Sulfonated Polyphenylene-Based Multiblock Membranes with Fluorine Moiety for Fuel Cell Applications

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Sulfonated poly(phenylene-co-arylene ether sulfone) multiblock copolymers are synthesized via Colon’s nickel-mediated cross-coupling reaction and are investigated as a proton-exchange membrane fuel cell. To investigate the influence of the fluorine moieties on the membrane properties, two different membranes are prepared, one containing a fluorinated hydrophobic poly(arylene ether) block (6F polymer membrane) and a nonfluorinated biphenyl (BP) polymer membrane. The proton transport, morphology, mechanical properties, and oxidative stabilities of the membranes are examined in relation to the ion-exchange capacity (IEC). 6F polymer membranes show superior proton conductivity and oxidative stability (results of Fenton’s oxidative stability and hydrogen peroxide exposure tests) compared with the BP polymer membranes. In water at 25°C, 6F and BP polymer membranes with IEC 2.0 meq g\(^{-1}\) exhibit proton conductivity of 0.11 S cm\(^{-1}\) with 6F having 16% lower water uptake than BP polymer. Meanwhile, at 30% RH and 80°C, 6F-X5Y9-(2.0) exhibits proton conductivity of 0.0026 S cm\(^{-1}\) that almost 50% higher than BP-X5Y7-(2.0) with 0.0018 S cm\(^{-1}\), while at 90% RH and 80°C, both polymers have an almost similar value of 0.10 S cm\(^{-1}\). Oxidative stability with the Fenton test under harsh conditions demonstrates that 6F-X5Y9-(2.0) has an extent degradation of 26%, almost 19% lower than BP-X5Y7-(2.0) with 32%, and the hydrogen peroxide exposure test demonstrates that 6F has 50% lower extent of degradation than BP with 5 and 9%, respectively. Fuel cell performance test at 80°C and 100% RH show that 6F-X5Y9-(2.0) exhibits a current density of 1.6 A cm\(^{-2}\) at 0.6 V (hydrogen/air) and outperforms Naion-NR211 and BP-X5Y7-(2.0), 1.4 A cm\(^{-2}\) and 1.2 A cm\(^{-2}\), respectively. Undoubtedly, incorporating fluorinated moieties could enhance proton transport properties and oxidative stability favorable for fuel cell application.

1. Introduction

Fuel cells have emerged as promising green energy devices for the electrochemical generation of electricity, heat, and water with almost zero emissions using green energy sources (e.g., compressed hydrogen) in combination with oxidants (e.g., atmospheric oxygen). Among the variety of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have become the most rapid growth and have reached commercial application in vehicles and portable/stationary energy sources owing to their high efficiency and power density [1, 2].

As PEMFC components, perfluorinated sulfonic acid (PFSA) membranes are the most widely used because of their high conductivity and durability. Nevertheless, PFSA membranes suffer from several disadvantages, including a low glass transition temperature (\(T_g\)) that limits its service temperature limited to 100°C and high manufacturing costs [3–5]. Therefore, most research on polymer electrolyte membranes (PEMs) focuses on developing alternative hydrocarbon-based membranes to replace PFSA. Hydrocarbon membranes exhibit high \(T_g\), low gas permeability, and a relatively low production cost [5–8]. Although advanced structures of hydrocarbon-based PEMs have been suggested, such as sulfonated poly(arylene ether ketone)s, sulfonated poly(arylene ether sulfone)s, sulfonated poly(arylene sulfide sulfone)s, and sulfonated polyimides, they exhibit poor
proton conductivity under low relative humidity (RH) and inadequate mecanochemical properties [1, 9–15]. To overcome these drawbacks, the development of a well-defined phase separation morphology with clustered water channels is essential to realize an efficient proton transport under low RH conditions. Multiblock copolymer designs have been demonstrated to enable a well-developed phase separation by intentionally separating hydrophilic and hydrophobic clusters, which results in the generation of proton transport channels when water percolation occurs [5, 9, 16, 17], enhancing the proton transport even under low RH conditions [17–20]. Furthermore, multiblock copolymers containing a p-phenylene structure and fluorinated moieties exhibit enhanced oxidative and mechanical stabilities, which are essential for PEMs to meet the practical requirements [16, 17, 21–27]. Thus, the combination of a multiblock design and the p-phenylene structure can be envisaged as an effective approach to realize an oxidatively stable multiblock membrane with well-defined phase separation [28, 29].

Owing to the high carbon–carbon bond dissociation energy that is present in the phenyl–phenyl group of the p-phenylene structure (478.6 ± 6.3 kJ mol⁻¹ at 298 K) [30, 31], p-phenylene is chemically and thermally more stable than other aromatic polymers containing ether, arylene sulfone, and ketone linkages [28, 32–36]. However, the p-phenylene architecture exhibits low solubility in most aprotic solvents, which hinders the membrane casting process [16, 37] and complicates the design of p-phenylene multiblocks. Using p-phenylene as the hydrophilic block in combination with poly(arylene ether) as the hydrophobic block can help to circumvent this issue [30, 31]. Combining m- and p-phenylene as the hydrophilic structures can also enhance the solubility even for long phenylene blocks, as we previously reported [28, 34, 38–40], because the linearity of phenylene and, in turn, the intermolecular attraction between phenylene groups are reduced. As a hydrophobic block, the flexible poly(arylene ether) can help increase the solubility of the resulting block copolymers. These approaches have enabled the synthesis of soluble sulfonated phenylene multiblock polymers with reduced oxidative degradation and synthetic cost [18, 28, 41]. In addition, incorporating fluorinated moieties in the hydrophilic poly(arylene ether) block could be expected to further enhance the solubility and phase separation between hydrophilic and hydrophobic blocks [35, 42–46].

