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Synthesis and properties of novel sulfonated polyimides bearing sulfophenyl pendant groups for polymer electrolyte fuel cell application

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Abstract

A novel sulfonated diamine bearing sulfophenyl pendant groups of 2,2′-(4-sulfophenyl) benzidine (BSPhB) was synthesized. Sulfonated polyimides (SPIs) derived from 1,4,5,8-naphthalene tetracarboxylic dianhydride, BSPhB and other non-sulfonated diamines were successfully synthesized. The SPIs with ion exchange capacity (IEC) of 1.5–2.8 meq g^{-1} showed high reduced viscosity of 3–10 dL g^{-1} and high desulfonation temperature of 320 °C. The SPI membranes were tough and flexible, having high stress at break of more than 80 MPa and elongation of 80–100%. They showed highly anisotropic membrane swelling in water with larger swelling in thickness direction than in plane direction. They showed fairly high proton conductivity (σ). For example, the membrane with IEC of 1.77 meq g^{-1} exhibited σ values of 120 and 260 mS cm^{-1} at 60 and 120 °C, respectively, in water. They also showed fairly high water stability.

Keywords: Polymer electrolyte membrane; Sulfonated polyimide; Water stability

1. Introduction

Polymer electrolyte fuel cell (PEFC) is considered as one of the promising energy sources in future in the field of transportation, stationary and portable devices because of their high energy efficiency and low pollution to environment [1]. In a PEFC, polymer electrolyte membrane (PEM) is one of the key components. Although perfluorinated PEMs such as Nafion are still the state-of-the-art materials, their high cost, limited operation temperature below 80 °C and high methanol crossover restrict their wide applications. This triggered intense research of alternative materials, such as partially fluorinated or aromatic hydrocarbon polymers, as witnessed by large quantity of patents, papers and reviews [2–7].

Among aromatic hydrocarbon polymers, six-membered ring sulfonated polyimides (SPIs) are considered as promising candidates for PEM materials because of their high thermal stability, high mechanical strength, good film-forming ability, superior chemical resistance and low fuel gas (or liquid) crossover. In 1997, Mercier and his coworkers first reported on SPIs derived from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), benzidine-2,2′-disulfonic acid (BDSA, commercially available sulfonated diamine) and other non-sulfonated diamines. They reported a fairly high performance and durability for H_2/O_2 fuel cells using these SPI membranes at 60 °C [8]. Since then, BDSA-based SPIs with different non-sulfonated diamine moieties were widely studied [9–12]. However, the BDSA-based SPIs had poor water stability

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especially at moderate temperatures above 70 °C because of relatively easy hydrolysis of imide rings [13,14].

To investigate the relationship between water stability and chemical structure of SPIs and to achieve the high water stability, many types of SPIs based on novel sulfonated diamines have been developed [15–26]. In the case of SPIs based on 4,4′-bis(4-aminophenoxy) biphenyl-3,3′-disulfonic acid (BAPBDS), after aging the membranes in water at 130 °C for 192 h, the tensile strength decreased largely but remained at a fairly high level, and the proton conductivity hardly changed [27]. Short-term durability tests for a PEFC with BAPBDS-based SPI membrane indicated that the cell voltage of 0.75 V under a constant current density of 0.5 A cm^{-2} at 90 °C was maintained for more than 300 h [28]. The BAPBDS-based SPI membranes are expected to be applicable at temperatures up to 100 °C. In the case of SPIs based on 2,2′- or 3,3′-bis(3-sulfopropoxy) benzidine (BSPB), after the aging in water at 130 °C for 192 h, the tensile strength remained at the reasonably high level but the proton conductivity decreased largely especially at low relative humidity (RH) region [27]. This was due to the relatively easy cleavage of sulfopropoxy groups. On the other hand, PEFCs and direct methanol fuel cells (DMFCs) with BSPB-based SPI membranes displayed high performance at temperatures below 90 °C [7,29]. Recently, Watanabe et al. reported on the long-term durability for PEFC with BSPB-based SPI membrane, which was operated at a constant current density of 0.2 A cm^{-2} at 80 °C for 5000 h [30]. The BSPB-based SPI membranes are expected to be applicable at temperatures below 80 °C.

To develop PEMs applicable at temperatures above 90 °C, SPIs with the much higher water stability are required. 2,2′-(4-Sulfophenoxy) benzidine (BSPOB) is a homologous diamine of BSPB, where the sulfopropoxy group is replaced with sulfophenoxy one. Recently, BSPOB-based SPIs were reported to show much higher water stability than the BSPB-based ones, because of higher stability of pendant sulfophenoxy group [31]. It is interesting to investigate the effect of replacement of sulfophenoxy group in sulfonated benzidine with sulfophenyl one on the properties of the resulting SPIs.

Herein, in this paper, we report on the synthesis and characterizations of novel side-chain-type diamine bearing sulfophenyl pendant groups, 2,2′-(4-sulfophenyl) benzidine (BSPhB), and the corresponding SPIs derived from it.

2. Experimental

2.1. Materials

2,2′-Diphenyl benzidine (PhB) was synthesized according to the reported method [32]. Benzoic acid, isoquinoline, concentrated sulfuric acid, and fuming sulfuric acid (60%) were purchased from Wako and used as received. NTDA (Aldrich) was purified by vacuum sublimation. 4,4′-Bis(*p*-aminophenoxy) biphenyl (BAPB), and 1,3-bis(4-aminophenoxy) benzene (BAPBz) were purchased from Wako and recrystallized from ethanol. Triethylamine (TEA) was dried with molecular sieve of 4 Å. Dimethyl sulfoxide (DMSO), *m*-cresol, *N*,*N*-dimethyl acetamide (DMAc), and 1-methyl-2-pyrrolidone (NMP) were purchased from Wako and used as received. Ultra-pure water was obtained from a Millipore Mill-Q purification system.

