

# Synthesis and Properties of Sulfonated Poly(siloxane imide)s Bearing Dimethyl Siloxane Oligomers for Fuel Cell Applications

Xinbing Chen,<sup>1,2</sup> Pei Chen,<sup>1,3</sup> Ken-Ichi Okamoto<sup>3</sup>

<sup>1</sup>Key Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education), School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, People's Republic of China

<sup>2</sup>Venture Business Laboratory, Yamaguchi University, Japan

<sup>3</sup>Graduate School of Science and Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan

Received 6 June 2008; accepted 28 October 2008

DOI 10.1002/app.29593

Published online 11 March 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of sulfonated poly(siloxane imide)s (SPSIs) were synthesized from 4,4'-ketone dinaphthalene 1,1',8,8'-tetracarboxylic dianhydride (KDNTDA), a dimethyl siloxane oligomer-based diamine, and a sulfonated diamine. The reduced viscosities ranged from 1.0 to 3.5 dL/g at 35°C in the triethylamine (TEA) salt form. The SPSIs showed anisotropic membrane swelling with larger swelling in thickness than in plane. They displayed reasonably high proton conductivity, thermal stability and good me-

chanical properties. The KDNTDA-based SPSIs showed good solubility in common aprotic solvents not only in TEA salt form but also in proton form. The <sup>1</sup>H-NMR results indicated that the molar content of the dimethyl siloxane oligomer in the SPSIs was 50–80% of that in the feed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3560–3568, 2009

**Key words:** films; high performance polymers; ionomers; polyimides; polysiloxanes

## INTRODUCTION

Polymer electrolyte membranes are one of the most important components in polymer electrolyte membrane fuel cells and direct methanol fuel cells.<sup>1,2</sup> Most research is focused on perfluorinated ionomer membranes, such as DuPont's Nafion, because of their high performance in polymer electrolyte membrane fuel cells. However, shortcomings such as high cost, large fuel crossover, and lower operating temperatures (<80°C) critically limit their industrial applications.<sup>3</sup>

Extensive efforts have been made to develop alternative proton-conducting membranes based on sulfo-

nated aromatic hydrocarbon polymers,<sup>4–8</sup> such as sulfonated poly(aryl ether sulfone),<sup>9,10</sup> sulfonated polyphenylene,<sup>11</sup> sulfonated poly(ether ether ketone),<sup>12</sup> and sulfonated polyimides (SPIs).<sup>13</sup> As one of the most promising polymer electrolyte membrane candidates for fuel cell applications, SPIs with six-membered imide rings have attracted much attention in recent years. SPIs reported to date have mainly been those derived from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA).<sup>14–18</sup> Recently, flexible dianhydrides of 4,4'-ketone dinaphthalene 1,1',8,8'-tetracarboxylic dianhydride (KDNTDA)<sup>19,20</sup> and 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride<sup>21,22</sup> have been synthesized and used for preparing SPI ionomers. A few studies on the effect of nonsulfonated diamine structures have also been reported,<sup>23,24</sup> and modifications of nonsulfonated diamine have been mainly focused on the aromatic structure.

A siloxane monomer such as a flexible and hydrophobic dimethyl siloxane oligomer-based diamine (SiRDA) can improve the solubility and reduce the glass temperature of polyimides. Thus, it has been widely used for preparing functional poly(siloxane imide)s with five-membered imide rings.<sup>25,26</sup> Zou and Anthamatten<sup>27</sup> developed a one-pot synthesis of SPI-polysiloxane segmented copolymers and studied their morphology. Their results showed the difficulty of incorporating siloxane segments into the

Correspondence to: X. Chen (chenxinbing@snnu.edu.cn) or K.-I. Okamoto (okamotok@yamaguchi-u.ac.jp)

Contract grant sponsor: New Energy and Industrial Technology Development (through the Fuel Cell and Hydrogen Technology Development Department).

Contract grant sponsor: Venture Business Laboratory of Yamaguchi University (through "Research and Development of Polymer Electrolyte Fuel Cells").

Contract grant sponsor: Ministry of Education, Culture, Sports, Science, and Technology of Japan (through a grant-in-aid for developmental science research); contract grant number: 19550209.

*Journal of Applied Polymer Science*, Vol. 112, 3560–3568 (2009)  
© 2009 Wiley Periodicals, Inc.

copolymer. However, there are a few reports on the application of SiRDA to SPIs with five- or six-membered imide rings. Sulfonated poly(siloxane imide)s (SPSIs) derived from SiRDA are expected to exhibit high solubility, which is favorable for processing and for other fuel cell operations for fuel cell applications.

In this study, a series of KDNTDA-based SPSIs bearing dimethyl siloxane oligomers were synthesized, and their properties were investigated.

## EXPERIMENTAL

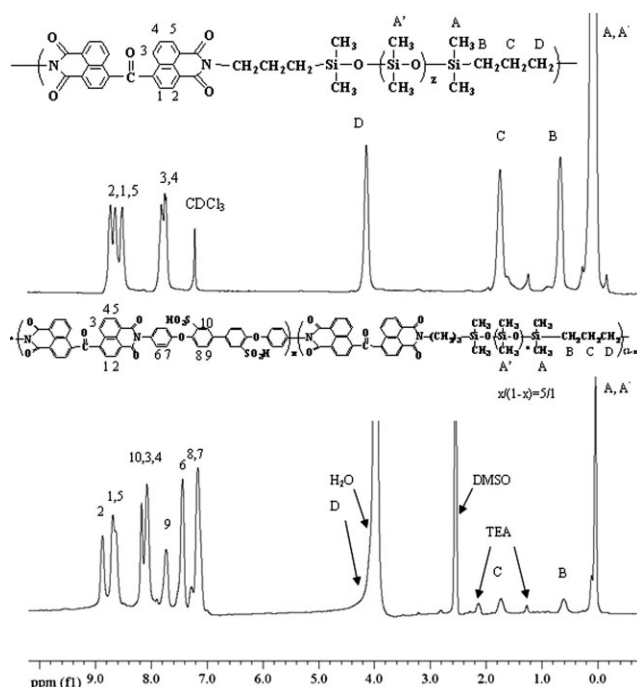
### Materials

Triethylamine (TEA), *m*-cresol, sulfuric acid (95%), benzoic acid, isoquinoline, dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and 1-methyl-2-pyrrolidone (NMP) were purchased from Wako (Osaka, Japan) and used as received. 1,3-Bis(4-aminophenoxy) benzene (BAPBz) was purchased from Wako and recrystallized from ethanol before use. SiRDA was provided by Shin-Etsu Chemical Co. (Tokyo, Japan), and ultra-pure water was obtained with a Millipore Milli-Q purification system (Watertown, Massachusetts). 4,4'-Bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS) and KDNTDA were prepared according to the literature.<sup>16,19</sup>