On the basis of these considerations, we prepared in this study a sulfonated poly(phenylene-co-arylene ether) multiblock membrane by combining the hydrophilic structure of phenylene and a poly(arylene ether) hydrophobic block containing the superhydrophilic trifluoromethyl (–CF₃) moiety (hereinafter referred to as 6F linkage), which was expected to increase the hydrophobicity of the hydrophobic blocks [44, 45, 47] and, therefore, to trigger a substantial phase separation between hydrophobic and hydrophilic clusters, even more upon water percolation [44, 45, 48, 49]. Furthermore, the presence of the 6F linkage was expected to increase the polymer solubility and oxidative stability [50–52]. Using Colon’s nickel-mediated cross-coupling reaction for the polymerization, we prepared two kinds of membranes containing fluorinated or nonfluorinated hydrophobic poly(arylene ether) blocks, i.e., a fluorinated and flexible membrane containing the 6F linkage and a biphenyl- (BP-) polymer membrane comprising nonfluorinated BP moieties, to investigate the influence of the fluorinated groups on the properties of the membrane as a function of the ion-exchange capacity (IEC), which include the water uptake and water vapor uptake, proton conductivity, morphology, mechanical and thermal properties, oxidative stability, and fuel cell performance. According to our findings, the sulfonated block copolymer membranes containing fluorinated moieties exhibit significantly enhanced proton transport and oxidative stability, highlighting fluorinated moieties’ potential as materials that need to be considered and applied in the chemical molecular design of polymeric membranes to achieve high oxidative stability–proton transport performance for PEMFC applications.

2. Experimental Section

2.1. Materials. 3,5-Dichlorobenzene-1-sulfonyl chloride (3,5-DCBSC, ≥98%), 2,5-dichlorobenzene-1-sulfonyl chloride (2,5-DCBSC, >98%), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (6F-BPA, >98%), 4,4′-dichlorodiphenyl sulfone (DCDSP, >98%), 2,2′-bipyridyl (>99%), neopentyl alcohol (NPA, >98%), and sodium iodide (NaI) (>99%) were purchased from TCI, Inc. Bis(1,5-cyclooctadiene)-nickel(0) (Ni(COD)₂), 4,4-dihydroxy biphenyl (DHBP, 97%), potassium carbonate (K₂CO₃, ACS reagent, ≥99%), NaHCO₃ (ACS reagent, >99.7%), lithium bromide (LiBr, ReagentPlus, ≥99%), dichloromethane (DCM, anhydrous, ≥99.8%), dimethylacetamide (DMAc, anhydrous, ≥99.9%), N-methylpyrrolidinone (NMP, anhydrous, ≥99.9%), pyridine (anhydrous, ≥99.8%), hexadeuteromethyl sulfoxide (DMSO-d₆), and deuterochloroform (CDCl₃) were procured from Sigma-Aldrich. DMAc (HPLC grade), hydrochloric acid (HCl, extra pure grade, and 3 N), and chloroform were procured from Duskan, Inc. Ethyl acetate (≥99.5%), ethanol, methanol, toluene, and sodium hydroxide solution (0.01 mol/L or N/100) were procured from Samchun Pure Chemicals. Nafion-NR211 was procured from Membranes. Nafion-NR211 was procured from Chemours Company FC, LLC. Sulfonated poly(arylene ether sulfone) with a degree of sulfonation of 50% (SPES50) was procured from Yanjin Co., Ltd. K₂CO₃ was dried for 24 h at 150 °C (vaccum) prior to use. Other than stated here, the reagents were used as received. Neopentyl 3,5-dichlorobenzenesulfonate (mDCBS) and neopentyl 2,5-dichlorobenzenesulfonate (pDCBS) were synthesized via a previously reported method [28].

2.2. Preparation of Sulfonated Block Copolymer Membrane

2.2.1. Synthesis of the Partially Fluorinated Hydrophobic Oligomer Poly(Arylene Ether Sulfone) Oligomer (6F-PES). The partially fluorinated hydrophobic oligomer 6F-PES containing five repeating units (X₅) was prepared according to the following procedure. 6F-BPA (1.00 g, 2.97 mmol), DCDPS (1.03 g, 3.56 mmol), and DMAc (4 mL) were added to a round-bottomed four-neck flask (100 mL) fitted with a
magnetic stirrer, a nitrogen inlet/outlet, and a condenser, which was heated at 120°C. To initiate the reaction, K₂CO₃ (0.62 g, 4.46 mmol) was added at 160°C, and the reaction was continued under nitrogen for 3–5 h while monitoring the progress of oligomerization by gel permeation chromatography (GPC). DCDPS (0.10 g, 0.36 mmol) was added to terminate the reaction while acting as an end-capping agent. After further reaction for 1 h, the temperature of the oligomer mixture was decreased to 80°C and treated with methanolic 1 M HCl twice. The resulting oligomer precipitate was rinsed with pure methanol twice, followed by drying at 80°C (vacuum) overnight to obtain the high purity of 6F-PES oligomer with X5 as a white powder (1.71 g, 95%). Following the same procedure except for using DHBP instead of 6F-BPA and different monomer ratios, the nonfluorinated hydrophobic BP-PES oligomer was formed.

2.2.2. Synthesis of the 6F Multiblock Copolymer 6F-X5Y9-(2.0). The 6F-X5Y9-(2.0) notation refers to a block copolymer composed of a hydrophobic 6F-PES block with five repeating units (X5) and a hydrophilic phenylene block with nine repeating units (Y9) having an IEC of 2.0 meq g⁻¹. This polymer was prepared according to the following procedure [27, 28, 41]: the hydrophobic X5 6F-PES oligomer (1.58 g, 0.53 mmol), mDCBS (0.79 g, 2.64 mmol), and pDCBS (0.79 g, 2.64 mmol) and NMP (10 mL) were added to a round-bottomed flask (100 mL) fitted with a mechanical stirrer, an argon inlet/outlet, and a condenser and was heated at 80°C. The clear solution of the precursor was complemented with 2,2'-bipyridyl (2.27 g, 14.54 mmol) as the additive ligand and Ni(COD)₂ (2.00 g, 7.27 mmol) as the nickel complex catalyst. The polymerization reaction was conducted under argon for 3 h. To terminate the reaction, the polymer mixture temperature was decreased to 50°C and precipitated into a methanolic 6 M HCl solution. The obtained precipitate was filtered, rinsed in methanol twice, and then dried at 80°C (vacuum) for 24 h resulting in the high purity of neopentyl-protected 6F-X5Y9-(2.0) polymer (2.48 g, 91% yield). According to the molecular ratio between oligomers and monomers precursor, the hydrophilic block length (Y) was being determined.

