Highly Sulfonated Poly(Arylene Biphenylsulfone Ketone) Block Copolymers Prepared *via* Post-Sulfonation for Proton Conducting Electrolyte Membranes

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A series of the block copolymers were successfully synthesized from post-sulfonated hydrophilic and hydrophobic macromers *via* three-step copolymerization. The degrees of sulfonation (DS) of the copolymers (10%, 30%, or 50%) were controlled by changing the molar ratio of the hydrophilic and hydrophobic parts. The resulting block copolymers were characterized by ^{1}H NMR and other technologies. The membranes were successfully cast using dimethyl sulfoxide (DMSO) solution at 100 °C. The copolymers were characterized to confirm chemical structure by ^{1}H NMR and FT-IR. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) demonstrated that all sulfonated block copolymers exhibited good thermal stability with an initial weight loss at temperatures above 240 °C. The membranes showed acceptable ion exchange capacity (IEC) and water uptake values in accordance with DS. The maximum proton conductivity was 184 mS cm^{-1} in block copolymer-50 at 60 °C and 100% relative humidity, while the conductivity of Nifion-115 was 160 mS cm^{-1} under the same measurement conditions. AFM images of the block copolymer membranes showed well separated the hydrophilic and hydrophobic domains. From the observed results it is that the prepared block membranes can be considered as suitable polymer electrolyte membranes for the application of polymer electrolyte membrane fuel cells (PEMFC).

Key Words : Proton exchange membrane, Post-sulfonation, Thermal stability, Ion conductivity, Morphology

Introduction

The proton exchange membrane is one of the key materials of a polymer electrolyte membrane fuel cell (PEMFC). Among the different types of membranes, Nafion has been primarily used as a standard PEMFC membrane. However, the high cost, low glass transition temperature, and environmental incompatibility of the membranes have impeded the widespread commercialization of PEMFCs. In order to overcome these drawbacks, a number of alternative membranes have been studied for PEM.[1]

Several approaches to improve the proton conductivity of membranes without sacrificing their excellent physical and other properties have been investigated.[2-6] Control of morphology has been suggested as a strategy for this purpose. A multi block structure enhances the phase separation between hydrophilic and hydrophobic domains, thus allowing for much higher proton conductivity. Block copolymer membranes containing a high density of sulfonic acid groups in the hydrophilic component show a unique phase-separated morphology with well-interconnected ion transport pathways.[3-6] In addition to the chemical and physical properties, the synthesis route of sulfonated block copolymers is an important issue. There are typically two synthetic methods: by direct copolymerization of sulfonated monomers or by post-sulfonation of copolymer. Extensive research efforts were devoted on the synthesis of sulfonated block copolymers using post-sulfonation method.[3,4] The tetrasulfonated poly(arylene biphenylsulfone ether) random copolymers based ion conducting electrolytes[7] were reported by our group. In more recent papers, we have also published the tetrasulfonated poly(arylene biphenylsulfone ether/ketone) block copolymers prepared by copolymerization reaction of sulfonated monomers.[5,6,8] Related to these reports, we synthesized newly designed and highly sulfonated block copolymers *via* the post-sulfonation of macromer, as dipicted in Scheme 1.

In this paper, we report the synthesis of highly sulfonated poly(arylene biphenylsulfone ketone) block copolymer membranes by post-sulfonation method. In addition, the structure analysis, oxidative and thermal stabilities, water uptake, IEC, proton conductivity and morphological properties of the prepared hydrocarbon polymeric membranes were thoroughly investigated.

