Synthesis of 4,4'-Diacryloylphenyl Ether to Conveniently Crosslink Sulfonated Poly(ether ether ketone) Membranes via Electron Beam Irradiation

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Nafion membranes have been widely used in the fabrication of polymer electrolyte membrane fuel cells (PEMFCs) owing to their good thermal and chemical stabilities and high proton conductivities.^{1,2} However, these polymer membranes have some disadvantages such as high cost and decreased proton conductivity at elevated temperatures. Sulfonated aromatic hydrocarbon polymer membranes including poly(ether ether ketone) (PEEK), poly(ether sulfone), poly(ether ketone), poly(phosphazene), and polybenzimidazole have been actively investigated as alternatives to the commercial membranes owing to their good stability and high proton conductivity.^{3–6} These highly sulfonated membranes, however, usually have serious problems such as low-dimensional stability and mechanical strength, because of excess water uptake.

The problems of the highly sulfonated polymer membranes associated with water uptake can be overcome by crosslinking of the membranes. Among various crosslinking methods, $7-1\overline{4}$ the electron beam-induced crosslinking appears to be a very convenient method, because it does not require any additive and heating. Furthermore, not only the membrane surface, but also the membrane interior can be crosslinked. For the crosslinking of the sulfonated aromatic polymer membranes, the crosslinking agent should be acid-resistant, because protons move across the membranes during the operation of PEMFCs. Divinylbenzene, a nonhydrolyzable crosslinking agent, is commercially available; however, it is so highly reactive that it can undergo inhomogeneous and inefficient crosslinking with other comonomers.¹⁵ One approach to overcome this problem is to synthesize a new agent such as 1,6-bis(4vinylphenyl)hexane (BVPH), where two styrene molecules are separated by a hexane chain, but the synthesis of such compound was reported to be difficult.7,15

One possible alternative may be 4,4'-diacryloylphenyl ether (DAPE) for the crosslinking of such aromatic polymers because of the following characteristics: (1) it cannot be hydrolyzed under acidic conditions; (2) it can be easily

synthesized in a large quantity; and (3) it is a polar compound and readily dissolves in solutions of sulfonated polymers in highly polar organic solvents such as dimethylacetamide (DMAc). Nonpolar crosslinking agents such as divinylbenzene are not immediately dissolved in DMAc.

DAPE was reported to be synthesized in two steps.¹⁶ However, we synthesized the compound via one-step reaction with an isolation yield of 75%, and employed it for the preparation of crosslinked sulfonated PEEK (c-SPEEK) via electron beam irradiation. The properties of the resulting membranes were characterized with respect to the swelling ratio, water uptake, thermal stability, mechanical property, proton conductivity, oxidative stability, and methanol permeability.

Experimental

Materials. Sulfuric acid (95–98%), DMAc, diphenyl ether, acryloyl chloride, AlCl₃, and MgSO₄ were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA) NaCl, NaOH, CH₂Cl₂, and ethyl acetate were purchased from Samchun (Gyeonggi-do, Korea). Aqueous phenolphthalein (1%), and 1.0 N HCl, H₂O₂ (35%) solutions were purchased from Daejung (Gyeonggi-do, Korea). PEEK was purchased from Victrex[®] USA Inc. (West Conchohocken, PA, USA). All the chemicals were used as received without purification. Sulfonated PEEK. PEEK was sulfonated following the reported procedure.⁸ PEEK powder (35 g) was dissolved in concentrated sulfuric acid (500 mL) at 40 °C for 1 h. The temperature was increased to 60 °C and maintained for 2 h. The reaction mixture was cooled to 5 °C and then poured into water with stirring. The coagulated solid was washed several times with water and dried in a vacuum oven at 50 °C for 12 h and then at 70 °C for 24 h. The degree of sulfonation of the SPEEK was estimated to be 60% based on its ¹H NMR spectrum.⁹ Diphenyl ether (0.5 g, 4,4'-Diacryloylphenyl ether. 2.94 mmol), acryloyl chloride (0.8 g, 8.81 mmol), and CH₂Cl₂ (18 mL) were added in a two-neck flask under a nitrogen atmosphere and stirred for 30 min, followed by the addition of AlCl₃ (1.12 g, 8.41 mmol) at 0 °C. The mixture was allowed to react for 4 h, quenched by the addition of water (1 mL), and then extracted thrice with CH₂Cl₂. The combined organic phase was dried over anhydrous magnesium sulfate and concentrated using a rotary evaporator. The crude product was purified by column chromatography (hexane/ethyl acetate 10/1) to afford a white solid (0.61 g, 75%). ¹H-NMR (400 MHz, CDCl₃): δ 7.99–8.02 (d, 2H), 7.16–7.2 (t, 1H), 7.1–7.13 (d, 2H), 6.44–6.48 (d, 1H), 5.92–5.95 (d, 1H). Anal. Calcd. for C₁₆H₁₄O₃: C, 77.68; H, 5.07. Found: C, 77.65; H, 5.14.

