

Synthesis and Characterization of Novel Poly(arylene ether)s Based on 9,10-Bis-(4-fluoro-3-trifluoromethylphenyl) anthracene and 2,7-Bis-(4-fluoro-3-trifluoromethylphenyl) fluorene

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ABSTRACT: Two new bisfluoro monomers 9,10-bis-(4-fluoro-3-trifluoromethylphenyl) anthracene and 2,7-bis-(4-fluoro-3-trifluoromethylphenyl) fluorene have been synthesized by the cross-coupling reaction of 2-fluoro-3-trifluoromethyl phenyl boronic acid with 9,10-dibromo anthracene and 2,7-dibromo fluorene, respectively. These two bisfluoro compounds were used to prepare several poly(arylene ether)s by aromatic nucleophilic displacement of fluorine with various bisphenols; such as bisphenol-A, bisphenol-6F, bishydroxy biphenyl, and 9,9-bis-(4-hydroxyphenyl)-fluorene. The products obtained by displacement of the fluorine atoms exhibits weight-average molar masses up to 1.5

$\times 10^5 \text{ g mol}^{-1}$ and number average molecular weight up to $6.8 \times 10^4 \text{ g mol}^{-1}$ in GPC. These poly(arylene ether)s show very high thermal stability even up to 490°C for 5% weight loss occurring at this temperature in TGA in synthetic air and showed glass transition temperature observed up to 310°C. All the polymers are soluble in a wide range of organic solvents, e.g., CHCl_3 , THF, NMP, and DMF. Films cast from DMF solution are brittle in nature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 664–672, 2007

Key words: poly(arylene ether)s; thermal properties; solubility; characterization

INTRODUCTION

Poly(arylene ether)s are a class of high performance polymers that have received considerable attention, they are very processable with good mechanical properties, and have moderately high glass transition temperature and operating temperatures.^{1–3} They also possess good thermo-oxidative stability.

Polymers that are stable at higher temperatures have become increasingly important over the last few decades particularly for aerospace applications. A wide range of aromatic poly(arylene ether)s have so far been synthesized, and the relationship between their primary structures and polymer properties has been studied extensively. To increase the thermal and mechanical properties, generally heterocyclic units are incorporated in to the main polymer units. Earlier we reported the increase in thermal stability with heterocyclic as well as rigid moieties.^{4,5}

Poly(arylene ether)s are synthesized via nucleophilic substitution polymerization of bisphenols with aromatic dihalides. The dihalides activated by strong electron withdrawing groups are generally chosen with bisphenols containing heterocyclic rings, amide linkages, ketonic groups, etc.^{6–9} A common characteristic of these activating groups is their electron withdrawing character and the presence of a site of un-saturation, which can stabilize the negative charge developed in the displacement through resonance to an electronegative atom. This requires the formation of Meisenheimer complex, which lowers the activation energy of the displacement reaction.

The perfluoro alkyl group is also used for activating the monomers either as a pendant or in the main chain. Since electron withdrawing perfluoroalkyl groups cannot participate in the resonance stabilization, the activation by this group is expected to be due to the stabilization of negative charges at the 2- or 4-position by hyper conjugation and by the negative inductive effect.^{9–12} The steric congestion due to a bulky trifluoromethyl group may also facilitate the formation of a stable Meisenheimer complex with release of steric strain.

Fluorine containing polymers are of special interest because of their low dielectric constant and remarkably low water absorption. The presence of

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pendant trifluoromethyl group in polymers increases fractional free volume and lowers its dielectric constants while increasing its solubility without forfeiture of thermal stability. The pendant trifluoromethyl group also decreases the crystallinity.^{11,12} Because of all these properties fluorine-containing polymers are used as membranes for gas separation and electrical insulation. In continuation of our research on semi-fluorinated poly(arylene ether)s, we would like to report the synthesis and characterization of a series of novel poly(arylene ethers).

EXPERIMENTAL

Characterization techniques

The elements, carbon, hydrogen, and nitrogen were analyzed by a Heraeus Carlo Erba 1106 elemental analyzer. ¹H NMR (400 MHz), ¹³C NMR (100 MHz) spectra were recorded on a Bruker 400 MHz instrument [reference 0 ppm with TMS (¹H and ¹³C NMR and ¹⁹F NMR)]. IR spectra were recorded with a Bruker IFS 55 spectrophotometer using KBr pellets. Gel permeation chromatography was obtained by using a Waters 1515 instrument equipped with a differential refractive index detector 2410. THF was used as mobile phase and the stationary phase was crosslinked polystyrene gel (Styragel HR-4) packed in stainless steel columns. Polymers were dissolved in THF (4 mg/mL) and filtered through 0.2 μm PTFE disposable filter prior to analysis. Molecular weight and polydispersity are reported versus monodisperse polystyrene standards. DSC measurements were made on a TA Instruments DSC-2920 instrument, at a heating/cooling rate of 20°C/min. under nitrogen. Glass transition temperature (*T_g*) was taken at the middle of the step transition in the second heating run. Thermogravimetry was measured on a TA Instruments thermo gravimetric analyzer, Model TGA-2950. A heating rate of 10°C/min was used for determination of the decomposition temperature in synthetic air (nitrogen 80 and oxygen 20 parts).

Materials

All reagents were purchased from Acros, Lancaster or Fluorochem Chemical Company and used as received unless otherwise noted. *N*-Methyl-2-pyrrolidone (NMP) (Lancaster) was purified by stirring with NaOH and distilled twice from P₂O₅ under reduced pressure.