Experimental Section

Materials. 4,4'-Bis[(4-chlorophenyl)sulfonyl]-1,1'-biphenyl (BCPSBP), 4,4'-dichlorobenzophenone (DBP), and 4,4'-(hexafluoroisopropylidene) diphenol (6F-BPA) were purchased from Sigma-Aldrich, and dried at 50 °C in an oven for 15 h before use. Chlorosulfuric acid, *N,N*-dimethylacetamide
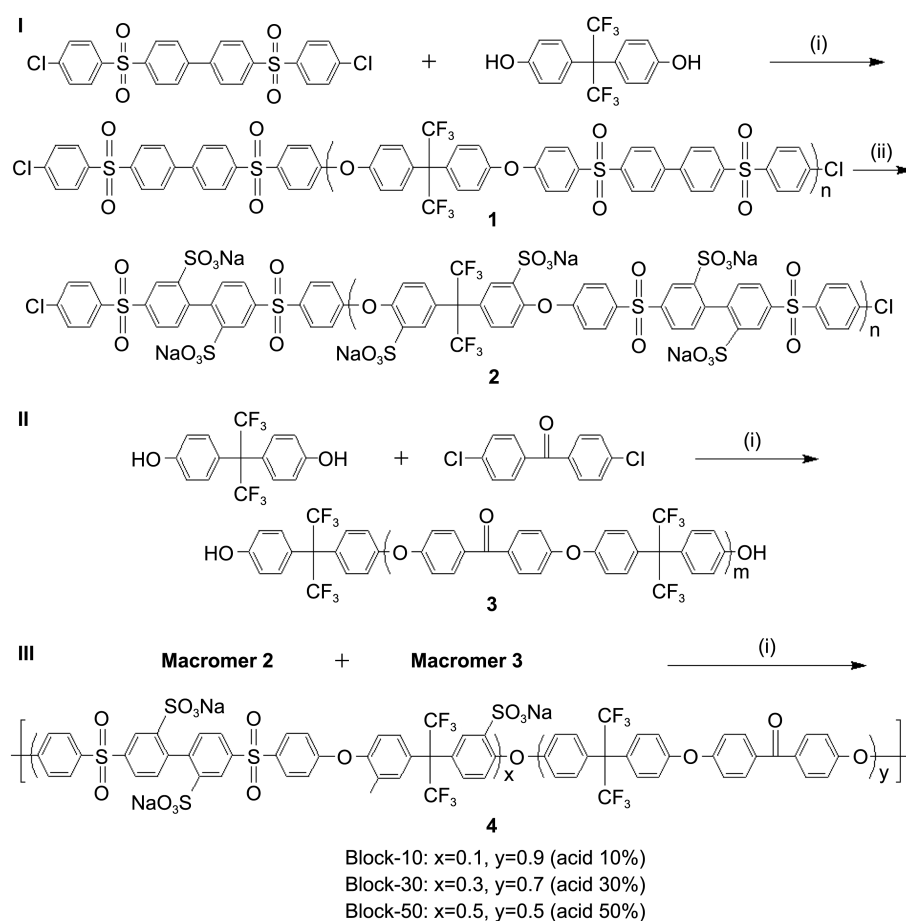
Scheme 1. Synthesis of the block copolymers: (i) K_2CO_3, DMAc/toluene, 140-185 °C, 24 h, and (ii) $ClSO_3H$, CH_2Cl_2, rt, 7 h; NaOH/NaCl, rt, 24 h.

(DMAc), anhydrous toluene, methylene chloride, anhydrous potassium carbonate, anhydrous sodium chloride and DMSO were purchased from Sigma-Aldrich and used without further purification.

Precursor (1) Synthesis. The polymerization was conducted in a 100 mL two-neck flask equipped with a mechanical stirrer and Dean-Stark trap under N_2 gas. In a typical polymerization, BCPSBP (6.80 g, 13.5 mmol), 6F-BPA (5.00 g, 14.9 mmol) and potassium carbonate (3.73 g, 27.0 mmol) are added into the flask. Subsequently DMAc (25 mL) and toluene (20 mL) were added into the flask as a solvent. The reaction mixture was heated under reflux at 135 °C for 6 h, and then most of the toluene was removed at 160 °C for 12 h. The temperature was raised slowly to 190 °C for 24 h until the solution was viscous. The viscous solution was slowly cooled to 60 °C and diluted with DMAc for easier filtering. The solution was poured into 800 mL of co-solvent (methanol/acetone/deionized water, 6:1:1, v/v/v). The precipitation was washed with methanol and deionized water several times and dried for 15 h at 100 °C in a vacuum oven for the post-sulfonation reaction. The precursor (**1**) for the hydrophilic part with the following data was produced in about 97% yield and is shown in Figure 1: FT-IR (KBr, cm^{-1}) 3068, 1633, 1588, 1510, 1489, 1408, 1389, 1326, 1247, 1206, 1173, 1152, 1104, 1072, 1015, 967, 928, 874, 855,

831, 822, 790, 725, 545, 522; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.2-8.0 (8H), 7.9-7.6 (4H), 7.4 (4H), 7.2-7.6 (8H).

Hydrophilic Macromer (2) Synthesis. The precursor of hydrophilic macromer was dissolved completely in methylene chloride (25 mL) and then added dropwise to 0.1 M chlorosulfuric acid/methylene chloride at room temperature over the course of about 1 h.^{9,10} The resulting mixture was stirred vigorously for 7-10 h until a pale brown product precipitated out of the solution. After the reaction solution was precipitated into *n*-hexane/deionized water (6:4, v/v), the precipitate was washed with deionized water several times until pH 7 was measured to remove the residual salt, and filtered with filter paper. The sulfonated hydrophilic macromer was dried in a vacuum oven at 80 °C for 24 h. The hydrophilic macromer **2** with the following data was produced in about 71% yield and is shown in Figure 1: FT-IR (KBr, cm^{-1}) 3406, 3098, 3072, 1688, 1632, 1587, 1486, 1408, 1250, 1211, 1182, 1152, 1091, 1024, 975, 877, 855, 834, 822, 721, 571; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10-7.98 (12H), 7.33 (2H), 7.17 (2H), 7.13-7.12 (4H).

