

# Sulfonated polyimides: Synthesis, proton conductivity and water stability

Jianhua Fang<sup>a,\*</sup>, Xiaoxia Guo<sup>a</sup>, Hongjie Xu<sup>a</sup>, Ken-ichi Okamoto<sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

<sup>b</sup> Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

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## Abstract

Six-membered ring sulfonated polyimides (SPIs) are promising membrane materials for low temperature (<100 °C) fuel cell application. This paper describes our recent work on the synthesis of various sulfonated diamine monomers and the related sulfonated polyimides. The relationship between the chemical structure and the proton conductivity and water stability of various sulfonated polyimide membranes is discussed in detail.

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## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted much attention in the past decade because they provide clean, quiet and portable power for vehicular transportation, electronic devices, and for other applications. The polymer electrolyte membrane is the key component of a PEMFC. At present, sulfonated perfluoropolymers such as DuPont's Nafion are typical membranes that are practically used due to their high proton conductivity, good mechanical properties, and high thermal, electrochemical and chemical stability. However, the high cost, low conductivity at low humidity and/or high temperature, and high methanol crossover are the major drawbacks of these perfluoropolymers. The development of low cost and high performance polymers as alternative materials is strongly desired. Up to now, a large number of sulfonated hydrocarbon polymers have been developed and among them six-membered ring sulfonated polyimides (SPIs) have been identified as one of the most promising membrane materials for PEMFC application [1–25]. This article describes the synthesis of various sulfonated diamine monomers and the related polyimides. The relationship between polymer struc-

ture and the water stability and proton conductivity is also discussed.

## 2. Experimental

### 2.1. Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) was purchased from Tokyo Kasei Co. and vacuum sublimed before use. 4,4'-Bis(3-aminophenoxy)biphenyl (*m*BAPB) was synthesized according to a literature method [1]. The syntheses of sulfonated diamines, 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS), 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS), 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS), 2,2'-bis(4-aminophenoxy)biphenyl-5,5'-disulfonic acid (*o*BAPBDS), 3-(2',4'-diaminophenoxy)propane sulfonic acid (DAPPS), 2,2'-bis(3-sulfopropoxy)benzidine (2,2'-BSPB) and 3,3'-bis(3-sulfopropoxy)benzidine (3,3'-BSPB) have been previously reported [6–12]. The synthesis of 3,3'-bis(4-sulfophenoxy)benzidine (BSPOB) will be reported elsewhere. Palladium/active carbon (10 wt.%) was purchased from Wako Co. Benzoic acid, *m*-cresol, triethylamine (Et<sub>3</sub>N), dimethylsulfoxide (DMSO), toluene, anhydrous potassium carbonate, concentrated sulfuric acid (96%), fuming sulfuric acid (SO<sub>3</sub>, 50%), concentrated hydrochloric acid (35–37%), hydrazine monohydrate were purchased from

\* Corresponding author. Tel.: +86 21 54747504; fax: +86 21 54741297.  
E-mail address: [jhfang@sjtu.edu.cn](mailto:jhfang@sjtu.edu.cn) (J. Fang).

Shanghai Chemicals Co. DMSO was distilled under reduced pressure and dried with molecular sieve 4A prior to use. Et<sub>3</sub>N was also dried with molecular sieve 4A. Other compounds were used as received.

### 2.2. Synthesis of 4,4'-bis(3-aminophenoxy)biphenyl-3,3'-disulfonic acid (*mBAPBDS*)

To a 100 mL three-neck flask equipped with a mechanical stirring device was charged 1.84 g (5 mmol) of *mBAPB*. The flask was cooled in an ice-bath, and then 3.0 mL of concentrated sulfuric acid was slowly added with stirring. After sulfuric acid was completely added, the mixture was continued to stir at 0 °C for 0.5 h and then slightly heated till *mBAPB* was completely dissolved. The mixture was again cooled in an ice-bath and 0.84 mL of fuming sulfuric acid (50% SO<sub>3</sub>) was slowly added. After fuming sulfuric acid was completely added, the mixture was continued to stir at 0 °C for 0.5 h and then slowly heated to 50 °C and kept at this temperature for 2 h. After cooling to room temperature, the mixture was poured into 20 g of crushed ice. The solid was filtered off and then re-dissolved in a sodium hydroxide solution. The basic solution was filtered and the filtrate was acidified with concentrated hydrochloric acid. The precipitate was filtered off, washed with deionized water and methanol successively, and dried at 90 °C in vacuo. About 1.40 g of product was obtained. Yield: 53%. m.p. (DSC): 200.3 °C. IR spectrum (KBr, cm<sup>-1</sup>): 3465, 2924, 2629, 1596, 1471, 1377, 1259, 1227, 1182, 1146, 1093, 1022, 952, 828, 792, 713, 681, 625, 560. <sup>1</sup>H NMR spectrum (in DMSO-*d*<sub>6</sub> in the presence of a drop of Et<sub>3</sub>N for dissolution of *mBAPBDS*) 8.11 (*J*=2.6 Hz, 2H); 7.60 (*J*=8.6 Hz, 2H); 7.07 (*J*=7.9 Hz, 2H); 6.93 (*J*=8.6 Hz, 2H); 6.41 (*J*=7.9 Hz); 6.28 (m, 6H); 5.29 (s, 4H of amino groups).

