A Novel Bisphenol Monomer with Grafting Capability and the Resulting Poly(arylene ether sulfone)s†

Zhao Li, Jianfu Ding, Gilles P. Robertson, and Michael D. Guiver*

Institute for Chemical Process and Environmental Technology (ICPET), National Research Council of Canada (NRC), 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada

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ABSTRACT: A new bisphenol monomer, 1,1-bis(4-hydroxyphenyl)-1-(4-(4-fluorophenyl)thio)phenyl-2,2,2-trifluoroethane (3FBPT), containing a masked grafting site was readily synthesized in high yield in two reaction steps. A conventional aromatic nucleophilic substitution (S_NAr) was used for copolymerization of this monomer with difluorodiphenyl sulfone and hexafluorobisphenol A, which gave high molecular weight linear poly(arylene ether sulfone)s containing 4-fluorophenyl sulfide pendant groups. After oxidation to convert the sulfide to sulfone, the para fluorine on the pendant group becomes activated for further S_NAr reaction for the introduction of other functionality onto the pendant side chains such as sulfonated species for fuel cell applications. All the polymers are thoroughly characterized by ^1H, ^{19}F, and ^{13}C NMR spectroscopy. Thermal analysis study shows that these polymers have T_gs between 180 and 230 °C according to the monomer ratio and have excellent thermal stability up to 500 °C.

Introduction

As a class of high-performance engineering thermoplastic materials, poly(arylene ether)s have high glass transition temperature, high thermal stability, good mechanical properties, and excellent resistance to hydrolysis and oxidation.[1] However, for some special applications, the modification of the polymer structure is frequently required in order to obtain desired properties. One objective of polymer structural modification is to alter chemical structure to some degree or introduce functionality without sacrificing the basic underlying desired physical and other properties. Functionalized poly(arylene ether)s may find many applications as membrane materials for gas separation, water desalination, and, more recently, fuel cells as proton exchange membrane.[2]

Generally, there are two methods to functionalize poly(arylene ether)s. One is to chemically modify the preformed polymer after polymerization, sometimes called postpolymerization modification. Another is to use a functionalized monomer to prepare the polymer via direct copolymerization. Both methods have advantages and disadvantages. For example, the first method can lead to polymer degradation or cross-linking during the reaction. The second method may require a tedious approach for monomer synthesis.

Until now, there have been few reports about the synthesis of poly(arylene ether)s with pendant activated aromatic fluorine atoms. One postpolymerization method is to first react polysulfone with butyllithium and then react the lithiated polysulfone with 4-fluorobenzoyl chloride to introduce 4-fluorobenzoyl side chains to polymer main chain.[3,4] However, while this method is convenient, it requires stringent reaction conditions. Recently, a divergent approach with an activation/condensation sequence was developed.[5,6] The reported monomers contain either one tertiary carbon connected with four phenyl or three phenyl and one methyl groups, which may show limited stability, especially in the presence of a strong acid.[7]

Here, we report a new bisphenol monomer, 3FBPT. This monomer was synthesized in two steps, and it shows similar reactivity for S_NAr reactions as other bisphenol monomers such as hexafluorobisphenol A. High molecular weight linear polymers have been synthesized from this monomer. The sulfide group in this unit was then converted to the sulfone group by a simple postpolymerization oxidation, which activates the fluorine atom in this unit for a further S_NAr condensation reaction. Consequently, the polymer chain can be grafted with other functional groups, as in the present work, whereby a disulfonated phenol was attached for fuel cell application. The resulting polymer series have been designed as a strategy for preparing polymer electrolyte membranes (PEM)s for fuel cell applications, whereby the main chain is comprised of thermally and chemically stable repeat units and the side chain is similarly stable and flexible, allowing the formation of ionic domains. The present work demonstrates the feasibility and success of this synthetic approach, and we will report on other polymers utilizing the same strategy in following publications.

Experimental Section

Measurements. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector. THF was used as eluant, and the μ-Styragel columns were calibrated by polystyrene standards. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere (50 mL/min) using a TA Instruments DSC 2920 at a heating rate of 10 °C/min, calibrated with the melting transition of indium. The reported data were taken from the second heating scan. The thermal gravimetric analysis (TGA) was performed using a TA Instruments TGA 2950 at a heating rate of 20 °C/min under a nitrogen atmosphere (60 mL/min). MS data were obtained using a Prince capillary electrophoresis system coupled to an API3000 mass spectrometer via a microspray interface. A sheath solution of 1 μL/min 2-propanol/methanol (2:1) was used, with 30 mM ammonium acetate dichloromethane/methanol (3:1) as the running buffer. The inherent viscosities of 0.050 g/mL polymer solutions in DMAc were measured at 30 °C by using an Ubbelohde viscometer.

NMR spectra were recorded in DMSO-d_6 using a Varian Unity Inova spectrometer at a resonance frequency of 399.96 MHz for ^1H, 376.29 MHz for ^{19}F, and 100.58 MHz for ^{13}C. ^1H and ^{19}F NMR

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* Corresponding author. E-mail Michael.Guiver@nrc-cnrc.gc.ca.

