Sulfonated Poly(aryl ether ketone) Random Copolymers Having Crosslinking Structure for Proton Exchange Membrane of Fuel Cell

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We have succeeded in developing a new methodology for proton exchange membrane (PEM) of direct methanol fuel cell (DMFC), which stemmed formation of a crosslinking structure by UV irradiation to sulfonated poly (aryl ether ketone) (PAEK) copolymer. A new class of the aromatic PAEKs with pendant sulfonate groups and methyl groups have been prepared by a direct aromatic nucleophilic substitution polycondensation reaction of 3,3'-disulfonated-4,4'-difluorobenzophenone (DSDFBP), 4,4'-difluorobenzophenone (DFBP) and the biphenols that have methyl groups. The polymerization quantitatively proceeded to form a high intrinsic viscosity of copolymer. Membranes having high mechanical strength were successfully obtained from the copolymers of DSDFBP, DFBP and the biphenols that have methyl groups including tetramethyl bisphenol A (TMBPA), tetramethyl bisphenol F (TMBPF) and tetramethyl biphenol (TMBP). The ketone of benzophenone group and the methyl group in the repeating structure unit of these PAEKs were easily crosslinked by UV irradiation and induced a crosslinked structure that improved their methanol blocking properties drastically. The membrane of crosslinking copolymer, DSDFBP/DFBP/TMBPF = 5/5/10 mole ratio (**F1**), was stable at 240 °C in air and showed the high proton conductivity at 90 °C of 0.23 S/cm and the low methanol permeation rate at 25 °C of 5.5 $\mu\text{mol}/\text{cm}^2/\text{min}$. This proton conductivity and methanol permeability are comparable to and half of the values of fluorinated copolymer Nafion112[®] that is known as the representative material of a PEM of DMFC respectively. These new copolymers, which have proton conductive sites and crosslinking structures, are candidates as new polymeric electrolyte materials for proton exchange membrane fuel cells, especially for DMFCs.

KEY WORDS: Sulfonated Poly(aryl ether ketone) / Crosslink / Proton Exchange Membrane / Fuel Cell /

The large interest in using polymer electrolyte membrane fuel cells (PEMFCs) as power sources of vehicles or portable applications has been greatly promoted these years. Among many kinds of PEMFCs, direct methanol fuel cells (DMFCs) are promising candidates for portable power sources and transport applications because they don't require fuel process equipment (such as reformers or catalytic burners) and can be operated at room temperature.

A DMFC consists of a proton exchange membrane (PEM) sandwiched between an anode and a cathode. The PEM for DMFC requires three major functions, as a proton conductor, as a fuel barrier and as a mechanical separator between the two electrodes. Nafion[®] that is known as a superior membrane for PEMFC has high proton conductivity and suitable mechanical strength. However, methanol goes through the Nafion[®] membrane, so that a large amount of methanol is lost in the DMFC. This is so-called "methanol crossover." To improve DMFC performance, the high methanol blocking property is required while the proton conductivity, the thermo oxidation stability and the mechanical strength are maintained. Methanol permeates through the ionic channels of membranes and the size of these channels increases as swelling of the membrane increases. Thus the easiness of swelling of the membrane caused permeation of methanol easily. Therefore, it becomes necessary to suppress the swelling of membrane by methanol to get the low methanol permeability. In general, suppressing the

swelling of membrane is a cause of reduction of the proton conductivity. So, the balance of the value of methanol permeate with the value of proton conductivity is important.

Several attempts have been made to limit the swelling by pore-filling method or crosslinking method. Yamaguchi¹ investigated pore-filling electrolyte membranes for use as PEM in DMFC. Although the membranes having pores filled with a polymer electrolyte can control methanol permeation, non-conductivity of the porous substrate caused decreasing of proton conductivity. For an example of crosslinking method, Yen² reported the crosslinking of sulfonate groups among themselves enhanced protection of methanol crossover. However, the decreasing of sulfonate groups caused decreasing of proton conductivity, and the chemical reaction of sulfonate groups was caused voids in the membrane.³ Moreover, Yoshida⁴ proposed crosslinking of Nafion[®] by radioactive rays. This method was effective to protect methanol crossover, but radioactive rays gave damages to the membrane.

