High Glass-Transition Temperature and Organosoluble Novel Arylene Ether Polymers

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ABSTRACT: Three novel 2-trifluoromethyl-activated bisfluoro monomers have been synthesized successfully using a Suzuki-coupling reaction of 4-fluoro-3-trifluoromethyl phenyl boronic acid with 4,4′-dibromo-*p*-terphenyls with varied phenyl substitution on the middle phenylene ring. Three monomers were converted to a series of phenyl substituted poly(arylene ether)s by nucleophilic displacement of the fluorine atoms on the terminal benzene ring, with several bisphenols. The polymers obtained by displacement of the fluorine atoms exhibit weight-average molecular weight up to 1.44×10^5 g/mol in GPC. Thermal analysis studies indicated that these polymers did not show melting endotherms but did show ultrahigh glass-transition temperature (T_g) values up to 332 °C in differential scanning calorimetry (DSC) and outstanding thermal stability up to 671 °C for 5% weight loss in TGA under nitrogen atmosphere. The polymers are soluble in a wide range of organic solvents: tetrahydrofuran (THF), chloroform ($CHCl_3$), *N*-methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF), toluene, etc., and are insoluble in dimethyl sulfoxide (DMSO) and acetone at room temperature. Transparent and flexible films were easily prepared by solution casting from a chloroform solution of each of the polymers. The UV absorption spectra of thin films showed no absorption in the visible light region of the spectrum, suggesting a good application to optical transparent materials in the visible light region of the spectrum.

Introduction

Poly(arylene ether)s (PAEs)[1−6] have been attracting a considerable amount of attention due to their excellent physical properties, such as high level of strength, high glass transition temperature, good processability, good electrical properties, thermo-oxidative stability, and chemical resistance.

Most success in preparation of PAEs is achieved by nucleophilic displacement reactions of dihalo or dinitro compounds with alkali metal bisphenolates. Nucleophilic aromatic substitution occurs when the leaving group is activated by electrowithdrawing substituents. Examples of three commercial engineering plastics prepared this way are polyethersulfone,[7,8] polyetherimide,[9] and polyetheretherketone.[10,11] The polyethersulfone involves displacement of halo groups activated by SO_2, usually referred to as a polysulfone even though ether linkages are formed in the polymerization reaction. With the polyetherimide, displacement of the nitro groups is promoted by the electron-withdrawing imide. The polyetherketone, involving displacement of halo groups activated by ketone, provides a polymer called polyetheretherketone (PEEK). On the basis of the common characteristics of the stabilization of negative charges developed on the aryl moiety in the transition state of the nucleophilic halogen displacement reaction through a Meisenheimer complex,[12] which lowers activation energy for displacement, Hedrick et al.[1] reported that perfluoroalkyl groups,

either in a pendent position or in the main chain, activate fluoro or nitro displacement by phenoxides.

Panel substrates used for conventional display panels have been made exclusively of inorganic glass, and plastic panels have not yet been put to practical use for a number of reasons. One of the major reasons is that plastic substrates for displays[13−15] must satisfy the following requirements at the same time: (1) to be optically transparent to light in the visible region of the spectrum; (2) to be impervious to moisture, and (3) to be sufficiently stable to withstand the manufacturing thermal processes with high temperatures up to 300 °C.

Because of rapid advancement in the microelectronic industry, the enhanced performance of tightly packed circuitry has become an increasingly relevant issue. Decreasing the dielectric constant, while maintaining thermal and mechanical properties of the thin film interlayer dielectric materials,[16,17] is highly desirable. Fluorine containing polymers[10,18,19] are of special interest because of their possible use as gas selective membranes and their enhanced flame resistance, low dielectric constant, and remarkably low water absorption. The trifluoromethyl groups in the polymer backbone enhance polymer solubility without any forfeiture of thermal stability. They also increase the glass transition temperature with a concomitant decrease of crystallinity. This bulky group also serves to increase various properties of polymers, including gas permeabilities[12] and electrical insulating properties. Because of all these interesting properties of the fluorinated polymers, considerable attention has been devoted to the preparation of new classes of fluorine-containing polymers.

In this paper, we report the successful synthesis of the bisfluoro monomers shown in Scheme 1 via a Suzuki cou-

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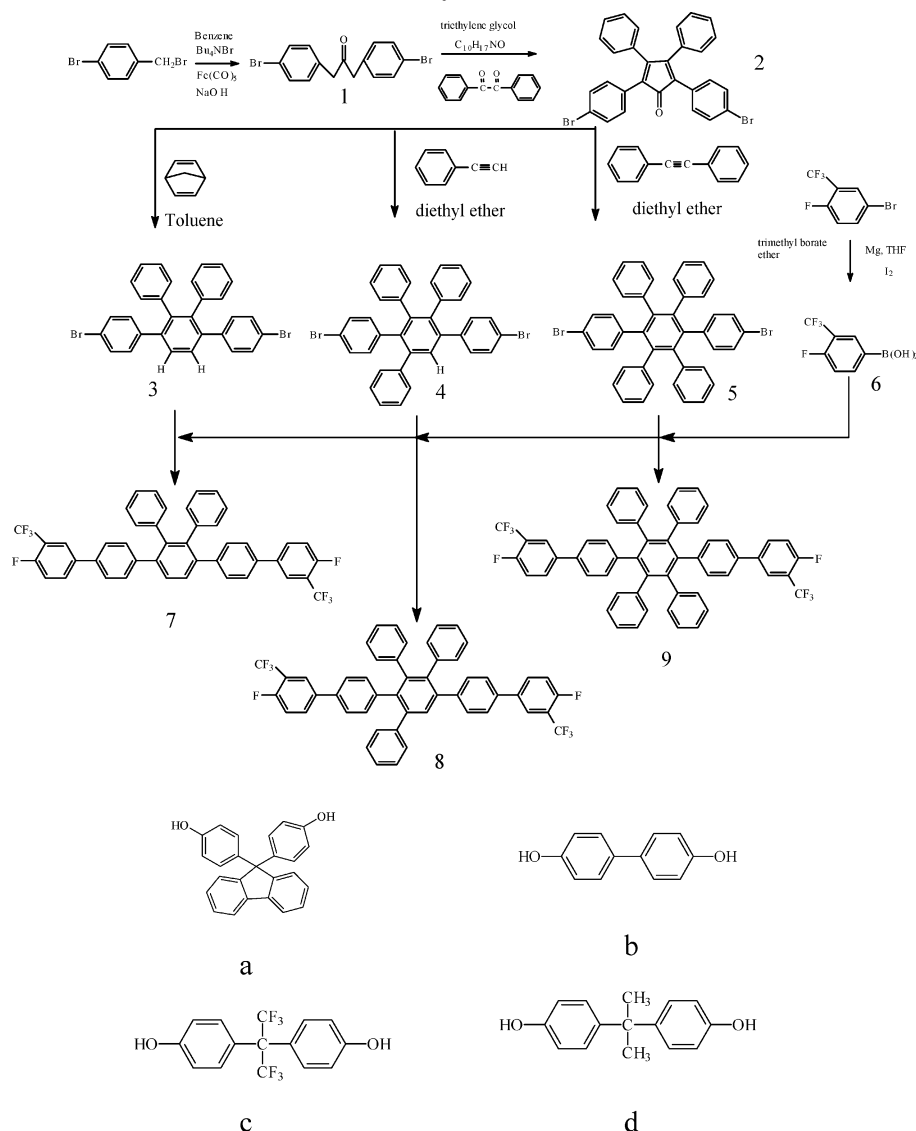† National Sun Yat-Sen University.
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Scheme 1. The Synthesis of Monomers

pling[20,21] and subsequent utilization of these monomers in a nucleophilic aromatic substitution polymerization with different bisphenols,[12,22−24] as well as their characterization.

