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Synthesis and Characterization of Highly Fluorinated Cross-linked Aromatic Polyethers for Polymer Electrolytes

Kwan-Soo Lee,[†] Myung-Hwan Jeong, Jung-Pil Lee, Young-Jea Kim, and Jae-Suk Lee*

Department of Nanobio Materials and Electronics and School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 1 Oryong-dong, Buk-gu, Gwangju 500-712, Republic of Korea. [†]Current address: Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

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New series of ethynyl-terminated sulfonated-fluorinated poly(arylene ether)s (ESF-6Fs) were synthesized via nucleophilic aromatic substitution reaction (SNAr) from potassium 2,5-dihydroxybenzenesulfonate (SHQ), 4,4′-(hexafluoroisopropylidene)diphenol (6FBPA), and decafluorobiphenyl (DFBP), followed by the reaction with 3-ethynylphenol. The cross-linked ESF-6F membranes exhibited high glass-transition temperatures in the range of 258−276 °C and good thermal degradation temperatures in the range of 308−328 °C. To optimize the proton conductivity and water uptake of the cross-linked ESF-6F membranes, various volume-related parameters (length-scaled parameters) were introduced. Using those parameters, the proton conductivity and water uptake of the cross-linked ESF-6F membranes were compared with sulfonated poly(arylene ether sulfone) random copolymer (BPSH), Nafion membrane, and another cross-linked membrane. In addition, the proton conductivity of optimized ESF-6F membrane was observed as a function of relative humidity (RH) at 80 °C and compared with other membranes. Excellent proton conductivity was observed at the percent conducting volume (PCV) (0.39, ESF90-6F) corresponding to the maximum volume-based ion exchange capacity in the hydrate state ($\mathrm{IECv}_{(\mathrm{wet})}$) and the atomic force microscopy (AFM) image showed good ionic channels at that point. Also, for the direct methanol fuel cell (DMFC) application, the cross-linked ESF-6F membranes exhibited lower methanol crossover ($11 \times 10^{-8}-103 \times 10^{-8}$ cm^2/s) and higher selectivities ($130 \times 10^3-492 \times 10^3$ s Ω^{-1} cm^{-3}) than those of Nafion 117 (167×10^{-8} cm^2/s and 55×10^3 s Ω^{-1} cm^{-3}).

Introduction

Economic and environmental issues facing global society are forcing industry to explore renewable energy sources for vehicles and electronic power devices. The concept of hydrogen economy was introduced, which is an energy system based on hydrogen for energy storage, distribution, and utilization. Polymer electrolyte fuel cells (PEFCs) (including hydrogen (PEMFCs) and direct methanol fuel cells (DMFCs)) have attracted a great deal of interest, because of their potential applications as the alternative clean energy source in wide various applications for transport, stationary, and portable devices.[1,2] Currently, the most common perfluorinated sulfonic acid (PFSA) ionomers such as Nafion, Flemion, Aciplex, and Dow membranes, which have excellent proton conductivity, good mechanical and chemical properties, and long-term durability, are commercially used. However, these ionomers not only limit the fuel cell operating temperature to the glass-transition temperature (ca. 110 °C), which leads to decrease proton conductivity and mechanical property, but also have high fuel crossover. Furthermore, their high cost and difficult synthesis procedure are critical drawbacks for commercial applications.[3−6]

These problems of PFSA ionomers have stimulated many efforts in the development of alternative hydrocarbon-based polymer electrolyte membranes (PEMs) such as poly(arylene ether)s,[7−13] polyimides,[14−16] poly(*p*-phenylene)s,[17] and

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*Author to whom correspondence should be addressed. Tel.: +82-62-970-2306. Fax: +82-62-970-2304. E-mail: jslee@gist.ac.kr.

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polybenzimidazoles.[18,19] Although many membrane materials as PEMs have been developed, the performance for PEFCs is still not satisfactory for practical applications. One of the major challenges of hydrocarbon-based PEMs is to increase the ion exchange capacity (IEC) of PEMs for better fuel cell performance. In general, most established structure—property relationships of PEMs show that the proton conductivity and water uptake of membranes increase as the IEC (or degree of sulfonation (DS)) increases. However, the high IEC of PEMs has caused excessively high water uptake with the durability problem of PEMs. Furthermore, it decreased the proton conductivity of the membrane, because of the dilution effect between the charges of sulfonated groups.[20,21] This dilution effect not only weakens the dimensional stability and durability of PEMs but it also induces problems of the membrane electrode assembly (MEA) preparation processing, such as cracking during hot pressing and delamination between the membrane and the electrode during acidification. Many researchers have studied attempts to reduce the water uptake with the increased IEC value of PEMs.[22−27] There are several modifications for reducing the water uptake, such as the introduction of fluorine components and polar functional groups (i.e., nitrile(CN) and phosphine oxide (PO)) in the polymer structures,[22] rigid backbone structure in polymer matrix,[23,24] blend (or mixing) system of inorganic materials with the polymer electrolyte,[25] pore-filling type structure,[26] and ionically or covalently cross-linking system of PEMs.[27]

Consequently, optimization of the proton conductivity and controllability of the water uptake is needed for better fuel cell performance and durability of PEMs. In addition, their structure—property relationship using the volume-related parameter, which represents ion concentration and the equivalent volume, and the proton-transporting ability of hydrophilic domains of the hydrated PEMs should be studied for better evaluation and comparison between the PEMs, because the electrochemical properties occur under operating conditions related to the volume of the PEM, regardless of the weight of the PEM and transporting of protons taking place in the hydrophilic phase region of the hydrated membrane. Recently, few reports presented the density, volume-based ion exchange capacity (IECv), and volume-based water uptake (WUv) of PEMs and explained their tendency between the sulfonated polymers using the volume-related parameters.[21,22,28] These reports have discussed that the volume-related parameters are regarded as a more appropriate criteria for the comparison between the sulfonated polymers than the weight-related parameters. In addition, when the weight-related parameters are used for the comparison between the polymer electrolytes, it might be very difficult to compare not only between the structurally modified and the original polymer electrolyte, but also between aromatic-based and aliphatic-based polymer electrolyte. For example, in our previous report, the cross-linked and noncross-linked ESF-BPs having the same IECw value showed different proton conductivity values.[21] The proton conductivity of cross-linked ESF90-BP is 110 mS/cm, while that of noncross-linked ESF90-BP could not be measured (expected data from calculation, 24 mS/cm), because of extremely high water uptake and swelling. The comparison between aromatic main-chain polymers such as BPSHs, 6Fs (6F bisphenol-based poly(arylene ether sulfone)s), sPEEKs (sulfonated polyetheretherketones), and etc., and aliphatic main-chain polymers such as Nafion, Dow membrane, sulfonated polystyene, and etc., could be open to misinterpretation about the real contents of sulfonated group and water in the polymer electrolyte under fuel cell operation, because of their different densities. In a very recent review, Kim and Pivovar have suggested new types of volume-related parameters which can be used to compare the proton conductivity among different polymer electrolytes.[29] Introduction of new volume-related parameters, which are the molar volume per charge (MVC) and percent conducting volume (PCV), has offered an easy explanation and comparison of proton conductivities among various types of sulfonated polymer electrolytes and the estimation of how many protons can transport through the PEM having the same active area and thickness from the anode to the cathode during fuel cell operation.

