Preparation of segmented semifluorinated poly(aryl ether)s from aromatic trifluorovinyl ethers and oligo(ethylene glycol)s

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ABSTRACT: A series of new segmented semifluorinated polyaryl ethers (PAEs) containing a biphenyl segmented by semifluorinated oligo-ethylene (SFE) units were prepared by nucleophilic addition of a commercial oligo(ethylene glycol)s to 4,4′-bis(4-trifluorovinyloxy)bi-phenyl. These new thermoplastics were characterized by ^{1}H and F^{19} nuclear magnetic resonance (NMR) and attenuated total reflectance Fourier transform infrared (ATR-FTIR). Gel permeation chromatography (GPC) analysis displayed number average molecular weights (M_ns) from 9000 to 13,000. Thermal properties of the polymers were studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). DSC chromatograms displayed glass transition temperatures (T_gs) from 11 to 1°C. The onsets of degradations were observed by TGA analysis between 313 to 333°C in air and 326 to 363°C in nitrogen, respectively. A second onset of degradation was observed from 452 to 470°C for all polymers. In addition, crystalline morphologies were studied by tapping mode atomic force microscopy (TM-AFM) and showed needle-like crystallites. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41798.

INTRODUCTION

Poly (aryl ether)s (PAEs) attained a lot of commercial success due to their high thermal stability, hydrolytic stability, and superior compatibility with commodity polymers such as polystyrene. This led to a multitude of engineered plastics such as poly(phenylene oxides) (PPOs), poly(ether ether ketone)s (PEEKs), and poly(ether sulfone)s (PESs). Despite these attractive features, PAEs typically have a high melt viscosities and high melt temperatures (T_ms), which leads to oxidation and gelation during processing.[1,2] Recent structural modifications have led to solution processable polymers with high glass transition temperatures (T_gs) and excellent thermal stability.[3] For example, semifluorinated poly(aryl ethers) polymerized from 9,10-bis-(4-fluoro-3-trifluoromethylphenyl) anthracene and 2,7-bis-(4-fluoro-3-trifluoromethylphenyl) fluorene monomers showed high thermal stability, high glass temperatures, and were solution processable.[4] Recently, PAEs containing naphthyl moieties were amorphous and soluble in common organic solvents.[5–7]

Perfluorocyclobutyl (PFCBs) aryl ether polymers and fluoro-ethylene/vinylene aryl ether (FAVE) polymers are two unique classes of semifluorinated PAEs.[8,9] Both polymers are prepared by step-growth polymerization of aromatic trifluorovinyl ether (TFVE) monomers and are illustrated in Scheme 1. PFCB aryl ether polymers, Scheme 1(a), are prepared by thermally induced [2+2] cycloaddition of aromatic TFVE ether monomers. While, FAVE polymers are prepared by nucleophilic addition of aryl bis-diols to TFVE monomers, Scheme 1(b). FAVE polymers can be selectively enriched with difluorovinylene (CF=CF) or hydrofluoroethylene (CHFCF2) groups by utilization of sodium hydride or cesium carbonate as a base, respectively.

PFCB aryl ether and FAVE polymers are typically solution and melt processable, amorphous, have excellent optical clarity, and are tunable through the utilization of (co)monomers.[8–10] PFCB aryl ether polymers have been investigated for many applications including polymer electrolytic membranes (PEMs) for fuel cells,[11,12] optical waveguides in telecommunications,[13] and
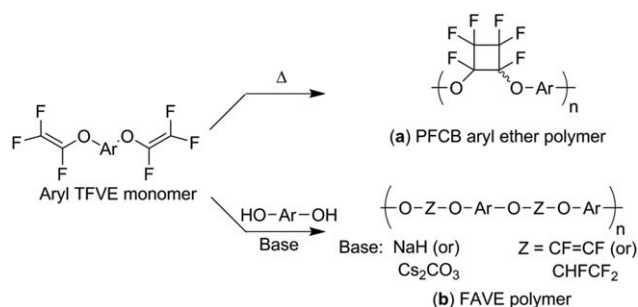
Scheme 1. Polymerization pathways to semifluorinated aromatic ether polymers from aromatic TFVE monomers via thermally induced [2+2] cycloaddition to produce PFCB aromatic ether polymers (a) or nucleophilic addition of bis-phenols to afford FAVE polymers (b).[8–10]

liquid crystalline (LC) polymers for displays.[14] FAVE polymers have been tailored for proton electrolyte membranes (PEMs)[15] and ion sensing.[16–19]