The deprotection process of the neopentyl-6F-X5Y9-(2.0) polymer was carried out according to the following procedure: an insulated round-bottomed four-neck flask (100 mL) fitted with a magnetic stirrer was added with the neopentyl-protected 6F-X5Y9-(2.0) polymer (2.40 g, 0.46 mmol) and DMAc (28.8 mL), and then the polymer mixture was heated at 100°C. The clear solution was added with NaI (5.00 g, 33.38 mmol) as the deprotecting agent and stirred for 24 h. The mixture was then diluted to 5 wt% with the addition of DMAc and precipitated into methanol. The obtained polymer precipitate was filtered, then rinsed with methanol twice, chloroform and methanol, and dried at 100°C (vacuum) overnight, resulting in high purity of the deprotected product in sodium form reddish-brown precipitate (1.95 g, 90%).

In an insulated vessel fitted with a magnetic bar and a thermometer, the sodium form of the 6F-X5Y9-(2.0) polymer was treated with 3 M aqueous HCl for 6 h at 80°C, and then the temperature was decreased to room-ambient temperature for 24 h. The precipitated proton form of the 6F-X5Y9-(2.0) polymer was filtered, rinsed with deionized water to neutralize the pH, and dried at 100°C (vacuum) overnight.

2.2.3. Preparation of 6F-X5Y9-(2.0) Membranes. Typically, the proton form of the 6F-X5Y9-(2.0) polymer (2.00 g) was dissolved to a concentration of 20 wt% with NMP-based solvent, and the polymer solution was spread-cast controlled using the doctor blade method on the surface of a glass plate, then dried at 70°C for overnight on a hot plate, and subsequently dried in an oven at 120°C (vacuum) for overnight. The as-obtained membrane was cooled down at room-ambient temperature, detached from the glass plate by being immersed in deionized water, and subsequently dried at room-ambient temperature. In an insulated vessel fitted with a magnetic bar and a thermometer, the membrane was treated with 3 M aqueous HCl at 80°C for 6 h and then cooled down at room-ambient temperature overnight. The membrane was then rinsed with deionized water to neutralize the pH and dried at room-ambient temperature overnight. The resulting proton form of the membrane was 25 ± 2 μm thick. The SPES50 membrane was prepared according to the same procedure [28, 53].

2.3. Characterization of the Membranes

2.3.1. Identification of the Chemical Structure. The molecular weights of the block copolymers and its precursor were analyzed using a GPC system complemented with a YL 9112 isocratic pump and a Younglin YL 9120 UV–vis detector (Young Lin Instruments). To analyze molecular weights of oligomers and polymers, Shodex SB-803HQ and ShodexKF-805L columns were used with 0.01 M aqueous LiBr as the eluent, respectively. GPC samples were filtered through a syringe filter of 0.2 μm polytetrafluoroethylene, and the obtained molecular weight was estimated using polystyrene standards. A Bruker BioSpin AVANCE III (600 MHz) spectrometer (Bruker Corp.) was used to obtain ¹H NMR spectra, while CDCl₃ (25°C) or DMSO-d₆ (80°C) was used as the solvent and with internal reference of tetramethylsilane (0.03 vol%).

The IEC of the membrane was determined using the back-titration method. The membranes (2 × 2 cm) in the proton form were treated with aqueous NaCl (5 M, 40 mL) for 48 h to exchange proton ions with sodium ions. The generated HCl from ion exchange was then quantified using a Metrohm 848 Titrino Plus titrator (Metrohm AG) by titration with a titrant of 0.01 N aqueous NaOH. The IEC was calculated using the following equation:

\[
\text{IEC} \left( \text{meq g}^{-1} \right) = \frac{\Delta V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_d} \times 100, \quad (1)
\]

where \( \Delta V_{\text{NaOH}} \) represents the volume of the NaOH solution, \( C_{\text{NaOH}} \) represents the concentration of the NaOH solution (0.01 N), and \( W_d \) represents the weight of the dried membrane.
2.3.2. Proton Conductivity. The proton conductivity ($\sigma$) of the proton form of the membrane ($1 \times 4 \text{ cm}$) was evaluated in a four-electrode conductivity cell (MCC, WonAtech) analyzed with a system made of an impedance/gain-phase analyzer Solartron 1260 and electrochemical interface Solartron 1287 at an amplitude of 100 mV and the frequency range of $10^{-3}$–$10^5$ Hz. The proton conductivity ($\sigma$) was calculated using the following equation:

$$\left( \frac{S}{\text{cm}} \right) = \frac{D}{L \times T \times R} \times 100, \quad (2)$$

where $D$ denotes the electrode distance, $L$ and $T$ are the width and thickness of the membranes, respectively, and $R$ denotes the membrane's resistance value obtained after extrapolating the Nyquist plot to the $x$-intercept. Before the test, the membrane was immersed in deionized water for 24 h at room-ambient temperature. The humidity dependent conductivity was measured at 80°C with an RH of 30%, 50%, 70%, and 90%.

2.3.3. Water Uptake and Swelling Ratio. The proton form of the membranes ($2 \times 2 \text{ cm}$) was evaluated for properties of the water uptake ($W$) and swelling ratios of in-plane ($A$) and through-plane ($T$). The membranes were immersed in deionized water for 24 h at room-ambient temperature, and membranes sample dimensions and weight were measured after the removal of excess water from the surface. The weight of the membranes before and after swelling was obtained using an EM 120-HR analytical balance (Precisa Gravimetrics AG). The humidity-dependent water vapor uptake was measured using a TGA Q5000 instrument at 80°C (30%, 50%, and 70% RH). $W$ and the $A$ and $T$ ratios were calculated as follows:

$$W\% = \frac{W_w - W_d}{W_d} \times 100,$$

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$$W\% = \frac{W_w - W_d}{W_d} \times 100, \quad (3)$$

where $W_w$ and $W_d$ denote the weights in wet and dry, $A_w$ and $A_d$ denote the total areas in wet and dry, while $T_w$ and $T_d$ represent the thickness in wet and dry states of the membranes.

