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ORIGINAL PAPER

Synthesis and properties of novel side-chain-type sulfonated polyimides

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Abstract A series of side-chain-type sulfonated polyimides (SPIs) were synthesized from 4,4′-ketone dinaphthalene-1,1′,8,8′-tetracarboxylic dianhydride (KDNTDA), 2,2′-(4-sulfophenoxy) benzidine, and nonsulfonated diamines. The SPIs showed anisotropic membrane swelling in water with 2–4 times larger swelling in thickness direction than that in plane one, being much different from SPIs derived from 1,4,5,8-naphthalenetetracarboxylic dianhydride. They exhibited good solubility in dimethyl sulfoxide and 1-methyl-2-pyrrolidone even in proton form, which is favorable for processing in fuel cell applications. KDNTDA-based SPIs displayed good mechanical properties with reduced viscosities ranged from 1.1 to 2.4 dl g^{-1} at 35 °C in triethylamine salt form. They also showed reasonably high proton conductivity and thermal stability.

Keywords Sulfonated polyimides · Proton conductivity ·
Polymer electrolyte membrane

Introduction

Polymer electrolyte membranes (PEMs) are one of the most important components in polymer electrolyte membrane fuel cells (PEFCs) and direct methanol fuel cells

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(DMFCs) [1, 2]. Most research focus on perfluorinated ionomer membranes, such as DuPont's Nafion, because of their high performance in PEFCs. However, shortcomings such as high cost, large fuel crossover, and lower operating temperature below 80 °C, critically limit their industrial application [3]. Extensive efforts have been made to develop alternative proton-conducting membranes based on sulfonated aromatic hydrocarbon polymers [4–8], such as sulfonated poly (aryl ether sulfone) [9, 10], sulfonated polyphenylene [11], sulfonated poly (ether ether ketone) [12], and sulfonated polyimides (SPIs) [13].

As one of the most promising PEM candidates for fuel cell application, 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA)-based SPIs have attracted much attention in recent years [14–18]. Many novel side-chain-type and main-chain-type sulfonated diamines are prepared to develop high performance SPI ionomers. Some structure-property relationships of NTDA-based SPIs are also discovered. It is reported [19, 20] that the change in hydrolytic stability of the polyimides is related to the basicity of the sulfonated diamine monomer. The further research [21] suggests that side-chain-type sulfonated monomer with sulfonated pendant groups are favorable for preparing high performance SPIs, due to the formation of the microphase-separated structure composed of hydrophilic side chain domains and hydrophobic polyimide main chain domains. To date, 2,2′-(4-Sulfophenoxy) benzidine (BSPOB)-based SPIs are reported to show the highest performance among side-chain-type SPIs [13]. However, NTDA-based SPIs displayed poor processing property in fuel cell applications due to their poor solubility. Recently, flexible dianhydrides of 4,4′-ketone dinaphthalene-1,1′,8,8′-tetracarboxylic dianhydride (KDNTDA) [22, 23] and 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) [24, 25] are being synthesized and used for preparing SPI ionomers. The results show that the solubility of SPIs has been improved.

Here, a series of KDNTDA-based side-chain-type SPIs are synthesized from BSPOB and several nonsulfonated diamines. Their properties such as proton conductivity, mechanical property, and thermal stability are 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 and used as received. 1,3-Bis(4-aminophenoxy)benzene (BAPBz), 4,4′-bis(4-aminophenoxy)biphenyl (BAPB), bis [4-(4-aminophenoxy)phenyl] sulfone (BAPPS), and 2,2′-bis(aminophenyl) hexafluoropropane (BAHF) were purchased from Wako and recrystallized from ethanol before use. Ultra-pure water was obtained from a Millipore Milli-Q purification system. KDNTDA and BSPOB were prepared according to the literature [22, 26].

Measurements

Infrared (IR) spectra were recorded on a Horiba FT-200 spectrometer while the ^{1}H-NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument. 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^{-1}. Thermogravimetric analysis (TGA) was carried out with a Rigaku TG-8120 in helium (flow rate: 100 cm^{3} min^{-1}) at a heating rate of 10 °C min^{-1}, standing at 150 °C for 0.5 h. Solubility tests were carried out in six solvents with a concentration of 5% (w/v) at room temperature. The studied solvents were *m*-cresol, DMAc, DMF, NMP, DMSO, and methanol. The reduced viscosity (η_r) was measured with an Ostwald viscometer using 0.5 g dL^{-1} *m*-cresol solution of SPI in TEA salt form at 35 °C.