Alternatively, segmented PAEs are being studied as novel thermoplastic materials. Guiver et al. recently prepared segmented copoly(arylene ether sulfone)s with sulfonated pendent phenyls as new PEMs for fuel cells.[20] Another class of segmented PAEs, segmented poly(aryl ether ketone-co-sulfone)s (PAEKs) have been widely studied as high performance materials due to high T_gs and high thermal stability.[21] Poly(arylidene-ether)s containing cyclopentanone and linked with polymethylene spacers displayed thermotropic liquid crystalline properties.[22] In addition, hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) (BAF PAES) segmented with polydimethylsiloxane (PDMS) block copolymer (BAF PAES–b–PDMS) showed thermal stabilities as high as 450°C and can be solution casted with THF.[23] Despite these attractive features, many segmented PAEs suffer from the same processability problems of their nonsegmented counterparts.

The introduction of semifluorinated ether (SFE) unit to PAEs should render solution processable PAEs. In this paper we prepare a series of new segmented semifluorinated PAE from step growth addition of oligo(ethylene glycol)s to 4,4′-bis(4-trifluorovinyloxy)biphenyl. These polymers differ in the flexible SFE units; while maintaining a rigid biphenyl segment from the aromatic TFVE monomer.

EXPERIMENTAL

Materials
4,4′-bis(4-trifluorovinyloxy)biphenyl was donated by Tetramer Technologies, L.L.C. and is commercially available through Oakwood Chemicals. All other chemicals and solvents were obtained from Sigma-Aldrich. Ethylene glycol (2a), diethylene glycol (2b), triethylene glycol (2c), tetraethylene glycol (2d) were stirred in magnesium sulfate for 30 minutes and filtered using 0.45 μm filter. All diols were further dried at 65°C under high vacuum for 6 h and stored with 3 Å molecular sieves. All reactions were carried out in flamed dried glassware in nitrogen atmosphere. All polymers (3a-c) were dried at 65°C under high vacuum before any analysis. Solvents were purified and dried according to well-known procedures.[24]

Characterization
[1]H- and ^{19}F-nuclear magnetic resonance (NMR) spectra were obtained from a JOEL Eclipse+ 300. DMSO-d_6 was used as a solvent and all chemical shifts are reported in parts per million (δ ppm). ^{1}H- and ^{19}F-NMR were internally referenced to tetramethylsilane (0 ppm) and CFCl$_3$ (0 ppm), respectively.

All IR spectra were acquired neat from an attenuated total reflectance Fourier transform infrared (ATR-FTIR) utilizing a ThermoNicolet Magna IR 550 FTIR spectrophotometer. All gel permeation chromatography (GPC) data were performed using a Waters 2690 alliance system. CHCl$_3$ was utilized as an eluent. Waters 2690 Alliance system was equipped with a Waters 2998 photodiode array detector, Mixed-I low molecular weight, and Mixed-I high molecular weight columns. All columns were obtained from viscotek and maintained at 35°C during all analysis. All polymers were compared with polystyrene standards.

AFM images were obtained by tapping mode from a Veeco Dimension 3100 equipped with a Nanoscope IIIa controller (Veeco inc.) and 40 n/M tip with a radius of 10 nm (Mikromash). The scan rate was 1 Hz.

Differential scanning calorimetry (DSC) analysis were performed using a TA Q1000 instrument. The DSC was calibrated with indium standards. All samples were prepared under nitrogen. DSC analysis were performed at a rate of 10°C/min from −70 to 220°C. All transition temperature were measured from the second heating cycle. Crystallization temperatures (T_cs), melting temperatures (T_ms), and glass transition temperatures (T_gs) were measured at the maximum exothermic peak, endothermic minimum, and the half-height of the heat capacity jump, respectively.