Hydrophobic Macromer (3) Synthesis. The hydrophobic component synthesis is synthesized as shown in Scheme 1. 6F-BPA (5.00 g, 14.9 mmol), DBP (4.11 g, 16.4 mmol) and potassium carbonate (4.12 g, 26.2 mmol) were added to a 100 mL two-neck flask equipped with a mechanical stirrer, a
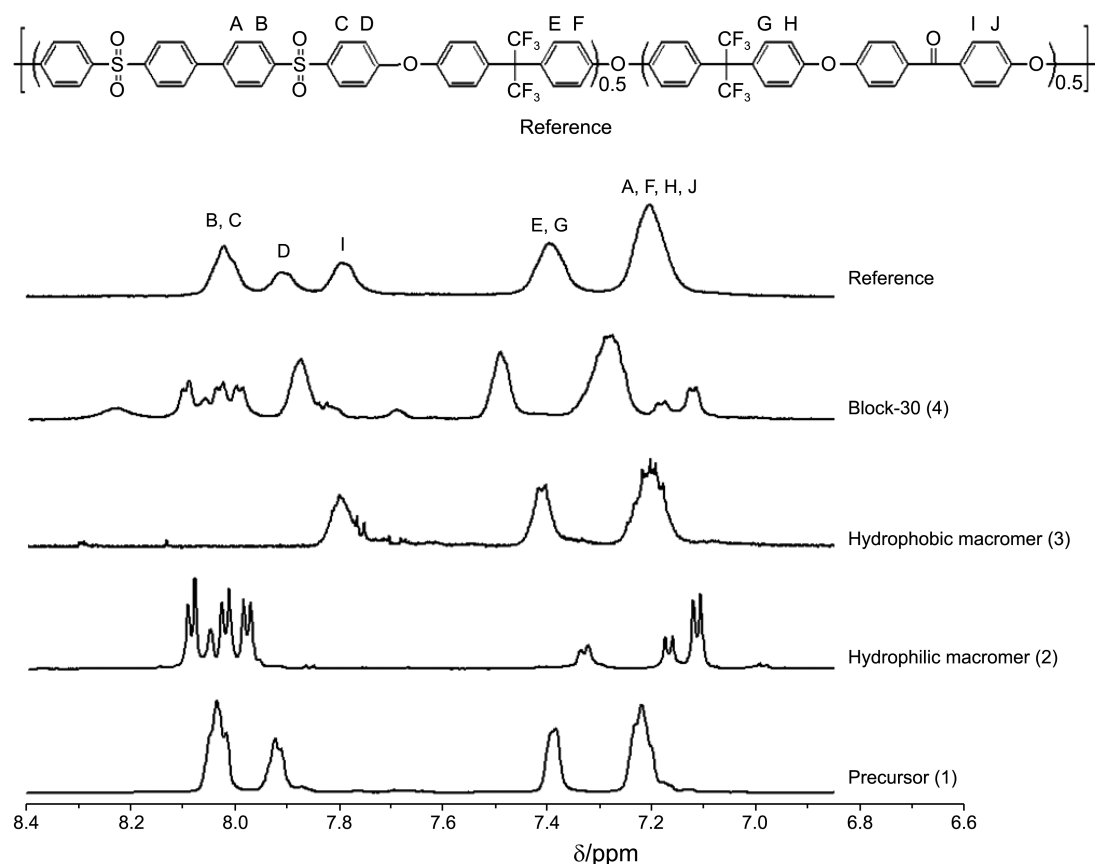
Figure 1. The ^{1}H NMR spectra of hydrophilic and hydrophobic macromers, reference, and Block-30.

Dean-Stark trap, and an argon trap. The reaction conditions and work-up procedures were carried out as described for the preparation of the hydrophilic part to obtain a hydrophobic macromer **3** (*ca.* 97% yield). Hydrophobic part is characterized by: FT-IR (KBr, cm^{-1}) 3054, 1659, 1596, 1502, 1414, 1307, 1247, 1206, 1173, 1163, 1016, 968, 928, 874, 834, 766, 738, 705, 639, 610, 560, 524; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.8 (4H), 7.4 (4H), 7.2 (8H).

