

# Sterically Encumbered Fluorene-Based Poly(arylene ether)s Containing Spiro-Annulated Substituents on the Main Chain

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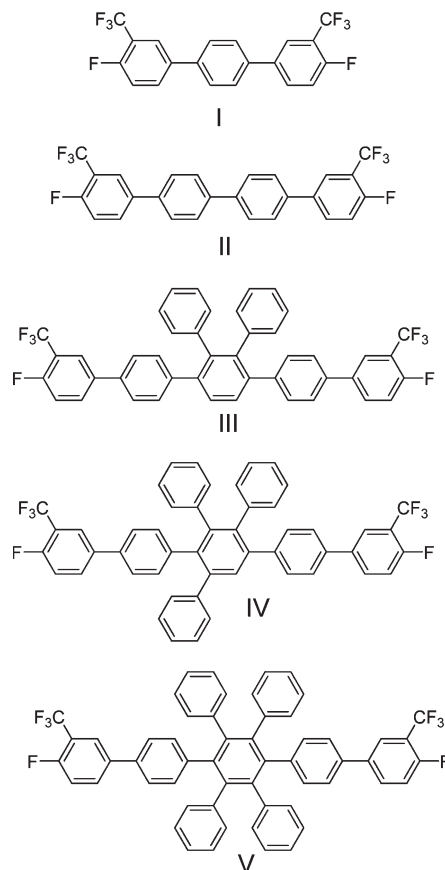
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**ABSTRACT:** Two novel fluorene-based bisphenol monomers containing spiro-annulated substituents on the middle biphenylene moiety have been synthesized in this study. Through reacting with four 2-trifluoromethyl-activated bisfluoro monomers, two monomers were converted into a series of fluorene-based poly(arylene ether)s by nucleophilic displacement of the fluorine atoms on the terminal benzene ring of bisfluoro monomers. The obtained polymers exhibit weight-average molecular weight up to  $2.41 \times 10^5$  g/mol in GPC. Thermal analysis studies indicated that these polymers did not show melting endotherms but did show ultrahigh  $T_g$  values up to 356 °C in DSC and outstanding thermal stability up to 643 °C for 5% weight loss in TGA under nitrogen atmosphere. The polymers are soluble in a wide range of organic solvents, THF,  $\text{CHCl}_3$ , NMP, DMAc, DMF, toluene, etc., and are insoluble in DMSO and acetone at room temperature. Transparent and flexible films were easily prepared by solution casting from chloroform solution of each of the polymers.

## Introduction

Poly(arylene ether)s (PAEs)<sup>1–6</sup> 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.

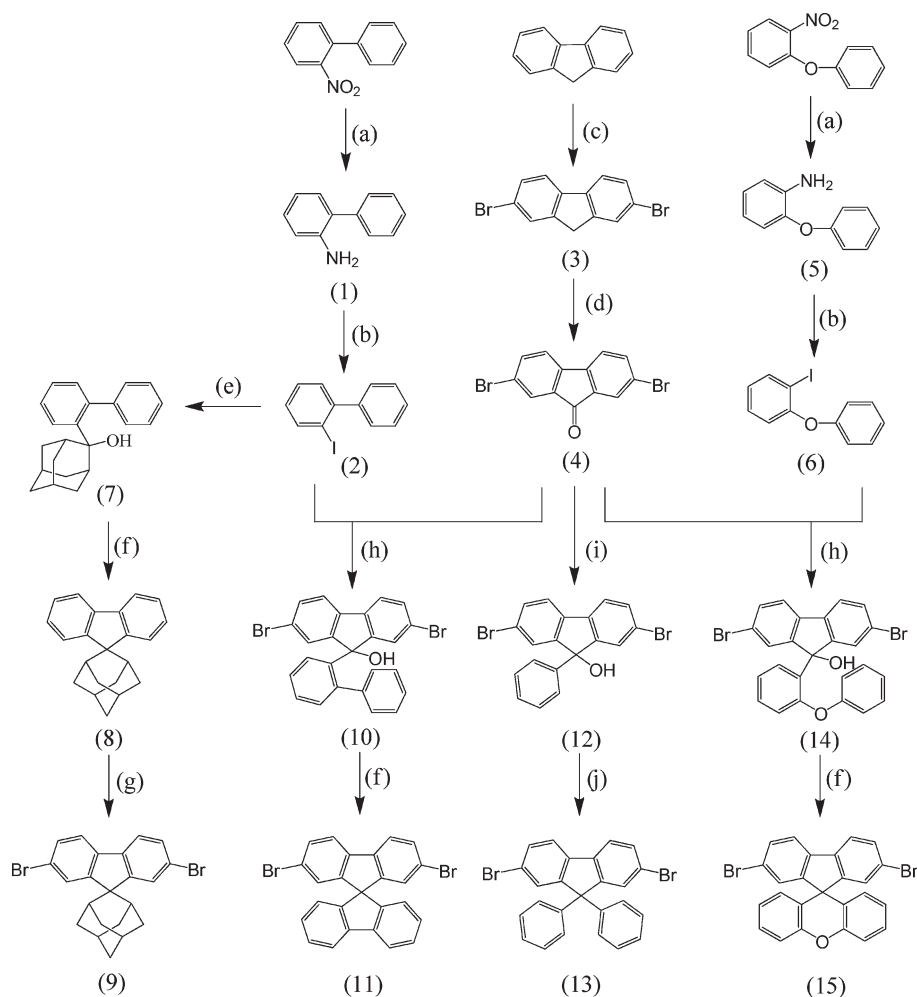
Most success in preparation of PAEs is achieved by nucleophilic displacement reactions of dihalo or dinitro compounds with alkali-metal bisphenolates. Nucleophilic aromatic substitution occurs when the leaving group is activated by electron-withdrawing substituents. Examples of three commercial engineering plastics prepared this way are poly(ether sulfone),<sup>7,8</sup> poly(ether imide),<sup>9</sup> and poly(ether ether ketone).<sup>10,11</sup> The poly(ether sulfone) involves displacement of halo groups activated by  $\text{SO}_2$ , usually referred to as a polysulfone even though ether linkages are formed in the polymerization reaction. With the poly(ether imide), displacement of the nitro groups is promoted by the electron-withdrawing imide. The poly(ether ketone), involving displacement of halo groups activated by ketone, provides a polymer called 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,<sup>12</sup> which lowers activation energy for displacement, Hedrick et al.<sup>1</sup> reported that trifluoromethyl groups, either in a pendent position or in the main chain, activate fluoro or nitro displacement by phenoxides. Accordingly, the bisfluoro monomers **I–II** and **III–V** shown below had been synthesized by Maier et al.<sup>2</sup> and our group,<sup>3,4</sup> respectively.



The poly(arylene ether)s based on the above bisfluoro monomers present many highly desirable properties, such as extraordinarily high glass transition temperature, excellent thermal

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Scheme 1. Synthesis of Monomer Precursors



and mechanical properties, low dielectric constant, and remarkably low water absorption.

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,<sup>13,14</sup> is highly desirable. Fluorene containing polymers<sup>6,15,16</sup> 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<sup>12</sup> 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.

