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Synthesis of New Poly(biphenylene oxide) with Pendent Trifluoromethyl Group

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A new AB type of monomer 4′-fluoro-3,5-dimethyl-3’-trifluoromethyl-biphenyl-4-ol has been synthesized that leads to a new poly(arylene ether) by self polycondensation reaction. The monomer and the polymer have been well characterized by elemental analyses, FT-IR and NMR spectroscopy. Both FT-IR and NMR spectra of the polymers did not show any terminal phenoxy group indicating high conversion. The polymer showed glass transition at 278°C and very good thermal stability in synthetic air. GPC results indicate high molar mass development; Mw = 53200 and MWD = 2.29.

Keywords: AB monomer, poly(arylene ether), glass transition temperature

1 Introduction

Poly(arylene ether)s (PAE) and related structures are an important class of engineering thermoplastics owing to their good thermal stabilities and high glass transition temperatures (T_g) (1,2). Poly(arylene ether) (PAE), also known as poly(phenylene oxide) (PPO), is a well-known synthetic polymeric material widely used in electrical or electronic equipment, vehicle parts and business machines due to its balanced mechanical properties, low moisture absorption, excellent electrical insulation property and dimension stability (3). PPO is commercially prepared from 2,6-dimethylphenol through oxidative coupling polymerization route in the presence of copper/amine catalysts (4). A typical example is poly(2,6-dimethyl-1,4-oxyphenylene) (PPO$^{\ominus}$)commercialized by General Electric. Large numbers of PPO derivatives with various pendent groups were prepared, but the structural variation was confined to side groups because of the limitation of the oxidative coupling reaction (5).

PPO prepared by this route has few limitations such as promotion of branching via Ar-CH_3 groups during high temperature processing by the un-reacted amine and copper salts (6). Now, the current research in this field is the synthesis of PPO free from the amine and copper salts for new applications and environmental safety. Sulfone, ketone, and imide groups are known as effective activating groups for the S_NAr reaction, and poly(ether sulfone)s, poly(ether ketone)s, and poly(ether imide)s have been successfully commercialized using this reaction (7–9).

Aromatic substitution (S_NAr) reaction is a very effective method among the various reactions with a leaving group activated with an electron-withdrawing group that produces an aromatic ether linkage (7,9,10). Generally, leaving groups are fluorine, chlorine and nitro groups. The fluorine leaving group shows good reactivity due to its small size and high electronegativity. However, trifluoromethyl group acts further as an effective activating group for the fluoro displacement. Another advantage of perfluoroalkyl activation in S_N!Ar reaction is that it can be an effective way to incorporate fluorines into the polymer chains, which provides some desirable properties, such as low dielectric constant, low moisture absorption, and good solubility (6,11). Poly(biphenylene oxide) (PBPO) can be considered as a class of poly(arylene ether)s and expected to have superior physical properties but high molecular weight PBPOs have not been prepared because of the absence of an appropriate polymerization reaction (12). It can be prepared by the Ullmann C-O coupling reaction or from 4,4’-dichlorodiphenyl ether (13). Incorporation of one phenyl ring into the main chain of PPO$^{\ominus}$ results in PBPO that is likely to have superior performance than PPO$^{\ominus}$(14).

In this study, new PBPO containing trifluoromethyl groups were prepared from a new AB type monomer through nucleophilic displacement reaction, and the properties of this novel PBPO have been investigated.

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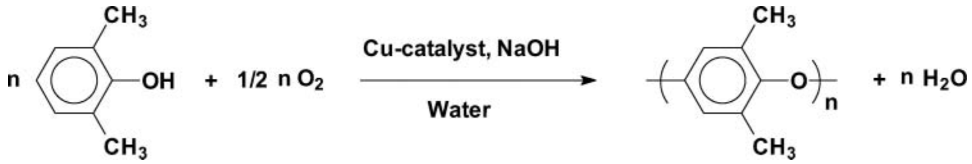


