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Polymer Electrolyte Membranes Based on Poly(phenylene ether)s with Pendant Perfluoroalkyl Sulfonic Acids

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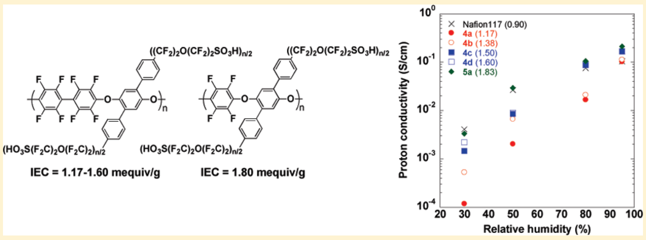

ABSTRACT: Poly(phenylene ether)s containing pendant perfluoroalkyl sulfonic acids with ion exchange capacity (IEC) of 1.17−1.83 mequiv/g were synthesized by the aromatic nucleophilic substitution reaction of a perfluoromonomer (decafluorobiphenyl or hexafluorobenzene) with 2,5-bis(4′-iodophenyl)hydroquinone, followed by the Ullman coupling reaction with potassium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonate. The membranes prepared by solution casting showed high oxidative stability against hot Fenton's reagent. Even in the hydrated state, water uptake of the membranes was significantly low (19.3−28.0 wt %) due to the high fluorine content. High proton conductivity (∼1.0 × 10^{-1} S/cm) was observed in all membranes under high relative humidity (95% RH). Furthermore, the membrane with IEC = 1.83 mequiv/g still maintained high proton conductivity of 3.3 × 10^{-3} S/cm even under low relative humidity (30% RH), which was comparable to that of the Nafion 117 membrane (4.1 × 10^{-3} S/cm). This proton conductivity was the highest data among the aromatic polymers containing pendant perfluoroalkyl sulfonic acids. Atomic force microscopy observation supported the formation of the phase-separated structure that the hydrophilic domains were well dispersed and connected to each other.

■ INTRODUCTION

Polymer electrolyte membranes (PEMs) based on sulfonated perfluoropolymers (e.g., Nafion and Flemion) have been widely used for polymer electrolyte fuel cells (PEFCs) because of their high proton conductivity and high stability.[1,2] However, their drawbacks, such as high cost, high methanol permeability, and limited operation temperature (<80 °C), restrict their practical use in PEFCs. Thus, the development of well-balanced alternatives of the perfluorinated PEMs, which should meet several requirements (e.g., high proton conductivity, high membrane stability, low fabrication cost, etc.), is essential today for the realization and spread of PEFCs. For alternatives of the perfluorinated PEMs, the application of aromatic polymers for PEMs has been of current interest over the past decades because of low fabrication cost, high thermal stability, and a wide variety of polymer designs.[3−6]

For the development of well-balanced aromatic PEMs, sulfonated multiblock copolymers[7−14] and highly sulfonated polymers,[15−17] as the representatives, have been widely investigated. The driving force to improve the PEM performance in these two examples is basically due to the well-controlled morphology derived from the difference in the polarity between the hydrophilic and hydrophobic domains as well as the perfluorinated PEMs,[1,2] which forms proton transportation channel and enhances the membrane stability.

As well as the well-controlled morphology, their strong acidity contributes to the effective proton concentration and proton mobility, leading to high proton conductivity in sulfonated perfluopolymers. For example, the pK_a values of sulfonated perfluoropolymers are estimated to be ca. −6, whereas those of the sulfonated aromatic polymers are estimated to be ca. −1.[18] The weak acidity of the sulfonated aromatic polymers leads to poor proton conductivity under low relative humidity. Thus, poly(arylene ether)s with pendant perfluoroalkyl sulfonic acids (IEC ∼ 1.50 mequiv/g) have been recently prepared to overcome the weak acidity of conventional sulfonated aromatic polymers by Miyatake et al.[19,20] and Iwasaki et al.[21] Drastic improvement of proton conductivity, which was 3−60 times higher than that of corresponding sulfonated aromatic polymers, was accomplished. These results revealed that the introduction of perfluoroalkyl sulfonic acids into aromatic polymers effectively improved proton conductivity. Furthermore, ion exchange capacity (IEC) values of polymers are quite an important factor because proton conductivity is strongly affected by IEC values. Although sulfonated aromatic membranes with high IEC values can achieve high proton conductivity, such membranes show excess water swelling or even dissolve in water.[4,15] Thus, the trade-off between proton conductivity and water resistance is generally a tough issue to overcome in sulfonated aromatic polymers. On the other hand, in the case of the fluorinated aromatic polymers with pendant perfluoroalkyl sulfonic acids, water resistance will be maintained even for high IEC values due