Ion exchange capacity (IEC) was calculated from the molar ratio of sulfonated diamine to nonsulfonated diamine in feed, and also evaluated by titration method. For the titration method, a sample membrane in proton form was soaked in 15 wt% of NaCl solution at 30 °C for 72 h to exchange the H^{+} ion with the Na^{+} ion. Then, the released H^{+} ion was titrated with 0.05 M of NaOH solution, using phenolphthalein as the indicator.

Water uptake (WU) was measured by immersing completely dried SPI membrane samples into de-ionized water at room temperature for 5 h. Then the samples were taken out, wiped with tissue paper, and quickly weighted on a microbalance to calculate WU, using the following equation:

$$\mathrm{WU} = [(W_\mathrm{s} - W_\mathrm{d})] \times 100\%, \tag{1}$$

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

The dimensional changes in membrane thickness (Δt_c) and in plane (Δl_c) were measured according to the method described elsewhere [16, 17]. The dimensional changes of the membrane were characterized by Eq. 2:

$$\begin{aligned} \Delta t_c &= (t - t_\mathrm{s})/t_\mathrm{s} \\ \Delta l_c &= (l - l_\mathrm{s})/l_\mathrm{s}, \end{aligned} \tag{2}$$

where t_s is the thickness and l_s is the diameter of the membrane equilibrated at 70% RH; t and l refer to those of the swollen membrane in water. In this case, the dry membrane was difficult to be measured due to the shrink after being dried at 150 °C for 10 h. The shrinked membrane was first immersed in water to get smooth sample and then taken out and placed at ambient condition (70% RH) for 24 h, followed by the measurement of size (t_s and l_s) as standards.

Proton conductivity in the plane direction of the membrane was determined using electrochemical impedance spectroscopy over a frequency ranging from 10 Hz to 100 kHz (Hioki 3532-80). The proton conductivity was calculated from the following equation:

$$\sigma = d/(t_\mathrm{s} w_\mathrm{s} R), \tag{3}$$

where d is the distance between the two electrodes, t_s is the thickness, and 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 σ for the measurement in water.

General procedure for synthesis of SPIs

Homo sulfonated polyimide

Under nitrogen flow, 0.528 g (1 mmol) of BSPOB, 5.5 mL of *m*-cresol, and 0.34 mL of TEA were added to a completely dried 100 mL three-neck flask. After BSPOB was completely dissolved, 0.422 g (1 mmol) of KDNTDA, and 0.171 g of benzoic acid were added to the flask. The mixture was stirred and heated at 90 °C for 4 h, and then heated at 180 °C for 20 h after 0.161 g of isoquinoline was added. After cooling to room temperature, the solution was poured into 100 mL of methanol, and washed three times with methanol. The resulting precipitate was collected by filtration and dried in vacuo.

Random co-SPIs

As an example, the synthesis of KDNTDA-BSPOB/BAPBz(2/1)-r (**BS-2**) is described as follows. Under a nitrogen flow, 0.845 g (1.6 mmol) of BSPOB, 11.5 mL of *m*-cresol, and 0.54 mL of TEA were added to a completely dried 100 mL three-neck flask. After BSPOB was completely dissolved, 0.234 g (0.8 mmol) of BAPBz, 1.014 g (2.4 mmol) of KDNTDA, and 0.410 g of benzoic acid were added to the flask. The mixture was stirred and heated at 90 °C for 4 h, and then heated at 180 °C for 20 h after 0.385 g of isoquinoline was added. After cooling to room temperature, the solution was poured into 250 mL of methanol, and washed three times with methanol. The resulting precipitate was collected by filtration and dried in vacuo.

