

# Synthesis and Characterization of Sulfonated Block Copolyimides Derived from 4,4'-Sulfide-bis(naphthalic anhydride) for Proton Exchange Membranes

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**ABSTRACT:** A series of sulfonated copolyimides (SPIs) with hydrophilic segment length of 20–60 based on 4,4'-sulfide-bis(naphthalic anhydride) (SBNA) have been successfully synthesized to improve hydrolytic stability and proton conductivity. The SPI membranes were cast from their *m*-cresol solutions, and they were characterized by determining the water uptake, water swelling ratio, mechanical properties, hydrolytic stability, oxidative stability, and proton conductivity. It was found that the water uptake of SPI membranes was low and decreased as the hydrophilic segment length increased, which led to good dimensional stability. In addition, the SPI membranes with low ion-exchange capacity (IEC) value displayed excellent hydrolytic stability and retained good mechanical properties even after harsh hydrolysis testing, in which the block SPI with hydrophilic segment length of 40 had the best hydrolytic stability, while those with high IEC value showed an apparent decrease. All of the block SPI membranes show better conductivity than the random ones at the temperature range from 30 to 70°C. Interestingly, the proton conductivities of random SPI membranes were higher than that of corresponding block ones at 90°C. The block SPI with hydrophilic segment length of 40 gave the highest proton conductivity as the temperature increased among the block SPIs. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41501.

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## INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) is considered to be one of the most promising clean energy technologies in the 21st century.<sup>1–3</sup> As the key component of the PEMFC, proton exchange membrane (PEM) is responsible for proton migration from the anode to the cathode. Currently, the well studied and practically used PEMs are perfluorinated sulfonated ionomer membranes, such as Nafion<sup>®</sup> (DuPont), Aciplex<sup>®</sup> (Asahi Kasei), and Flemion<sup>®</sup> (Asahi Glass), because of their high proton conductivity, high mechanical strength and satisfactory chemical stability.<sup>4</sup> However, these membranes can only be used at low temperature (<80°C) because of their low conductivity at high temperature/low humidity. Therefore, much efforts in PEMFC researches are focused on sulfonated aromatic hydrocarbon polymers, which include sulfonated poly(arylene ether sulfone)s,<sup>5–7</sup> poly(arylene ether ketone)s,<sup>8–10</sup> polyimides,<sup>11,12</sup> polybenzimidazoles,<sup>13–15</sup> to develop high temperature PEMFCs in order to afford higher energy efficiency and preferable performances.<sup>16–18</sup>

Among these sulfonated aromatic hydrocarbon polymers, sulfonated polyimides (SPIs) have been deemed to be a potential can-

didate owing to the excellent thermal and mechanical stabilities, extremely low methanol permeation, and low electro-osmotic drag coefficients.<sup>19</sup> However, because of the hydrolytic instability of imide moiety in the SPIs, which affects the lifetime of membranes in fuel cell application,<sup>20</sup> a lot of novel SPIs have been designed and synthesized using naphthalene tetracarboxylic dianhydride (NTDA) with many high basic sulfonated diamines to enhance their hydrolytic stability.<sup>21–23</sup> In addition, the hydrolytic stability of SPIs also could be improved by using dianhydrides with low electron affinity, such as 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNTDA),<sup>24–26</sup> benzophenone-4,4'-bis(4-thio-1,8-naphthalic anhydride) (BPBTNA).<sup>27,28</sup> Recently, our group has reported the SPIs obtained from another dianhydride monomer with calculated electron affinity (*E<sub>a</sub>*) value of 2.03 eV, 4,4'-sulfide-bis(naphthalic anhydride) (SBNA), showed comparable hydrolytic stability and higher proton conductivity.<sup>28</sup> However, only random SPI membranes were investigated to relate their structure and property relationships in these reports.

As we all known, the morphology of proton exchange membranes is expected to play an important role in determining the

membrane properties such as water uptake, proton conductivity, etc.<sup>29</sup> As observed in Nafion, well-connected ionic channel network is formed by microphase or nanophase separation between the hydrophilic proton transport sites and the hydrophobic domain, which leads to high proton conductivity even with low ion-exchange capacity (IEC).<sup>30</sup> Therefore, block SPIs were synthesized via block copolymerization to achieve phase separation and improve the proton conductivity. Mercier and coworkers first reported sulfonated block copolyimides from NTDA and 2,2'-bendizine sulfonic acid (BDSA) showed best proton conductivity with proper block length of 3 in 2001, although the water uptake of block SPI was lower than random one.<sup>31</sup> However, similar block SPIs but using different unsulfonated diamines showed very different properties. The proton conductivity strongly depended on the block chain lengths and increased with an increase in the block lengths among 49–122, which were reported by Kawakami and coworkers.<sup>32,33</sup> Besides those, various NTDA-based block SPIs with different sulfonated diamines containing sulfonic acid groups in side chain and/or with flexible aliphatic moiety in the polymer chain were considered to be favorable to the aggregation of the hydrophilic phase, thus benefited the microphase separation.<sup>34–38</sup> In addition, Zhang and coworkers reported block SPI obtained by sulfonated dianhydride BNTDA and sulfonated diamine with high ion-exchange capacity (IEC) showed better microphase separated morphology.<sup>39,40</sup> As far as we know, there was no report on the block SPIs using dianhydrides with lower electron affinity.

