CHEMISTRY OF MATERIALS
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Fluorinated Aromatic Polyether Ionomers Containing Perfluorocyclobutyl as Cross-Link Groups for Fuel Cell Applications

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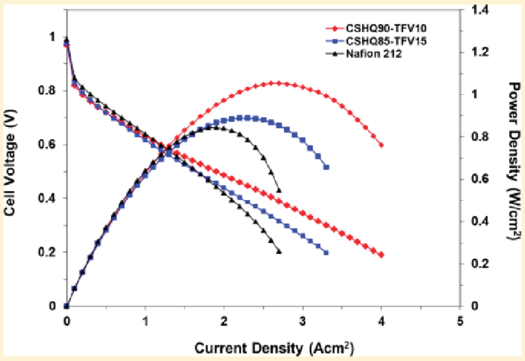
Ⓢ *Supporting Information*



ABSTRACT: The cross-linkable copolymers (SHQ*x*-TFV*y*s) with varying degrees of sulfonation (DS) from 70 to 95% were prepared from potassium-2,5-dihydroxybenzenesulfonate (SHQ), decafluorobiphenyl (DFBP), and 4-(trifluorovinyloxy)-biphenyl-2,5-diol (TFVOH) as a cross-linkable moiety. To develop a highly stable polymer electrolyte membrane (PEM) for application in polymer electrolyte fuel cells (PEFC)s, cross-linked membranes were prepared by chemical cross-linking. The cross-linked membranes were synthesized by varying the amount of TFVOH (5−30 mol %) in order to achieve desirable PEM properties. The structures of the cross-linkable monomer and polymers were investigated by ^1H and ^{19}F NMR and FT-IR spectra. The cross-linked membranes exhibited good glass transition temperature and thermal stability up to 239−271 °C and 290−312 °C, respectively. The crosslinked membranes (DS range 80−95%) exhibited higher proton conductivity (0.098−0.151 S/cm) than Nafion 212 (0.092 S/cm). Moreover, all membranes possessed lower methanol permeability ($13-132 \times 10^{-8}$ cm^2/s) compared with Nafion 212 (163×10^{-8} cm^2/s) under the same measurement conditions. The H_2/O_2 single cell performance tests of the cross-linked membranes and Nafion 212 were performed. The CSHQ90-TFV10 exhibited the higher maximum power density (1.053 W/cm^2) than that of Nafion 212 (0.844 W/cm^2).

KEYWORDS: *cross-linking, fuel cell, perfluorocyclobutane (PFCB), polymer electrolyte membrane, proton conductivity*

■ INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) are receiving increasing attention due to their potential abilities as alternative power sources for stationary, automobile, and portable applications. The main features of the PEFCs are high energy density, low operational temperature, and pollution free operation.[1] Polymer electrolyte membranes (PEMs) have attracted considerable attention because they play the key role in PEFCs, acting as a proton transport media and as a separator of fuel and oxidant. The current widely used perfluorosulfonic acid copolymer (Nafion) is considered as the state-of-the-art PEM, because it has excellent chemical and mechanical stability with good proton conductivity. However, the drawbacks of Nafion, which include a low glass transition temperature (ca. −20 °C)[2] and high fuel permeability, give rise to a decrease in the performance during the fuel cell operation for high temperature fuel cell and direct methanol fuel cell (DMFC) applications. In addition, the material cost and difficult synthetic procedure limit the availability for commercial use.[3−5] In order to overcome those problems of Nafion, extensive efforts have been made to develop alternative aromatic-based ionomers, such as poly(arylene ether)s,[6−13] polyimides (PI)[14−16] and polybenzimidazoles (PBI),[17−19] due to their thermal stability, low cost, and low fuel permeability. Also, there is much research related to improving proton conductivity and mechanical strength by cross-linked polymer. The low relative humidities (<50% RH) and high temperature (>80 °C) condition are researched to develop the PEFCs.[20−25] However, it has drawbacks, such as rapidly decreased proton conductivity.[43]

PEMs usually require high proton conductivity and low methanol permeability, and both factors contribute high selectivity, which shows overall performance of the membrane. The polymers with high degree of sulfonation (DS) are widely used to achieve high proton conductivity, but it also has drawbacks such as high water uptake and methanol permeability. Therefore, some research groups have studied the improvement of the selectivity under the high methanol concentration condition. Besides, the polymers lose their mechanical stability and limit their practical application in PEFCs and DMFCs.[26,40−44]

Cross-linking is a promising approach to improve mechanical property and to lower methanol permeability while maintains

Received: November 27, 2011
Revised: March 20, 2012
Published: March 26, 2012

ACS Publications

higher proton conductivity. So far, there have been several studies on the application of cross-linking.[27−46] Ionic cross-linking is an interaction between different ionomer types such as acid−base blend membranes.[27−34] It showed good mechanical and chemical stabilities. However, ionic cross-links break down in an aqueous environment when the temperature is raised above 70 °C. To overcome this instability, covalently cross-linked membranes have also been developed.[35−46] The introduction of chemical bonds has the strongest impact on the polymer structure, because covalent cross-links fix the polymer morphology. In general, covalently cross-linked membranes also have excellent chemical and thermal stability, even at elevated temperatures.

A few chemical cross-linking systems have been developed for the aromatic based PEMs. In general, chemically cross-linked PEMs have been prepared by three approaches.[35−46] The first uses the sulfonate (SO_3) groups directly as cross-linkable moieties.[35] The second adds the cross-linking media between (or/and among) the sulfonate groups of inter- and/or intra-polymer electrolytes.[36,37] These two methods are very simple and easy procedures for the preparation of cross-linked PEMs. On the other hand, controlling the ion exchange capacity (IEC) is somewhat difficult. In addition, the IEC of the PEM is decreased due to the elimination of sulfonate groups for cross-linking. The third option is to use other cross-linkable moieties regardless of the sulfonate group in the PEM.[38−46] The cross-linkable components are placed in various positions of the polymer such as "in the main chain of the polymer",[38,39] "at the end group of the polymer",[40−43] and "at the side group of the polymer".[44−46] The membrane preparation by this method usually suffers from the thermal- or photo-cross-linking procedure. This approach does not result in the loss of sulfonic acid, and therefore, the PEM has the same IEC before and after cross-linking, meaning that the IEC controllability and treatment are much easier than other methods.

Our group has developed cross-linkable PEMs containing an ethynyl group at the polymer end group and side group.[40−44] The appropriate curing time and temperature were investigated to optimize the PEM having good transport properties and dimensional stability. Cross-linking densities of the PEMs also were studied as a function of curing time for end group cross-linkable polymers and as controlling the cross-linkable monomer ratio for the side group cross-linkable polymers. The former exhibited the better effective degree of cross-linking (DC) than the side group cross-linkable polymers, due to higher free volume and more flexibility of the polymer end group, while the latter showed more controllability of DC than the end group cross-linkable polymers. However, for the preparation of PEMs, they all needed a high curing temperature above 220 °C, and the enthalpy for the cross-linking of the ethynyl cross-linkable group is around 130 kcal/mol.[44] Also, the tight packing cross-linked membranes have reduced conductivity due to the formation of four phenyl groups from three ethynyl groups, even though they have chance to increase the chemical stability.[42−44]