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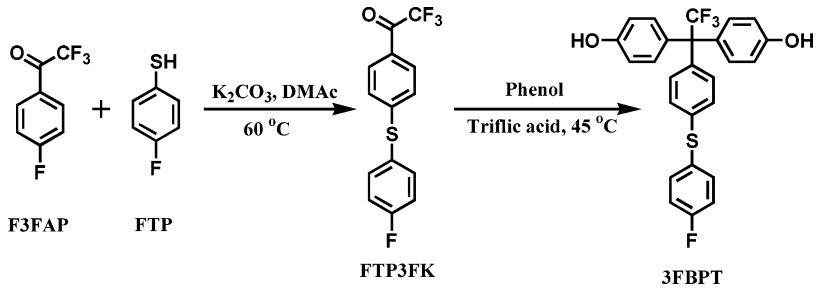
Scheme 1. Synthesis of 3FBPT Monomer



and 2D spectra were obtained using a 5 mm indirect detection probe. A 5 mm broadband probe was used for acquiring 1D ^{13}C NMR spectra. $CFCl_3$ was used as an internal standard (0 ppm) for the ^{19}F NMR measurements. Signals from DMSO-d_6 were used as the reference for ^1H (2.50 ppm) and ^{13}C NMR (39.43 ppm) measurement. The 2D $^1H-^1H$ correlated spectroscopy (COSY), $^1H-^{13}C$ heteronuclear single quantum coherence (HSQC), and $^1H-^{13}C$ heteronuclear multiple bond correlation (HMBC) spectra were recorded to assist assignment of all NMR signals. Coupling constants of $^1J_{CH} = 150$ Hz and $^3J_{CH} = 7.5$ Hz were used for HSQC and HMBC experiments.

Materials. Hexafluorobisphenol A (6F-BPA), 4,4′-difluorodiphenyl sulfone (DFS), anhydrous dimethylacetamide (DMAc), and 1-naphthol-3,6-disulfonic acid disodium salt (N36DS) were purchased from Sigma-Aldrich Ltd. 6F-BPA and DFS were purified by recrystallization in toluene before use. DMAc and N36DS were used as received. 4-Fluoro-2,2,2-trifluoroacetophenone (F3FAP), trifluoromethanesulfonic acid (triflic acid), and 4-fluorothiophenol (FTP) were purchased from Oakwood Products Inc. and used as received. Anhydrous K_2CO_3 was purchased from EMD and used as received. Phenol was purchased from Anachemia Ltd. and used as received.

Synthesis of Monomer. *4-((4-Fluorophenyl)thio)phenyl Trifluoromethyl Ketone (FTP3FK).* A mixture of F3FAP (25.0 g, 130 mmol), FTP (18.34 g, 143.15 mmol), K_2CO_3 (10.8 g, 78.1 mmol), and DMAc (300 mL) was stirred under nitrogen for 24 h at 60 °C. Then the mixture was poured into 1 L of water and extracted with 500 mL of diethyl ether. The organic phase was further washed with water, and the solvent was removed by a rotary evaporator. The yellowish oily product was purified by chromatographic column (using 1/4 v/v hexanes/ethyl acetate). Yield: 96%. ^1H NMR (DMSO-d_6, ppm): 7.93−7.95 (d, $J = 8.4$ Hz, 2H), 7.68 (m, 2H), 7.41 (t, 2H), 7.28 (d, $J = 8.4$ Hz, 2H). ^{19}F NMR (DMSO-d_6, ppm): −70.0(s, 3F), −110.1 (m, 1F). MS (*m*/*z*): 318.1 ($[M + NH_4]^+$). FT-IR (diamond plate, cm^{-1}): 1711 (C═O), 835 (Ar).

1,1-Bis(4-hydroxyphenyl)-1-(4-(4-fluorophenyl)thio)phenyl-2,2,2-trifluoroethane (3FBPT). FTP3FK (18.0 g, 60.0 mmol) and phenol (22.6 g, 240 mmol) were added to a round-bottom flask. The system was purged with nitrogen three times before heating to 45 °C to form a homogeneous solution. Then triflic acid (2.34 g, 15.6 mmol) was added, and the solution was stirred at 60 °C for 1 h until a pale yellowish solid formed. The product was washed with boiling water three times and recrystallized from toluene to give a white solid. The synthetic scheme for the monomer is shown in Scheme 1. Yield: 94%. ^1H NMR (DMSO-d_6, ppm): 9.63 (s, 2H), 7.52 (dd, 2H), 7.29 (t, 2H), 7.18 (d, $J = 8.8$ Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 4H), 6.74 (d, $J = 8.8$ Hz, 4H). ^{19}F NMR (DMSO-d_6, ppm): −57.9(s, 3F), −112.5(m, 1F). MS (*m*/*z*): 488.2 ($[M + NH_4]^+$). FT-IR (diamond plate, cm^{-1}): 3400 (−OH), 820 (Ar).