Thermal gravimetric analysis (TGA) were executed using a Mettler-Toledo 851. All TGA analysis were performed at 10°C per min to 700°C. Quench-cool methods were performed by heating the **3a** in a DSC pan to 200°C. The pan was quenched in liquid nitrogen and reintroduced to the DSC at −50°C and 0°C for first and second quench-cool, respectively. Similar methods have been used to enhance T_gs for other polymers.[25]

Preparation of Segmented Semifluorinated Poly(aryl ether)s
Preparation of 3a. 4,4′-bis(4-trifluorovinyloxy)biphenyl, **1**, (1.6 mmol, 558 mg) and dried ethylene glycol, **2a**, (1.6 mmol, 100 mg) were added to 5-mL round bottom flask containing 0.5 mL of anhydrous DMF and a magnetic stir bar. The mixture was heated at 80°C under nitrogen purge and anhydrous cesium carbonate (0.8 mmol, 260 mg) was added. After 24 h, the reaction mixture was added drop wise to water, filtered, and washed with hexanes. After drying in the vacuum oven at 65°C for 24 h, polymer **3a** was afforded as a white powder (499 mg, 76%). ^{1}H-NMR (DMSO-d_6, 300 MHz, δ): 4.11-4.12 (m, 4H), 6.50 (broad dt, $J=56.8$ 1H, CHFCF$_2$), 7.21 (d, $J=9.0$ Hz, 4H), 7.61 (d, $J=9.0$ Hz, 4H); ^{19}F-NMR (DMSO-d_6, 283 MHz, δ): −88.3 and 87.8 (AB pattern, $J=141.5$ Hz CHFCF_2), −141.0 (d, $J=56.6$, CHFCF$_2$). ATR-FTIR (neat): ν 2965 (m), 1607 (s), 1497 (s), 1124 (s), 739 (w). Molecular weight and selected properties are reported in Table I.

Preparation of 3b. 4,4′-bis(4-trifluorovinyloxy)biphenyl, **1**, (326 mg, 0.94 mmol), dried diethylene glycol, **2b**, (100 mg, 0.94

Table I. Selected Properties of Polymers **3a** to **3d**

Polymer	x	M_n^a	M_w^a	M_w/M_n^a	$T_g (°C)^b$	$T_m (°C)^b$	$T_c (°C)^b$
3a	1	9,000	19,800	2.2	–	189	185
3b	2	10,000	17,000	1.7	11	63	27
3c	3	12,000	19,200	1.6	11	–	–
3d	4	13,000	22,100	1.7	−1	–	–

[a] Determined by gel permeation chromatography (GPC) using $CHCl_3$ as an eluate and polystyrene standards.
[b] Determined by DSC under nitrogen (10°C/min).

mmol), anhydrous cesium carbonate (154 mg, 0.47 mmol), and 0.5 mL of anhydrous DMF were used according to the procedure outlined in the preparation of **3a**. Polymer **3b** was isolated as a white solid (349 mg, 82%). ^{1}H-NMR (DMSO-d_6, 300 MHz, δ): 3.65-3.71 (m, 4H), 4.11-4.12 (m, 4H), 6.50 (broad dt, J=56.8 2H, C*H*FCF$_2$), 7.21 (d, J = 9.0 Hz, 4H), 7.61 (d, J = 9.0 Hz, 4H); ^{19}F-NMR (DMSO-d_6, 283 MHz, δ): −88.3 and 87.8 (AB pattern, J = 141.5 Hz CHFC*F*$_2$), −141.0 (d, J = 56.6, CH*F*CF$_2$), ATR-FTIR (neat): v 2877 (m), 1607 (s), 1497 (s), 1121 (s), 738(w). Molecular weight and selected properties are reported in Table II.