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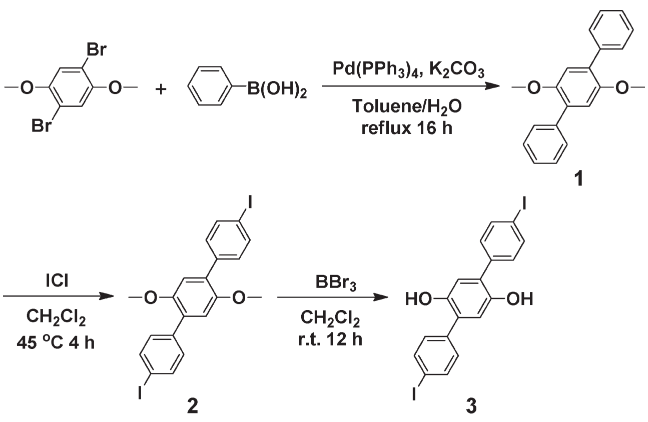
Scheme 1. Synthesis of 3



to the high hydrophobicity of the fluorinated units. Thus, further enhancement of proton conductivity is expected by increasing IEC values (IEC $>$ 1.50 mequiv/g) while maintaining the membrane stability, although the proton conductivity of the polymers described above[19−21] (IEC $\sim$ 1.50 mequiv/g) could not reach that of the sulfonated perfluoropolymers.

Herein, in this article, we prepared novel poly(phenylene ether)s with pendant perfluoroalkyl sulfonic acid groups (IEC $\sim$ 1.80 mequiv/g) by the aromatic nucleophilic substitution reaction of a perfluoromonomer (decafluorobiphenyl (DFB) or hexafluorobenzene (HFB)) to enhance water resistance of the resulting polymers with 2,5-bis(*p*-iodophenyl)hydroquinone, followed by the Ullman coupling reaction with potassium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonate. The introduction of the perfluoroalkyl sulfonic acids was successfully carried out with high conversion ($\sim$85%) to yield the desired polymers. These polymers consist of the rigid polymer backbones with the high fluorine content and the flexible perfluoroalkyl sulfonic acid side chains; that is, the structure mimics that of the sulfonated perfluoropolymers. The membrane prepared by solution casting (IEC = 1.83 mequiv/g) showed higher proton conductivity than that of the Nafion 117 membrane under high relative humidity, and in addition, the high proton conductivity of 3.3×10^{-3} S/cm was maintained at 80 °C and 30% RH. This proton conductivity was the highest value among aromatic polymers with pendant perfluoroalkyl sulfonic acids. The membrane properties, such as thermal stability, oxidative stability, water uptake, and morphology, were also investigated in detail.

■ EXPERIMENTAL SECTION

Materials. Potassium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonate (PTES) was prepared according to a previous report.[21] *N,N*-Dimethylacetamide (DMAc) was distilled from calcium hydride before use. Other solvents and reagents were used as received.

Characterization. ^{1}H (300 MHz) and ^{19}F (400 MHz) spectra were recorded with Bruker DPX300S and JEOL JNM-AL400 spectrometers, respectively. 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 polystyrene gel columns (TSKgel GMHHR-M) eluted with *N,N*-dimethylformamide (DMF) containing 0.01 M LiBr at a flow rate of 1.0 mL/min 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) under a nitrogen atmosphere.

1,4-Dimethoxy-2,5-diphenylbenzene (1). The mixture of 1,4-dibromo-2,5-dimethoxybenzene (10 mmol, 2.96 g), phenylboronic acid (30 mmol, 3.66 g), $Pd(PPh_3)_4$ (0.6 mmol, 0.69 g), toluene (50 mL), and 2 M K_2CO_3 aqueous solution (25 mL) was refluxed for 16 h under a nitrogen atmosphere. After cooling to room temperature, the organic layer was dried over $MgSO_4$ and evaporated. The residue was purified with column chromatography (dichloromethane:hexane = 3:7) to yield a white powder (2.5 g, 86%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.58 (4H, d), 7.43 (4H, t), 7.34 (2H, t), 6.97 (2H, s), 3.78 (6H, s); mp 149−150 °C (lit. mp 147−149 °C[22]).

1,4-Bis(4′-iodophenyl)-2,5-dimethoxybenzene (2). To the dry dichloromethane solution (60 mL) of **1** (10 mmol, 2.9 g) was added iodine monochloride (40 mmol, 2.1 mL) under a nitrogen atmosphere. The mixture was stirred at 45 °C for 4 h. After cooling to room temperature, the mixture was poured into Na_2SO_3 aqueous solution and extracted with dichloromethane. The organic layer was washed with Na_2SO_3 aqueous solution, dried over $MgSO_4$, and evaporated. The residue was purified with column chromatography (dichloromethane: hexane = 1:3) to yield a white powder (3.1 g, 57%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.51−7.35 (10H, m), 3.44 (6H, s).