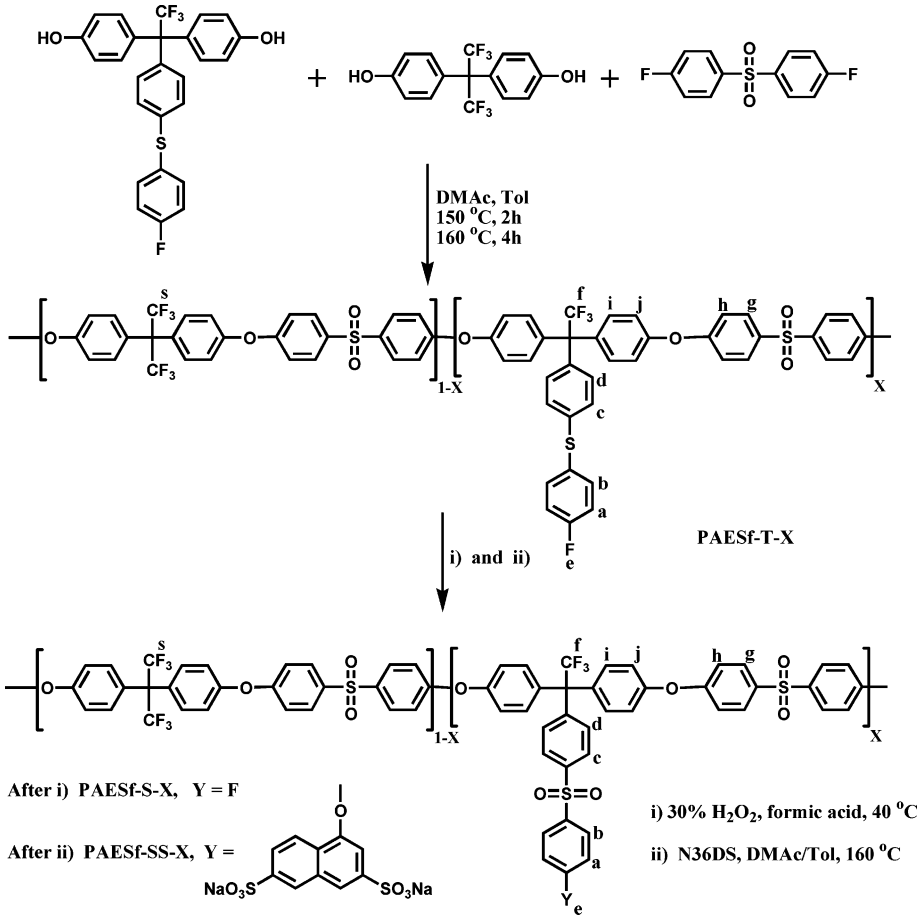
Synthesis and Oxidation of Poly(arylene ether sulfone). The following procedure represents a typical polymerization that gave the polymer PAESf-T-67 shown in Scheme 2. 6F-BPA (0.673 g, 2.0 mmol), 3FBPT (1.882 g, 4.0 mmol), K_2CO_3 (1.66 g, 12.0 mmol), DMAc (40 mL), and toluene (20 mL) were added into a 100 mL three-necked round-bottom flask equipped with a Dean−Stark trap and a nitrogen inlet. The system was purged with nitrogen, and a slow flow of nitrogen was maintained during the entire reaction period. The mixture was heated with continuous stirring. After reaction at 140 °C for 2 h, water and toluene were removed by azeotropic distillation at 150 °C. The system was then cooled to room temperature, and DFS (1.526 g, 6.0 mmol) was added. The temperature was increased to 165 °C, and the mixture was stirred at this temperature for 4 h. The solution was filtered before being precipitated into 500 mL of methanol. The resulting white polymer product, in the form of fiber, was then filtered and dried under vacuum at 60 °C overnight. Yield: 93%; GPC: $M_n = 58\,700$, $M_w = 111\,000$, PDI = 1.90. ^1H NMR (DMSO-d_6, ppm): 7.84−8.00 (Ar−SO_2−Ar), 7.42−7.58 (Ar−S−Ar), 7.32−7.42 (Ar−O−Ar), 6.90−7.30 (m, Ar). ^{19}F NMR (DMSO-d_6, ppm): −57.8 (s, 3F), −62.9 (s, 3F), −112.0 (m, 1F).

In a typical oxidation procedure, polymer PAESf-T-67 (3.0 g) was added into 130 mL of formic acid, and 13 mL of 30% hydrogen peroxide was added dropwise at 40 °C. The heterogeneous dispersion was stirred vigorously for 1.5 h before being filtered and washed with methanol. The white polymer powder was then dried under vacuum at 60 °C overnight to give polymer PAESf-S-67 containing sulfone in the pendant group. Yield: 99%; GPC: $M_n = 55\,800$, $M_w = 103\,000$, PDI = 1.85. ^1H NMR (DMSO-d_6, ppm): 7.86−8.18 (Ar−SO_2−Ar), 7.30−7.50 (m, Ar), 7.00−7.10 (Ar−O−Ar), 7.10−7.28 (m, Ar). ^{19}F NMR (DMSO-d_6, ppm): −57.7 (s, 3F), −62.9 (s, 3F), −103.7 (m, 1F).