Herein, we report the synthesis of novel fluorinated aromatic polyether (SHQ*x*-TFV*y*) ionomers containing a new cross-linkable group, trifluorovinyl (TFV) group, as the polymer side group for the improvement of the cross-linked membrane preparation procedure, and properties which exceed those of PEMs made using ethynyl group as a side cross-linkable moiety. This SHQ*x*-TFV*y* polymer containing the TFV group has a big advantage for the preparation of PEMs, which is to lower the energy needed for PEM preparation. The lower onset point around 150 °C for the reaction between the TFVs and the lower enthalphy value around 57 kcal/mol than those of ethynyl group (~220 °C, ~130 kcal/mol) make the preparation of cross-linked PEM easier with lowering curing temperature and/or shorter curing time.[42,47] In addition, the polymerization step is an one-step synthetic procedure compared with the end group cross-linkable polymer. After cross-linking, the cross-linked region, perfluorocyclobutyl (PFCB) moieties, gives rise to a more flexible cross-linking point and better chemical resistance due to its perfluorinated alkyl ether linkage (PFCB group with ether linkage), compared with the cross-linking component consisting of four phenyl moieties formed from the ethynyl side group in polyethers. Membrane properties of cross-linked membranes (CSHQ*x*-TFV*y*s) are evaluated and compared with those of non-cross-linked membranes (NSHQ*x*-TFV*y*s) and our previous side-group cross-linked membranes (SFPE*x*-CM*y*s). The CSHQ*x*-TFV*y*s resulted in the improvement of mechanical properties and good hydrogen fuel cell performance at the same DS and DC and/or similar IEC, compared to the previous structure.[44]

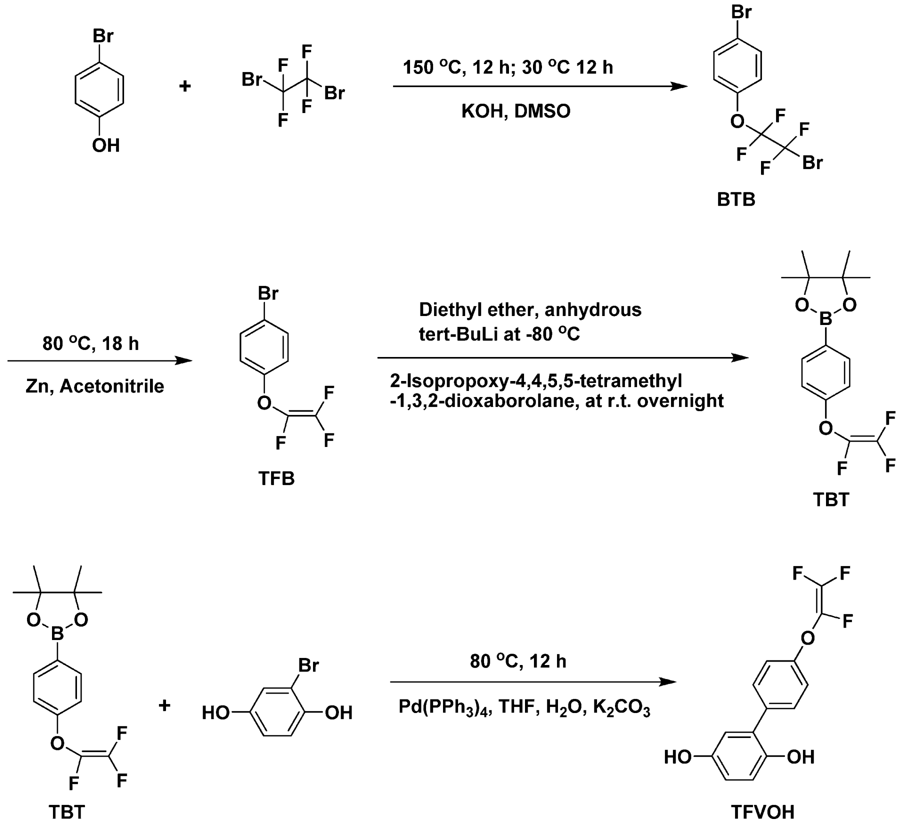
■ EXPERIMENTAL SECTION

Materials. 4-Bromophenol, bromohydroquinone, zinc, tetrakis(triphenylphosphine)palladium(0), potassium-2,5-dihydroxybenzenesulfonate, decafluorobiphenyl, acetonitrile, diethyl ether, tert-butyllithium, potassium-2,5-dihydroxybenzenesulfonate (SHQ), benzene, and N,N-dimethylacetamide were supplied by Aldrich Chemical Co. Potassium carbonate was dried at 120 °C before use. The compounds, 4-(2-bromotetrafluoroethoxy)bromobenzene (BTB), 4-(trifluorovinyloxy) bromobenzene (TFB), and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-yl)-phenyl trifluorovinyl ether (TBT) were prepared according to the reported procedure.[47,48]

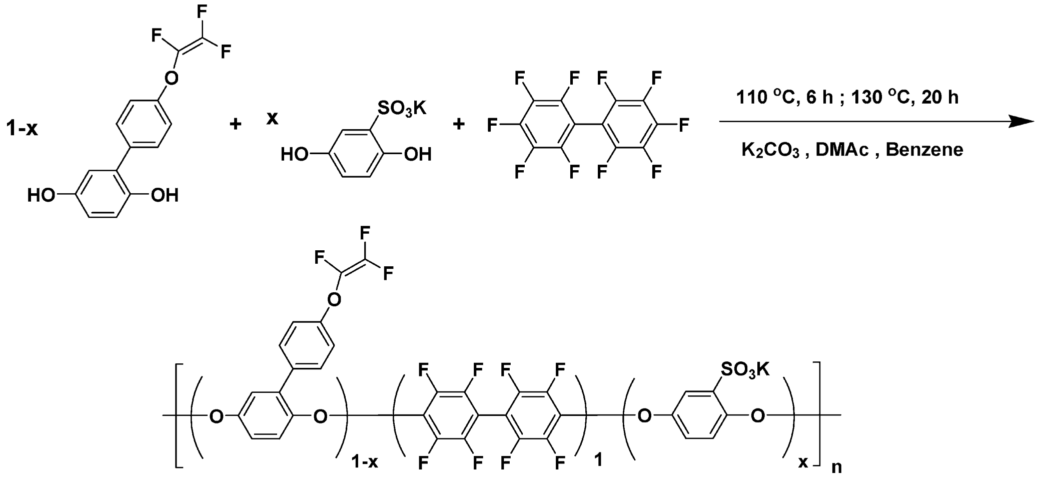
4-(Trifluorovinyloxy)biphenyl-2,5-diol (TFVOH). To a stirred solution of bromohydroquinone (2.88 g, 15.0 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-yl)-phenyl trifluorovinyl ether (5.00 g, 16.0 mmol) in THF (100 mL), K_2CO_3 solution (2M) in water (50 mL), and $Pd(PPh_3)_4$ (0.400 g, 0.350 mmol) as a catalyst were added (Scheme 1).[12] The reaction mixture was heated at 80 °C under a nitrogen atmosphere for 12 h. The solution was extracted with diethyl ether and washed with H_2O. The extracts were dried over $MgSO_4$. The crude product was purified by chromatography on silica gel using hexane as the eluent. The yield of product, TFVOH, was above 80% after purification. ^1H NMR ($CDCl_3$): $\delta = 6.85$ (3H, m), 7.19 (2H, d), 7.53 (2H, dd). ^{19}F NMR ($CDCl_3$): $\delta = -118.3$ (1F, dd, cis-$CF{=}CF_2$), -126.2 (1F, dd, trans-$CF{=}CF_2$), -135.3 (1F, dd, $CF{=}CF_2$). IR (KBr, cm^{-1}): ν 1833 (w, $CF{=}CF_2$), 1483 (st, Ar). MS (EI, *m*/*z*): 282 (M^+, 100%). Anal. calcd for $C_{22}H_{10}F_{12}O_2$: C, 59.58; H, 3.21. Found: C, 59.41; H, 3.19.