Preparation of 3c. 4,4′-bis(4-trifluorovinyloxy)biphenyl, **1**, (231 mg, 0.666 mmol), dried triethylene glycol, **2c**, (100 mg, 0.666 mmol), anhydrous cesium carbonate (108 mg, 0.333 mmol), and 0.2 mL of anhydrous DMF were used according to the procedure outlined in the preparation of **3a**. Polymer **3c** was isolated as a white semi-solid (295 mg, 89%). ^{1}H-NMR (DMSO-d_6, 300 MHz, δ): 3.48-3.56 (m, 8H), 4.08-4.10 (m, 4H), 6.50 (broad dt, J=56.8 2H, C*H*FCF$_2$), 7.21 (d, J = 9.0 Hz, 4H), 7.62 (d, J = 9.0 Hz, 4H); ^{19}F-NMR (DMSO-d_6, 283 MHz, δ): −88.3 and −87.8 (AB pattern, J = 141.5 Hz CHFC*F*$_2$), −141.0 (d, J = 56.6, CH*F*CF$_2$), ATR-FTIR (neat): v 2875 (m), 1607 (s), 1497 (s), 1119 (s), 734(w). Molecular weight and selected properties are reported in Table I.
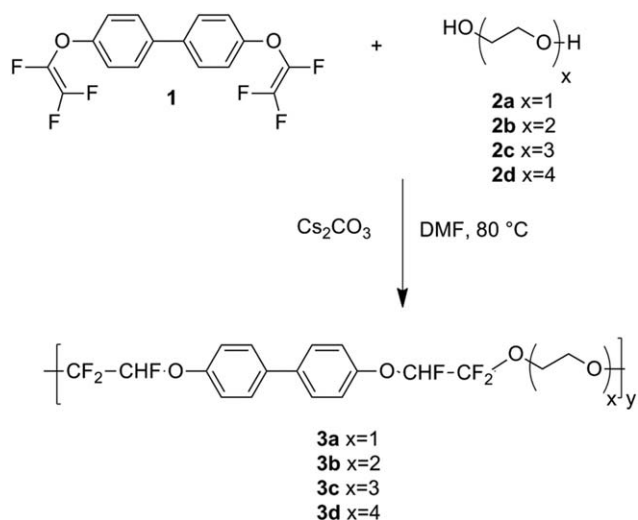
Preparation of 3d. 4,4′-bis(4-trifluorovinyloxy)biphenyl, **1**, (178 mg, 0.51 mmol), dried tetraethylene glycol, **2d**, (100 mg, 0.51 mmol), anhydrous cesium carbonate (84 mg, 0.26 mmol), and 0.17 mL of anhydrous DMF were used according to the procedure outlined in the preparation of **3a**. Polymer **3d** was isolated as a

Scheme 2. Polymerization of segmented semifluorinated polyaryl ethers (PAEs).

white semi-solid (204 mg, 73%). ^{1}H-NMR (DMSO-d_6, 300 MHz, δ): 3.48-3.64 (m, 12H), 4.08-4.10 (m, 4H), 6.50 (broad dt, J=56.8 2H, C*H*FCF$_2$), 7.22 (d, J = 9.0 Hz, 4H), 7.65 (d, J = 9.0 Hz, 4H); ^{19}F-NMR (DMSO-d_6, 283 MHz, δ): −88.3 and 87.8 (AB pattern, J = 141.5 Hz CHFC*F*$_2$), −141.0 (d, J = 56.6, CH*F*CF$_2$), ATR-FTIR (neat): v 2875 (m), 1607 (s), 1496 (s), 1120 (s), 733(w). Molecular weight and selected properties are reported in Table I.

RESULTS AND DISCUSSION

Polymerization Conditions

Step-growth polymerization of segmented semifluorinated polyaryl (ether)s (PAEs) were achieved using commercially available diols (Scheme 2, 2**2a-d**) and 4,4′-bis(4-trifluorovinyloxy)biphenyl (Scheme 2, 1**1**) in 1 : 1 molar ratios. Polymerizations were performed using anhydrous cesium carbonate at 50 mol % of the diol monomer in anhydrous DMF at 80°C for 24 h. Cesium carbonate was selected as base due to its higher (co) monomer conversion rates compared to sodium hydride.[26,27] All copolymers were precipitated in water and washed with hexanes. Polymers were dried by high vacuum and isolated as a white powder (**3a**) to a white semi-solid (**3d**) in moderate yields from 73 to 89%. Gel permeation chromatography (GPC) revealed number average molecular weights (M_ns) from 9000 to 13,000 and polydispersities (M_w/M_n) from 2.2 to 1.6, Table II. All polymers were soluble in dichloromethane, chloroform, DMF, DMSO, and THF; polymers **3c** and **3d** showed additional solubility in acetone, and methanol. All polymers were film-forming by solution casting. **3a** formed an opaque brittle film. All other polymers, **3c** to **3d**, formed clear films by solution casting. **3c** and **3d** formed tacky films.