### Measurements

Infrared (IR) spectra were recorded on a Horiba FT-200 spectrometer (Kyoto, Japan), whereas the <sup>1</sup>H-NMR spectra were recorded on a JEOL EX270 (270-MHz) (Tokyo, Japan) instrument. The tensile strength was measured with an Intesco model 2005 instrument at 25°C and around 50% relative humidity (RH) at a crosshead speed of 10 mm/min. Thermogravimetric analysis was carried out with a Rigaku TG-8120 apparatus in helium (flow rate = 100 cm<sup>3</sup>/min) at a heating rate of 10°C/min, and the sample was allowed to stand at 150°C for 0.5 h. Solubility tests were carried out in five solvents with a concentration of 5% (w/v) at room temperature. The studied solvents were *m*-cresol, DMAc, DMF, NMP, and DMSO. The reduced viscosity was measured with an Ostwald viscometer with a 0.5 g/dL *m*-cresol solution of SPSI in TEA salt form at 35°C.

The ion-exchange capacity (IEC) was calculated from the molar feed ratio of the sulfonated diamine to the nonsulfonated diamine in the feed and was evaluated by <sup>1</sup>H-NMR and titration methods. In the <sup>1</sup>H-NMR method, a proton-exchanged SPSI membrane was dissolved in DMSO-*d*<sub>6</sub> [without tetramethylsilane (TMS)] at a concentration of 1–2 wt %. Figure 1 shows a typical <sup>1</sup>H-NMR spectrum. The IEC was evaluated from the peak intensity ratios of H<sub>9</sub> to H<sub>2+1+5</sub>, H<sub>A+A'</sub> to H<sub>2+1+5</sub>, and H<sub>B+C</sub> to H<sub>2+1+5</sub> for



**Figure 1** <sup>1</sup>H-NMR spectra of the poly(siloxane imide) (K0) in CDCl<sub>3</sub> without TMS and SPSI (K3) in proton form in DMSO-*d*<sub>6</sub> without TMS.

SPSIs bearing dimethyl siloxane oligomers. For the titration method, a sample membrane in proton form was soaked in a 15 wt % NaCl solution at 30°C for 72 h to exchange the H<sup>+</sup> ion with the Na<sup>+</sup> ion. Then, the released H<sup>+</sup> ion was titrated with a 0.05M NaOH solution with phenolphthalein as the indicator.

The water uptake (WU) was measured by the immersion of completely dried SPSI membrane samples into deionized water at room temperature for 5 h. Then, the samples were taken out, wiped with tissue paper, and quickly weighed on a microbalance to calculate WU with the following equation:

$$WU = (W_s - W_d) / W_d \times 100 \quad (1)$$

where  $W_s$  and  $W_d$  are the weights of the swollen and dry membranes, respectively.

The dimensional changes in the membrane thickness ( $\Delta t_c$ ) and in plane ( $\Delta l_c$ ) were measured according to a method described elsewhere.<sup>16,17</sup> The dimensional changes of the membrane were characterized with eq. (2):

$$\begin{aligned} \Delta t_c &= (t - t_s) / t_s \\ \Delta l_c &= (l - l_s) / l_s \end{aligned} \quad (2)$$

where  $t_s$  and  $l_s$  are the thickness and diameter of the membrane equilibrated at 70% RH, respectively, and  $t$  and  $l$  refer to swollen membranes in water.

The proton conductivity ( $\sigma$ ) in the plane direction of the membrane was determined with electrochemical impedance spectroscopy over a frequency range

of 10 Hz to 100 kHz (3532-80, Hioki).  $\sigma$  was calculated with the following equation:

$$\sigma = d/(t_s w_s R) \quad (3)$$

where  $d$  is the distance between the two electrodes,  $t_s$  is the thickness,  $w_s$  is the width of the membrane at a standard condition of 70% RH, and  $R$  is the measured resistance value. The swollen membrane thickness was used to calculate  $\sigma$  for the measurement in water.

### General procedure for the synthesis of the SPSIs

#### Homopoly(siloxane imide)

Under a nitrogen flow, 0.8 g (1 mmol) of SiRDA, 6 mL of DMAc, and 0.422 g (1 mmol) of KDNTDA were added to a completely dried 100-mL, three-necked flask. The mixture was stirred at 60°C for 20 h, at 130°C for 4 h, and at 160°C for 20 h. After being cooled to room temperature, the solution was poured into 30 mL of methanol and was washed three times with methanol. The resulting precipitate was collected by filtration and dried *in vacuo*.

#### Random co-SPSIs

As an example, the synthesis of KDNTDA-BAPBDS/SiRDA(4/1)-r can be described as follows. Under a nitrogen flow, 0.845 g (1.6 mmol) of BAPBDS, 11 mL of *m*-cresol, and 0.54 mL of Et<sub>3</sub>N were added to a completely dried 100-mL, three-necked flask. After BAPBDS was completely dissolved, 0.320 g (0.4 mmol) of SiRDA, 0.845 g (2 mmol) of KDNTDA, and 0.342 g of benzoic acid were added to the flask. The mixture was stirred and heated at 90°C for 4 h and then was heated at 180°C for 20 h after 0.321 g of isoquinoline was added. After cooling to room temperature, the solution was poured into 50 mL of methanol and washed three times with methanol. The resulting precipitate was collected by filtration and dried *in vacuo*.