1,4-Bis(4′-iodophenyl)hydroquinone (3). To the dry dichloromethane solution (70 mL) of **2** (5.7 mmol, 3.1 g) was added boron tribromide (1.0 M in dichloromethane, 23 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 12 h, then quenched at 0 °C with water, and extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified with recrystallization (ethanol/water) to yield a white crystal (2.5 g, 86%). ^{1}H NMR (DMSO-d_6, δ, ppm): 8.55 (2H, s), 7.51−7.34 (6H, m), 7.28 (4H, d). mp: 229−231 °C.

Polymer with Decafluorobiphenyl (4). **3** (0.9 mmol, 0.30 g), decafluorobiphenyl (0.9 mmol, 0.46 g), and K_2CO_3 (1.35 mmol, 0.19 g) were added into a round-bottomed flask equipped with a Dean−Stark trap, condenser, and gas adapter. Then, DMAc (5.1 mL) and cyclohexane (20 mL) were charged into the flask under a nitrogen atmosphere. The mixture was heated to 120 °C. After dehydration and removal of cyclohexane, the mixture was stirred at 120 °C for 20 h. After cooling to room temperature, the mixture was slowly poured into water, then filtered, and washed with methanol. The precipitated polymer was dried at 80 °C in vacuo to yield a brown powder (0.68 g, 94%). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.59−7.24 (6H, m), 7.24−6.71 (4H, bs).

Polymer with Hexafluorobenzene (5). The dry DMAc solution (7.3 mL) of **3** (1.56 mmol, 0.80 g), hecafluorobenzene (1.56 mmol, 0.18 mL), and K_2CO_3 (2.34 mmol, 0.32 g) was stirred at 80 °C for 20 h and then at 120 °C for 20 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was slowly poured into water, then filtered, and washed with methanol. The precipitated polymer was dried at 80 °C in vacuo to yield a brown powder (0.82 g, 80%). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.72−7.24 (6H, m), 7.24−6.77 (4H, bs).

Polymer with Pendant Perfluoroalkyl Sulfonic Acids (4a−5a). A typical procedure (**4d**) is as follows: the dry DMAc solution (6 mL) of **4** (0.15 mmol, 0.12 g) and copper powder (dendritic, 3 μm) (1.5 mmol, 0.1 g) was stirred at 120 °C for 4 h under a nitrogen atmosphere. Then, the dry DMAc solution (2 mL) of **PTES** (0.75 mmol, 0.35 g) was added dropwise to the mixture, and the reaction was continued at 160 °C for 72 h. After cooling to room temperature, copper was removed by Celite filtration. The filtrate was slowly poured into water, and the precipitate was collected. For protonation, the filtrate was stirred in 1 M H_2SO_4 aqueous solution at 50 °C for 12 h, then washed with water several times, and dried in vacuo at 80 °C to yield a light brown powder. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.73−6.50 (10H, bs). ^{19}F NMR

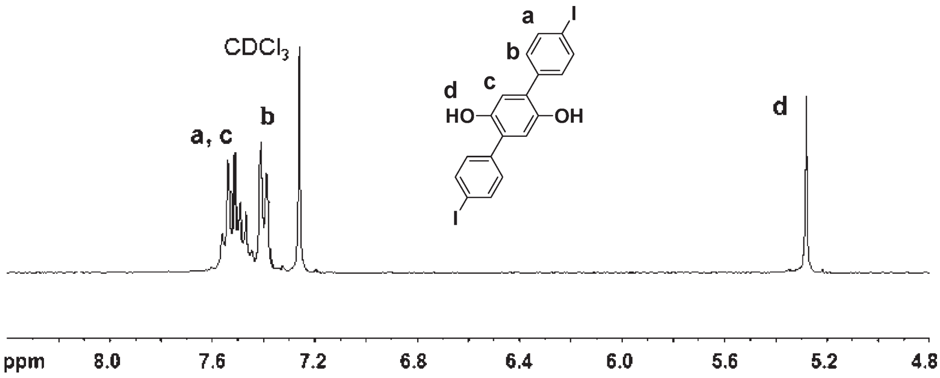
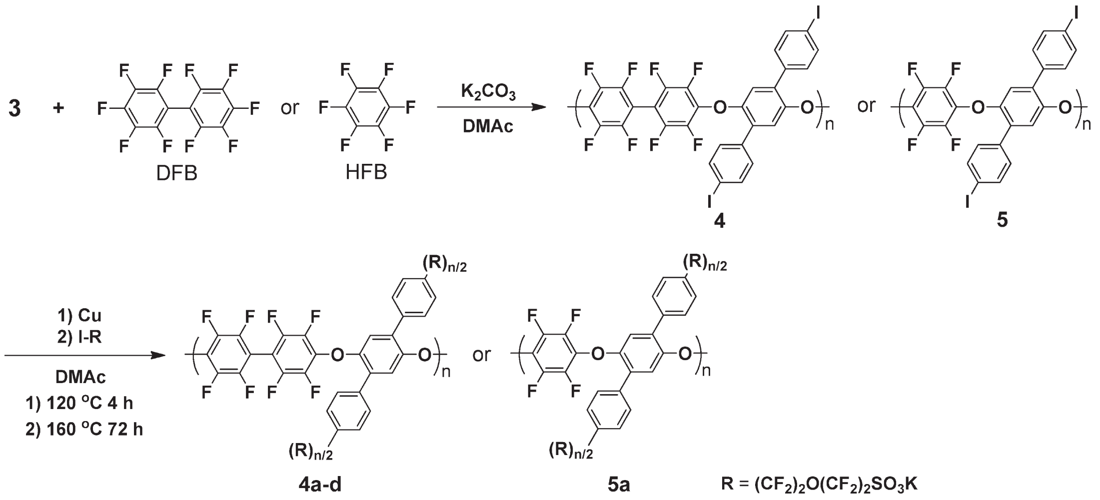


