Locally and Densely Sulfonated Poly(ether sulfone)s as Proton Exchange Membrane

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Received November 24, 2008; Revised Manuscript Received January 3, 2009

ABSTRACT: New locally and densely sulfonated poly(ether sulfone)s were successfully prepared for fuel cell applications by the nucleophilic substitution of 4,4′-dichlorodiphenylsulfone with 1,2,4,5-tetrakis([1,1′-biphenyl]-2-oxy)-3,6-bis(4-hydroxyphenoxy)benzene and 2,2-bis(4-hydroxyphenyl)hexafluoropropane, followed by sulfonation using chlorosulfonic acid. The polymers gave tough, flexible, and transparent membranes by solvent casting. The large difference in polarity between the locally and densely sulfonated units and hydrophobic units of the polymers resulted in the formation of well-defined phase-separated structures, which induced efficient proton conduction in a wide range of 30−95% RH at 80 °C.

Introduction

Polymer electrolyte fuel cells (PEFCs), which convert chemical energy to electrical energy, are regarded as promising future power sources owing to their advantages, such as high efficiency, high energy density, quiet operation, and environmental friendliness. One of the key materials for PEFCs is a proton exchange membrane (PEM), which allows for the proton transport from the anode to the cathode. The current state-of-the-art PEM materials are perfluorinated polymers such as Nafion or Flemion because of their good physical and chemical stability along with high proton conductivity under a wide range of relative humidity at moderate operation temperatures.[1,2] However, they suffer from disadvantages such as limited operation temperature (<80 °C), high cost, and high methanol permeability. These problems have driven the investigation of aromatic hydrocarbon polymers as alternative PEM materials[3−5] and a number of sulfonated aromatic polymers such as poly(phenylene)s,[6,7] poly(ether ether ketone)s,[8,9] poly(ether ether sulfone)s,[10,11] poly(arylene ether)s,[12,13] and polyimides[14−16] have been developed as capable candidates. Generally, membranes based on these polymers require high ion exchange capacities (IECs) to achieve comparable proton conductivity for perfluorinated polymers.

The proton conducting properties of PEMs basically rely on IECs and water uptake, especially for sulfonated aromatic polymers. Although highly sulfonated polymers show high proton conductivity, their massive water uptake results in a dramatic loss of mechanical properties. As a strategy to improve proton conductivity and mechanical properties, a multiblock copolymer system has been extensively studied.[17−19] Multiblock copolymers composed of hydrophilic and hydrophobic segments are expected to form ion transport channels which enable efficient proton conduction, derived from hydrophilic/hydrophobic phase-separated structures. Improvement of proton conductivity, especially under low relative humidity conditions, is reported in that system. On the other hand, Hay et al. reported poly(arylene ether)s with highly sulfonated units only on the end groups in order to enhance the difference between hydrophilic and hydrophobic units.[20−23] Their membranes show a significantly phase-separated morphology. However, their structures are limited in the number of sulfonated units because the number of terminated groups is restricted. Furthermore, hydrophilic units at the periphery increase the water solubility of polymers, which prevents an increase in IEC values. For this reason, we have recently reported star-shaped sulfonated block copoly(ether ketone)s having inner hydrophilic segments surrounded by outer hydrophobic segments.[24] The membranes obtained showed relatively good dimensional stability, high bound-water content, and excellent proton conductivity which were comparable to those of Nafion 117 in the range of 50−95% RH at 80 °C. Locally and densely sulfonated polymers are also expected to form hydrophilic/hydrophobic phase-separated structures because of the high contrast in polarity between them.

In this article, we report the synthesis and the properties of locally and densely sulfonated poly(ether sulfone)s for PEM applications. The pendant side phenyl groups along the main chains were selectively postsulfonated and yielded densely sulfonated hydrophilic units. Introduction of hydrophilic units in the main chains is an excellent way to prepare PEMs because of the easy control of IEC values and the wide variety of monomer choices. As new poly(ether sulfone)s have local and eight sulfonation positions in the polymer chains, sulfonic acid groups are introduced locally and densely in comparison with previous reports.[25,26] The large difference in polarity between the densely sulfonated hydrophilic units and the hydrophobic units is expected to produce clear phase-separated structures, which can induce effective proton conduction.

Experimental Section

Materials. 1,2,4,5-Tetrafluoro-3,6-bis(4-methoxyphenoxy)benzene (**1**) was synthesized from 4-methylphenol and hexafluorobenzene according to the previous report.[27] Dichloromethane was distilled from calcium hydride before use. Other solvents and reagents were used as received.