### 2.3. Synthesis of 2-fluoro-5-nitrobenzenesulfonic acid sodium salt

To a 100 mL three-neck flask equipped with a mechanical stirring device were charged 7.06 g (50.0 mmol) of *p*-fluoronitrobenzene and 3.5 mL of concentrated sulfuric acid. The flask was cooled in an ice-bath, and then 6.0 mL of fuming sulfuric acid (50% SO<sub>3</sub>) was slowly added with stirring. The reaction mixture was slowly heated to 120 °C and kept at this temperature for 6 h. After cooling to room temperature, the reaction mixture was poured into 35 g of crushed ice. Sodium chloride was added to "salt out" the product. The precipitate was filtered off, washed with saturated sodium chloride solution, and dried in vacuo. The crude solid was dissolved in DMSO and the insoluble part was removed by filtration. The filtrate was distilled under reduced pressure, and the residual was thoroughly washed with acetone and dried at 90 °C in vacuo. About 9.88 g of product was obtained. Yield: 82%. m.p. (DSC): 132.5 °C, 252.9 °C. IR spectrum (KBr, cm<sup>-1</sup>): 3105, 2925, 2854, 1710, 1617, 1585, 1542, 1469, 1349, 1315, 1261, 1207, 1148, 1122, 1079, 1038, 927, 913, 897, 845, 746, 729, 644, 629, 574, 518. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>): 8.46 (1H); 8.29 (1H); 7.48 (dd, *J*=8.9 Hz, 1H).

### 2.4. Synthesis of 4,4'-bis(4-nitro-2-sulfophenoxy)biphenyl disodium salt

To a 100 mL four-neck flask equipped with a condenser and a Dean-Stark trap were charged 1.86 g (10.0 mmol) of 4,4'-dihydroxybiphenyl and 15.0 mL of DMSO with magnetic stirring under nitrogen flow. About 0.80 g (20.0 mmol) of NaOH solution in 3.2 g of water was slowly added, and the mixture was stirred at room temperature for 0.5 h. Fifteen millilitres of toluene was added and the mixture was refluxed for 3 h. After cooling to room temperature, 4.86 g (20.0 mmol) of 2-fluoro-5-nitrobenzenesulfonic acid sodium salt and additional 5.0 mL of DMSO were added. The reaction mixture was heated at 170 °C for 36 h. After cooling to room temperature, the mixture was filtered, and the filtrate was distilled under reduced pressure. The resulting solid was thoroughly washed with acetone, and dried in vacuo. Four grams of yellow solid was obtained. Yield: 63%. m.p. (DSC): 212.7 °C. IR spectrum (KBr, cm<sup>-1</sup>): 3465, 3107, 1642, 1604, 1583, 1520, 1491, 1467, 1348, 1259, 1195, 1144, 1076, 1031, 901, 831, 789, 745, 617, 517. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>): 8.62 (*J*=3.0 Hz, 2H); 8.20 (*J*=8.9 Hz, 2H); 7.78 (*J*=8.6 Hz, 4H); 7.18 (*J*=8.6 Hz, 4H); 7.00 (*J*=8.9 Hz, 2H).

### 2.5. Synthesis of 4,4'-bis(4-amino-2-sulfophenoxy)biphenyl (*iBAPBDS*)

To a 100 mL four-neck flask equipped with a condenser were added 3.16 g (10.0 mmol) of 4,4'-bis(4-nitro-2-sulfophenoxy)biphenyl disodium salt, 20 mL of ethanol, 5.0 mL of water and 0.30 g of palladium/active carbon (10 wt.%) with magnetic stirring under nitrogen flow. The mixture was heated to 100 °C, and then 8.0 mL of hydrazine monohydrate solution in 10 mL of ethanol was added dropwise over 6 h. After hydrazine monohydrate solution was completely added, the reaction mixture was heated and stirred at 110 °C for 36 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was directly poured into 100 mL of 2.0N hydrochloric acid. The resulting precipitate was filtered off, washed with water, and dried in vacuo. About 1.90 g of light grey solid was obtained. Yield: 72%. m.p. (DSC): 136.5 °C. IR spectrum (KBr, cm<sup>-1</sup>, in triethylamine salt form): 3437, 3337, 3230, 3002, 2705, 1609, 1479, 1398, 1304, 1222, 1195, 1085, 1023, 852, 703, 632, 531. <sup>1</sup>H NMR spectrum (in DMSO-*d*<sub>6</sub> in the presence of a drop of Et<sub>3</sub>N for dissolution of the product): 7.45 (*J*=8.9 Hz, 4H); 7.10 (*J*=2.6 Hz, 2H); 6.83 (*J*=8.6 Hz, 4H); 6.61 (*J*=8.6 Hz, 2H); 6.53 (*J*=2.6 Hz, 2H); 5.04 (s, 4H of amino groups).

