

## NOTE

## Influence of Polymer Structure in Sulfonated Block Copoly(ether sulfone) Membranes for Fuel Cell Application

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Proton-conducting polymers have a great interest in the field of polymer electrolyte membrane fuel cells (PEMFCs). Presently, perfluorosulfonic acid polymers such as Nafion<sup>®</sup> and Flemion<sup>®</sup> have been widely used as polymer electrolyte membranes (PEMs) for PEMFCs because of their excellent chemical, physical stability and high proton conductivity.<sup>1,2</sup> Despite their advantages of high conductivity and good mechanical and chemical properties, certain drawbacks exist that restrict their use in fuel cells, such as high cost, limited operating temperature (> 80 °C), and the high fuel permeation property in direct methanol fuel cells (DMFCs). To overcome these drawbacks, extensive efforts have been made to develop alternative acid-functionalized aromatic hydrocarbon-based polymers,<sup>3–5</sup> and a class of high-performance sulfonated aromatic polymers such as poly(phenylene)s,<sup>6–8</sup> poly(ether ether ketone)s,<sup>6</sup> poly(ether sulfone)s,<sup>9,10</sup> poly(arylene ether)s,<sup>11–13</sup> and polyimides<sup>14,15</sup> have been investigated as potential PEMs. Generally, these polymers exhibit excellent conductivities only at high ion-exchange capacities (IEC), resulting in extensive water uptake above a critical temperature, or a dramatic loss of mechanical properties. One promising way to avoid these problems is to prepare sulfonated block copolymers, which can control the hydrophilic and hydrophobic domain structure. The phase of the hydrophobic block should enable good mechanical properties under a fully hydrated state whereas the hydrophilic block should provide high proton conductivity. Therefore, the synthesis of sulfonated block copolymers has been extensively investigated.<sup>16–18</sup> McGrath and coworkers reported the synthesis of sulfonated multiblock poly(arylene ether sulfone) copolymers from highly activated fluorine-terminated and hydroxyl-terminated oligomers. The resulting multiblock copolymers showed a well defined phase separation and higher proton conductivities compared to the random copolymers.

In a previous paper, we demonstrated a facile synthetic method of sulfonated multiblock copoly(ether sulfone)s by the coupling reaction of hydroxyl-terminated poly(ether sulfone) oligomers and hydroxyl-terminated sulfonated poly(ether sul-

fone) oligomers in the presence of decafluorobiphenyl (DFB) as the chain extender. The high reactivity of DFB enabled the reaction to be conducted at a low temperature, avoiding the ether-ether interchange reaction and a small amount of DFB was enough to obtain multiblock copolymers with high molecular weight ( $M_w > 100000$ ). Those membranes showed higher proton conductivity than that of a corresponding random copolymer and maintained good proton conductivity under low relative humidity ( $6.0 \times 10^{-3}$  S/cm under 80 °C, 50% RH). However, the obtained multiblock copolymers are random multiblock copolymers in which hydrophilic and hydrophobic oligomer segments are statistically distributed. Thus, it is interesting to compare the properties of the random multiblock copolymers and alternating multiblock copolymers in which A and B segments are alternatively connected (see Figure 1), because the latter is expected to produce highly phase-separated morphology as compared to the former.

In this article, we report the influence of multiblock polymer structure to the membranes' properties such as water uptake and proton conductivity. Two sulfonated block copoly(ether sulfone)s with the same chemical compositions such as a random multiblock copolymer and an alternating multiblock copolymer were prepared by a chain extender method<sup>19</sup> and an end-capping method,<sup>20</sup> respectively.

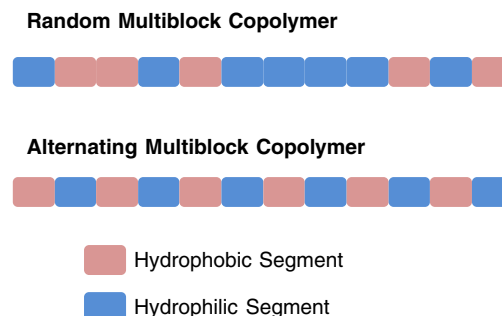


Figure 1. Images of random multiblock copolymer and alternating multiblock copolymer.

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## EXPERIMENTAL

### Materials

4,4'-Dichlorodiphenylsulfone (DDS), 4,4'-biphenol (BP), and decafluorobiphenyl (DFB) were purchased from TCI. Co., Inc. 3,3'-Disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS) was synthesized from DDS according to the previous report.<sup>21</sup> *N*-Methyl-2-pyrrolidinone (NMP) was distilled from calcium hydride before use. Other solvents and reagents were used as received.