1,2,4,5-Tetrakis([1,1′-biphenyl]-2-oxy)-3,6-bis(4-methoxyphenoxy)benzene (2). To a round-bottomed flask equipped with a Dean−Stark trap, **1** (0.79 g, 2.0 mmol), 2-phenylphenol (2.04 g, 12 mmol), and K_2CO_3 (1.66 g, 12 mmol) were charged. Then, 1,3-dimethyl-2-imidazolidinone (8 mL) and toluene (5 mL) were added into the flask under nitrogen. The reaction mixture was stirred at 150 °C for 2 h. After removal of toluene, the reaction temperature was increased to 220 °C, and the reaction was continued for 48 h. After cooling to room temperature, the mixture was poured into 10 wt % NaOH(aq). The resulting precipitate was collected and dissolved in DMF. The solution was poured into 10 wt % NaOH(aq), and the resulting solid was collected and purified by column chromatography on a silica gel (dichloromethane:hexane = 1:1) to yield a white solid. The yield was 1.73 g (87%). IR (KBr,

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10.1021/ma802637w CCC: $40.75

ν, cm^{-1}); 1250 (−O−), 2939 (−CH$_3$). ^{1}H NMR (CDCl$_3$, δ, ppm): 3.67 (s, 6 H), 6.38−6.49 (m, 8 H), 6.57 (d, J = 8.0 Hz, 4 H), 6.87−6.97 (m, 12 H), 6.99−7.17 (m, 20 H). ^{13}C NMR (CDCl$_3$, δ, ppm): 55.77, 114.13, 114.47, 117.18, 122.68, 126.65, 127.70, 128.06, 129.55, 130.70, 130.98, 137.62, 139.29, 140.18, 151.65, 154.01, 155.00. Anal. Calcd for ($C_{68}H_{50}O_8$): C, 82.07; H, 5.06. Found: C, 81.73; H, 5.25.

1,2,4,5-Tetrakis([1,1′-biphenyl]-2-oxy)-3,6-bis(4-hydroxyphenoxy)benzene (3). To a solution of **2** (1.20 g, 1.2 mmol) in dry dichloromethane (21 mL) was added a solution of BBr$_3$ in dichloromethane (2.9 mL, 2.9 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, and the reaction temperature was increased to room temperature. The reaction was continued for 12 h, and the mixture was diluted with CH_2Cl_2, washed with water, dried over MgSO$_4$, and concentrated in vacuo. The resulting solid was purified by column chromatography on a silica gel (dichloromethane) to yield a white solid. The yield was 1.07 g (92%); mp 233.0 °C (by DTA). IR (KBr, ν, cm^{-1}); 1250 (−O−), 3417 (−OH). ^{1}H NMR (CDCl$_3$, δ, ppm): 4.44 (s, 2 H), 6.32−6.42 (m, 8 H), 6.56 (d, J = 8.0 Hz, 4 H), 6.86−6.97 (m, 12 H), 6.98−7.19 (m, 20 H). ^{13}C NMR (CDCl$_3$, δ, ppm): 114.48, 115.56, 117.38, 122.72, 126.66, 127.72, 128.06, 129.54, 130.70, 130.98, 137.60, 139.28, 140.15, 150.77, 151.71, 153.99. Anal. Calcd for ($C_{66}H_{46}O_8$): C, 81.97; H, 4.79. Found: C, 82.15; H, 5.06.

Synthesis of Poly(ether ether sulfone) (Typical Example). To a round-bottomed flask equipped with a Dean−Stark trap, 4,4′-dichlorodiphenylsulfone (0.43 g, 1.5 mmol), **3** (0.29 g, 0.3 mmol), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (0.40 g, 1.2 mmol), and K_2CO_3 (0.62 g, 4.5 mmol) were charged. Then, *N*,*N*-dimethylacetamide (DMAc) (3 mL) and cyclohexane (3 mL) were added into the flask under nitrogen. The reaction mixture was stirred at 100 °C for 2 h. After removal of cyclohexane, the reaction temperature was increased to 165 °C, and the reaction was continued for 16 h. After cooling to room temperature, the mixture was poured into methanol. The resulting fiber was filtered and washed with water and hot methanol. The polymer was dried in vacuo at 100 °C for 8 h to give **4b**. The yield was 0.96 g (95%). IR (KBr, ν, cm^{-1}); 1250 (−O−), 1327 (−SO$_2$−).