Figure 1. ^{1}H NMR spectrum of **3** in CDCl$_3$.

Scheme 2. Synthesis of 4a−5a



(DMSO-d_6, δ, ppm): −81.7, −85.2, −108.3, −117.3, −141.6, −160.4.

Preparation of Membranes and Ion Exchange Capacity (IEC). The DMAc solutions of each polymer were filtered and cast onto a flat glass plate. Drying the solution at 80 °C for 12 h under reduced pressure gave membranes. IEC values of polymers were determined by titration with 0.02 M NaOH aqueous solution.

Oxidative Stability. Oxidative stability of membranes was tested by immersing the films into Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C. The dissolved time of membranes into the reagent was used to evaluate their oxidative stability.

Water Uptake and Dimensional Change. The humidity dependence of water uptake was measured by plating a membrane in a thermo-controlled humid chamber for 3−4 h. Then the membrane was taken out and quickly weighed on a microbalance. Water uptake was calculated from

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

where W_s and W_d are the weights of wet and dried membrane, respectively. Water uptake and dimensional change of a hydrated membrane were also investigated by using the membrane plated in water for 24 h. The changes of thickness and length were calculated from

$$\begin{aligned} \Delta l &= (l - l_s) / l_s \\ \Delta t &= (t - t_s) / t_s \end{aligned}$$

where t_s and l_s are the thickness and length of the dried membrane, respectively; t and l refer to those of the hydrated membrane.

Table 1. Synthesis of 4a−5a[a]

run	PTES (equiv)	n	conversion (%)	IEC (mequiv/g)[b]
4a	3.0	1.0	50	1.17
4b	4.0	1.3	65	1.38
4c	5.0	1.5	75	1.50
4d	6.0	1.7	85	1.60
5a	6.0	1.6	80	1.83

[a] Detailed reaction conditions are described in the Experimental Section. [b] Estimated by titration with 0.02 M NaOH aqueous solution.

Proton Conductivity. Proton conductivity in plane direction of a membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 5 to 10^5 Hz (Hioki 3532-80). A two-point-probe conductivity cell with two platinum plate electrodes was fabricated. The cell was placed under a thermo-controlled 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.

Atomic Force Microscopic (AFM) Observation. Tapping mode AFM observation was performed with a Digital Instrument, SII-NT SPA400, using microfabricated cantilevers with a force constant of