### 2.6. Polymerization

The detailed procedures for preparation of NTDA-*mBAPBDS* are described as follows.

To a 100 mL completely dried four-neck flask were added 1.584 g (3 mmol) of *mBAPBDS*, 12 mL of *m*-cresol, and 1.02 mL of triethylamine successively under nitrogen flow. After the *mBAPBDS* was completely dissolved, 0.804 g (3 mmol) of NTDA and 0.52 g of benzoic acid were added. The mixture was stirred at room temperature for a few minutes and then heated

at 80 °C for 4 h and 180 °C for 20 h. After cooling to 80 °C, additional 5 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into acetone. The fiber-like precipitate was filtered off, washed with acetone thoroughly, and dried in vacuo at 60 °C for 20 h.

NTDA-*i*BAPBDS was synthesized by the same approach as described above, while the synthesis of other SPIs has been previously reported [6–15].

### 2.7. Film formation and proton-exchange

The SPIs (in triethylammonium salt form) were dissolved in *m*-cresol or DMSO, and the solution was cast onto glass plates at 110 °C (*m*-cresol solution) or 80 °C (DMSO solution) for 10 h. The as-cast films were soaked in methanol at 60 °C for 1 h and in 1.0N hydrochloric acid at room temperature for 10–15 h successively. The proton-exchanged films were thoroughly washed with deionized water and then dried in vacuo at 150 °C for 20 h. The preparation of other SPI membranes has been previously reported [6–15].

### 2.8. Measurements

Infrared (IR) spectra were recorded on a Horiba FT-200 spectrometer as KBr pellets. <sup>1</sup>H NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument. Differential scanning calorimetry (DSC) was performed with a Seiko DSC-5200 at a heating rate of 10 °C min<sup>-1</sup>.

Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) [6]. A sheet of membrane (1.0 cm × 0.5 cm) and two pairs of blacken platinum plate electrodes were set in a Teflon cell. The distance between two electrodes was 0.5 cm. The cell was placed in either a thermo-controlled humidic chamber for measurement at relative humidity (RH) lower than 100% or distilled deionized water for measurement in liquid water. The resistance value associated with the membrane conductance was determined from high frequency intercept of the impedance with the real axis. Proton conductivity was calculated from the following equation:

$$\sigma = \frac{d}{t_s w_s R} \quad (1)$$

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 measurement in liquid water, as the dimensional changes could not be neglected, the measured or corrected membrane thickness was used in the calculation of  $\sigma$ .

Water uptake (WU) was measured by immersing three sheets of films (20–30 mg per sheet) of each polyimide into water at a given temperature for 5 h. Then the films were taken out, wiped with tissue paper, and quickly weighed on a microbalance. WU of the films was calculated from:

$$\text{WU}(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

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

Dimensional changes were measured by immersing the membranes into deionized water at a given temperature for 5 h. The size change in thickness direction  $\Delta L$  and the area change in planar direction  $\Delta A$  were calculated from the following equations:

$$\Delta L = \frac{L - L_0}{L_0} \quad (3)$$

$$\Delta A = \frac{A - A_0}{A_0} \quad (4)$$

where  $L_0$  and  $L$  are the thickness, and  $A_0$  and  $A$  the area of membrane before and after soaking treatment, respectively.