Optimization of polymerization was achieved using ethylene glycol (**2a**) and 4,4′-bis(4-trifluorovinyloxy)biphenyl (**1**) as a model compound. Initial polymerizations had low yields and higher polymer dispersities (M_w/M_n) by GPC analysis (Figure 2). Further drying of **2a** before polymerization led to stoichiometric amounts, a higher yield, and a lower polydispersity. Polymerization conditions were further improved by varying the amount of
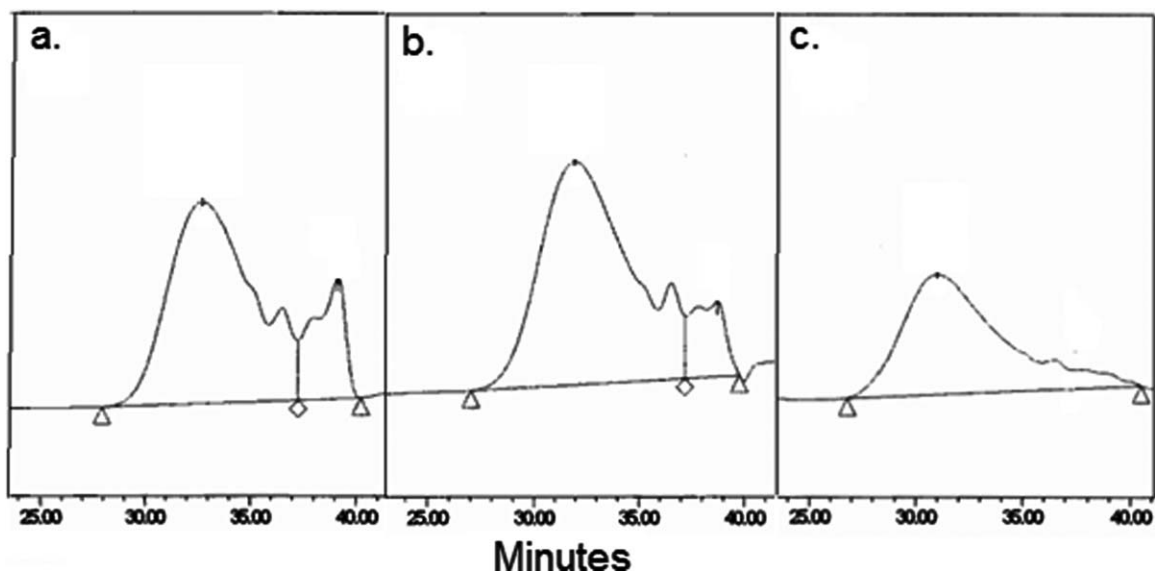
Table II. Summary of Thermal Decomposition of Polymers **3a-d**

Polymer	wt % SFE[a]	in N$_2$ T_d (°C)[b] Initial	T_d (°C)[b] Initial, Second	Initial weight loss (%)
			In air	
3a	62	363	320, 452	62
3b	66	334	333, 475	61
3c	70	325	313, 450	64
3d	72	326	316, 441	67

[a] Semifluorinated ether (SFE) was measured by ^{1}H NMR using the ratio of aryl to ether repeat unit.
[b] Determined by TGA at 10°C/min from 0 to 700°C. Initial refers to onset of degradation and second refers to second onset of degradation.

Figure 1. Gel permeation chromatogram of polymer (**3a**) prepared in: (a) 0.2 wt %, (b) 0.1 wt %, and (c) 0.08 wt % of DMF.

DMF to maximize the M_n and lower oligomeric product. Figure 1 displays gel permeation chromatograms (GPCs) using 0.2 wt %, 0.1 wt %, and 0.08 wt % of DMF to 4,4'-bis(4-trifluorovinyloxy)-biphenyl (**1**), and ethylene glycol (**2a**) monomers. GPC analysis showed that an increase in DMF led to a bimodal distribution and more oligomeric product as expected.
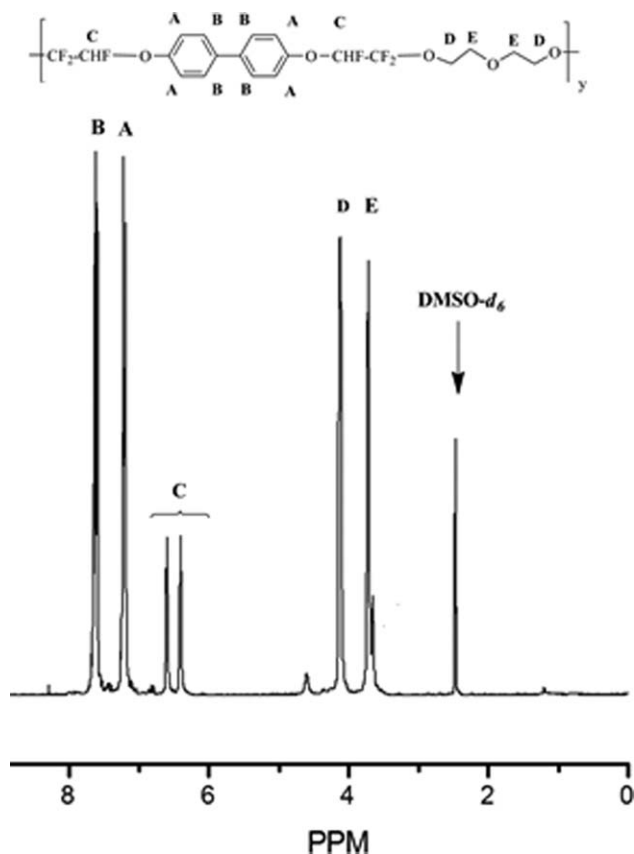
Characterization

