Star-Shaped Sulfonated Block Copoly(ether ketone)s as Proton Exchange Membranes

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ABSTRACT: New star-shaped sulfonated block copolymers with hydrophilic and hydrophobic segments as arms have been developed. The star-shaped block copolymers were synthesized via the Friedel−Crafts reaction of a trifunctional core with AB monomers using trifluoromethanesulfonic acid, followed by sulfonation using concentrated sulfuric acid. High molecular-weight polymers over 37 000 in number average molecular weight were easily obtained and gave tough and flexible membranes by solvent casting. The membranes showed relatively good dimensional stability despite high water uptake due to their star-shaped structure. Moreover, the star-shaped structure having hydrophilic segments surrounded by hydrophobic segments enabled the achievement of high bound-water content. The membranes showed excellent proton conductivity which was comparable to that of Nafion 117 in the range of 50−95% RH at 80 °C.

Introduction

The fuel cell is one of the promising future power sources owing to its advantages such as high efficiency, high energy density, quiet operation, and environmental friendliness. The proton exchange membrane fuel cell (PEMFC) is considered to be the most promising power source for portable and automotive applications. Currently, perfluorinated polymers such as Nafion or Flemion are the state of the art materials 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, high operation temperatures, which are required for actual operations, cause weakening of their properties. In addition, their shortcomings such as high cost and high methanol permeation property, limit their application. To remedy these problems, aromatic hydrocarbon polymers have been extensively studied as alternative materials for proton exchange membranes (PEMs)[3−5] and many 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 alternate candidates. Generally, membranes based on these polymers can achieve high proton conductivity by increasing their ion exchange capacities (IECs), resulting in huge water uptake and a dramatic loss of mechanical properties.

Recently, introduction of block copolymer structures to PEMs has been considered as a strategy to overcome the weak points of a random copolymer system.[17] Block copolymers composed of hydrophilic and hydrophobic segments are expected to form ion transport channels due to hydrophilic/hydrophobic phase-separated structures and show improved proton conductivity. McGrath et al. reported that sulfonated hydrophilic/hydrophobic multiblock copolymers showed high proton conductivity comparable to that of Nafion.[18]

Unique polymer forms, such as stars, dendrimers and hyperbranched polymers, impart properties distinctly different from linear polymers of similar compositions. For PEMs, unique structural designs such as graft,[19] comb-shaped,[20,21] and branched polymers[22] were reported to improve proton conductivity compared to that of conventional polymers. Thus, it is interesting to study the star-shaped sulfonated block copolymer as a candidate for PEMs. We designed well-defined star-shaped block copolymers which have AB block copolymers as arms. The AB block copolymers are composed of hydrophilic and hydrophobic segments, where the hydrophilic segments are attached to the core, and the hydrophobic ones are placed at the periphery of the star polymers to increase their dimensional stability.

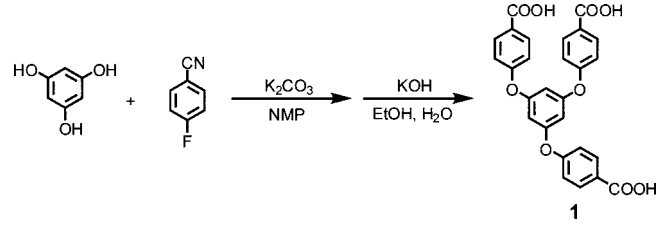
In this article, we report the synthesis of new star-shaped sulfonated block copoly(ether ketone)s. Star-shaped block copoly(ether ketone)s were prepared by the direct polycondensation of tricarboxylic acids as the core molecule with 4-(4′-phenoxyphenoxy)benzoic acid, followed by 3-phenoxy benzoic acid using trifluoromethanesulfonic acid (TFMSA) as a solvent and activating reagent, and then these polymers were sulfonated by using concentrated sulfuric acid. The properties of their membranes, such as proton conductivity, water uptake, dimensional stability, and oxidative stability, are also reported.

Experimental Section

Materials. Phloroglucinol, anisole, *p*-fluorobenzonitrile, 4-bromoanisole, 2-phenylphenol, and trifluoromethanesulfonic acid (TFMSA) were purchased from TCI. Copper powder, boron tribromide (BBr_3) dichloromethane solution, and concentrated sulfuric acid were purchased from Wako. 4-(4′-Phenoxyphenoxy)-benzoic acid (**3**) was synthesized from 4-phenoxyphenol and *p*-chlorobenzonitrile according to the previous report.[23] 3-Phenoxybenzoic acid (**5**) was prepared from 3-phenoxytoluene by the reported method.[24] Dichloromethane and *N*-methyl-2-pyrrolidinone (NMP) was distilled from calcium hydride before use. Other solvents and reagents were used as received.