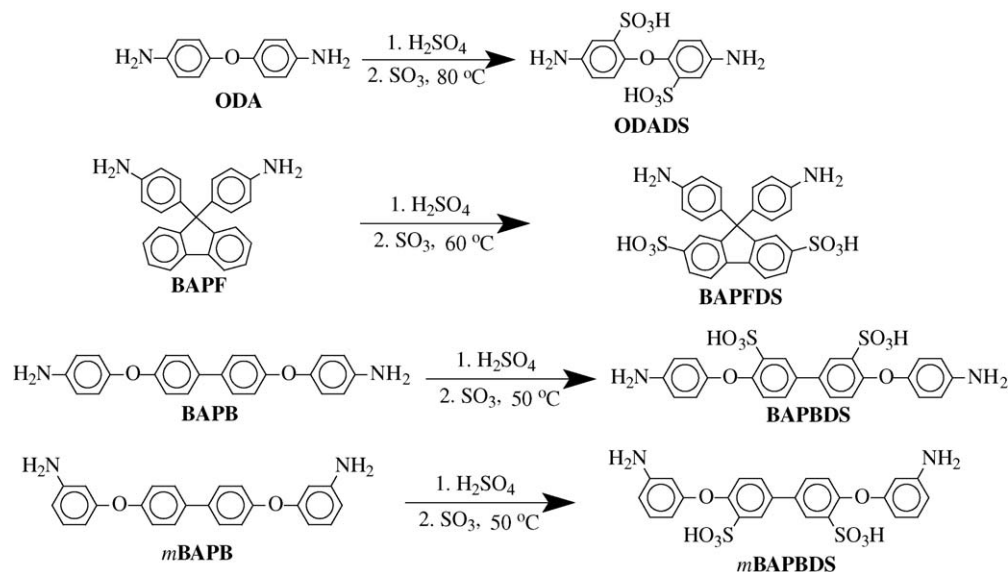
Tensile measurement was performed with an Intesco Model 2005 instrument at 25 °C in ambient atmosphere (~50% relative humidity) at a crosshead speed of 1 mm min<sup>-1</sup>. Sulfonated polyimide membranes were soaked in distilled water at 100 °C for a given time and subject to tensile measurement as soon as they were taken out. The thickness of hydrated membranes was used for tensile strength calculation.

## 3. Results and discussion

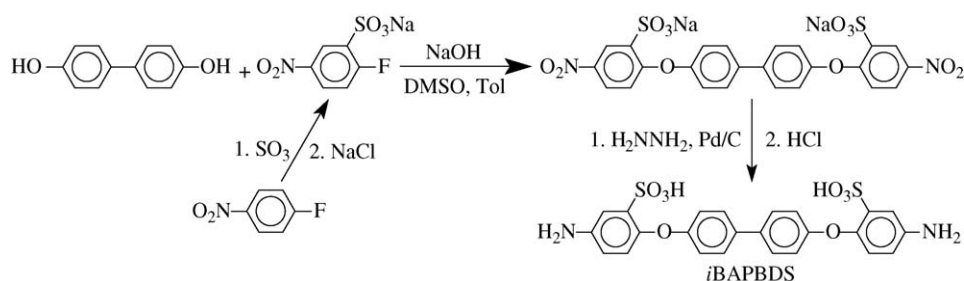
### 3.1. Monomer synthesis

Because the commercially available sulfonated diamine monomers are quite few and the sulfonated polyimide membranes derived from those monomers showed rather poor water stability [4–7], a series of novel sulfonated diamine monomers were synthesized and the related sulfonated polyimides were prepared. The sulfonated diamines could be classified into two types. One is the main-chain-type diamines of which sulfonic acid groups are directly attached to the backbone of the molecules. Another is the ‘so-called’ side-chain-type diamines of which sulfonic acid groups are pendant in side chains. Examples of main-chain-type monomers include the commercially available monomer 2,2'-benzidinedisulfonic acid (BDSA), BAPFDS [6], ODADS [7], BAPBDS [10], *o*BAPBDS [11], *i*BAPBDS and *m*BAPBDS. The side-chain-type monomers include DAPPS [9], 2,2'-BSPB [8,12], 3,3'-BSPB [8,12] and BSPOB.

The synthesis of sulfonated diamines was carried out by direct sulfonation of the corresponding non-sulfonated diamines using fuming sulfuric acid as the sulfonating reagent or by multiple-step reactions. The direct sulfonation method has been successfully employed to prepare many main-chain-type monomers such as ODADS, BAPFDS, BAPBDS, *m*BAPBDS and *o*BAPBDS (Scheme 1). The risk of oxidation of amino groups was eliminated by dissolving the non-sulfonated diamines in concentrated sulfuric acid at low temperature (ice bath) in the primary stage because of the formation of protonated amino groups. The protonated amino group is a meta-directing group and the phenyl ring bonded with the amino group is thus deactivated, and therefore, the sulfonation



Scheme 1.