c-SPEEK Membranes. The dried SPEEK was dissolved in DMAc (10 wt %), followed by the addition of DAPE. The solutions were cast on glass plates and then dried at 70 °C for 1 h. The casting membranes were irradiated with electron beams at a dose of 350 kGy with a dose rate of 6 kGy/min at room temperature (Korea Atomic Energy Research Institute, Advanced Radiation Technology Institute, Jeongup, Korea). The irradiated membranes were dried at 120 °C for 4 h. The c-SPEEK membranes were designated as 5c-SPEEK, 10c-SPEEK, 15c-SPEEK, and 20c-SPEEK, where the numbers indicate the wt % of DAPE with respect to the SPEEK.

Measurements. Gel fraction, ion-exchange capacity (IEC), dimensional stability, water uptake, proton conductivity, and methanol permeability of polymer membranes were determined following the reported procedures.¹⁷ The thermal and mechanical properties were also measured following the reported procedures, using a Q-50 thermogravimetric analyzer (TA instruments, New Castle, DE, USA) and an INSTRON Series IX Universal Testing System Model 4400 (Instron Co. Norwood, MA, USA), respectively.

Results and Discussion

DAPE was synthesized from diphenyl ether and acryloyl chloride via a simple one-step Friedel-Craft acylation in 75% yield. Its proton NMR spectrum (Figure 1) along with the elemental analysis data confirmed that DAPE was successfully synthesized with high purity. DAPE is well soluble in polar aprotic



solvents such as DMAc and dimethylformamide. As mentioned earlier, the solubility characteristics are very important for the crosslinking of SPPEK, because nonpolar hydrocarbon crosslinking agents are not readily dissolved in highly polar solvents that are required to dissolve highly polar SPEEK.

A commercial PEEK was sulfonated to obtain the SPEEK, following the reported procedure.⁸ The degree of sulfonation (DS) of the SPEEK, defined as the average number of sulfonic acid groups per repeat unit of SPEEK, was estimated to be 60% based on its ¹H NMR spectrum.⁹ The gel fractions of the membranes were determined from the difference in the weights before and after dissolving in DMAc. The c-SPEEK membranes prepared by irradiation at 400 kGy were brittle, and thereafter all the SPEEK membranes were irradiated at a constant dose of 350 kGy. When PEEK membranes without DAPE were irradiated with electron beam, the resulting membranes were completely dissolved in DMAc, indicating that the SPEEK chains are not effectively crosslinked in the absence of the crosslinking agent. As expected, the gel fraction of the c-SPEEK membranes gradually increased from 96 to 98% with increasing DAPE loading from 5 to 20 wt %, because of a higher degree of crosslinking at higher loadings of DAPE. The gel fractions of the c-SPEEK membranes (96-98%) are similar to those (93-98%) of the crosslinked membranes (DS: 55%, BVPH loading: 5-15 wt %) prepared using BVPH under similar conditions.⁷ DAPE is expected to crosslink polymer chains via radical process. We proposed one of possible mechanisms for crosslinking SPEEK with 4-vinylbenzyl chloride on electron beam irradiation.¹⁷ A similar mechanism may also occur in this system.

The IEC of the membranes decreased with increasing DAPE loading, because the addition of DAPE decreased the weight fraction of the sulfonic acid groups in the membranes. The experimentally measured IEC value of the SPEEK membrane (1.69 mmol/g) is very close to the theoretical value (1.71 mmol/g), whereas the experimental IEC values of all the c-SPEEK membranes were smaller than their corresponding calculated values, as listed in Table 1. Perhaps, this discrepancy resulted from incomplete ion exchange between —SO₃H groups in the c-SPEEK membranes and NaCl dissolved in the aqueous solution, probably because it may be more difficult for Na⁺ ions to diffuse into —SO₃H groups for ion exchange within the more highly crosslinked membranes.¹⁷

As expected, the dimensional change and water uptake of the c-SPEEK membranes decreased with increasing DAPE

Table 1. IEC values of SPEEK and c-SPEEK membranes.

