Synthesis, and Structural and Thermal Characterizations of Tetrasulfonated Poly(arylene biphenylsulfone ether) Copolymer Ion Conducting Electrolytes

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High molecular weight tetrasulfonated poly(arylene biphenylsulfone ether) (TsPBPSEH) copolymers containing up to four pendant sulfonate groups per repeat unit were synthesized *via* aromatic nucleophilic displacement condensation from 4,4'-bis(4-chloro-3-sulfonatophenylsulfonyl)biphenyl-2,2'-disulfonate (SBCSBPD), 4,4'-dichlorodiphenylsulfone (DCDPS) and 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA). The synthesized copolymers were structurally characterized using ^{1}H NMR and FT-IR techniques. They were analytically pure, amorphous and were readily soluble in a wide range of organic solvents. Electrolyte membranes were successfully cast using the synthesized polymers with various sulfonation levels and *N*-methyl-2-pyrrolidinone. This new class of polymer membranes exhibited elevated thermal and physical stabilities and reduced swelling at high temperatures. An increase of acidic functional groups in the copolymer yielded high ion exchange capacity and moderate ionic conductivity values even at higher temperatures, which makes them potential ion conducting candidates.

Key Words : Molecular weight, Tetrasulfonated monomer, Tetrasulfonated poly(arylene biphenylsulfone ether), Thermal stability, Ionic conductivity

Introduction

Booming power demand has triggered research into fuel cells in which high temperature operation *via* hydrocarbon polymer electrolyte membranes is sought.[1-4] Though perfluorinated polymer electrolyte membranes are commercially available, cost and performance limitations have hindered large-scale commercialization and market penetration of polymer electrolyte membrane fuel cells (PEMFC) in mobile and stationary systems.[5,6] This has encouraged researchers to design alternative hydrocarbon polymer electrolyte membrane materials with high ionic conductivity and elevated thermal, physical and chemical stabilities at low cost.[7,8]

Recently, acidified aromatic polymers such as poly(ether ketone) (PEK),[9] poly(ether sulfone) (PES),[10] poly(imide) (PI),[11] poly(benzimidazole) (PBI),[12] poly(phenylene oxide),[13] poly(phenylene sulfide)[14] and poly(phthalazinone ether ketone)[15] have been studied for fuel cell applications. Most of these polymeric membranes exhibit prompt chemical and electrochemical stabilities. As a class of high-performance engineered thermoplastic materials, poly(arylene ether sulfone)s containing sulfonate groups have a high glass transition temperature, high thermal stability, good mechanical properties and excellent resistance to hydrolysis and oxidation, making them good candidates for high temperature fuel cell applications. Based on the degree of sulfonation (DS), these copolymers exhibit hydrophilic-

hydrophobic phase separation. The ionic conductivity, ion-exchange capacity (IEC) and water uptake for this series of copolymers also increase with increasing DS.[15,16] In general, conventional post-sulfonation synthesis techniques limit large scale application in corresponding membranes due to their side reactions and the high level of control that is needed over the degree of sulfonation. These demerits of polymer post-acidification have been effectively tackled by the pre-acidification process. Pre-sulfonated halides afford the power to (i) control the exact location of ion conducting sulfonic acid groups; (ii) precisely vary the degree of sulfonation with monomer feed stoichiometry; and (iii) sustain the chemical stability of sulfonic acid groups by attaching them with electron-deficient aromatic rings. In general, pre-sulfonated halides are prepared by direct polymerization of the disulfonated activated halide with a bisphenol using a method similar to nucleophilic substitution condensation polymerization.

Harrison *et al*. reported a detailed account of the synthesis, characterization, and fuel cell performances of disulfonated poly(arylene ether sulfone) copolymers prepared from the disodium salt of 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS), 4,4'-dichlorodiphenyl sulfone (DCDPS), and 4,4'-biphenol (BP) *via* direct step-growth polycondensation.[8] The high oxidative stability of biphenol-based copolymers guarantees the durability of fuel cells. Disulfonated poly(arylene biphenylsulfone ether) (sPBPSEH) copolymers using SDCDPS, 4,4'-bis[(4-chlorophenyl)-

sulfonyl]-1,1'-biphenyl (BCPSBP) and bisphenol A (BPA) for fuel cell applications have also been reported.[16] Though elevated thermal and chemical stabilities have been maintained for the reported random copolymers, imbalances between the physical and electrochemical properties of the copolymers decrease fuel cell performance and limit large scale applications. Here, we report novel proton conducting copolymer membranes containing tetrasulfonated groups in each repeat unit to meet the mentioned objective. The main objective of this work was to generate ion conducting hydrocarbon electrolyte membranes with elevated thermal and physical stabilities.

Experimental Section

Materials. 4,4'-Bis[(4-chlorophenyl)sulfonyl]-1,1'-biphenyl (BCPSBP), 4,4'-dichlorodiphenylsulfone (DCDPS) and 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA) were purchased from Aldrich and dried at 50 °C under vacuum for 15 h before use. Anhydrous potassium carbonate (K_2CO_3), acetone, chloroform, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *N,N*-dimethylsulfoxide (DMSO), methanol, *N*-methyl-2-pyrrolidinone (NMP), sodium chloride (NaCl), toluene and 30% fuming sulfuric acid were also purchased from Aldrich and used without further purification.