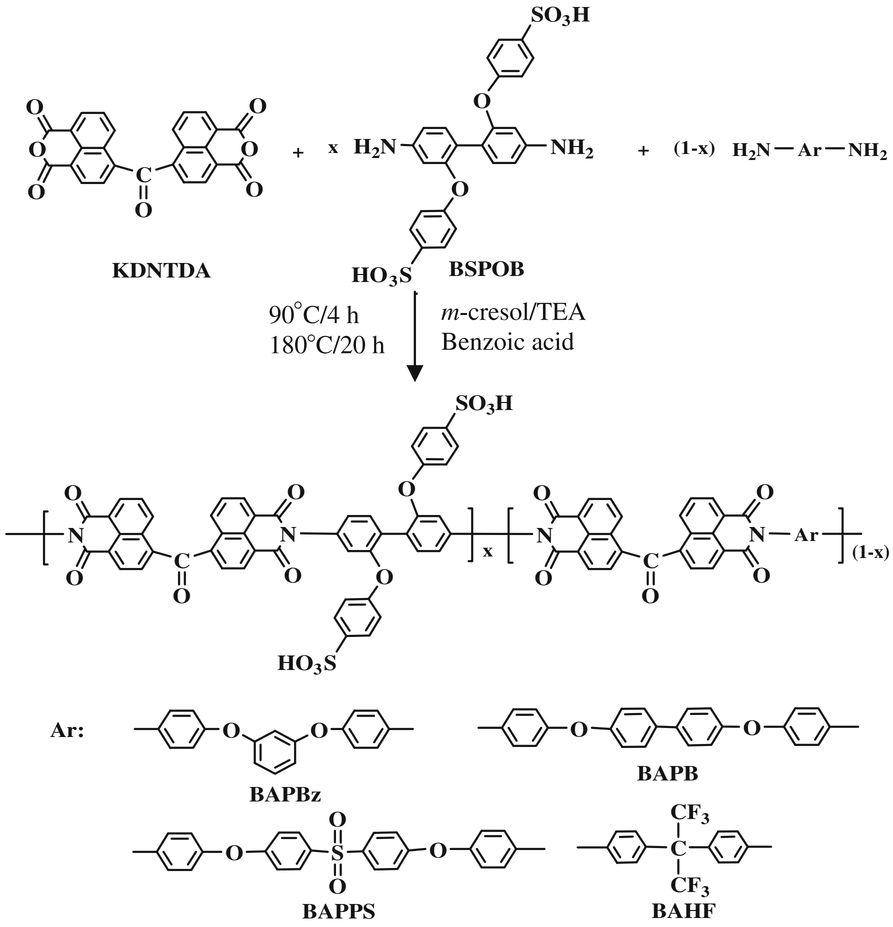
Membrane formation and proton exchange

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

Results and discussion

Synthesis and characterization of SPIs

The synthesis of KDNTDA-based homo-polyimide and random co-polyimides was carried out by a one-step method in *m*-cresol in the presence of TEA and using benzoic acid as the catalyst (Scheme 1).



Scheme 1 Synthesis of homo and random co-SPIs

The structures of the KDNTDA-based SPIs in proton form were confirmed by the ^{1}H-NMR and IR spectra. Figure 1 shows the protons of KDNTDA-based SPIs. It is obvious that there are three kinds of naphthalenic protons based on their different chemical environments. The protons nearer to the naphthalimide or carbonyl linkage (H_1, H_2, and H_5 in Fig. 1) appear in the range of 8.5–9.0 ppm, while the protons far from the naphthalimide or carbonyl linkage (H_3, H_4 in Fig. 1) shift to 7.9–8.1 ppm because of the smaller electron-withdrawing effect of the naphthalimide and carbonyl groups. The protons on the sulfophenoxy group (H_9 and H_{10} in Fig. 1) overlap each other in the range of 7.5–7.8 ppm. The peaks appeared in the range of 6.8–7.5 ppm are attributed to the protons of biphenyl group in BSPOB and the protons of nonsulfonated diamine moiety. These peaks are difficult to definitely assign due to their overlap.

