

Effects and Properties of Poly(arylene ether benzonitrile)s of Various Molecular Weights Blended with Sulfonated Poly(ether ether ketone)

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Received 6 April 2007; accepted 21 August 2007

DOI 10.1002/app.27400

Published online 27 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(arylene ether benzonitrile) (PAEBN) was synthesized with 2,6-dichlorobenzonitrile and biphenol. PAEBNs with various molecular weights (MWs), 1,640,000 and 185,000 g/mol, were synthesized by control of the stoichiometry of the monomers and were blended with sulfonated poly(ether ether ketone) (SPEEK). The effects of MW on the water uptake, swelling, methanol permeability, and proton conductivity of the SPEEK/

PAEBN blend membranes were investigated. The molecular mobility of the SPEEK/PAEBN blends was also examined in this study. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3236–3243, 2008

Key words: blends; gel permeation chromatography (GPC); ionomers; membranes; NMR; poly(ether ketones); swelling

INTRODUCTION

Proton-exchange membranes (also termed *polymer electrolyte membranes*; PEMs) have been used in direct methanol fuel cells (DMFCs) to separate methanol and oxygen, where it allows protons to transfer from the anode to the cathode.^{1,2} The requirements for PEMs are (1) a high proton conductivity, (2) a low electronic conductivity, (3) the ability to block fuel and oxidants, (4) a low water drag during proton transfer, (5) oxidative and hydrolytic stability, (6) good mechanical properties, (7) low cost, and (8) electrode/membrane interface resistance.¹ Perfluorinated polymer materials are typically used currently because of their high proton conductivity, long-term stability, and good mechanical properties.¹ However, drawbacks, such as water repelling over 80°C and a relatively high methanol cross-over, limit the applications of perfluorinated materials both high-temperature fuel cells and DMFCs. In view of this, alternative materials, such as poly(arylene ethers),^{3–5} polyimide,^{6,7} and polyphosphazene,^{8,9} have been widely investigated. Proton conductivity can be achieved by the postsulfonation of these high-performance polymers.

Among the aforementioned nonperfluorinated materials, sulfonated poly(ether ether ketone) (SPEEK) has potential because of its good mechanical properties, high proton conductivity, and lifetime of longer than 3000 h.^{10,11} However, the degree of sulfonation (DS) not only leads to a high proton conductivity but also increases the hydrophilicity, which can lead to extreme water uptake and methanol permeability.¹² Consequently, many approaches have been proposed to reduce the water uptake and swelling at high DS.^{13–16}

In this study, SPEEK was chosen for the major component of PEMs and, further, was blended with poly(arylene ether benzonitrile) (PAEBN). Sumner et al.¹⁷ proposed the synthesis of sulfonated poly(arylene ether) copolymers containing aromatic nitriles. They anticipated that the nitrile functional groups would afford hydrogen bonding sites for heteropolyacid particles in future nanocomposites. Similar to that of their polymer structures, the synthesis of PAEBNs was conducted by the direct polymerization of 2,6-dichlorobenzonitrile (CN) and biphenol (BP). Nitrile groups are strong electron withdrawers, which facilitates the polymerization via nucleophilic aromatic substitution.^{17,18} Various molecular weights (MWs) of PAEBN were derived by control of the molar ratio of CN to BP. In this study, the effects of MW on the water uptake, swelling, methanol permeability, and proton conductivity of SPEEK/PAEBN blend membranes were investigated. The molecular mobility was also examined in this study.

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Contract grant sponsor: Ministry of Economic Affairs of the Republic of China; contract grant number: 94-EC-17-A-008-S1-0003.

EXPERIMENTAL

Materials

Poly(ether ether ketone) (PEEK; PEEK 450PF) was provided by Victrex (South Yorkshire, UK). Sulfuric acid (95–98 wt %) was obtained from the Union Chemicals Co. (Taiwan). Potassium carbonate was received from Showa Co. (Tokyo). CN, BP, and *N*-methyl-2-pyrrolidinone (NMP) were purchased from the Tedia Co., Inc. (Farfield, OH).

Synthesis of PAEBN

BP and potassium carbonate were dried in a vacuum oven overnight at 80°C before they were weighed. CN was used without further drying. Equal moles of CN and BP, potassium carbonate (1.15 molar ratio to BP), dry NMP (afforded a 20 wt % solid content), and toluene (50 vol % of NMP) were charged into a three-necked, round-bottom flask equipped with a mechanical stirrer, a Dean–Stark trap, and a nitrogen inlet. The synthesis of PAEBN is shown in Figure 1. The reaction mixture was heated in an isothermal oil bath at 155°C to remove water. The oil bath temperature was raised slowly to 175°C and was maintained for 10 h. At the end of the reaction, the viscous product was diluted with NMP and was cooled to room temperature, following by the addition of excess methanol to the product to precipitate PAEBN. The polymer product was collected and washed two times with methanol and deionized water to remove salts and oligomers. The product was dried at 80°C for 1 day and was milled before blending.

