Processable High T_g High Strength Fluorinated New Poly(arylene ether)s Containing Imido Aryl Group

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ABSTRACT: A series of poly(arylene ether)s (**7a–7f**) were successfully synthesized by aromatic nucleophilic substitution reactions of imidoaryl biphenol (5), 4,9-*bis*-(4-hydroxy-phenyl)-2-phenyl-benzo[*f*]isoindole-1,3-dione with six different trifluoromethyl substituted bisfluoro monomers (**6a–6f**). The weight-average molar masses of the polymers were up to 280 kD as measured by GPC. These poly(arylene ether)s exhibited glass transition temperatures up to 361°C in DSC. These polymers showed very high thermal stability up to 558°C for 10% weight loss under synthetic air in TGA. Except **7d–7f**, remaining polymers **7a–7c** were soluble in a wide range of organic solvents. Transparent thin films of these polymers cast from DCM or NMP exhibited tensile strengths up to 75 MPa and elongation at break up to 41% depending on their exact repeating unit structures. These poly(arylene ether)s showed cut-off wavelength in between 400 and 450 nm except **7d** and water absorption were in the range of 0.4 to 0.6%. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3038–3047, 2011

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

INTRODUCTION

Poly(arylene ether)s are considered as an important class of engineering thermoplastics and possess useful physical properties such as high modulus, toughness, high thermal, thermo oxidative stability, and chemical resistance.[1–3] These polymers find applications in a variety of fields such as coatings, adhesives, composites, and molded components.[1,2,4] Poly(arylene ether)s are very useful in microelectronics as insulating materials[5,6] and are also used as membrane materials, mainly for gas separation.[7] Poly(arylene ether)s are generally prepared by a step growth polymerization of activated aryl dihalo or dinitro monomers with bisphenoxides.[6,7] Perfluoroalkyl groups as a pendent or in the main chain are used for activating haloaryls for nucleophilic displacement by phenoxides. Perfluoroalkyl groups stabilizes the negative charges at the 2- or 4-position by hyperconjugation and by the negative inductive effect.[8,9] The steric congestion due to a bulky trifluoromethyl group may also facilitate the formation of a stable Meisenheimer complex with release of steric strain.[10]

The continued search for new bishydroxy groups leading to the formation of highly processable as well as highly thermal stable poly(arylene ether)s has been a very active area of polymer research. In an attempt to increase the polymer property, Korshak et al. introduced cyclic cardo group (for example; fluorene, phthalide, or phthalimidine) in the polymer backbone which increased the glass transition temperature, thermo-oxidative stability, and also good solubility of the polymers.[11] Strukelji and Hay reported the synthesis of a number of imido aryl biphenols derived from phenolphthalein.[12] These biphenols were used to react readily with different activated aromatic bishalides to prepare poly(arylene ether)s, poly(imidoaryl ether sulfone)s, poly(imidoaryl ether ketone)s.[12,13] These imido biphenol based polymeric materials exhibited high Young's moduli, high thermo oxidative stability ($T_{d10\%} > 545°C$), and glass transition temperature as high as 245 to 330°C. The variation of different pendent groups at nitrogen atom of the imido biphenol resulted in variation of different properties depending on exact molecular structure.[12,14] Various research groups also introduced different functionality like, amino, amino acids as future sites for crosslinking at the substituted imido nitrogen before or after the polymerisartion.[15]

Fluorine containing polymers are of special interest because of their low dielectric constant and remarkably low water absorption. The presence of pendant trifluoromethyl group in polymers increases fractional free volume and lowers its dielectric constant values while increasing its solubility without forfeiture of thermal stability.[16,17] The pendant trifluoromethyl group also decreases the crystallinity. Because of all these properties fluorine-containing

polymers are used as membranes for gas separation and electrical insulation. These groups decreases crystallinity, color, water absorption as well as increase optical transparency, environmental stability, and flame resistance.[18,19]

In continuation of our research for the preparation of high temperature, high T_g, and high strength materials, we designed number of new semifluorinated poly(arylene ether)s.[20,21] In this article we report six new poly(arylene ether)s derived from the polycondensation of six different fluorinated bis-fluoro monomers with the imidoaryl biphenol (5). Detailed characterization of these polymers 7a–7f including thermal, mechanical, optical transparency, and water absorption is discussed.

EXPERIMENTAL

General consideration

Elemental analyses of carbon, hydrogen, and nitrogen content of the compounds were done by pyrolysis method. FTIR spectra of the monomers and polymers were recorded from a NEXUS 870 FTIR (Thermo Nicolet) spectrophotometer at room temperature and humid free atmosphere using KBr pellets. ^{1}H-NMR and proton decoupled ^{13}C-NMR of monomers and polymers were recorded on a Bruker 500 MHz instrument (Switzerland), using CDCl$_3$ or DMSO-d[6] as solvent and TMS as reference. DSC measurements were made on Q 2000 of TA instrument, at a heating rate of 20°C/min under nitrogen. Glass transition temperatures (T_g) were taken as the middle point of the step transition in the second heating run. Thermogravimetric analyses were done on a TGA Q 500 of TA thermal analyzer instrument at a heating rate of 10°C/min to determine the decomposition temperature under synthetic air. Inherent viscosities of the polymer solutions of 0.5 g/dL concentration in NMP were measured using an Ubbelohde viscometer at (30 ± 1)°C. Molecular weights and molecular weight distributions of the polymers were determined using a Waters gel permeation chromatography (Waters 2414) instrument. Tetrahydrofuran (THF) was used as eluent (flow rate 0.8 mL/min), polystyrene was used as narrow standard for calibration, and RI detector was used to record the signal. Stress-strain behavior of the thin polymer films was measured at room temperature using UTM-Instron, Plus-800 at a strain rate of 5% of sample length. Five film specimens of 100 to 120 micron (25 mm × 10 mm) were used for the measurements. The films prepared from 7a to 7c were cast using dichloromethane (DCM) and from 7d to 7f were cast from N-methyl-2-pyrrolidone (NMP) from their 10% (w/v) solution. Wide angle X-ray diffractograms were recorded on Rigaku, Ultema III X-ray diffractometer using a CuKα (β = 0.154 nm) source, operated at 40 kV and 40 mA for the 2θ range of 2° to 40°. Optical characterization was done with Perkin–Elmer λ 750 UV-Visible spectrometer for 300 to 800 nm wavelength range. Water absorption test of the polymer films were done at room temperature by immersing rectangular pieces of samples (30 × 10 mm) in distilled water after drying to a constant initial weight. Final weight was taken after 72 h and %water absorption was measured by using a Sartorious balance of sensitivity 10^{-6} g.

