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Novel Poly(arylene ether)s with Pendent Trifluoromethyl Groups

Susanta Banerjee,[†] Gerhard Maier,* and Martin Burger

Technische Universität München, Lehrstuhl für Makromolekulare Stoffe, Lichtenbergstrasse 4, D-85747 Garching, Germany

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ABSTRACT: Six novel perfluoroalkyl-activated bishalo monomers **4a,b**−**6a,b** have been synthesized successfully using Pd(0)-catalyzed cross-coupling reaction of 4-chloro- or 4-fluoro-3-trifluoromethylphenylboronic acid with 1,4-dibromobenzene, 2,6-dibromopyridine, and 2,5-dibromothiophene. These monomers were converted to poly(arylene ether)s by nucleophilic displacement of the halogen atoms on the benzene ring with several bisphenols. The products obtained by displacement of the fluorine atoms exhibit weight-average molar masses up to 3.52×10^5 g mol^{-1} in GPC. Displacement of the chlorine atoms from the analogous monomer structures by bisphenols was not successful in obtaining high molar mass products. These poly(arylene ether)s showed very high thermal stability even up to 536 °C for 5% weight loss in TGA in synthetic air. Comparatively low thermal stability for the thiophene ring containing polymers was attributed to the oxidation of the sulfur atom of the thiophene ring at high temperature in air, which destroyed the aromatic character of the thiophene ring. This was confirmed by investigating the thermal stability of these polymers in an inert environment. The polymers exhibit glass transition temperatures (T_g) up to 234 °C in DSC. The glass transition temperatures taken as peak in tan δ in DMTA measurements are in good agreement with the DSC T_g values. All the polymers are soluble in a wide range of organic solvents, e.g., $CHCl_3$, THF, NMP, and DMF. Transparent thin films of these polymers cast from THF exhibited tensile strengths up to 70 MPa, a modulus of elasticity up to 2.69 GPa, and elongation at break up to 30% depending on their exact repeating unit structures.

Introduction

Much emphasis is placed today on the synthesis of poly(arylene ether)s and related structures which can be used as moldable or castable tough matrix resins having high glass transition temperatures and good thermal stability.[1] Poly(arylene ether)s are generally prepared by a step growth polymerization of activated aryl dihalo or dinitro monomers with bisphenoxides.[2] It is well-known that both sulfone and ketone groups are very effective in activating aryl halides toward nucleophlic displacement. Therefore, they are used in the synthesis of poly(aryl ether sulfone)s[3] and poly(aryl ether ketone)s,[4] respectively. Heterocyclic rings[5] and amide groups[6] have also been used as activating groups to produce high molar mass poly(arylene ether)s. A common feature of these groups is stabilization of negative charges developed at the 2- or 4-position of the aryl moiety in the transition state of the nucleophlic halogen displacement reaction through a Meisenheimer complex.[2] Labadie et al.[7] have reported that perfluoroalkyl groups, either pendent or in the main chain, activate fluoro or nitro displacement by phenoxides. Since electron-withdrawing perfluoroalkyl groups cannot participate in resonance stabilization, the activation by this group is expected due to the stabilization of the negative charges at the 2- or 4-position by hyperconjugation and by the negative inductive (−I) effect. The steric congestion due to a bulky trifluoromethyl group may also facilitate the formation of a stable Meisenheimer complex with release of steric strain.[8]

Among the possible applications of poly(arylene ether)s are the use as insulating materials in microelectronics (ILD and IMD) and the use as membrane materials, e.g., for gas separations. Fluorine-containing polymers are of special interest because of their low dielectric constants and remarkably low water absorption.[9−11] The 6F groups in the polymer backbone enhance polymer solubility (commonly referred to as the “fluorine effect”) without forfeiture of thermal stability. They also increase the glass transition temperature with concomitant decrease of crystallinity.[2b,c] The bulky $-CF_3$ group also serves to increase the free volume of the polymer, thereby improving various properties of polymers, including gas permeabilities 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. We have already reported a number of poly(arylene ether)s based on the following oxazole and thiazole monomers (Figure 1).[12]

The oxazole monomer **1** is extremely reactive, because the fluorine atom is activated not only by the $-CF_3$ group but also by the electron deficiency of the oxazole ring, and therefore produces high molar mass poly(arylene ether)s under mild conditions when reacted with bisphenols.[12a] In contrast, the thiazole monomer **2** failed to produce high molar mass polymers under similar conditions.[12d] The low reactivity of this monomer toward nucleophilic attack can be attributed to the fact that the electron-deficient character of the thiazole ring is much less pronounced than that of the oxazole ring. The polyethers derived from bisoxazole monomer **1** possess only limited thermal stability, whereas the polyethers derived from bisthiazole monomer **2** possess the expected high thermal stability. This can be attributed to the higher aromaticity of sulfur heteroaromatic rings as compared to their oxygen analogues. The polyethers derived from **3** have very good thermal stability due to the absence of any substituent in the 4-position of the oxazole, which precludes a certain decomposition reaction.[12a] It is anticipated that polymers with low dielectric constant and higher thermal stability can be achieved if the oxazole group can be replaced with a less polar and more aromatic phenyl unit. Considering all these points, we designed a new

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[†] Permanent address: Defence Research & Development Establishment, Jhansi Road, Gwalior-474002, India.

* Correspondening author.

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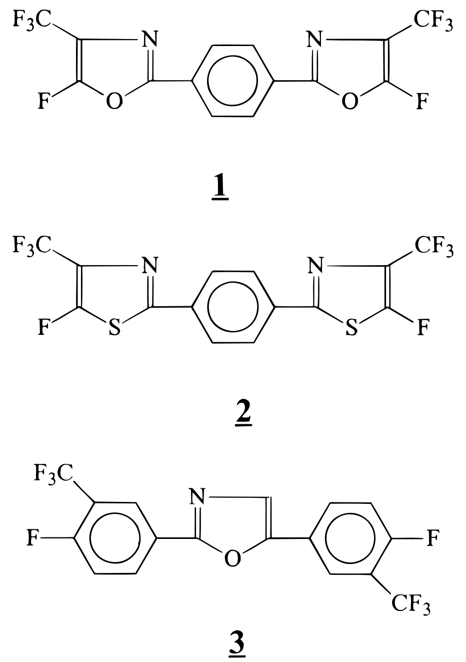


Figure 1.

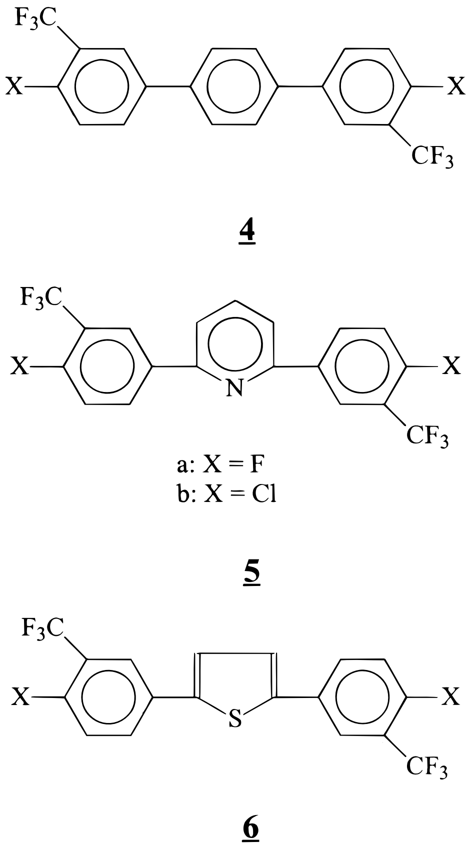


Figure 2.

class of poly(arylene ether)s from the monomers shown in Figure 2.

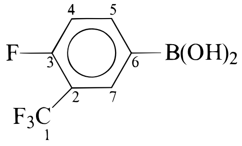
The preparation of this new class of semifluorinated poly(arylene ether)s relied, first, on the preparation of trifluoromethyl-activated bishalo monomers via Suzuki coupling[13] and, second, the subsequent utilization of these monomers in a nucleophilic aromatic substitution polymerization.[6] In this paper, we report the successful synthesis of these monomers, their polymerization with different bisphenols, and their characterization, including thermal and mechanical properties. In a future publication, the gas permeabilities and dielectric properties of these poly(arylene ether)s will be reported.