Economical and commercially viable engineering polymers have been focused on as PEMs for fuel cells because of their high thermo oxidation stability and high solvent resistance. Concerning synthetic methods of sulfonated polymers, many groups have been investigating postsulfonated aromatic polymers. The postsulfonation of polymers has been accomplished using sulfonation agents such as chlorosulfonic acid,⁵ sulfonic acid⁶⁻⁸ and sulfur trioxide/triethyl phosphate complexes⁹ etc.

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However, in the case of the postsulfonation of polymers, undesirable chain scission, branching and crosslinking can occur with chlorosulfonic acid, and also decrease in the molecular weight and partial gelation are observed with sulfonic acid. In order to control the positions and the quantity of sulfonate groups, the monomer sulfonation and the subsequent controlled copolymerization are quite suitable. Wang¹⁰ reported the sulfonation of 4,4'-difluorobenzophenone (DFBP) with copolymerization of 3,3'-disulfonated-4,4'-difluorobenzophenone (DSDFBP), DFBP and bisphenol A (BPA) to generate copolymer with up to 40 mol % DSDFBP. This approach allows for the much better control of the position and the degree of sulfonation.

We have designed a new approach, whose key step, our own technology, is the formation of a crosslinking structure by UV irradiation to sulfonated poly (aryl ether ketone) (PAEK) copolymer shown in Figure 1. The technology was reported as the method for the introduction of a crosslinked structure to the PAEK having a benzophenone group and an alkyl group in the repeating structure unit by Goto.¹¹ We anticipated that the most suitable balance of methanol permeation and proton conductivity can be achieved through introduction of crosslinking by UV irradiation and control of the position and quantity of sulfonated groups. We have chosen the PAEK having methyl groups and pendant sulfoate groups in the repeating structure unit because of in particular excellent chemical property of PAEK. This repeating structure unit has the benzophenone groups and methyl groups readily crosslinkable by UV irradiation and the degree of sulfonation is controlled by quantity of sulfonated monomer. The sulfonation extent and the degree of crosslinking were carefully controlled so as to maximize the proton conductivity and to minimize the methanol crossover. In this paper, the effects of the repeating structures and the degree of crosslinking are investigated by assessing performances of membranes and characters of their structures.

EXPERIMENTAL

Materials

50% Fuming sulfuric acid, sodium hydroxide (NaOH), sodium chloride (NaCl) and ethanol were obtained from Wako Pure Chemical Industries, Ltd.

4,4'-Difluorobenzophenone (DFBP), tetramethyl bisphenol A (TMBPA), tetramethyl bisphenol F (TMBPF) and tetramethyl biphenol (TMBP) were obtained from Tokyo Kasei Industries, Ltd. (TCI) were used as received (Figure 2). Anhydrous dimethylsulfoxide (DMSO) and toluene were obtained from Wako Pure Chemical Industries, Ltd. Potassium carbonate was obtained from Tokuyama Co., Ltd., and dried at 150 °C for 12 h under nitrogen.

Synthesis of Disodium Salt of DSDFBP

A modified procedure from previously reported approaches¹⁰ was developed and used for the synthesis of DSDFBP from DFBP. A typical procedure is as follows:

Figure 1. UV crosslinking of poly (aryl ether ketone) having benzophenone and alkyl group.

Figure 2. Structures of biphenols.

DFBP (114.56 g, 0.525 mol) was dissolved in 50% fuming sulfuric acid (210 mL) in a three-necked flask equipped with a mechanical stirrer, a thermometer, a condenser tube and a nitrogen inlet/outlet. The solution was heated at 100 °C for 12 h. The resultant was added to ice water (1000 g) and neutralized with NaOH (210 g). Next, NaCl (210 g) was added and the mixture was heated to obtain a clear solution. After cooling, the resulting suspension was allowed to stand over night. The white precipitated crystals were filtered out and then deionized water (400 mL) and ethanol (400 mL) were added. The mixture was heated, dissolved, and air-cooled for carrying out the recrystallization. The precipitated crystals were filtered out and then dried at 100 °C for 6 h to obtain white crystals of the disodium salt of DSDFBP (yield of 70%), which was identified with ¹H-NMR spectroscopy, and the atomic composition was confirmed by elemental analysis.