2.2. Monomer and polymer syntheses

2.2.1. Synthesis of 2,2′-disulfophenyl benzidine (BSPhB)

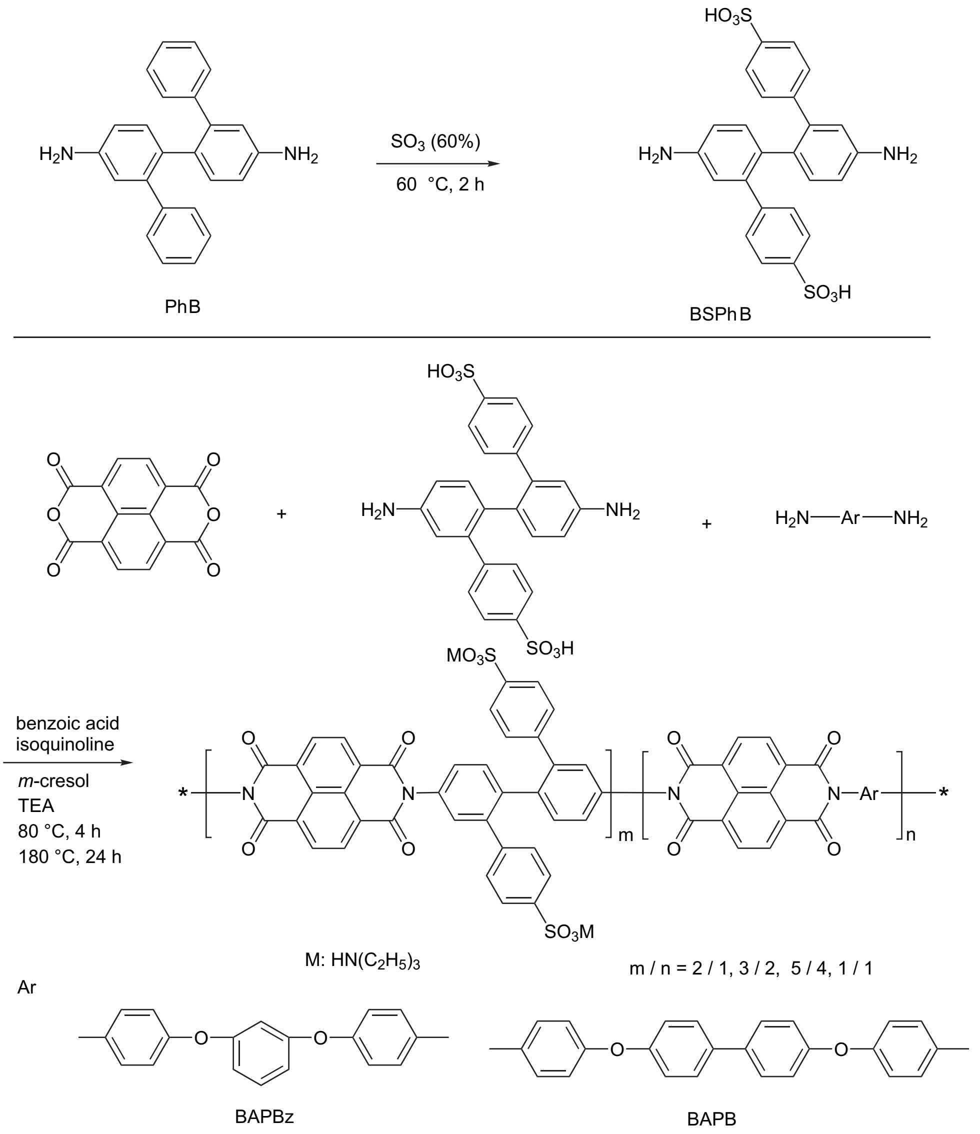
Scheme 1 shows the synthesis route of the novel sulfonated side-chain-type diamine and SPIs derived from it.

To a 100 mL of three-necked flask equipped with a magnetic stirring device and a nitrogen inlet was charged 10 g of PhB. The flask was cooled in an ice bath, and then 15 mL of concentrated sulfuric acid was slowly added with stirring. After PhB was completely dissolved, 5 mL of fuming sulfuric acid (SO_3, 60%) was slowly added to the flask. The reaction mixture was stirred at 0 °C for 0.5 h and then slowly heated to 60 °C and kept at this temperature for additional 2 h. After cooling to room temperature, the transparent solution was carefully poured into cold methanol. The resulting white precipitate was filtered off, washed with large amount of methanol until neutral, and dried at 60 °C *in vacuo*. The crude product was recrystallized from water to give 12.5 g (yield: 80%) of white product. ^1H NMR (270 MHz, DMSO-d_6): δ (ppm): 6.36–6.47 (4H), 6.66–6.75 (6H), 7.35–7.45 (4H) (see Fig. 1(a)). Elemental analysis results: Calculated for $C_{24}H_{20}N_2O_6S_2$: C, 58.05%; H, 4.06%; N, 5.64%. Calculated for 2.8% water in the sample: C, 56.41%; H, 4.26%; N, 5.48%. Found: C, 56.42%; H, 4.54%; N, 5.56%.

2.2.2. Synthesis of sulfonated random (co)polyimides

A series of co-SPIs derived from NTDA, BSPhB and BAPB or BAPBz were synthesized. As an example, the synthesis of NTDA–BSPhB/BAPB (3/2) is described below, where the data in parenthesis refer to the ratio of BSPhB to BAPB or BAPBz.

To a 200 mL completely dried four-necked flask equipped with a mechanical stirrer, a condenser and a nitrogen inlet were charged 4.387 g of BSPhB (8.83 mmol), 58 mL of *m*-cresol and 3.4 mL of TEA. After BSPhB was completely dissolved, 2.167 g of BAPB (5.89 mmol), 3.949 g of NTDA (14.72 mmol) and 2.52 g of benzoic acid were added to the flask. The mixture was stirred at room temperature for a few minutes and heated at 80 °C for 4 h and at 180 °C for 12 h, and then 2.67 g of isoquinoline was added and the reaction was continued for another 12 h. The viscous solution was diluted with 80 mL of *m*-cresol at 100 °C and then precipitated into acetone. The precipitated fiber-like polymer was collected by filtration and dried at 100 °C *in vacuo*. Fig. 1(b) shows the ^1H NMR of NTDA–BSPhB/BAPBz (1/1) in proton form in DMSO-d_6 at 90 °C. Elemental analysis results: Calculated for NTDA–BSPhB/BAPBz (1/1) in TEA salt form ($C_{82}H_{66}N_6O_{16}S_2$): C, 67.66%; H, 4.57%; N, 5.77%. Calculated for containing 2.1% water in the sample: C, 66.27%; H, 4.71%; N, 5.65%. Found: C, 66.27%; H, 4.62%; N, 5.78%.