Block Copolymer (4) Synthesis. Typical procedure for the synthesis of the block copolymer (**4**) was as follows. The block copolymer-30 (Block-30) was synthesized from hydrophilic (524 mg, 3.36 × 10^{-2} mmol) and hydrophobic (1.50 g, 7.8 × 10^{-2} mmol) macromers, and potassium carbonate (19.0 mg, 1.40 × 10^{-1} mmol) in DMAc/toluene through nucleophilic aromatic substitution reaction. The reaction conditions and work-up procedures were carried out as described for the preparation of the hydrophilic part. The Block-30 with the following data was produced in about 94% yield and is shown in Figure 1: FT-IR (film, cm^{-1}) 3056, 1656, 1593, 1498, 1413, 1235, 1203, 1169, 1159, 1135, 1064, 1015, 967, 953, 926, 873, 855, 831, 764, 736, 705, 686, 608, 546, 522; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10-7.98 (12H), 7.94-7.85 (4H), 7.52-7.45 (4H), 7.35-7.22 (10H), 7.20-7.18 (2H), 7.13 (4H).

Reference block copolymer with the following data was produced in about 98% yield and is shown in Figure 1: FT-IR (film, cm^{-1}) 3068, 1657, 1594, 1508, 1413, 1247, 1206, 1173, 1155, 1106 1074, 1015, 968, 928, 874, 832, 791, 766,

726, 707, 682, 610, 588, 569, 545, 523; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.91 (4H) 7.79 (4H), 7.40 (8H), 7.20 (16H).

Membrane Preparation. The copolymers were dissolved in 10% (w/v) DMSO solutions at 100 °C and then directly cast onto a glass plate and dried in vacuum at 90 °C for 15 h. After membranes were peeled off from the glass plate by immersing into deionized water, the membrane was acidified in 1 M H$_2$SO$_4$ solution at room temperature for 24 h and washed with deionized water several times to remove the residual H$_2$SO$_4$ for 12 h. The membranes were carefully dried in vacuum oven at 80 °C for 12 h. The thickness of the dried membranes was measured in the range 180-220 μm (for comparison, Nafion-115 is 152 μm thick in its dried state).

Characterizations. The solubility of the block copolymer was determined at a concentration of 10% (w/v) in a number of solvents, including water, methanol, acetone, tetrahydrofuran (THF), chloroform, dimethylformamide (DMF), NMP, DMAC, or DMSO at room temperature. Fourier transform infrared (FT-IR) spectroscopy was used to confirm the pendant functional groups on the polymers. Measurements were recorded with a Nicolet Impact 400 FT-IR spectrometer in the range 400-4000 cm^{-1} using a KBr pellet or a film. The ^{1}H NMR (600 MHz) spectra were recorded using a JNM-ECA600 instrument (JEOL Ltd.). The precursors and block copolymer samples were prepared in deuterated dimethyl sulfoxide (DMSO-d_6) and tetramethylsilane (TMS) was used as internal standard reference. Gel permeation chromatography

(GPC) was performed in DMF at 40 °C using semi-micro GPC columns from Tosoh Corporation (HLC-8320GPC) with an RI detector. For suppression of intra- and intermolecular polymer interactions and interactions of the macromolecules with the column material, LiBr (10 mmol L^{-1}) was added to the polymer solution prior to measurement. The column was calibrated with standard polyethylene oxide, and DMF was used as the eluent at a flow rate of 1.0 mL min^{-1} at 40 °C. Oxidative stability of membranes was evaluated by immersing the film into Fenton's reagent (3% H$_2$O$_2$ containing 2 ppm FeSO$_4$) at 60 °C for 24 h. Thermal stability of polymers was measured using a TA Instruments Thermal Analysis System (Q 50) from 30 to 800 °C at a heating rate of 10 °C min^{-1} under nitrogen gas (N$_2$ flow rate: 60 mL min^{-1}). Before measuring, the polymers were dried for 12 h at 90 °C in vacuum to remove moisture. DSC of the polymers was measured using a TA Instruments Thermal Analysis System (Q 20) from 20 to 200 °C at a heating rate of 10 °C min^{-1} under nitrogen gas (N$_2$ flow rate: 50 mL min^{-1}). The glass transition temperatures (T$_g$) were determined from a second scan. Tapping-mode atomic force microscopy (TM-AFM) images were obtained using a Veeco Multimode Atomic force microscope with a NanoScope IV controller. All samples were dried at 80 °C for 24 h under vacuum conditions. Samples were then imaged in equilibrated 100% relative humidity (RH) in deionized water for at least 24 h.

Water Uptake. All membranes were vacuum-dried at 90 °C for 24 h, then weighed and immersed in deionized water at room temperature for 24 h. The wet membranes were wiped with tissue paper to remove the water, and then directly weighed again on a balance. The water uptake of the membranes was calculated using the following equation:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

where W_{wet} and W_{dry} are wetted and dried membrane weights, respectively.

Ion Exchange Capacity. The ion exchange capacity (IEC; meq g^{-1}) of the membranes was measured by titration method.[11,12] To this end, 0.05-0.1 g of the membranes were immersed into 40 mL of saturated NaCl solution (2 mol L^{-1}) at room temperature for 48 h to exchange H$^+$ with Na$^+$. The samples were titrated with a 0.01 N NaOH solution, and phenolphthalein was used as an indicator. The IEC of the membranes were calculated using the following equation:

$$\text{IEC} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_{\text{dry}}}$$

where V_{NaOH} is the volume of NaOH consumed (mL), C_{NaOH} is the concentration of NaOH (N) and W_{dry} is the weights of dry membranes.