2.3.4. Proton Diffusion Coefficient and Characteristic Factor. The Nernst–Einstein equation was calculated using Equation (4) to determine the proton diffusion coefficient ($D_p$) at 25°C, while Equation (5) was used to calculate the characteristic factor as follows:

$$D_p \left( \text{cm}^2/\text{s} \right) = \frac{RT}{F^2 c(H^+)} \sigma,$$

$$\phi = \frac{D_p}{f(H_2O)} \quad (4)$$

where $R$ represents the universal gas constant, $T_k$ represents the absolute temperature (K), $F$ represents the Faraday constant, and $c(H^+)$ represents the concentration of the proton charge carrier (M). The density ($\rho$) of the sulfonated multiblock copolymer membrane and SPE50 is assumed to be equal to 1.5 g cm$^{-3}$ [54, 55], while the Nafion membrane has a density of 1.99 g cm$^{-3}$ [54, 55]. Equation (6) was used to calculate the water volume fraction ($f(H_2O)$) as follows:

$$f(H_2O) = \frac{\rho_{H_2O}}{(\rho_{H_2O})/2/polymer \times 200/(W\%)} + 2/fH2O \times 100/(W\%)(%) \quad (5)$$

where $\rho_{H_2O}$ represents the density of water (25°C), $M_{H_2O}$ represents the molecular weight of water, and $W$ (%) represents the water uptake.

2.3.5. Small-Angle X-Ray Scattering (SAXS) Analysis. SAXS observation was conducted with the 3C Beamline of Pohang Light Source (PLS) II at Pohang Accelerator Laboratory. The SAXS instrument was equipped with a storage ring energy of 3.0 GeV, in-vacuum undulator 20 (IVU 20) as the synchrotron light source, DCM Si (111) crystal as the monochromator, and Rayonix 2D MAR165 as the detector (source: https://pal.postech.ac.kr/paleng/bl/3C/). The membrane samples were located at a distance of 2 m and characterized in the wet state to observe the effect of water percolation by being immersed in deionized water for 24 h prior to characterization.

2.3.6. Transmission Electron Microscopy (TEM) Analysis. Prior to characterization, the proton-form membranes were stained with lead ions using 0.5 M aqueous lead (II) acetate, rinsed with water, vacuum dried for 24 hours at room temperature, and placed in epoxy resin, sectioned using an ultramicrotome, and positioned onto copper grids.

2.3.7. Dynamic Mechanical Analysis (DMA) and Tensile Test. Before the test, the proton form of the membrane sample ($5 \times 25 \text{ mm}$) was dried in a desiccator at room-ambient temperature for 24 h. The samples were examined using the multifrequency strain mode with a 0.05 N starting force, a 10 m oscillation amplitude, and a 125.0% force track at 10 Hz. This test was conducted by varying the temperature from 30°C to 250°C at a rate of 5°C min$^{-1}$. The glass transition temperature ($T_g$) of the membrane was determined using the collected stress-temperature data on the basis of the storage modulus, loss modulus, and $\tan \delta$. An elongation test machine was used to test the tensile strength of the membranes (exclusively designed for a thin film) using a TopTac 2000 (Yeojin Corp.). The proton form of the membrane sample was cut in accordance with the JIS K 6251-7 standard into a dumbbell shape with a $35 \times 6 \text{ mm}^2$ total area and a $15 \times 2 \text{ mm}^2$ test area, and the measurement was performed at room-ambient temperature with a 10 mm min$^{-1}$ strain rate. The results were plotted as stress versus strain curves.
2.3.8. Oxidative Stability. The proton form of the membrane (2 cm × 2 cm) was subjected to an oxidative stability test under harsh conditions by immersing the membrane in Fenton’s reagent, i.e., 10% hydrogen peroxide (H₂O₂) containing 10 ppm FeSO₄ at 60°C for 2 h and under mild conditions by immersing the membrane into 3% H₂O₂ containing 3 ppm FeSO₄ at 30°C for 15 h. GPC was used to determine the subsequent changes in molecular weight.

An oxidative durability test was also conducted using an H₂O₂ exposure apparatus [56] complemented with a nitrogen inlet/outlet and a humidity/temperature controller. Nitrogen (Ultrapure, >99.99%) was used as the carrier gas. The proton form of the membrane (2 × 2 cm) was attached to a polytetrafluoroethylene rack using a thread and then exposed to a vapor mixture in the combination of deionized water and 10% aqueous H₂O₂ for 38 h. After the test, the membranes were rinsed with deionized water and dried at room-ambient temperature. The pristine membranes and membranes after being treated with H₂O₂ were measured using GPC to determine the changes in molecular weight.

2.3.9. Fuel Cell Performance. Membrane electrode assemblies (MEAs) were prepared using the solution of Na₂SO₄ as the binder and Pt/C (40 wt% Pt/C, under harsh conditions by immersing the membrane in Fenton’s reagent, i.e., 10% hydrogen peroxide (H₂O₂) containing 10 ppm FeSO₄ at 60°C for 2 h and under mild conditions by immersing the membrane into 3% H₂O₂ containing 3 ppm FeSO₄ at 30°C for 15 h. GPC was used to determine the subsequent changes in molecular weight.

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2.3.9. Fuel Cell Performance. Membrane electrode assemblies (MEAs) were prepared using the solution of Na₂SO₄ as the binder and Pt/C (40 wt% Pt/C, 0.25mg Pt cm⁻²) as the catalyst, respectively, and the catalyst layer transferred to the surface of the membrane through decal transfer. In preparation, catalyst slurries were mixed homogeneously for 12 h in a roll mill and a paste mixer for three. The molecular weight was not affected by the different structures of the PES hydrophobic oligomers, which implies that the 6F- and BP-PES oligomers exhibited similar reactivity due to the presence of the same end group. Figure S6c shows the proton NMR spectrum of the 6F-PES oligomer, as shown in Table 1. Similarly, 6F-PES and BP-PES were successfully obtained with a length (X) value of five, which we previously reported as the optimal length for a hydrophobic block [28].