Experimental Section

General Considerations. Melting points are uncorrected and were determined with a Mettler-FP 5 + FP 51 Uni-Melt capillary melting point apparatus. Elemental analysis (C, H, N) was provided by Mikro-analytisches Labor Anorganische Chemie, TUM, Germany. GC-MS analysis of the monomers was performed on a HP 5890 instrument equipped with a MSD 5970 detector, EI 70 eV, to check their purity and mass. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{19}F NMR (282 MHz) spectra were recorded on a Bruker ARX 300 instrument [reference 0 ppm with TMS (^{1}H and ^{13}C NMR) or $CFCl_3$ (^{19}F NMR)]. IR spectra were recorded with a Bruker IFS 55 spectrophotometer with KBr pellets. Gel permeation chromatograms were obtained using a Waters instrument equipped with UV and RI detectors (Waters 510 HPLC Pump, Waters 410 differential refractometer, Waters 486 turnable detector at $\lambda = 254$ nm). Chloroform and THF were used as eluents at a flow rate of 0.5 mL/min, and Shodex K-802.5, K-804, and K-805 columns from Showa Denko ($CHCl_3$) and Waters Ultrastyragel 10^4, 10^5, and Styragel HR-2 (THF) columns were employed. Molecular weights and polydispersity are reported vs monodisperse polystyrene standards from Polymer Standard Service. DSC measurements were made on a Perkin-Elmer DSC-7 instrument, equipped with a TAC 7/DX thermal analyzer controller, at a heating/cooling rate of 20 K/min under nitrogen. Glass transition temperatures (T_g) were taken as the center of the step transition in the second heating run. Thermogravimetry was measured on a PL-STA 1500 instrument. A heating rate of 10 K/min was used for determination of the decomposition temperature (T_d) at 5% weight loss under synthetic air and nitrogen. Dynamic mechanical thermal analysis (DMTA) was performed on a PL-DMTA instrument equipped with a Rheometric Scientific mechanical thermal analysis controller in the tension mode on thin-film samples with a heating rate of 2 K/min (1 and 10 Hz). Stress−strain behavior of the thin polymer films (cast from THF solutions onto glass plates, the solvent was allowed to evaporate slowly at room temperature followed by drying at 100 °C for 24 h under vacuum) was observed at room temperature with a Miniature Materials Tester, PL Thermal Sciences, with strain rate 10%/min.

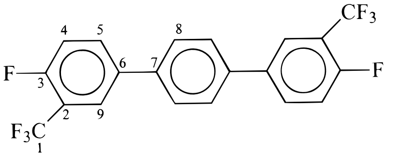
Starting Materials. All reagents were purchased from Aldrich, Fluka, Chempure, or Fluorochem Chemical Co. and used as received unless otherwise noted. The monomer 6F−BPA (Aldrich) was purified by recrystallization from toluene/ethyl acetate (95:5), BPA (Fluka) was recrystallized from toluene, and 4,4′-biphenyl (Aldrich) was recrystallized from ethanol/water. THF, diethyl ether (Et_2O), and toluene were refluxed over Na/K alloy to remove water and distilled freshly before use. NMP (Fluka) was purified by stirring with NaOH and distilled twice from P_2O_5 under reduced pressure.

Synthesis of Monomers. Synthesis of 4-Fluoro-3-trifluoromethylphenylboronic Acid. A solution of 5-bromo-2-fluorobenzotrifluoride (22 g, 90.49 mmol) in 100 mL of THF (peroxide free) was added slowly to a stirred mixture of magnesium turnings (2.4 g, 98.74 mmol) and 300 mL of dry THF under nitrogen. The reaction was initiated by the addition of a trace of iodine. The resulting mixture was stirred at 25 °C for 4−5 h, until consumption of almost all magnesium turnings. The resulting solution was added dropwise to a cooled (−78 °C) solution of trimethylborate (45 mL, 473.29 mmol) in dry Et_2O (400 mL). After complete addition the mixture was allowed to warm to room temperature and stirred overnight at 25 °C. Subsequently, 3 M HCl (375 mL) was added. The organic layer was separated, and the aqueous layer was extracted with ET_2O (2 × 150 mL). The combined organic phases were washed with water (2 × 200 mL) and dried ($MgSO_4$). The extract was evaporated, and the white powdered boronic acid derivative was washed several times with *n*-hexane to remove any impurity.



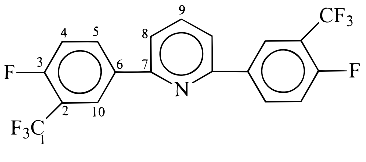
Yield: 15.50 g (83%). Melting point: 203 °C. Anal. Calcd for $C_7H_5F_4BO_2$ (207.92 g/mol): C, 40.44; H, 2.42. Found: C, 39.82; H, 2.25. IR (KBr): $\bar{\nu}$ (cm^{-1}) 1671, 1593, 1507, 1364, 1305, 1278, 1242, 1226, 1058, 844, 753, 725, 658, 540. ^{1}H NMR ($CDCl_3$/DMSO-d_6, 1: 1): δ (ppm) 8.2−7.9 (m); 7.5−7.4 (m). ^{13}C NMR ($CDCl_3$/DMSO-d_6): δ (ppm) 115.4 (m, C4); 116.2 (m, C2); 122.2 (q, J = 271.6 Hz, C1); 127.7 (m, C5); 133.9 (m, C6); 139.0 (m, C7); 159.9 (d, J = 255.8 Hz, C3). ^{19}F NMR ($CDCl_3$/DMSO-d_6): δ (ppm) 60.44 (m, 3F, F1); 114.7 (m, 1F, F3).

Synthesis of Bis(fluoro) Monomers 4a, 5a, and 6a. 4-Fluoro-3-trifluoromethylphenylboronic acid (6.0 g, 28.8 mmol) and a dibromo compound (12.0 mmol; 1,4-dibromobenzene, 2.83 g; 2,6-dibromopyridine, 2.84 g; 2,5-dibromothiophene, 2.90 g), toluene (90 mL), aqueous Na_2CO_3 (90 mL, 1 M), and Pd-$(Ph_3P)_4$ (0.416 g, 3 mol %) were intensely stirred and refluxed for 5 days. The organic layer was separated and the aqueous phase extracted with toluene (2 × 100 mL). The combined organic layers were washed with water (2 × 100 mL), dried ($MgSO_4$), and concentrated. The concentrated (100 mL) organic layer was filtered over Al_2O_3 (type 100−125 mesh; activity 1, bed length 20 cm, diameter 2 cm) to remove the catalyst Pd-$(Ph_3P)_4$. The column was washed with 600 mL of toluene to obtain the desired compounds. Finally, the compounds were obtained after removal of the toluene in a vacuum. The compounds were further purified by recrystallization from a 1:10 mixture of toluene/hexane.



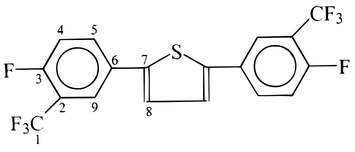
4a

Yield: 83%. Melting point: 164 °C. m/z: 402. Anal. Calcd for $C_{20}H_{10}F_8$ (402.283 g/mol): C, 59.71; H, 2.50. Found: C, 59.91; H, 2.52. IR (KBr): $\bar{\nu}$ (cm^{-1}): 3035, 1621, 1530, 1494, 1439, 1399, 1337, 1238, 1120, 1056, 905, 850, 823, 765, 687, 644, 524, 486. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.815 (d, J = 9.1 Hz, 2H, H5); 7.762 (m, 2H, H9); 7.627 (s, 4H, H8); 7.285 (t, J = 9.1 Hz, 2H, H4). ^{13}C NMR ($CDCl_3$): δ (ppm) 117.46 (d, J = 21.4 Hz, C4); 118.94 (dq, J_1 = 20.6 Hz, J_2 = 12.2 Hz, C2); 122.56 (q, J = 272.3 Hz, C1); 125.68 (d, J = 3.8 Hz, C9); 127.70 (s, C8); 132.28 (d, J = 9.1 Hz, C5); 136.84 (d, J = 3.8 Hz, C6); 138.52(s, C7); 159.41 (d, J = 257.1, C3). ^{19}F NMR ($CDCl_3$): δ (ppm) −61.83 (d, J = 13.4 Hz, 6F, F1); −117.11 (m, 2F, F3).



5a

Yield: 94%. Melting point: 149 °C. m/z = 403. Anal. Calcd for $C_{19}H_9NF_8$ (403.361 g/mol): C, 56.59; H, 2.24; N, 3.47. Found: C, 56.57; H, 2.31; N, 3.43. IR (KBr): $\bar{\nu}$ (cm^{-1}) 1623, 1573, 1508, 1462, 1446, 1383, 1327, 1259, 1242, 1161, 1124, 1053, 843, 800, 667, 571. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.33 (d, J = 9.1 Hz, 2H, H5); 8.28 (m, 2H, H10); 7.88 (t, J = 8.0 Hz, 1H, H9); 7.70 (d, J = 8.0 Hz, 2H, H8); 7.32 (t, J = 9.1 Hz, 2H, H4). ^{13}C NMR ($CDCl_3$): δ (ppm) 117.35 (d, J = 21.4, Hz, C4); 118.52 (m, C2); 118.99 (s, C8); 122.57 (q, J = 271 Hz, C1); 125.81 (d, J = 4.6 Hz, C10); 132.28 (d, J = 8.4 Hz, C5); 135.37 (d, J = 3.1 Hz, C6); 138.24 (s, C9); 154.70 (s, C7); 160.42 (d, J = 257.1, C3). ^{19}F NMR ($CDCl_3$): δ (ppm) −61.88 (d, J = 13.4 Hz, 6F, F1); −114.64 (m, 2F, F3).



