Synthesis and Properties of Fluorocarbon–Hydrocarbon Hybrid Block Copolymers with Perfluorosulfonimide Acid

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ABSTRACT: Novel fluorocarbon–hydrocarbon hybrid block copolymer electrolytes were synthesized. The block copolymer electrolytes consist of poly(perfluoropropyl sulfonimide) (PC3SI) as a perfluorinated hydrophilic segment and poly(ether ether sulfone) as a hydrocarbon hydrophobic segment. The sulfonimide group of poly(perfluoropropyl sulfonimide) has superacidity, very low equivalent weight (EW = 293 g/equiv), and a proton conductivity of 1.2 × 10⁻² S/cm under dry conditions and 25 °C, although soluble in water. The proton conductivity of the block copolymer was 1.7 × 10⁻³ S/cm at 20% relative humidity and 25 °C, which is three times as high as that of Nafion 112.

INTRODUCTION

Fuel cell (FC) vehicles that are equipped with polymer electrolyte fuel cells (PEFCs) and use hydrogen gas as the fuel have received considerable attention in recent years due to their lack of harmful emissions. The performance of PEFC systems is dependent on membrane-electrode assembly materials. The PEFC has been typically operated under humidified conditions using humidifying systems at 60–80 °C. Operation under low humidity could simplify the humidifying systems and, in the end, reduce the cost of FC systems. The proton conductivity of conventional polymer electrolyte membranes, however, is so low under low humidity. The main issue in the development of polymer electrolyte membranes is the improvement of proton conductivity under low humidity, and the electrolyte membranes should have high acid density (low EW) and strong acidity to form continuous proton conduction pathways. Perfluorosulfonic acid electrolytes meet these requirements because of the super acidity derived from the electronegativity of fluorine. However, perfluorosulfonic acid membranes have some issues with respect to high processing costs and a low glass transition temperature.¹

Many studies have been conducted on aromatic hydrocarbon polymer electrolytes as alternative membranes, which consist of hydrophilic hydrocarbon segments and hydrophobic hydrocarbon segments.²⁻⁶ For hydrocarbon electrolytes to exhibit high proton conductivity, it has been reported that a block copolymer that consists of a regular arrangement of hydrophobic and hydrophilic segments maintains significantly higher proton conductivity under low humidified conditions than that which consists of a random arrangement of the segments.⁷⁻¹⁰ However, hydrocarbon-hydrophilic segments with sulfonic acids exhibit weaker acidity than perfluorosulfonic acids, and there have been a few reports on embedded perfluorosulfonic acids or perfluorosulfonimide acids as side chains of hydrophilic segments.²⁵⁻²⁸ Poly-(perfluoroalkyl sulfonimides) (PCSIs) are promising candidates as the hydrophilic segment of block copolymers. Hu and DesMarteau reported the synthesis and properties of PCSIs, and the advantage of PCSIs in the control of equivalent weight (EW) by changing the alkyl chain length, and synthesized a polymer with a number of sulfonimide repetitions as intended.²⁹⁻³¹ There has been no report of the incorporation of segments with highly repetitive sulfonimide into main chains of hydrophilic segments. We have focused on poly-(perfluoropropyl sulfonimide) (PC3SI), which should satisfy the requirements of a very low EW (293 g/equiv) together with super acidity similar to that of perfluorosulfonic acid. For hydrophobic segments, poly(ether ether sulfone) (PEES) was selected because of its ease of synthesis of hydrocarbon polymers.

For the block copolymer to achieve high proton conductivity, the control of block length in hydrophilic segments and hydrophobic segments is also important. MacGrath and co-worker have reported that proton conductivity of block copolymer membranes increased as the block length increased due to the sharply developed microphase-separated structure.⁴

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In this paper, we report studies on novel fluorocarbon–hydrocarbon hybrid block copolymer electrolyte membranes including the synthesis of telechelic hydrophilic and hydrophobic segments by polycondensation (Scheme 1) and the properties of the obtained electrolyte membrane with different block lengths of j and k. The microphase-separated structure of the block copolymers may change not only by the block lengths of j and k but also by the ratio (j/k). In this paper, the effects of block lengths on the properties were investigated with j/k kept constant.

**Experimental Section**

**Materials.** Perfluoropropylyl-1,3-bissulfonylfluoride (C3F) was purchased from Daikin Industries, Ltd. (Osaka, Japan) and used as received. Lithium bromide was purchased from Sigma-Aldrich and used as received. 4-Fluorobenzenesulfonyl chloride, sodium hydroxide, potassium carbonate, magnesium sulfate, diethyl ether (Et2O), ethanol (EtOH), chloroform (CH2Cl2), dimethyl sulfoxide (DMSO), DMSO-d6 acetonitrile-d3 (MeCN-d3), anhydrous acetonitrile (MeCN), anhydrous N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), p-cresol, 1,4-dioxane, hexane, and tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries, Ltd., distilled with CaH2, and used as received. Lithium hexamethyldisilazide (LiHMDS) solution in THF was as received. 4-Fluorobenzenesulfonyl chloride, magnesium sulfate, diethyl ether (Et2O), ethanol (EtOH), chloroform (CH2Cl2), dimethyl sulfoxide (DMSO), DMSO-d6 acetonitrile-d3 (MeCN-d3), anhydrous acetonitrile (MeCN), anhydrous N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), p-cresol, 1,4-dioxane, hexane, and tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries, Ltd., distilled with CaH2, and used as received. Lithium bromide was purchased from Sigma-Aldrich and used as received. Lithium bromide was purchased from Sigma-Aldrich and used as received. Lithium hexamethyldisilazide (LiHMDS) solution in THF was as received. Lithium hexamethyldisilazide (LiHMDS) solution in THF was as received. Lithium hexamethyldisilazide (LiHMDS) solution in THF was as received.