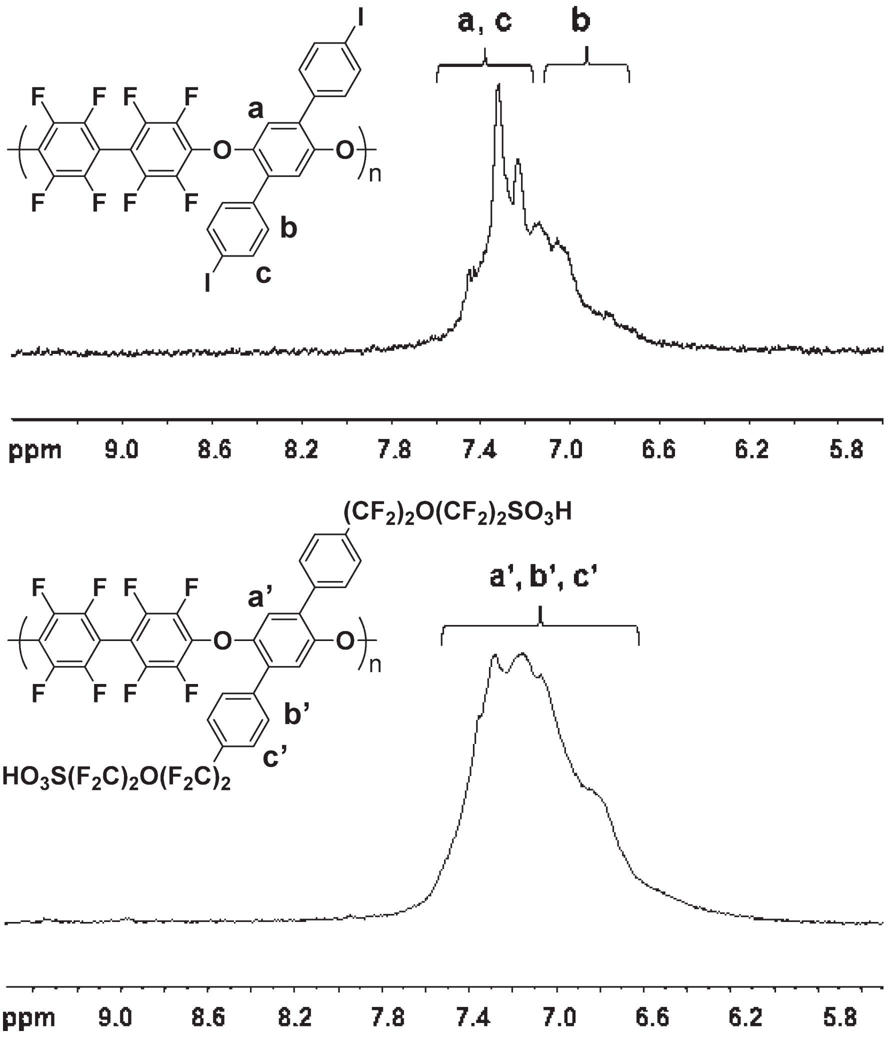


Figure 2. ^{1}H NMR spectra of **4** (top) and **4d** (bottom) in DMSO-d_6.

~20 N/m. A treated sample was allowed to equilibrate by exposuring under 100% relative humidity at room temperature for at least 24 h before testing.

RESULTS AND DISCUSSION

Synthesis of Polymers with Pendant Perfluoroalkyl Sulfonic Acids. 1,4-Bis(4′-iodophenyl)hydroquinone (**3**) was synthesized from 1,4-dibromo-2,5-dimethoxybenzene as a starting material via the three-step reaction according to Scheme 1. The crude product was recrystallized with ethanol/water to yield **3** as a white crystal. The structure of **3** was confirmed by the ^{1}H NMR spectrum (Figure 1). Although the copolymerization of 2,5-diiodohydroquinone with the perfluoromonomer was suitable considering IEC values of polymers, the solubility of the resulting polymers was poor. Thus, the phenyl-substituted **3** was selected as the monomer.

Then **3** was polymerized with DFB or HFB under aromatic nucleophilic substitution reaction conditions (Scheme 2). Polymerization with DFB for 20 h at 120 °C under a nitrogen atmosphere gave a brown powder (**4**: M_w = 33 000, M_w/M_n = 2.2). On the other hand, polymerization with HFB was carried out for 20 h at 80 °C and then for 20 h at 120 °C to yield a brown powder (**5**: M_w = 30 000, M_w/M_n = 2.5). Moderate reaction temperature (<120 °C) was applied for both polymerizations to prevent the elimination of iodine groups according to previous reports,[20,21] and the high reactivity of DFB and HFB for the aromatic nucleophilic substitution reaction enabled the polymerization under moderate reaction temperature. The introduction of the perfluoroalkyl sulfonic acids was carried out under Ullman coupling reaction conditions with PTES (Scheme 2 and Table 1). The conversion of perfluoroalkyl sulfonic acids into polymers (i.e., IEC values of polymers) could be readily adjusted by changing the amount of PTES, and the polymer with IEC = 1.60 mequiv/g corresponding to conversion of 85% (**4d**) was finally obtained by using 6 equiv of PTES for **4**. The reaction of **5** and PTES (6 equiv) also gave **5a** with IEC = 1.83 mequiv/g, which corresponds to conversion of 80%. The IEC values of **4a**–**5a** were determined by titration with 0.02 M NaOH aqueous solution. Obtained polymers dissolved well in polar solvents, such as DMAc, NMP, and DMSO.