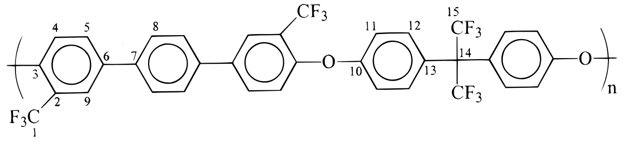
6a

Yield: 71%. Melting point: 106 °C. m/z = 408. Anal. Calcd for $C_{18}H_8SF_8$ (408.311 g/mol): C, 52.94; H, 1.97. Found: C, 52.76; H, 2.18. IR (KBr): $\bar{\nu}$ (cm^{-1}) 1617, 1547, 1496, 1427, 1327, 1261, 1247, 1169, 1133, 1053, 896, 834, 800, 674. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.77 (d, J = 8.8 Hz, 2H, H5); 7.70 (m, 2H, H9); 7.24 (s, 2H, H8); 7.18 (d, J = 8.8 Hz, 2H, H4). ^{13}C NMR ($CDCl_3$): δ (ppm) 117.65 (d, J = 21.6 Hz, C4); 119.1 (dq, J_1 = 19.7 HZ, J_2 = 13.5 Hz, C2); 122.3 (q, J = 272 Hz, C1); 124.28 (dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, C9); 125.1 (s, C8); 130.6 (dd, J_1 = 20.6 Hz, J_2 = 4.5 Hz, C5); 132.42 (d, J = 9.0, C6); 147.77 (s, C7); 159.13 (d, J = 257.6 Hz, C3). ^{19}F NMR ($CDCl_3$): δ (ppm) −61.98 (d, J = 13.4 Hz, 6F, F1); −116.05 (m, 2F, F3).

Synthesis of 4-Chloro-3-trifluoromethylphenylboronic Acid and Bis(chloro) Monomers 4b, 5b, and 6b. These compounds were prepared by analogous procedures. Details will be given elsewhere.

Polymerization. Polymerization reactions were carried out in a 100 mL, three-necked round-bottom flask equipped with a stir bar, a Dean−Stark trap fitted with condenser, and a nitrogen inlet. The flask was charged with equimolar amounts of a bishalogen monomer and a bisphenol (approximately 3 mmol each), K_2CO_3 (approximately 6.6 mmol), NMP (25 mL), and toluene (50 mL). The mixture was then heated to reflux (140−150 °C, oil bath temperature) for 4−5 h as water was removed azeotropically with toluene. After removing the toluene from the Dean−Stark trap, the reaction temperature was increased to 180 °C and maintained for 8 h. After cooling to room temperature, 20 mL of THF was added to dilute the mixture; the polymer was recovered by precipitation from about 800 mL of methanol, containing a few milliliters of HCl. Fibrous solids were isolated. These products were washed several times in boiling water to remove any inorganic impurities, dried in a vacuum, dissolved in THF, reprecipitated in excess methanol, and dried in a vacuum at 70 °C for 24 h.

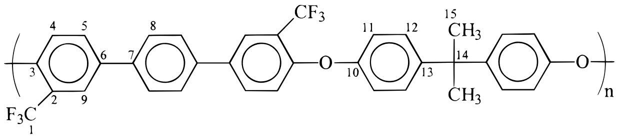
Polymer 7a: 1.3 g (3.23 mmol) of bisfluoro monomer **4a**; 1.0865 g (3.23 mmol) of 6F−BPA; 1.05 g (7.6 mmol) of K_2CO_3; 25 mL of NMP/40 mL of toluene.



Anal. Calcd for $(C_{35}H_{18}O_2F_{12})_n$, $(698.51)_n$ g/mol: C, 60.18; H, 2.59. Found: C, 59.95; H, 2.62. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3052, 1608, 1512, 1486, 1473, 1333, 1250, 1207, 1174, 1132, 1053, 824. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.94 (s, 2H, H5); 7.76 (d, J = 8.3 Hz, 2H, H9); 7.67 (s, 4H, H8); 7.42 (d, J = 8.3 Hz, 4H, H12); 7.14 (d, J = 8.3 Hz, 2H, H4); 7.07 (d, J = 8.3 Hz, 4H, H11). ^{13}C NMR ($CDCl_3$): δ (ppm) 156.84 (s, C10); 153.30 (s, C3); 138.19 (s, C7); 135.81 (s, C6); 131.52 (s, C13); 131.28 (s, C5); 128.20 (s, C12); 127.16 (s, C8); 125.52 (m, C9); 121.6(q, J = 272.8 Hz, C1, C15); 122.32 (q, J = 20.4 Hz, C2); 120.31 (s, C11); 117.89 (s, C4); not found (C14). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.27 (s, 6F, F1); − 64.42 (s, 6F, F15).

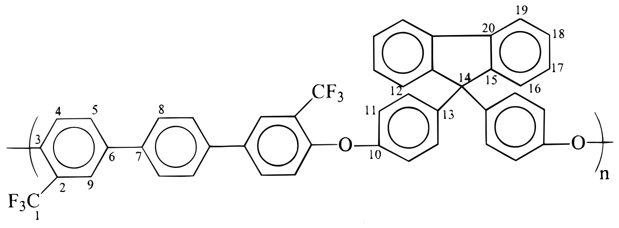
Polymer 7b: 1.300 g (3.23 mmol) of bisfluoro monomer **4a**; 0.7377 g (3.23 mmol) of BPA; 1.05 g (7.6 mmol) of K_2CO_3; 25 mL of NMP/40 mL of toluene.

Anal. Calcd for $(C_{35}H_{24}O_2F_6)_n$, $(590.56)_n$ g/mol: C, 71.18; H, 4.09. Found: C, 70.41; H, 4.27. IR (KBr): $\bar{\nu}$ (cm^{-1}) 2968, 1618, 1484, 1436, 1332, 1251, 1134, 1053, 1013, 821. ^{1}H NMR



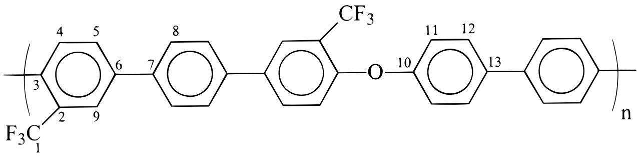
($CDCl_3$): δ (ppm) 7.82 (s, H5); 7.62−7.56 (m, 6H, H9, H8); 7.19 (d, $J = 6.5$ Hz, 4H, H12); 6.98−6.90 (m, 6H, H4, H11); 1.63 (s, 6H, H15). ^{13}C NMR ($CDCl_3$): δ (ppm) 154.77 (s, C3); 153.69 (s, C10); 146.16 (s, C7); 138.19 (s, C6); 134.57 (s, C5); 131.60 (s, C13); 127.87 (s, C12); 127.02 (s, C8); 125.28 (d, $J = 3.4$ Hz, C9); 121.13 (q, $J = 19.7$ Hz, C2); 119.2 (q, $J = 272.8$ Hz, C1); 118.87 (s, C4); 118.68 (s, C11); 41.90 (s, C14); 30.56 (s, C15). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.33 (s, F1).

Polymer 7c: 1.3 g (3.23 mmol) of bisfluoro monomer **4a**; 1.1324 g (3.23 mmol) of 4,4′-dihydroxy diphenyl fluorene; 1.05 g (7.6 mmol) of K_2CO_3; 25 mL of NMP/40 mL of toluene.



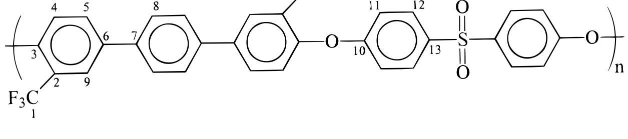
Anal. Calcd for $(C_{45}H_{26}O_2F_6)_n$, $(712.69)_n$ g/mol: C, 75.84; H, 3.67. Found: C, 73.22; H, 3.8. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3036, 1603, 1484, 1332, 1275, 1248, 1162, 1132, 1052, 819, 739. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.85 (s, 2H, H5); 7.77 (d, 2H, $J = 8.0$ Hz, H9); 7.65−7.55 (m, 6H, H8, H19); 7.44−7.16 (m, 10 H, H16, H18, H17, H12); 7.03−6.87 (m, 6H, H4, H11). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.54 (s, C10); 155.28 (s, C3); 151.44 (s, 15); 142.14 (s, C20); 140.47 (s, C13); 139.00 (s, C7); 135.61 (s, C6); 131.85 (s, C5); 130.06 (s, C12); 128.27 (s, C17); 128.15 (s, C19); 127.85 (s, C8); 126.51 (s, C16); 126.09 (d, $J = 4.5$ Hz, C9); 123.90 (q, $J = 272.50$ Hz, C1); 122.00 (q, $J = 26.0$ Hz, C2); 120.75 (s, C18), 119.99 (s, C4); 119.59 (s, C11); 64.89 (s, C14). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.32 (s, F1).

Polymer 7d: 0.6921 g (1.72 mmol) of bisfluoro monomer **4a**; 0.3204 g (1.72 mmol) of 4,4′-dihydroxy biphenyl; 0.522 g (3.78 mmol) of K_2CO_3; 12 mL of NMP/18 mL of toluene.



