

# Preparation and Solubility of Water–Methanol Mixtures in Sulfonated Poly(etherketone) Containing a Cardo-Ring Structure

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**ABSTRACT:** The preparation and solubility of water–methanol mixtures in sulfonated (1,3-dihydro-3-oxoisobenzofuran-1,1-diyl-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene) (C-PEK) was systematically studied. The sulfonation was carried out by reacting C-PEK with 98% sulfuric acid at 60°C. This reaction obeys a first-order reaction mechanism up to 4 h. The sulfonic acid group was uniformly dispersed in a sulfonated C-PEK (SC-PEK) membrane. The introduction of sulfonic acid groups in C-PEK could increase polymer segmental gaps because of the size of a bulky sulfonic acid group or decrease polymer segmental gaps as a result of polar interactions. The former effect is dominant for SC-PEK with low sulfonic acid content, whereas the latter occurs for SC-PEK with high sulfonic

acid content. The uptake of pure water or an aqueous methanol solution (e.g., 3, 5, and 10 wt % methanol concentration) in the sulfonated C-PEK membranes increases with increasing sulfonic acid group content. However, the sulfonated C-PEK with high sulfonic acid content selectively sorbs water rather than methanol in the membrane. This suggests that the sulfonated C-PEK membrane could prevent crossover of methanol through the membrane and has potential as a polymer electrolyte for the direct methanol fuel cell. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1113–1123, 2006

**Key words:** direct methanol fuel cell; polymer electrolytes; membranes; solubility; poly(ether ketones)

## INTRODUCTION

An integral component of a polymer electrolyte fuel cell (PEFC) is the electrolyte membrane that separates the cell's anode and cathode. High performance polymer electrolyte membranes allow for fuel cell miniaturization and high output densities necessary to power automobile, electronics, etc. The optimum properties of the electrolyte membrane in a fuel cell are high proton conductivity, low gas permeability, chemical resistance, thermal stability, mechanical properties, and low cost.

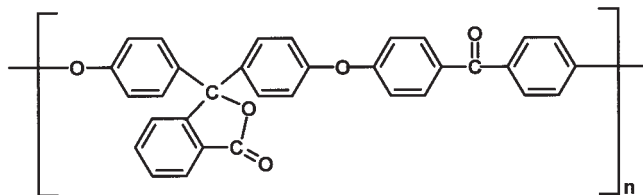
Among PEFC, the direct methanol fuel cell (DMFC) has an advantage of using an easily-stored liquid fuel. The electrolyte membranes used for PEFC are mainly sulfonated perfluoropolymers, such as Nafion<sup>®</sup> (DuPont, DE), Flemion<sup>®</sup> (Asahi Glass Co. Ltd., Tokyo, Japan), and Aciplex<sup>®</sup> (Asahi Chemical Co. Ltd., Tokyo, Japan). However, because of the high methanol affinity of these perfluoropolymer membranes, methanol crossover occurs and causes a significant loss in system efficiency. The operating temperature with perfluoropoly-

mers must be below 100°C, because the glass transition temperature of sulfonated perfluoropolymers is around 130°C.<sup>1</sup> In addition, perfluoropolymers are expensive relative to hydrocarbon-based polymers.

In general, hydrocarbon-based aromatic polymers such as poly(oxy-1,4-phenylene-1,4-phenylene-carbonyl-1,4-phenylene) (PEEK) have excellent thermal stability with high glass transition, chemical stability, and mechanical strength suitable to engineering plastic applications. In this regard, sulfonated hydrocarbon-based aromatic polymers have been widely studied as candidate electrolyte membranes in DMFC.<sup>2–14</sup>

A new type of PEEK contains poly(1,3-dihydro-3-oxoisobenzofuran-1,1-diyl-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene) (C-PEK, Fig. 1). A C-PEK membrane is amorphous and soluble in aprotic polar solvents such as *N,N*-dimethylformamide and *N*-methyl-2-pyrrolidone (NMP), but insoluble in methanol. So far, various modifications such as nitration, sulfonation, blends with other polymers, and copolymerization have been reported.<sup>15–20</sup> Gas permeation and pervaporation experiments have also been performed for these modified materials.<sup>21–24</sup> Recently, the proton conductivity, gas permeability, and water and methanol vapor permeability in sulfonated C-PEK were reported.<sup>25</sup>

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**Figure 1** Chemical structure of poly(1,3-dihydro-3-oxoisobenzofuran-1,1-diyl-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene).

The ideal electrolyte membrane in a DMFC has to sorb water for proton conductivity and reject methanol to prevent fuel loss (i.e., methanol crossover) during operation. Therefore, the solubility behavior of water–methanol mixtures in an electrolyte membrane is an important factor in designing the membrane. However, there is no report about solubility selectivity of water–methanol mixtures in sulfonated C-PEK. In this article, a systematic study of the preparation and solubility of water–methanol mixtures in sulfonated poly(etherketone) containing a cardo-ring structure is reported.

## EXPERIMENTAL

### Materials and chemicals

C-PEK was purchased from Xu Zhou Engineering Plastique Factory (Jiangsu, China). Sodium chloride, methanol, phosphorus(V) oxide, and phenolphthalein (Junsei Chemistry Co. Ltd., Tokyo, Japan), sulfuric acid, sodium carbonate, and NMP (Prolabo, Paris, France), dimethyl- $d_6$  sulfoxide for NMR (Isotec, OH) were used without further purification.

### Sulfonation of C-PEK

C-PEK powder was dissolved in 98% sulfuric acid and stirred at 60°C. After a determined reaction time, the reaction medium was poured into 0.5M sodium carbonate solution cooled with ice under stirring and sulfonated C-PEK (SC-PEK) was precipitated in a bead form. SC-PEK beads were washed with pure water to remove excess acids and then dried under vacuum at 80°C for 48 h.

### Membrane preparation

C-PEK and SC-PEK were dissolved in NMP. The solutions were filtered and cast on a glass petri dish. The solvent was evaporated in an oven at 80°C for 48 h and then dried at 80°C for 12 h under vacuum. After drying, C-PEK membranes were stored in desiccators in the presence of  $P_2O_5$  as a desiccant under vacuum until experiments began.

SC-PEK membranes were immersed in 0.01M HCl solution and then washed with pure water to convert the membranes from  $-\text{SO}_3\text{Na}$  (Na-form) to the  $-\text{SO}_3\text{H}$  (H-form).<sup>26</sup> Like C-PEK, the H-form SC-PEK membranes were stored in desiccators with  $P_2O_5$  under vacuum.