	IEC (m	mol/g)	
Sample	Calculated	Measured	
SPEEK	1.71	1.69	
5c-SPEEK	1.63	1.43	
10c-SPEEK	1.56	1.41	
15c-SPEEK	1.48	1.32	
20c-SPEEK	1.43	1.17	

loading, owing to a higher degree of crosslinking (Table 2). For example, the crosslinking with 15 wt % DAPE reduced the increment in length of the membranes from 18 to 2% and water uptake from 28 to 11%. It was reported that the crosslinking SPEEK membranes (DS: 55%) with 15 wt % BVPH reduced the increment in length from 18 to 4% and water uptake from 28 to 13%.⁷ This comparison indicates that DAPE improves the dimensional stability of the membranes to the almost same degree as BVPH.

As shown in Figure 2, the SPEEK membrane exhibited a two-step thermal degradation, a typical behavior of most SPEEK membranes.^{18,19} The first weight loss in the range of 270–380 °C and the second weight loss above 430 °C were attributed to the elimination of the sulfonic acid groups and the decomposition of the polymer main chains, respectively. All the c-SPEEK membranes exhibited similar degradation patterns as the SPEEK membrane; however, their degradation onset temperatures were slightly lower than that of the original SPEEK membrane. The lowered degradation temperatures may be because of the unreacted or partially reacted DAPE. If some polymer chains had been cleaved into shorter chains during the electron beam irradiation process, the resulting

Table 2. Dimensional stability and water uptake of membranes.

$\Delta l^{a}\left(\% ight)$		Δt^b	(%)	Water uptake (%)	
25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
18	25	25	36	28	65
4	12	13	28	14	40
3	10	10	26	12	35
2	9	9	17	11	21
1	5	8	13	10	15
5	20	7	16	16	20
	$ \frac{\Delta l^a}{25 ^{\circ}\mathrm{C}} $ 18 4 3 2 1 5	$ \frac{\Delta l^a (\%)}{25 ^{\circ}\text{C}} 80 ^{\circ}\text{C}}{18} 25 \\ 4 12 \\ 3 10 \\ 2 9 \\ 1 5 \\ 5 20 $	$ \frac{\Delta l^{a} (\%)}{25 ^{\circ} \text{C}} \frac{80 ^{\circ} \text{C}}{80 ^{\circ} \text{C}} \frac{25 ^{\circ} \text{C}}{25 ^{\circ} \text{C}} $ $ 18 25 25 $ $ 4 12 13 $ $ 3 10 10 $ $ 2 9 9 $ $ 1 5 8 $ $ 5 20 7 $	$\begin{array}{c cccc} & & & & & & & & \\ \hline \Delta l^a \left(\%\right) & & & & & & & \\ \hline 25 \ ^\circ C & 80 \ ^\circ C & 25 \ ^\circ C & 80 \ ^\circ C & \\ \hline 18 & 25 & 25 & 36 & \\ \hline 4 & 12 & 13 & 28 & \\ 3 & 10 & 10 & 26 & \\ 2 & 9 & 9 & 17 & \\ 1 & 5 & 8 & 13 & \\ 5 & 20 & 7 & 16 & \\ \hline \end{array}$	Δl^a (%) Δt^b (%) uptak 25 °C 80 °C 25 °C 80 °C 25 °C 18 25 25 36 28 4 12 13 28 14 3 10 10 26 12 2 9 9 17 11 1 5 8 13 10 5 20 7 16 16

^{*a*} Swelling ratio in length = $(l - l_{dry})/l_{dry} \times 100$ where l_{dry} and *l* represent the length of the membranes before and after the swelling experiment, respectively.

^b Swelling ratio in thickness = $(t - t_{dry})/t_{dry} \times 100$ where t_0 and t represent the thickness of the membranes before and after the swelling experiment, respectively.