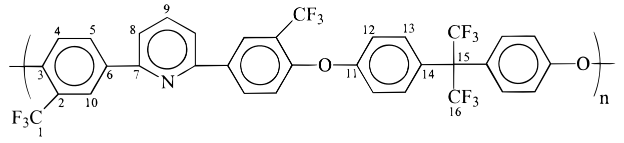
Anal. Calcd for $(C_{32}H_{18}O_2F_6)_n$ $(548.48)_n$ g/mol: C, 70.07; H, 3.30. Found: C, 70.09; H, 3.55. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3051, 1604, 1483, 1437, 1333, 1247, 1161, 1133, 1053, 820. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.94 (s, 2H, H5); 7.72 (d, $J = 8.8$ Hz, 2H, H9); 7.65 (s, 4H, H8); 7.58 (d, $J = 8.8$ Hz, 4H, H11); 7.18−7.00 (m, 6H, H12, H4). ^{13}C NMR ($CDCl_3$): δ (ppm) 156.39 (s, C10); 155.28 (s, C3); 139.06 (s, C7); 136.93 (s, C6); 135.87 (s, C13); 131.99 (s, C5); 128.91 (s, C12); 127.95 (s, C8); 126.19 (m, C9); 122.00 (m, C2); 120.16 (s, C11, C14). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.28 (s, F1).

Polymer 7e: 1.000 g (2.49 mmol) of bisfluoro monomer **4a**; 0.6221 g (2.49 mmol) of 4,4′-dihydroxydiphenyl sulfone; 0.754 g (5.46 mmol) of K_2CO_3; 15 mL of NMP/22 mL of toluene.



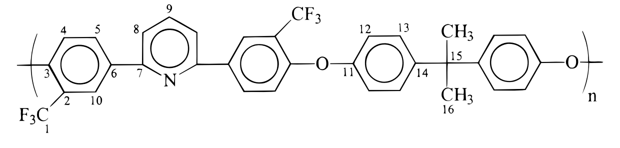
Anal. Calcd for $(C_{32}H_{18}O_4SF_6)_n$, $(612.54)_n$ g/mol: C, 62.74; H, 2.96. Found: C, 63.11; H, 3.3. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3053, 1585, 1527, 1436, 1428, 1332, 1249, 1151, 1106, 1053, 825. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.23−7.7 (m, 12H, H5, H9, H12, H8); 7.45−7.10 (m, 6H, H4, H11). ^{13}C NMR ($CDCl_3$): δ (ppm) 161.02 (s, C10); 159.70 (s, C3); 152.09 (s, C13); 137.82 (s, C7); 137.06 (s, C6); 133.13 (s, C5); 130.44 (s, C12); 127.90 (s, C8); 125.67 (m, C9); 122.7 (m, C2); 123.5 (q, $J = 272.0$ Hz, C1); 120.26 (s, C4); 118.77 (s, C11). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.28 (s, F1). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.29 (s, F1).

Polymer 8a: 1.000 g (2.48 mmol) of bisfluoro monomer **5a**; 0.8339 g (2.48 mmol) of 6F−BPA; 0.754 g (5.46 mmol) of K_2CO_3; 20 mL of NMP/32 mL of toluene.



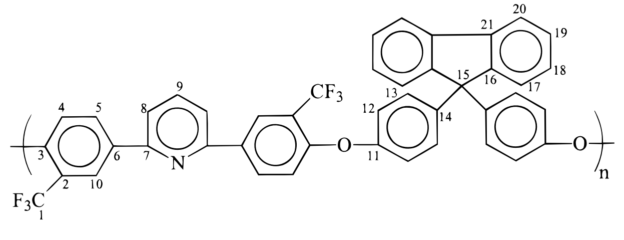
Anal. Calcd for $(C_{34}H_{17}NO_2F_{12})_n$, $(699.49)_n$ g/mol: C, 58.38; H, 2.45; N, 2.00. Found: C, 58.43; H, 2.4; N, 1.98. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3056, 1609, 1570, 1499, 1458, 1420, 1327, 1253, 1207, 1174, 1132, 1052, 803. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.41 (s, 2H, H5); 8.24 (d, $J = 8.7$ Hz, 2H, H10); 7.85 (t, 7.9 Hz, 1H, H9); 7.68 (d, $J = 7.9$ Hz, 2H, H8); 7.40 (d, $J = 8.7$ Hz, 4H, H13); 7.13 (d, $J = 8.7$ Hz, 2H, H4); 7.05 (d, $J = 8.7$ Hz, 4H, H12). ^{13}C NMR ($CDCl_3$): δ (ppm) 156.98 (s, C3); 155.14 (s, C7); 154.93 (s, C11); 138.25 (s, C9); 134.54 (s, C6); 131.95 (s, C14); 131.80 (s, C5); 128.82 (s, C13); 126.03 (d, $J = 4.6$ Hz, C10); 123.01 (q, $J = 272.8$ Hz, C1, C16); 122.00 (q, $J = 20.2$ Hz, C2); 120.18 (s, C12); 118.84 (s, C4); 118.56 (s, C8); not found (C15). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.33 (s, 6F, F1); −64.40 (s, 6F, F16).

Polymer 8b: 1.000 g (2.48 mmol) of bisfluoro monomer **5a**; 0.5662 g (2.48 mmol) of BPA; 0.754 g (5.46 mmol) of K_2CO_3; 20 mL of NMP/32 mL of toluene.



Anal. Calcd for $(C_{34}H_{23}NO_2F_6)_n$, $(591.55)_n$ g/mol: C, 69.03; H, 3.91; N, 2.36. Found: C, 69.39; H, 4.1; N, 2.23. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3052, 2969, 1618, 1595, 1568, 1498, 1458, 1420, 1327, 1253, 1161, 1131, 1051, 803. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.39 (d, $J = 1.9$ Hz, 2H, H5); 8.18 (dd, $J_1 = 1.9$ Hz, $J_2 = 8.7$ Hz, 2H, H10); 7.81 (t, $J = 7.9$ Hz, 1H, H9); 7.64 (d, $J = 7.9$ Hz, 2H, H8); 7.23 (d, $J = 8.3$ Hz, 4H, H13); 7.05−6.96 (m, 6H, H4, H12); 1.69 (s, 6H, H16). ^{13}C NMR ($CDCl_3$): δ (ppm) 156.18 (s, C3); 154.64 (s, C11); 153.41 (S, C7); 146.32 (s, C9); 137.68 (s, C6), 132.92 (s, C5); 131.17 (s, C14); 127.88 (S, C13); 125.40 (m, C10); 122.2 (q, $J = 272.8$ Hz, C1); 121.1 (q, $J = 31.5$ Hz, C2); 118.86 (s, C12); 118.37 (s, C8); 118.05 (s, C4); 41.92 (s, C15); 30.54 (s, C16). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.40 (s, F1).

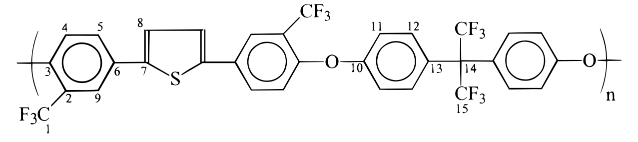
Polymer 8c: 1.000 g (2.48 mmol) of bisfluoro monomer **5a**; 0.8691 g (2.48 mmol) of 4,4′-dihydroxy diphenyl fluorene; 0.754 g (5.46 mmol) of K_2CO_3; 20 mL of NMP/32 mL of toluene.



Anal. Calcd for $(C_{44}H_{25}O_2F_6N)_n$, $(713.67)_n$ g/mol: C, 74.05; H, 3.53; N, 1.96. Found: C, 74.44; H, 3.7; N, 1.83. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3057, 1618, 1497, 1458, 1420, 1326, 1250, 1131, 1051,

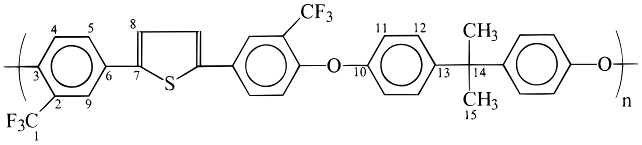
740. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.20 (s, 2H, H5); 8.13 (d, J = 8.7 Hz; 2H, H10); 7.76 (d, J = 7.2 Hz, 3H, H9, H20); 7.60 (d, J = 7.2 Hz, 2H, H8); 7.43−7.19 (m, 10H, H19, H18, H17, H13); 7.02−6.88 (m, 6H, H4, H12). ^{13}C NMR ($CDCl_3$): δ (ppm) 156.19 (s, C3); 155.02 (s, C7); 151.52 (s, C16); 141.89 (s, C21); 140.03 (s, C14); 137.96 (s, C9); 135.80 (s, C6); 133.73 (s, C5); 129.67 (s, C13); 127.88 (s, C20); 127.73 (s, C18); 126.08 (s, C17); 125.72 (d, J = 4.6 Hz, C10); 125.52 (s, C8); 123.00 (q, J = 272 Hz, C1); 121.54 (q, J = 29.6 Hz, C2); 120.33 (s, C19); 119.36 (s, C4); 64.48 (s, C15). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.36 (s, F1).