Experimental Section

Characterization. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were collected on a Bruker AM-300WB spectrometer in chloroform-*d* as solvent and tetramethylsilane (TMS) as the internal standard. UV spectra were recorded by a DMS-300 spectrophotometer. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer Pyris 1 system with a Hi-Res thermogravimetric analyzer under a heating rate of 20 °C/min and a nitrogen or air flow rate of 20 cm³/min. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer Pyris 1 system. All melting (Tm) and glass transition (Tg) temperatures were obtained using DSC. Tg was taken from the reflection point of the step transition, while Tm was taken from the maximum of the endothermic peak in the second heating run. Gel permeation chromatography (GPC) analysis was conducted with a Polymer Laboratories HPLC system equipped with Polymer Laboratories ultra Styragel Mixed-D 3, 2, and 1 (7.8 mm i.d. × 300 mm) columns in series using polystyrene as the standard and tetrahydrofuran as the eluent. Optical quality thin films of polymers were obtained by solvent casting from chloroform solutions onto quartz substrates. All the films were dried at 80 °C for 12 h first and then 120 °C for 24 h in vacuum before measurement. Dynamic mechanical analysis (DMA) were per-

formed on a Perkin-Elmer Pyris 1 system with a mechanical thermal analysis controller in the tension mode on thin film samples under a heating rate of 20 °C/min and a frequency of 1 Hz.

Materials. All reagents and solvents were purchased from Aldrich Chemical Co., Merck, Lancaster, Fluoko, or Fisher. Spectroscopic grade dichloromethane was used for all absorption and emission experiments. Diphenyl ether was purchased as dry solvent and used as received. Diethyl ether and tetrahydrofuran (THF) were dried over sodium benzophenone and distilled under argon atmosphere before use. Toluene was dried over CaH and then distilled under argon atmosphere and deoxygenated by purging with argon for 30 min before use in the monomer synthesis. Bisphenols 4,4′-dihydroxybiphenyl, 4,4′-(1-methylethylidenelbisphenol (BPA), 4,4′-(hexafluoroisopropylidene)bisphenol (6F BPA), and 9,9′-bis(4-hydroxyphenyl)fluorene were purchased from Aldrich Chemical Co. and used without further purification. All polymerizations were conducted using standard vacuum-line techniques, and in order to remove water produced by the reaction, a slow stream of argon was passed through the reaction vessel during the course of polymerization.

Monomer Synthesis. For successful preparation of PAEs via nucleophilic displacement reactions of dihalo compounds with alkali metal bisphenolates, the corresponding monomers **7−9** have to be prepared in large quantities and good yields (Scheme 1). The synthetic procedures for monomers **7−9** are provided below. Self-coupling[19] of 4-bromobenzyl bromides with catalyst Fe(CO)₅ and

phase transfer reagent Bu$_4$NBr in an alkali aqueous solution afforded **1** in fair yield, which were cyclized after recrystallization without further characterization. Cyclization of **1** with benzil in a solvent mixture of triethylene glycol, benzyltrimethyl ammonium hydroxide, and methanol gave **2** in fair to good yield. Diels–Alder reactions[25] of cyclopentadienone **2** were carried out with 1.1 equiv of cyclodiene or acetylenes in dry diphenyl ether furnished six-member ring precursors **3–5** in good to excellent yields. Couple reactions of compounds **3–5** were carried out using the Suzuki reaction with 2.3 equiv of compound **6** in solvent mixture of toluene, sodium carbonate aqueous solution (1 M), and tetrakis(triphenyl phosphine) palladium(0) and furnished monomers **7–9** in good to excellent yields. The detailed procedure for each precursor is given separately below.

1,3-Bis-(4-bromophenyl)-propan-2-one (1). To a solution containing 4-bromobenzyl bromide (20.0 g, 80 mmol), 33% NaOH aqueous solution (160 mL), tetrabutylamonium bromide (3.09 g, 9.6 mmol), and toluene (160 mL) were slowly added to iron pentacarbonyl (15.68 g, 80 mmol). The reaction mixture was stirred at room temperature for 6 h. The resultant solution was poured onto icily diluted HCl aqueous solution and extracted with chloroform (3 × 100 mL). The combined organic layers were washed with H$_2$O (3 × 100 mL) and dried over MgSO$_4$. Then the solvent was removed under reduced pressure, and the resultant was purified by column chromatography using hexane as the eluent, which gives compound **1** as a white solid (14.9 g, 50.6%); R_f (ethyl acetate (EAC)–hexane = 1:20) = 0.3. MS (fast atom bombardment, FAB) *m/z* ([ion], rel. intensity): 368.0 ([M$^+$], 20); 195.1 ([M – C$_8$H$_3$BrO]$^+$, 20); 167.0 ([M – C$_7$H$_3$Br]$^+$, 100). ^{1}H NMR (CDCl$_3$): δ(ppm) = 3.68 (s, 4H), 7.00–7.03 (d, 4H), 7.43–7.46 (d, 4H).

2,5-Bis-(4-bromophenyl)-3,4-diphenylcyclopenta-2,4-dienone (2). A reaction mixture containing compound **1** (16.0 g, 43 mmol), 40% benzyltrimethyl ammonium hydroxide methanol solution (6.6 mL), benzil (9.14 g, 43 mmol), and triethylene glycol (70 mL) was stirred at 120 °C for 1 h. The mixture was poured into methanol. The compound **2** was obtained as a black solid (20.7 g, 89%); R_f (EAC–hexane = 1:20) = 0.8. MS (FAB) *m/z* [ion] (rel. intensity): 541.2 ([M$^+$], 100); 513.4 ([M – C$_{28}$H$_{17}$Br$_2$]$^+$, 35); 353.9 ([M – C$_{28}$H$_{17}$]$^+$, 20); 258.1 ([M – C$_{19}$H$_{14}$O]$^+$, 30); 176.6 ([M – C$_{14}$H$_9$]$^+$, 38). ^{1}H NMR (CDCl$_3$): δ(ppm) = 6.88–6.91 (d, 4H), 7.07–7.12 (d, 4H), 7.17–7.22 (m, 4H), 7.25–7.26 (s, 2H), 7.35–7.38 (d, 4H).

4,4″-Dibromo-2′,3′-diphenyl-[1,1′;4′,1″]-terphenyl (3). A reaction mixture containing compound **2** (7.0 g, 13 mmol), bicyclo-(2,2,1)hepta-2,5-diene (2.37 g, 26 mmol), and toluene (45 mL) was stirred at reflux for 24 h. The mixture was poured into methanol. After filtration, the compound **3** was obtained as a white solid (6.0 g, 85%); R_f (EAC–hexane = 1:20) = 0.75. Melting point: 278 °C. MS (*m/z*): 537.9. Anal. Calcd for C$_{30}$H$_{20}$Br$_2$: C, 66.69; H, 3.73; Br, 29.58. Found: C, 65.95; H, 3.95; Br, 30.10. ^{1}H NMR (CDCl$_3$): δ(ppm) = 6.75–6.90 (m, 12H), 6.96–7.02 (m, 8H).

4,4″-Dibromo-2′,3′-5′-triphenyl-[1,1′;4′,1″]-terphenyl (4). A reaction mixture containing compound **2** (5.0 g, 9.2 mmol), phenylacetylene (1.13 g, 11.1 mmol), and diphenyl ether (6 mL) was stirred at 150 °C overnight under nitrogen atmosphere. The mixture was poured into methanol. After filtration, the compound **4** was obtained as a white-gray solid (5.12 g, 90%); R_f (EAC–hexane = 1:20) = 0.7. Melting point: 275 °C. MS (*m/z*): 615.1. Anal. Calcd for C$_{36}$H$_{24}$Br$_2$: C, 70.15; H, 3.92; Br, 25.93. Found: C, 70.60; H, 4.16; Br, 25.24. ^{1}H NMR (CDCl$_3$): δ(ppm) = 6.72–6.90 (m, 16H), 7.11–7.23 (m, 8H).