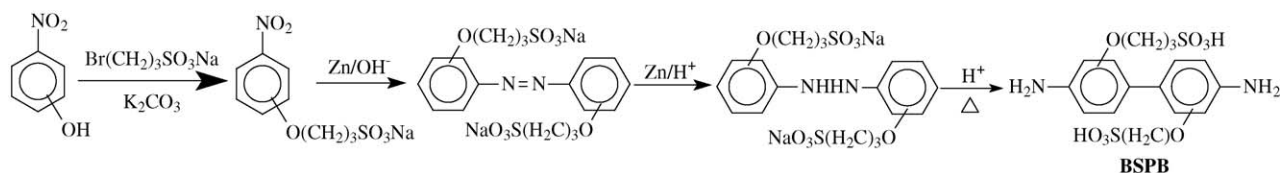


Scheme 2.

of ODA occurs in 2,2'-positions. In the case of sulfonation of 9,9-bis(4-aminophenyl)fluorene (BAPF) and 4,4'-bis(4-aminophenoxy)biphenyl (BAPB), the sulfonation preferentially occurs in the central fluorenylidene and biphenylene parts at moderate temperature ( $50\text{--}60\text{ }^\circ\text{C}$ ) because they are more active than other phenyl rings. The situation is the same for **mBAPBDS** and **oBAPBDS** although the parent non-sulfonated diamines, **mBAPB** and 2,2'-bis(4-aminophenoxy)biphenyl (**oBAPB**), are not commercially available and had to be synthesized through two-step reactions as reported in the literature [1]. When the sulfonation reaction is performed at high temperature ( $>80\text{ }^\circ\text{C}$ ), sulfonation may extend to the phenyl rings bonded with protonated amino groups. To prepare sulfonated diamines of their sulfonic acid groups bonded to relatively less active phenyl rings, an appropriate intermediate product with sulfonic acid group in the desired sites is needed. **iBAPBDS**, for example, was synthe-

sized through the reaction of 2-fluoro-5-nitrobenzenesulfonic acid sodium salt and 4,4'-dihydroxybiphenyl followed by reduction reaction of the dinitro compound (Scheme 2).

Side-chain-type diamines are generally synthesized via multiple-step reactions. 2,2'-BSPB and 3,3'-BSPB, for example, were synthesized by analogous method through four-step reactions (Scheme 3) [8,12]. First, 2-(or 3-)nitrophenol was allowed to react with 3-bromopropanesulfonic acid sodium salt to give 3-(2'-(or 3'-)nitrophenoxy)propanesulfonic acid sodium salt which was then reduced into the sulfonated azo compounds with zinc dust under basic condition. The azo compounds were further reduced to yield hydrazine derivatives with zinc dust under weak acid condition in the third step reaction. Finally, the hydrazine derivatives were converted to 2,2'-BSPB or 3,3'-BSPB through rearrangement reaction in hydrochloric acid.



Scheme 3.

### 3.2. Polymerization

The preparation of various SPIs was performed via condensation polymerization of NTDA, sulfonated diamines in *m*-cresol in the presence of triethylamine ( $\text{Et}_3\text{N}$ ) and benzoic acid at around  $180^\circ\text{C}$ . This is a literature method first reported by Mercier and co-workers [1].  $\text{Et}_3\text{N}$  was used to liberate the protonated amino groups of sulfonated diamines for polymerization with NTDA, and benzoic acid functioned as catalyst. Non-sulfonated diamines are often used as comonomers to control the sulfonation degree of the polymers. The copolymerization can be conducted in two manners. One is the random copolymerization that both sulfonated and non-sulfonated diamines are added to the reaction flask prior to the addition of NTDA. Another way is that sulfonated diamines are allowed to react with NTDA to form anhydride-end-capped oligomers, which were then further reacted with non-sulfonated diamines to give sequenced copolymers [1,4–6]. The sequence length can be controlled by regulating the molar ratio between the sulfonated diamines and NTDA.

### 3.3. Proton conductivity

Table 1 lists the proton conductivity of various SPI membranes in liquid water at  $50^\circ\text{C}$ . The ion exchange capacities (IECs) of these SPI membranes are in the range of  $1.73\text{--}3.37\text{ mequiv. g}^{-1}$ . It can be seen that the proton conductivity strongly depends on the IEC but hardly depends on the structure of membranes. Higher IEC resulted in higher conductivity, and vice versa. In addition, most of the SPI membranes showed higher conductivity than Nafion 117 because of the much higher IECs of the former. The proton conductivities of SPI membranes are also closely dependent on the relative humidity (RH). As shown in Fig. 1, for all the membranes the proton conductivity increases rapidly as the RH increases. In the range of RH above 80%, SPI membranes showed higher proton conduc-

