene (*t*-Bu-TFVE), and 2-(2-phenoxy ethoxy)-1,1,2-trifluoroethene (Ph-TFVE). The monomers have an ethylene glycol pendant group in common and different terminal functional groups. The presence of the oligoethylene oxide group may render the fluoropolymer less protein adsorptive,[6]

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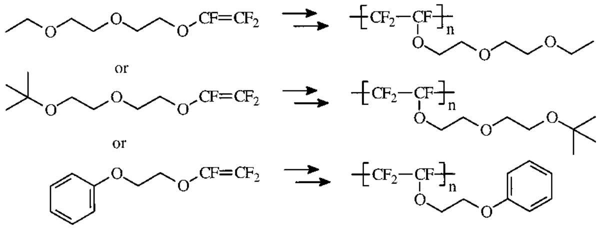

**Figure 1.** Homopolymerization of 1-(2-alkoxy ethoxy)-1,2,2-trifluoroethenes (TFVE)s: Et-TFVE, *t*-Bu-TFVE, and Ph-TFVE.

thereby making it desirable for biomedical applications.[7] Although the Et-TFVE has a pendant group structure similar to that of poly(ethylene oxide), the *t*-Bu-TFVE is a protected alcohol, allowing for modification after polymerization. The Ph-TFVE provides a more rigid polymeric structure and may serve as a precursor to an ionic polymer.

We were interested in preparing these new TFVE polymers because we anticipated that they would have properties different from those with fluorinated pendant groups. In particular, we thought that the inherent incompatibility between the hydrophobic/oleophobic perfluorinated backbone and the hydrophilic oligoether pendant group would lead to micro- or nanoscale domains. When used as additives in blends, the fluorocarbon backbone would enrich the surface, whereas the pendant oligoether group would anchor the polymer within the bulk, thereby enhancing the longevity of the additive at the surface.

Before investigating their properties, the new polymers had to be synthesized. We took advantage of the methodology previously described for the polymerization of fluorocarbon TFVEs[8,9] and used a redox-initiated aqueous emulsion polymerization. Given the unique structure of our monomers, we anticipated that the polymerization would be complex; thus, we have investigated the effects of reaction temperature and initiator concentration in terms of polymer molar mass, polydispersity index (PDI), and yield. To gain insight into the mechanisms of termination and chain transfer, the polymers were characterized by $^1$H–NMR, $^{19}$F–NMR, and FTIR.

## EXPERIMENTAL

*Reagents.* The three TFVE monomers, Et-TFVE, *t*-Bu-TFVE, and Ph-TFVE, were prepared as previously described[5] and according to published methods.[10] The monomers were purified by fractional distillation to greater than 99% purity, as determined by gas chromatography, $^1$H–NMR, 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 other reagents were purchased from Aldrich (Ontario, Canada) and used as received.

*Characterization.* Polymers were characterized for molar mass using a gel permeation chromatograph (Waters 2690, Bedford, MA), equipped with a refractive index detector (Waters 410, Bedford, MA) and a series of Styragel® columns (Waters $10^5$, $10^4$, and 500 Å, Bedford, MA). Using a THF mobile phase, polymer molar mass was calculated relative to polystyrene standards (Aldrich, Ontario, Canada). $^1$H– and $^{19}$F–NMR spectra were obtained on a Varian Gemini 300 MHz spectrometer in $CDCl_3$, using TMS and $CFCl_3$ as external references, respectively. FTIR spectra were obtained using a Galaxy Series 5000 spectrometer. Glass transition temperatures ($T_g$) were measured using a Perkin–Elmer DSC-7 differential scanning calorimeter under an inert nitrogen atmosphere at a heating rate of 10°C/min, either from −120 to 0°C for poly(Et-TFVE) and poly(*t*-Bu-TFVE) or from −50 to +50°C for poly(Ph-TFVE).