All polymers were characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR), ^{19}F nuclear magnetic resonance (NMR), and ^{1}H-NMR. ^{1}H-NMR spectrum of **3b** in DMSO-d_6 is shown in Figure 2. Aromatic protons are illustrated as doublets at 7.21 [Figure 2(A)] and 7.65 [Figure 2(B)] ppms. A broad doublet of triplets are located at 6.50 ppm [Figure 2(C)] are from hydrofluoroethylene (CHFCF$_2$) proton. Ether protons alpha and beta to hydrofluoroethylene are shown as 4.11−4.12 [Figure 2(D)] ppm and 3.65 to 3.71 [Figure 2(E)] ppm, respectively. All other protons of (–CH$_2$-CH$_2$-O-)$_n$ are seen as a multiplet from 3.48 to 3.64 ppm. Integration ratio of aromatic protons to protons diols agree with 1 : 1 feed ratios for both monomers.

^{19}F-NMR spectrum of **3b** in DMSO-d_6 is shown as Figure 3. Hydrofluoroethylene fluorines can be seen as a AB pattern at

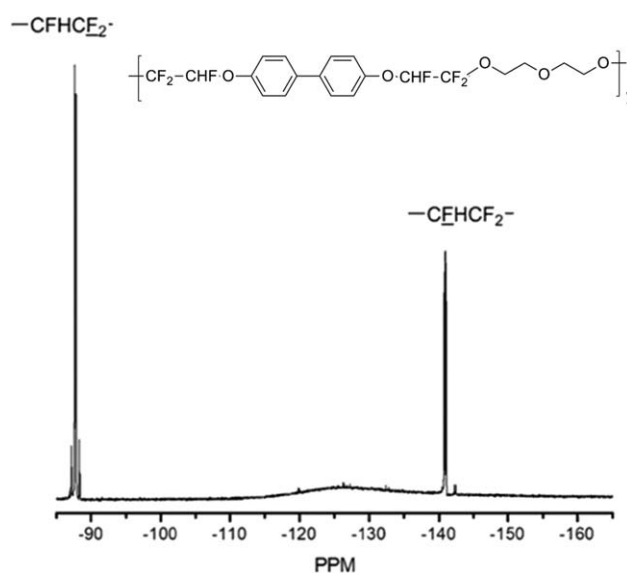**Figure 2.** ^{1}H-NMR spectrum of **3b** in DMSO-d_6.

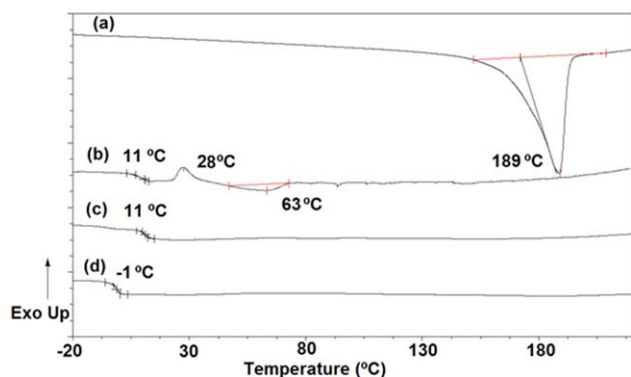**Figure 3.** F[19]-NMR spectrum of **3b** in DMSO-d_6.