### Synthesis of Hydroxyl-terminated Hydrophilic Oligo(ether sulfone) (1)

The hydroxyl-terminated hydrophilic oligomer was synthesized from SDCDPS and BP according to the previous reports.<sup>19,20</sup> <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.32 (2H, d), 7.86 (2H, dd), 7.70 (4H, d), 7.59 (end-group, d), 7.46 (end-group, d), 7.13 (4H, d), 7.07 (end-group, d), 7.02 (2H, d), 6.84 (end-group, d).

### Synthesis of Hydroxyl-terminated Hydrophilic Oligo(ether sulfone) (2)

The hydroxyl-terminated hydrophilic oligomer was also synthesized from DDS and BP according to the previous reports.<sup>19</sup> <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 7.92 (4H, s), 7.72 (4H, s), 7.32 (end-group, d), 7.17 (8H, s).

### Synthesis of End-capping Hydrophobic Oligo(ether sulfone) (3)

**2** ( $M_n = 4000$ , 0.2 mmol, 0.8 g), DFB (2.0 mmol, 0.7 g), and  $K_2CO_3$  (0.6 mmol, 0.08 g) were placed into a round-bottomed flask equipped with a condenser, and a gas adapter. NMP (10 mL) was charged into the reaction flask under a nitrogen atmosphere. The reaction temperature was increased to 105 °C. After 12 h, the mixture was cooled to room temperature and poured into methanol to precipitate a white polymer. Then the polymer was washed with water and dried *in vacuo* at 80 °C for 10 h. The reaction yield was quantitative. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 7.94 (4H, d), 7.71 (4H, s), 7.61 (end-group, d), 7.44 (end-group, d), 7.16 (4H, s), 6.84 (end-group, d).

### Synthesis of Sulfonated Multiblock Copoly(ether sulfone) by End-capping System (4EP)

**1** ( $M_n = 10000$ , 0.09 mmol, 0.9 g), **3** ( $M_n = 4600$ , 0.09 mmol, 0.4 g), and  $K_2CO_3$  (0.18 mmol, 0.025 g) were placed into a round-bottomed flask equipped with a condenser, and a gas adapter. NMP (12 mL) was charged into the reaction flask under a nitrogen atmosphere. The reaction temperature was increased to 120 °C. After 18 h, the mixture was cooled to room temperature and poured into isopropanol to precipitate a brown polymer. The precipitated polymer was stirred in 1 M  $H_2SO_4$  aq at room temperature for 2 d for protonation. Then the polymer was thoroughly washed with water, and dried *in vacuo* at 80 °C for 10 h. The reaction yield was quantitative. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.31, 7.99–7.81, 7.77–7.60, 7.24–7.00.

### Synthesis of Sulfonated Multiblock Copoly(ether sulfone) by a Chain Extender System (4CE)

The general polymerization method for the sulfonated multiblock copoly(ether sulfone) by a chain extender system has been described in the previous papers.<sup>19,20</sup> IR (KBr,  $\nu$ ,  $cm^{-1}$ ): 1234 (-O-), 1325 (-SO<sub>2</sub>-). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.30, 7.98–7.81, 7.76–7.60, 7.24–6.98.

### Membrane Preparation and Ion Exchange Capacity (IEC)

The NMP solutions of **4EP** and **4CE** were filtered and cast onto a flat glass plate. Drying the solution at 80 °C for 10 h under reduced pressure gave a tough, flexible, and transparency membranes. IEC values were determined by <sup>1</sup>H NMR spectra.

### Proton Conductivity

Proton conductivity in plane direction of membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 5 Hz to 1 MHz (Hioki 3532-80). A two-point-probe conductivity cell with two platinum plate electrodes was fabricated. The cell was plated under a thermocontrolled humid chamber. Proton conductivity ( $\sigma$ ) was calculated from:

$$\sigma = d/(L_s w_s R)$$

where  $d$  is the distance between the two electrodes,  $L_s$  and  $w_s$  are the thickness and width of the membrane, and  $R$  is the resistance value measured.

### Water Uptake and Dimensional Change

Water uptake of a hydrated membrane was measured by immersing the membrane into water at room temperature for 24 h. Then the membrane was taken out, wiped with a tissue paper, and quickly weighed on a microbalance. Water uptake was calculated from:

$$WU = (W_s - W_d)/W_d \times 100 \text{ wt } \%$$

Where,  $W_s$  and  $W_d$  are the weights of wet and dried membranes, respectively.

