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Synthesis and Characterization of Novel Poly(Arylene Ether)s from 4,4′-Thiodiphenol

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Four novel perfluoroalkylated poly(arylene ether)s have been synthesized successfully using four perfluoroalkyl-activated bisfluoro monomers. These polymers are synthesized through nucleophilic displacement of the fluorine atoms on the benzene ring with 4,4′-thiodiphenol and are named as 1a, 1b, 1c and 1d, respectively. The polymers obtained by displacement of the fluorine atoms exhibit weight-average molar masses up to 3.9×10^4 g · mol^{-1} in Gel permeation chromatography. These poly(arylene ether)s showed very high thermal stability up to 548°C for 10% weight loss in TGA under nitrogen and high glass transition temperature (T_g) up to 178°C in DSC depending on the repeat unit structures. The glass transition temperatures taken as peak in tan δ in DMA measurements are in good agreement with the DSC T_g values. All the polymers synthesized are soluble in a wide range of organic solvent such as $CHCl_3$, $CHCl_2$, THF, NMP, DMF and toluene. Transparent thin films of these polymers cast from THF exhibited tensile strengths up to 72 MPa, modulus up to 1.69 GPa with low elongation at break depending on their exact repeating unit structures. Rheological properties showed ease of processability of these polymers with no change in melt viscosity with temperature.

Keywords: poly(arylene ether)s; thermal stability; glass transition temperature; rheology

1 Introduction

Poly(aryl ether)s are an important class of polymers for their outstanding physical properties such as excellent strength, high modulus, toughness, high thermal stability, chemical resistance and hydrolytic stability. Because of such attractive properties poly(arylene ether)s are categorized as high performance engineering thermoplastics (1–3).

These materials are very useful for microelectronics as optical wave guide materials. Kim et al. (4) synthesized sulphur containing novel poly(arylene ether) containing ethynyl group by nucleophilic aromatic substitution from 4,4′-(hexafluoroisopropylidene)diphenol (6FBPA) and an excess of pentafluorophenyl sulfide, followed by a reaction with 3-ethynylphenol as a suitable material for optical wave devices, and optical loss as reported by them was less than 0.40 dB/cm. Qi et al. (5) have prepared novel crosslinkable, highly fluorinated poly(arylene ether ketones/sulfones) by copolycondensation reactions of perfluorinated aromatic ketone/sulfone with 4,4′-(hexafluoroisopropylidene)diphenol and a tetrafluorostyrol-containing bisphenol (i.e., 1,1-bis(4-hydroxyphenyl)ethyl-1-phenyl 2,3,5,6-tetrafluorostyrol ether). The crosslinked polymer thin films exhibited low optical loss (~0.5 dB/cm). Poly(arylene ether)s are also promising as membrane materials for gas separations. Xu et al. (6) studied the gas transport properties of two novel poly(arylene ether)s, one containing diphenylfluorene (FBP) and 2,6-bis(trifluoromethylphenylene)pyridine (6FPPr) groups and the other containing FBP and 2,5-bis(3-trifluoromethylphenylene)thiophene (6FPT) groups in the main chain. It is reported that these FBP-containing poly(arylene ether)s show higher gas permeabilities than most of the earlier reported FBP-containing polymer membranes. Poly (arylene ether)s are also promising materials for fuel cell applications. Miyatake et al. (7) synthesized poly(arylene ether sulfone) membrane containing sulfofluorenyl groups, which showed a lower resistance than expected from its conductivity, indicating superior water-holding capability at high temperature and low humidity.