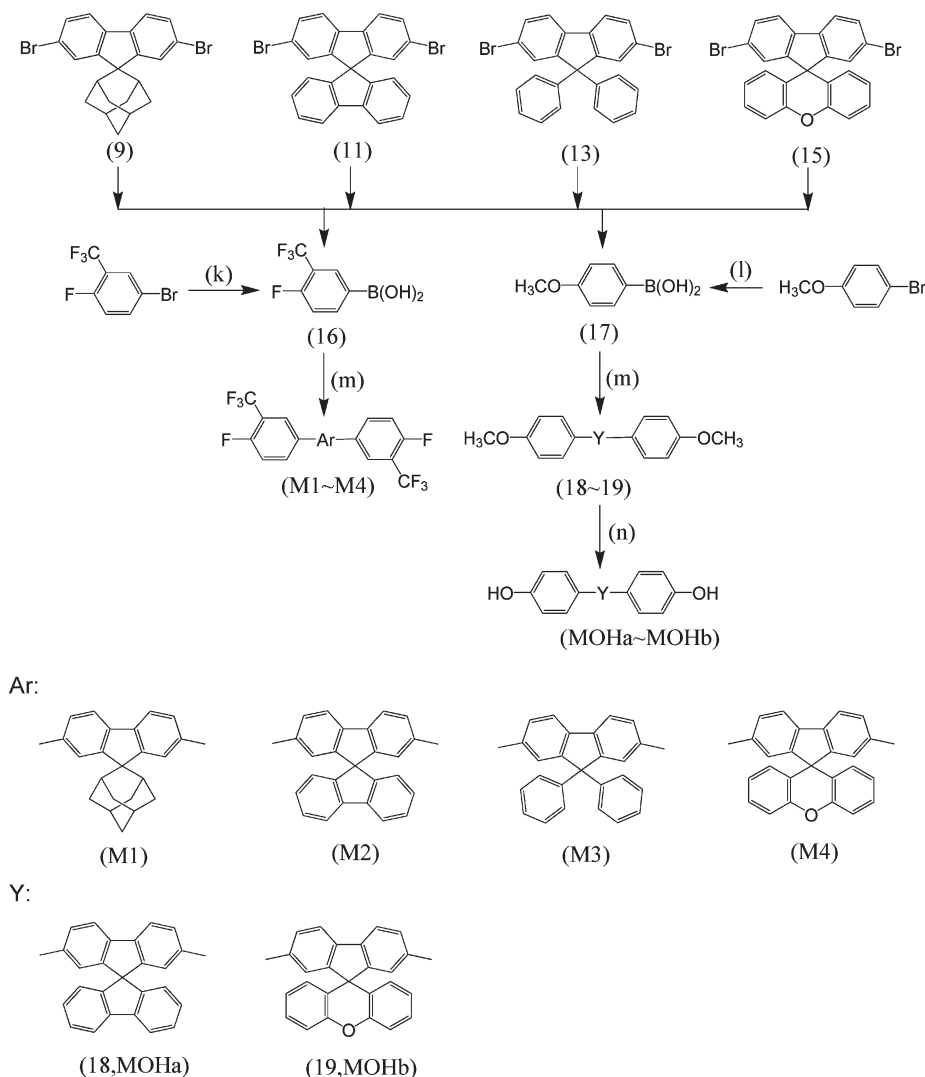
Nevertheless, the spiro-annulated structure caused by the 9,9-disubstituted fluorene skeleton is of significance in polymers for optical use.<sup>20</sup> Some other characteristic properties including light-emitting and carrier transporting abilities for light emission

devices and high thermal stability of fluorine-based molecules have also been demonstrated.<sup>20,22</sup> On the basis of all above observations, we have recently designed two novel fluorine-based bisphenol monomers shown in Schemes 1 and 2 for synthesis of PAEs. This paper discloses the synthesis of PAEs via a nucleophilic aromatic substitution polymerization utilizing the two novel fluorine-based bisphenol monomers and four 2-trifluoromethyl-activated bisfluoro monomers previously published by our group,<sup>19</sup> as a high performance polymer with exceptional chemical, thermal, and optical properties.

## Experimental Section

**Characterization.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were collected on a Bruker AM-500WB spectrometer in chloroform-*d* or tetrahydrofuran-*d* as solvent and tetramethylsilane (TMS) as the internal standard. Thermogravimetric analysis (TGA) was conducted on a PerkinElmer Pyris 1 system with a Hi-Res thermogravimetric analyzer under a heating rate of  $20^\circ\text{C}/\text{min}$  and a nitrogen or air flow rate of  $50\text{ cm}^3/\text{min}$ . Differential scanning calorimetry (DSC) was run on a PerkinElmer Pyris 1 system. All melting temperature ( $T_m$ ) and glass transition ( $T_g$ ) were obtained using DSC.  $T_g$  was taken from the middle point of the step transition, while  $T_m$  was taken from the

Scheme 2. Synthesis of Monomers



(k) Mg, I<sub>2</sub>, dry Ethyl ether, dry THF, Trimethyl borate, HCl;

(l) Mg, I<sub>2</sub>, dry THF, Trimethyl borate, HCl;

(m) Pd(PPh<sub>3</sub>)<sub>4</sub>, 1M Na<sub>2</sub>CO<sub>3</sub> sol'n, Toluene;

(n) dry CH<sub>2</sub>Cl<sub>2</sub>, BBr<sub>3</sub>;

maximum of the endothermic peak in the second heating run. GPC analysis was conducted with a Polymer Laboratories HPLC system equipped with Polymer Laboratories ultra Plgel 5  $\mu$  Mixed column (7.8 mm i.d.  $\times$  300 mm) 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  $^{\circ}$ C for 12 h first and then 120  $^{\circ}$ C for 24 h in vacuum before measurement. Dynamic mechanical analysis (DMA) were performed on a PerkinElmer Pyris 1 system with a mechanical thermal analysis controller in the tension mode on thin film samples under a heating rate of 20  $^{\circ}$ C/min and a frequency of 5 Hz.

**Materials.** All reagents and solvents were purchased from Aldrich, Merk, Lancaster, or Fisher Chemical Co. 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 nitrogen atmosphere and deoxygenated by purging with nitrogen for 30 min before use in monomer synthesis. 4,4'-(Hexafluoroisopropylidene)bisphenol (6F BPA) was 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 nitrogen 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 **M1**–**M4** and **MOHa**–**b** have to be prepared in large quantities and good yields (Scheme 1 and Scheme 2). The synthetic procedures for monomers **M1**–**M4** could be found in a previous publication,<sup>19</sup> and those for **MOHa**–**b** are provided below. Hydrogenation of 2-nitrobiphenyl and 2-nitrophenyl phenyl ether with catalyst 5% Pd/C remaining at 5 atm hydrogen atmosphere afforded **1** and **5**, respectively, in good yields, which were iodized after purification without further characterization. Iodization of **1** and **5** with potassium iodide in an aqueous solution of 35% hydrogen chloride and sodium nitrate gave **2** and **6**, respectively, in fair to good yields. Bromination of fluorene with N-bromosuccinimide in propylene carbonate gave **3** in good yield. Ketonation of **3** with oxidation reagent CrO<sub>3</sub> in acetic acid provided **4** in good yield. After Grignard reactions of **2** and **6**, the

resulted Grignard reagents were reacted with **4** to afford **10** and **14**, respectively, in fair yields. Cyclizations of **10** and **14** with 35% hydrogen chloride in acetic acid solution provided **11** and **15**, respectively, in good to excellent yields. Grignard reaction product of 4-bromoanisole was reacted with trimethyl borate in dry THF gave **17** in good yields. Couple reactions of compounds **11** and **15** were carried out using Suzuki reaction with 2.3 equiv of compounds **17** in solvent mixture of toluene, sodium carbonate aqueous solution (1 M) and tetrakis(triphenyl phosphine) palladium (0) furnished compounds **18** and **19** in good to excellent yields. Deprotection of compounds **18** and **19** with BBr<sub>3</sub> in dry dichloromethane gave monomers **MOHa** and **MOHb**. The detailed procedure for each precursor is given separately below.

**2-Aminobiphenyl (1).** To a high pressure reactor containing 2-nitrobiphenyl (25.0 g, 125 mmol), 5% Pd/C (0.3 g) and ethyl acetate (80 mL) was slowly introduced hydrogen gas until 5 atm. The reaction mixture was maintained at 5 atm and stirred at room temperature for 24 h. The resultant solution was filtered to remove solid contents. Then the solvent was removed under reduced pressure and the resultant was purified by column chromatography using hexane as eluent, which gives compound **1** as a light brown liquid (16.9 g, 80%);  $R_f$  (EAC:hexane = 1:20) = 0.2. MS ( $m/z$ ): 169.1. Anal. Calcd for C<sub>12</sub>H<sub>11</sub>N: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.08; H, 6.47; N, 8.20.

**2-Iodobiphenyl (2).** An aqueous sodium nitrite solution (2.1 M, 77.0 mL) was added dropwise into a reaction mixture containing compound **1** (23.0 g, 136 mmol) and 35% hydrochloric acid (70.0 mL), and the resulting mixture was stirred at 0 °C for 15 min. The above mixture was poured into a solution containing potassium iodide (83.4 g, 502 mmol) and water (280 mL) and the combined reaction solution was stirred at room temperature overnight. The mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with H<sub>2</sub>O (3 × 100 mL) and dried over MgSO<sub>4</sub>. Then the solvent was removed under reduced pressure and the resultant was purified by column chromatography using hexane as eluent, which gives compound **2** as a light red liquid (28.5 g, 75%);  $R_f$  (EAC:hexane = 1:20) = 0.7. MS ( $m/z$ ): 280.0. Anal. Calcd for C<sub>12</sub>H<sub>9</sub>I: C, 51.46; H, 3.24; I, 45.31. Found: C, 51.42; H, 3.19; I, 45.25.