*Emulsion Homopolymerization of Et-TFVE, t-Bu-TFVE, or Ph-TFVE.* To a 100 mL round-bottom flask equipped with a magnetic stirrer and nitrogen purge, 22 or 29 mL of deionized water and 8 or 1 mL of a $3.1 \times 10^{-5}$ $M$ aqueous ferrous ion solution [Fe(II) as $FeSO_4 \cdot 7H_2O$] were added for a total volume of 30 mL. Dissolved oxygen was removed using a nitrogen purge (1 h). Sodium hydrogen phosphate (0.15 g), sodium dodecylsulfate (0.20 to 0.25 g), and sodium hydrogensulfite (50, 100, or 200 mg) were added to the flask. The temperature of the flask was adjusted to the desired polymerization temperature (2 to 50°C) using a Haake K15 water bath with a DC3 temperature controller. Potassium persulfate (1 wt equiv to $NaHSO_3$; 50 to 200 mg) was added to the flask prior to the addition of monomer (3.0 g). The monomer was polymerized for 2 to 4 days, after which ~0.5 mL of concentrated HCl was added to poly(Et-TFVE) and poly(*t*-Bu-TFVE) syntheses, followed by centrifugation. Poly(Et-TFVE) and poly(*t*-Bu-TFVE) were dissolved in ethanol and then precipitated in water (twice) before drying under vacuum ($P \approx 0.1$ mmHg, 40°C). The poly-

**Table I.** Aqueous Emulsion Homopolymerization of Ph-TFVE, Et-TFVE, and *t*-Bu-TFVE ($T = 26°C$)

| Polymer | $M_n$ (gmol$^{-1}$) | $M_w$ (gmol$^{-1}$) | PDI | Yield (%) |
|---|---|---|---|---|
| Poly(Ph-TFVE)[a] | 21,700 | 42,900 | 1.98 | 28 |
| Poly(Et-TFVE) | 7,850 | 23,400 | 2.98 | 64 |
| Poly(*t*-Bu-TFVE) | 8,200 | 26,200 | 3.20 | 78 |

[a] Polymerization at 30°C.

merization of Ph-TFVE was terminated by the addition of ~300 mL of acidified methanol (i.e., with ~0.5 mL concentrated HCl). The polymer was vacuum filtered on a coarse fritted funnel and washed with ~50 mL methanol (three times) before drying under vacuum ($P \approx 0.1$ mmHg, 40°C).

For poly(Et-TFVE): $^1$H–NMR: $\delta = 5.7$ (broad d, $CF_2CFH$), $\delta = 4.15$ (broad s, 2H, $CFOCH_2$), 3.8–3.4 (broad m, 8H, $OCH_2$), 1.2 (t, 3H, $CH_3$). $^{19}$F–NMR: $\delta = -111$ to $-117$ (broad m, 2F, $CF_2$), $-134$ to $-137$ (broad m, 1F, CF)

For poly(*t*-Bu-TFVE): $^1$H–NMR: $\delta = 5.7$ (broad d, $CF_2CFH$), $\delta = 4.15$ (broad s, 2H, $CFOCH_2$), 3.8–3.4 (broad m, 6H, $OCH_2$), 1.2 [s, 9H, $C(CH_3)_3$]. $^{19}$F–NMR: $\delta = -111$ to $-117$ (broad m, 2F, $CF_2$), $-134$ to $-137$ (broad m, 1F, CF)

For poly(Ph-TFVE): $^1$H–NMR: $\delta = 7.4$–6.6 (broad m, 5H, Ph), 4.2 (broad s, 2H, $CFOCH_2$), 3.8 (broad s, 2H, $OCH_2$). $^{19}$F–NMR: $\delta = -111$ to $-115$ (broad d, $J = \sim 85$ Hz, 2F, $CF_2$), $-134$ to $-136$ (broad m, 1F, CF)