Starting materials

Phenolphthalein (Loba Chemie Pvt, India), zinc granules, maleic anhydride, aniline, toluene, K$_2$CO$_3$, and dichloromethane (DCM) (E. Merck, India) were used as received. N-methyl-2-pyrrolidone (NMP) (E. Merck, India) was purified from NaOH and distilled from P$_2$O$_5$ before use. Toluene (Merck) was refluxed over sodium metal to remove water and freshly distilled before use. Methanol was purchased from Ranbaxy Fine Chem. Ltd., India. The fluorinated monomers namely 1,3-bis(4′-fluoro-3′-trifluoromethylphenyl)benzene, 1,4-bis(4′-fluoro-3′-trifluoromethylphenyl)benzene, 4,4′-bis(4′-fluoro-3′-trifluoromethylphenyl)biphenyl, 9,10-bis(4-fluoro-3-trifluoromethylphenyl)anthracene, 2,6-bis(4′-fluoro-3′-trifluoromethylphenyl)pyridine, and 2,5-bis(4′-fluoro-3′-trifluoromethylphenyl)thiophene were prepared according to our previous publications.[22–25]

Synthesis of (5)

Imido aryl biphenol (5) was prepared according to the procedure already reported elsewhere with adoption of some modifications.[12] The synthesis of 5 is presented in Figure 1. Phenolphthalein (1) (40 g) was reduced after refluxing with sodium hydroxide (6 M, 300 mL) in ethyl alcohol (300 mL) in presence of zinc granules (30 g). The disappearance of the pink color of phenolphthalein (1) confirmed the complete conversion toward 2-[bis(4-hydroxyphenyl)methyl]benzoic acid (2). The finely crushed reduced compound 2 (20 g, 62.4 mmol) reacted with concentrated sulfuric acid (50 mL) in a round bottom flask immersed in ice-salt bath. The mixture was stirred vigorously to dissolve all the material within 5 to 7 min. Stirring for a longer period leads to lower yield due to unwanted sulfonation while generating the isobenzofuran derivative (3). [12] The orange-brownish colored slurry was poured into 900 mL of ice-water in a beaker. The greenish-yellow precipitate of 3 obtained was filtered, washed with cold water, and dried within 10 to 15 min before next step. The greenish yellow color turns to fully yellow due to oxidation if it is kept for longer time
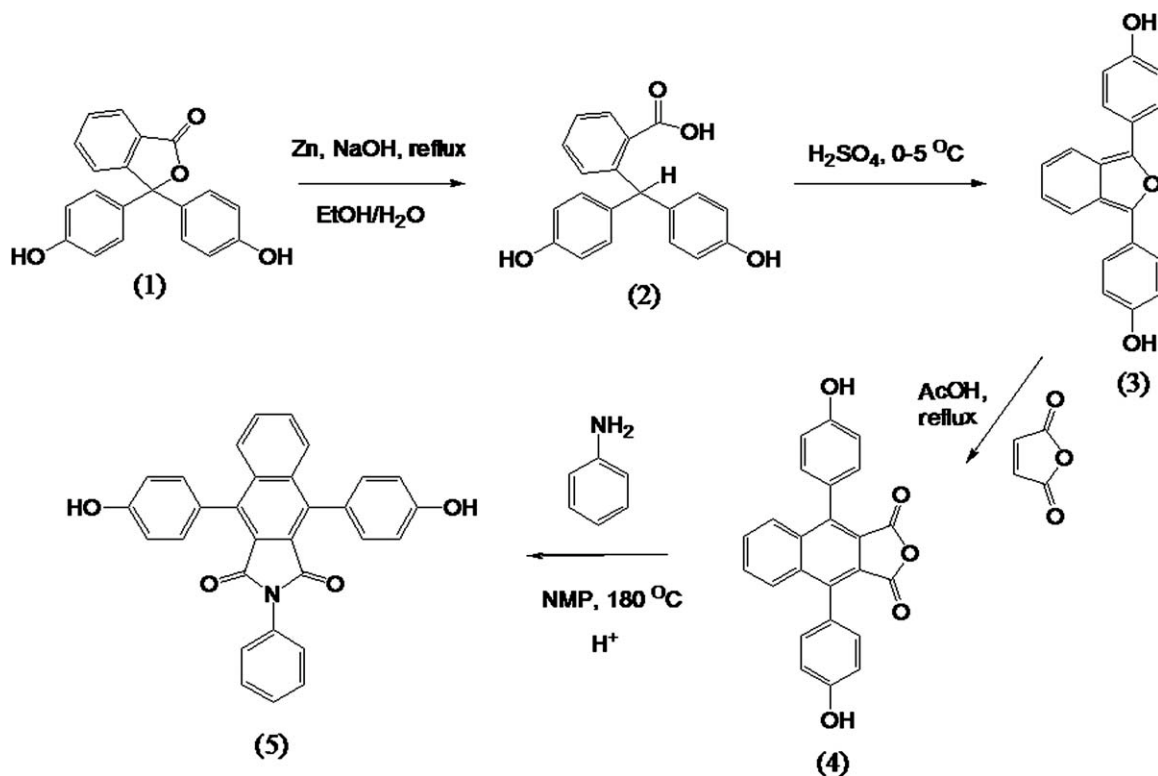
Figure 1   Reaction scheme for the synthesis of imidoaryl biphenol.