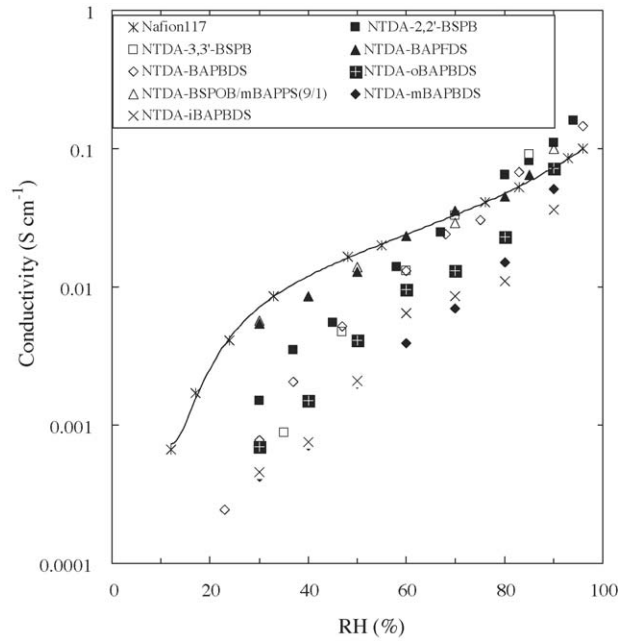


Fig. 1. Proton conductivities of various SPI membranes as a function of relative humidity at  $50^\circ\text{C}$ .

tivities than Nafion 117. However, at low RH (<40%) most of SPI membranes showed significantly lower conductivities than Nafion 117 despite the higher IECs of the former. This is likely because of the less acidity of sulfonic acid groups and the lack of channel structure for proton transport as has been observed with Nafion 117. It is well-known that the acidity of sulfonic acid group is greatly affected by the electronic withdrawing/donating effect of the substituent, i.e., electronic withdrawing substituent leads to high acidity and vice versa. Thus the acidity of the sulfonic acid groups in Nafion 117 and SPI membranes should be in the order: Nafion 117 (perfluorocarbon sulfonic)  $\gg$  wholly aromatic SPIs (aryl sulfonic) > sulfoalkoxy-substituted SPIs (alkyl sulfonic). This is likely the reason that although the side-chain-type SPI membrane, NTDA-BSPB, had fairly high IEC ( $2.89\text{ mequiv. g}^{-1}$ ) as well as microphase-separated structure resulting from the hydrophobic polyimide backbone and the hydrophilic ionic domains (average size: about 5 nm) [12], the conductivity is still lower than that of Nafion 117 in low RH. If the sulfoalkoxy side chain is perfluorinated, the conductivity is expected to be greatly enhanced.

### 3.4. Water stability

The water stability test for the sulfonated polyimide membranes was performed by immersing the membranes into deionized water at a given temperature and the stability was characterized by the elapsed time when the hydrated membranes start to lose mechanical properties. The criterion for the judgment of the loss of mechanical properties is that the membrane is broken into pieces naturally (soaking temperature:  $100^\circ\text{C}$ ) or when lightly bent (soaking temperature:  $80^\circ\text{C}$ ).

Table 2 lists the water uptake, water stability and dimensional changes of various SPI membranes. It can be seen that the water

Table 1  
Proton conductivity ( $\sigma$ ) of various SPI membranes in water at  $50^\circ\text{C}$

Membrane	IEC (mequiv. $\text{g}^{-1}$ ) <sup>a</sup>	$\sigma$ ( $\text{S cm}^{-1}$ )	References
NTDA-ODADS	3.37	0.30	[7]
NTDA-2,2'-BSPB	2.89 (2.72)	0.22	[8,12]
NTDA-3,3'-BSPB	2.89 (2.80)	0.21	[12]
NTDA-BAPFDS	2.70	0.21	[6]
NTDA-ODADS/ODA(3/1)	2.70	0.21	[6]
NTDA-BAPBDS	2.63	0.20	[10]
NTDA-iBAPBDS	2.63	0.21	This
NTDA-mBAPBDS	2.63	0.17	This
NTDA-oBAPBDS	2.63	–	[11]
NTDA-BSPOB/mBAPPS(9/1)	2.40	0.23	This
NTDA-BAPFDS/ODA(2/1)	2.09	0.17	[6]
NTDA-BAPFDS/ODA(2/1)-s	2.09	0.19	[6]
NTDA-DAPPS	2.09 (1.98)	0.18	[9]
NTDA-ODADS/ODA(1/1)	1.95	0.12	[7]
Nafion 117	0.91	0.11	[10]

<sup>a</sup> The data in parenthesis are experimental values and others are calculated values.