**2,7-Dibromofluorene (3).** A reaction mixture containing fluorene (12.5 g, 75 mmol), N-Bromosuccinimide (27.4 g, 153 mmol) and propylene carbonate (90 mL) was stirred at reflux for 3 h. The mixture was poured into methanol. After filtration and recrystallization from ethanol, the compound **3** was obtained as a white solid (18.2 g, 75%);  $R_f$  (hexane) = 0.8. MS ( $m/z$ ): 323.7. Anal. Calcd for C<sub>13</sub>H<sub>8</sub>Br<sub>2</sub>: C, 48.19; H, 2.49; Br, 49.32. Found: C, 48.09; H, 2.41; Br, 49.25.

**2,7-Dibromo-9-fluorenone (4).** To a reaction mixture containing compound **3** (15.0 g, 46 mmol) and acetic acid (190 mL) was added CrO<sub>3</sub> (20.0 g, 200 mmol) in 10 portions. The above reaction solution was stirred at 120 °C for 1 h. The mixture was poured into methanol. After filtration and washing with water twice, the compound **4** was obtained as a yellow solid (10.9 g, 70%);  $R_f$  (EAC:hexane = 1:10) = 0.5. MS ( $m/z$ ): 337.7. Anal. Calcd for C<sub>13</sub>H<sub>6</sub>Br<sub>2</sub>O: C, 46.20; H, 1.79; Br, 47.28; O, 4.73. Found: C, 46.14; H, 1.71; Br, 47.08; O, 4.71.

**2-Aminophenyl Phenyl Ether (5).** To a high pressure reactor containing 2-nitrophenyl phenyl ether (25.0 g, 116 mmol), 5% Pd/C (0.28 g) and ethyl acetate (74 mL) was slowly introduced hydrogen gas until 5 atm. The reaction mixture was maintained at 5 atm and stirred at room temperature for 20 h. The resultant solution was filtered to remove solid contents. Then the solvent was removed under reduced pressure and the resultant was purified by column chromatography using EAC:hexane = 1:20 as eluent, which gives compound **5** as a light brown liquid (16.9 g, 85%);  $R_f$  (EAC:hexane = 1:5) = 0.4. MS ( $m/z$ ): 185.0. Anal. Calcd for C<sub>12</sub>H<sub>11</sub>NO: C, 77.81; H, 5.99; N, 7.56; O, 8.64. Found: C, 77.83; H, 5.92; N, 7.52; O, 8.67.

**2-Iodobiphenyl Phenyl Ether (6).** An aqueous sodium nitrite solution (2.1 M, 66.0 mL) was added dropwise into a reaction

mixture containing compound **5** (21.6 g, 116 mmol) and 35% hydrochloric acid (60.0 mL) and the resulted mixture was stirred at 0 °C for 15 min. The above mixture was poured into a solution containing potassium iodide (71.5 g, 400 mmol) and water (240 mL) and the combined reaction solution was stirred at room temperature overnight. The mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with H<sub>2</sub>O (3 × 100 mL) and dried over MgSO<sub>4</sub>. Then the solvent was removed under reduced pressure and the resultant was purified by column chromatography using hexane as eluent, which gives compound **6** as a light red liquid (24.0 g, 70%);  $R_f$  (EAC:hexane = 1:10) = 0.8. MS ( $m/z$ ): 295.8. Anal. Calcd for C<sub>12</sub>H<sub>9</sub>IO: C, 48.67; H, 3.06; I, 42.86; O, 5.40. Found: C, 48.58; H, 3.02; I, 42.82; O, 5.48.

**9-(2-Biphenyl)-2,7-dibromo-9-fluorenone (10).** To a solution of magnesium (0.32 g, 13 mmol), iodine (0.05 g), and 5 mL of anhydrous THF was slowly added compound **2** (2.5 g, 9 mmol) in 25 mL of anhydrous THF via dropping funnel under nitrogen atmosphere. During the addition period, the reaction mixture was stirred at reflux for 2 h.

To a solution of compound **4** (2.3 g, 7 mmol) in anhydrous THF (30 mL) was slowly added the above Grignard reagent at room temperature under nitrogen atmosphere. After complete addition, the reaction mixture was stirred at reflux for 12 h. The mixture was poured into an HCl aqueous solution (3M, 200 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with H<sub>2</sub>O (3 × 100 mL) and dried over MgSO<sub>4</sub>. Then the solvent was removed under reduced pressure and the resultant was purified by column chromatography using hexane as eluent. The pure product was obtained as a light yellow solid (2.2 g, 63%);  $R_f$  (EAC:hexane = 1:10) = 0.4; MS ( $m/z$ ): 491.8. Anal. Calcd for C<sub>25</sub>H<sub>16</sub>Br<sub>2</sub>O: C, 61.00; H, 3.28; Br, 32.47; O, 3.25. Found: C, 60.91; H, 3.23; Br, 32.42; O, 3.28.

**Spiro-9-(2,7-dibromofluorene)-9'-fluorene (11).** A reaction mixture containing compound **10** (6.3 g, 13 mmol), 35% hydrochloric acid (0.3 mL) and acetic acid (60 mL) was stirred at 140 °C for 2.5 h. The mixture was poured into methanol. After filtration and washing with water twice, the compound **11** was obtained as a brown solid (5.5 g, 89%);  $R_f$  (EAC:hexane = 1:10) = 0.8; MS ( $m/z$ ): 473.9; Anal. Calcd for C<sub>25</sub>H<sub>14</sub>Br<sub>2</sub>: C, 63.32; H, 2.98; Br, 33.70. Found: C, 63.26; H, 2.95; Br, 33.66.

**2,7-Dibromo-9-(2-phenoxyphenyl)-9-fluorenone (14).** To a solution of magnesium (0.85 g, 35 mmol), iodine (0.05 g) and 10 mL of anhydrous THF was slowly added compound **6** (7.0 g, 23 mmol) in 60 mL of anhydrous THF via dropping funnel under nitrogen atmosphere. During the addition period, the reaction mixture was stirred at reflux for 2 h.

To a solution of compound **4** (4.8 g, 14 mmol) in anhydrous THF (30 mL) was slowly added the above Grignard reagent at room temperature under nitrogen atmosphere. After complete addition, the reaction mixture was stirred at reflux for 20 h. The mixture was poured into an HCl aqueous solution (3M, 200 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with H<sub>2</sub>O (3 × 100 mL) and dried over MgSO<sub>4</sub>. Then the solvent was removed under reduced pressure and the resultant was purified by column chromatography using hexane as eluent. The pure product was obtained as a light yellow solid (4.6 g, 65%);  $R_f$  (EAC:hexane = 1:10) = 0.5; MS ( $m/z$ ): 507.9. Anal. Calcd for C<sub>25</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>2</sub>: C, 59.08; H, 3.17; Br, 31.45; O, 6.30. Found: C, 58.88; H, 3.14; Br, 31.37; O, 6.35.

**Spiro-9-(2,7-dibromofluorene)-9'-xanthene (15).** A reaction mixture containing compound **14** (9.0 g, 18 mmol), 35% hydrochloric acid (0.8 mL) and acetic acid (80 mL) was stirred at 140 °C for 2 h. The mixture was poured into methanol. After filtration and washing with water twice, the compound **15** was obtained as a gray solid (5.6 g, 64%). Melting temperature: 273–275 °C.  $R_f$  (EAC:hexane = 1:10) = 0.7. MS ( $m/z$ ): 440.3. Anal. Calcd for C<sub>25</sub>H<sub>14</sub>Br<sub>2</sub>O: C, 61.26; H, 2.88; Br, 32.60; O, 3.26. Found: C, 61.15; H, 2.82; Br, 32.51; O, 3.24. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) = 6.38–6.40 (m, 2H), 6.81–6.84 (m, 2H),



7.22–7.26 (m, 4H), 7.27 (m, 2H), 7.49–7.51 (m, 2H), 7.62–7.64 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 54.21, 117.11, 121.38, 122.40, 123.04, 123.53, 127.78, 128.69, 129.04, 131.35, 137.56, 151.09, 156.57.