Synthesis of monomers

9,10-Bis-(4-fluoro-3-trifluoromethylphenyl) anthracene was synthesized by reacting 4-fluoro-3-trifluoro-

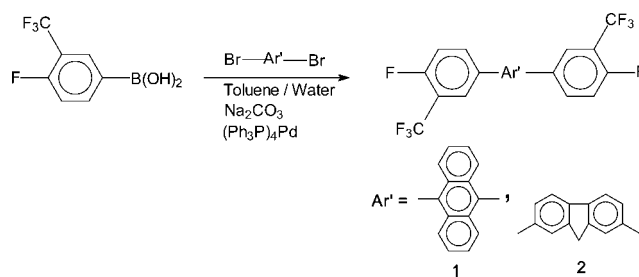


Figure 1 Reaction scheme and structure of monomers.

methylphenyl boronic acid (4 g, 19.23 mmol), 9,10-dibromo anthracene (2.68 g, 8 mmol), toluene (45 mL), aqueous Na₂CO₃ (45 mL, 1M), and Pd(PPh₃)₄ (0.208 g; 3 mol % with respect to dibromo anthracene) refluxed for 5 days, with vigorous stirring (Fig. 1). The organic layer was separated and the aqueous phase extracted with 50 mL toluene. The combined organic layers were washed with excess water, dried over (MgSO₄), and concentrated. The concentrated organic layer was filtered over Al₂O₃ (type 100–125 mesh; activity 1, bed length 20 cm, and diameter 2 cm) to remove the catalyst Pd(PPh₃)₄. The column was washed with 100 mL of toluene to obtain the desired product. Finally the compound was obtained after removal of the toluene. The compound was further purified by recrystallization from 1 : 10 mixture of toluene/hexane. Similarly 2,7-bis-(4-fluoro-3-trifluoromethylphenyl) fluorene was also synthesized taking 2,7-dibromofluorene compound (4 g, 19.23 mmol), 4-fluoro-3-trifluoromethylphenyl boronic acid (2.59 g, 8 mmol), Toluene (60 mL), aqueous Na₂CO₃ (60 mL, 1M), and Pd(PPh₃)₄ (0.285g; 3 mol % with respect to dibromo compound)

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 bishalide monomer and a bisphenol (~ 3 mmol, each), K₂CO₃ (~ 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 2–3 h (in case of bisfluoro fluorene containing moiety). After cooling to room temperature, 20 mL of THF was added; the polymer was recovered by precipitation from about 500 mL of methanol, containing a few milliliters of HCl and the solids were isolated. These products were washed several times with boiling water

to remove any inorganic impurities, dried under vacuum, dissolved in THF, re-precipitated in excess methanol, and dried under vacuum at 70°C for 24 h.

9,10-Bis-(4-fluoro-3-trifluoromethylphenyl) anthracene

Melting point: 219.7°C (DSC). Anal. Calcd. for $C_{28}H_{14}F_8$ (502.4 g/mol) C, 66.9; H, 2.8. Found: C, 67.2; H, 2.97. IR (KBr): (cm^{-1}): 2966 (aromatic C—H band out of plane), 1603 (C=C ring stretching band), 1494, 1385, 1313, 1248, 1134, 1054, 1014 (band due to C—F absorption), 829, 765, 556 (aromatic C—H band out of plane). 1H NMR($CDCl_3$): δ (ppm) 7.72 (H11, 2H, d, $J = 2.4$ Hz); 7.67–7.64 (H5, 2H, m); 7.59 (H9, 4H, q, $J = 3.2$ Hz); 7.47 (H11, 2H, t, $J = 8.2$ Hz); 7.41 (H10, 4H, q, $J = 3.2$ Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 159.45 (C3, $d = 255.7$ Hz), 136.78 (C7), 135.09 (C8), 129.82 (C6), 126.63 (C9), 124.0 (C10), 123.20 (C1, q, $J = 271$ Hz), 121.29 (C5), 121.21 (C4), 119.32 (C2, C11). ^{19}F NMR($CDCl_3$): δ (ppm) –116.13 (F2); –61.58 (F1).

2,7-Bis-(4-fluoro-3-trifluoromethylphenyl) fluorene

Melting point: 212.3°C (DSC). Anal. Calcd. for $C_{27}H_{14}F_8$ (502.4 g/mol) C, 66.9; H, 2.8. Found: C, 67.2; H, 2.97. IR (KBr): (cm^{-1}): 3042, 2925, (Aromatic C—H stretching) 1618 (C=C ring stretching band), 1499, 1466, 1253, 1128 (band due to C—F absorption), 1051, 829, 543 (aromatic C—H band out of plane). 1H NMR($CDCl_3$): δ (ppm): 7.89 (H11, 2H, m); 7.87 (H5, 2H, d, $J = 8$ Hz); 7.82–7.78 (H9, 2H, m); 7.74 (H4, 2H, m); 7.58 (H12, 2H, s); 7.29 (H8, 2H, $J = 8$ Hz); 4.04 (H14, 2H, s) ^{13}C NMR ($CDCl_3$): δ (ppm) 159.15 (C3, $d, J = 254.8$ Hz); 144.4 (C12); 140.95 (C13); 137.81 (C6); 132.35 (C5); 126.11 (C11); 125.72 (C8); 122.78 (C1, q, $J = 272$ Hz); 121.29 (C10); 120 (C7); 118.58 (C9); 117.42 (C4); 37.02 (C14) 117.32 (C2, $d = 29$ Hz); ^{19}F NMR($CDCl_3$): δ (ppm) –117.80 (F2); –61.77 (F1).