Synthesis of Sulfonated Poly (aryl ether ketone) Copolymers with DSDFBP

In this study, we used three different types of biphenols, TMBPA, TMBPF and TMBP. Even though the reactivities of biphenols were different, the copolymerization procedure was very useful as the following description. A typical copolymerization for all the sulfonated copolymers is described by the A4 series.

First, DFBP (10.91 g, 0.050 mol), salt-formed DSDFBP (21.11 g, 0.050 mol), TMBPA (28.44 g, 0.100 mol) and potassium carbonate (17.30 g, 0.125 mol) were added to a four-necked flask equipped with an overhead mechanical stirrer, a nitrogen inlet, and a Dean-Stark trap. DMSO (250 mL) was introduced to afford a 20% (w/v) solid concentration. Toluene (100 mL, usually DMSO/toluene = 25/10 (v/v)) was used as the azeotroping agent. The reaction mixture was refluxed at 140 °C for 8 h to remove the water generated by proceeding copolymerization reaction. The temperature was slowly raised to 160 °C by the controlled removal of the toluene. The reaction was allowed to proceed for 8–12 h, during which time the solution became very viscous. The solution was cooled to 100 °C and diluted with enough DMSO to allow easier filtering. After filtering with celite to remove the salts, the copolymer was isolated by coagulation in stirred toluene and then decanted. The precipitated copolymer was washed several times with acetone to completely remove the DMSO. Finally, it was dried at 50 °C for 8 h, and then at 150 °C for 4 h under nitrogen.

The copolymers with other biphenols and compositions were prepared using similar procedures. And the sulfonation degree of polymers could be controlled easily by changing the ratio of DFBP and salt-formed DSDFBP. The sulfonation degree of polymers was represented by equivalent weight (EW, g/mol) value of their membranes.

Membrane Preparation

The solution of the copolymer in DMSO to afford 10–20% transparent solution was prepared. Salt-formed membranes were prepared by casting of the solutions onto clean glass

substrates, and heated to 200 °C at the rate of 40 °C/h and then dried at 200 °C for 4 h under nitrogen. The thickness of the final membranes was controlled between 40 and 80 μm.

UV Irradiation

The UV irradiation was carried out with up to 30000 mJ/cm² light using a metal halide lamp. The crosslinking reactions were confirmed indirectly by the decrease in the absorption strength of a carbonyl group in the IR measurement.

Acidification of Sulfonated Copolymer Membranes

The sulfonated polymer membranes in the salt sulfonate form were converted into the corresponding free sulfonic acid form by immersion in 1 mol/l sulfuric acid for 24 h and followed by extraction with distilled water for 24 h.

The acidified membranes were dried at 100 °C for 2 h and at 150 °C for 2 h under nitrogen. That sulfuric acid was not remained in membrane was confirmed by accordance with the measured EW values and the calculated EW values of membranes.

Characterization

¹H-NMR spectrum of the DSDFBP was recorded for structural characterization. The data was collected with a JEOL GSX FT NMR Spectrometer using 10% solution (w/v) in D₂O at room temperature. The monomer purity was analyzed by NMR spectroscopy.

The EW of the membrane was estimated by acid-base titration. Pieces of each protonated membranes were placed in 1 mol/l NaCl solutions for 24 h. The solution was then titrated with 0.01 mol/l NaOH solution using phenolphthalein as indicator. Triple titrations of each membrane were made in order to ensure accurate data. The EW value was calculated from the titration results as the ratio of the number of mole of consumed NaOH to the weight of dried membrane sample. The EW value was estimated as:

$$EW = W_{\text{dry}} / (0.01 \times (m/1000)) \text{ g/mol} \quad (1)$$

where W_{dry} is the weight (g) of dry membrane, 0.01 is the molar concentration of NaOH solution (mol/l) and m is the titration quantity (ml).

Water Uptake and Methanol Dissolution

The water uptake and methanol dissolution were measured about membranes of all the sulfonated PAEKs in free sulfonic acid forms. The membranes were first thoroughly dried at 100 °C for 2 h and at 150 °C for 2 h under nitrogen to a constant weight, which was then recorded. The dried membrane was then immersed in distilled water or methanol at 25 °C and periodically weighed on an analytical balance until a constant weight was obtained. Typically, the apparent equilibrium of water absorption or methanol dissolution occurred within 24 h. The water uptake is reported as a percentage and estimated as follows:

$$\text{Water uptake} = (W_{\text{wet}} - W_{\text{dry}}) / (W_{\text{dry}}) \times 100\% \quad (2)$$

where W_{wet} and W_{dry} are the weights of the wet and the dry membranes, respectively. The methanol dissolution is reported as a percentage and determined as follows:

$$\text{Methanol dissolution} = (W_1 - W_2)/(W_1) \times 100\% \quad (3)$$

where W_1 and W_2 are the weights of the membranes before and after soaking in methanol, respectively.