*Bulk Homopolymerization of Ph-TFVE.* The initiator, 2,2′-azobisisobutyronitrile (AIBN, 15 mg, 2 mol %), was added to a 2 mL glass vial that was sealed with a screw cap and a septum and purged with nitrogen (5 min). To the vial was added either 1.00 g of Ph-TFVE or a mixture of 1.00 g of Ph-TFVE and 41 mg of *n*-butanethiol (10 mol %). The vial was placed in a 55°C oven for 3 days, after which most of the unreacted monomer was removed under vacuum ($P \approx 0.1$ mmHg, $T = 55°C$). The $^1$H–NMR and $^{19}$F–NMR data are in accord with those reported for the emulsion-polymerized Ph-TFVE; however, an additional $^1$H–NMR peak was observed for poly(Ph-TFVE) prepared in the presence of *n*-butanethiol: $\delta = 5.7$ (broad d, $CF_2CFH$).

## RESULTS

*Emulsion Homopolymerization of Et-TFVE, t-Bu-TFVE, or Ph-TFVE.* Poly(Et-TFVE), poly(t-Bu-TFVE), and poly(Ph-TFVE) were synthesized by an aqueous emulsion polymerization using sodium dodecylsulfate surfactant; potassium persulfate/iron (II)/sodium hydrogensulfite redox initiator at 1 mol % relative to monomer. The polymers were initially characterized by gel permeation chromatography (GPC) relative to polystyrene standards and differential scanning calorimetry (DSC). Poly(Et-TFVE) and poly(*t*-Bu-TFVE) were transparent, highly viscous liquids, both of which had a glass transition temperature ($T_g$) of −60°C. Poly(Ph-TFVE) was a white powder with a $T_g$ of 23°C. As shown in Table I, the polymers were initially prepared at either 26 or 30°C.

The effects of temperature and initiator concentration were further investigated to determine their effects on polymer molar mass and yield. In order to determine the effect of temperature on polymer molar mass, a series of Et-TFVE polymers were prepared between 2 and 50°C at constant initiator concentrations ($\sim 6 \times 10^{-3}$ *M*, 1 mol % relative to monomer). As shown in Figure 2, $M_n$, as determined by GPC, increased with decreasing temperature and reached a maximum of approximately 13,000 g mol$^{-1}$ ($M_w = 33{,}800$ g mol$^{-1}$) at the lowest practical temperature of 2°C. The PDIs for all polymers were typically between 2.6 and 3.6, with those polymers synthesized at the lower temperatures having the lower PDIs. The polymer yields were typically between 60 and 70% after 2 to 4 days.

Given the increase in molar mass observed for poly(Et-TFVE) at reduced temperatures, we repeated this experiment with poly(Ph-TFVE). The synthesis of poly(Ph-TFVE) at 10°C with 1 mol % potassium persulfate initiator was unsuccessful, with no polymer isolated after 4 days. Given that a 28% yield of poly(Ph-TFVE) was obtained at 30°C (cf. Table I) and a 0% yield at 10°C, there appeared to be an inverse correlation between