#### Sequenced block co-SPSIs

*Method A [KDNTDA-BAPBDS/SiRDA(4/1)-s]*. Under a nitrogen flow, 0.845 g (1.6 mmol) of BAPBDS, 9.5 mL of *m*-cresol, and 0.54 mL of Et<sub>3</sub>N were added to a completely dried 100-mL, three-necked flask. After BAPBDS was completely dissolved, 0.845 g (2 mmol) of KDNTDA and 0.342 g of benzoic acid were added. The reaction was kept at 90°C for 4 h and at 180°C for 5 h. After the mixture cooled to room temperature, 2.5 mL of *m*-cresol and 0.320 g (0.4 mmol) of SiRDA were successively added to the solution. The reaction mixture was stirred for a few minutes,

and then 0.321 g of isoquinoline was added to the flask. The mixture was heated at 90°C for 4 h and at 180°C for 20 h. The crude product was purified similarly to random co-SPSIs.

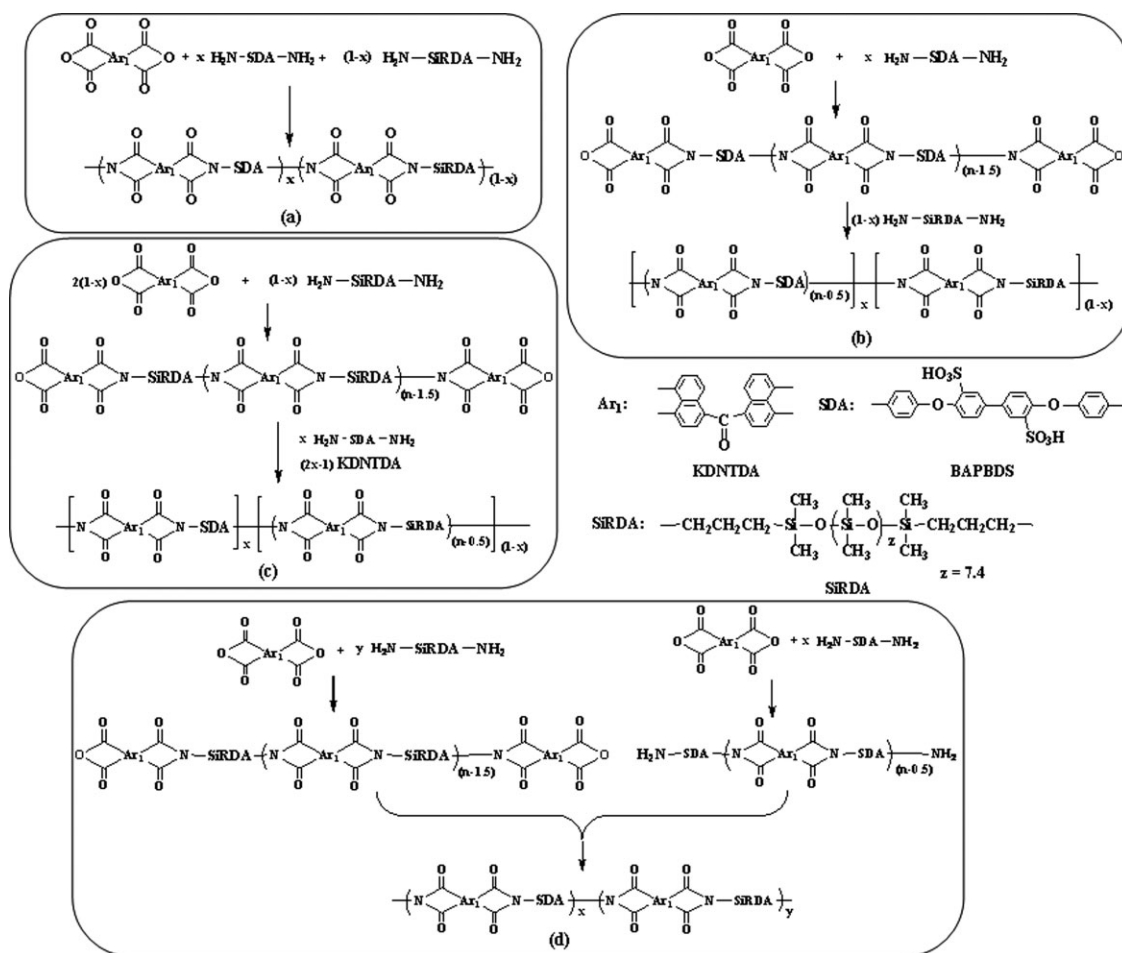
*Method B [KDNTDA-BAPBDS/SiRDA(5/1)-s]*. After 0.320 g (0.4 mmol) of SiRDA, 0.338 g (0.8 mmol) of KDNTDA, and 4 mL of *m*-cresol were added to a completely dried 100-mL, three-necked flask, the mixture was stirred under a nitrogen flow at room temperature for 5 h, at 90°C for 12 h, and at 130°C for 10 h. After the mixture was cooled to room temperature, 10 mL of *m*-cresol, 1.057 g (2 mmol) of BAPBDS, 0.64 mL of Et<sub>3</sub>N, 0.676 g (1.6 mmol) of KDNTDA, and 0.410 g of benzoic acid were added. The reaction was kept at 90°C for 24 h, at 130°C for 10 h, and at 180°C for 15 h after 0.341 g of isoquinoline was added to the flask. The crude product was purified similarly to random co-SPSIs.