### Structural analysis

To determine the chemical structure of the products, Fourier transform infrared spectrometry (FT-IR) analysis was performed using Avatar 360 FT-IR (Thermo Electron Co., WI) and nuclear magnetic resonance (NMR) experiments were carried out using JNM-ECA500 (JEOL Ltd., Tokyo, Japan) in 500 MHz  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.  $\text{DMSO}-d_6$  was used as a solvent for these NMR analyses.

### Ion exchange capacity

The ion exchange capacity (IEC) of SC-PEK membranes was determined by the following titration method procedure. The weight of dry state H-form SC-PEK membranes was determined. These membranes were immersed in pure water for 24 h and then continuously stored in 0.01M HCl solution for more than 24 h. They were rinsed using pure water until the water became neutral. Afterward, the membranes were immersed in 0.01M NaCl solution for more than 48 h. Ten milliliter of this solution was collected and titration was performed using a 0.005M NaOH solution whose concentration was determined by  $(\text{COOH})_2$  beforehand with phenolphthalein as an indicator.

The degree of sulfonation indicated the amount of sulfonic acid group per repeat unit in C-PEK as:

$$\text{Degree of sulfonation} = \frac{496 \times \text{IEC}}{1 - (80 \times \text{IEC})} \quad (1)$$

where 496 and 80 are the molecular weights of C-PEK and a  $-\text{SO}_3^-$  group, respectively.

### Density

The density ( $\rho$ ) of membranes was obtained geometrically with membrane weight and volume as:

$$\rho(\text{g}/\text{cm}^3) = \frac{M_d}{S \times l} \quad (2)$$

where  $M_d$  is the membrane weight,  $S$  is the membrane area, and  $l$  is the thickness of the dry state H-form membrane.

### Glass transition temperature ( $T_g$ )

Differential scanning calorimeter analysis was performed to determine the  $T_g$  using a Perkin–Elmer DSC7 (Perkin–Elmer Inc., MA) with a heating rate of 10°C/min. The temperature range varied from 180 to 430°C under nitrogen atmosphere.

### $d$ -spacing

Wide angle X-ray diffraction (WAXD) analysis was performed to determine the  $d$ -spacing using a RINT-1200 X-ray diffractometer (Rigaku Corp., Tokyo, Japan) in dry and water-swollen states with a scanning speed of 2°/min, using Cu K $\alpha$  radiation at 40 kV and 20 mA in the dispersion angle from 3° to 50°. The  $d$ -spacing value was calculated from Bragg's equation:

$$n\lambda = 2d \sin\theta \quad (3)$$

where  $\lambda$  is 1.54 (Å) of the X-ray wavelength and  $\theta$  is the X-ray diffraction angle.

### Static contact angle

Static contact angles to water or water–methanol mixtures (3, 5, and 10 wt % methanol) onto a membrane were determined using a video microscope system, VMS-1000S (Scala), and a color video printer, Mavi-graph UP-5000 (Sony Corp., Tokyo, Japan). One microliter of pure water or water–methanol mixtures was placed onto the surface of the dried membrane. Thereafter, the shape of a drop was recorded to a computer and the contact angle determined.

### Water–methanol uptake and solubility selectivity

The degree of swelling by pure water or water–methanol mixtures (3, 5, and 10 wt % methanol) was measured at 30°C. The membranes were stored in each solution for more than 24 h until sorption equilibrium was attained. The membrane surface was wiped off and the weight was measured immediately. Then, the membrane was evacuated for 24 h with P<sub>2</sub>O<sub>5</sub> under vacuum and the weight of the dry membrane was measured. The degree of swelling was obtained from:

$$\text{Degree of swelling (wt\%)} = \frac{M_s - M_d}{M_d} \times 100 \quad (4)$$

where  $M_s$  is the weight of a swollen membrane and  $M_d$  is the weight of a dry membrane.

The composition of water and methanol sorbed in a membrane at equilibrium was analyzed. The surface of an equilibrated membrane was wiped off and sorbate evaporated by heating at 150°C under vacuum for more than 2 h. The sorbed solution was collected

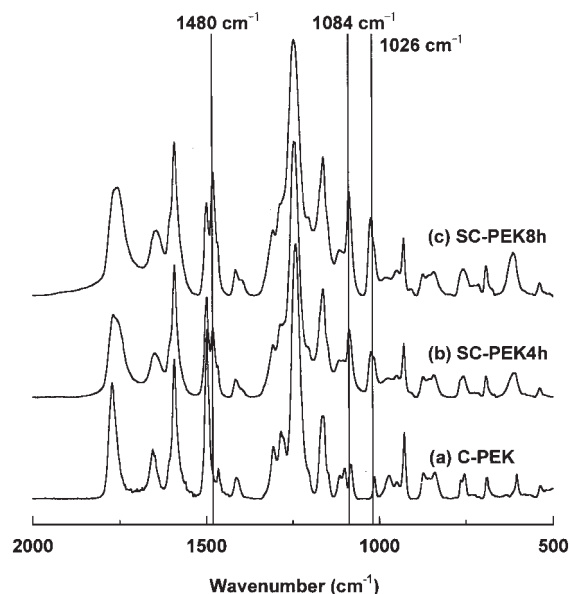


Figure 2 FT-IR spectra of (a) C-PEK, (b) SC-PEK4h, and (c) SC-PEK8h.

with a cold trap cooled by liquid nitrogen and the composition determined using a gas chromatograph GC-8A (Shimadzu Corp., Kyoto, Japan). The water/methanol solubility selectivity  $\alpha_s$  was obtained from:

$$\alpha_s = \frac{X_W/X_M}{Y_W/Y_M} \quad (5)$$

where  $X_W$  and  $X_M$  are the weights of water or methanol sorbed in a membrane.  $Y_W$  and  $Y_M$  are the weights of water or methanol in a solution, respectively.

