A Convenient Crosslinking Method for Sulfonated Poly(ether ether ketone) Membranes via Friedel–Crafts Reaction Using 1,6-Dibromohexane and Aluminum Trichloride

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ABSTRACT: In this study, sulfonated poly(ether ether ketone) (SPEEK) was very efficiently crosslinked via a Friedel–Craft reaction using 1,6-dibromohexane and AlCl$_3$. The resulting crosslinked SPEEK (c-SPEEK) membranes exhibited improved dimensional stability, thermal and chemical stability, and mechanical strength with slight reduction in the elongation. The methanol permeability was reduced by approximately two orders of magnitude by the crosslinking reaction. The proton conductivities of c-SPEEK membranes were greater than Nafion-212 in the temperature range of 30–90°C. Overall, this new crosslinking method can be conveniently and efficiently applicable to most aromatic hydrocarbon polymer membranes. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40695.

INTRODUCTION

Perfluorosulfonic acid ionomers such as Nafion membranes have been most frequently used in the fabrication of polymer electrolyte membrane fuel cells, because they have good mechanical and chemical properties, excellent proton conductivity, and long-term durability.[1] However, those membranes have some problems such as the complexity of the manufacturing process, high cost, and performance degradation at high temperature.

Several aromatic hydrocarbon polymers, including poly(ether sulfone)s, poly(ether ketone)s, poly(phenylene)s, polyimides, and polybenzimidazoles, have been recognized as very promising alternatives due to their excellent thermal property, chemical resistance, and mechanical integrity.[1–4] These membranes require a high degree of sulfonation (DS) to obtain enhanced proton conductivities. However, the introduction of excess sulfonic acid groups causes excess water uptake, leading to mechanical instability and high methanol permeability of membranes.[5]

Crosslinking is considered to be a simple way to mitigate such problems associated with the highly sulfonated aromatic hydro-carbon polymers. Among various crosslinking reactions,[5–27] electrophilic aromatic substitution reactions (Friedel–Craft alkylation or acylation) appear most useful. For example, Lee and coworkers reported that poly(phenylene sulfide sulfone nitrile) membranes were crosslinked by heating membranes containing 4,4′-oxybis(benzoic acid), and the resulting crosslinked membranes exhibited improved dimensional stability while maintaining high proton conductivity.[6] However, the crosslinking procedure is not efficient as the gel fraction, the ratio of the weight of polymer after extraction from *N,N*-dimethylacetamide to the initial weight, was only 0.68–0.78 and subsequently did not significantly change the tensile strength (13–56% increase) and methanol permeability (16–58% decrease). Han et al. reported that sulfonated poly(ether ether ketone) (SPEEK) membranes were crosslinked by heating membranes containing a carboxyl-terminated benzimidazole trimer, and the crosslinked SPEEK membranes exhibited high proton conductivity [up to 0.22 S/cm at 80°C and 100% relative humidity (RH)], significantly improved thermal stability and dimensional stability.[5] However, the methanol permeability was not greatly reduced by the crosslinking method (1.05–2.38 × 10^{-7} cm^2/s at 25°C). Another representative example is crosslinking highly

sulfonated PEEK membranes (0.96 sulfonic acid group per repeat unit) using 1,4-benzenedimethanol (BDM) and ZnCl$_2$.[7] However, the crosslinking temperature, which was increased to 200°C, may be too high because the color of the membranes changed from clear yellow to dark brown, likely due to decomposition of sulfonic acid groups. In addition, a significant amount of the crosslinking agent (50%) was lost via evaporation from the membrane surface. Furthermore, the crosslinked membranes were brittle (only 5.5–6% elongation at break). Radiation-induced crosslinked SPEEK membranes were also prepared using a mixture of various crosslinking agents, but some of the radical crosslinking agents have acid-sensitive functional groups.[7,8]

In this study, SPEEK membranes were crosslinked via Friedel–Crafts alkylation using 1,6-dibromohexane and AlCl$_3$. The crosslinked membranes were characterized with respect to dimensional stability, thermal and chemical stability, mechanical strength, proton conductivity, and methanol permeability.

