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Sulfonated Block Poly(arylene ether sulfone) Membranes for Fuel Cell Applications via Oligomeric Sulfonation

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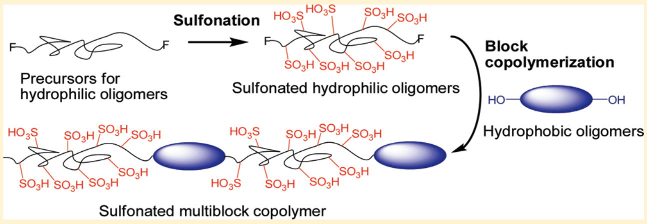
Supporting Information



ABSTRACT: Poly(arylene ether sulfone) multiblock copoly. were synthesized via oligomeric sulfonation. The successful oligomeric sulfonation enabled multiblock copolymer membranes with different hydrophobic block moiety (biphenyl and naphthalene units). High local concentration of sulfonic acid groups within the hydrophilic blocks enhanced the phase separation between hydrophilic and hydrophobic moiety. Rigid, nonpolar, and planar hydrophobic moiety such as naphthalene groups were effective in increasing proton conductivity and decreasing gas permeability. The multiblock copolymers with naphthalene hydrophobic units with IEC = 2.01 mequiv/g showed comparable proton conductivity to Nafion NRE 212 membrane (0.91 mequiv/g) at >40% RH. The longer blocks were found to increase a characteristic factor (ratio of the proton conductivity to the water volume fraction) as well as phase separation. The membrane showed relatively low oxidative stability under Fenton's test conditions due to higher water uptake and swelling. However, low gas permeability could compensate this drawback for fuel cell applications.

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) have received considerable attention as clean, efficient energy devices. Their applications range from mobile electrical power to transportation.[1,2] The proton exchange membrane is one of the key materials of the PEMFC in term of performance and production cost. Perfluorosulfonic acid (PFSA) ionomer membranes such as Nafion have been most used as a standard PEMFC membrane; however, the high cost, low glass transition temperature, and environmental incompatibility of the PFSA membranes have impeded the widespread commercialization of PEMFCs. A number of alternative membranes have been proposed for PEMs. Hydrocarbon-based polymer electrolyte membranes are attractive candidates due to their flexibility in molecular design and synthesis. Aromatic polymers such as poly(arylene ether sulfone)s,[3−6] poly(arylene ether ketone)s,[7−9] polyimides,[10−13] and others[14−24] have been investigated as a base skeleton for sulfonation. Some of these sulfonated membranes have been reported to exhibit improved fuel cell performance.[25−28] For the practical PEMFC application, the conductivity and durability under high temperature, low relative humidity (RH) conditions need further improvement.

Block copolymerization of sulfonated aromatic polymers has been suggested as one of the successful strategies for this purpose.[29−32] The sequential block structure can enhance the phase separation between hydrophilic and hydrophobic moiety, and therefore much higher proton conductivity has been achieved without sacrificing other favorable properties such as mechanical and thermal stability. McGrath and co-workers reported that partially fluorinated multiblock sulfonated poly(arylene ether sulfone)s have comparable proton conductivity to that of Nafion 112 at 80 °C and 30% RH.[33] Recently, introduction of sulfonic acid clusters has been proved to be effective in increasing proton conductivity under low RH conditions.[34]

In addition to the chemical and physical properties, the synthetic route for the sulfonated block copolymers is another important issue. There are typically two synthetic methods: copolymerization of presulfonated monomers and postsulfonation of block copolymers. In the former, available presulfonated monomers are few and limit the flexibility in the design of hydrophilic blocks. In the latter, more choices are available as reactive monomers for providing high molecular weight precursor block copolymers. However, the sulfonation of block copolymers is sometimes accompanied by the production of structural defects, which can be difficult to remove from the final products.

Recently, we have reported a series of sulfonated block copolymers by the postsulfonation method.[35,36] The block copolymer (SPESK, sulfonated block poly(arylene ether sulfone ketone)) membranes contained a high density of sulfonic acid groups in the hydrophilic component and showed a unique phase-separated morphology, with well-interconnected proton transport pathways. The SPESK membranes were highly proton conductive at high temperature (110 °C) and low relative humidity (40% RH) and showed fuel cell performance comparable to that obtained with a Nafion membrane.[37] While the SPESK membranes already appear to be promising as alternative PEMs, our

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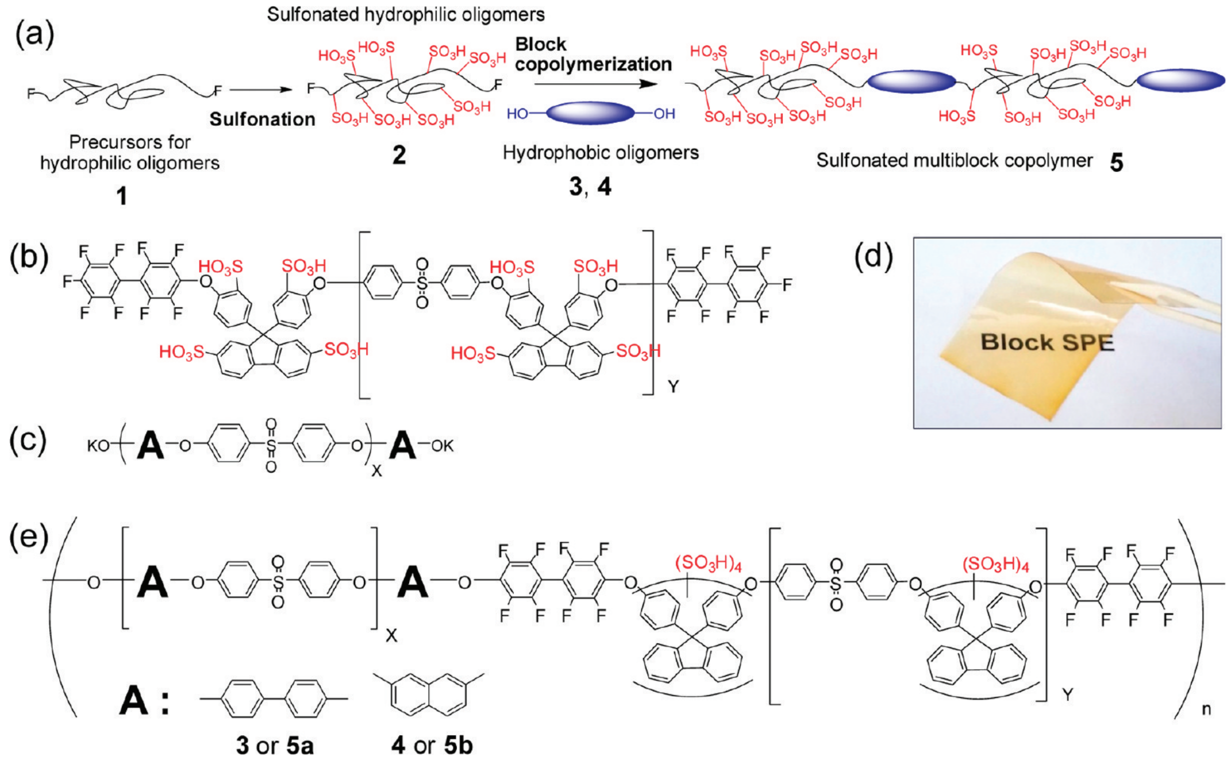