Scheme 1. Synthesis of BSPhB and the corresponding SPIs.

2.3. Membrane preparation and proton exchange

SPI membranes were prepared by casting from *m*-cresol solution (5–6 wt% in TEA salt form) onto glass plates and drying at 120 °C for 12 h. The as-cast membranes were soaked in methanol for 24 h to remove the residual solvent, and then treated with 1.0 N sulfuric acid at 50 °C for 5 days for proton exchange. The proton-exchanged membranes were soaked in water for 48 h at 30 °C and cured *in vacuo* at 150 °C for 1 h and at 180 °C for 1 h.

2.4. Polymer characterization

2.4.1. Measurements

^{1}H NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument in DMSO-d_6. FT-IR spectra were recorded on a Horiba FT-200 Spectrometer by ATR (attenuated total reflection). Thermogravimetry analysis (TGA) was performed on Rigaku TG-8120 in helium (flow rate: 100 cm^3 min^{-1}) at a heating rate of 10 °C min^{-1}. The reduced viscosity η_r was measured with an Ostwald viscometer with 0.5 g dL^{-1} *m*-cresol solution at 35 °C. Mechanical tensile tests were performed on a universal testing machine (Orientic, TENSILON TRC-1150A) at 25 °C and around 60%RH.

Ion exchange capacity (IEC) of the SPIs was calculated from the feed molar ratio of sulfonated diamine to non-sulfonated diamine, or determined by the titration method. A sample membrane in proton form was soaked in a 15 wt% NaCl solution for 24–72 h at 30 °C to exchange the H$^+$ ion with Na$^+$ ion. Then the H$^+$ ion released into the solution was titrated with a 0.02 N NaOH solution using phenolphthalein as an indicator.

2.4.2. Water uptake and dimensional change

Water uptake (WU), dimensional change in membrane thickness (Δt_c) and diameter (Δl_c) were measured according

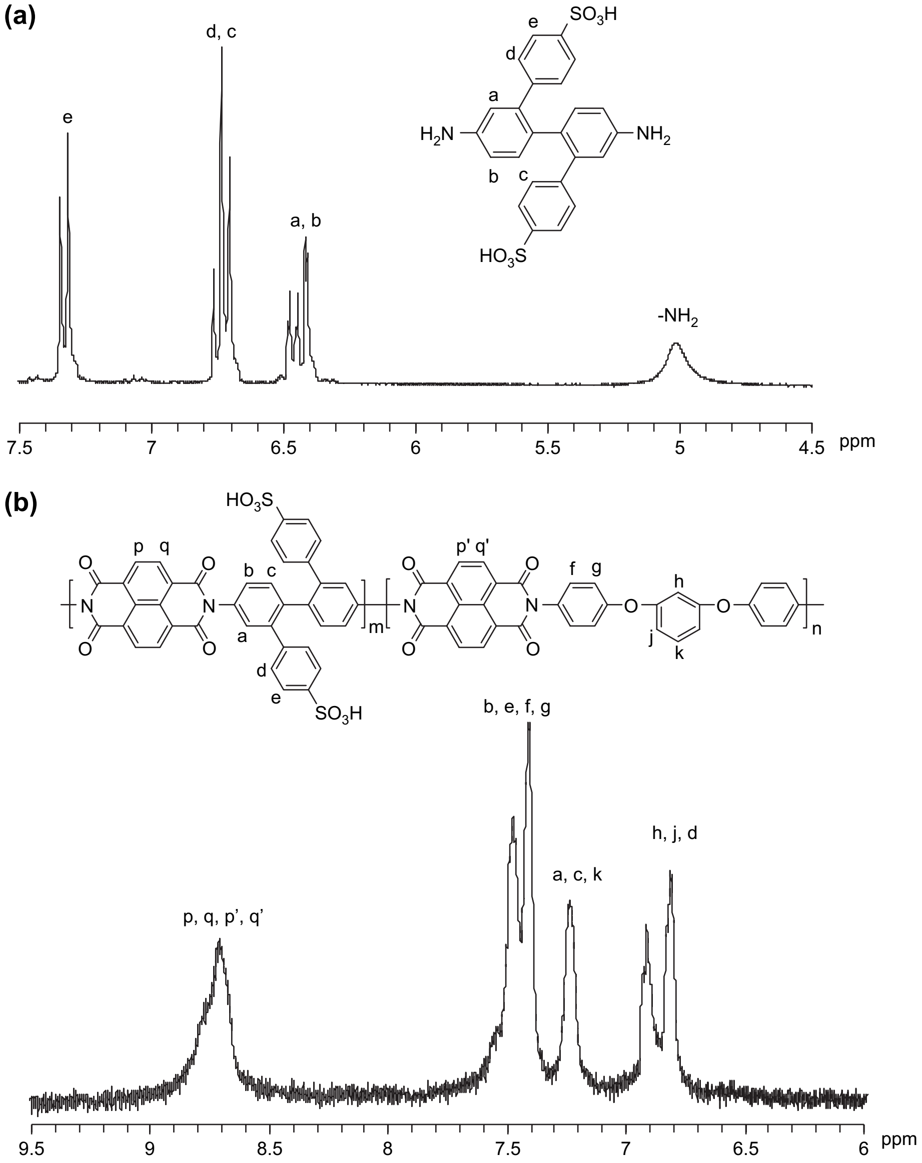


Fig. 1. (a) ^{1}H NMR spectrum of BSPhB in DMSO-d_6 and (b) ^{1}H NMR spectra of NTDA–BSPhB/BAPBz (1/1) in DMSO-d_6 as proton form at 90 °C.

to the method described elsewhere [16]. Water uptake was measured by immersing a sample sheet into water at 30 °C for 5 h. Then the membrane was taken out, wiped with tissue paper very quickly, and weighed on a microbalance. Water uptake was calculated from

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

where W_d and W_s are the weights of dry and corresponding water-swollen membranes, respectively.