EXPERIMENTAL

Materials
PEEK powder was purchased from Victrex . N,N-Dimethylformamide (DMF, anhydrous), sulfuric acid (95–98 wt %), aluminum trichloride, and 1,6-dibromohexane were purchased from Sigma-Aldrich and used without further purification.

Preparation of SPEEK Membranes
PEEK was sulfonated following the reported method.[8] Briefly, PEEK powder (18 g) was added slowly to sulfuric acid (500 mL) at room temperature under a nitrogen atmosphere. After the PEEK was dissolved completely, the resulting solution was stirred at 65°C for 3 h. The polymer solution was then cooled to 5°C in an ice-water bath to terminate the reaction and poured into a large amount of ice water (ca. five times the volume) under vigorous mixing with a glass rod to form SPEEK. The polymer was washed with deionized water until a neutral pH was achieved. The prepared SPEEK was dried at 80°C for 12 h and then 130°C for 5 h in a vacuum oven. The SPEEK was dissolved in DMF to form a 10 wt % solution. The resulting solution was cast onto a glass plate, dried at 60°C for 12 h, and finally 100°C for 6 h.

Preparation of crosslinked SPEEK (c-SPEEK) Membranes
To a solution of SPEEK in DMF (10 wt %), AlCl$_3$ was added and the mixture was stirred for 1 h in a nitrogen atmosphere, followed by addition of 1,6-dibromohexane. The solution was stirred at 30°C for 1 h, followed by addition of water (1 mL) at room temperature. The resulting solution was cast onto a glass plate, dried at 60°C for 12 h, and then 100°C for 6 h. The as-prepared membranes were washed with water several times and dried. The loading of 1,6-dibromohexane with respect to the SPEEK was 3, 4, or 5 wt %.

Measurements
Ion Exchange Capacity.
Dry polymer membranes were immersed in an aqueous 1.0M NaCl solution for 24 h. The solution was subsequently back titrated with a 0.01M NaOH solution using phenolphthalene as an indicator. The ion exchange capacity (IEC) value was calculated using the following equation

$$IEC \ (mmol/g) = [C_{NaOH} \times V_{NaOH}]/W_{dry}$$

where C_{NaOH} is the concentration of the NaOH solution, V_{NaOH} is the volume of the 0.01M NaOH solution consumed in the titration, and W_{dry} is the weight of dry polymer membranes.

Water Uptake and Dimensional Change. To determine the water uptake, all the samples were dried in a vacuum oven at 120°C for 1 day before the measurements. The samples were then immersed and maintained in deionized water for 1 day to obtain an equilibrium water uptake. The water uptake value was calculated using the following equation

$$Water \ uptake \ (\%) = (W_{wet} - W_{dry})/W_{dry} \times 100$$

where W_{wet} and W_{dry} are the weight of wet and dry membranes, respectively. The dimensional change of membranes was calculated using the following equation

$$Dimensional \ change \ (\%) = (\Delta t_{wet} - \Delta t_{dry})/\Delta t_{dry} \times 100$$

where Δt_{wet} and Δt_{dry} are the thickness of wet and dry membranes, respectively.

Proton Conductivity. The proton conductivity of polymer membranes was measured by a four-electrode AC impedance method over a frequency range of 0.01–100 kHz at 30, 45, 60, 75, and 90°C using a SI 1260 (Solatron Company). The humidity was maintained at 90% during the measurements, and the proton conductivity (σ, S/cm) was calculated from the following equation

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

where L is the distance between the two electrodes (cm), A is the cross-sectional area of the membrane (cm^2), and R is resistance of polymer membranes (Ω).