stability of the SPIs is greatly affected by the chemical structure of the sulfonated diamine moieties. First, side-chain-type SPI membranes generally showed better water stability than the main-chain-type ones. The two side-chain-type SPI membranes, NTDA-2,2'-BSPB and NTDA-BSPOB/*m*BAPPS(9/1), for example, displayed the highest water stability despite their high IEC level. They did not lose mechanical strength even after being soaked in deionized water for more than 2000 h indicating excellent water stability. NTDA-BAPBDS represents the most stable main-chain-type SPI membrane, but this stability is significantly lower than that of NTDA-2,2'-BSPB and NTDA-BSPOB/*m*BAPPS(9/1). The second structural factor affecting water stability is the configuration of the sulfonated diamine moieties. Linear configuration is favorable for maintaining water stability of SPI membranes, whereas nonlinear configuration leads to poor water stability. For example, BAPBDS, *m*BAPBDS and *o*BAPBDS are isomers to each other but have different configurations. BAPBDS has linear configuration, whereas the others are nonlinear molecules. As shown in Table 2, the water stability of the SPI membranes from these diamine monomers is quite different. NTDA-*o*BAPBDS is water soluble even at room temperature. NTDA-*m*BAPBDS can also be dissolved in hot water (80 °C, 2 h). In contrast, NTDA-BAPBDS could maintain mechanical strength after being soaked in deionized water at 100 °C for 1000 h. The isomeric effect on water stability was also observed with side-chain-type SPI membranes. 2,2'-BSPB and 3,3'-BSPB are isomers to each other and both have linear configuration. However, NTDA-2,2'-BSPB displayed significantly better water stability than NTDA-3,3'-BSPB. This is might because the *ortho*-substituted sulfopropoxy groups in 3,3'-BSPB are relatively unfavorable for dense packing of polymer chains in comparison with the case of 2,2'-BSPB. Another side-chain-type monomer, DAPPS, is nonlinear molecule, and therefore, NTDA-DAPPS showed much poorer water stability than NTDA-2,2'-BSPB and NTDA-3,3'-BSPB despite the much

lower IEC of the former. The third structural factor is the basicity of sulfonated diamine moieties. Higher basicity results in better water stability of the SPI membranes. BAPBDS and *i*BAPBDS are isomers to each other and both have linear configuration, but the former is much more basic than the latter due to the strong electron-withdrawing effect of sulfonic acid groups. The high basicity (high electron density) lowered the positive electricity of carbonyl groups of imido rings and thus the hydrolytic reaction is depressed. This is the reason that NTDA-BAPBDS showed much better water stability than NTDA-*i*BAPBDS. The fourth structural factor is the chain flexibility of SPI membranes. Flexible chains can undergo relaxation more easily than the rigid ones. This is why ODADS-based SPIs had better water stability than BDSA-based ones [7].

IEC is also an important factor affecting water stability of membranes. Generally higher IEC causes larger water uptake (swelling degree) or even dissolution of membranes in water. However, SPI membranes do not simply obey this law. As discussed before, the structure of sulfonated diamine monomers had much greater effects on water stability than the IEC. This indicates that with proper molecular design of sulfonated diamines SPI membranes with high IEC as well as high water stability can be developed. 2,2'-BSPB, BSPOB and BAPBDS are successful examples of which SPI membranes showed fairly good performance.

The water stability of SPI membranes was also determined by tensile strength measurement. As shown in Table 3, NTDA-BSPOB/*m*BAPPS(9/1) had a stress at break of 80 MPa at ambient atmosphere before soaking in deionized water and 27 MPa in fully hydrated state (soaked in deionized water at room temperature for 6 h). The stress decreased to 14 MPa after the membrane was soaked in deionized water at 100 °C for 12 h. Further soaking treatment led to very slow reduction in tensile strength. The membrane still had a stress at break of 12 MPa even after being soaked in deionized water at 100 °C for

Table 2  
Water uptake, water stability, and dimensional changes of various SPI membranes

Membrane	IEC <sup>a</sup> (mequiv. g <sup>-1</sup> )	WU <sup>b</sup> [g 100 g polymer <sup>-1</sup> ]	Water stability		Dimensional changes (%) <sup>c</sup>		Reference
			Temperature (°C)	Time (h)	$\Delta L$	$\Delta A$	
NTDA-ODADS	3.37	–	50	<2 (dissolved)	NM	NM	[7]
NTDA-ODADS/ODA(1/1)	1.95	87 <sup>d</sup>	80	25	NM	NM	[7]
NTDA-BDSA/ODA(1/1)	1.98	79 <sup>d</sup>	80	5.5	NM	NM	[7]
NTDA-BAPFDS	2.70	122	80	<5 (dissolved)	NM	NM	[6]
NTDA-BAPBDS	2.63 (2.43)	107 <sup>d</sup>	100	1000	16	32	[10]
NTDA- <i>i</i> BAPBDS	2.63	213 <sup>d</sup>	80	80	NM	NM	This
NTDA- <i>m</i> BAPBDS	2.63	184	80	<2 (dissolved)	NM	NM	This
NTDA- <i>o</i> BAPBDS	2.63	–	r.t.	Dissolved	–	–	[11]
NTDA-DAPPS	2.09	105	80	200	12	15	[9]
NTDA-2,2'-BSPB	2.89 (2.72)	222	100	2500	220	2	[12]
NTDA-3,3'-BSPB	2.89 (2.80)	250	100	700	180	23	[12]
NTDA-BSPOB/ <i>m</i> BAPPS(9/1)	2.40	160 <sup>e</sup>	100	>2000	150 <sup>e</sup>	7 <sup>e</sup>	This

–: Infinite (dissolution); NM: not measured.

