

# Synthesis and Characterization of Postsulfonated Poly(arylene ether sulfone) Diblock Copolymers for Proton Exchange Membranes

SHOGO TAKAMUKU, KEN AKIZUKI, MITSUTAKA ABE, HIROYUKI KANESAKA

Fuel Cell Laboratory, Nissan Research Center, Nissan Motor Co., Ltd., 1 Natsushima-cho, Yokosuka-shi, Kanagawa 237-8523, Japan

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**ABSTRACT:** Sulfonated poly(arylene ether sulfone) diblock copolymers were studied through the postsulfonation process. Two kinds of hydrophobic oligomers with a molecular weight of 20 kDa were prepared in advance as block sequences and then coupled together to obtain diblock copolymers. One oligomer was synthesized from bis(4-hydroxyphenyl) sulfone (BHPS) and 4,4'-difluorodiphenyl sulfone (DFDPS), which was thought to be incapable of postsulfonation. The other oligomer was synthesized from hydroquinone (HQ) and 4,4'-dichlorodiphenyl sulfone (DCDPS), which successfully proceeded to a hydrophilic sequence as a result of sulfonation onto the HQ moiety after the coupling reaction. Consequently, a diblock copolymer with high molecular weight was obtained; although its intrinsic viscosity was too low to form a tough membrane because of its high rigidity and high crystallinity. Therefore, the use of decafluorobiphenyl (10F) as a termination reagent was investigated with the aim of achieving higher coupling reactivity and a kinky property. As a result, a sulfonated diblock copolymer was successfully obtained with sufficient molecular weight and intrinsic viscosity to form the membrane, as well as with adequate thermal properties. It was observed that proton conductivity, water uptake, and the water diffusion coefficient increased with higher ion exchange capacity. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 700–712, 2009

**Keywords:** block copolymers; polycondensation; polyelectrolytes

## INTRODUCTION

For the last several decades, there has been increasing interest in polymer electrolyte membrane (PEM) fuel cells for application as stationary, transportation, and portable power sources.<sup>1</sup> Extensive research efforts have produced a wide variety of PEMs such as perfluorinated sulfonic

acidic (PSA) polymers, partially fluorinated polymers, and all hydrocarbon (HC) polymers.<sup>2–4</sup> Nafion® developed by DuPont has been used as a benchmark that meets almost all of the requirements for PEMs, such as high proton conductivity (PC), adequate mechanical properties, and good adhesiveness between the PEM and electrodes. In addition, it can be used as a polyelectrolyte with catalyst particles. However, there are still some drawbacks of using PSA membranes like Nafion. In the case of application to fuel cell vehicles, the operation temperature should be increased to over 90 °C to enhance thermal efficiency. Since PSA

Correspondence to: S. Takamuku (E-mail: s-takamuku@mail.nissan.co.jp)

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membranes have a glass transition point near 100 °C, higher operation temperatures result in poor thermal stability and greater fuel permeation.

In general, HC membranes made of engineering plastics such as poly(arylene ether sulfone) (PES) surpass PSA membranes in terms of thermal stability; although they also have some weak points, including poor PC under low relative humidity (RH), which is the main issue.<sup>5</sup> For example, in random copolymers, the PC of HC membranes is not as good as that of PSA membranes, owing to the isolated proton paths under low RH, despite having equal or higher PC under a fully hydrated condition. In recent years, many researchers have been searching for ways to compensate for this low PC such as by providing microphase separations. For direct-methanol fuel cell (DMFC) applications, a number of block copolymers based on poly(styrene-co-olefin) have been developed, resulting in better selectivities, yet they still have some inherently similar problems to those of PSA membranes, because of their lower thermal stability than engineering plastics.<sup>6</sup> Recently, McGrath et al.<sup>7–9</sup> have proposed that multiblock copolymers based on PES consisting of hydrophilic and hydrophobic sequences could improve PC under low RH because of the formation of continuous effective proton paths. However, there is a problem in synthesizing such multiblock copolymers via a polycondensation reaction because of the poor coupling reactivity between the two oligomers, which results in a lower molecular weight than that needed to form tough membranes. Considering the nucleophilicity of the terminated structures, poly(imide) type block copolymers can be easily polymerized; although the issue of hydrolysis has not been thoroughly resolved so far.<sup>10–13</sup>

Therefore, the aim of this study was to enhance the reactivity of the coupling reaction by using two hydrophobic oligomers that can be expected to provide more mutual miscibility than hydrophilic–hydrophobic oligomers, as well as highly reactive fluorine-extermination moieties instead of chlorine.<sup>7,14–16</sup> With regard to the raw material cost, hydroquinone (HQ), as a commercially available dihydroxyl monomer, is more readily usable, compared with even well-known monomers such as biphenol, bisphenol A, and bisphenol AF. Some researchers have been investigating the use of a sulfonated HQ monomer<sup>17,18</sup> or a postsulfonation process after polymerization,<sup>19</sup> but these approaches have not been examined for block copolymers. In general, HQ moiety possibly leads

to precipitation-out during polymerization reaction. Thus, the use of nonsulfonated HQ to polymerize oligomers suitable for postsulfonation was investigated in this study to prevent such a phenomenon. Furthermore, as another point, this article discussed the controllability of the degree of sulfonation after obtaining block copolymers, whereas the ionic concentration on block copolymers compromised of hydrophilic and hydrophobic sequences is designed mostly when coupling reaction conducts between two oligomers.