Sulfonation of Polymer. To a round-bottomed flask equipped with a dropping funnel, 0.3 g of **4b** was charged. Then, dry dichloromethane (9 mL) was added into the flask, and the mixture was cooled to 0 °C. To the mixture was added dropwise a solution of chlorosulfonic acid (0.19 mL, 2.8 mmol) in dry dichloromethane (2 mL) at 0 °C and stirred at RT for 5 h. After the reaction, the mixture was poured into hexane. The resulting polymer was dissolved in DMAc, and several drops of water and triethylamine were added to the solution. The solution was stirred at RT for 2 h and poured into 2 M H_2SO_4(aq). The resulting polymer was washed with 2 M H_2SO_4(aq) and water. The polymer was dried in vacuo at 100 °C for 10 h to give **5b**. IR (KBr, ν, cm^{-1}); 1250 (−O−), 1327 (−SO$_2$−), 1119 (−SO$_3$H).

Membrane Preparation and Ion Exchange Capacity (IEC). A *N*-methylpyrrolidinone (NMP) solution of a sulfonated polymer was filtered and cast onto a flat glass plate. The film was heated at 60 °C for 3 h, 80 °C for 3 h, 100 °C for 3 h, and 120 °C for 1 h. Then the film was dried in vacuo at 100 °C for 12 h. The dried film was immersed in 2 M H_2SO_4(aq) at 60 °C for 3 h and then thoroughly washed with water at 80 °C to give a tough and flexible membrane. IECs were determined by titration with 0.02 M NaOH(aq).

Proton Conductivity. Proton conductivity in plane direction of the membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 5 Hz to 100 kHz (Hioki 3532-80). A two-point-probe conductivity cell with two platinum plate electrodes was fabricated. The cell was placed under a thermocontrolled humid chamber. Proton conductivity (σ) was calculated from

$$\sigma = d/(L_s W_s R) \qquad (1)$$

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 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

$$\mathrm{WU} = (W_s - W_d)/W_d \times 100 \text{ wt } \% \qquad (2)$$

where W_s and W_d are the weights of hydrated and dried membranes, respectively. The weights of dried membranes were measured after drying in vacuo at 100 °C for 8 h.

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

$$\Delta t = (t - t_s)/t_s \qquad (3)$$

$$\Delta l = (l - l_s)/l_s \qquad (4)$$

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.

Oxidative Stability. Small pieces of membrane samples were soaked in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm FeSO$_4$) for 1 h at 80 °C. The stability was evaluated by changes in weight and appearance of the test samples.

Atomic Force Microscopic Observations. Tapping mode atomic force microscopic (AFM) observations were performed with a Digital Instrument SII-NT SPA400, using microfabricated cantilevers with a force constant of ~20 N/m. All samples were cast onto flat glass plates and heated at 60 °C for 3 h, 80 °C for 3 h, 100 °C for 3 h, and 120 °C for 1 h. Then the films were dried in vacuo at 100 °C for 12 h. The resulting films were allowed to stand under 100% relative humidity at room temperature for 12 h before testing.

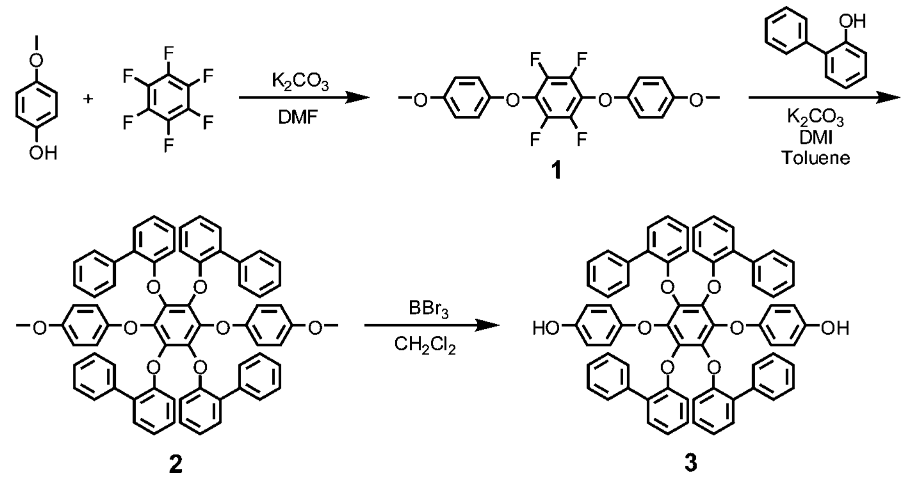
Transmission Electron Microscopic Observations. The membranes was stained with lead by ion exchange of the sulfonic acid groups by immersing it in a large excess of PbNO$_3$ aqueous solution for 3 days and then rinsed with water. The stained membrane was embedded in epoxy resin and sectioned to give 70 nm thick membrane. Transmission electron microscopic (TEM) observations were performed with a JEOL JEM-2010 transmission electron microscope.