in air. So, it was used immediately for Diels–Alder reaction with maleic anhydride (6.73 g, 68.7 mmol) in acetic acid (60–70 mL) in 500 mL round bottom flask. The clean reaction mixture was heated to reflux. After 15 to 20 min, a yellow color product precipitated from reaction mixture. However, the reaction was left in reflux condition for another 2 to 3 h for complete dehydration. The yellow product **4** was isolated by filtration, washed, and dried at 70 to 80°C under vacuum. Purity of the material was checked through calorimetric method (DSC) and NMR spectroscopy. Finally, imidization reaction was carried out by taking product **4** (5.0 g, 13.7 mmol) with aniline (1.3 mL, 14.3 mmol) in 20 to 25 mL of NMP in round bottom flask connected with Dean-Stark trap. The temperature was raised to 165°C and then to 185°C. After 7 to 8 h, a yellow color product was precipitated from the reaction mixture. Completion of reaction was confirmed from thin layer chromatography (TLC). The yellow imido aryl biphenol **5** was isolated by filtration, washed with dilute hydrochloric acid (1 M), water (200 mL), and dried at 120°C under vacuum. A single narrow peak (mp 404°C obtained against reported values 383°C) in DSC confirms the purity of the material. ^{1}H-NMR (DMSO-d^6): δ (ppm) 9.68 (s, 2H, H^{15}); 7.84-7.81 (m, 2H, H^9); 7.69-7.68 (m, 2H, H^3); 7.46-7.42 (m, 2H, H^{10}); 7.38-7.32 (m, 3H, H^1, H^2); 7.25 (d, J = 8.4Hz, 4H, H^{12}), 6.91 (d, J = 8.4Hz, 4H, H^{13}).


(5)
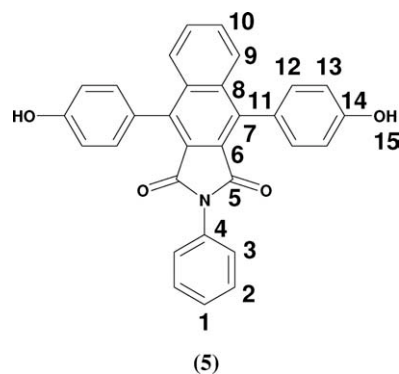
Polymerization

Polycondensation reactions were carried out in a 50 mL, three-necked round-bottomed flask equipped with a nitrogen inlet, a stir bar, and a Dean-Stark trap fitted with condenser. The reactions were conducted under constant flow of nitrogen. A representative polycondensation reaction procedure for **7a**: the flask was charged with equimolar amounts of a 1,3-bis(4′-fluoro-3′-trifluoromethylphenyl)benzene (**6a**) and compound **5** (2.5 mmol each), K$_2$CO$_3$ (6 mmol), NMP (10 mL), and toluene (25 mL). The mixture was then heated to reflux (140–150°C, oil bath temperature) for 2 to 3 h to remove the water azeotopically with toluene. After removal of the toluene from the Dean-Stark trap, the reaction temperature was increased to 180°C and maintained for

another 6 h. After cooling to room temperature, the polymer was precipitated in about 500 mL of methanol containing 10 mL of HCl. Fibrous solids were isolated. These products were washed several times in boiling water to remove any inorganic impurities and dried in a vacuum oven at 65°C for overnight.
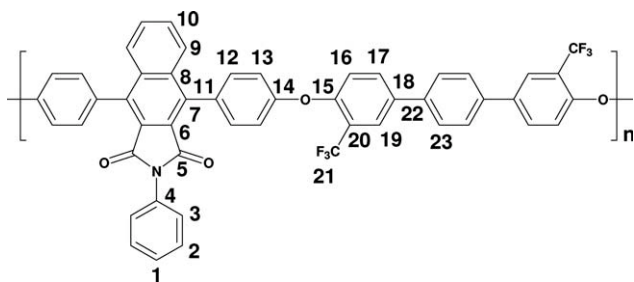
Poly(arylene ether) 7a
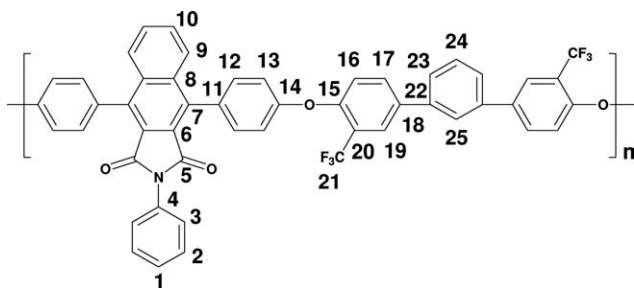
Anal. cal. for $C_{50}H_{27}F_6NO_4$ (819.74)$_n$ g/mol: C, 73.26; H, 3.32; N, 1.71. Found: C, 73.15; H, 3.57; N, 1.73.

FTIR (KBr, cm^{-1}): 3042 (aromatic C-H stretching), 1769 (imide >C=O asymmetric stretching), 1721 (imide >C=O symmetric stretching), 1599 (aromatic C=C stretching), 1484, 1331 (C-O-C asymmetric stretching), 1246, 1133 (C-F stretching), 1052 (C-O-C symmetric stretching), 760 (C-N bending).

^{1}H-NMR (CDCl$_3$, δ ppm): 7.99 (m, 5H, H^3, H^9, H^{25}); 7.79-7.70 (m, 6H, H^{17}, H^{19}, H^{23}); 7.61–7.54 (m, 5H, H^{12}, H^{24}); 7.43 (m, 4H, H^2, H^{10}); 7.31 (m, 7H, H^1, H^{13}, H^{16}).

^{13}C-NMR (CDCl$_3$, δ ppm): 166.31; 156.78; 154.76; 140.25; 139.61; 136.12; 135.94; 132.06; 131.75; 130.49; 129.78; 129.25; 128.97; 128.89; 128.65; 128.22; 126.98; 126.48; 126.07; 125.76; 123.57; 123.4 (q, J = 271.25 Hz, C^{21}); 122.01 (q, J = 31.13 Hz, C^{20}); 120.22; 119.17.