Dimensional change of SPI membranes was investigated by immersing more than two sample sheets in water at 30 °C for 5 h. The changes of thickness and diameter were calculated from

$$\Delta t_\mathrm{c} = (t - t_\mathrm{s})/t_\mathrm{s}$$
$$\Delta l_\mathrm{c} = (l - l_\mathrm{s})/l_\mathrm{s} \tag{2}$$

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

2.4.3. Proton conductivity

Proton conductivity in plane direction of SPI membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 10 Hz to 100 kHz (Hioki 3532-80). A single cell with two platinum plate electrodes was mounted on a Teflon plate at 0.5 cm distance. The cell was placed under either in a thermo-controlled humidic chamber or in liquid water. Proton conductivity, σ, was calculated from

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

where d is the distance between the two electrodes, t_s and w_s are the thickness and width of the membrane at a standard condition of 70%RH, respectively, and R is the resistance value measured. For the measurements in liquid water, the swollen membrane thickness was used in the calculation of σ.

2.4.4. Water stability

Water stability tests were carried out by immersing SPI membrane sheets (150–200 mg of dry weight, in proton form) into ultra-pure water (90 mL) at 130 °C in an autoclave, which was set in the thermo-controlled oven, for a given time.

3. Results and discussion

3.1. Monomer synthesis

As seen in Scheme 1, BSPhB was prepared by direct sulfonation of the precursor diamine bearing phenyl pendant groups, using fuming sulfuric acid as the sulfonating agent. The synthesis was performed through changing sulfonation temperature (40–70 °C) and/or sulfonation time (2–8 h). The optimum sulfonation condition was found to be at 60 °C for 2 h. The sulfonation reaction mainly occurred in the *para* position of the phenyl pendant groups due to the strong electron-withdrawing protonized amino groups and the steric effect of the bulky sulfonic acid group. The chemical structure of resulting product was characterized by ^{1}H NMR spectrum as shown in Fig. 1, all peaks are well assigned to each proton and the integration intensity ratio of the protons was found to be 2:3:2, which was in agreement with the theoretical data. The elementary analysis results were slightly different from the calculated ones, but this was attributed to a small amount (2.8%) of sorbed water in the sample.

3.2. Polymer synthesis and characterization

The preparation of BSPhB-based co-SPIs was carried out through one-pot high temperature polymerization method in *m*-cresol as shown in Scheme 1. The presence of isoquinoline was reported on being advantageous to facilitate the imidization process and improve molecular weight [33]. Tough and transparent membranes were obtained.

The elementary analysis of polymer showed differences between the calculated and found data due to the sorbed water in the sample. After correction of water content of 2.1% in the sample, the calculated and found data were in good agreement. The ^{1}H NMR spectrum (see Fig. 1(b)) was performed at 90 °C due to its incomplete dissolution in DMSO at room temperature, and the integration intensity ratio of protons of diamine moieties over naphthalenic protons was found to be 3.30, which was in agreement with the theoretical one (3.29). These indicated the complete polycondensation.

Fig. 2 shows the IR spectra of the SPI membranes in proton form. Typical absorption bands for naphthalene imido rings are found at 1710 (C=O, symmetric), 1660 (C=O, asymmetric) and 1350 cm^{-1} (C–N, asymmetric). The bands at 1200, 1100 and 1030 cm^{-1} are assigned to the stretch vibration (O=S=O) of sulfonic acid groups.

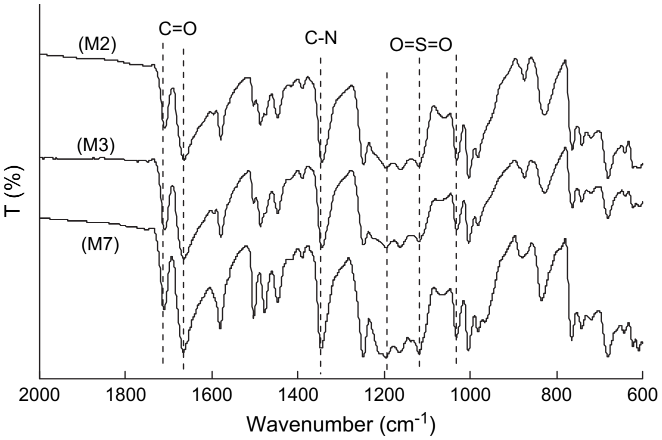


Fig. 2. IR spectra of BSPhB-based SPI membranes in proton form.

Properties such as IEC, reduced viscosity (η_r), water uptake (WU), first decomposition temperature (T_{d1}), dimensional change (Δt_c, Δl_c) and proton conductivity (σ) are summarized in Table 1. In this study, two kinds of non-sulfonated diamines, BAPB and BAPBz, were used as co-monomer to obtain SPIs with various IECs. The properties such as water uptake and proton conductivity significantly depended on IEC, but hardly depended on the type of co-monomer diamine. For comparison, the data for the BSPB-, BSPOB- and BAPBDS-based SPIs (R1, R2 and R3–4, respectively) and Nafion 112 are also listed. The experimental IEC values for the BSPhB-based SPI membranes obtained by the titration method were 87–89% of the theoretical ones.

Table 2 lists the solubility behavior of SPIs in common organic solvents. All the SPIs in TEA salt form showed good solubility in *m*-cresol, but not in proton form. Although all the BSPhB-based SPIs were insoluble in NMP, DMAc and DMF, some of them were soluble in DMSO in both forms.

3.3. Water uptake

The SPIs in TEA salt form showed high reduced viscosities (3.1–10 dL g^{-1}), indicating the high molecular weight. The SPI membranes showed highly anisotropic membrane swelling in water, that is, much larger swelling in membrane thickness direction than in plane direction. For instance, the membrane M3 showed 10 times larger swelling in thickness direction (34%) than in plane direction (3%). The similar tendency was found in the SPIs from other benzidine-type diamines, such as BSPB and BSPOB [19,31]. The anisotropic membrane swelling is considered due to the polymer chain alignment in plane direction. The rigid imide backbone from NTDA and benzidine with sulfonated pendants seemed to cause the better alignment in plane direction.

