

A facile approach for the preparation of cross-linked sulfonated polyimide membranes for fuel cell application†

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A facile approach has been successfully developed for the preparation of a series of cross-linked sulfonated polyimide (SPI) membranes *via* the condensation reaction between the sulfonic acid groups and the activated hydrogen atoms of SPIs in the presence of phosphorous pentoxide : methanesulfonic acid in the ratio of 1 : 10 by weight (PPMA, method 1) or phosphorous pentoxide only (method 2). The resulting sulfonyl linkages are very stable and the cross-linked SPI membranes showed greatly improved water stability in comparison with the uncross-linked ones while high proton conductivity was maintained.

Introduction

Polymer electrolyte membrane (PEM) is the key component of a fuel cell system. Current state-of-the-art PEMs used in practical systems are sulfonated perfluoropolymers, typically DuPont's Nafion, which have high proton conductivity, good mechanical properties, and high thermal, chemical and electrochemical stability. However, some drawbacks such as the high cost, low conductivity at high temperature, and high methanol permeability of the perfluoropolymers seriously limit their industrial application. In the past decade many efforts have been made on the development of low cost and high performance sulfonated hydrocarbon polymers as the alternative membrane materials for fuel cell application. Many sulfonated hydrocarbon polymer membranes such as sulfonated polystyrene and derivatives,^{1–3} sulfonated polysulfones,^{4–6} sulfonated poly(ether ketone)s,^{7,8} sulfonated polyphenylenes,^{9,10} and six-membered ring sulfonated polyimides (SPIs)^{11–21} have been reported to have comparable or even higher proton conductivities than Nafion when fully hydrated. However, a major problem associated with most of the sulfonated hydrocarbon polymer membranes is their poor water stability, *i.e.*, the membranes highly swell or even dissolve in water and thus lose mechanical properties especially when their ion exchange capacities (IECs) are at high levels (*e.g.* IEC > 2.0 meq g^{−1}) which are generally essential to provide high proton conductivity. To enhance the water stability while maintaining high proton conductivity, one approach is to optimize the chemical structure and/or to control the morphology of membranes. Successful examples have been reported with SPI membranes of which proton conductivities are around 0.20 S cm^{−1} (in water) and the water

stability is 1000–2500 h at 100 °C.^{14–17} On the other hand, cross-linking is a common and effective method to enhance the mechanical properties, to suppress membrane swelling degree and to improve the membrane durability. There are many reports on the preparation of cross-linked sulfonated polymer membranes in the literature. Kerres and coworkers extensively investigated the preparation of various ionically cross-linked acid–base blends and ionomer membranes [acid: sulfonated poly(ether sulfone), sulfonated poly(ether ether ketone), sulfonated poly(phenylene oxide); base: polybenzimidazole],^{22–25} covalently cross-linked membranes through the reaction between sulfinate groups of sulfonated polymers and alkyl or aryl dihalides (cross-linkers),^{26,27} and covalent–ionically cross-linked membranes.^{28–30} However, as pointed out by Kerres in the review article,³¹ the ionically cross-linked acid–base (blend) membranes showed unacceptable swelling in water at the temperatures above 70–90 °C leading to possible destruction of the membranes in fuel cell operation. The covalently cross-linked (blend) membranes are stable but have the disadvantage that much effort is involved in the synthesis of the polymers containing both sulfonate and sulfinate groups.³¹ Pintauro and coworkers reported on a photo-cross-linking method which is based on the photochemical reaction between the α -methyl groups of the sulfonated polyphosphazene and benzophenone (photoinitiator) under the exposure of UV.³² However, it is well known that α -methyl group-containing polymers such as sulfonated polystyrene are unstable toward radical oxidation. Guiver and coworkers prepared a series of cross-linked sulfonated poly(ether ether ketone) membranes by using polyatomic alcohols as the cross-linker and the cross-linking is based on the condensation reaction between sulfonic acid groups of the polymer and polyatomic alcohols.³³ This method seems, in principle, applicable to all kinds of sulfonated polymers, but the water stability of the resulting membranes was not investigated. Theoretically the resulting sulfonic acid ester linkages can still undergo hydrolysis and therefore they are expected not to be very stable. Han and coworkers prepared a series of cross-linked SPI membranes by self-cross-linking of maleimido-end-capped SPI oligomers and by reaction of the oligomers with a diacrylate compound, but