2 Experimental

2.1 General Consideration

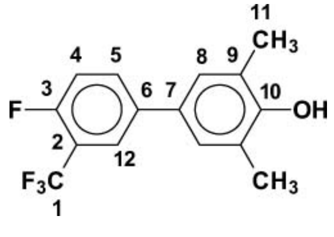
^{1}H and ^{13}C-NMR were recorded on a Bruker 200 MHz instrument (Switzerland) using $CDCl_3$ as a solvent having a small amount of TMS as the internal standard. The synthesized monomer and polymer were characterized by FT-IR to analyze the functional groups present. Analyses were done in a humidity-free atmosphere at room temperature using a NEXUS 870 FT-IR (Thermo Nicolet) spectrophotometer. Samples were prepared by dispersing the materials in KBr and compressing the mixture to form discs. At least 32 scans at a resolution of 4 cm^{-1} were used. The elements, carbon, hydrogen, and oxygen of the monomer and polymer were analyzed by a Heraeus Carlo Erba 1106 elemental analyzer. Thermogravimetric data were recorded on a Pyris thermal analyzer, using Al_2O_3 crucible, with the flow rate of (XL) grade synthetic air 100 mL/min, to obtain the decomposition temperature (T_d) at 5% wt loss and 10% wt loss. Glass transition temperature (T_g) of the polymer samples were analyzed by differential scanning calorimetry (DSC) using NETZSCH DSC 200PC differential scanning calorimeter with 10 ± 2 mg samples, at a heating rate of 20°C/min. Glass transition temperatures were taken as the midpoint of the change in slope of the thermogram for the second heat cycle. X-ray diffaction study was conducted by Rigaku, Ultema III X-ray diffractometer with a CuK_α ($\lambda = 0.154$ nm) source, operated at 40 kV and 40 mA between 10° and 70° with a continuous scan rate of 3°/min. Molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) at ambient temperature using a Waters Gel Permeation Chromatography equipped with 2487 dual λ absorbance detector and a 2414 RI detector. Data analysis was collected using empower software.

2.2 Starting Materials

5-Bromo-2-fluorobenzotrifluoride, tetrakis(triphenylphosphine)palladium(0) magnesium turnings, 4-bromo-2,6-dimethyl-phenol and trimethylborate were purchased from (Fluorochem Chemical Co.), (Acros Organics, USA), (Sigma Aldrich, USA) and used as received unless otherwise noted. *N*-methyl-2-pyrrolidone (NMP) (E Merck, India) was purified by stirring with NaOH and subsequent distillation over P_2O_5under reduced pressure. Toluene (E Merck, India) was refluxed over sodium metal to remove water and was freshly distilled before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) (E Merck, India) were refluxed over sodium metal and sodium hydride to remove water and were also freshly distilled before use. The compound 4-fluoro-3-trifluoromethylphenylboronic acid was prepared according to the procedure reported earlier (7).

2.3 Synthesis of Monomer4’-fluoro-3,5-dimethyl-3′-trifluoromethyl-biphenyl-4-ol

The synthesis procedure of the 4-fluoro-3-trifluoromethylphenylboronic acid from 5-bromo-2-fluorobenzotrifluoride was already reported in a previous publication (8). 4-Fluoro-3-trifluoromethylphenylboronic acid (4.03 g, 19.4 mmol), 4-bromo-2,6-dimethyl-phenol (3.00 g, 14.9 mmol), $Pd(Ph_3P)_4$(0.26 g, 0.25 mmol), Na_2CO_3 (6.43 g, 60.6 mmol), toluene (60 mL) and water (60 mL) were placed in a 250 mL round bottom flask. The reaction mixture was stirred and refluxed for 3 days under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was treated with acid and the organic layer was later separated using a separating funnel and the aqueous phase was extracted twice with toluene. The combined organic layer was washed with excess water, dried over anhydrous $MgSO_4$, and concentrated. The concentrated organic layer was filtered over Al_2O_3, bed length 20 cm and diameter 2 cm, to remove the catalyst $Pd(PPh_3)_4$. The column was washed with toluene. The compound was further purified by recrystallization from a 1:10 mixture of toluene/hexane. The detailed synthesis procedure of the monomer is shown in Figure 1.



Yield: 3.49 g (82%), Melting point: 112°C (DSC heating rate 10°C/min). Anal. Calcd. for $C_{15}H_{12}OF_4$ (284.25 g/mol): C 63.38, H 4.26, O 5.63; Found: C 63.32, H 4.17, O 5.65; FT-IR (KBr): 3602, 2923, 1615, 1485, 1237, 1124, 829. ^{1}H-NMR (ppm): 7.72 (s, 1H, H12); 7.67-7.65 (m, 1H, H5); 7.22-7.16 (m, 3H, H4 and H8); 4.78 (s, 1H, -OH); 2.32 (s, 6H, H11).