Measurement. FT-IR spectra were measured on a Horiba FT-720 spectrometer. ^{1}H (300 MHz) and ^{13}C spectra (75 MHz) were recorded with a Bruker DPX300S spectrometer. Molecular weight measurement was performed via gel permeation chromatography with JASCO PU-2080Plus with two polystyrene gel columns (TSK GELs; GMH$_{HR}$-M). *N*,*N*-Dimethylformamide (DMF) containing 0.01 M LiBr was used as a solvent at a flow rate of 1.0 mL min^{-1}. M_n and M_w were calibrated by standard polystyrene samples. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and differential thermal analysis (DTA).

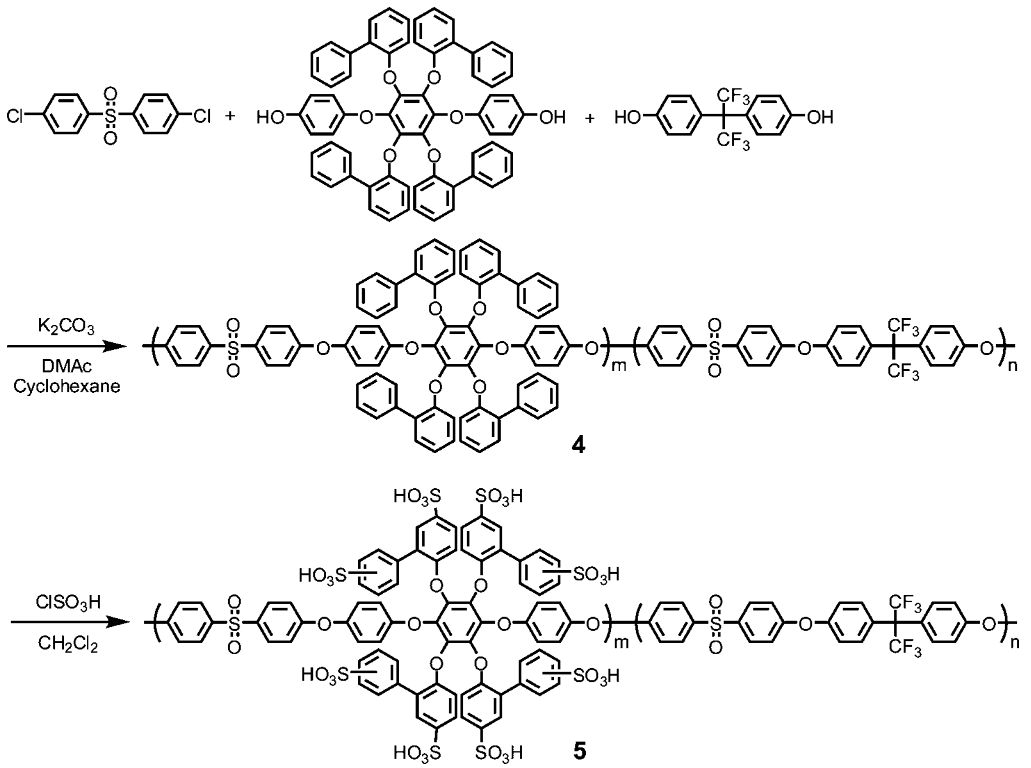
Results and Discussion

Synthesis of Monomer. As a new monomer having eight sulfonation positions in the polymers, 1,2,4,5-tetrakis([1,1′-biphenyl]-2-oxy)-3,6-bis(4-hydroxyphenoxy)benzene (**3**) was designed and prepared as shown in Scheme 1. The aromatic nucleophilic substitution reaction between 4-methoxyphenol and hexafluorobenzene gave disubstituted compound **1**. Compound **2** was prepared by the reaction of 2-phenylphenol with **1**, which required a high temperature (220 °C) and a long reaction time (48 h) due to the steric hindrance of 2-phenylphenol. Compound **3** was obtained by the demethylation of **2** using BBr$_3$. The structure of **3** was confirmed by IR and NMR spectroscopy and

Scheme 1. Synthesis of Monomer 3



Scheme 2. Synthesis of Polymers 4 and 5



elemental analysis. The IR spectrum of **3** showed characteristic absorptions corresponding to C−O−C and OH stretching at 1250 and 3417 cm^{-1}, respectively. Figure 1 shows the ^{1}H NMR spectrum of **3**, consisting of a singlet peak at 4.44 ppm and multiplets at 6.32−7.19 ppm that are assigned to OH and aromatic protons, respectively. Furthermore, the structure of **3** was confirmed by elemental analysis.