In this study, we present the synthesis and characterization of new ethynyl-terminated sulfonated poly(arylene ether) copolymers containing high fluorine components (ESF-6Fs; End-group cross-linkable Sulfonated Fluorinated 6F-bisphenol-based copolymers, abbreviated as ESFx-6F, where x is the degree of sulfonation (DS)) with the aim of achieving high proton conductivity and low water uptake of cross-linked ESF-6F membranes. For the cross-linked ESF-6F membranes to meet the above demands, cross-linkable moiety (ethynyl group) and fluorine components (decafluorobiphenyl and CF_3 groups) are introduced into the polymer structure, which induced the increase of thermal stability and chemical resistance and the

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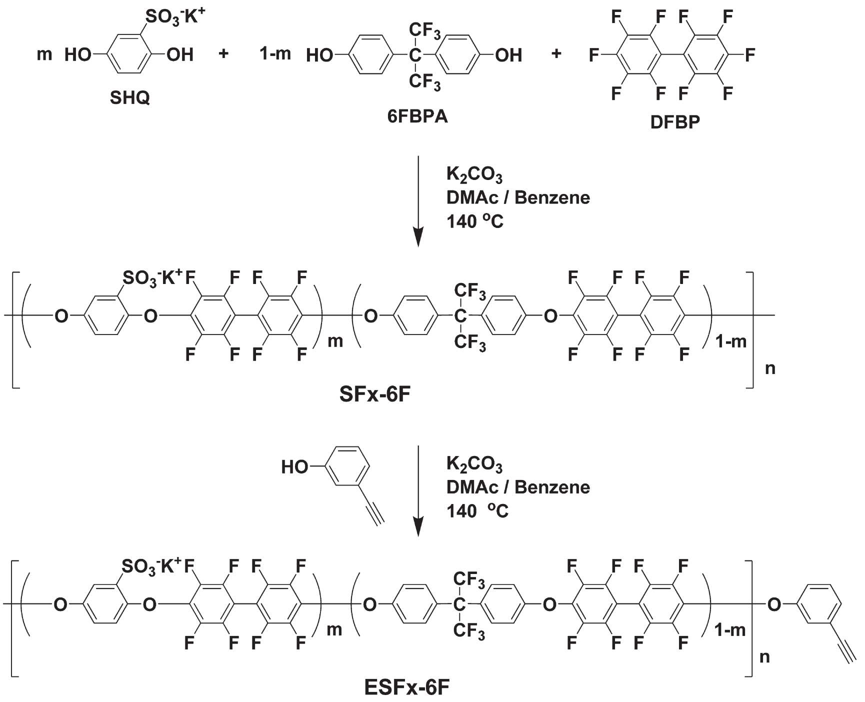
Scheme 1. Synthesis and Chemical Structure of ESF*x*-6Fs



decrease of the methanol permeability.[15,21,30] In addition, to evaluate and optimize proton conductivity and water uptake, the cross-linked ESF-6F membranes are investigated using various volume-related parameters (length-scaled parameters) such as density, IECv, WUv, molar volume per charge in the hydrated state (MVC$_{(wet)}$), and PCV, and are compared with the BPSHs as a representative for random copolymers, the state-of-the-art Nafion membranes, and another cross-linked membranes prepared from biphenol-based monomer structures (ESF-BPs) and 6H-bisphenol-based monomer structures (ESF-6Hs).

Experimental Section

Materials. Potassium 2,5-dihydroxybenzenesulfonate (SHQ), 4,4′-bis(4-hydroxyphenyl)hexafluoropropane (6FBPA) and potassium carbonate were purchased from Aldrich Chemical Co. and used after vacuum drying at 100 °C for 2 days. Benzene and *N,N*-dimethylacetamide (DMAc) were purchased from Aldrich Chemical Co. and used without further purification. Decafluorobiphenyl (DFBP) was purchased from Fluorochem, Ltd., and used without purification. 3-Ethynylphenol was purchased from Alfa Aesar Co.

Polymer Synthesis. Highly fluorinated and cross-linkable ESF-6F random copolymers were synthesized via direct sulfonation polymerization of the SHQ and 6FBPA with DFBP, followed by the reaction with 3-ethynylphenol (Scheme 1). The DS of polymers was precisely controlled, by changing the feed ratio of two dihydroxy monomers: sulfonated monomer (SHQ) and nonsulfonated monomer (6FBPA). One typical copolymerization for an ESF-6F series will be described using ESF90-6F (where 90 is the DS for the polymer) as follows. SHQ (18.0 mmol, 4.11 g) and 6FBPA (2.0 mmol, 0.67 g) were dissolved in a mixture of DMAc (40 mL) and benzene (20 mL) with K_2CO_3 (3.40 g, 1.15 equiv of dihydroxy monomer). The reaction mixture was in a 250-mL two-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and Dean–Stark trap and heated to 140 °C for 5 h to ensure complete dehydration. Benzene was used as an azeotropic agent to remove the water produced in the system. After removing benzene completely, the reaction mixture was stirred at this temperature for an additional period of 2 h. A solution of DFBP (6.70 g, 1.002 eq. of dihydroxy monomers) in DMAc (20 mL) was added and reacted for an additional 12 h. A mixture of 3-ethynylphenol (0.40 g, 0.17 equiv of dihydroxy monomer), DMAc (10 mL), and benzene (10 mL) then was added to the reaction mixture for end-capping and the reaction was continued for 3 h. The reaction mixture was cooled to room temperature and filtered to remove the salt and then precipitated into 1 L of ethanol/water (9.8:0.2). The precipitated polymer was filtered and washed with ethanol. The brown solid was dried under vacuum (60 °C) for 3 days.

Membrane Preparation. The noncross-linked ESF-6F copolymers (K^+ form) were cast from a 30% (w/v) DMAc solution onto clean glass substrates. The polymer solutions were filtered to remove particulates using a 1-μm Teflon syringe filter prior to casting. The removal of DMAc was accomplished in an oven at 50 °C in an inert (N_2) environment over 3 h. Thermal cross-linking of ESF-6Fs was subsequently performed on a hot plate at 250 °C. The degree of cross-linking was controlled by varying cross-linking times.[21,30] The salt form membranes were acidified by boiling in a 0.5 M sulfuric acid (H_2SO_4) solution for 2 h, followed by treatment with boiling deionized water for 2 h.[31] All acidified membranes were stored at room temperature in deionized water for at least 1 day before testing.

Characterization and Measurements. *Nuclear Magnetic Resonance* (*NMR*) *Spectroscopy*. ^{1}H and ^{19}F NMR spectra were obtained on a JEOL Model JNM-LA 300 WB Fourier transform–nuclear magnetic resonance (FT-NMR) system with DMSO-d_6 as a solvent and tetramethylsilane (TMS) and fluorinated trichlorofluoromethane as internal and external references, respectively. The molecular weights of ESF*x*-6F were determined

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by the ratio of end groups to aromatic groups in the polymer, as determined from relative ^{1}H NMR signals.[32]

Fourier Transform Infrared (*FT-IR*) *Spectroscopy*. Fourier transform infrared (FT-IR) spectroscopy was utilized to confirm the functional groups of synthesized polymers. Measurements were conducted on a Jasco Model FT/IR-400 Plus system, using thin solution-cast polymer films.

Inherent Viscosity Determinations. Inherent viscosity (η_{inh}) values of potassium-form ESFx-6F were measured at 25 °C in DMAc, using an Ubbelohde viscometer that was thermostatically controlled in a water bath. The thermal properties of polymers were determined with a TA Instrument 2100 series system.

Thermal Analysis. Glass-transition temperature (T_g) values of ESF-6Fs were measured in the range of 40−300 °C at a heating rate of 10 °C/min in N_2 gas. Thermal degradation temperature (T_d, 5% weight loss) values were measured in the range of 40−800 °C at a heating rate of 10 °C/min in air. The temperatures at which a 5% weight loss was observed and the percentages of char remaining were recorded as an evaluation of thermal stability.

Atomic Force Miscroscope (*AFM*). AFM images were obtained from a Nanoscope IIIa (Digital Instruments Inc., Santa Barbara, CA). Super Sharp Silicon tapping mode with a cantilever resonance frequency (ca. 330 kHz) was used (NanoSensors, Wetzlar-Blankenfeld, Germany). A nominal radius of curvature (ca. 2 nm.) was used for the tip of the cantilever. Scan rates of 0.5 Hz were used. All treated samples were allowed to equilibrate by exposure to 100% relative humidity (RH) at room temperature for at least for 24 h before testing. Surface phase images of the samples then were obtained immediately, under ambient conditions.