4,4″-Dibromo-2′,3′-5′-6′-tetraphenyl-[1,1′;4′,1″]-terphenyl (5). A reaction mixture containing compound **2** (5.0 g, 9.2 mmol), diphenylacetylene (2.0 g, 11.1 mmol), and diphenyl ether (3 mL) was stirred at 220 °C for 3 days under nitrogen atmosphere. The mixture was poured into methanol. After filtration, the compound **5** was obtained as a white-gray solid (6.07 g, 96%); R_f (EAC–hexane = 1:20) = 0.7. MS (*m/z*): 691.1. Anal. Calcd for C$_{42}$H$_{28}$Br$_2$: C, 72.85; H, 4.07; Br, 23.08. Found: C, 72.97; H, 4.18; Br, 22.85. ^{1}H NMR (CDCl$_3$): δ(ppm) = 6.67–6.92 (m, 20H), 6.98–7.03 (m, 8H).

4-Fluoro-3-trifluoromethyl Phenyl Boronic Acid (6). Grignard Reagent. To a solution of magnesium (1.94 g, 81 mmol), iodine (0.05 g), and 7 mL of anhydrous THF was slowly added 4-bromo-1-fluoro-2-trifluoromethylbenzene (15.0 g, 61.7 mmol) in 55 mL of anhydrous THF via a dropping funnel under nitrogen atmosphere. During the addition period, the reaction mixture was stirred at reflux for 2 h.

To a solution of trimethyl borate (43.7 g, 421 mmol) in anhydrous ethyl ether (215 mL) was slowly added the above Grignard reagent at −78 °C under nitrogen atmosphere. After complete addition, the reaction mixture was stirred at room temperature overnight. The mixture was poured into an HCl aqueous solution (3 M, 200 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with H$_2$O (3 × 100 mL) and dried over MgSO$_4$. Then the solvent was removed under reduced pressure and the resultant solution was purified by recrystallization twice from hexane. The pure product was obtained as a white solid (9.1 g, 71%). Melting point: 203 °C. MS (*m/z*): 208.7. Anal. Calcd for C$_7$H$_5$F$_4$BO$_2$: C, 40.44; H, 2.42. Found: C, 39.88; H, 2.24.

General Procedure for the Preparation of the Monomers (7–9). Couple reactions of compound **3–5** were carried out using the Suzuki reaction[25] with 2.3 equiv of compound **6** in a solvent mixture of toluene, sodium carbonate aqueous solution (1 M), and tetrakis-(triphenyl phosphine) palladium(0) and furnished monomers **7–9** in good to excellent yields. The detailed procedure for each monomer is given separately below.

Amounts of 1 molar equiv of precursors (**3–5**), 0.03 molar equiv of Pd(PPh$_3$)$_4$, 3.7 molar equiv of Na$_2$CO$_3$ were placed in a flame-dried flask. A proper amount of toluene–H$_2$O (1/1) was added into the reaction vessel. Before the reaction took place, the solution was purged with a slow stream of nitrogen for 10 min and then 2.3 molar equiv of 4-fluoro-3-trifluoromethyl phenyl boronic acid (**6**) was introduced into the solution. The reaction mixture was stirred at reflux for 24 h. The resultant mixture was then passed through a short column packed with silica gel. Evaporation of solvent yields a crude product, which is purified by column chromatography. The above procedure was used in the synthesis of monomers **7–9**.

4,4⁗-Difluoro-3,3⁗-bistrifluoromethyl-2″,3″-bisphenyl-[1,1′;4′,1″;4″,1‴;4‴,1⁗]-pentaphenyl (7). Combination of **3** (4.38 g, 8.1 mmol), **6** (3.90 g, 18.6 mmol), Pd(PPh$_3$)$_4$ (0.28 g, 0.243 mmol), Na$_2$CO$_3$ (3.18 g, 30.0 mmol), H$_2$O (30 mL), and toluene (30 mL) gives **7** as a white solid purified from silica gel column chromatography (4.57 g, 80%). R_f (EAC–hexane = 1:20) = 0.48. MS (FAB) *m/z* (rel. intensity): 706 (100); 707 (53); 708 (16). Anal. Calcd for C$_{44}$H$_{26}$F$_8$: C, 74.78; H, 3.71. Found: C, 73.96; H, 3.88. ^{1}H NMR (CDCl$_3$): δ(ppm) = 6.92–6.93 (s, 4H), 7.00–7.02 (d, 6H), 7.26–7.29 (m, 6H), 7.39–7.41 (d, 4H), 7.62 (s, 2H), 7.69 (Br, 2H), 7.72 (Br, 2H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 117.58, 118.99, 121.83, 124.58, 126.13, 127.76, 130.12, 131.24, 132.77, 132.84, 137.90, 137.95, 140.48, 141.15, 141.38, 142.53, 158.87. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.28 (d, 6F, CF$_3$), −118.37 (d, 2F, CF).

4,4⁗-Difluoro-3,3⁗-bistrifluoromethyl-2″,3″,5″-triphenyl-[1,1′;4′,1″;4″,1‴;4‴,1⁗]-pentaphenyl (8). Combination of **4** (5.01 g, 8.1 mmol), **6** (3.90 g, 18.6 mmol), Pd(PPh$_3$)$_4$ (0.28 g, 0.243 mmol), Na$_2$CO$_3$ (3.18 g, 30.0 mmol), H$_2$O (30 mL), and toluene (30 mL) gives **8** as a white solid purified from silica gel column chromatography (5.26 g, 83%). MS (FAB) *m/z* (rel. intensity): 782 (100); 783 (78); 784 (27). Anal. Calcd for C$_{50}$H$_{30}$F$_8$: C, 76.72; H, 3.86. Found: C, 75.94; H, 3.88. ^{1}H NMR (CDCl$_3$): δ(ppm) = 6.88–6.95 (t, 12H), 7.13–7.36 (Br, 14H), 7.62–7.70 (Br, 5H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 117.43, 117.60, 119.06, 119.19, 121.82, 124.57, 125.87, 126.00, 126.12, 126.47, 127.25, 127.51, 128.14, 128.27, 128.86, 129.24, 129.74, 130.21, 131.24, 132.86, 136.35, 137.34, 137.90, 139.56, 139.82, 140.41, 141.25, 141.29, 142.45, 142.78, 158.72, 158.86. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.30 (d, 6F, CF$_3$), −118.48 (d, 2F, CF).