#### Block-block co-SPSIs

As an example, the synthesis of KDNTDA-BAPBDS/SiRDA(7.5b/1.5b) can be described as follows. To prepare the nonsulfonated poly(siloxane imide) block, 0.320 g (0.4 mmol) of SiRDA, 0.338 g (0.8 mmol) of KDNTDA, and 4 mL of *m*-cresol were added to a completely dried 100-mL, three-necked flask. The mixture was then stirred under a nitrogen flow at room temperature for 5 h, at 90°C for 12 h, at 130°C for 72 h, and at 180°C for 4 h. Another completely dried 100-mL, three-necked flask also received 1.057 g (2 mmol) of BAPBDS, 0.64 mL of Et<sub>3</sub>N, 0.676 g (1.6 mmol) of KDNTDA, 0.410 g of benzoic acid, and 10 mL of *m*-cresol. The mixture was stirred under a nitrogen flow at 90°C for 4 h and at 180°C for 15 h to prepare the SPI block. The two blocks were mixed together under a nitrogen flow after both were cooled to room temperature. The block mixture was stirred under a nitrogen flow at 90°C for 1 week and at 180°C for 10 h after 0.341 g of isoquinoline was added to the flask. The crude product was purified similarly to random co-SPSIs.

#### Membrane formation and proton exchange

A 5 wt % SPSI solution in *m*-cresol or DMSO was prepared and cast onto glass plates and then was dried at 120°C for 12 h. The resulting membranes were about 50  $\mu$ m thick; they were soaked in methanol at room temperature for 48 h to remove the residual solvent and then in 1M sulfuric acid at 40°C for 120 h. The proton-exchanged membranes were soaked in water for 48 h and then cured *in vacuo* at 150°C for 1 h and at 180°C for 1 h.



**Scheme 1** Synthesis of KDNTDA-based SPSIs: (a) the homopolymer and a random co-SPSI, (b) a sequenced block co-SPSI by method A, (c) a sequenced block co-SPSI by method B, and (d) a block–block co-SPSI.

## RESULTS AND DISCUSSION

### Synthesis and characterization of the copolymer

The synthesis of the KDNTDA–SiRDA homopolymer differed from the synthesis of SPI as it was prepared in DMAc under a nitrogen flow. The homopolymer prepared in *m*-cresol with the same procedure showed a low viscosity. The synthesis of KDNTDA-based random copoly(siloxane imide)s was carried out by a one-step method in *m*-cresol in the presence of TEA and with benzoic acid as the catalyst [Scheme 1(a)]. The KDNTDA-based sequenced block copoly(siloxane imide)s were obtained in two steps. First, the anhydride-terminated SPI oligomer [or the anhydride-terminated poly(siloxane imide) oligomer] was prepared, and the nonsulfonated SiRDA (or sulfonated diamine) was then introduced into the reaction system [Scheme 1(b,c)]. For the block–block SPSI, the amine-terminated SPI oligomer and the anhydride-terminated poly(siloxane imide) oligomer were prepared, and the sulfonated and nonsulfonated oligomers were then mixed together for further polymerization [Scheme 1(d)].

The structures of the KDNTDA-based homopolymer and co-SPSIs in proton form were confirmed by  $^1\text{H-NMR}$  and IR spectra. Figure 1 shows the protons of the KDNTDA-based homopolymer and co-SPSIs. They are different from NTDA-based SPIs as they have three kinds of naphthalenic protons based on their different chemical environments. The protons nearer the naphthalimide or carbonyl linkage ( $\text{H}_1$ ,  $\text{H}_2$ , and  $\text{H}_5$  in Fig. 1) appear in the range of 8.5–9.0 ppm, which overlaps with the NTDA-based protons (8.7 ppm). The protons far from the naphthalimide or carbonyl linkage ( $\text{H}_3$  and  $\text{H}_4$  in Fig. 1) shifted to 7.9–8.1 ppm because of the smaller electron-withdrawing effect of the naphthalimide and carbonyl groups. The weak peaks of TEA protons in the spectrum revealed that the proton exchange was almost complete for the KDNTDA-based SPSI membrane.

The characteristic peaks of the four kinds of protons in the dimethyl siloxane oligomer moiety appeared in the ranges of  $-0.2$ – $0.2$ ,  $0.4$ – $0.7$ ,  $1.5$ – $1.8$ , and  $3.8$ – $4.2$  ppm for the KDNTDA-based homopolymer and co-SPSIs. The integrated intensity ratios of methyl protons A and A' ( $-0.2$ – $0.2$  ppm) and

methylene protons B and C (0.37–0.73 ppm and 1.50–1.83 ppm) to KDNTDA protons (8.5–9.0 ppm)— $H_{A+A'}/H_{2+1+5}$  and  $H_{B+C}/H_{2+1+5}$ —were found to be 9.45 and 1.32, respectively, for homopolymer K0, which agreed with the theoretical values (9.4 and 1.33). This indicated the complete polycondensation of KDNTDA with SiRDA. However, the values were 0.83 and 0.15 for KDNTDA–BAPBDS/SiRDA(5/1)-s (K3), that is, much smaller than the theoretical values (1.57 and 0.22, respectively). From these observed ratios, the molar percentages of the KDNTDA–SiRDA unit in the SPSI were evaluated to be 9.7 and 11.4% (K3 in Table I), respectively, indicating that only 60–68% of SiRDA in the feed was incorporated into the copolymer. Similar results were found for other KDNTDA-based co-SPSIs and short block–block co-SPSIs [KDNTDA–BAPBDS/SiRDA(7.5b/1.5b) (K4)]. This may be due to the lower encounter probability of the terminal anhydride groups of hydrophilic SPI [or hydrophobic poly(siloxane imide)] oligomers with the amino groups of hydrophobic dimethyl siloxane (or hydrophilic SPI) oligomers because SiRDA has high reactivity that is enough to form a KDNTDA–SiRDA homopolymer with a high molecular weight.