3. Results and Discussion

3.1. Synthesis of the Partially Fluorinated Hydrophobic 6F-PES Block Oligomer. Figure S3a shows the GPC profile of the 6F-PES oligomer, Table S1 summarizes the molecular weight, polydispersity index (PDI), and X values (based on NMR analysis), and Figure S3b illustrates the protons assigned to the main chain in the corresponding NMR spectra. The obtained PDI of 1.8 suggests that the oligomerization was uniform. Using the GPC data and NMR spectra, the X value was determined to be five, which was in accord with the stoichiometry of the 6F-PES oligomer and with the value obtained according to the intensity ratio of the signals of the main chain to the end group in the 1H NMR spectra. Meanwhile, the GPC profile and properties of the nonfluorinated hydrophobic BP-PES block oligomer are shown in Figures S4a, S4b, and Table S2. A similar PDI of 1.7 was obtained, indicating the uniform oligomerization of the BP-PES oligomer. These results demonstrate that the hydrophobic PES blocks 6F-PES and BP-PES were successfully obtained with a length (X) value of five, which we previously reported as the optimal length for a hydrophobic block [28].

3.2. Synthesis and Characterization of the Sulfonated Multiblock Copolymer. Figure 1 shows the proton NMR spectra of the synthesized sulfonated multiblock copolymers with two different IECs. For a fair comparison, those having the same length of the hydrophobic block (X5) are shown. The feeding ratio during the synthesis determined the Y value. The 1H NMR spectra confirmed the final length of X and Y. Samples are named to indicate the X, Y, and IEC values; for instance, BP-X5Y7-(2.0) refers to a polymer with a hydrophobic BP block with five repeating units (X5), a phenylene hydrophilic block with seven repeating units (Y7), and an IEC of 2.0 meq g⁻¹. As control samples, commercially available SPES50 and a PFSA membrane of Nafion NR211 having the same thickness as the block copolymers (25 μm) were used. In addition, considering our previous finding that pure mDCBS or pDCBS for the hydrophilic block resulted in poor solubility of the final multiblock copolymers, a 1:1 mDCBS-to-pDCBS mixture was selected for the hydrophilic block.

As shown in Table 1, the 6F block copolymers exhibited a number-average molecular weight (Mn) of 20–26 kDa and a weight-averaged molecular weight (Mw) of 50–64 kDa, and the corresponding values of the BP block copolymers were 21–26 kDa and 50–70 kDa, respectively. In all cases, the synthesized polymers showed PDI values lower than three. The molecular weight was not affected by the different structures of the PES hydrophobic oligomers, which implies that the 6F- and BP-PES oligomers exhibited similar reactivity due to the presence of the same end group. Figure S5c shows the proton NMR spectrum of the 6F-PES oligomer, revealing that the a', b', c', and d' peaks were not affected by the carbon–carbon coupling reaction. Meanwhile, the two end-group peaks (e and f) shifted downfield from 7.9 and 7.6 to 8.0 and 7.8 ppm, respectively. The deprotection and proton-exchange treatment also resulted in a peak shift, confirming the successful synthesis of the desired structures. The same behavior was observed for the BP-PES oligomer, as shown in Figure S6c. The proton form of the sulfonated 6F and BP multiblock copolymers was cast on a glass plate to obtain flexible and transparent membranes with a thickness of 25 ± 2 μm. Notably, the 6F block copolymers were more soluble during the casting process than the BP block copolymers, affording more transparent solutions. The IECs of the membranes were obtained by comparing the intensity ratio of the 1H NMR signals of the hydrophobic block and the hydrophilic block (Figure 1), and the results were consistent with those obtained via back titration (Table 1).

3.3. Proton Conductivity and Water Uptake. The 6F-X5Y9-(2.0) membrane showed a proton conductivity at 25°C of 0.11 S cm⁻¹, which was identical to that of BP-X5Y7-(2.0), while the water uptake was 16% lower for the former membrane, as shown in Table 1. Similarly, 6F-X5Y11-(2.3) showed the same proton conductivity as BP-X5Y8-(2.3)
but a 10% lower water uptake. This trend could also be observed for the RH dependence of the block copolymers on the proton conductivity (Figure 2). Thus, the 6F-X5Y9-(2.0) membrane exhibited comparable proton conductivity to the Naﬁon-NR211 reference at an RH of 90% and 80°C.

Moreover, 6F-X5Y9-(2.0) outperformed BP-X5Y7-(2.0) and SPES50 in all RH conditions and was only inferior to BP-X5Y8-(2.3). Similarly, 6F-X5Y11-(2.3) outperformed BP-X5Y8-(2.3) and showed almost 30% higher proton conductivity than the Naﬁon control at 90% RH (0.13 vs. 0.09 S cm⁻¹). This result indicates that owing to the superhydrophobicity of the −CF₃ moiety, introducing a ﬂexible 6F linkage as the hydrophobic main chain moiety, maintains the proton conductivity and lowers the water uptake [45, 46, 57]. According to Harrison et al. [51], a similar trend was observed for random copolymers, in which the 6F linkage lowered the water uptake even at a higher degree of sulfonation. Liu et al. [46] also demonstrated that incorporating the 6F linkage into the polymer main chain was undoubtedly beneﬁcial and provided a simple alternative compared to ﬂuorinated biphenyl, such as 3,5-bis(trifluoromethyl)-1,1′-biphenyl. In the present study, the multiblock copolymers showed much higher conductivity than random SPES50 at the same IEC under low RH conditions.