Fluorine–containing polymers (8) are of special interest because of their low dielectric constants and reduced water uptake. This is because of the greater steric volume of fluorine compared to that of hydrogen which thereby reduces the number of polarizable groups per unit volume resulting in reduced dielectric constant. The presence of pendant trifluoromethyl groups in polymers increases fractional free volume (9) thereby improving solubility and other properties such as crystallinity (10) without forfeiture

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of thermal stability (11). Ding et al. (12) reported highly fluorinated poly(arylene ether-1,3,4-oxadiazole)s (FPAEOx), where the presence of the highly electron-withdrawing oxadiazole group in FPOx significantly enhanced the reactivity of the *p*-fluorine substituents such that the reaction could be completed under mild reaction conditions. The polymer was a fit candidate for fluoride sensory without displaying any response to other tested anions including Cl^-, Br^-, ClO_4^-, HSO_4^-, and PF_6^-. Ding et al. (13) recently developed highly fluorinated poly(arylene alkylene ether sulfone)s using a nucleophilic polycondensation reaction of decafluorodiphenyl sulfone (DPSO) with a series of fluorinated linear or branched alkylene diols.

In continuation of our research in the preparation of semifluorinated poly(arylene ether)s (6, 14, 15), considerable attention has been devoted towards the preparation of new classes of fluorine containing polymers by alterations of molecular structure of the polymers which dramatically influences the performance and processing properties. In this paper we report four new poly(arylene ether)s derived from 4,4′-thiodiphenol as bisphenoxide along with four different perfluoroalkylated monomers. Detailed characterization of the resulting polymers including thermal, mechanical, dynamic mechanical and rheology is discussed.

2 Experimental

2.1 General Considerations

Spectroscopic studies of the synthesized polymers were done. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz instrument [reference zero ppm with respect to TMS]. IR spectra were recorded with a Nexus 870 spectrophotometer with KBR pellets. Gel permeation chromatography (GPC) was obtained using a Waters 2414 instrument equipped with RI detectors. THF was used as eluent at a flow rate of 1 mL/min. Solution viscosity was measured manually with the help of a Ubbelhode viscometer at room temperature using toluene as solvent. DSC measurements were made on a NETZSCH DSC 200 PC instrument, at a heating/cooling rate of 20°C/min. Glass transition temperatures (T_g) were taken at the center of the step transition in the second heating run. Thermogravimetry analysis was done on a NETZSCH TG 209 F1 instrument. A heating rate of 10°C/min was used to determine the decomposition temperature (T_d) at 10% weight loss under nitrogen. Mechanical properties were measured with a H10KS-0547 instrument with a strain rate of 5%/min at room temperature. For this analysis, the thin polymer films prepared by casting from THF solution onto glass plates, was allowed to evaporate the solvent slowly at room temperature, then dried overnight under vacuum at 80°C. Dynamic mechanical thermal analysis (DMA) was done on a DMA 2980 instrument under tension mode on thin-film samples at a heating rate of 10°C/min with a 1 Hz frequency. Dry specimens were made by keeping the samples at 80°C overnight under high vacuum, and water absorption of the films was measured by using a Sartorius balance of sensitivity of 10^{-6} g. The dry films were immersed into double distilled water for 72 h at 30°C. A rheology study was done on a AR 1000 (TA instrument) advanced rheometer using polymer films.

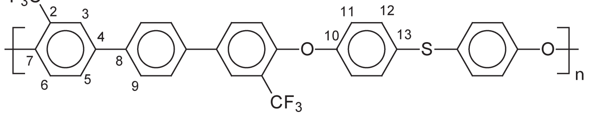
2.2 Starting Materials

All the reagents were purchased from Merck, Aldrich, Fluka and used as received unless otherwise noted. The compounds 4,4′-*bis*(4-fluoro-3-trifluoromethyl benzyl) benzene, 4′4″-*bis*(4-fluoro-3-trifluoromethyl benzyl) biphenyl, 2,6-*bis*(4-fluoro-3-trifluoromethyl benzyl)pyridine and 2,5-*bis*(4-fluoro-3-trifluoromethyl benzyl) thiophene were prepared according to the previously reported procedure (14, 15). The bisphenoxide 4,4′-thiodiphenol was purified by recrystallization from toluene. THF and toluene (Merck) was refluxed over Na alloy to remove water and freshly distilled before use. NMP (Merck) was purified by stirring with NaOH and distilled twice from P_2O_5 under reduced pressure. Methanol was purchased from Ranbaxy Fine Chem. Ltd., India.