1a

Anal. Calcd. for $C_{43}H_{28}O_2F_6$ (690.68 g/mol) C, 74.77; H, 4.08. Found: C, 75.12; H, 4.18. IR (KBr): (cm^{-1}): 3065, 2924 (Aromatic C—H stretching), 2853, 1617 (C=C ring stretching band), 1493, 1386, 1313, 1248, 1135 (band due to C—F absorption), 1054, 1020 (symmetric C—O—C stretch), 881, 828, 764, 603 (aromatic C—H band out of plane). 1H NMR ($CDCl_3$): δ (ppm) 7.8 (H5, 2H, s); 7.55–7.58 (H5 and H9, 6H, m); 7.33 (H14, 4H, d, $J = 8$ Hz); 7.38–7.15 (H10, H13, 4H, m); 6.97–6.89 (H4, 2H, m); 1.63 (H17, 6H, s). ^{13}C NMR ($CDCl_3$): δ (ppm): 156 (C3); 155.8 (C11); 140 (C7); 139 (C8); 136.7 (C9); 135.9 (C12); 132.4 (C6); 129.5 (C5); 128 (C14); 126.2 (q, $J = 272$ Hz, C1); 126.7

(C10); 126.2 (C4); 125.4 (C8); 121.4 (q, $J = 31$ Hz, C2); 120.5 (C13); 41.23 (C16); 30.54 (C17). ^{19}F NMR ($CDCl_3$): δ (ppm) –62.23 (F1)

1b

Anal. Calcd. for $C_{43}H_{22}O_2F_{12}$ (798.62 g/mol): C, 64.67; H, 2.77. Found: C, 64.91; H, 2.79. IR (KBr): (cm^{-1}): 3080, 2925 (Aromatic C—H stretching), 2854, 1606 (C=C ring stretching band), 1496, 1423, 1386, 1313, 1250, 1170, 1136 (band due to C—F absorption), 1055, 968 (symmetric C—O—C stretch), 928, 828, 766, 736, 637 (aromatic C—H band out of plane). 1H NMR ($CDCl_3$): δ (ppm) 7.8 (H11, 2H, s); 7.7–7.6 (H9 and H5, 6H, m); 7.53 (H14, 4H, d, $J = 8$ Hz); 7.45–7.39 (H10, 4H, m); 7.31 (H4, 2H, d, $J = 8$ Hz); 7.2 (H13, 4H, d, $J = 8$ Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 157.8 (C12); 153.9 (C3); 136.19 (C6); 135.24 (C5); 134.35 (C8); 132.7 (C15); 129.95 (C14); 128.86 (C9); 126.47 (C7); 125.84 (C11); 124.57 (C10), 123.22 (C1 and C17, q, $J = 272$ Hz); 122.19 (C2, d, $J = 31$ Hz); 121.15 (C13); 118.65 (C4); Not found (C16); ^{19}F NMR($CDCl_3$): δ (ppm) –62.02 (F1), –117.38 (F17).

1c

Anal. Calcd. for $C_{53}H_{30}O_2F_6$ (812.80 g/mol) C, 78.31; H, 3.72. Found: C, 75.84; H, 3.81. IR (KBr): (cm^{-1}): 3064, 3038, 2925 (Aromatic C—H stretching), 2853, 1681, 1605 (C=C ring stretching band), 1493, 1447, 1385, 1312, 1244, 1134 (band due to C—F absorption), 1054, 1014 (symmetric C—O—C stretch), 915, 823, 740, 637 (aromatic C—H band out of plane). 1H NMR($CDCl_3$): δ (ppm) 7.94 (H5, 2H, s); 7.73 (H21, 2H, d, $J = 8$ Hz); 7.6 (H11, 2H, s); 7.53–7.55 (H9, 4H, m); 7.43 (H14, 4H, d, $J = 8$ Hz); 7.36–7.24 (H10, H13, 8H, m); 7.03–6.93 (H19, H20, 4H, m); 7.1 (H18, 2H, d, $J = 8$ Hz); 6.87 (H4, 2H, d, $J = 8$ Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.02 (C12); 151.07 (C3); 147.43 (C17), 142.24 (C22); 140.098 (C15); 135.93 (C6); 135.37 (C5); 133.1 (C8); 131.02 (C14); 130 (C21); 129.8 (C19); 127.8 (C9); 126.5 (C7); 126.08 (C11); 125.68 (C10); 121.87 (q, $J = 272$ Hz, C1); 120.39 (C20); 120.02 (C18); 119.46 (C4); 118.45 (C2, d, $J = 31$ Hz); 118.73 (C13); C16 (not found); ^{19}F NMR($CDCl_3$): δ (ppm) –62.23 (F1).

1d

Anal. Calcd. for $C_{40}H_{22}O_2F_6$ (648.60 g/mol) C, 74.07; H, 3.41. Found: C, 74.36; H, 3.55. IR (KBr): (cm^{-1}): 3039 (Aromatic C—H stretching), 1603 (C=C ring stretching band), 1489, 1441, 1423, 1387, 1314, 1244, 1161, 1136 (band due to C—F absorption), 1054, 1006 (symmetric C—O—C stretch), 964, 916, 825, 767, 649 (aromatic C—H band out of plane). Insoluble in the solvents commonly used for NMR.

