Synthesis and Properties of Sulfonated Block Copolymers Having Fluorenyl Groups for Fuel-Cell Applications

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ABSTRACT A series of sulfonated poly(arylene ether sulfone)s (SPEs) block copolymers containing fluorenyl groups were synthesized. Bis(4-fluorophenyl)sulfone (FPS) and 2,2-bis(4-hydroxy-3,5-dimethylpheny)propane were used as comonomers for hydrophobic blocks, whereas FPS and 9,9-bis(4-hydroxyphenyl)fluorene were used as hydrophilic blocks. Sulfonation with chlorosulfonic acid gave sulfonated block copolymers with molecular weight (M_w) higher than 150 kDa. Proton conductivity of the SPE block copolymer with the ion exchange capacity (IEC) = 2.20 mequiv/g was 0.14 S/cm [80% relative humidity (RH)] and 0.02 S/cm (40% RH) at 80 °C, which is higher or comparable to that of a perfluorinated ionomer (Nafion) membrane. The longer hydrophilic and hydrophobic blocks resulted in higher water uptake and higher proton conductivity. Scanning transmission electron microscopy observation revealed that phase separation of the SPE block copolymers was more pronounced than that of the SPE random copolymers. The SPE block copolymer membranes showed higher mechanical properties than those of the random ones. With these properties, the SPE block copolymer membranes seem promising for fuel-cell applications.

KEYWORDS: poly(arylene ether sulfone)s • block copolymers • ionomers • fuel cells

INTRODUCTION

The polymer electrolyte membrane fuel cell (PEMFC) has received considerable attention because of its high energy efficiency and lack of carbon dioxide emission. Its application ranges from mobile electronic devices to electric vehicles and stationary power sources (1). Perfluorosulfonic acid (PFSA) polymers such as Nafion (Du Pont) membranes have been most used as the polymer electrolyte membrane of the PEMFC. PFSA, however, suffers from several problems such as high production cost, environmental inadaptability (poor recyclability), and poor thermomechanical properties above 80 °C (2). Aromatic hydrocarbon polymers bearing acid functions are a possible candidate to replace the PFSA polymers. Aromatic hydrocarbon polymers are generally much less expensive than the fluorinated polymers; typical aromatic hydrocarbon polymers cost less than a few dollars per pound. Postsulfonation of these polymers is an easy and inexpensive step. Such polymers include sulfonated poly(arylene ether sulfone)s (SPEs) (3, 4), poly(arylene ether ether ketone)s (SPEEKs) (5–7), poly(arylene sulfide sulfone)s (SPSSs) (8), polyimides (SPIs) (9), polyphosphazenes (10), polybenzimidazoles (11), and polyphenylenes (12). Some of these ionomer membranes are highly proton conductive when fully hydrated; however, the conductivity at low humidity is insufficient for practical PEMFC applications. Fuel-cell operation under low relative humidity (RH) conditions has significant advantages because of a smaller size balance of the plant within the

Scheme 1. Synthesis of OH-Terminated Telechelic Oligomers
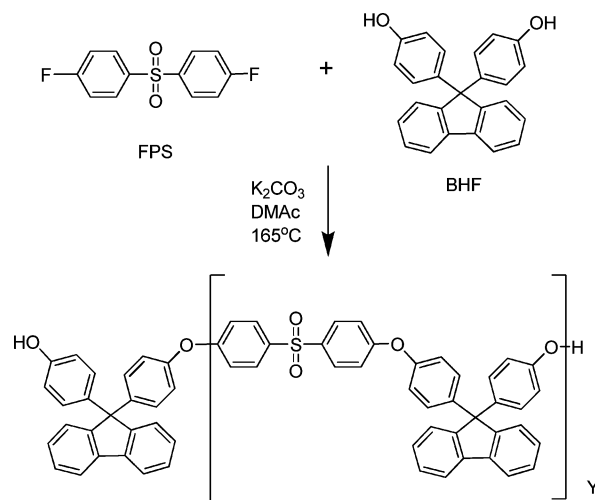
PEMFC systems. For example, the U.S. Department of Energy suggested that alternative membranes should be operable up to 120 °C and their proton conductivity should be higher than 0.1 S/cm at 10% RH and 80 °C, exceeding that of Nafion at 100% RH and 80 °C (13).