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these cross-linked membranes displayed rather poor water stability (around 200 h at 80 °C) probably because of the very poor hydrolytic stability of maleimido rings.³⁴ Okamoto and coworkers reported on a series of interesting branched/cross-linked SPI membranes which were prepared through the reaction of anhydride-end-capped SPI oligomers and a triamine monomer. These SPI membranes showed good water stability as well as high proton conductivity,¹⁷ but the application of this method to other kinds of sulfonated polymers such as sulfonated polysulfones and sulfonated poly(ether ether ketone)s is not easy. Very recently Lee *et al.* reported on the preparation of a series of cross-linked SPI membranes based on the chemical reaction between the carboxyl groups from a non-sulfonated diamine moiety and the hydroxyl groups of *N,N*-bis(2-hydroxyethyl)-2-aminothanesulfonic acid (cross-linker).³⁵ It seems that their cross-linked SPI membranes are still organo-soluble judging from the fact that they got ¹H NMR spectra of the cross-linked samples. They reported that their cross-linked SPI membranes had water stability of around 12–42 days at 80 °C but no information is available for the stability test under severer conditions such as in boiling water. In fact, the ester cross-links they have can still undergo hydrolysis. The development of a facile approach to produce stable cross-linking is strongly desired. In this paper, we report on a novel and facile approach for preparation of cross-linked and highly stable SPI membranes and their water stability and proton conductivities are also described.

Experimental section

Materials

1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), 1,8-naphthalenedicarboxylic anhydride (NDA) and 2,2'-benzidinedisulfonic acid (BDSA) were purchased from TCI. NTDA was vacuum sublimed before use. BDSA was purified by decolorization with activated carbon in methanol in the presence of a slight excess of triethylamine (Et₃N) under nitrogen flow followed by acidification, thoroughly washing the precipitate with methanol and de-ionized water successively and finally drying at 120 °C in vacuo for 20 h. 9,9-bis(4-aminophenyl)fluorene (BAPF) was synthesized according to a literature method.³⁶ The syntheses of sulfonated diamines, 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS) and 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS) have been previously reported.^{12,15} The synthesis of 3,3'-bis(4-sulfophenoxy)benzidine (BSPOB) is described as follows. Other compounds were purchased from SCRC and used as received except that 1-methyl-2-pyrrolidinone (NMP) and triethylamine (Et₃N) were distilled under reduced (for NMP) or normal (for Et₃N) pressure and dried with 4 Å molecular sieve prior to use.

Synthesis of 4-fluorobenzenesulfonic acid sodium salt (FBSNa)

14.42 g (150 mmol) of fluorobenzene was added to a 300 mL 3-neck flask which was pre-cooled in an ice-bath. 22.8 mL of fuming sulfuric acid (SO₃, ~165 mmol) was added with magnetic stirring. The ice-bath was removed after the fuming

sulfuric acid was completely added, and the reaction mixture was stirred at room temperature for half an hour followed by heating at 80 °C for 6 h. After cooling to room temperature, the solution mixture was poured into 100 g of crushed ice. Sodium chloride was added and the mixture was stirred overnight. The mixture was filtered, and the solid was washed with saturated sodium chloride solution and then dried in vacuo at 80 °C for 20 h. The obtained solid was added to 200 mL of DMSO with stirring. The mixture was filtered, and the filtrate was distilled under reduced pressure. The obtained solid was washed with acetone, and dried in vacuo at 100 °C for 20 h. 28.77 g of white product was obtained. Yield: 96.9%. IR (KBr, cm⁻¹): 3448, 2358, 1598, 1502, 1216, 1134, 1048, 830, 696, 568. ¹H NMR spectrum (in DMSO-d₆, δ (ppm)): 7.48–7.52 (2H), 7.08–7.14 (2H).

Synthesis of 3,3'-bis(4-sulfophenoxy)benzidine (BSPOB)

To a dry 200 mL 3-neck flask were added under nitrogen flow 3.244 g (15 mmol) of 3,3'-dihydroxybenzidine, 15 mL of NMP, 6.237 g (31.5 mmol) of 4-fluorobenzenesulfonic acid sodium salt, 10 mL of toluene and 6.0 g of anhydrous potassium carbonate. The mixture was magnetically stirred at room temperature for 0.5 h, and then heated at 140 °C for 4 h and 170 °C for 24 h. The produced water was evaporated together with toluene as an azeotrope and collected in a Dean–Stark trap. After cooling to room temperature, the reaction mixture was added to methanol with stirring. It was filtered and the solid was dissolved in water followed by acidification with concentrated hydrochloric acid. The resulting precipitate was filtered, washed with water and ethanol successively, and dried in vacuo. The crude product was de-colored with activated carbon in methanol in the presence of an excess amount of Et₃N and re-acidified with concentrated hydrochloric acid. The precipitate was washed with methanol and water and dried in vacuo at 120 °C for 15 h. 5.2 g of off-white solid was obtained. Yield: 65%. IR (KBr, cm⁻¹): 3478, 2920, 2632, 1638, 1596, 1530, 1496, 1388, 1252, 1214, 1166, 1128, 1030, 1006, 838, 734, 690, 604, 572, 490. ¹H NMR spectrum (in DMSO-d₆ in the presence of a drop of Et₃N), δ (ppm): 7.51–7.54 (m, 4H), 7.11 (d, 2H, J = 8.0 Hz), 6.99 (s, 2H), 6.78–6.83 (m, 6 H), 4.89 (4 H, NH₂).