Synthesis of Polymers. Poly(ether sulfone) was selected as the main chain because of its high adaptability to PEM application. As a comonomer, 2,2-bis(4-hydroxyphenyl)hexafluoropropane (Bis-AF) was used for the hydrophobic unit due to its high hydrophobicity. Random copolymers **4** were synthesized via polycondensation (Scheme 2). The feed ratio of monomer **3** to Bis-AF was changed to get polymers with different IEC values after sulfonation. Polymers with over 60 000 Da of number-average molecular weights were easily obtained (Table 1) and were soluble in chloroform, THF, and polar aprotic solvents.

The structure of polymers **4** was confirmed by IR and ^{1}H NMR spectroscopy. In the IR spectra of polymers **4**, characteristic absorption due to the sulfone groups was observed at 1327 cm^{-1}. The ^{1}H NMR spectrum of polymer **4a** is shown in Figure 2. All signals were well assigned, and the expected copolymer structure was confirmed. The integral ratio of the peaks at 7.84 and 7.96 ppm, which were assigned to the *b* and *m* protons, respectively, was calculated to determine the polymer composition. The calculated composition from the ^{1}H NMR spectrum ($m/n = 17/83$) matched well with the feed ratio (**3**/Bis-AF = 17/83).

Sulfonation of Polymers. Sulfonation of polymers **4** was performed by using chlorosulfonic acid to give sulfonated polymers **5** (Scheme 2). Generally, the introduction of sulfonic acid groups by chlorosulfonic acid preferentially occurs on electron-rich aromatic rings because sulfonation is an electrophilic reaction. In this case, phenyl rings of 2-phenylphenoxy groups should be sulfonated. In order to achieve complete

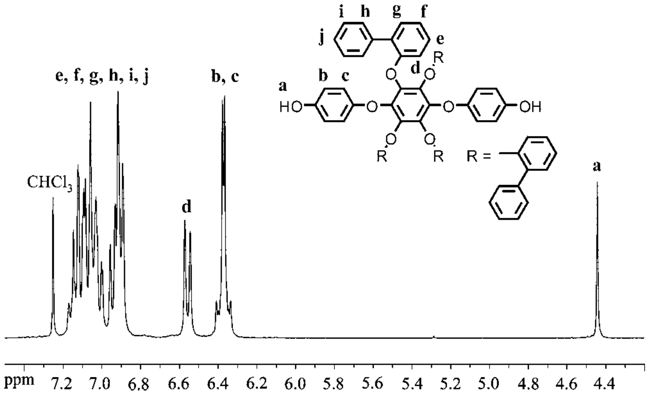


Figure 1. ^{1}H NMR spectrum of monomer **3**.

Table 1. Properties of Polymers 4

sample	composition[a] (mol/mol) *m*/*n*	M_n[b] (kDa)	M_w/M_n[b]
4a	0.17/0.83	61.5	1.6
4b	0.20/0.80	67.2	1.5

[a] Determined by ^{1}H NMR. [b] Determined by GPC based on polystyrene standards.

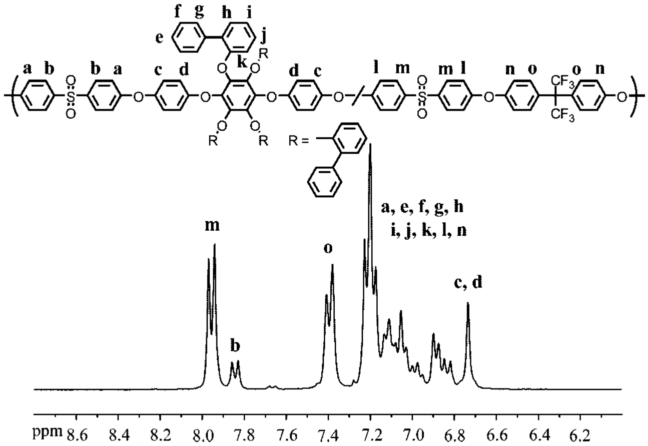


Figure 2. ^{1}H NMR spectrum of polymer **4a**.

sulfonation to **3**, an excess amount of chlorosulfonic acid was used. After sulfonation, a part of the sulfonic acid groups existed as sulfonyl chlorides because of the excess chlorosulfonic acid. Therefore, all sulfonyl chloride groups were hydrolyzed using triethylamine and water. The sulfonated polymers were readily soluble in polar aprotic solvents such as DMF, DMAc, NMP, and dimethyl sulfoxide (DMSO). Tough, flexible, and transparent membranes of polymers **5** were obtained by solvent casting.

The structure of polymers **5** was confirmed by IR and ^{1}H NMR spectroscopy. A characteristic sulfonic acid absorption was observed at 1119 cm^{-1} in the IR spectra. The ^{1}H NMR spectrum of polymer **5a** is shown in Figure 3. The signals at 6.7−7.2 ppm decreased and new signals assigned to the f′, h′, and j′ protons, which were neighbors of the sulfonic acid groups, appeared at around 7.5 ppm. The integral ratio between signals at 7.3−7.6 ppm (f′, h′, j′, o′) and at 7.8−8.1 ppm (m′, b′) was 6:4, which accorded with that of the desired structure.