**4-Methoxyphenylboronic Acid (17).** To a solution of magnesium (1.95 g, 81 mmol), iodine (0.05 g) and 5 mL of anhydrous THF, 4-bromoanisole (10.0 g, 53 mmol) was slowly added to 25 mL of anhydrous THF via dropping funnel under nitrogen atmosphere. During the addition period, the reaction mixture was stirred under reflux for 2 h.

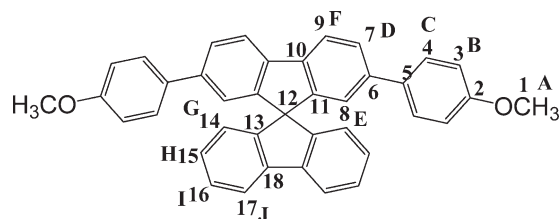
To a solution of trimethyl borate (14.0 g, 135 mmol) in anhydrous ethyl ether (50 mL), the above Grignard reagent was slowly added at  $-78^\circ\text{C}$  in a nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred at room temperature overnight. The mixture was poured into an HCl aqueous solution (3M, 200 mL) and extracted with diethyl ether ( $3 \times 100$  mL). The combined organic layers were washed with  $\text{H}_2\text{O}$  ( $3 \times 100$  mL) and dried over  $\text{MgSO}_4$ . Then the solvent was removed under reduced pressure and the resultant was washed with hexane twice. The pure product was obtained as a white solid (9.1 g, 89%).  $R_f$  (EAC:hexane = 1:1) = 0.4. MS ( $m/z$ ): 151.9. Anal. Calcd for  $\text{C}_7\text{H}_9\text{BO}_3$ : C, 55.33; H, 5.97. Found: C, 55.25; H, 5.89.

**General Procedure for the Preparation of the Monomers.** Couple reactions of compounds **11** and **15** were carried out using Suzuki reactions<sup>17,18</sup> with 2.3 equiv of compound **17** in solvent mixtures of toluene, sodium carbonate aqueous solution (1M) and tetrakis(triphenyl phosphine) palladium (0). These reactions produced precursors **18** and **19**, respectively, in good to excellent yields. After demethylation of **18** and **19**, monomers **MOHa** and **MOHb** could be obtained in good yields. The detailed procedure for creating each monomer is given separately below.

First 1 equiv mol of precursors (**11** and **15**), 0.03 equiv mol of  $\text{Pd}(\text{PPh}_3)_4$ , and 3.7 equiv mol of  $\text{Na}_2\text{CO}_3$  were placed in a flame-dried flask. A proper amount of toluene/ $\text{H}_2\text{O}$  (1/1) was added to 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 equiv mol of **17** was introduced into the solution. The reaction mixture was stirred under reflux for 24 h. The resultant mixture was then passed through a short column packed with silica gel. Evaporation of solvent yielded a crude product (**18** and **19**), which was purified by column chromatography.

To a 10 wt % solution containing precursors **18** and **19** and anhydrous dichloromethane was added a proper amount of  $\text{BBr}_3$ . The reaction mixture was stirred at  $0-5^\circ\text{C}$  in a nitrogen atmosphere. The mixture was poured into a  $\text{NaHCO}_3$  aqueous solution (1M) and extracted with dichloromethane twice. The combined organic layers were washed with  $\text{H}_2\text{O}$  and dried over  $\text{MgSO}_4$ . Then the solvent was removed under reduced pressure and the resultant was purified by column chromatography using ethyl acetate: hexane = 1:10 as eluent. The monomers **MOHa**–**b** were obtained as a white solid in good yields. The above procedure was used in the synthesis of monomers **MOHa**–**b**.

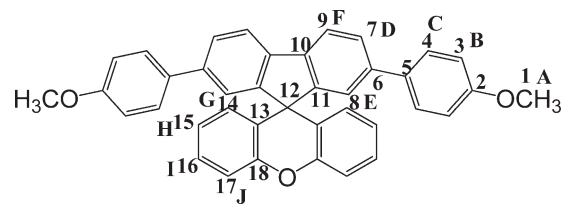
*Spiro-9-{2,7-bis[4-methoxyphenyl]fluorene}-9'-fluorene (18).*



**11** (2.50 g, 5.27 mmol), **17** (2.33 g, 11.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.10 g, 0.08 mmol),  $\text{Na}_2\text{CO}_3$  (2.12 g, 20.0 mmol),  $\text{H}_2\text{O}$  (20 mL), and toluene (20 mL) gives **18** as a white solid purified from silica gel column chromatography (5.07 g, 48%).  $R_f$  (EAC:hexane = 1:10): 0.3. MS ( $m/z$ ): 528.3. Anal. Calcd for  $\text{C}_{39}\text{H}_{28}\text{O}_2$ : C, 88.61; H, 5.34. Found: C, 88.50; H, 5.29.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 3.79 (s, 6H,  $\text{H}_\text{A}$ ), 6.86–6.88 (m, 6H,  $\text{H}_\text{B}, \text{H}_\text{H}$ ), 6.94 (s, 2H,  $\text{H}_\text{E}$ ),

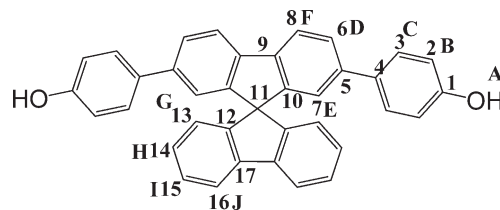
7.13–7.16 (m, 2H,  $\text{H}_\text{I}$ ), 7.38–7.42 (m, 6H,  $\text{H}_\text{C}, \text{H}_\text{D}$ ), 7.60–7.62 (m, 2H,  $\text{H}_\text{G}$ ), 7.89–7.92 (m, 4H,  $\text{H}_\text{F}, \text{H}_\text{J}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 66.06 ( $\text{C}_1$ ), 158.99 ( $\text{C}_2$ ), 113.98 ( $\text{C}_3$ ), 127.69 ( $\text{C}_4$ ), 133.45 ( $\text{C}_5$ ), 140.33 ( $\text{C}_6$ ), 119.96 ( $\text{C}_7$ ), 122.14 ( $\text{C}_8$ ), 127.86 ( $\text{C}_9$ ), 140.14 ( $\text{C}_{10}$ ), 149.71 ( $\text{C}_{11}$ ), 55.24 ( $\text{C}_{12}$ ), 148.82 ( $\text{C}_{13}$ ), 128.01 ( $\text{C}_{14}$ ), 124.26 ( $\text{C}_{15}$ ), 120.16 ( $\text{C}_{16}$ ), 126.39 ( $\text{C}_{17}$ ), 141.75 ( $\text{C}_{18}$ ).