Sulfonation of PEEK

The sulfonation of PEEK was similar to the procedure described elsewhere.¹¹ The sulfonation of PEEK was performed according to the following procedure: PEEK was dried for more than 12 h in an oven at 80°C; 40 g of the polymer was dissolved in 400 g of concentrated sulfuric acid (> 95%) at 40°C for up to 7 h to the desired conversion. The product solution was gradually added to a large excess of water in an ice bath and washed with distilled water until the pH value was over 6. The polymer was then dried in an oven at 80°C for 1 day.

Blends of SPEEK and PAEBN and membrane preparation

SPEEK and PAEBN were dissolved in NMP at concentrations of 10 wt %. The SPEEK solution and the PAEBN solution were blended at given compositions and were stirred for 12–24 h. The mixing solutions were cast onto a glass plate and placed in a vacuum oven at 40°C for 1 day, 60°C for 1 more day, and



Figure 1 Synthesis of BPCN. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

100°C for 2 additional days. The initial and final thicknesses of the membranes were 800 and 80 μm, respectively.

Characterization

NMR

¹H-NMR spectra were performed on a Bruker DMX-500 NMR spectrometer (Bruker BioSpin Co., Billerica, MA). A 2–5 wt % polymer solution was prepared in DMSO-*d*₆ for each analysis.

High-resolution solid-state ¹³C-NMR experiments were performed on a Bruker DSX 400WB NMR spectrometer. Solid-state ¹³C-NMR was performed at resonance frequencies of 300.13 and 75.475 MHz for ¹H and ¹³C, respectively. The ¹³C cross-polarization/magic-angle spinning spectra were measured for 3.9 μs with a 90° pulse width, a 3-s pulse delay time, a 12.8-ms acquisition time, a spectral width of 200 ppm, and 2048 scans. Proton spin-lattice relaxation time in a rotating frame, or spin lock relaxation time (*T*_{1ρ}^H), was measured via carbon signal intensity with a 90°-τ-spin lock pulse sequence, where τ is the spin lock time, before the cross-polarization.

Intrinsic viscosities

Approximately 30 mg of the polymer was dissolved in 30 mL of NMP. The intrinsic viscosities of solutions were measured at 25°C with a Cannon Ubbelohde viscometer (Hsinchu, Taiwan).

Gel permeation chromatography (GPC)

MW was measured on a gel permeation chromatograph (Waters, Milford, MA) with a Waters 510 iso-

cratic high performance liquid chromatography (HPLC) pump and a Waters 2410 refractive-index detector. The columns were calibrated with polystyrene standards. Three columns (Styragel HR 0.5, 4, and 5) were used with NMP as the mobile phase with a 1.0 mL/min flow rate at 100°C.

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the SPEEK/PVP blend membranes were recorded between 4000 and 400 cm^{-1} on a Nicolet Avatar 320 FTIR spectrometer (WI). Thin films were prepared by solution casting onto KBr pellets. A minimum of 32 scans were signal-averaged with a resolution of 2 cm^{-1} in the 4000–400- cm^{-1} range.

Atomic force microscopy (AFM)

A tapping mode atomic force microscope (SPA-400, SII Nanotechnology, Inc., Tokyo) was used. The membranes were imaged under a relative humidity of about 50%.

Water uptake and swelling

The membrane was dried in a vacuum oven at 80°C for 4 h and was weighed at its dry weight (W_{dry}). The wet weight (W_{wet}) was obtained after the membrane was immersed in distilled water isothermally at 60°C for 2 h. The water uptake was calculated with the following equation:

$$\text{Water uptake} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\% \quad (1)$$

The water swelling was the extent of the increase in thickness when the sample membrane had soaked in water at 60°C for 2 h compared to that of dry membrane.

Ion-exchange capacity (IEC) and number of water molecules per sulfonic acid site (λ)

The amount of acid equivalents per gram of polymer could be obtained by the following steps. First, the membrane in the acid form was immersed in a 2M NaCl solution to convert sulfonic acid to its sodium form. Next, the released H^+ was back-titrated with a 0.01N NaOH solution with phenolphthalein as the indicator.⁴

λ could be calculated with the following equation:

$$\lambda = \text{Water uptake}/(18 \times \text{IEC}) \quad (2)$$

where the water uptake could be obtained from eq. (1) and 18 is the MW of water.