Synthesis of 9,9-bis[4-(1,5-naphthylimido)phenyl]fluorene (BNIPF)

To a dry 100 mL 3-neck flask were added under nitrogen flow with stirring 1.1890 g (6.0 mmol) of 1,8-naphthalenedicarboxylic anhydride (NDA), 1.044 g (3.0 mmol) of BAPF, 20 mL of *m*-cresol, 0.732 g (6.0 mmol) of benzoic acid and 0.775 g (6.0 mmol) of isoquinoline. The reaction mixture was slowly heated to 150 °C and kept at this temperature for 10 h. Subsequently the reaction temperature was raised to 180 °C and maintained for 10 h. After cooling to room temperature, the reaction mixture was poured into 250 mL of isopropanol. The resulting precipitate was filtered off, washed with isopropanol a couple of times, and dried in vacuo. 1.85 g yellow–brownish solid was obtained. Yield: 87%. The FT-IR and ¹H NMR spectra are shown in Fig. S1 and S2†, respectively.

Synthesis of 2,7-bis(4-methylphenylsulfonyl)-9,9-bis[4-(1,5-naphthylimido)phenyl]fluorene (BMPS–BNIPF)

To a dry 100 mL 3-neck flask were added under nitrogen flow with stirring 0.708 g of BNIPF (1.0 mmol), 0.418 g (2.2 mmol) of *p*-toluenesulfonic acid monohydrate and 15 mL of PPMA. The reaction mixture was heated at 80 °C for 4 h. After cooling to room temperature, the mixture was poured into ice water. The resulting precipitate was filtered off, thoroughly washed with deionized water and dried in vacuo at 100 °C. 0.96 g white product was obtained. Yield: 95%. The FT-IR and ¹H NMR spectra are shown in Figs. S3 and S4†, respectively.

Polymerization

The experimental procedures for sulfonated polyimides are described as follow using NTDA–BSPOB/BAPF (9/1) copolyimide as an example.

To a dry 100 mL 3-neck flask were added under nitrogen flow with stirring 1.901 g (3.6 mmol) of BSPOB, 0.1392 g (0.4 mmol) of BAPF, 25 mL of *m*-cresol and 1.22 mL of Et₃N. After the diamines were completely dissolved, 1.072 g (4.0 mmol) of NTDA and 0.693 g of benzoic acid were added. The reaction mixture was stirred at room temperature for half an hour, and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to around 120 °C, the highly viscous mixture was diluted with an additional 20 mL of *m*-cresol and then slowly poured into 250 mL of acetone. The fiber-like precipitate was filtered off, washed with acetone a couple of times, and dried in vacuo.

Film formation and proton exchange

Films were prepared by casting the sulfonated polyimide (in their triethylammonium salt form) solutions in DMSO (BSPOB, ODADS and BDSA-based SPIs) or *m*-cresol (BAPBDS-based SPI) onto glass plates and dried at 80 °C (DMSO solutions) or 120 °C (*m*-cresol solution) for 10 h. The as-cast films were soaked in methanol at 60 °C for 6 h. Proton exchange was performed by immersing the films in 1.0 M hydrochloric acid at room temperature for two days. The proton exchanged films were washed with deionized water and then dried in vacuo at 100 °C for 20 h.

Cross-linking treatment

Two methods were used for the preparation of cross-linked membranes and the experimental details are described as follows:

Method 1: dry SPI membranes in their proton form were immersed into phosphorus pentoxide : methanesulfonic acid (1 : 10 by weight, PPMA) in a glass vessel at 80 °C for 3–48 h under nitrogen atmosphere. The membranes were taken out, thoroughly rinsed with deionized water till the water was neutral and dried in vacuo 100 °C for 20 h.