2.3 Synthesis of Poly(arylene ether)s

Polymerization reactions were carried out in a 250 mL, three-necked round bottom flask equipped with a magnetic stir bar, a Dean-Stark trap fitted with condenser, and a nitrogen inlet. The reaction flask was charged with equimolar amounts of a bis (fluoro) monomer and 4,4′-thiodiphenol (approximately 3.0 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 5 h to remove water 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 mL of HCl. The products were washed several times with boiling water to remove any organic impurities and dried in a vacuum. The products were redissolved in THF, reprecipitated in excess of methanol, and dried in vacuum at 80°C for 24 h.

2.4 Polymer 1a

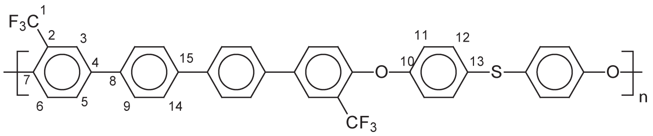


IR (KBR) (Cm^{-1}): 3034, 1610, 1482, 1436, 1332, 1246, 1132, 050, 1010, 818.

^{1}H-NMR ($CDCl_3$): δ (ppm) 7.91 (s, 2H, H_3); 7.72–7.65 (m, 6H, H_5, H_9); 7.4 (d, $J = 8.4$, 4H, H_{12}); 7.07–7.02 (m, 6H, H_6, H_{11}).

^{13}C-NMR ($CDCl_3$): δ (ppm) 155.97, 154.39, 138.55, 135.68, 132.87, 131.59, 131.03, 127.50, 125.82, 123.83 (q, C_1, $J = 271$ Hz), 122.21 (q, C_2, $J = 30$ Hz), 120.05, 119.98.

2.5 *Polymer 1b*

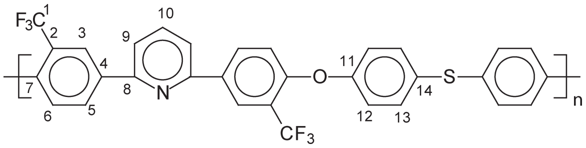


IR (KBR) (Cm^{-1}): 3787, 3032, 1615, 1482, 1429, 1331, 1247, 1133, 1049, 1009, 815.

^{1}H-NMR ($CDCl_3$): δ (ppm) 7.93 (s, 2H, H_3); 7.74–7.64 (m, 10H, H_5, H_9); 7.40 (d, $J = 8.1$, 4H, H_{11}); 7.07–7.02 (m, 6H, H_6, H_{12}).

^{13}C-NMR ($CDCl_3$): δ (ppm) 156.02, 154.28, 139.77, 138.26, 135.91, 132.87, 131.57, 130.99, 127.58, 127.37, 125.79, 123.82 (q, C_1, $J = 271$ Hz), 122.19 (q, C_2, $J=$ 30 Hz), 120.42, 120.03.

2.6 *Polymer 1c*

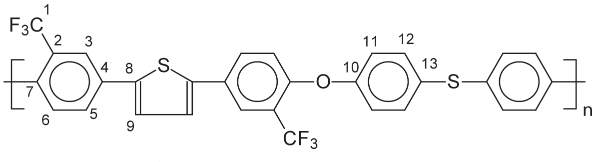


IR (KBR) (Cm^{-1}): 3052, 1618, 1596, 1484, 1484, 1419, 1326, 1248, 1248, 1202, 1130, 1051, 1011, 908, 881, 801.