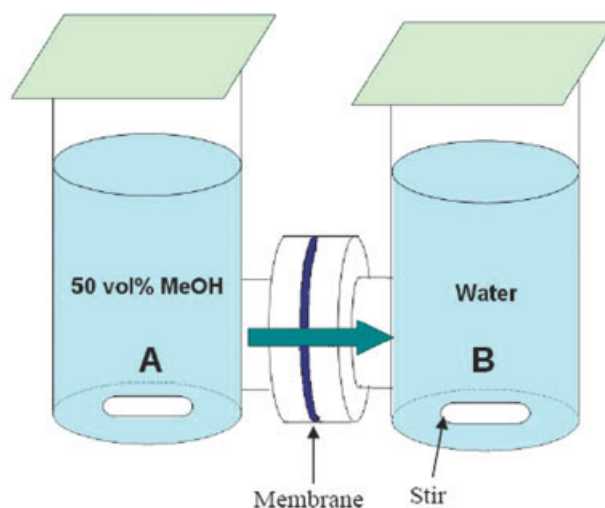


Figure 2 Methanol permeability cell. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Methanol permeability

The methanol permeability of the sample was determined with test cells, as illustrated in Figure 2. Each compartment was stirred constantly during the experiment to ensure the uniformity of cell concentration. The refractive index of compartment B and the temperature were detected with time. The detected refractive indices were converted to methanol concentration by the calibration curve. The methanol permeability was obtained by analysis of the methanol concentration with time.

Proton conductivity

Proton conductivities were measured by an alternating-current impedance method with an electrochemical interface (1260 interface/gain phase analyzer, Solartron, Hampshire, United Kingdom) at room temperature. The membrane was soaked in a water bath (60°C) for 1 h before conductivity testing. The membrane sample was sandwiched between two circular electrodes. A spring linked to one of the electrodes kept the membrane under a slight but constant pressure and thereby provided good contact between the electrodes and the membrane. The conductivity (σ) was calculated from the following equation: $\sigma = L/(RA)$, where L is the membrane thickness, A is the surface area of the electrodes, and R is the resistance.

Differential scanning calorimetry (DSC)

A differential scanning calorimeter (Q10, TA Instruments) was used to measure the glass-transition temperature (T_g) of the test membrane. The heating rate

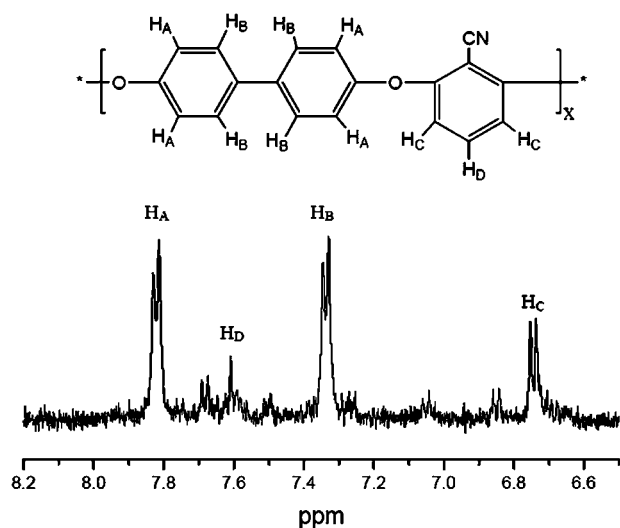


Figure 3 $^1\text{H-NMR}$ of poly(arylene ether benzonitrile) (BPCN).

was $5^\circ\text{C}/\text{min}$ within a temperature range of $50\text{--}250^\circ\text{C}$. T_g was determined at the midpoint of the transition point of the heat-capacity change.

RESULTS AND DISCUSSION

Synthesis and characterization of SPEEK and PAEBN

The characterization of the chemical structure of PAEBN was done by $^1\text{H-NMR}$, and the results are shown in Figure 3. The chemical shifts and the integrals of each peak were as follows: $H_A = 7.82$ ppm, $H_B = 7.33$ ppm, $H_C = 6.74$ ppm, $H_D = 7.61$ ppm, $I_A = 4$, $I_B = 4$, $I_C = 2$, and $I_D = 1$.