Figure 1. (a) Conceptual preparation scheme of sulfonated block copolymers; (b) structure of sulfonated hydrophilic oligomers **2**; (c) structure of hydrophobic oligomers **3** and **4**; (d) photo of **5a** membrane; (e) structure of sulfonated block copolymers **5a** and **5b**.

interest has focused on further improvements of the synthetic method that could afford more freedom in the molecular structures, more choices in the monomer compounds, higher reactivity to obtain high molecular weight, soluble polymers, and fewer structural defects.

In this report, we present a novel method to synthesize sulfonated block copolymers via sufonation of oligomers. The sulfonation of oligomers represented in Figure 1a enables various monomers to be used for the hydrophobic block moiety. Monomers that are susceptible to sulfonation can be used. With this method, we synthesized two types of hydrophobic oligomers (biphenyl, **3**, and naphthalene unit, **4**) and incorporated them into block copolymers, as shown in Figure 1e. The membrane properties were investigated and compared with those of our previous version of the sulfonated block copolymer SPESK membrane.

■ EXPERIMENTAL SECTION

Materials. Bis(4-fluorophenyl)sulfone (FPS), 9,9-bis(4-hydroxyphenyl)fluorene (BHF), 2,7-dihydroxynaphthalene (DHNT), 4,4′-biphenol (BP), and decafluorobiphenyl (DFB) were purchased from TCI, Inc., and crystallized from toluene or toluene/ethanol depending on its purity. Potassium carbonate, calcium carbonate, cyclohexane, toluene, chlorosulfonic acid, and 1,2-dichloromethane were purchased from Kanto Chemical Co. and used as received. *N*,*N*-Dimethylacetamide (DMAc, organic synthesis grade, 99%) and *N*-methyl-2-pyrrolidone (NMP, organic synthesis grade, 99%) were purchased from Kanto Chemical Co. and dried over 3 Å molecular sieves prior to use. Nafion NRE212 membrane was purchased from Du Pont and treated with hot 5 wt % H_2O_2 aqueous solution for 1 h and boiling 1 M H_2SO_4 aqueous solution for 1 h and washed several times with deionized water.

Synthesis of Decafluorobiphenyl (DFB)-Terminated Telechelic Oligomers (1). A typical synthetic procedure is as follows ($Y = 4$). A 200 mL round-bottom flask was charged with FPS (5.8 g, 22.8 mmol), BHF (10.0 g, 28.5 mmol), potassium carbonate (7.9 g, 57.1 mmol), 50 mL of DMAc, and 25 mL of toluene. The reaction was carried out at 140 °C for 3 h with a Dean–Stark trap. Then, the temperature was elevated to 165 °C, and the reaction was continued for another 3 h to obtain a slightly viscous mixture. After the reaction, the temperature was decreased to room temperature and end-capping reagent, DFB (6.3 g, 18.8 mmol), was added to the reaction mixture. Further reaction at 100 °C for 12 h gave DFB-terminated telechelic oligomer (**1**). The reaction mixture was poured dropwise into a large excess of water. The crude product was washed with hot deionized water and hot methanol several times. Drying in vacuum oven overnight gave a DFB-terminated telechelic oligomer **1**.

Sulfonation of Oligomers 1. 300 mL of dichloromethane containing 14 g of chlorosulfonic acid was charged in a round-bottom flask. 4.1 g of DFB-terminated telechelic oligomer (**1**, $Y = 4$) was dissolved in 150 mL of dichloromethane. The solution of **1** was added dropwise into the chlorosulfonic acid in dichloromethane solution with stirring. The amount of chlorosulfonic acid was adjusted to be 5 excess equimolar to fluorenylide diphenylene unit of the oligomers **1**. The sulfonation reaction was carried out for 24 h until all of the sulfonated oligomers precipitated from the reaction mixture. The product was poured into 500 mL of cold water, and the mixture was evaporated under reduced pressure to remove most of dichloromethane. Addition of NaCl into the mixture gave a precipitation of target oligomer (**2**). The crude product was filtered, dissolved in water, and basified with 1 M NaOH to transform sulfonic acid groups in sodium salt form. The product was reprecipitated by addition of NaCl. The precipitate was filtered, redissolved in water, and dialyzed to give a pure oligomer **2** in ca. 70% yield. The product was well-dried under vacuum at 120 °C overnight prior to block copolymerization.