Figure 2 shows the IR spectra of the KDNTDA-based SPIs. The spectra display KDNTDA-based naphthalimide absorption bands at 1,711 cm^{-1} (C=O,

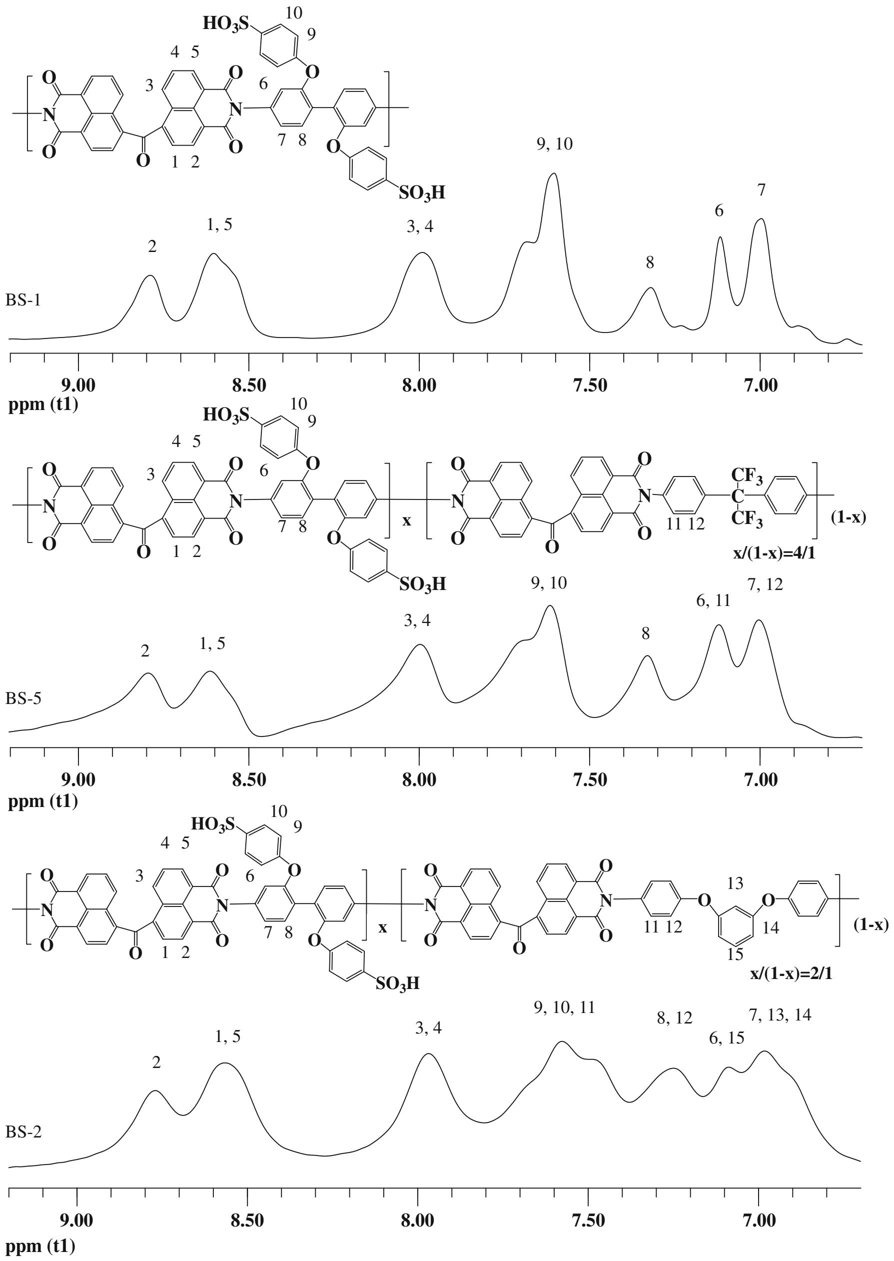


Fig. 1 ^{1}H-NMR spectra of SPIs in proton form in DMSO-d_6

asymmetric), 1,664 cm^{-1} (C=O, symmetric), and 1,370 cm^{-1} (C–N–C, asymmetric). The stretching vibration of the carbonyl group in the aryl ketone skeleton overlap with the symmetric stretching vibration of the carbonyl group at 1,664 cm^{-1} (C=O, symmetric). The peaks appeared at 1,003, 1,028, 1,124, and 1,173 cm^{-1} are