Preparation of Sulfonated Polymer, PAESf-SS-*X*. The following represents a typical procedure to attach sulfonated phenol to the pendant group of the polymers. PAESf-S-80 (0.854 g, 1.0 mmol para fluorine atom), N36DS (0.697 g, 2.0 mmol), K_2CO_3 (0.276 g, 2.0 mmol), 30 mL of DMAc, and 10 mL of toluene were added into a nitrogen-flushed reactor which was equipped with a Dean−Stark trap. The mixture was heated at 140 °C for 2 h before water and toluene were removed at 150 °C. The reaction was continued at 160 °C for 16 h before the solution was filtered. The solution was precipitated into diethyl ether, and the precipitate was washed with distilled water before being dried under vacuum overnight at 60 °C. Yield: 95%. ^1H NMR (DMSO-d_6, ppm): 8.23 (s, H−Ar−SO_3H), 7.90−8.10 (m, Ar−SO_2−Ar), 7.84 (d, $J = 8.4$ Hz, H−Ar−SO_3H), 7.75 (d, $J = 8.4$ Hz, H−Ar−SO_3H), 7.30−7.49 (m, Ar), 7.02−7.28 (m, Ar). ^{19}F NMR (DMSO-d_6, ppm): −57.6(s, 2F), −62.9 (s, 1F). FT-IR (diamond plate, cm^{-1}): 3500 (−SO_3H), 1296, 1121 (−SO_3H).

Membrane Casting and Characterization. Polymer PAESf-SS-80 membranes were cast from DMAc solutions (10 wt %) in a custom-built flat glass dish at 50 °C under slow nitrogen flow for 2 days. The resulting membranes in the salt form were then soaked in 2 N HCl for 2 days to exchange the ion and obtain the protonated form, before soaking and washing thoroughly with deionized water several times. The ion exchange capacity (IEC) was determined by titration with 0.025 N NaOH. Water uptake was measured as previously reported.[8] A four-probe conductivity cell from BekkTech was used for proton conductivity measurement. Membranes samples were cut into strips that were 1.0 cm wide, 2.0 cm long, and about 100 μm thick prior to mounting in the cell. The cell was placed in deionized water in a temperature-controlled stainless steel chamber. Impedance measurements were made using Solartron SI1260 impedance/gain-phase analyzer by a four-probe ac impedance technique. The scan frequency was between 100 and 10^7 Hz at a maximum perturbation amplitude of 100 mV.[8]

Scheme 2. Synthesis of PAESf-T-*X*, PAESf-S-*X*, and PAESf-SS-*X*



Results and Discussion

Monomer Synthesis. As shown in Scheme 1, the synthesis of monomer 3FBPT comprises two steps. First, the fluoride of F3FAP was displaced with FTP using K_2CO_3 under mild conditions.[6] The resulting FTP3FK was then condensed with 2 mol of phenol to produce the bisphenol, 3FBPT using the superacid catalyst triflic acid.[9] The overall yield of the two step reactions was above 90%, and the proposed structure was confirmed by ^{1}H and ^{19}F NMR spectra. This bisphenol monomer contains a 1,1,1-trifluoroethylidene group as the linkage for the two phenol units in the molecule, which was shown to provide excellent stabilities in a monomer with a similar structure, 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane.[9,10]

Polymerization and Oxidation. Poly(arylene ether sulfone)s containing pendant 4-fluorophenyl sulfide groups (PAESf-T-*X*) were synthesized by the S_NAr polycondensation using various feed ratios of 3FBPT/6F-BPA, so that polymers with different molar percentage of pendant group (Scheme 2) have been obtained. Their characterization results are listed in Table 1, and the polymers are named as PAESf-T-*X* or PAESf-S-*X*, where PAESf represents poly(arylene ether sulfone), T (thio) represents the 4-fluorophenyl sulfide pendant group, and S (sulfone) represents the 4-fluorophenyl sulfone pendant group. *X* is the molar percent of 3FBPT in total bisphenol monomers. The polymerization reactions proceeded smoothly, and no cross-linking was evident when the system was carefully purged with nitrogen and the temperature was well controlled by oil bath (less than 170 °C). GPC results (Table 1, Figure 1) showed that high molecular weight polymers (M_n > 50 000 g/mol) were obtained, and the polydispersity index is around 2, which is consistent with the results of a typical polycondensation reaction. All these demonstrate the much higher selectivity of the reaction to the activated para fluorine on the sulfonyl phenyl group than to the para fluorine on the pendant phenyl sulfide group during the nucleophilic substitution. It was found that higher temperature (above 170 °C) or longer reaction time (longer than 5 h) would lead to some cross-linked gel-like polymer remaining attached on the glassware, indicating that the comparative selectivity decreased when the temperature was higher than 170 °C. In this case, GPC analysis showed a shoulder peak in the high molecular weight region of the main peak. There is also a trend that higher *X* value polymers show higher PDI (Table 1). A higher *X* value infers more para fluorines on the pendant phenyl sulfide groups per polymer chain, which have the potential to compete with the condensation reaction and form cross-linked or branched structures.