Poly(arylene ether) 7b

Anal. cal. for $C_{50}H_{27}F_6NO_4$ (819.74)$_n$ g/mol: C, 73.26; H, 3.32; N, 1.71. Found: C, 73.31; H, 3.35; N, 1.68.
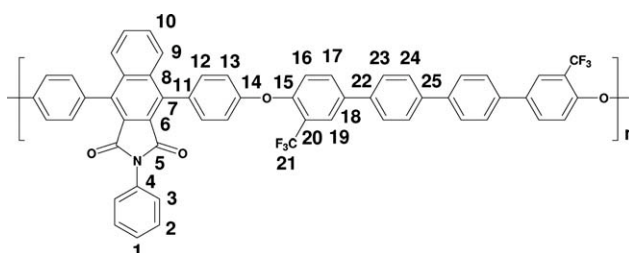
FTIR (KBr, cm^{-1}): 3039 (aromatic C-H stretching), 1770 (imide >C=O asymmetric stretching), 1720 (imide >C=O symmetric stretching), 1599 (aromatic C=C stretching), 1484, 1331 (C-O-C asymmetric

stretching), 1247, 1132 (C-F stretching), 1051 (C-O-C symmetric stretching), 819 (C-N bending).

^{1}H-NMR (CDCl$_3$, δ ppm): 7.99 (m, 4H, H^3, H^9); 7.78 (m, 2H, H^{19}); 7.71 (m, 6H, H^{17}, H^{23}); 7.54 (m, 4H, H^{12}); 7.45-7.44 (m, 4H, H^2, H^{10}); 7.37-7.16 (m, 7H, H^1, H^{13}, H^{16}).

^{13}C-NMR (CDCl$_3$, δ ppm): 166.34; 156.76; 154.69; 139.63; 138.68; 135.94; 135.64; 132.58; 131.75; 130.56; 130.24; 129.27; 128.99; 128.65; 128.24; 127.75; 127.01; 125.81; 123.56; 123.43 (q, J = 271 Hz, C^{21}); 121.99 (q, J = 30.75 Hz, C^{20}); 120.18; 119.19.

Poly(arylene ether) 7c

Anal. cal. for $C_{56}H_{31}F_6NO_4$ (895.84)$_n$ g/mol: C, 75.08; H, 3.49; N, 1.56. Found: C, 75.17; H, 3.61; N, 1.52.

FTIR (KBr, cm^{-1}): 3036 (aromatic C-H stretching), 1769 (imide >C=O asymmetric stretching), 1721 (imide >C=O symmetric stretching), 1599 (aromatic C=C stretching band), 1483, 1330 (C-O-C asymmetric stretching), 1246, 1131 (C-F stretching), 1050 (C-O-C symmetric stretching), 817 (C-N bending).

^{1}H-NMR (CDCl$_3$, δ ppm): 7.99 (m, 4H, H^3, H^9); 7.77 (m, 6H, H^{19}, H^{23}); 7.70 (m, 6H, H^{17}, H^{24}); 7.54 (m, 4H, H^{12}); 7.45–7.43 (m, 4H, H^2, H^{10}); 7.37–7.20 (m, 7H, H^1, H^{13}, H^{16}).

^{13}C-NMR (CDCl$_3$, δ ppm): 166.31; 156.79; 154.59; 139.85; 139.62; 138.43; 135.95; 135.85; 131.73; 130.55; 130.46; 129.23; 128.97; 128.65; 128.22; 127.72; 127.64; 127.45; 127.00; 125.80; 123.57; 123.46 (q, J = 271 Hz, C^{21}); 121.99 (q, J = 30.88 Hz, C^{20}); 120.18; 119.15.

## Poly(arylene ether) 7d
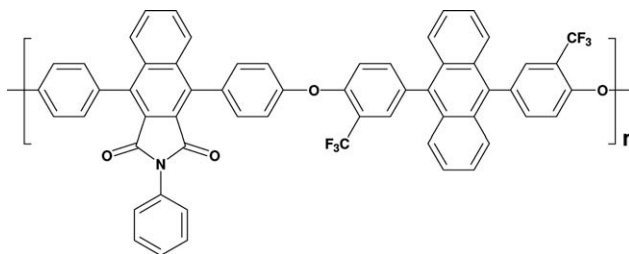
Anal. cal. for $C_{58}H_{31}F_6NO_4$ (919.86)$_n$ g/mol: C, 75.73; H, 3.40; N, 1.52. Found: C, 75.59; H, 3.47; N, 1.57.

FTIR (KBr, cm^{-1}): 3040 (aromatic C-H stretching), 1768 (imide >C=O asymmetric stretching), 1721

(imide >C=O symmetric stretching), 1598 (aromatic C=C stretching), 1482, 1330 (C-O-C asymmetric stretching), 1244, 1131 (C-F stretching), 1050 (C-O-C symmetric stretching), 762 (C-N bending).

NMR: NMR spectroscopy for polymer **7d** was not done because of their insolubility in CDCl$_3$ or DMSO-d^6.

Poly(arylene ether) 7e
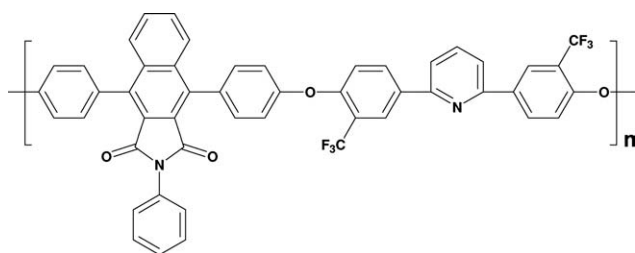
Anal. cal. for C$_{49}$H$_{26}$F$_6$N$_2$O$_4$ (820.73)$_n$ g/mol: C, 71.71; H, 3.19; N, 3.41. Found: C, 71.75; H, 3.67; N, 3.47.