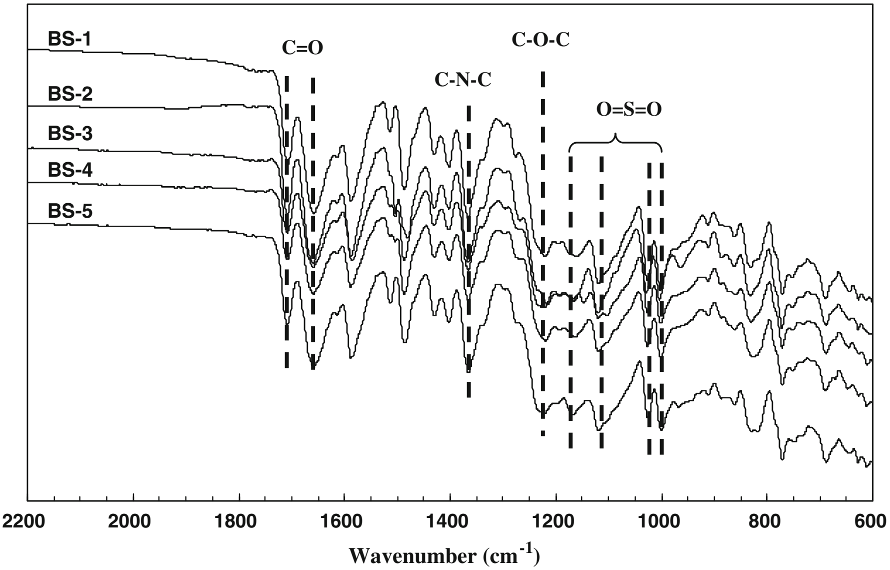


Fig. 2 IR spectra of SPI membranes in proton form

attributed to the symmetric and asymmetric vibration of O=S=O bond in the sulfonic acid group for KDNTDA-based SPIs. The vibrations of C–O–C bond in the aryl ether backbone appear at 1,230 cm^{-1}.

Physical properties of SPIs

The properties of the KDNTDA-based side-chain-type SPIs are listed in Table 1. The IEC was evaluated from the molar ratio of sulfonated diamine to nonsulfonated diamine in the feed (theoretical IEC) as well as by the titration method. As listed in Table 1, the IEC values calculated by the titration method are as large as 89–98% of the corresponding theoretical values, which indicates that the proton exchange is almost complete for KDNTDA-based side-chain-type SPIs.

The WU significantly depends on the IEC, therefore, the number of sorbed water molecules per sulfonic acid group (λ) was used to evaluate the relationship between the polymer structure and WU. λ can be calculated from the equation $\lambda = (10 \times \mathrm{WU})/(\mathrm{IEC} \times 18)$. As listed in Table 1, λ in water for KDNTDA-based SPIs with IEC of 1.58–2.19 meq g^{-1} is in the range of 12–16. λ is slightly larger for higher IECs due to the molecular relaxations that cause upon sorption. KDNTDA-based side-chain-type SPI, **BS-5**, with an IEC of 1.83 meq g^{-1}, has WU of 47% and λ of 14, which is much lower than those of the NTDA-based one (78% and 23, respectively), **N1**, with a comparable IEC of 1.88 meq g^{-1}. The low WU and λ suggest the low molecular relaxations of the KDNTDA-based SPIs in the water.

As shown in Table 1, KDNTDA-based side-chain-type SPIs display anisotropic membrane swelling. The dimensional change is 2–4 times larger in thickness direction than that in plane one for KDNTDA-based SPIs, whereas it is nearly 14

Table 1 Properties of SPIs

No	Code	IEC (meq/g)		η_r^a(dL/g)	WU (%)	λ	Dimensional change		T_{ds}^b(°C)	σ (mS/cm)^c		
		Theoretical	Titr.				Δt_c	Δl_c		50%RH	70%RH	In water
BS-1	KDNTDA-BSPOB	2.19	2.05	1.1	65	16	0.20	0.099	308	18	44	149
BS-2	KDNTDA-BSPOB/BAPBz(2/1)-r	1.58	1.41	1.3	34	12	0.12	0.035	300	3	15	56
BS-3	KDNTDA-BSPOB/BAPPS (3/1)-r	1.62	1.59	1.1	39	13	0.10	0.044	317	4	20	61
BS-4	KDNTDA-BSPOB/BAPB (3/1)-r	1.71	1.60	1.8	40	13	0.17	0.038	305	6	22	68
BS-5	KDNTDA-BSPOB/BAHF (4/1)-r	1.83	1.70	2.4	47	14	0.13	0.051	296	6	24	85
N1	NTDA-BSPOB/BAPB(2/1)-r	1.88	1.80	3.9	78	23	0.39	0.026	–	7	30	168
	Nafion 112	0.91	0.89	–	39	24	0.13	0.12	–	26	59	141