Measurement of Gel Fraction. Gel fraction of the cross-linked membranes was measured by solvent extraction. Several pieces of cross-linked membranes of ~1.0 g were extracted by Soxhlet extractor using *N*,*N*-dimethylacetamide (DMAc) as the extraction solvent at room temperature. The membranes were place in an excess of DMAc, and the solvent was replaced for 24 h until no further extractable polymer could be detected. The extracted samples were dried until constant weight. The gel fractions were calculated as follows:

$$\text{gel fraction (\%)} = \frac{W_2}{W_1} \times 100$$

where W_1 is the weight of the sample before extraction and W_2 is the weight of the dried sample after extraction.

Density of Membrane. The membrane density was measured using 3 cm × 3 cm membranes in acid form. The membranes were prepared after acidification and washing under boiling conditions. Before measurement, the prepared membranes were dried using a vacuum plate at 80 °C for 2 h. The density of each membrane was measured at least five times, to ensure data reproducibility.

Water Uptake (*WU*). Weight-based water uptake (WUw) was determined on all membranes in acid form. After boiling acid-form membranes in deionized water for 2 h, the membranes were immersed in deionized water at room temperature for 1 day. The membranes then were weighed for WUw measurement after the removal of surface water. The acid-form membranes were dried at 80 °C under vacuum to a constant weight that was recorded. The WUw was calculated from the difference between the wet membrane weight (W_{wet}) and the dry membrane weight (W_{dry}), divided by the dry membrane weight W_{dry}, and converted to a percentage:

$$\text{WUw (wt \%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

Volume-based water uptake (WUv) was estimated using the densities of water (δ_W) and the dry membrane (δ_M), assuming no free-volume effects (experimental errors associated with measuring actual membrane volumes under dry and wet conditions were likely no worse than the estimates applied here):

$$\text{WUv (vol \%)} = \frac{(W_{wet} - W_{dry})/\delta_W}{(W_{dry}/\delta_M)} \times 100$$

Ion Exchange Capacity (*IEC*). Multiple ion exchange capacities (IEC, IECv, and IECv$_{(WET)}$) were calculated using titration and other physical properties. IEC measurement of membranes was performed using titration methods. The acid-form membranes were immersed in a large excess of 0.1 M NaCl solution for 24 h. The remaining liquid was titrated with 0.1 M NaOH solution, using phenolphthalein as an indicator. IEC, expressed in terms of mequivalents of ($-SO_3H$) per gram of dry polymer (denoted as mequiv ($-SO_3H$)/g of dry polymer), was obtained by the consumed NaOH and the weight of dried membrane. Volume-based IEC (IECv) was obtained by multiplying the (mass-based) IEC value by the (dry) membrane density. Membrane density was calculated from dimension measurements and weight after drying at 80 °C for 2 h. The volume-based IEC for a fully hydrated membrane (IECv$_{(WET)}$)) was calculated using the following equation:[22]

$$\text{IECv}_{(wet)} = \frac{\text{IECv}}{1 + 0.01\text{WUv(vol \%)}} \times 100$$

Hydrated Molar Volume per Charge (*MVC*$_{(wet)}$). The fully hydrated molar volume per charge (MVC$_{(wet)}$) was calculated from van der Waals volume increments of composing atoms or structural groups of sulfonated polymers and membrane water uptake, which is given by[29,33]

$$\text{MVC}_{(wet)} = \sum_i n_i V_i + 18\lambda$$

Here, V_i is the volumetric contribution of the ith structural group which appears n_i times per charge and λ is the number of water molecules per charge; the value 18 represents the molar volume of water (in units of cm^3/mol).

Percent Conducting Volume (*PCV*). Percent conducting volume (PCV), which is the ratio of volume water uptake to acid volume concentration, was calculated using the following equation:[29]

$$\text{PCV} = \frac{18\lambda}{\text{MVC}_{(wet)}}$$

Recently, Kim and Pivovar[29] suggested this equation for the better comparison of proton conductivity among the sulfonated polymers in a fully hydrated state of polymer electrolyte membranes.

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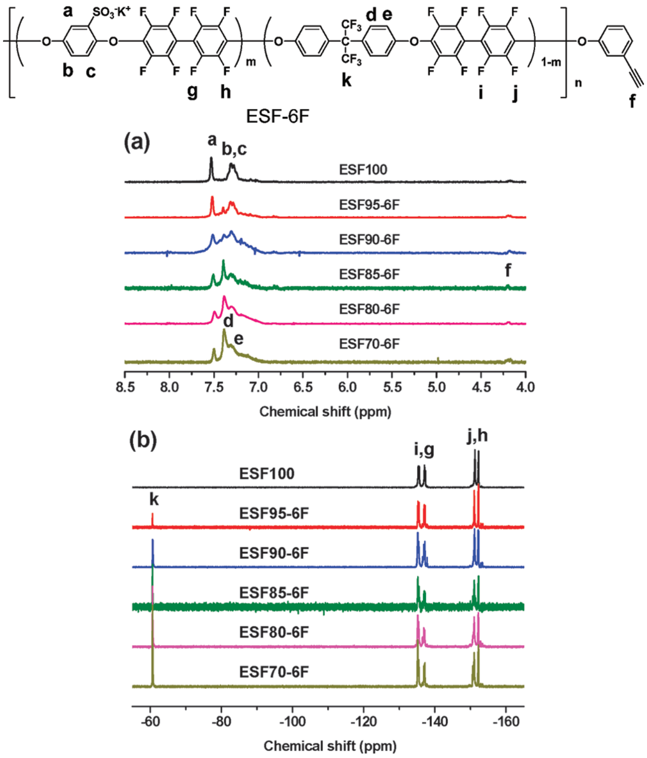

Figure 1. Nuclear magnetic resonance ((a) ^{1}H NMR and (b) ^{19}F NMR) spectra of ESF-6Fs.[30]

Methanol Permeability. The methanol permeability of the membranes was determined using a diffusion cell, using previous methods and equations.[30] The diffusion cell consisted of two separated reservoirs (150 mL), and the membrane was placed between two reservoirs. The methanol permeability was observed using 2 M methanol/water solution at 25 °C. The methanol concentration in deionized water compartment is monitored with time using a refractive index detector (RI750F, Younglin Instrument Co., Korea) through 1-mm-diameter silicon tube at a constant speed of 1.0 mL/min, driven by a Masterflex pump. The output signal was converted by a data module (Autochro, Younglin Instrument Co., Korea) and recorded by a personal computer.

Proton Conductivity. Proton conductivity was estimated from the electrochemical impedance spectroscopy (Solatron 1280Z) at 30 °C and measured as a change in relative humidity (RH) at 80 °C, using an Espec Model SH-240 environmental chamber. Before measuring proton conductivity, prepared membranes were equilibrated with deionized water for 24 h. The proton conductivity was calculated from the following equation:

$$\sigma = \frac{L}{RS}$$

where σ is the proton conductivity (expressed in units of S/cm or Ω^{-1} cm^{-1}), L the distance between two electrodes used (in centimeters), R the resistance of the membrane (in ohms (Ω)), and S the cross-sectional surface area of the membrane sample (given in square centimeters). The cross-sectional surface area was measured fully hydrated. The impedance of each sample was measured at least five times, to ensure data reproducibility.

Results and Discussion

Polymer Synthesis. ESF-6F copolymers with DS values of 70%−100% were synthesized via direct copolymerization from SHQ, 6FBPA, and DFBP, followed by a reaction with 3-ethynylphenol as a cross-linkable end-group. The molecular weights of the prepared copolymers were controlled using the reaction time, the temperature, and the molar feed ratio of monomers.[21,30,34]

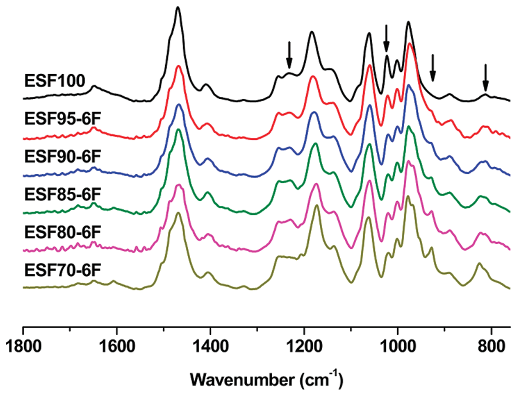

Figure 2. Fourier transform infrared (FT-IR) spectra of cross-linked ESF-6F membranes.