Monomer Synthesis: Tetrasodium Salt of 4,4'-bis(4-chloro-3-sulfonatophenylsulfonyl)biphenyl-2,2'-disulfonate (SBCSBPD). 4,4'-Bis[(4-chlorophenyl)sulfonyl]-1,1'-biphenyl (BCPSBP, 3.0 g, 5.96 mmol) was dissolved in 10 mL of 30% fuming sulfuric acid (*ca.* 6-equiv excess) in a 250 mL three-neck flask under an argon inlet/outlet. The solution was magnetically stirred for 6 h at 110 °C, cooled to room temperature and poured into 100 mL of cold water. A white precipitate was obtained after the addition of 1.2 g sodium chloride and was identified as SBCSBPD. The powder was filtered, redissolved in 100 mL of deionized water and the pH was maintained between 6 and 7. Excess sodium chloride (NaCl) content (~1.2 g) was added to salt-out the sodium form of the tetrasulfonated monomer. The crude product was filtered, recrystallized from a heated mixture of alcohol (methanol or isopropanol) and deionized water (7/3, v/v), which yielded 70% of the product. ^{1}H NMR, ^{13}C NMR, and elemental analysis (EA) were used to confirm the structure and purity of the monomer. No melting point was observed for this ionic compound below 300 °C. SBCSBPD: FT-IR (KBr, cm^{-1}) 3584, 3441, 3085, 3028, 2569, 2469, 2099, 1942, 1637, 1593, 1581, 1478, 1451, 1393, 1378, 1322, 1284, 1216, 1165, 1144, 1111, 1086, 1065, 1020, 912, 824, 810, 757, 711, 696, 676; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 (2H, d, $J = 1.48$ Hz), 8.53 (2H, d, $J = 8.28$ Hz), 8.41 (2H, dd, $J = 1.48, 8.32$ Hz), 8.40 (2H, d, $J = 2.44$ Hz), 8.12 (2H, dd, $J = 8.28, 2.44$ Hz), 7.73 (2H, d, $J = 8.32$ Hz); Elem Anal Calcd for $C_{24}H_{12}Cl_2Na_4O_{16}S_6$: C, 31.62; H, 1.33; S, 21.10. Found: C, 31.94; H, 1.50; S, 20.33.

Synthesis of Tetrasulfonated Poly(arylene biphenyl-sulfone ether) (TsPBPSE) and Poly(arylene biphenyl-

sulfone ether) (PBPSE) Polymers. For a typical copolymerization of a TsPBPSE-30 system, SBCSBPD (2.63 g, 2.68 mmol), DCDPS (1.79 g, 6.25 mmol) and 6F-BPA (3.00 g, 8.92 mmol) were added to a 100 mL two-neck flask under an argon inlet and a Dean-Stark trap. K_2CO_3 (2.71 g, 19.63 mmol), DMAc (18 mL) and toluene (45 mL) were then added to the mixture. The reaction mixture was refluxed at 150 °C for 12 h to dehydrate the system and then the reaction temperature was raised to 200 °C for 24 h. The resulting copolymer was filtered and isolated using methanol/ deionized water. The precipitated copolymer was washed with deionized water several times to completely remove salts and was then extracted in deionized water at 60 °C overnight. Finally, the product was vacuum-dried at 120 °C for 24 h. Copolymers with other compositions were prepared by similar procedures. TsPBPSE-30: FT-IR (KBr, cm^{-1}) 3604, 3453, 3090, 3074, 2922, 2037, 1910, 1675, 1613, 1587, 1509, 1488, 1467, 1410, 1391, 1325, 1297, 1247, 1205, 1172, 1150, 1105, 1073, 1028, 1018, 969, 953, 927, 875, 855, 830, 792, 745, 731, 717, 705; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.56 (1.0H, s), 8.25-8.45 (4.3H, m), 8.07-8.25 (2.3H, m), 7.96 (13.8H, d, $J = 7.32$ Hz), 7.75-7.90 (0.85H, m), 7.47-7.70 (1.23H, m), 7.30-7.44 (17.82H, m), 7.21 (28.47H, s), 7.00-7.14 (3.52H, m).

Control polymer (PBPSE): BCPSBP (2.99 g, 5.95 mmol), DCDPS (1.71 g, 5.95 mmol) and 6F-BPA (4.0 g, 11.90 mmol) were added to a 100 mL two-neck flask under an argon inlet and a Dean-Stark trap. K_2CO_3 (3.62 g, 26.17 mmol), DMAc (20 mL) and toluene (40 mL) were then added to the mixture. The reaction conditions and work-up procedures were carried out as described for the preparation of TsPBPSE-30 to obtain a reference polymer. PBPSE: FT-IR (KBr, cm^{-1}) 3639, 3556, 3069, 2588, 2421, 2034, 1906, 1776, 1676, 1613, 1586, 1509, 1490, 1410, 1387, 1325, 1296, 1249, 1205, 1174, 1153, 1106, 1072, 1018, 1002, 966, 953, 927, 874, 856, 834, 790, 724, 705; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (4.0H, dd, $J = 5.52, 5.96$ Hz), 7.97 (2.0H, d, $J = 5.48$ Hz), 7.91 (2.0H, d, $J = 5.04$ Hz), 7.39 (4.0H, d, $J = 3.64$ Hz), 7.21 (8.0H, dd, $J = 5.96, 7.32$ Hz).

Preparation of Polymer Membranes. An appropriate amount of copolymer (salt form) was dissolved in NMP (8 wt %) at 140 °C and cast as membranes. The membranes were then dried at 80 °C for 2 h and vacuum-dried at 100-120 °C for 24 h. To convert the fabricated membranes into the acid form, membranes were activated with 10 wt % sulfuric acid for 24 h at 60 °C. Finally, the membranes were thoroughly washed with deionized water several times and stored in deionized water.