Method 2: dry SPIs in their proton form were dissolved in DMSO containing 5 wt% phosphorus pentoxide at room temperature. The weight ratio between SPI and phosphorus pentoxide was controlled at 1 : 1. The solution mixture was cast onto glass plates and dried at 80 °C for 10 h in an air oven. The glass plates were moved to a vacuum oven and dried at

80 °C for 1 h, 120 °C for 2 h, and 170 °C for 10 h, successively. The membranes were thoroughly rinsed with deionized water till the water was neutral and then dried in vacuo at 100 °C for 20 h.

Measurements

Infrared (IR) spectra were recorded on a Perkin-Elmer Paragon 1000PC spectrometer. ¹H NMR spectra were recorded on a Varian Mercury Plus 400 MHz instrument.

Proton conductivity in the membrane planar direction was measured by an ac impedance method with two platinum electrodes using a Hioki 3552 Hitester instrument over the frequency range from 100 Hz to 100 KHz as has been reported in previous papers.^{12,13} Proton conductivity σ was calculated from the following equation:

$$\sigma = D/(LBR) \quad (1)$$

where D is the distance between the two electrodes, L and B are the thickness and width of membrane (measured from the samples stored at ambient atmosphere when the conductivity measurements were performed at relative humidities below 90% or from the hydrated samples when the conductivity measurements were performed at relative humidities above 90% or in liquid water), respectively, and R is the resistance measured.

Water sorption experiments were carried out by immersing three sheets of film (20–30 mg per sheet) of a polyimide into water at 100 °C for 5 h. Then the films were taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake of the films, S , was calculated from

$$S = (W_s - W_d)/W_d \times 100 (\%) \quad (2)$$

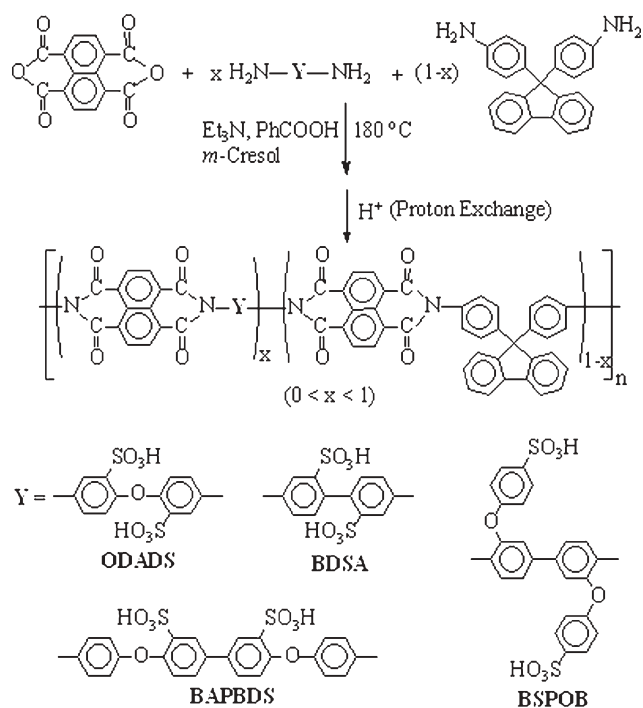
where W_d and W_s are the weight of the dry and corresponding water-swollen film sheets, respectively. Water uptake of a polyimide was estimated from the average value of S of each sheet.

Tensile measurements were performed with an Instron 4456 instrument at room temperature in an ambient atmosphere (~80% relative humidity) at a crosshead speed of 1 mm min⁻¹. Sulfonated polyimide membranes were soaked in distilled water at 100 °C for one month and subjected to tensile measurement as soon as they were taken out. The thickness of the hydrated membranes was used for tensile strength calculation.

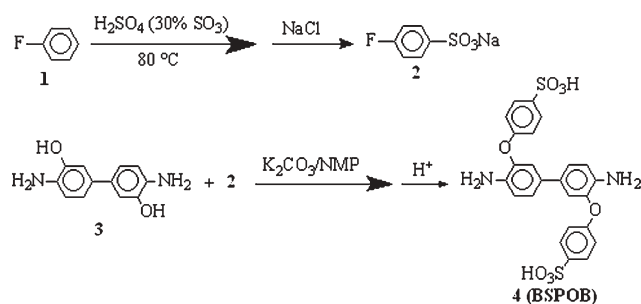
Results and discussion

Polymer synthesis and cross-linking

A series of SPIs were synthesized by one-step condensation polymerization of NTDA, sulfonated diamines and BAPF in *m*-cresol in the presence of triethylamine (Et₃N) and benzoic acid at 180 °C for 20 h (Scheme 1). This is a literature method which was first reported by Mercier.³⁷ Four kinds of sulfonated diamines, BSPOB, BAPBDS, ODADS and BDSA, were employed for polymerization. The side chain-type sulfonated diamine, BSPOB, was synthesized *via* the reaction