## RESULTS AND DISCUSSION

### Structural analysis

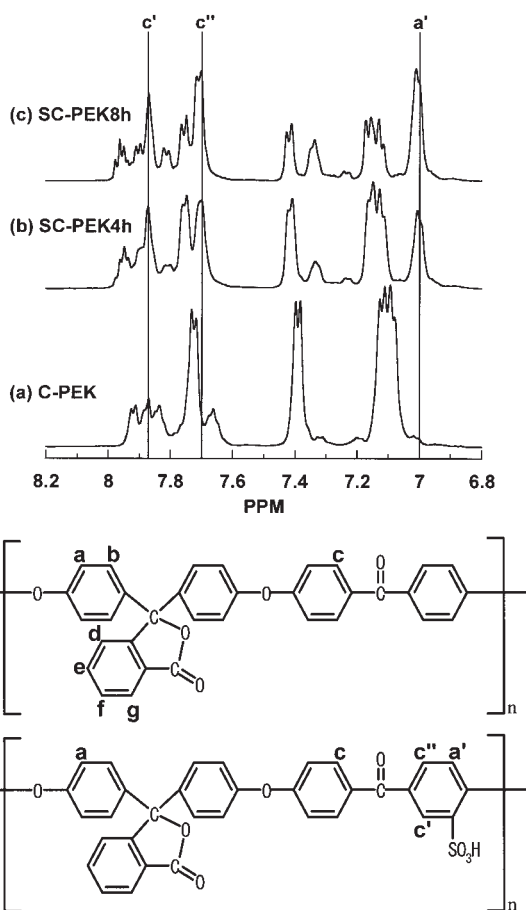
FT-IR spectra of C-PEK and SC-PEK are shown in Figure 2. The characteristic absorption bands are observed with SC-PEK at 1084 and 1026 cm<sup>-1</sup> assigned to aromatic —SO<sub>3</sub>H symmetric and asymmetric stretching vibrations. The absorption of the 1,4-aromatic ring substitution at 1500 cm<sup>-1</sup> becomes weaker and a new absorption of the 1,2,4-aromatic ring substitution at 1480 cm<sup>-1</sup> representing a sulfonic acid group increases, as does the peak intensity, with increasing reaction time. Moreover, C-PEK and SC-PEK membranes show absorption of a carbonyl group at 1649 cm<sup>-1</sup> and the C—O—C bond between aromatic rings at 1236 cm<sup>-1</sup>.<sup>3,7,21,22</sup>

<sup>1</sup>H- and <sup>13</sup>C NMR spectra in Figures 3 and 4 indicate the chemical structures of C-PEK and SC-PEK. C-PEK: <sup>1</sup>H NMR: 7.92 (H<sub>g</sub>), 7.87 (H<sub>d</sub>), 7.83 (H<sub>e</sub>), 7.72 (H<sub>c</sub>), 7.66 (H<sub>f</sub>), 7.39 (H<sub>b</sub>), and 7.10 (H<sub>a</sub>), <sup>13</sup>C NMR: 193.02 (C<sub>10</sub>),

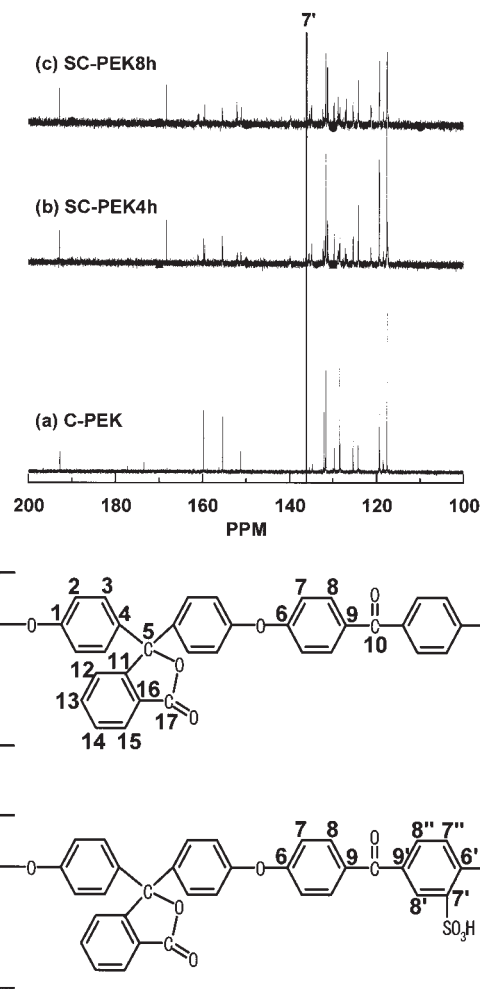
168.45 ( $C_{17}$ ), 159.93 ( $C_6$ ), 155.60 ( $C_1$ ), 151.40 ( $C_{11}$ ), 136.47 ( $C_4$ ), 132.34 ( $C_9$ ), 131.92 ( $C_8$ ), 129.96 ( $C_{15}$ ), 128.70 ( $C_{3, 14}$ ), 128.56 ( $C_{12}$ ), 125.57 ( $C_{16}$ ), 124.44 ( $C_{13}$ ), 119.53 ( $C_7$ ), 118.77 ( $C_5$ ), and 117.77 ( $C_2$ ). SC-PEK:  $^1\text{H}$  NMR: 7.88 ( $H_{c'}$ ), 7.72 ( $H_c$ ), 7.70 ( $H_{c''}$ ), 7.11 ( $H_a$ ), and 7.00 ( $H_{a'}$ ),  $^{13}\text{C}$  NMR: 159.62 ( $C_{6'}$ ), 136.24 ( $C_{7'}$ ), 134.94 ( $C_{8'}$ ), 132.46 ( $C_{9'}$ ), 131.38 ( $C_{8''}$ ), and 121.35 ( $C_{7''}$ ).

### Characterization

Table I summarizes the physical properties of C-PEK and SC-PEK membranes. IEC increases from 0.68 meq/g (SC-PEK1h) to 1.90 meq/g (SC-PEK8h) with increasing reaction time. FT-IR and NMR analyses indicated an increase in sulfonic acid group content in the polymer with increasing reaction time. The degree of sulfonation was estimated from IEC. The degree of sulfonation approaches 1 at 6 h (SC-PEK6h) and then increases up to 1.11 at 8 h (SC-PEK8h). This means that SC-PEK8h contains two sulfonic acid groups in 11% of the total repeating units. However, the second sulfonated position was not clear because the  $^1\text{H}$ - and  $^{13}\text{C}$  NMR peaks were overlapped and it was difficult to separate them. On the basis of previous work, C-PEK



**Figure 3**  $^1\text{H}$  NMR spectra of (a) C-PEK, (b) SC-PEK4h, and (c) SC-PEK8h.



**Figure 4**  $^{13}\text{C}$  NMR spectra of (a) C-PEK, (b) SC-PEK4h, and (c) SC-PEK8h.

sulfonated by 98% sulfonic acid became mechanically weak because of the degradation of polymer chains when the degree of sulfonation exceeded 0.8.<sup>18</sup> In fact, SC-PEK8h (degree of sulfonation: 1.11) was brittle in the dry state consistent with the result in the literature. However, SC-PEK6h was still mechanically strong enough to be tested in this study.