For improvement of the proton conductivity at low humidity without sacrificing water swelling (or dimensional stability), the acidity of the sulfonic acid groups and the membrane morphology are important parameters (14). The former is directly related to the number of effective protons taking part in proton conduction; i.e., higher acidity of the sulfonic acid groups leads to a higher concentration of mobile protons because of the increased number of dissociated protons. The high acidity could also enhance hydro-
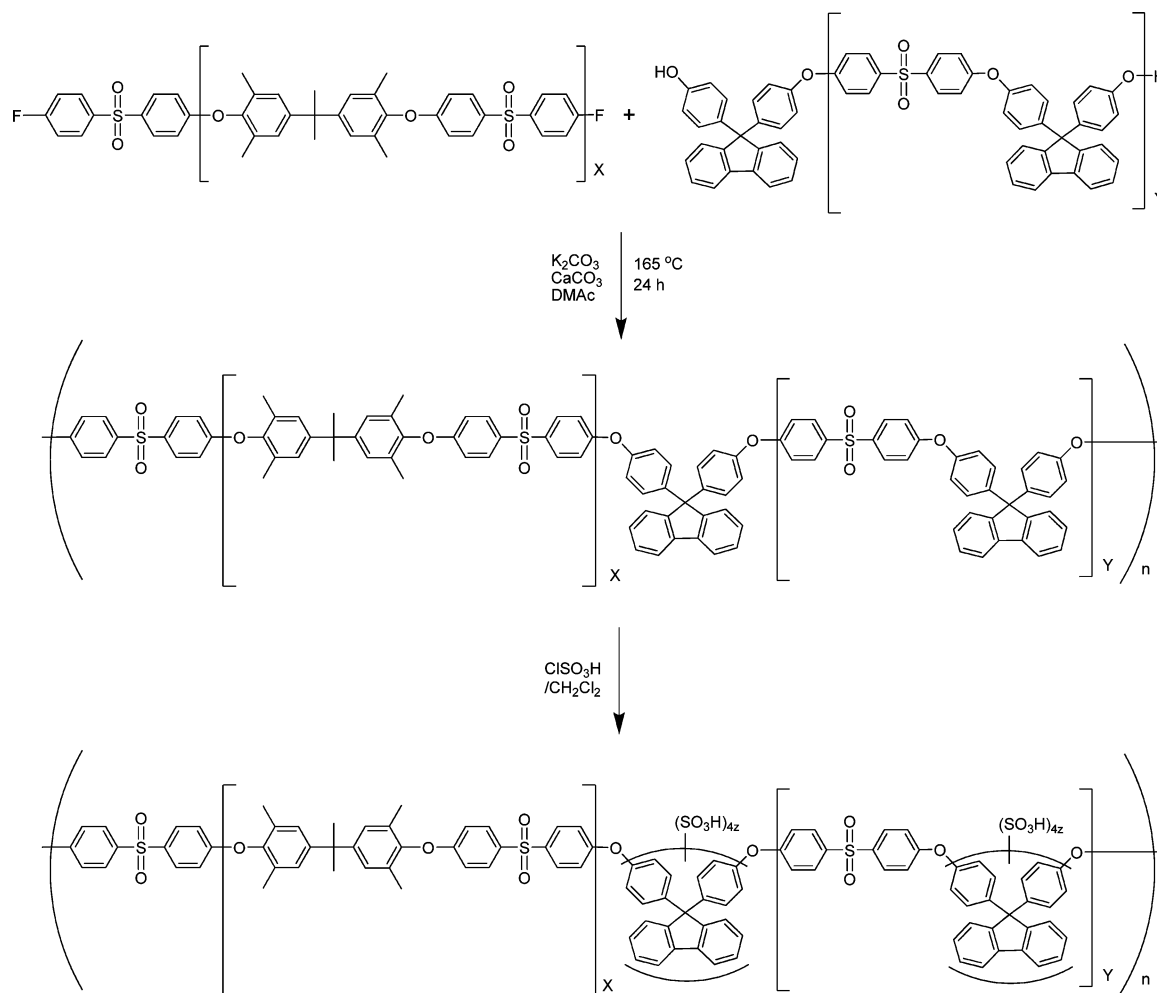
Scheme 2.   Synthesis of F-Terminated Telechelic Oligomers
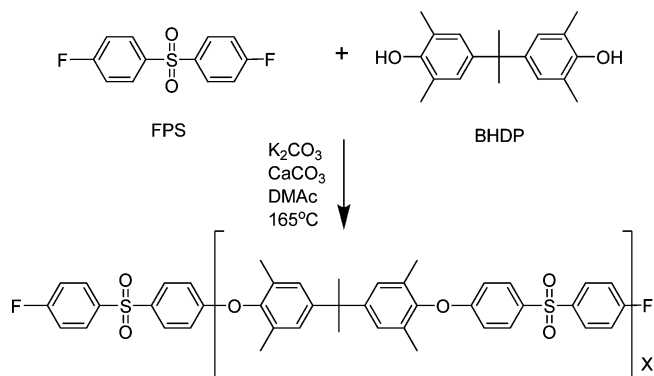
philic/hydrophobic phase separation due to increased polarity and thus provide a well-connected proton-transporting pathway (15). The membrane morphology is alternatively controllable by an appropriate molecular design. Recently, ordered morphology has been reported in hydrocarbon ionomer membranes, which contain highly sulfonated moieties (16, 17) or sequenced hydrophilic and hydrophobic groups as block copolymers (18–20). These ionomer membranes showed higher proton conductivity than those of the conventional random ones at the same hydration level even at low humidity.

Another issue for the practical synthesis of polymer electrolyte membranes is the sulfonation step. Although membranes from the polymerization of sulfonated monomers easily control the degree of sulfonation and block structure (3, 18, 19), available sulfonated monomers are very limited and high-molecular-weight enough ductile membranes can be achieved only when reactive dihydroxy comonomers are used (21). On the other hand, high-molecular-weight polymer electrolytes can be more easily realized in a postsulfonation method because of highly reactive unsulfonated monomers. The flexible choice of monomers is another great advantage of the postsulfonation method. However, the hydrophobic blocks have to be carefully designed not to be sulfonated during postsulfonation reactions in order to achieve hydrophilic/hydrophobic multiblock structures.