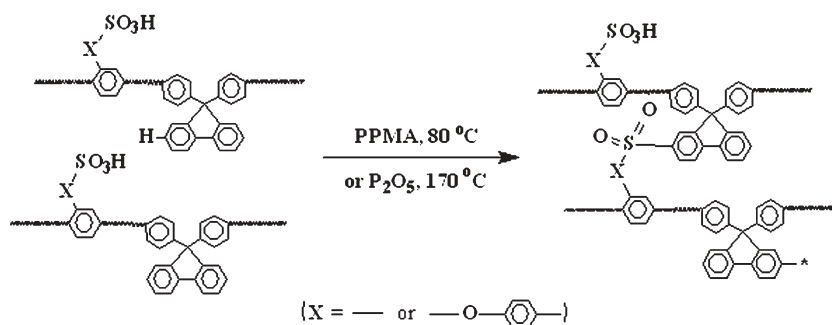
Scheme 1



Scheme 2

between 3,3'-dihydroxybenzidine and 4-fluorobenzenesulfonic acid sodium salt in the presence of anhydrous potassium carbonate in NMP at 180 °C for 24 h (Scheme 2). To achieve high IECs ($>2.0 \text{ meq g}^{-1}$) and thus high proton conductivities of SPIs, the molar fraction of the non-sulfonated diamine, BAPF, in the diamine monomers was controlled to be no higher than 25%.

The preparation of cross-linked SPI membranes was performed in two ways. Method 1 is that the dry SPI membranes (in their proton form) were immersed into PPMA at 80 °C for a given time. Method 2 is that the SPI (in proton form) solutions in DMSO containing 5 wt% phosphorus pentoxide were cast into films which were subsequently thermally treated at high temperature (170 °C) in vacuo for 10 h. For both methods, the cross-linking reaction of SPIs is based on the chemical reaction between the sulfonic acid groups of a sulfonated diamine moiety and the activated hydrogen atoms of a non-sulfonated diamine moiety (BAPF) in the presence of a condensation agent (PPMA or phosphorus pentoxide), and the resulting cross-linking bonds are the very stable sulfonyl groups (Scheme 3). Ueda *et al.* have found that many diaryl sulfones could be readily synthesized by condensation reactions of arenesulfonic acids and activated (electron-rich) aromatic hydrocarbons in PPMA, and sodium 4-phenoxybenzenesulfonate could even undergo self-condensation polymerization in PPMA to form high molecular weight poly(ether sulfone).^{38,39} Based on the discovery by Ueda *et al.* we expect that sulfonated polymer membranes might also be readily cross-linked by just treating them with PPMA or phosphorus pentoxide without introducing additional cross-linkers. To meet the requirement of reactivity of phenyl rings for the cross-linking reaction with sulfonic acid groups, BAPF was used as the diamine co-monomer because the 2,7-positions of this compound are highly reactive. Table 1 lists the cross-linking treatment conditions and results for a series of SPI membranes. Although all the SPI membranes are insoluble in PPMA, cross-linking reactions could still occur by immersing them in PPMA at 80 °C for a given time. The formation of cross-links is judged from the insolubility of the membranes in organic solvents (DMSO and *m*-cresol) in which the membranes were soluble before treating with PPMA. The thickness of the membranes for cross-linking treatment was in the range of 20–60 μm , and it was observed that the sorption of PPMA in SPI membranes was very fast and the cross-linking rate was almost identical for the same kind of membranes with different thickness. The cross-linking rate is mainly determined by the structure of the sulfonated diamine moiety. As shown in Table 1, with method 1 the cross-linking rate is in the order: NTDA–BSPOB/BAPF (9/1) \gg NTDA–BAPBDS/BAPF (3/1) $>$ NTDA–BDSA/BAPF (3/1), NTDA–ODADS/BAPF (3/1) and NTDA–ODADS/BAPF (5/1). BSPOB is a side chain-type diamine with pendent sulfonic acid groups and there are no



Scheme 3

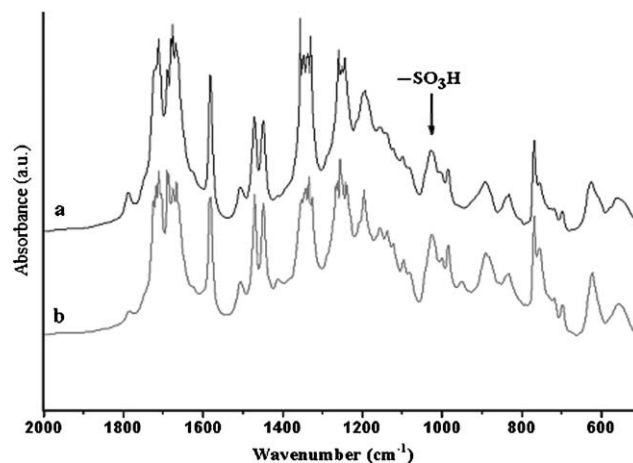
Table 1 Solubility changes of SPI membranes before and after immersing in PPMA at 80 °C