Kinetics of the sulfonation of C-PEK is considered as the second-order reaction and it can be described as:



$$\frac{dc}{dt} = k_2(a-x)(b-x) \quad (7)$$

where  $a$  and  $b$  are the initial concentration of C-PEK and sulfonic acid respectively,  $x$  is the concentration of SC-PEK and water at time  $t$ , and  $k_2$  is the rate constant. Because  $\text{H}_2\text{SO}_4$  exists much excessively rather than C-PEK, it can be approximated  $(b-x) \approx b$ .

TABLE I  
Physical Properties of Sulfonated Poly(1,3-dihydro-3-oxoisobenzofuran-1,1-diyl-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene)

Polymer	Reaction time (h)	IEC (meq/g)	Degree of sulfonation	Film density (g/cm <sup>3</sup> )	$T_g$ (°C)	$\Delta C_{pp}$ (J/g)	$d$ -spacing (Å)		FFV
							Dry	Swollen	
C-PEK	0	0.00	0.00	1.18	207.0	0.11	4.94	5.02	0.215
SC-PEK1h	1	0.68	0.36	1.08	255.7	0.12	5.10	5.25	0.294
SC-PEK2h	2	1.03	0.56	1.09	326.2	0.11	5.02	5.20	0.294
SC-PEK3h	3	1.18	0.65	1.18	339.0	0.18	5.01	5.08	0.238
SC-PEK4h	4	1.48	0.83	1.21	352.2	0.17	4.96	5.07	0.225
SC-PEK6h	6	1.74	1.00	1.24	372.4	0.35	4.79	5.13	0.211
SC-PEK8h	8	1.90	1.11	1.26	386.9	0.31	4.74	5.32	0.202

$$\frac{dc}{dt} = k_2 b(a - x) \quad (8)$$

Moreover, because  $b$  is a constant value, it is rewritten as  $k_2 b = k_1$  and this reaction can be considered as the first-order reaction.

$$\frac{dc}{dt} = k_1(a - x) \quad (9)$$

The following eq. (10) is then obtained by integrating with eq. (9).

$$\ln \frac{a}{a - x} = k_1 t \quad (10)$$

As shown in Figure 5, the value of  $\ln(a/(a-x))$  increases linearly with increasing reaction time up to 4 h, indicating a first-order reaction up to 4 h. The kinetic constant  $k_1$  is  $1.14 \times 10^{-4} \text{ s}^{-1}$  ( $0.411 \text{ h}^{-1}$ ).

C-PEK and all SC-PEK membranes have a single glass transition temperature ( $T_g$ ). This indicates that the sulfonation occurred homogeneously, that is, the

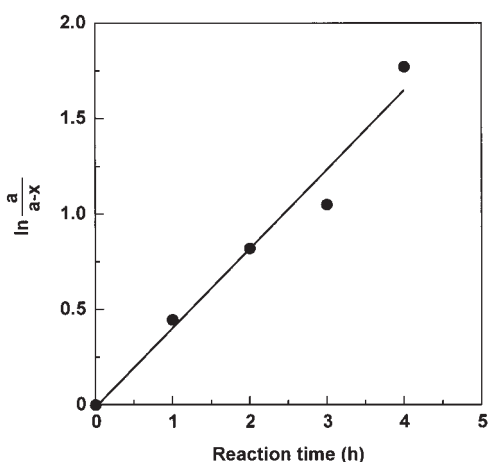


Figure 5  $\ln(a/(a-x))$  as a function of reaction time. The line represents the first-order reaction in eq. (10).

sulfonic acid group was uniformly dispersed in a membrane. If the sulfonation proceeds heterogeneously, there would be two  $T_g$ s: one is for unreacted C-PEK regions and the other one for sulfonated C-PEK regions. C-PEK has a  $T_g$  of 207°C.  $T_g$  increases with increasing degree of sulfonation. For instance, the  $T_g$  of SC-PEK6h (degree of sulfonation: 1.00) is 372.4°C. The interaction between polar groups prevents polymer segment motion and causes an increase in  $T_g$ .<sup>5,8</sup> The sulfonic acid groups probably provide interactions among sulfonic acid groups and/or between a sulfonic acid group and polar substituents in C-PEK such as a carbonyl group. In fact, the  $\Delta C_p$  value tends to increase with increasing degree of sulfonation.

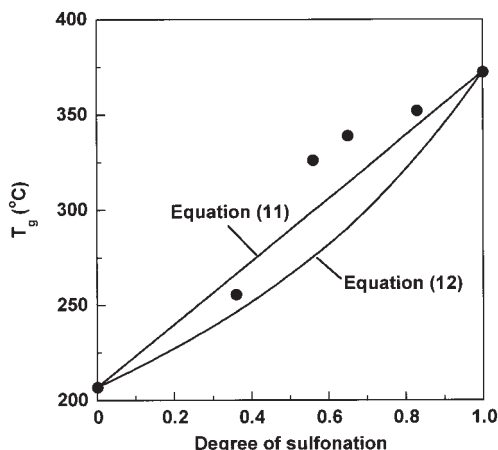
$T_g$ s can be estimated from two predictive equations: the rule of mixtures in eq. (11) and the Fox equation in eq. (12).<sup>27</sup>

$$T_g = w_i T_{g,i} + w_j T_{g,j} \quad (11)$$

$$\frac{1}{T_g} = \frac{w_i}{T_{g,i}} + \frac{w_j}{T_{g,j}} \quad (12)$$

where  $T_{g,i}$  and  $T_{g,j}$  are the  $T_g$  of components  $i$  and  $j$ , respectively. The  $w_i$  and  $w_j$  are the weight fractions of components  $i$  and  $j$ , respectively. We have assumed that C-PEK (degree of sulfonation: 0) and SC-PEK6h (degree of sulfonation: 1.00) are components  $i$  and  $j$ , respectively, and estimated  $T_g$ s of SC-PEK. Figure 6 presents the  $T_g$  values as a function of degree of sulfonation. Because SC-PEK has a single  $T_g$ , it could obey a simple mixing rule described as eq. (11). However, the experimental  $T_g$  values do not simply follow these two equation curves in Figure 6. C-PEK contains three polar structures (i.e., a carboxyl group, an ester group, and an ether group). A subtle interplay between these groups and a sulfonic acid group probably influences the glass transition of SC-PEK.