The water uptake of the SPI membranes was mainly determined by IEC. The λ (the number of water molecules sorbed per sulfonic acid group) values of the BSPhB-based SPI membranes were slightly larger than those of BAPBDS-based SPIs and similar to those of BSPOB-based SPIs [16,31]. The rigid structure of imide repeating units from NTDA and benzidine

Table 1
Properties of SPI membranes

Code	NTDA-based SPIs	IEC[a] (meq g^{-1})	η_r[b] (dL g^{-1})	T_{d1} (°C)	WU[c] (%)	λ	Dimensional change[c]		σ[d] (mS cm^{-1})		
							Δt_c	Δl_c	50%RH	70%RH	In water
M1	BSPhB	2.75	6.6	–	207	42	1.78	–	15	54	172
M2	BSPhB/BAPB (2/1)	1.95(1.74)	4.4	325	72(92)	20	0.34	0.03	8	31	141
M3	BSPhB/BAPB (3/2)	1.77(1.58)	5.7	320	60(79)	19	0.34	0.03	8	27	121
M4	BSPhB/BAPB (5/4)	1.65(1.43)	5.6	–	62(81)	21	0.34	0.03	6	22	118
M5	BSPhB/BAPB (1/1)	1.51(1.35)	9.2	–	62	23	0.25	0.03	2	18	118
M6	BSPhB/BAPBz (5/4)	1.74(1.55)	–	320	59(76)	19	0.38	0.03	7	25	132
M7	BSPhB/BAPBz (1/1)	1.60	10.2	–	50(63)	17	0.29	0.04	4	14	98
R1	BSPB/BAPB (2/1)	2.02	4.5	250	72	20	0.47	0.04	3	15	154
R2	2,2′-BSPOB/BAPB (2/1)	1.89	4.4	300	78(109)	23	0.39	0.03	7	30	168
R3	BAPBDS/BAPB (2/1)	1.89(1.86)	4.4	300	57	17	0.14	0.05	5	29	127
R4	BAPBDS/BAPBz (2/1)	1.96	2.0	–	55	16	0.14	0.07	2.3	13	102
	Nafion 112	0.91	–	–	39	24	0.14[e]	0.14[e]	30	59	141

[a] Calculated data, data in parenthesis were obtained by titration.
[b] 0.5 g dL^{-1} in *m*-cresol at 35 °C.
[c] At room temperature, the data in parenthesis were measured at 100 °C.
[d] At 60 °C.
[e] Provided by DuPont technical information.

moieties with bulky and rigid sulfonated pendants seemed to cause slightly loose packing of polymer chains, resulting in the large λ values. Fig. 3 shows the temperature dependence of water uptake and λ. The water uptake increased almost linearly with increasing temperature without any critical increase.

3.4. Thermal and mechanical properties

Fig. 4 shows the TGA curves of SPIs in proton form. The first step with large weight loss in the range of 50–150 °C was due to the loss of sorbed water. The second step in the range of 300–350 °C was attributed to the cleavage of the sulfonic acid group. The first decomposition temperature (T_{d1}) attributed to the cleavage of sulfonic acid group was 320 °C for the BSPhB-based SPIs, which was much higher than that of BSPB-based ones (about 250 °C), indicating the improved thermal stability for the sulfonic acid group.

Fig. 5 shows the strain–stress curves of BSPhB-based SPI membranes and Nafion 112. The result for Nafion 112 was close to DuPont's product information, showing Young's modulus (M), maximum stress (S) and elongation degree at break point (E) of 0.24 GPa, 40 MPa and 380%, respectively. It was noted that all the SPI membranes had much higher Young's modulus above 1.2 GPa than Nafion 112, and reasonably large maximum stress and elongation at break point, showing their excellent mechanical properties. For example, the membrane M3 showed M, S and E of 1.3 GPa, 100 MPa and 103%, respectively.

Table 2
Solubility of SPIs in TEA salt form and proton form

Code	*m*-Cresol	DMSO	NMP	DMAc
M1	++ (−)	+ (+)	− (−)	− (−)
M2	++ (+−)	+ (+)	− (−)	− (−)
M3	++ (−)	+ (+−)	− (−)	− (−)
M4	++ (−)	− (−)	− (−)	− (−)
M5	++ (−)	− (−)	− (−)	− (−)
M6	++ (+−)	+ (+)	− (−)	− (−)
M7	++ (+−)	+ (+)	− (−)	− (−)
R1	+ (−)	+ (−)	+− (−)	− (−)
R2	++ (−)	− (−)	− (−)	− (−)
R3	++ (−)	− (−)	− (−)	− (−)

The data in parenthesis refer to the proton form.
'++' easily soluble, '+' soluble by heating, '+−' partially soluble, '−' insoluble.

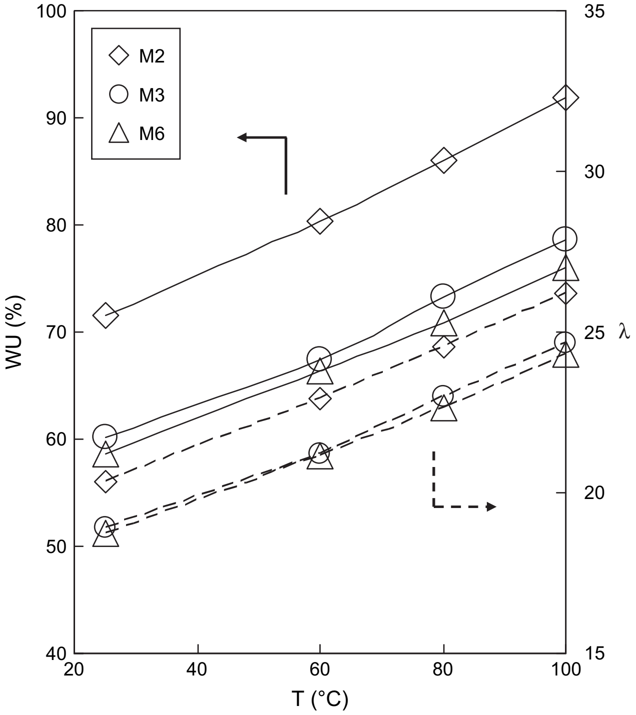


Fig. 3. Water uptake and λ in liquid water as a function of temperature for SPI membranes.