2a

Anal. Calcd. for $C_{42}H_{28}O_2F_6$ (678.67 g/mol) C, 74.55; H, 3.87. Found: C, 74.81; H, 3.68. IR (KBr): (cm^{-1}): 3038, 2966, 2926 (Aromatic C—H stretching), 2871 (aliphatic C—H stretching), 1604 (C=C ring stretching band), 1499, 1468, 1430, 1331, 1252, 1135, 1052, 1014 (symmetric C—O—C stretch), 817, 604, 469 (aromatic C—H band out of plane). 1H NMR: ($CDCl_3$): δ (ppm) 7.96 (H14, 2H, s); 7.84 (H5, 2H, d, $J = 8$ Hz); 7.68 (H9, 2H, s); 7.65–7.51 (H4, H16, 6H, m); 7.049 (H17, 4H, d, $J = 8$ Hz); 6.68 (H4, 2H, d, $J = 8$ Hz); 3.9 (H13, 2H, s); 1.62 (H20, 6H, s). ^{13}C NMR ($CDCl_3$): δ (ppm) 153.85 (C3); 153.21(C15); 148.5 (C12); 145.46 (C11); 137.08 (C6), 134.98(C5); 130.52 (C9); 127.22 (C7); 126.91(C10); 124.88 (C17); 124.70 (C18); 122.56 (C14); 122.36 (C1, q, $J = 271.2$ Hz); 120.30 (C8); 119.46 (C4); 119.45 (C2, d, $J = 31$ Hz); 118.13 (C16); 41.27 (C19); 36.09 (C13); 29.96 (C20); ^{19}F NMR($CDCl_3$): δ (ppm) –62.23 (F1).

2b

Anal. Calcd. for $C_{42}H_{22}O_2F_{12}$ (786.44 g/mol) C, 64.14; H, 2.81. Found: C, 64.31; H, 2.76. IR (KBr): (cm^{-1}): 2924 (Aromatic C—H stretching), 1607 (C—C ring stretching band), 1501, 1467, 1330, 1250, 1171, 1052 (band due to C—F absorption), 967, 928, 825 (aromatic C—H band out of plane). 1H NMR: ($CDCl_3$): δ (ppm) 7.98 (H5, 2H, s); 7.56–7.74 (H8, H9, H11, H14, H17, 12H, m); 7.47–6.69 (H4, H16, 6H, m); 3.9 (H13, 2H, s); ^{13}C NMR ($CDCl_3$): δ (ppm) 174.39 (C14); 166.63 (C20); 156.42 (C10); 153.88 (C3), 137.96 (C7), 137.81 (C17), 136.29 (C18), 135.83 (C6), 128.81(q, $J = 272$ Hz, C1), 133.44 (C16), 133.04 (C15), 129.86 (C5), 127.91 (C8), 125.11 (C9), 124.85 (C12), 124.08 (C19), 123.28 (C13), 121.71 (C11), 121.20 (q, $J = 32$ Hz, C2); 120.04 (C4). ^{19}F NMR ($CDCl_3$): δ (ppm) –62.25 (F1).

2c

Anal. Calcd. for $C_{53}H_{30}O_2F_6$ (812.808 g/mol) C, 78.31; H, 3.72. Found: C, 78.37; H, 3.63. IR (KBr): (cm^{-1}): 3042 (Aromatic C—H stretching), 2925, 1618 (C=C ring stretching band), 1499, 1466, 1253, 1128, 1051 (band due to C—F absorption), 829, 543, 435. 1H NMR: 7.88 (H 14, 2H, s); 7.86 (H5, 2H, s); 7.81 (H21, 2H, d, $J = 8$ Hz); 7.75 (H11, 2H, s); 7.74–7.71 (H9, H17, 6H, m); 7.45 (H8, 2H, s); 7.37 (H16, 4H, d, $J = 8$ Hz); 7.33 (H22, 2H, d, $J = 8$ Hz); 7.23 (H23, 2H, d, $J = 8.4$ Hz); 7.1 (H21, 2H, d, $J = 8$ Hz); 6.97 (H4, 2H, d, $J = 8$ Hz); 3.9 (H13, 2H, s). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.28 (C14); 154.52 (C3); 151.5 (C17); 141.96 (C22); 140.27 (C15); 140.2 (C7); 135.78 (C6); 132.73 (C5); 131.13 (C12); 131.07 (C23); 128.8 (C19); 128.67 (C21); 127.21(C8); 126.8 (C18); 126.65

(C11); 125.65(C9); 125.42 (C24); 124.81 (C10); 120.87 (q, $J = 272$ Hz, C1); 120.56 (C20); 120.13 (C4); 119.69 (C13); 64.613 (C16); not found (C2). ^{19}F NMR($CDCl_3$): δ (ppm) –62.23 (F1).