**Synthesis of Perfluoropropylyl-1,3-bissulfonylfluoride (C3F).** 1 M LiHMDS solution in THF (66 mL, 66 mmol) was added to a 100 mL two-necked round-bottomed flask under a N2 atmosphere, and then, 9.48 g (30 mmol) of C3F was slowly added at −80 °C. The mixture was stirred for 1 h at −80 °C and then for 12 h at room temperature. After removal of the volatiles, the remaining solid was dissolved in 1 N HCl solution and extracted with 300 mL of Et2O. The organic phase was dried with anhydrous MgSO4 and then stirred with activated carbon for 20 min until the color of the solution disappeared. The colorless solution was evaporated to give C3A as white powder (7.6 g, 82%). 19F nuclear magnetic resonance (NMR) (MeCN-d3, 500 MHz): δ = −118.28 (s, 2F), −112.84 (s, 4F).

**Synthesis of PC3SI.** C3F 2.50 g (7.92 mmol), C3A 2.48 g (8 mmol), DIPEA 6.13 mL (40 mmol), and anhydrous MeCN (8 mL) were added to a 30 mL Schlenk flask and stirred under a N2 atmosphere at 80 °C for 2 days. The volatile contents were removed by N2 flow, and the remaining oily product was dissolved in 50 mL of 1 N NaOH aqueous solution. The alkaline solution was bubbled with N2 gas to remove DIPEA. The solution was then washed with Et2O to remove impurities, and the Na salt was extracted with MeCN. The organic phase was evaporated, and the residue was dried under vacuum at 60 °C overnight to give the Na salt. The salt was acidified with 100 mL of 1 N HCl solution, and the acidic solution was washed again with Et2O to remove impurities. This ether washing caused three-phase separation, the top layer was aqueous solution, the middle layer was Et2O including impurities, and the bottom layer was Et2O solution including PC3SI. The bottom layer was separated, and the residue was dried under vacuum at 80 °C to give PC3SI as pale yellow powder (5.0 g, 85%, i = 25, Scheme 2).

**Scheme 1. Synthesis of Perfluorocarbon–Hydrocarbon Hybrid Block Copolymer Electrolyte**

**Scheme 2. Chemical Structure of PC3SI**

**Synthesis of F-Ph-Terminated Telechelic Poly(perfluoropropyl sulfonimide) Potassium Salt (1 in Scheme 1).** F-Ph-terminated telechelic poly(perfluoropropyl sulfonimide) was synthesized with the comonomer compositions shown in Table 1. The polymerization is described as follows for run 1 in Table 1. C3F (13.8 g, 43.6 mmol), C3A (20.3 g, 64.6 mmol), and anhydrous MeCN (40 mL) were added to a Schlenk flask equipped with a PTFE stopcock, under a N2 atmosphere. DIPEA (38 mL, 0.22 mol) was then added to the flask, and the solution was stirred at 80 °C for 2 days. After evaporation of the volatiles, 1 N NaOH (aqueous) was added to the remaining mixture, and the mixture was extracted with MeCN. The organic phase was evaporated to
and the mixture was dried under vacuum at room temperature. A condenser, a Dean Stark apparatus, and a 3-way stopcock, and the mixture was dried under vacuum for 2 h. Anhydrous DMAc (28 mL) and toluene (28 mL) were added to the flasks under a N₂ atmosphere, and the solution was refluxed at 120 °C for 2 h. The reaction temperature was gradually increased to 150 °C, while azeotropic water was removed with the Dean–Stark apparatus. The solution was kept at 165 °C for 24 h. The excess K₂CO₃ and KF byproducts were then filtered out from the reaction solution. The filtrate was precipitated in EtOH, and the precipitate was retrieved by centrifugation. The target compound was obtained after drying at 60 °C under vacuum overnight (4.7 g, 99%).