*Spiro-9-{2,7-bis[4-methoxyphenyl]fluorene}-9'-xanthene (19).*



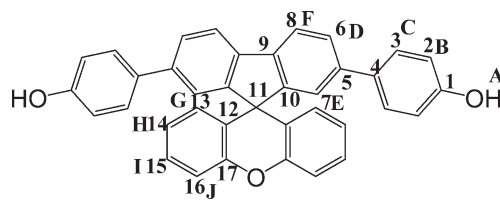
**15** (3.00 g, 6.12 mmol), **17** (2.76 g, 18.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.06 g, 0.05 mmol),  $\text{Na}_2\text{CO}_3$  (2.54 g, 24.0 mmol),  $\text{H}_2\text{O}$  (24 mL), and toluene (24 mL) gives **19** as a white solid purified from silica gel column chromatography (2.13 g, 64%).  $R_f$  (EAC:hexane = 1:10): 0.3. MS ( $m/z$ ): 543.6. Anal. Calcd for  $\text{C}_{39}\text{H}_{28}\text{O}_3$ : C, 86.01; H, 5.18. Found: C, 85.92; H, 5.10.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 3.82 (s, 6H,  $\text{H}_\text{A}$ ), 6.56–6.58 (m, 2H,  $\text{H}_\text{I}$ ), 6.81–6.83 (m, 2H,  $\text{H}_\text{H}$ ), 6.91–6.92 (m, 4H,  $\text{H}_\text{B}$ ), 7.20–7.24 (m, 2H,  $\text{H}_\text{I}$ ), 7.26–7.29 (m, 2H,  $\text{H}_\text{D}$ ), 7.39 (m, 2H,  $\text{H}_\text{E}$ ), 7.45–7.47 (m, 4H,  $\text{H}_\text{C}$ ), 7.61–7.63 (m, 2H,  $\text{H}_\text{G}$ ), 7.86–7.87 (m, 2H,  $\text{H}_\text{F}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 60.37 ( $\text{C}_1$ ), 159.11 ( $\text{C}_2$ ), 114.07 ( $\text{C}_3$ ), 128.10 ( $\text{C}_4$ ), 124.97 ( $\text{C}_5$ ), 140.81 ( $\text{C}_6$ ), 123.36 ( $\text{C}_7$ ), 128.04 ( $\text{C}_8$ ), 128.10 ( $\text{C}_9$ ), 138.03 ( $\text{C}_{10}$ ), 151.37 ( $\text{C}_{11}$ ), 54.38 ( $\text{C}_{12}$ ), 133.38 ( $\text{C}_{13}$ ), 126.46 ( $\text{C}_{14}$ ), 120.15 ( $\text{C}_{15}$ ), 123.81 ( $\text{C}_{16}$ ), 116.74 ( $\text{C}_{17}$ ), 155.94 ( $\text{C}_{18}$ ).

*Spiro-9-{2,7-bis[4-hydroxyphenyl]fluorene}-9'-fluorene (MOHa).*



**18** (1.06 g, 3.03 mmol),  $\text{BBr}_3$  (0.5 mL), and dichloromethane (15 mL) gives **MOHa** as a white solid purified from silica gel column chromatography (0.76 g, 50%). Melting temperature:  $339-340^\circ\text{C}$ .  $R_f$  (EAC:hexane = 1:1): 0.6. MS ( $m/z$ ): 500.2. Anal. Calcd for  $\text{C}_{37}\text{H}_{24}\text{O}_2$ : C, 88.78; H, 4.83. Found: C, 88.70; H, 4.79.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 6.68–6.70 (m, 4H,  $\text{H}_\text{A}, \text{H}_\text{D}$ ), 6.76–6.78 (m, 2H,  $\text{H}_\text{G}$ ), 6.84 (s, 2H,  $\text{H}_\text{E}$ ), 7.08–7.11 (m, 2H,  $\text{H}_\text{H}$ ), 7.23–7.25 (m, 4H,  $\text{H}_\text{B}$ ), 7.33–7.36 (m, 2H,  $\text{H}_\text{I}$ ), 7.58–7.60 (m, 2H,  $\text{H}_\text{F}$ ), 7.91–7.93 (m, 4H,  $\text{H}_\text{C}$ ), 8.32 (s, 2H,  $\text{H}_\text{J}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 158.37 ( $\text{C}_1$ ), 116.28 ( $\text{C}_2$ ), 128.54 ( $\text{C}_3$ ), 132.82 ( $\text{C}_4$ ), 141.82 ( $\text{C}_5$ ), 120.87 ( $\text{C}_6$ ), 122.41 ( $\text{C}_7$ ), 128.54 ( $\text{C}_8$ ), 140.98 ( $\text{C}_9$ ), 150.72 ( $\text{C}_{10}$ ), 60.55 ( $\text{C}_{11}$ ), 150.09 ( $\text{C}_{12}$ ), 128.65 ( $\text{C}_{13}$ ), 124.96 ( $\text{C}_{14}$ ), 120.99 ( $\text{C}_{15}$ ), 126.99 ( $\text{C}_{16}$ ), 142.89 ( $\text{C}_{17}$ ).

*Spiro-9-{2,7-bis[4-hydroxyphenyl]fluorene}-9'-xanthene (MOHb).*



**19** (5.00 g, 9.18 mmol),  $\text{BBr}_3$  (1.0 mL), and dichloromethane (95 mL) gives **MOHb** as a white solid purified from silica gel column chromatography (2.84 g, 60%). Melting temperature:  $261-263^\circ\text{C}$ .  $R_f$  (EAC:hexane = 1:3): 0.2; MS ( $m/z$ ): 515.6. Anal. Calcd for  $\text{C}_{37}\text{H}_{24}\text{O}_3$ : C, 86.03; H, 4.68. Found: C, 85.87; H, 4.65.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 6.49–6.51 (m, 2H,  $\text{H}_\text{A}$ ), 6.71–6.73 (m, 4H,  $\text{H}_\text{B}$ ), 6.75–6.78 (m, 2H,  $\text{H}_\text{H}$ ), 7.16–7.19

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

polymer	yield (%)	$M_n^a$	$M_w^a$	$M_w/M_n$
P1a	89	128 490	241 300	1.88
P2a	90	89 800	175 890	1.96
P3a	90	23 060	39 950	1.73
P4a	87	41 220	68 270	1.66
P1b	91	27 360	48 500	1.77
P2b	88	31 470	63 560	2.02
P3b	86	31 430	54 740	1.74
P4b	89	20 940	35 070	1.68

<sup>a</sup> Given in  $\text{g mol}^{-1}$  determined by gel permeation chromatography in THF by UV–vis detector versus polystyrene standards.

(m, 2H,  $H_I$ ), 7.22–7.23 (m, 2H,  $H_D$ ), 7.31–7.32 (m, 6H,  $H_C, H_G$ ), 7.59–7.61 (m, 2H,  $H_J$ ), 7.87–7.89 (m, 2H,  $H_F$ ), 8.35 (s, 2H,  $H_E$ ). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 158.50 ( $C_1$ ), 116.36 ( $C_2$ ), 128.99 ( $C_3$ ), 126.23 ( $C_4$ ), 142.32 ( $C_5$ ), 124.12 ( $C_6$ ), 128.68 ( $C_7$ ), 128.93 ( $C_8$ ), 138.90 ( $C_9$ ), 152.50 ( $C_{10}$ ), 55.42 ( $C_{11}$ ), 132.74 ( $C_{12}$ ), 127.07 ( $C_{13}$ ), 121.00 ( $C_{14}$ ), 124.20 ( $C_{15}$ ), 117.49 ( $C_{16}$ ), 157.11 ( $C_{17}$ ).

**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 **M1–M4** (0.9 mmol), bisphenol monomer **MOHa–b** (0.9 mmol), potassium carbonate (1.8 mmol), DMAc (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 work up, the resultant polymer solution was diluted with 8 mL of THF and poured into a stirring methanol (250 mL) and the fibrous polymer was precipitated in situ. The precipitated polymers **P1a–P4b** were collected by filtration and washed with 10% HCl and  $\text{H}_2\text{O}$  and then vacuum-dried until no solvent was detected in TGA experiment. For yields and molecular masses, see Table 1.

**Polymer P1a.** Applying general procedure to monomers **M1** and **MOHa** affords **P1a** in 89% yield, which is soluble in chloroform under reflux. GPC analysis shows that the number-average and weight-average molecular weight of **P1a** are 128 500 and 241 300, respectively. Anal. Calcd for  $(\text{C}_{75}\text{H}_{54}\text{F}_6\text{O}_2)_n$  (1101.2)<sub>n</sub>: C, 81.80; H, 4.94. Found: C, 81.79; H, 4.78.

**Polymer P1b.** Applying general procedure to monomers **M1** and **MOHb** affords **P1b** in 91% yield, which is soluble in chloroform at room temperature. GPC analysis shows that the number-average and weight-average molecular weight of **P1b** are 27 400 and 48 500, respectively. Anal. Calcd for  $(\text{C}_{75}\text{H}_{54}\text{F}_6\text{O}_3)_n$  (1117.2)<sub>n</sub>: C, 80.63; H, 4.87. Found: C, 80.48; H, 4.81.

**Polymer P2a.** Applying general procedure to monomers **M2** and **MOHa** affords **P2a** in 90% yield, which is soluble in chloroform under reflux. GPC analysis shows that the number-average and weight-average molecular weight of **P2a** are 89 800 and 175 900, respectively. Anal. Calcd for  $(\text{C}_{78}\text{H}_{48}\text{F}_6\text{O}_2)_n$  (1131.2)<sub>n</sub>: C, 82.82; H, 4.28. Found: C, 82.27; H, 4.16.