Membrane	Method	Cross-linking treatment	Solubility ^a	
			<i>m</i> -Cresol	DMSO
NTDA–BSPOB/BAPF (9/1)	1	No	+	+
	2	3 h	–	–
NTDA–BAPBDS/BAPF (9/1)	1	No	+	–
	2	10 h	–	–
NTDA–ODADS/BAPF (5/1)	1	No	+	+
	2	24 h	–	–
NTDA–ODADS/BAPF (3/1)	1	No	+	+
	2	24 h	–	–
NTDA–BDSA/BAPF (3/1)	1	No	+	+
	2	10 h	–	–
NTDA–BDSA/BAPF (3/1)	1	No	+	+
	2	24 h	–	–
NTDA–BDSA/BAPF (3/1)	1	No	+	+
	2	10 h	–	–

^a +, soluble; +–, partially soluble; –, insoluble on heating.

substituents in the *ortho* positions of the sulfonic acid groups leading to less steric effects in the cross-linking reaction than the rest of the main chain-type ones. This is the main reason that NTDA–BSPOB/BAPF (9/1) had a much faster cross-linking rate than the other ones. Another structural factor affecting cross-linking rate is the reactivity of the sulfonic acid groups. Ueda *et al.* have investigated that with the same aromatic hydrocarbons electron-rich phenyl rings to which sulfonic acid groups are attached are favorable for the formation of diaryl sulfones.³⁸ This is also true for the present cross-linking reactions of SPI membranes. NTDA–BAPBDS/BAPF (3/1), for example, underwent a cross-linking reaction significantly faster than NTDA–ODADS/BAPF (3/1). This should be attributed to the relatively higher reactivity of the sulfonic acid groups of the BAPBDS moiety because the steric effect is similar. Polymer chain flexibility has little effect on cross-linking rate judging from the fact that NTDA–ODADS/BAPF (3/1) and NTDA–BDSA/BAPF (3/1) displayed the same cross-linking rate although ODADS is flexible whereas BDSA is highly rigid. In addition, the cross-linking rate hardly depends on the molar fraction of BAPF because the same cross-linking rate was observed for NTDA–ODADS/BAPF (3/1) and NTDA–ODADS/BAPF (5/1). In the case of method 2, all the SPIs except NTDA–BAPBDS/BAPF (3/1) could be readily cross-linked under the same conditions. The inapplicability of method 2 to NTDA–BAPBDS/BAPF (3/1) is because of its insolubility in DMSO.

To confirm if the cross-linking reaction indeed occurred between sulfonic acid groups and the fluorenylidene groups, a model compound, 9,9-bis[4-(1,5-naphthylimido)phenyl]fluorene (BNIPF), was synthesized *via* the reaction of 1,5-naphthalenedicarboxylic anhydride (NDA) and 9,9-bis(4-aminophenyl)fluorene (BAPF) at 190 °C in *m*-cresol in the presence of benzoic acid and isoquinoline (see ESI†). Then BNIPF and *p*-toluenesulfonic acid were dissolved in PPMA and the mixture were heated at 80 °C for 4 h. The resulting crude product (yield: 94%) was directly used for ¹H NMR and

**Fig. 1** FT-IR spectra of NTDA–BDSA/BAPF (3/1) membranes: (a) cross-linked, (b) uncross-linked.

FT-IR measurement. As shown in Figs. S3 and S4†, both spectra suggest formation of the desired product, 2,7-bis(4-methylphenylsulfonyl)-9,9-bis[4-(1,5-naphthylimido)phenyl]fluorene (BMPS–BNIPF).

Fig. 1 shows the FT-IR spectra of NTDA–BDSA/BAPF (3/1) before and after cross-linking treatment. No significant change was observed between these two spectra except that the relative intensity of the absorption band at 1030 cm^{–1} which is assigned to the stretch vibration of the sulfonic acid group decreased after cross-linking. This is because some of the sulfonic acid groups were consumed (formation of sulfonyl groups) during the cross-linking process. Similar phenomena were observed with other SPI membranes. The consumption of sulfonic acid groups due to the cross-linking reaction was also reflected in the reduction of IEC which was determined by a titration method. As shown in Table 2, for both NTDA–BAPBDS/BAPF (3/1) and NTDA–BDSA/BAPF (3/1) membranes, cross-linking led to a reduction in IEC by a factor of about 20% which is close to the theoretical maximum value (content of BAPF moiety, 25% by mole).