WAXD spectra of C-PEK and SC-PEK do not show any peaks attributed to crystalline structures, indicating that these polymer membranes are 100% amorphous. The top of the amorphous peak on each X-ray



**Figure 6** Relationship between glass transition temperature and degree of sulfonation for SC-PEK. Curves represent the theoretical values in eqs. (11) and (12).

pattern is attributed to the average intersegmental distance of polymer chains<sup>28</sup> and the  $d$ -spacing can be estimated from eq. (3). In the dry membranes, the  $d$ -spacing value of C-PEK is 4.94 Å. As the degree of sulfonation increases, the  $d$ -spacing value initially increases and then decreases gradually. As previously mentioned, the increase in  $T_g$  by the addition of sulfonic acid groups indicates interactions between sulfonic acid groups and other polar groups in C-PEK. Because of an increase in cohesive energy of polymer segments, this effect predicts a decrease in  $d$ -spacing. In contrast, an increase in  $d$ -spacing suggests an increase in polymer segmental gaps in the presence of sulfonic acid groups. Sulfonic acid groups on the side chains in C-PEK probably create a space between C-PEK segments. The latter effect appears to be dominant at lower sulfonic acid content. With increasing degree of sulfonation, this steric effect becomes less important.

$d$ -Spacing increases in all membranes when water is absorbed. Water molecules sorbed in a membrane reduce interaction between sulfonic acid groups and other polar groups in C-PEK, causing swelling of the membrane. After removing water molecules from a membrane, increased polymer segmental gaps could still remain. In the dry membranes, the  $d$ -spacing value decreases at higher sulfonic acid content. However, in the swollen membranes, the  $d$ -spacing value increases from the degree of sulfonation of 1.00 (SC-PEK6h). As will be discussed later, the water uptake increases exponentially with increasing the degree of sulfonation. At higher sulfonic acid group content, extremely expanded polymer segments may not recover immediately. As a result, the  $d$ -spacing value is larger than the value expected from the trend in the dry membranes.

The membrane density of C-PEK is 1.18 g/cm<sup>3</sup>. The membrane density initially decreases at a reaction

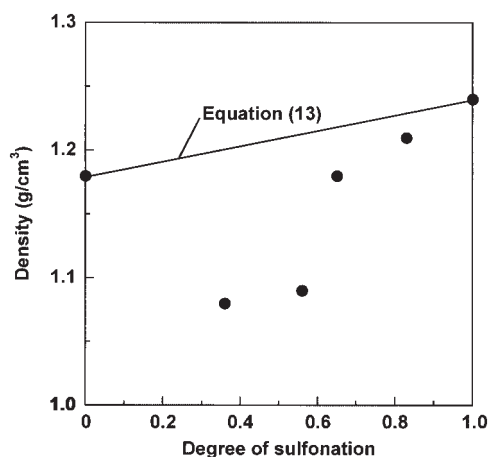
time of 1 h (SC-PEK1h) and then increases with increasing time. The SC-PEK8h membrane has a density of 1.26 g/cm<sup>3</sup>. A simple mixing rule of binary homogeneous polymer blends and copolymers estimates the density as:

$$\rho = w_i\rho_i + w_j\rho_j \quad (13)$$

where  $w_i$  and  $w_j$  are weight fraction and  $\rho_i$  and  $\rho_j$  are the density of components  $i$  and  $j$ , respectively. We have assumed that C-PEK (degree of sulfonation: 0) and SC-PEK6h (degree of sulfonation: 1.00) are components  $i$  and  $j$ , respectively, and estimated SC-PEK densities. Figure 7 presents the experimental membrane density and estimated densities of SC-PEK membranes. When the density obeys eq. (13), it increases linearly with increasing degree of sulfonation. All experimental values are below the estimated ones. For example, the experimental density of SC-PEK1h is 10% lower than its estimated value. As the degree of sulfonation increases, the experimental density initially decreases and then increases to the density of SC-PEK6h (degree of sulfonation: 1.00). The introduction of sulfonic acid groups in C-PEK could provide a combination of an increase in polymer segmental gaps because of the steric effects and a decrease in polymer segmental gaps resulting from polar interactions. The former effect dominates density effects at low degrees of sulfonation. However, as the degree of sulfonation increases in the polymer, the interaction effects gradually contribute to the density.

The fractional free volume (FFV) of membranes is given by:

$$\text{FFV} = \frac{V - 1.3V_w}{V} \quad (14)$$



**Figure 7** Membrane density of SC-PEK as a function of the degree of sulfonation. The line represents the theoretical density data in eq. (13).

**TABLE II**  
**Characteristics of Sulfonated Poly(1,3-dihydro-3-oxoisobenzofuran-1,1-diyl-1,4-phenylene-oxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene) Membranes for Water-Methanol Mixtures**

Sample	Contact angle (deg.)				Degree of swelling (wt%)					$\alpha_s$		
	methanol concentration				methanol concentration							
	0 wt%	3 wt%	5 wt%	10 wt%	0 wt%	3 wt%	5 wt%	10 wt%	100 wt%	3 wt%	5 wt%	10 wt%
C-PEK	89.4	85.6	86.7	87.2	2.2	1.0	0.6	1.2	0.0	—	—	—
SC-PEK1h	86.2	85.0	85.5	85.6	10.3	7.8	8.9	9.0	16.4	0.72	0.69	0.81
SC-PEK2h	78.3	80.0	82.3	80.2	19.9	14.1	14.3	14.7	28.2	2.04	2.44	2.22
SC-PEK3h	78.1	81.0	79.4	79.5	21.7	16.5	20.3	24.2	34.9	2.68	3.84	2.50
SC-PEK4h	75.1	79.4	78.6	77.7	27.8	27.8	29.8	31.2	Soluble	2.49	3.46	3.04
SC-PEK6h	69.9	74.9	77.5	74.1	53.9	46.8	48.9	62.1	Soluble	3.68	3.68	3.01
SC-PEK8h	67.9	73.0	70.4	70.4	67.8	88.2	96.0	158.6	Soluble	3.90	2.88	2.72

