

Synthesis and Properties of Novel Sulfonated Polyimides for Fuel Cell Application

Jianhua Fang*¹, Xiaoxia Guo¹ and Morton Litt²

*¹School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, P.R. China.

Fax: 86-21-54741297, e-mail: jhfang@sjtu.edu.cn

²Department of Polymer Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202, USA

ABSTRACT: A new sulfonated diamine monomer, 3,3'-bis(4-sulfophenoxy)benzidine (BSPOB), was synthesized and a series of sulfonated (co)polyimides were prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), BSPOB and common nonsulfonated diamine monomers. The solubility behavior, thermal stability, mechanical strength, water uptake, proton conductivity, water stability and methanol permeability of the resulting sulfonated (co)polyimides were investigated. The copolyimide prepared from NTDA, BSPOB, and 4,4'-bis(3-aminophenoxy)diphenyl sulfone (*m*BAPPS), with the diamine molar ratio of 9:1 (BSPOB to *m*BAPPS) showed unusually high water stability as well as high proton conductivity, i.e., it did not lose mechanical strength even after being soaked in deionized water at 100 °C for more than 2000 h, while its proton conductivity was 0.18 S/cm in liquid water at 25 °C which is higher than that of Nafion 117.

Key words: synthesis, sulfonated polyimide, membrane, proton conductivity, water stability

1. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted much attention in the past decade because they provide cleaning, quiet and portable power for vehicular transportation and for other applications [1, 2]. The key component of a PEMFC is the polymer electrolyte membrane. For practical use, an ideal polymer electrolyte membrane material should satisfy the following requirements: 1) low cost, 2) low resistance (i.e., high proton conductivity) under fuel cell operating conditions, 3) good mechanical strength, preferably with resistance to swelling, 4) long-term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments, 5) low gas (reactant) crossover, and 6) interfacial compatibility with catalyst layers. At present, sulfonated perfluoropolymers such as DuPont's Nafion are typical membranes that are used in practical systems 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 for 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 such as sulfonated polysulfone [3, 4], sulfonated poly(ether ether ketone) [5, 6], sulfonated polysulfide [7] have been developed. These hydrocarbon polymers are much cheaper than the perfluoropolymers, however, the poor water stability is a serious problem associated with most of the sulfonated hydrocarbon polymers that limits their application.

On the other hand, aromatic polyimides have found wide application in industry due to their excellent thermal stability, high mechanical strength and modulus, superior electrical properties, and good chemical resistance. These merits are just what are required for the polyelectrolyte membrane materials used in fuel cell systems. Recent researches have demonstrated that six-membered ring sulfonated polyimides are promising membrane materials for PEMFC application [8-17]. The

sulfonated polyimides are generally synthesized by condensation polymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), sulfonated diamines, and common nonsulfonated diamines when the control of sulfonation degree and the morphology of polymers is needed. The often used and commercially available sulfonated diamine monomer is 2,2'-benzidinedisulfonic acid (BDSA). However, many researches have demonstrated that the water stability of BDSA-based polyimide membranes is still poor and one cannot expect to improve it much by only modifying the chemical structure of the nonsulfonated diamine comoieties and/or the morphology of the polymers [8, 12-17]. This is because BDSA-based polyimides are readily hydrolyzed especially at elevated temperatures. We have previously reported that the hydrolysis stability of sulfonated polyimide membranes could be greatly improved by using suitably designed sulfonated diamine monomers with high basicity, linear configuration and flexible structure to replace BDSA [12, 13, 17]. In this paper, we report on our recent progress in the development of highly water stable sulfonated polyimide membranes.

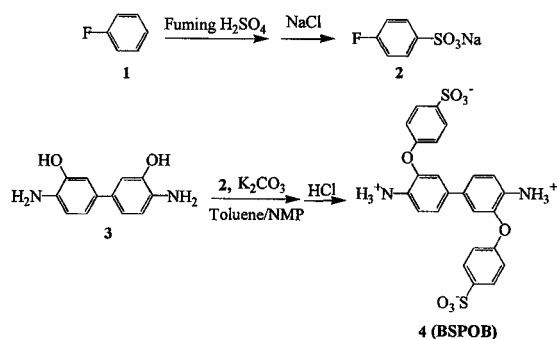
2. EXPERIMENTAL

2.1 Materials

Fluorobenzene was purchased from Aldrich and used as-received. 3,3'-dihydroxybenzidine, 2,4,6-trimethyl-1,3-phenylenediamine (TrMPD), and 4,4'-bis(3-aminophenoxy)diphenyl sulfone (*m*BAPPS) were purchased from Tokyo Kasei Co.. TrMPD was purified by vacuum sublimation prior to use.