Mechanical properties

The mechanical properties of the cross-linked and uncross-linked SPI membranes in both the dry state and the wet state were investigated and the results are listed in Table 2. It can be seen that for NTDA–BSPOB/BAPF(9/1) the cross-linked membrane displayed both higher maximum stress (MS) and larger elongation at break (EB) than the uncross-linked membrane indicating improved mechanical properties due to cross-linking. Unlike NTDA–BSPOB/BAPF (9/1), in dry state other SPI membranes displayed significantly lower MS than the corresponding uncross-linked ones. However, in wet state for all the SPI membranes cross-linking led to significant improvement in mechanical properties, *i.e.*, cross-linking is more favorable for maintaining mechanical properties of the wet membranes. Moreover, all the cross-linked membranes showed reasonably good toughness judging from the fact that their EB values are larger than 5%. More studies are needed to elucidate the effect of cross-linking density and polymer structure on membrane mechanical properties.

Table 2 IEC, water uptake (WU) at 100 °C, maximum stress (MS), elongation at break (EB), proton conductivity (σ) at 100% relative humidity and 60 °C and water stability of cross-linked and uncross-linked SPI membranes

Membrane	Cross-linking treatment	IEC/meq g ⁻¹	WU/wt%	MS/MPa	EB ^c (%)	σ /S cm ⁻¹	Water stability/h
NTDA-BSPOB/BAPF(9/1)	No	2.02	130	114 (44)	5.5 (10)	0.21	150
	Yes (method 1)	1.96	60	128 (62)	13 (13)	0.16	>720
NTDA-BAPBDS/BAPF(3/1)	No	2.16	110	59 (19)	14 (5.0)	0.16	150
	Yes (method 1)	1.80	90	44 (24)	21 (9.5)	0.12	>720
NTDA-ODADS/BAPF(5/1)	No	2.82 ^a	120 ^b	70 (8.0)	15 (1.8)	0.22	0.5
	Yes (method 1)	2.08	85	33 (11)	22 (5.2)	0.13	>720
NTDA-BDSA/BAPF(3/1)	No	2.55	200 ^b	97 (18)	11 (8.7)	NM ^d	10 min
	Yes (method 2)	2.11	120	77 (27)	8.3 (14)	0.15	400

^a Theoretical value. ^b Measured at room temperature. ^c The data in parentheses refer to wet membranes. ^d NM: not measured.

Proton conductivity and water stability

The water uptake, proton conductivity and water stability of the cross-linked and uncross-linked SPI membranes are shown in Table 2. It can be seen that cross-linking caused significant suppression of membrane swelling and lower water uptake was obtained with the cross-linked membranes. The proton conductivities of the cross-linked membranes also slightly decreased but were still at a high level [>0.1 S cm⁻¹ at 100% relative humidity (RH) and 60 °C]. Fig. 2 shows the variation in proton conductivity of the cross-linked and uncross-linked SPI membranes as a function of relative humidity (RH). For both cross-linked and uncross-linked membranes, the proton conductivity decreased drastically as RH decreased which is a common phenomenon observed with many other sulfonated polymer membranes. Moreover, in the whole range of RH the cross-linked membranes generally displayed lower proton conductivities than the corresponding uncross-linked ones. It's a big challenge to enhance the proton conductivity at low humidities from the viewpoint of practical use. The variation of proton conductivity of various cross-linked SPI membranes as a function of temperature is shown in Fig. 3. For all the membranes the conductivity increased with an increase in temperature which is superior to Nafion in which proton

conductivity dropped drastically as temperature increased above 120 °C.