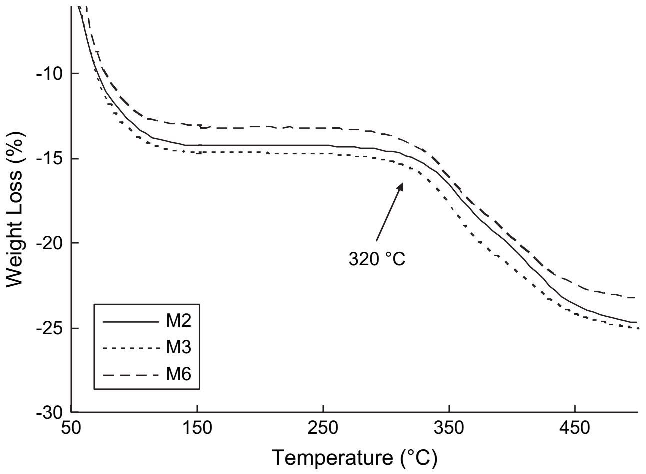


Fig. 4. TGA curves of SPI membranes in proton form.

3.5. Proton conductivity

Table 1 lists proton conductivities at 50 and 70%RH and in water at 60 °C for the SPI membranes and Nafion 112. Fig. 6 shows the RH dependence of conductivity at 60 °C. The proton conductivity depends significantly on IEC, hydration state, and membrane morphology. The homo-SPI membrane M1 of a high IEC of 2.75 meq g^{-1} showed conductivities of 172 and 15 mS cm^{-1} in water and 50%RH, respectively. The conductivities were larger in water but 2 times smaller at 50%RH compared with Nafion 112. For the co-SPI membranes with IEC of 1.95 to 1.65 meq g^{-1}, M2, M3, M4 and M6, the conductivities in water were similar to or slightly smaller than that of Nafion 112, whereas the conductivities at 50%RH were about 4 times smaller. Thus, the RH dependence of conductivity was stronger for the SPI membranes than for Nafion 112. This was because the SPI membranes did clearly not have the hydrophilic proton conducting channel structure which was proposed for Nafion membranes. Comparison of the proton conductivity of M3 with that of other SPI membranes R1–R3 with the similar IEC of 1.9–2.0 meq g^{-1} indicates the following. The BSPhB- and BSPOB-based SPI membranes, M2 and R2, showed the similar proton conducting behavior in magnitude and in RH dependence. Compared with these membranes, the BAPBDS-based SPI membrane, R3, showed the slightly smaller conductivity especially at the lower RH region, suggesting that the side-chain-type SPI membranes generally have slightly larger proton conductivity than the main-chain-type one. The BSPB-based SPI membrane, R1, showed the similarly high conductivity of 154 mS cm^{-1} in water, but fairly lower one at lower RH region than the other SPI membranes. The lower proton conductivity in the lower RH region for the BSPB-based SPI membranes have been reported to be due to the lower water vapor sorption [19].

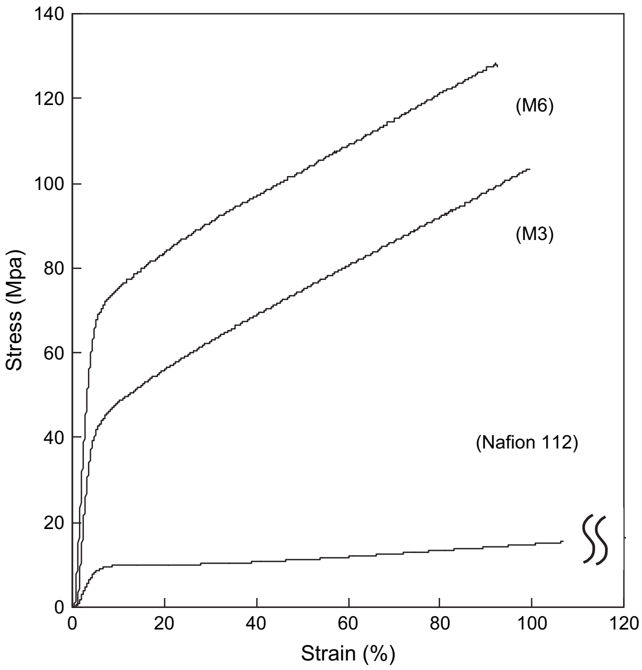


Fig. 5. Tensile stress–strain curves of SPI membranes and Nafion 112.

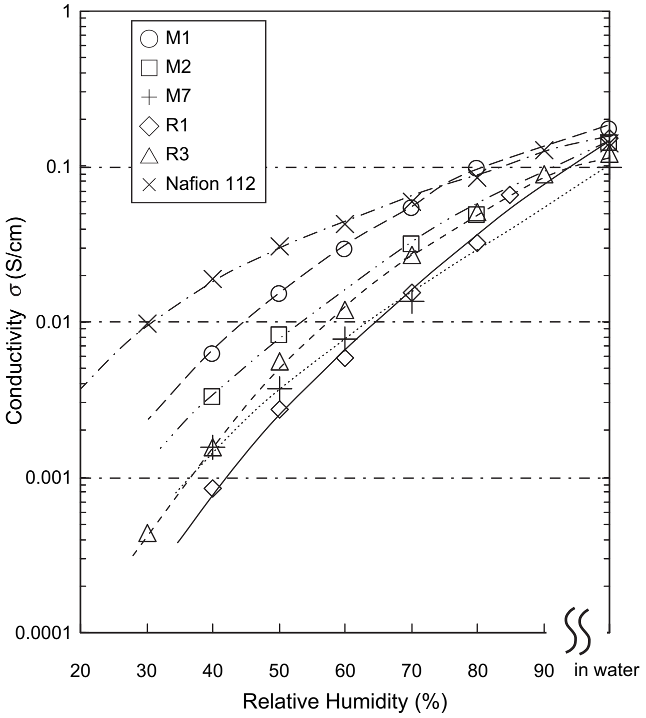


Fig. 6. RH dependence of proton conductivity of SPI membranes and Nafion 112 at 60 °C.

Fig. 7 shows the temperature dependence of proton conductivity of the SPI membranes in water from 50 to 140 °C. The activation energy was in the range of 9–11 kJ mol^{-1}. All the SPI membranes displayed high σ values about 100–460 mS cm^{-1} in water. For example, the membranes M2 and M3 displayed σ values of 300 and 250 mS cm^{-1} at 120 °C, respectively.