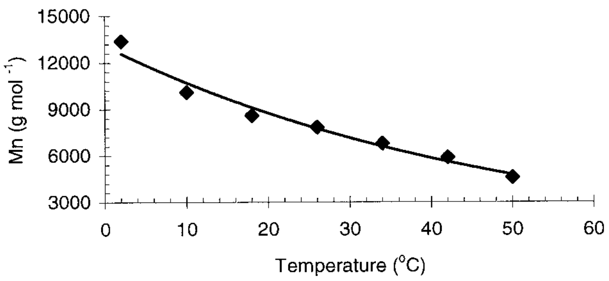

**Figure 2.** The molar mass of poly(Et-TFVE), as determined by GPC, decreased with increasing temperature.

**Table II.** Effect of Initiator Concentration of Poly(Ph-TFVE) Molar Mass and Yield ($T$ = 30°C)

| [Ferrous Ion] ([$M$]) | [Potassium Persulfate] ([$M$]) | $M_n$ (gmol$^{-1}$) | $M_w$ (gmol$^{-1}$) | PDI | Yield (%) |
|---|---|---|---|---|---|
| $3.1 \times 10^{-5}$ | $6.2 \times 10^{-3}$ | 21,700 | 42,900 | 1.98 | 28 |
| $3.1 \times 10^{-5}$ | $12 \times 10^{-3}$ | 21,600 | 48,800 | 2.26 | 53 |
| $3.1 \times 10^{-5}$ | $25 \times 10^{-3}$ | 16,000 | 45,600 | 2.85 | 75 |
| $25 \times 10^{-5}$ | $6.2 \times 10^{-3}$ | 19,200 | 39,300 | 2.05 | 14 |
| $25 \times 10^{-5}$ | $12 \times 10^{-3}$ | 24,000 | 59,000 | 2.46 | 53 |
| $25 \times 10^{-5}$ | $12 \times 10^{-3}$ [a] | 21,500 | 43,300 | 2.01 | 13 |

[a] Polymerization at 20°C.

temperature and polymer yield for poly(Ph-TFVE). However, at the higher temperature of 50°C, the yield did not increase and molar mass decreased relative to results obtained at 30°C: at 50°C, the yield was 23%, whereas $M_n$ was 9800 g mol$^{-1}$, $M_w$ was 22,500 g mol$^{-1}$, and PDI was 2.3. For 1 mol % potassium persulfate, the optimal temperature in terms of molar mass and yield appeared to be 30°C.

Since $25 \times 10^{-3}$ $M$ potassium persulfate has been used to initiate the emulsion polymerization of other fluorocarbon TFVEs,[8] we thought that the initiation process for poly(Ph-TFVE) may be inefficient. In an attempt to produce higher molar mass poly(Ph-TFVE) in greater yields, the initiator concentration was investigated by successively doubling the concentration of potassium persulfate. As shown in Table II, the isolated yield of poly(Ph-TFVE) increased with potassium persulfate concentration. The potassium persulfate concentration had no significant effect on $M_n$ until the highest concentration ($25 \times 10^{-3}$ $M$, 4 mol %) where $M_n$ decreased by approximately 25% overall. Although the yield was high (75%), the latex was unstable at this high initiator concentration, resulting in partial precipitation of the polymer and likely accounting for the lower $M_n$ observed.

When 1 mol % ($6.2 \times 10^{-3}$ $M$) potassium persulfate was used, the molar mass of poly(Ph-TFVE) did not change appreciably with different concentrations of the Fe(II) electron transfer reagent ($3.1 \times 10^{-5}$ $M$ versus $25 \times 10^{-5}$ $M$). Instead, the eightfold increase of Fe(II) concentration resulted in a decreased isolated yield from 28 to 14%, indicating that the initiator was consumed prior to most of the monomer's being polymerized. By increasing the concentration of the potassium persulfate from 1 mol % ($6.2 \times 10^{-3}$ $M$) to 2 mol % ($12 \times 10^{-3}$ $M$), the yield almost doubled to 53% (cf. entries 1 and 2); the compounded effect of increasing Fe(II) as well, from $3.1 \times 10^{-5}$ $M$ to $25 \times 10^{-5}$ $M$ (cf. entries 2 and 5), did not affect the yield but did result in an increase in $M_w$. Using the identical conditions at a lower temperature of 20°C, instead of 30°C (cf. entries 5 and 6), the yield decreased to 13%, as may have been expected given the relation previously observed between yield and temperature for poly(Ph-TFVE). This experiment was complicated by partial precipitation of the surfactant upon addition of the potassium persulfate, indicating that the surfactant was incompatible with high concentrations of potassium persulfate at lower temperatures.