The pendant 4-fluorophenyl sulfide groups of these polymers were oxidized, initially using Oxone for this purpose.[5] It was found that the sulfide group could be oxidized completely to sulfone using excess Oxone in refluxing chloroform solution overnight. However, substantial polymer degradation was detected under these conditions, as indicated by the GPC curves in Figure 1B. Shorter reaction times with Oxone lead to incomplete oxidation. A second method was developed using hydrogen peroxide in heterogeneous polymer formic acid suspension.[12] ^{19}F and ^{1}H NMR confirm the success of complete oxidation, which occurred without accompanying polymer degradation as shown by unchanged GPC curves (Figure 1C).

^{1}H NMR. ^{1}H NMR spectra of homopolymer PAESf-T-100 and PAESf-S-100 are shown in Figure 2; all the proton signals were unambiguously assigned from 1D and 2D C−H correlation NMR spectra. As expected, the ortho sulfonyl protons appear

Table 1. Characterization of Polymer PAESf-T-*X* and PAESf-S-*X*

polymer sample[a]	X^b	X^c	molecular weight[d] ($\times 10^4$ mol/g) M_n	M_w	PDI[d]	T_g	T_d[e]
PAESf-T-10	0.10	0.10	14.0	26.2	1.87	203	508
PAESf-T-20	0.20	0.20	6.92	11.9	1.72	197	506
PAESf-T-33	0.33	0.33	19.5	44.8	2.30	198	508
PAESf-T-40[f]	0.40	0.41	12.3	37.3	3.03	197	499
PAESf-T-67	0.67	0.67	5.87	11.1	1.90	190	499
PAESf-T-80	0.80	0.80	6.56	12.3	1.88	227	508
PAESf-T-100	1.0		5.57	9.47	1.70	187	509
PAESf-S-10	0.10	0.10	13.3	24.8	1.87		516
PAESf-S-20	0.20	0.20	6.43	10.9	1.69	207	508
PAESf-S-33	0.33	0.34	18.9	41.4	2.19		500
PAESf-S-40[f]	0.40	0.40	11.9	33.3	2.81	216	508
PAESf-S-67	0.67	0.67	5.58	10.3	1.85	220	514
PAESf-S-80	0.80	0.80	6.29	11.6	1.84	227	508
PAESf-S-100	1.0		5.02	7.56	1.51	227	508
PAESf-SS-80	0.80	0.80				264	374

[a] PAESf represents poly(arylene ether sulfone), -T-*X* represents percent of 4-fluorophenyl sulfide pendant group, -S-*X* represents percent of 4-fluorophenyl sulfone pendant groups, and -SS-*X* represents disulfonic acid naphthol attached polymer with *X* percent of side group grafted monomer. [b] Molar ratio of 3FBPT in total bisphenol monomers. [c] Molar ratio measured from ^{19}F NMR spectrum. [d] Measured by GPC using THF as solvent. The small molecular weight cyclic polymer peak was not included for calculation of M_n, M_w, and PDI. [e] 5% weight loss temperature in nitrogen atmosphere. [f] Some branching and cross-linking detected.

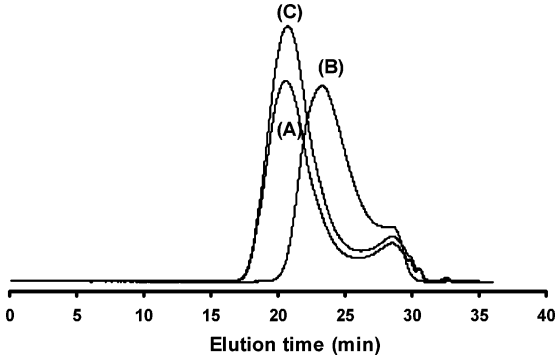


Figure 1. GPC curve of (A) PAESf-T-10, (B) after oxidation using Oxone for 16 h in reflux chloroform, and (C) after oxidation using H_2O_2.

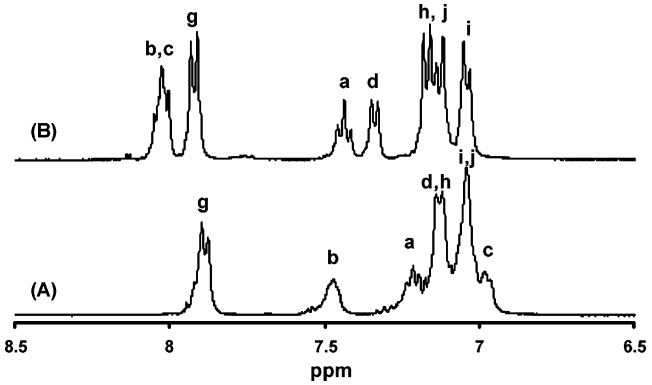


Figure 2. ^{1}H NMR spectra of polymer (A) PAESf-T-100 and (B) PAESf-S-100 (see Scheme 2 for proton labels).

at higher frequencies due to deshielding from the sulfone groups. On the other hand, the electron-rich protons such as the ortho ether linkage appear at lower frequencies. The integration ratios are as expected from the molecular structures of polymers.