<sup>a</sup> The data in parenthesis are experimental values and others are calculated values.

<sup>b</sup> 50 °C.

<sup>c</sup> Room temperature.

<sup>d</sup> 80 °C.

<sup>e</sup> 100 °C.

Table 3  
Changes of mechanical properties of sulfonated polyimide membranes before and after soaking in deionized water under different conditions

Membrane	Soaking treatment conditions	Maximum of stress (MPa)	Elongation at break (%)	References
NTDA- BSPOB/ <i>m</i> BAPPS(9/1)	No treatment	80	2.5	This
	25 °C, 6 h	27	7.5	This
	100 °C, 12 h	14	6.5	This
	100 °C, 100 h	12	2.7	This
NTDA- BAPBDS	No treatment	54	58	[10,13]
	100 °C, 10 min	31	109	[10,13]
	100 °C, 10 h	22	64	[10,13]
NTDA- ODADS/ODA(1/1)	No treatment	103	102	[10,13]
	100 °C, 3 h	32	46	[10,13]
	100 °C, 10 h	–	–	This
NTDA- BAPFDS/ODA(2/1) <sup>a</sup>	No treatment	65	39	[13]
	100 °C, 10 min	18	25	[13]
	100 °C, 30 min	12	11	[13]
	100 °C, 2 h	–	–	[13]
NTDA-BDSA/ODA(1/1)	100 °C, 10 min	–	–	[13]

–: Could not be measured because the membrane became highly brittle.

100 h indicating excellent water stability. NTDA-BAPBDS also showed good water stability. It could maintain relatively high tensile strength (22 MPa) after being soaked in deionized water for 10 h. The water stability of NTDA-ODADS/ODA(1/1) and NTDA-BAPFDS/ODA(2/1) is significantly poorer than that of NTDA-BSPOB/*m*BAPPS(9/1) and NTDA-BAPBDS but better than that of NTDA-BDSA/ODA(1/1). NTDA-BDSA/ODA(1/1) displayed the worst water stability, i.e., the tensile measurement could not be performed because the membrane broke into pieces after being soaked in deionized water at 100 °C for only 10 min [10]. The tensile strength measurement results are just consistent with that of the foregoing discussed method.

It is interesting that the dimensional changes of the two side-chain-type SPI membranes, NTDA-2,2'-BSPB and NTDA-BSPOB/*m*BAPPS(9/1), are anisotropic before and after soaking in water. In membrane planar direction, the dimensional changes are quite small and can be neglected. This should be very favorable for enhancing the lifetime of fuel cells because the cycling shrink/expansion processes are eliminated as the membrane is in drying/hydrated state. The anisotropic dimensional changes of these SPI membranes are likely attributed to their microphase-separated structure and the rod-like backbones. For other SPI membranes, the dimensional changes are almost isotropic.

#### 4. Summary

The synthetic approaches for various sulfonated diamine monomers were described. Some of the sulfonated diamines such as ODADS, BAPFDS, BAPBDS, *m*BAPBDS and *o*BAPBDS can be synthesized by direct sulfonating the parent non-sulfonated diamines using fuming sulfuric acid as the sulfonating reagent under proper conditions, whereas other sulfonated diamines have to be synthesized via multiple-step reactions. The proton conductivities of SPI membranes strongly depend on the relative humidity, i.e., the conductivity increases rapidly as the humidity increases. At high relative humidities (>80%), SPI membranes generally show comparable or higher proton conductivities than Nafion 117 which are high enough for practical use (>10<sup>-2</sup> S cm<sup>-1</sup>). However, at low relative humidities (<40%), the conductivities of these SPI membranes are too low to meet the requirement for practical use. It is a great challenge to enhance the proton conductivities of SPI and other sulfonated polymer membranes to the order of 10<sup>-2</sup> S cm<sup>-1</sup> at low relative humidities. The water stability of SPI membranes is mainly determined by the structure of the sulfonated diamine moieties including the flexibility, basicity and configuration. Flexible structure, high basicity and linear configuration resulted in high water stability of SPI membranes. The two side-chain-type SPI membranes, NTDA-2,2'-BSPB and NTDA-BSPOB/*m*BAPPS(9/1), displayed excellent water stability despite their high IEC levels, i.e., they did not lose mechanical strength even after being soaked in deionized water for more than 2000 h.

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