3.6. Water stability

Water stability of SPI membranes was investigated from the viewpoints of weight loss, mechanical properties and proton conductivity.

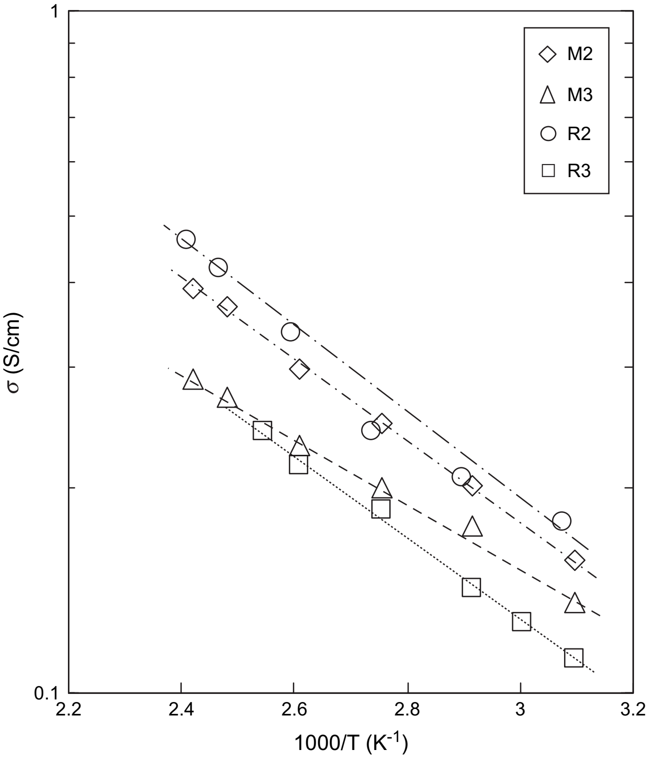


Fig. 7. Temperature dependence of proton conductivity of SPI membranes in water.

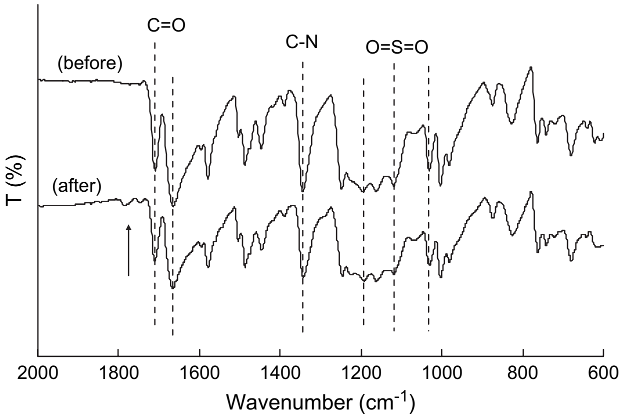


Fig. 8. IR spectra of BSPhB/BAPB (3/2) before and after aging in water at 130 °C for 48 h.

Fig. 8 shows the IR spectra of M3 before and after the aging for 48 h. After the aging, new bands around 1783 and 1747 cm^{-1} appeared, which were assigned to the carbonyl groups of acid anhydride. This indicates that the hydrolysis of imide ring took place during the aging, judging from the fact that the dicarboxylic acid of the model compound, *N*-(3-sulfophenyl)-4,5-dicarboxylic-1,8-naphthalimide, was easily converted to the acid anhydride by drying it under vacuum at 100 °C.

Table 3 lists the weight loss, proton conductivity and mechanical properties of SPI membranes before and after the aging tests. For comparison purpose, the data of other SPI membranes, R1, R2 and R4 are also listed. The BSPhB-based SPIs showed fairly larger weight loss than the BSPOB-based one, in spite of the slightly lower IECs. For example, the weight losses for M3 were 12% and 25% after aging for 48 and 192 h, respectively, whereas those for R2 were 7.6% and 12%, respectively.

Mechanical properties were evaluated by means of tensile strength and membrane toughness. The membrane toughness level was specified as follows. In level I, the membrane is

Table 3
Properties of the SPI membranes before and after aging tests

Code	Time[a] (h)	Weight loss (%)	σ^b (mS cm^{-1})			M^c (GPa)	S^d (MPa)	E^e (%)	Toughness
			50%	70%RH	In water				
M3	0		8	27	121	1.3	99	103	V
	48	12	8	20	112	1.2	38	7	V
	192	25	2	13	97	1.3	36	5	V
M4	0		6	22	118	1.2	81	85	V
	48	12	6	17	108	1.0	31	4	V
	192	23	2	6	88	1.3	26	3	V
R1	0		2.8	15.4	154	2.1	127	86	V
	96[f]	9.4	0.4	6.2	123	2.1	33	3	IV
R2	0		6	28	160	2.5	200	50	V
	48	7.6	5	29	143	2.1	82	9	V
	192	12	7	34	160	2.0	76	8	V
R4	0		2.3	13	102	1.4	81	95	V
	192	7.3	2.9	13	103	1.2	55	10	V

[a] At 130 °C in water.
[b] At 60 °C.
[c] Young's modulus.
[d] Stress at break.
[e] Elongation at break.
[f] At 130 °C in 100%RH vapor.

brittle and breaks into pieces by handling. In level II, the membrane sheet breaks when being bent by holding both ends between fingers. In level III, the membrane sheet breaks along a fold when it is folded to zero degree. In level IV, the membrane sheet breaks when it is folded back. In level V, the membrane sheet does not break after it is folded back [7]. M3 and M4 still kept reasonably high Young's modulus above 1.0 GPa and toughness of level V after aging for 192 h at 130 °C. However, after the aging, the stress and elongation at break decreased down to 26–36 MPa (the third of the original value) and 3–5%, respectively. This tensile strength property was at the similar level to that of the aged membrane of BAPBDS-based SPI (R4) and much lower than that of the aged membranes of R2 [7,27]. After the aging for 192 h, R2 kept the reasonably high tensile strength property.