2d

Anal. Calcd. for $C_{39}H_{22}O_2F_6$ (636.59 g/mol) C, 73.58; H, 3.48. Found C, 73.61; H, 3.53. IR (KBr): (cm^{-1}): 3046 (Aromatic C—H stretching), 2918, 1616 (C=C ring stretching band), 1492, 1468, 1252, 1129, 1050 (band due to C—F absorption), 831, 541. 1H NMR: 7.9(H14, 2H, s); 7.83 (H5, 2H, d, $J = 8$ Hz); 7.72 (H9, 2H, s); 7.66 (H11, 2H, s); 7.53 (H16, 4H, d, $J = 8.8$ Hz); 7.49 (H8, 2H, d, $J = 8$ Hz); 7.1 (H17, 4H, d, $J = 8$ Hz); 6.84 (H4, 2H, d, $J = 8$ Hz); 3.91 (H13, 2H, s). ^{13}C NMR ($CDCl_3$): δ (ppm): 156 (C7); 155.8 (C14); 140 (C8); 139 (C16); 136.7 (C9); 135.9 (C15); 132.4 (C6); 129.5 (C5); 128 (C12); 127.7 (C17); 126.2 (q, $J = 272$ Hz, C1); 126.7 (C10); 126.2 (C4); 125.4 (C8); 122.73 (18); 121.9 (C11); 121.4 (q, $J = 31$ Hz, C2); 120.5 (C13). ^{19}F NMR($CDCl_3$): δ (ppm) –62.2 (F1).

RESULTS AND DISCUSSION**Synthesis of monomers**

9,10-Bis-(4-fluoro-3-trifluoromethylphenyl) anthracene and 2,7-bis-(4-fluoro-3-trifluoromethylphenyl) fluorene compounds were prepared by a palladium-catalyzed cross-coupling reaction of an aryl bromide with boronic acid commonly known as Suzuki cou-

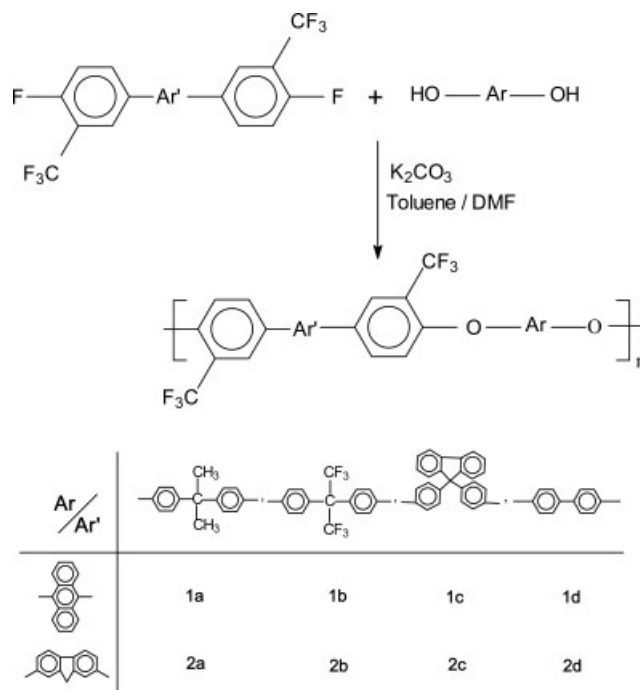


Figure 2 Reaction scheme and structures of the polymers.