Therefore, we intend to adopt block copolymerization strategy by using dianhydrides with low electron affinity to not only achieve phase separation and improve the proton conductivity but also enhance hydrolytic stability of SPIs. Herein, we will describe the synthesis and related properties of block SPIs obtained from SBNA and discuss the differences between block SPIs with different hydrophilic segment lengths and random ones.

## EXPERIMENTAL

### Materials

4-Bromo-1,8-naphthalic anhydride (TCI, 95+%) was recrystallized from acetic anhydride and then dried at 140°C under vacuum. Anhydrous sodium sulfide was purchased from Inner Mongolia Lichuan Chemistry (Bayannur, China). 4,4'-Diaminodiphenyl ether (ODA, TCI, 98%) was purified by sublimation before use. *N,N*-Dimethylacetamide and *N,N*-dimethylformamide (DMAc and DMF, Sinopharm Chemical Reagent) were distilled from calcium hydride before use. All other reagents in this study were commercially obtained and used as received without further purification.

### Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Thermo Nicolet 6700 FTIR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker 400 AVANCE III spectrometer operating at 400 MHz, using dimethylsulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) as solvent. The inherent viscosities were measured with an Ubbelohde Viscometer at 30°C in *m*-cresol at a concentration of 0.5 g/dL. The molecular weight measurement was performed via gel permeation chromatogra-

phy (TOSOH HLC-8320) equipped with a differential refractometer. *N,N*-Dimethylformamide was used as the eluent at a flow rate of 0.6 mL/min.  $M_w$  and  $M_n$  were calibrated with standard polystyrene samples.

For the TEM observation, membranes were stained with silver by ion exchange of sulfonic acid groups by immersing them in a 0.5 M AgNO<sub>3</sub> aqueous solution overnight, rinsed with water, and dried at room temperature for 12 h. The stained membranes were embedded in epoxy resin and sectioned to yield 70 nm thick using an RMC PT-XL microtome, and placed on copper grids. Images were taken on a Tecnai F20 transmission electron microscope using an accelerating voltage of 200 kV.

The water uptake of the sulfonated copolyimide was gravimetrically determined from the dried and humidified membranes. The hydrated membrane was dried at 120°C under vacuum for 12 h until constant weight as dry material was obtained. It was immersed into deionized water at room temperature for 20 h. Then the membrane was taken out, wiped with tissue paper, and quickly weighted on a microbalance. Water uptake of the SPI membranes was calculated from

$$\text{water uptake (\%)} = [(W_w - W_d) / W_d] \times 100\% \quad (1)$$

where  $W_d$  and  $W_w$  are the weight of dry and corresponding water swollen membranes, respectively.

The dimensional stability of SPI membranes was investigated by immersing the membranes into deionized water at room temperature or 80°C for 20 h. The changes of thickness and in-plane direction were calculated from

$$\Delta T = (T - T_s) / T_s \quad \Delta L = (L - L_s) / L_s \quad (2)$$

where  $T_s$  and  $L_s$  are the thickness and length of the membrane at dry state, respectively;  $T$  and  $L$  refer to those of the membrane immersed in deionized water for 20 h.

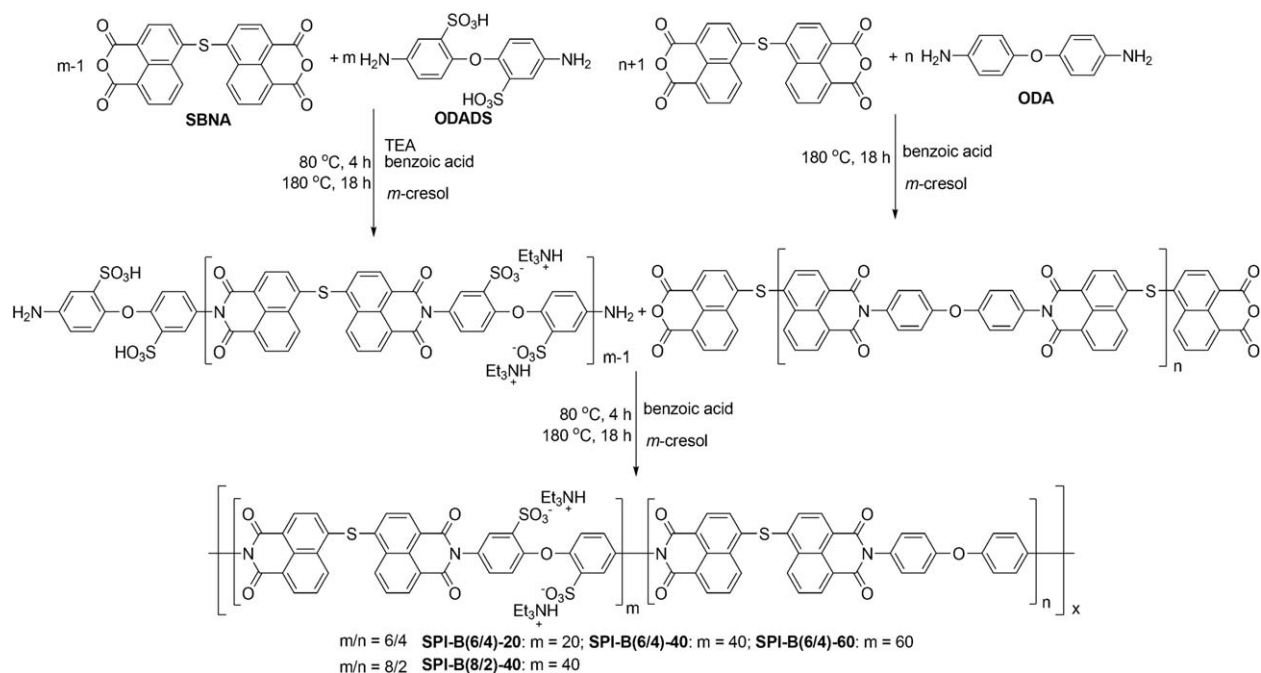
The oxidative stability of the fresh SPI membranes was determined by immersing the membrane samples (10 mm × 10 mm) with a thickness about 30 μm into Fenton's reagent (30 ppm FeSO<sub>4</sub> in 30% H<sub>2</sub>O<sub>2</sub>) at room temperature, which was evaluated by recording the time when the membranes began to dissolve ( $\tau_1$ ) and dissolved completely ( $\tau_2$ ).