4,4⁗-Difluoro-3,3⁗-bistrifluoromethyl-2″,3″,5″,6″-tetraphenyl-[1,1′;4′,1″;4″,1‴;4‴,1⁗]-pentaphenyl (9). Combination of **5** (5.62 g, 8.1 mmol), **6** (3.90 g, 18.6 mmol), Pd(PPh$_3$)$_4$ (0.28 g, 0.243 mmol), Na$_2$CO$_3$ (3.18 g, 30.0 mmol), H$_2$O (30 mL), and toluene (30 mL) gives **9** as a white solid purified from silica gel column

Table 1. Yields and Molar Masses of Poly(arylene ether)s

polymer	yield (%)	$M_n{}^a$	$M_w{}^a$	M_w/M_n	DP^b
10a	94	60 200	108 360	1.80	59
10b	95	15 000	32 250	2.15	18
10c	98	28 900	66 470	2.30	29
10d	96	8 400	16 210	1.93	10
11a	96	62 100	128 550	2.07	57
11b	93	19 300	52 110	2.70	21
11c	89	15 500	33 320	2.15	15
11d	91	10 700	21 400	2.00	11
12a	95	82 400	144 200	1.75	71
12b	97	17 000	37 570	2.21	17
12c	92	12 500	25 500	2.04	11
12d	96	14 000	37 100	2.65	13

^{a} Given in g mol^{-1}, determined by gel permeation chromatography in THF by UV−vis detector versus polystyrene standards. ^{b} Degree of polymerization calculated from M_n according to comonomer composition.

chromatography (6.05 g, 87%). MS (FAB) *m/z* (rel. intensity): 858 (100); 859 (83); 860 (29). Anal. Calcd for $C_{56}H_{34}F_8$: C, 78.31; H, 3.99. Found: C, 77.97; H, 3.96. ^{1}H NMR (CDCl$_3$): δ(ppm) = 6.84−6.85 (t, 20H), 6.89−6.92 (d, 14H), 7.04−7.06 (m, 6H), 7.32−7.36 (m, 4H). ^{13}C NMR(CDCl$_3$): δ(ppm) = 117.36, 118.97, 121.67, 123.75, 125.64, 125.86, 127.39, 132.05, 132.78, 133.06, 135.86, 139.90, 140.57, 141.15, 141.28, 141.42, 158.65. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.34 (d, 6F, CF$_3$), −118.87 (s, 2F, CF).

General Procedure for the Polymerizations. Polymerization reactions were carried out in a 50 mL, three-necked round-bottom flask equipped with a stir bar, a Dean−Stark apparatus fitted with a condenser, and a nitrogen inlet. The flask was charged with monomer **7**−**9** (0.9 mmol), bisphenol monomer **a**−**d** (0.9 mmol), potassium carbonate (1.8 mmol), *N*-methylpyrrolidone (NMP, 8 mL), and toluene (15 mL). The solution mixture was then stirred at 130−150 °C for several hours, and during the course of reaction, a slow stream of nitrogen was passed through the reaction vessel for removing the water, produced by the reaction and azeotroped with toluene. After complete removal of the water, the reaction solution was stirred at reflux (165 °C) for 8 h. For workup, the resultant polymer solution was diluted with 8 mL of THF and poured into a stirring methanol solution (250 mL) and the fibrous polymer was precipitated in situ. The precipitated polymer **10**−**12** was collected by filtration and washed with 10% HCl and H$_2$O and then vacuum-dried until no solvent was detected in the TGA experiment. For yields and molecular masses, see Table 1.

Polymer 10a. 10a is soluble in common organic solvents. Anal. Calcd for $(C_{69}H_{42}F_6O_2)_n$ (1017.1)$_n$: C, 81.48; H, 4.16. Found: C, 80.79; H, 4.22. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.80 (d, 4H), 7.56 (d, 4H), 7.40 (m, 8H), 7.21 (m, 8H), 6.95 (bs, 12H), 6.90 (s, 2H), 6.86 (br, 4H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 155.3, 151.1, 141.6, 141.4, 140.5, 140.4, 140.0, 139.7, 136.8, 135.6, 131.5, 131.3, 130.5, 129.6, 129.4, 127.8, 127.7, 127.1, 126.0, 125.8, 120.3, 119.6, 119.0. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.75 (s, 6F, CF$_3$).

Polymer 10b. 10b is soluble in common organic solvents. Anal. Calcd for $(C_{56}H_{34}F_6O_2)_n$ (852.9)$_n$: C, 78.86; H, 4.02. Found: C, 78.88; H, 4.21. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.54−7.67 (bs, 6H), 7.32−7.49 (bs, 6H), 7.10−7.21 (bs, 10H), 6.87−6.93 (bs, 12H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 157.2, 155.3, 142.6, 142.2, 141.6, 140.8, 140.4, 139.1, 137.4, 136.7, 136.3, 132.9, 132.1, 131.2, 129.1, 128.6, 128.0, 127.6, 126.7, 126.0, 125.4, 122.7, 120.5, 120.2. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.77 (s, 6F, CF$_3$).

Polymer 10c. 10c is soluble in common organic solvents. Anal. Calcd for $(C_{59}H_{34}F_{12}O_2)_n$ (1002.9)$_n$: C, 70.66; H, 3.42. Found: C, 71.14; H, 3.45. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.62−7.73 (bs, 6H), 7.19−7.41 (bs, 16H), 6.91−7.01 (bs, 12H). ^{13}C NMR (CDCl$_3$): δ-(ppm) = 157.5, 153.1, 141.5, 141.3, 140.2, 139.5, 138.8, 136.5, 135.1, 132.4, 132.0, 131.8, 131.4, 130.5, 128.4, 127.2, 126.2, 125.4, 125.3, 122.5, 121.2, 120.7, 118.1, 106.4, 68.2. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.74 (s, 6F, CF$_3$), −64.99 (s, 6F, CF$_3$).

Polymer 10d. 10d is soluble in common organic solvents. Anal. Calcd for $(C_{59}H_{40}F_6O_2)_n$ (894.9)$_n$: C, 79.18; H, 4.51. Found: C,

78.86; H, 4.56. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.45−7.73 (bs, 6H), 7.18−7.43 (bs, 16H), 6.85−6.97 (bs, 12H), 1.65 (d, 6H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 155.7, 155.3, 147.4, 142.5, 142.1, 140.7, 140.4, 139.3, 137.2, 136.5, 136.0, 132.8, 132.2, 131.7, 131.4, 130.1, 128.7, 128.3, 127.8, 127.3, 126.2, 125.7, 125.1, 121.2, 119.9, 115.1, 41.9, 30.6. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.81 (d, 6F, CF$_3$).

Polymer 11a. 11a is soluble in common organic solvents. Anal. Calcd for $(C_{75}H_{46}F_6O_2)_n$ (1093.1)$_n$: C, 82.40; H, 4.24. Found: C, 82.21; H, 4.27. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.42 (s, 2H), 2.88 (bs, 4H), 2.12 (s, end group), 1.74 (bs, 4H), 1.36 (bs, 20H), 0.89 (bs, 6H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 141.3, 132.1, 122.5, 92.4, 34.2, 31.8, 30.8, 30.2, 29.7, 22.5, 14.2. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.78 (d, 6F, CF$_3$).

Polymer 11b. 11b is soluble in common organic solvents. Anal. Calcd for $(C_{62}H_{38}F_6O_2)_n$ (929.0)$_n$: C, 80.16; H, 4.12. Found: C, 81.08; H, 4.23. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.62 (s, 5H), 7.35−7.50 (bs, 6H), 7.16−7.24 (bs, 11H), 6.87−6.95 (bs, 16H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 157.2, 157.1, 155.4, 155.2, 142.7, 142.4, 142.0, 141.8, 141.0, 140.9, 140.6, 140.5, 140.2, 139.6, 137.7, 137.1, 136.9, 136.7, 136.5, 132.9, 132.2, 131.9, 131.3, 130.6, 129.1, 129.0, 128.8, 128.4, 128.1, 127.8, 127.5, 127.1, 126.7, 126.4, 126.2, 126.0, 125.9, 125.3, 122.6, 122.5, 122.2, 120.4, 120.3, 120.1, 119.9. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.76 (s, 6F, CF$_3$).