The polymer structures and functional groups of ESF-6Fs were characterized by ^{1}H NMR, ^{19}F NMR, and FT-IT spectra. The ^{1}H NMR spectra of ESF-BP (Figure 1a), as a function of sulfonation level, showed clear trends in their peaks near 7.51 ppm, corresponding to the prevalence of the SHQ moiety, compared to the 6FBPA moeity. For example, the peak at 7.51 ppm became much more pronounced at high sulfonation level (higher SHQ content). On the other hand, the peaks centered at 7.39 ppm (peak "d") (corresponding to the 6FBPA moiety) decreased with increasing DS (reduced 6FBPA content). The subpeak at 4.2 ppm was due to the ethynyl moiety and was used for molecular weight determination. The ^{19}F NMR spectra of ESF-6Fs were dominated by peaks centered at −60.64 ppm, corresponding to the 6FBPA moiety, and at −135.30, −136.91, −150.86, and −152.20 ppm, corresponding to two *ortho* and two *meta* F atoms of DFBP moiety, respectively (identified in Figure 1b). The fluorine peak at the *para* position of DFBP expected at −146.82 ppm was not observed, confirming complete nucleophilic aromatic substitution. These ESF-6F copolymers were soluble in aprotic polar solvents such as DMAc, DMSO, NMP, and DMF, allowing processing into membranes and confirming no side reaction during the polymerization. The FT-IR spectrum of ESF-6Fs (see Figure 2) was normalized using the absorption of the Ar−O−Ar (benzene ring−ether−benzene ring) linkage at 1003 cm^{-1} in the polymer backbone. The obvious increase in intensity of the symmetric and asymmetric stretching peaks of sulfonate (SO_3) moieties was observed at 1023 and 1233 cm^{-1}, as the DS increased. This phenomenon provides proof of the successful incorporation between the dihydroxy monomer and the sulfonated dihydroxy monomer. The aromatic C−H out of plane (OOP) peak of *para* substitution of benzene ring (1,4-disubstitution) was observed at 815 cm^{-1} without any overlapped peaks. The FT-IR spectra of ESF-6F showed that the decrease in

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Table 1. Properties of the ESF-6F Copolymers

sample[a]	Weight-Based Ionic Exchange Capacity, IECw (mequiv/g) calcd	obsd	inherent viscosity, η_{inh} (dL/g)	molecular weight, M_n	gel fraction (%)	Glass-Transition Temperature, T_g (°C)[b] non-cross-linked	cross-linked	thermal degradation temperature, T_d (°C)[b]
ESF95-6F	1.93	1.93	0.83	16700	96.2	158	258	308
ESF90-6F	1.80	1.79	1.51	22800	97.2	155	276	310
ESF85-6F	1.68	1.68	1.44	21800	99.3	151	272	313
ESF80-6F	1.56	1.55	1.34	19500	97.8	148	270	320
ESF70-6F	1.33	1.32	1.14	18800	96.4	146	260	328

[a] η_{inh} and M_n were measured in the salt form of the non-cross-linked ESF-6F copolymers. [b] T_g and T_d values were obtained from the H^+ form of cross-linked ESF-6F membranes.

intensity of the aliphatic fluoroakylated peak ($-CF_3$ peak) was observed at 928 cm^{-1} with increasing DS as a sufficient evidence. (See Figure 2.)

The molecular weight (M_n) of the ESF-6F copolymers was measured by end-group analysis from the relative ^1H NMR integrals of the proton in the ethynyl end-groups, and the aromatic resonances and inherent viscosity (η_{inh}) determinations were determined using an Ubbelohde viscometer with a thermostatically controlled water bath, as described in the literature.[21,32] As shown in Table 1, the η_{inh} and M_n values of the ESF-6F copolymers were in the range of 0.83−1.51 dL/g and 16700−22800 g/mol, respectively.

Gel Fractions. The cross-linking density (the degree of cross-linking) of cross-linkable polymers affect various important factors for PEM properties, such as water uptake, dimensional changes, fuel permeability, and chemical and mechanical stability. Our group has tried to determine the degree of cross-linking of the end-group and side-group cross-linkable copolymers using differential scanning calorimetry (DSC) analysis through the calculation using the heat flow,[21] the effect on the various properties of changing the cross-linking time,[30] and the gel fraction measurement of controlled cross-linkable moiety using the different cross-linkable monomer feed ratios for the polymerization.[35] In this study, the measurement of gel fractions of the cross-linked membranes was used for evaluating the degree of cross-linking of membranes. The measured gel fractions of the cross-linked membranes are given in Table 1, which shows gel fractions in the range of 96.2%−99.3%. These results support the previous results which were the heat flow calculation obtained from DSC analysis.[21] In addition, those indicate that the cross-linking of end-group of copolymers is a more effective way than that of copolymers that have short cross-linkable side-groups, while controllability of the degree of cross-linking is still more difficult than that of the side-group cross-linkable polymer.

Thermal Properties. Thermal stabilities of the cross-linked ESF-6F membranes in acid form were investigated using thermogravimetry (TG) and DSC analysis. The thermal degradation temperature (T_d) and glass-transition temperature (T_g) values of the cross-linked ESF-6F membranes are listed in Table 1. The T_g values of non-cross-linked ESF-6F membranes were also observed, for comparison with the cross-linked membranes (see Figure 3a). In general, the T_g values of sulfonated copolymers increase as DS increases, because of the increase of intermolecular interactions and the bulkiness of the sulfonic acid groups.[36] As shown in Figure 3, the T_g values of non-cross-linked ESF-6F membranes increase as DS increases, while the T_g values of cross-linked membranes do not exhibit the same trend, because of the differing molecular weights between the cross-links (M_c), which may be affected by various polymer properties (such as gel fraction, inherent viscosity (η_{inh}), molecular weight (M_n), controllability of membrane fabrication procedure, etc.) of each polymer membrane. The T_g values of non-cross-linked and

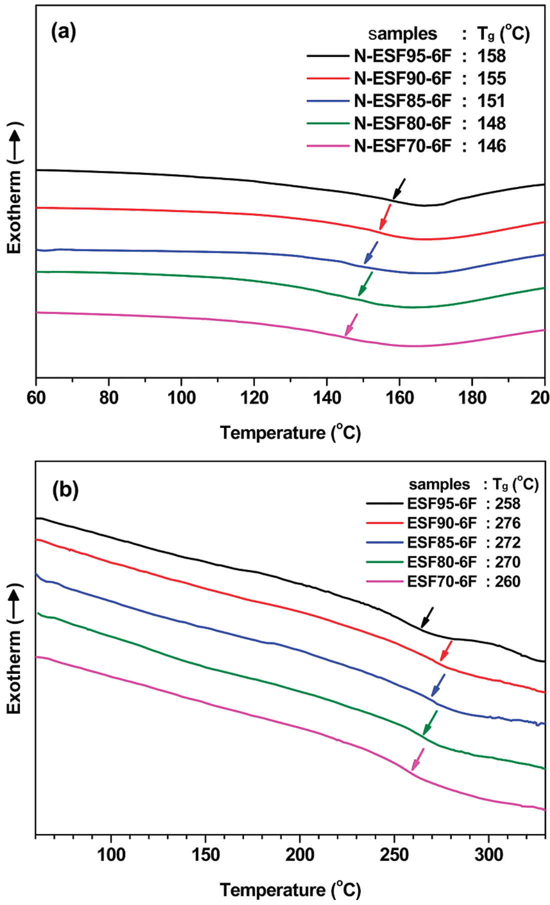

Figure 3. Differential scanning calorimetry (DSC) curves of (a) non-cross-linked and (b) cross-linked ESF-6F membranes.