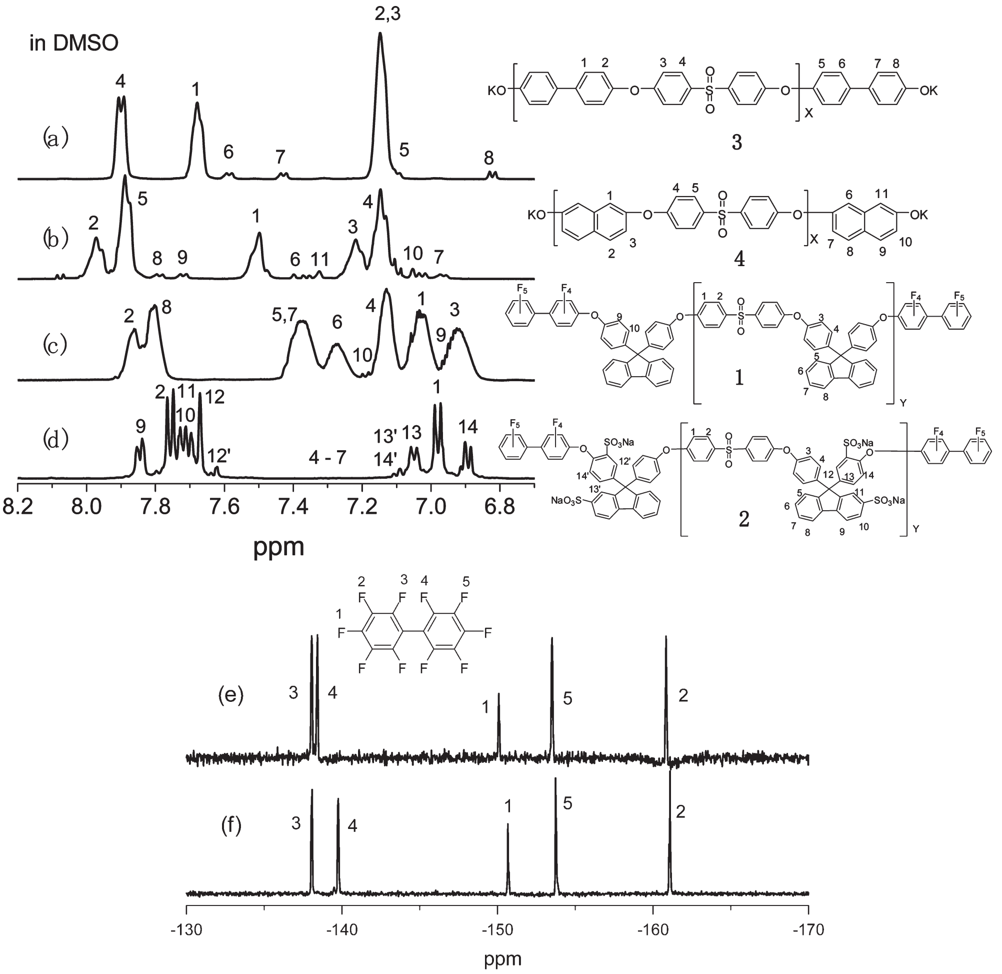

Figure 2. ^{1}H NMR spectra of (a) **3** (X = 15), (b) **4** (X = 15), (c) **1** (Y = 4), and (d) **2** (Y = 4). ^{19}F NMR spectra of (e) **1** (Y = 4) and (f) **2** (Y = 4).

Synthesis of Hydroxy-Terminated Telechelic Oligomers 3 and 4. A typical synthetic procedure for oligomers **3** is as follows (X = 15). A 100 mL round-bottom flask was charged with FPS (4.00 g, 15.7 mmol), BP (3.12 g, 16.7 mmol), potassium carbonate (4.62 g, 33.4 mmol), 32 mL of DMAc, and 16 mL of toluene. The reaction was carried out at 140 °C for 3 h with a Dean–Stark trap. Then, the temperature was elevated to 165 °C, and the reaction was continued for another 12 h to obtain a slightly viscous mixture. The mixture was diluted with 30 mL of additional DMAc and poured dropwise into 1 L of water. The crude product was washed with hot deionized water and hot methanol several times. Drying in vacuum oven overnight gave the hydroxy-terminated telechelic oligomers (**3**).

Block Copolymerization and Membrane Preparation. The mixture containing sulfonated DFB-terminated hydrophilic (**2**) and hydroxy-terminated hydrophobic oligomers (**3** or **4**) was copolymerized at 100 °C for 24–48 h in the presence of potassium carbonate and calcium carbonate (Scheme S1). DMAc or NMP was used as polymerization solvent and cyclohexane as azeotropic solvent. After the polymerization, additional DMAc was added in order to lower the viscosity. The mixture was poured into a large excess of dilute hydrochloric acid (10 mL of concentrated HCl in 1 L of water) to precipitate the product. The crude product was washed with dilute hydrochloric acid and hot methanol several times. Finally, the product was changed to sodium form by washing with 3 M NaCl aqueous solution and filterated. A white fiber of the product (**5**) was dried at 80 °C in vacuum oven overnight. The block copolymer **5** (1 g) in 10 mL of DMAc or NMP solution was cast onto a flat glass plate. Drying the solution at 60 °C for overnight gave a 50 ± 5 μm thick, transparent, and tough film. The film was further dried in vacuum oven at 80 °C for at least 6 h. The membrane was treated with 1 M H_2SO_4 aqueous solution for 4 h, washed with water several times, and dried at room temperature.

Measurements. ^{1}H and ^{19}F NMR spectra were obtained on a JEOL JNM-ECA 500 using deuterated dimethyl sulfoxide (DMSO-d_6) or chloroform ($CDCl_3$) as a solvent and tetramethylsilane (TMS) as an internal reference. Ion exchange capacities (IEC) of the membranes were measured by back-titration. A piece of the membrane (ca. 80 mg) was equilibrated in a large excess of 5 M NaCl aqueous solution for 3 days. The released HCl by the ion exchange was titrated with standard 0.01 N NaOH aqueous solution. Apparent molecular weight was measured with gel permeation chromatography (GPC) with a Jasco 805 UV detector. DMF containing 0.01 M LiBr was used as eluent. Two Shodex KF-805 columns were used for polymers and a Shodex SB-803HQ column was used for oligomers, respectively. Molecular weight was calibrated with standard polystyrene samples.

For scanning transmission electron microscopy (STEM) observations, the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 0.5 M lead acetate aqueous solution, rinsed with deionized water, and dried in vacuum oven for 12 h. The stained membranes were embedded in epoxy resin, sectioned to 90 nm thickness with Leica microtome Ultracut UCT, and placed on copper grids. Images were taken on a Hitachi HD-2300C STEM with an accelerating voltage of 200 kV.