The hydrolytic stability was evaluated by treating the membrane samples in water at 140°C for 24 h as an accelerated testing. Mechanical properties before and after the hydrolytic testing were measured and averaged on at least three film specimens by an Instron model 5567 at ambient conditions (25°C and 50% RH). The wet samples for testing mechanical properties were equilibrated at ambient conditions for 24 h before measurement.

The proton conductivity ( $\sigma$ , S/cm) was calculated by the formula from

$$\sigma = L / (RA) \quad (3)$$

where  $L$ ,  $R$ , and  $A$  are the distance between two electrodes, the resistance value, and the cross-sectional area of membranes, respectively. The resistance value ( $R$ ) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-



Scheme 1. Synthesis of sulfonated block polyimides.

phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287).

#### Monomer Synthesis

4,4'-Diaminodiphenyl ether-2,2'-disulfonic acid (ODADS)<sup>41</sup> and 4,4'-sulfide-bis(naphthalic anhydride) (SBNA)<sup>28</sup> were prepared according to the reported procedures.

#### Polymer Synthesis

The synthesis of sulfonated block copolyimide SPI-B(6/4)-40 is described below as an example to illustrate the general synthetic route for the preparation. A flask was charged with ODADS (0.6618 g, 1.84 mmol), triethylamine (0.4467 g, 4.41 mmol), and *m*-cresol (8 mL) under nitrogen atmosphere with stirring. After ODADS was dissolved completely, SBNA (0.7640 g, 1.79 mmol), and benzoic acid (0.3274 g, 2.68 mmol) were added and the mixture was stirred at room temperature for 30 min. Then the reaction was heated at 80°C for 4 h and 180°C for 18 h to afford amine-terminated polyimide oligomers. In another flask, the anhydride-terminated polyimide oligomers were prepared from ODA (0.2454 g, 1.23 mmol), an excess of SBNA (0.5420 g, 1.27 mmol), and benzoic acid (0.2324 g, 1.91 mmol) in *m*-cresol (8 mL) at 180°C for 18 h. After the two flasks were cooled to 80°C, the solution of anhydride-terminated polyimide oligomers was transferred to another flask containing amine-terminated polyimide oligomers. *m*-Cresol (6 mL) was used for complete transfer to avoid any loss. Then the mixture was stirred at 80°C for 4 h and 180°C for 18 h. After cooling to 80°C, the viscous solution was diluted with *m*-cresol and trickled into 500 mL of acetone to afford a precipitate. Then the precipitate was collected by filtration, extracted with acetone in a Soxhlet extractor for 20 h, and dried at 150°C for 24 h under vacuum.

**SPI-B(6/4)-40.** FTIR (film): 1704  $\text{cm}^{-1}$  ( $\nu_{\text{asym}} \text{C=O}$ ), 1656  $\text{cm}^{-1}$  ( $\nu_{\text{sym}} \text{C=O}$ ), and 1363  $\text{cm}^{-1}$  ( $\nu_{\text{C-N}}$  imide), 1229, 1186, 1081, 1025  $\text{cm}^{-1}$  (sulfonic acid group stretching).

**SPI-B(6/4)-20.** FTIR (film). 1708  $\text{cm}^{-1}$  ( $\nu_{\text{asym}} \text{C=O}$ ), 1666  $\text{cm}^{-1}$  ( $\nu_{\text{sym}} \text{C=O}$ ), and 1367  $\text{cm}^{-1}$  ( $\nu_{\text{C-N}}$  imide), 1239, 1193, 1085, 1028  $\text{cm}^{-1}$  (sulfonic acid group stretching).