For M3 and M4, the proton conductivity hardly decreased after aging for 48 h, in spite of the weight loss of 12%. However, after the aging for 192 h, the weight loss became large upto 23–25% and the conductivity decreased by 20–30% in water and by 65–75% at 50%RH. In the case of R4, the aging for 192 h at 130 °C caused weight loss of about 7–8% but no appreciable decrease in the conductivity [7,27]. For R2, the proton conductivity did not decrease even after the aging for 192 h, in spite of 12% weight loss. For these SPI membranes, the weight loss was due to elution of oligomers of NTDA and sulfonated diamine caused by hydrolysis of imide bonds [27]. As a result, the weight loss upto 12% led to no appreciable reduction in the conductivity. The large weight loss of 25% resulted in the fairly large decreases in the conductivity at low RHs, because the weight loss took place mainly in hydrophilic segments which are responsible for proton conduction. On the other hand, the BSPB-based SPI membrane (R1), showed large decreases in the conductivity especially at lower RHs with the weight loss of less than 10 wt%, because of preferential breaking out of sulfopropoxy group [27].

From the viewpoints of mechanical properties and proton conductivity, the BSPhB-based SPI membranes showed the better water stability than the BSPB-based ones because of the higher stability of sulfophenyl group than that of sulfopropoxy one. However, the water stability of BSPhB-based SPI membranes was not so high as that of BSPOB-based ones, because of the larger weight loss. The reason for the large weight loss should be investigated to improve their water stability. Further study is in progress.

4. Conclusion

A novel diamine bearing sulfophenyl pendant groups of BSPhB was synthesized successfully. A series of SPIs based on it were prepared. The resulting SPIs showed high molecular weight and gave tough and transparent membranes. The SPI membranes showed highly anisotropic membrane swelling in water with much larger swelling in thickness direction and high desulfonation temperature of 320 °C. They showed reasonably high proton conductivity of more than 100 mS cm^{-1} in water at 60 °C. They showed fairly high water stability, but not high enough because of larger weight loss after aging at 130 °C in water for 192 h.

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Reference

[1] Mauritz K, Moore R. Chem Rev 2004;104:4535–85.
[2] Savadogo O. J New Mater Electrochem Syst 1998;1:47–66.
[3] Rikukawa M, Sanui K. Prog Polym Sci 2000;25:1463–502.
[4] Kerres J. J Membr Sci 2001;185:3–27.
[5] Roziere J, Jones D. Annu Rev Mater Res 2003;33:503–55.
[6] Hickner M, Ghassemi H, Kim Y, Einsla B, McGrath J. Chem Rev 2004;104:4587–612.
[7] Yin Y, Yamada O, Tanaka K, Okamoto K. Polym J 2006;38:197–219.
[8] Faure S, Cornet N, Gebel G, Mercier R, Pineri M, Sillion B. In: Savadogo O, Roberge P, editors. Proceedings of the second international symposium on new materials for fuel cells and modern battery systems, Montreal, Canada; 1997. p. 818.
[9] Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M. Polymer 2001;42:359–73.
[10] Miyatake K, Asano N, Watanabe M. J Polym Sci Part A Polym Chem 2003;41:3901–7.
[11] Lee C, Sundar S, Kwon J, Han H. J Polym Sci Part A Polym Chem 2004;42:3612–20. and 3621–30.
[12] Miyatake K, Zhou H, Matsuo T, Uchida H, Watanabe M. Macromolecules 2004;37:4961–6.
[13] Meyer G, Perrot C, Gebel G, Gonon L, Morlat S, Gardette J. Polymer 2006;47:5003–11.
[14] Meyer G, Gebel G, Gonon L, Capron P, Marscaq D, Marestin C, et al. J Power Sources 2006;157:293–301.
[15] Guo X, Fang J, Harada S, Watari T, Tanaka K, Kita H, et al. Macromolecules 2002;35:6707–13. and 9022–8.
[16] Watari T, Fang J, Guo X, Tanaka K, Kita H, Okamoto K, et al. J Membr Sci 2004;230:111–20.
[17] Guo X, Fang J, Tanaka K, Kita H, Okamoto K. J Polym Sci Part A Polym Chem 2004;42:1432–40.
[18] Yin Y, Fang J, Cui Y, Tanaka K, Kita H, Okamoto K. Polymer 2003;44:4509–18.
[19] Yin Y, Fang J, Watari T, Tanaka K, Kita H, Okamoto K. J Mater Chem 2004;14:1062–70.
[20] Yin Y, Yamada O, Suto Y, Mishima T, Tanaka K, Kita H, et al. J Polym Sci Part A Polym Chem 2005;43:1545–53.
[21] Yasuda T, Miyatake K, Hirai M, Nanasawa M, Watanabe M. J Polym Sci Part A Polym Chem 2005;43:4439–45.
[22] Einsla B, Kim Y, Hickner M, Hong Y, Hill M, Pivovar B, et al. J Membr Sci 2005;255:141–8.
[23] Hu Z, Yin Y, Chen S, Yamada O, Tanaka K, Kita H, et al. J Polym Sci Part A Polym Chem 2006;44:2862–72.
[24] Chen S, Yin Y, Tanaka K, Kita H, Okamoto K. Polymer 2006;47:2660–9.
[25] Yin Y, Chen S, Guo X, Fang J, Tanaka K, Kita H, et al. High Perform Polym 2006;18:617–35.
[26] Fang J, Guo X, Litt M. Trans Mater Res Soc Jpn 2004;29:2541–6.

[27] Yin Y, Suto Y, Sakabe T, Chen S, Hayashi S, Mishima T, et al. Macromolecules 2006;39:1189–98.

[28] Yamada O, Yin Y, Tanaka K, Kita H, Okamoto K. Electrochim Acta 2005;50:2655–9.

[29] Yin Y, Yamada O, Hayashi S, Tanaka K, Kita H, Okamoto K. J Polym Sci Part A Polym Chem 2006;44:3751–62.

[30] Asano N, Aoki M, Suzuki S, Miyatake K, Uchida H, Watanabe M. J Am Chem Soc 2006;128:1762–9.

[31] Suto Y, Yin Y, Kita H, Okamoto K. J Photopolym Sci Technol 2006;19:273–4.

[32] Leung M, Lin H, Chou M, Wang S, Yang K. US patent; 2005; 0236976.

[33] Sek D, Pijet P, Wanic A. Polymer 1992;33:190–3.