The effects of temperature and initiator concentration on polymer molar mass were evident and could be used to elucidate the polymerization mechanism. As was shown in Figure 2, the resulting $M_n$'s of poly(Et-TFVE) were lower than may have been expected, given that relatively low initiator concentrations were used and propagation is fast relative to termination on a carbon radical that bears electron withdrawing groups.[11] Although for fluorinated polymer systems radical recombination has been suggested as the predominant mode of termination,[4] this was unlikely for our TFVEs, which had PDIs greater than or equal to 2. As was shown in Table II, for low isolated yields of poly(Ph-TFVE) (i.e., less than 30%), the PDI approached a limiting value of 2, suggesting termination by disproportionation.[11] In an attempt to rationalize the limited molar masses achieved for poly(Et-TFVE) and understand the disproportionation mechanism suspected for poly(Ph-TFVE), the polymers were further analyzed by FTIR and $^1$H–NMR to lend greater insight into the mechanism of polymerization.

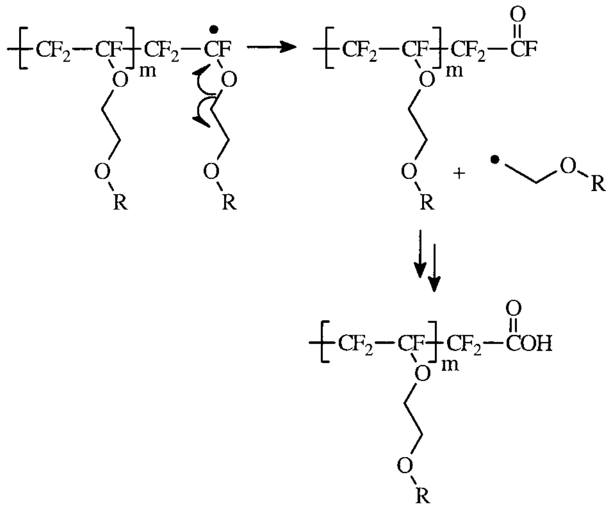

**Figure 3.** Chain transfer by $\beta$-scission of the propagating polymer radical results in carboxylic acid end groups. R is 2-ethoxy-ethyl, 2-*t*-butoxy-ethyl, or phenyl.

*Mechanisms of Chain Transfer and Termination.* In order to investigate possible modes of chain transfer or termination, the polymers were characterized by FTIR. A weak carbonyl peak at $\sim$1770 cm$^{-1}$, which was not present in any of the reagents prior to polymerization, was observed in the FTIR spectra of all three homopolymers. The peak intensity was not affected by repeated precipitation of the polymer, indicating the carbonyl's association with the polymers and not an impurity or by-product. A similar peak has previously been observed during the polymerization of 1-fluoroalkoxy-1,2,2-trifluoroethenes and explained by $\beta$-scission.[12] We ascribed the FTIR carbonyl peak to $\beta$-scission as well. As shown in Figure 3, $\beta$-scission results from homolytic cleavage of the carbon–oxygen bond that is beta to the propagating radical, leading to the formation of a carboxylic acid end group, via an acid fluoride intermediate, and a radical species that may initiate a new polymer chain. The acid fluoride intermediate was observed directly by FTIR with a peak at 1874 cm$^{-1}$ for bulk-polymerized Ph-TFVE. We confirmed our FTIR peak assignment by comparison to a small molecule, $ClF_2CCO_2H$, which has a carboxylic acid stretch at 1772 cm$^{-1}$.

The GPC polydispersity data coupled with the FTIR evidence of $\beta$-scission indicate a unimolecular disproportionation mechanism for poly(Ph-TFVE). Thus, unlike previous $\beta$-scission chemistry, it is likely that $\beta$-scission is the predominant mode controlling $M_n$ of poly(Ph-TFVE) under the aqueous emulsion conditions employed herein. For poly(Et-TFVE), molar mass increased as the polymerization temperature decreased, likely as a result of suppressed $\beta$-scission relative to propagation (cf. Fig. 2).