Thermal and Mechanical Property. The thermal stability of polymer membranes was determined by a Q-50 thermogravimetric analyzer (TA Instruments). Before testing, all the membrane samples were preheated to 160°C, equilibrated for 15 min, and heated from 50 to 800°C in a nitrogen atmosphere at a heating rate of 20°C/min. The mechanical property of the membranes (40 × 5 mm^2) was measured by an INSTRON Series IX (Universal Testing System model 4400, Instron Co.) at a test speed of 50 mm/min. Prior to the measurements in the wet state, the membranes were immersed in water for 24 h at room temperature, and any remaining water on the surface of the membranes was wiped off with absorbent paper. Each sample was tested at least three times, and the average value was taken.

Methanol Permeability. The methanol permeability was measured using a membrane-separated diffusion cell in an isothermal bath at 35°C with a 1.0M methanol solution (Cell A).

Figure 1. Photographs of the dried SPEEK products obtained after precipitation in cold water under two different mixing conditions: gentle stirring with a mechanical stirrer (left) and vigorous stirring with a glass rod (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Methanol concentrations in the water cell (Cell B) were determined using a RI detector 750F equipped with a SP930D pump (Young Lin, Korea). The methanol concentration in Cell B as a function of time (t) is given by the following equation

$$C_B(t) = \frac{A}{V_B} \frac{P}{L} C_A(t - t_0)$$

where C_A and C_B are the concentrations of methanol in Cell A and Cell B, respectively. A, V_B, P, and L are the area of membranes, the volume of Cell B, the methanol permeability, and the thickness of membranes, respectively.

Oxidative Stability. The prepared membranes were soaked in a 3 wt % H_2O_2 aqueous solution containing 2 ppm $FeSO_4$ (Fenton's reagent) at 80°C. The oxidative stability was evaluated by recording the time when the membranes are broken into smaller pieces.

RESULTS AND DISCUSSION

Synthesis

A commercial PEEK was sulfonated using concentrated sulfuric acid (95–98%) as previously reported.[8,28] When the SPEEK

Figure 2. ^{1}H NMR of SPEEK in DMSO-d_6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction mixture was slowly poured into ice water while mixing with a mechanical stirrer, SPEEK fibers were obtained. However, possible impurities captured between the strands were not easily removed by simply washing with water. Alternatively, when the reaction mixture was poured into ice water under vigorous mixing with a glass rod, a SPEEK film was formed on the surface of the resulting aqueous solution (Figure 1). This procedure may produce more highly purified SPEEK due to better mixing between the reaction mixture and ice water.

Figure 2 shows the ^{1}H NMR spectrum of SPEEK dissolved in DMSO-d_6, where all of the aromatic protons appear at chemical shifts, similar to the reported data.[8,28] The DS, defined as the average number of sulfonic acid groups per repeat unit of SPEEK, was calculated based on the ^{1}H NMR spectrum. A peak at 7.5 ppm corresponds to Ha' near the sulfonic acid group, and its area relative to the other aromatic protons shows that the DS of the SPEEK is 0.80,[8,29] corresponding to an IEC of 2.27 mmol/g.