**SPI-B(6/4)-60.** FTIR (film). 1708  $\text{cm}^{-1}$  ( $\nu_{\text{asym}} \text{C=O}$ ), 1686  $\text{cm}^{-1}$  ( $\nu_{\text{sym}} \text{C=O}$ ), and 1367  $\text{cm}^{-1}$  ( $\nu_{\text{C-N}}$  imide), 1239, 1193, 1085, 1029  $\text{cm}^{-1}$  (sulfonic acid group stretching)

**SPI-B(8/2)-40.** FTIR (film). 1703  $\text{cm}^{-1}$  ( $\nu_{\text{asym}} \text{C=O}$ ), 1655  $\text{cm}^{-1}$  ( $\nu_{\text{sym}} \text{C=O}$ ), and 1364  $\text{cm}^{-1}$  ( $\nu_{\text{C-N}}$  imide), 1231, 1186, 1082, 1025  $\text{cm}^{-1}$  (sulfonic acid group stretching).

#### Membrane Preparation and Proton Exchange

Polymer membranes were prepared by solution casting from *m*-cresol. The dried SPI powders (in triethylammonium salt form) were dissolved in *m*-cresol to form 8 wt % solutions, and then filtered to eliminate any particulates. The filtrate was cast onto glass plate and dried at 80°C for 12 h, and 120°C for 24 h. Then the membrane was soaked in ethanol for 48 h to remove the residual *m*-cresol. The membrane (in triethylammonium salt form) was treated with 1 M HCl at room temperature for 24 h and 1 M H<sub>2</sub>SO<sub>4</sub> at 50°C for 24 h for proton exchange to afford the corresponding sulfonic acid-form membranes. All membranes were carefully washed with deionized water and dried.

## RESULTS AND DISCUSSION

#### Polymer Synthesis and Properties

As shown in Scheme 1, the sulfonated block copolyimides SPI-B(6/4) series and SPI-B(8/2) were prepared via a two-pot procedure from SBNA, ODADS, and ODA in the presence of triethylamine and benzoic acid with the ratio of ODADS to ODA was 60:40 and 80:20, respectively. The amine-terminated hydrophilic segment was prepared from SBNA and ODADS in a pot, while the anhydride-terminated hydrophobic segment was prepared

**Table I.** Inherent Viscosity, IEC, Water Uptake, and Dimensional Stability of the SPI Membranes

SPI	$\eta_{inh}^a$ (dL/g)	IEC <sup>b</sup> (meq/g)	IEC <sup>c</sup> (meq/g)	WU <sup>d</sup> (%)	$\lambda^e$ (H <sub>2</sub> O/SO <sub>3</sub> <sup>-</sup> )	Dimensional stability <sup>f</sup>	
						$\Delta T$	$\Delta L$
SPI-B(6/4)-20	0.53	1.75	1.74	27.9	8.6	0.06 (0.07)	0.05 (0.06)
SPI-B(6/4)-40	0.59	1.75	1.73	26.8	8.5	0.06 (0.07)	0.05 (0.06)
SPI-B(6/4)-60	0.60	1.75	1.74	26.1	8.3	0.06 (0.07)	0.06 (0.07)
SPI-B(8/2)-40	0.63	2.23	2.23	35.2	8.8	0.09 (0.12)	0.06 (0.08)

<sup>a</sup> Measured in *m*-cresol at a concentration of 0.5 g/dL at 30°C in triethylammonium salt form.

<sup>b</sup> Calculated.

<sup>c</sup> Measured by titration with NaOH.

<sup>d</sup> Measured in water (100% RH) at room temperature.

<sup>e</sup> Number of water molecules per ion exchange site (SO<sub>3</sub><sup>-</sup>).

<sup>f</sup> Measured in water at room temperature or 80°C (given in parentheses).

from SBNA and ODA in another pot. Finally, the two pots were combined to synthesize the sulfonated block copolyimides. Take **SPI-B(6/4)** series with same ODADS content ( $m/n = 6/4$ ) but different lengths of hydrophilic and hydrophobic segments for example, the amine-terminated hydrophilic segment was prepared from SBNA and ODADS in a pot. The molar ratio of SBNA to ODADS in the first step was controlled to be **m-1/m**. Then the sequence length of repeat units was calculated to be **m-1** according to the following equation:  $l = r/(1 - r)$ , where the  $l$  is the sequence length and the  $r$  is the molar ratio of one component monomer to another excess component monomer.<sup>42</sup> The anhydride-terminated hydrophobic segment was prepared from SBNA and ODA with sequence length **n** in another pot. Finally, the two pots were combined to synthesize a series of block copolyimide **SPI-B(6/4)-m** with hydrophilic segment length of **m** and hydrophobic segment length of **n**. In this article, three different **SPI-B(6/4)-m** were prepared with increasing average repeating unit number **m** of the amine-terminated hydrophilic segment from 20 to 40, 60, respectively.