**Polymer P2b.** Applying general procedure to monomers **M2** and **MOHb** affords **P2b** in 88% yield, which is soluble in chloroform at room temperature. GPC analysis shows that the number-average and weight-average molecular weight of **P2b** are 31 500 and 63 600, respectively. Anal. Calcd for  $(\text{C}_{78}\text{H}_{48}\text{F}_6\text{O}_3)_n$  (1147.2)<sub>n</sub>: C, 81.66; H, 4.22. Found: C, 81.21; H, 4.17.

**Polymer P3a.** Applying general procedure to monomers **M3** and **MOHa** affords **P3a** in 90% yield, which is soluble in chloroform at room temperature. GPC analysis shows that the number-average and weight-average molecular weight of **P3a** are 23 100 and 40 000, respectively. Anal. Calcd for  $(\text{C}_{78}\text{H}_{50}\text{F}_6\text{O}_2)_n$  (1133.2)<sub>n</sub>: C, 82.67; H, 4.45. Found: C, 82.52; H, 4.36.

**Polymer P3b.** Applying general procedure to monomers **M3** and **MOHb** affords **P3b** in 86% yield, which is insoluble in

chloroform. GPC analysis shows that the number-average and weight-average molecular weight of **P3b** are 31 400 and 54 700, respectively. Anal. Calcd for  $(\text{C}_{78}\text{H}_{50}\text{F}_6\text{O}_3)_n$  (1149.2)<sub>n</sub>: C, 81.52; H, 4.39. Found: C, 80.79; H, 4.11.

**Polymer P4a.** Applying general procedure to monomers **M4** and **MOHa** affords **P4a** in 87% yield, which is soluble in chloroform at room temperature. GPC analysis shows that the number-average and weight-average molecular weight of **P4a** are 41 200 and 68 300, respectively. Anal. Calcd for  $(\text{C}_{78}\text{H}_{48}\text{F}_6\text{O}_3)_n$  (1147.2)<sub>n</sub>: C, 81.66; H, 4.22. Found: C, 81.48; H, 4.18.

**Polymer P4b.** Applying general procedure to monomers **M4** and **MOHb** affords **P4b** in 89% yield, which is soluble in chloroform at room temperature. GPC analysis shows that the number-average and weight-average molecular weight of **P4b** are 20 900 and 35 100, respectively. Anal. Calcd for  $(\text{C}_{78}\text{H}_{48}\text{F}_6\text{O}_4)_n$  (1163.2)<sub>n</sub>: C, 80.54; H, 4.16. Found: C, 79.94; H, 3.91.

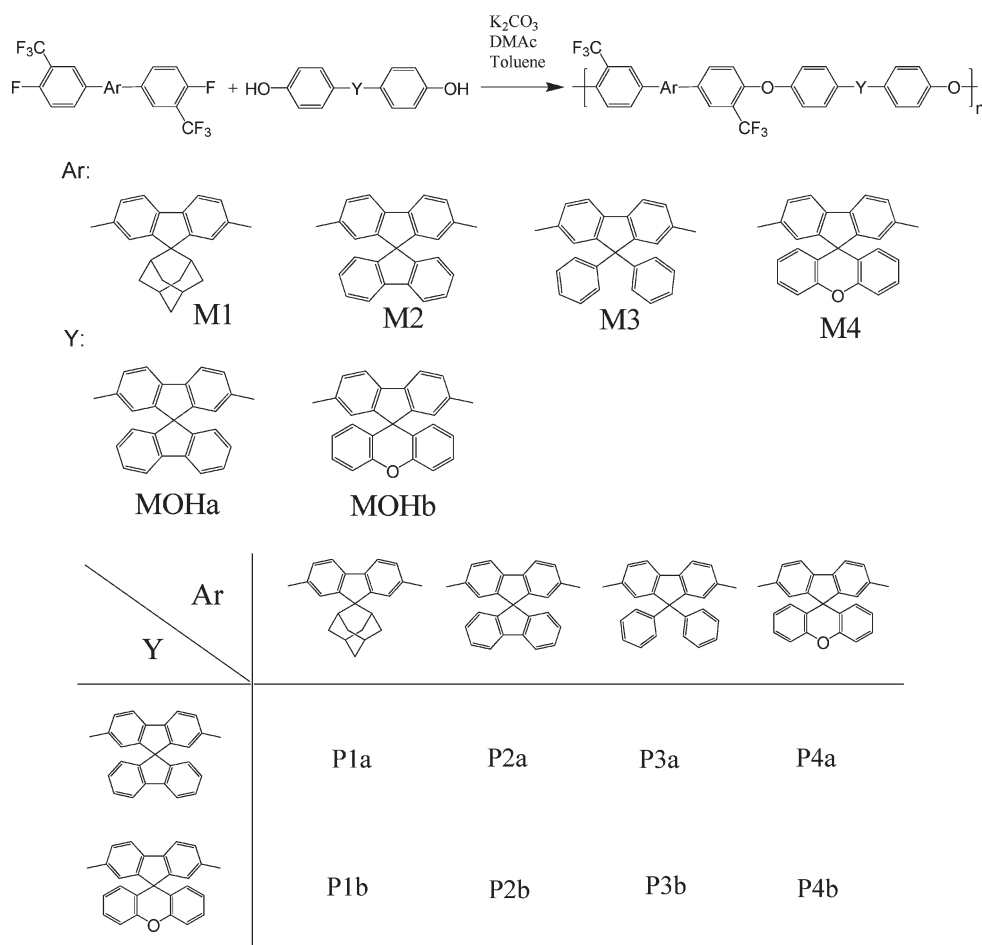
## Results and Discussion

**Polymerizations.** The bisfluoro monomers **M1–M4** were each polymerized with bisphenols **MOHa–b** to provide a series of poly(arylene ether)s (Scheme 3). The poly(arylene ether)s were prepared using equimolar amounts of monomers in a mixed solvent system of 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 under 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.

Gel permeation chromatography 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 <sup>1</sup>H NMR signals of –OH 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 rigid and bulky pendant of 9,9'-bis(4-hydroxyphenyl) fluorene (**MOHa**) have a higher degree of polymerization than the ones having soft pendants (**MOHb**). 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 DMF, DMAc, and

Scheme 3. Synthesis of Polymers



NMP. Surprisingly, the polymers were only swelled in the presence of DMSO and ethyl acetate.

**NMR Spectroscopy.** With aid of  $^{13}\text{C}$  DEPT spectrum, the positions of chemical shifts of  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR for monomers **M2** and **MOHa** are readily assigned as shown in Figure 1 and Supporting Information Figure 1, respectively, on the basis of the chemical shielding effect. Because of a nearly fully aromatic structure the chemical shifts for all carbons (Figure 1) locate between 116 and 160 ppm except for alkyl carbons **14** and **11**, which appear at 66 and 70 ppm for **M2** and **MOHa**, respectively. In addition, all tertial carbons, which are upward in DEPT spectra, display the chemical shifts between 116 and 132 ppm for both **M2** and **MOHa** monomers. Because of fluoro-coupling effect the  $^{13}\text{C}$  NMR spectrum of the bis-fluoro monomer **M2** (Figure 1a) shows quartet and doublet for carbons at positions **1** and **3**, respectively. In addition, splitting of the **2**, **4**, and **6** carbon absorptions are observed owing to long-range effects by the  $\text{CF}_3$  and C–F fluorine. The  $^1\text{H}$  NMR chemical shifts for both **M2** and **MOHa** are assigned and shown as Supporting Information. When above-mentioned monomers **M2** and **MOHa** were polymerized into **P2a**, due to fluoro-displacement occurred in polymerization reaction the corresponding  $^{13}\text{C}$  NMR spectrum of the polymer **P2a** (not shown here) presents merely a peak at 154 ppm attributed to the oxy-carbon of the oxy-phenyl groups instead of the doublet of fluoro-carbon **3** in monomer **M2**. Concurrently, the chemical shift of hydroxyl-protons on **MOHa** at 6.70 ppm disappears owing to polymerization. Besides NMR characterization, X-ray diffraction analysis in our previous study<sup>19</sup> also confirmed the structures of monomers **M1–M4**. Furthermore,

Table 2. Solubility of Poly(arylene ether)s<sup>a</sup>

polymer	NMP	DMF	DMSO	THF	chloroform	EAc	toluene	DMAc
P1a	○	–	–	+	○	–	+	○
P2a	–	–	–	+	○	–	○	○
P3a	+	–	–	+	+	–	○	○
P4a	+	+	–	+	+	–	+	+
P1b	+	–	–	+	+	–	+	+
P2b	+	–	–	+	+	–	+	+
P3b	–	–	–	○	–	–	–	○
P4b	+	+	–	+	+	–	+	+

<sup>a</sup> Key: (+) soluble at room temperature; (○) soluble at refluxing; (–) insoluble at refluxing.

combined information on aforementioned characterization results and the elemental analysis data listed in the Experimental Section confirmed the presence of all new compounds.