The Friedel–Craft alkylation reaction was performed using 1,6-dibromohexane and $AlCl_3$. Under these conditions, carbocations are formed and added to aromatic rings of SPEEK as electrophiles. The reaction likely occurs in the electron-rich aromatic rings without a carbonyl group (Scheme 1). The reaction proceeds during the drying step because the reaction does not occur in DMF solutions, probably due to the complex
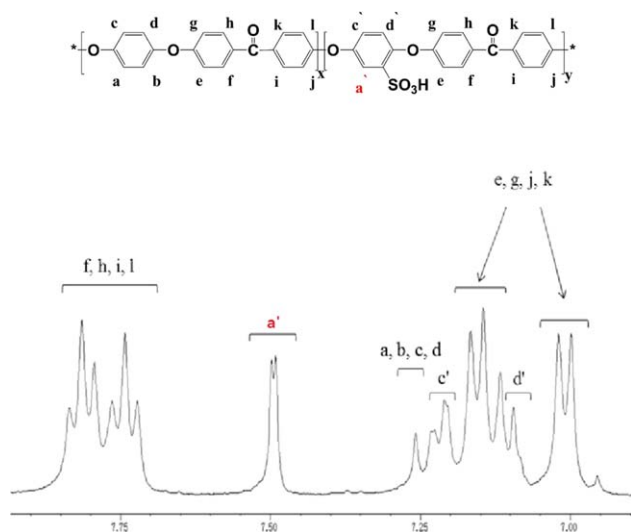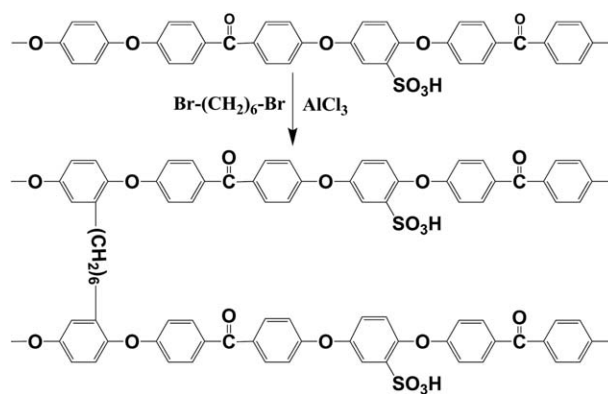

Scheme 1. Crosslinking reaction of SPEEK with 1,6-dibromohexane and $AlCl_3$.

Figure 3. Photograph of the as-prepared 3c-SPEEK. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. FT-IR spectra of SPEEK and 3c-SPEEK (KBr).

formation between $AlCl_3$ and DMF. Thus, compared to other reported electrophilic aromatic substitution reactions used for crosslinking of SPEEK, the current reaction is much simpler. The dried, crosslinked SPEEK (c-SPEEK) was obtained as a yellow-colored membrane (Figure 3).

The FT-IR spectra of the SPEEK and c-SPEEK are shown in Figure 4. The FT-IR spectrum of the SPEEK confirmed the presence of sulfonic acid groups (a broad band at 3400 cm^{-1} and two peaks at 1260 and 1020 cm^{-1}). Water molecules associated with sulfonyl groups also show the broad absorption peak near 3400 cm^{-1}. The c-SPEEK showed asymmetric and symmetric stretching vibrations of aliphatic chains in the range of 2800–2900 cm^{-1}, indicating that the aliphatic chains are covalently linked to the SPEEK molecules. The SPEEK membrane was dissolved in DMF at 80°C within 5 min, while the c-SPEEK membranes maintained their original shape, even after 1 day. This result indicates that the SPEEK molecules were successfully crosslinked. The gel fraction, the percentage of each c-SPEEK membrane remaining after dissolving in DMF, was calculated as 93–98% (Table I), which is much greater than those of poly (phenylene sulfide sulfone nitrile) membranes crosslinked using 4,4′-oxybis(benzoic acid).[9] This result indicates that our current crosslinking procedure is very efficient.

The measured IEC value of SPEEK was 2.28 mmol/g, which is in good agreement with the theoretical value (2.27 mmol/g) cal-
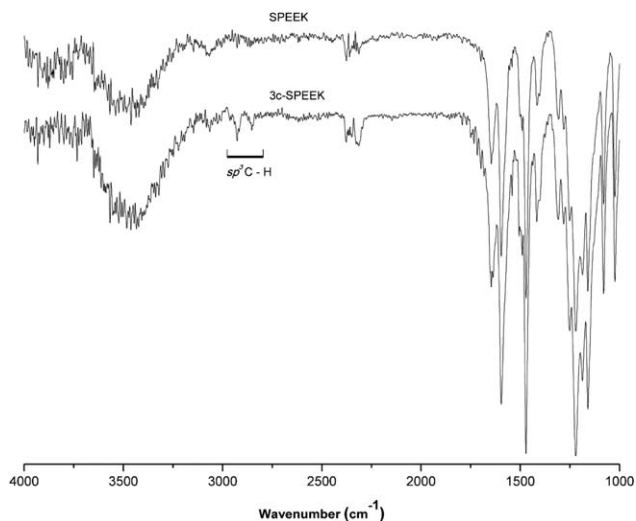
culated from the DS value (0.8). The measured IEC values of 3c-SPEEK, 4c-SPEEK, and 5c-SPEEK membranes were 2.09, 2.03, and 1.95, while their corresponding IEC values calculated based on their loadings are 2.25, 2.24, and 2.23, respectively. The deviations from the expected values are in the range of 8–13%, indicating that the measured IEC values are also in good agreement with the calculated values within the experimental errors.