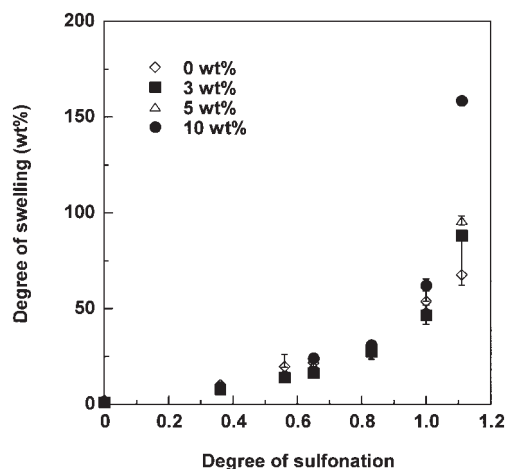
where  $V$  is the specific volume of polymer (i.e., reciprocal membrane density) and  $V_W$  is the van der Waals volume calculated by group contribution methods.<sup>29</sup> C-PEK has a FFV value of 0.215. As expected from the trend in polymer density and  $d$ -spacing, as the degree of sulfonation increases, the FFV value initially increases and then decreases gradually. The largest FFV value of 0.294 is observed for SC-PEK1h and SC-PEK2h. When the degree of sulfonation is greater than 1, the FFV value is lower than that of C-PEK (degree of sulfonation: 0). Like membrane density and  $d$ -spacing, a combination of the volume of sulfonic acid substituents and interactions among polar moieties provides this FFV behavior.

### Characteristics for water-methanol mixtures

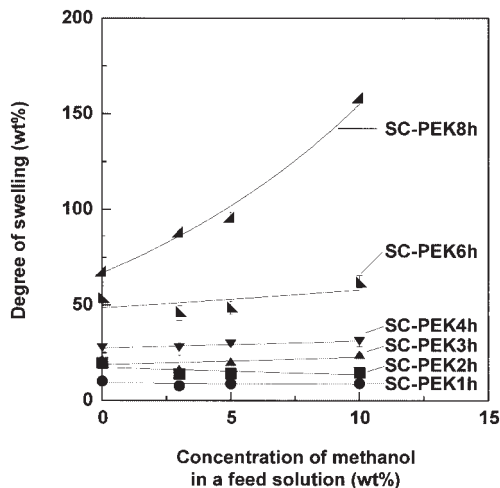
Table II summarizes the static contact angles, degree of swelling, and water/methanol solubility selectivity of water-methanol mixtures in C-PEK and SC-PEK membranes at 30°C. As the degree of sulfonation increases, the static contact angle of pure water (methanol concentration: 0 wt %, in Table II) decreases. This indicates that some sulfonic acid groups orient to the surface of the membrane. The hydrophilicity on the surface of a membrane increases with increasing the degree of sulfonation. C-PEK has a contact angle of 89.4°. The contact angle of SC-PEK6h (degree of sulfonation: 1.00) membranes is 22% lower than that of C-PEK. Regardless of methanol concentrations up to 10 wt %, like pure water, the contact angle of methanol solutions decrease with increasing the degree of sulfonation. In addition, methanol concentration does not significantly affect the contact angle for C-PEK and SC-PEK with lower sulfonic acid content. However, SC-PEK with higher sulfonic acid content tends to have larger contact angle for methanol mixtures than for pure water. Hence, sulfonic acid groups on a membrane surface probably prefer to interact with water molecules relative to methanol molecules.

The degree of swelling of pure water and methanol solutions (3, 5, and 10 wt % methanol) in C-PEK and SC-PEK membranes increases with increasing degree of sulfonation, as shown in Table II. For pure methanol (methanol concentration: 100 wt %, in Table II), C-PEK shows little sorption, whereas SC-PEK is soluble when the degree of sulfonation is greater than 0.83 (SC-PEK4h). The degree of swelling of pure water and methanol solutions (3, 5, and 10 wt % methanol) in C-PEK and SC-PEK membranes at 30°C is plotted in Figure 8 as a function of degree of sulfonation. The degree of swelling increases exponentially with increasing degree of sulfonation.

Figure 9 presents the degree of swelling in SC-PEK as a function of methanol concentration. At a lower degree of sulfonation, the dependence of methanol concentration on the degree of swelling is not distinctly observed. However, at a higher degree of sulfonation, the degree of swelling increases with increasing methanol concentration. For example, in SC-PEK8h (degree of sulfonation: 1.11), the degree of



**Figure 8** Relationship between degree of swelling and degree of sulfonation for ( $\diamond$ ) 0 wt %, ( $\blacksquare$ ) 3 wt %, ( $\triangle$ ) 5 wt %, and ( $\bullet$ ) 10 wt % methanol solutions at 30°C.

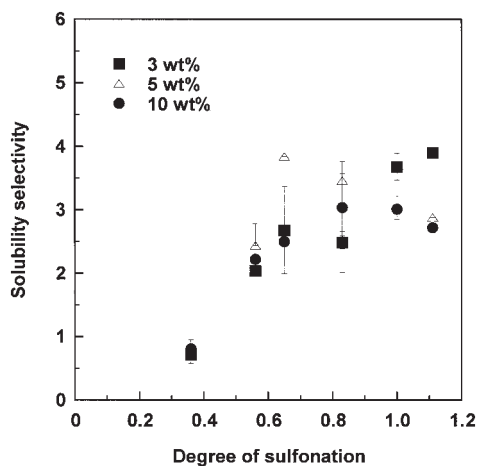


**Figure 9** Effect of methanol concentration for degree of swelling.

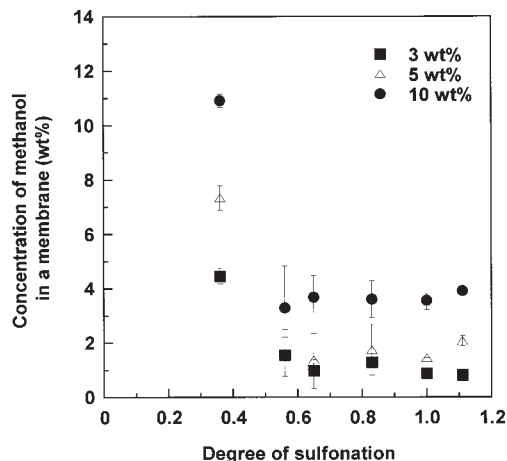
swelling of a 10 wt % methanol solution is 130% larger than that of pure water.