To control the MW of PAEBN, the molar ratio of CN to BP was controlled to obtain the required averaged degree of polymerization (DP). For the polymerization of the bifunctional monomers CN and BP, the number-average DP was expressed as¹⁸

$$\text{DP} = \frac{N_A(1 + 1/r)/2}{[N_A(1 - p) + N_B(1 - rp)]/2} = \frac{1 + r}{1 + r - 2rp} \quad (3)$$

where N_A and N_B are equal to twice the number of CN and BP molecules, respectively; r is the ratio of N_A to N_B ; and p is the reaction conversion. r was 0.995 for low-MW PAEBN and 0.9995 for high-MW PAEBN. With p assumed to be 0.99, which was practically reasonable, the DPs for $r = 0.995$ and $r = 0.9995$ were 80 and 98, respectively. The calculated number-average MWs were 22,800 and 27,900 g/mol for low-MW PAEBN and high-MW PAEBN, respectively.

The weight-average molecular weight (M_w) of SPEEK was measured with an intrinsic viscosity instrument and GPC; the results are listed in Table I. From GPC analysis, the MWs were 1,640,000 and 185,000 g/mol for high-MW PAEBN and low-MW

TABLE I
DS, $[\eta]_s$, and MW Values of SPEEK and BPCN

Sample	DS (%)	$[\eta]$ (dL/g)	M_w^a
SPEEK2	64	4.68	256,000
BPCN high	—	5.41	1,640,000
BPCN low	—	1.33	185,000

$[\eta]$ = intrinsic viscosity.

^a M_w was measured by GPC with NMP as the solvent at 100°C with polystyrene as the standard.

PAEBN, respectively. M_w from GPC analysis was much higher than the calculated number-average MW, especially for high-MW PAEBN. Presently, the exact reason is not clear. One suggestion is that the high p due to the strong electron-withdrawing functional group nitride of CN, which facilitated the nucleophilic substitution reactions, resulted in the great difference in DP with slightly changed molar ratios of the monomers.

The sulfonation of PEEK was carried out by the dissolution of PEEK in concentrated sulfuric acid (> 95%) for a given time. DS of SPEEK was correlated to the sulfonation time and the sulfonation temperature. Zaidi et al.⁴ reported that the DS of SPEEK was determined by $^1\text{H-NMR}$ and elemental analysis. DS of SPEEK was calculated from the following equation:⁴

$$\frac{\text{DS}}{12 - 2\text{DS}} = \frac{A_{H_E}}{\sum A_{H_{A,A',B,B',C,D}}} \quad (4)$$

where A is the peak area, H_E represents the protons closed to the sulfonated acid, and $H_{A,A',B,B',C,D}$ represents the other aromatic protons of SPEEK. The DS of SPEEK was 64% in this study. For determining MW of SPEEK, Devaus et al.¹⁹ proposed an empiri-

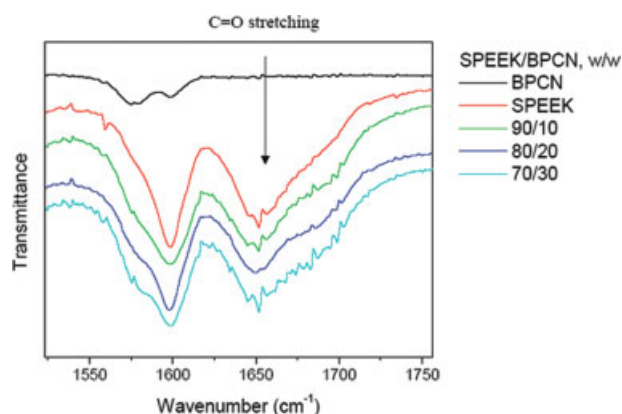


Figure 4 FTIR spectra of SPEEK/BPCN polymer blends ($\text{C}=\text{O}$ stretching at $1523\text{--}1756$ cm^{-1}). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

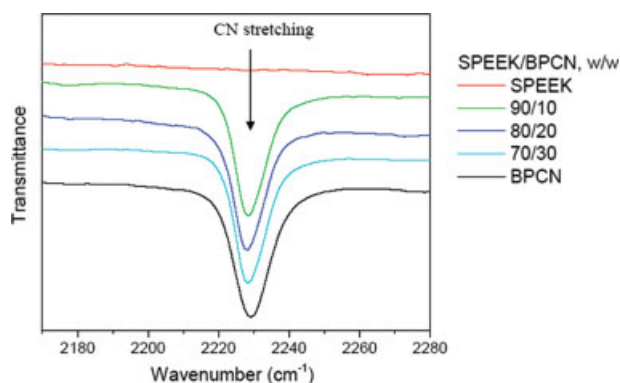


Figure 5 FTIR spectra of SPEEK/BPCN polymer blends (CN stretching at 2170–2280 cm^{-1}). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cal Mark–Houwink equation for relating the intrinsic viscosity of SPEEK ($[\eta]_s$):