The membrane cannot be cast beyond 30 or 35 mol % SBCSBPD. The lower reactivity of the deactivated 6F-BPA phenolate may produce lower molecular weight copolymers, which resulted in membranes with a less ductile nature in the dry state. Similar difficulties were apparently encountered for the 30 mol % of SDCDPS content by Ueda *et al.*.[17]

Characterizations. FT-IR spectra of the fabricated membranes were examined by a Nicolet Impact 400 FT-IR spectrometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR

spectra of the synthesized copolymers were recorded on Bruker AM-400 MHz spectrometers using DMSO-d_6 as a solvent with tetramethylsilane (TMS) as the internal standard. Chemical analyses of elemental C, H and S were performed for the tetrasulfonated monomer with a Vario EL Elemental Analyzer. Molecular weights and the molecular weight distribution of the synthesized copolymers were evaluated by gel permeation chromatography (GPC) on semi-micro GPC columns from Tosoh Corporation (HLC-8320GPC) with an RI detector. The column was conditioned with standard polyethylene oxide, and DMF was used as the eluent at a flow rate of 1.0 mL min^{-1}. The tensile strength of the prepared membranes was examined at room temperature using a Universal Testing Machine (UTM) (LR5KPlus 5KN, Lloyd). Thermo gravimetric analysis (TGA) of the prepared membranes was conducted on a TA Instruments Thermal Analysis System Q50 at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a TA Instruments Thermal Analysis System Q10 at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Tapping mode atomic force microscopy (TP-AFM) images were obtained using a Digital Instruments Multimode scanning probe microscope with a NanoScope IV controller. A silicon probe (Veeco) with an end radius of < 10 nm and a force constant of 5 N m^{-1} was used to image the prepared samples.

Water Uptake Measurement. Water uptake of the fabricated membranes was determined according to a procedure described elsewhere.[18]

Ion Exchange Capacity (IEC). Ion exchange capacity (IEC, meq. g^{-1}) values of the membranes were measured by a titration method. After sulfuric acid treatment, the membranes were rinsed with deionized water, and then the H$^+$ form membranes were immersed in 2.0 M NaCl solution for a day to exchange all the H$^+$ with Na$^+$. The H$^+$ ions in the NaCl solution were titrated with a 0.01 M NaOH solution, in which phenolphthalein was used as the endpoint indicator. The ion exchange capacity (IEC) of the membranes was

calculated from the titration data using the following equation:

$$IEC = [(V_{NaOH} \times C_{NaOH}) / W_{dry}] \qquad (1)$$
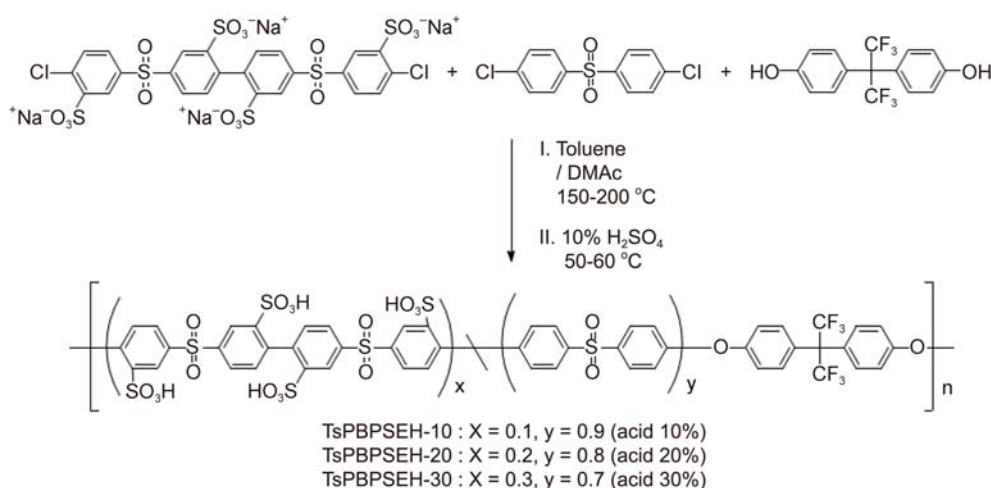
where V_{NaOH} is the volume of NaOH (mL) consumed, C_{NaOH} is the concentration of NaOH (M), and W_{dry} is the weight of dry membranes, respectively.

Ionic Conductivity. Ionic conductivity values of the fabricated membranes were examined by a BekkTech conductivity test cell in conjunction with a PGZ 301 Dynamic EIS voltammeter as reported elsewhere.[16,18]

Results and Discussion

Synthesis of Tetrasulfonated Poly(arylene biphenyl-sulfone ether) Copolymers and Membrane Preparation. A monomer, tetrasodium salt of 4,4'-bis(4-chloro-3-sul-fonatophenylsulfonyl)biphenyl-2,2'-disulfonate (SBCSBPD) was synthesized by sulfonating BCPSBP with fuming sulfuric acid (30% SO$_3$), followed by neutralization with NaOH and NaCl, according to a procedure described else-where.[17,19] Individual copolymers (Scheme 1) were synthe-sized as follows: Tetrasulfonated poly(arylene biphenyl-sulfone ether) (TsPBPSE) polymers were synthesized by the polymerization of SBCSBPD and DCDPS with 6F-BPA (ratio 1:9:10 for TsPBPSE-10, ratio 2:8:10 for TsPBPSE-20, ratio 3:7:10 for TsPBPSE-30 refer to the intended equivalent weight in g mol^{-1}). The reference copolymer, poly(arylene biphenylsulfone ether) (PBPSE) was prepared by a standard polycondensation reaction (nucleophilic aromatic sub-stitution) of BCPSBP and DCDPS with 6F-BPA (ratio 5:5:10 for PBPSE refers to the intended equivalent weight in g mol^{-1}). After precipitation in methanol/water co-solvent, the obtained sulfonated copolymers were purified by thoroughly washing with distilled water. The sodium salt form of the membranes was prepared by redissolving the sodium-neutralized copolymer in NMP to form 8 wt% transparent solution, which was cast onto clean glass sub-