We have reported that SPEs containing sulfofluorenyl groups are highly proton conductive and durable for 5000 h in operating fuel cells (22). In this paper, we report multiblock SPE copolymers having improved hydrophilic/hydrophobic phase separation by postsulfonation, which has not been reported yet in nucleophilic substitution polymerization. The postsulfonation enabled us to design a higher local concentration of sulfonic acid groups within the hydrophilic block. This novel polymer structure was based on the idea
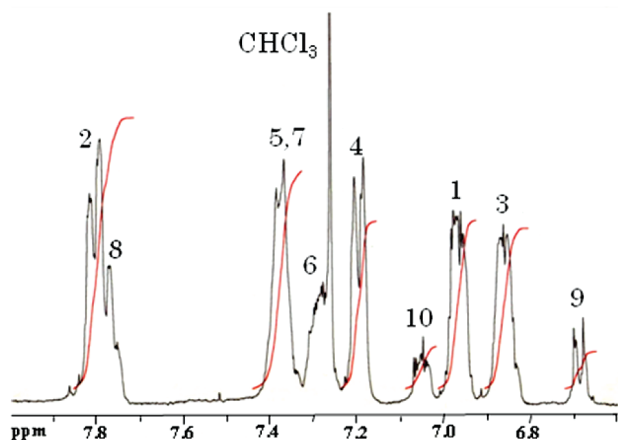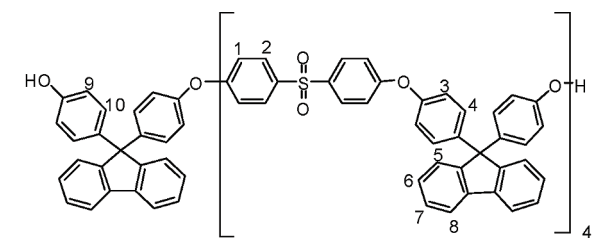
Scheme 3.   Synthesis of SPE Block Copolymers

CHCl₃

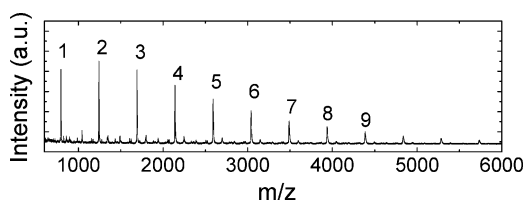FIGURE 1. ¹H NMR spectrum of a OH-terminated oligomer ($Y = 4$).

FIGURE 2. MALDI-TOF-MS spectrum of a OH-terminated oligomer ($Y = 4$).

that a higher local concentration of sulfonic acid groups should increase the hydrophilicity of the sulfonated blocks and thus result in pronounced phase separation. Such morphology may induce intermolecular proton transfer between sulfonic acid groups within hydrophilic blocks. A series of block SPEs with highly sulfonated hydrophilic blocks were synthesized. The morphology, water absorbability, proton conductivity, and mechanical properties of the membranes were investigated.

EXPERIMENTAL SECTION

Materials. Bis(4-fluorophenyl)sulfone (FPS) was purchased from TCI, Inc., and crystallized from toluene. 2,2-Bis(4-hydroxy-3,5-dimethylpheny)propane (BHDP) and 9,9-bis(4-hydroxyphenyl)fluorene (BHF) were purchased from TCI., Inc., and crystallized from toluene/ethanol. Potassium carbonate, calcium carbonate, and toluene were purchased from Kanto Chemical Co. and used as received. *N,N*-Dimethylacetamide (DMAc; organic synthesis grade, 99%) was purchased from Kanto Chemical Co. and dried over 3 Å molecular sieves prior to use. A Nafion NRE 212 membrane was purchased from Du Pont and treated with a 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 Hydroxy-Terminated Telechelic Oligomers. A typical synthetic procedure is as follows ($Y = 4$ in Scheme 1). A

100 mL round-bottomed flask was charged with FPS (0.3915 g, 1.54 mmol), BHF (0.6745 g, 1.925 mmol), potassium carbonate (0.5321 g, 3.85 mmol), 10 mL of DMAc, and 5 mL of toluene. The reaction was carried out at 140 °C for 4 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. After the reaction, the mixture was mixed with a fluorine-terminated telechelic oligomer, which was prepared in a different flask as below. Two batches of the oligomers were synthesized simultaneously, in which one was used for the block copolymerization and the other was used for matrix-assisted laser desorption time-of-flight mass spectroscopy (MALDI-TOF-MS) and NMR analyses.

Synthesis of Fluorine-Terminated Telechelic Oligomers. A typical synthetic procedure is as follows ($X = 12$ in Scheme 2). A 100 mL round-bottomed flask was charged with FPS (1.2713 g, 5.0 mmol), BHDP (1.3125 g, 4.615 mmol), potassium carbonate (1.3821 g, 10.0 mmol), calcium carbonate (10.009 g, 100 mmol), 20 mL of DMAc, and 10 mL of toluene. The reaction was carried out at 140 °C for 4 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. After the reaction, the temperature was decreased to room temperature and the mixture was mixed with a hydroxy-terminated telechelic oligomer, which was prepared in a different flask as above. Two batches of the oligomers were synthesized simultaneously, in which one was used for the block copolymerization and the other was used for NMR analyses.

Block Copolymerization. The above mixtures containing hydrophilic and hydrophobic oligomers were mixed, and the mixture was copolymerized at 165 °C for 24 h (Scheme 3). After polymerization, ca. 20 mL of additional DMAc was added in order to decrease 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. The obtained polymer was dissolved in DMAc and reprecipitated from acetone. A white fiber of the product was dried at 80 °C in a vacuum oven to obtain a block copolymer.