Synthesis of 1,3,5-Tri(4-carboxyphenoxy)benzene (1). To a round-bottomed flask equipped with a Dean−Stark trap were charged phloroglucinol (0.63 g, 5 mmol), *p*-fluorobenzonitrile (1.91

Scheme 1. Synthesis of Trifunctional Core



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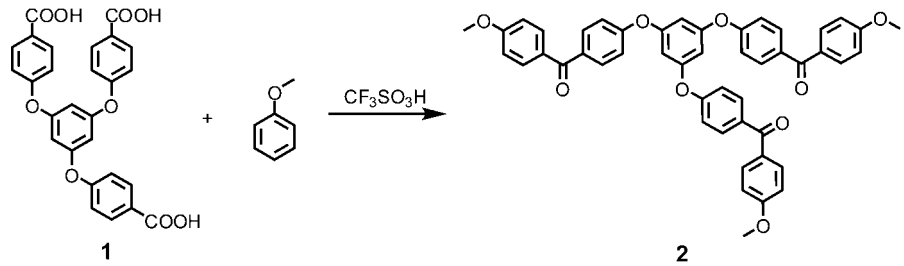
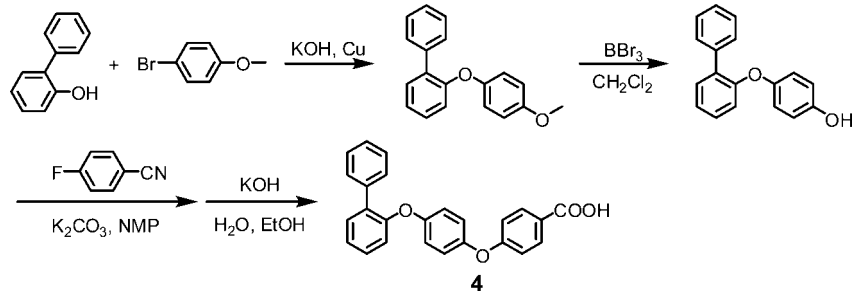
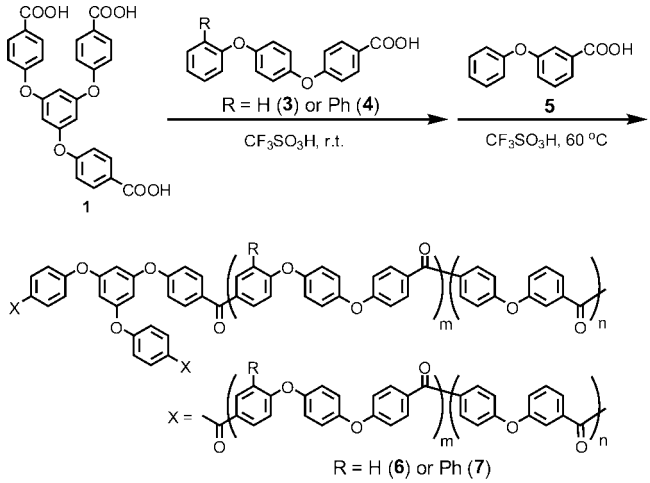
Scheme 2. Model Reaction of Trifunctional Core and Anisole



Scheme 3. Synthesis of 4-(4-([1,1′-Biphenyl]-2-yloxy)phenoxy)benzoic Acid



Scheme 4. Synthesis of Star-Shaped Copolymers 6 and 7



g, 15.8 mmol), and K_2CO_3 (3.11 g, 22.5 mmol). Then, NMP (10 mL) and toluene (10 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 180 °C and the reaction was continued for 16 h. After cooling to room temperature, the mixture was poured into water and acidified with 1 M HCl (aq). The resulting precipitate was collected and charged in a round bottomed flask containing KOH (13 g, 0.2 mol), H_2O (50 mL), and ethanol (50 mL), and the mixture was refluxed overnight. After removal of ethanol by distillation, the mixture was cooled to room temperature and poured into water and acidified with concentrated HCl (aq). The resulting precipitate was collected and recrystallized from ethanol and water (1/1, v/v) to yield white powder. The yield was 1.46 g (60%). Mp: 343.2 °C (by DTA). IR (KBr, ν, cm^{-1}): 1227 (−O−), 1689 (−COOH). ^1H NMR (DMSO-d_6, δ, ppm): 6.64 (s, 3 H), 7.16 (d, J = 8.7 Hz, 6 H), 7.96 (d, J = 9.0 Hz, 6 H). ^{13}C NMR (DMSO-d_6, δ, ppm)): 106.27, 118.04, 126.21, 131.59, 157.90, 159.63, 166.51. Anal. Calcd for $C_{27}H_{18}O_9$: C, 66.67; H, 3.73. Found: C, 66.67; H, 3.89.