2.4 Polymer Synthesis

Polymerization reactions was carried out in a 50 mL, three-necked round-bottom flask equipped with a nitrogen inlet,

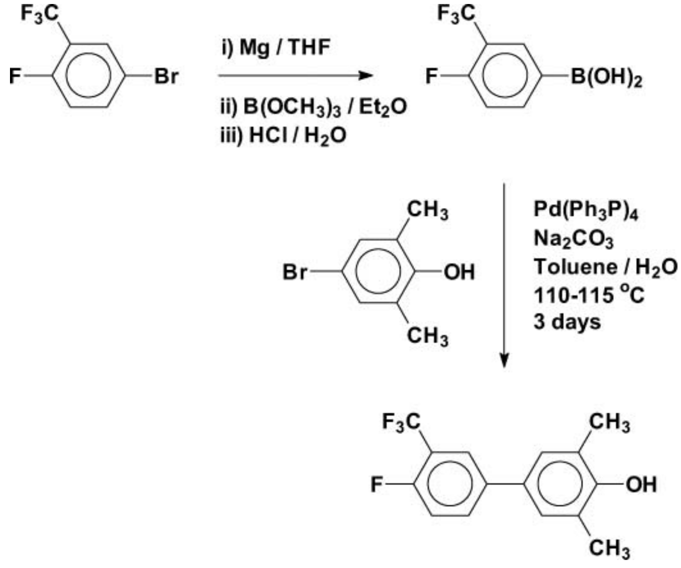
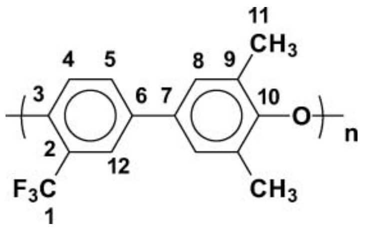


Fig. 1. Reaction scheme of synthesis of the monomer.

a stir bar and a Dean-Stark trap fitted with condenser. The flask was charged with 4′-fluoro-3,5-dimethyl-3’-trifluoromethyl-biphenyl-4-ol (1.00 g, 3.52 mmol), K_2CO_3 (0.58 g, 4.22 mmol), NMP (10 mL), and toluene (20 mL). The mixture was then heated to reflux at 145°C for 3 h and, water that formed due to deprotonation of phenol was removed azeotropically by toluene. After removal of the toluene, the reaction temperature was increased to 180°C and maintained for 6 h. After cooling to room temperature, the polymer was recovered by precipitation from about 300 mL of methanol; containing a few mL of HCl. A yellowish solid powder product was isolated by filtration. These products were washed several times in boiling water to remove acid, as well as inorganic impurities, and dried in a vacuum at 110°C overnight.



Yield: (95%), Glass transition temperature: 278°C (DSC heating rate 20°C/ min). Anal. Calcd. for $C_{15}H_{11}OF_3$ (264.24 g/mol): C 68.18, H 4.20, O 6.05; Found: C 68.12, H 4.17, O 6.07. FT-IR (KBr): 3037, 2924, 1311, 1239, 1125, 1048, 826. ^{1}H-NMR (ppm): 7.90 (s, 1H, H12); 7.55 (d, J = 8.5 Hz, 1H, H5); 7.30 (s, 2H, H8); 6.58 (d, J = 8.5 Hz, H4); 2.28 (s, 6H, H11). ^{13}C-NMR (ppm): 154.71; 149.86; 136.96; 133.72; 131.94; 13139; 127.63; 126.10; 121.01 (q, J= 19.07 Hz); 119.23 (q, J = 271 Hz); 113.70; 16.31.

3 Results and Discussion

3.1 Synthesis of Monomer

The reaction scheme for the synthesis of compound 4’-fluoro-3,5-dimethyl-3’-trifluoromethyl-biphenyl-4-ol named as AB monomer is shown in Figure 1. The synthesis of AB consists of firstly, the synthesis of 4-fluoro-3-trifluoromethylphenylboronic acid from 5-bromo-2-fluorobenzotrifluoride and, finally, the palladium-catalyzed cross-coupling reaction of 4-fluoro-3-trifluoromethyl-phenylboronic acid with 4-bromo-2,6-dimethyl-phenol adopting the reaction protocol as reported in earlier literature (7). The coupling reaction was very efficient, which resulted in a very high yield of the AB monomer. The chemical structure of the compound was confirmed by FT-IR and ^{1}H-NMR spectroscopic methods and elemental analysis. The ^{1}H-NMR spectra of the monomer is shown in Figure 3.