For the large block–block co-SPSI KDNTDA–BAPBDS/SiRDA(20b/10b) (K5), the integrated intensity ratios  $H_{A+A'}/H_{2+1+5}$  and  $H_{B+C}/H_{2+1+5}$  were observed to be 0.26 and 0.04, respectively, that is, much smaller than the theoretical values (3.13 and 0.44, respectively). The molar percentages of the KDNTDA–SiRDA unit in the sulfonated block–block poly(siloxane imide) were very low at 2.8 and 3.1%, respectively, revealing that only about 10% of SiRDA in the feed was incorporated into the copolymer. In other words, about 90% of the anhydride-terminated KDNTDA–SiRDA oligomer block failed to react with the amine-terminated KDNTDA–BAPBDS oligomer block even though the reaction time was prolonged to 1 week. This was attributed to the lower encounter probability of the two blocks due to the strong microphase separation between the hydrophobic poly(siloxane imide) block and the hydrophilic SPI block. Figure 2 shows the  $^1\text{H-NMR}$  spectrum of the residue derived from the postprocess of precipitating and washing K5. The peaks appearing at 8.4–8.8 and 7.6–8.0 ppm are attributable to the naphthalenic protons ( $H_1$ ,  $H_2$ , and  $H_5$  and  $H_3$  and  $H_4$ ). The  $H_{2+1+5}/H_{3+4}$  integration intensity ratio (1.55/1) agreed with the theoretical ratio (1.5/1). The peaks that appeared at 7.2, 7.0, and 6.6 ppm were assigned to the protons of  $\text{CDCl}_3$  and *m*-cresol. The characteristic peaks of the four kinds of protons in the dimethyl siloxane moiety appeared in the ranges of –0.2–0.2, 0.4–0.7, 1.6–1.8, and 4.0–4.2 ppm, respectively. This indicated that the residue was mainly composed of nonsulfonated anhydride-terminated KDNTDA–SiRDA

TABLE I  
Properties of the KDNTDA-Based SPSIs

No.	Code <sup>a</sup>	IEC (mequiv/g) <sup>b</sup>		Si (mol %) <sup>c</sup>		Reduced viscosity (dL/g) <sup>d</sup>		WU (%) <sup>e</sup>	Size change		$\sigma$ (mS/cm) <sup>g</sup>	
		Theoretical	Titration	$H_9/H_{2+1+5}$	$H_{A+A'}/H_{2+1+5}$	$H_9/H_{2+1+5}$	$H_{B+C}/H_{2+1+5}$		$\Delta\lambda_c$	$\Delta\lambda_c$	$T_{ds}$ (°C) <sup>f</sup>	50%
K0	PSI	—	—	—	100	100	0.55	—	—	—	—	—
K1	SPSI(4/1)-r	1.65	1.82	1.88	1.90	1.84	12.8	44(13)	0.20	0.062	—	4.5
K2	SPSI(4/1)-s	1.65	1.83	1.86	1.92	1.89	10.8	45(13)	0.14	0.040	300	4.0
K3	SPSI(5/1)-s	1.74	1.85	1.82	1.92	1.87	11.4	49(14)	0.08	0.058	310	4.8
K4	SPSI(7.5b/1.5b)	1.74	1.82	1.90	1.92	1.91	10.2	48(14)	0.11	0.042	306	5.6
K5	SPSI(20b/10b)	1.33	2.09	2.09	2.11	2.10	3.1	63(17)	—	—	—	13
K6	SPI	1.58	1.45	1.50	—	—	1.0	36(13)	0.14	0.040	297	2.7
Nafion 112		0.91	0.89	—	—	—	—	39(24)	0.13	0.12	—	26

<sup>a</sup> PSI = KDNTDA–SiRDA; SPSI = KDNTDA–BAPBDS/SiRDA; SPI = KDNTDA–BAPBDS/BAPBz(2/1)-s.

<sup>b</sup> Evaluated from titrations and the  $H_9/H_{2+1+5}$ ,  $H_{A+A'}/H_{2+1+5}$ , and  $H_{B+C}/H_{2+1+5}$  intensity ratios.

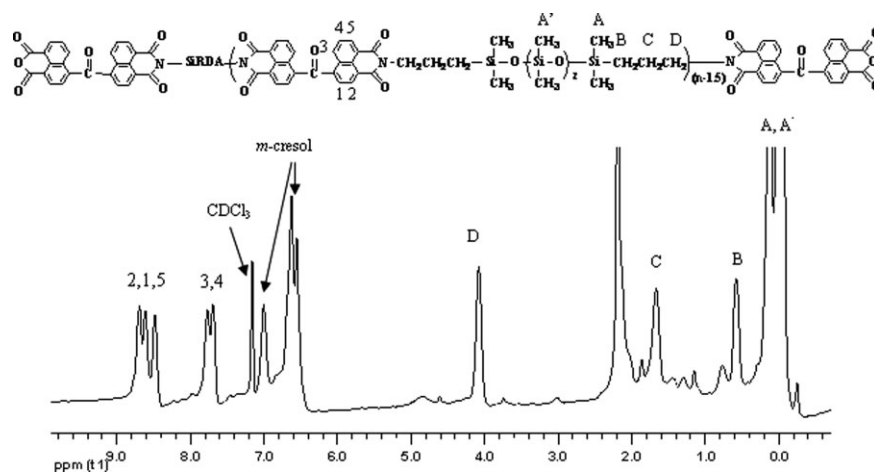
<sup>c</sup> Molar fraction of the KDNTDA–SiRDA unit in the polymer, which was evaluated from titrations and the  $H_9/H_{2+1+5}$ ,  $H_{A+A'}/H_{2+1+5}$ , and  $H_{B+C}/H_{2+1+5}$  intensity ratios.

<sup>d</sup> TEA salt form at 35°C in *m*-cresol.

<sup>e</sup> The  $\lambda$  values are based on the  $^1\text{H-NMR}$  IEC values of  $H_{A+A'}/H_{2+1+5}$ .

<sup>f</sup> Desulfonation temperature.

<sup>g</sup> At 60°C.



**Figure 2**  $^1\text{H-NMR}$  spectrum of the residue derived from the postprocess of K5 in  $\text{CDCl}_3$  without TMS.

oligomers. The results indicated that some of the KDNTDA–SiRDA oligomers did not react with sulfonated KDNTDA–BAPBDS oligomers and were washed off by the postprocess. This resulted in a lower molar percentage of the KDNTDA–SiRDA unit in the SPSI of K5.