Model Reaction. To a mixture of **1** (0.19 g, 0.4 mmol) and anisole (0.17 g, 1.2 mmol) was added TFMSA (0.8 mL) at room temperature. The mixture was stirred for 3 h. Then the mixture was poured into water and the resulting solid was filtered and dried in vacuo. The yield was 0.30 g (100%). IR (KBr, ν): 1227 (−O−), 1643 (C═O), 2931 (−CH_3). ^1H NMR (DMSO-d_6, δ, ppm)): 6.72 (s, 3H), 7.08 (d, J = 9.0 Hz, 6 H), 7.26 (d, J = 8.7 Hz, 6 H), 7.74 (d, J = 8.7 Hz, 6 H), 7.78 (d, J = 9.0 Hz, 6 H). ^{13}C NMR (DMSO-d_6, δ, ppm)): 55.40, 106.01, 113.71, 118.02, 129.48, 131.70, 131.80, 133.11, 157.95, 159.00, 162.73, 192.99. Anal. Calcd for $C_{48}H_{36}O_9$: C, 76.18; H, 4.79. Found: C, 75.87; H, 4.81.

Synthesis of 2-(4-Methoxyphenoxy)biphenyl. A mixture of 2-phenylphenol (2.55 g, 15 mmol) and KOH (0.99 g, 15 mmol) was stirred at 120 °C for 3 h under nitrogen. After removal of water in vacuo, 4-bromoanisole (1.50 g, 8 mmol), 2-phenylphenol (0.50 g, 2.9 mmol), and copper powder (0.0050 g, 0.08 mmol) were added to the flask and heated overnight at 200 °C under nitrogen. After cooling to room temperature, the mixture was diluted with ethyl acetate, and the organic layer was washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (dichloromethane) to yield a colorless viscous oil. The yield was 1.47 g (66%). IR (NaCl, ν, cm^{-1}): 1219 (−O−), 2946 (−CH_3). ^1H NMR (DMSO-d_6, δ, ppm)): 3.74 (s, 3 H), 6.81 (d, J = 8.7 Hz, 2 H), 6.90 (d, J = 9.3 Hz, 3 H), 7.10−7.43 (m, 6 H), 7.57 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (DMSO-d_6, δ, ppm)): 55.58, 114.74, 118.54, 119.98, 123.21, 127.11, 128.07, 128.54, 129.26, 131.16, 132.79, 137.89, 150.89, 154.81, 155.44.

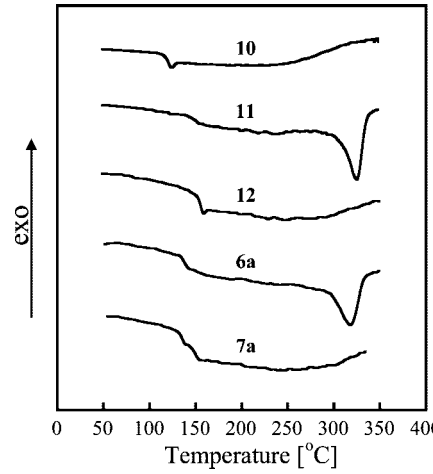


Figure 1. DSC profiles of **6a**, **7a,** and corresponding homopolymers.