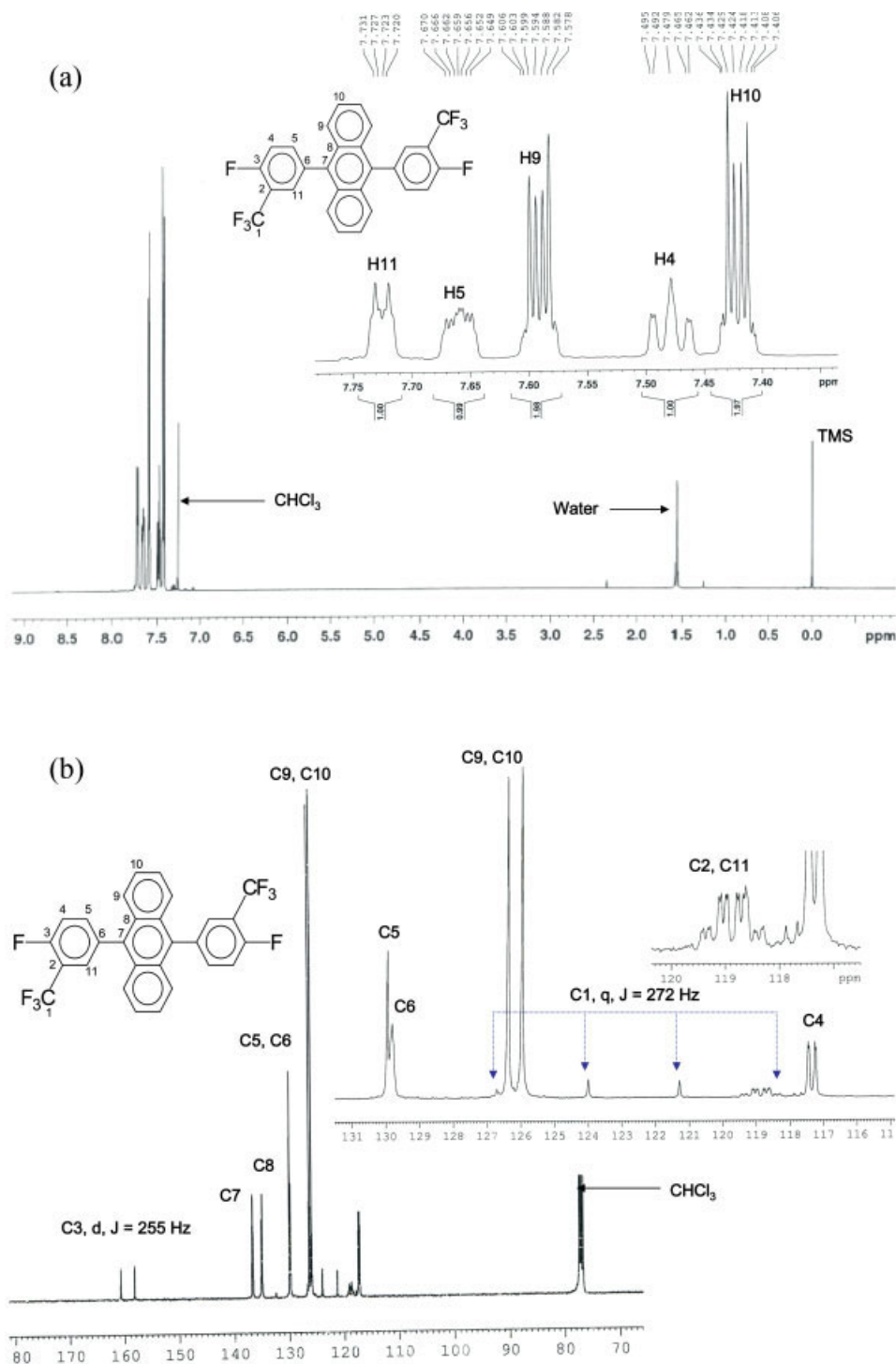


Figure 3 (a) ¹H NMR spectra of 9,10-bis-(4-fluoro-3-trifluoromethylphenyl) anthracene (NMR frequency 600 MHz). (b) ¹³C NMR spectra of 9,10-bis-(4-fluoro-3-trifluoromethylphenyl) anthracene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pling reaction as shown in Figure 1. The protocol of synthesis is quite similar as described earlier.^{12,13} Product obtained was confirmed by TLC single spot, DSC single melting peak, and was further characterized by elemental analysis, IR, NMR (¹H, ¹³C, ¹⁹F) spectroscopic methods. The representative proton and carbon NMR spectra of 9,10-bis-(4-fluoro-3-tri-

fluoromethylphenyl) anthracene is shown in Figure 3(a,b). The proton NMR spectra showed usual splitting pattern as expected from the fluorine containing polymers^{12,14,15} and gives the exact matching in the integrated ratios for different protons. The carbon NMR spectrum [Fig. 3(b)] also supports the structure. The C1, C3, and C4 carbons appeared as quartet,

TABLE I
Molar Masses of the Poly(arylene ether)s

Polymer	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_n/M_w	Color of 5% polymer solution in DMF
1a	68,740	150,544	2.19	Clear, Transparent
1b	58,520	120,550	2.09	Clear, Transparent
1c	63,527	114,834	1.71	Clear, Transparent
1d	–	–	–	–
2a	24,013	59,310	2.47	Orange
2b	31,860	77,748	2.44	Clear, Transparent
2c	29,375	62,570	2.13	Green
2d	18,185	78,409	2.78	Violet

doublet and doublet at 123.20, 159.45, and 114.4 ppm respectively, with a C-F coupling constants of 272, 255.7, and 14 Hz. C2 and C11 have merged together as multiplet, otherwise should appeared as quartet, C5 and C6 have also merged together but can be seen as two separate peak in the expanded spectrum and the NMR spectrum showed the exact number of carbons as expected from the structure.

Polymer synthesis

The synthesis of poly(arylene ether)s is based on nucleophilic displacement reaction of an activated aryl halide with bisphenoxide in polar aprotic solvents as shown in Figure 2. Polymerizations of activated bishalide compound with different bisphenols were carried by conventional carbonate process.^{11,12} The reaction mixture was maintained at 140°C until the presence of water was no longer observed in the Dean–Stark trap, which takes 4–5 h. During this stage of the reaction the solution underwent several color changes. As in initial stages, at the time of phenoxide formation; pale yellow color was observed, and as the refluxing proceeds; the color changed to dark brown. Upon dehydration the temperature was slowly increased to 180°C to effect the nucleophilic displacement reaction and reaction was allowed to run till rise in viscosity. Among the two system i.e., bisfluoro fluorene and bisfluoro anthracene, poly(arylene ether)s with fluorene moiety were

showing gelation. The time taken for gel formation was also different depending on the reactivity of the monomers. As the electron donating nature of methyl group in bisphenol-A makes CH₂ proton of bisfluoro fluorene monomer more acidic and leads to early gelation. Similarly bisphenol 6F makes –CH₂ proton of bisfluoro fluorene monomer less acidic due which it takes more time for gelation hence reaction can be run for longer time and leads to high molecular weight polymer. Similarly it was observed that bisphenol fluorene monomer also shows lesser tendency towards gelation. The reactivity of monomers can also be observed from the molecular weights (Table I).

In case of bisfluoro anthracene containing system no gelation was observed and increase in molecular weight was judged by dramatic increase of viscosity. However 1d polymer precipitates in due course of polymerization. Polymers obtained were brittle in nature, and films formed were not free standing. In anthracene containing polymers rigidity has shown dominating effect over the bulkiness of the anthracene.