To examine the water vapor absorption behavior of the sulfonated multiblock membranes, the water vapor uptake was analyzed at 80°C as a function of RH, as shown in Figure 3. At RH values of 30%, 50%, and 70%, the 6F block copolymers exhibited a little higher water vapor uptake than the BP copolymers at the same IECs of 2.0 and 2.3 meq g⁻¹. This result suggests that the 6F linkage contributed to the water vapor absorption as a ﬂexible hydrophobic channel, promoting the phase separation even under low RH conditions [57–59]. This would also explain the higher proton conductivity of the 6F block copolymers under low RH conditions despite their lower water uptake. According to the

### Table 1: Basic properties of selected sulfonated multiblock membranes.

<table>
<thead>
<tr>
<th>Sample-XY composition-(IEC)</th>
<th>Predicted IEC</th>
<th>Experimental IEC (meq g⁻¹)</th>
<th>Mₙ (kDa)</th>
<th>Mₘ (kDa)</th>
<th>PDI</th>
<th>WU (%) (at 25°C)</th>
<th>Swelling ratio (%) (at 25°C)</th>
<th>σ (S cm⁻¹) (at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6F-X5Y11-(2.3)</td>
<td>2.3</td>
<td>2.3</td>
<td>2.3</td>
<td>25.9</td>
<td>2.9</td>
<td>70</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>6F-X5Y9-(2.0)</td>
<td>2.0</td>
<td>1.9</td>
<td>1.9</td>
<td>20.3</td>
<td>2.1</td>
<td>60</td>
<td>26</td>
<td>28</td>
</tr>
<tr>
<td>BP-X5Y8-(2.3)</td>
<td>2.3</td>
<td>2.3</td>
<td>2.3</td>
<td>26.1</td>
<td>2.7</td>
<td>80</td>
<td>33</td>
<td>30</td>
</tr>
<tr>
<td>BP-X5Y7-(2.0)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>21.2</td>
<td>2.4</td>
<td>76</td>
<td>31</td>
<td>29</td>
</tr>
<tr>
<td>SPES50-(2.0)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>59.2</td>
<td>3.6</td>
<td>61</td>
<td>50</td>
<td>35</td>
</tr>
</tbody>
</table>

*Note: Naﬁon~0.9 represents Naﬁon with an IEC of 0.9 meq g⁻¹.*

**Figure 1:** ¹H FT-NMR spectra of the sulfonated multiblock membrane copolymer in DMSO-d₆ (80°C, 600 MHz).
dimensional swelling ratios shown in Figure S7, the sulfonated block copolymers exhibited anisotropic swelling ratios. This behavior was previously reported for multiblock copolymers [19], which showed higher through-plane than in-plane swelling [16, 24, 60]. The same phenomenon was observed for 6F-X5Y9-(2.0), with a through-plane and in-plane swelling of 28% and 26%, respectively, which is favorable for fuel cell applications. In contrast, the in-plane swelling of the random copolymer SPES50 was higher than the through-plane swelling.

3.4. Proton Diffusion Coefficient and Characteristic Factor as a Function of RH. To further disclose the proton transport behavior of the sulfonated multiblock copolymers, $D_\sigma$ and $\Phi$ were calculated as a function of RH using Equations (4) and (5), respectively (Figures 4 and 5). $D_\sigma$ describes the proton diffusion in terms of the concentration of charge carriers (protons), and $\Phi$ is defined as the ratio between the proton conductivity to the water volume fraction and is an indicator of the overall membrane performance. 6F-X5Y9-(2.0) and 6F-X5Y11-(2.3) showed higher $D_\sigma$ values than the BP block copolymer membranes having the same IEC under all RH conditions, indicating that the proton diffusion was more efficient for the fluorinated membranes. This is consistent with the flexible 6F linkage promoting the phase separation [45]. Further discussion is provided in the section "SAXS analysis of the polymer morphology."

In addition, the practical performance of the membranes can be assessed in terms of the $\Phi$ parameter because a higher conductivity with a lower water uptake is desirable for the performance and stability of the membranes. Figure 5 shows that the 6F block copolymers exhibited higher $\Phi$ values than the BP derivatives at IEC values of 2.0 and 2.3 meq g$^{-1}$, which indicates that the former copolymers are more effective in utilizing the absorbed water volume fraction per sulfonic acid for proton conduction. This behavior may be due to a more clustered hydrophilic domain originating from the flexibility and superhydrophobicity of the 6F linkage. Nevertheless, the $\Phi$ value of the sulfonated block copolymers was still highly dependent on RH, which should be solved to compete with the PFSA membrane.

3.5. SAXS Analysis of the Polymer Morphology. The SAXS patterns shown in Figure 6 revealed an interesting result. For the same IEC, the BP polymers showed a broader intensity distribution. In other words, the BP block copolymers showed higher intensities at a higher scattering vector ($q$) than the 6F block copolymers but similar intensities at lower $q$. This means that the fluorinated polymers experienced a steep decrease in $Iq^2$/(INV) with increasing $q$, which is
strong evidence for the existence of a distinct interface between hydrophilic and hydrophobic blocks [45]. These results demonstrate that the 6F block copolymers exhibited a well-developed phase separation, whereas the BP block copolymers and SPES50 exhibit limited and poor phase separation, respectively, since both polymers share the same hydrophobic moieties as hydrophobic structures.

As shown in Table 2, the $d$-spacing was calculated for the sulfonated block copolymer membranes and Na$_x$ion-NR-211. It should be noted that the random structure of SPES50 prevented the observation of the corresponding peak. For the same IEC values, the 6F block copolymers exhibited a smaller cluster size than the BP block copolymers, and Na$_x$ion-NR211 showed the smallest $d$-spacing. This result suggests that the 6F linkage acts as an interstitial supramolecular defect that promotes polymer phase separation, thereby increasing the polymer's flexibility and decreasing its strength [61–64].

3.6. TEM Analysis of the Polymer Morphology. Representative transmission electron microscopy (TEM) images of sulfonated block copolymers are provided in Figure S8. White areas represent the hydrophobic domains, while the lead-stained hydrophilic domains are depicted as black areas. The 6F polymer, with an ion exchange capacity (IEC) of 2.0 meq g$^{-1}$, exhibits distinct and clustered phase separation, with interconnected black channel areas observed as the hydrophilic domain. In contrast, the BP polymer with IEC values of 2.0 and 2.3 meq g$^{-1}$ displays less

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Table 2: Value of calculated $d$-spacing of sulfonated multiblock membranes at 25°C.