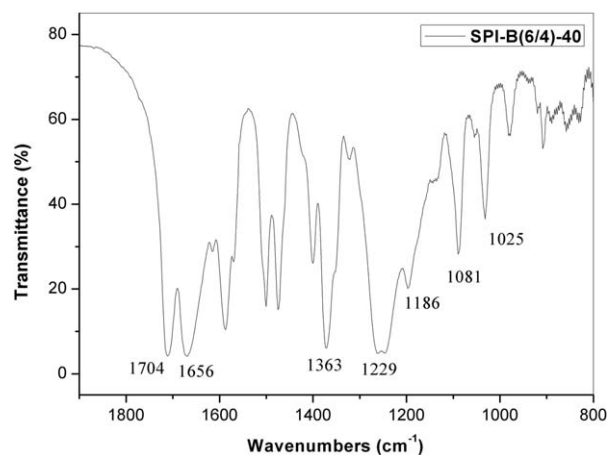
As shown in Table I, the inherent viscosities of these sulfonated polyimides (in triethylammonium salt form) ranged from 0.53 to 0.63 dL/g, indicating high-molecular weight polymers have been prepared. We found that the two-pot procedure for the synthesis of block SPIs and the increase of the amount of ODADS have no effect on the polymer formation. It should be noted that it was difficult to improve the molecular weights of these SPIs due to the low reactivity of SBNA. The "S" linkage of SBNA increased the electron density on the anhydride carbonyl groups, which was beneficial to enhance the hydrolytic stability, but made the nucleophilic attack of the amine group more difficult at the same time.<sup>43</sup> The block **SPI-B(6/4)** series has poor solubility in *N,N*-dimethylformamide while **SPI-B(8/2)-40** could be dissolved and measured molecular weight by GPC. The weight-average molecular weight ( $M_w$ ) and number-average molecular weight ( $M_n$ ) of **SPI-B(8/2)-40** were 88,000 and 27,300, respectively. However, all of the SPIs could be dissolved in *m*-cresol and give tough membranes.

The chemical structure of sulfonated polyimides in sulfonic acid form was confirmed by FTIR and <sup>1</sup>H NMR spectroscopy. The representative IR spectrum of **SPI-B(6/4)-40** is shown in Figure 1. The strong absorption bands around 1704 cm<sup>-1</sup>

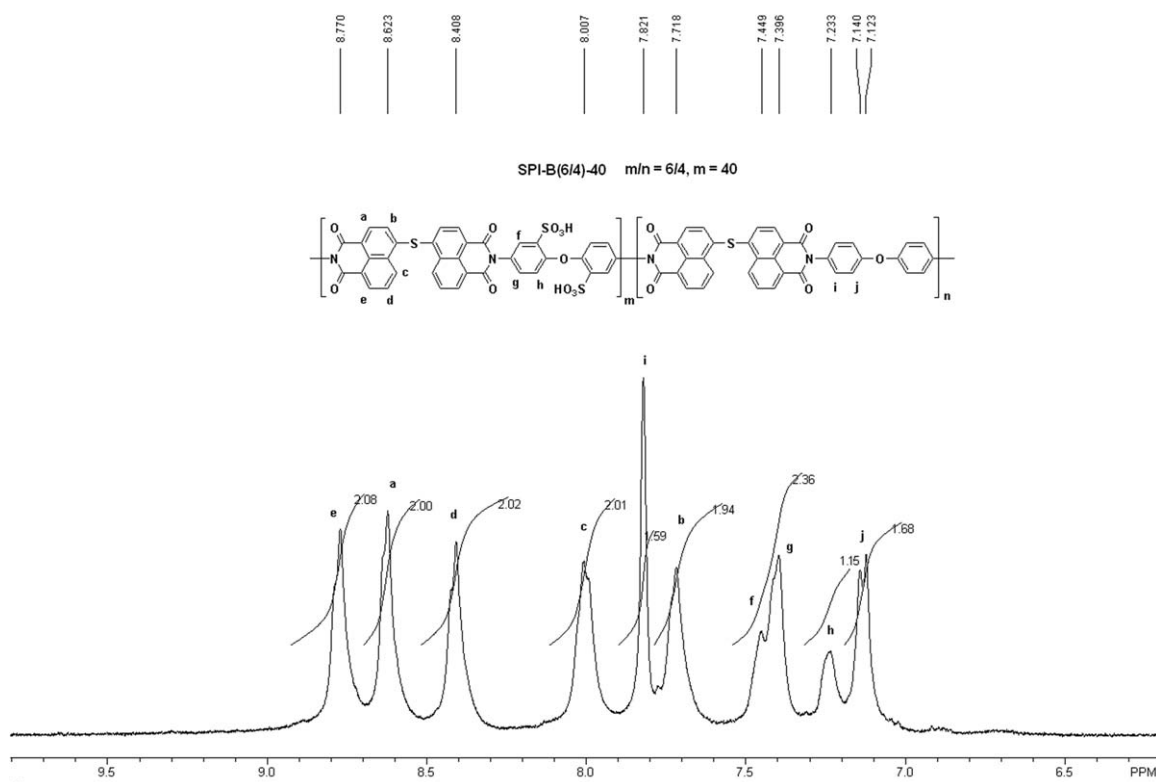
( $\nu_{asym} C=O$ ), 1656 cm<sup>-1</sup> ( $\nu_{sym} C=O$ ), and 1363 cm<sup>-1</sup> ( $\nu_{C-N}$  imide) were assigned to the naphthalenic imido ring. The observed bands at 1186, 1025 cm<sup>-1</sup> and 1229, 1081 cm<sup>-1</sup> were due to symmetric and asymmetric stretch vibrations of sulfonic acid groups, respectively. The typical <sup>1</sup>H NMR spectrum of proton exchanged **SPI-B(6/4)-40** is shown in Figure 2, in which all the signals were assigned. The signals in the peaks of 8.62, 7.72, 8.01, 8.41, 8.77 ppm are assigned to the aromatic hydrogens (H<sub>a</sub> to H<sub>e</sub>) of SBNA moiety in the polyimides, respectively. The signals corresponding to the hydrogens of ODADS were at 7.45, 7.40, and 7.23 ppm, and the hydrogens of ODA revealed signals at 7.82 and 7.13 ppm. The actual ratio of ODADS and ODA moiety ( $m/n$ ) in polyimide **SPI-B(6/4)-40** was 6/4 by calculating and converting the integral ratio of corresponding peak areas (H<sub>f</sub>, H<sub>g</sub>, and H<sub>h</sub>) to (H<sub>i</sub>, H<sub>j</sub>) in <sup>1</sup>H NMR spectrum, which was consistent with the feeding ratio of ODADS and ODA. It indicated that the synthesis conditions were convenient for producing the expected SPI.