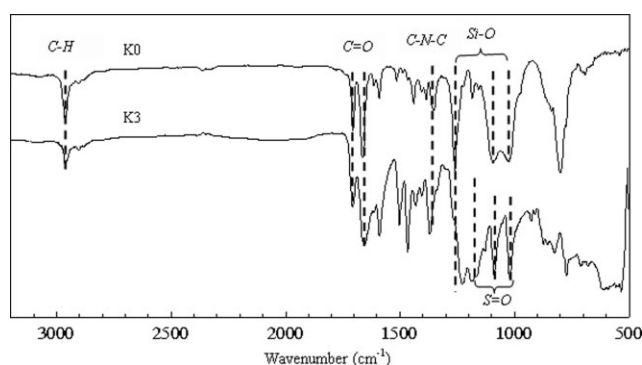
Figure 3 shows the IR spectra of the KDNTDA-based homopolymer and co-SPSIs. The spectra display KDNTDA-based naphthalimide absorption bands at  $1707$  ( $\text{C}=\text{O}$ , asymmetric),  $1662$  ( $\text{C}=\text{O}$ , symmetric), and  $1373$   $\text{cm}^{-1}$  ( $\text{C}-\text{N}-\text{C}$ , asymmetric). The stretching vibration of the carbonyl group in the aryl ketone skeleton overlapped with the symmetric stretching vibration of the carbonyl group at  $1662$   $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ , symmetric). The peaks appearing at  $1020$ ,  $1090$ , and  $1180$   $\text{cm}^{-1}$  were attributed to the symmetric and asymmetric vibrations of the  $\text{O}=\text{S}=\text{O}$  bond in the sulfonic acid group for the KDNTDA-based co-SPSI (K3). The  $1235$ - $\text{cm}^{-1}$  peak was assigned to the vibrations of the  $\text{C}-\text{O}-\text{C}$  or  $\text{Si}-\text{O}-\text{Si}$  bond in the aryl ether backbone or in the flexible dimethyl siloxane group of K3. The strong vibrations of the  $\text{Si}-\text{O}$  bond were observed obviously at  $1030$ ,  $1100$ , and  $1248$   $\text{cm}^{-1}$ , respectively, for K0 and partly overlapped with the vibrations of the  $\text{S}=\text{O}$  bond for the KDNTDA-based co-SPSI (K3). The vibration of the  $\text{C}-\text{H}$  bond in the methyl/methylene group appeared at  $2965$   $\text{cm}^{-1}$ , indicating that the dimethyl siloxane oligomer was incorporated into the SPSI chain.

### Physical properties of the SPSIs

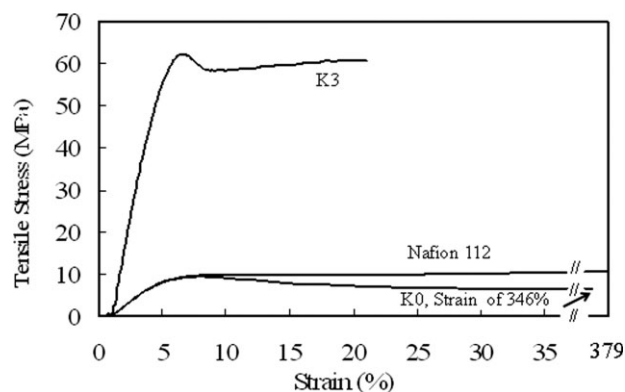
The properties of the KDNTDA-based homopolymer and co-SPSIs are listed in Table I. The reduced viscosities of the SPSIs (K1–K5) ranged from 1.0 to 3.5 dL/g and were higher than the viscosity of poly(siloxane imide) (K0; 0.55 dL/g). The IEC was evaluated from the molar ratio of the sulfonated diamine

to the nonsulfonated diamine in the feed (theoretical IEC) and by  $^1\text{H-NMR}$  and titration methods. As listed in Table I, the IEC values observed with the  $^1\text{H-NMR}$  and titration methods were 10–16% (according to the  $\text{H}_{\text{A}+\text{A}'}/\text{H}_{2+1+5}$  ratio) and 5–11% larger than the theoretical values of the co-SPSIs (K1–K4), whereas for the large block–block co-SPSI (K5), the corresponding IEC values were about 59 and 57% larger than the theoretical values. These results were attributed to the smaller molar fraction of the dimethyl siloxane oligomer moiety in the SPSIs as mentioned previously.

The molar fractions of the KDNTDA–SiRDA unit in the copolymers were evaluated with the titration method and the integrated intensity ratios  $\text{H}_9/\text{H}_{2+1+5}$ ,  $\text{H}_{\text{A}+\text{A}'}/\text{H}_{2+1+5}$ , and  $\text{H}_{\text{B}+\text{C}}/\text{H}_{2+1+5}$ . Table I shows that the molar fractions of the KDNTDA–SiRDA unit in SPSIs were about 11 and 13 mol % from the  $^1\text{H-NMR}$  and titration methods for K1 or K2, respectively, indicating that about half of SiRDA in the feed (20 mol %) was incorporated into the copolymer. The values were about 11 and 12 mol % for K3 and 10 and 13 mol % for K4, respectively, whereas the theoretical molar fraction of the



**Figure 3** IR spectra of the KDNTDA-based poly(siloxane imide) and SPSI membrane in proton form.



**Figure 4** Stress–strain curves of the KDNTDA-based poly(siloxane imide), SPSI membrane, and Nafion 112.

KDNTDA–SiRDA unit in K3 or K4 was 16.7 mol %. It was revealed that 60–80% of SiRDA in the feed was incorporated into the SPSIs for K3 and K4. The different molar fractions of the KDNTDA–SiRDA unit in the SPSIs for K1–K4 were attributed to the different synthetic methods. For K3 and K4, the KDNTDA–SiRDA oligomer was prepared first, and then the sulfonated monomer or oligomer was added to the reaction system to continue polymerization, with more KDNTDA–SiRDA incorporated. These results showed that the molar content of the dimethyl siloxane oligomer in the copolymers was about 50–80% of that in the feed for KDNTDA-based random, sequenced, and short block–block co-SPSIs. However, only about 10% of the SiRDA monomer was incorporated into the large block–block co-SPSI (K5). This could be attributed to the low encounter probability of the hydrophobic poly(siloxane imide) block with the hydrophilic SPI block due to microphase separation, as mentioned previously. The conclusion is that it is difficult to incorporate siloxane segments into SPSIs, and this is similar to literature results.<sup>27</sup>