Thermogravimetical Analysis (TGA)

The thermogravimetical behavior of both the salt-formed and the acid-formed copolymers was performed using a TGA-50 (manufactured by Shimadzu Corporation). The samples were pieces of thin membranes and had a weight total of 10–15 mg. The samples were evaluated over the range of 30–900 °C at the heating rate of 10 °C/min in air.

Proton Conductivity

Membranes of sulfonated PAEKs were cut into a 5 mm width and a 40 mm length, then positioned on a PTFE folder and four electrodes were pressure-joined to measure the resistivity from a circular arc obtained by the AC impedance method using the 4 terminal method. The interval between the voltage terminals was 20 mm. The impedance was measured using an LCR meter (3532, a product of Hioki E.E. Corporation). The temperature was held at 90 °C while an electrode-connected sample was put in a thermostatic chamber made of aluminum block to measure the conductivity. The humidity was supplied into the thermostatic chamber at atmospheric pressure by flowing vapor generated by heating the distilled water at the temperature of the thermostatic chamber +5 °C with a vapor generator. Furthermore, the membrane thickness was measured with a micrometer in the dried form.

Methanol Permeation Rate

At room temperature, the distilled water and an 1 mol/l methanol aqueous solution came into contact with each other *via* the sulfonated PAEKs membrane having a diameter of 23 mm to measure the concentration change in methanol of the distilled water side using a refractive index meter (RID-6A, manufactured by Shimadzu Corporation). The methanol permeation rate was calculated at the membrane thickness of 50 µm from the slope of the straight line of the increase in the obtained methanol concentrations.

Hot Water Test¹²

The stability toward water of crosslinking structures was examined by the hot water test. **F2** membrane was soaked in distilled water at 85 °C for 8, 15, 30 and 50 h. The stability was evaluated by comparing the values of before and after the test about its weight change, water uptake and proton conductivity. The weight change is reported as a percentage and estimated as follows:

$$\text{Weight change} = (W_{\text{before}} - W_{\text{after}})/(W_{\text{before}}) \times 100\% \quad (4)$$

where W_{before} and W_{after} are the dried weights of the before and the after the hot water test.

Figure 3. Synthesis of disodium salts of DSDFBP.

RESULTS AND DISCUSSION

Monomer Synthesis

A monomer, DSDFBP, was synthesized by direct sulfonation of DFBP in fuming sulfuric acid as shown in Figure 3. Salt-formed DSDFBP with high purity was obtained in a good yield (70%) after recrystallizing from a methanol/water mixture. The sulfonation occurred at the 3,3'-positions of the phenyl-rings because these positions are more active than others. The ¹H-NMR spectrum and the element analysis of salt-formed DSDFB confirmed the chemical structure of the product.

Copolymer Synthesis

The polycondensation reaction is depicted in Figure 4. The PEM of DMFC requires a high molecular weight for flexibility and high strength. Careful dehydration with toluene was important for the high molecular weight, which was recognized by high intrinsic viscosity. High temperature was required with the less reactive sterically hindered DSDFBP monomer. This polymerization proceeded smoothly and the procedure has been successfully applied to use with TMBPF and TMBP.

The intrinsic viscosities of the sulfonated PAEK copolymers, the calculated EW values and the observed EW values are shown in Table I. The intrinsic viscosity obtained 0.8–1.7 dl/g and were high enough to make membranes. Their intrinsic viscosities were not affected by biphenol structures and degrees of sulfonation. The mole ratio of DFBP and DSDFBP can adjust the desired EW value. The observed EW value accorded with the calculated EW value well. The agreement of the observed EW value and the calculated EW value proved that sulfuric acid used for acidification of membrane did not remain in membranes. In addition, this agreement shows that the sulfonic acid sodium groups are stable during the reaction at 160 °C and the dry at 200 °C.