Polymer 9a: 1.000 g (2.45 mmol) of bisfluoro monomer **6a**; 0.8235 g (2.45 mmol) of 6FBPA; 0.754 g (5.46 mmol) of K_2CO_3; 15 mL of NMP/22 mL of toluene.



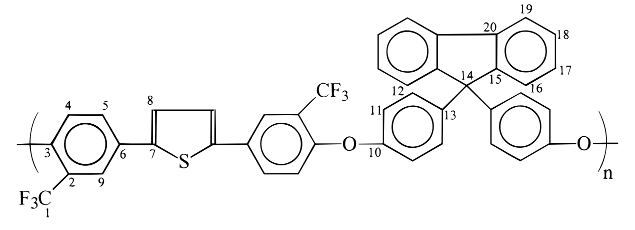
Anal. Calcd for $(C_{33}H_{16}SO_2F_{12})_n$, $(704.53)_n$ g/mol: C, 56.26; H, 2.29. Found: C, 56.22; H, 2.7. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3058, 1608, 1546, 1509, 1490, 1420, 1329, 1249, 1207, 1173, 1133, 1052, 968, 928. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.90 (s, 2H, H5); 7.71 (d, J = 8.7 Hz, 2H, H9); 7.40 (d, J = 8.7 Hz, 4H, H12); 7.28 (s, 2H, H8); 7.10−7.00 (m, 6H, H4, H11). ^{13}C NMR ($CDCl_3$): δ (ppm) 157.11 (s, C10); 153.59 (s, C3); 141.99 (s, C7); 131.94 (s, C13, C6); 130.29 (s, C12); 129.96 (s, C5); 124.93 (s, C8); 124.51 (m, C9); 122.4)q, J = 272.6 Hz, C1, C15); 122.21 (q, J = 20.4 Hz, C2); not found (C14). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.41 (s, 6F, F1); −64.41 (s, 6F, F15).

Polymer 9b: 0.8000 g (1.96 mmol) of bisfluoro monomer **6a**; 0.4473 g (1.96 mmol) of BPA; 0.600 g (4.37 mmol) of K_2CO_3; 12 mL of NMP/18 mL of toluene.



Anal. Calcd for $(C_{33}H_{22}SO_2F_6)_n$, $(596.59)_n$ g/mol: C, 66.43; H, 3.71. Found: C, 66.19; H, 4.10. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3051, 2968, 1617, 1545, 1489, 1419, 1329, 1253, 1131, 1052. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.79 (s, 2H, H5); 7.56 (d, J = 8.3 Hz, 2H, H9); 7.20−7.15 (m, 6H, H8, H12); 6.93−6.87 (m, 6H, H4, H11); 1.62 (s, 6H, H15). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.44 (s, C13); 154.35 (s, C10); 147.02 (s, C7); 142.36 (s, C6); 130.47 (s, C13); 129.20 (s, C5), 128.71 (s, C12); 124.89 (s, C8); 124.73 (m, C9); 123.2 (q, J = 272.8 Hz, C1); 122.0 (q, J = 31.4 Hz, C2); 119.74 (s, C4); 118.88 (s, C11); 42.69 (s, C14); 31.34 (s, C15). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.49 (s, F1).

Polymer 9c: 1.000 g (2.45 mmol) of bisfluoro monomer **6a**; 0.8582 g (2.45 mmol) of 4,4′-dihydroxydiphenylfluorene; 0.754 g (5.46 mmol) of K_2CO_3; 15 mL of NMP/22 mL of toluene.



Anal. Calcd for $(C_{43}H_{24}SO_2F_6)_n$, $(718.71)_n$ g/mol: C, 71.86; H, 3.36. Found: C, 71.7; H, 3.8. IR (KBr): $\bar{\nu}$ (cm^{-1}) 3055, 1603, 1544, 1488, 1419, 1328, 1251, 1132, 1052, 740. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.76 (s, 2H, H5); 7.70 (d, J = 7.1 Hz, 2H, H9); 7.58 (d, J = 8.3 Hz, 2H, H8); 7.42−7.18 (m, 12H, H17, H16, H18, H12, H19); 7.00−6.87 (m, 6H, H4, H11). ^{13}C NMR ($CDCl_3$): δ (ppm) 154.87 (s, C10); 154.62 (s, C3); 150.84 (s, C15); 141.84 (s, C7); 141.68 (s, C20); 139.91 (s, C13); 131.28 (s, C6); 129.96 (s, C12); 128.87 (s, C5); 127.74 (s, C17); 127.64 (s, C19); 125.94 (s, C16); 124.44 (s, C8); 124.16 (d, J = 4.4 Hz, C9); 123.41 (q, J = 272.6 Hz, C1); 121.53 (q, J = 20.6 Hz, C2); 120.23 (s, C18); 119.53 (s, C4); 119.05 (s, C11); 64.44 (s, C14). ^{19}F NMR ($CDCl_3$): δ (ppm) −62.47 (s, F1).

Results and Discussion

Synthesis of Bishalogen Monomers. These compounds were prepared by a palladium-catalyzed cross-coupling reaction of an aryl bromide with a boronic acid (commonly referred to as the Suzuki reaction)[13] as shown in Figure 3. The synthesis of these bishalogen monomers was targeted by two different routes as depicted in Figure 3. Initially, we were trying to synthesize the bisfluoro monomer **4a** as model compound by a cross-coupling reaction of 1,4-phenyldiboronic acid with 2-fluoro-5-benzotrifluoride, adapting the Suzuki protocol, in a 1:1 mixture of toluene/water (1 M Na_2CO_3) as solvent in the presence of 3 mol % $(Ph_3P)_4Pd$ as catalyst at 100−115 °C for 5 days (route II). The rationale behind selecting this route is the availability of a well-known synthetic procedure for preparation of different diboronic acids[14] and commercial availability of the counterpart, 2-fluoro-5-benzotrifluoride. Although the coupling reaction is expected to be very effective under these conditions,[15] we failed to get good yields of **4a**. Despite our repeated trial and varying the concentration of $(Ph_3P)_4Pd$ (0.5−5 mol %) and Na_2CO_3 up to 3 M, the yield was only about 5−8%. Apart from the desired product **4a**, some side products formed, which could not be separated completely. This may be due to aryl scrambling at the catalyst, tetrakis(triphenylphosphine)palladium(0), or the associated unselective aryl transfer of the phosphane to side products.[16] However, detailed investigations in this regard are required.

Because of low yield and associated problems in route II, we planned to reach to the same product in a different route using the same Suzuki protocol as shown in route I. This route required, first, the synthesis of boronic acids from 2-chloro- or 2-fluoro-5-bromobenzotrifluoride compounds and, finally, the cross-coupling with different dibromo compounds. Since there is no available synthetic procedure to make boronic acids from these compounds, initially we tried to make 4-fluoro-3-trifluoromethylphenylboronic acid from 2-fluoro-5-bromobenzotrifluoride by lithiation using BuLi and subsequent reaction with trimethyl borate followed by acid hydrolysis. We were successful to obtain the desired product, but at a low yield (33%),[17] which may be due to the high reactivity of BuLi toward the activated halogen compounds. We conducted the same reaction using the less reactive Grignard compound (route I, step I). The reactions were more successful; we achieved more than 80% yield of the boronic acids for both 2-chloro- and 2-fluorobenzotrifluoride compounds. These boronic acids were coupled with 1,4-dibromobenzene, 2,6-dibromopyridine, and 2,5-dibromothiophene using the same reaction conditions as route II. The coupling reactions were very successful; yields were 72−92% depending on the exact products. One single sharp peak on the gas chromatograph for these monomers indicated high purity. Their corresponding mass spectra show exact *m/z* peaks for these compounds. The chemical structures of the monomers were confirmed by IR and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic methods and elemental analysis.

Synthesis of Polymers. Polymerizations of the bishalogen monomers with stoichiometric amounts of

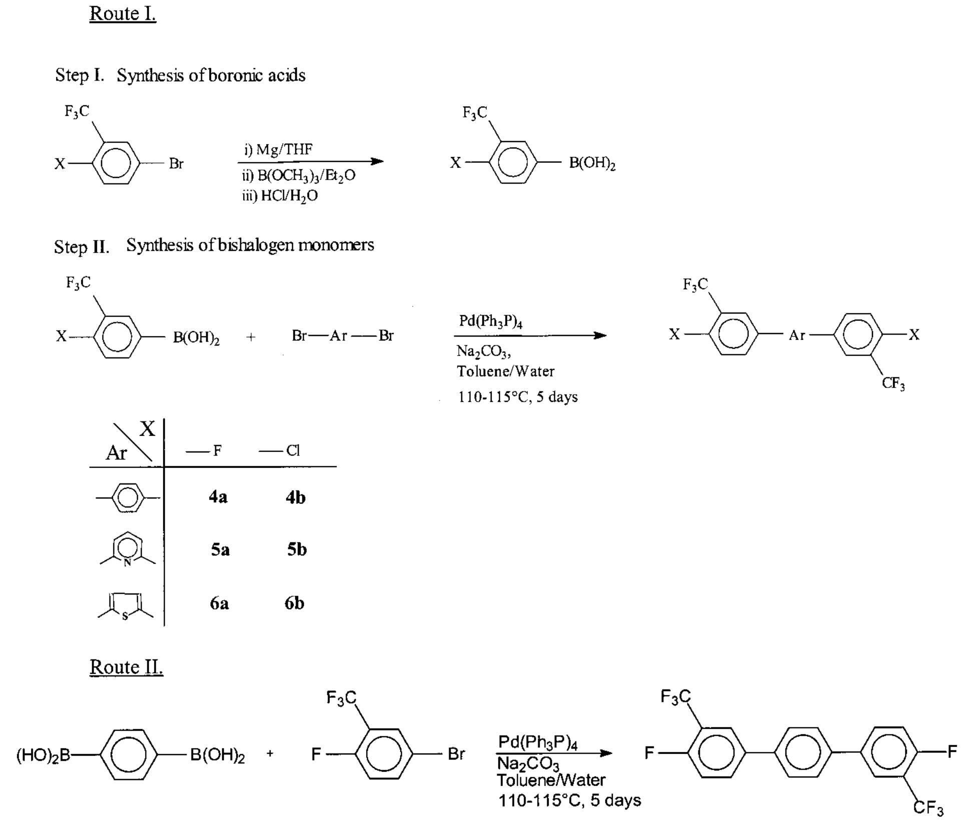


Figure 3. Reaction scheme and structures of the novel bishalogen monomers.