^{1}H-NMR ($CDCl_3$): δ (ppm) 8.42 (s, 2H, H_3); 8.23 (d, 2H, H_5); 7.87 (t, $J_1 = 7.2$, 2H, H_{10}, $J_2 = 7.2$); 7.68 (d, $J = 7.4$, 2H, H_9); 7.38 (d, $J = 8.1$, 4H, H_{13}); 7.07 (m, 6H, H_6, H_{12}).

^{13}C-NMR ($CDCl_3$): δ (ppm) 155.71, 154.93, 138.05, 134.20, 132.87, 131.62, 131.20, 125.88, 125.05, 123.48 (q, C_1, $J = 272$ Hz), 121.92 (q, C_2, $J = 30$ Hz), 120.22, 119.49, 118.59.

2.7 *Polymer 1d*



IR (KBR) (Cm^{-1}): 3052, 1689, 1617, 1584, 1482, 1416, 1328, 1244, 1202, 1160, 1131, 1051, 1010, 896, 875, 798, 684, 512.

^{1}H-NMR ($CDCl_3$): δ (ppm) 7.88 (s, 2H, H_3), 7.86 (d, 2H, $J = 8.5$, H_5), 7.37–7.30 (m, 6H, H_9, H_{12}), 7.05–6.97 (m, 6H, H_6, H_{11}).

^{13}C-NMR ($CDCl_3$): δ (ppm) 155.80, 154.66, 141.91, 134.40, 132.87, 131.59, 130.18, 129.44, 124.75, 123.53 (q, C_1, $J = 271$ Hz), 121.19 (q, C_2, $J = 31$ Hz), 120.04, 119.57.

3 Results and Discussion

The 4,4′-thiodiphenol compound reacts with different bisfluoro compounds to yield poly(arylene ether)s at the analogy of conventional polyether synthesis by nucleophilic displacement reaction (15, 16). Figure 1 shows the synthetic scheme of the poly(arylene ether)s.

The inherent viscosity of the polymers was measured in DMF solutions, and the results are shown in Table 1. The high inherent viscosities of these polymers are due to a rigid backbone structure. The molar mass of the polymers were evaluated by GPC, and the results in Table 1 indicate formation of a high molecular weight product. The polydispersity index values are in the range expected for condensation polymers.

3.1 *Polymer Solubility*

The synthesized poly(arylene ether)s exhibited good solubility in common organic solvents. It was attempted to obtain 10% (w/v) solution of all polymers in several organic solvents. These polymers are soluble in toluene, chloroform ($CHCI_3$), dichloromethane (CH_2CI_2), N,N′-dimethylformamide (DMF), N-methyl pyrrolidone (NMP) and tetrahydrofuran (THF) at room temperature. Here, toluene appears as a good solvent for all these polymers, despite its low polarity compared to the solvents that are commonly used for poly(arylene ether)s. This indicates that polarity alone is not the only parameter for selecting solvents for polymers. Although the synthesized polymers contain sulfide linkage (-S-), they are still observed to be insoluble in DMSO even on reflux. The new poly(arylene ether)s are readily soluble in dipolar aprotic solvents such as NMP and DMF, which have similar polarity. This behavior is similar to the previously reported semi-fluorinated poly(aryl ether)s (14). THF is a very good solvent for the synthesized polymers.

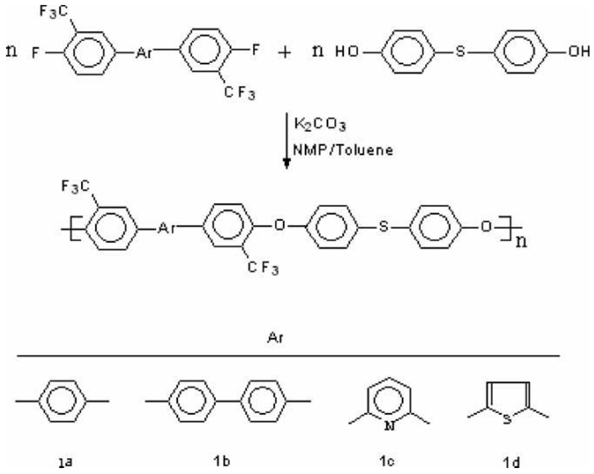
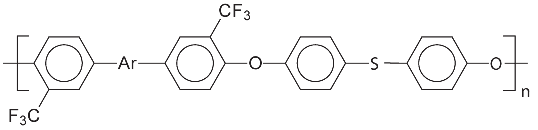