Cross-Linkable Copolymer Synthesis (SHQx-TFVy). The cross-linkable copolymers (SHQ*x*-TFV*y*s) were synthesized directly via an aromatic nucleophilic reaction between potassium-2,5-dihydroxybenzenesulfonate (SHQ) and 4-(trifluorovinyloxy) biphenyl-2,5-diol (TFVOH) in the presence of potassium carbonate in DMAc, with benzene as an azeotropic agent. The molar ratio of SHQ/TFVOH was varied to achieve desired target compositions of the copolymer, as shown in Scheme 2. The polymerizations were conducted in a 250 mL two-necked round-bottom flask with a nitrogen inlet and a Dean−Stark trap with reflux condenser. A 10 mmol concentration of SHQ, TFVOH, and 1.15 equivalent of potassium carbonate were added to the flask, followed by N,N-dimethylacetamide (DMAc), which was introduced to afford about 15 wt % solids concentration. Benzene was used as an azeotropic agent in a 70/30 volume ratio of DMAc/benzene. The reaction mixture was heated under reflux at 110 °C for 6 h in a nitrogen atmosphere to dehydrate the system. The most of the benzene was removed and cooled to room temperature. The dihalide monomer, decafluorobiphenyl (DFBP), was added using additional DMAc. The temperature was increased slowly to 130 °C and kept there for 20 h to achieve high molecular weight. The solution became

Scheme 1. Synthesis of the New Cross-Linkable Monomer, (4-(Trifluorovinyloxy) Biphenyl-2,5-diol) (TFVOH), through 4-(2-Bromotetrafluoroethoxy)bromobenzene (BTB), 4(Trifluorovinyloxy) Bromobenzene (TFB), and 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-yl)-phenyl Trifluorovinyl Ether (TBT)



Scheme 2. Synthesis of the Cross-Linkable Copolymers (CSHQ*x*-TFV*y*)



very viscous and was cooled to room temperature. It was filtered to remove most of the salt, and all polymers were precipitated into ethanol, filtered, and washed extensively with deionized water two times to remove the remaining salt.

Membrane Preparation. Membranes were prepared by casting solutions of SHQ*x*-TFV*y* ionomers dissolved in DMAc. The solution was filtered to remove particles using a disposable syringe. The solution placed on a hot plate with a gradually increasing temperature from 50 to 150 °C over 1 h. Then, the hot plate temperature was increased to 200 °C for 30 min for cross-linking through the reaction of trifluorovinyl ethers.[47−49] The membranes were acidified by immersing in boiling 0.5 M H_2SO_4 aqueous solution for 2 h, followed by treatment with boiling deionized water for 2 h.[50]

Characterization and Measurements. *Structural Characterizations.* ^{1}H and ^{19}F NMR spectra were measured on a JEOL JNM-LA 300 WB FT-NMR and were used to obtain the chemical composition of the monomers and polymers. The membranes were analyzed by FTIR-ATR (Jasco 460 Plus, Japan) spectra, with spectra recorded at a 4 cm^{-1} resolution.

Thermal Characterizations. The thermal behavior of the membranes in acid form was determined on a 2100 series TA Instrument. Thermal degradations (T_d) were determined by TGA in the range from 50 to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The glass transition temperatures (T_g) were determined by DSC in the range from 50 to 350 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

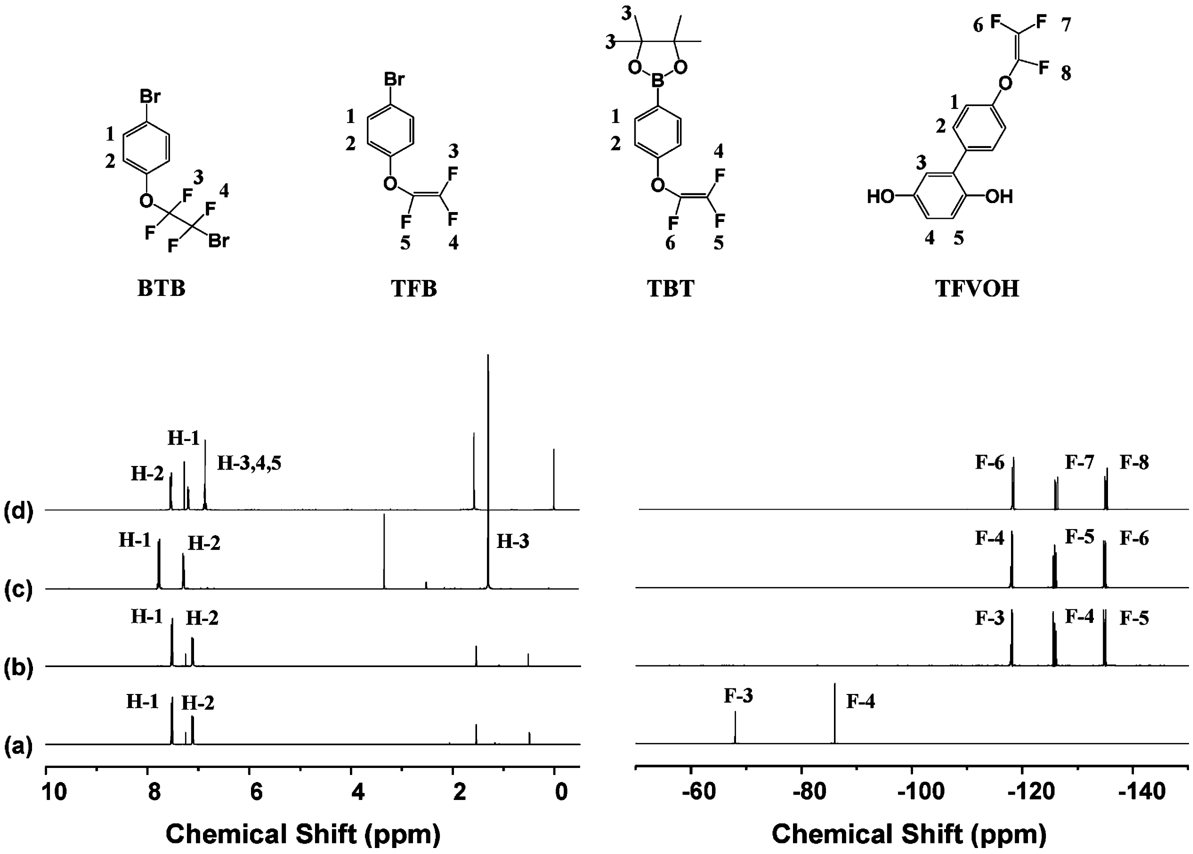


Figure 1. ^1H NMR and ^{19}F NMR spectra of (a) 4-(2-bromotetrafluoroethoxy)bromobenzene (BTB), (b) 4(trifluorovinyloxy) bromobenzene (TFB), (c) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-yl)-phenyl trifluorovinyl ether (TBT), and (d) (4-(trifluorovinyloxy) biphenyl-2,5-diol) (TFVOH).

Inherent Viscosity (η_{inh}). The inherent viscosity (η_{inh}) of sulfonated copolymers was measured at 25 °C in DMAc using an Ubbelohde viscometer, thermostatically controlled in a water bath.[40]

Ion Exchange Capacity (IEC). Ion exchange capacity (IEC) was determined using the classical titration method. After acidifying and washing the membranes, they were immersed into 0.1 M NaCl solution for 24 h to replace H^+ with Na^+. The remaining liquid was titrated with 0.1 M NaOH solution using phenolphthalein as an indicator.