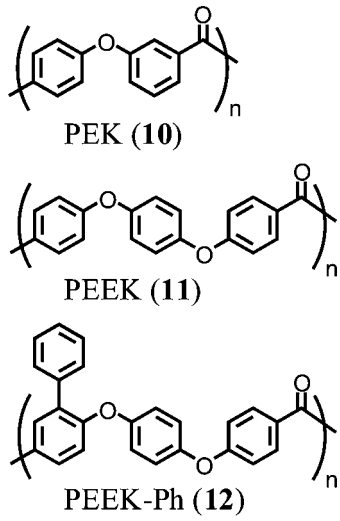
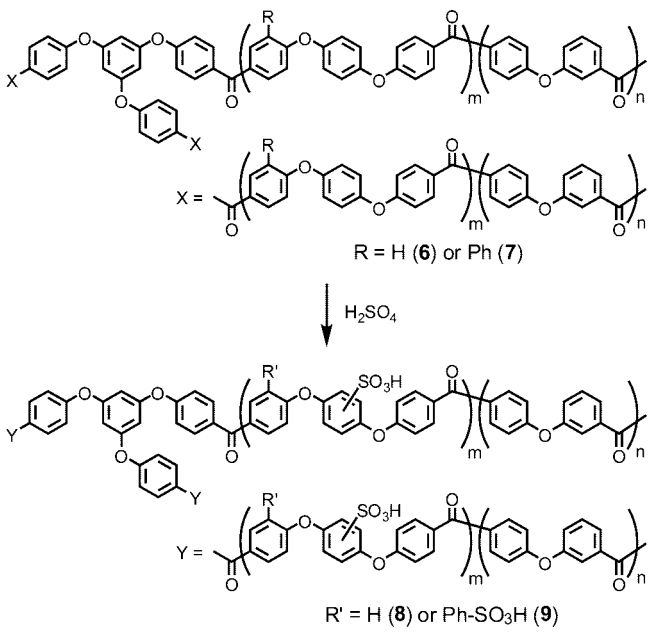


Figure 2. Polymer structure of poly(ether ketone)s.

Scheme 5. Sulfonation of Polymers 6 and 7



Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.50; H, 5.99.

Synthesis of 4-([1,1′-Biphenyl]-2-yloxy)phenol. To a solution of 2-(4-methoxyphenoxy)biphenyl (1.47 g, 5.3 mmol) in dry dichloromethane (30 mL) was added a solution of BBr_3 in CH_2Cl_2 (6 mL, 6 mmol) at −78 °C. The reaction mixture was stirred at room temperature for 12 h. The mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated in vacuo. The resulting solid was recrystallized from toluene and hexane (1/1, v/v) to yield a white product. The yield was 1.29 g (93%). Mp: 146.0−146.3 °C. IR (KBr, ν, cm^{-1}): 1219 (−O−), 3201 (−OH). ^{1}H NMR ($CDCl_3$, δ, ppm: 4.53 (s, 1 H), 6.75 (d)) J = 9.6 Hz, 2 H), 6.85, (d, J = 9.0 Hz, 2 H), 6.91 (dd, J = 8.1, 1.5 Hz, 1 H), 7.15 (td, J = 7.5, 1.5 Hz, 1 H), 7.30−7.44 (m, 5 H), 7.57 (d, J = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, δ, ppm)): 116.19, 118.61, 120.14, 123.29, 127.14, 128.08, 128.56, 129.27, 131.19, 132.85, 137.87, 151.03, 151.19, 154.75. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.01; H, 5.58.

Synthesis of 4-(4-([1,1′-biphenyl]-2-yloxy)phenoxy)benzoic acid (4). To a round-bottomed flask equipped with a Dean−Stark trap, 4-(biphenyl-2-yloxy)phenol (1.90 g, 7.2 mmol), *p*-fluorobenzonitrile (0.88 g, 7.2 mmol), and K_2CO_3 (1.50 g, 11 mmol) were charged. Then, NMP (16 mL) and toluene (16 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 180 °C and the reaction was continued for 16 h. After cooling to room temperature, the mixture was poured into water and acidified with 1 N HCl (aq). The resulting precipitate was collected and charged in a round bottomed flask. KOH (15 g, 0.23 mol), H_2O (50 mL), and ethanol (100 mL) were added to the flask and the mixture was refluxed overnight. After removal of ethanol by distillation, the mixture was cooled to room temperature and poured into water and acidified with conc. HCl aq. The resulting precipitate was collected and recrystallized from ethanol and water (1/1, v/v) to yield a white powder. The yield was 2.43 g (88%). Mp: 193.0−193.5 °C. IR (KBr, ν, cm^{-1}): 1227 (−O−), 1682 (−COOH). ^{1}H NMR (DMSO-d_6, δ, ppm): 6.96 (d, J = 9.0 Hz, 4 H), 7.06 (d, J = 9.0 Hz, 3 H), 7.25−7.54 (m, 8 H), 7.92 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (DMSO-d_6, δ, ppm)): 116.55, 119.34, 119.63, 121.42, 124.26, 124.94, 127.09, 128.02, 128.80, 129.01, 131.03, 131.41, 132.73, 137.11, 149.94, 153.08, 153.69, 161.27, 166.52. Anal. Calcd for $C_{25}H_{18}O_4$: C, 78.52; H, 4.74. Found: C, 78.86; H, 4.91.