FTIR (KBr, cm^{-1}): 3043 (aromatic C-H stretching), 1771 (imide >C=O asymmetric stretching), 1720 (imide >C=O symmetric stretching), 1597 (aromatic C=C stretching), 1483, 1329 (C-O-C asymmetric stretching), 1244, 1134 (C-F stretching), 1050 (C-O-C symmetric stretching), 761 (C-N bending).

NMR: NMR spectroscopy for polymer **7e** was not done because of their insolubility in CDCl$_3$ or DMSO-d^6.

Poly(arylene ether) 7f
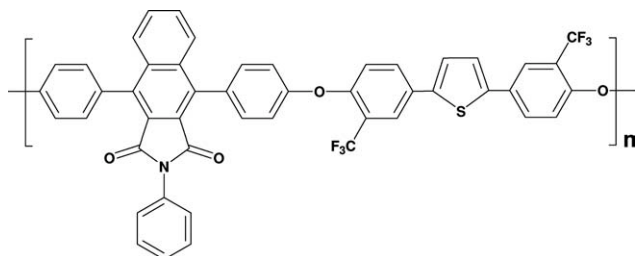
Anal. cal. for C$_{48}$H$_{25}$F$_6$NO$_4$S (825.77)$_n$ g/mol: C, 69.82; H, 3.05; N, 1.70. Found: C, 69.89; H, 3.15; N, 1.73.

FTIR (KBr, cm^{-1}): 3040 (aromatic C-H stretching), 1770 (imide >C=O asymmetric stretching), 1722 (imide >C=O symmetric stretching), 1601 (aromatic C=C stretching), 1484, 1330 (C-O-C asymmetric stretching), 1248, 1135 (C-F stretching), 1051 (C-O-C symmetric stretching), 760 (C-N bending).

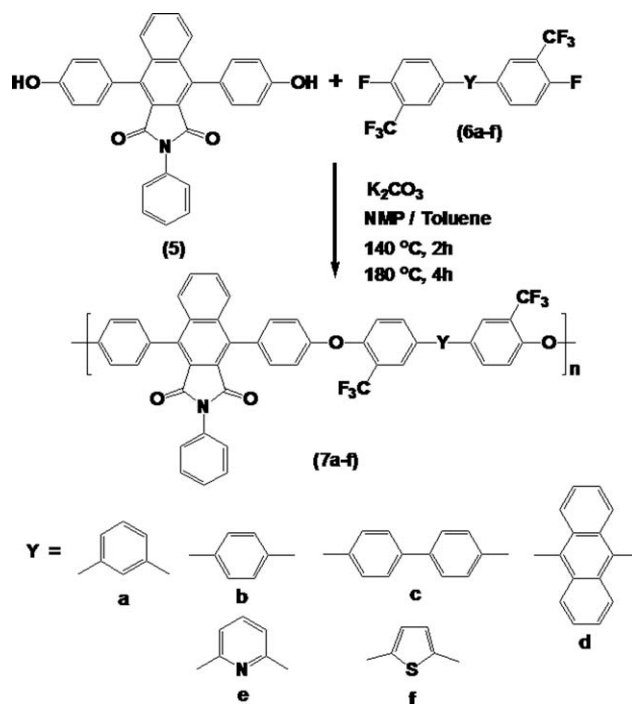NMR: NMR spectroscopy for polymer **7f** was not done because of their insolubility in CDCl$_3$ or DMSO-d^6.

Figure 2 Polymerization and structures of the poly(arylene ether)s.

RESULTS AND DISCUSSION

Synthesis of poly(arylene ether)s

Polymerizations of the bisfluoro monomers with stoichiometric amounts of **5** were carried out in the presence of excess of K$_2$CO$_3$ in NMP as solvent according to the reported protocol.[17,25] The solid content was maintained at 15 to 20%. Toluene was used for azeotropic removal of water. The detailed structures of the polymers prepared are shown in Figure 2. During the initial stage of the polymerization, the reaction temperature was maintained at 140 to 150°C, and the water generated was effectively removed along with toluene through a Dean-Stark trap. Upon completion of bisphenoxide formation, the reaction temperature was raised to 180°C for effective nucleophilic displacement reaction. High molar mass polymers were obtained within 6 h as judged by the remarkable increase of the viscosity of the reaction medium in all the cases. The resulting viscous reaction mixtures were diluted with THF and were precipitated in large excess of methanol containing a few milliliters of HCl for complete removal of the excess base present in the system. Fibrous solids were isolated. These products were washed several times with hot water for the removal of inorganic impurities present in the system, and the isolated products were dried in a vacuum at 65°C for overnight. About 1 g of each of the dry polymers were dissolved in 10 mL of dichloromethane or N-methyl pyrrolidone, and poured in flat

bottom Petri dishes. In case of dichloromethane as solvent, the solvent was evaporated at a control rate at room temperature for 24 h. The films were kept overnight at 120°C under vacuum to ensure the complete removal of any residual solvent in the film. When N-methyl pyrrolidone was used as solvent, a step wise drying was adopted with the sequential increase of temperature as 100°C (overnight), 150°C (3 h), 180°C (3 h), 220°C (2 h), and at 250°C (1 h). Transparent yellowish-brown films were obtained in almost all cases.