Gel Fraction. Gel fractions of the networks were measured by solvent extraction. An ~0.3 g sample was extracted by Soxhlet extractor using dimethyl sulfoxide (DMSO) as extraction solvent at room temperature. The samples were placed in an excess of DMSO, and the solvent was replaced for 24 h until no further extractable polymer could be detected. The extracted samples were dried until constant weight.[43,44]

Proton Conductivity. Proton conductivity measurement was performed on fully hydrated samples (in water) and was measured using a four-point probe electrochemical impedance analyzer (Solatron 1280Z) over a frequency range from 1 Hz to 1 MHz at room temperature. Using a Bode plot, the frequency region over which the impedance had a constant value was checked, and the resistance was obtained from a Nyquist plot. The impedance of each sample was measured at least five times to ensure data reproducibility.[43,44]

Methanol Permeability. The methanol permeability of the cross-linked membranes was determined using a diffusion cell consisting of two compartments, each compartment containing deionized water (150 mL) and 2 M methanol solution (150 mL). The test membrane was placed between the two compartments, and the diameter of the diffusion area was 1.0 cm. During the test, both compartments were continuously stirred and were maintained at room temperature. Methanol permeates across the membrane by the concentration gradient between the two compartments. The methanol concentration in the deionized water compartment was monitored using a refractive index detector (RI750F, Younglin Instrument Co., Korea) through a 1 mm diameter silicon tube with 1.0 mL/min constant flow 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.[43,44]

Single Cell Performance. Gas diffusion layers (GDL, from Sigracet) were sprayed with Pt/C catalyst slurry (40 wt % Pt), and the loading of Pt catalyst was 0.4 mg/cm^2. The membrane-electrode assembly (MEA) was obtained by sandwiching the membrane between two sheets of GDL without hot pressing. The MEA was then set into a fuel cell station with an effective area of 5 cm^2. The test was performed under atmospheric pressure with the cell temperature of 60 °C. The hydrogen for anode and the oxygen for cathode, both at a flow rate of 100 mL/min, were prebubbled in distilled water at 60 °C for humidification. The current−voltage (I−V) relation of the cell was recorded at a current sweep rate of 100 mA/min using an electronic loader. For comparison, Nafion 212 was tested under the same conditions.

■ RESULTS AND DISCUSSION

Synthesis of New Cross-Linkable Monomer (TFVOH).

A new type of fluorinated and cross-linkable monomer, TFVOH, designed for reducing the curing temperature for the membrane preparation procedure and for a more flexible cross-linking point in the cross-linked network membrane with high chemical resistance. Figure 1 shows the ^1H NMR and ^{19}F NMR spectra of the new cross-linkable monomer and its raw chemicals. After Suzuki cross-coupling reaction, a new peak was observed at 6.85 ppm in ^1H NMR spectra of TFVOH. The ^{19}F NMR spectra for TFVOH are dominated by peaks centered at −118, −125, and −134 ppm, corresponding to the trifluorovinyl of TFVOH. The integration ratio of each proton and fluorine peak was completely matched.

Synthesis of Cross-Linkable Copolymers (SHQ*x*-TFV*y*s). The cross-linkable sulfonated copolymers (SHQ*x*-TFV*y*s) were prepared by copolymerization of the perfluorinated monomer (DFBP; decafluorobiphenyl) with SHQ and TFVOH, depicted in Scheme 2. The polymer synthesis involved condensing a controlled amount of SHQ, TFV, and DFBP in DMAc, which contained benzene as an azeotropic agent. To avoid serious branching or cross-linking side reactions that have been observed in several polymer syntheses under traditional polymerization conditions, the polymerizations were therefore conducted under very mild reaction conditions.

The polymer structures were confirmed by ^{1}H NMR and ^{19}F NMR spectra, giving good agreement for the designed structures (Figure 2). The degree of sulfonation (DS) was determined by the ^{1}H NMR spectra for the SHQ*x*-TFV*y*. The peak H-6 at 7.45−7.54 ppm is assigned to the protons adjacent to the sulfonic acid group, and the DS is estimated by the integration ratio of the peak H-1 at 7.66−7.73 ppm over the peak at S_2. That is, the intensity of the H-6 signal shows a value that is equal to the sulfonic acid group contents.[12] The DS could be calculated by comparing the integral of S_1 with the integral of S_2 using eq 1, where S_1 (7.66−7.73 ppm) is the H-1 area ($2 \times (1 - X) = 2 - 2X$) and S_2 (7.45−7.54 ppm) is the H-6 area (X, X = ratio of SHQ (Table 1)),

$$\frac{S_1}{S_2} = \frac{2(1 - X)}{X} \qquad (1)$$

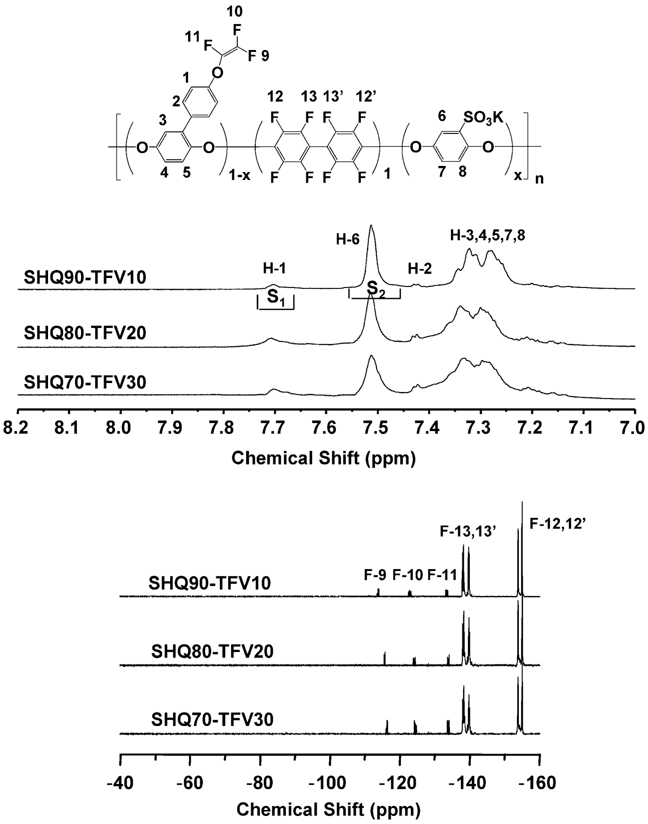


Figure 2. ^{1}H NMR and ^{19}F NMR spectra of SHQ*x*-TFV*y*s containing TFV10, TFV20, and TFV30.

Table 1. Inherent Viscosity, Gel Fraction, and Thermal Properties of SHQ*x*-TFV*y* Depending on the Concentration of Cross-Linking Moiety

membrane	DS[a] (%)	TFV[b] (mol %)	IV[c] (dL/g)	gel fraction[d] (%)	T_g[d] (°C)	$T_{d5\%}$[d] (°C)
SHQ95-TFV05	95	5	1.75	64.1	239	290
SHQ90-TFV10	91	9	1.67	75.8	247	298
SHQ85-TFV15	86	4	1.42	79.0	253	303
SHQ80-TFV20	82	18	1.18	87.5	258	308
SHQ75-TFV25	78	22	0.95	91.2	266	310
SHQ70-TFV30	73	27	0.80	97.3	271	312

[a] Determined by ^{1}H NMR. [b] The TFV means the contents of TFV in SHQ*x*-TFV*y*s and was determined by ^{1}H NMR. [c] Inherent viscosities were measured at a concentration of 0.5 g/dL in DMAc at 25 °C. [d] Measured using cross-linked SHQ*x*-TFV*y*s (CSHQ*x*-TFV*y*s).

In conclusion, degree of sulfonation (DS = x) of SHQ*x*-TFV*y* is given at eq 2, where S_1 and S_2 are integration ratios of H-1 and H-6 areas, respectively, as shown in Figure 2.

$$\mathrm{DS}(x) = 100X = \frac{2S_2}{S_1 + 2S_2} \qquad (2)$$

The experimentally determined DS values were found to be almost identical to the calculated DS values. Also, the cross-linking moiety content for SHQ*x*-TFV*y* was determined by the eq 3, where X is the ratio of SHQ moiety.

$$\text{ratio of cross-linking moiety (TFV)} = 1 - X \qquad (3)$$

The successful introduction of the sulfonate (SO_3) groups was also confirmed by the FT-IR spectra as shown in Figure 3.