Water uptake and proton conductivity were measured with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) equipped with a temperature and humidity controllable chamber. Weight of the membranes was measured by magnetic suspension balance at given humidity, and then water uptake ((weight of hydrated membrane − weight of dry membrane)/weight of dry membrane × 100) was calculated. Vacuum drying for 3 h at 80 °C gave the weight of dry membranes and exposure to a given humidity for at least 2 h gave the weight of hydrated membranes. Proton conductivity was measured using four-probe conductivity cell attached with impedance spectroscopy (Solartron 1255B and 1287, Solartron Inc.) simultaneously in the same chamber. Ion conducting resistances (R) were determined from the impedance plot obtained in the frequency range from 1 to 10^5 Hz. The proton conductivity (σ) was calculated from the equation $\sigma = l/(A \times R)$, where A and l are the conducting area and the membrane thickness, respectively.

Oxidative stability of membranes was tested by immersing membrane samples in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h. Hydrolytic stability test was conducted under long-term conditions (hot water of 100 °C for 1000 h). Loss of weight and molecular weight and changes in IEC were checked for the samples after the stability test.

Tensile strength was measured by universal test machine (AGS-J 500N, Shimadzu) attached with a temperature and humidity controllable chamber (Bethel-3A, Toshin Kogyo). Stress vs strain curves were obtained for samples cut into a dumbbell shape (DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)). The measurement was conducted at 60% RH and 80 °C at a stretching speed of 10 mm/min.

Hydrogen and oxygen permeability was measured with a gas permeation measurement apparatus (20XFYC, GTR-Tech Inc.) and concentration of the permeated gases was quantified with a gas chromatography (GC, G2700T, Yanaco) with thermal conductivity detector. Argon and helium were used as a carrier for the measurement of hydrogen and oxygen, respectively. Membranes were placed in the center of the permeation cell, and the test gas was introduced onto one side of the membrane at a flow rate of 20 mL/min. Carrier gas was introduced onto the other side of the membrane at the same flow rate and was analyzed by the GC. The same humidity conditions were applied to both test and carrier gases to ensure homogeneous wetting of the membrane samples. The membrane was equilibrated until stable permeation data were obtained. The gas permeability coefficient, Q (barrer = 1×10^{-10} cm^3 (STP) cm cm^{-2} cm^{-1} $mmHg^{-1}$), was calculated by eq 1

$$Q = \frac{273}{T} \times \frac{1}{A} \times B \times \frac{1}{t} \times l \times \frac{1}{76 - P_{\mathrm{water}}} \qquad (1)$$

where T (K) is the absolute temperature, A (cm^2) is the permeation area, B (cm^3) is the volume of the test gas permeated through the membrane, t (s) is the sampling time, l (cm) is the thickness of the membrane, and P_{water} (cmHg) is the water vapor pressure.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Telechelic and Sulfonated Oligomers. Oligomers for hydrophilic precursor (**1**) and two hydrophobic blocks (**3**, **4**) were successfully synthesized by polycondensation of hydroxy- and fluorine-terminated monomers. The prepared DFB-terminated precursor (**1**), sulfonated DFB-terminated (**2**), and OH-terminated (**3**, **4**) oligomers were analyzed by GPC and NMR as shown in Figures 2 and S1 and Table 1.

Figures 2c and S1 show the ^{1}H NMR spectrum in DMSO and GPC curve of **1** ($Y = 4$), respectively. Five distinct fluorine peaks assigned to the end groups were observed in the ^{19}F NMR spectrum (Figure 2e). The experimental Y value calculated from the GPC data was close to the expected value. The average Y values were 5.9 for $Y = 4$ and 9.8 for $Y = 8$, which were slightly higher than the values expected from the feed monomer compositions. Polydispersity was narrow as shown in Figure S1, implying no side reactions such as cross-linking by DFB.

Table 1. Expected and Experimental Degree of Polymerization and Molecular Weight of Oligomers

1				3				4			
Y^a	Y^b	$M_n{}^b$	M_w/M_n	X^a	X^b	$M_n{}^b$	M_w/M_n	X^a	X^b	$M_n{}^b$	M_w/M_n
4	5.9	4.3	1.8	15	28.1	11.4	2.2	15	11.5	4.6	2.6
8	9.8	6.5	2.2	30	34.4	13.9	2.5	30	23.2	8.9	2.7

[a] Calculated value from the feed monomer ratio. [b] Determined by GPC (calibrated by polystyrene standards).

On the basis of the experimental Y value of oligomeric precursor **1**, 5 excess equimolar chlorosulfonic acid was used for the sulfonation reaction. Sulfonation reaction of **1** with chlorosulfonic acid was conducted in dichloromethane solution. Excellent solubility of oligomers **1** compared to the corresponding block copolymers assured facile, complete sulfonation. Figure 2d shows ^{1}H NMR spectrum of the sulfonated oligomer **2** ($Y = 4$). All of the proton peaks of unsulfonated fluorenylidene biphenylene units (3−8 in **1**) disappeared, which confirmed complete sulfonation or 100% degree of the sulfonation. The other aromatic rings were intact and a set of five distinct peaks in the ^{19}F NMR spectrum (Figure 2f) was assigned to the perfluorinated biphenylene end-capped groups, supporting no degradation of the end groups during the sulfonation. Unlike the sulfonation of block copolymers, the oligomeric sulfonation was not interfered by the solubility of precursors due to good solubility of the oligomeric precursors in halogenated hydrocarbon solvents.

For the successful block copolymerzation, purification of the sulfonated oligomers was crucial. A combination of precipitation from aqueous solution with sodium chloride and subsequent dialysis was found to be effective in isolating pure sulfonated oligomers in high yield. High purity of the oligomers was confirmed by ^{1}H and ^{1}H−^{1}H gradient COSY 2D NMR spectra (Figures 2d and S2, respectively), in which degradation and/or side reactions were not detected.