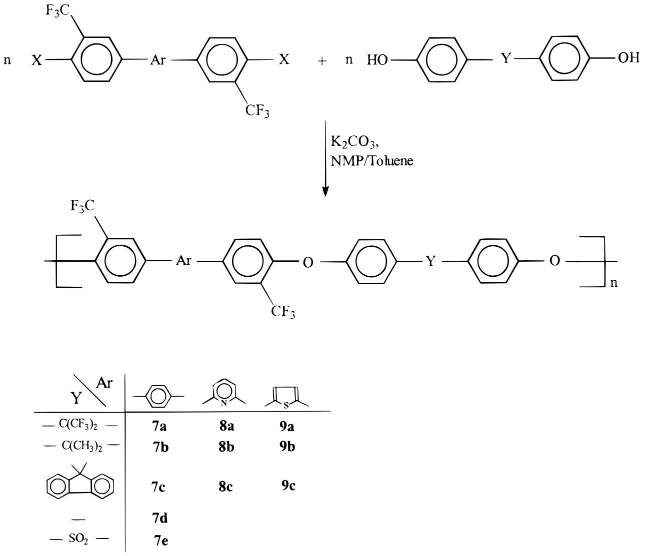


Figure 4. Reaction scheme and structures of the poly(arylene ether)s.

different bisphenols were carried out in the presence of excess potassium carbonate as base in NMP in analogy to conventional polyether synthesis[18] as shown in Figure 4. The polymerizations were run at solids contents of 25%, and toluene was used for azeotropic removal of water. During the initial stage of the polymerization, the reaction temperature was maintained at 140−150 °C, and the water generated by deprotonation of the phenols was most effectively removed through a Dean−Stark trap. Upon completion of bisphenoxides formation and dehydration (4−5 h), the reaction temperature was raised to 180 °C to effect the nucleophilic displacement. High molar mass polymers were obtained within 8 h as judged by the dramatic increase of the viscosity of the reaction medium in all the cases except **7e**. The resulting polymers were coagulated in a large excess of methanol. Fibrous solids were isolated. These products were boiled and washed several times with hot water to remove any inorganic impurities, dried in a vacuum, and dissolved in THF, and the concentrated solutions were reprecipitated in an excess of methanol. The fibrous polymers recovered by filtration were dried in vacuo at 50 °C for 24 h.

Table 1. Yields and Molar Masses of the Poly(arylene ether)s[a]

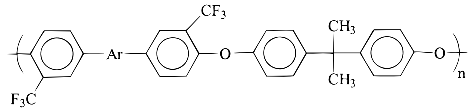
polymer	yield/%	$\bar{M}_n$/g/mol	$\bar{M}_w$/g/mol	$\bar{M}_w/\bar{M}_n$
7a	96	30 000	74 500	2.5
7b	97	43 200	83 400	1.9
7c	98	44 600	71 600	1.6
7d	94	21 200	62 200	2.9
7e	73	6500	16 400	2.5
8a	98	32 400	67 800	2.1
8b	99	148 200	352 000	2.4
8c	99	46 000	148 600	3.2
9a	99	27 800	57 700	2.1
9b	98	42 000	124 100	2.9
9c	99	32 500	93 700	2.9

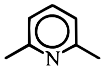
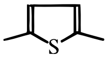
[a] Figure 4, synthesized by fluoro displacement.

Although Labadie et al.[19] reported that the use of 2-perfluoroalkyl activation of fluoro displacements appears to be insufficient for high conversion, our findings are different. We obtain very good conversion as indicated by the yields shown in Table 1. The GPC data for the polymers as reported in Table 1 indicate formation of high molecular weight polymers. The polydispersity values are within the range expected for condensation polymerization.

The displacement of a fluorine atom from 2-trifluoromethyl-activated bisfluoro momomers by several bisphenols was very successful, which caused us to

Table 2. Yields and Molar Masses of the Poly(arylene ether)s[a]



Ar	yield/%	$\bar{M}_n$/g/mol	$\bar{M}_w$/g/mol	$\bar{M}_w/\bar{M}_n$
	87	16 300	28 800	1.8
	88	17 800	31 600	1.8
	76	10 500	19 200	1.8

[a] Figure 4, synthesized by chloro displacement.

Table 3. Solubility of the Poly(arylene ether)s[a]

polymer	NMP	DMF	decalin	DMSO	THF	$CHCl_3$	acetone	toluene
7a	+	+	−	−	+	+	−	+
7b	+	+	−	−	+	+	o	+
7c	+	+	−	−	+	+	−	+
7d	+	+	−	−	+	+	−	+
7e	+	+	−	o	+	−	−	−
8a	+	+	−	−	+	+	−	o
8b	+	+	−	−	+	+	+	+
8c	+	+	−	−	+	+	−	+
9a	+	+	−	−	+	+	−	o
9b	+	+	−	−	+	+	+	+
9c	+	+	−	−	+	+	−	+

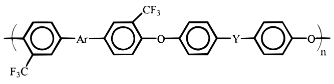
[a] + = soluble at room temperature; o = soluble at reflux; − = insoluble at reflux.

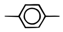
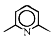
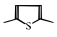
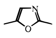
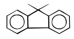
study the possibility of the displacement of chlorine atoms from the analogous 2-trifluoromethyl-activated bischloro monomers **4b**, **5b**, and **6b** by bisphenols. In contrast to the fluoro displacement reactions, the chloro displacement reactions were slower and required higher temperature (190 °C) for polymerization. The GPC data and yields of these reactions are summarized in Table 2. The chlorine atoms of the thiophene ring containing monomer **6b** are the least reactive ones. This can be attributed to the electron-rich character of the thiophene ring in comparison to the phenyl or pyridine ring. As expected, the displacement of chlorine or fluorine atoms from the bishalogen monomers containing pyridene is most facile, evidenced by the higher molar mass polymers derived from these monomers. Although the molar mass of the poly(arylene ether)s derived from the phenyl- or pyridine-containing 2-trifluoromethyl-activated bischloro monomers (**4b** and **5b**) and BPA are not very low, they failed to produce any free-standing films. High conversion and high molar mass materials might be obtained from these bischloro monomers by use of silylated bisphenols.[12d,20]

Polymer Solubilities. The solubilities of the resulting poly(arylene ether)s are shown in Table 3. These polymers also exhibit good solubility in common organic solvents such as previously reported semifluorinated poly(arylene ether)s derived from thiazole- and oxazole-based bisfluoro monomers (Figure 1).[12] It was attempted to obtain 10% (w/v) solutions of all polymers in several organic solvents.

All poly(arylene ether)s are soluble in chloroform at room temperature, with the exception of **7e**, derived from 4,4′-dihydroxy sulfone as bisphenol. The polymers containing pyridine (**8a**−**8c**) or thiophene (**9a**−**9c**) exhibit quite similar solubility behavior, whereas the analogous phenyl (**7a**−**7c**)-based polymers differ slightly. For example, polymer **7b** is only soluble in acetone on reflux, while polymers **8b** and **9b** are completely soluble at room temperature. Similarly, toluene is a very good solvent for **7a** but an equally poor solvent for **8a** and **9a**. It is somewhat surprising that toluene appears to be a fairly good solvent for most of these polymers, despite its low polarity compared to the solvents that are commonly used for poly(arylene ether)s. From this investigations and our previous experience with semifluorinated poly(arylene ether)s, we feel that polarity alone is not a sufficient parameter for selecting a polymer solvent.[12d] This was proved again when the solubility of these polymers in DMSO was examined. None of these polymers except **7e** are soluble in DMSO even on reflux, while they are soluble in the amide solvents such as NMP, DMF, and DMAc at room temperature, although these types of dipolar aprotic solvents have similar polarities. THF is a very good solvent for all of these polymers, and decalin is a nonsolvent.