The water/methanol solubility selectivity in SC-PEK membranes is plotted in Figure 10 as a function of degree of sulfonation. Only SC-PEK1h (degree of sulfonation: 0.36) shows methanol-selective behavior. All other SC-PEK membranes are water selective. As the degree of sulfonation increases, the solubility selectivity also increases for 3 wt % methanol solutions. For 5 and 10 wt % methanol solutions, initially the solubility selectivity increases and then stays almost constant when the uncertainties are considered. The highest water/methanol solubility selectivity was 3.90 for SC-PEK8h with a 3 wt % methanol solution.

Figure 11 shows the methanol concentration in SC-PEK membranes. As expected from the results in Figure 10, the methanol concentration in only SC-PEK1h (degree of sulfonation: 0.36) exceeds the feed concen-



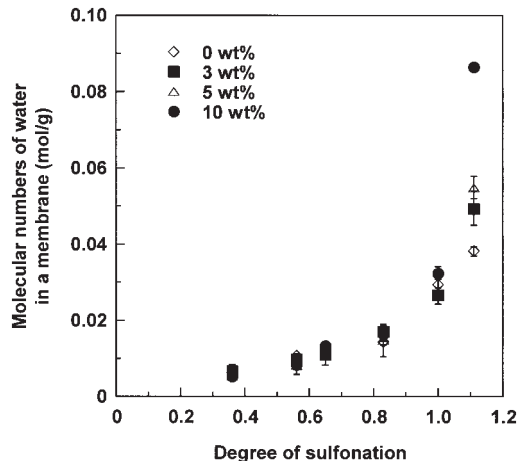
**Figure 10** Solubility selectivity for SC-PEK membranes in (■) 3 wt %, (△) 5 wt %, and (●) 10 wt % methanol solutions.



**Figure 11** Concentration of methanol in a membrane for (■) 3 wt %, (△) 5 wt %, and (●) 10 wt % methanol solutions.

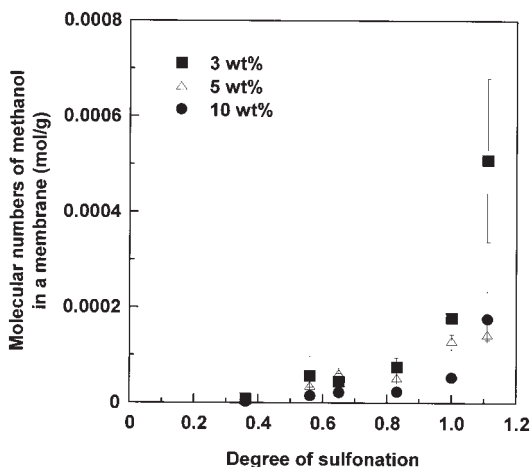
tration. In other SC-PEK membranes, the methanol concentration in a membrane decreases with increasing the degree of sulfonation for 3 wt % methanol solutions, whereas it is constant regardless of the degree of sulfonation for 5 and 10 wt % methanol solutions.

To understand these solubility results in more detail, the numbers of water and methanol molecules in each membrane are plotted in Figures 12 and 13 as a function of the degree of sulfonation, respectively. As expected, the total number of water molecules in a membrane is always much greater than that of methanol molecules. For instance, for 3 wt % methanol solutions, SC-PEK8h membranes sorb  $5 \times 10^{-2}$  mol/g of water and  $5 \times 10^{-4}$  mol/g of methanol. The number of water molecules increases exponentially with increasing the degree of sulfonation. The number of methanol molecules also increases exponentially with



**Figure 12** Comparison of molecular numbers of (◇) 0 wt %, (■) 3 wt %, (△) 5 wt %, and (●) 10 wt % methanol solutions.



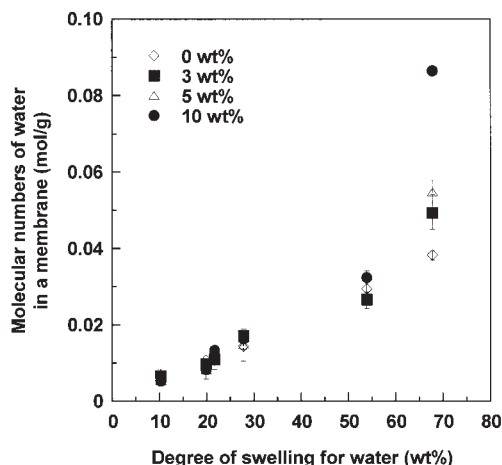


**Figure 13** Comparison of molecular numbers of methanol for (■) 3 wt %, (△) 5 wt %, and (●) 10 wt % methanol solutions.

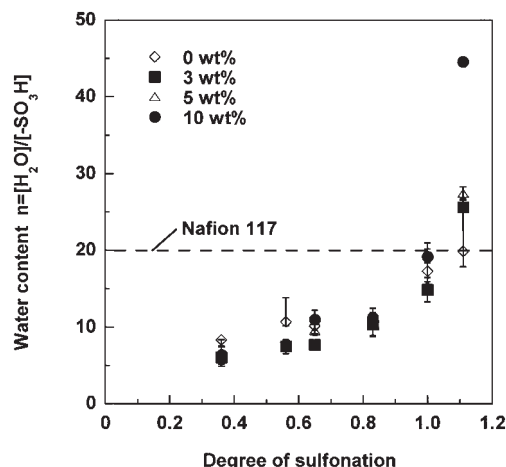
increasing degree of sulfonation, much like water molecules. On the basis of these results, SC-PEK membranes sorb both water and methanol. Water-selective behavior is due to the fact that SC-PEK membranes preferably sorb water relative to methanol in a membrane.

Figure 14 presents the number of water molecules in a membrane as a function of the degree of swelling for pure water. As expected, a linear relationship between the number of water molecules and the degree of swelling appears for pure water. In contrast, a linear relation is not observed for methanol solutions. This indicates that methanol molecules sorbed in a membrane contribute to the swelling of a membrane as well as water molecules.

Figures 15 and 16 present moles of water and methanol molecules per sulfonic acid group sorbed in SC-



**Figure 14** Comparison of molecular numbers of (◇) 0 wt %, (■) 3 wt %, (△) 5 wt %, and (●) 10 wt % methanol solutions (versus degree of swelling for water).