$$[\eta]_{25^\circ\text{C}} = (3.849 \times 10^{-5})(M_w)_s^{0.94} (\text{dL/g}) \quad (5)$$

where $(M_w)_s$ is the molecular weight of SPEEK, $[\eta]_s$ was 4.68 dL/g, and M_w was 257,000 g/mol from eq. (5). This corresponded with M_w from GPC, which was 256,000 g/mol. Xing et al.¹¹ found that when DS was less than 80%, the overestimated MW of SPEEK was derived from eq. (5). In this study, the estimated MW of SPEEK was similar to the value from the GPC method, which indicated that MW was also overestimated from the GPC method. The ion-containing SPEEK had a size-excluded effect due to the interaction between ionic groups; therefore, the higher MW could be obtained. So far, there is no suitable method for measuring such kinds of polymers.

FTIR study

Figures 4 and 5 show the FTIR spectra of the SPEEK/PAEBN blends in the ranges 1523–1756 and 2170–2280 cm^{-1} , respectively. SPEEK blended with different MW PAEBNs showed the same FTIR results. As

shown in Figure 4, the carbonyl stretching of SPEEK was at 1650 cm^{-1} . The shoulder peak around 1687 cm^{-1} was enhanced with increasing PAEBN content. Figure 5 displays the nitrile stretching of PAEBN. The nitrile peak of PAEBN was slightly shifted from 2229 to 2228 cm^{-1} as blended with SPEEK. At least three scans were done for each sample to confirm that the chemical shifts did not result from the experimental errors. In addition, the sulfonic acid group (SO_3H), for which the peak was between 1030 and 1010 cm^{-1} , exhibited no shift with increasing content of PAEBN. The FTIR results suggested that the CN interacted slightly with SO_3H , which lowered the presence of interactions between $\text{C}=\text{O}$ and SO_3H .

Morphology

The hydrophilic region and the hydrophobic domains were investigated with AFM in tapping mode. Phase diagrams of the SPEEK/PAEBN blend membranes are shown in Figure 6, where the dark parts represent the softer hydrophilic regions and the light parts represent the harder hydrophobic regions.²⁰ For SPEEK, the dark regions were continuously distributed over the polymer matrix with an averaged length of around 50 nm. However, it became 20 nm as 10 wt % low-MW PAEBN was incorporated. Moreover, SPEEK blended with 10 wt % high-MW PAEBN led to the disappearance of the light region, which indicated the hydrophilic region was substantially reduced and may have been embedded in the hydrophobic region. Different hydrophobic/hydrophilic phase behaviors have great influences on the properties, such as water uptake and swelling, of blend membranes; we discuss this later.

Water uptake and swelling

The water uptake, IEC, and the proton conductivity of the membrane are the most basic properties that should be measured in comparison to standard Nafion 117 materials and other systems.¹

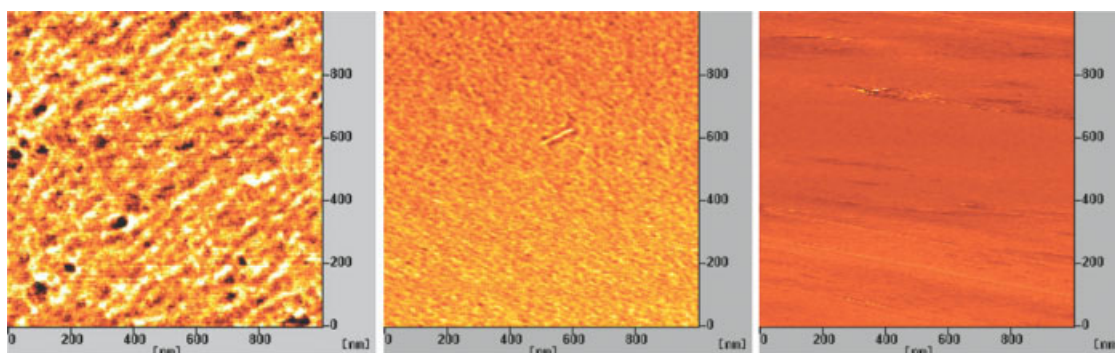


Figure 6 AFM phase images of (a) SPEEK, (b) SPEEK/low-MW BPCN (90/10 w/w), and (c) SPEEK/high-MW BPCN (90/10 w/w). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