The humidity dependence of water uptake was measured by plating the membrane in a thermo-controlled humid chamber for 6 h. Then the membrane was taken out, and quickly weighed on a microbalance.

Dimensional change of a hydrated membrane was investigated by immersing the membrane into water at room temperature for 24 h, the changes of thickness and length were calculated from:

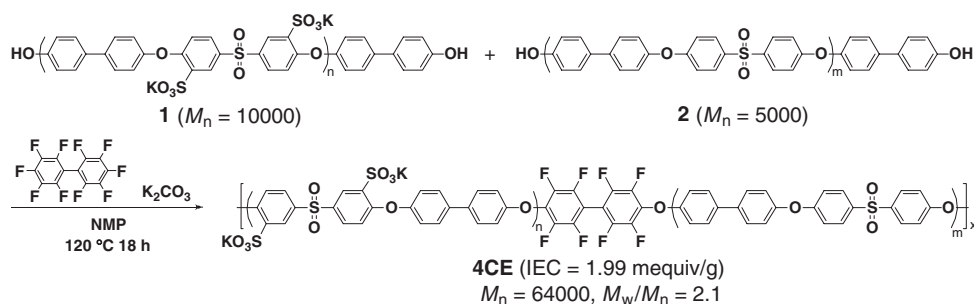
$$\Delta t = (t - t_s)/t_s$$

$$\Delta l = (l - l_s)/l_s$$

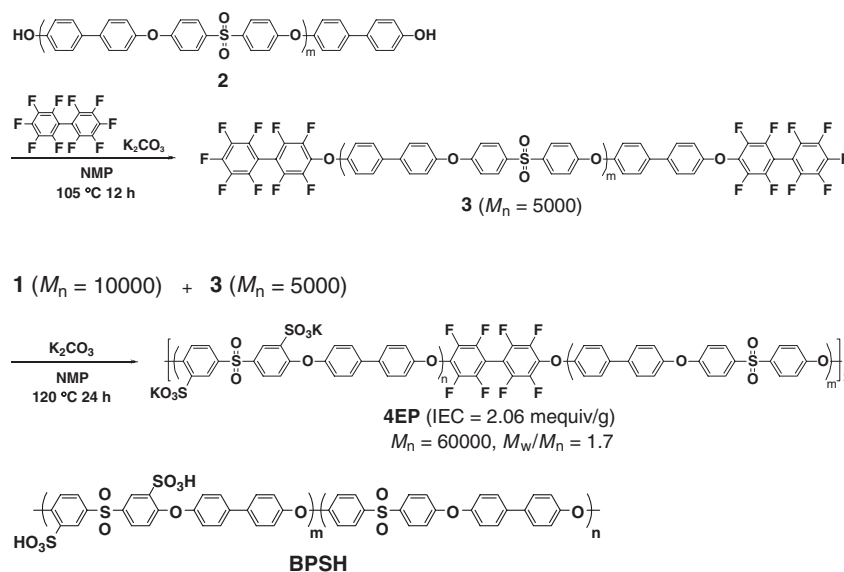
where  $t_s$  and  $l_s$  are the thickness and diameter of the dried membrane, respectively;  $t$  and  $l$  refer to those of the membrane in water for 24 h.

### Atomic Force Microscopic (AFM) Observations

Tapping mode AFM observations were performed with a Digital Instrument, SII-NT SPA400, using micro-fabricated



**Scheme 1.** Synthesis of **4CE** by chain extender method.



**Scheme 2.** Synthesis of **4EP** by end-capping method and the structure of BPSH.

cantilevers with a force constant of approximately 20 N/m. All treated samples were allowed to equilibrate by exposing under 100% relative humidity at room temperature for at least 24 h before testing.

### Measurement

$^1\text{H}$  (300 MHz) and  $^{13}\text{C}$  spectra (75 MHz) were recorded with a Bruker DPX300S spectrometer. Number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) were measured by gel permeation chromatography (GPC) on a Hitachi LC-7000 system equipped with a polystyrene gel column (TSKgel GMHHR-M) eluted with *N,N*-Dimethylformamide (DMF) containing 0.01 M LiBr at a flow rate of  $1.0\text{ mL min}^{-1}$  calibrated by standard polystyrene samples.