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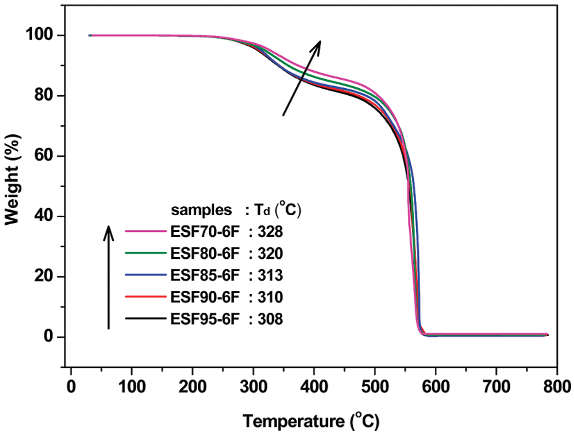

Figure 4. Thermogravimetry (TG) analysis of cross-linked ESF-6F membranes.

cross-linked ESF-6F membranes are in the ranges of 146−158 and 258−276 °C, respectively, allowing these membranes, especially cross-linked ESF-6F membranes, to be used for the high-temperature PEFC applications.

The T_d values at 5% weight loss of the cross-linked ESF-6F membranes observed under air conditions, in the range of 308−328 °C, are shown in Figure 4. To remove the absorbed water, the TGA measurement was performed after drying at 150 °C for 1 h. As shown in Figure 4, a two-step degradation procedure is clearly observed for all cross-linked ESF-6F membranes in their acid form, indicating the decomposition of sulfonic acid groups and polymer backbone at ~300 and ~500 °C, respectively. The initial weight loss temperature occurred between 250 °C and 420 °C, which is related to the degradation of sulfonic acid groups and the bound state of water hydrogen bonded with the sulfonic acid groups in the membranes.[37] The weight loss increased as the DS increased. The second weight loss step, at ~500−600 °C, is related to the degradation of the main polymer chain.

Ion Exchange Capacity (IEC). Table 2 displays the various IEC values, water uptake (WU), proton conductivity, molar volume per charge at fully hydrated state (MVC$_{(\mathrm{wet})}$), percent conducting volume (PCV) of cross-linked ESF-6Fs (compared to that of BPSH (biphenol-based sulfonated poly(arylene ether sulfone))), ESF-BPs, and Nafion. Generally, the aromatic backbone based sulfonated polymers show the percolation threshold, which is the point at which a sudden increase is exhibited as the IECw of the polymers increases, and the inflection point at high IECv$_{(\mathrm{wet})}$, where a percolation threshold is reached and substantially increased water uptake results in decreased IECv$_{(\mathrm{wet})}$ (and where polymer has the highest ion concentration in the hydrated state).[22]

As shown in Figure 5, cross-linked ESF-6Fs and ESF-BPs exhibit a trend similar to that of the BPSH-type polymer. The cross-linked ESF-6Fs and ESF-BPs have even higher IECv$_{(\mathrm{wet})}$ values than that of BPSH series polymer, because of cross-linking and a fluorination effect, which give rise to low water uptake and high density of the polymers. Figure 6 displays the volume-based water uptake (WUv) of the non-cross-linked ESF70-6F and ESF70-BP, cross-linked ESF-6Fs and ESF-BPs, BPSH, 6Fs, and Nafion membranes, as a function of the IECv$_{(\mathrm{wet})}$.[29,38] Representative hydrocarbon sulfonated polymer, BPSH series, has a much lower IECv$_{(\mathrm{wet})}$ value at the inflection point, compared to fluorine-containing sulfonated polymers such as 6Fs, Nafion, ESF-6Fs, and ESF-BPs. Moreover, ESF-6Fs and ESF-BPs show higher IECv$_{(\mathrm{wet})}$ values at the inflection point, compared to 6Fs and Nafion. This is due to the fluorine components and cross-linked components in the polymer structure, which induces the low water uptake and high density of the polymers. The IECv$_{(\mathrm{wet})}$ values of cross-linked ESF-6Fs and ESF-BPs were also compared with those of non-cross-linked polymers (N-ESF70-6F and N-ESF70-BP) in Figure 6. Dramatic changes in the IECv$_{(\mathrm{wet})}$ value were observed after cross-linking. This cross-linking affects the increase of the IECv$_{(\mathrm{wet})}$ value from 1.37 and 1.36 mequiv/cm^3 to 1.62 and 1.67 mequiv/cm^3 for ESF70-6F and ESF70-BP, respectively. These cross-linked membranes exhibit even higher IECv$_{(\mathrm{wet})}$ values than those of hydrocarbon membranes and even with the Nafion membranes, which have a high density (~2.00 g/cm^3). The cross-linked ESF-6F membranes show higher IECv$_{(\mathrm{wet})}$ values at DS $>$ 85%, compared to the cross-linked ESF-BP membranes at the same DS value, which may be due to the structural difference between the biphenol-based polymer (ESF-BP) and bisphenol-based polymer (ESF-6F). As the nonsulfonated dihydroxy monomer (6FBPA) ratio for the synthesis of ESF-6F copolymers increases (decreasing the DS of ESF-6F copolymers), the amorphous property of 6FBPA not only accentuates the flexibility but also decreases the crystallinity of ESF-6F copolymers. These results support that the chemical cross-linking system with high fluorine contents produces the high ion concentration per volume of the membrane in the hydrated state. These cross-linking and fluorine effects are discussed in detail later in this work.

Proton Conductivity. The most important transport property for the fuel cell application is proton conductivity of the polymer electrolyte. Figures 7 and 8 show the proton conductivity as a function of IECw, IECv$_{(\mathrm{wet})}$, MVC$_{(\mathrm{wet})}$, and PCV of cross-linked ESF-6Fs and ESF-BPs, BPSHs, and Nafion membranes under fully hydrated conditions at ambient temperature. The proton conductivity of cross-linked ESF-6Fs exhibits similar values, compared to that of the cross-linked ESF-BPs, even with the low water uptake at the same DS (Table 2 and Figure 5a) and increases as IECw increases. However, unlike the relationship between the proton conductivity and the IECw, for the case of IECv$_{(\mathrm{wet})}$, the maximum point was observed with the increase of proton conductivity. The maximum IECv$_{(\mathrm{wet})}$ value of ESF-6Fs was observed at DS = 90% and results from the cross-linking and the high fluorine contents, compared to BPSHs, and cross-linked ESF-BPs. This represents an optimum condition with the high ion concentration at the point for fuel cell performance. The cross-linked

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Table 2. Effect of Degree of Sulfonation on Density, IEC, Water Uptake, Hydration Number (λ), Proton Conductivity, $MVC_{(wet)}$, and PCV

sample[a]	density (g/cm^3)	IECw (mequiv/g)	$IECv_{(dry)}$ ($mequiv/cm^3$)	$IECv_{(wet)}$ ($mequiv/cm^3$)	WUw (wt %)	WUv (vol %)	λ[b] (H_2O/SO_3H)	conductivity (mS/cm)	$MVC_{(wet)}$	PCV
ESF70-6F	1.52	1.32	2.01	1.62	16	24	6.7	54	567	0.21
ESF80-6F	1.56	1.55	2.41	1.72	26	41	9.3	77	546	0.31
ESF85-6F	1.58	1.68	2.65	1.78	31	49	10.2	100	534	0.35
ESF90-6F	1.61	1.79	2.89	1.79	38	61	11.8	111	537	0.39
ESF95-6F	1.65	1.93	3.18	1.29	89	147	25.6	133	764	0.60
ESF70-BP	1.50	1.45	2.18	1.67	20	30	7.7	53	552	0.25
ESF80-BP	1.54	1.66	2.56	1.75	30	46	10.1	74	541	0.34
ESF85-BP	1.56	1.76	2.75	1.76	36	56	11.4	94	541	0.38
ESF90-BP	1.60	1.86	2.98	1.76	43	69	12.9	110	549	0.42
ESF95-BP	1.65	1.96	3.23	1.26	95	157	26.9	131	783	0.62
N-ESF70-6F	1.50	1.32	1.98	1.37	30	45	12.6	58	673	0.34
N-ESF80-6F	1.53	1.55	2.37	1.02	86	132	30.9	91	934	0.60
N-ESF70-BP	1.48	1.45	2.14	1.36	39	58	14.9	64	683	0.39
N-ESF80-BP	1.51	1.66	2.50	0.91	116	175	38.9	82	1060	0.66
BPSH20	1.22	0.92	1.12	0.93	17	21	10.2	16	1000	0.18
BPSH25	1.26	1.11	1.40	1.09	23	29	11.5	23	869	0.24
BPSH30	1.30	1.34	1.74	1.24	31	40	12.9	40	790	0.29
BPSH35	1.34	1.54	2.06	1.34	40	54	14.4	72	743	0.35
BPSH40	1.38	1.72	2.37	1.30	60	83	19.4	104	778	0.45
BPSH45	1.41	1.92	2.74	1.15	98	138	28.4	140	897	0.57
Nafion 117	1.98	0.91	1.80	1.21	25	50	15.3	91	799	0.34
Nafion 212	1.97	0.98	1.93	1.28	26	51	14.7	100	742	0.36

[a] Data of ESF-BPs are taken from ref 21; data of the BPSH series are taken from ref 22. N-ESF-6Fs and N-ESF-BPs membranes are noncross-linked membranes. [b] Hydration number is the number of water molecules per sulfonic acid group: $\lambda = H_2O/SO_3H$.