3.2 Polymer Synthesis

The polymerization of the AB monomer was carried out in the presence of excess potassium carbonate as a base in NMP in analogy to conventional polyether synthesis(5,14) as shown in Figure 2. The polymerizations were run at solids contents of 25%, and toluene was used for azeotropic removal of water. During the initial stage of the polymerization, the reaction temperature was maintained at 140–150°C, and the water generated by deprotonation of the phenols was most effectively removed through a Dean-Stark trap. Upon completion of bisphenoxides formation and dehydration (4–5 h), the reaction temperature was raised to 180°C to affect the nucleophilic displacement. High molar mass polymers were obtained within 8 h as judged by the increase of the viscosity of the reaction medium. The resulting polymers were coagulated in a large excess of methanol. The solid product obtained was boiled and washed several times with hot water to remove any inorganic impurities, dried in a vacuum, and dissolved in THF, and the concentrated solutions were reprecipitated in an excess of methanol. The precipitated polymer recovered by filtration was dried in vacuum at 50°C for 24 h. The polymer showed very good solubility in different organic solvents like chloroform, toluene, and tetrahydrofuran, as well as polar aprotic solvents such as dimethylformamide (DMF), DMAc, and NMP. However, the polymer is insoluble in dimethyl sulfoxide even after boiling.

3.3 Polymer Characterization

The molecular weight of the polymer soluble in THF was determined by GPC using a polystyrene standard. The weight average molecular weight of the polymer was 53200 with a polydispersity index of 2.29. The molecular weight

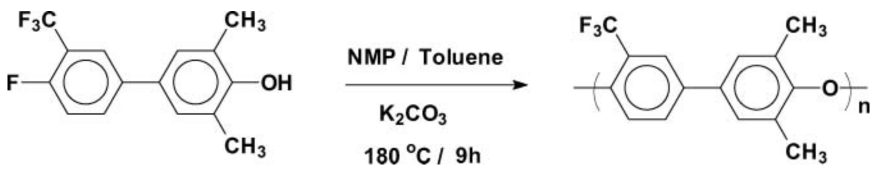


Fig. 2. Reaction scheme of synthesis of the poly(biphenylene oxide).

distribution was essentially unimodal with no evidence of oligomeric or unreacted species, which is also attested by undetectable ^{1}H-NMR signals of the hydroxyl end groups of the polymer. In any case, this value has to be taken as merely indicative, since calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the polymers studied deviate strongly from those of polystyrene. All spectroscopic data from FT-IR and ^{1}H, and ^{13}C-NMR spectroscopy support the structures of the poly(arylene ether). These characterization methods, as well as elemental analysis, do not indicate a degradation of the trifluoromethyl groups. The FT-IR spectrum of this polymer show the aryl ether linkages (1140−1050 cm^{-1}) that are generated in the polymer-forming reaction and also the stretching frequencies (1240−1150 cm^{-1}) corresponding to -CF_3 groups. ^{1}H-NMR and expanded FT-IR spectra of the polymer as shown in Figures 3 and 4, respectively do not show any signals corresponding to the terminal −OH or −F groups, indicating a high conversion. The exact analytical data for all these polymers are listed in the experimental section.

The thermal properties of the polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results of TGA thermogram of the polymer is shown in Figure 5. The 5 and 10% wt loss temperature in air is 433 and 462°C, respectively. The thermal stability of this polymer in air is comparable to that of the commercial PPO resin derived from 2,6-dimethylphenol (15) and trifluoromethyl substituted PBPO reported in the literature (14).