^{19}F NMR. ^{19}F NMR of copolymer PAESf-T-67 is shown in Figure 3A; the three sharp signals at −57.8, −62.9, and −112.0 ppm belong to Ff, Fs, and Fe, respectively, as labeled in Scheme 2. After oxidation, the fluorine signal on the phenylsulfide group at −112.0 ppm shifts to −103.7 ppm (Figure 3B) due to the formation of phenyl sulfone group. In addition, a small signal (inset in Figure 3) was also detected at −108.3 ppm, which is believed to arise from the partially oxidized product, phenyl

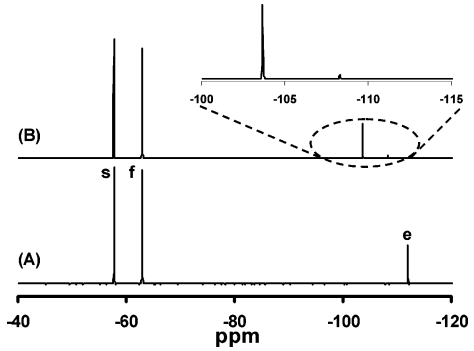


Figure 3. ^{19}F NMR spectra of copolymer (A) PAESf-T-67 and (B) PAESf-S-67 (see Scheme 2 for labels).

sulfoxide group. The relative intensity of this signal is less than 5% compared with the fluorine signal on the phenyl sulfone group.

^{13}C NMR. The ^{13}C NMR spectra of the copolymers are very complicated due to the large number of the different carbons present. Therefore, only the spectra of homopolymer, PAESf-T-100 and PAESf-S-100, are presented in Figure 4 as examples. These two polymers contain 18 different carbon atoms each, and HSQC and HMBC spectra (Figures 5 and 6) have been applied for assignment of all these carbon peaks.

Useful information can be extracted simply from studying the ^{13}C NMR spectrum of PAESf-S-100 (Figure 4B). Since $^1J_{CF}$ is usually about 200−310 Hz,[11] the doublet at 164.4 and 166.9 ppm ($^1J_{CF}$ = 253.2 Hz) can be assigned to Ce, and this assignment was confirmed by $^3J_{Ce-Hb}$ correlation in HMBC. For the same reason, the quartet at 122.9, 125.7, 128.6, and 131.4 ppm ($^1J_{CF}$ = 285.6 Hz, last signal overlapped with other large signal at 131 ppm) can be assigned to Cf. $^2J_{CF}$ is expected near 20−50 Hz; the doublet at 117.1 ppm ($^2J_{CF}$ = 23.0 Hz) and the quartet at 63.7 ppm ($^2J_{CF}$ = 23.5 Hz) can be assigned to Ca and Ck, respectively.

The ^{1}H−^{13}C HSQC spectrum of this polymer is shown in Figure 5; Cb, Cc, Cg, Cd, and Ch can be easily assigned on the basis of their correlation signals via $^1J_{CH}$. The ^{1}H−^{13}C HMBC spectrum of this polymer is shown in Figure 6, and the correlation signals via $^3J_{CH}$ are yielded. From the correlation $^3J_{Ck-Hi}$ with Ck, the Hi signal can now be distinguished from Hj as labeled in Figure 2B. All the other carbons, such as Ci,

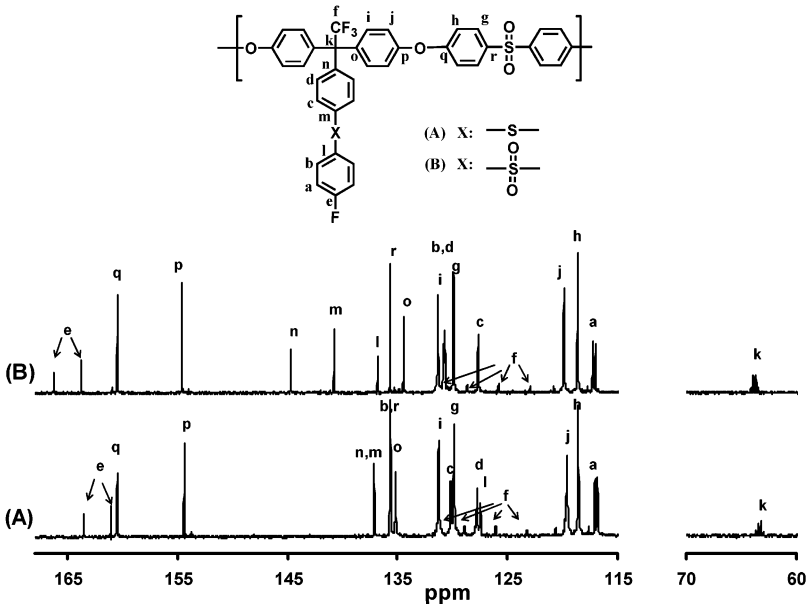


Figure 4. ^{13}C NMR spectra of homopolymer (A) PAESf-T-100 and (B) PAESf-S-100.