Figure 4. DSC thermograms of (a) **3a**, (b) **3b**, (c) **3c**, and (d) **3d** performed at 10°C/min under nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. TGA thermogram overlay of **3a** and **3d** in nitrogen and air.

88.3 and 87.8 ($J = 141.5$ Hz, CHFCF_2) ppm and as a doublet at -141.0 ppm ($J = 56.6$, CHFCF$_2$). ^{19}F-NMR spectrum also revealed the slight appearance of AMX pattern associated with the 4,4′-bis(4-trifluorovinyloxy)biphenyl monomer (**1**), indicating a high consumption of trifluorovinyl ether (TFVE).

Thermal Properties

Table I shows differential scanning calorimetry (DSC) analysis of polymers **3a** to **3d**. Figure 4 shows thermograms of polymers **3a** to **3d**. Glass transition temperatures (T_gs) for amorphous, semifluorinated PAEs were from 11 to -1°C. Although an increase of ether units from three to four led to a decrease in T_g, this trend was not exhibited in **3b** to **3c**. Polymer **3a** exhibited no T_g by initial DSC analysis. To observe the T_g of **3a** a quench-cooling method was applied.[25] Polymer **3a** was heated to 200°C in a DSC pan, removed, and quickly added to liquid nitrogen to maximize amorphous structure and slow crystallization. The quench-cooling method was unsuccessful in obtaining a T_g value.

Polymer **3a** exhibited a melt transition temperature (T_m) of 189°C by DSC. No thermally induced crystallization was observed on the heating cycle of **3a**, but upon cooling a crystallization transition (T_c) was observed at 185°C. **3b** displayed a T_c at 27°C and a T_m at 63°C. Thermograms of **3c** and **3d** polymers did not produce a T_m or T_c indicating that the increasing the ether units imparts chain flexibility producing exclusively amorphous polymers.

Degradation Analysis

Polymer thermal stability was studied by thermal gravimetric analysis (TGA) in air and nitrogen. Initial and second thermal degradation (T_d) values with the corresponding weight percent of the semifluorinated ether (SFE) units are reported in Table II. SFE units were determined by ^{1}H-NMR using the ratio of the aryl protons to the ether protons. All polymers displayed a two-step weight loss in air and a one-step weight loss in nitrogen by TGA analysis. Polymer **3a** has an onset of degradation of 363°C in nitrogen. In air, **3a** has an onset of degradation of 320°C for the initial weight loss followed by a second weight loss at 452°C. Initial degradation in this case corresponds to the weight percent of the SFE unit. Polymers **3b** to **3d** showed an initia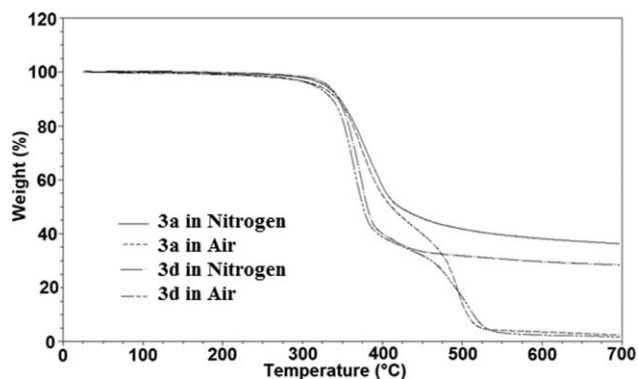l weight loss in air that closely corresponds to thermal degradation of SFE and then the degradation of aromatic portion. An overlay of TGA thermograms of **3a** and **3d** in nitrogen and air can be seen in Figure 5. Semifluorinated polyethers are well known for thermal stability due to the high bond dissociation energy of the C—F bond (116 kcal/mol) compared with the bond dissociation energy of the C—H bond (98 kcal/mol).[26] Polymers still degrade by autoxidation of ether units in air,[27] which explains the two-step weight loss of polymers **3a-d** in air.

Surface Morphology

Surface morphology of polymers **3a** and **3b** were studied by tapping mode atomic force microscopy (TM-AFM) due to their crystalline nature. AFM phase and height images are shown on the top and bottom of Figure 6. Needle-like crystallites were observed quite well in height images of **3a** [Figure 6(A)] and **3b** [Figure 6(B)]. Height images showed small crystallite domains with larger areas of roughness. This formation may be due to phase separation of aromatic segment. Needle or ribbon morphologies are commonly reported with many segmented polyurethanes, poly (ether amides), and PAEs.[23,28–30] Crystallization of these polymers are due to aggregation of the hard chain segments and is suspected to be occurring with these new semifluorinated PAEs. In addition, the crystallite morphology observed in the phase images of **3b** are less continuous than **3a**. This may be due to the much larger SFE units.