Since radicals on carbon bonded to fluorine are very electrophilic and can abstract hydrogen from many hydrocarbon-containing compounds,[13] we suspected that hydrogen abstraction might be further limiting molar mass. It is for this reason that high molar mass polymers of 1-perfluoropropoxy-1,2,2-trifluoroethene and tetrafluoroethylene are limited to media such as aqueous emulsions, fluorinated solvents, and supercritical $CO_2$.[12] We used $^1$H–NMR to determine whether hydrogen abstraction was involved in the polymerization mechanism. In addition to the peaks expected based on the monomer composition, the $^1$H–NMR spectra of poly(Et-TFVE) and poly(*t*-Bu-TFVE) had a broad doublet at 5.7 ppm ($J$ = 60 Hz). Given that a similar small molecule, $CH_3OCFHCF_3$, was reported to have a $^1$H–NMR hydride peak at 5.3 ppm (dq, $J$ = 62.3 Hz),[14] we attributed the new peak observed at 5.7 ppm to a proton coupled to a fluorine on the same carbon atom. Notwithstanding that the corresponding geminal fluorine could not be identified in the $^{19}$F–NMR spectra of poly(Et-TFVE) and poly(*t*-Bu-TFVE), the $^1$H–NMR peak indicated hydride formation during polymerization, as shown in Figure 4.

Interestingly, the $^1$H–NMR and $^{19}$F–NMR spectra of poly(Ph-TFVE) showed only those peaks expected based on the monomer composition. The broad doublet at 5.7 ppm, identified as a proton coupled to a geminal fluorine for the other two polymers, was not observed for poly(Ph-TFVE). Thus, for poly(Ph-TFVE), the $^1$H–NMR spectrum suggested that hydrogen abstraction did not occur during its synthesis and that only $\beta$-scission was molar mass–limiting.

To further test this hypothesis of hydrogen abstraction, poly(Ph-TFVE) was synthesized by

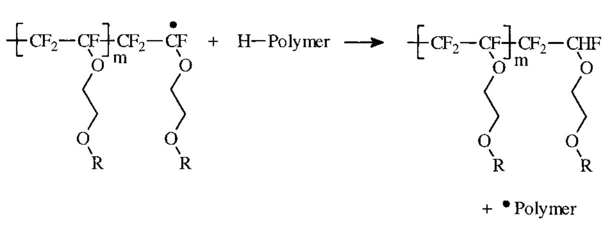

**Figure 4.** Hydrogen abstraction by the propagating polymer radical results in hydride end groups. R is 2-ethoxy-ethyl or 2-*t*-butoxy-ethyl.

bulk polymerization in the presence and absence of a chain transfer agent, $n$-butanethiol, using AIBN initiation at 55°C. We suspected that the use of a chain transfer agent would result in the observation of a hydride peak in the $^1$H–NMR, which would be similar to that observed for poly(Et-TFVE) and poly($t$-Bu-TFVE). The $^1$H–NMR spectrum of bulk poly(Ph-TFVE) formed in the presence of the chain transfer agent (cta) [bulk poly(Ph-TFVE-cta)] showed a small peak at 5.7 ppm ($J = \sim 57$ Hz), whereas that of bulk poly(Ph-TFVE), formed in the absence of the chain transfer agent, showed no hydride peak. The presence of a weak carbonyl peak at ~1770 cm$^{-1}$ in the FTIR spectra of both polymers indicated $\beta$-scission. As determined by GPC, the bulk poly(Ph-TFVE-cta) had a $M_n$ of 6600 g mol$^{-1}$ and a $M_w$ of 11,200 g mol$^{-1}$, whereas bulk poly(Ph-TFVE) had a $M_n$ of 8100 g mol$^{-1}$ and a $M_w$ of 15,400 g mol$^{-1}$.