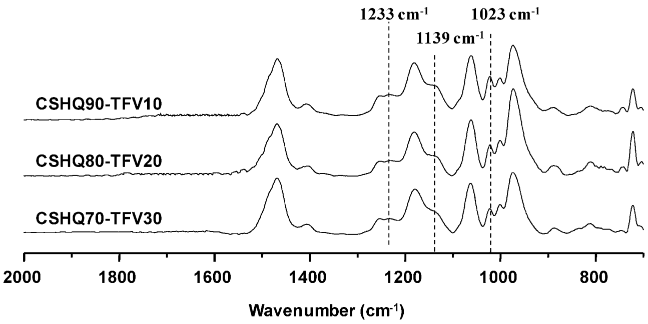


Figure 3. FT-IR spectra of CSHQ*x*-TFV*y*s containing TFV10, TFV20, and TFV30.

The characteristic absorption peaks of the sulfonate groups in CSHQ*x*-TFV*y* membranes were observed at 1023, 1139, and 1233 cm^{-1}, corresponding to the symmetric, asymmetric, and wagging peaks, respectively. The intensity of these absorption peaks increases with the increase of SHQ (Figure 3). All of the results clearly indicate that the sulfonate groups were quantitatively incorporated into the copolymer without any side reactions and that the DS could be easily controlled by changing the ratio of monomers of SHQ/TFVOH.

The inherent viscosity of SHQ*x*-TFV*y* was in range from 0.80 to 1.75 dL/g, measured in DMAc at 25 °C. These results show that the high molecular weight copolymers were successfully synthesized (Table 1). However, the higher the molar ratio of the TFVOH to the repeating unit of the copolymer is, the lower the inherent viscosities of the copolymer are, as a result of the decrease of reactivity of TFVOH.

Cross-Linking Reaction of Cross-Linkable Copolymers (SHQ*x*-TFV*y*s). The maximum exothermic peak for the PFCB formation through the thermal reaction between TFV groups in DSC measurement appears at about 230 °C.[47−49] In this study, cross-linked membranes (CSHQ*x*-TFV*y*s) were prepared by curing at 200 °C for 30 min.[48] This curing temperature and time for CSHQ*x*-TFV*y* membranes provides an advantage for PEM preparation by saving energy, compared with the previous cross-linking system which used ethynyl groups as a cross-linkable moiety.[40−44] Also of note were the single cell performances and mechanical properties of CSHQ*x*-TFV*y* membranes, which exhibited better performances and properties compared with the previous side-group cross-linked membrane (SFPE*x*-CM*y*) (see Figure S1 in the Supporting Information).[44] These are discussed in detail later in this work. The FT-IR spectra of membranes before and after curing are shown in Figure 4. The R-CF═CF_2 vibration peak (1833 cm^{-1}) disappeared after curing, indicating that the TFV groups formed PFCB groups, as shown in Scheme 3.[47,48]

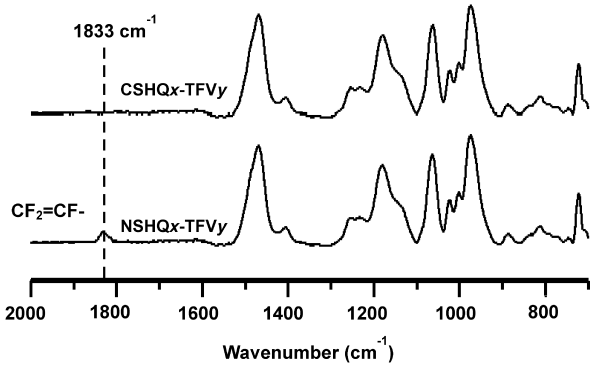


Figure 4. FT-IR spectra of CSHQ70-TFV30 (cross-linked membrane) and NSHQ70-TFV30 (non-cross-linked membrane).

The solubilities of CSHQ*x*-TFV*y* and NSHQ*x*-TFV*y* membranes were tested in various solvents at room temperature, and the cross-linked membranes were not soluble in any solvent. The solubility of the cross-linked membrane is different from that of the non-cross-linked membrane at room temperature. For example, CSHQ70-TFV30 (cross-linked membrane) is insoluble in all solvents, but NSHQ70-TFV30 (non-cross-linked membrane) is soluble in DMSO, DMAc, and NMP (Table 2). It confirms that the cross-linked membrane forms cross-linking network structure by thermal curing and has good chemical resistance.[40]

The degree of cross-linking (DC, the cross-linking density) of cross-linkable polymers affects various PEM properties, such as water uptake, swelling ratio, fuel permeability, and chemical and mechanical stability. The DC of the cross-linkable copolymers was determined through the heat flow calculation using differential scanning calorimetry (DSC) analysis,[42] the effect of cross-linking time on the various properties,[40] and the gel fraction measurement of controlled cross-linkable moiety using the various cross-linkable monomer feed ratios for the polymerization.[44] In this study, the gel fraction measurement of the cross-linked membranes was used for evaluating the DC of membranes.[44,46] The gel fraction values of CSHQ*x*-TFV*y*s were in the range 64.1−97.3%, as shown in Table 1. The gel fractions of the membranes increased with the molar ratio of TFVOH. This indicates that the increase of TFV group in the polymer improves the DC of polymer membrane. These results support the previous results of the side-group cross-linking system.[44] Overall, the gel fraction of CSHQ*x*-TFV*y*s was higher than that of SFPE*x*-CM*y*s.

Thermal Properties. The thermal behavior of CSHQ*x*-TFV*y* membranes in acid form was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and was compared with that of SFPE*x*-CM*y* membranes containing rigid cross-linking component which consists of four phenyl group.[44] All the CSHQ*x*-TFV*y* samples were first preheated to 120 °C for 15 min in the TGA furnace to remove any moisture and followed by dynamic TGA experiments which were run from 50 to 800 °C, at a heating rate of 10 °C/min under nitrogen. The influence of the DS on both 5% weight loss temperature is shown in Figure 5. All films displayed a two-step degradation profile. The initial weight loss was observed at 290 °C, which was assigned to the decomposition of sulfonic acid groups on the copolymer. The second decomposition, which was observed at around 500 °C, was attributed to degradation of the copolymer backbone.

The glass transition temperatures (T_g) of the CSHQ*x*-TFV*y* copolymers in acid forms were analyzed by DSC through heating the polymers from 50 to 350 °C at a rate of 10 °C/min under a nitrogen atmosphere (Figure 6). The DSC results show that the T_g of CSHQ*x*-TFV*y* copolymer occurs in the range 239−271 °C, depending on the cross-linking density (Table 1). The introduction of the cross-linking moiety (TFV) into the copolymer raises the T_g by decreasing the flexibility of the polymer chains because cross-linking hinders the rotational ability of the chains, thereby leading to the increased T_g for the sulfonated copolymers.

CSHQ*x*-TFV*y*s showed lower T_g and $T_{d5\%}$ than SFPE*x*-CM*y* at the same DS and DC, due to the two different cross-linking components of each cross-linked membrane. This means that the PFCB group as a cross-linking component in CSHQ*x*-TFV*y*s gives more flexibility in the cross-linked membranes. This flexible component in cross-linked membranes affects the transport properties and single cell performances of the membranes. These properties are explained in detail later in mechanical properties and single cell performance sections in this work.

Mechanical Properties. Good mechanical properties of PEMs are one of necessary requirements for their applications because the mechanical strength of membranes affects the fabrication conditions of the MEA and durability of the PEFC. The membranes with various amounts of the cross-linking moiety (TFV) were tested in the dry state to evaluate the effect of cross-linking density on the mechanical properties. The mechanical properties of CSHQ*x*-TFV*y* were investigated with those of the previous cross-linked membrane (SFPE*x*-CM*y*) for the comparison of the effect of the cross-linking component on the properties (Figure 7).