Flexible and tough SPSI membranes were obtained in this study with reasonably high stress–strain behavior. Figure 4 shows that KDNTDA–BAPBDS/SiRDA(5/1)-s (K3) displayed a Young's modulus (YM) of 1.1 GPa, a maximum stress (MS) of 61 MPa,

and an elongation at break (EB) of 21%, whereas KDNTDA–SiRDA (K0) showed values of 0.3 GPa, 9.5 MPa, and 346%, respectively. K3 showed much larger YM and MS than K0 because of its high molecular weight and rigid sulfonated aryl polyimide group. The small YM and MS but very large EB of K0 were due to the flexible dimethyl siloxane oligomer incorporated into the poly(siloxane imide) chain. The large EB of K0 indicated that SiRDA had sufficient reactivity to form high-molecular-weight poly(siloxane imide)s with six-membered imide rings.

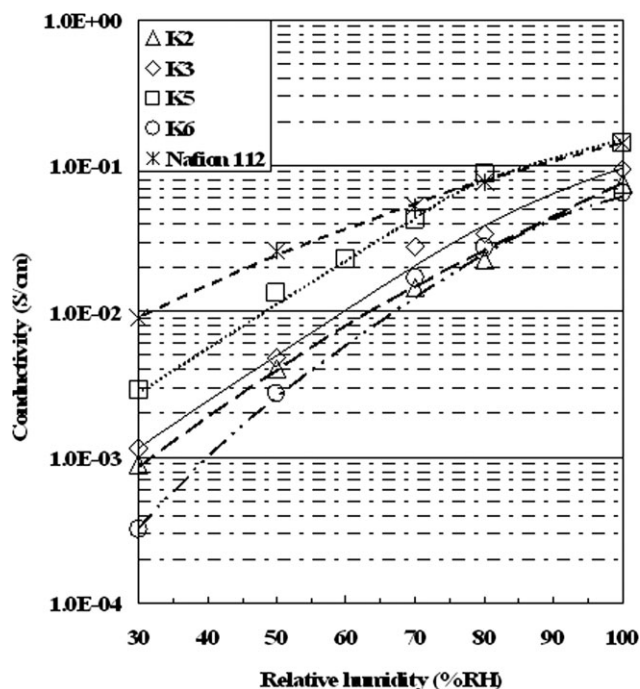
The thermal stability of the KDNTDA-based SPSIs was examined by thermogravimetric analysis, and the results are given in Table I. The desulfonation temperatures of the decomposition of sulfonic acid groups were 300 and 306°C for KDNTDA–BAPBDS/SiRDA(4/1)-s (K2) and KDNTDA–BAPBDS/SiRDA(7.5b/1.5b) (K4), respectively. These values are similar to those of KDNTDA–BAPBDS-based SPSIs.<sup>19,20</sup> The results reveal that the desulfonation temperature of SPSIs is mainly determined by the sulfonated oligomer.

Table II lists the solubility properties of SPSIs. KDNTDA-based SPSIs in TEA salt form generally show good solubility in polar aprotic solvents such as DMSO, DMAc, DMF, and NMP. On the other hand, SPIs in proton form generally have poor solubility. However, the KDNTDA-based SPSIs in proton form displayed better solubility in more than two kinds of aprotic solvents at a concentration of 5 wt % (K1–K4). This revealed that the KDNTDA-based SPSIs had higher solubility than the KDNTDA-based sulfonated aryl polyimide (K6). The KDNTDA-based homopolymer (K0) displayed better solubility in chloroform and polar aprotic solvents such as DMAc and NMP. The SPSIs did not dissolve in methanol or chloroform whether in TEA salt form or proton form. This suggests that SPSIs may be potential candidates for direct methanol fuel cells. KDNTDA-based SPSIs generally show good solubility properties versus KDNTDA- or NTDA-based sulfonated aryl polyimides, and this is favorable for processing and other operations in fuel cell applications.

**TABLE II**  
Solubility Properties of the KDNTDA-Based SPSIs

No.	<i>m</i> -Cresol	DMSO	DMAc	DMF	NMP	CHCl <sub>3</sub>	CH <sub>3</sub> OH
K0	+	+-	++	+-	+	++	-
K1	++ (-)	+(+)	++ (+-)	++ (+)	+- (+)	- (-)	- (-)
K2	++ (-)	++ (+)	++ (+-)	++ (+)	++ (+)	- (-)	- (-)
K3	++ (-)	++ (+)	++ (+-)	++ (+-)	++ (+)	- (-)	- (-)
K4	++ (-)	++ (+)	++ (+-)	++ (+-)	++ (+)	- (-)	- (-)
K5	++ (-)	++ (+)	++ (+)	++ (+-)	++ (+-)	- (-)	- (-)
K6	++ (-)	++ (+)	+	++ (+-)	+- (-)	- (-)	- (-)

The data in parentheses refer to the proton form, and the other data refer to the TEA salt form. + = soluble at an elevated temperature; ++ = soluble at room temperature; +- = partially soluble; - = insoluble.



**Figure 5** RH dependence of  $\sigma$  at 60°C for the SPSI membranes, SPI membrane, and Nafion 112.

#### WU, size change, and $\sigma$

The WU significantly depends on the IEC; therefore, the number of sorbed water molecules per sulfonic acid group ( $\lambda$ ) was used to evaluate the relationship between the polymer structure and WU.  $\lambda$  can be calculated with the equation  $\lambda = 10 \times \text{WU}/\text{IEC} \times 18$ . As listed in Table I,  $\lambda$  in water for KDNTDA-based SPSIs with an IEC of 1.90–2.11 mequiv/g (the  $^1\text{H-NMR}$  values) was in the range of 13–17.  $\lambda$  was slightly larger for higher IECs because of molecular relaxations caused upon sorption.