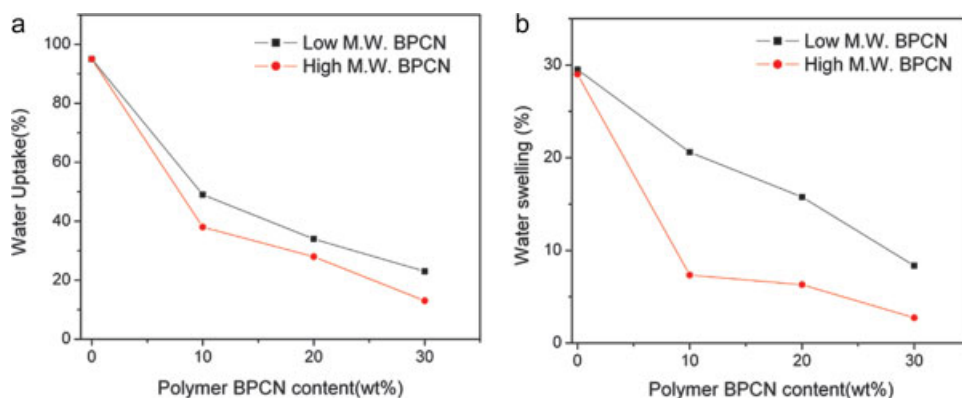


Figure 7 (a) Water uptake and (b) water swelling of the SPEEK/BPCN blend membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

First, the water uptake and the swelling are very crucial because they are closely related to the proton conductivity and the mechanical strength of proton conducting membranes. Compared with Nafion, SPEEK exhibited smaller water-containing channels due to the rigidity of the polymer backbone and the attachment of the pendent group.²¹ Water molecules facilitated proton transfer within the polymer membrane. However, excess water uptake decreased the dimensional stability and reduced the mechanical strength. Figure 7 displays the water uptake and the water swelling of the SPEEK/PAEBN blend membranes. As expected, the water uptake and the swelling of the blend membranes decreased with increasing content of PAEBN. Also, SPEEK blended with high-MW PAEBN showed a lower water uptake and less swelling than low-MW PAEBN. Compared with the low-MW sample, the high-MW sample possessed more polymer entanglement, which led to less water in the hydrophilic region, that is, sulfonic acid groups. Polymer entanglements in the blend membranes could be considered physical crosslinking, which constrained the water swelling of the polymer

backbone of SPEEK. SPEEK blended with 10 wt % high-MW PAEBN or 30 wt % low-MW PAEBN showed good dimensional stability. Moreover, the dimensional change was less than 10% at 60°C. The water uptake of the blend with 10 wt % high-MW sample was 47%, which was higher than that of Nafion (19%). Overall, the membrane samples possessed higher water uptakes than that of Nafion.

IEC, λ , and proton conductivity

IEC is an important property for PEM; it represents the amount of sulfonic acid per gram of polymer membrane. Figure 8 shows the IEC and λ of the SPEEK/PAEBN membranes of various PAEBN contents. IEC was decreased in proportion to the increased PAEBN content regardless of the MW of PAEBN. Also, λ was correlated to both IEC and water content. The low-MW sample showed a higher water uptake; hence, a higher λ was obtained. The λ value of the 10 wt % high-MW sample was similar to that of the 30 wt % low-MW sample.

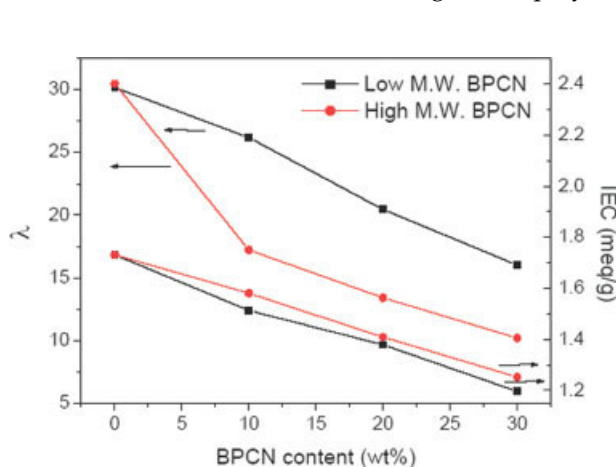


Figure 8 λ and IEC values of the SPEEK/BPCN blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