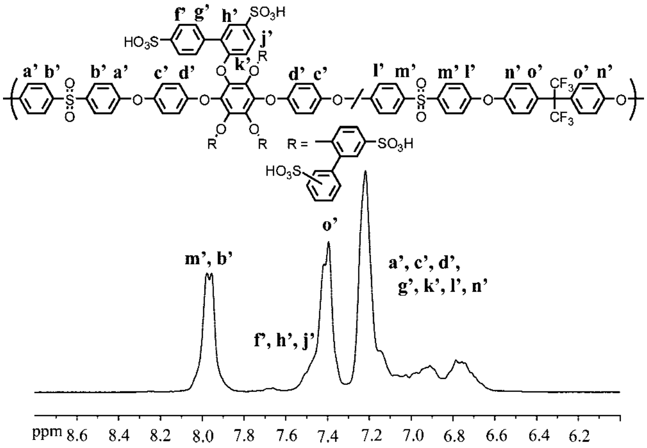


Figure 3. ^{1}H NMR spectrum of polymer **5a**.

The IEC values of polymers **5** were determined by titration and agreed well with the calculated values (Table 2). This result indicates that selective and complete sulfonation to the **3** moiety was achieved.

Thermal Stability. The thermal stability of polymers **5** was evaluated by TG analysis. A three-step weight loss was observed from 50 to 200 °C, from 320 to 450 °C, and above 450 °C. The first weight loss is due to the evaporation of hydrated water, and the second and third ones are attributed to the decomposition of the sulfonic acid groups and the polymer main chains, respectively. Generally, the decomposition of sulfonic acid groups attached to electron-rich benzene rings starts at around 250 °C.[15,28] Although half of the sulfonic acid groups of polymers **5** are attached to the electron-rich benzene rings (the i position in Figure 2), their decomposition temperature is higher than 300 °C. This decomposition behavior may be explained as follows: the electron-donating effect of the phenoxy group in the **3** moiety is weakened by resonance with the pendant phenyl group and the electron-withdrawing effect of the sulfonic acid group attached to the pendant phenyl group.

Oxidative Stability. The oxidative stability of the membranes **5** was evaluated in a hot Fenton's reagent (80 °C) for 1 h as an accelerated test. BPSH-40, which is a typical sulfonated poly(ether ether sulfone),[13] was used for comparison. The results are summarized in Table 2. For all samples, no weight loss was observed, and their film properties such as flexibility and transparency were maintained even after the test. Generally, large weight losses are observed for membranes with high IEC values, and the oxidative degradation mainly occurs on the main chains.[11] The high oxidative stability of the membranes **5** can be considered to be derived from their moderate IEC values (up to around 2.0 mequiv/g) and localized hydrophilic units.

Water Uptake and Dimensional Change. Water uptake is an important factor in proton conductivity because water in a membrane acts as a transportation medium of protons. However, high water uptake causes a large dimensional change in the membranes.

The water uptake of **5** and BPSH-40 membranes after being immersed in water is summarized in Table 2. Membrane **5a** showed water uptake similar to BPSH-40, which has an IEC

Table 2. Properties of Polymers 5 and BPSH-40

sample	composition[a] (mol/mol) *m*/*n*	IEC[b] (mequiv/g)	IEC by titration[c]	water uptake (%)	Δ*l*	Δ*t*	weight residue[d] (%)
5a	0.17/0.83	1.77	1.80	36.5	0.12	0.12	100
5b	0.20/0.80	1.99	2.03	197	0.34	0.38	100
BPSH-40			1.71	45.2			100

[a] Determined by ^{1}H NMR. [b] Theoretical IEC value. [c] Determined by titration with 0.02 M NaOH(aq). [d] After treatment with Fenton's reagent (3% H_2O_2(aq) containing 2 ppm $FeSO_4$).

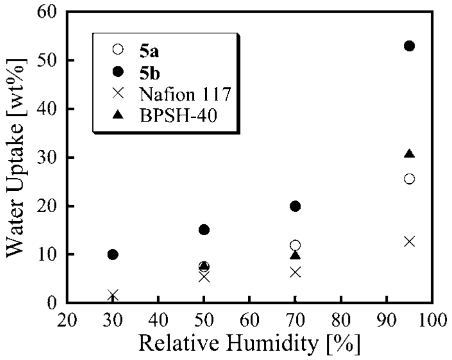


Figure 4. Relative humidity dependence of water uptake of polymers **5**, BPSH-40, and Nafion 117 at 80 °C.