## RESULTS AND DISCUSSION

### Synthesis of Sulfonated Block Copoly(ether sulfone)s

Sulfonated random multiblock copoly(ether sulfone)s (**4CE**:  $M_n = 64000, M_w/M_n = 2.1$ ) was prepared by the coupling reaction of hydroxyl-terminated hydrophilic oligomer (**1**) and hydroxyl-terminated hydrophobic oligomer (**2**) in the presence

of DFB as the chain extender (Scheme 1). On the other hand, sulfonated alternating multiblock copoly(ether sulfone)s (**4EP**:  $M_n = 60000, M_w/M_n = 1.7$ ) was prepared from **1** and fluorine-terminated hydrophilic oligomer (**3**) obtained by the end-capping method (Scheme 2).<sup>20</sup> Block copolymers with high molecular weights gave tough, flexible, and transparent films by NMP solution casting. The IEC values of **4CE** and **4EP** calculated by  $^1\text{H}$  NMR spectra were 1.99 and 2.06 mequiv/g, respectively, which were in good agreement with the theoretical IEC values (2.10 mequiv/g) calculated from the feed ratios of oligomers. This indicates that each polycondensation was carried out successfully.

### Characterization of Block Copolymers

The  $^{13}\text{C}$  NMR spectra of **4CE**, **4EP**, and a corresponding random copolymer BPSH polymer are shown in Figure 2. The carbons of the random copolymer have several multiplet peaks, suggesting an irregular connection of the repeating sequences. In contrast, the carbons of **4CE** and **4EP** have sharp narrow peaks. Moreover, the carbons of **4EP** show sharper and narrower peaks in comparison with those of **4CE**. As described before, **4CE** is not an alternating multiblock copolymer but a

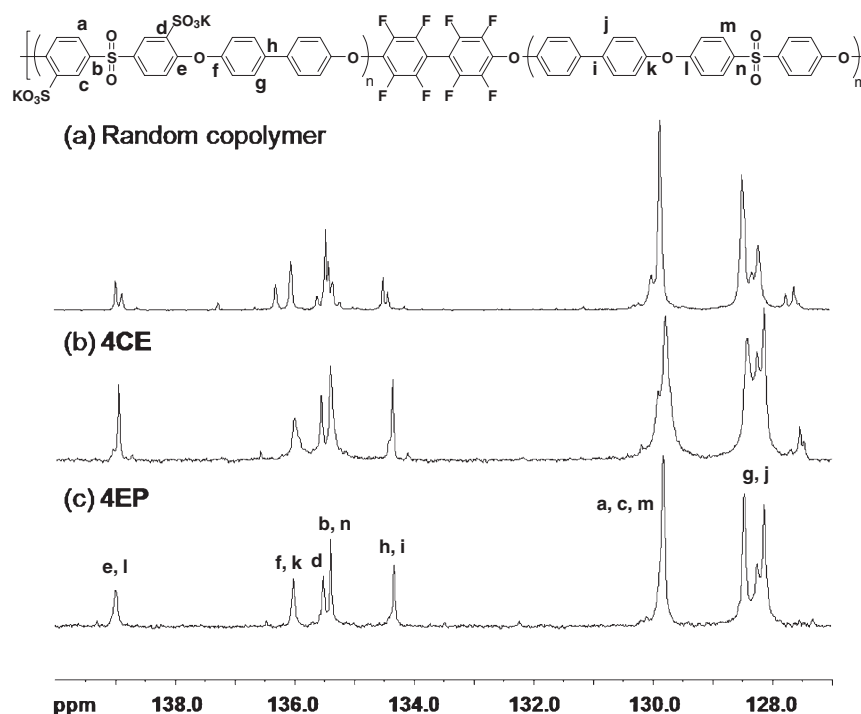


Figure 2.  $^{13}\text{C}$  NMR spectra of (a) random copolymer, (b) **4CE**, and (c) **4EP** in  $\text{DMSO-}d_6$ .

Table I. Water uptake and dimensional change of **4CE** and **4EP**

Run	IEC (mequiv/g) <sup>b</sup>	WU (wt%) <sup>c</sup>	$\Delta l^d$	$\Delta t^d$
<b>4CE</b> (2.10 mequiv/g <sup>a</sup> )	1.99	63	0.09	0.28
<b>4EP</b> (2.10 mequiv/g <sup>a</sup> )	2.06	96	0.16	0.45

<sup>a</sup>IECs calculated from feed ratios. <sup>b</sup>IECs calculated from  $^1\text{H}$  NMR spectra. <sup>c</sup>At the hydrated state. <sup>d</sup>At the hydrated membranes.

random multiblock copolymer. The difference of the  $^{13}\text{C}$  NMR spectra between them is due to the controlled degree of the polymer structure.