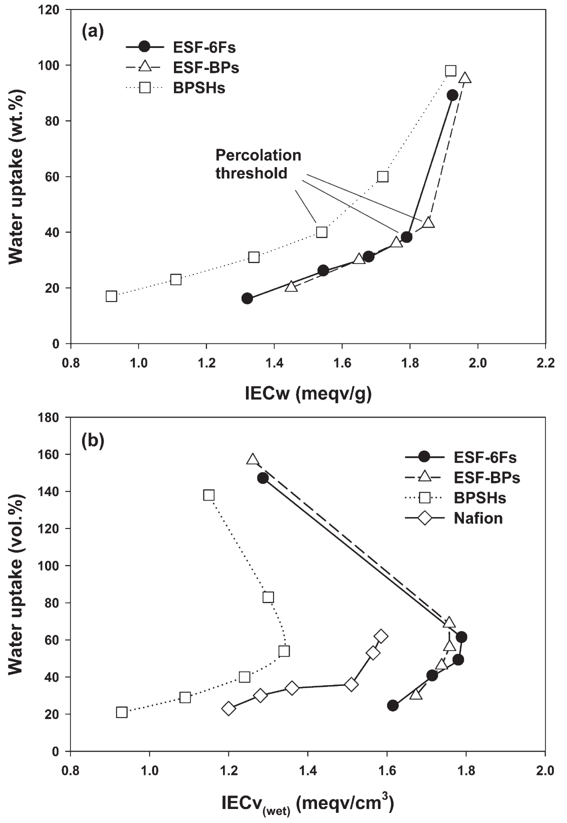

Figure 5. Comparison of the water uptake, using (a) weight-based IEC (IECw) and (b) fully hydrated, volume-based IEC ($IECv_{(wet)}$).[29]

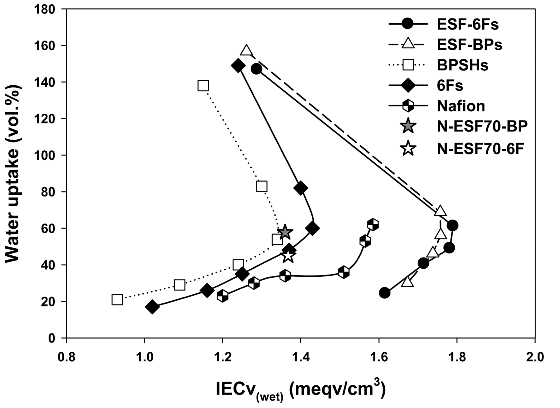

Figure 6. Effect of fluorine and cross-linking on membrane water uptake (WU), as a function of $IECv_{(wet)}$.[29]

ESF90-6F membrane at the maximum $IECv_{(wet)}$ had excellent proton conductivity (111 mS/cm), which was higher than that of Nafion membranes (91 mS/cm for Nafion 117 and 100 mS/cm for Nafion 212). Figure 8a shows the proton conductivity as a function of the $MVC_{(wet)}$ value. It not only gives good information about the relationship between the molar volume and proton conductivity of the polymer per sulfonic acid group, but it also has the inverse effect of $IECv_{(wet)}$. The $MVC_{(wet)}$ of cross-linked ESF-6Fs and ESF-BPs showed a low equivalent molar volume ($MVC_{(wet)}$) of ~550 cm^3/mol, compared with that of BPSHs and Nafion membranes (~750 cm^3/mol), which indicates a high ion concentration in the fully hydrated state. The $MVC_{(wet)}$ of cross-linked ESF-6F membranes especially has a slightly lower value at DS = 85%, 90%, and 95% and a higher value at DS = 70% and 80%, compared to cross-linked ESF-BP membranes at the same DS value. This may result from the complex effect of fluorine content, hydration number, and their nature of monomer components (6FBPA for ESF-6F and BP for ESF-BP). Cross-linked ESF-6Fs have generally higher fluorine contents and a lower hydration number (water molecule number per sulfonic acid) than cross-linked ESF-BPs, even at the low IECw value. These two factors give a more practical effect on $MVC_{(wet)}$ at

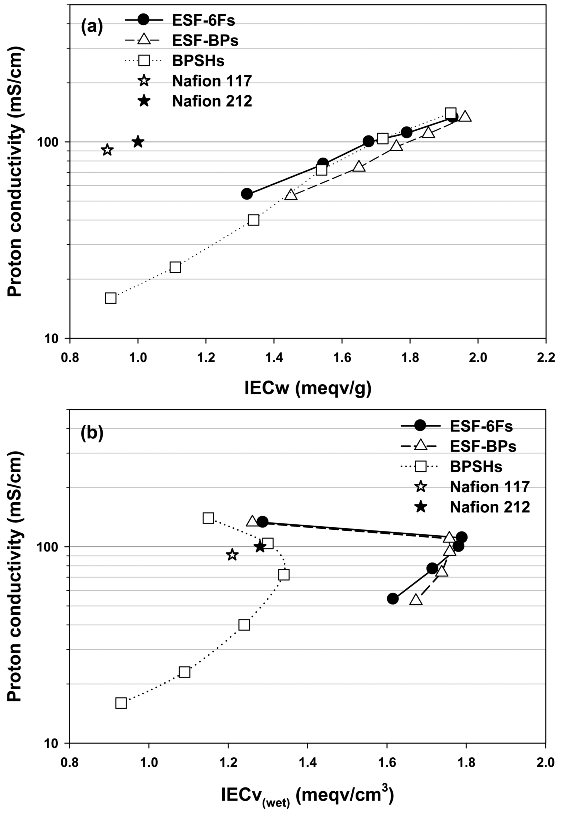

Figure 7. Comparison of proton conductivity versus (a) weight-based IEC (IECw), fully hydrated, and (b) volume-based IEC ($IECv_{(wet)}$) of ESF-6Fs, ESF-BPs, BPSHs, Nafion 117, and Nafion 212 under fully hydrated conditions at ambient temperature.[22]

DS = 85%, 90%, and 95% for both ESF-6Fs and ESF-BPs. However, they show different phenomena at DS = 70% and 80%, because of the nature of monomer components. The 6FBPA monomer shows the amorphous property (each angle between the carbons at the centered quaternary carbon is ~109°), which induces mobility of the free volume of the polymer, while the BP monomer shows the crystalline property (the angle between two benzenes is 180°) and the aromaticity (complete delocalization of the π-electrons), which induce the $\pi-\pi$ stacking between the benzene rings of the intermolecules (and/or intramolecules). Consequently, with increasing 6FBPA moiety (decreasing the DS of ESF-6F), the amorphous property of 6FBPA in the ESF-6F membrane gradually increases the free volume with increases in the molar volume of the ESF-6Fs, whereas with increasing BP moiety (decreasing the DS of ESF-BP), the crystalline property of BP in the ESF-BP membrane gradually increases the $\pi-\pi$ stacking between the benzene rings as the molar volume of the ESF-BPs decreases. This relative effect of two monomers in the each polymer structure results in the slightly higher $MVC_{(wet)}$ of ESF-6Fs than that of ESF-BPs at DS = 70% and 80%. For the definite effect of this fluorine component on the $MVC_{(wet)}$ value, a comparison between cross-linked ESF-6Fs and ESF-6Hs (the 6HBPA-based polymer structure; see Figure S1 in the Supporting Information) was investigated. Unlike the ESF-BP polymer, these two polymers have almost the same contour length of the polymer structure and similar MVC, which means that these polymers have similar molar volumes in the dry state (see Table S1 in the Supporting Information). As shown in Figure Figure S2 in the Supporting Information, cross-linked ESF-6Fs exhibit higher $MVC_{(wet)}$ than ESF-6Hs at the same DS value, indicating higher proton conductivity and ion concentration in the fully hydrated state.