Figure 4. Synthesis of random TMBPA-based sulfonated poly(aryl ether ketone) copolymer.

Table I. Sample codes and structures of poly(aryl ether ketone)s

Sample Codes	Monomer composition	η_{inh}^a (dl/g)	EW ^b (g/mol)	EW ^c (g/mol)
A1	DSDFBP/DFBP/TMBPA = 10/0/10	0.9	311	—
A2	DSDFBP/DFBP/TMBPA = 9/1/10	0.8	335	—
A3	DSDFBP/DFBP/TMBPA = 8/2/10	0.8	369	—
A4	DSDFBP/DFBP/TMBPA = 5/5/10	0.8	543	—
A5	DSDFBP/DFBP/TMBPA = 3.5/6.5/10	0.8	741	765
F1	DSDFBP/DFBP/TMBPF = 5/5/10	1.1	514	—
F2	DSDFBP/DFBP/TMBPF = 3.5/6.5/10	1.1	701	742
B1	DSDFBP/DFBP/TMBP = 4.5/5.5/10	1.7	547	—
B2	DSDFBP/DFBP/TMBP = 3/7/10	1.3	781	805

^aInherent viscosity was measured at a concentration of 0.5% in DMSO at 35 °C. ^bCalculated value. ^cDetermined by acid-base titration with NaOH solution.

Membrane Preparation and Characterization

UV Irradiation. The flexible and durable membranes were crosslinked by UV irradiation to improve not only methanol permeability but also solvent dissolution. As shown in Figure 1, a radical on the benzophenone generated at the first stage of an irradiation with UV pulls out hydrogen from a methyl group. Subsequently, the crosslinking is carried out by dimerization of a benzyl radical, a coupling reaction of the benzyl radical with an alcohole carbon radical or dimerization of an alcohole carbon radical. These crosslinking reactions were confirmed indirectly by the decrease in the absorption strength of a carbonyl group in the IR measurement. The UV irradiation caused the drying and the shrinkage of a membrane, therefore UV had to be irradiated in 1000 mJ/cm² repeatedly to prevent transformation of a membrane. Figure 5 shows the absorption strength change of carbonyl groups of **A4** membrane by the UV irradiation. This figure shows that as the quantity of the UV irradiation increased, the absorption strength of carbonyl groups decreased. About half of carbonyl groups can finally contribute to the crosslinking reaction.

The absorption strength change of carbonyl groups of **A4**, **F1** and **B1** membranes, which have similar EW values, is shown in Figure 6. This figure shows that the crosslinking degree of **A4**, **F1** and **B1** membranes were different by each

Figure 5. UV irradiation dependence of absorption of carbonyl group of **A4**.

Figure 6. UV irradiation dependence of absorption of carbonyl group of sulfonated PAEKs.

and the crosslinking degree of **F1** membrane was the highest. The IR absorption spectra of the methyl groups and the carbonyl groups in **A4**, **F1** and **B1** membranes are shown in Figures 7–9, respectively. As the crosslinking system is shown in Figure 1, the change of IR absorption strengths of the methyl groups and the carbonyl groups should be at the same rate. However, the decrease rate of absorption of the carbonyl groups was faster than that of the methyl groups for **F1** membrane. This difference shows that the carbonyl groups crosslinked with other unit except the methyl group, the methylene group of the **F1** structure. The crosslinking degree of **F1** was the highest in these three structures because **F1** structure has two crosslinkable units that are the methyl groups and the methylene groups.

TGA

The thermo-oxidative stability of the crosslinked membranes was measured by the weight reduction temperature in air, using TGA at heating rate of 10 °C/min. The TGA result of **A4** is shown in Figure 10. This figure shows that the weight didn't change until 240 °C apart from decrease of water, which was taken in membrane as moisture. Moreover, the result of using a TGA coupled to mass spectrometry (MS) showed that sulfone acid groups came off at first at about 250 °C. The thermo-oxidative stabilities of other polymers were similar with **A4**. Each T_{d1} are shown in Tables II and III. The thermo-

Figure 7. UV irradiation dependence of absorption of methyl group and carbonyl group of A4.

Figure 8. UV irradiation dependence of absorption of methyl group and carbonyl group of F1.