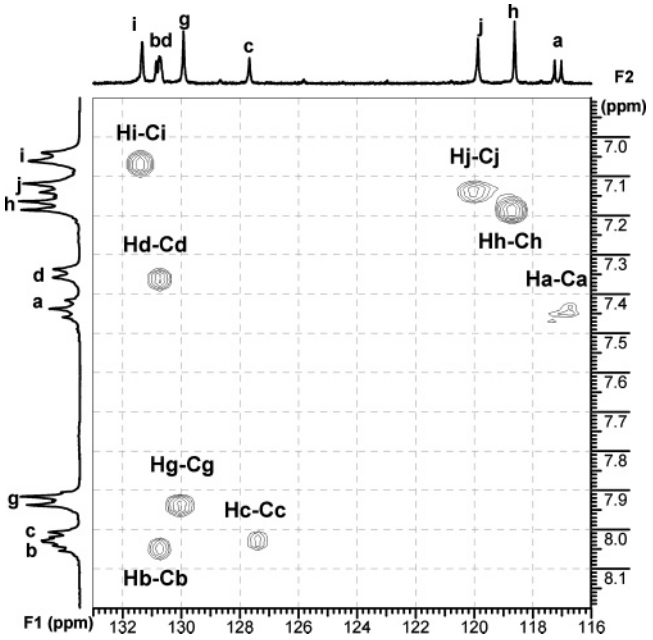


Figure 5. $^{1}H-^{13}C$ HSQC spectrum of polymer PAESf-S-100.

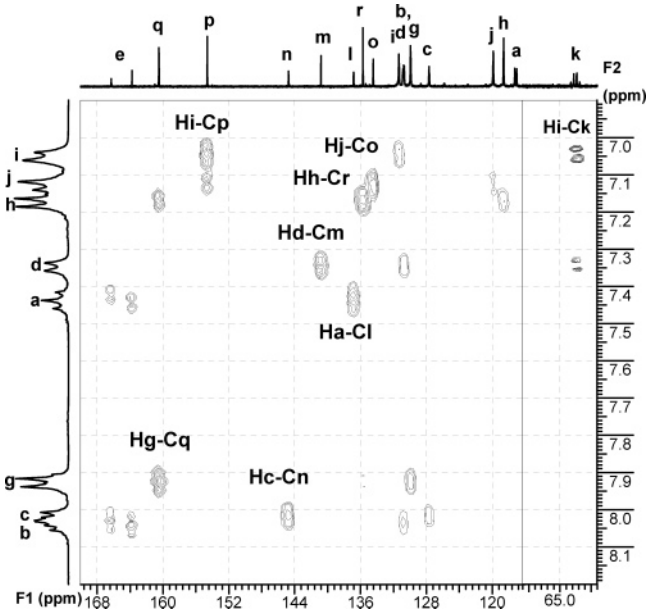


Figure 6. $^{1}H-^{13}C$ HMBC spectrum of polymer PAESf-S-100.

Cj, Cp, Cm, Cl, Cr, Co, Cq, and Cn, can all be assigned from their correlation with the corresponding protons three bonds away.

In the same manner, all of the signals in the ^{13}C NMR spectrum of PAESf-T-100 can be assigned as indicated in Figure 4 using the $^{1}H-^{13}C$ HSQC and HMBC analysis (spectra not shown). It is interesting that Hi and Hj signals in PAESf-T-100 overlapped with each other (Figure 2A), but their counterpart signals in the oxidized product were distinctly separated as shown in Figure 2B, even though the oxidation occurred at the position several bonds away. An explanation for this could be from the anisotropic effect of the sulfone group through space on Hi and Hj.

Thermal Analysis. Thermal analyses for most of the polymers with either sulfide or sulfone linkage in the pendant group were carried out as summarized in the data in Table 1. All the polymers have T_g between 180 and 230 °C. Interestingly, as the content of pendant group increased, the T_g of the polymer

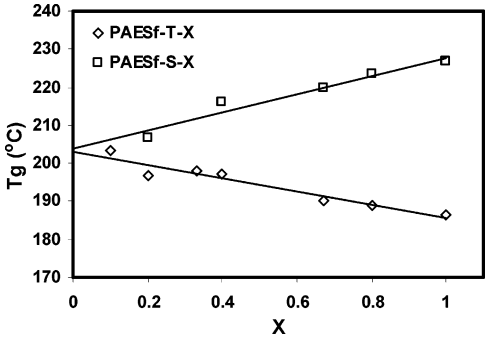


Figure 7. Relationship between T_g and pendant group content *X*.

with the sulfide linkage showed a linear decrease, while the T_g of the polymer with the sulfone linkage had a linear increase (Figure 7). The best-fit straight lines for the two sets of data crossed at the *Y* axis, where only one T_g should be present, representing the homopolymer of 6F-BPA with DFS. The difference between the T_g of homopolymer PAESf-T-100 and

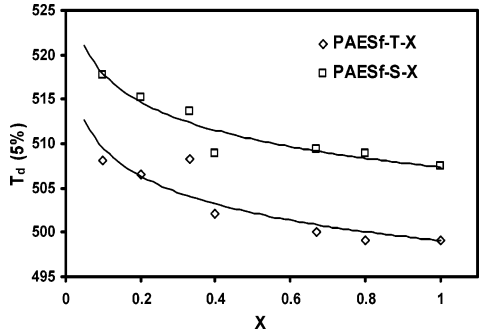


Figure 8. Relationship between 5% weight loss temperature and pendant group content *X*.