Proton Conductivity. The proton conductivity of the block copolymers and Nafion-115 were measured by AC electrochemical impedance spectroscopy (Gamry Reference 600 TM potentiostat and Gamry EIS 300 software) over a frequency range of 1 Hz-1 MHz at 20 °C, 40 °C, or 60 °C.

Prior to the proton conductivity measurements the membranes were immersed in deionized water for 24 h to reach hydration equilibrium. The typical sizes of all membranes were 40 mm × 10 mm or 20 mm × 10 mm. The proton conductivity was calculated using the following equation:

$$\sigma(\text{S/cm}) = \frac{L}{R \times T \times W}$$

where σ is the proton conductivity, L (cm) is the distance between the two electrodes, R (Ω) is the resistance of the membrane, T (cm) is the thickness of the membrane, and W (cm) is the width of the fully hydrated membrane.

Results and Discussion

Block Copolymer Synthesis and Membrane Preparation. Block copolymers (**4**) were prepared from hydrophilic (**2**) and hydrophobic (**3**) macromers as follows (Scheme 1). First, the precursor (**1**) of hydrophilic macromer was prepared from BCPSBP, 6F-BPA, and excess K$_2$CO$_3$ in DMAC/toluene. The precursor was treated with 0.1 M chlorosulfuric acid in methylene chloride at room temperature for 1 h to afford hydrophilic macromer (**2**).[12] Second, hydrophobic macromer (**3**) was made from DBP, 6F-BPA, and excess K$_2$CO$_3$ in the same solvent. Finally, we synthesized block copolymers (**4**) from the phydrophilic (16 kDa) and hydrophobic (19 kDa) macromers (1:9 ratio for the block copolymer-10, 3:7 ratio for the block copolymer-30, 1:1 ratio for the block copolymer-50) using a nucleophilic substitution reaction. After precipitating in a methanol/water co-solvent, the obtained sulfonated copolymers were purified by thoroughly washing with deionized water for 24 h, dried in vacuum oven at 80 °C for 24 h. The block copolymer-50 had a high molecular weight of 66 kDa, which supported the formation of a block structure.

Membrane were prepared by dissolving the copolymer in DMSO to yield 10 wt % transparent solutions which were then casting onto a clean glass plate. After peeling off the glass plate by immersing into deionized water, the fabricated membranes were acidified by 1 M sulfuric acid, washed with deionized water several times, and carefully dried in vacuum oven. The thickness of the membranes was maintained between 180-220 μm.

Characterization of Block Copolymers. The solubility of the copolymers was determined at 10% (w/v) in various solvents at room temperature as shown in Table 1. All block copolymers were quite soluble in a wide range of polar aprotic solvents such as DMAc, NMP, DMSO and DMF, but partially soluble in chloroform and THF. All copolymers were insoluble in polar protic solvents such as methanol, ethanol and water.

Figure 1 shows the ^{1}H NMR spectrum (DMSO-d_6) spectra of hydrophilic and hydrophobic macromers and reference and block copolymers. The ^{1}H NMR spectrum of Block-30 in Figure 1 is a representative spectrum of block copolymer series. A broad signal can be observed in the range of 6.9-8.3 ppm, which corresponds to the protons on aromatic rings of

Table 1. Solubility behavior of the synthesized block copolymers in various solvents; (++) highly soluble, (+) soluble, (±) partially soluble, and (−) insoluble at 50 ℃

Solvent	Block-10	Block-30	Block-50
DMAc	++	++	++
NMP	++	++	++
DMSO	++	++	++
DMF	++	++	++
Chloroform	±	±	+
THF	±	±	±
Acetone	−	−	−
Methanol	−	−	−
Water	−	−	−

the polymer main chain.[13] Due to the strong electron-with-drawing property of the sulfone group, NMR signals of the aromatic protons were usually shifted to low fields (de-shielding effect). However, the aromatic protons of our block copolymers fabricated by post-sulfonation method had resonance at higher field than expected, probably due to the sulfonation of the aromatic protons which are activated by an adjacent electron-donating groups. Therefore, the proton signals of the adjacent sulfonated aromatic ring (> 7.96 ppm) did not shift a lot to downfield compared to the starting polymers (precursor (**1**)). ^{1}H NMR analysis of block copoly-mer-50 was confirmed as 48% sulfonation (the degree of sulfonation on each phenylene ring in the repeating unit).[5,14]