<table>
<thead>
<tr>
<th>Sample-XY composition–(IEC)</th>
<th>$d$-spacing (nm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_x$ion</td>
<td>5.69</td>
</tr>
<tr>
<td>6F-X5Y11-(2.3)</td>
<td>8.47</td>
</tr>
<tr>
<td>6F-X5Y9-(2.0)</td>
<td>7.33</td>
</tr>
<tr>
<td>BP-X5Y8-(2.3)</td>
<td>8.83</td>
</tr>
<tr>
<td>BP-X5Y7-(2.0)</td>
<td>7.46</td>
</tr>
</tbody>
</table>

Table 3: Mechanical properties of the sulfonated multiblock membranes at 25°C.

<table>
<thead>
<tr>
<th>Sample-XY composition–(IEC)</th>
<th>Maximum stress (MPa)</th>
<th>Maximum strain (%)</th>
<th>Young's modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6F-X5Y11-(2.3)</td>
<td>30.5</td>
<td>13.1</td>
<td>1.4</td>
</tr>
<tr>
<td>6F-X5Y9-(2.0)</td>
<td>24.3</td>
<td>11.5</td>
<td>1.3</td>
</tr>
<tr>
<td>BP-X5Y8-(2.3)</td>
<td>37.8</td>
<td>8.7</td>
<td>1.4</td>
</tr>
<tr>
<td>BP-X5Y7-(2.0)</td>
<td>34.4</td>
<td>15.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 5: Characteristic factor ($\Phi$) of the sulfonated multiblock membranes as a function of the RH.

Figure 6: Normalized intensity, $I_q^2/(INV)$ vs. scattering vector ($q$) plots for the investigated membranes in the wet state.

Figure 7: Extent of degradation (%Mw) of the sulfonated multiblock membranes after Fenton’s test under harsh conditions.

This result suggests that the 6F linkage acts as an interstitial supramolecular defect that promotes polymer phase separation, thereby increasing the polymer’s flexibility and decreasing its strength [61–64].
distinctive phase separation, with smaller and scattered hydrophilic domains. These observations suggest that the 6F polymer possesses superior phase separation morphology between hydrophilic and hydrophobic domains compared to the BP polymer, in agreement with small-angle X-ray scattering (SAXS) results. This finding can be attributed to the flexibility and superhydrophobicity properties of the 6F linkage, which promote enhanced phase separation.

3.7. Thermomechanical Analysis. DMA was used to assess the thermomechanical properties of the sulfonated block copolymers. The storage modulus (E'), loss modulus (E''), and tan δ (E''/E') were investigated to observe the effect of introducing the 6F linkage (Figure S9). The Tg values of the 6F block copolymers, the BP block copolymers, and SPES50 were 243°C, 289°C–295°C, and 294°C, respectively. The lower Tg of the fluorinated polymers is indicative of their enhanced flexibility caused by the fluorine moiety, which is consistent with the smaller d-spacing (Table 2) and with previous reports [46, 47, 65]. Despite the decrease in the Tg of the 6F block copolymers, this value is still relatively high. In fact, it is not a bad result, considering the increase in proton conductivity. This result is in accord with the SAXS analysis, indicating that the flexible 6F structure would be more sensitive to water uptake than the BP block copolymers. When sulfonated polymers absorb water, the water molecules can function as a plasticizer of the polymer matrix [9, 66–68]. The absorbed water molecules tend to aggregate into clusters, which results in the wet polymers exhibiting a Bragg pattern. Owing to their lower Tg, the flexible 6F block copolymers are more rubbery and form clusters more easily than the BP block copolymers. Figure S10 shows the strain–stress curves and Table 3 summarizes the mechanical properties of the sulfonated multiblock membranes at ambient-room temperature. According to these results, the 6F block copolymers were more flexible, with lower Young's modulus and maximum stress than the BP block copolymers. This result indicates that the 6F linkage could increase the average molecular mobility in the polymeric membrane by decreasing the load-bearing carbon content from the polymeric main chain [14, 61, 69, 70], thereby lowering Young's modulus and strength of the polymer, that is, in agreement with the morphology and DMA observations.

3.8. Oxidative Stability Evaluation. Figures 7 and S11 show the extent of degradation of the multiblock copolymer membranes after performing Fenton's test under both harsh and mild conditions. The 6F block copolymers showed better oxidative stability than the BP block copolymers under both conditions. For example, 6F-X5Y9-(2.0) showed an extent of degradation of 26%, whereas that of BP-X5Y7-(2.0) was 32% (Figure 7). The same trend was observed for an IEC value of 2.3 meq g−1, with 6F-X5Y11-(2.3) showing almost 20% lower degradation than BP-X5Y8-(2.3). Meanwhile, the commercial SPES50 membrane having an IEC of 2.0 meq g−1 showed almost 90% degradation. Under mild conditions, Fenton's test revealed that the 6F block copolymers were more stable than the BP derivatives, as shown in Figure S11. Both types of block copolymers showed less than 10% degradation for IECs of 2.0 and 2.3 meq g−1.

Other methods of membrane degradation were also explored to mimic real fuel cell conditions. Thus, the results obtained after exposure to H2O2 (Figure S12) matched those of Fenton's test, showing the higher stability of the 6F block copolymers. This can be explained in terms of the lower water uptake of the 6F block copolymers compared with their BP counterparts, as presented in Table 1. Specifically, the lower water uptake can suppress the diffusion of peroxide in the polymer matrix, thereby reducing membrane degradation. Lawrence et al. observed a similar behavior for random copolymers upon introducing the 6F linkage [50] while having lower water absorption [51] as described.
above. Furthermore, the 6F linkage acts as a strong electron- withdrawing group in the phenyl ring, thus reducing the electron density of the arylene ether structure to protect the backbone from oxidative attack [50, 71, 72].