The structure of the polymers was characterized by ^{1}H and ^{19}F NMR spectra. As can be seen in Figure 2, the peaks of **4d** are shifted compared to those of **4** in ^{1}H NMR spectra, which indicates that the introduction of the perfluoroalkyl sulfonic acids was successfully performed. Furthermore, all peaks of **4b** can be clearly assigned in the ^{19}F NMR spectrum (Figure 3).

Thermal Stability. The thermal stability of polymers was evaluated by TG analysis. Figure 4 shows the TG curves

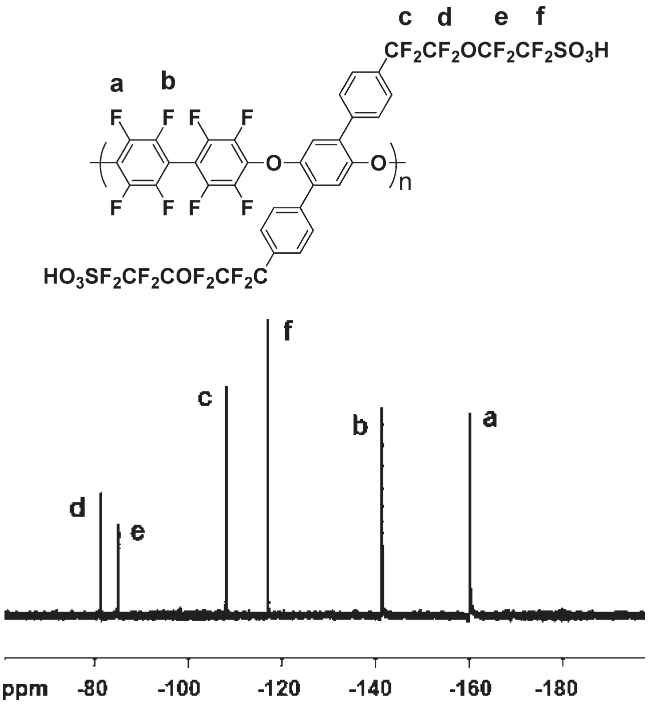


Figure 3. ^{19}F NMR spectrum of **4d** in DMSO-d_6.

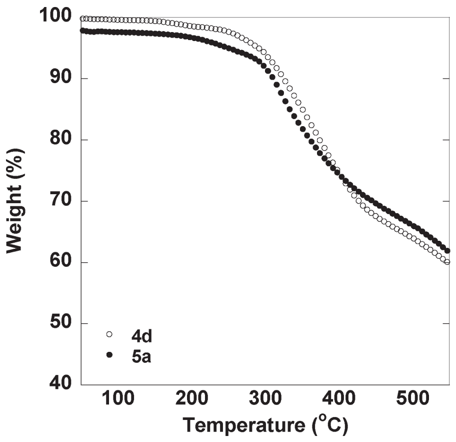


Figure 4. TG curves of **4d** and **5a**.

of **4d** and **5a**, in which a two-step weight loss is observed from 50 to 250 and above 250 °C. The first weight loss is due to the evaporation of hydrated water, and the second is attributed to the decomposition of the pendant perfluoroalkyl sulfonic acids. The decomposition temperature of **4d** and **5a** was almost the same as that of the sulfonated aromatic polymers,[11,14,15,18] which indicates that the polymers with perfluoroalkyl sulfonic acids also have good thermal stability for fuel cell operation. Furthermore, no glass transition of **4d** and **5a** was observed up to the decomposition temperature, which is probably due to the rigid aromatic polymer backbones.

Oxidative Stability. The oxidative stability of the **4a**−**5a** membranes was evaluated in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C as an accelerated test (Table 2). Regardless of the IEC values, all membranes showed high oxidative stability (>100 h). High oxidative stability similar to that of sulfonated perfluoropolymers cannot be easily achieved even with moderate (or low) IEC values in sulfonated aromatic polymers.[1−5,23] The oxidative degradation is likely to occur at the carbon atoms linking the ether bond due to the high electron density by the attack of hydroxyl radicals.[24] The fluorine-substituted DFB and HFB units decrease the electron density around the ether bonds, and besides the chemically stable C−F bonds prevent the decomposition of pendant perfluoroalkyl sulfonic acids, which led to high oxidative stability.

Table 2. Properties of 4a−5a Membranes in the Hydrated State

run	IEC (mequiv/g)[a]	WU (wt %)[b]	Δl[b]	Δt[b]	τ (h)[c]
4a	1.17	19.3	0.06	0.06	>100
4b	1.38	20.0	0.06	0.06	>100
4c	1.50	23.5	0.10	0.08	>100
4d	1.60	25.2	0.10	0.11	>100
5a	1.83	28.0	0.14	0.15	>100

[a] Measured by titration with 0.02 M NaOH aqueous solution. [b] In the hydrated state. [c] Dissolution time of membranes in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C.