TsPBPSEH-10 : X = 0.1, y = 0.9 (acid 10%)
TsPBPSEH-20 : X = 0.2, y = 0.8 (acid 20%)
TsPBPSEH-30 : X = 0.3, y = 0.7 (acid 30%)

Scheme 1. Synthesis of tetrasulfonated poly(arylene biphenylsulfone ether) (TsPBPSEH) copolymers and chemical structures of poly(arylene biphenylsulfoneether) (PBPSE) copolymers.

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Table 1. Solubility behavior of the synthesized copolymers in various solvents; [a](++) highly soluble, (+) soluble, (±) partially soluble, and (−) insoluble at room temperature

Solvent	PBPSE	TsPBPSEH-10	TsPBPSEH-20	TsPBPSEH-30
DMAc	++	++	++	++
DMF	++	++	++	++
DMSO	++	++	++	++
NMP	++	++	++	++
THF	+	+	+	+
Chloroform	±	±	±	±
Acetone	±	±	±	±
Methanol	-	-	-	±
Water	-	-	-	-

strates. The films were carefully dried at 120 °C for 24 h and then the sodium salt form of the polymer films was acidified with 10 wt % sulfuric acid for 24 h at 50-60 °C. The thickness of the membranes was maintained between 95-185 μm.

Solubility Behavior. The solubility behaviors of the synthesized copolymers in selected solvents are summarized in Table 1. The solubility of the polymers was measured at room temperature by dissolving 10 mg of polymer in 10 mL of solvent. All TsPBPSEH polymers were quite soluble in a wide range of aprotic polar solvents such as DMAc, DMF, DMSO, NMP and THF, but partially soluble in chloroform and acetone. All TsPBPSEH co-polymers except TsPBPSEH-30 were insoluble in protic polar solvents such as methanol, ethanol and water. TsPBPSEH-30 alone was partially soluble in methanol. The absence of a cross-linking reaction in the executed direct polymerization processes was directly evident based on the high solubility of TsPBPSEH in DMSO.
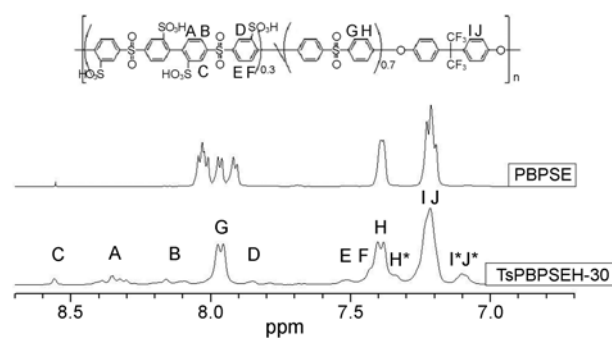
Structural Characterization of the Copolymers. Standardized FT-IR spectra allowed for qualitative and quantitative determination of the functional groups of the synthesized copolymers. Figure 1 depicts FT-IR spectra of the TsPBPSEH copolymer series. The absorption band
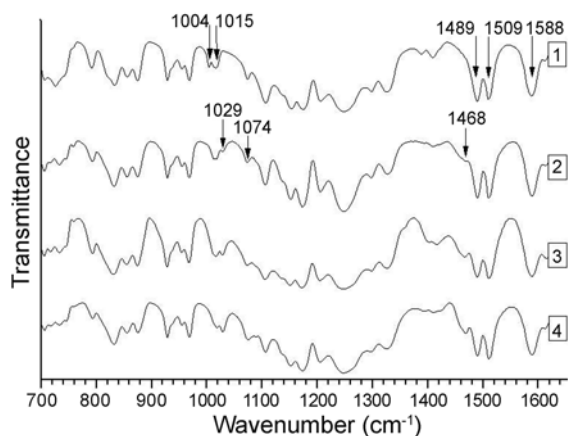
located at 1004 cm^{-1} was assigned to the split symmetric stretching vibration mode of in-chain diphenyl ether (Ar-O-Ar) units of the *para*-substituted benzene ring, and this band was used to normalize each of the sulfonated copolymers.[16] The peaks at 1489, 1509 and 1588 cm^{-1} arose from the C=C stretching vibration of the aromatic groups, and these peaks were observed in all of the obtained spectra. The successful inclusion of SO$_3$H groups in all copolymers was confirmed by the two characteristic peaks at 1029 and 1074 cm^{-1}, which were assigned to the symmetric and asymmetric stretching vibration modes of the SO$_3$H group, respectively.[15] The intensities of the mentioned modes increased with an increase in the SBCSBPD content, indicating that the SO$_3$H groups were successfully incorporated into the polymer chain without any detectable cross-linking, as expected from previous results. The degree of SO$_3$H substitution increased with an increase in the concentration of SBCSBPD monomer in the feed. Additionally, the number of SO$_3$H groups could be easily controlled by varying the ratio of SBCSBPD and DCDPS monomers, provided the amount of 6F-BPA was fixed.