### Water Uptake and Dimensional Change

The water uptake of polymer membranes is very important, since the water facilitates the transportation of protons from the anode to the cathode and affects other membrane performances. However, excessive water uptake can lead to unacceptable dimensional changes and a decrease in the mechanical properties. The water uptake and dimensional changes of hydrated **4CE** and **4EP** membranes are summarized in Table I. The **4EP** membrane exhibited higher water uptake (96 wt %) than that of the **4CE** membrane (63 wt %) in the hydrated state. As for their dimensional change, the **4EP** membrane showed bigger dimensional change than that of the **4CE** membrane due to its higher water uptake, and both membranes showed an anisotropic dimensional change, which is a larger swelling in the membrane thickness direction than in the plane direction.

The humidity dependence of water uptake was measured for **4CE** and **4EP** membranes at  $80^\circ\text{C}$ . The results are shown in Figure 3, in comparison with those of Nafion 117. The water

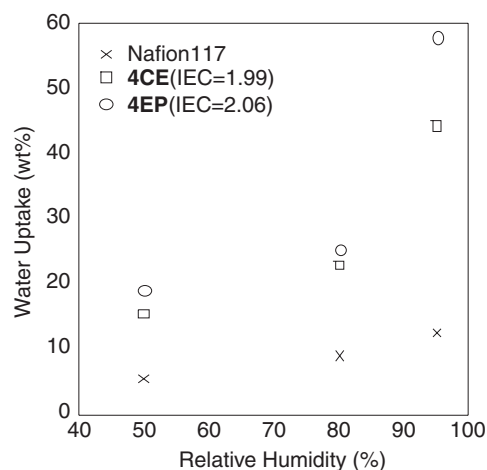
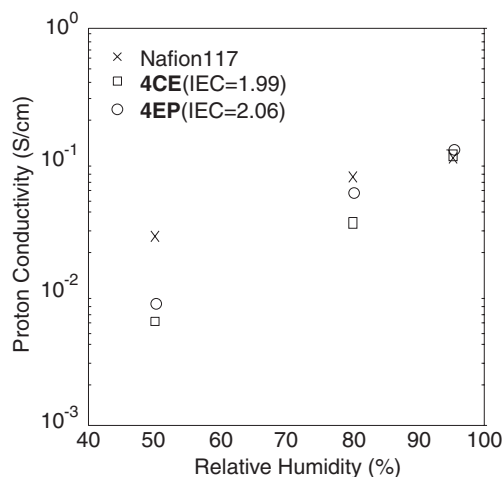
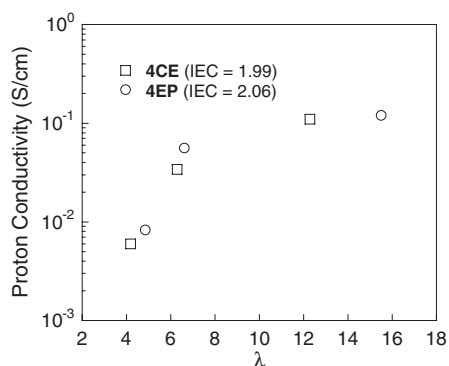


Figure 3. Humidity dependence of water uptake of **4CE**, **4EP**, and Nafion 117 membranes at  $80^\circ\text{C}$ .

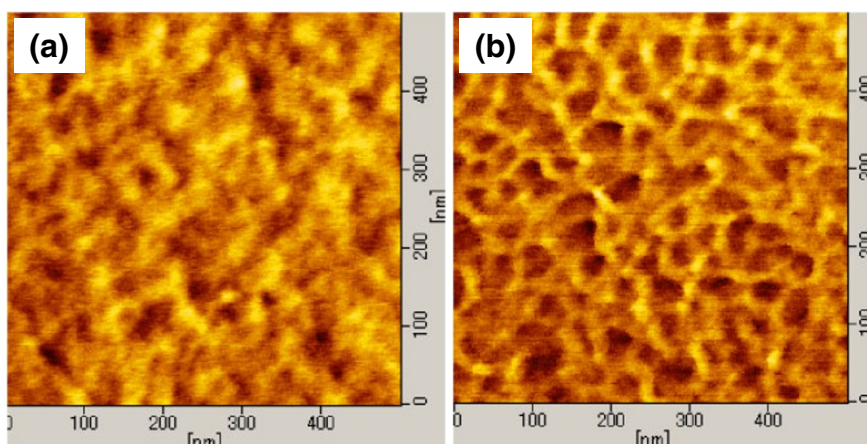
uptake of Nafion 117 is lower than those of block copolymer membranes due to its low IEC value (0.90 mequiv/g). As can be seen in Figure 3, **4CE** membrane absorbs 44.4, 23.0, and 15.6 wt % of water at 95, 80, and 50% RH, respectively. On the other hand, **4EP** membrane absorbs 58.1, 25.6, and 19.1 wt % of water at 95, 80, and 50% RH, respectively. The water uptake of **4EP** membrane is slightly higher than that of **4CE** membrane even under low relative humidity, probably due to an enhanced phase separation of **4EP**.<sup>22</sup> This difference of water uptake between **4CE** and **4EP** membranes would affect their proton conductivities.