## EXPERIMENTAL

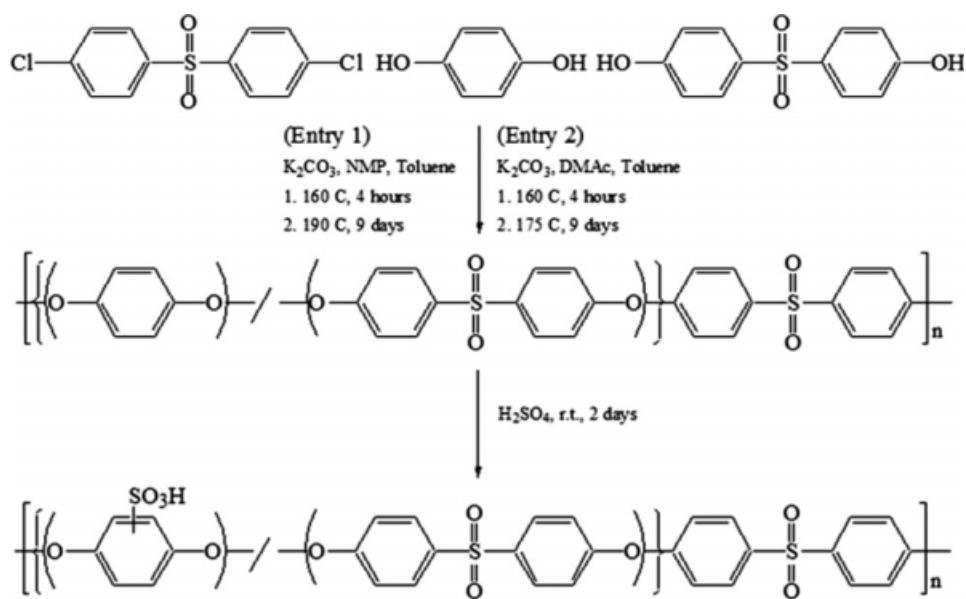
### Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS) was obtained from Solyve Advanced Polymers and Eastman Chemicals. HQ, 4,4'-difluorodiphenyl sulfone (DFDPS), and potassium carbonate ( $K_2CO_3$ ) were purchased from Aldrich. Bis(4-hydroxyphenyl) sulfone (BHPS), anhydrous toluene, and 1-methyl-2-pyrrorridone (NMP) were purchased from Alfa Aesar. Decafluorobiphenyl (10F) was purchased from Lancaster and used as received. All other reagents were dried well at 60 °C for 24 h before use.

### Polymerization of Random Copolymers

HQ (1.6974 g, 15.416 mmol), BHPS (2.6939 g, 10.765 mmol), DCDPS (7.5176 g, 26.181 mmol), and  $K_2CO_3$  (4.16 g, 30.1 mmol) were added to either NMP or DMAc (60 mL, 20 v/w%) with toluene (30 mL, equivalent to half of the solvent volume), using a three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a Dean Stark trap with both a condenser and a calcium chloride outlet, as schematized in Figure 1. The solution was heated to 160 °C for at least 4 h to remove the byproducts of water inside and then heated for 9 days to either 190 °C for NMP or 175 °C for DMAc to complete the step-growth polymerization. After that, the solution was cooled to room temperature, filtered to remove salts, and then precipitated in an excess amount of methanol. The product was dried well in a vacuum oven at 80 °C for 24 h and redissolved in NMP for further purification.

<sup>1</sup>H NMR [Fig. 7(1)]:  $\delta$  7.09 (d, 4H), 7.17 (d, 4H), 7.22 (d, 4H), ~7.9 (4H); <sup>1</sup>H NMR [Fig. 7(2)]:  $\delta$  6.95 (d, 2H), 7.05 (d, 4H), 7.12 (d, 4H), 7.25 (d, 4H), 7.39 (s, 1H), 7.82 (d, 4H), 7.9 (4H).

**Figure 1.** Polymerization and sulfonation of random copolymers.

### Polymerization of Diblock Copolymers

#### *OH-Terminated Poly(ether ether sulfone) Oligomer (Target $M_n$ : 20 kDa)*

As indicated in Figure 2, HQ (3.4311 g, 31.161 mmol), DCDPS (5.0335 g, 30.6610 mmol), and  $K_2CO_3$  (5.03 g, 36.1 mmol) were put together in NMP (60 mL, 20 v/w%) with toluene (30 mL). The solution was first heated to 60 °C for 4 h and then to 190 °C for 2 days. The filtered solution was kept in nitrogen gas without any isolation treatment until the coupling reaction. This oligomer is referred to as PEES in this article.

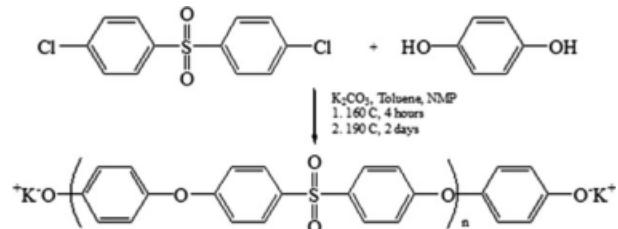
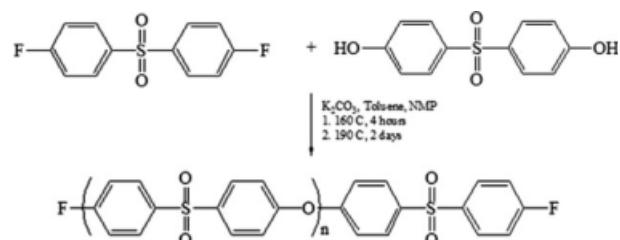
#### *F-Terminated Poly(ether sulfone) Oligomer (Target $M_n$ : 20 kDa)*

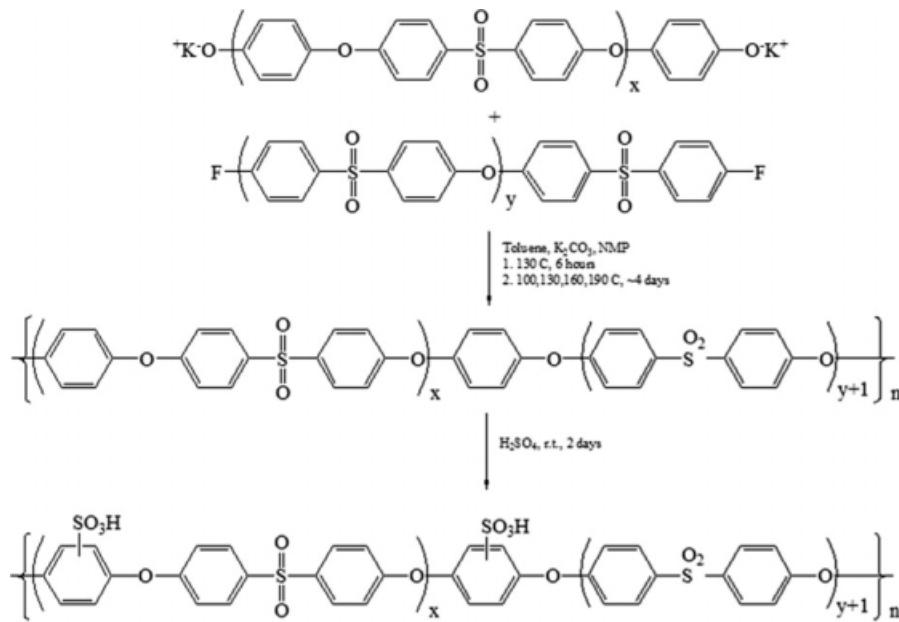
BHPS (5.3192 g, 21.255 mmol), DFDPS (5.5311 g, 21.755 mmol), and  $K_2CO_3$  (3.38 g, 24.5 mmol) were added to NMP (60 mL) with toluene (30 mL). The solution was first heated to 160 °C for 4 h and

then to 190 °C for 2 days, as indicated in Figure 3. The filtered solution was kept in the same way as PEES. This oligomer is referred to here as PES-F.