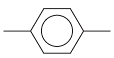
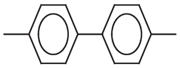
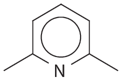
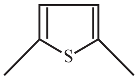
Fig. 1. Reaction scheme and structures of novel poly(arylene ether)s.

Table 1. Physical properties of poly(arylene ether)s

Polymer	η_{inh}	M_n	PDI	Film quality
1a	0.84	35000	1.88	Clear, flexible
1b	0.70	39200	1.89	Clear, flexible
1c	0.68	37900	1.84	Clear, flexible
1d	0.66	31000	1.82	Clear, brittle

Table 2. Thermal properties of the poly(arylene ether)s



Polymer	Ar	DSC T_g (°C)	DMA (tan ∂) T_g (°C)	T_d (°C) 10% weight loss
1a		167	162	545
1b		178	175	548
1c		147	142	540
1d		142	—	528

3.2 *Spectroscopy*

All spectroscopy data obtained from FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy support the desired structures of the poly(arylene ether)s. The FT-IR spectra shows the aryl ether linkages (1140–1050) cm^{-1}, those are generated in the polymer forming reaction and the stretching frequencies (1240–1150) cm^{-1} corresponding to CF_3 groups (14, 15, 17). Also, the FT-IR and ^{1}H-NMR spectra of the polymers do not show any signals corresponding to the terminal -OH groups, supporting high conversion. The absence of peaks at 1350 or 1150 cm^{-1} for S═O stretching indicates that the sulfide linkage of thiodiphenol monomer is not oxidized during polymerization reaction. The number of magnetically different protons that were obtained from the integrated ratios of the different peaks in proton NMR spectra matches exactly with the proposed polymer repeat unit structure. The detailed spectral data of the polymers are given in the experimental section.

3.3 *DSC Measurements*

The four poly(arylene ether)s synthesized exhibited no crystallization or melting transitions in DSC measurements. Figure 2 shows the representative DSC plots of polymers 1a and 1b, respectively. These polymers show glass transition temperature, which indicates their amorphous or glassy morphology. This indicates that incorporation of the 4,4′-thiodiphenol in the polymer backbone creates more amorphous regions and the thio groups do not take part in the formation of crystalline structure. The glass transition temperatures are mentioned in Table 2. The synthesized poly(arylene ether)s show lower glass transition temperatures than the poly(arylene ether)s reported earlier (14). It is probable that the C-S-C bond provides free rotation around the main axis, hence resulting in a loose conformation resulting in lowering of T_g values.

The values given in Table 2 indicates that the glass transition temperatures of the pyridine and thiophene ring containing polymers 1c and 1d are lower than those of their corresponding phenyl analogues. 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. This can be explained on the basis of catenation angle, which is one of the important parameters affecting T_g of polymers. The catenation angle at the benzene ring is 180°, while at the pyridine and thiophene ring is only 120° and 148°, respectively. 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 (Fig. 3).

The above discussed factor alone is not sufficient to explain the varied T_g's of the polymers. The other factor, which affects the T_g, is the polarity of the material. The high T_g of the polymer containing pyridine moiety may be due to the polarity of the pyridine ring. As we observed, the thiophene ring has more extended geometry than the pyridine ring at the same time the pyridine ring has four times more polarity ($\mu_{thiophene} = 1.83 \times 10^{-30}$ Cm; $\mu_{pyridine} = 7.4 \times 10^{-30}$ Cm) (16) than that of the thiophene ring.