Spectroscopy

All spectroscopic data obtained from FTIR, ^{1}H, and ^{13}C-NMR spectroscopy supported the structures of the poly(arylene ether)s. In FTIR spectra the presence of absorption band at 1050 cm^{-1} corresponding to Ph-O-Ph symmetric stretching and absorption band at 1330 and 1481 cm^{-1} corresponding to Ph-O-Ph asymmetric stretching of all polymers confirmed the formation of poly(arylene ether)s. The FTIR spectra showed the absorption band at 1770 cm^{-1} corresponding to >C=O asymmetric stretching, 1720 cm^{-1} to >C=O symmetric stretching, 1599 cm^{-1} to aromatic C=C stretching, (1250–1130) cm^{-1} to -C-F stretching frequencies.[17,18,25] Both the FTIR and ^{1}H-NMR spectra of the polymers did not show any signals corresponding to the terminal -OH groups, supporting high conversion. The number of magnetically different protons that were obtained from the integrated ratios of the different peaks in spectra was in exactly match with the proposed polymer repeat unit structures. The desired numbers of ^{13}C signals were obtained in ^{13}C-NMR spectra of all the polymers. The C-F coupling constant values for the quartet due to one bond coupling ($^1J_{C-F}$) were around 271 Hz and due to two bond coupling ($^2J_{C-F}$) were around 31 Hz. The detailed spectral data of the polymers are given in the Experimental section. NMR spectroscopy for polymer 7d–7f was not done because of their insolubility in CDCl$_3$ or DMSO-d^6.

Polymer solubility

Poly(arylene ether)s 7a–7c exhibited good solubility in common organic solvents like other semifluorinated poly(arylene ether)s.[20,21] It was attempted to obtain 10% (w/v) solution of all polymers in several organic solvents. These polymers were soluble in halogenated solvents like chloroform, dichloromethane (DCM) and in polar aprotic solvents like tetrahydrofuran (THF), N,N'-dimethylformamide (DMF), N-methyl pyrrolidone (NMP), dimethylacetamide (DMAc) at room temperature. Polymer 7d showed relatively lower solubility in all these common solvents except in NMP. All these poly(arylene ether)s

TABLE I
Physical Properties of the Poly(arylene ether)s

Polymer	Yield (%)	M_n	M_w	PDI	η_{inh} (dL/g)
7a	99	108,000	286,000	2.3	0.92
7b	99	86,000	194,000	2.2	0.83
7c	99	111,000	262,000	2.6	0.87
7d[a]	99				0.86
7e[a]	99				0.91
7f[a]	99				0.94

η_{inh}, inherent viscosity of poly(arylene ether)s measured at a concentration of 0.5 g/dL in NMP at 30°C; M_n, number average molecular weight; M_w, weight average molecular weight; PDI, polydispersity index.
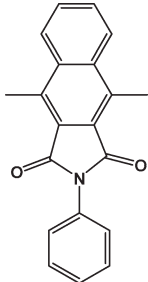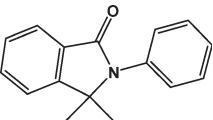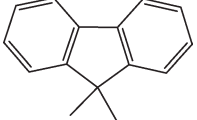[a] Due to their insolubility in THF, GPC could not be done.
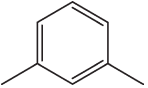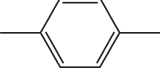
were insoluble in dimethyl sulfoxide (DMSO) and acetone. Poly(arylene ether)s 7e–7f were soluble only in NMP. So, in addition to chemical structure, and/or rigidity and/or catenation angle, polarity play a major role i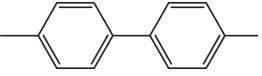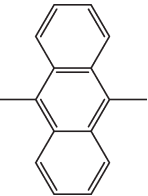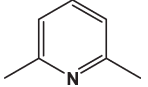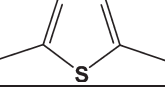n the solubility in these polymers. The presence of polar pyridine and thiophene unit may have profound effect contributing to the interchain/intermolecular interaction resulted in their large insolubility in common solvent. The inherent viscosity of the synthesized poly(arylene ether)s in NMP [concentration 0.5% (w/v)] were evaluated with highest as 0.94 dL/g and lowest as 0.83 dL/g among the polymers. These values along with the GPC results of the polymers are shown in Table I. GPC results, along with viscosity values indicate the formation of high molar masses. GPC analysis for polymers 7d–7f was not done because of their insolubility in THF.

Glass transition temperature and comparison with other polymers

None of the six synthesized poly(arylene ether)s exhibited any crystallization or melting transitions in DSC measurements. It indicated their amorphous character. The amorphous nature of all the polymers was further supported by the broad peaks in X-ray diffraction experiment. The absence of well-defined long ranged order or crystanillity in these polymers is expected because of the presence of pendent imido aryl group, and pendent trifluoromethyl group in the main backbone. The pendent imido aryl moiety and trifluoromethyl groups substantially reduce the interchain cohesion leading to amorphous nature. All these polymers showed higher glass transition temperature in comparison to their analogous phenolphthalein/fluorene based poly(arylene ether)s reported earlier.[20,21,25] The increase in glass transition temperature of all these polymers is attributed to the presence of rigid napthylimido moiety in the

TABLE II
Thermal Properties of the Poly(arylene ether)s and a Comparison with Similar Types of Polymers

Ar								
			Refs. [20,21]		Refs. [22–25]		Refs. [22–25]	
	DSC	TGA	DSC	TGA	DSC	TGA	DSC	TGA
Y	(T_g)	(T_{d5}/T_{d10})	(T_g)	(T_{d5}/T_{d10})	(T_g)	(T_{d5}/T_{d10})	(T_g)	(T_{d5}/T_{d10})
	271 (**7a**)	495/554 (**7a**)	241	518/540	–	–	176	507/–
	317 (**7b**)	512/557 (**7b**)	264	536/549	234	530/–	209	514/–
	334 (**7c**)	522/558 (**7c**)	291	532/556	300	534/–	257	549/–
	361 (**7d**)	488/528 (**7d**)	–	–	303	484/508	–	–
	298 (**7e**)	513/543 (**7e**)	260	497/533	186	536/–	218	492/–
	287 (**7f**)	451/497 (**7f**)	–	493/524	–	494/–	–	470/–

DSC, heating rate 20°C/min under nitrogen; T_g, glass transition temperature; TGA, heating rate 10°C/min under synthetic air; T_{d5}, 5% weight loss temperature; T_{d10}, 10% weight loss temperature.