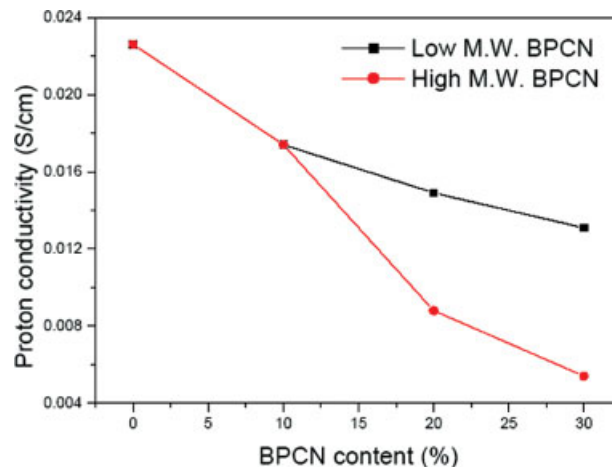


Figure 9 Proton conductivity of the SPEEK/BPCN blend membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

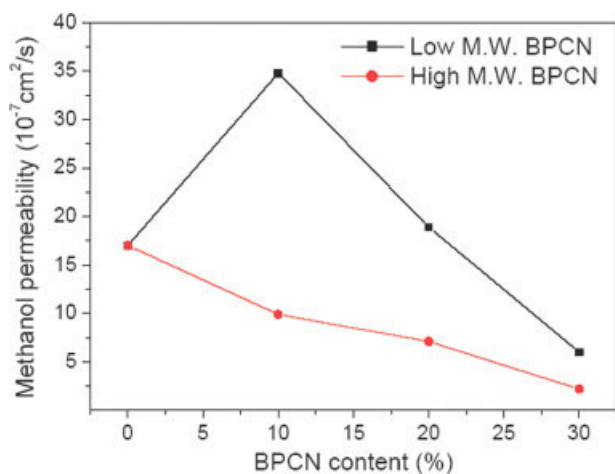


Figure 10 Methanol permeability of the SPEEK/BPCN blend membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The foremost basic property of the membranes is the proton conductivity due to the direct effect on the membrane electrode assembly performance. McGrath's and coworkers^{1,20} used a simple cell to determine the proton conductivity in the plane, which allows equilibration in a variety of environments. On the other hand, the proton conductivity through the plane is more like the real conditions in a fuel cell. Through the plane, the proton conductivities of the SPEEK/PAEBN blend membranes are shown in Figure 9. The self-measured proton conductivity of Nafion was 0.09 S/cm, which was higher than that of the blend samples, the values of which ranged from 0.004 to 0.024 S/cm. The proton conductivity of all the blend membranes behaved similarly: low-MW samples showed a lower decrease in proton conductivity than high-MW samples. The proton conductivity was related to water uptake, IEC, and temperature. Blends with higher PAEBN contents exhibited even lower water uptakes, which led to a higher reduction in proton conductivity.

Methanol permeability

The methanol permeability is also very important, in addition to the proton conductivity, for DMFCs. As shown in Figure 10, the high-MW sample showed a lower methanol permeability than the low-MW sam-

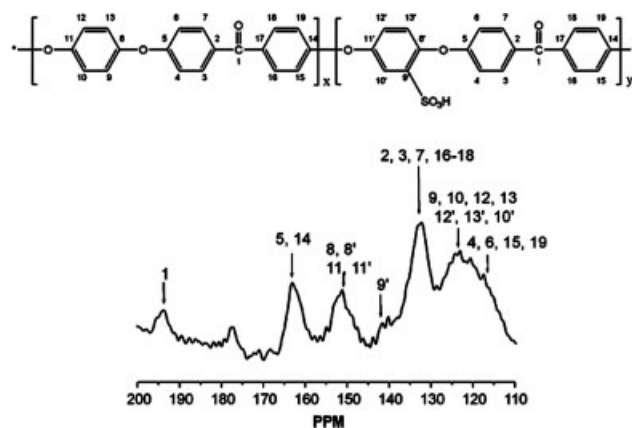


Figure 11 Solid-state ¹³C-NMR spectrum of SPEEK.

ple. Again, the lower methanol permeability was due to the decreasing hydrophilic region with the blending with PAEBN. The methanol permeability of the 10 wt % high-MW sample was 1×10^{-6} cm²/s, which was significantly lower than that of Nafion, which was 2.4 cm²/s, as measured in our laboratory.

Molecular mobility study

Solid-state ¹³C-NMR can provide evidence to explain the molecular motion of various types of polymers. The magnetization (M) of each polymer chain can be modulated or averaged by molecular motions. The NMR relaxation behavior of polymers shows the molecular structure with respect to the mobility of polymer chains. The relaxation time of ¹³C after the spin lock process is called $T_{1\rho}^H$. $T_{1\rho}^H$ can be expressed as the following equation:²²

$$M(\tau) = M_0 \exp(-\tau/T_{1\rho}) \quad (6)$$

where M_0 is the initial magnetization.