### Coupling Reaction of Diblock Copolymers

Figure 4 shows the coupling reaction of the diblock copolymer consisting of the PEES and PES-F oligomers. The stoichiometric ratio (1:1) of PEES to PES-F was calculated from the ideal molar numbers in each solution under the assumption that each could have a molecular weight of 20 kDa. Both prepared solutions were put in a flask in addition to a small amount of  $K_2CO_3$  (equivalent to 1.15 times the amount of PEES) and toluene (half the volume of NMP). The solution mixture was heated to 130 °C for 6 h, and then the completion temperature was investigated by setting the temperature at various levels of 100, 130, 160, and 190 °C. After 4 days, the solution was isolated in methanol and dried in a vacuum oven at 80 °C.

**Figure 2.** Synthesis of OH-terminated poly(ether ether sulfone) oligomer (PEES).**Figure 3.** Synthesis of F-terminated poly(ether sulfone) oligomer (PES-F).



**Figure 4.** Polymerization and sulfonation of diblock copolymers via PEES and PES-F.

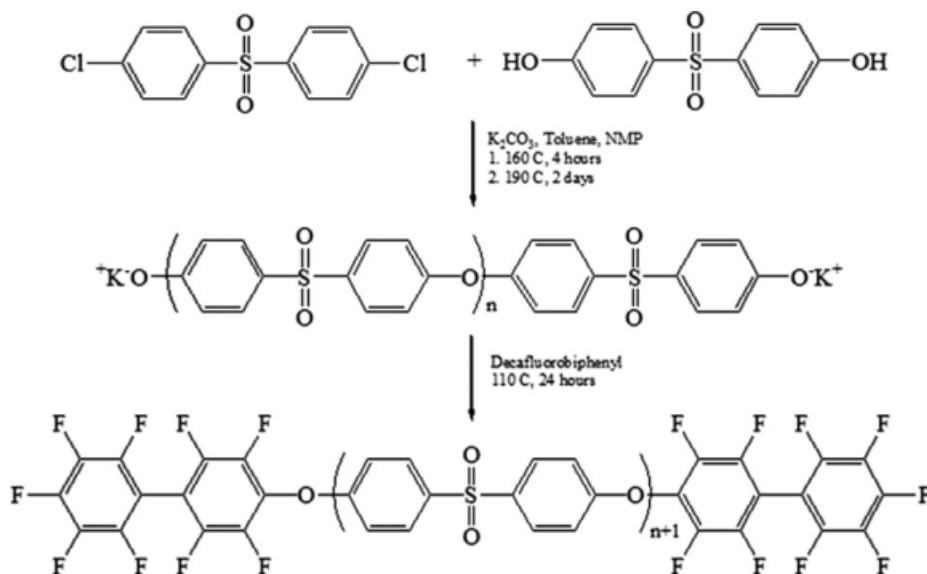
$^1H$  NMR [Fig. 8(1)–(4)]:  $\delta$  7.08 (d, 4H), 7.15 (d, 4H), 7.22 (d, 4H), 7.88 (d, 4H), 7.94 (d, 4H);  $^1H$  NMR [Fig. 8(5)]:  $\delta$  6.95 (d, 2H), 7.10 (d, 4H), 7.16 (d, 4H), 7.22 (d, 4H), 7.39 (s, 1H), 7.81 (4H), 7.9 (4H).

#### Polymerization of Diblock Copolymer with Decafluorobiphenyl

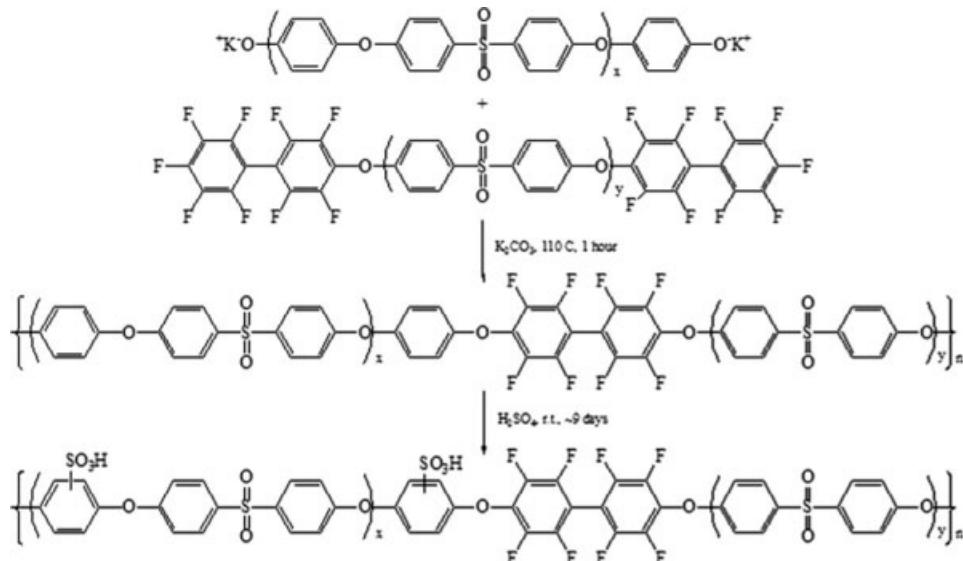
##### 10F-Terminated Poly(ether sulfone) (Target $M_n$ : 20 kDa)

An OH-terminated poly(ether sulfone) oligomer was prepared first as shown in Figure 5.<sup>11,12</sup>

BHPS (5.4456 g, 21.760 mmol), DFDPS (6.1046 g, 21.260 mmol), and  $K_2CO_3$  (3.54 g, 25.6 mmol) were added to NMP (60 mL) with toluene (30 mL). The solution was first heated to 160 °C for 4 h and then to 190 °C for 2 days. After the solution was cooled to 110 °C, 10F (1.0024 g, 3.000 mmol) was added, followed by stirring for 24 h. The filtered solution was precipitated in a methanol/acetone mixture and dried in a vacuum oven at 80 °C for 24 h. This product is referred to here as PES-10F.



**Figure 5.** Synthesis of 10F-terminated poly(ether sulfone) oligomer.



**Figure 6.** Polymerization and sulfonation of diblock copolymer with a connection of 10F.

### Coupling Reaction of Diblock Copolymer with 10F as a Connection

The stoichiometric ratio (1:1) of PES-10F to PEES was calculated from the gel permeation chromatography (GPC) results for PES-10F and the hypothesis that PEES could have a molecular weight of 20 kDa. PES-10F was dissolved well in NMP (20 wt %) at  $110\text{ }^\circ\text{C}$ , and then PEES was added as well as  $K_2CO_3$  (equivalent to 1.15 times the volume of PEES), as indicated in Figure 6. After 1 h, the filtered solution was isolated in methanol. The product was dried well in a vacuum oven at  $80\text{ }^\circ\text{C}$  for 24 h and then redissolved in NMP for further purification.