OH-terminated hydrophobic oligomers **3** and **4** were also characterized by ^{1}H NMR and GPC as shown in Figure 2a,b, Figure S1, and Table 1. Protons attached to OH-terminated phenylene rings (7 and 8) of oligomer **3** appeared at higher magnetic field than those attached to the repeating unit (1 and 2) due to the electron donating property of hydroxy groups. The similar trend was also observed for the oligomer **4**. The experimental X value calculated from the GPC data for the oligomer **3** was slightly higher than the expected one, whereas the oligomer **4** showed lower experimental value. The differences might be due to different reactivity of hydroxy phenyl group.

Synthesis and Characterization of Sulfonated Block Copolymers. Block copolymerization of hydrophobic and hydrophilic oligomers was successfully conducted by a nucleophilic aromatic substitution reaction, as shown in Scheme S1. Apparent molecular weight measured by GPC was higher than 200 kDa (M_w) to form tough and flexible membranes. High apparent molecular weight as shown in Table 2 indicates that the obtained copolymers are of multiblock structure. The polydispersity index (PDI, M_w/M_n) values were relatively higher than those of our

Table 2. Properties of Block Copolymers 5a and 5b

	block copolymer	targeted IEC (mequiv/g)	experimental IEC (mequiv/g)[a]	molecular weight (kDa)[b] M_n	M_w	M_w/M_n	casting solvent
5a	X15Y4	1.8	1.78	48	240	5.0	DMAc
	X30Y4	1.2	1.29	48	507	10.6	DMAc
	X30Y8	1.7	1.71	27	689	25.5	DMAc
5b	X15Y4	1.9	2.01	36	332	9.2	DMAc
	X30Y4[d]	1.2	1.26	29	374	12.9	NMP[c]
	X30Y8[d]	1.8	1.85	37	626	16.9	NMP[c]

[a] By titration. [b] By GPC (calibrated by polystyrene standards). [c] Insoluble in DMAc. [d] Synthesized in NMP solution.

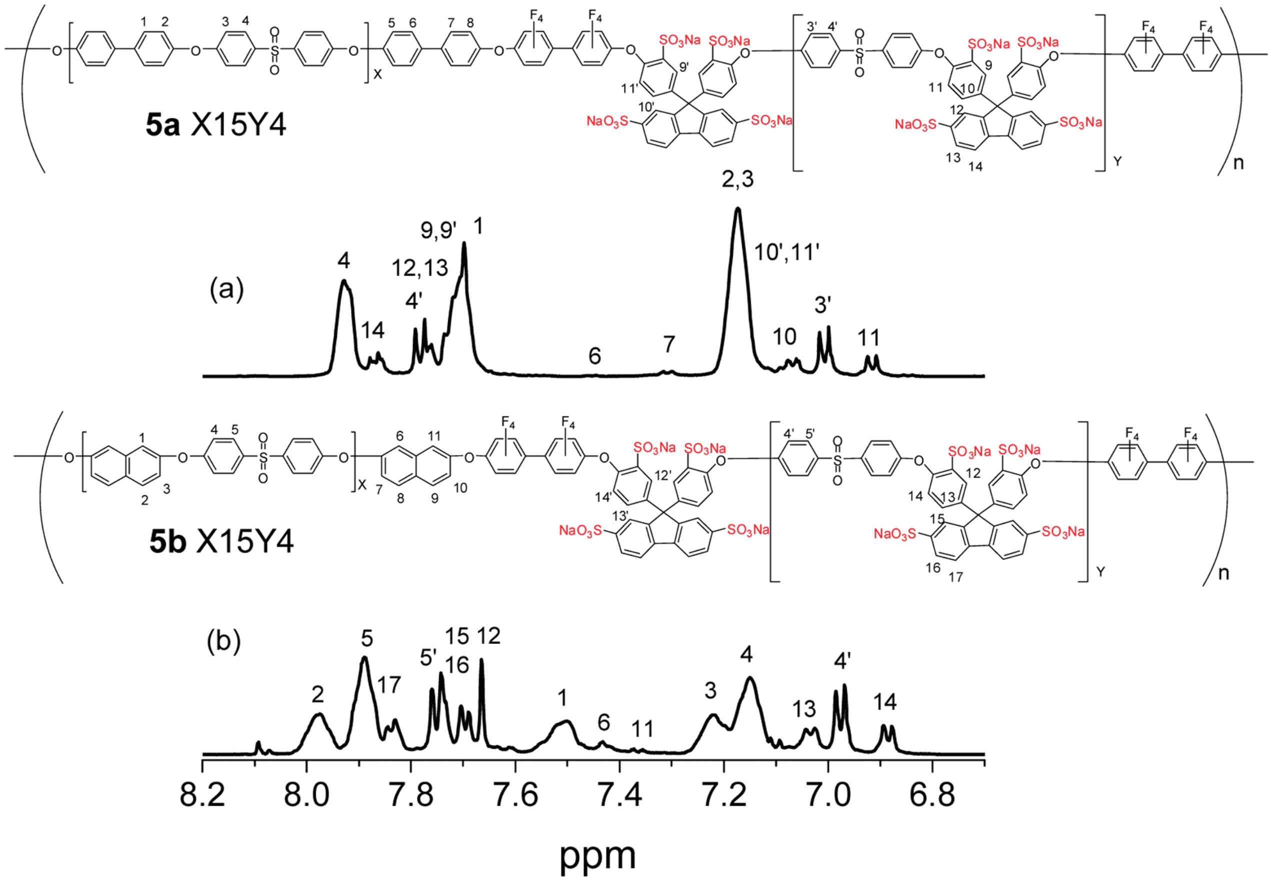

Figure 3. ^{1}H NMR spectra of X15Y4 SPE block copolymers (a) **5a** and (b) **5b**.

postsulfonated block copolymers.[35] A small amount of crosslinking via DFB terminal groups in **2**, which could not be detected in the NMR spectra, might have occurred during the block copolymerization reaction.