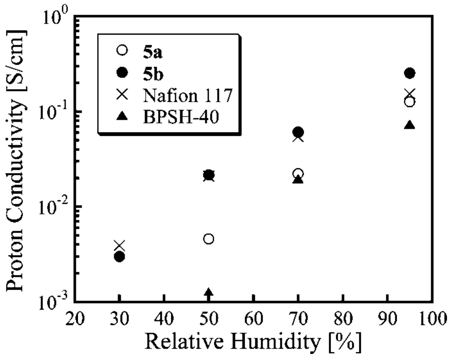


Figure 5. Relative humidity dependence of proton conductivity of polymers **5**, BPSH-40, and Nafion 117 at 80 °C.

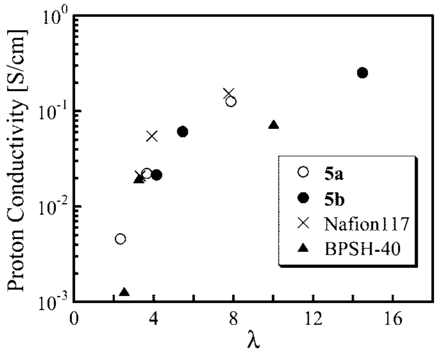


Figure 6. Relationship between hydration number (λ) and proton conductivity for polymers **5**, BPSH-40, and Nafion 117 at 80 °C.

value similar to membrane **5a**. On the other hand, membrane **5b**, which had a higher IEC value than **5a** and BPSH-40 membranes, showed high water uptake of 197%. The large increase in water uptake of membranes **5** would suggest that the IEC value of 1.99 mequiv/g is a critical value for polymers **5**. In fact, polymers **5** with IEC values over 2.3 mequiv/g were highly swelled or soluble in water.

The humidity dependence of water uptake was measured for membranes **5** at 80 °C. The results are shown in Figure 4, in comparison with BPSH-40 and Nafion 117. For all samples, water uptake tended to decrease with decreasing relative humidity. The water uptake of membrane **5a** in the range of 50−95% RH was almost the same as that of BPSH-40. On the other hand, the water uptake of membrane **5b** was higher than that of **5a**, BPSH-40, and Nafion 117 membranes in the measured range. Moreover, membrane **5b** exhibited high water uptake of around 10 wt % even at 30% RH. These results indicate that water uptake depends on IEC values.

The dimensional changes of membranes **5** were evaluated by comparing their hydrated state with dry state (Table 2). Membrane **5a** presented small dimensional changes (12%) in both the length and thickness directions. For membrane **5b**, a higher swelling degree for both length and thickness was observed due to its higher IEC value. It is reported that the anisotropy of proton conductivity for in plane and thickness directions of membranes was observed in membranes which showed anisotropic swelling.[16] In the case of membranes **5**, the isotropy of proton conductivity is expected due to their isotropic swelling nature.

Proton Conductivity. The proton conductivities of membranes **5** were measured at 80 °C in the range of 30−95% RH. The results are shown in Figure 5, in comparison with those of BPSH-40 and Nafion 117. The proton conductivity of membrane **5a** was almost the same as that of Nafion 117 at 95% RH. Although the IEC value of BPSH-40 (1.71 mequiv/g) was similar to that of membrane **5a** (1.80 mequiv/g), BPSH-40 showed lower proton conductivity than Nafion 117 at 95% RH. Moreover, BPSH-40 showed a greater dependence of proton conductivity on the relative humidity, and its proton conductivity at 50% RH was lower than that of **5a** and Nafion 117 membranes. On the other hand, membrane **5b**, which had a higher IEC value than membrane **5a**, showed higher proton conductivity than Nafion 117 at 95% RH. Furthermore, membrane **5b** showed a smaller dependence of proton conductivity on the relative humidity than **5a** and BPSH-40 membranes. The proton conductivity of membrane **5b** was maintained at the same level as that of Nafion 117 over the measured range (30−95%