**Synthesis of the Targeted Block Copolymer.** F-Ph-terminated telechelic poly(3-fluoropropylsulfonimide) potassium salt (run 1 in Table 1; 18.2 g, F-Ph 11 mmol), OH-Ph-terminated PEES (run 1 in Table 2; 15.9 g, OH-Ph 11 mmol), and K₂CO₃ (3.06 g, 22 mmol) were added to a 1 L three-necked round-bottomed flask equipped with a condenser, a Dean–Stark apparatus, and a 3-way stopcock, and the mixture was dissolved at 120 °C. The reaction temperature was gradually increased to 150 °C, while azeotropic water was removed with the Dean–Stark apparatus. The solution was kept at 165 °C for 2 weeks. The excess K₂CO₃ and KF byproducts were then retrieved from the reaction solution. The filtrate was precipitated in 1 N HCl aq, and the precipitate was retrieved by centrifugation. After the obtained precipitate was dried under vacuum overnight, the reaction solution was added to the water under a N₂ atmosphere, and the solution was refluxed at 110 °C for 2 h. The reaction temperature was gradually increased to 150 °C, while azeotropic water was removed with the Dean–Stark apparatus. The solution was precipitated and kept at 165 °C for 2 weeks. The excess K₂CO₃ and KF byproducts were then retrieved from the reaction solution. The filtrate was precipitated in EtOH, and the precipitate was retrieved by centrifugation. After the obtained precipitate was dried under vacuum and dissolved in MeCN, the insoluble part was filtered, and the filtrate was evaporated to dryness (30 g, 89%). The dried copolymer (0.5 g) was dissolved in MeCN (5 g), and CHCl₃ (45 g) was added to the solution. The obtained precipitate was recovered by centrifugation, and the target compound was obtained after drying at 60 °C under vacuum (0.28 g, 56%).

### Table 1. Reaction Conditions of OH-Ph-Terminated PC3SI

| run | feed j | C3F (g) | C3A (g) | DIPEA (mL) | MeCN (mL) | PC3SI (g) | FPhSO₂Cl (g) | DIPEA (mL) | MeCN (mL) |
|-----|--------|---------|---------|------------|-----------|-----------|--------------|------------|-----------|
| 1   | 5      | 13.8    | 20.3    | 38         | 40        | 16.9      | 5.33         | 20         | 20        |
| 2   | 15     | 18.1    | 20.3    | 50         | 20        | 39.3      | 5.00         | 30         | 30        |

### Table 2. Reaction Conditions of OH-Ph-Terminated Telechelic PEES

| run | feed k | 4,4’-dichlorodiphenyl sulfone (g) | 4,4’-bisphenol (g) | K₂CO₃ (g) | DMAc (mL) | toluene (mL) |
|-----|--------|---------------------------------|-------------------|-----------|----------|-------------|
| 1   | 4      | 12.0                            | 9.73              | 28.9      | 65       | 65          |
| 2   | 10     | 12.0                            | 8.56              | 25.4      | 65       | 65          |

**Synthesis of the Cl-Ph-Terminated Hydrophobic Segment (for Polymer Structural Analysis).** 4,4’-Bisphenol (1.3 g, 7.0 mmol), 4,4’-dichlorodiphenyl sulfone (6.0 g, 21 mmol), and K₂CO₃ (0.97 g, 21 mmol) were added to a 100 mL three-necked round-bottomed flask equipped with a condenser, a Dean–Stark apparatus, and a 3-way stopcock, and the mixture was dried under vacuum at room temperature for 2 h. Anhydrous DMAc (28 mL) and toluene (28 mL) were added to the flasks under a N₂ atmosphere, and the solution was refluxed at 120 °C for 2 h. The reaction temperature was gradually increased to 150 °C, while azeotropic water was removed with the Dean–Stark apparatus. The solution was kept at 165 °C for 24 h. The excess K₂CO₃ and KF byproducts were then retrieved from the reaction solution. The filtrate was precipitated in EtOH, and the precipitate was retrieved by centrifugation. After the obtained precipitate was dried under vacuum overnight, the reaction solution was added to the water under a N₂ atmosphere, and the solution was refluxed at 110 °C for 2 h. The reaction temperature was gradually increased to 150 °C, while azeotropic water was removed with the Dean–Stark apparatus. The solution was precipitated and kept at 165 °C for 2 weeks. The excess K₂CO₃ and KF byproducts were then retrieved from the reaction solution. The filtrate was precipitated in EtOH, and the precipitate was retrieved by centrifugation. After the obtained precipitate was dried under vacuum and dissolved in MeCN, the insoluble part was filtered, and the filtrate was evaporated to dryness (30 g, 89%). The dried copolymer (0.5 g) was dissolved in MeCN (5 g), and CHCl₃ (45 g) was added to the solution. The obtained precipitate was recovered by centrifugation, and the target compound was obtained after drying at 60 °C under vacuum (0.28 g, 56%).
membrane was separated from the Petri dish and dried under vacuum overnight at 60 °C. The membrane was immersed in 1 N H2SO4 aqueous solution at 60 °C overnight and then washed with pure water until the pH of the water became neutral. The membrane was dried at 60 °C overnight.

**Measurements.** 1H NMR (500 MHz) and 19F NMR (500 MHz) measurements were conducted using samples dissolved in MeCN-d3 or dimethyl sulfoxide (DMSO-d6) on a JEOL JMTJC-400/54/SS spectrometer.