In order to understand the role of hydrogen abstraction in the polymerization mechanism, the $^1$H–NMR data were used to calculate the degree of polymerization ($X_n$) by end-group analysis, using the normalized ratio of protons in the pendant ether group to that of the hydride. Poly(Et-TFVE) had an $X_n$ of 7.7 ± 0.4, corresponding to a $M_n$ of 1650 g mol$^{-1}$ as determined by end-group analysis, yet a GPC-determined $M_n$ of 7850 g mol$^{-1}$. Similarly, poly($t$-Bu-TFVE) had an $X_n$ of 9.1 ± 0.4, corresponding to a $M_n$ of 2200 g mol$^{-1}$ as determined by end-group analysis, yet a GPC-determined $M_n$ of 8200 g mol$^{-1}$. Notwithstanding the different hydrodynamic volumes between polystyrene and our poly(TFVE)s, the differences in $M_n$ may indicate that multiple hydrides formed per polymer chain, thereby lowering the $M_n$ calculated by end-group analysis relative to that calculated by GPC. Multiple chain transfer reactions per polymer chain may have occurred if the radical that was formed by abstraction continued to propagate. Figure 5 summarizes the effect of temperature on the $M_n$ of poly(Et-TFVE), as calculated by end-group analysis from $^1$H–NMR data. The data in Figure 5 are consistent with those in Figure 2, where $M_n$ increased as temperature decreased. The data in Figure 5 indicate that hydrogen abstraction was suppressed relative to propagation at lower temperatures.

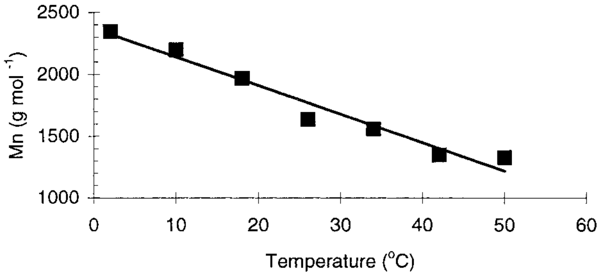

**Figure 5.** The molar mass of poly(Et-TFVE), calculated by end-group analysis from $^1$H–NMR data, decreased with increasing temperature.

## DISCUSSION

The emulsion polymerizations of Et-TFVE and $t$-Bu-TFVE appeared to follow similar mechanisms, leading to an FTIR carbonyl peak at 1770 cm$^{-1}$, ascribed to $\beta$-scission, and a $^1$H–NMR peak at 5.7 ppm, ascribed to hydride abstraction. By comparison to small molecules, we were confident that we correctly assigned both the FTIR and $^1$H–NMR peaks. It was unlikely that the carboxylic acid resulted from hydrolysis of the persulfate-initiated end groups because we observed the acid fluoride peak by FTIR for AIBN-initiated polymers. For greater certainty of the $^1$H–NMR assignment, we prepared poly(Ph-TFVE) by bulk polymerization in the presence and absence of $n$-butanethiol, a chain transfer agent. The $^1$H–NMR spectrum of bulk poly(Ph-TFVE-cta) had a peak at 5.7 ppm, similar to that observed for poly(Et-TFVE) and poly($t$-Bu-TFVE), thereby confirming the hydrogen abstraction mechanism in the synthesis of poly(Et-TFVE) and poly($t$-Bu-TFVE).

Although we had clearly demonstrated the presence of hydride formation during the polymerization of Et-TFVE and $t$-Bu-TFVE, we were not certain from where hydrogen was being extracted. As was shown in Figure 4, it was likely that the propagating radical abstracted hydrogen from the pendant hydrocarbon ether group, leading to hydride formation and possibly low molar mass polymers. However, it was not clear which pendant group or what parts of the pendant group were undergoing hydrogen abstraction. If hydrogen was abstracted from the pendant group adjacent to the propagating radical, part of the pendant group may be incorporated into the backbone of the polymer. Alternatively, if hydrogen was abstracted from a pendant group further away from the propagating radical, or a pendant group in a separate molecule, branched polymers may be formed.