Figure 2 depicts FT-IR spectra of the block copolymer series. The absorption band located at 1003 cm^{−1} and 1015 cm^{−1} are 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 nor-malize each of the sulfonated copolymers. The peaks at 1412, 1508, and 1594 cm^{−1} arise from the C=C stretching vibration of the several aromatic groups and was observed in all spectra. A peak at 1657 cm^{−1} arises from C=O stretching vibration of the ketone group and was also observed in all spectra. Usually the typical C=O stretching vibration band arises at 1715 cm^{−1}, but this C=O band shifts to lower fre-quency due to the conjugation of the carbonyl group with aromatic double bond (conjugation effect). The successful
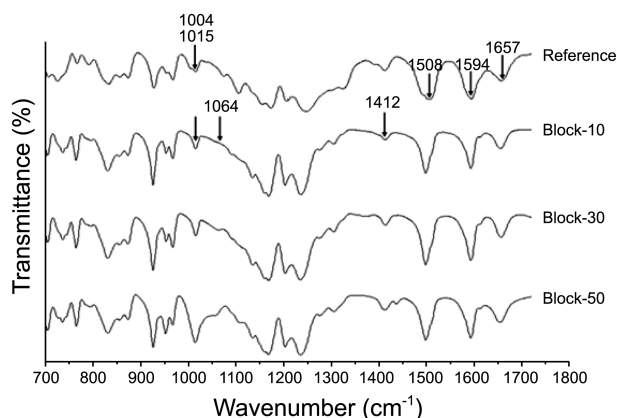
Figure 2. FT-IR spectra of the block copolymers.

inclusion of SO₃H groups was confirmed by two peaks at 1015 cm^{−1} and 1064 cm^{−1}, which were assigned to the sym-metric and a symmetric stretching vibration modes, respec-tively.[15]

In order to obtain information about the molecular weight, GPC measurement of the fabricated block copolymers in DMF at 40 ℃ was performed. The reference block copoly-mer was a high molecular weight polymer having a distri-bution with $M_{max} \approx 68,000$ g mol^{−1}. The maximum of the molecular weight distribution for the block copolymer-50 ($M_{max} \approx 204,400$ g mol^{−1}) was higher than that of the refer-ence copolymer, and any amounts of low molecular weight components were not detected in all copolymers. The number-average molecular weights (M_n) of the copolymers by GPC were measured in the range of 8-16 kDa, whereas the theoretical M_n values were calculated in 16-19 kDa. Deviations between the experimental and the targeted M_n values might be occurred by some contributions in the experimental polycondensation reaction. The polydispersity indices (PDI) varied from 2.4 to 6.6 and in Table 2 the M_n, M_w, M_{max}, and PDI values of the copolymers are listed.

Oxidative Stability. A Fenton's reagent test was perform-ed with all fabricated membranes and commercial Nafion-115 to examine the radical oxidative stability of the polymer membranes. The membranes were soaked in 3% H_2O_2 at 60 ℃ for 1 h before testing. The stability was characterized by the remaining weight (RW) percentage of the membranes and the time at which the membrane began to dissolve (τ_1). This method has been used to simulate the oxidative reaction by the attack of radical species (HO• and HOO•) during the fuel cell operation.[16] As shown in Table 3, block copolymer-10 and -30 and Nafion-115 membranes showed greater than 96% RW after the Fenton's reagent test and were still very tough, indicating highly oxidative stability. However, the highly sulfonated block copolymer-50 membranes displayed much weaker radical oxidative stability than the block copolymer-10 and -30 membranes. The tendency of τ_1 has also shown almost consistent with that of RW(%) as listed in Table 3.

Thermal Properties. The thermal stabilities of the fabri-cated copolymers and Nafion-115 were characterized by TGA and DSC techniques. The results are summarized in Table 3. The thermal spectra of all except the reference copolymer exhibited two distinct weight-losses (Figure 3). The first noticeable weight loss observed near 310 ℃ was attributed to the loss of sulfonic acid groups, and the second

Table 2. Number average molecular weight (M_n), weight average molecular mass (M_w), maximum molecular weight (M_{max}) and PDI (polydispersity index) of the block copolymers

Copolymers	M_n^{target}	M_n^{exp}	M_w	M_{max}	PDI (M_w/M_n)
Reference	15800	16000	38000	68000	2.4
Block-10	18700	9400	28000	60700	3.0
Block-30	18100	8000	52700	192200	6.6
Block -50	17500	12500	66000	204400	5.3

**Table 3.** Oxidative and thermal stability of the block copolymers and Nafion-115

Polymers	Oxidative stability		T_g (^{o}C)	T_d (^{o}C)	
	RW(%)[a]	τ_1(h)[b]		5%	10%
Reference	99	> 12	174	479	502
Block-10	96	5.5	140	432	510
Block-30	97	5.5	143	240	445
Block-50	91	2.5	151	291	335
Nafion-115	99	> 12	~100[c]	355	397