$^1\text{H}$  NMR [Fig. 9(1)]:  $\delta$  7.15 (8H), 7.25 (d, 4H), 7.90 (d, 4H), 7.97 (4H);  $^1\text{H}$  NMR [Fig. 9(2)]: 6.98 (d, 2H), 7.17 (d, 4H), 7.27 (d, 4H), 7.42 (s, 1H), 7.85 (4H), 7.9 (4H).

### Postsulfonation

Postsulfonation was carried out in a concentrated sulfuric acid at room temperature for several days. The typical procedure used for a random copolymer is described here. A polymer of 10 g was dissolved in sulfuric acid of 100 mL and stirred for 2 days at room temperature. The polymer solution was isolated in an excess amount of deionized water. The water was refreshed repeatedly until the water was neutralized. The product was dried well in a vacuum oven at  $80\text{ }^\circ\text{C}$  for 24 h and then dissolved in NMP for further purification as

usual. Lastly, the product was washed for 24 h in boiled water to remove isolated hydrophilic oligomers.

### Membrane Preparation

A polymer solution was prepared in NMP (5 wt %) and filtered with a  $0.45\text{-}\mu\text{m}$  porous PTFE membrane. The filtrate was cast onto a glass plate and dried under an infrared lamp for 48 h to form the membrane. After drying in a vacuum oven at  $80\text{ }^\circ\text{C}$  for 24 h, the membrane was immersed into deionized water for a while to detach it from the substrate and then boiled in 0.5 M sulfuric acid for 2 h for acidification.<sup>5</sup> Finally, it was rinsed several times, boiled for 2 h, and then rinsed again in deionized water.

### Characterization

#### Proton Nuclear Magnetic Resonance Spectra

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were obtained with a Varian Unity 400 NMR spectrometer in dimethyl sulfoxide ( $DMSO-d_6$ ) at room temperature.

#### GPC Measurement and Intrinsic Viscosity ( $\eta$ )

GPC measurements were conducted using a Waters 1515 HPLC pump, a Waters 717 plus autosampler, and a Viscotek 270 dual detector to obtain universal and light scattering calibrations,

using poly(styrene) as a standard. A solution of 0.05 M lithium bromide (LiBr) in NMP was used to avoid ionic aggregations. Intrinsic viscosity was determined with a viscometer at 25 °C in 0.05 M LiBr in NMP.

### ***Ion Exchange Capacity***

The ion exchange capacity (IEC) (mequiv/g) value was measured by a back-titration method as described here. The sample membrane was put in a 1 M sodium chloride (NaCl) solution that was stirred for several hours to change it to the Na form at room temperature. It was then rinsed in deionized water and put in a 1 M hydrochloric acid (HCl) solution that was stirred for several hours. This procedure was conducted twice. The membrane was then thoroughly acidified by immersing it in a 1 M HCl solution for 1 day, rinsed in ionized water, and dried in a vacuum oven at 60 °C for a minimum of 12 h. The weight of the dry membrane was regarded as  $W(g)$ .

Sodium hydroxide (NaOH) and HCl solutions of 0.01 M were prepared. The concentration of the NaOH solution was determined precisely by titrating it with a standardized oxalic acid  $[(COOH)_2]$ , using phenolphthalein as an indicator. The concentration of the HCl solution was then determined precisely on the basis of the NaOH solution. The HCl concentration was regarded as  $C$  (mol/mL). The sample membrane was put in a NaOH solution of 20.00 mL with a 1 M NaCl solution of 20.00 mL and stirred for 1 day. A solution of 5.00 mL was taken out for titration with the HCl solution, using methyl orange as an indicator. The titrated amount of the HCl solution was regarded as  $A$  (mL). In addition, a solution consisting of a NaOH solution of 20.00 mL and a 1 M NaCl solution of 20.00 mL without a sample membrane was titrated in the same procedure as a blank test. The titrated amount of the HCl solution was regarded as  $B$  (mL). Lastly, the IEC value was calculated with the following equation:

$$\text{IEC(mequiv/g)} = \frac{1000 \times C \times (B - A) \times 40}{5 \times W}$$

### ***Differential Scanning Calorimetry and Thermogravimetric Analysis***

The thermal properties of the diblock copolymers were investigated with both a thermogravimetric analysis (TGA) instrument (TGA Q500) and a dif-

ferential scanning calorimetry (DSC) instrument (DSC Q1000) at a heating rate of 5 °C/min in nitrogen in a temperature range of 50–300 °C for DSC and 50–400 °C for TGA. The sample powder was kept at 150 °C for 1 h to remove any residual water or solvent before the test.

### ***Mechanical Properties***

Mechanical tensile tests were performed at room temperature and 44–50% RH using an Instron 5500R universal testing machine equipped with a 200-lb load cell. The crosshead displacement speed was 5 mm/min and gauge lengths were set to 40 mm. A dogbone die was used to punch out specimens 50 mm long with a minimum width of 4 mm. Before testing, the specimens tested in the dry state were dried under vacuum at 100 °C for at least 12 h and then equilibrated at 40% RH and 30 °C. The specimens tested after hydration were immersed in deionized water at room temperature overnight and blotted dry just prior to testing. All specimens were mounted in manually tightened grips.

### ***PC Measurement***

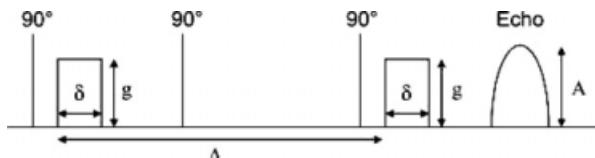
Proton conductivity at 30 °C at full hydration (in liquid water) was determined in a window cell geometry<sup>20</sup> using a Solartron 1252 + 1287 Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz to 1 MHz following the procedure reported in the literature.<sup>21</sup> In determining proton conductivity in liquid water, membranes were equilibrated at 30 °C in deionized water for 24 h prior to testing. For determining proton conductivity under partially hydrated conditions, membranes were equilibrated in a humidity-temperature oven (ESPEC SH-240) at the specified RH and 80 °C for 24 h before each measurement.