Among all synthesized poly(arylene ether)s, polymer 1b exhibits a considerably higher T_g value. This is attributed to

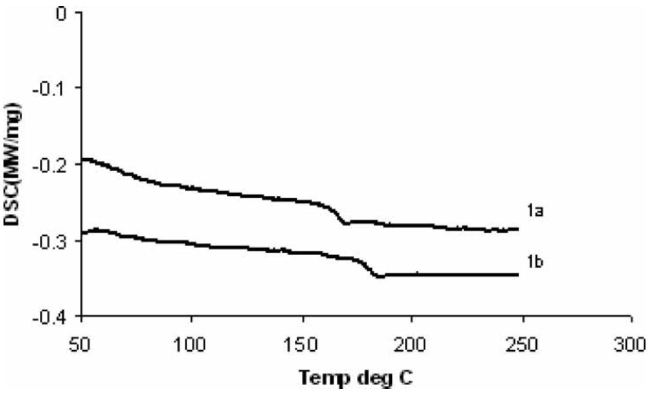


Fig. 2. DSC plots of poly(arylene ether)s 1a and 1b.

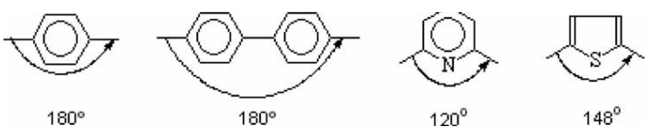


Fig. 3. Catenation angle of different arylene rings.

the more rigid structure of this polymer, because of the presence of a quadriphenyl unit in the polymer backbone.

3.4 *Thermal Stability*

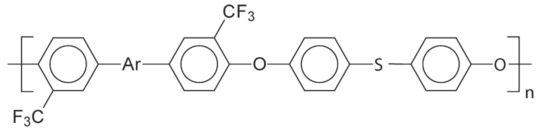
The poly(arylene ether)s exhibit good thermal stability. The TGA thermograms are shown in Figure 4. The high thermal stability of these polymers is due to rigid structure and pendent trifluoromethyl groups. Depending upon the exact structures, these polymers showed 10% weight loss between 528°C and 548°C in nitrogen. Lower thermal stability of these polymers compared to the poly(arylene ether)s reported earlier (14) is due to the lower bond energy value of S-C bond (272 kJ/mol) compared to C-C bond (348 kJ/mol). Thermo oxidative stability of the polymers also depends on the monomers from which they have been synthesized. The polymers showed very high char residue up to 66% at 800°C. However, this corresponds to the investigation under nitrogen atmosphere.

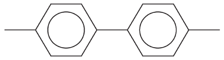
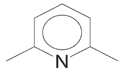
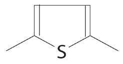
3.5 *Mechanical Properties*

The mechanical properties of poly(arylene ether)s are studied using thin films of poly(arylene ether)s cast from THF solutions. In general, the polymers showed very good tensile strength but low elongation at break. The mechanical properties of these polymers are summarized in Table 3.

The representative dynamic mechanical behavior of the polymer film 1b is shown in Figure 5. The T_g's taken from the tan δ peaks of dynamic mechanical behavior at 1 Hz are given in Table 2. These values are in good agreement with the calorimetric T_g values. Due to the brittle nature, it was not possible to record the DMA for the polyether film 1d.

Table 3. Mechanical properties of the poly(arylene ether)s



Polymer	Ar	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
1a		71	1.66	6.0
1b		72	1.54	6.4
1c		69	1.37	5.0
1d		65	1.69	4.7

3.6 *Rheology*

It is interesting to know that apparent viscosity changes when shear rates are changing in a very wide range. In order to make this dependence more visual, logarithmic scales are frequently used. The flow curve of the polymers in Figure 6 show very pronounced non-Newtonian flow as a gradual decrease of apparent viscosity. The polymer showed low melt viscosity and hence, good melt processability. At low shear rates, Newtonian behavior is observed and apparent viscosity corresponding to this region of the flow curve is called zero-shear or initial or maximum Newtonian viscosity then the decrease of apparent viscosity is observed — typical of non-Newtonian behavior.