[a]Weights retained after treating the membrane in Fenton's reagent at 60 ^{o}C for 1 h. [b]Began to dissolve in Fenton's reagent at 60 ^{o}C. [c]Reference [18]
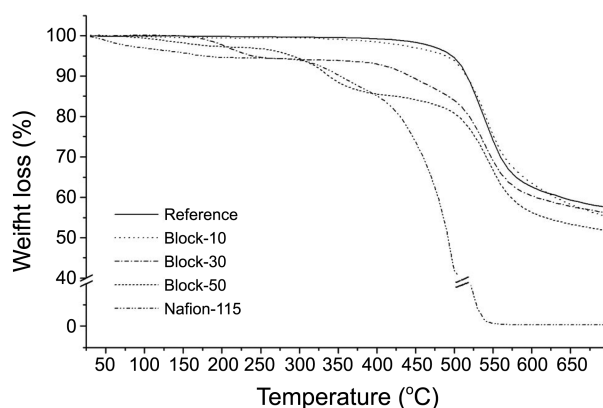
Figure 3. Comparison of TGA curves of block copolymers and Nafion-115 measured at 10 ^{o}C min^{-1} under N_2 gas.

weight loss near 500 ^{o}C is primarily due to decomposition of the polymeric backbone. Reference and block copolymer-10 were quite stable which were much higher than anticipated. However, the other two copolymers and Nafion-115 were less stable because they have the high-level degree of sulfonation and the intrinsic nature of aliphatic polymer, respectively. The weight loss of the block copolymer-30, -50, and Nafion-115 in the range of 100-240 ^{o}C was attributed to the desorption of water bonded to the sulfonic groups.[14] At the higher DS, the initial 5% weight loss of block copolymer-30 and -50 were significantly lower, approximately 240 and 290 ^{o}C, respectively. This may be due to difficulty with the water removal, or there could be more than one origin of the weight loss while investigating post-sulfonated polymer samples.[17] The observed thermal behaviors confirmed the suitability of the prepared membranes for use in elevated temperature applications.

Figure 4 shows DSC thermograms (second heat) of block copolymers as a function of the DS. Although the reference block copolymer had a higher T_g than the other block copolymers, the T_g of the other fabricated copolymers increased with increasing ionic groups in the polymer backbone (ionomer effect). This trend should be purely attributed to the increment in molecular bulkiness and enhancement of the intermolecular interaction between pendant ions *via* hydrogen bonding. The range of T_g values was measured between 140 and 151 ^{o}C. A summary of the thermal pro-
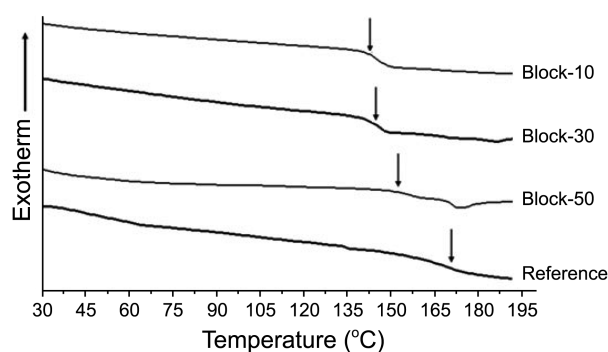
Figure 4. DSC analysis of the block copolymers.

perties of the copolymers is given in Table 3.

Water Uptake and IEC. Water uptake of some membranes is correlated with their IEC. Water plays an important role in allowing protons of an anode to smoothly transfer to the cathode. However, if water uptake is higher, it can be difficult to keep the mechanical strength and morphology of the membranes.[19] Therefore, the control of water uptake is a very important aspect. In general, hydrocarbon-based electrolyte membranes require number of sulfonic acid groups to achieve the comparable proton conductivity with the Nafion 115 membrane. However, increasing -SO_3H groups in the polymer is often accompanied by excessive water uptake and dimensional change of the membranes, which leads to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly. In our case, we also could not measure the water uptake for increasing temperature due to the weakness of membranes arising from excessive swelling.[19] Therefore, we measured proton conductivity just at ambient conditions providing adequate water uptake (Table 4).

IEC is an important indicator of the extent of sulfonation, which is related to the exchangeable ions in polymer membranes. IEC of copolymers was measured using titration methods at room temperature. The IEC values increases with increasing the hydrophilic macromer content due to the effect of sulfonic acid groups.[11,12] The water uptake and IEC values are listed in Table 4.