The poly(arylene ether) exhibit no crystallization or melt transition in DSC measurement (Fig. 6). These polymers manifest a T_g indicative of an amorphous or glassy morphology. The glass transition temperature of the polymer is 278°C. These polymer exhibit considerably higher T_g values than the commercial PPO resin and many reported poly(arylene ether)s (5,7,8,14). This is attributed to the more rigid structures of this polymer because of the presence of biphenyl unit in the polymer backbone than phenyl unit in PPO. It is somewhat unexpected that the polymer exhibits amorphous character; it seems that trifluoromethyl groups are bulky enough to prevent crystallization of the

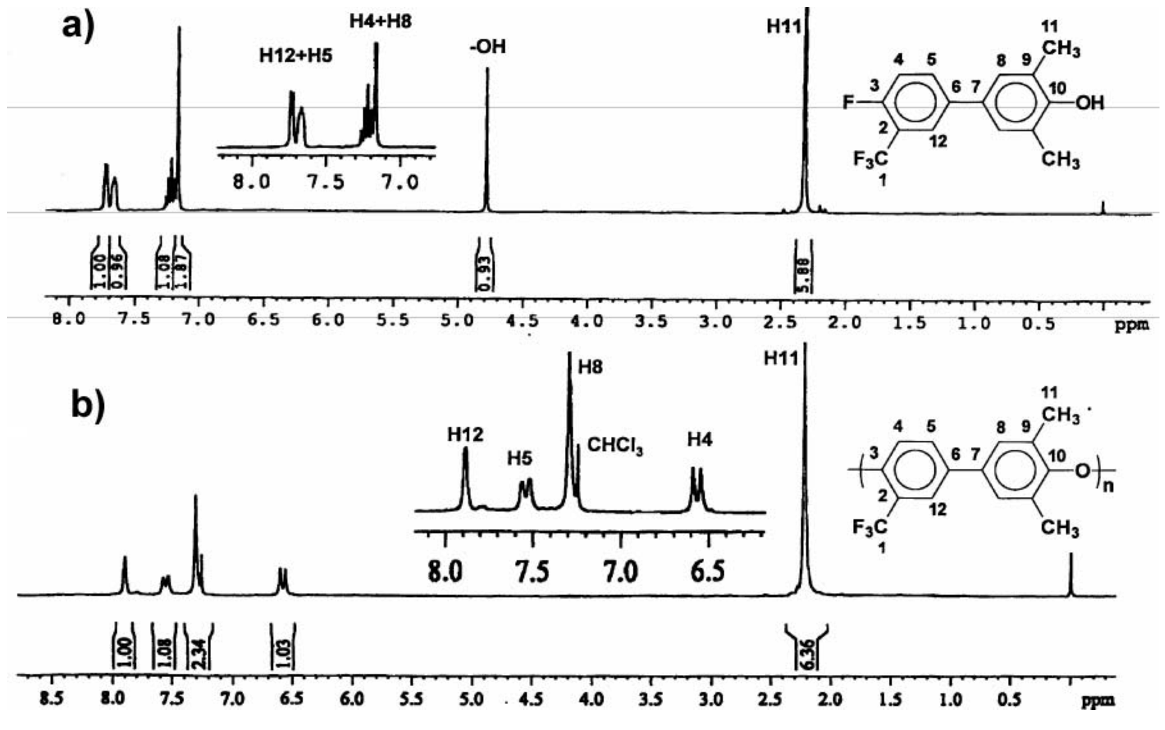


Fig. 3. The proton NMR spectra of a) monomer; b) poly(arylene ether) in $CDCl_3$.

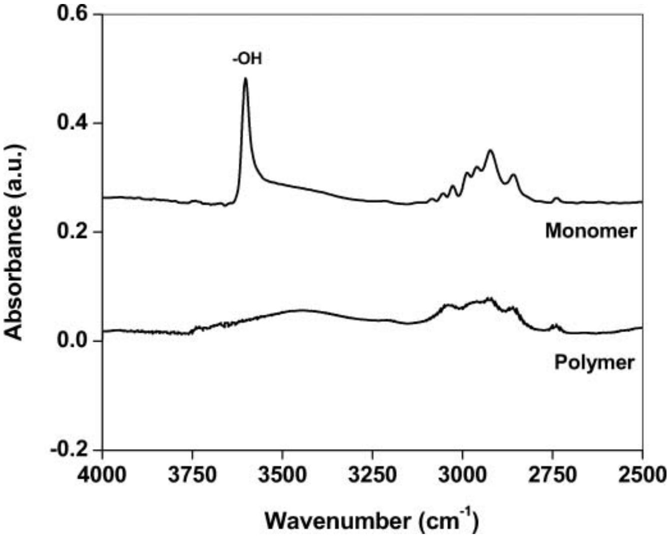


Fig. 4. The FT-IR spectra of poly(arylene ether).