Molecular weight and molecular weight distributions (Mn/Mn) were determined using gel permeation chromatography (GPC; Tosoh HPC-8120GPC) with a UV detector (Tosoh UV-820; 270 nm) and a TSK gel α-M column (Tosoh) with DMSO (50 mM LiBr) as the eluent at a flow rate of 0.5 mL/min at 40 °C. A molecular weight calibration curve was obtained using a polystyrene standard (Tosoh).

Transmission electron microscopy (TEM) observations were conducted using ultrathin sections of the membranes. The samples were embedded with epoxy resin and then cross-sectioned with an ultra-microtome (Leica ULTRACUT-S) at 20 °C to obtain 50 nm-thick sections. Bright-field images of the ultrathin sections were obtained using TEM (JEOL JEM-2000EX) at an acceleration voltage of 200 kV.

**Evaluation of Membrane Properties. Water Uptake.** The weight of the membrane after immersion in water at room temperature (Ww-H2O) and that of the membrane after drying overnight at 80 °C (Wdry) were measured. The water uptake was calculated using formula 1

\[ \text{water uptake (\%) = } \left( \frac{W_{\text{w-H2O}} - W_{\text{dry}}} {W_{\text{dry}}} \right) \times 100 \]  

(1)

**Swelling Ratio.** The size in plain and through plain of the membrane after immersion in water at room temperature (Lw-1H2O) and that of the membrane after drying overnight at 80 °C (Ldry) were measured. The swelling ratio was calculated using formula 2

\[ \text{swelling ratio (\%) = } \left( \frac{L_{\text{w-1H2O}} - L_{\text{dry}}} {L_{\text{dry}}} \right) \times 100 \]  

(2)

**Proton Conductivity.** The obtained membrane was set on a pair of platinum electrodes at a distance of 0.4 cm. The resistance of the membrane was measured using a chemical impedance meter (Hioki 3532-80) over the frequency range of 50 Hz to 1 MHz. The proton conductivity (σ) was calculated from the membrane resistance (R) and the distance between the electrodes (L = 0.4 cm) using the membrane thickness (T) and width (W) under the given measurement conditions using formula 3

\[ \sigma \ (\text{S/cm}) = \frac{1}{R} \times \frac{L}{(T \times W)} \]  

(3)

**Equivalent Weight.** The obtained membrane was dried at 80 °C under vacuum overnight, and the weight of the dried membrane was measured. The dried membrane was immersed in 10 wt % NaCl aqueous solution (30 mL) at room temperature overnight to obtain an acidic aqueous solution for titration. After immersion, the membrane was removed from the solution and rinsed with water. The solution was diluted to a total volume of 80 mL with water as a titration sample. The titration was performed using an automatic titrator (GT-100, Mitsubishi Chemical Corporation) with 0.05 mol/L NaOH aqueous solution. The EW was calculated from the weight of the dried membrane (Wdry), the dripped volume of the basic aqueous solution (VNaOH), and the concentration of the NaOH aqueous solution (CNaOH) using formula 4

\[ \text{EW (g/eq.) = } V_{\text{NaOH}} \times C_{\text{NaOH}} / W_{\text{dry}} \]  

(4)

**RESULTS AND DISCUSSION**

**Synthesis of PC3SI and F-Ph-Terminated Telechelic Poly(perfluoropropyl sulfonimide) Potassium Salt (Hydrophilic Segment).** Table 3 shows the results for the synthesis of hydrophilic segments. The progress in these syntheses was confirmed by 19F NMR as follows. Figure 1

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c01972)
likely because the lower molecular weight oligomers were removed, and the higher molecular weight polymers were recovered by purification.

![Chemical structure image]

**Synthesis of OH-Ph-Terminated Telechelic PEES (Hydrophobic Segment).** Table 4 shows the results for the hydrophobic segments. In the 1H NMR spectra of the hydrophobic segments, it was derived from the ratio of the integral value of polymer terminals (Hg) and repeat units (Hb, HB, and Hc) in the 1H NMR spectra, was calculated from the ratio of the hydrophilic segments to the hydrophobic segments, which indicates that implementation of the OH-Ph end groups was 100%. The degree of polymerization for the hydrophobic segments, which was calculated from the ratio of the remaining F-Ph groups in the hydrophilic segments before reaction [(b) run 1 in Table 5] and the hydrophobic segments before reaction [(b) run 1 in Table 4]. The peak top of (b) was shifted to that of (a) for high molecular weight; therefore, it was also confirmed by SEC that the block copolymerization was successful.

**Table 4. Results for Obtained OH-Ph-Terminated Telechelic PEESs**

| run | feed % | yield % | obtained | Mw (×10^3) | Mn (×10^3) | Mw/Mn |
|-----|--------|---------|----------|-------------|-------------|-------|
| 1   | 4      | 81      | 6.7      | 2.9         | 6.7         | 1.8   |
| 2   | 10     | 88      | 15       | 6.0         | 16          | 33    |

“Calculated from 1H NMR. “Calculated from GPC (PS standard).