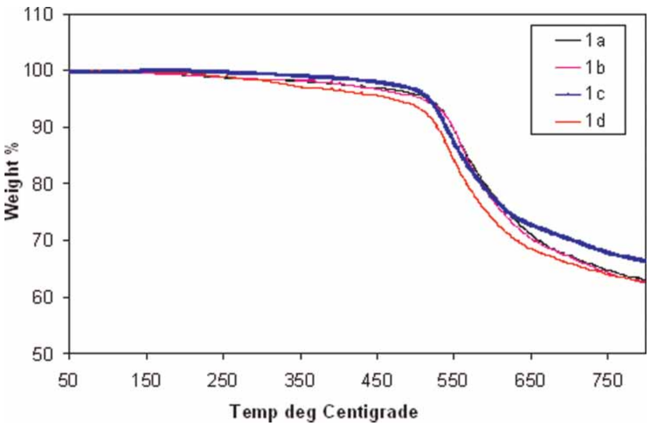


Fig. 4. TGA thermograms of the poly(arylene ether)s.

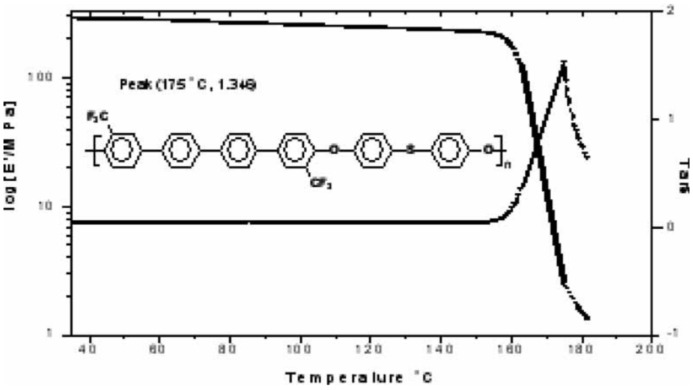


Fig. 5 DMA plot of poly(arylene ether) 1b.

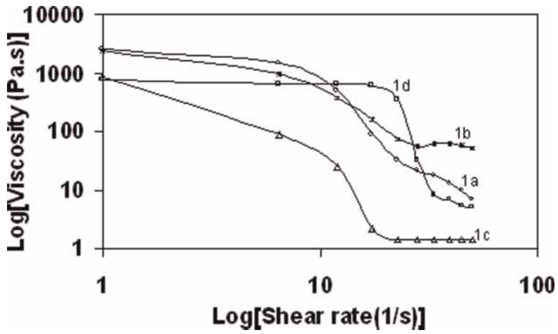


Fig. 6. Flow curves of the poly(arylene ether)s.

3.7 Water Absorption

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 less than 0.2%. Negligibly small water uptake of these polymers is possibly due to the contribution from fluorine as trifluoromethyl groups in the polymer structure.

4 Conclusions

Four novel poly(arylene ether)s have been successfully synthesized from 4,4′-thiodiphenol on reaction with 4,4′-*bis*(4-fluoro-3-trifluoromethyl benzyl) benzene, 4′4″-*bis*(4-fluoro-3-trifluoromethyl benzyl) biphenyl, 2,6-*bis*(4-fluoro-3-trifluoromethyl benzyl)pyridine and 2,5-*bis*(4-fluoro-3-trifluoromethyl benzyl) thiophene through nucleophilic displacement polymerization. The new polymers are amorphous in nature. The polymers exhibit good thermal stabilities in nitrogen. The polymers show excellent solubility in common organic solvents. The polymers showed very good tensile strength, good Young's modulus values, and low water absorption however low elongation at break.

5 References

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