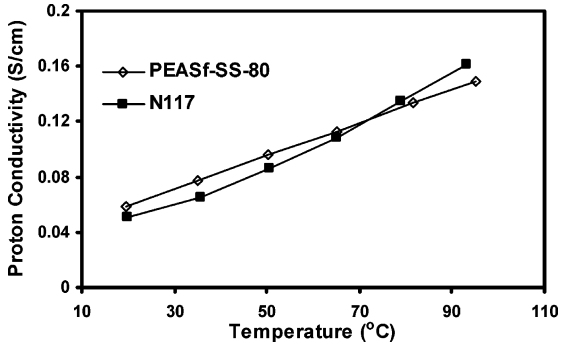


Figure 9. Temperature dependence of the proton conductivity of PEASf-SS-80 and that of Nafion-117 at 100% RH.

PAESf-S-100 is 40 °C. These data were unexpected and surprising since these two polymers have the same main-chain structure. Theoretical calculation by a semiempirical equation[12] shows that the difference should be about 27 °C. Compared with sulfide, the higher polar sulfone side groups can form stronger intermolecular interactions. In addition, the sulfone group is less flexible than sulfide to offer a higher steric hindrance effect.

TGA experiments show that all the polymers have excellent thermal stabilities, and the 5% weight loss temperature in nitrogen is around 500 °C. There is also some trend between this temperature and monomer ratio. As shown in Figure 8, all the sulfone side-chain copolymers show better thermal stability than their sulfide counterparts by about 10 °C. As the molar ratio of the pendant group increases from 10% to 100%, the 5% weight loss temperature decreased nearly 10 °C, for both PAESf-T-*X* and PAESf-S-*X* copolymers.

Sulfonated Side-Chain Attachment. To demonstrate the reactivity of the fluorine atom on the pendant group of the sulfone polymer, PAESf-S-80 was further reacted with a phenol compound N36DS. A preliminary ^{1}H and ^{19}F NMR study showed that more than 85% of fluorine reacted with this phenol. This ionomer PAESf-SS-80 is soluble in DMAc and formed transparent, flexible, and tough membranes after solution casting, which implies that no cross-linking or degradation occurred during the side-group attachment reaction. Further evidence comes from the viscosity measurement; PAESf-T-80 has an inherent viscosity of 0.39 dL/g, and PAESf-S-80 gives 0.40 dL/g. This result agrees well with the previous GPC data. Polymer PAESf-SS-80 shows a much higher inherent viscosity of 1.06 dL/g because of the attachment of disulfonic naphthol, which gives a much stronger interaction between polymer chains, and this result agrees well with previous reports.[2] A titration experiment shows this membrane had an IEC of 1.52 mequiv/g, which agrees well with the theoretical calculation (1.57 mequiv/g). The equilibrium water uptake at 20 °C is 52%, which means the number of water molecules per sulfonic acid groups (λ) is equal to 18. The proton conductivity, perhaps the most critical property of proton exchange membranes, is shown in Figure 9. For comparison, the data from Nafion 117 is also shown in the same figure. PAESf-SS-80 has a very similar proton conductivity compared with Nafion 117 throughout the whole measured temperature range (20−95 °C). This result is promising considering the novel sulfonated side group grafted structure.[2] More detailed studies of these series of polymers are still underway.

It should be noted that this bisphenol monomer, 3FBPT, is a universal monomer which can be used for preparation of other kinds of poly(arylene ether) polymers by condensation polymerization, and we are currently investigating these polymer systems as potential PEM materials. The pendant 4-fluorophenyl sulfide group serves as a masked reactive site for further S_NAr reaction. The fluorine in this group is easily activated for reaction with any functional phenolic or similar compounds by converting the sulfide to sulfone.[14] It is also possible to control the end groups and molecular weight by adjusting the ratio of two kinds of monomers.

Conclusions

A new general bisphenol monomer 3FBPT containing a masked grafting site was readily synthesized in two steps. The bisphenol monomer has general utility for preparing a wide variety of thermally and chemically stable poly(arylene ether)s, which when "unmasked" can be converted to graft polymers. In the present work, we report the preparation of a series of high molecular weight poly(arylene ether sulfone) copolymers with excellent thermal stability from this monomer. After oxidation, these copolymers were activated for a further S_NAr reaction through the fluorine atoms on the pendant groups of polymer chains. This approach provides a novel methodolgy for the preparation of chemically and thermally stable functional poly(arylene ether) polymers with flexible graft side chains. As an example, the present work demonstrates the attachment of a disulfonated side group, and the preliminary study shows these kinds of polymers have excellent potential as PEMFC materials. A more detailed report on PEM properties will follow in a later publication.

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