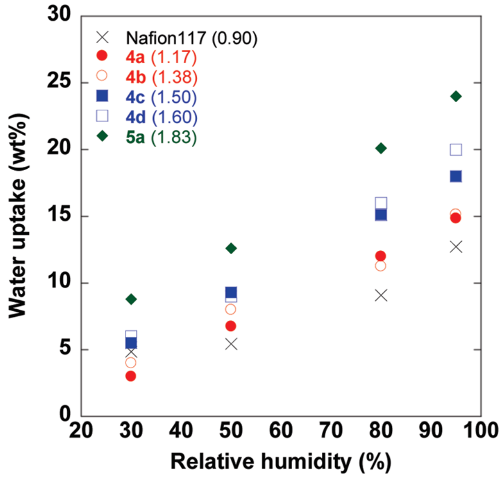


Figure 5. Humidity dependence of water uptake of **4a**−**5a** and Nafion 117 membranes at 80 °C.

Water Uptake and Dimensional Change. The water uptake and dimensional changes of the hydrated **4a**−**5a** membranes at room temperature are summarized in Table 2. Compared to the sulfonated aromatic polymers, the water uptake of the **4a**−**5a** membranes is significantly low (19.3−28.0 wt %) due to the high hydrophobicity, thus leading to good dimensional stability.

The humidity dependence of water uptake was investigated for the **4a**−**5a** membranes at 80 °C. The results are shown in Figure 5, in comparison with that of the Nafion 117 membrane. The water uptake of the **4a** and **4b** membranes is almost the same as that of the Nafion 117 membrane in a whole range of relative humidity. On the other hand, the **4c**, **4d**, and **5a** membranes with relatively high IEC values show higher water uptake compared to the Nafion 117 membrane, which indicate the strong relationship between IEC values and water uptake. The **5a** membrane still maintains good water uptake of 12.6 and 8.8 wt % at 50 and 30% RH, respectively.

Furthermore, the hydration number (λ), which is the number of water molecules per a sulfonic acid group, is plotted against

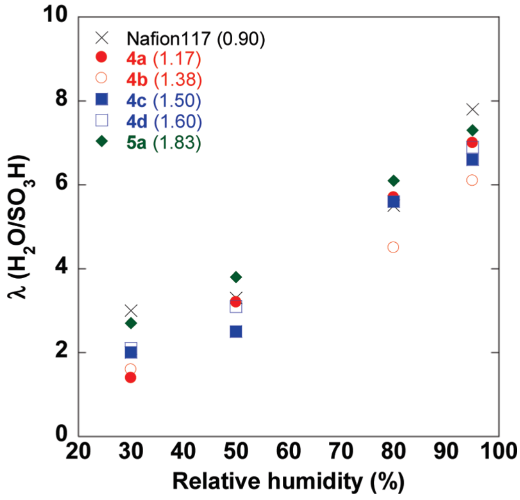


Figure 6. Humidity dependence of hydration number (λ) of **4a**−**5a** and Nafion 117 membranes at 80 °C.

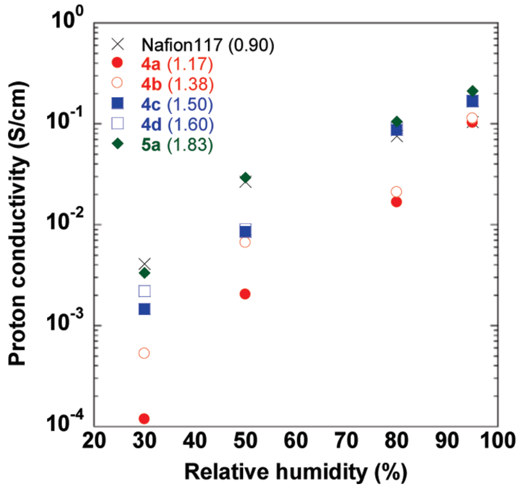


Figure 7. Humidity dependence of proton conductivity of **4a**−**5a** and Nafion 117 membranes at 80 °C.