Water Uptake and Dimensional Change

The water uptake of c-SPEEK membranes at 80°C decreased from 48% to 39% with increasing the crosslinker content (20% for Nafion 212). The dimensional change in the thickness of c-SPEEK membranes at 80°C also decreased from 27% to 17% with increasing the crosslinker content (16% for Nafion 212). Even though the water uptake and dimensional change of c-SPEEK membranes were somewhat greater than those of Nafion 212 membranes, the values are much smaller than those of SPEEK membranes (water uptake 2700%, dimensional change 73% at 80°C). The decreased water uptake and dimensional change of c-SPEEK membranes are primarily due to the crosslinking bonds that help to hold the polymer chains together. The decreased IEC of the membranes resulting from the inclusion of the hydrophobic crosslinker also contributed to the

Table I. IEC, Dimensional Change, Water Uptake, and Gel Fraction of SPEEK, 3c-SPEEK, 4c-SPEEK, 5c-SPEEK, and Nafion 212 Membranes

Sample	Crosslinker (wt %)	IEC (mmol/g)	Dimensional change (Δt, %)[a]		Water uptake (%)		Gel fraction[b] (%)
			25°C	80°C	25°C	80°C	
SPEEK	–	2.28	28	73	8	2700	–
3c-SPEEK	3	2.09	22	27	28	48	93
4c-SPEEK	4	2.03	14	22	25	42	96
5c-SPEEK	5	1.95	11	17	20	39	98
Nafion 212	–	–	7	18	16	20	–

[a] $\Delta t = t - t_o$ where t_o and t represent the thickness of each membrane before and after the swelling experiment for 24 h, respectively.
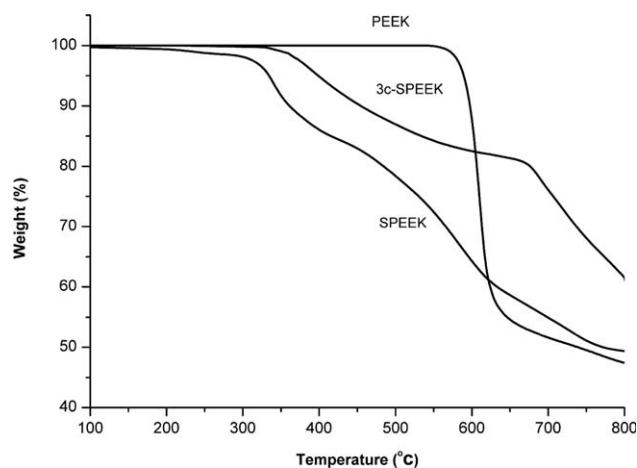[b] weight percentage of each c-SPEEK membrane remaining after dissolving in DMF for 24 h.

Figure 5. TGA curves of PEEK, SPEEK and 3c-SPEEK in a nitrogen atmosphere.
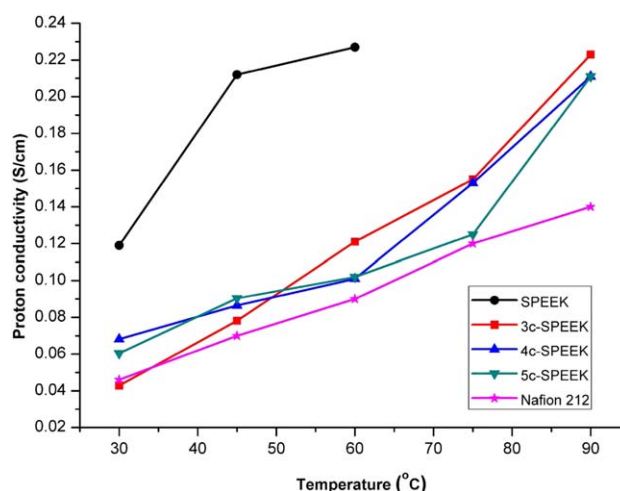