Figure 9. UV irradiation dependence of absorption of methyl group and carbonyl group of B1.

oxidative stabilities of A4 and the other polymers were sufficient to use in the DMFC. The UV irradiation didn't decrease stability of the membranes.

Water Uptake and Methanol Dissolution

Measuring the water uptakes of PEMs is very important,

Figure 10. TGA thermogram of crosslinked A4 membrane in air at 10 °C/min.

Table II. UV irradiation dependence of properties of A4

UV irradiation (mJ/cm ²)	Water uptake ^a (%)	Proton conductivity ^b (S/cm)	Methanol permeation rate ^c (μmol/cm ² /min)	Methanol dissolution ^d (%)	<i>T</i> _{d1} ^e (°C)
1000	45	0.15	6.6	73	245
5000	43	0.17	5.3	46	242
10000	64	0.15	4.7	37	239
15000	35	0.14	5.2	11	239
30000	31	—	—	11	—

^aAt 25 °C. ^bAt 90 °C and under humidification (100% RH). ^cAt 25 °C and with 1 mol/l methanol. ^dAt 25 °C and in 100% methanol. ^e1% weight loss temperature measured by TGA in air at 10 °C/min heating rate.

Table III. Properties of sulfonated PAEKs after 15000 mJ/cm² UV irradiation

Sample Code	EW ^a (g/mol)	Water uptake ^b (%)	Proton conductivity ^c (S/cm)	Methanol permeation rate ^d (μmol/cm ² /min)	Methanol dissolution ^e (%)	<i>T</i> _{d1} ^f (°C)
A4	543	35	0.14	5.2	11	239
F1	515	40	0.23	5.5	0	342
F2	701	19	0.10	2.1	0	—
B1	547	41	0.11	5.2	7	258
B2	781	16	0.09	2.5	0	—

^aCalculated value. ^bAt 25 °C. ^cAt 90 °C and under humidification (100% RH). ^dAt 25 °C and with 1 mol/l methanol. ^eAt 25 °C and in 100% methanol. ^f1% weight loss temperature measured by TGA in air at 10 °C/min heating rate.

since the proton conductivity is influenced a great deal by the presence of water. Moreover characterizing the behaviors of PEMs in contact with methanol is very important, since the higher density of methanol aqueous solution is necessary to larger energy capacity of DMFC.

The relationship between the water uptakes and the quantity of UV irradiation to A4 membrane are shown in Table II. As the quantity of UV irradiation increased, the water uptakes were decreased. The water uptakes of other A-polymer membranes, F-polymer membranes and B-polymer membranes are shown in Table III. Figure 11 shows the relationship between the EW values and the water uptakes of 15000 mJ/cm² UV irradiation. When the EW values were similar and the quantity of UV irradiation was the same, the water uptakes

Figure 11. EW dependence of water uptake for sulfonated PAEKs.

Table IV. Methanol dissolution of A-polymer membranes

Sample Code	Methanol dissolution ^a (%)	
	0 mJ/cm ² ^b	6000 mJ/cm ² ^b
A1	100	100
A2	100	55
A3	100	51
A4	100	22
A5	56	1

^aAt 25 °C. ^bUV irradiation quantity.

were similar in these similar type polymer membranes of PAEK structures. This result was shown in Figure 11.

The methanol dissolutions of the A-polymer membranes are summarized in Table II. The copolymers, which had DSDFBP/DFBP/TMBPA mole ratio of 10/0/10, 9/1/10, 8/2/10 and 5/5/10, were soluble in methanol, but the UV irradiation to these membranes improved their methanol soluble resistance. The crosslinking of PAEK membranes by the UV irradiation was very effective to improve the methanol dissolution clearly. The relationship of the properties of the A4 membranes and the quantity of the UV irradiation are shown in Table IV. As the quantity of UV irradiation increased, and the crosslinking reaction occurred, the dissolution in methanol was suppressed. The relationship between the UV irradiation quantity and the solubility in methanol is shown in Figure 12. When the quantity of UV irradiation was over 15000 mJ/cm², the solubility became almost constant. About half of the crosslinkable groups contribute to crosslinking reaction as shown in Figure 6, and the crosslinking reaction almost reacted until irradiation of 15000 mJ/cm². The methanol dissolutions of F-polymer membranes and B-polymer membranes are shown in Table III. At the same quantity of UV irradiation and the similar value of EW, for example A4, F1 and B1, the methanol dissolutions were different greatly in each structure. The methanol dissolution of each EW values and structure are shown in Figure 13. The methanol dissolution characteristics had structure dependence and F-polymer structure had the lowest solubility. The lowest solubility was caused by the high crosslinking degree of F-polymer structure.