[a] At 0.5 g dL^{-1} *m*-cresol solution of SPI in TEA salt form

[b] Desulfonation temperature

[c] At 60 °C

times larger in thickness than that in plane for NTDA-based one, **N1**. The results reveal that KDNTDA-based side-chain-type SPIs has much smaller anisotropy than NTDA-based ones. Which are corresponded to the low WU and λ of the KDNTDA-based SPIs. The anisotropic membrane swelling of SPI membranes is considered due to the polymer chain alignment in plane direction. The anisotropic degree of membrane swelling ($\Delta t_c/\Delta l_c$) for KDNTDA-based SPIs is much smaller than that for NTDA-based ones, which suggest that the rigid imide backbone from NTDA seemed to cause the better alignment of polymer chain in plane direction compared with the imide backbone containing flexible KDNTDA. It is observed that the dimensional change of **BS-5** in plane direction is about two times of that for **N1**, but in thickness direction, the dimensional change is only one-third as that for **N1**. Generally, side-chain-type SPIs derived from NTDA display large dimensional change especially in thickness direction because of their flexible side chain and rigid main chain structure [13]. However, for KDNTDA-based SPIs, side chain increase the thickness change while flexible main chain help to improve the plane change of the SPI membranes. As a result, with the introduction of the flexible KDNTDA moiety into the side-chain-type SPIs, large dimensional change is improved obviously, which is useful for the operations in fuel cell applications under high relative humidity.

Reduced viscosities of the KDNTDA-based side-chain-type SPIs ranged from 1.1 to 2.4 dL g^{-1}, which ensured that flexible and tough SPI membranes were obtained in this study with a reasonably high stress-strain behavior. As shown in Fig. 3, KDNTDA-BSPOB/BAPB(3/1)-r (**BS-4**) displays in Young's modulus (YM) of 2.3 GPa, a maximum stress (MS) of 85 MPa and an elongation-at-break (EB) of 39%, whereas NTDA-BSPOB/BAPB(2/1) (**N1**) with viscosity of 3.9 dL g^{-1} shows 2.9 GPa, 122 MPa, and 45% EB, respectively. Compared with NTDA-based SPIs, slightly lower mechanic properties of KDNTDA-based ones are attributed to their flexible main chain and low molecular weight. Compared with Nafion 112, KDNTDA-based side-chain-type SPIs show much larger tensile stress but much lower EB.

The thermal stability of the KDNTDA-based SPIs was examined by TGA and the results are given in Fig. 4 and Table 1. The first weight loss observed around 100 °C is due to the loss of sorbed water. The second weight loss appeared around