The structures of the TsPBPSEH copolymer series were elucidated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the TsPBPSEH-30 copolymer is depicted in Figure 2. As a consequence of the strongly electron-withdrawing properties of the sulfone groups, NMR signals of the aromatic protons were shifted to lower fields (deshielding effect). The position of the signals at low fields, between δ = 8.06 and 8.6 ppm, are consistent with ^{1}H NMR resonances reported for sulfonated poly(phenylene sulfone).[20] Several multi-signals in the same range of the ^{1}H NMR spectrum of the TsPBPSEH-30 copolymer were observed, suggesting the formation of random copolymers. These multi-signals can be approximately assigned to the nine groups of aromatic protons as follows: δ 8.56 (H$_C$), 8.25-8.45 (H$_A$), 8.07-8.25 (H$_B$), 7.97 (H$_G$), 7.75-7.90 (H$_D$), 7.47-7.70 (H$_E$), 7.30-7.44 (H$_F$, H$_H$, H$_{H*}$), 7.21 (H$_{IJ}$), 7.00-7.14 (H$_{I*J*}$).

The successful introduction of SO$_3$H groups was confirmed by several peaks between 8.06 and 8.6 ppm. Intensity increased with increases in the number of SBCSBPD moieties. The integration and appropriate analysis of the known reference protons of the copolymers allowed the relative compositions of the various copolymers to be

Figure 1. FT-IR spectra of (1) PBPSE, (2) TsPBPSEH-10, (3) TsPBPSEH-20 and (4) TsPBPSEH-30 tetrasulfonated poly(arylene biphenylsulfone ether) copolymers.

Figure 2. Representative ^{1}H NMR spectra of TsPBPSEH-30 and the reference polymer, PBPSE.

Table 2. Degree of sulfonation (DS), tensile strength, T_d and T_g of the fabricated membranes

Copolymers	Mol % SBCSBPD	DS by ^{1}H NMR	Tensile Strength (MPa)	T_g (^{o}C)	T_d (^{o}C) 5%	T_d (^{o}C) 10%
PBPSE	0	0	28.2	145	509	523
TsPBPSEH-10	10	8.8	27.7	195	500	529
TsPBPSEH-20	20	19.5	24.3	204	308	480
TsPBPSEH-30	30	28.3	19.2	214	279	361

determined. The three protons (H_A, H_B and H_C at > 8.06 ppm) in the biphenyl moiety derived from the tetra-sulfonated bishalophenylsulfonyl biphenyl monomer were separated from the other aromatic protons (H_D, H_E, H_F, H_G, H_H, H_{H*}, H_{IJ} and H_{I*J*}). The degree of sulfonation (DS) in the copolymers was determined *via* ^{1}H NMR spectra using the following equation:

$$\text{Degree of sulfonation (DS\%)}$$
$$= I_{ABC}/6 \div (I_{IJ}/8 + I_{ABC}/6) \times 100 \qquad (2)$$

where I_{ABC} is the integration for the A, B, and C protons of the biphenyl moiety and I_{IJ} is the integration for the I and J protons of the 6F-BPA moiety. The integration indicated that 28.3 mol % of TsPBPSEH-30 was incorporated into the polymer. Similar calculations were performed for all of the sulfonated copolymers and the results are listed in Table 2.

GPC measurement of the TsPBPSEH copolymers in DMF at 40 ^{o}C was performed in order to determine the molecular weight. LiBr was added (0.86 g L^{-1}) to the copolymer solution in order to suppress the polyelectrolyte effect. The reference (PBPSE) copolymer was a low molecular weight polymer having an unimodal distribution with $M_{max} \approx 22{,}000$ g mol^{-1}. The maxima of the molecular weight distributions for TsPBPSEH-10 and TsPBPSEH-30 ($M_{max} \approx 33{,}000$ and $34{,}000$ g mol^{-1}, respectively) were higher than that of the reference copolymer, and even small amounts of low molecular components ($M_{max} \approx 1{,}500$ g mol^{-1}) were detected in TsPBPSEH-10, suggesting slight deviations from ideal progress of the polycondensation reaction. The number-average molecular weights (M_n) of the copolymers were in the range of 13,000-27,000 Da, and the poly-dispersity indices (M_w/M_n) varied from 2.2 to 2.6 as shown in Table 3 and Figure 3.

Mechanical Strength. The tensile strength of the fabri-cated membranes was evaluated and the results are shown in Table 2. Among the fabricated membranes, the reference

Table 3. Number average molecular weight (M_n), weight average molecular mass (M_w), maximum molecular weight (M_{max}) and PDI (polydispersity index) of the synthesized copolymers

Copolymers	M_n (g mol^{-1})	M_w (g mol^{-1})	M_{max} (g mol^{-1})	PDI (M_w/M_n)
PBPSE	13000	29000	22000	2.2
TsPBPSEH-10	22000	57000	33000	2.6
TsPBPSEH-20	22000	49000	27000	2.3
TsPBPSEH-30	27000	61000	34000	2.3
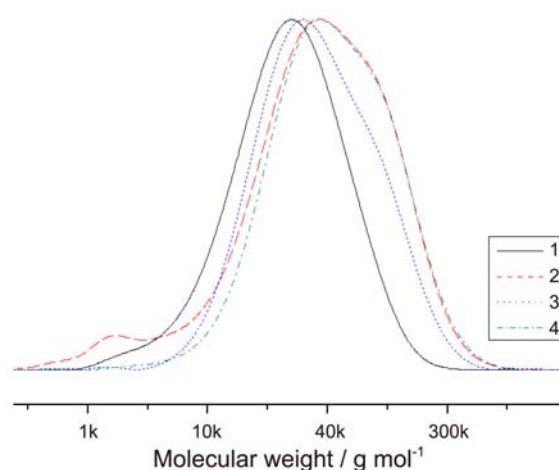
Figure 3. GPC profiles of (1) PBPSE, (2) TsPBPSEH-10, (3) TsPBPSEH-20 and (4) TsPBPSEH-30 copolymers in DMF at $T = 40$ ^{o}C with LiBr addition (10 mM in DMF) relative to the polystyrene standard.