**Figure 4.** Humidity dependence of proton conductivity of **4CE**, **4EP**, and Nafion 117 membranes at 80 °C.



**Figure 5.** Relationship between hydration number ( $\lambda$ ) and proton conductivity for **4CE** and **4EP** membranes at 80 °C.



**Figure 6.** AFM tapping mode phase images of (a) **4CE** and (b) **4EP** membrane: Scan sizes are 500 × 500 nm<sup>2</sup>.

### Proton Conductivity

The humidity dependence of proton conductivity was measured for **4CE** and **4EP** membranes at 80 °C. The results are shown in Figure 4, in comparison with those of Nafion 117. The proton conductivities of **4CE** and **4EP** membranes are comparable to that of Nafion 117 at 95% RH. The proton conductivity of **4EP** membrane is a little higher than that of **4CE** membrane at 80 and 50% RH. The proton conductivity of **4CE** and **4EP** membranes are  $3.4 \times 10^{-2}$ ,  $5.8 \times 10^{-2}$  S/cm at 80% RH, and  $6.1 \times 10^{-3}$ ,  $8.6 \times 10^{-3}$  S/cm at 50% RH, respectively. These results reflect the difference of water uptake between **4CE** and **4EP** membranes discussed above. Considering other factors of **4CE** and **4EP**, that is, block lengths and feed ratios of each unit, and IEC values are same; the difference of proton conductivity between them is due to the controlled degree of the polymer structure. This data demonstrates that the controlled polymer structure (alternating multiblock copolymer) is presumably necessary and promising for high proton conductivity. The proton conductivities of **4CE** and **4EP** membranes are lower at lower humidity than that of Nafion 117, which indicates that **4CE** and **4EP** membranes are

unlikely to have well-developed hydrophilic domains as compared to Nafion 117.

The relationship between water uptake and proton conductivity was investigated for **4CE** and **4EP** membranes. In Figure 5, proton conductivity is plotted versus hydration number,  $\lambda$ , which is the number of water molecules per a sulfonic acid unit. As shown in Figure 5, proton conductivity tends to increase with increasing the  $\lambda$  values of the membranes. Compared to **4CE** membrane, **4EP** membrane shows slightly higher proton conductivity in similar IEC values. This result suggests that **4EP** membrane has effective proton paths, which are induced by controlled structure.

### Atomic Force Microscope (AFM) Observations

To get information on the phase-separated morphology of copolymers, the tapping mode phase images of **4CE** and **4EP** were recorded under ambient conditions on 500 × 500 nm<sup>2</sup> size scales. In Figure 6, the dark and bright regions were assigned to the soft structure corresponding to the hydrophilic sulfonic acid groups containing water and the hard structure corresponding to the hydrophobic polymer matrix, respectively.



Although both copolymers show a phase-separated structure, **4EP** membrane exhibits a clearer phase separation where the domains are better connected each other continuously. This difference of the phase-separated morphology between them results in a small change of proton conductivity probably because of still less connectivity of proton paths under low humidity conditions.

## CONCLUSIONS

Sulfonated random multiblock and alternating multiblock copoly(ether sulfone)s with the same chemical compositions were prepared by the chain extender method and end-capping method, respectively, to investigate the influence of the polymer structure on membranes' properties, such as water uptake and proton conductivity. This polymer structural change induced higher water absorption and consequent higher proton conductivity, probably due to the enhanced phase separation. Thus, the controlled polymer structure (alternating multiblock copolymer) is presumably necessary and promising for achieving high proton conductivity.

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