Table 3 shows the tensile strength, Young's modulus, and elongation at break of the CSHQ*x*-TFV*y* membranes. CSHQ*x*-TFV*y* membranes showed excellent tensile strength ranging from 51.4 to 85.9 MPa and reasonable elongation at break ranging from 6.01 to 10.9%. Young's modulus for the membranes was from 1.33 to 2.10 GPa with the increase of the cross-linking density. On the other hand, tensile strength and elongation at break of CSHQ*x*-TFV*y* membranes decreased with an increase in cross-linking density. The result could be explained from the increase of brittleness with increasing

Scheme 3. Postulated Cross-Linking Mechanism: (a) Cross-Linking Reaction of Trifluorovinyl Ether after Thermal Curing and (b) Effect of Amount of TFV in CSHQ*x*-TFV*y*

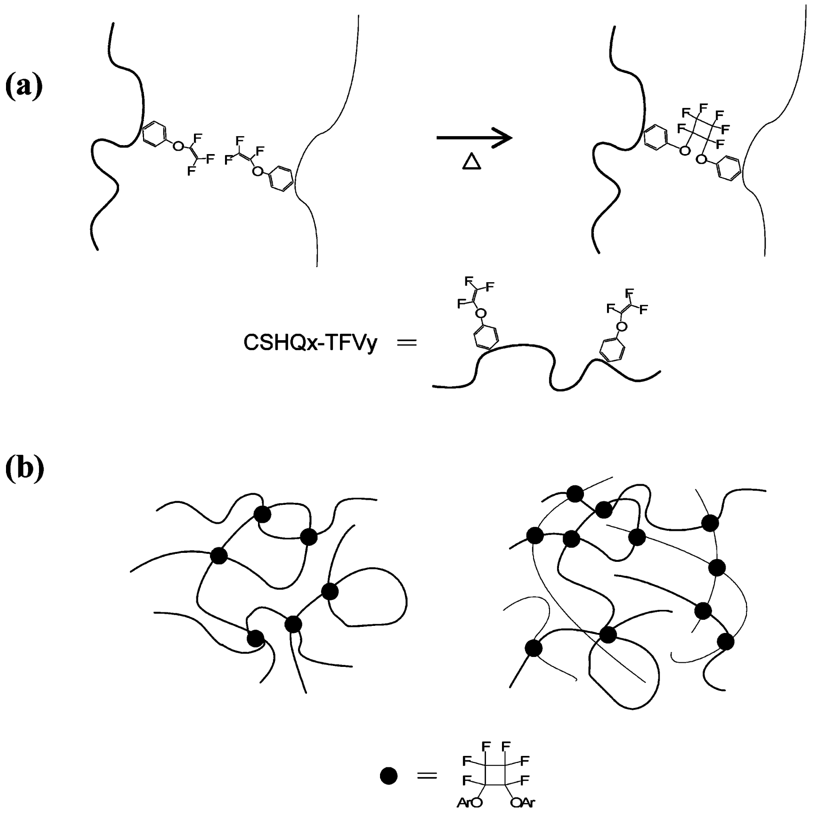


Table 2. Solubility of Non-Cross-Linked and Cross-Linked Membrane in Various Common Organic Solvents[a]

sample	DMSO[b]	DMAc[c]	NMP[d]	THF[e]	methanol	water
NSHQ70-TFV30	S	S	S	I	I	I
CSHQ70-TFV30	I	I	I	I	I	I

[a] S = soluble, I = insoluble at room temperature. [b] DMSO: dimethylsulfoxide. [c] DMAc: N,N-dimethylacetamide. [d] NMP: N-methylpyrrolidone. [e] THF: tetrahydrofurane.

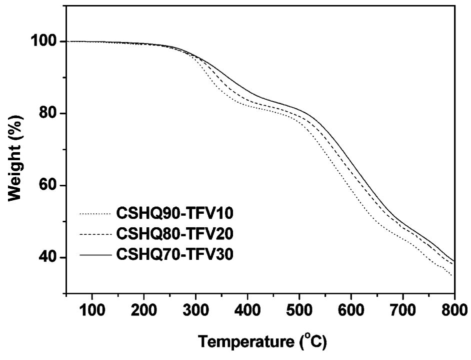


Figure 5. TGA curves of CSHQ*x*-TFV*y*s as a function of TFV mole ratio.

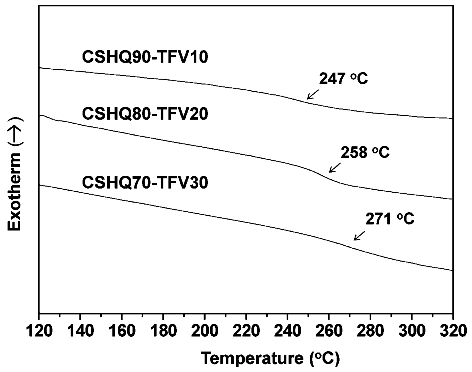


Figure 6. Glass transition temperatures of cross-linked SHQ*x*-TFV*y*s as a function of TFV mole ratio.

cross-linking component, which induces a decrease of toughness. Figure 7 shows the effect of cross-linking component on the mechanical properties as a function of the feed ratio of the cross-linked moiety. Tensile strength and elongation at break of CSHQ*x*-TFV*y* membranes were higher than those of SFPE*x*-CM*y* membranes at the same feed ratio of cross-linkable moiety. These results indicated that the CSHQ*x*-TFV*y* membranes exhibited better mechanical properties compared with SFPE*x*-CM*y* membranes and were strong and tough enough for use as PEMs.

Swelling Ratio and Water Uptake. The swelling ratio of the membranes was measured at room temperature (Table 4). As expected, the swelling ratio of the CSHQ*x*-TFV*y* membranes increased with DS, because the sulfonic acid groups on the polymer backbone increase the ionic nature of the sulfonated copolymer. The cross-linking increased the

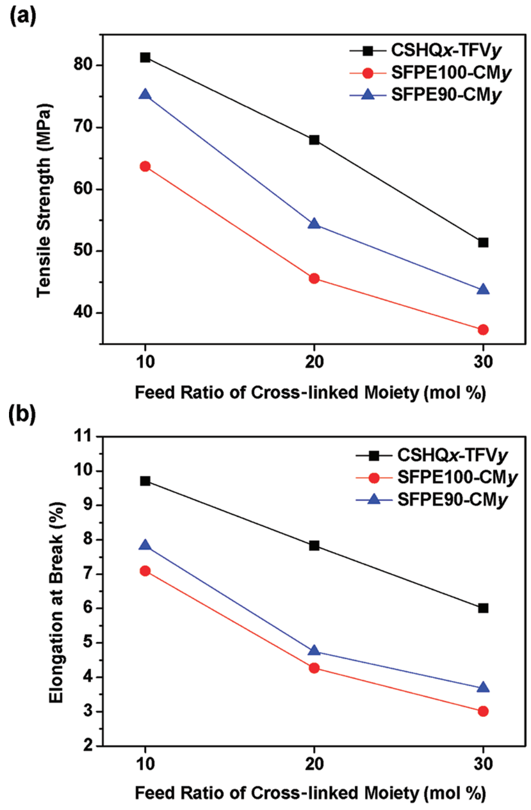


Figure 7. (a) Tensile strength (MPa) and (b) elongation at break (%) of CSHQ*x*-TFV*y*s and SFPE*x*-CM*y*s in dry state as a function of feed ratio of cross-linked moiety.

Table 3. Mechanical Properties of CSHQ*x*-TFV*y*s[a]

membrane	tensile strength (MPa)	Young's modulus (GPa)	elongation at break (%)
CSHQ95-TFV05	85.9	1.33	10.9
CSHQ90-TFV10	81.3	1.47	9.71
CSHQ85-TFV15	76.5	1.54	9.03
CSHQ80-TFV20	68.0	1.60	7.83
CSHQ75-TFV25	57.1	1.86	6.76
CSHQ70-TFV30	51.4	2.10	6.01
Nafion 212	27.7	0.25	157

[a] Mechanical properties of the thin dry membranes were evaluated at room temperature on an Instron instrument at a strain rate of 10 mm/min, and a 500 N load cell was used.

interaction of the copolymers, and the cross-linking restrained the swelling volume to hold water; therefore, the cross-linked membranes showed a smaller swelling ratio than the virgin membranes (Table 4). For example, the swelling ratio of CSHQ80-TFV20 is 16%, while that of NSHQ80-TFV20 is 79%. The cross-linking methodology can effectively improve the dimensional stability of the membranes. As shown in Figure 8a, the swelling ratio of CSHQ*x*-TFV*y* films decreased linearly from 50 to 7%.