(PBPSE) membrane exhibited the greatest tensile strength due to its highly crystalline character. The hydrophobic nature of the reference copolymer further supports the physical integrity of the corresponding membranes. An increase in the SBCSBPD content yielded hydrophilicity, which in turn reduced the mechanical stability of the fabricated membranes (Table 2). However, the mechanical strengths of the fabricated membranes were comparable to those of conventional polymer electrolyte membranes.[21]

Thermal Properties. The thermal properties of the fabri-cated copolymers were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. The results are summarized in Table 2. The thermal spectra of all but the control polymer exhibited two distinct weight-losses (Figure 4). The first noticeable weight loss observed at around 300 ^{o}C was attributed to the loss of sulfonic acid groups, and the second weight loss near 550 ^{o}C is primarily due to decomposition of the polymeric back-bone.[22] The weight loss of the TsPBPSEH-30 copolymer in the range of 100-200 ^{o}C was attributed to the desorption of water molecules bonded to the sulfonic groups in the polymers.[23,24] All copolymers were stable up to 300 ^{o}C. However, the 30% sulfonated copolymer was less stable due to its high level of sulfonation. At a higher degree of sulfonation (TsPBPSEH-30), the initial 5% weight loss occurred at approximately 280 ^{o}C, whereas the second 10% weight loss was around 360 ^{o}C. The observed thermal
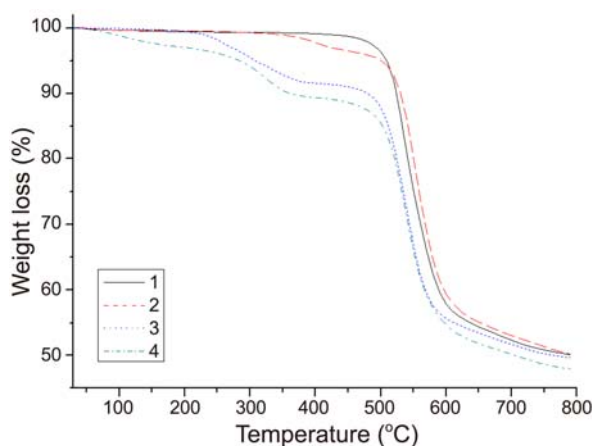
Figure 4. Thermogravimetric analysis of the (1) PBPSE, (2) TsPBPSEH-10, (3) TsPBPSEH-20 and (4) TsPBPSEH-30 membranes.
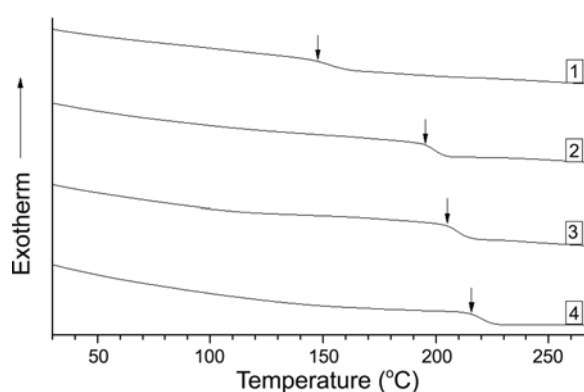

Figure 5. DSC analysis of the (1) PBPSE, (2) TsPBPSEH-10, (3) TsPBPSEH-20 and (4) TsPBPSEH-30 copolymers.

behaviors clearly confirmed the suitability of the prepared membranes for use in elevated temperature applications.

Figure 5 depicts DSC thermoscans (second heat) of the TsPBPSEH copolymers as a function of sulfonation degree. The reference polymer had a lower T_g than the other TsPBPSEH copolymers. In general, the T_g increased with the increase in ionic groups in the polymer chain (ionomer effect).[25,26] The fabricated membranes also followed the same general trend, *i.e.*, an increase in the sulfonic acid content increased the T_g values and was purely attributed to the increment in molecular bulkiness and enhancement of the intermolecular interaction between pendant ions *via* hydrogen bonding. A summary of the thermal properties of the prepared copolymers is given in Table 2.

Water Uptake, Ion Exchange Capacity and Proton Conductivity. The presence of adequate amounts of water in PEMs is vitally important for ion transport and is dependent on several parameters such as DS, temperature, and relative humidity.[27] The absorption of water molecules increases linearly with an increase in the number of sulfonic acid groups. The water uptake values of the sulfonated membranes at room temperature are exhibited in Figure 6.