Polymer 11c. 11c is soluble in common organic solvents. Anal. Calcd for $(C_{65}H_{38}F_{12}O_2)_n$ (1079.0)$_n$: C, 72.36; H, 3.55. Found: C, 72.52; H, 3.51. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.63−7.72 (bs, 5H), 7.18−7.39 (bs, 17H), 6.89−7.01 (bs, 16H). ^{13}C NMR (CDCl$_3$): δ-(ppm) = 157.5, 157.4, 141.5, 141.0, 140.1, 139.8, 139.4, 136.6, 132.2, 131.9, 131.6, 131.5, 131.4, 130.6, 130.0, 127.8, 127.1, 126.8, 126.5, 126.1, 125.8, 125.5, 125.3, 120.7, 118.1, 118.0, 106.2, 68.0. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.73 (s, 6F, CF$_3$), −64.96 (s, 6F, CF$_3$).

Polymer 11d. 11d is soluble in common organic solvents. Anal. Calcd for $(C_{65}H_{44}F_6O_2)_n$ (971.0)$_n$: C, 80.40; H, 4.57. Found: C, 79.79; H, 4.41. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.46−7.72 (bs, 5H), 7.19−7.45 (bs, 17H), 6.88−6.96 (bs, 16H), 1.67 (d, 6H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 155.3, 155.2, 147.3, 147.2, 142.8, 142.4, 142.0, 141.7, 140.9, 140.6, 140.4, 140.2, 139.6, 137.8, 136.7, 136.1, 132.9, 132.2, 131.9, 131.2, 130.2, 128.9, 128.8, 128.6, 128.4, 127.7, 127.4, 127.1, 126.6, 126.4, 126.1, 125.8, 125.4, 119.9, 119.5, 119.3, 115.2, 41.8, 30.4. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.82 (d, 6F, CF$_3$).

Polymer 12a. 12a is soluble in common organic solvents. Anal. Calcd for $(C_{81}H_{50}F_6O_2)_n$ (1169.3)$_n$: C, 83.20; H, 4.31. Found: C, 82.32; H, 4.32. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.42 (s, 2H), 2.88 (bs, 4H), 2.12 (s, end group), 1.74 (bs, 4H), 1.36 (bs, 20H), 0.89 (bs, 6H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 141.3, 132.1, 122.5, 92.4, 34.2, 31.8, 30.8, 30.2, 29.7, 22.5, 14.2. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.77 (d, 6F, CF$_3$).

Polymer 12b. 12b is soluble in common organic solvents. Anal. Calcd for $(C_{68}H_{42}F_6O_2)_n$ (1005.1)$_n$: C, 81.26; H, 4.21. Found: C, 81.48; H, 4.31. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.56−7.66 (bs, 4H), 7.34−7.52 (bs, 6H), 7.08−7.23 (bs, 12H), 6.82−6.95 (bs, 20H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 157.4, 155.6, 142.9, 141.7, 140.6, 139.1, 137.4, 136.5, 132.8, 132.0, 131.5, 129.2, 128.7, 128.2, 127.4, 126.5, 126.1, 125.4, 122.5, 120.4, 120.1. ^{19}F NMR (CDCl$_3$): δ-(ppm) = −62.78 (s, 6F, CF$_3$).

Polymer 12c. 12c is soluble in common organic solvents. Anal. Calcd for $(C_{71}H_{42}F_{12}O_2)_n$ (1155.1)$_n$: C, 73.83; H, 3.61. Found: C, 72.94; H, 3.51. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.63−7.72 (bs, 5H), 7.20−7.43 (bs, 17H), 6.90−7.18 (bs, 20H). ^{13}C NMR (CDCl$_3$): δ-(ppm) = 157.4, 153.0, 141.3, 141.1, 140.5, 139.3, 138.9, 136.5, 135.4, 132.5, 132.2, 131.3, 130.7, 128.2, 127.1, 126.2, 125.2, 122.5, 121.5, 120.2, 118.0, 106.2, 68.1. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.72 (s, 6F, CF$_3$), −64.96 (s, 6F, CF$_3$).

Polymer 12d. 12d is soluble in common organic solvents. Anal. Calcd for $(C_{71}H_{48}F_6O_2)_n$ (1047.1)$_n$: C, 81.44; H, 4.62. Found: C, 82.18; H, 4.41. ^{1}H NMR (CDCl$_3$): δ(ppm) = 7.45−7.73 (bs, 6H), 7.18−7.43 (bs, 16H), 6.85−6.97 (bs, 12H), 1.65 (d, 6H). ^{13}C NMR (CDCl$_3$): δ(ppm) = 155.5, 155.2, 147.3, 142.8, 142.2, 140.7, 139.2, 137.8, 136.5, 136.2, 132.4, 132.1, 131.6, 131.1, 130.0, 128.9, 128.2,

Scheme 2. The Synthesis of Polymers
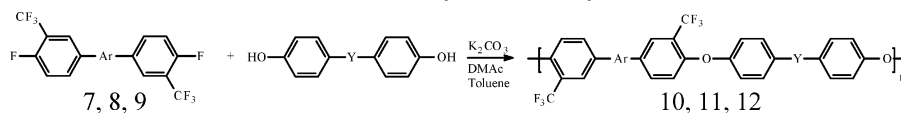
Y \ Ar			
a (9,9-fluorenylidene)	10a	11a	12a
b −	10b	11b	12b
c −C(CF₃)₂−	10c	11c	12c
d −C(CH₃)₂−	10d	11d	12d

127.6, 126.1, 125.6, 125.1, 121.4, 119.7, 115.3, 41.7, 30.8. ^{19}F NMR (CDCl$_3$): δ(ppm) = −62.84 (d, 6F, CF$_3$).

Results and Discussion

Monomer Synthesis. The 4,4″-dibromo-phenyl-substituted *p*-terphenylene compounds **3**−**5** used in this study were prepared by a modification of the published procedure[25] as outlined in Scheme 1. Self-coupling[19] of 4-bromobenzyl bromides with catalyst Fe(CO)$_5$ and phase transfer reagent Bu$_4$NBr in an alkali aqueous solution afforded **1** in fair yield, which were cyclized after recrystallization without further characterization. Cyclization of **1** with benzil in a solvent mixture of triethylene glycol, benzyltrimethyl ammonium hydroxide, and methanol gave **2** in fair to good yield. Diels−Alder reactions of cyclopentadienone **2** were carried out with 1.1 equiv of cyclodiene or acetylenes in dry diphenyl ether and furnished the 4,4″-dibromo-phenyl-substituted *p*-terphenylene compounds **3**−**5** in good to excellent yields. Couple reactions of compounds **3**−**5** were carried out using the Suzuki reaction with 2.3 equiv of compound **6** in a solvent mixture of toluene, sodium carbonate aqueous solution (1 M), and tetrakis(triphenyl phosphine) palladium(0) and furnished the 4,4″″-difluoro-phenyl-substituted quinquephenyl monomers **7**−**9** in good to excellent yields.

Polymerizations. The bisfluoro monomers **7**−**9** were each polymerized with bisphenols **a**−**d** to provide a series of poly-(arylene ether)s (Scheme 2). The poly(arylene ether)s were prepared using equimolar amounts of monomers in a mixed solvent system of dimethylacetamide (DMAc) and toluene with an excess of anhydrous potassium carbonate. All polymerizations involved two reaction steps. First, the dipotassium salt of the desired bisphenol was synthesized by reacting the bisphenol with potassium carbonate at reflux (130 °C) for 2 h in a DMAc−toluene solution. Water was removed from the reaction via the toluene−water azeotrope which was separated using a Dean−Stark trap. Toluene was then removed from the reaction flask by distillation until the reaction temperature reached 155−160 °C. The desired bisfluoro monomer was then added to the reaction flask and stirred at reflux under an inert atmosphere

for 3−6 h. As end groups could affect the thermal stability of the polymers, to ensure that most of the chains were fluorine terminated, an excess of 5 mol % of the bisfluoro monomer was added 30 min before stopping the polymerization. The resulting reaction mixtures were diluted with twice the volume of DMAc and then filtered to remove excess potassium salts. The filtrates were slowly poured into water to yield flaky, white precipitates. Purification of the resultant polymers was accomplished by dissolving in chloroform, precipitation into methanol, and drying in vacuo at 110 °C for 24 h.