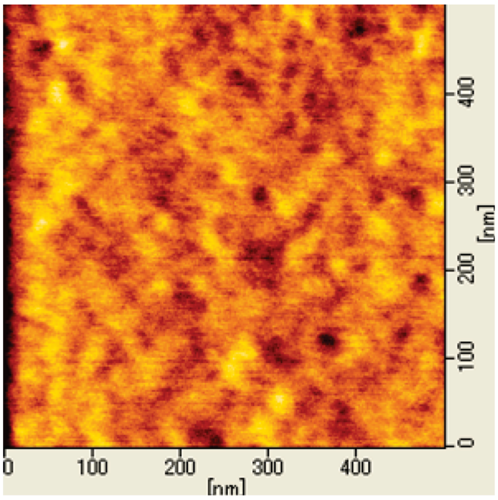


Figure 8. AFM tapping mode phase image of **5a** membrane. Scan sizes are 500 × 500 nm^2.

relative humidity. As can be seen in Figure 6, IEC values are principally reflected in λ values; that is, the **5a** membrane with the highest IEC value (1.83 mequiv/g) shows the highest λ values in the whole range of relative humidity among the **4a**−**5a** membranes. Furthermore, note that the Nafion 117 membrane shows high λ values comparable to the **5a** membrane regardless of the low IEC value (0.90 mequiv/g). The high retention capacity of water molecules (i.e., high λ values) is one of the reasons why sulfonated perfluoropolymers can achieve efficient proton conduction in the whole range of relative humidity. Thus, high proton conductivity like sulfonated perfluoropolymers is also expected in the **5a** membrane with high λ values (see the next section).

Proton Conductivity. The humidity dependence of proton conductivity was measured for the **4a**−**5a** and Nafion 117 membranes at 80 °C. Proton conductivity is generally considered to play an important role in the performance of fuel cells. Thus, higher levels of proton conductivity can achieve higher power densities in PEFCs. As shown in Figure 7, all membranes show high proton conductivity comparable to that of the Nafion 117 membrane at 95% RH. The proton conductivity of the **4a** and **4b** membranes, however, decreases rapidly with decreasing relative humidity from 95 to 30% RH. The **4c** and **4d** membranes maintain relatively high proton conductivity ((1.5−2.2) $\times 10^{-3}$ S/cm) even at 30% RH. On the other hand, the proton conductivity of the **5a** membrane with the highest IEC value is higher than that of the Nafion 117 membrane at 80 and 50% RH (1.1×10^{-1} and 3.0×10^{-2} S/cm, respectively) and still comparable (3.3×10^{-3} S/cm) to the Nafion 117 membrane even at 30% RH. The high λ values of the **5a** membrane should contribute to high proton conductivity. Compared to sulfonated aromatic polymers (IEC ∼ 1.80 mequiv/g),[4,5,9−11] the **4a**−**5a** membranes (even the **4a** and **4b** membranes) show higher proton conductivity in the whole range of relative humidity. Although the water uptake of the **4a**−**5a** membranes and polymers with pendant perfluoroalkyl sulfonic acids in previous reports[19,20] is significantly low compared to those of the sulfonated aromatic polymers, their λ values are particularly superior to those of the sulfonated aromatic polymers under low relative humidity. Such high retention capacity of water molecules and high proton mobility due to low pK_a values obviously contributed to high proton conductivity.

Atomic Force Microscope (AFM) Observation. The tapping mode phase image of the surface of the **5a** membrane as the representative was recorded under ambient conditions on 500 × 500 nm^2 size scales to investigate the phase separation between the hydrophilic and hydrophobic domains (Figure 8). The dark and bright regions were assigned to the soft structure corresponding to the hydrophilic domains with sulfonic acid groups containing water and the hard structure corresponding to the hydrophobic domains, respectively. As can be seen in Figure 8, the phase separation in which the hydrophilic domains are well dispersed and connected to each other is clearly observed, which contributes to the formation of proton transportation channel and high λ values, resulting in high proton conductivity in the whole range of relative humidity.

■ CONCLUSIONS

Poly(phenylene ether)s with pendant perfluoroalkyl sulfonic acids (IEC = 1.17−1.83 mequiv/g) were successfully synthesized by the aromatic nucleophilic substitution reaction of the fluorine monomer (DFB or HFB) with 2,5-bis(*p*-iodophenyl)hydroquinone, followed by the Ullman coupling reaction with PTES. All polymers showed high oxidative stability against hot Fenton's reagent. Even in the hydrated state, the water uptake of the membranes was significantly low (19.3−28.0 wt %) due to the high fluorine content. The strong acidity of the perfluoroalkyl sulfonic acids contributed to high proton conductivity of all membranes in the wide range of relative humidity. The **5a** membrane with the highest IEC value (1.83 mequiv/g), in particular, showed higher proton conductivity than that of the Nafion 117 membrane in the range of 50−95% RH and still maintained high proton conductivity (3.3×10^{-3} S/cm) comparable to that of the Nafion 117 membrane even at 30% RH. Consequently, novel aromatic polymers with pendant perfluoroalkyl sulfonic acids, which mimicked the structure of the sulfonated perfluoropolymers, are a promising candidate for fuel cell applications.

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