Figure 12. UV irradiation dependence of methanol dissolution of A4.

Figure 13. EW dependence of methanol dissolution for sulfonated PAEKs.

Proton Conductivity

Table II shows the relationship between the quantity of UV irradiation and the proton conductivity. The quantity of UV irradiation didn't affect the proton conductivity with these ranges. The proton conductivities of the sulfonated PAEKs are shown in Table III. The EW dependence of the proton conductivity is shown in Figure 14. In these similar structures of PAEKs, the change of proton conductivity was dependent on EW value without being dependent on structure of a polymer. The proton conductivities of these sulfonated PAEKs were in the same range as reported for other sulfonated aromatic polymers and their values were high enough to be used in DMFCs.

Methanol Permeation Rate

The methanol permeation rate also decreased as the crosslinking increased as shown in Table II. Crosslinking membrane limits swelling of membrane with water. When a membrane swells with water, a channel of water is formed in a membrane. Methanol goes through this channel with water and methanol crossover occurs. Therefore, swelling limit of a membrane by crosslinking is very effective to protect methanol crossover. As shown in Table III and Figure 15, in these similar structures of PAEKs, the methanol permeation rates are dependent on the

Figure 14. EW dependence of proton conductivity for sulfonated PAEKs.

Figure 15. EW dependence of methanol permeation rate for sulfonated PAEKs.

EW value without depending on their structure, same as the water uptake and the proton conductivity. If the EW value significantly increases, the values of these properties decrease. Therefore, selecting the optimized quantity of UV irradiation is important to maintain the balance of all properties. The UV irradiation of 15000 mJ/cm² is the most suitable in these sulfonated PAEKs.

Hot Water Test

The hot water test was done in order to examine the stability toward water of the crosslinking structure. The result of hot water test of **F2** membrane is shown in Table V. There was no particular change with its weight change, water uptake and proton conductivity of before and after soaking in water at 85 °C for 8, 15, 30 and 50 h. This shows that the crosslinking structure of **F2** membrane is stable in water.

CONCLUSIONS

1. An improved method was developed for preparing the salt-formed DSDFBP monomer in high yield. A new class of sulfonated PAEKs was synthesized *via* the direct copolymer-

Table V. Hot water test of F2 membrane

Soaking Time ^a (h)	Appearance ^b	Weight change ^c (%)	Water uptake ^d (%)	Proton conductivity ^e (S/cm)
0		0.0	24	0.10
8	N	0.6	28	0.10
15	N	0.3	25	0.09
30	N	0.5	26	0.11
50	N	-0.4	22	0.09

^aAt 85 °C in water. ^bN: no change. ^c($W_{\text{before}} - W_{\text{after}}$)/ $W_{\text{before}} \times 100\%$. ^dAt 25 °C. ^eAt 90 °C and under humidification (100% RH).

ization of the disulfonated dihalide benzophenone monomers with DFBP and any of three different biphenols. Varying the stoichiometric ratio of the DSDFBP and the DFBP easily controlled the degree of sulfonation in the copolymers.

2. These sulfonated PAEKs having benzophenone groups and methyl groups in their structures were easily crosslinked by UV irradiation. This crosslinking can improve the methanol blocking properties, methanol dissolution and methanol permeation rate, required as the important properties for the DMFCs.

3. The **F**-polymer structure shows high crosslinking characteristic because of having crosslinkable methylene groups in its structure besides methyl groups.

4. Especially the crosslinked **F1**, consisting of DSDFBP/DFBP/TMBPF = 5/5/10, in these sulfonated PAEKs has an excellent property as the PEM for DMFC. Its proton conductivity was 0.23 S/cm at 90 °C, the methanol permeation rate was 5.5 μmol/cm²/min and it was not dissolved in methanol. This proton conductivity and methanol permeability are comparable to and half of the values of fluorinated copolymer Nafion112[®] that is known as the representative material of a PEM of DMFC respectively.

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