Polymer solubilities

These polymers exhibited good solubility behavior in common organic solvents like the previously reported semifluorinated poly(arylene ether)s.^{12,15} It was attempted to obtain 10% (w/v) solution of all

TABLE II
Solubility of Polymers in Various Common Organic Solvents

Polymer	NMP	DMF	DMSO	THF	Toluene	Acetone	CHCl ₃
1a	+	+	–	+	+r	–	+
1b	+	+	+rr	+	+	–	+
1c	+	+	+rr	+r	+rr	–	+r
1d	+	–	–	–	–	–	–
2a	+	+	+rr	+	+	–	+
2b	+	+	+rr	+	+	–	+
2c	+	+	+rr	+	+	–	+
2d	+	+	+rr	+	+	–	+

+ = soluble at room temperature; – = insoluble at room temperature; +r = partially soluble at reflux; +rr = soluble at reflux.

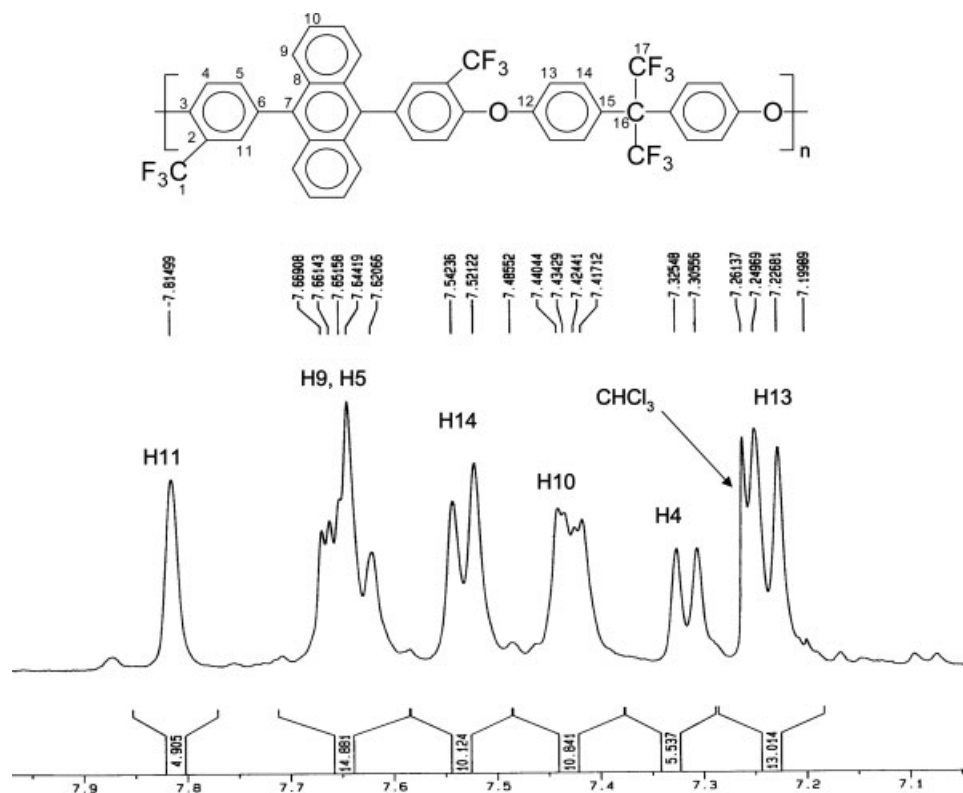


Figure 4 ^1H NMR spectra of polymer 1b.

polymers in several organic solvents, which are summarized in Table II. These polymers are soluble in CHCl_3 , THF, DMF, DMAc, NMP, and toluene at room temperature. Here toluene appeared to be good solvent for these polymers, despite its low polarity compared with the solvents that are commonly used for poly(arylene ether)s. Polymer 1d is not at all soluble in any of the solvent except the NMP, this may be due to the highly rigid nature of this polymer. The polymer 1c was soluble partially even after refluxing for long time. It was anticipated that presence of bulky moieties in the polymer should enhance the solubility by increasing the fractional free volume but rigidity of the polymer dominated over the bulkiness in these cases. Polymer 1a is soluble in various solvents while polymer 1b has shown best solubility among the entire four-anthracene moiety-containing polymer.

Gelation was observed in fluorene moiety containing polymers. Between gel-sol, we had taken soluble portion of polymer and further evaluated the properties. Therefore, fluorene moiety containing polymer showed good solubility in most of the organic solvents as mentioned above.

Although, the polymers have good solubility in many organic solvents, the solution cast films of these polymers are brittle in nature that limits the evaluation of the mechanical properties of these polymers.

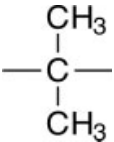


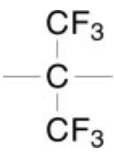

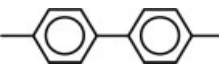
Spectroscopy

The spectroscopic data from FTIR and ^1H , ^{13}C and ^{19}F NMR spectroscopy support the structure of poly(arylene ether)s. These characterization methods as well as elemental analysis do not indicate any degradation of trifluoromethyl group. The FTIR spectra of these polymers show the aryl ether linkages ($1140\text{--}1050\text{ cm}^{-1}$) that are generated in the polymer forming reaction, and also the stretching frequencies ($1240\text{--}1150\text{ cm}^{-1}$) corresponding to trifluoromethyl group.^{11,12} FTIR and ^1H NMR do not show any signals corresponding to the terminal $-\text{OH}$ or $-\text{F}$ groups, indicative of high conversion. Figure 4 shows the ^1H NMR spectra of the polymer 1b. The spectrum shows exact matching for integrated peak areas for different protons. The exact analytical data for all these polymers are listed in the experimental section. It was not possible to record the NMR spectra of the insoluble polymers.