As expected, water uptake increased with an increase in the sulfonation degree due to the strong hydrophilicity of the
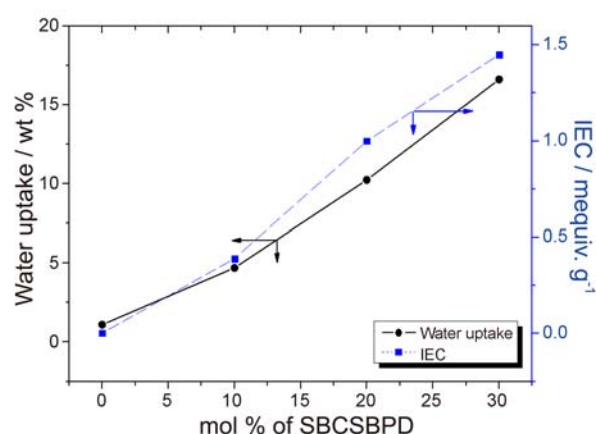
Figure 6. Water uptake and ion-exchange capacity (IEC) values of the prepared membranes as a function of SBCSBPD mole fraction.

sulfonic acid groups. The water uptake values increased almost linearly from 4.7 wt % for TsPBPSEH-10 to 16.6 wt % for TsPBPSEH-30 at room temperature. The water uptake of the TsPBPSEH-30 membrane containing 30 mol % of SBCSBPD monomer was about quadruple that of TsPBPSEH-10. Moreover, the water uptake values for all of the sulfonated TsPBPSEH membranes were higher than that of the control membrane and were purely attributed to high IEC values (Table 4 and Figure 6).

Ion exchange capacity (IEC) is an important indicator of the extent of sulfonation, which is related to the exchangeable ions in polymer membranes. The IEC values of the copolymers were consistent with the results of the ^{1}H NMR intensities. The experimentally determined IECs of the TsPBPSEH films were greater than that of the reference film. The IEC values were highly dependent upon the mol fraction of SBCSBPD as illustrated in Figure 6. The figure shows that the degree of sulfonation was associated with IEC as well as water uptake values. We also found that higher IEC values decreased the decomposition temperature (T_d) (Table 4 and Figure 6).

Figure 7 depicts the ionic conductivity values of the fabricated membranes as a function of sulfonation degree at 30 ℃. As expected from the water uptake and IEC values, an increase in the sulfonation degree increased the ionic conductivity of the prepared membranes. The acid-form membranes, TsPBPSEH-10 (IEC 0.39 meq g^{-1}) and TsPBPSEH-30 (IEC 1.45 meq g^{-1}), exhibited ionic conductivity values

Table 4. Water uptake, ion exchange capacity (IEC), and proton conductivity values of the fabricated membranes

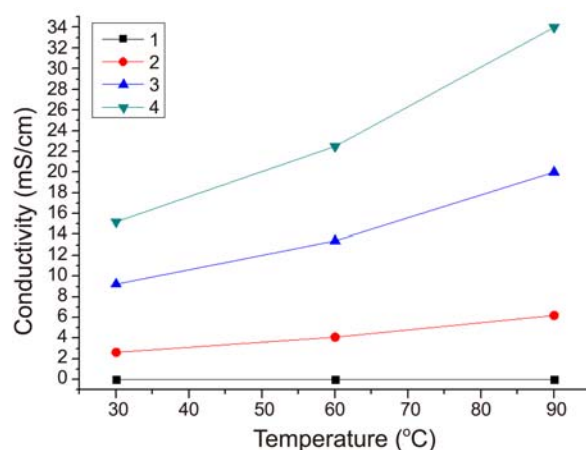| Copolymers	Water uptake (wt %)	IEC (meq g^{-1})	Conductivity (mS cm^{-1})[a]		
			30 ℃	60 ℃	90 ℃
PSPSE	1.1	0	0	0	0
TsPBPSEH-10	4.7	0.39	2.6	4.1	6.2
TsPBPSEH-20	10.2	1.00	9.2	13.4	20.2
TsPBPSEH-30	16.5	1.45	15.2	22.5	34.1

[a]Measured at 30 ℃ with 100% RH.
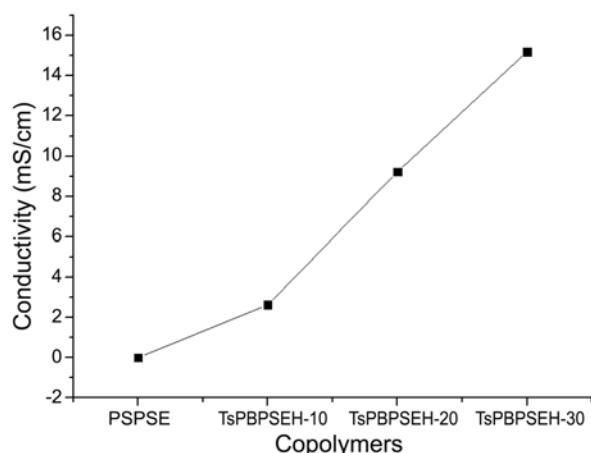
Figure 7. Ionic conductivity values of the prepared membranes at 30 °C and 100% RH.

Figure 8. Ionic conductivity values of the (1) PBPSE, (2) TsPBPSEH-10, (3) TsPBPSEH-20 and (4) TsPBPSEH-30 membranes as a function of temperature at 100% RH.

of 2.6 and 15.2 mS cm^{-1}, respectively, while the conductivity of Nafion 115 was 34 mS cm^{-1} (data not shown) under comparable conditions.