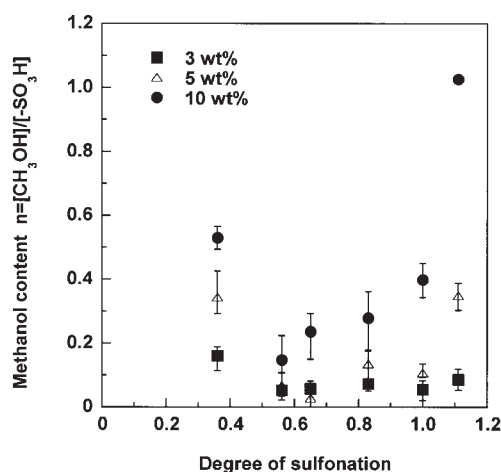


**Figure 15** Water content of (◇) 0 wt %, (■) 3 wt %, (△) 5 wt %, and (●) 10 wt % methanol solutions.

PEK as a function of degree of sulfonation, respectively. Nafion<sup>®</sup> 117 is widely used as a proton exchange perfluorinated polymer membrane for fuel cells. Its sulfonic acid group sorbs 20 water molecules.<sup>25,30,31</sup> In Figure 15, the number of water molecules per sulfonic acid group increases with increasing degree of sulfonation. Except for SC-PEK8h (degree of sulfonation: 1.11), this ratio of SC-PEK is lower than that of Nafion<sup>®</sup> 117. On the other hand, the number of methanol molecules per one sulfonic acid group is less than one in Figure 16. The ratio of SC-PEK is independent of the degree of sulfonation.

To understand the selective solubility characteristics of SC-PEK, Hansen's three-dimensional solubility parameters for C-PEK were estimated using the following equations.<sup>32</sup>

$$\delta = (\delta_d + \delta_p + \delta_k)^{1/2} \quad (15)$$



**Figure 16** Methanol content of (■) 3 wt %, (△) 5 wt %, and (●) 10 wt % methanol solutions.

**TABLE III**  
**Solubility Parameters of Water, Methanol, and Poly(1,3-dihydro-3-oxoisobenzofuran-1,1-diyl-1,4-p henyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene oxy-1,4-phenylene)**  
**(MPa<sup>1/2</sup>)**

	$\delta_d$	$\delta_p$	$\delta_h$	$\delta$
Water <sup>a</sup>	15.6	16.0	42.3	47.8
Methanol <sup>a</sup>	15.1	12.3	22.3	29.6
C-PEK <sup>b</sup>	18.4	0.1	6.2	19.4

<sup>a</sup> Reference 32.

<sup>b</sup> Estimated using eq. (15), (17), (18), and (19).

$$V = \sum_z zV \quad (16)$$

$$\delta_z = \frac{\sum_z zF_d}{V} \quad (17)$$

$$\delta_{zr} = \frac{\left( \sum_z zF_r^2 \right)^{1/2}}{V} \quad (18)$$

$$\delta_k = \left( \frac{-\sum_z zU_h}{V} \right)^{1/2} \quad (19)$$

where  $\delta_d$  is the dispersion component,  $\delta_p$  is the polar component,  $\delta_h$  is the hydrogen bonding component,  $zF_d$  is the group contribution to the dispersion,  $zF_p$  is the group contribution to the polar parameter,  $zU_h$  is the group contribution to the hydrogen bonding parameter, and  $V$  is the group molar volume.

The solubility parameters of water, methanol, and C-PEK are summarized in Table III. Unfortunately, a parameter for a sulfonic acid group is not available. It is, however, expected that a sulfonic acid group possesses a large hydrogen bonding force. The total solubility parameter ( $\delta$ ) is 47.8 MPa<sup>1/2</sup> for water and 29.6 MPa<sup>1/2</sup> for methanol. The  $\delta_d$  values of water and methanol are almost the same. The difference in  $\delta$  results in  $\delta_p$  and, specifically,  $\delta_h$ . C-PEK has a  $\delta$  value of 19.4 MPa<sup>1/2</sup>, much lower than that of water and methanol. SC-PEK must have a larger  $\delta$  value than C-PEK, with a significantly larger  $\delta_p$  value because of the existence of a sulfonic acid group in its structure. On the basis of the results in Figures 15 and 16, water molecules were sorbed selectively in SC-PEK when compared with methanol because of the effects of  $\delta_h$ .

As previously explained, among SC-PEK, only SC-PEK1h (degree of sulfonation: 0.36) selectively sorbs methanol when compared with water. In Table I, SC-PEK1h showed the widest  $d$ -spacing and the largest FFV among SC-PEK. Because methanol has smaller  $\delta_p$

and  $\delta_h$  than water, methanol molecules are probably sorbed preferably around polar structures in C-PEK and in SC-PEK with low sulfonic acid groups. In this regard, continuous sulfonic acid groups in a membrane are necessary to provide water selective sorption from methanol–water solutions. If the domain of sorbed water molecules is large and acts like bulk water, methanol molecules would be dispersed into the domains of water molecules. The small methanol solubility in SC-PEK with high sulfonic acid content suggests that the domain of water molecules sorbed in a membrane around sulfonic acid groups must be small; that is, the channel of water transport in SC-PEK membranes is narrow.

## CONCLUSIONS

The preparation and solubility of water–methanol mixtures in sulfonated C-PEK was systematically studied. The sulfonation was carried out by reacting C-PEK with 98% sulfuric acid at 60°C. This reaction obeys a first-order reaction mechanism up to 4 h. The sulfonic acid group was uniformly dispersed in sulfonated C-PEK (SC-PEK) membranes. The introduction of sulfonic acid groups in C-PEK can increase polymer segmental gaps because of a size effect or decrease polymer segmental gaps because of polar interactions. The former effect is dominant for SC-PEK with low sulfonic acid content, whereas the latter one is for SC-PEK with high sulfonic acid content. The uptake of pure water or a methanol aqueous solution (e.g., 3, 5, 10 wt % methanol concentration) in the sulfonated C-PEK membranes increases with increasing sulfonic acid group content. However, the sulfonated C-PEK with high sulfonic acid content selectively sorbs water rather than methanol in the membrane. This suggests that the sulfonated C-PEK membrane could prevent methanol crossover and has a potential as a polymer electrolyte for the DMFC.

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