### ***Water Self-Diffusion Coefficient***

Water self-diffusion coefficients were measured using a Varian Inova 400 MHz (for protons) nuclear magnetic resonance spectrometer with a 60 G/cm gradient diffusion probe. A total of 16 points were collected across the range of gradient strength, and the signal-to-noise ratio was enhanced by recording four scans. The standard stimulated-echo NMR pulse sequence is shown later. The sample membrane was immersed in deionized water at room temperature overnight and blotted dry just prior to testing.

**Table 1.** Various Reaction Conditions and Molecular Information

Sample	Structure	Solvent	Temp. (°C)	Time	$M_n^a$ (kDa)	$M_w^a$ (kDa)	IV <sup>a</sup> (dL/g)	IV <sup>b</sup> (dL/g)
R <sub>1</sub>	Random copolymer	NMP	190	9 days	75.6	85.8	0.17	0.17
R <sub>2</sub>	Random copolymer	DMAc	175	9 days	14.5	19.3	0.25	0.25
s-R <sub>2</sub>	Sulfonated R <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	RT	2 days	22.2	26.7	0.28	0.22
B <sub>1</sub>	Block copolymer	NMP	100	4 days	16.7	23.1	0.22	— <sup>c</sup>
B <sub>2</sub>	Block copolymer	NMP	130	4 days	16.9	23.2	0.24	0.25
B <sub>3</sub>	Block copolymer	NMP	160	4 days	31.0	35.7	0.25	0.20
B <sub>4</sub>	Block copolymer	NMP	190	4 days	70.3	79.4	0.21	0.13
s-B <sub>4</sub>	Sulfonated B <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	RT	2 days	81.5	92.9	0.22	0.23
B <sub>5</sub>	Block copolymer <sup>d</sup>	NMP	110	1 h	56.4	613.9	0.65	0.71
s-B <sub>5</sub>	Sulfonated B <sub>5</sub>	H <sub>2</sub> SO <sub>4</sub>	RT	9 days	126.8	1445.0	0.97	0.90

<sup>a</sup> Determined by GPC measured in NMP with 0.05 M LiBr.<sup>b</sup> Determined with a viscometer measured in NMP with 0.05 M LiBr at 25 °C.<sup>c</sup> Impossible to measure because of its poor solubility.<sup>d</sup> Obtained by means of decafluorobiphenyl as a connection, as shown in Figure 6.

### Water Uptake

The sample membrane was immersed in deionized water at room temperature for 2 h and then dried in a vacuum oven at 60 °C for 2 h. After weighing the dry membrane ( $W_d$ ), it was repeatedly immersed in deionized water at room temperature for 2 h. The hydrated membrane was weighed ( $W_w$ ) after removing water on the surface, and lastly the water uptake was calculated with the following equation:

$$\text{Water Uptake}(\%) = \frac{(W_w - W_d)}{W_d} \times 100$$

The amount ( $\lambda$ ) of the adsorption water relative to one sulfonic acid group was calculated from the combination of water uptake and IEC values using the following equation:

$$\lambda = \frac{1000 \times (W_w - W_d)}{18 \times W_d \times \text{IEC}}$$

### Atomic Force Microscopy

Atomic force microscopy (AFM) images were obtained with a Digital Instruments multimode scanning probe microscope with a NanoScope IVa controller (Veeco) in a tapping mode. A silicon

probe (Veeco) with a tip radius of less than 10 nm and a constant force of 5 N/m was used to image samples. The ratio of the amplitude used in the feedback control was adjusted to 0.83 of the free-air amplitude. The samples were dried in a vacuum oven at 60 °C for 3 h and then equilibrated at 30% RH for at least 12 h before being imaged immediately at room temperature and RH of approximately 15–20%.

## RESULTS AND DISCUSSION

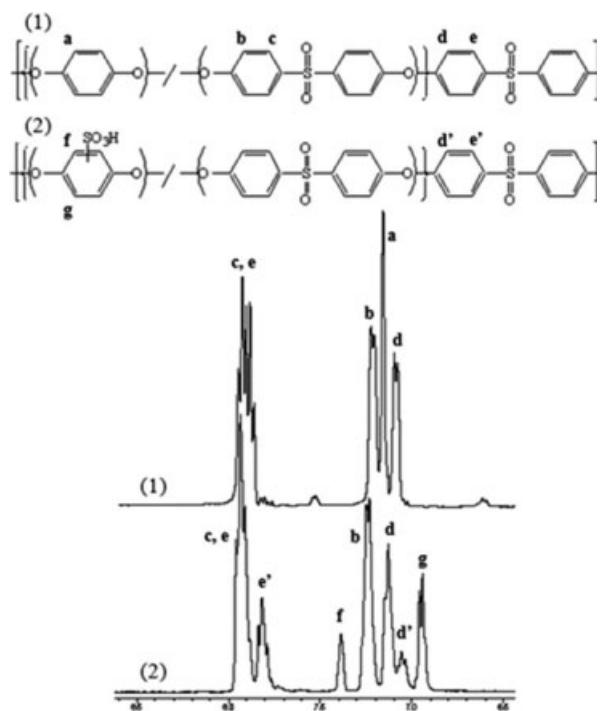
### Polymerizations

#### Random Copolymers

Two conditions were investigated for polymerizing random copolymers consisting of HQ, DCDPS, and BHPS, in either NMP or DMAc as a solvent.

Table 1 shows their molecular weights obtained from GPC and IV measurements (R<sub>1</sub> for NMP, R<sub>2</sub> for DMAc). Unique behavior correlating the molecular weight ( $M_w$ ) and IV was observed; that is, the higher the  $M_w$ , the lower is the IV. We believe that the introduction of HQ into copolymers leads to such behavior, reflecting HQ's crystalline property. In short, the degree of crystallinity that led to poorer entanglement between polymer chains was increased, resulting in lower viscosity with increasing  $M_w$ .

Figure 7(1) shows the <sup>1</sup>H NMR spectra of the random copolymers synthesized in DMAc. It was found that peaks (b and d) corresponding to the same schematic structure of the ether sulfone moiety appeared separately because of the



**Figure 7.**  $^1\text{H}$  NMR spectra of random copolymers (1) before and (2) after postsulfonation.

surrounding circumstance; although other peaks (c and e) appeared at almost the same position.

Postsulfonation was successfully induced into these copolymers synthesized in DMAc, as shown in Figure 7(2). Compared with the spectra before sulfonation, four new peaks clearly appeared. Peaks f and g were assigned to the sulfonated HQ moiety, since the integral value ratio of f to g was almost 1:2. By contrast, peaks d' and e' could not be clearly assigned, but we believe that the sulfonyl induction of HQ caused peaks d and e to shift partially to peaks d' and e'. Using the integral values of peak f due to sulfonated HQ and the sum of peaks c, e, and e' due to ether sulfone, the conversion ratio was calculated to be almost 100%. Additionally, a peak completely disappeared after sulfonation. The PES sequence was confirmed to be incapable of postsulfonation, using PES oligomers; although the results are not discussed in this article. From these observations, it was concluded that sulfonation was conducted almost perfectly onto PEES.