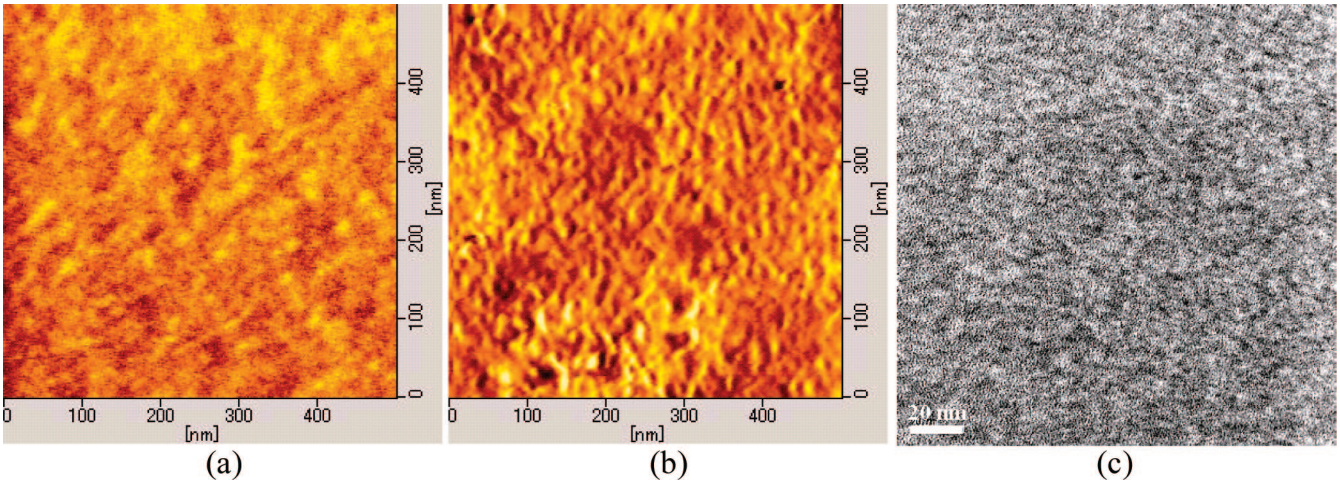


Figure 7. AFM tapping phase images of (a) BPSH-40 and (b) membrane **5b**; (c) cross-section TEM image of membrane **5b**.

RH). This result suggests that membranes **5**, especially the membrane **5b**, have defined phase-separated structures because of their high proton conductivity under low relative humidity conditions.

The relationship between water uptake and proton conductivity was investigated to clarify the advantage of locally and densely sulfonated units. In Figure 6, proton conductivity is plotted against hydration number, λ, which is the number of water molecules per sulfonic acid unit. As seen in Figure 6, all samples except for BPSH-40 showed a relatively moderate decrease in proton conductivity with a decrease in their hydration numbers. On the other hand, BPSH-40 exhibited great dependence of proton conductivity on hydration number, especially under low hydration number conditions. For example, membrane **5a** showed 4 times higher proton conductivity than BPSH-40 despite a similar hydration number of 2 for each sample. This result suggests that the proton paths of BPSH-40 are narrow and less connected under low water uptake conditions in comparison with **5** and Nafion 117 membranes. In the case of membranes **5**, the formation of developed and connected proton paths is assumed from this result.

AFM Observations. Tapping mode phase images of BPSH-40 and **5b** membranes were recorded under ambient conditions on a scale of 500 × 500 nm^2 to clarify their hydrophilic/hydrophobic morphology (Figure 7a,b). The bright and dark regions are derived from the hard segments corresponding to the hydrophobic units and the soft segments corresponding to the hydrophilic units containing water, respectively. Distinguished separation of the bright and dark region was not observed for BPSH-40 due to its small difference between hydrophilic and hydrophobic units. On the other hand, membrane **5b** showed that the well-defined phase-separated structures and hydrophilic domains, which are assigned to the dark region, were well connected to each other. Such a hydrophilic/hydrophobic separation of membrane **5b** would be induced by the large difference in polarity between the locally and densely sulfonated units and hydrophobic units. These morphological observations agree well with the results from the proton conductivity measurement. The advantageous contribution of locally and densely sulfonated units is recognized by the improvement in proton conductivity derived from the well-defined phase-separated structures.

TEM Observations. To investigate the morphology of membrane **5b** in cross section, transmission electron microscopy (TEM) was used. The cross-section TEM image of membrane **5b** is shown in Figure 7c. The dark and bright regions correspond to hydrophilic and hydrophobic domains, respectively, because the membrane was stained with lead nitrate. As shown in Figure 7c, clear phase separation, where hydrophilic domains were surrounded by hydrophobic domains, was observed. This defined phase-separated structure would assist the proton conduction of membrane **5b**.

Conclusions

Novel locally and densely sulfonated poly(ether sulfone)s were successfully synthesized for fuel cell applications. The pendant side phenyl groups along the main chains were selectively postsulfonated and yielded densely sulfonated hydrophilic units. The polymers gave tough, flexible, and transparent membranes by solvent casting. The large difference in polarity between the locally and densely sulfonated units and hydrophobic units of the polymers resulted in the formation of well-defined phase-separated structures, which enabled efficient proton conduction in a wide relative humidity range (30−95% RH) at 80 °C.

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MA802637W