**Figure 2.** 1H NMR spectra for the hydrophobic segments. In the 1H NMR spectra of 4,4'-bisphenol (a), OH-Ph-terminated PEES [run 1 (b) and run 2 (c) in Table 4] and Cl-Ph-terminated model compound (d) in DMSO-d6 at RT.

spectra for the Cl-Ph-terminated model compound and 4,4'-bisphenol, Cl-Ph was not observed in the end groups of the hydrophobic segments, which indicates that implementation of the OH-Ph end groups was 100%. The degree of polymerization for the hydrophobic segments, which was calculated from the ratio of the integral value of polymer terminals (Hg) and repeat units (Hb, HB, and Hc) in the 1H NMR spectra, was 1.5 times that of the feed. This is also likely because the lower molecular weight oligomers were removed, and the higher molecular weight polymers were recovered by purification.

**Synthesis of the Hydrophilic–Hydrophobic Block Copolymer.** Table 5 shows the results for the block copolymerization. The charged j/k values were set so that the ratio of the hydrophilic segments to the hydrophobic segments in the block copolymers was almost equal. The progress in the reaction between the obtained hydrophilic and hydrophobic segments was confirmed by 19F and 1H NMR, as follows. Figure 3 shows 19F and 1H NMR spectra for the obtained block copolymers (run 2 in Table 5). The peaks derived from the F-Ph end groups of the hydrophilic segments (−109.5 ppm in 19F NMR spectrum) and the end groups of the hydrophilic segments [H (7.46 ppm) and H (6.85 ppm) in 1H NMR spectrum] disappeared; these NMR results confirmed that the block copolymerization was successful.

**Figure 4** shows the ratio of the remaining F-Ph groups in the copolymerization reaction to the feed and the molecular weight of each as a function of the reaction time (run 1 in Table 5). It took 2 weeks to consume all the F-Ph groups because the collision frequency between end groups of the hydrophilic segments and hydrophobic segments in this copolymerization was much lower than in typical reactions between low molecular weight compounds.

**Figure 5** shows size-exclusion chromatography (SEC) profiles for the purified block copolymer [(a) run 1 in Table 5] and the hydrophobic segments before reaction [(b) run 1 in Table 4]. The peak top of (b) was shifted to that of (a) for high molecular weight; therefore, it was also confirmed by SEC that the block copolymerization was successful. The profile for the block copolymer was monomodal, and the molecular weight distribution (Mw/Mn) of approximately 2.5 was larger than that of the theoretical value of 2 for the polycondensation polymer; therefore, multi block copolymers with various degrees of polymerization were obtained.

The EW values, 510 and 558, of the obtained block copolymers in runs 1 and 2 in Table 5, respectively, were smaller than the theoretical EW values of 592 and 574 of the feed. This is because of the purification process; in the purification step by reprecipitation of the block copolymers, the EW values in runs 1 and 2 for the block copolymer dissolved in the top clear layer were higher at 782 and 610 g/ equiv, respectively. Therefore, the block copolymers recovered as a precipitate had lower EWs.

**Evaluation of Physical Properties.** The obtained block copolymer was dissolved in a mixture of NMP and p-cresol at room temperature, and the solution was cast onto a flat Petri dish, dried at 80 °C, and then annealed at 100 °C. After immersion in 1 N H2SO4 aqueous solution, the membrane was washed with pure water. Table 6 shows the physical properties of the obtained block copolymers. Phase separation of hydrophilic and hydrophobic segments in the membrane can affect properties such as the water uptake and proton conductivity. Figure 6 shows a TEM image of a section of the block copolymer (run 2 in Table 6) membrane. Dark parts and clear parts are hydrophilic segments and hydrophobic segments, respectively. Dark parts were partially continuous at the nanometer level and, therefore, the hydrophilic segments formed continuous proton conductive pathways to provide high proton conductivity. Although the phase separation occurred, the contrast between hydrophilic segments and hydrophobic segments was not clear, and the diameter of ion...
channels (a few nanometers) was smaller than that of the previously reported electrolyte membranes (tens of nanometers).\textsuperscript{3,5,6} Watanabe et al. have reported the relationship between the phase separation of block copolymer electrolytes and block length, in which the contrast becomes clearer and the diameter becomes thicker as the block length increases.\textsuperscript{5} Using long block length, the similar effects can be obtained in this block copolymer system. The block copolymer, whose block length of $j$ was greater than 21, was not obtained because the implementation of F-Ph end groups of hydrophilic segments was too low to copolymerize.

Despite of lower $N_{H}$ (proton density) of block copolymer 2, the water uptake was higher than that of block copolymer 1. Calculating the ratio of the block length of the hydrophilic segments ($j$) to that of the hydrophobic segments ($k$) in Table 5, the ratio of block copolymer 2 ($j/k = 1.40$) is higher than that of block copolymer 1 ($j/k = 1.28$). The reason for high water uptake of the block copolymer 2 was that the hydrophobic segment had no enough length to sufficiently suppress the hydrophilic segment from absorbing water.

Although the obtained block copolymers (runs 1 and 2 in Table 6) were insoluble in hot water at 80 °C, the water uptake was extremely high (more than 100%) as with S-PEEK [sulfonated-poly(ether ether ketone)]. This suggests that the hydrophobic segments formed were not effectively continuous to resist swelling of the hydrophilic segments with water.