Figure 6. Proton conductivities of SPEEK, 3c-SPEEK, 4c-PEEK, 5c-SPEEK, and Nafion 212 membranes at different temperatures (RH 90%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decrease in water uptake and dimensional change of c-SPEEK membranes.

Thermal Stability

The thermogravimetric analysis (TGA) of PEEK, SPEEK, and c-SPEEK membranes was performed in a nitrogen atmosphere, and the results are shown in Figure 5. The PEEK showed one-step weight loss at 580°C, while the SPEEK exhibited two degradation steps in the ranges of 300–360°C and 450–625°C. The first and second weight losses are due to the degradation of sulfonic acid groups and SPEEK backbones, respectively.[8,28–31] The c-SPEEK membranes also showed a two-step degradation pattern, but their degradation ranges were 300–450°C and 500–680°C, indicating that the thermal stability of SPEEK membrane was improved via the crosslinking process.

Oxidative Stability

The oxidative stability of membranes was performed in the presence of Fenton's reagent at 80°C as an accelerated test, and the results are shown in Table II. The SPEEK membranes broke apart quickly (5 min), but the c-SPEEK membranes remained unchanged for a much longer time (210–257 min). This result indicates that the c-SPEEK membranes exhibited much better oxidative stability than the SPEEK membranes due to incorporation of crosslinking bonds between the polymer backbones. The breaking time increased as the crosslinker content increased, primarily due to increased crosslinking density and reduced water uptake.

Proton Conductivity and Methanol Permeability

The proton conductivity of the membranes was measured at various temperatures and 90% RH. The results are shown in Figure 6 and summarized in Table III. It should be noted that our SPEEK membranes showed a high proton conductivity (0.227 S/cm at 60°C and 90% RH) compared to other reported membranes with a DS of 0.76 (0.107 S/cm at 60°C and 100% RH).[6] The higher proton conductivity resulted from the higher purity of our SPEEK membranes (due to the better mixing procedure), even though the purity of the membranes was not measured. The membranes exhibited a substantial increase in proton conductivity with increasing temperature. This observation can be attributed to increased activity of protonated water molecules (hydronium ions, H_3O^+) and formation of more hydrogen-bonded cluster network channels resulting from the increased water uptake at higher temperatures.[8,10,31,32]

The proton conductivities of c-SPEEK membranes were less than that of SPEEK membranes, and decreased with increasing the crosslinker content, primarily due to the increased hydrophobic domain and reduced IEC by addition of the crosslinker in the membranes. The reduction in water uptake as a result of

Table II. Breaking Time of SPEEK, 3c-SPEEK, 4c-SPEEK, and 5c-SPEEK Membranes in the Presence of Fenton's Reagent at 80°C

Sample	Breaking time (min)
SPEEK	5
3c-SPEEK	210
4c-SPEEK	240
5c-SPEEK	257

Table III. Proton Conductivity and Methanol Permeability of SPEEK, 3c-SPEEK, 4c-SPEEK, 5c-SPEEK, and Nafion 212 Membranes

Sample	Proton conductivity at 90% RH (S/cm)		Methanol permeability at 35°C (cm²/S)
	30°C	90°C	
SPEEK	0.119	–	5.2×10^{-6}
3c-SPEEK	0.043	0.223	4.2×10^{-8}
4c-SPEEK	0.068	0.211	3.6×10^{-8}
5c-SPEEK	0.060	0.211	2.7×10^{-8}
Nafion 212	0.046	0.140	2.2×10^{-6}