Figure 2. TGA curves of SPEEK and c-SPEEK membranes.

small polymer molecules would also contribute to the slightly decreased thermal stability of the c-SPEEK membranes.¹⁷

As shown in Table 3, the tensile strength and Young's modulus of the c-SPEEK membranes gradually increased with increasing DAPE loading up to 15 wt % and decreased thereafter (increment: 62% in tensile strength, 77% in Young's modulus). In contrast, the elongation at break decreased significantly from 130 to 15% with increasing DAPE loading up to 15 wt % (reduction: 88%). The increased tensile strengths and Young's moduli at high loadings of DAPE are because of the increased compactness of the membranes. However, the decreased tensile strength and Young's modulus of the 20c-SPEEK membrane probably resulted from its brittleness, because of a high degree of crosslinking. However, the crosslinking of SPEEK membranes with 15 wt % BVPH was reported to slightly increase the tensile strength and modulus of the membranes (increment: 13% in tensile strength, 10% in Young's modulus) but reduce the elongation at break from 47 to 18% (reduction: 62%).⁷ This comparison indicates that DAPE increases the tensile strength and Young's modulus more effectively with more reduction in the elongation than BVPH, probably due to the difference in the chemical structures of BVPH and DAPE where DAPE is shorter and more rigid than BVPH.

The proton conductivity of the membranes increased with increasing temperature as shown in Figure 3. Even though the SPEEK membrane exhibited higher proton conductivity than Nafion 212 at various temperatures up to 75 °C, its proton conductivity could not be measured at 90 °C owing to its excessive water uptake and swelling. In contrast, the proton conductivities of the c-SPEEK membranes were lower than that of SPEEK and decreased with increasing DAPE loading, because of the decrease in the water uptake and IEC value as a result of the crosslinking. The decreased proton conductivities of the c-SPEEK membranes may also result from the decrease in the free volume, and subsequently narrowed water channels within the polymer membranes.¹⁴ However, notably, the proton conductivities of the c-SPEEK membranes did not decrease too much from that of the original SPEEK membrane and were comparable to that of Nafion 212. A similar result was also reported for the BVPH-derived membranes.

The membranes were immersed in Fenton's reagent (2 ppm $FeSO_4 + 2\% H_2O_2$) at 80 °C, and the breaking times of the

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	Tensile strength	Young's modulus	Elongation at
Sample	(MPa)	(GPa)	break (%)
SPEEK	22.0	0.66	130
5c-SPEEK	33.5	1.09	21
10c-SPEEK	35.5	1.15	18
15c-SPEEK	35.7	1.17	15
20c-SPEEK	26.5	1.05	14
Nafion212	33.3	0.19	240



Figure 3. Proton conductivities of SPEEK and c-SPEEK membranes.

resulting membranes were assessed by the naked eye. The original SPEEK membrane was broken apart into pieces within 7 min, but the c-SPEEK membranes became so highly oxidation-resistant that the breaking times of the c-SPEEK membranes increased from 208 to 272 min as the DAPE loading increased from 5 to 15 wt % (Table 4). This experimental data indicate that the oxidative stability of the SPEEK membrane increases with increasing DAPE loading owing to a higher degree of crosslinking of the membranes are lower than those of the BVPH-derived membranes (breaking time: 33–38 h), probably due to the radical-sensitive carbonyl groups of DAPE moiety.²⁰

The methanol permeabilities of the membranes were measured in an aqueous 3.0 M methanol solution at 35 °C, following the reported procedure.¹⁷ The methanol permeability of the original SPEEK membrane (2.8×10^{-6} cm²/s) was close to that of Nafion 212, because of the high content of the sulfonic acid group. However, as the DAPE loading increased from 5 to 15%, the methanol permeability decreased progressively from 1.5×10^{-7} to 3.8×10^{-8} cm²/s, because of more compact membrane structures. The degree of reduction in the methanol permeability is close to that of the BVPH-derived membranes (1.7×10^{-8} cm²/s).⁷

In summary, DAPE was successfully synthesized in a moderately high isolated yield and used for the crosslinking of the SPEEK membranes via electron beam irradiation. The c-SPEEK membranes exhibited significantly improved dimensional and oxidative stability, methanol permeability, and mechanical strength with the decrease in the elongation at break. The proton conductivities of the c-SPEEK membranes were lower than those of the SPEEK membrane, but were still comparable to that of Nafion 212. This study indicates that DAPE can be very easily synthesized in a large quantity and conveniently used as a nonhydrolizable crosslinking agent for the preparation of crosslinked ionic aromatic polymer membranes.

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Sample	Breaking time (min)	Methanol permeability (cm ² /s)
SPEEK	7	2.8×10^{-6}
5c-SPEEK	208	1.5×10^{-7}
10c-SPEEK	233	5.3×10^{-8}
15c-SPEEK	272	3.8×10^{-8}
20c-SPEEK	310	1.0×10^{-8}
Nafion 212	—	2.2×10^{-6}

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