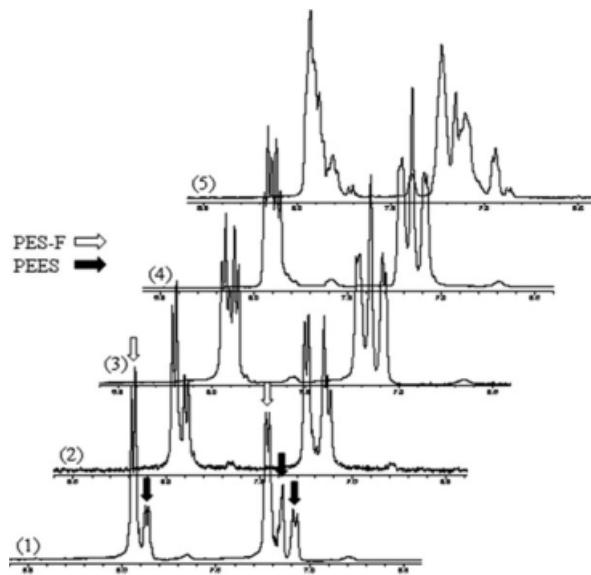
With regard to the molecular weight before and after postsulfonation, Table 1 indicates a small increase in  $M_w$  for samples R<sub>1</sub> and R<sub>2</sub>. However, their IV of 0.2–0.3 dL/g was too low to make a film with adequate mechanical properties.

### Diblock Copolymers

Diblock copolymers were investigated using PEES and PES-F oligomers with a target  $M_n$  of 20 kDa. When PEES oligomers were synthesized, as shown in Figure 2, a solubility problem was found. Although PEES with a target  $M_n$  of 5 kDa was soluble in aprotic solvents such as DMAc or NMP after isolation in methanol, PEES with a target  $M_n$  of 10 kDa was partially insoluble, and PEES oligomers with a target  $M_n$  of 15 and 20 kDa were not soluble at all. Therefore, the oligomer solution was not isolated by keeping it under nitrogen until the coupling reaction. One of the presumed reasons is that HQ causes high crystallinity, resulting in poor solubility.

On the other hand, PES with a target  $M_n$  of 20 kDa was terminated by fluorine (DFDPS), as shown in Figure 3, to enhance the termination reactivity for combining with the PEES oligomer. Although PES-F was soluble in aprotic solvents even with a high  $M_n$  after isolation, the PES-F oligomer solution was also kept without isolation under nitrogen until the coupling reaction, to make it compatible with the PEES oligomer.

The coupling reaction condition between the PEES and PES-F oligomers was studied by optimizing the reaction temperature, as indicated in Figure 4. Figure 8 shows the  $^1\text{H}$  NMR spectra of



**Figure 8.**  $^1\text{H}$  NMR spectra of diblock copolymers as a function of completion reaction temperature: (1) 100 °C; (2) 130 °C; (3) 160 °C; (4) 190 °C; in addition to (5) sulfonated diblock copolymer.

coupled diblock copolymers after changing the reaction temperature from 100 to 190 °C. The identification of the chemical structure was almost the same as that shown in Figure 7, where there is a white arrow attributed to PES-F and a black one attributed to PEES. The peaks at around 7.8–8.0 ppm in Figure 8 were apparently increased and further combined as a function of the reaction temperature. The existence ratio of PEES to PES-F at 100 °C [Fig. 8(1)] was calculated to be around 20%, much lower than expected. Further, some partially insoluble products were observed after isolation in methanol, leading to the same behavior as described before, presumably because there was a lot of unreacted PEES insoluble in NMP after isolation. It can be inferred that the product becomes soluble after isolation, only when the coupling reaction is successful, in spite of the insolubility of PEES. Furthermore, the result at 130 °C seemed to be almost the same as that at 100 °C. Therefore, a temperature of 160 °C or higher was found to be necessary to attain the coupling reaction.

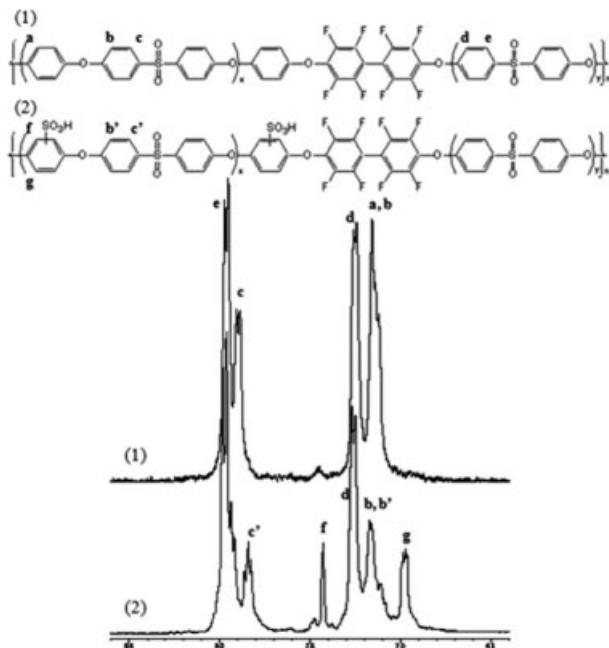
Looking at  $B_1$  to  $B_4$  in Table 1, the same tendency between  $M_w$  and IV is observed as in the random copolymers. The product ( $B_4$ ) polymerized at 190 °C with the highest  $M_w$  of 79.4 kDa had the lowest IV of 0.13–0.21 dL/g.

With regard to postsulfonation application of these diblock copolymers, an attempt was made to sulfonate the product at 190 °C in the same way as the random copolymers. As a result, the sulfonated structure was identified as shown in Figure 8(5), while Figure 9 shows almost the same explanation for identifying the sulfonated diblock copolymers. Unfortunately, it was impossible to form a tough film because of the low IV, despite the high  $M_w$ .

#### Diblock Copolymer with 10F as an End-Group

As mentioned previously, no polymerization was successful in producing sufficiently tough mechanical properties. In this study, the use of 10F as the termination reagent was examined with the aim of enhancing the coupling reactivity. The procedure for synthesizing 10F-terminated PES-based oligomers (PES-10F) is shown in Figure 5 and that for polymerizing diblock copolymers in Figure 6.