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



Y	Ar			
				
	DSC / DMTA	DSC / DMTA	DSC / DMTA	DSC
-$C(CH_3)_2$-	174 / 210	119 / 125	120 / 130	185
-$C(CF_3)_2$-	197 / 218	153 / 140	155 / 150	205
	234 / 240	186 / 179	175 / 163	—
—	209 / 198	—	—	200
-SO_2-	214 / —	—	—	210

Spectroscopy. All spectroscopic data from FT-IR and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy support the structures of the poly(arylene ether)s. These characterization methods, as well as elemental analysis, do not indicate a degradation of the trifluoromethyl groups. The FT-IR spectra of these polymers show the aryl ether linkages (1140−1050 cm^{-1}) that are generated in the polymer-forming reaction and also the stretching frequencies (1240−1150 cm^{-1}) corresponding to CF_3 groups. FT-IR and ^{1}H and ^{19}F NMR spectra of the polymers do not show any signals corresponding to the terminal −OH or −F groups, indicating a high conversion. The ^{19}F NMR spectra of the polymers (**7a**, **8a**, **9a**) which are derived from bisfluoro monomers **4a**, **5a**, **6a** and 6F−BPA show two different signals at about −64.4 and −62.2 ppm of equal intensity corresponding to the fluorine signals from the trifluoromethyl groups in the 6F-BPA unit and from the bisfluoro monomers, respectively. The exact analytical data for all these polymers are listed in the Experimental Section.

DSC Measurements. None of the poly(arylene ether)s exhibit crystallization or melt transition in DSC measurements. The glass transition temperatures are summarized in Table 4. Table 4 also contains the T_g values of the analogous poly(aryl ether oxazole)s for comparison.

As Table 4 shows, the glass transition temperatures of the thiophene (**9**) and pyridine (**8**) ring containing

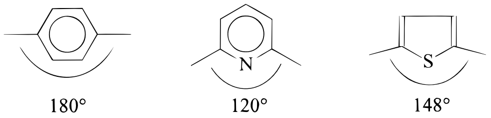


Figure 5. Catenation angle of different arylene rings.

polymers are about 50 °C lower than those of their corresponding phenyl analogues (**7**). A possible explanation for the low T_g's for pyridine and thiophene ring containing polymers can be found in the geometry of the repeating units. The catenation angle at the benzene is 180°, while at the thiophene and pyridine ring it is only about 148° and 120°, respectively (Figure 5).[21] Consequently, the backbones of the pyridine- and thiophene ring-containing polymers are less restricted in their mobility, which causes lower glass transition temperatures in comparison to the analogous phenyl ring-containing polymers.

However, the same explanation is not valid when we compare the glass transition temperatures of these polymers with the oxazole ring-containing poly(arylene ether)s. They exhibit higher glass transition temperatures, although the catenation angle at the oxazole ring is only 132°. We feel that the catenation angle in combination with the polarity of the ring may give a better explanation about the glass transition temperature of polymer molecules. As we observed, the thiophene ring has a more extended geometry than the pyridine ring at the same time the pyridine ring has a higher polarity than the thiophene ring ($\mu_{\text{pyridine}} = 7.4 \times 10^{-30}$ C m, $\mu_{\text{thiophene}} = 1.83 \times 10^{-30}$ C m),[21] and as a consequence the pyridine- and thiophene ring-containing poly(arylene ether)s have comparable glass transition temperatures.

Glass transition temperatures of the poly(arylene ether)s also depend significantly on the bisphenol from which they are derived. In general, the polymers containing bulky fluorene units in the backbone (**7c**, **8c**, **9c**) exhibit the highest T_g's, and the most flexible polymers **7b**, **8b**, **9b** with a BPA unit in the polymer backbone show the lowest glass transition temperatures.

DMTA Measurements. The dynamic mechanical behaviors for several pol(arylene ether)s are shown in Figure 6. The T_g's taken as maximum in the tan δ curves are presented in Table 4 for comparison with the calorimetry results. Young's modulus values for these polymers are shown in Table 6.

Thermal Stability. The poly(arylene ether)s exhibit excellent thermal stability as summarized in Table 5. Depending on the exact structures, these polymers show a 5% weight loss between 444 and 536 °C in synthetic air determined by dynamic TGA. The bisphenol moiety has a significant influence on the thermal stability. Those structures based on fluorene units were found to be the most thermally stable polymers. BPA units in the polymer backbone result in lower thermal stability, which can be attributed to the presence of the oxidizable isopropylidine group.[22]

Thermooxidative stability of these polymers also depends on the bisfluoro monomers from which they were derived. The polymers containing thiophene units in the backbone exhibit the lowest thermal stability. This can be explained by oxidation of thiophene to thiophene dioxide.[23] The thiophene ring loses its aromaticity, and as a consequence a lower thermal stability results. To confirm this, we investigated the thermal stability of three similar polymer structures containing phenyl (**7a**), pyridine (**8a**), and thiophene (**9a**) units in nitrogen. A dramatic increase in thermal stability by 35 °C for the thiophene-based polymer **9a** was observed, whereas for **7a** and **8a** it was only 10−20 °C. Figure 7 shows the thermogravimetry curves of polymers **7a**, **8a**, and **9a** in synthetic air and nitrogen as examples. Comparable oxazole-containing polymers exhibit decomposition temperatures that are 50 °C lower. This is attributed to the higher aromaticity of the phenyl, pyridine, or thiophene rings compared to that of the oxazole ring.[21,24]

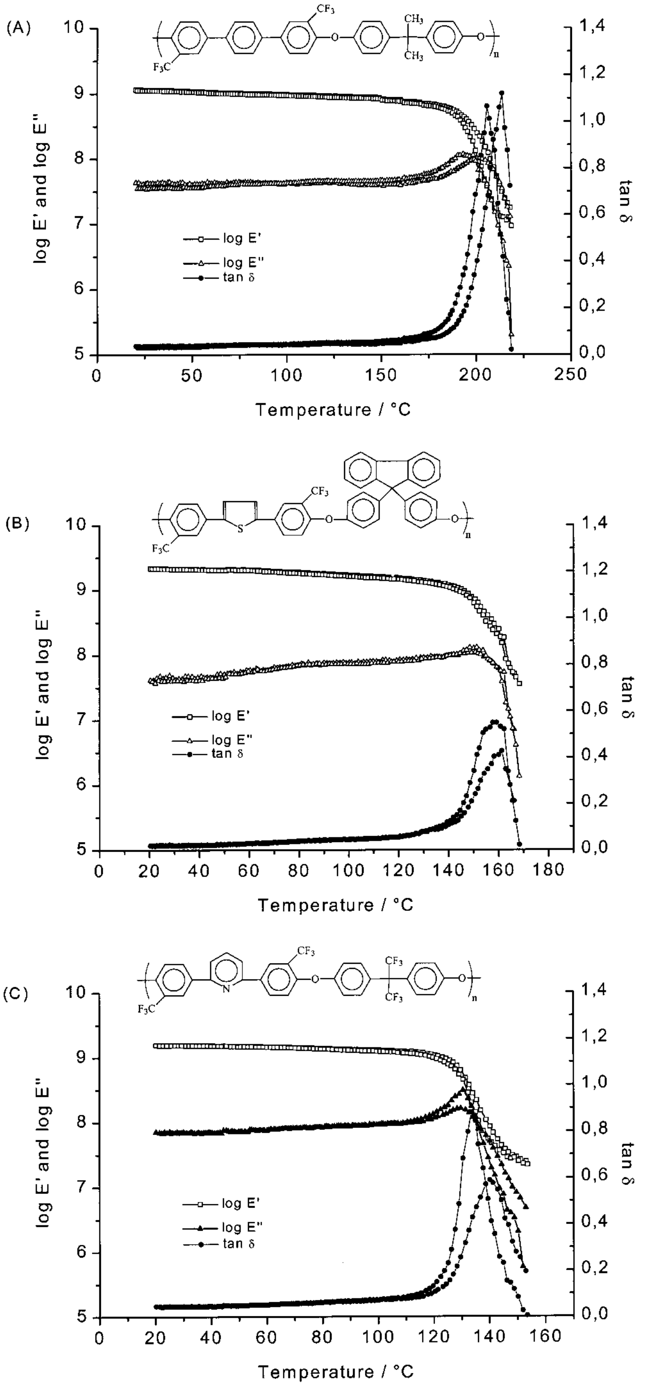


Figure 6. DMTA plots of poly(arylene ether)s: (A) **7b**, (B) **9c**, (C) **8a**.