3.9. MEA Performance Test. The 6F and BP block copolymer membranes with an IEC of 2.0 meq g$^{-1}$ and a thickness of 25 μm, i.e., 6F-X5Y9-(2.0) and BP-X5Y7-(2.0), were selected for the evaluation of the MEA fuel performance because they showed the most balanced results in terms of conductivity and mechanical properties. Figure 8 displays the cell performance at 80°C at 100% and 50% RH. At 100% RH, 6F-X5Y9-(2.0) delivered the highest current density of 1.6 A cm$^{-2}$ at 0.6 V (hydrogen/air), outperforming the Nafion-NR211 reference (1.4 A cm$^{-2}$ under the same conditions). 6F-X5Y9-(2.0) and Nafion-NR211 showed almost the same high-frequency resistance (HFR) value of ca. 45 mΩ cm$^{-2}$. Meanwhile, BP-X5Y7-(2.0) showed the lowest current density of 1.2 A cm$^{-2}$. Similarly, at 50% RH, 6F-X5Y9-(2.0) delivered a current density of 1.3 A cm$^{-2}$ at 0.6 V (hydrogen/air) and an HFR value of 73 mΩ cm$^{-2}$, which exceeded those of Nafion (1.1 A cm$^{-2}$ and 96 mΩ cm$^{-2}$, respectively). Moreover, BP-X5Y7-(2.0) showed the lowest current density of 0.8 A cm$^{-2}$ and an HFR of 124 mΩ cm$^{-2}$. The effect of IEC was compared for the BP block copolymers, as shown in Figure S13. The BP copolymer with an IEC of 2.3 meq g$^{-1}$ showed a performance comparable to that of Nafion-NR211 and 6F-X5Y9-(2.0), which implied that higher IEC values are required for the BP block copolymers to compete with the 6F block copolymers. The results are in accord with the high value of the 6F block copolymers. Taken together, the results demonstrate that the 6F block copolymer with an IEC of 2.0 meq g$^{-1}$ can compete with Nafion in terms of MEA performance, which renders it a strong candidate for PEMFCs.

4. Conclusions

Partially fluorinated sulfonated 6F multiblock membranes showed enhanced proton conductivity, oxidative stability, and fuel cell performance compared with the nonfluorinated derivatives. The proton conductivity of 6F-X5Y9-(2.0) exceeds that of the commercial PFSA membrane Nafion-NR211 at 100% at 80°C with a value of 0.10 and 0.09 S cm$^{-1}$, respectively. Furthermore, 6F-X5Y9-(2.0) demonstrates the enhanced proton diffusion coefficient and characteristic factor superior to nonfluorinated BP multiblock membranes with IEC 2.0 and 2.3 meq g$^{-1}$. However, further enhancement of the water uptake and conductivity at low RH is required. UTM and DMA analyses revealed that the structural flexibility lowered the mechanical properties and $T_g$. This study highlights the importance of incorporating fluorinated moiety as the hydrophobic molecular structure and the relevance of the molecular design in polymer structure flexibility, which is essential to be considered to enhance the electrochemical performance of PEMs. Future work to develop a flexible structure for both hydrophobic and hydrophilic blocks with consideration for improving the flexibility of proton transport in polymeric membranes containing rigid hydrophilic phenylene would be highly desirable, e.g., a hydrophilic phenylene with a flexible and oxidatively stable sulfonated side chain.

Data Availability

The data supporting this study’s findings are available from the corresponding author upon reasonable request.

Additional Points

The description of experimental details and additional characterization data is shown; figures show NMR of monomer precursor, oligomer, and polymer; figures and tables show GPC data of monomer, oligomer, and polymer; the figure shows in-plane and through-plane swelling ratio; TEM images; DMA curves; strain–stress curves; extent of degradation after Fenton’s test under mild condition and after hydrogen peroxide exposure test and cell performance.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors’ Contributions

Farid Wijaya contributed to the conceptualization, methodology, synthesis and characterization, sample preparation, validation, formal analysis, investigation, and writing—original manuscript. Seunghee Woo, Minji Chon, and Hyerin Lee were responsible for the MEA performance test. Hyejin Lee was assigned to the methodology. Jonghak Kim and Hansung Kim were tasked with the review and supervision. Su yeon Kim contributed to the synthesis. Dongwon Shin was responsible for the conceptualization, methodology, and resources. Byungchan Bae was responsible for the conceptualization, methodology, writing—review and editing, supervision, and project administration. All authors have given approval to the final version of the manuscript.

Acknowledgments

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Supplementary Materials

$^{1}$H NMR spectra of mDCBS; $^{1}$H NMR spectra of pDCBS; GPC graph of the hydrophobic 6F-PES oligomer; Table S1: summarizing the molecular weight properties of the hydrophobic 6F-PES oligomer; GPC graph of the hydrophobic 6F-PES oligomer; Scheme of the synthesis of the hydrophobic 6F-PES oligomer; Table S2: listing the molecular weight properties of the hydrophobic BP-PES oligomer; $^{1}$H NMR
spectra of the hydrophobic BP-PES oligomer; scheme of the synthesis of the hydrophobic BP-PES oligomer precursor; GPC graph of the 6F polymer; Table S4: summarizing the molecular weight properties of the 6F polymer; scheme of the synthesis of the 6F polymer; \(^{1}H\) NMR spectra of the hydrophobic 6F polymer; dimensional swelling of sulfonated block copolymer membranes; (a) in-plane (b) through-plane swelling ratios; TEM images of sulfonated block copolymer membranes (∼300 magnification); extent of degradation (%Mw) of the sulfonated multiblock copolymer membranes after Fenton’s test under mild conditions; extent of degradation (%Mw) of the sulfonated multiblock copolymer membranes after \(\text{H}_2\text{O}_2\) exposure test; cell performances of 6F-X5Y9-(2.0), BP-X5Y7-(2.0), BP-X5Y8-(2.3), and Na\text{fli} membrane at 80°C (H\text{fli}/air, 1 atm, no back pressure) and (a) 100% RH and (b) 50% RH. (Supplementary Materials)

References