Synthesis of Star-Shaped Polymer (Typical Example). To a solution of **1** (0.0097 g, 0.02 mmol) in TFMSA (2 mL) was added 4-(4′-phenoxyphenoxy)benzoic acid (0.61 g, 2 mmol) in three portions over a period of 1 h at room temperature. The mixture was stirred for 12 h and 2 mL of TFMSA was then added. Then 3-phenoxybenzoic acid (0.43 g, 2 mmol) was added to the mixture in three portions over a period of 1 h at 60 °C. The mixture was stirred at 60 °C for 24 h. The mixture was then poured into water. Resulting polymer was washed with 3% Na_2CO_3 aq, hot water, and hot methanol. The polymer was dried in vacuo at 100 °C for 8 h to give **6a**. The yield was 0.97 g (100%). IR (KBr, ν, cm^{-1}): 1226 (−O−), 1651 (C═O).

Sulfonation of Polymer. To a round-bottomed flask, 0.4 g of **6a** and 6 mL of concentrated sulfuric acid (95−98%) were added and the mixture was stirred at 45 °C for 24 h. The mixture was then poured into cold water. Then the polymer was thoroughly washed with water, and dried in vacuo at 100 °C for 8 h. IR (KBr, ν, cm^{-1}): 1126 (−SO_3H), 1227 (−O−), 1643 (C═O).

Membrane Preparation and Ion Exchange Capacity (IEC). A NMP solution of 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 to give a tough and flexible membrane. The resulting membrane was immersed in 2 M H_2SO_4 (aq) at room temperature for 24 h. The membrane were then thoroughly washed with water and dried in vacuo at 100 °C for 12 h. IECs were determined by titration with 0.02 M NaOH (aq).

Proton Conductivity. Proton conductivity in the 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:

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

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

Table 1. Properties of 8 and 9

sample	composition[a] (mol/mol) [**3**] or [**4**]/[**5**]	M_n[b] (kDa)	M_w/M_n[b]	IEC[c] (mequiv/g)	IEC by titration[d]	Δl	Δt	weight residue[e] (%)
8a	0.50/0.50	146	3.0	1.77	1.84	0.26	0.31	100
8b	0.59/0.41	140	3.4	1.98	2.06	0.24	0.38	0
9a	0.25/0.75	37	2.7	1.80	1.88	0.11	0.40	100
9b	0.33/0.67	39	2.9	2.18	2.27	0.08	0.70	80

[a] Calculated from feed ratio. [b] Determined by GPC based on polystyrene standards. [c] Theoretical IEC value. [d] Determined by titration with 0.02 M NaOH (aq). [e] After treatment with Fenton's reagent (3% H_2O_2 (aq) containing 2 ppm of $FeSO_4$).

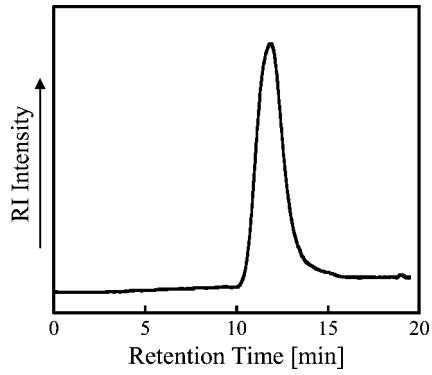


Figure 3. GPC trace of polymer **8a**.

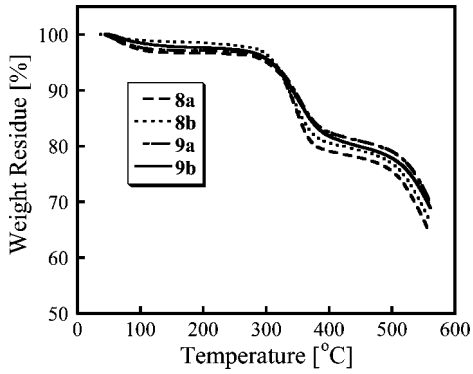


Figure 4. TG curves of **8** and **9**.

Table 2. Water Uptake and Water State of 8 and 9

sample	IEC[a]	water content (%)	free water (%)	bound water (%)	ratio [bound]/[total]
8a	1.84	53.4	18.0	35.4	66.3
8b	2.06	76.8	47.5	29.3	38.1
9a	1.88	147	95.3	51.7	35.2
9b	2.27	313	257	56.0	17.8

[a] Determined by titration with 0.02 M NaOH (aq).

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:

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

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

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.

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.

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 column (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), differential thermal analysis (DTA), and a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen.