#### IEC, Water Uptake, and Dimensional Stability

The calculated IEC value of 1.75 and 2.23 meq/g in Table I for **SPI-B(6/4)** series and **SPI-B(8/2)-40** was calculated according to the structural formulas, in which the mole ratio of ODADS to ODA in copolymer ( $m/n$ ) was 6/4 and 8/2, respectively. Therefore, the hydrophilic segment length **m** (repeating unit) of



**Figure 1.** FTIR spectrum of SPI-B(6/4)-40.



block SPI-B(6/4) series was changed by feeding ratio control but without any change of  $m/n$  ratio, leading to no change in IEC value of SPI-B(6/4) series. As shown in Table I, the IEC values determined experimentally from soaking and titration were in good agreement with the calculated ones, indicating the complete proton exchange. The water uptake of SPI membranes in acid form at room temperature was measured at 100% relative humidity. As expected, water uptake increased along with the increasing IEC. However, the water uptake of block SPI-B(6/4) series slightly decreased along with the increasing hydrophilic segment length from 27.9% to 26.1%, which showed that block length had less effect on the water uptake of the block SPI-B(6/4) series, and was much lower than that of the corresponding random one which was reported as 35.7%.<sup>28</sup> In addition, although the water uptake changed with IEC, the values for the average number of water molecules ( $H_2O$ ) per ion exchange site ( $SO_3^-$ ) ( $\lambda$ ) were within a narrow range from 8.3 to 8.8 at room temperature. The  $\lambda$  value of Nafion 212 is 9.8<sup>27</sup> and the  $\lambda$  values of other SPI<sup>28,30,32,34</sup> are much higher than that block SPIs. The low value of  $\lambda$  was probably due to the rigid nature of the SPI structure<sup>31</sup> and the hydrophobic thioether linkage in the polymer chain.<sup>44</sup>

Dimensional stability of SPI membranes was also tested at room temperature and 80°C by water swelling ratio, which was defined as increased length or thickness of membrane at swelling divided by the dimension of dry samples. The SPI membranes with high IEC value SPI-B(8/2)-40 displayed swelling behavior with relative larger dimensional change in through-plane direction than in in-plane direction which showed 9%

swelling in thickness direction at room temperature, whereas its in-plane direction swelling was 6%. This phenomenon was more pronounced at higher temperature. For example, at 80°C, the SPI-B(8/2)-40 swelled 12% and 8% in thickness direction and in-plane direction, respectively, which was increased more than 30% in both through-plane and in-plane direction. However, there was no obvious difference between thickness direction and in-plane direction in block SPI-B(6/4) series with low IEC value and different hydrophilic segment length. In addition, when the temperature was changed from room temperature to 80°C, the swelling ratios of SPI-B(6/4) series increased less than 20% in both through-plane and in-plane direction. It should be noted that the block SPI membranes showed lower dimensional change than the random ones<sup>28</sup> and other reported SPI membranes<sup>36,37</sup> with similar IEC value. Such good performance on swelling behavior was important for PEMFC application.

#### Mechanical Properties, Hydrolytic Stability, and Oxidative Stability

The mechanical properties of the SPI membranes were measured at room temperature and 50% relative humidity, which are listed in Table II. The tensile strengths, tensile moduli, and elongation at breaks of the membranes are in the ranges of 53.5–67.1 MPa, 1.76–2.11 GPa, and 10.7–16.9%, respectively, which indicated that these SPI membranes were strong and tough enough for fuel cell application even at high IEC value. The SPI membrane SPI-B(8/2)-40 showed lower tensile strength and tensile modulus than SPI-B(6/4) series due to the SPI membranes with high IEC value would promote the

**Table II.** Mechanical Properties, Hydrolytic Stability, and Oxidative Stability of the SPI Membranes

SPI	Mechanical properties and hydrolytic stability <sup>a</sup>			Oxidative stability <sup>b</sup>	
	$T_s$ (MPa)	$T_m$ (GPa)	$E$ (%)	$\tau_1$ (h)	$\tau_2$ (h)
SPI-B(6/4)-20	65.0 (64.9)	1.89 (1.69)	16.9 (11.5)	20	29
SPI-B(6/4)-40	67.1 (67.4)	2.08 (1.71)	10.7 (13.0)	20	24
SPI-B(6/4)-60	63.9 (62.0)	2.11 (1.83)	15.0 (9.6)	20	24
SPI-B(8/2)-40	53.5 (34.7)	1.76 (1.39)	13.8 (3.9)	20	23

$T_s$ , tensile strength;  $T_m$ , tensile modulus;  $E$ , elongation at break.