^{1}H NMR spectra (Figure 3) confirmed the existence and composition of both hydrophobic and hydrophilic blocks, supporting the block copolymer structure. The apparent molecular weight of the resulting block copolymers was dependent on the polymerization solvent. We have previously reported that DMAc was the best solvent for the block polymerization of poly(arylene ether sulfone)s. However, block copolymer **5b** with X30 hydrophobic block showed rather lower solubility in DMAc than **5a**. Therefore, NMP was used as polymerization solvent for **5b** X30Y4 and X30Y8 in order to increase apparent molecular weight. The planar structure of the naphthalene moiety seems to increase physical interaction between polymer chains to cause lower solubility. During the membrane casting, DMAc had to be replaced with NMP to dissolve longer block copolymers **5b**. Solution casting of both copolymers gave tough, flexible membranes (Figure 1d), whose experimental IECs (measured by titration) were fairly consistent with the targeted IEC values (calculated from the copolymer composition).

Morphologies of 5 Membranes. One of the unique properties of sequential block copolymers is the microphase-separated morphology. Figure 4 shows STEM images of some selected **5a**

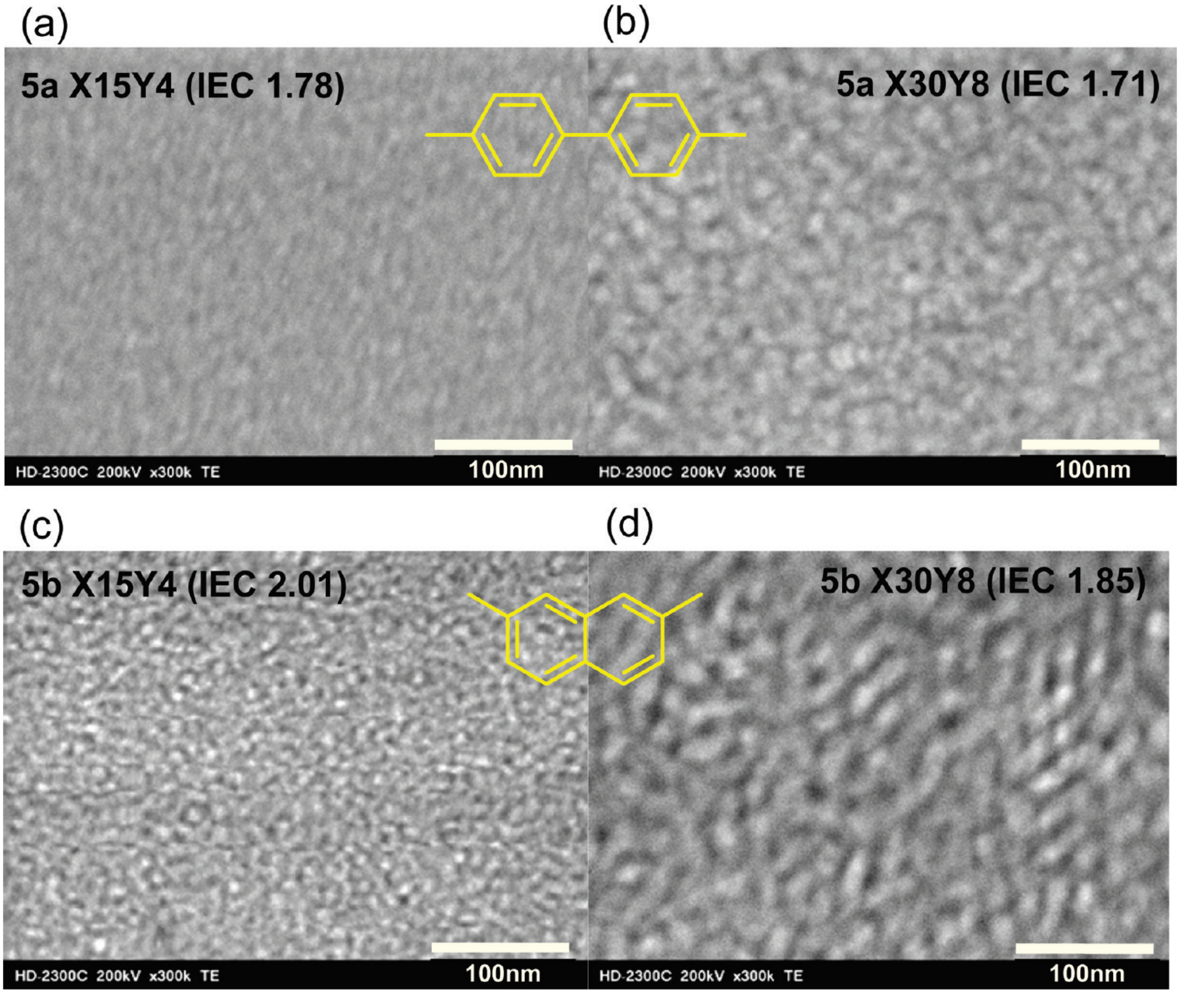

Figure 4. STEM images of lead ion-stained (a) **5a** X15Y4, (b) **5a** X30Y8, (c) **5b** X15Y4, and (d) **5b** X30Y8. All images were taken in the direction normal to the plane of the membrane, with a magnification of 300K.

and **5b** membranes at the 100 nm scale (lower magnification images are available in Figure S3). Black areas represent hydrophilic domains originating from lead ion-exchanged sulfonic acid groups, whereas light areas are hydrophobic domains. The block copolymer membranes showed distinct phase separation between hydrophilic and hydrophobic blocks. This well-defined phase separation originates from the sequential structure of the block copolymers, especially the highly sulfonated hydrophilic block. Similar phase-separated morphology was observed in our previous version of the sulfonated block copolymer (SPESK) membranes prepared by the postsulfonation method[36] and other block copolymers.[32]

The dependence of the morphology on the block length is meaningful. The hydrophilic domains became larger with increasing block length. Size of the black areas was associated not only with the hydrophilic block but also with the hydrophobic one but was less dependent on IEC. For instance, **5a** X30Y4 (IEC = 1.29 mequiv/g) showed larger hydrophilic domains than **5a** X15Y4 (IEC = 1.78 mequiv/g) in spite of the former's lower IEC (Figure S3). The trend was similar for both **5a** and **5b**. We also noticed some differences in the morphology between **5a** and **5b**. The phase separation was more distinct in **5b**. The results are well in accordance with the results of our previous random copolymers, in which a compact naphthalene hydrophobic moiety induced more developed phase separation than bulky ones.[38]

It is considered that degree of phase separation in diblock or triblock copolymer system is associated with χN and f, where χ is the Flory−Huggins interaction parameter, N is the degree of polymerization, and f is volume fraction of one block component.[39] Recent researches on sulfonated block copolymers have revealed that higher value of χN induced more phase segregation in given block copolymers.[40−42] Although the present multiblock copolymers have high PDI values, the phase separation seems yet to be related with χN value. The longer length of hydrophobic block and naphthalene moiety would contribute to increasing χN and accordingly facilitating phase segregation.