**Thermal Properties.** The thermal properties of the polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results of TGA measurements for polymers **P1a–P4b** are listed in Table 3. The polymers were stable up from 482 to 637 °C in nitrogen atmospheres (Table 3). On the basis of polymer structures, TGA thermograms (Figure 2) show that the polymers could be briefly classified into two categories. The first category, polymers **P2–P4a** and **P2–P4b** having almost fully aromatic main chain, show only one decomposition process, starting at about 550 °C with char residues of about 75% at 800 °C, which was attributed to the degradation of the main chain. In polymers **P1a** and **P1b** the second category, possessing pendent groups of adamantyl attached to the main chain also show one decomposition



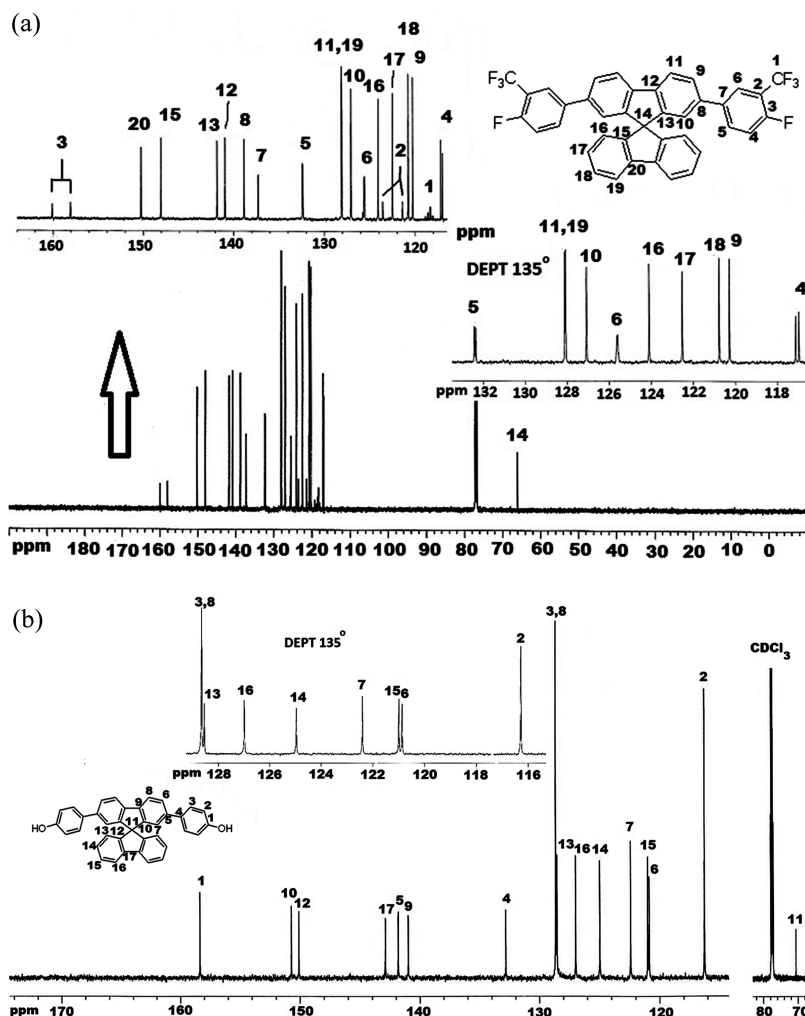


Figure 1.  $^{13}\text{C}$   $135^\circ$  DEPT and  $^{13}\text{C}$  NMR spectra for (a) monomer M2, and (b) monomer MOHa.

process; however, it starts at a lower temperature of about  $460^\circ\text{C}$  with char residues of about 70% at  $800^\circ\text{C}$ . This is owing to the alkyl pendent groups, which cause the degradation to occur at somewhat lower temperatures than the ones of first category. In order to make a clear comparison, the temperature of 5% weight loss as a function of monomer for each polymer was depicted in Figure 3. Besides above observations the data basically shows that on the basis of bisphenol monomer structures, the polymers prepared from **MOHb** monomer have better thermal stability than the polymers derived from **MOHa** monomer. This is because compared to the stress sourced from spiro-fluorenyl group (**MOHa**) the one from the spiro-xanthenyl group (**MOHb**) is somewhat reduced by ether linkage in the structure and consequently resulting in a better thermal stability for the polymers prepared from **MOHb** monomer. On the other hand, on the basis of bifluoro monomer structures the polymers made from **M1–M4** have increased thermal stability successively. This is quite interesting because the trend is substantially different from the one of glass transition temperature, which is presented and discussed in the next paragraph. 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  $482^\circ\text{C}$  was well above the highest temperature ( $380^\circ\text{C}$ ) 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.

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

polymer	$T_g$ ( $^\circ\text{C}$ ) <sup>a,b</sup>	$T_d$ ( $^\circ\text{C}$ ) <sup>c</sup>	$T_d^5$ ( $^\circ\text{C}$ ) <sup>d</sup>
P1a	356 (362)	482	490
P2a	353 (360)	554	561
P3a	307 (316)	562	570
P4a	313 (327)	568	572
P1b	322 (330)	484	492
P2b	318 (326)	568	575
P3b	300 (310)	590	596
P4b	313 (324)	637	643

<sup>a</sup> Glass transition temperature was measured by DSC and the reflection point was taken as  $T_g$ . <sup>b</sup> Glass transition temperature in the parentheses was measured by DMA. <sup>c</sup> Initial decomposition temperature was recorded on TGA at a heating rate of  $20^\circ\text{C}/\text{min}$  under  $\text{N}_2$  and the onset temperature was taken as  $T_d$ . <sup>d</sup> Temperature at which 5% weight loss recorded on TGA at a heating rate of  $20^\circ\text{C}/\text{min}$  under  $\text{N}_2$ .

In the DSC scans of **P1a–P4b** (Figure 4),  $T_g$  values were in the range  $300\text{--}356^\circ\text{C}$ , depending on the monomer used in the synthesis.  $T_g$  is known to depend on several factors such as the rigidity of the main polymer chain, chain symmetry, intermolecular forces, and the bulkiness of side pendants. As shown in Figure 4 and Table 3, when comparing  $T_g$  values in different bisfluoro monomer structures, the results indicate that the adamantylidene-substituted polymers **P1a–P1b** have the highest  $T_g$  values followed by fluorenylidene-substituted polymers **P2a–P2b**, xanthenylidene-substituted polymers **P4a–b**, and then diphenylmethylenesubstituted polymers **P3a–P3b**, due to a gradual decrease in the stiffness



and/or bulkiness of substituents on middle biphenyl of the polymer main chain, which causes less restriction for rotating the substituents along the polymer main chain. Additionally, an unignorable factor of influence on  $T_g$  values is molecular weight, which should be noticed here. Table 1 shows that in polymers **P1–P4a** a successive sequence of molecular weights is presented as follows: **P1a** > **P2a** > **P4a** > **P3a**, which has the same trend of sequence in  $T_g$  values. Therefore, molecular weights might play an important part in affecting  $T_g$  values although a similar trend does not occur in polymers **P1–P4b**.