main chain. In comparision with corresponding fluorene/phenolphthalein analogues, the rigid napthylimido group makes the biphenol more rigid; thereby, hinders the motions around the polymer backbone and increases glass transition temperatures. The glass transition temperatures of the polymers are summarized in Table II. The DSC plot for all the synthesized polymers are shown in Figure 3. The glass transition temperatures of all these polymers were obtained in the order: **7d** > **7c** > **7b** > **7e** > **7f** > **7a**. This order could be explained considering three factors: rigidity, catenation angle of the
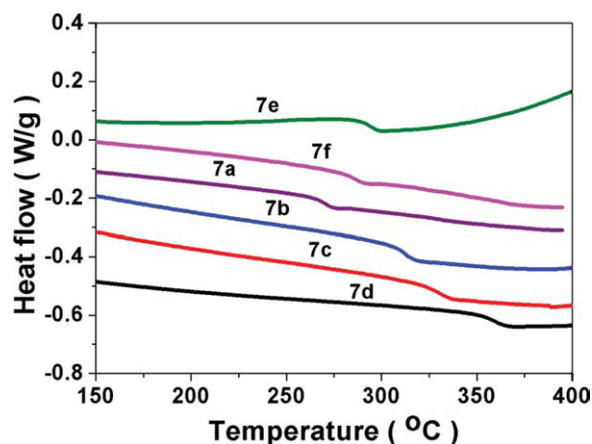
Figure 3 DSC plot of the poly(arylene ether)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

different groups, and polarity. A macromolecule having higher catenation angle (more extended geometry) and rigid units is expected to have higher glass transition temperature and *vice versa*. The highest glass transition temperature (364°C) of the polymer **7d** is due to its extended geometry and most rigid backbone structure compared to others. The catenation angle between 4,4′-diphenyl biphenyl **7c** and 1,4-diphenyl benzene **7b** is the same (180°); however, as the rigidity decreases from **7c** to **7b,** the glass transition temperature also decreases in the same order from **7c** to **7b**. The lower glass transition temperature of poly(arylene ether)s **7a** containing 1,3-diphenyl benzene unit compared to poly(arylene ether)s **7b–7d** is due to its less extended geometry (catenation angle 120°). When we compared the glass transition temperatures of the poly(arylene ether)s **7a**, **7e**, and **7f** containing 1,3-diphenyl benzene, 2,6-diphenyl pyridine, and 2,5-diphenyl thiophene units respectively, the above observed order of glass transition temperature could not be explained on the simple basis of catenation angle (catenation angle: 1,3-diphenyl benzene (120°), 1,6-diphenyl pyridine unit (120°), and thiophene is 148°).[25] The obtained T_g order for **7a**, **7e**, and **7f** could be explained through polarity of the corresponding involved heterocyclic units in **7e** and **7f**. The higher T_g of polymer **7e** containing pyridine moiety may be due to the polarity of the pyridine ring. Thiophene has a more extended geometry than pyridine; but four times more polarity of pyridine over thiophene ($\mu_{pyridine} = 7.4 \times 10^{-30}$ Cm; $\mu_{thiopene} = 1.83 \times 10^{-30}$ Cm),[26] diminishes the catenation effect and thus contributes to its higher T_g by increasing the intermolecular polar interaction.

Thermal stability

The thermal stability of the polymers was evaluated by TGA under synthetic air. The TGA plot for the

polymers is shown in Figure 4 and the thermal properties of the polymers along with other similar polymers are summarized in Table II. The 5 and 10% weight loss temperatures for these polymers are in the range of 451 to 522°C and 497 to 558°C, respectively. All these polymers showed similar and in few cases better thermal stability in air as compared with their phenolphthalein/fluorene based poly(arylene ether)s except **7f**.[20,21,22] The improved thermoxidative stability of the polymers may be due to stabilization of ether linkages by the electron withdrawing effect of napthylimido group.[12] The poly(arylene ether)s bearing imido aryl cardo groups were more thermally stable in comparison with the similar structure of poly(arylene ether)s without cardo moiety.[22–25] High thermal stability observed in case of polymer **7c** containing quadriphenyl unit in the main chain attributed due to the greater chain rigidity. The polymer **7b** showed similar thermal stability as of polymer **7c**. Lower thermo oxidative stability of polymer **7f** in comparison to others is due to the presence of thermally less stable thiophene ring in the polymer. The thiophene ring loses its aromaticity as it oxidizes to thiophene dioxide at high temperatures.[24]

Mechanical properties

The mechanical properties of thin poly(arylene ether)s films cast from DCM or NMP are shown in Table III and a representative stress-strain plots for **7b** is shown in Figure 5. All the poly(arylene ether)s films showed good mechanical properties and exhibited very high tensile strength and modulus. Higher tensile strength up to 96 MPa, and Young's modulus up to 1.58 GPa was obtained for the poly(arylene ether) **7f**. The highest tensile strength of poly(arylene ether) **7f** among the series is probably due to the higher molecular weight development as indicated
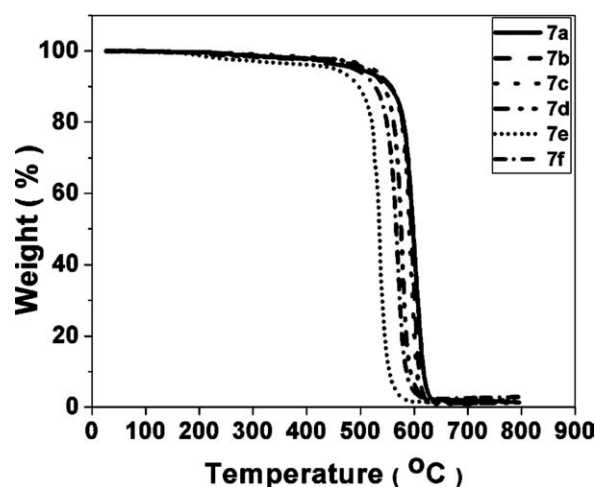

Figure 4 TGA thermograms of the poly(arylene ether)s.