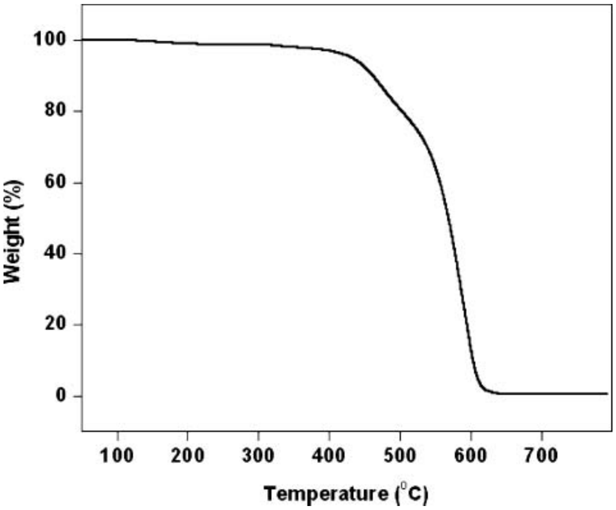


Fig. 5. TGA plot of the poly(arylene ether).

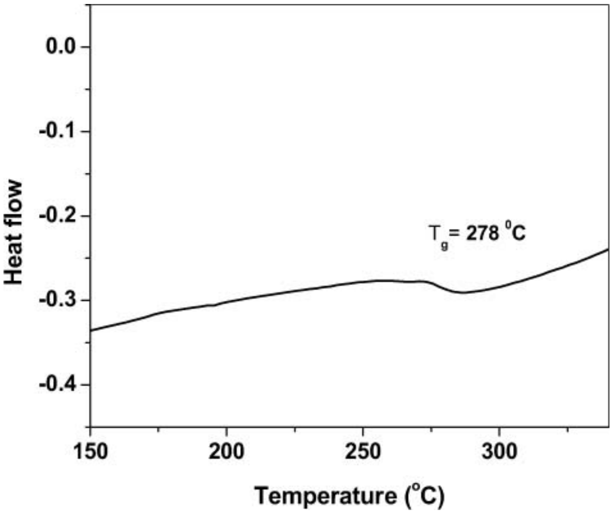


Fig. 6. DSC plot of the poly(arylene ether).

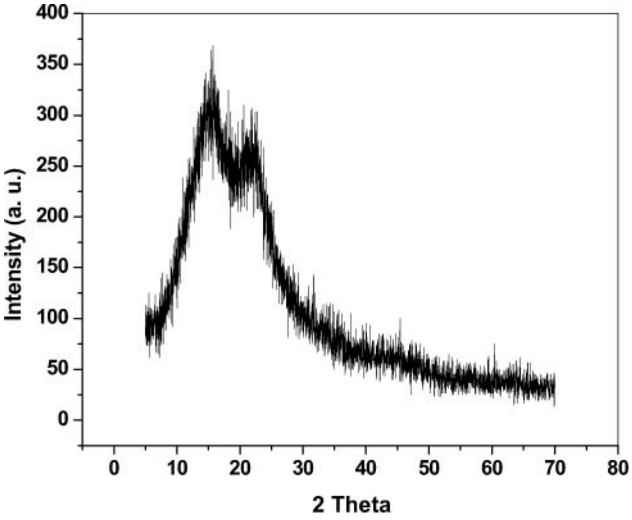


Fig. 7. X-ray diffractogram of the poly(arylene ether).

polymer chain in this case. The X-ray diffractogram of the polymer as shown in Figure 7 supported the glassy morphology of the polymer.

4 Conclusions

A new fluoro-hydroxy AB monomer has been synthesized successfully using a Pd(0)-catalyzed reaction. The fluoro group of the AB monomer is activated by the electron withdrawing trifluoromethyl group in the ortho position in the leaving group and the hydroxyl group is activated by the electron donating methyl groups in the two ortho positions. This monomer led to a novel poly(arylene ether) by self polycondensation and resulted in high molar mass with weight average molecular weight 53200. The resulting polymer is amorphous with glass transition temperatures of 278°C and exhibits good thermooxidative stability. Despite very good solubility of this polymer in several organic solvents, it was not possible to obtain a free standing film from this polymer.

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