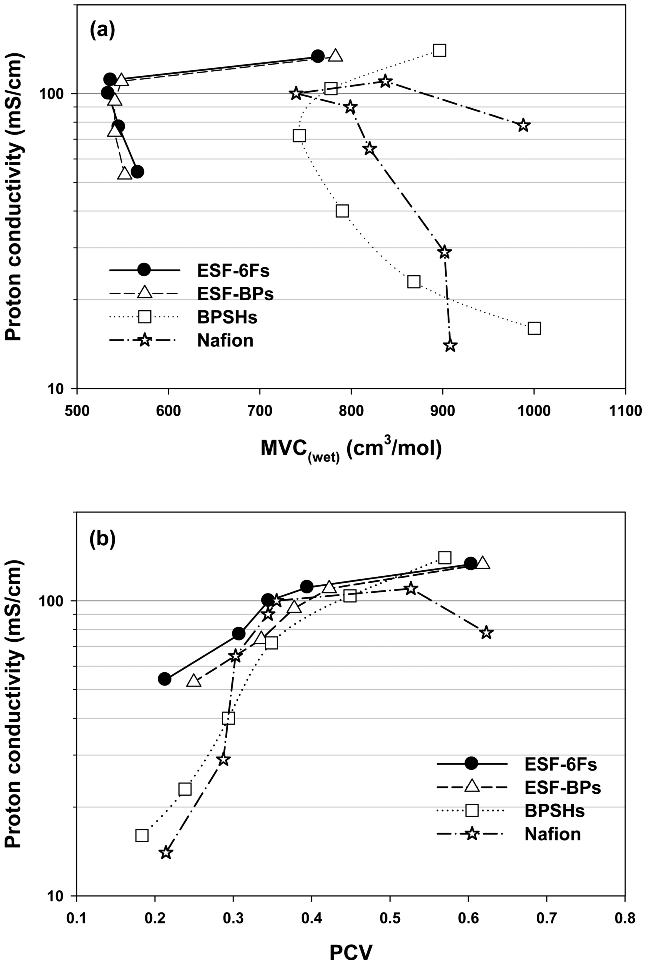

Figure 8. Proton conductivity as a function of (a) $MVC_{(wet)}$ and (b) PCV of ESF-6Fs, ESF-BPs, BPSHs, and Nafion membranes under fully hydrated conditions at ambient temperature.[29]

PCV was introduced to compare the proton conductivity of cross-linked ESF-6Fs with different polymer electrolytes, such as BPSHs and Nafion membranes (see Figure 8b).[29] PCV represents the total water volume per equivalent volume and per sulfonic acid group (or total water volume per hydrated volume of charges). In other words, it may indicate the number or the volume of waters that one sulfonic acid group possesses at the given equivalent volume. The proton conductivity at the given PCV could be also be interpreted as the power and ability of one sulfonic acid of the sulfonated polymer electrolyte membrane. As shown in Figure 8b and Figure S2b in the Supporting Information, the proton conductivities of cross-linked ESF-6Fs, presented as a function of the PCV (especially at PCV values under 0.4), exhibited mostly higher values than those of cross-linked ESF-BPs and ESF-6Hs, BPSHs, and Nafion membranes at the same PCV. It means that cross-linking and fluorination of the membrane result in a better effect on the proton conduction of PEMs that have a smaller amount of hydrophilic phase, relative to the hydrated membrane (lower value of PCV). ESF90-6F especially showed higher proton conductivity than those of BPSHs and ESF-BPs and a similar value, compared to Nafion membranes, at the same PCV.

To evaluate the proton conductivity of cross-linked ESF-6Fs at low relative humidity (RH) and high temperature, the proton conductivity of cross-linked ESF90-6F and ESF90-BP, BPSH35, and Nafion 212 with the lowest $MVC_{(wet)}$ of each polymer was observed as a function of RH at 80 °C. As shown in Figure 9, cross-linked ESF90-6F shows a higher proton conductivity from 95% RH to 70% RH, compared with other membranes. However, with further decrease of the RH, the proton conductivity of cross-linked ESF-6F is lower than that of Nafion 212. Cross-linked ESF90-BP exhibited a slightly lower proton conductivity, compared to the cross-linked ESF90-6F. Among observed membranes, the conductivity of BPSH35 was more dependent on RH than that of other membranes.

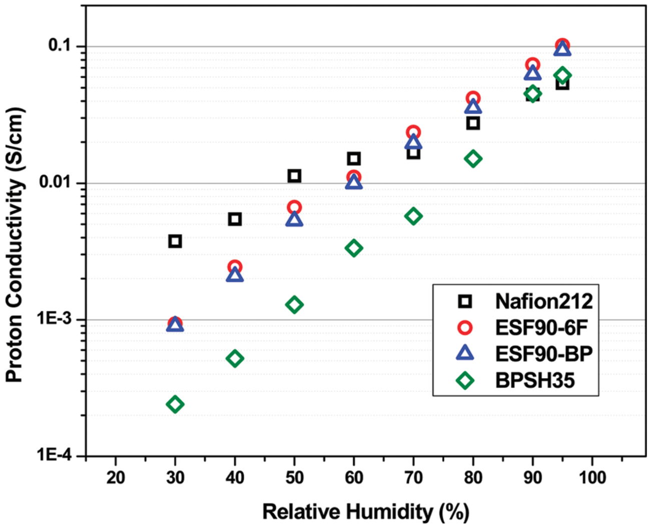

Figure 9. Proton conductivity as a function of relative humidity (RH) at 80 °C.

Methanol Permeability and Selectivity. Polymer electrolyte membranes for DMFC application must have both high proton conductivity and low methanol permeability. The combined two properties usually represent as a selectivity, which is defined as the ratio of proton conductivity to methanol permeability. Selectivity is often used to evaluate the potential performance of polymer electrolyte membrane for DMFC.[28,35] Figure 10 presents the proton conductivity, methanol permeability, and selectivity of cross-linked ESF-6Fs as a graph and compares the values to those of Nafion 117. The proton conductivity of cross-linked ESF-6Fs is in the range of 54−133 mS/cm, which is 59%−146% of that of Naion 117. In addition, cross-linked ESF-6Fs exhibited lower methanol permeability (11×10^{-8}−103×10^{-8} cm^2/s) than that of Nafion 117 (167×10^{-8} cm^2/s) (see Table 3). The proton conductivity and the methanol permeability of cross-linked ESF-6Fs resulted in good selectivity as a polymer electrolyte membrane for DMFC. The selectivity of cross-linked ESF-6Fs increases as DS decreases. The cross-linked ESF-6F membranes exhibit selectivities in the range from 130×10^3 s Ω^{-1} cm^{-3} to 492×10^3 s Ω^{-1} cm^{-3}. As listed in Table 3, the relative selectivity of ESF-6Fs is ~2.4−9.0 times higher than the selectivity of Nafion 117. Especially, the low methanol permeability of cross-linked ESF70-6F induces the high relative selectivity (~9.0 times greater than that of Nafion 117), while the high methanol permeability of cross-linked ESF95-6F gives rise to low selectivity among cross-linked ESF-6F membranes (see Figure 10). As shown in Table 3, the methanol permeability, selectivity, and relative selectivity of ESF-6Fs and N-ESF-6Fs are displayed with those of representative hydrocarbon-based BPSH membranes. After cross-linking, the membranes exhibits a selectivity that is ~2 times higher than that of non-cross-linked membranes at the same DS value. In addition, the cross-linked ESF-6F membranes exhibit a higher selectivity (or relative selectivity) than that of BPSH membranes. For example, the selectivity (or relative selectivity) of ESF80-6F and ESF85-6F membranes is > 2 times higher, compared to that of BPSH35 and BPSH40 at the similar proton conductivity and WUv (vol %). Furthermore, even N-ESF-6F membranes exhibit good selectivity, compared to that of the BPSH membranes and Nafion 117. These results demonstrate that both fluorine components of DFBP and CF_3 moieties and cross-linking system of the membrane have an effect on the methanol permeability and