Figure 8 exhibits the ionic conductivity values of the studied membranes as a function of temperature (Table 4). A maximum conductivity of 34.1 mS cm^{-1} was achieved for the TsPBPSEH-30 membrane at 90 °C with 100% RH. Ion transport of these sulfonated membranes solely depends on the temperature and mole fraction of SBCSBPD. The increase in temperature influences ion transfer and structural reorganization, which results in increased ionic conductivity.[28] The number of hydrophilic domains gradually increased with an increase in the sulfonation level. It gradually brings the water clusters closer to each other, which increases the ionic conductivity values. The ionic conductivity of the sulfonated polymers depends upon the type of charge carrier and its mobility, and mobility is

mainly ensured by the presence of water molecules and their clusters. Hence, the hydrophilic pathway, through which ions could easily pass, may broaden with increasing sulfonated monomer content due to an increase in the space accessible for water molecules around the charged groups. The acidity of the pendant perfluorosulfonic acid is much stronger than the aryl sulfonic acid. Therefore, more acid moieties are required in sulfonated poly(arylene ethers) to achieve the desired conductivity. The observed ionic conductivity values of the tetrasulfonated TsPBPSEH-30 copolymer under the same conditions were measured to be approximately three times higher than that of a disulfonated sPBPSEH-30 copolymer reported elsewhere,[16] and this difference was attributed purely to the four pendant sulfonate groups per repeat unit.

Morphology. Tapping mode AFM phase images of the TsPBPSEH system were recorded under ambient conditions
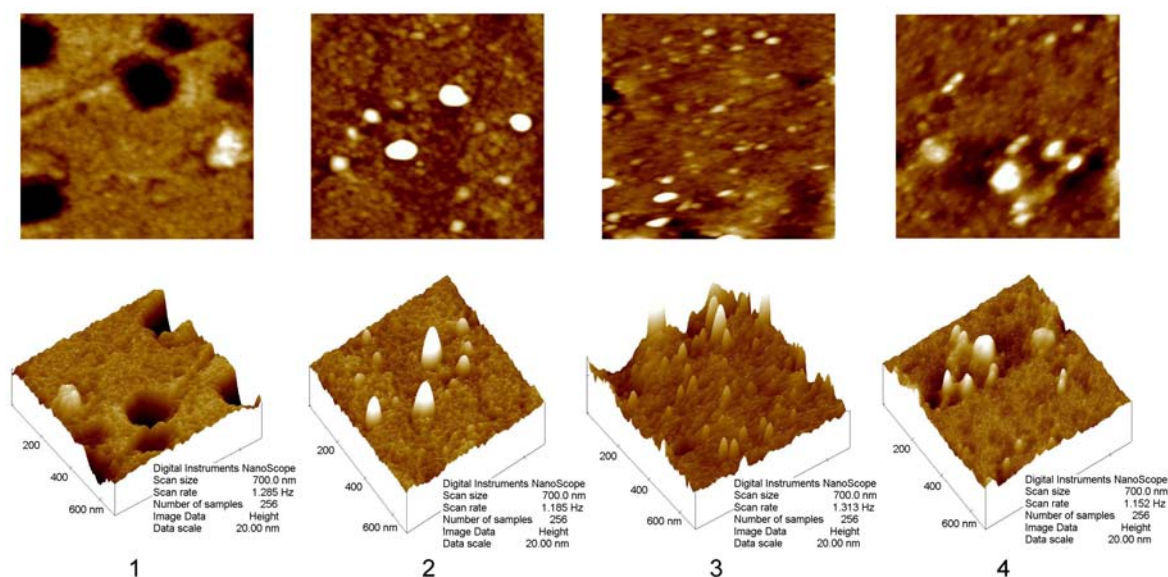
Figure 9. AFM (atomic force microscopy) surface images (700 × 700 nm scale) of the (1) PBPSE, (2) TsPBPSEH-10, (3) TsPBPSEH-20, (4) TsPBPSEH-30 membranes.

on a 700 nm × 700 nm scale in order to investigate ionic clusters of the sulfonated poly(arylene biphenylsulfone ether) polymers (Figure 9). Featureless phase morphology with some marks of solvent emissions was observed for the control copolymer (PBPSE). In contrast, dark cluster-like structures were clearly visible in the phase images of the TsPBPSEH copolymers. The dark phases were assigned to a softer region that represents the hydrophilic sulfonic acid groups, whereas the lighter phases were assigned to a hard region representing the hydrophobic domain.[15,29] The variation in the domain size and connectivity depends solely on the degree of sulfonation in the copolymers. The increase in the water uptake values is due to the hydrophilic nature of the copolymers, which may be further amplified by the introduction of hydrogen bonding with water. Based on the AFM phase images of the TsPBPSEH copolymers, it can be concluded that water uptake, IEC and ion transport increase with increasing ionic clusters in the polymers.

Conclusions

New tetrasulfonated poly(arylene biphenylsulfone ether) copolymers with four sulfonic acid groups per high molecular weight repeat unit were successfully synthesized by aromatic nucleophilic substitution polymerization. An increase in the SBCSBPD portion enhances hydrophilicity, which in turn reduces the tensile strength of the prepared membranes. The functionalized TsPBPSEH copolymers were found to possess a higher T_g than the reference (PBPSE) copolymer and exhibited good thermal stability. The T_g, water uptake, IEC, and ionic conductivity values of the synthesized copolymer membranes increased with increasing numbers of ionic clusters in the polymers. Due to the combination of high IEC and water absorption values, high ionic conductivity values were observed for the TsPBPSEH-30 membrane even under high temperature conditions. AFM phase images showed that the hydrophilic ionic domains increased in proportion to the DS. The observed results clearly indicate that the tetrasulfonated aromatic hydrocarbon membranes prepared from the tetrasulfonated monomer can be considered suitable candidates for polymer electrolyte membrane fuel cells. Further research on hydrocarbon membranes containing tetrasulfonated monomer moieties is in progress.

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