GPC was used to determine the molecular weight of the polymers soluble in THF, and the results are listed in Table 1. The molecular weight distributions were essentially unimodal with no evidence of oligomeric or unreacted species, which is also attested by undetectable ^{19}F NMR signals of the fluorine end groups of poly(arylene ether)s. The reported values are polystyrene equivalent weights. In any case, these values have to be taken as merely indicative, since calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the polymers studied deviate strongly from those of polystyrene. Results of the polymerizations are summarized in Table 1. Table 1 shows that the polymers derived from bisphenols with the bulky pendant of 9,9′-bis(4-hydroxyphenyl) fluorene (**a**) have a higher degree of polymerization than the ones having smaller pendants (**b**−**d**). This can be attributed to the difference in catenation angle, which results in different backbone curvature.

Solubilities of the polymers are reported in Table 2. It shows that all of the polymers are soluble in common organic solvents such as chloroform, toluene, and tetrahydrofuran, as well as polar aprotic solvents such as dimethylformamide (DMF), DMAc, and NMP. Surprisingly, the polymers were only swelled in the presence of dimethyl sulfoxide (DMSO), and the enhanced solubility afforded by six F groups can be observed in ethyl acetate. Polymers **10c, 11c**, and **12c**, having six F BPA, were rapidly dissolved by ethyl acetate while the other polymers were only swelled by this solvent.

Table 2. Solubility of Poly(arylene ether)s[a]

polymer	NMP	DMF	DMSO	THF	chloroform	ethyl acetate	toluene	DMAc
10a	+	+	−	+	+	−	+	+
10b	+	+	−	+	+	−	+	+
10c	+	+	o	+	+	+	+	+
10d	+	+	−	+	+	−	+	+
11a	+	+	−	+	+	−	+	+
11b	+	+	−	+	+	−	+	+
11c	+	+	o	+	+	+	+	+
11d	+	+	−	+	+	−	+	+
12a	+	+	−	+	+	−	+	+
12b	+	+	−	+	+	−	+	+
12c	+	+	o	+	+	+	+	+
12d	+	+	−	+	+	−	+	+

[a] Key: (+) soluble at room temperature; (o) soluble at refluxing; (−) insoluble at refluxing.

Table 3. Thermal Properties of Poly(arylene ether)s

polymer	Tg (°C)[a,b]	Td (°C)[c]	Td5 (°C)[d]
10a	294(304)	648	658
10b	243(254)	667	671
10c	240(248)	619	626
10d	210(217)	610	617
11a	305(310)	650	657
11b	274(284)	636	643
11c	249(258)	635	640
11d	237(246)	628	632
12a	332(338)	668	671
12b	299(305)	635	635
12c	271(280)	640	644
12d	262(271)	621	625

[a] Glass transition temperature was measured by DSC and the reflection point was taken as Tg. [b] Glass transition temperature in the parentheses was measured by DMA. [c] Initial decomposition temperature was recorded on TGA at a heating rate of 20 °C/min under N$_2$, and the onset temperaturet was taken as Td. [d] Temperature at which 5% weight loss recorded on TGA at a heating rate of 20 °C/min under N$_2$.

NMR Spectroscopy. Typical spectroscopic data from ^{19}F and ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy (see the Supporting Information) support the structures of the bisfluoro monomer **8** and polymer **11d**, respectively. The ^{19}F NMR spectrum of the bisfluoro monomer **8** shows two peaks at the chemical shifts of −62.3 and −118.5 ppm of equal intensity, attributed to the fluorines of the trifluoromethyl groups and of the bisfluoro groups, respectively. After polymerization, the corresponding ^{19}F NMR spectrum of the polymer **11d** presents only a peak at −62.8 ppm, attributed to the trifluoromethyl groups, while the signal at −118.5 ppm caused from the bisfluoro groups of the monomer **8** completely disappears due to nucleophilic displacement of the fluorine atoms. The ^{1}H and ^{19}F NMR spectra of the polymers do not show any signals corresponding to the terminal −OH or −F groups, which is indicative of a high degree of conversion. The exact analytical data for all these polymers are listed in the Experimental Section.

Thermal Properties. The thermal properties of the polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results of TGA measurements (see the Supporting Information) for **12a−d** are listed in Table 3. The polymers were stable from 610 to 668 °C in nitrogen atmosphere (Table 3). On the basis of the bisphenols' structures, the polymers could be briefly classified into two categories. The first category, polymers **12a** and **12b**, having almost fully aromatic main chains, show only one decomposition process, starting at about 600 °C with char residues of 70 and 59% at 800 °C, which was attributed to the degradation of the main chain. In polymers **12c** and **12d**, the second category, possessing small pendent groups of methyl and trifluoromethyl attached to the main chain, also show one decomposition process; however, it starts at a lower temperature of about 500 °C with char residues of 34 and 31% at 800 °C. This is owing to the alkyl pendent groups, which cause the degradation to occur at somewhat lower temperatures than the ones of the first category. The high thermal stability of these polymers was confirmed by the high char residues reported in Table 3. The lowest initial thermal degradation temperature of about 500 °C was well above the highest temperature (350 °C) used in DSC experiments; furthermore, the samples were solvent-free within the TGA limits of detection. This guarantees that no artifact will be seen in the DSC studies, which are shown below.

In the DSC scans of **12a−d** (see the Supporting Information), Tg values were in the range 262−332 °C, depending on the bisphenol used in the synthesis. Tg is known to depend on several factors such as the rigidity of the main polymer chain, chain symmetry, and intermolecular forces, but in our PAEs it most likely depends on the barriers to rotation along the main polymer chain. As expected, when comparing Tg values (shown in Figure 1) in different bisfluoro monomer structures, it was predicted and confirmed that all the tetraphenyl-substituted polymers **12a−d** would have the highest Tg values followed by triphenyl-substituted polymers **11a−d**, and then diphenyl-substituted polymers **10a−d**, due to a gradual decrease in the number of substituents on the middle phenylene, which causes less restriction for rotating the substituents along the polymer backbone. On the other hand, the Tg values listed in Table 3 decrease gradually from polymer **12a−d** due to a gradual decrease in rigidity of pendent groups sourced from bisphenols. The Tg of **12a** is 33 °C higher than that of the poly(arylene ether) based on biphenyl (**12b**) because the fluorenylidene connector group is quite rigid and has a higher molecular mass than does the biphenyl group. On the other hand, owing to rigidity, polymer **12b** shows higher Tg than polymers **12c** and **12d**, and polymer **12c** exhibits a higher Tg with respect to polymer **12d** because of the stronger interchain interactions due to the polar −CF$_3$ groups which partially balance their flexibilizing effect. Similar trends are also observed in polymers **10a−d** and **11a−d**.

By comparison with previous studies,[2] the published Tg values are collected and listed in Table 4. It shows that the Tg values increase gradually from *p*-terphenylene, *p*-quaterphenylene, to tetraphenyl-substituted *p*-pentaphenylene PAEs, based on different bisfluoro monomer structures due to a gradual increase in the rigidity of the main-chain structures. On the other hand, when comparing Tg values in different bisphenol monomer structures, it indicates the Tg values increase gradually from BPA, 6F BPA, biphenyl, to fluorenylidene PAEs due to a gradual increase in rigidity and/or steric hindrance of substituent structures.