Mechanical Properties. The mechanical properties of thin poly(arylene ether) films cast from THF are shown in Table 6. The polymers containing BPA (**7b**, **8b**, **9b**) or 6F-BPA (**7a**, **8a**, **9a**) exhibit ductile mechan-

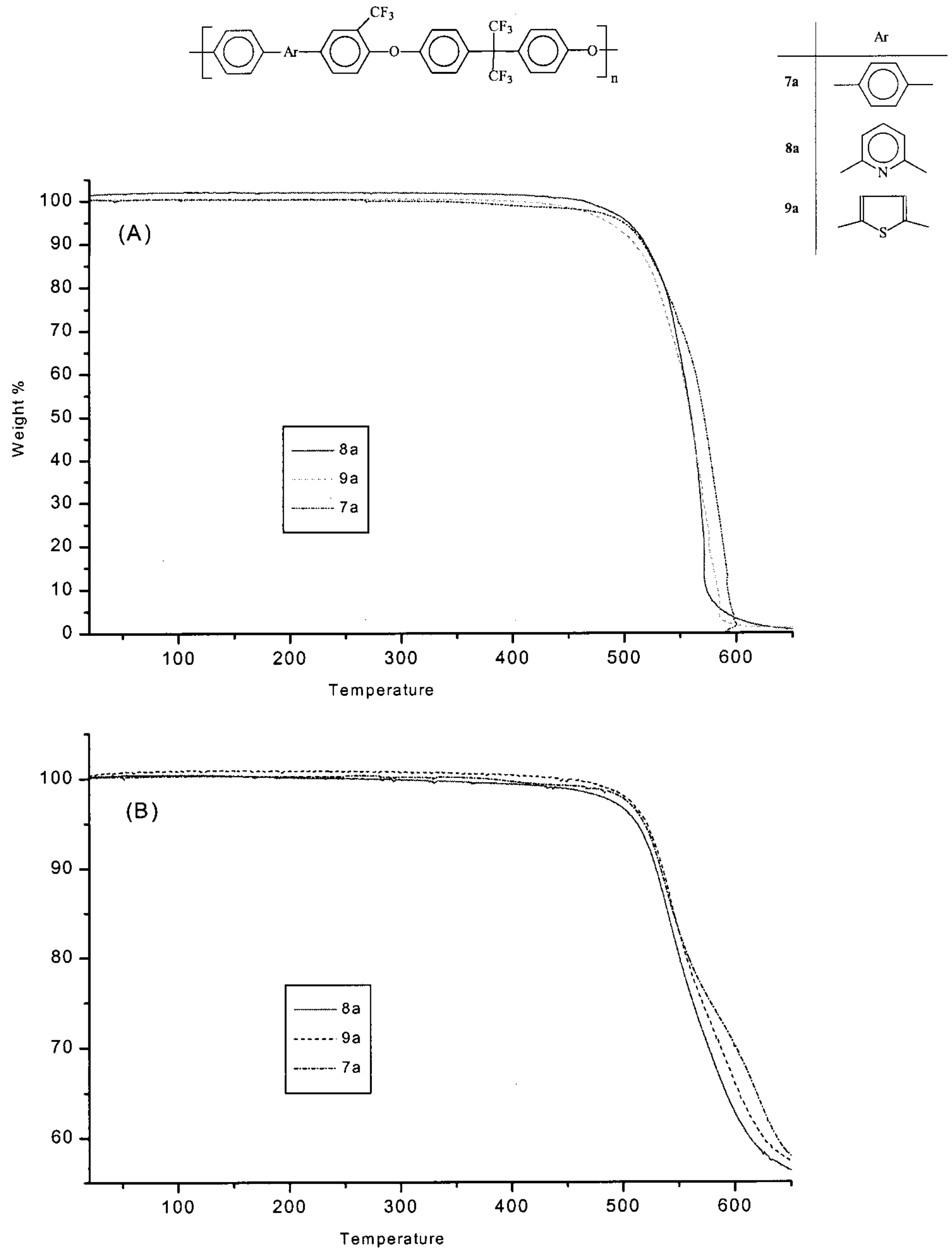


Figure 7. TGA thermograms of poly(arylene ethers) **7a**, **8a**, and **9a** (A) in air and (B) in nitrogen.

ical behavior with an elongation up to 30%. In contrast, the analogous poly(arylene ether)s (**7c**, **8c**, **9c**) containing bulky fluorene units exhibited relatively high tensile and yield stresses but somewhat brittle mechanical behavior with an elongation at break under 8%.

The 6F poly(arylene ether)s exhibit yield points with necking and drawing typical to many other engineering plastics. It is reported in the literature that many engineering plastics with ductile mechanical behavior show a secondary relaxation (β transition) in the dynamic mechanical spectra at low temperatures.[25] We also observed a secondary relaxation at −70 °C in the DMTA measurements of the BPA and 6F-BPA polymers at 10 Hz. A representative stress−strain plot for three different poly(arylene ether)s is shown in Figure 8.

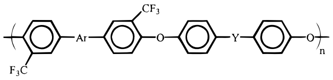
Dielectric Constants. So far, only preliminary results of the measurements of the dielectric constant of polymer **7c** could be obtained (1 μm film spin-coated on Ti surface, sputtered Ti counter electrode; measured at 1 kHz). A value of $\epsilon = 2.67 \pm 0.2$ was observed. This is very close to the values calculated by the methods and from the increments given in Van Krevelen's book on properties of polymers.[26] Using the free volume method, $\epsilon = 2.67$ is calculated, while the mass increment method yields $\epsilon = 2.60$.

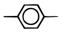
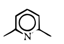
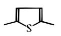
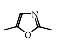
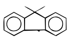
Conclusion

Six new trifluoromethyl-activated bishalo monomers **4a,b**−**6a,b** have been synthesized successfully using Pd(0)-catalyzed reaction. The versatility of the monomer synthesis allows the preparation of various structures which lead to several novel poly(arylene ether)s by nucleophilic displacement polymerization with different bisphenols. We obtained very high conversion for all the polymers and very high molar masses with weight-average molecular weights up to 3.52×10^5 g mol^{-1}. Chloro displacement of analogous monomers by bisphenols was not very successful.

The resulting poly(arylene ether)s are amorophous with glass transition temperatures between 125 and 240

Table 5. Thermal Stabilities of the Poly(arylene ether)s in Synthetic Air Expressed as 5 % Weight Loss Temperatures (°C) and Their Comparison with Similar Oxazole Polymers



Y	Ar			
				
-C(CH$_3$)$_2$-	464	461	444	443
-C(CF$_3$)$_2$-	500 (520)$^{a)}$	503 (512)$^{a)}$	486 (521)$^{a)}$	441
	530	536	494	—
—	514	—	—	460
-SO$_2$-	422	—	—	441

[a] Parentheses values are for 5% weight loss temperature (°C) in TGA under nitrogen.

Table 6. Mechanical Properties of the Poly(arylene ether)s[a]

polymer	yield stress/MPa	tensile strength/MPa	Young's modules/GPa	elongation at break/%
7a	62	55	2.51	28
7b	52	58	1.32	18
7c	61	61	2.69	7
7d	65	70	1.77	10
8a	56	59	1.98	30
8b	60	67	2.04	28
8c	55	58	1.58	7
9a	58	52	1.71	27
9b	42	51	1.66	23
9c	64	68	2.58	8

[a] The 6F poly(arylene ether)s exhibit yield points with necking and drawing typical to many.

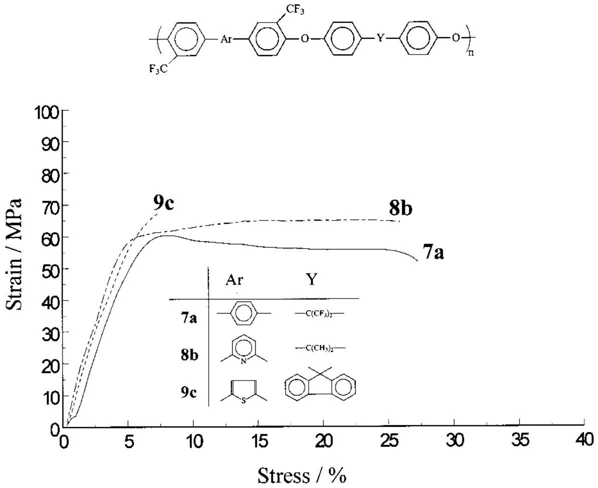


Figure 8. Stress–strain plot of poly(arylene ether)s.

°C, depending on the exact structure of the repeating unit. The polymer structures containing pyridine and thiophene rings in the polymer backbone exhibit 70–80 °C lower glass transition temperatures than their corresponding 1,4-phenyl analogous polymers. This can be explained by different catenation angles introduced by different rings into the polymer chains. Also, the polarity of the different rings must be considered. The T_g's taken as maxima in the tan δ curves of the DMTA measurements are in good agreement with the DSC values.These polymers exhibit high thermal stability. A 5% weight loss occurred between 444 and 536 °C in TGA under synthetic air, depending on the exact polymer structures. The poly(arylene ether)s containing thiophene rings in the backbone exhibit 20–30 °C lower thermal stability than their corresponding phenyl and pyridine analogues. This can be attributed to the loss of aromaticity of the thiophene ring at high temperature due to oxidation of the sulfur atom, resulting in formation of thiophene dioxide. This was confirmed further when the thermal stability of these polymers was investigated under nitrogen, where the thiophene polymers exhibit thermal stabilities that are comparable to those of the other polymers.

These poly(arylene ether)s are soluble in common organic solvents such as $CHCl_3$ like many other semifluorinated polymers. The mechanical properties of these polymer films cast from THF are typical of high-performance engineering thermoplastics (Young's modulus 2.69 GPa, tensile strength 70 MPa, elongation at break 30%).

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