Proton Conductivity. The proton conductivity of block copolymer and Nafion-115 membranes was described in Table 4 and Figure 5. As expected from water uptake and

Table 4. Water uptake, ion exchange capacity (IEC) and proton conductivity values of the block copolymer membranes and Nafion-115

Polymers	Water uptake (%)	IEC (meq/g)	Conductivity (mS cm^{-1})[a]		
			20 ^{o}C	40 ^{o}C	60 ^{o}C
Reference	0	0	0	0	0
Block-10	9	0.23	15	27	37
Block-30	21	0.74	57	72	98
Block-50	31	1.05	79	120	184
Nafion-115	24	0.87	80	115	160

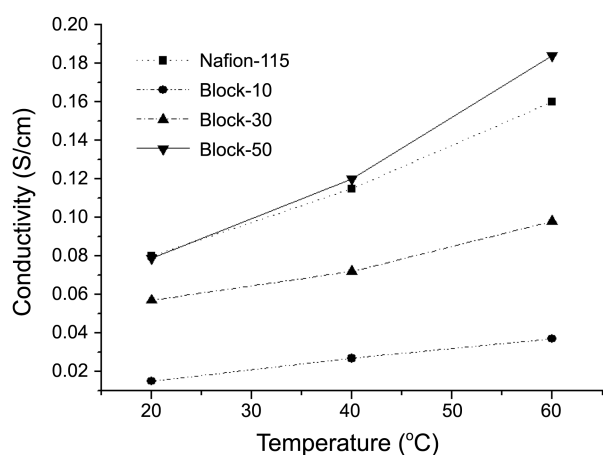[a]Membranes were soaked in deionized water for 24 h before testing and measured at 100% RH.

Figure 5. Comparison of the proton conductivity of Nafion-115 and the block copolymers as a function of temperature at 100% RH.
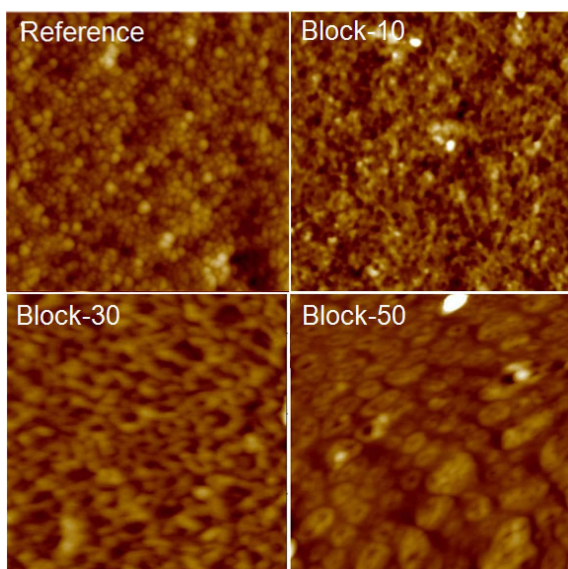

Figure 6. AFM phase image of the block copolymers (1 μm × 1 μm).

IEC, the proton conductivity increases with increasing DS. The block copolymer-10, -30, and -50 exhibited the proton conductivity values of 15, 57 and 79 mS cm^{-1}, respectively, while the conductivity of Nafion-115 is 80 mS cm^{-1} under the same conditions. Block copolymer-50 showed better performance than Nafion-115 at elevated temperature. It might be indicated that block copolymers have formed good cation-transport pathways *via* block formation within the membrane.[3-6]

Morphological Characterization. Microphase-separated morphologies of the cast film surfaces as shown in Figure 6 were characterized by TM-AFM.[5,6,20] It has been shown that water adsorbed on the surface of a sample increases adhesive forces between the tip and the sample. The membrane samples were usually immersed in deionized water under ambient conditions on a 1 μm × 1 μm scale before the test, in order to detect ionic cluster in the membranes. AFM images of the membranes in 100% RH were separated between hydrophilic and hydrophobic domains. In these films, the ionic groups adsorb water, resulting in an increased phase lag. Consequently, the hydrophilic domains of the films appear darker in the TM-AFM phase images while the hydrophobic domains appear brighter. Based on the AFM phase images, it can be concluded that IEC and proton conductivity increase with an increase in the hydrophilic macromer content due to the formation of effective cation-transport pathways.

Conclusions

In conclusion, we have synthesized hydrophilic and hydrophobic macromers *via* nucleophilic aromatic substitution polymerization. The block copolymers have also been successfully synthesized from the hydrophilic and hydrophobic parts by the same reaction. The resulting block copolymers showed good thermal stability and were soluble in some organic solvents. This suggests that these hydrocarbon polymer membranes have adequate thermal properties for application in fuel cells because their thermal decomposition is detected at temperature above 240 °C. The proton conductivity of block copolymer-50 was 184 mS cm^{-1} at 60 °C and 100% RH. The block copolymer-50 showed higher proton conductivity than Nafion-115 at the same conditions. This result indicates that the morphology of block copolymer-50 effectively makes well-formed ion rich phase compared to Nafion-115. Further research including a sing cell test on the title polymers under progress in this laboratory will be reported elsewhere.

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