The swelling ratio of block copolymers 1 and 2 was anisotropic in comparison to Naion 112. Both the swelling ratio in-plane and through-plane was decreased with increasing the block length. Long block length may be effective in controlling of the swelling ratio.

Figure 7 shows the dependency of the proton conductivity on the humidity for PC3SI ($i = 25$) and the block copolymer membrane (runs 1 and 2 in Table 6). The conductivity of PC3SI at 20% relative humidity (RH) was $1.2 \times 10^{-2}$ S/cm, which is approximately 10 times as high as that of Naion 112. The conductivity of PC3SI at more than 50% RH was not obtained because the membrane was dissolved. The conductivity of the block copolymer decreased when humidity became low, but did not decrease suddenly as with the hydrocarbon S-PEEK, Figure 7e, which has randomly arranged sulfonic acid groups. The conductivity of the block copolymer at 20% relative humidity (RH) was $1.7 \times 10^{-3}$ S/cm, which is approximately three times that of Naion 112 and approximately 930 times that of S-PEEK. Although EW of the block copolymer 2 was higher than that of block copolymer 1, the conductivity of 2 was higher than that of 1. It is expected that the clearer phase-separated structure and more continuous proton conduction pathways of block copolymer 2 are formed because of long block lengths.

According to the Nernst–Einstein equation, the proton conductivity is proportional to the proton diffusion coefficient and proton density:

![Table 5. Results for Block Copolymerization](https://example.com/table5.png)

| Run | Block Copolymer | Feed | $j/k$ | EW (g equiv$^{-1}$) | Yield (%) | EW$_{c}$ (g equiv$^{-1}$) | $M_{n}$ (x10$^{3}$) | $M_{w}$ (x10$^{3}$) | $M_{w}/M_{n}$ |
|-----|----------------|------|------|-------------------|-----------|-------------------------|------------------|----------------|-------------|
| 1   | 1              | 8.6  | 6.7  | 1.28              | 56        | 510                     | 2.6              | 6.4            | 2.5         |
| 2   | 2              | 21   | 15   | 1.40              | 63        | 558                     | 3.3              | 6.0            | 2.3         |

\textsuperscript{a}Calculated from $^{19}$F NMR. \textsuperscript{b}Calculated from $^{1}$H NMR. \textsuperscript{c}Theoretical. \textsuperscript{d}Calculated from titration (NaCl method). \textsuperscript{e}Calculated from GPC.

![Figure 3. $^{19}$F NMR (upper) and $^{1}$H NMR (lower) spectra for the obtained block copolymer (run 2 in Table 5) in DMSO-$d_6$ at RT. Asterisk peak is unknown.](https://example.com/fig3.png)

![Figure 4. (a) $[F\text{-Ph}]/[F\text{-Ph}]_0$ and (b) $M_n$ as a function of reaction time.](https://example.com/fig4.png)

![Figure 5. SEC curves for the obtained copolymer [(a) run 1 in Table 5] and the obtained OH-Ph-terminated PEES [(b) run 1 in Table 4].](https://example.com/fig5.png)
Table 6. Properties of the Obtained Block Copolymers

| run  | electrolyte      | EW (g/equiv) | density (g/cm³) | N_H2O (mmol/cm³) | water uptake (%) | swelling ratio |
|------|------------------|--------------|-----------------|------------------|-----------------|---------------|
| 1    | block copolymer 1| 510          | 2.31            | 4.5              | 113             | 44            |
| 2    | block copolymer 2| 558          | 2.27            | 4.1              | 153             | 36            |
| 3    | Naflon112        | 1075         | 2.03            | 1.9              | 22              | 14            |
| 4    | S-PEEK           | 418          | 1.32            | 3.1              | 165             | 54            |

Proton density (N_H2O = density/EW×1000).

Figure 6. TEM image of the obtained block copolymer (run 2 in Table 6).

Figure 7. Proton conductivity of PC3SI [(a) EW 293 g/equiv], the obtained block copolymer [(b) EW558 g/equiv run 2 in Table 6, (c) EW510 g/equiv run 1 in Table 6], Naflon112 [(d) EW1075 g/equiv], and S-PEEK [(e); EW 418 g/equiv].

\[
\sigma = Z^2F^2D_pN_H2O/(R\cdot T) \tag{5}
\]

where \(\sigma\) is the conductivity, \(Z\) is the charge of a proton, \(F\) is the Faraday constant, \(D_p\) is the proton diffusion coefficient, \(N_H2O\) is the proton density, \(R\) is the gas constant, and \(T\) is the temperature.

\(N_H2O\) for the block copolymer was approximately twice that for Naflon 112 (Table 6). \(D_p\) at 20% RH for the block copolymer was calculated from eq 5 and was approximately 1.5 times as high as that for Naflon 112, which indicates that continuous proton conductive pathways were formed in the block copolymer, even at low humidity. The high proton conductivity of the block copolymer is attributed to both the low EW and the continuous proton conductive pathways.