4-Fluorobenzenesulfonic acid sodium salt was synthesized by sulfonation of fluorobenzene at 80 °C using fuming sulfuric acid (30% SO₃) as the sulfonating reagent. 3,3'-Bis(4-sulfophenoxy)benzidine (BSPOB) was synthesized via the reaction between 3,3'-dihydroxybenzidine and 4-fluorobenzenesulfonic acid sodium salt in the presence of anhydrous potassium carbonate as a base (Scheme 1). The detailed procedures will be reported elsewhere.

Scheme 1

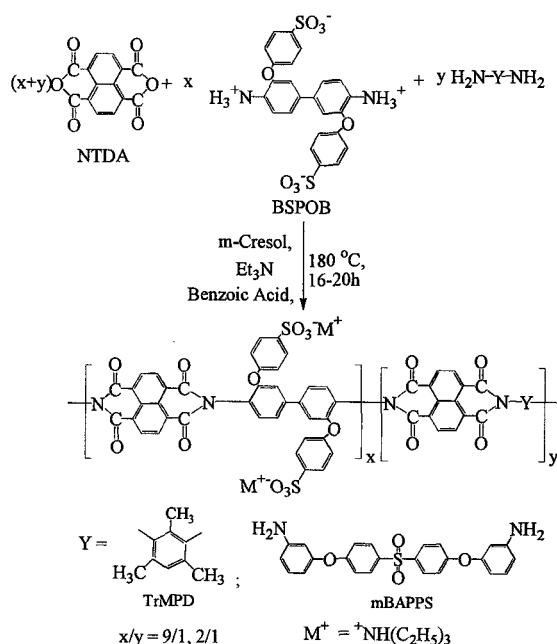


2.2 Polymerization

The preparation procedures of sulfonated (co)polyimides were described as follow using NTDA-BSPOB/*m*BAPPS(9/1) copolyimide as an example.

To a dry 50 mL 3-neck flask were added under nitrogen flow with stirring 0.7128 g (1.35 mmol) of BSPOB, 0.0648 g (0.15 mmol) of *m*BAPPS, 8.0 mL of *m*-cresol and 0.46 mL of triethylamine. After the diamines were completely dissolved, 0.402 g (1.5 mmol) of NTDA and 0.26 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 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 for a few times, and dried in vacuo.

Scheme 2



2.3 Film formation and proton exchange

Films were prepared by casting the sulfonated polyimide (in triethylammonium salt form) solutions onto glass plates and dried at 80 °C 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 into 1.0 N 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.

2.4 Measurements

¹H NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument. Thermogravimetry-mass spectroscopy (TG-MS) was measured with a JEOL MS-TG/DTA220 in helium (flow rate: 100 cm³/min) at a heating rate of 5 °C/min. Inherent viscosity was measured in DMSO at a polymer concentration of 0.5 g/dL at 35 °C using a viscometer.

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

$$\sigma = D/(L \cdot B \cdot R) \quad (1)$$

where D is the distance between the two electrodes, L and B are the thickness and width of membrane (measured from the samples store 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 films (20-30 mg per sheet) of a polyimide into water at 80 °C for 5 h. Then the films were taken out, wiped with tissue paper, and quickly weighted 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 dry and corresponding water-swollen film sheets, respectively. Water uptake of a polyimide was estimated from the average value of S of each sheet.