Appropriate membrane hydration is critical for fuel cell applications, because of its profound effect on the proton conductivity and mechanical property. Water can influence the interaction between the proton and the fixed sulfonic acid groups within the membrane. Moreover, water can change the structure of the ionic cluster and improve proton transportation. A lack of water in the electrolyte membrane leads to poor proton conductivity, on the other hand, an excess of water can result in electrode flooding and the morphological instability of the membrane. The water uptake also increases with the DS of membrane, due to the strong hydrophilicity of the sulfonic acid groups. On the other hand, the cross-linked membranes had lower water uptake than non-cross-linked membranes and the water uptake decreased with the increase of the cross-linking density (Figure 8b) and the decrease of the DS. Table 4 displays the water uptake of both cross-linked and non-cross-linked membranes as changing DS and DC of the membranes. Similar to the tendency of swelling ratio, the water uptake difference of membranes between before and after cross-linking was very huge at the same DS. For example, the water uptake of CSHQ80-TFV20 (42%) exhibits about 6.5 times lower than that of NSHQ80-TFV20 (271%). In case of 90% DS or 95% DS membranes, the difference of water uptake between them is presumably over 10 times. The previous research about end-group cross-linked membranes supports this expectation.[42] In the study, the water uptake difference between cross-linked and non-cross-linked membranes at 90−95% DS was over 13 times.

Proton Conductivity. Proton conductivity of the membranes is the most important factor for the fuel cell applications. In general, the cross-linked membrane shows lower proton conductivity than the non-cross-linked membrane because of the reduced water uptake in the membrane. Figure 8c shows the proton conductivity as a function of the TFVOH feed ratio. As expected, the proton conductivity of CSHQ*x*-TFV*y* membranes linearly decreases with increase of the TFV feed ratio (cross-linking density). The proton conductivity of CSHQ*x*-TFV*y* membranes is in the range 0.055−0.151 S/cm. In particular, the proton conductivity of CSHQ*x*-TFV*y* membranes with higher than 80% DS exhibited excellent values (0.098−0.151 S/cm), compared with Nafion 212 (0.092 S/cm). The proton conductivity of CSHQ*x*-TFV*y*s was compared with the previous side-group cross-linked membranes, SFPE*x*-CM*y*s.[42] CSHQ*x*-TFV*y*s (0.130 S/cm for CSHQ90-TFV10 and 0.098 S/cm for CSHQ80-TFV20) exhibited higher proton conductivity than SFPE*x*-CM*y*s (0.106 S/cm for SFPE90-CM10 and 0.058 S/cm for SFPE80-CM20) at the same DS and cross-linking density. The proton conductivity of CSHQ90-TFV10 also was higher than that of SFPE100-CM10 at the same cross-linking density and at even higher IEC and water uptake. These results indicate that the more flexible PFCB groups (the cross-linked components) of CSHQ*x*-TFV*y* membranes are better than the four phenyl groups of SFPE*x*-CM*y* membranes for improving of proton conductivity of membranes as the cross-linked networking system.

Methanol Permeability and Selectivity. The methanol permeability at room temperature is plotted in Figure 8d as a function of the feed ratio of TFVOH. The methanol permeability of CSHQ*x*-TFV*y* membranes is in the range 13−132 × 10^{-8} cm^2/s, which was lower than that of Nafion 212 (163 × 10^{-8} cm^2/s). The methanol permeability was significantly reduced by the cross-linking. CSHQ75-TFV25, for example, showed the methanol permeability (26 × 10^{-8} cm^2/s), which is about one-fourth of that of the NSHQ75-TFV25.

The ratio of proton conductivity to methanol permeability (selectivity) is often used to evaluate the overall performance of the membranes and the higher the selectivity, the better the performance is in direct methanol fuel cell (DMFC). All the cross-linked membranes exhibited better selectivity than Nafion

Table 4. Membrane Properties of NSHQ*x*-TFV*y* and CSHQ*x*-TFV*y*

membranes	IEC (meq g^{-1}) cal. IEC[a]	IEC (meq g^{-1}) exp. IEC[b]	water uptake (%)	swelling ratio (%)	proton conductivity (S/cm)	methanol permeability (10^{-8}cm^2/s)
NSHQ95-TFV05	2.05	c.m.[c]	c.m.	c.m.	c.m.	c.m.
NSHQ90-TFV10	2.03	c.m.	c.m.	c.m.	c.m.	c.m.
NSHQ85-TFV15	2.01	c.m.	c.m.	c.m.	c.m.	c.m.
NSHQ80-TFV20	1.99	1.93	271	79	0.180	c.m.
NSHQ75-TFV25	1.97	1.89	88	35	0.122	101
NSHQ70-TFV30	1.95	1.86	34	13	0.081	40
CSHQ95-TFV05	2.05	2.02	158	50	0.151	132
CSHQ90-TFV10	2.03	1.99	94	36	0.130	108
CSHQ85-TFV15	2.01	1.95	69	24	0.114	64
CSHQ80-TFV20	1.99	1.93	42	16	0.098	41
CSHQ75-TFV25	1.97	1.89	31	11	0.079	26
CSHQ70-TFV30	1.95	1.86	19	7	0.055	13
Nafion 212	0.95−1.01[d]	0.97	33	16	0.092	163

[a] Calculated ionic exchange capacity (IEC). [b] Measured ionic exchange capacity (IEC). [c] c.m.: cannot be measured. [d] Data obtained from ref 52.

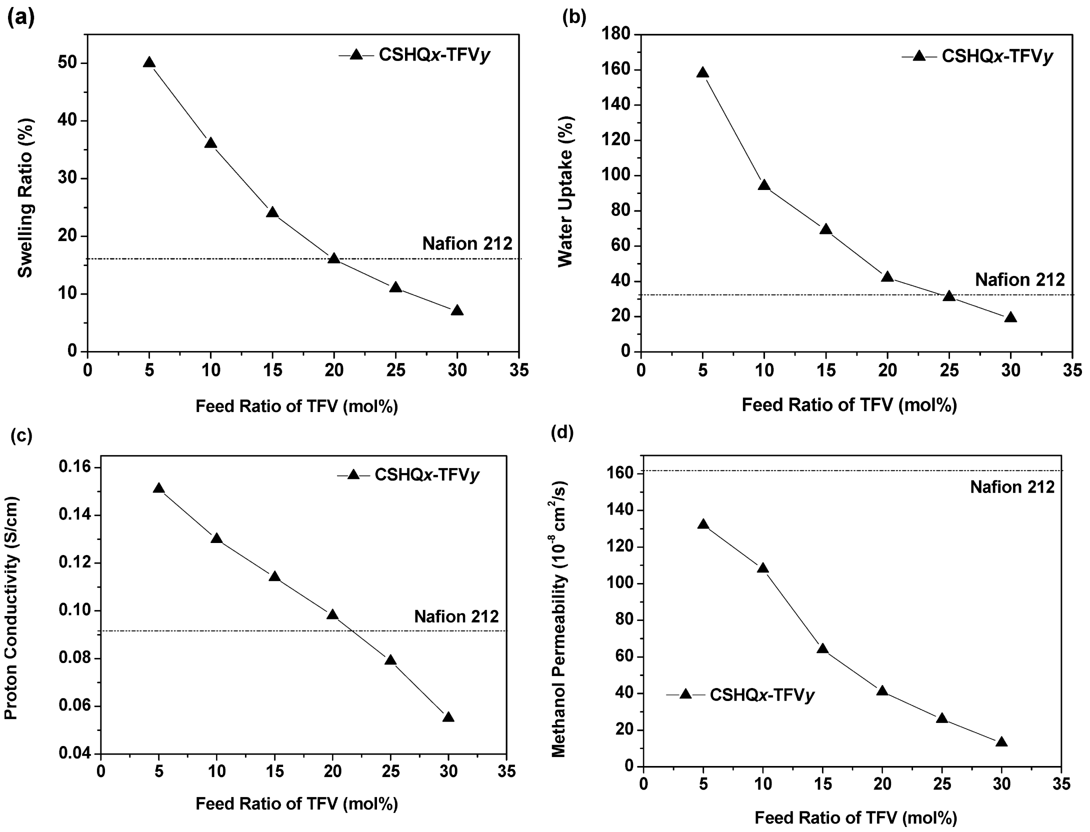


Figure 8. Influence of the TFV feed ratios on membrane properties for CSHQ*x*-TFV*y*.