Since hydrogen abstraction was observed only in the polymerization of poly(Et-TFVE) and

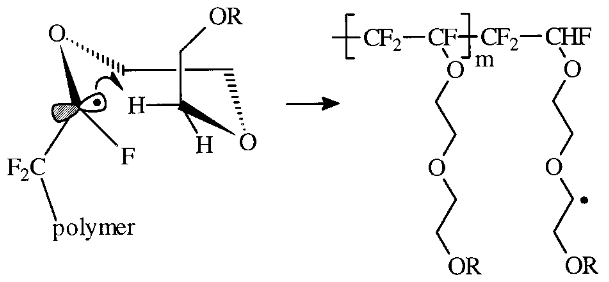

**Figure 6.** Hydrogen abstraction from the pendant group adjacent to the propagating radical. R is ethyl or *t*-butyl.

poly(*t*-Bu-TFVE), and not in the polymerization of poly(Ph-TFVE), this suggested that hydrogen was abstracted from the pendant group adjacent to the propagating radical, at a position that was six, and possibly more, atoms away. Although all three polymers have an oxygen atom at the fifth position of the pendant group, at the sixth position, poly(Ph-TFVE) has an aromatic ring, whereas poly(Et-TFVE) and poly(*t*-Bu-TFVE) have methylene groups. The difference at position six, and possibly beyond, likely accounts for the source of hydrogen; otherwise, hydrogen abstraction would have been evident in the poly(Ph-TFVE). Figure 6 represents a possible mechanism for hydrogen abstraction at the methylene group. Although others have observed hydrogen abstraction from additives or solvents in the polymerization of fluorinated/perfluorinated trifluorovinyl ethers, to the best of our knowledge, this is the first example of hydrogen abstraction from the pendant group of the trifluorovinyl ether polymer itself.

Under identical reaction conditions, by comparison to polystyrene standards, the molar masses of poly(Et-TFVE) and poly(*t*-Bu-TFVE) were lower than that of poly(Ph-TFVE); however, this comparison is limited due to the different chemical compositions of the polymers. The polymerization mechanism of poly(Et-TFVE) and poly(*t*-Bu-TFVE) involved both hydrogen abstraction and $\beta$-scission, whereas poly(Ph-TFVE) involved only $\beta$-scission. The $^1$H–NMR data, used to calculate molar mass based on end-group analysis, indicated that the radical formed as a result of hydrogen abstraction continued to propagate. This may account for the greater polydispersity observed for poly(Et-TFVE) and poly(*t*-Bu-TFVE) relative to poly(Ph-TFVE). Since the radical formed as a result of hydrogen abstraction may not always continue to propagate, hydrogen abstraction may result in termination and thereby account for the apparently lower molar masses of poly(Et-TFVE) and poly(*t*-Bu-TFVE) relative to poly(Ph-TFVE), as observed by GPC.

The yield of poly(Et-TFVE) was greater than that of poly(Ph-TFVE) under similar polymerization conditions. Although the yield of poly(Et-TFVE) was unaffected by temperature, that of poly(Ph-TFVE) seemed to be temperature-dependent. In addition, the yield of poly(Ph-TFVE) increased with initiator concentration. These results suggest that the initiation of Ph-TFVE is less efficient than that of Et-TFVE and may result from a difference in monomer partitioning in the aqueous phase.

## CONCLUSIONS

We have successfully synthesized three new polymers, poly(Et-TFVE), poly(*t*-Bu-TFVE), and poly(Ph-TFVE), by a redox-initiated aqueous emulsion polymerization and determined optimal conditions for obtaining higher molar mass polymers by varying temperature and initiator concentration. We found that $\beta$-scission limited molar mass for all three polymers, whereas hydrogen abstraction was evident for only poly(Et-TFVE) and poly(*t*-Bu-TFVE). The results suggested that the structure of the polymer's pendant group determined whether hydrogen abstraction occurred. Poly(Et-TFVE) and poly(*t*-Bu-TFVE) were viscous liquids at room temperature, with low $T_g$'s, suggesting their potential use in solventless-coating applications. Although not probed herein, de-protection of the *t*-butyl group of poly(*t*-Bu-TFVE) will facilitate further modification, such as with crosslinking agents. Poly(Ph-TFVE) had a higher $T_g$ due to the increased rigidity of the pendant group and may be used as an additive or alone. Future studies will investigate alternate methods of polymerization, properties, and potential applications for these novel fluoropolymers.

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