Dimensional changes were measured by immersing the membranes into deionized water at 100 °C for 24 h. The size change in thickness direction ΔL and the area change in planar direction ΔA were calculated from the following equations:

$$\Delta L = (L - L_0)/L_0 \quad (3)$$

$$\Delta A = (A - A_0)/A_0 \quad (4)$$

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

Methanol permeability of membranes was measured according to a previously reported method [15]. The sulfonated polyimide membranes were soaked in deionized water at room temperature for 2-4 h to get well-swollen samples and then the thickness was measured immediately. The fully hydrated membrane

was vertically set into a liquid permeation cell composed of two compartments. One compartment (A) of the cell was filled with a solution mixture of methanol and deionized water (volume $V_A = 350$ mL). The other compartment (B) was filled with deionized water (volume $V_B = 109$ mL). The compartments were continuously stirred during the whole process of permeability measurement. The methanol concentrations in the two compartments, C_A and C_B , were analyzed on a gas chromatography (SHIMADZU, GC-8A) equipped with 3-m column packed with Polarpak Q (poly(ethylene glycol)-1000 supported on Shimalite F). The effective area of the membrane for methanol permeation was 16 cm². The methanol permeability, P_M , was determined by the following equation:

$$q = A \cdot P_M \cdot \Delta C_{av} \cdot t / L$$

$$\Delta C_{av} = (C_{A0} + C_A - C_B) / 2 \quad (5)$$

where q is the methanol mole permeated into compartment B, t measuring time, ΔC_{av} the average methanol concentration difference between the two compartments during the permeation measurement process, A and L are the area and thickness of the fully hydrated membrane, respectively. C_{A0} is the initial methanol concentration in feed, and C_A and C_B are the methanol concentrations in feed and permeate at time t , respectively.

Tensile measurement was performed with an Intesco Model 2005 instrument at 25 °C in ambient atmosphere (~80% relative humidity) at a crosshead speed of 1 mm/min. 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 Polymerization and solubility behaviors

BSPOB-based (co)polyimides with controlled ion exchange capacities (IECs) were prepared by one-step (co)polymerization of NTDA, BSPOB, and nonsulfonated diamines (TrMPD and *m*BAPPS) in *m*-cresol in the presence of triethylamine (Et_3N) and benzoic acid (Scheme 2). This is a literature method which has been used for preparation of many other sulfonated polyimides [8, 9]. Table I lists the solubility behaviors and the inherent viscosity values of the resulting BSPOB-based (co)polyimides. The homopolyimide NTDA-BSPOB showed very limit solubility in *m*-cresol and gelation occurred during the polymerization process. The inherent viscosity of

NTDA-BSPOB is not very high in dimethylsulfoxide (DMSO), and the cast film is somewhat brittle due to the insufficiently high molecular weight. Although it is soluble in DMSO, the use of DMSO as the polymerization solvent to replace *m*-cresol failed to give the high molecular weight homopolymer. To improve polymer solubility in *m*-cresol, two nonsulfonated diamine TrMPD and *m*BAPPS were used as the comonomers. The selection of TrMPD and *m*BAPPS is based on the fact that many TrMPD and *m*BAPPS-based polyimides have been reported to have excellent solubility properties in common organic solvents. As expected, the incorporation of these nonsulfonated diamines (even in small fraction) led to significant improvement in solubility of the polymers. All the copolyimides were soluble in *m*-cresol and DMSO and showed very high inherent viscosity (except the moderate viscosity of NTDA-BSPOB/TrMPD(2/1)) and the cast films were very tough indicating that high molecular weight copolyimides were obtained.

The thermal stability of BSPOB-based copolyimides was investigated by TG-MS measurement. For NTDA-BSPOB/*m*BAPPS(9/1), the decomposition of sulfonic acid groups started from around 270 °C judging from the fact that the evolution of sulfur dioxide and sulfur monoxide was detected. This indicates fairly high thermal stability of the copolyimide. Other BSPOB-based copolyimides showed similar thermal stability.

The copolyimide membranes were fabricated by the conventional solution cast method. The as-cast films were in their triethylammonium form. Proton exchange was achieved by soaking the films in 1.0 N hydrochloric acid solution with magnetic stirring for two days. The completion of proton exchange for all the samples was examined by judging from the disappearance of the ¹HNMR peaks corresponding to triethylammonium.