Sulfonation of Block Copolymers and Membrane Preparation. The block copolymers were sulfonated using a flow reactor as described in our previous report (23). A typical procedure is as follows for X12Y4. A 200 mL syringe was charged with 50 mL of a 0.01 M copolymer in dichloromethane, and another 200 mL syringe was charged with 76 mL of 0.1 M chlorosulfonic acid in dichloromethane (12 equimolar amount of chlorosulfonic acid to a fluorenylide diphenylene unit). Both syringes were connected to the reactor via a Teflon tube. Each solution was supplied to the flow reactor simultaneously using a microfeeder. The flow rates of the copolymer solution and the chlorosulfonic acid solution were set independently to maintain the same concentration in the flow reactor during the reaction. The obtained mixture was poured dropwise into 500 mL of hexane. The resulting product was washed with hexane and water several times and dried under vacuum at 80 °C overnight to obtain a white powder of the sulfonated copolymer (SPE).

The SPE (1 g) in DMAc (10 mL) solution was cast onto a flat glass plate. Drying the solution at 60 °C overnight gave a 50 ± 5 μm thick, transparent, and tough film. The film was further dried in a vacuum oven at 80 °C for at least 6 h. The membrane was treated with a 1 M H_2SO_4 aqueous solution for 4 h, followed by washing with water several times and drying at room temperature.

Measurements. ¹H NMR spectra were obtained on a Bruker AVANCE 400S using deuterated dimethyl sulfoxide as a solvent and tetramethylsilane as an internal reference. MALDI-TOF-MS spectra were recorded by orthogonal TOF-MS (JEOL AccuTOF), and dithranol was used as a matrix. The ion exchange capacity (IEC) of the SPE membranes was calculated from back-titration.
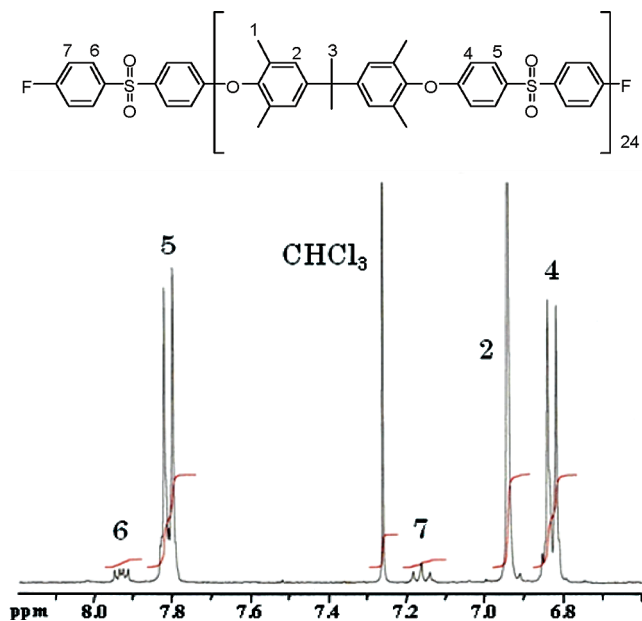
FIGURE 3. ^{1}H NMR spectrum of a F-terminated oligomer ($X = 24$).

A piece of the SPE membranes (ca. 80 mg) was equilibrated in a large excess of a 0.2 M NaCl aqueous solution overnight. The released HCl by the ion exchange was titrated with a standard 0.01 N NaOH aqueous solution. The molecular weight was measured by gel permeation chromatography (GPC) with a Jasco 805 UV detector. N,N-Dimethylformamide containing 0.01 M LiBr was used as an eluent. Two Shodex KF-805 columns were used for the polymers, and a Shodex SB-803HQ column was used for the oligomers. The molecular weight was calibrated with standard polystyrene samples.

For scanning transmission electron microscopy (STEM) observations, the membranes were stained with silver ions by ion exchange of the sulfonic acid groups in a 0.5 M AgNO$_3$ aqueous solution, rinsed with deionized water, and dried in a vacuum oven for 12 h. The stained membranes were embedded in an

epoxy resin, sectioned to 90 nm thickness with a Leica microtome Ultracut UCT, and placed on copper grids. Images were taken on a Hitachi HD-2300C scanning transmission electron microscope with an accelerating voltage of 200 kV.

The 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. The weight of the membrane was measured by a magnetic suspension balance at a given humidity, and then the 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 the dry membrane, and exposure to a given humidity for at least 2 h gave the weight of hydrated membranes. The proton conductivity was measured using four-probe conductivity cell attached with impedance spectroscopy (Solartron 1255B and 1287, Solartron Inc.). 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 $\sigma = l/AR$, where A and l are the conducting area and membrane thickness, respectively.