Mechanical Properties. According to X-ray diffraction (no diffractions) and DSC analysis (no melting points), all PAE polymers are amorphous at room temperature, even after annealing at temperatures higher than the glass transition temperature. Unlike typical polymers with high Tg values, the PAE polymers in this study show the expected ductile mechanical behavior characteristic of many materials containing aryl ether linkages and were somewhat soft with elongations above 5%. In Figure 2, the dynamic mechanical spectra of PAE **12**, **11**, and **10b** show the primary relaxations, the large-scale chain motions characteristic of the glass transition (tan δ), ranging from 338 to 304 °C. These data are consistent with the calorimetric results shown in Table 3, clearly showing the high Tg values and good dimensional stability exhibited by these
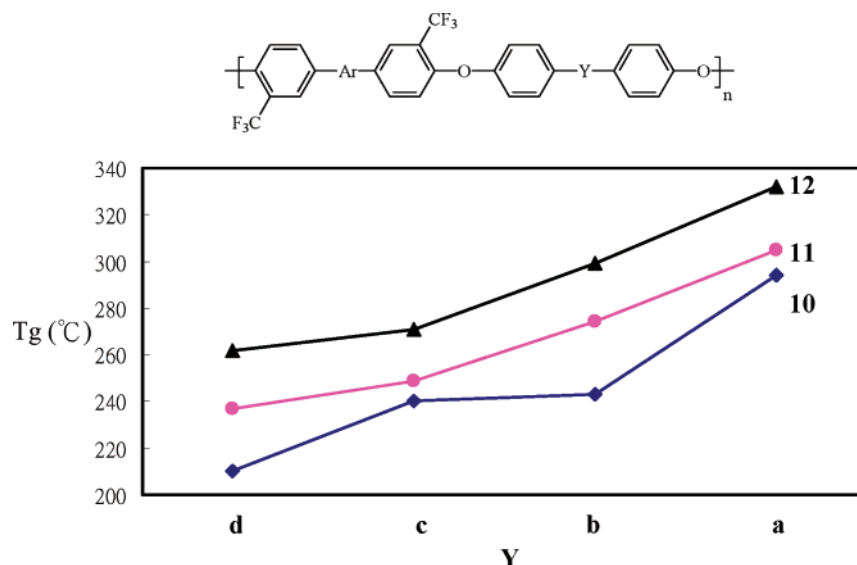
Figure 1. Glass transition temperatures (Tg/°C) of the Poly(arylene ether)s by DSC versus bisphenols' geometries (Y).

Table 4. Glass Transition Temperatures (Tg/°C) of the Poly(arylene ether)s by DSC and Their Comparison with Similar Polymers

Y \ Ar	(single ring)	(biphenyl)	(tetraphenyl)
C(CH₃)₂	174	—	262
C(CF₃)₂	179	210	271
—	209	257	299
(fluorenyl)	234	300	332

materials. The Tg values of these polymers are among the highest reported for ary1ene ether polymers prepared by nucleophilic aromatic substitution and are even higher than those poly(aryl ether-phenylquinoxalines) reported by Hedrick et al. and Connell et al.[1,27] on similar structures. In addition to the primary relaxations, the secondary relaxations also were observed and held still even though sub-Tg annealing was conducted to reduce or eliminate the nonequilibrium packing defects in the glass or the stresses introduced during fabrication. Therefore, we believe this indicates that the molecular motions of individual units or small segments of the polymer backbone existed. However, more investigation is needed to elucidate what is really going on in the secondary relaxations in these polymers; such a study is underway and the results are going to be published in a separate paper.

Photophysical Properties. UV Absorption Spectra. The UV absorption spectra of monomers **7**−**9** in dichloromethane are shown in Figure 3, and for comparison, the absorption and emission λ_{max} of monomers **7**−**9** and the PAEs **10**−**12a** are summarized in Table 5. The UV absorption spectra (Figure 3) in dichloromethane revealed that three monomers have π−π^* transitions with λ_{max} between 292 and 228 nm. The spectrum

of monomer **7** shows a λ_{max} at 292 nm and two small shoulders at approximately 260 and 228 nm. When the spectrum of monomer **7** (two substituents) is compared with that of monomer **8** (three substituents), it is seen that the extra substituent on the middle phenylene ring has caused a blue shift to 290 nm and a decreased intensity of the peak. At the same time the shoulder at approximately 260 nm has been increased in intensity. In comparing the tetra-substituted monomer **9**, the effects are enhanced; the peak at 292 nm has now been blue-shifted to 287 nm and further decreased in intensity, while the intensity of the peak at approximately 228 nm has been increased. The observations deduced above show that the π−π^* transitions showed gradual blue shifts from **7** to **9**, suggesting decreasing electron delocalization along the chain as the side groups changed from diphenyl-substituted monomer **7** to triphenyl-substituted monomer **8** and tetraphenyl-substituted monomer **9**.

It should be noted that the wavelengths are shifted only by a small amount with the number of substituents on the central phenylene ring, but the intensities are changed significantly as the number of substituents is altered. Upon comparison of the absorption bands of monomers **8** and **9** with those of monomer **7**, in both instances (monomers **8** and **9**) the intensities are greatly shifted. Therefore, it may be that intensities are, in general, more sensitive to slight changes in the angle between the rings than they are to wavelengths. This also indicates that although there are three major absorption bands for each monomer, the number of excitons responsible for each absorption band varies substantially as the number of substituents is altered.

A similar trend of blue shift is observed in corresponding polymer solutions as seen by comparing the absorption spectra of PAEs **10a**−**d** (diphenyl-substituted) and PAEs **11a**−**d** (triphenyl-substituted) to those of PAEs **12a**−**d** (tetraphenyl-substituted), nearly independent of the bisphenol monomers. However, the degrees of blue shift caused by substituted side groups for polymers decrease, which indicates lesser reduction in the electron delocalization of the polymer main chain than that of the monomers. From Table 5, it is clear that the UV absorption λ_{max} of polymers becomes longer than that of the corresponding monomers. In the sense of effective conjugation length, this indicates that it becomes longer after polymerization. On the other hand, however, the effect of twist between adjacent planes of the phenylene rings of the main chain, which varies
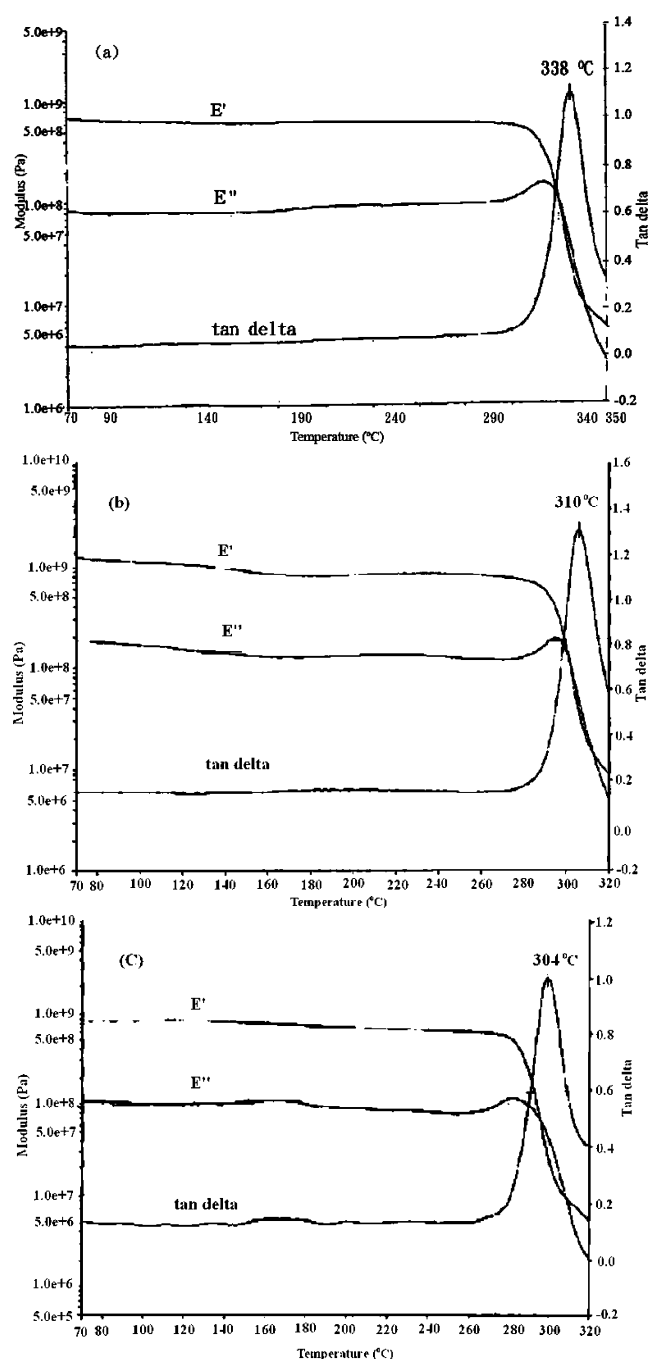
Figure 2. Dynamic mechanical analysis of the Poly(arylene ether)s: (a) **12a**, (b) **11a**, (c) **10a**.