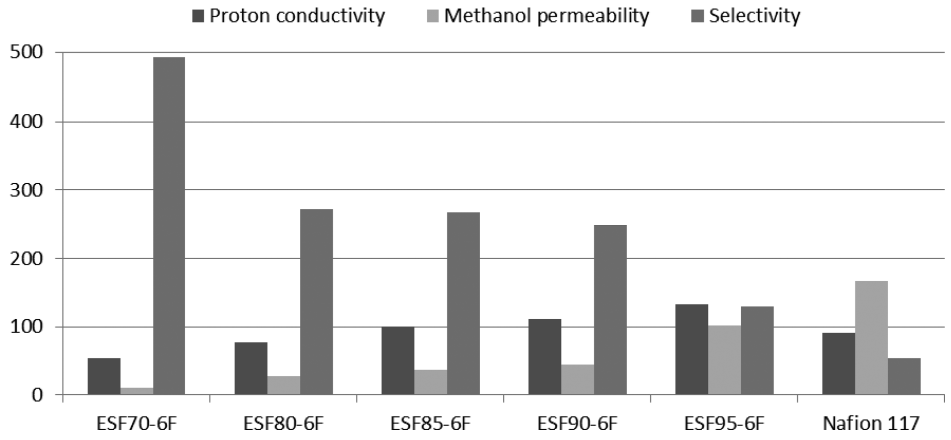

Figure 10. Proton conductivity (expressed in terms of mS/cm), methanol permeability (expressed in units of 10^{-8} cm^2/s), and selectivity (expressed in units of 10^3 s Ω^{-1} cm^{-3}) of ESF-6Fs.

Table 3. Effect of Degree of Sulfonation on Methanol Permeability and Selectivity

sample[a]	IECw (mequiv/g)	IECv$_{(wet)}$ (mequiv/cm^3)	WUv (vol %)	conductivity (mS/cm)	methanol permeability ($\times 10^{-8}$ cm^2/s)	selectivity ($\times 10^3$ s Ω^{-1} cm^{-3})[b]	relative selectivity[c]
ESF70-6F	1.32	1.62	24	54	11	492	9.0
ESF80-6F	1.55	1.72	41	77	28	271	5.0
ESF85-6F	1.68	1.78	49	100	37	267	4.9
ESF90-6F	1.79	1.79	61	111	45	249	4.6
ESF95-6F	1.93	1.29	147	133	103	130	2.4
N-ESF70-6F	1.32	1.37	45	58	25	232	4.3
N-ESF80-6F	1.55	1.02	132	91	62	147	2.7
BPSH20	0.92	0.93	21	16	22	73	1.3
BPSH30	1.34	1.24	29	40	36	111	2.0
BPSH35	1.54	1.34	40	72	56	129	2.4
BPSH40	1.72	1.30	83	104	81	128	2.4
BPSH45	1.92	1.15	138	140	151	93	1.7
Nafion 117	0.91	1.21	50	91	167	55	1.0

[a] Data of BPSH series were from ref 39. [b] Selectivity = proton conductivity/methanol permeablility. [c] Relative selectivity = membrane selectivity/Nafion selectivity.

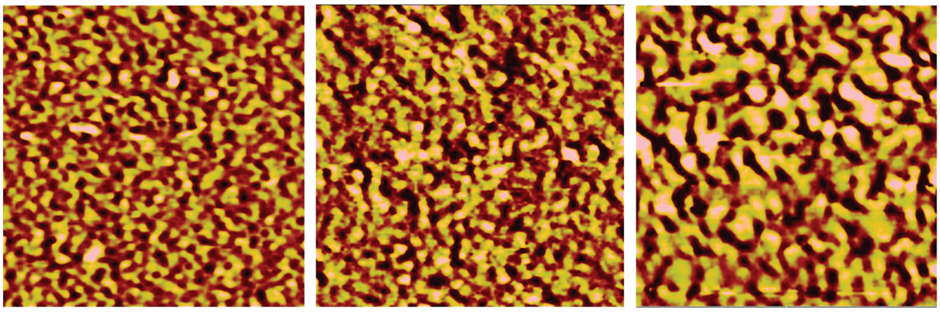

Figure 11. AFM images of cross-linked ESF85-6F, ESF90-6F, and ESF95-6F (image dimensions: 500 nm × 500 nm).

the selectivity. Consequently, for the DMFC applications, cross-linked ESF-6F membranes, especially cross-linked ESF85-6F and ESF90 6F membranes, which have good proton conductivity and low methanol permeability, are promising candidates as DMFC membranes.

Morphological Study. As shown in the AFM phase images in Figure 11, the dark region indicates the hydrophilic sulfonic acid groups that contain a large fraction of water, and the bright region indicates the hydrophobic aromatic region.[31,39] Our previous report with AFM study has demonstrated that the cross-linking of the membrane affected their morphology, which was changed to the smaller hydrophilic domain size, because of the decrease in water uptake after cross-linking.[30] Figure 11 shows the effect of the DS on the morphology of cross-linked ESF-6Fs. The dark softer region of cross-linked ESF-6Fs increases as the DS value increases and their size distribution of hydrophilic domain widens with increasing DS. After reaching the percolation threshold of cross-linked ESF-6F copolymers in Figure 5, the cross-linked ESF95-6F showed a dramatic increase in hydrophilic domain size (10−25 nm), compared to that of the cross-linked ESF85-6F (5−15 nm) and ESF90-6F (5−18 nm), because of the large water uptake. The AFM phase image of cross-linked ESF90-6F showed good hydrophilic domain connectivity, compared to the cross-linked ESF85-6F, giving rise to good proton conduction in the membrane. These observations suggest that the cross-linked ESF90-6F is an optimum morphology for the fuel cell application.

Conclusions

End-group cross-linkable poly(arylene ether) ionomers (ESF-6Fs) that contain high fluorine contents were successfully synthesized via direct sulfonation polymerization using SHQ, DFBP, and 6FBPA with an ethynyl end-group. The thermal properties of cross-linked ESF-6Fs for fuel cell applications showed thermal degradation temperature (T_d) values in the range of 258−276 °C and glass-transition temperature (T_g) values in the range of 308−328 °C. Various volume-related parameters were introduced for the evaluation of the optimized membrane properties and for comparison between the cross-linked ESF-6F membranes and other sulfonated ionomers. The optimum membrane from the parameters is the cross-linked ESF90-6F, which has excellent proton conductivity (111 mS/cm) and low methanol crossover (45 $\times 10^3$ s Ω^{-1} cm^{-3}), compared to those of Nafion 117 (91 mS/cm and 167 $\times 10^{-8}$ cm^2/s). The cross-linked ESF90-6F exhibited the low MVC$_{(wet)}$, which means high ion concentration per volume, and high proton conductivity at the same PCV value, compared to that of BPSH random copolymer, Nafion membrane, and another cross-linked membrane (ESF-BP). The AFM phase images of cross-linked ESF-6F membranes also showed the same result for the optimized

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(39) Kim, Y. S.; Hickner, M.; Dong, L.; Pivovar, B. S.; McGrath, J. E. *J. Membr. Sci.* **2004**, *243*, 317.

membrane. These results indicate that cross-linked ESF-6F membranes are promising candidates as a proton exchange membrane for hydrogen fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs).

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Supporting Information Available: The definition of molar volume per charge (MVC), MVC of ESF-BPs, ESF-6Fs, and ESF-6Hs, and the proton conductivity as a function of $MVC_{(wet)}$ and PCV of cross-linked ESF-6Hs. This information is available free of charge via the Internet at http://pubs.acs.org/.