Water Uptake and Proton Conductivity of 5 Membranes. Figure 5 shows humidity dependence of the proton conductivities of the **5a** and **5b** membranes at 80 °C. The **5a** and **5b** membranes showed higher water uptake than that of Nafion due to their higher IEC values. Water uptake of the membranes was highly dependent on IEC. Longer block length resulted in higher proton conductivity when IEC was similar (compare X15Y4 and X30Y8 in **5a**). **5b** with IEC = 2.01 mequiv/g showed comparable proton conductivity to Nafion NRE 212 membrane at >40% RH and 0.17 S/cm at 90% RH. Compared to the other block

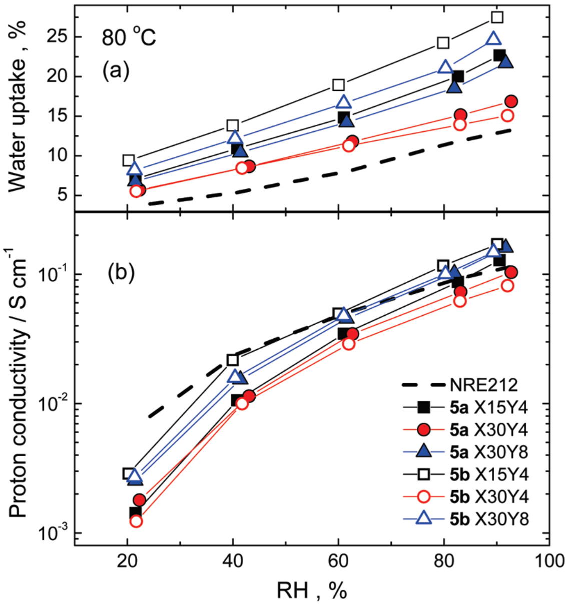

Figure 5. (a) Water uptake and (b) in-plane proton conductivity of NRE 212 and **5a** and **5b** membranes as a function of RH at 80 °C.

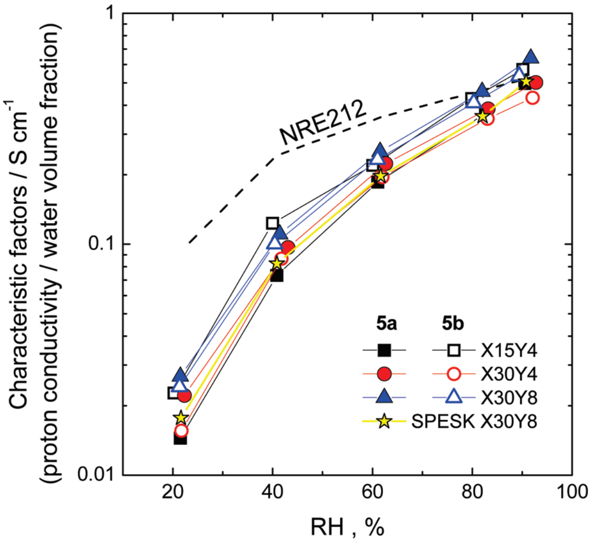

Figure 6. Characteristic factor Φ (proton conductivity/water volume fraction) of Nafion and **5a** and **5b** membranes as a function of RH at 80 °C.

copolymers such as partially fluorinated poly(arylene ether sulfone)[31] and polyimide,[30] this is one of the highest value under these conditions.

In order to facilitate a more exact, precise discussion, we propose a new parameter, a characteristic factor (Φ), which we define as the ratio of the proton conductivity to the water volume fraction. The Φ factor is a measure for evaluating membranes with similar volumetric IEC values in terms of the practical fuel cell application. Figure 6 shows the humidity dependence of Φ for Nafion NRE212, SPESK (our previous sulfonated block poly(arylene ether sulfone ketone) membrane prepared by the postsulfonation method),[43] and the **5a** and **5b** membranes. The Φ values of X30Y4 **5a** and **5b** can be compared with that of NRE212, since these membranes share similar volumetric IEC over whole RH range (e.g., ca. 1.44–1.49 mequiv/cm^3 at 80 °C and 90% RH).[43] The Φ values of X30Y4 **5a** and **5b** were similar or slightly lower than that of NRE212 at 90% RH. The results indicate that the **5a** and **5b** membranes utilized water effectively for proton conduction, as effectively as Nafion at high humidity. However, there was still a gap at low and medium RH between **5** and Nafion NRE membranes. Nevertheless, it is noteworthy that **5a** and **5b** revealed a higher Φ value than that of SPESK X30Y8 with the same block length and similar volumetric IEC (e.g., ca. 2.02 mequiv/cm^3 at 80 °C and 90% RH). This effect was more pronounced under lower RH conditions. The Φ value of **5a** X30Y8 was 0.027 at 20% RH, which was ca. 50% higher than that of SPESK X30Y8 at the same humidity. The differences in compactness and hydrophobicity of the hydrophobic block should be responsible. Compact, rigid biphenyl and naphthalenic groups were found to be effective as the hydrophobic component in improving the proton conducting behavior, which was realized by the new oligomeric sulfonation method.