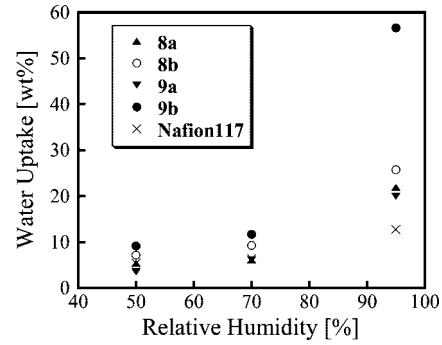


Figure 5. Relative humidity dependence of water uptake of **8**, **9**, and Nafion 117.

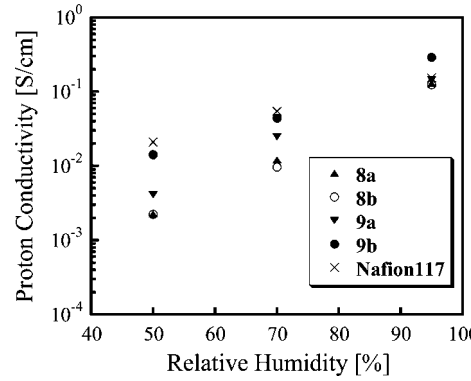


Figure 6. Relative humidity dependence of proton conductivity of **8**, **9**, and Nafion 117.

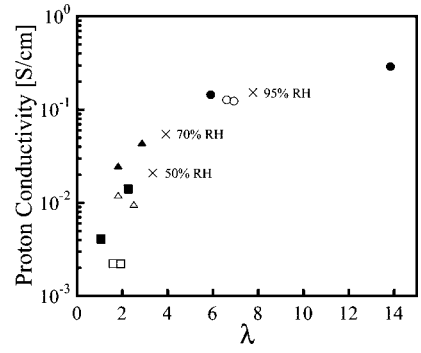


Figure 7. Proton conductivity of **8** (open symbols), **9** (filled symbols), and Nafion 117 (×) as a function of hydrated number (λ) at 80 °C and at 95% RH (circle symbols), 70% RH (triangle symbols), and 50% RH (square symbols).

Results and Discussion

Synthesis of Core and Monomers. Poly(ether ketone), which is a typical matrix polymer for PEMs, was selected as the main chain for a star-shaped block copolymer. As a trifunctional core, 1,3,5-tri(4-carboxyphenoxy)benzene (**1**) was prepared by the reaction of phloroglucinol with *p*-fluorobenzonitrile, followed by hydrolysis of the resulting trinitrile compound (Scheme 1). It is known that an acylation of a phenoxy group by benzoic acid in TFMSA occurs at the *para* position selectively.[25] To investigate the reactivity of the core molecule, the model reaction between the core (**1**) and anisole was performed at room temperature in TFMSA (Scheme 2). The reaction produced the desired tri-*para*-acylated compound (**2**) in a quantitative yield, which suggests that **1** can be used for the synthesis of star-shaped polymers.

As monomers for linear units, 4-(4′-phenoxyphenoxy)benzoic acid (**3**) and 3-phenoxy benzoic acid (**5**) were prepared by the reported methods.[23,24] Another new monomer, 4-(4-([1,1′-biphenyl]-2-yloxy)phenoxy)benzoic acid (**4**), was prepared as shown in Scheme 3. The resulting polymer from monomer **4** can be used for the hydrophilic segment after sulfonation and the sulfonated polymer should have a densely sulfonated structure due to its phenyl side group, which is readily sulfonated.

Synthesis and Characterization of Star-Shaped Block Copolymers. Star-shaped block copolymers were prepared by polycondensation between the trifunctional core (**1**) and two types of AB monomers such as **3** and **5**, as shown in Scheme 4. At first, AB monomer **3** in limited amounts was added to **1** in TFMSA at room temperature to preferentially promote the reaction between **1** and **3**. After polycondensation of **3** was completed, the second monomer **5** was added slowly to the polymer solution at 60 °C and the reaction was continued for 24 h to produce star-shaped block copolymer **6**. Polymer **7** was also prepared by the same method using monomer **4** instead of monomer **3**. The IR spectra of **6** showed characteristic absorptions due to the carbonyl and ether groups at 1651 and 1226 cm^{-1}, respectively. The NMR spectroscopy and GPC measurement of **6** and **7** could not be performed due to their poor solubility in chloroform, tetrahydrofuran, and polar aprotic solvents.