The water stability test for cross-linked and uncross-linked SPI membranes was performed by immersing them in deionized water at 100 °C and characterized by the time elapsed when the hydrated membranes began to lose mechanical strength. The criterion for the judgment of the loss of mechanical properties is that the membranes were broken when lightly bent. As shown in Table 2, among the uncross-linked membranes, BSPOB and BAPBDS-based SPIs displayed much better water stability than ODADS and BDSA-based ones. This is because BSPOB and BAPBDS have higher basicity than ODADS and BDSA as we have previously reported.^{13–16} Cross-linking caused great improvement in water stability for all the SPI membranes. NTDA-BSPOB/BAPF (9/1) membrane in its uncross-linked state, for example, started to lose mechanical strength after being soaked in deionized water at 100 °C for 150 h. However, the cross-linked membrane could maintain mechanical strength at the same soaking temperature for more than one month indicating much improved water stability. In fact, after this soaking treatment the cross-linked membrane was still tough and had a tensile strength of about 10 MPa in fully hydrated state which

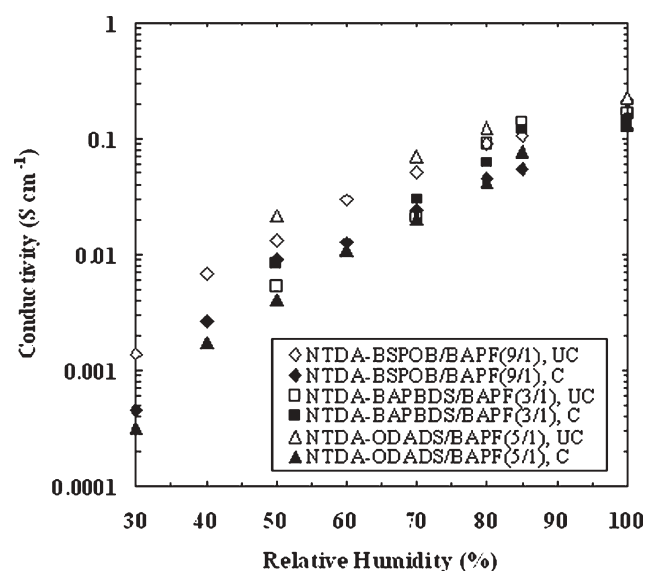


Fig. 2 Variation of proton conductivity of cross-linked (C, by method 1) and uncross-linked (UC) SPI membranes as a function of relative humidity at 60 °C.

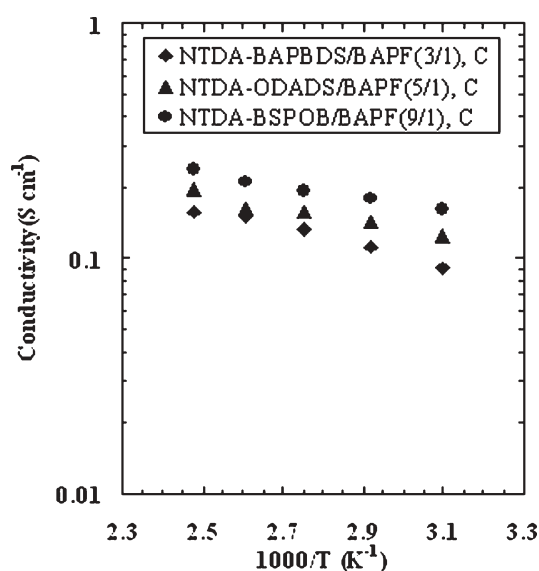


Fig. 3 Variation of proton conductivity of cross-linked (C, by method 1) SPI membranes as a function of temperature at 100 °C relative humidity.

should be high enough for fuel cell use. BDSA is a commercially available sulfonated diamine which has been widely used for preparation of various SPIs. However, the poor water stability of BDSA-based SPI membranes is a very serious problem which made them hard to use. In this study, NTDA-BDSA/BAPF (3/1), although insoluble in hot water, became highly brittle after being soaked in deionized water at 100 °C for only ten minutes indicating very poor water stability. After cross-linking, however, it could maintain reasonable high mechanical strength (~10 MPa) after being soaked in deionized water at 100 °C for 400 h, *i.e.*, the stability is about three orders longer than that of the uncross-linked membrane.

It should be noted that the cross-linking method developed in this study is also applicable to many other sulfonated polymers such as sulfonated polystyrenes, sulfonated poly(ether sulfone)s, sulfonated poly(ether ketone)s, sulfonated polyphenylenes and sulfonated polybenzimidazoles. Sulfonated polystyrene of a degree of sulfonation of 42%, for example, was water soluble at room temperature. However, it could be readily cross-linked by immersing the membrane into PPMA at 80 °C for half an hour. The resulting membrane was insoluble and its dimensions were stable even in boiling deionized water. The detailed studies will be reported elsewhere.

Conclusions

(1) A new and facile approach has been successfully developed for preparation of cross-linked SPI membranes *via* a condensation reaction between the sulfonic acid groups and the activated hydrogen atoms of SPIs in the presence of a condensation agent (PPMA or phosphorus pentoxide).

(2) The resulting cross-linked SPI membranes showed greatly improved water stability in comparison with the uncross-linked ones while high proton conductivity was maintained.

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