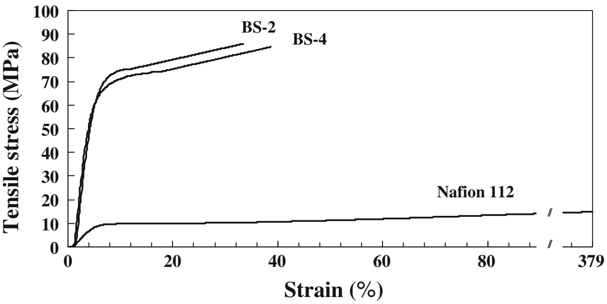


Fig. 3 Stress-stain curves of SPI membranes and Nafion 112

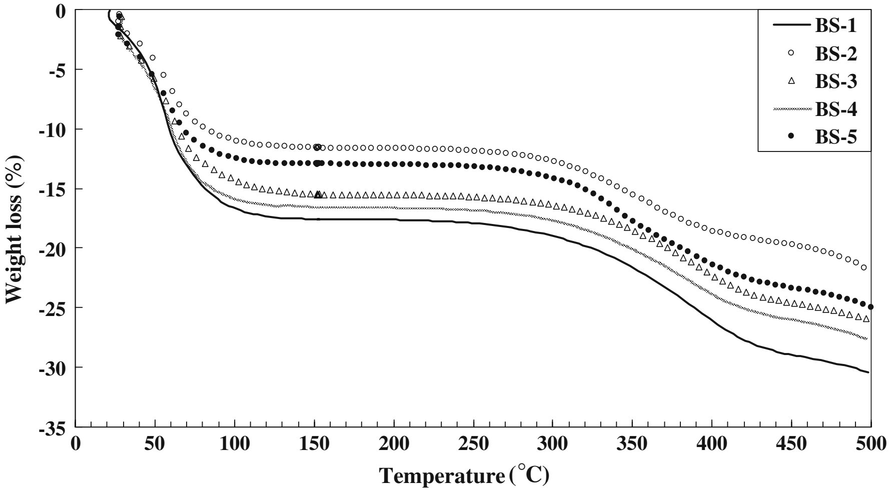


Fig. 4 TG curves of SPI membranes in proton form

Table 2 Solubility properties of SPIs

No	m-Cresol	DMSO	DMAc	DMF	NMP	CH_3OH
BS-1	++ (−)	++ (+)	++ (S)	++ (S)	++ (−)	− (−)
BS-2	++ (−)	++ (+)	++ (±)	++ (±)	++ (+)	− (−)
BS-3	++ (−)	++ (+)	++ (±)	++ (±)	++ (+)	− (−)
BS-4	++ (−)	++ (+)	++ (−)	++ (±)	++ (+)	− (−)
BS-5	++ (−)	++ (+)	++ (±)	++ (±)	++ (+)	− (−)
N1	++ (−)	− (−)	− (−)	− (−)	− (−)	− (−)

++, soluble at room temperature; +, soluble at elevated temperature; ±, partially soluble; −, insoluble; S, swelling. The data in parentheses refer to proton form and others refer to TEA salt form

300 °C is attributed to the decomposition of sulfonic acid group. As shown in Fig. 4 and Table 1, the desulfonation temperatures (T_{ds}) are 308 and 317 °C for KDNTDA-BSPOB (**BS-1**) and KDNTDA-BSPOB/BAPPS(3/1) (**BS-3**), respectively. The results reveal that the KDNTDA -based side-chain-type SPIs have high thermal stability with high desulfonation temperature around 300 °C.

The solubility properties of SPIs are listed in Table 2. KDNTDA-based SPIs in TEA salt form generally show good solubility in polar aprotic solvents, such as DMSO, DMAc, DMF, and NMP. On other hand, SPIs in proton form generally have poor solubility. However, the KDNTDA-based co-SPIs in proton form display better solubility in two kinds of aprotic solvents (DMSO and NMP) at a content of 5 wt%. This reveals that the KDNTDA-based SPIs have a higher solubility than NTDA-based one, **N1**. Different from KDNTDA-based co-SPIs, the homo-polymer (**BS-1**) display better solubility in DMSO, but it is insoluble in NMP and only swells in DMAc and DMF. This suggests that the introduction of the flexible nonsulfonated diamine moiety into SPIs main-chain could improve the solubility of SPIs. It was observed that KDNTDA-based side-chain-type SPIs did not dissolve in methanol either in TEA salt or in proton forms. This reveals that the SPIs may be potential candidates for DMFCs. It is obvious that KDNTDA-based SPIs generally show much better solubility properties than NTDA-based ones, which is due to the much improved flexibility of the SPI main chain with the introduction of the flexible KDNTDA. The high solubility properties provide an advantage of easy processing and other operations in fuel cell applications, being different from NTDA-based SPIs.

Proton conductivity

Figure 5 shows the proton conductivities of SPI membranes as a function of RH at 60 °C. Compared with Nafion 112, all of the SPI membranes display larger humidity dependence. With an increase in RH, the proton conductivities increased significantly. The SPI membranes exhibit much lower σ values at a lower RH than Nafion 112, whereas they show similar or slightly lower σ values in water. The proton conductivities of co-SPI membranes incorporated with nonsulfonated diamines were much smaller than those of homo-SPI (**BS-1**), especially at lower RHs as a result of lower IEC, smaller water uptake, and poor ionic channel structure. KDNTDA-BSPOB (**BS-1**) with a high IEC of 2.19 meq g^{-1} and high WU of 65% displays high σ values of 149, 44, and 18 mS cm^{-1} in water, 70% RH, and