On the other hand, the polymers **P1–P4a** prepared from **MOHa** possess the higher  $T_g$  values than the polymers

**P1–P4b** made from **MOHb** because compared to **MOHb**, **MOHa** has higher rigidity in molecular structure due to ether linkage softening effect of **MOHb**. The  $T_g$  of **P1a** is 3 °C higher than that of **P2a** due to multicyclic structural effect. In our previous studies<sup>3,4</sup> we found that compared to adamantylidene group (**P1a**) although fluorenylidene group (**P2a**) possesses higher molecular mass and more aromatic structure, the multicyclic structural effect of adamantylidene group outweighs the influence of molecular mass and aromatic structure of fluorenylidene group. The  $T_g$  of **P4a** is 37 °C lower than that of **P2a** owing to softening effect of ether linkage in xanthenylidene group (**P4a**). On the other hand, because of hardening effect from cyclic structures, polymers **P2a** and **P4a** exhibit higher  $T_g$ 's than polymer **P3a** (diphenylmethylene group) by 46 and 9 °C, respectively. Similar trends are also observed in polymers **P1–P4b**.

By comparison with previous studies,<sup>2</sup> the published  $T_g$  values are collected and listed in Table 4. It shows that the  $T_g$  values increase gradually from *p*-terphenylene, *p*-quaterphenylene without and with substituents to tetraphenyl-substituted *p*-pentaphenylene PAEs, based on different bisfluoro monomer structures due to a gradual increase in the rigidity of main chain structures. On the other hand, when comparing  $T_g$  values in different bisphenol monomer structures, it indicates the  $T_g$  values increase gradually from 6F BPA, fluorenylidene, adamantylidene to spiro fluorenyl 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  $T_g$ 's, 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%. The representative dynamic mechanical spectra of PAE **P2a** are shown in Figure 5. It indicates that the primary relaxations, the large-scale chain motions characteristic of the glass transition ( $\tan \delta$ ), appear at 360 °C for **P2a**. The mechanical relaxation spectra of the other polymers in this study resemble those of **P2a**.

The polymers in this study show  $T_g$ 's measured by DMA ranging from 310 to 362 °C. These data are consistent with the calorimetric results shown in Table 3, clearly showing the high  $T_g$ 's and good dimensional stability exhibited by these materials. The  $T_g$ 's of these polymers are among the highest reported values for arylene 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.<sup>1,21</sup> on similar

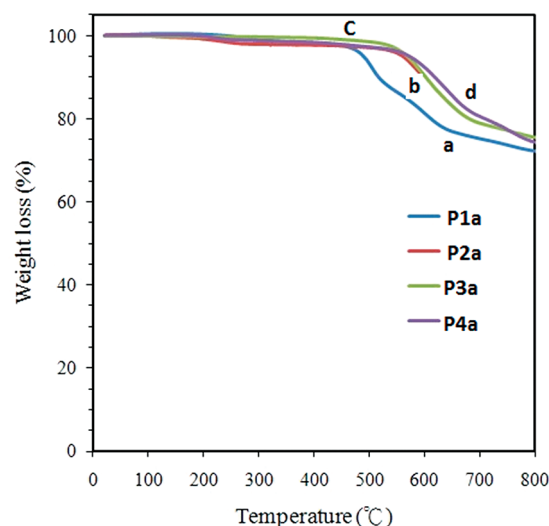


Figure 2. TGA thermograms of the poly(arylene ether)s.

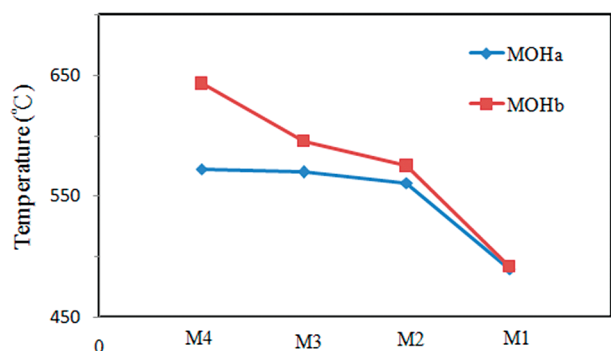


Figure 3. Polymer 5% weight loss temperature as a function of monomer.

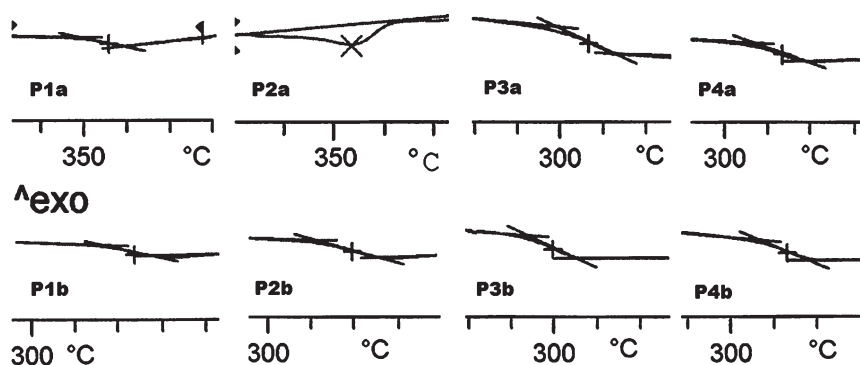

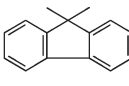

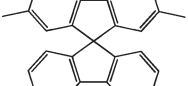

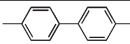
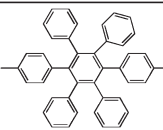
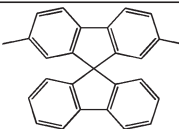
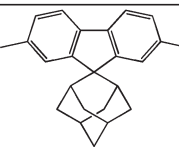
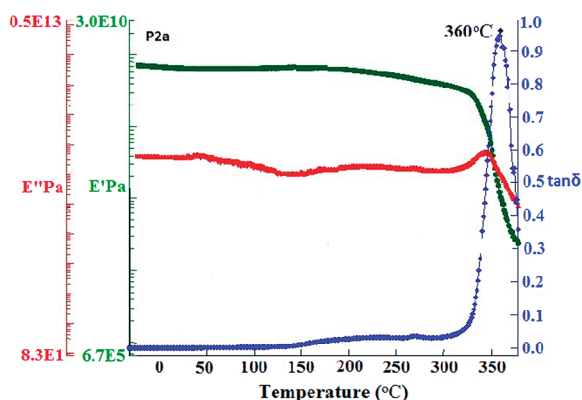


Figure 4. DSC thermograms of the poly(arylene ether)s.

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

$$\left[ \text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{Ar}-\text{C}_6\text{H}_3(\text{CF}_3)-\text{O}-\text{C}_6\text{H}_4-\text{Y}-\text{C}_6\text{H}_4-\text{O} \right]_n$$

Ar \ Y				
	179	234	—	—
	210	300	—	—
	271	332	334	—
	265	—	—	353
	270	—	—	356

**Figure 5.** Dynamic mechanical analysis of P2a.

structures. In addition to the primary relaxations, the secondary relaxations at ca. 0–90 °C also were observed for these polymers. This second relaxation is associated with a steady decrease in  $G'$ . Such a transition has generally been attributed to the rotation or oscillations of the pendent groups around the polymer main chain. Furthermore, these relaxations held still even though sub- $T_g$  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.

### Conclusion

The following conclusions were reached. (a) A new class of high-temperature, high- $T_g$  polymers, the poly(arylene ether)s, have been synthesized via a nucleophilic aromatic substitution reaction of bisfluoro-*p*-quaterphenylene monomers, with bisphenolates generating the arylene ether linkages. (b) The electro-withdrawing pendent groups of trifluoromethyl activate a nucleophilic fluoro displacement polymerization. (c) The nucleophilic displacement polymerization reactions were conducted in DMAc in the presence of potassium carbonate to give high molecular weight polymers. (d) Glass transition temperatures of the poly(arylene ether)s increase with increasing spiro-pendant stiffness in the monomers. (e) The materials experienced 5% weight losses above 490 °C by thermogravimetric analysis, indicative of their high thermal stability. (f) In comparison with previously reported analogues, owing to spiro-annulated substituents on the backbone the poly(arylene ether)s in this study possess rather better thermal properties, i.e., higher  $T_g$ 's and  $T_d$ 's, which have become an imperative for the engineering plastics applying on flexible electronics. Furthermore, all of the polymers in this study could be readily processed from solution to derive flexible transparent films. Combining all the above merits suggests that a good application to optical transparent materials in the visible light region of the spectrum is feasible.

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**Supporting Information Available:**  $^1\text{H}$  NMR spectra of monomer **M2** and **MOHa**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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