The termination reaction was run for 24 h after the synthesis of the PES-OH oligomer. To prevent excessive growth of PES-OH, 10F equivalent to six times the molar fraction of PES-OH was added

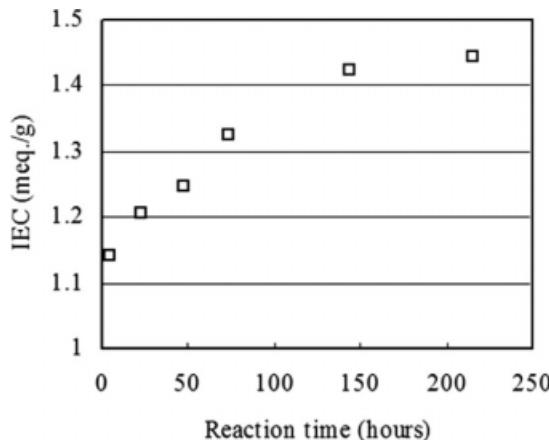


**Figure 9.**  $^1\text{H}$  NMR spectra of diblock copolymers with 10F as a connection (1) before and (2) after post-sulfonation.

to the system. After the termination reaction, the solution was isolated in an acetone/methanol mixture, since 10F is soluble in acetone. PES-10F was dried at 80 °C in a vacuum oven for 24 h, allowing 10F to vapor out easily. The GPC results revealed that PES-10F had  $M_n$  of 25.5 kDa and  $M_w$  of 43.3 kDa.

The prepared PES-10F was dissolved in NMP to afford a 20% solid concentration, and then the PEES solution was added to the solution. The coupling reaction between them was so fast that it was completed in only 1 h. When the reaction was run for a few hours, the solution clearly gelated. From the  $^1\text{H}$  NMR spectrum in Figure 9(1), it was concluded that polymerization using 10F was successfully accomplished. In addition, the product was found to have a very high  $M_w$  of 613.9 kDa, as indicated for sample  $B_5$  in Table 1.

With respect to postsulfonation, the reaction time dependency was studied by sampling the solution in a concentrated sulfuric acid at certain given intervals. All of the solution samples were isolated in water, filtered, redissolved in NMP, and isolated in methanol. The products were washed well in water and then dried well in a vacuum oven at 80 °C. A film was cast from each product for measuring the IEC values by back-titration. The results revealed that IEC increased with a longer reaction time, as summarized in



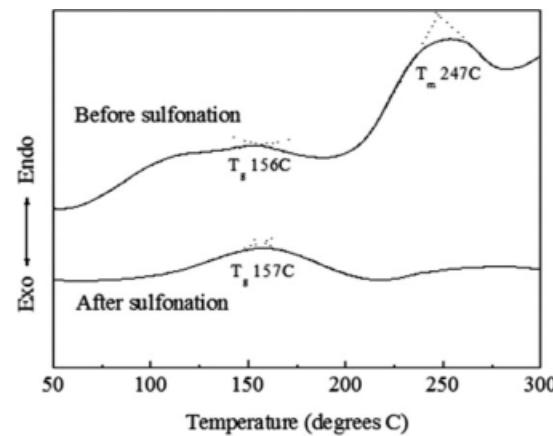
**Figure 10.** Correlation between IEC values and reaction time of postsulfonation on diblock copolymers with 10F as a connection.

Figure 10. The IEC value eventually increased to 1.44 mequiv/g after 9 days, rising from 1.14 mequiv/g after 5 h. Furthermore, the identification of the sulfonated diblock copolymer is clearly seen in Figure 9(2). The molecular weight was high enough, more than 1000 kDa, according to the GPC results in Table 1 for sample s-B<sub>5</sub>; although values more than 1000 kDa may not be so reliable owing to the limited molecular range of polystyrene used as a standard. The IV behavior was significantly different from that of the random diblock copolymers without 10F. The  $M_w$  of this sample was markedly high at 1445 kDa, and its IV was 0.97 dL/g. Presumably, the multifunctional property of 10F enabled the formation of kinky polymer chains that resulted in highly entangled polymeric physical structures, which would account for the high values. This successful diblock copolymer (B<sub>5</sub>, s-B<sub>5</sub>) is discussed in the following section.

## Characterization

### Thermal Properties

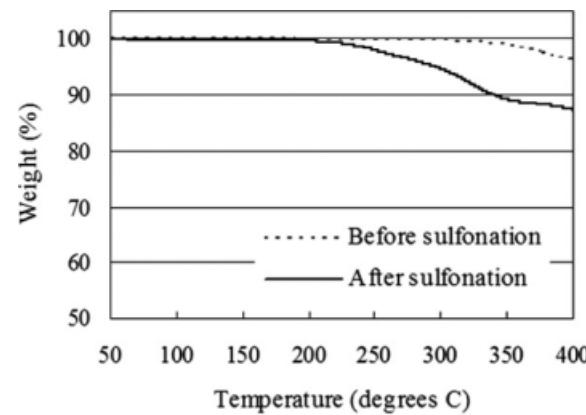
The glass transition point ( $T_g$ ) of the 10F-based diblock copolymer was evaluated using DSC measurement by heating samples from 50 to 300 °C at a rate of 5 °C/min, as shown in Figure 11. Looking at the diblock copolymer before sulfonation, a peak due to  $T_g$  was detected at 156 °C, corresponding to the PES block sequences, since it also appeared at almost the same temperature after sulfonation. A large peak also appeared at 247 °C, which is likely the melting point ( $T_m$ ) mainly due



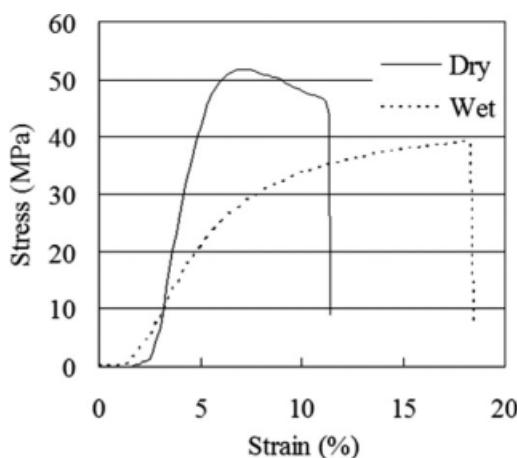
**Figure 11.** DSC curves of diblock copolymers with 10F as a connection before (B5) and after sulfonation (s-B<sub>5</sub>), at a heating rate of 5 °C/min.

to PEES. After sulfonation, the peak intensity decreased. This is because the sulfonate group associates and increases intermolecular interaction, hence reducing molecular mobility.