212, indicating better performance of the cross-linked membranes (Figure 9). For example, CSHQ80-TFV20 showed a selectivity (239 × 10^3 S·s/cm^3). It is approximately 4 times higher than the selectivity of Nafion 212 (56 × 10^3 S·s/cm^3). These results indicate that CSHQ*x*-TFV*y* membranes are promising candidates for DMFC.

Single Cell Performance. The fabrication of a membrane−electrode assembly (MEA) with newly synthesized cross-linked membranes requires considerable effort to identify the proper electrode/binder composition and attachment conditions. Often, an MEA preparation using hot pressing method was failed, not because the membrane performs poorly, but rather due to poor adhesion of the electrodes to the membrane and insufficient catalyst utilization due to problems associated with the catalyst binder and electrode/membrane interfacial microstructure. To avoid such difficulties, cross-linked membranes and Nafion 212 were prepared without hot pressing under same condition and sufficient catalyst was supplied (Pt catalyst loading of 0.400 mg/cm^2).

Figure 10 shows the single cell performance of CSHQ90-TFV10, CSHQ85-TFV15, and Nafion 212 at 60 °C. The maximum power densities of CSHQ90-TFV10 and CSHQ85-TFV15 were 1.05 and 0.889 W/cm^2, respectively. CSHQ90-TFV10 and CSHQ85-TFV15 showed better performance than

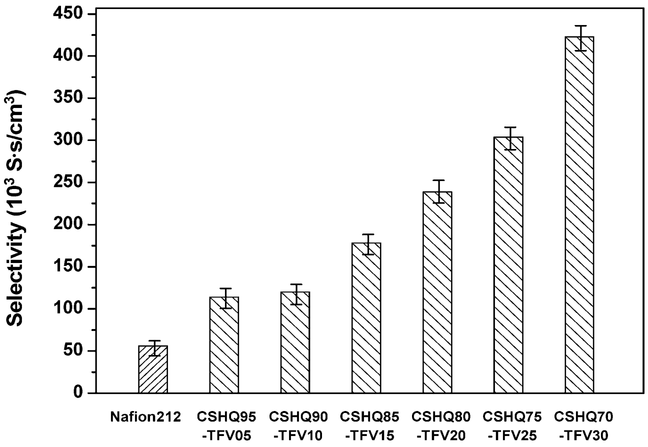


Figure 9. Selectivity of CSHQ*x*-TFV*y*s with various concentrations of TFV moiety.

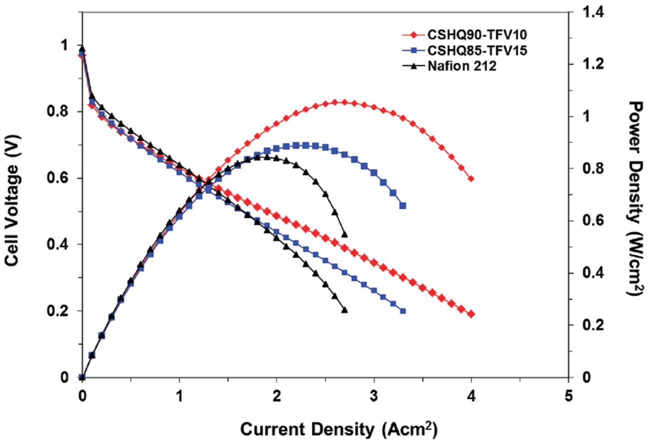


Figure 10. Single cell performance of CSHQ90-TFV10, CSHQ85-TFV15, and Nafion 212.

Nafion 212 (0.844 W/cm^2) due to a lower membrane resistance. The difference of the maximum power density between CSHQ90-TFV10 and CSHQ85-TFV15 is bigger than that between CSHQ85-TFV15 and Nafion 212 compared with the differences of their proton conductivity values. That is, the difference of the maximum power density between the cross-linked membranes and Nafion 212 can also be explained by Nafion binder solution that was used for the electrode fabrication, because the interaction between the Nafion binder solution and cross-linked membranes is incompatibility. That is, both Nafion 212 and CSHQ*x*-TFV*y* membranes have excellent proton conductivity and good mechanical and chemical properties, while fuel cell performance using the CSHQ*x*-TFV*y* membranes often suffers from their poor interfacial compatibility with Nafion-bonded electrodes. Poor interfacial compatibility results in difficulties in membrane−electrode fabrication, increased cell resistance (reduced cell performance), local flooding, and gradual performance degradation over time.[51]

The single cell performance of CSHQ*x*-TFV*y* membranes was compared to that of SFPE*x*-CM*y*. Membranes that were used for these cell performance comparisons have similar IEC (1.91−1.99 meq g^{-1}) and DS values. Figure 10 and Figure S2 (see the Supporting Information) show the cell performances of CSHQ*x*-TFV*y*, SFPE*x*-CM*y*, and Nafion 212. CSHQ*x*-TFV*y* membranes exhibited higher cell performance than SFPE*x*-CM*y* and Nafion 212.

■ CONCLUSIONS

Novel cross-linkable polymers (SHQ*x*-TFV*y*s) were synthesized containing the trifluorovinyl ether (TFV) group at the polymer side chain as a cross-linkable moiety. A thermal cross-linking reaction was conducted between the TFV groups at lower temperature and for shorter time (200 °C and 30 min) compared with the previous method for ethynyl groups (250 °C and 2 h). No IEC change was observed after completion of the cross-linking reaction. The CSHQ*x*-TFV*y* membranes showed a huge reduction of proton conductivity, water uptake, swelling ratio, and methanol permeability compared with those of the NSHQ*x*-TFV*y* membranes, and the difference in properties increased with the DS. The proton conductivity of the membrane ranged between 0.055 and 0.151 S/cm depending on DS and DC. These copolymers have relatively lower methanol permeability with comparable proton conductivity to Nafion 212. This cross-linked membrane (CSHQ*x*-TFV*y*) exhibited better mechanical properties and single cell performances than our previous cross-linked membrane (SFPE*x*-CM*y*). Tensile strength and elongation at break of CSHQ*x*-TFV*y* were higher than those of SFPE*x*-CM*y*, indicating that the flexibility of cross-linking point (PFCB group for CSHQ*x*-TFV*y* and four phenyl group for SFPE*x*-CM*y*) affects those mechanical properties. CSHQ*x*-TFV*y* membranes showed excellent single cell performance (power density) as compared to SFPE*x*-CM*y* membranes and Nafion 212. These results indicate that CSHQ*x*-TFV*y* series is a promising candidate for optimizing the structure of cross-linked membrane and for a polymer electrolyte membrane for fuel cells (DMFCs and PEMFCs).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by New & Renewable Energy R&D program (20093020030030-11-1-000) under the Ministry of Knowledge Economy, World Class University (WCU) Program (Project Number: R31-20008-000-10026-0), the Research Foundation of Korea(NRF) funded by the Korean government (MEST) (Grant No. 2010-0027330), and the Core Technology Development Program for Next-Generation Energy Storage of Research Institute for Solar and Sustainable Energies (RISE), GIST.

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