The tensile strength was measured by a universal test machine (AGS-J 500N, Shimadzu) attached to a temperature- and humidity-controllable chamber (Bethel-3A, Toshin Kogyo). Stress versus 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 93 % RH and 85 °C at a stretching speed of 10 mm/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of Oligomers. The synthetic procedure of the OH-terminated telechelic oligomers is shown in Scheme 1. The monomer composition was set so that the degree of polymerization (Y) would be 4, 8, or 16. The oligomerization reaction proceeded well in DMAc under typical nucleophilic substitution reaction conditions using potassium carbonate as a base. The oligomers were obtained as a white fiber and characterized by ^{1}H NMR
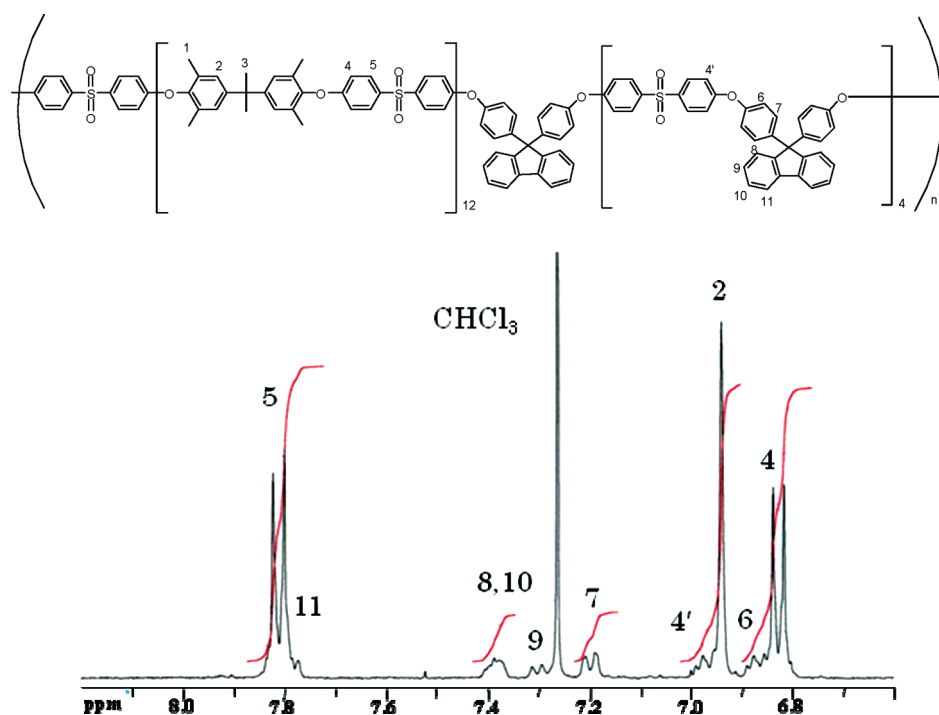

FIGURE 4. ^{1}H NMR spectrum of a X12Y4 SPE block copolymer.

Table 1. IEC and Molecular Weight of the SPE Block Copolymers

| | | | | molecular weight (kDa)[a] | | | |
| | | | | before sulfonation | | after sulfonation | |
block SPE	targeted IEC (mequiv/g)[b]	experimental IEC (mequiv/g)[c]	degree of sulfonation, z (%)	M_n	M_w	M_n	M_w
X12Y4	1.85	1.24	64	55	152	45	250
X12Y8	2.53	2.20	85	59	142	33	172
X24Y8	1.78	1.25	67	75	112	32	151
X24Y16	2.53	1.66	62	69	169	58	357

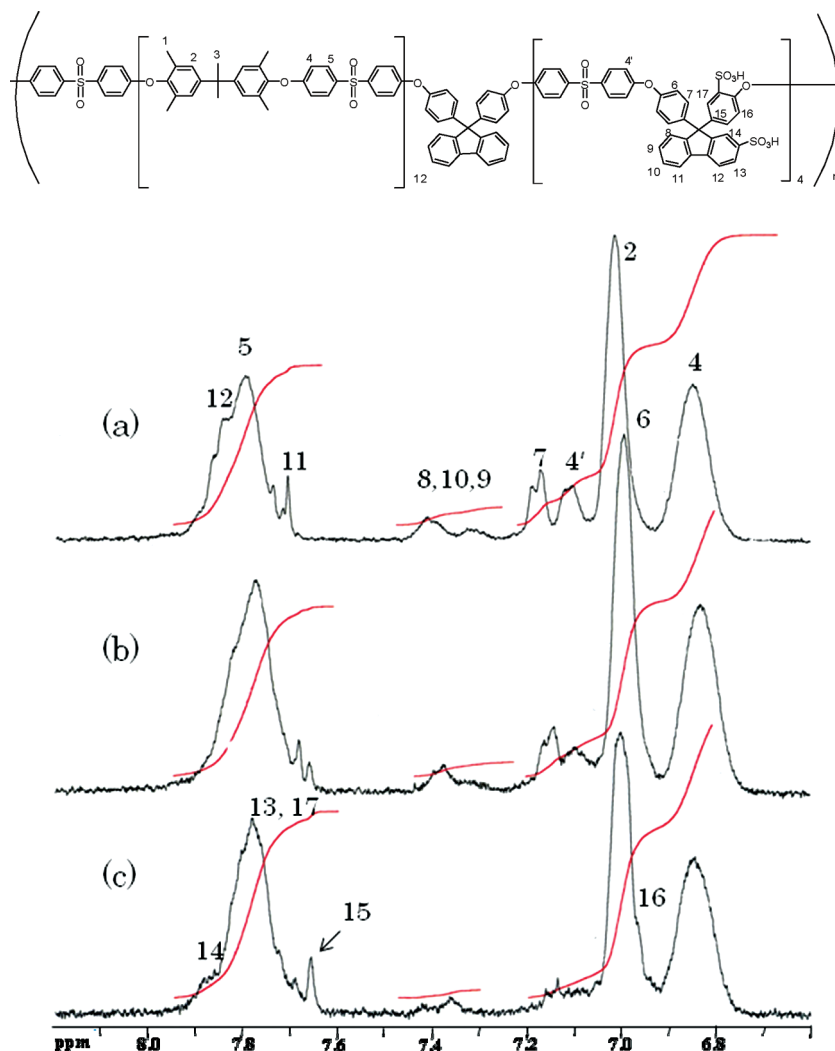[a] Determined by GPC. [b] Supposed to be 100% sulfonation. [c] Obtained from back-titration.