The thermal decomposition point ( $T_d$ ) was also studied using TGA measurement in a temperature range from 50 to 400 °C at a heating rate of 5 °C/min. The results are shown in Figure 12. Although the diblock copolymer before sulfonation was stable until 300 °C without any weight loss, the sulfonated sample showed slight degradation at 200 °C, resulting in a 5% weight loss at 295 °C and a 10% weight loss at 340 °C. The  $T_d$  for this sulfonated diblock copolymer was lower than that reported in the reference.<sup>22</sup> The reason can be explained by the differences between pre and postsulfonation. These results consequently



**Figure 12.** TGA curves of diblock copolymers with 10F as a connection before (B5) and after sulfonation (s-B<sub>5</sub>), at a heating rate of 5 °C/min.



**Figure 13.** Tensile strength of sulfonated diblock copolymer before and after immersion in water.

indicated that the sulfonate groups cleaved to electron-rich sites in the postsulfonation system were not as chemically stable as those in the presulfonation. However, it can be concluded that the sulfonated diblock copolymer has sufficient thermal properties, because there is no degradation until at least 200 °C.

#### Mechanical Properties

The mechanical properties under the wet and dry conditions were evaluated in a tensile test, and the results are shown in Figure 13. As summarized in Table 2, maximum tensile strength of 51.82 MPa was sufficient in the dry state. Even when hydrated, it was still tough at 38.98 MPa. Looking at both the tensile strain at fracture and the modulus between the dry and wet conditions, it is concluded that water molecules serve as a plasticizer, since the former increased from 7%

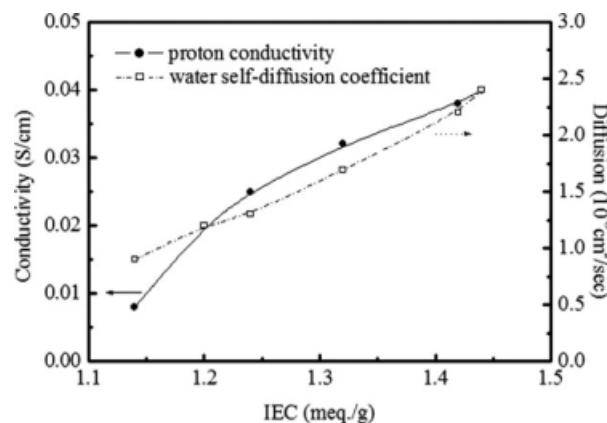
**Table 2.** Mechanical Properties of Sulfonated Diblock Copolymer

	Maximum Tensile Strength (MPa)	Tensile Strain at Fracture (%)	Modulus (GPa)
Dry condition <sup>a</sup>	51.82	7.00	2.00
Wet condition <sup>b</sup>	38.98	18.33	0.70

This corresponds to Figure 13.

<sup>a</sup>Dried in a vacuum oven at RT.

<sup>b</sup>Immersed in water at RT overnight.



**Figure 14.** Correlation between IEC, proton conductivity, and water diffusion coefficient of sulfonated diblock copolymer.

to 18.33%, while the latter decreased from 2.0 to 0.7 GPa.

#### Water Behavior

The correlation between PC and the water self-diffusion coefficient was investigated as a function of IEC by controlling the sulfonation time. The results are shown in Figure 14. The data indicate that the water self-diffusion coefficient and PC increased with increasing IEC. Water uptake also increased as a function of IEC, as summarized in Table 3. A calculation of  $\lambda$  revealed that it increased from 12 to 14 because of the thickening of the hydrophilic phase. However, there seems to be a saturation limit of 14 because of its physical

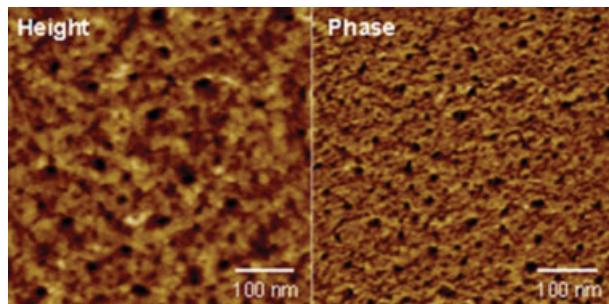
**Table 3.** Proton Conductivity, Water Self-Diffusion Coefficient and Water Uptake of Sulfonated Diblock Copolymer

IEC <sup>a</sup> (mequiv/g)	Proton Conductivity <sup>b</sup> (S/cm)	Water Self-Diffusion Coefficient <sup>c</sup> ( $10^{-6}$ cm $^2$ /s)	Water Uptake (wt %)	$\lambda$
1.14	0.008	0.9	24	12
1.20	0.02	1.2	29	13
1.24	0.025	1.3	31	14
1.32	0.032	1.7	34	14
1.42	0.038	2.2	36	14
1.44	0.04	2.4	37	14

<sup>a</sup>Determined by back-titration.

<sup>b</sup>Measured in liquid water at 30 °C.

<sup>c</sup>Measured in the hydrated state at RT.



**Figure 15.** AFM images [height mode (left), phase mode (right)] of sulfonated diblock copolymer.

and chemical properties. The AFM images in Figure 15 also confirmed the phase separation of the hydrophobic region (light color) and hydrophilic region (dark color), indicating that both partially continuous and isolated phase separations exist. In summary, both PC and the water self-diffusion coefficient were lower than we expected, because of the strength of proton association that is dependent on the chemical structure, as well as the insufficient phase separation due to randomly postsulfonated structure.

## CONCLUSIONS

The synthesis of postsulfonated, hydroquinone-based diblock copolymers was investigated by means of highly reactive fluorine-terminated reagents.

The use of HQ led to some crystallinity and solubility problems in the oligomer consisting of HQ and 4,4'-dichlorodiphenyl sulfone. 4,4'-Difluorodiphenyl sulfone was used as the termination reagent for the ether sulfone-based oligomer. It was found that intrinsic viscosity decreased with a higher molecular weight, even for the random copolymers.

In contrast, decafluorobiphenyl worked very effectively as the termination reagent and resulted in a successful synthesis of a diblock copolymer with sufficient molecular weight and intrinsic viscosity to form a tough membrane. Postsulfonation was successfully induced in the diblock copolymer without any degradation. It was observed that the degree of sulfonation was controllable by changing the reaction time. In addition, the postsulfonated diblock copolymer was confirmed to have sufficient thermal stability.

The characterization results confirmed thermal stability at a temperature of at least 200 °C,  $T_g$  of 156 °C and  $T_m$  of 247 °C. Additionally, tensile

strength at fracture was confirmed to be 38.98 MPa even in the hydrated state. It was observed that proton conductivity, water uptake, and the water self-diffusion coefficient increased with increasing IEC.

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