The DSC profiles of **6a** (composition (mol/mol): [**3**]/[**5**] = 0.50/0.50) and **7a** (composition (mol/mol): [**4**]/[**5**] = 0.25/0.75) are shown in Figure 1. The structures of the homopolymers corresponding to polymers **6** and **7** are depicted in Figure 2. The glass transition temperature (T_g) values of PEK (**10**), PEEK (**11**) PEEK-Ph (**12**) are 122, 155, and 157 °C, respectively, and the melting point of **11** is observed at 326 °C. On the other hand, **6a** has a melting point at 318 °C and its T_g at 138 °C, corresponding to each unit, that clearly indicates the formation of the block copolymer. The DSC trace of **7a** shows two T_gs at 135 and 149 °C, and the T_g values agree with those of corresponding homopolymers **10** and **12**. This result clearly indicates the block copolymer architecture of **7a**.

Sulfonation of Star-Shaped Block Copolymers. Selective sulfonation is a big issue in preparing hydrophilic and hydrophobic block copolymers. The phenyl rings activated by two phenoxy units in poly(ether ether ketone) and the pendant phenyl groups are known to be easily sulfonated in concentrated sulfuric acid under mild conditions because sulfonation is an electrophilic reaction.[9,26] On the other hand, the poly(ether ketone) segment tends not to be sulfonated under mild conditions because all phenyl rings are deactivated by strong electron-withdrawing carbonyl groups. In fact, sulfonation of **10** was carried out with concentrated sulfuric acid at 45 °C for 24 h. However, no absorption due to sulfonic acid groups was observed in the IR spectrum.

Based on these findings, **6** and **7** were sulfonated with concentrated sulfuric acid at 45 °C (Scheme 5). Characteristic sulfonic acid absorption at 1126 cm^{-1} was observed in both sulfonated block copolymers **8** and **9**.

The properties of the resulting sulfonated polymers are shown in Table 1. Samples **8** and **9** are readily soluble in polar aprotic solvents and give tough and flexible membranes by solvent casting. The number-average molecular weights (M_n)s of polymers are over 37 000. Polymers **9** show lower (M_n)s than polymers **8,** probably because the electron-donating effect of the phenoxy group in monomer **4** is weakened by the resonance with the pendant phenyl group, resulting in the lower reactivity toward the acylation. The GPC trace of **8a** is shown in Figure 3. The chromatogram has an unimodal distribution and its molecular weight distribution is relatively narrow. This indicates that **8a** is star-shaped and that there is no free arm which is not attached to the core.

The IEC values were determined by titration. The theoretical IEC values of **8** and **9** were calculated from sulfonated structures which have one and two sulfonic acid groups in a hydrophilic repeating unit, respectively. The resulting IEC values corresponded to the theoretical values. Thus, selective sulfonation, as shown in Scheme 5, was confirmed. Although the IEC values of copolymers are relatively high, the copolymers are insoluble in hot water. It is noteworthy that sulfonated linear poly(ether ether ketone), which has the same structure as the hydrophilic segment of **8**, is soluble in hot water in spite of a lower IEC value (1.92 mequiv/g) than **8b** (IEC = 2.06 mequiv/g).[27] The insolubility of these copolymers in hot water is a result of the star-shaped structure, which has hydrophobic segments at the periphery.

Thermal Stability. Figure 4 shows the TG curves of **8** and **9**. A three-step weight loss is observed from 50 to 200 °C, from 250 to 350 °C, and above 350 °C. The first weight loss is due to the evaporation of hydrated water, the second is attributed to the decomposition of the sulfonic acid groups, and the third is because of the decomposition of the polymer main chains. There is no significant difference in all sulfonated polymers, regardless of their IEC values and chemical compositions.

Oxidative Stability. The oxidative stability of the **8** and **9** membranes was evaluated in a hot Fenton's reagent for 1 h as an accelerated test. The results are summarized in Table 1. No weight loss was observed for the **8a** and **9a** membranes with an IEC value of around 1.8 mequiv/g, while the **8b** membrane with an IEC value of 2.0 mequiv/g was completely dissolved. On the other hand, the **9b** membrane showed higher oxidative stability than the **8b** membrane despite a higher IEC value for **9b** than that of **8b**. A decrease in oxidative stability with an increase in the IEC value of the polymer is generally observed.[11,28] However, the result from the **9b** membrane does not correspond with the general result. Compared to **8b**, **9b** has shorter hydrophilic segments because of a higher density of sulfonic acid groups. Thus the hydrophilic segments of **9b** seem to be effectively surrounded by hydrophobic segments. The higher oxidative stability of **9b** may be derived from the surrounding hydrophobic segments.

Water Uptake and Dimensional Change. Water uptake and water state are closely related to membrane properties such as proton conductivity, dimensional stability, and mechanical strength. Generally, the water in membranes is regarded as a transportation medium of protons and enables high proton conductivity. Especially, the water content of a membrane under a low relative humidity condition is a critical factor in proton conductivity.