<sup>a</sup>The mechanical properties of SPI membranes after the hydrolytic testing are given in parentheses.

<sup>b</sup>Measured in Fenton's reagent (30 ppm  $\text{FeSO}_4$  in 30%  $\text{H}_2\text{O}_2$ ) at room temperature.  $\tau_1$ : the time when the membranes began to dissolve.  $\tau_2$ : the time when the membranes dissolved completely.

swelling and decrease the mechanical properties, which was consistent with the random ones.<sup>28</sup>

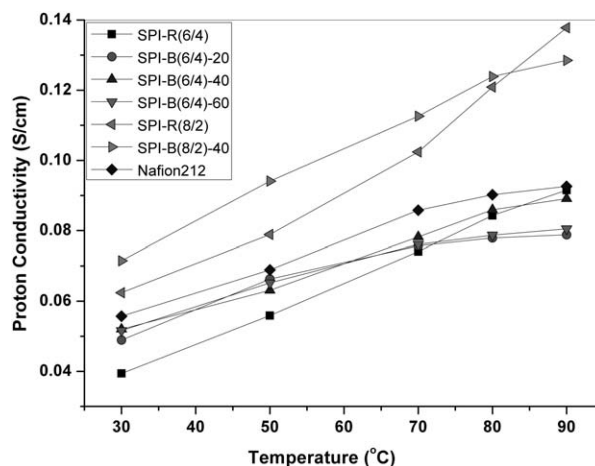
For accelerated hydrolytic stability test, SPI membranes were tested at 140°C in water with an autoclave for 24 h, and the results are summarized in Table II. After the treatment, **SPI-B(6/4)** series with low IEC value showed good hydrolytic stability without detectable changes in appearance, flexibility, and toughness. The improved hydrolytic stability was attributed to the higher electron density in carboxyl carbon atoms through the introduction of dianhydride SBNA with low electron affinity.<sup>28</sup> It should be noted that the tensile strength and elongation at break of **SPI-B(6/4)-40** even showed a slight increase after aging among the **SPI-B(6/4)** series, which showed that the best hydrolytic stability was given when the hydrophilic segment length **m** was 40. Similar to the random one, for the **SPI-B(8/2)-40** with high IEC value, although there was no obvious change in appearance, the mechanical properties decreased apparently, especially at the elongation at break, which was probably because of the more obvious increase in water swelling ratio at high temperature.<sup>27,28</sup>

The oxidative stability of the SPI membranes was investigated by immersing the membranes in Fenton's reagent (30 ppm  $\text{FeSO}_4$  in 30%  $\text{H}_2\text{O}_2$ ) at room temperature. The oxidative stability was characterized by the time that had elapsed when the membranes started to dissolve ( $\tau_1$ ) and the time when the membranes dissolved completely ( $\tau_2$ ). As listed in Table II, compared with other aromatic polyimide ionomers,<sup>34,39</sup> these fresh SPI membranes after proton exchange exhibited equivalent oxidative stability, but slightly lower oxidative stability than random ones,<sup>28</sup> which was quite different with the reported results that block SPI membranes displayed much poorer oxidative stability than random ones.<sup>34</sup> The hydrophilic segment length of block SPIs had no effect on the oxidation stability in the **SPI-B(6/4)** series. However, the oxidative stability should be further enhanced by crosslink or other methods, because the SPI membranes showed still much lower stability compared with Nafion with  $\tau_1$  value of more than 50 h.<sup>39</sup> In addition, it should be noted that the aged SPI membranes showed significant decrease in oxidative stability with low  $\tau_1$  value of less than 5 h. This significant change was probably because of the apparent decreased IEC value of the aged SPI membranes, which were determined experimentally by soaking and titration again. The oxidative stability of aged SPI membranes could be improved to the same as