DSC measurements

The glass transition temperatures for 1a–1d and 2a–2d, measured during the second heating cycles are summarized in Table III. Representative graphs (1b and 2a) are shown in Figure 5. The glass transition temperatures of poly(arylene ether)s were in the range $180\text{--}303^\circ\text{C}$. T_g is known to depend on several

TABLE III
Glass Transition Temperatures (°C) of the Poly(arylene ether)s by DSC

Y/Ar	235	254
		
	275	282
	303	310
	280	292

factors such as chain symmetry and intermolecular forces, but primarily depends on the rigidity of the main polymer chain.^{16,17} Polymers with bisphenol-6F exhibits higher T_g with respect to polymers containing bisphenol-A. This is due to stronger interchain interactions due to the polar trifluoromethyl groups and also bulkiness of trifluoromethyl group restricts their flexibilizing effect.¹⁷ Since, the fluorene containing polymers shows gelation during polymerization, only soluble portion has been taken for evaluation of the properties. However, except 2a all other polymers exhibit weight average molecular weight

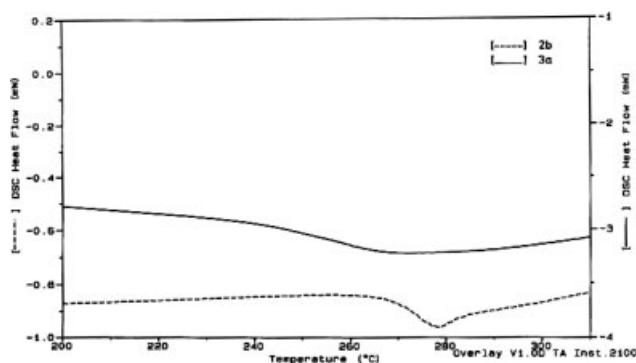


Figure 5 DSC curves of polymers 1b and 2a.

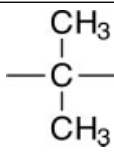
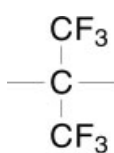

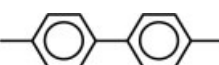
above 75,000, which shows that 2a is more effective for gelation and does not give high molecular weight (24,000) and as a consequence exhibited low T_g .

Polymer 1c exhibited glass transition temperature up to 333°C is the highest among the series because of the rigid and bulky nature of both bisfluoro anthracene and bishydroxy fluorene. It is known that with the increase in rigidity, glass transition temperature also increases.¹⁸

Thermal stability

The thermal stability of polymers was studied by TGA. All polymers exhibited excellent thermal stability as summarized in Table IV. Representative graphs are shown in Figure 6. Depending upon exact structures, these polymers show a 5% weight loss between 345 and 495°C in synthetic air. The bisphenol components in the polymer chain significantly influence the thermal stability. The polymer based on isopropylidene generally exhibits lower thermal stability than corresponding hexafluoro-isopropylidene.¹⁹ However, our observation was different for polymer 1b, which showed early decomposition. Polymer 2b exhibited the highest thermal

TABLE IV
Thermal Stability of Poly(arylene ether)s by TGA in Air for 5 and 10 % Weight Loss Temperature (°C)

Y/Ar	5%	10%	5%	10%
	430	483	454	492
	481	531	482	497
	484	508	491	598
	486	517	488	510

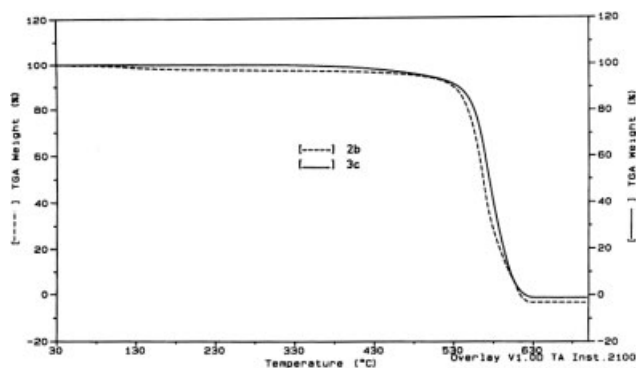


Figure 6 TGA curves of polymers 1b and 2c.

stability among all the polymers. The higher stability of 1d and 2d can be attributed to the higher aromaticity in comparison to bisphenol-6F and bisphenol-A whereas higher thermal stability of polymer 1c and 2c is because of the rigid fluorene moiety.

CONCLUSIONS

Two new trifluoromethyl activated bispheno monomers have been synthesized successfully using Suzuki protocol. The versatility of the monomer synthesis allows the preparation of various novel poly(arylene ether)s by nucleophilic displacement polymerization with different bisphenols. We obtained very high conversion for most of the polymers with weight average molecular weight even up to 3×10^5 g mol⁻¹. The resulting poly(arylene ether)s were semicrystalline in nature with glass transition temperatures between 180 and 333°C depending on the exact structures of the repeating unit. These polymers exhibit high thermal stability at 5% weight loss occurred between 345 and 495°C in TGA under syn-

thetic air, depending on the exact polymer structures. The polymers were soluble in most of the common organic solvents such as CHCl₃, THF, NMP, and DMF. However, the solution cast films are of brittle in nature, this limits the evaluation of the mechanical properties of these polymers.

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