As shown in Table I, the KDNTDA-based SPSIs displayed anisotropic membrane swelling. The dimensional change was 2–3 times larger in the thickness direction than in the plane direction. This anisotropy was comparable to that of the KDNTDA-based sulfonated aryl polyimide (K6).

$\sigma$  values at 50% RH, 70% RH, and in water at 60°C are listed in Table I. Figure 5 shows the RH dependence of  $\sigma$  at 60°C. Compared with Nafion 112, all of the SPSI membranes displayed larger humidity dependence. The SPSI membranes exhibited much lower  $\sigma$  values at lower RH than Nafion 112, whereas they showed similar or slightly lower  $\sigma$  values in water.  $\sigma$  significantly depends on the IEC. KDNTDA–BAPBDS/SiRDA (K2) with a relatively high IEC of 1.92 mequiv/g displayed relatively low  $\sigma$  values of 75, 15, and 4 mS/cm in water, 70% RH, and 50% RH, respectively, which are comparable to those of the KDNTDA-based SPI (K6), which had an

IEC of 1.58 mequiv/g. This might be due to any differences in their membrane morphologies.

Random, sequenced, and short block–block co-SPSIs (K1–K4) showed similar WUs, size changes, and  $\sigma$  values. K1 was considered to have a short sequenced block structure rather than a random structure because of the reactivity difference between BAPBDS and SiRDA. K2–K4 were considered to have a short block length ( $<3.5$ ) of KDNTDA–BAPBDS or KDNTDA–SiRDA. Therefore, the membrane morphologies may not be obviously different among random, sequenced, and short block–block co-SPSIs.

## CONCLUSIONS

A series of KDNTDA-based SPSIs bearing dimethyl siloxane oligomers were synthesized with reduced viscosities of 1.0–3.5 dL/g. The SPSIs displayed reasonably high  $\sigma$  values, thermal stability, and mechanical properties. They also showed anisotropic membrane swelling with a larger effect in thickness than in plane. The KDNTDA-based SPSIs had good solubility in common aprotic solvents in both TEA salt and proton forms. The molar content of the dimethyl siloxane oligomer in the copolymers was 50–80% of that in the feed for KDNTDA-based random, sequenced, and short block–block co-SPSIs.

## References

1. Roziere, J.; Jones, D. J. *Annu Rev Mater Res* 2003, 33, 503.
2. Beuschern, U.; Cleghorn, S. J. C.; Johnson, W. B. *Int J Energy Res* 2005, 29, 1103.
3. Mehta, V.; Cooper, J. S. *J Power Sources* 2003, 114, 32.
4. Savadogo, O. *J New Mater Electrochem Syst* 1998, 1, 47.
5. Rikukawa, M.; Sanui, K. *Prog Polym Sci* 2000, 25, 1463.
6. Kerres, J. A. *J Membr Sci* 2001, 185, 3.
7. Kreuer, K. D. *J Membr Sci* 2001, 185, 29.
8. Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem Rev* 2004, 104, 4587.
9. Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. *J Membr Sci* 2002, 197, 231.
10. Taeger, A.; Vogel, C.; Lehmann, D.; Lenk, W.; Schlenstedt, K.; Meier-Haack, J. *Macromol Symp* 2004, 210, 175.
11. Hickner, M. A.; Fujimoto, C. H.; Cornelius, C. J. *Polymer* 2006, 47, 4238.
12. Regina, A.; Fontananova, E.; Drioli, E.; Casciola, M.; Sganappa, M.; Trotta, F. *J Power Sources* 2006, 160, 139.
13. Yin, Y.; Yamada, O.; Tanaka, K.; Okamoto, K. I. *Polym J* 2006, 38, 197.
14. Besse, S.; Capron, P.; Diat, O.; Gebel, G.; Jousse, F.; Marsacq, D.; Pinéri, M.; Marestin, C.; Mercier, R. *J New Mater Electrochem Syst* 2002, 5, 109.
15. Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. I. *Macromolecules* 2002, 35, 6707.
16. Watari, T.; Fang, J.; Tanaka, K.; Kita, H.; Okamoto, K. I.; Hirano, T. *J Membr Sci* 2004, 230, 111.
17. Einsla, B. R.; Hong, Y. T.; Kim, Y. S.; Wang, F.; Gunduz, N.; McGrath, J. E. *J Membr Sci* 2005, 255, 141.



18. Asano, N.; Aoki, M.; Suzuki, S.; Miyatake, K.; Uchida, H.; Watanabe, M. *J Am Chem Soc* 2006, 128, 1762.
19. Chen, X.; Yin, Y.; Tanaka, K.; Kita, H.; Okamoto, K. *High Perform Polym* 2006, 5, 637.
20. Chen, X.; Yin, Y.; Chen, P.; Kita, H.; Okamoto, K. *J Membr Sci* 2008, 313, 106.
21. Yan, J.; Liu, C.; Wang, Z.; Xing, W.; Ding, M. *Polymer* 2007, 48, 6210.
22. Li, N.; Cui, Z.; Zhang, S.; Li, S.; Zhang, F. *J Power Sources* 2007, 172, 511.
23. Lee, C.; Sundar, S.; Kwon, J.; Han, H. *J Polym Sci Part A: Polym Chem* 2004, 42, 3612.
24. Lee, C.; Sundar, S.; Kwon, J.; Han, H. *J Polym Sci Part A: Polym Chem* 2004, 42, 3621.
25. Chang, Y.-H.; Kim, J.-H.; Lee, S.-B.; Rhee, H.-W. *J Appl Polym Sci* 2000, 77, 2691.
26. Wu, K. H.; Chang, T. C.; Yang, J. C.; Chen, H. B. *J Appl Polym Sci* 2001, 79, 965.
27. Zou, L.; Anthamatten, M. *J Polym Sci Part A: Polym Chem* 2007, 45, 3747.