FIGURE 5. ^{1}H NMR spectra of X12Y4 SPE block copolymers obtained with (a) 6, (b) 9, and (c) 12 equimolar amounts of chlorosulfonic acid, respectively.

spectra. A typical example is shown in Figure 1 for the oligomer with $Y = 4$, in which protons attached to OH-terminated phenylene rings (9 and 10) appeared at higher magnetic field than those attached to oxyphenylene rings (3 and 4) because of the strong electron-donating property of the hydroxy groups. The experimental Y value calculated from the integration ratio of these peaks was 4.3, reasonably close to the expected value. MALDI-TOF-MS and GPC analyses were also used to elucidate the Y value and molecular weight distribution, as shown in Figures 2 and S1 and Table S1 in the Supporting Information. Although a relatively large molecular weight distribution was observed (for example,

the Y value ranged from 1 to 12 in the MALDI-TOF-MS spectrum), the averaged Y value was 4.1 for the MALDI-TOF-MS spectrum and 4.6 for the GPC. These values are in good agreement with the value obtained from the NMR spectra. The experimental Y values were 8.6 (NMR) and 9.8 (GPC) and 18.0 (NMR) and 15.5 (GPC) for oligomers with theoretical $Y = 8$ and 16, respectively.

The synthetic procedure of F-terminated telechelic oligomers is shown in Scheme 2. The monomer composition was set so that the degree of polymerization (X) would be 12 or 24. While the oligomerization conditions were similar to those above, excess calcium carbonate was effectively added
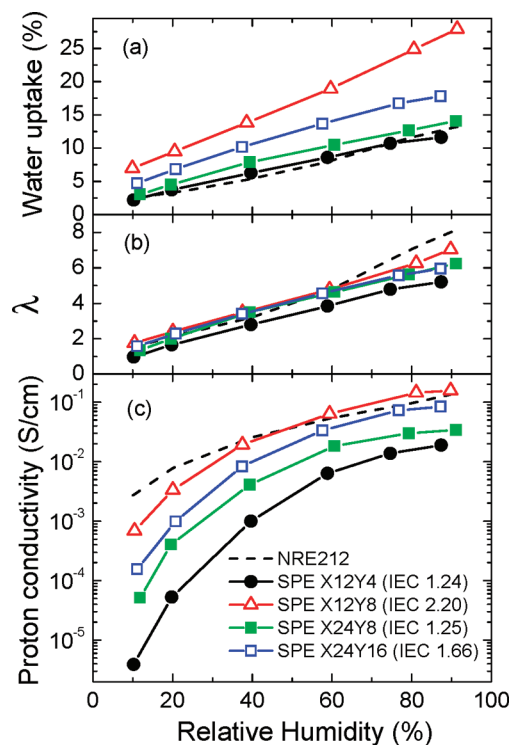
FIGURE 6. (a) Water uptake, (b) λ, and (c) proton conductivity of Nafion NRE 212 and SPE block copolymers at 80 °C as a function of the RH.

to complete the oligomerization reaction without reverse polymerization or main-chain cleavage (16, 24). The products were obtained as a white fiber and characterized by ^{1}H NMR spectra. A typical example is shown in Figure 3 for the oligomer with $X = 24$, in which protons of F-terminated sulfonylphenylene rings (6 and 7) appeared at lower magnetic field than those attached to the sulfonylphenyleneoxy rings (4 and 5) because of the strong electron-withdrawing property of the fluorine groups. The experimental X value from the integration ratio was 23.1, close to the targeted value. Similarly, the experimental X value of 11.0 was obtained for the oligomer with theoretical $X = 12$. In order to achieve the designed block copolymer structure, reactivity toward the sulfonation reaction of the F-terminated telechelic oligomers was tested by use of chlorosulfonic acid. The oligomers were intact under the tested conditions without any evidences of sulfonation, as confirmed by ^{1}H NMR spectra.

Synthesis and Sulfonation of Block Copolymers. Block copolymerization of the oligomers was conducted in the presence of potassium carbonate and calcium carbonate (Scheme 3). Four block copolymers, X12Y4, X12Y8, X24Y8, and X24Y16, were synthesized, each of which had high molecular weight ($M_n > 55$ kDa and $M_w > 112$ kDa), as confirmed by GPC analyses (Table 1). The molecular weight data suggest that the obtained copolymers were of a multiblock structure. Figure 4 shows the ^{1}H NMR spectrum of the X12Y4 block copolymer. A comparison with the NMR spectra (Figures 1 and 3) of the parent oligomers revealed that the protons of both hydroxy- and fluorine-substituted phenylene groups were absent and the other

peaks were consistent with those of the oligomers. The results support the formation of block copolymers.