Stability, Gas Permeability, and Mechanical Properties of 5 Membranes. The oxidative and hydrolytic stabilities of the **5** membranes were investigated, as summarized in Table 3. Fenton's reagent at 80 °C was used for the oxidative stability test. The **5** membranes degraded to some extent with losses in weight and apparent molecular weight. Such oxidative instability was similar to that of the SPESK membrane and was due mainly to the hydrophilic component. However, the lower gas permeability (see below) could compensate for this drawback in the practical fuel cell operation. The **5** membranes were hydrolytically more stable. Although **5b**, with a high IEC (2.01 mequiv/g), dissolved during a 1000 h hydrolytic stability test, the other **5** membranes showed minor losses in weight and apparent molecular weight. Since there are no standard methods for evaluating oxidative and hydrolytic stability of ionomer membranes, comparison with the other sulfonated aromatic membranes is unavailable. However, the stability of **5** membranes needs further improvement for practical applications.

Gas permeability is another important parameter for fuel cell membranes. The hydrogen and oxygen permeabilities of the **5** membranes were investigated under both dry and humidified conditions, as shown in Figures 7 and S4. The gas permeabilities of **5a** and **5b** were much lower than that of Nafion NRE 212 under all investigated conditions, despite the former's higher water absorbing capability (swellability). The **5b** membrane showed lower gas permeability than that of **5a**. The results seem reasonable taking their morphology into account. Planar, compact naphthalene groups are more likely to aggregate by themselves to form closely packed (or dense) hydrophobic domains, which is the major permeation pathway of the gases. Similar results were obtained for our previous random copolymers containing naphthalene groups.[38]

The physical properties of the water-swollen membranes were investigated by use of an elongation test at 80 °C and 60% RH (Figure 8 and Table S1). All of the test membranes showed high mechanical strength with Young's moduli greater than 0.6 GPa, which was much higher than that of Nafion NRE212. Maximum stress was dependent on IEC of membranes due to the change in water uptake. A general trend was that the lower IEC resulted in higher maximum stress. **5b** showed a higher Young's modulus than that of **5a**. Similar to the gas permeability, the naphthalene groups can engender

Table 3. Results of Oxidative and Hydrolytic Stability Tests

block copolymer		IEC[a]	after oxidative stability test[b] residual weight (%)	after oxidative stability test[b] residual molecular weight (%)	after hydrolytic stability test[c] IEC[a]	after hydrolytic stability test[c] residual weight (%)	after hydrolytic stability test[c] residual molecular weight (%)
5a	X15Y4	1.78	0[d]	N/A	1.78	96	96
	X30Y4	1.29	59	13	1.31	100	92
	X30Y8	1.71	45	9	1.70	94	78
5b	X15Y4	2.01	0[d]	N/A	N/A	0[d]	N/A
	X30Y4	1.26	58	13	1.25	93	95
	X30Y8	1.85	29	9	1.57	92	88
SPESK	X30Y8	1.86	33	26	1.58	99	100

[a] In mequiv/g. [b] In Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h. [c] Hydrolytic test in water at 100 °C for 1000 h. [d] Dissolved after the test.

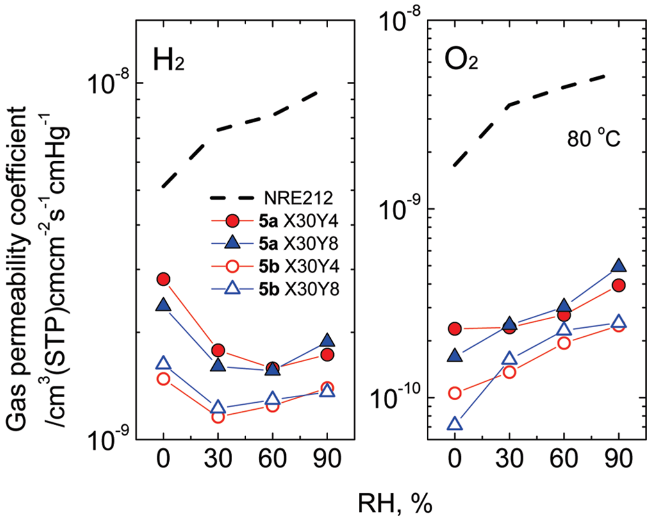

Figure 7. Humidity dependence of hydrogen and oxygen permeability coefficients of Nafion NRE212, **5a** X30Y4, **5a** X30Y8, **5b** X30Y4, and **5b** X30Y8 membranes at 80 °C.

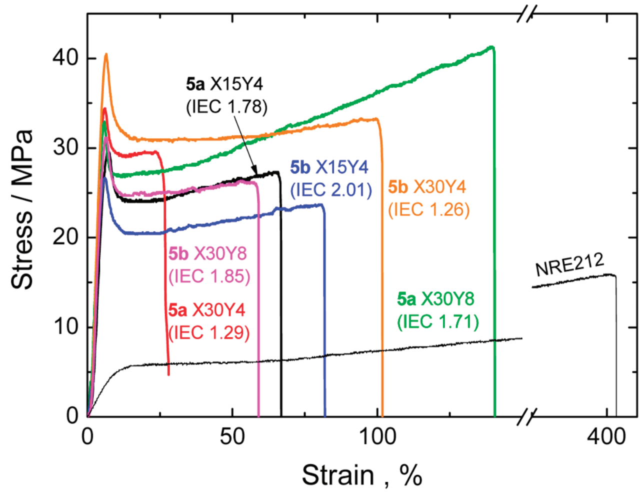

Figure 8. Stress vs strain curves of Nafion NRE212, **5a**, and **5b** at 80 °C and 60% RH.

strong hydrophobic interactions and thus increase the mechanical strength of the **5** membranes.

CONCLUSIONS

We successfully synthesized a series of novel multiblock poly(arylene ether sulfone) membranes having highly sulfonated hydrophilic block via oligomeric sulfonation. The resulting copolymers, **5a** and **5b**, revealed improved membrane performances (50% improvement in Φ at 20% RH) than our previous SPESK block membrane prepared by the postsulfonation method. The rigid and compact naphthalene unit was effective in improving nanophase separation and proton conductivity. This new synthetic route enables us not only to incorporate sulfonic acid groups into various hydrophilic blocks but also to design aromatic ionomers with multiblock architectures for finely tuning their properties.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed preparation scheme and GPC profiles of oligomers and polymers, 2D ^{1}H COSY NMR of sulfonated hydrophilic oligomers, STEM images with low magnification, temperature dependence of gas permeability under dry condition, and result of elongation test of **5a** and **5b** polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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