The water uptake and hydrated state of **8** and **9** after being immersed in water are summarized in Table 2. The hydrated state of the membranes was estimated from the endothermic peaks corresponding to the water melting measured by DSC. The amount of water increased with increasing the IEC values and the water uptake of **9a** and **9b** was higher than that of **8a** and **8b**, which indicates that **9a** and **9b** having sulfonated side chains in hydrophilic segments can absorb and hold a lot of water because of the high density of sulfonic acid groups. The water state of hydrated polymers is also important. The bound water content of **9a** and **9b** (around 50%) is higher than that of **8a** and **8b** (around 30%). This result confirms that the density of sulfonic acid groups is an important factor in capturing water. In addition, the star-shaped structure with hydrophilic segments surrounded by hydrophobic segments tends to enhance the water-holding property.

The humidity dependence of water uptake was measured for **8** and **9** at 80 °C and is shown in Figure 5. The water uptake of sulfonated polymers at 95% RH is in the range of 20−26 wt %, except for **9b**, which shows 57 wt % water uptake. The water uptake is decreased with decreasing relative humidity and reaches below 10 wt % at 50% RH for all samples. The highest water uptake at 50% RH was obtained for **9b** probably because of its high IEC value and high density of sulfonic acid groups in the hydrophilic segments.

The dimensional stability of the **8** and **9** membranes was evaluated by comparing their hydrated state with dry-state membranes (Table 1). The **8a** and **8b** membranes show similar dimensional changes and the swelling degree of thickness is slightly higher than that of length. On the other hand, the **9a** and **9b** membranes show different swelling behavior from the **8a** and **8b** membranes. For the **9a** and **9b** membranes, the swelling degree of thickness is 4 times and 9 times higher than that of length, respectively. In addition, the swelling degree of length for the **9** membranes is lower than that of the **8** membranes. This result indicates that the **8** membranes show isotropic swelling probably because of the almost same ratios of the hydrophilic/hydrophobic units. In contrast, the **9** polymers with high content of hydrophobic unit exhibit anisotropic swelling, suggesting the formation of ionic domains in the direction of thickness. This morphological structure directs water into hydrophilic domains.[20]

Proton Conductivity. The proton conductivities were measured for the **8** and **9** membranes at 80 °C in the range of 50−95% RH. The results are shown in Figure 6, in comparison with those of Nafion 117. The proton conductivities of **8a**, **8b**, and **9a** are comparable to that of Nafion 117 at 95% RH. On the other hand, **9b** shows a higher proton conductivity of 0.29 S/cm than that of Nafion 117 at 95% RH. Generally, sulfonated aromatic polymers require high IEC values to attain high proton conductivity because of the lower acidity of sulfonic acid group, the smaller flexibility, and the smaller hydrophilic/hydrophobic difference compared to Nafion.[29] In this case, **8** and **9** membranes also requires high IEC values over 1.8 to achieve high proton conductivity, while that of Nafion 117 is only 0.91. With decreasing the relative humidity, proton conductivities decrease for all samples. Compared to **8a** and **8b**, **9a** and **9b** show a smaller dependence on the relative humidity and maintain relatively high proton conductivities under low relative humidity. This result is consistent with the result from water uptake and the amount of bound water in the membranes. To clarify the relationship between water uptake and proton conductivity, proton conductivity is plotted versus hydration number, λ, which is the number of water molecules per a sulfonic acid unit (Figure 7). Proton conductivities of all membranes tend to increase with increasing λ values. For each relative humidity, the **9** membranes show higher proton conductivities than the **8** membranes with the similar λ values. The difference in the contribution of λ to proton conductivity for **8** and **9** membranes may be caused by the difference in the density of sulfonic acid groups and in phase-separated structures. The **9b** membrane shows a high proton conductivity of 0.014 S/cm at 50% RH, which is comparable to that of Nafion 117 (0.021 S/cm at 50% RH). The advantageous contribution of the star-shaped structure to the proton conductivity is recognized.

Conclusions

Novel star-shaped block copolymers having hydrophilic and hydrophobic segments as arms were synthesized for fuel cell applications. The polymers could give tough and flexible membranes by solvent casting. The membranes showed high water uptake and high bound water content due to the star-shaped structure which has hydrophilic segments surrounded by hydrophobic segments. The membranes showed excellent proton conductivity which was comparable to that of Nafion 117 in the range of 50−95% RH at 80 °C. The advantage of the star-shaped structure was confirmed by its water-holding ability and proton conductivity under low relative humidity.

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