**CONCLUSIONS**

Novel fluorocarbon and hydrocarbon hybrid block copolymer electrolytes that consist of poly(perfluoropropyl sulfonimide) as hydrophilic segments and PEES as hydrophobic segments were prepared. The membranes of the obtained block copolymers had insufficient microphase-separated structures but had partially continuous proton conduction paths. The proton conductivity of the block copolymer did not suddenly decrease with a decrease in the humidity and was \(1.7 \times 10^{-3}\) S/cm at 20% RH, which is approximately three times as high as that for Naflon 112. The proton diffusivity for the block copolymer was approximately 1.5 times of Naflon 112 because of the formation of continuous proton conductive pathways at low humidity.

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**Notes**
The authors declare no competing financial interest.

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**REFERENCES**

1. James, C. W., Jr.; Roy, A.; McGrath, J. E.; Marand, E.; Marand, E. Determination of the effect of temperature and humidity on the \(O_2\) sorption in sulfonated poly(arylene ether sulfone) membranes. J. Membr. Sci. 2008, 309, 141–145.
2. Lee, H.-S.; Roy, A.; Lane, O.; Dunn, S.; McGrath, J. E. Hydrophilic-hydrophobic multiblock copolymers based on poly(arylene ether sulfone) via low-temperature coupling reactions for proton exchange membrane fuel cells. Polymer 2008, 49, 715–723.
3. Einsla, M. L.; King, Y. S.; Hawley, M.; Lee, H.-S.; McGrath, J. E.; Liu, B.; Guiver, M. D.; Pivovar, B. S. Toward Improved Conductivity of Sulfonated Aromatic Proton Exchange Membranes at Low Relative Humidity. Chem. Mater. 2008, 20, 5636–5642.
4. Takimoto, N.; Takamuku, S.; Abe, M.; Ohira, A.; Lee, H.-S.; McGrath, J. E. Conductive area ratio of multiblock copolymer electrolyte membranes evaluated by e-AFM and its impact on fuel cell performance. J. Power Sources 2009, 194, 662–667.
PSU/PPSU Poly(ether sulfone)s as solid electrolytes for proton transport: a review. J Membr. Sci. 2010, 363, 234–240.

(2) Miyake, J.; Saito, M.; Akiyama, R.; Watanabe, M.; Miyatake, K. A Proton Conductive Aromatic Block Copolymer Containing Dibenzo-furan Moieties. Chem. Lett. 2015, 44, 964–966.

(3) Miyahara, T.; Miyake, J.; Matsumo, S.; Watanabe, M.; Miyatake, K. A sulfonated polybenzophenone/polyimide copolymer as a novel proton exchange membrane. RSC Adv. 2015, 5, 50082–50086.

(4) Miyake, J.; Miyake, K. Fluorine-free sulfonated aromatic polymers as proton exchange membranes. Polym. J. 2017, 49, 487–495.

(5) Hu, Z.; Yin, Y.; Yaguchi, K.; Endo, N.; Higa, M.; Okamoto, K.-i. Synthesis and properties of sulfonated multiblock copolycalohalimides. Polymer 2009, 50, 2933–2943.

(6) Yamazaki, K.; Tang, Y.; Kawakami, H. Proton conductivity and stability of low-IEC sulfonated block copolyimide membrane. J. Membr. Sci. 2010, 362, 234–240.

(7) Sannigrahi, A.; Takamuku, S.; Jannasch, P. Block copolymers combining semi-fluorinated poly(arylene ether) and sulfonated poly(arylene ether sulfone) segments for proton exchange membranes. Int. J. Hydrogen Energy 2014, 39, 15718–15727.

(8) Ahn, J.; Lee, H.; Yang, T.-H.; Kim, C.-S.; Bae, B. Synthesis and characterization of multiblock sulfonated poly(arylene ether sulfone) membranes with different hydrophobic moieties for application in polymer electrolyte membrane fuel cell. J. Polym. Sci., Part A: Polym. Chem. 2014, 52, 2947–2957.

(9) Yuk, J.; Lee, S.; Nugraha, A. F.; Lee, H.; Park, S.-H.; Yim, S.-D.; Bae, B. Synthesis and characterization of multi-block poly(arylene ether sulfone) membranes with highly sulfonated blocks for use in polymer electrolyte membrane fuel cells. J. Membr. Sci. 2016, 518, 50–59.

(10) Jung, M. S.; Kim, T.-H.; Yoon, Y. J.; Kang, C. G.; Yu, D. M.; Lee, J. Y.; Kim, H.-J.; Hong, Y. T. Sulfonated poly(arylene sulfone) multiblock copolymers for proton exchange membrane fuel cells. J. Membr. Sci. 2014, 459, 72–85.

(11) Lee, J. Y.; Yu, D. M.; Kim, T.-H.; Yoon, S. J.; Hong, Y. T. Multi-block copolymers based on poly(p-phenylene)s with excellent durability and fuel cell performance. J. Membr. Sci. 2015, 492, 209–219.