Table IV. Tensile Property of SPEEK, 3c-SPEEK, 4c-SPEEK, 5c-SPEEK, and Nafion 212 Membranes

Sample	Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)	
	Dry	Wet	Dry	Wet	Dry	Wet
SPEEK	87	16	3.0	0.3	28	45
3-cSPEEK	122	30	4.0	0.6	23	143
4-cSPEEK	130	33	4.0	0.4	45	165
5-cSPEEK	111	30	4.0	0.5	15	140
Nafion 212	37	32	0.3	0.2	246	248

crosslinking is also considered to cause the decrease in proton conductivity. More importantly, all of the c-SPEEK membranes showed greater proton conductivities than Nafion 212 at high temperatures, likely due to the higher IEC of the c-SPEEK membranes. This result suggests that the proton-conducting channel may be reduced only slightly by the crosslinking process, possibly because the aliphatic crosslinker is highly flexible.

Methanol permeability is another important property for a direct methanol fuel cell and should be as low as possible to prevent methanol crossover.[5,33] The methanol permeability of our membranes was determined using an aqueous 1.0M methanol solution at 35°C, and the results are listed in Table III. The methanol permeability of SPEEK membranes (5.23×10^{-6} cm^2/s) was comparable to Nafion 212 (2.2×10^{-6} cm^2/s). The relatively high methanol permeability of SPEEK membranes is likely due to the high content of sulfonic acid groups, even though aromatic hydrocarbon polymers have lower methanol solubility than fluorinated polymers. However, the methanol permeability of SPEEK membranes was significantly reduced (by about two orders of magnitude) by the crosslinking procedure and decreased gradually with increased the crosslinker content. The c-SPEEK membranes showed much lower methanol permeability ($2.7–4.2 \times 10^{-8}$ cm^2/s) than Nafion 212 (2.0×10^{-6} cm^2/s). The significant reduction in the methanol permeability of c-SPEEK membranes compared to that of SPEEK membranes is primarily due to the more compact membrane structures caused by the crosslinking reaction.[5]

Mechanical Property

As shown in Table IV, the tensile strength and Young's modulus of c-SPEEK membranes increased with increasing the crosslinker content, which was greater than those of SPEEK and Nafion 212 membranes in both the dry and wet states. Alternatively, the membranes' elongation was slightly less than those of SPEEK and Nafion 212 membranes. The reduced elongation of c-SPEEK membranes compared to SPEEK membranes was due to the crosslinked networks between the polymer chains in the membranes. However, the elongations of c-SPEEK membranes are still slightly larger (140–165% in the wet state) than the crosslinked membranes prepared using a carboxyl-terminated benzimdazole trimer (10–17%, wet condition)[5] and BDM (maximum 6%, dry condition).[11] More importantly, the c-SPEEK

membranes exhibited greater tensile strength (111–130 MPa) than the reported crosslinked SPEEK membranes prepared using a carboxyl-terminated benzimdazole trimer (70–75 MPa) and BDM (39–40 MPa). The greater elongation of our membranes may be due to the crosslinker, which is a flexible alkyl chain. The 5c-SPEEK membranes exhibited reduced tensile strength and elongation at break compared to 3c-SPEEK and 4c-SPEEK membranes, which may be due to increased brittleness.

CONCLUSIONS

SPEEK with a DS of 0.8 was successfully crosslinked via a Friedel–Craft reaction using various amounts of 1,6-dibromohexane and AlCl$_3$ in DMF, and the resulting mixtures were cast to form c-SPEEK membranes. Compared to SPEEK membranes, c-SPEEK membranes exhibited significantly reduced methanol permeability but enhanced dimensional stability, thermal and chemical stability, and mechanical property with slight reduction in elongation. The proton conductivities of c-SPEEK membranes were slightly less than those of SPEEK membranes but were still greater than those of Nafion-212. Therefore, the current crosslinking method can be readily applicable to the crosslinking of various aromatic hydrocarbon polymer membranes.

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