The prepared block copolymers were sulfonated with chlorosulfonic acid in a dichloromethane solution. In order to control the degree of sulfonation (z in Scheme 3), 6, 9, and 12 equimolar amounts of chlorosulfonic acid to the fluorenylide diphenylene unit were reacted with the polymers. Figure 5 shows the ^{1}H NMR spectra of a SPE X12Y4 block copolymer obtained with (a) 6, (b) 9, and (c) 12 equimolar amounts of chlorosulfonic acid, respectively. As the amount of chlorosulfonic acid was increased, the proton peaks of unsulfonated fluorenylide biphenylene groups (6−11) became smaller and new peaks of sulfonated fluorenylide biphenylene groups (12−17) became larger. Under the investigated conditions, the other aromatic rings were intact during the sulfonation reaction. Although there exists the possibility of sulfonation of the phenyl ring of the bisphenol A part (2 in Figure 4) in a hydrophobic component, steric hindrances by substituent groups seem to inhibit this sulfonation reaction. A higher degree of sulfonation was achieved with higher concentration of chlorosulfonic acid; however, a too high concentration (12 equimolar condition) of chlorosulfonic acid caused main-chain degradation to some extent. As a result, 9 equimolar amount of chlorosulfonic acid was the upper limit for the sulfonation reaction. Table 1 summarizes the block length, IEC, degree of sulfonation (z), and molecular weight of the SPE block copolymers. The degree of sulfonation was determined by titration to be 64−85%. and, thus, the IEC of the SPE block copolymers ranged from 1.24 to 2.20 mequiv/g. Although 9 times excess condition was chosen as the best condition, a decrease in M_n was observed in the sulfonated polymer, implying a slight degradation of the block polymers during the sulfonation step. Also, an increase in M_w was observed because its increased hydrodynamic volume originated from repulsion between sulfonic acid groups even in the lithium salt form. Nevertheless, SPE block copolymers showed acceptable molecular weights to give ductile membranes by casting.

Water Uptake and Proton Conductivity of SPE Block Copolymers. Figure 6 shows the water uptake, λ (number of absorbed water molecules per sulfonic acid group), and proton conductivity of the SPE block copolymer membranes as a function of the RH at 80 °C. As expected, higher IEC membranes absorbed more water because of increased hydrophilicity (Figure 6a). The water uptake can be converted to the λ value, which takes both water uptake and IEC into account. It is noteworthy that λ slightly increases with an increase of the IEC value (Figure 6b). The result is consistent with our previous result of a SPE random copolymer (15). Generally, the degree of water swelling is a balance between the absorbing ability of sulfonic acid and the suppressing ability of the hydrophobic component. The SPEs bearing higher IEC are expected to possess a more developed water cluster than those of a lower IEC membrane. As a result, the high λ was observed in the SPE
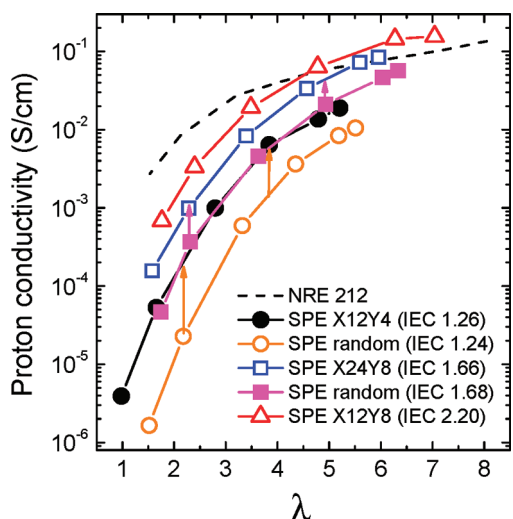
FIGURE 7. Proton conductivity of Nafion NRE 212, SPE block, and SPE random copolymers at 80 °C as a function of λ.

membrane bearing high IEC. This reason is also applied to explain the high λ of the Nafion membrane.

Similar to the water uptake, the higher IEC membranes showed higher proton conductivity from 10 to 90 % RH (Figure 6c). The SPE X12Y8 block polymer membrane with the highest IEC value (2.20 mequiv/g) showed the highest proton conductivity among the four SPEs. Its conductivity was comparable or even higher than that of the Nafion NRE 212 membrane at >40 % RH. The block length affected the water uptake and proton conductivity. When X12Y4 and X24Y8 membranes with similar IEC (1.24 and 1.25 mequiv/g, respectively) were compared, the X24Y8 membrane with a longer block length showed higher water uptake and higher proton conductivity than those of the X12Y4 membrane. This result implies that the longer block can induce a more developed phase separation than that of the shorter one. A similar behavior was observed by Lee et al., who reported higher water uptake and higher proton conductivity in their block SPEs having longer block segments (19).

The proton conductivity of SPE block copolymer membranes was plotted as a function of λ and compared with that of Nafion NRE212 and SPE random copolymer membranes in Figure 7. The X12Y4 block copolymer (IEC = 1.26 mequiv/g) showed much higher proton conductivity than that of a random copolymer with a similar IEC (1.24 mequiv/g) at any λ value. This was also the case for the higher IEC SPE X24Y8 block membrane (1.66 mequiv/g). It should be noted that the difference in proton conductivity between block and random SPE copolymer membranes was more significant at lower λ values for both high and low IEC

membranes. At $\lambda = 1-2$, a SPE X12Y4 block membrane showed ca. 5 times higher proton conductivity than the random one. The reason for the high proton conductivity might be explained by its block structure and highly concentrated sulfonic acid. In the literature, a developed phase separation between hydrophilic and hydrophobic domains accounted for the higher proton conductivity of the block copolymer membranes (25, 26). In addition, the block SPE copolymers in this report possess highly sulfonated hydrophilic blocks. This higher concentration of sulfonic acid makes the SPE more hydrophilic than other reported block copolymer membranes. We therefore have investigated the morphology of our block SPE membranes and compared it with those of the Nafion and the random SPE membranes.