(12) Ureña, N.; Pérez-Prior, M. T.; Río, C. d.; Vázquez, A.; Sanchez, J.-Y.; Ioioiu, C.; Levenfeld, B. Multiblock copolymers of sulfonated PSU/PPSU Poly(ether sulfone)s as solid electrolytes for proton exchange membrane fuel cells. Electrochim. Acta 2019, 302, 428–440.

(13) Kang, K.; Kwon, B.; Choi, S. W.; Lee, J.; Kim, D. Properties and morphology study of proton exchange membranes fabricated from the pendant sulfonated poly(arylene ether ketone) copolymers composed of hydrophobic and hydrophilic multi-blocks for fuel cell. Int. J. Hydrogen Energy 2015, 40, 16443–16456.

(14) Kang, K.; Kim, D. Comparison of proton conducting polymer electrolyte membranes prepared from multi-block and random copolymers based on poly(arylene ether ketone). J. Power Sources 2015, 281, 146–157.

(15) Kim, B.; Kannan, R.; Nahm, K. S.; Yoo, D. J. Development and Characterization of Highly Conducting Nonfluorinated Di and Tri-block Copolymers for Polymer Electrolyte Membranes. J. Dispersion Sci. Technol. 2016, 37, 1315–1323.

(16) Lee, K. W.; Chu, J. Y.; Kim, A. R.; Yoo, D. J. Enhanced Performance of a Sulfonated Poly(arylene ether ketone) Block Copolymer Bearing Pendant Sulfonic Acid Groups for Polymer Electrolyte Membrane Fuel Cells Operating at 80% Relative Humidity. ACS Appl. Mater. Interfaces 2018, 10, 20835–20844.

(17) Oh, K.; Kietpang, K.; Kim, H.; Shanmugam, S. Synthesis of sulfonated poly(arylene ether ketone) block copolymers for proton exchange membrane fuel cells. J. Membr. Sci. 2016, 507, 135–142.

(18) Yoo, T.; Aziz, M. A.; Oh, K.; Shanmugam, S. Modified sulfonated Poly(arylene ether) multiblock copolymers containing highly sulfonated blocks for polymer electrolyte membrane fuel cells. J. Membr. Sci. 2017, 542, 102–109.

(19) Hu, Z.; Lu, Y.; Zhang, X.; Gao, Q.; Yan, X.; Chen, S. Poly(arylene ether) sulfones bounded with disulfonanaphthoxyl pendants by post functionalization for polymer electrolyte membrane application in fuel cells. Int. J. Hydrogen Energy 2017, 42, 12064–12075.

(20) Lu, Y.; Zhang, X.; Yan, X.; Hu, Z.; Chen, S. The structure–property–performance relationship of disulfonated naphthyl pendant bearing poly(aryl ether)s for polymer electrolyte membrane applications. J. Membr. Sci. 2018, 555, 45–55.

(21) Assumma, L.; Ioioiu, C.; Mercier, R.; Lyonard, S.; Nguyen, H. D.; Planes, E. Synthesis of partially fluorinated poly(arylene ether sulfone) multiblock copolymers bearing perfluorosulfonic functions. J. Polym. Sci., Part A: Polym. Chem. 2015, 53, 1941–1956.

(22) Assumma, L.; Nguyen, H.-D.; Ioioiu, C.; Lyonard, S.; Mercier, R.; Escude, E. Effects of Block Length and Membrane Processing Conditions on the Morphology and Properties of Perfluoro-sulfonated Poly(arylene ether sulfone) Multiblock Copolymer Membranes for PEMFC. ACS Appl. Mater. Interfaces 2015, 7, 13808–13820.

(23) Nguyen, H.-D.; Assumma, L.; Judeinstein, P.; Mercier, R.; Porcar, L.; Jestin, J.; Ioioiu, C.; Lyonard, S. Controlling Microstructure—Transport Interplay in Highly Phase-Separated Perfluorosulfonated Aromatic Multiblock Ionomers via Molecular Architecture Design. ACS Appl. Mater. Interfaces 2017, 9, 1671–1683.

(24) Cho, C. G.; Kim, Y. S.; Yu, X.; Hill, M.; McGrath, J. E. Synthesis and characterization of poly(arylene ether sulfone) copolymers with sulfonamide side groups for a proton exchange membrane. J. Polym. Sci., Part A: Polym. Chem. 2006, 44, 6007–6014.

(25) Hu, L.; DesMarie, D. D. Synthesis of perhalokeline-sulfonyl halides and their sulfonamide derivatives. Inorg. Chem. 1993, 32, 5007–5010.

(26) DesMarie, D. D. Novel perfluorinated ionomers and ionenes. J. Fluorine Chem. 1995, 72, 203–208.

(27) Thomas, B. H.; Schafer, G.; Ma, J. J.; Tu, M.-H.; DesMarie, D. D. Synthesis of 3,6-dioxa-7-4-trifluoromethyl perfluoroctyl trifluoromethyl sulfonamide: bis{[perfluoroalkyl]sulfonyl} superacid monomer and polymer. J. Fluorine Chem. 2004, 125, 1231–1240.