TABLE III
Tensile Properties of the Poly(arylene ether)s

Polymer	Tensile strength/MPa	Young's modulus/GPa	Elongation at break (%)
7a[a]	64	1.53	6
7b[a]	75	1.59	38
7c[a]	74	1.51	41
7d[b,c]			
7e[c]	67	1.58	5
7f[c]	96	1.58	12

[a] Film cast from DCM.
[b] Due to brittle character, tensile testing could not be done.
[c] Film cast from NMP.

from its viscosity value. The GPC analysis for this polymer **7f** was not possible as it was insoluble in tetrahydrofuran. The poly(arylene ether)s **7b and 7c** showed ductile characteristic of materials containing aryl ether linkages with elongation at break as high as 38 to 41%. The lower elongation at break for polymer **7a** (6%) and **7e** (5%) are due to their lower extended geometry (lower catenation angle for both 1,3-diphenylbenzene unit and 2,6-diphenylpyridine unit). The poly(arylene ether) **7d** showed brittle character.

Optical properties and water absorption study

UV-Visible spectroscopic studies (Figure 6) of the polymers revealed that all the polymer thin films (thickness between 104 and 124 μm) showed high optical transparency. Except **7d**, cut-off wavelength in the range 400 to 450 nm was obtained for all the polymers; depending on the thickness and exact structures. High optical transparency of these films can be attributed to the amorphous nature of the polymeric films originated from the flexible ether linkages, pendent trifluoromethyl group, and bulky
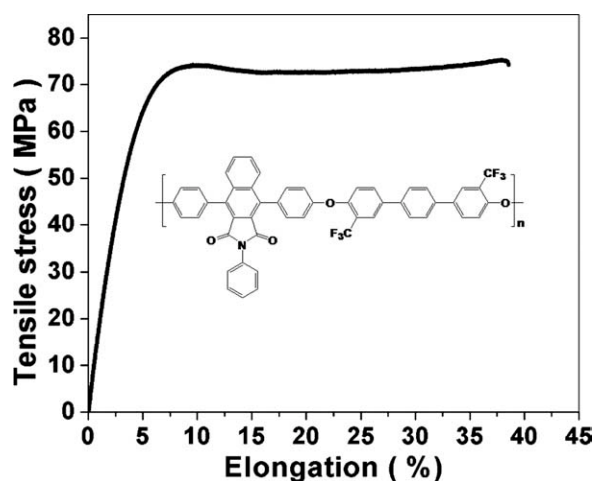
cardo imido aryl group in the polymer backbone which hinders the inter chain close packing.

Besides high optical transparency, low water absorption is also an important criterion for application in optoelectronic devices. Water absorption study of the poly(arylene ether)s were done by immersing rectangular pieces of samples (30 × 10 mm) in double distilled water after taking the initial weight at room temperature. Final weight was taken after 72 h and water absorption was calculated; % water absorbed = [(weight of the wet film − weight of the dry film)/Weight of the dry film] × 100. The water uptake values are as less as 0.4%. Lower water uptake values of these polymers are possibly due to the contribution from fluorine as trifluoromethyl groups in the polymer structure. The detailed values of water absorption and cut-off wavelength are summarized in Table IV.

CONCLUSIONS

Six new poly(arylene ether)s were successfully synthesized via activated aromatic nucleophilic displacement polymerization reaction of 4,9-bis(4-hydroxy-phenyl)-2-phenyl-benzo[f]isoindole-1,3-dione (**5**) with six different trifluoromethyl substituted monomers **6a–6f**. All the synthesized poly(arylene ether)s were amorphous in nature as indicated from DSC and XRD measurements. The poly(arylene ether)s exhibited very high T_g (271–361°C) and very high thermal stabilities in synthetic air in comparison with similar semifluorinated poly(arylene ether)s reported earlier. Polymers **7a–7c** showed good solubility in several organic solvents, whereas **7d–7f** showed good solubility only in NMP. The polymers showed very good tensile strength, high Young's modulus values, and low water absorption. The properties of these
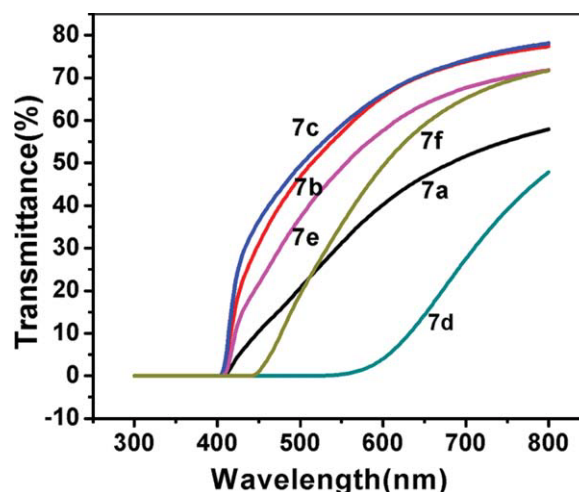

Figure 5   Stress-strain plot of the poly(arylene ether) **7b.**

Figure 6 UV-Visible spectra of poly(arylene ether)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
Cut-Off Wavelength and Water Absorption Data of the Poly(arylene ether) Films

Polymers	Thickness (µm)	Cut-off wavelength (nm)	Water absorption (%)[a]	Color and quality
7a[b]	117	408	0.5	Yellowish-brown, transparent, flexible
7b[b]	111	404	0.4	Yellowish-brown, transparent, flexible
7c[b]	104	404	0.6	Yellowish-brown, transparent, flexible
7d[c]	124	534	0.6	Dark-brown, translucent, brittle
7e[c]	113	408	0.5	Yellowish-brown, transparent, flexible
7f[c]	105	444	0.5	Yellow, transparent, flexible

[a] After 72 h.
[b] Film cast from DCM.
[c] Film cast from NMP.

polymers are comparable or better than many other engineering thermoplastics and these polymers may find application in the field of gas permeation and optoelectronic devices.

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