CONCLUSIONS

Semifluorinated polyaryl ethers (PAEs) were successfully prepared via nucleophilic addition of a oligo(ethylene glycol)s to 4,4′-bis(4-trifluorovinyloxy)biphenyl to produce a novel series of polymers containing a new fluoroethylene alkyl bond. ^{1}H-NMR showed a one to one diol to 4,4′-bis(4-trifluorovinyloxy)-biphenyl ratio, DSC thermograms revealed that crystallinity depends on the diol monomer utilized during polymerization and in one case a high melting point of 189°C was obtained. In addition, glass transition temperatures from 11 to -1°C were observed for all polymers. TGA analysis displayed a step-wise degradation in air that closely corresponded to less thermally stable ether. In the AFM phase and height images, needle-like crystalline morphologies were observed indicating phase separation. These polymers have a unique solubility and significantly lower thermal transitions that are not usually associated with
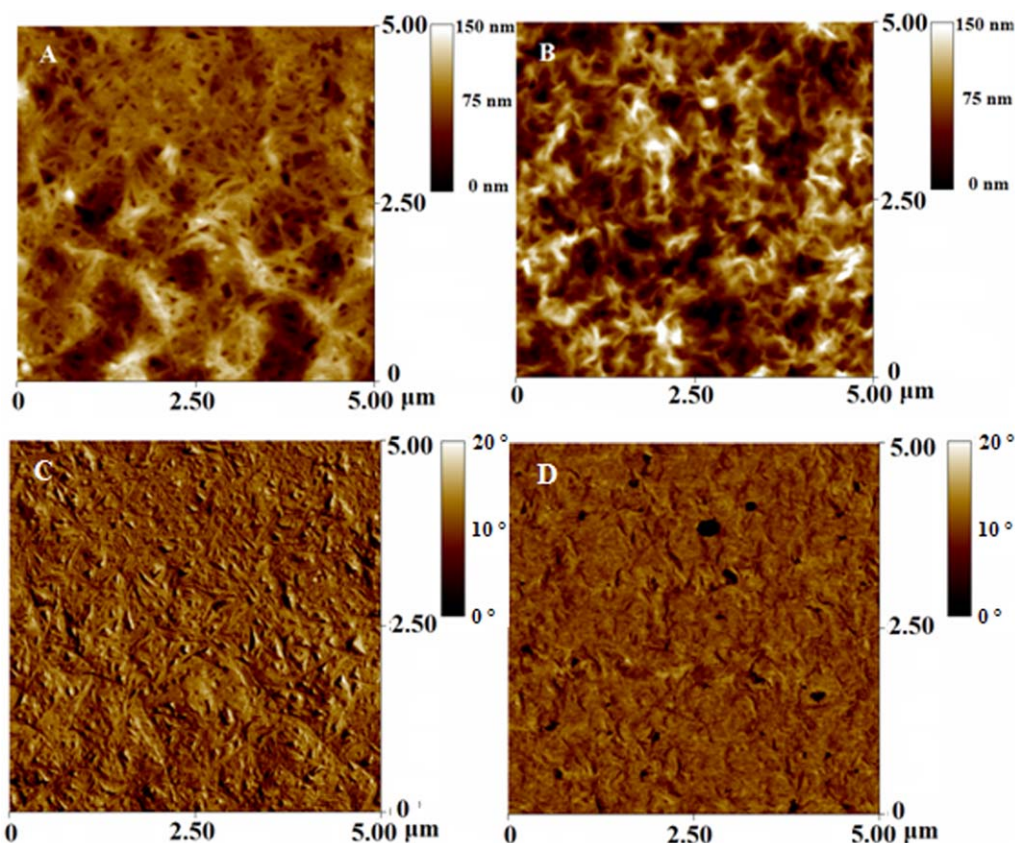
Figure 6. AFM height (top) and phase (bottom) images of solution cast films of **3a** (a,c) and **3b** (b,d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PAEs. These thermoplastics could possibly be utilized as a plasticizer for PAEs.

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