with the number of side-chain substituents of the bisfluoro monomers, is reduced due to polymerization and thus results in a smaller geometric effect on the ground-state electronic structure of the PAEs. This indicates that the stress caused by the twist between adjacent planes of the phenylene rings of the main chain can be somehow released by introducing a soft ether linkage via polymerization.

Photoluminescence Spectra. The photoluminescence (PL) spectra of the monomers and polymers were investigated in solution. The emission spectra in dilute dichloromethane solutions (0.0001 g/dL) are shown in Figures 3 and 4, and the data are summarized in Table 5. The PL spectra are insensitive to the excitation wavelength in the range 230−300 nm. All the data presented here were obtained by excitation at the wavelength of the respective absorption maximum. All the PL spectra
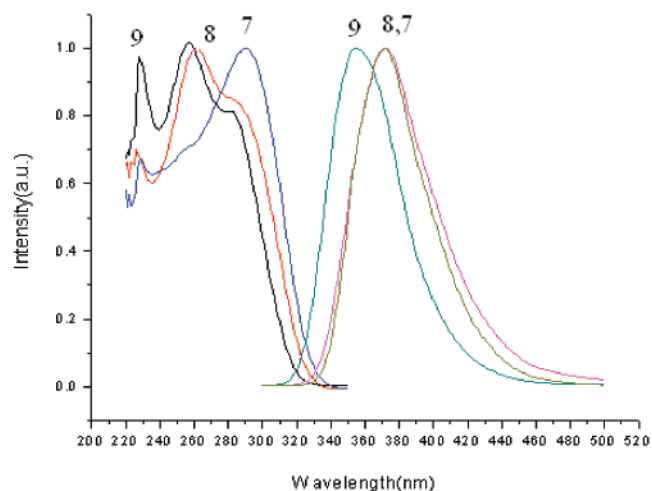

Figure 3. UV absorption and photoluminescence spectra of the bisfluoro monomers **7**−**9** in dichloromethane.

Table 5. Absorption and Photoluminescence Characteristics of Monomers and Polymers

compound	absorption λ_{max} (nm)^a	emission λ_{max} (nm)^{a,b}	Stokes shift (nm)^c
7	228/260/292^d	371	45
8	228/261^d/291	370	49
9	228^d/259^d/287	355	39
10a	228/260/298^d	372	35
10b	228/261/299^d	373	35
10c	228/261/298^d	373	35
10d	228/260/299^d	372	34
11a	228/260^d/297^d	370	41
11b	228/262^d/297^d	370	41
11c	228/263^d/298^d	370	40
11d	228/263^d/297^d	371	41
12a	228^d/259/288	352	24
12b	228^d/261/289	353	26
12c	228^d/260/288	353	26
12d	228^d/261/289	352	26

^{a} 10^{-3}g/dL in THF. ^{b} Excited at absorption λ_{max} ^{c} Stokes shift = emission λ_{max}− absorption onset. ^{d} The major bands in the spectrum.
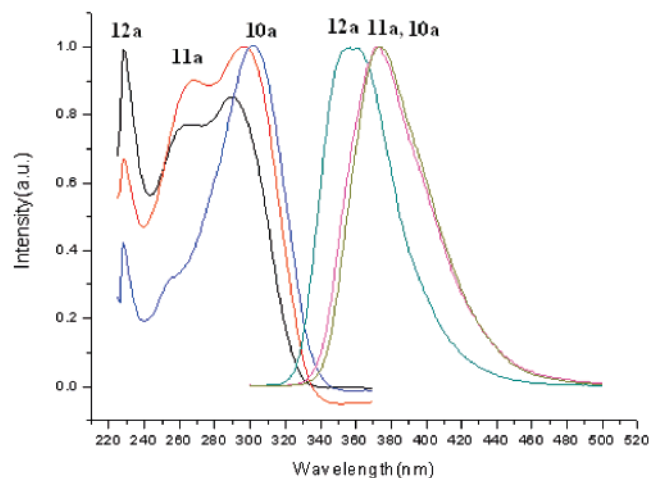

Figure 4. UV absorption and photoluminescence spectra of the PAEs **10a**, **11a**, and **12a** in dichloromethane.

in dilute solution show a very similar pattern with only one featureless peak. In addition, the PL spectra show relatively small Stokes shifts of 24 to ∼49 nm between the emission λ_{max} and the absorption onset, which is consistent with emission from localized states of the 0−0 band. Interestingly, we also found that the emission λ_{max} of the lower energy state was gradually blue shifted as the substituent was changed from diphenyl to

triphenyl and tetraphenyl. This indicates that the emission band was strongly associated with the size and number of the substituents, which affected the torsion angle and the relative movement of the phenyl rings. Therefore, we tentatively conclude that the emission spectrum is characterized by effective conjugation length which could be manipulated by the size and number of the substituents.

Conclusion

A new class of high-temperature, high-Tg polymers, the poly-(ary1ene ether)s, have been synthesized via a nucleophilic aromatic substitution reaction of bisfluoro- pentaphenyl monomers, with bisphenolates generating the arylene ether linkages. The electrowithdrawing pendent groups of trifluoromethyl activate a nucleophilic fluoro displacement polymerization. The nucleophilic displacement polymerization reactions were conducted in NMP in the presence of potassium carbonate to give high molecular weight polymers. Glass transition temperatures of the poly(ary1ene ether)s increase with increasing pendent phenyls in the bisfluoro-pentaphenyl monomers. The materials experienced 5% weight losses above 500 °C by thermogravimetric analysis, indicative of their high thermal stability. All of the polymers could be readily processed from solution to derive flexible transparent films. The effects of the number of substituents on the UV absorption and PL spectra of bisfluoro-pentaphenyl monomers and respective polymers are also studied. The band position and intensity shifts observed are correlated with the number of substituents. It is suggested that the substituents may modify the energies and population of both the ground and the excited states of the molecules.

Supporting Information Available: NMR spectra of monomer **8** and polymer **11d**, TGA thermograms of polymer **12** series, and DSC thermograms of polymer **12** series. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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