The chemical shift of each carbon on SPEEK was assigned as illustrated in Figure 11. The $T_{1\rho}^H$ values are summarized in Table II. All $T_{1\rho}^H$'s of the carbons on SPEEK increased with increasing PAEBN content, which indicated that the molecular motion of the SPEEK polymer chain was reduced. The reduced molecular motion was due to the rigid PAEBN polymer chain, which restricted the segmental motion of SPEEK or the specific interaction between PAEBN and SPEEK. In addition, SPEEK blended with low-molecular PAEBN showed a lower molecular mobil-

TABLE II
 $T_{1\rho}^H$ Measured at 300 K of the Corresponding Segmental Motions of SPEEK in the SPEEK/BPCN Blends

SPEEK/ BPCN ratio	C1 (ms)	C2, C3, C7, C16–C18 (ms)	C5, C14 (ms)	C8, C8', C11, C11' (ms)	C9, C10, C12, C13 C10', C12', C13' (ms)
100/0	1.0	1.0	1.4	0.9	1.5
70/30 low		5.7	8.5	12.2	7.4
70/30 high		5.4	5.1	5.5	6.8

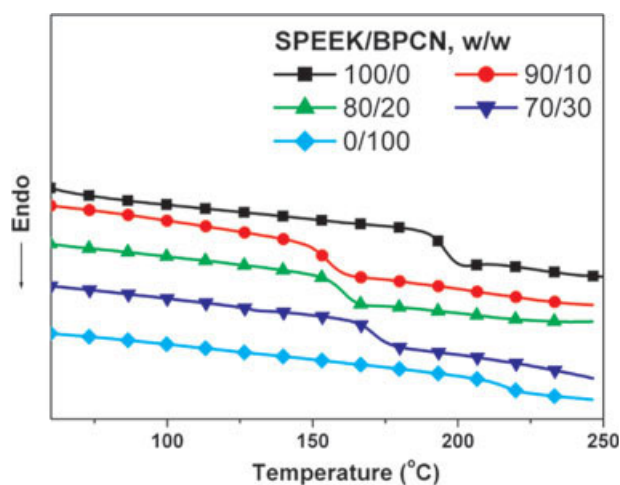


Figure 12 DSC results for the SPEEK/BPCN blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ity than that blended with high-MW PAEBN. Low-MW PAEBN could be blended with SPEEK in molecular levels more easily because when it was dissolved in the solvent, a greater presence of polymer entanglement in low-MW PAEBN could be untangled compared to that in high-MW PAEBN.

T_g

T_g of the SPEEK/PAEBN blend membrane was measured by DSC, and the results were shown in Figure 12. The T_g 's of SPEEK and PAEBN were 196 and 219°C, respectively. In general, the polymer blends followed the rule of mixture, which means that T_g of the polymer blends was between the T_g value of each component polymer. However, the SPEEK/PAEBN blended membranes showed a decreased T_g compared to that of SPEEK. This suggests that the increased interaction by hydrogen bonding between each sulfonic acid group led to an increasing T_g .^{4,23} That is, the T_g of PEEK was between 143 and 155°C and increased with increasing DS.⁴ In other words, the T_g of SPEEK also increased as its IEC increased. We propose that decreased T_g of SPEEK resulted from the reduced IEC with the addition of PAEBN.

CONCLUSIONS

Various MW PAEBN samples were synthesized and characterized by FTIR and NMR spectroscopies and GPC. The MW was controlled by the molar ratio of the monomers. This study first demonstrated the effect of MW on the performance of PEM. Blending high-MW PAEBN led to lower hydrophilic sizes than that of the low-MW sample because it could form more polymer entanglements, which limited

the swelling of the SPEEK polymer chain; thus, fewer water molecules could enter into the polymer network. The high-MW samples possessed a lower water uptake, λ and swelling than that of the low-MW samples. Because the proton transfer was bound to the water molecules, the extent of water greatly affected the proton conductivity. Therefore, the high-MW sample had lower water uptake; hence, lower proton conductivity was observed. All $T_{1\rho}^H$ values of the carbons on SPEEK increased with increasing of PAEBN content, which indicated that the molecular motion of the SPEEK polymer chain was reduced. In addition, the SPEEK blended with low-molecular PAEBN showed a lower molecular mobility than that of high-MW PAEBN. Compared to Nafion, the blend membrane showed a lower proton conductivity and methanol permeability.

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