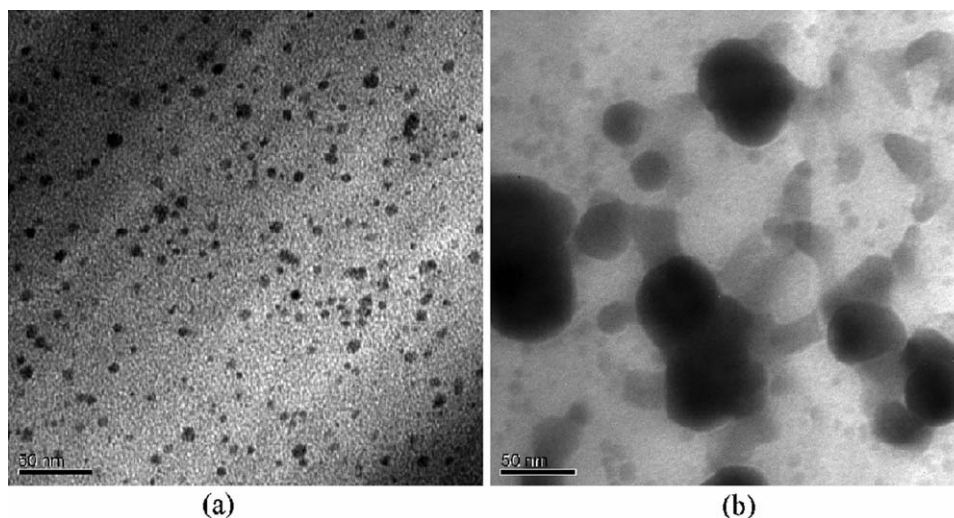
the original ones through proton exchange procedure again, which showed such changes were not irreversible.

### Proton Conductivity

The proton conductivities of SBNA-based block polyimide membranes as well as Nafion 212 were measured at 100% relative humidity at different temperatures, which is shown in Figure 3. The proton conductivities of random polyimide membrane **SPI-R(6/4)** and **SPI-R(8/2)** were also tested and shown in Figure 3 for comparison.<sup>28</sup> As expected, the proton conductivity of the membranes increased with IEC and temperature increasing. The SPI membranes with IEC value of 2.23 meq/g showed higher proton conductivities than that of SPI membranes with IEC value of 1.75 meq/g and Nafion 212 with IEC value of 1.75 meq/g at the temperature range from 30 to 90°C.<sup>27</sup> The proton conductivity of block SPIs is obviously higher than that of random ones with the same IEC value at lower temperature, which is attributed to the microphase separation in block SPI membranes.<sup>35</sup> However, the difference in conductivity between block polyimides and random ones decreases when temperature increases, which is similar to the report by Kawakami et al.<sup>32</sup> Interestingly, the random SPIs even showed higher proton conductivity than the block ones at 90°C. This is because with the increase in temperature the molecular mobility increases and hence the water molecules can easily penetrate through the polymer backbone and the



**Figure 3.** Proton conductivities of SPI membranes and Nafion 212 under fully hydrated conditions (in water) at different temperatures.



**Figure 4.** TEM micrographs of (a) SPI-R(8/2) and (b) SPI-B(8/2)-40.

transportation of protons in SPI membranes becomes quite easy, making the effect of microphase separation and ion-channels less important.<sup>39</sup> Furthermore, other elements, such as water uptake and stability, become the key factor affecting the proton conductivity of SPI membranes as the temperature increases. On the other hand, the hydrophilic segment length of block SPIs also has an impact on the proton conductivity.<sup>31,32</sup> The SPI-B(6/4)-40 showed the highest proton conductivity among the SPI-B(6/4) series with same IEC value but different hydrophilic segment lengths at the temperature range from 70 to 90°C although there was no apparent difference on the proton conductivity at low temperature 30–50°C.

#### Microscopic Morphology

To investigate and confirm hydrophilic/hydrophobic microphase separation and the proton transport pathway in the membranes, the scanning transmission electron microscopy (TEM) for random polyimide membrane SPI-B(8/2)-40 as well as random polyimide membrane SPI-R(8/2) stained with silver ions by ion exchange was performed. In the TEM images, the dark areas represent the hydrophilic (ionic) domain and the brighter areas represent the hydrophobic domain. As clearly seen in Figure 4, large ionic clusters (>40 nm) were formed obviously in the TEM image of SPI-B(8/2)-40 while spherical ionic clusters with relatively uniform size about 10 nm were found in corresponding random ones SPI-R(8/2).<sup>28</sup> Such developed microphase separation and large ionic clusters could be the reason to enhance the proton conductivity of block SPIs,<sup>35</sup> which was well consistent with the aforementioned results of the determined proton conductivity.

#### CONCLUSIONS

A series of novel aromatic block copolyimides derived from 4,4'-sulfide-bis(naphthalic anhydride) (SBNA) have been successfully synthesized by solution polycondensation. The resulting SPI membranes with low IEC value displayed excellent hydrolytic stability because of the low electron affinity of SBNA, and the performance degraded along with the IEC increased. In addition, the SPI membranes showed low water uptake and

good dimensional stability due to the rigid SPI structure and hydrophobic thioether linkage. It was revealed that the block SPIs display higher proton conductivity compared with the random ones at lower temperature owing to the better microphase separated morphology. Interestingly, along with the increase of temperature, the difference on the proton conductivity between block and random SPIs became smaller. At 90°C, the random SPI membranes even showed better proton conductivity than corresponding block ones, which indicated that the effect of microphase separation on the proton conductivity became less important at higher temperature. The SPI-B(6/4)-40 with hydrophilic segment length of 40 gave the best hydrolytic stability and proton conductivity among the SPI-B(6/4) series, which showed the hydrophilic segment length was also played an important role in determining the membrane properties.

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