Morphology of the SPE Block Copolymer Membranes. Morphologies of the membranes were investigated by STEM observation with silver-ion-exchanged samples. The images were taken at transmission electron mode, in which the black domain represents silver-ion-exchanged sulfonic acid groups (hydrophilic cluster). The Nafion NRE 212 membrane showed distinct and well-connected hydrophilic clusters even under dry conditions (Figure 8a), which are accountable for its high proton conductivity. The random SPE membrane showed much smaller hydrophilic clusters in spite of its high IEC (2.0 mequiv/g) (Figure 8b). This is a typical morphology of hydrocarbon-based ionomer membranes with a less developed phase separation. In contrast, much larger and well-developed hydrophilic clusters were observed in the SPE block copolymer membranes. The SPE X12Y4 block copolymers with IEC = 1.24 mequiv/g showed hydrophilic clusters of ca. 5−10 nm in diameter throughout the image. The hydrophilic clusters were somewhat larger and better connected for the higher IEC (1.66 mequiv/g) SPE X24Y16 block membrane. The developed hydrophilic cluster is responsible for the high proton conductivity of the SPE block copolymers at low RH or low λ.

Mechanical Properties. Figure 9 shows stress versus strain curves of selected SPE block and random copolymer membranes at 85 °C and 93 % RH. The results are summarized in Table 2. Both SPE block membranes showed high Young's moduli, 293 MPa for X24Y8 and 172 MPa for X24Y16, respectively. However, these values were smaller than that of the SPE random membrane (372 MPa). The major difference in the stress versus strain curves between random and block membranes is that only the random SPE membrane showed stress relaxation after maximum stress. The results may imply that the molecular rearrangement during stretching is unlikely to happen for the block SPE
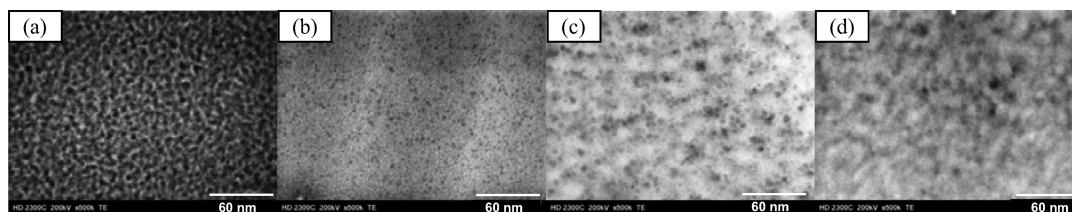

FIGURE 8. STEM images of silver-ion-exchanged (a) Nafion NRE 212, (b) SPE random (IEC = 2.0 mequiv/g), (c) X12Y4 (IEC = 1.24 mequiv/g), and (d) X12Y16 (IEC = 1.66 mequiv/g) block copolymers.
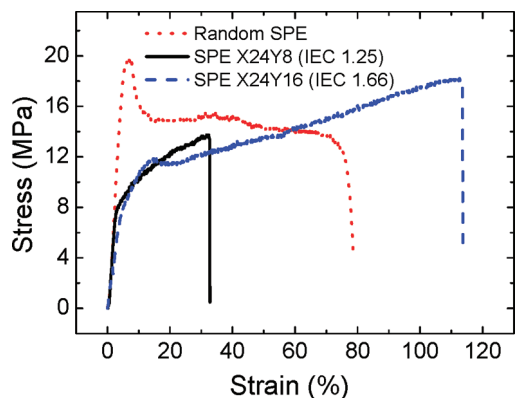
FIGURE 9. Stress versus strain curves of SPE block and random copolymers at 85 °C and 93% RH.

Table 2. Results of Elongation Tests of SPE Random and Block Copolymers at 85 °C and 93% RH

SPE copolymer	experimental IEC (mequiv/g)	strain (%)	maximum stress (MPa)	Young's modulus (MPa)
random	1.97	78	20	372
X24Y8	1.25	32	14	293
X24Y16	1.66	113	18	172

membranes. X24Y16 SPE showed high elongation due to higher water uptake than that of X24Y8. The elongation of the block copolymer was larger than that of the random SPE membrane. This is probably because in the block membranes the hydrophilic domains are of higher IEC locally and thus extend significantly under wet conditions.

CONCLUSIONS

The SPE block copolymers having highly sulfonated hydrophilic blocks were successfully synthesized. These block copolymers showed much higher proton conductivity than the random copolymers. The effect was more distinctive at low humidity conditions or low λ values. The higher proton conductivity of the block SPE membranes originated from a more developed hydrophilic and hydrophobic phase separation and better connected hydrophilic channels, which were clearly confirmed by STEM observation. Block copolymer membranes showed larger elongation than the random copolymer membrane. These properties of the SPE block membranes seem promising for fuel-cell applications. The fuel-cell performance is under investigation.

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AM900165W