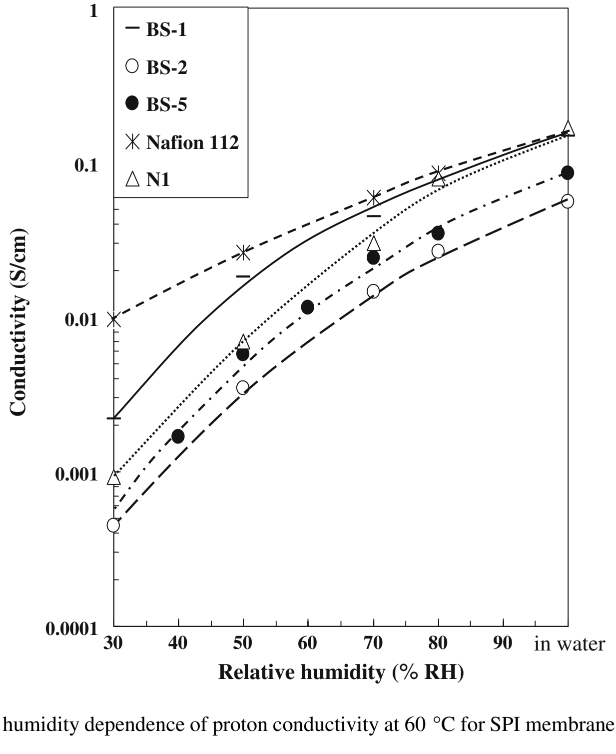


Fig. 5 Relative humidity dependence of proton conductivity at 60 °C for SPI membranes and Nafion 112

50% RH, respectively, whereas KDNTDA-BSPOB/BAHF(4/1) (**BS-5**) with a relative low IEC of 1.83 meq g^{-1} and low WU of 47% shows relative low σ values of 85, 24, and 6 mS cm^{-1}, respectively. However, in water, the co-SPI membranes displayed values closer to that of homo-SPI. The proton conductivities of co-SPI membranes incorporated with other nonsulfonated diamines, such as BAPBz, BAPPS, and BAPB, are listed in Table 1. The SPI membrane from BAPBz (**BS-2**) displays lower conductivities at 50% RH, 70% RH, and in water compared with other KDNTDA-based co-SPIs, probably due to its slightly lower IEC of 1.58 meq g^{-1} and smaller WU of 34%. For co-SPIs from BAPBz, BAPPS, BAPB, and BAHF, with an increase of their IECs, the proton conductivity values at 50% RH, 70% RH, and in water increase gradually as a result of their increased water uptakes. It is noted that, in water, **BS-5** shows much lower proton conductivity than **N1**, which are corresponded to their dimensional change, WU, and λ, although they have comparable IEC value. However, under low relative humidity (50% RH), **BS-5** and **N1** display similar proton conductivity. These might be due to their different structures and any difference in their membrane morphologies.

Water stability

Water stability tests were carried out by soaking the membrane sheets (250 mg) of KDNTDA-BSPOB/BAPB(3/1) (**BS-4**) in proton form in water (70 mL) at 130 °C under pressure for 96 h. After being kept under an aging condition, the membrane sheets were dried under vacuum at 120 °C for 3 h and then subjected to the characterization experiments including mechanical property, proton conductivity, and weight loss. The mechanical property was evaluated via tensile strength. The low weight loss of 4.3% with the aging was obtained. The aged membrane shows a smaller MS of 55 MPa and much smaller EB of 7% than the unaged one (MS of 85 MPa and EB of 39%, respectively). However, it was obvious that the aged membrane still kept reasonably toughness with relatively high tensile strength. The proton conductivity values of the aged membrane at 50% RH, 70% RH, and in water at 60 °C are 5, 20, and 69 mS cm^{-1}, respectively, and there are no appreciable change on proton conductivity before and after aging. As a result, KDNTDA-based side-chain-type SPIs display high water stability, which are comparable to NTDA-based ones.

Conclusions

A series of KDNTDA-based side-chain-type SPIs were synthesized with a reduced viscosity of 1.1-2.4 dL g^{-1}. SPIs displayed reasonably high proton conductivity, thermal stability, water stability, and mechanical properties. Compared with NTDA-based SPIs, KDNTDA-based ones showed lower anisotropic membrane swelling with a larger effect in thickness than in plane, which is useful for the operations in fuel cell applications. They also had good solubility in common aprotic solvents in both TEA salt and proton forms, which provide an advantage of easy processing in fuel cell applications.

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