3.2 Proton Conductivity

Fig. 1 shows the variations of proton conductivity of NTDA-BSPOB/TrMPD(9/1) as functions of relative humidity (RH) and temperature. It can be seen that the conductivity increased rapidly as the relative humidity increased. At high RH (> 70%), the membrane showed fairly high conductivities (> 10^{-2} S/cm), whereas at low RH (e.g. 20%), the conductivities are in rather low level (in the order of 10^{-4} S/cm). This has been observed with many other sulfonated polymer membranes [12-17]. In addition, it is well known that for Nafion the conductivity decreased drastically as temperature increased above 100 °C due to the rather low water retention of the membrane. However, in the present case NTDA-BSPOB/TrMPD(9/1) did not show significant reduction in proton conductivity decrease as temperature

Table I Inherent viscosity (η) and solubility behaviors of BSPOB-based polyimide membranes.

Polyimide	η [dL/g]	Solubility			
		<i>m</i> -cresol	DMSO	NMP	DMAc
NTDA-BSPOB	1.7	+/-	+	-	-
NTDA-BSPOB/TrMPD(19/1)	16.1	+	+	-	-
NTDA-BSPOB/TrMPD(9/1)	6.3	+	+	-	-
NTDA-BSPOB/TrMPD(2/1)	2.0	+	+	-	-
NTDA-BSPOB/ <i>m</i> BAPPS(9/1)	8.9	+	+	-	-

NMP and DMAc refers to 1-methylpyrrolidone and N,N-dimethylacetamide, respectively.

+: soluble, +/-: partially soluble, -: insoluble.

increased up to 160 °C. In fact, at high RH (above 80%) the conductivity increased gradually as temperature increased from 80 to 140 °C. This is very favorable for use in medium-temperature (120 – 150 °C) fuel cells.

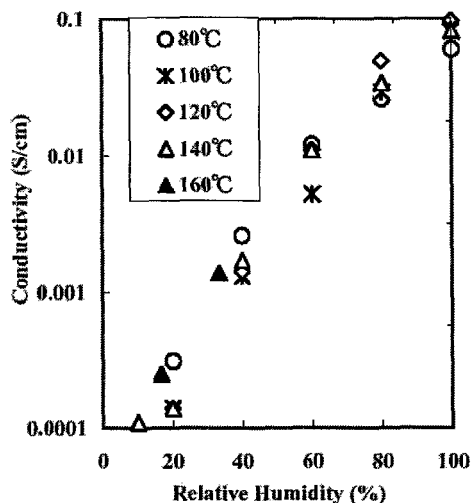


Fig. 1 Variations of proton conductivity of NTDA-BSPOB/TrMPD(9/1) as functions of relative humidity and temperature.

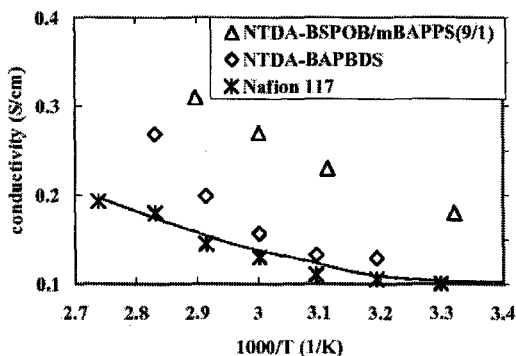


Fig. 2 Variations of proton conductivity of sulfonated polymer membranes as functions of temperature in liquid water.

Fig. 2 shows the temperature dependence of conductivity of NTDA-BSPOB/*m*BAPPS(9/1) and other membranes in liquid water. It is obvious that for all the membranes the conductivity increased as temperature increased. In addition, NTDA-BSPOB/*m*BAPPS(9/1) showed higher conductivities than Nafion 117 and another type of sulfonated polyimide NTDA-BAPBDS (BAPBDS refers to 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid) with slightly higher IEC, indicating high proton conducting performance of the polymer.

3.3 Water uptake, water stability, and dimensional stability

The water stability test for the sulfonated polyimide membranes was performed by immersing the membranes into deionized water at 80 °C or 100 °C (boiling) and the stability was characterized by the elapsed time when the hydrated membranes lost mechanical properties. The criterion for the judgment of the loss of mechanical properties is that the membrane sheets were broken into pieces.

Table II lists the water uptake, water stability, and dimensional stability of BSPOB-based copolyimide membranes. For comparison purpose, the data of other sulfonated polyimide membranes reported in the literature [8, 14-17] are also listed in this Table. It can be seen that NTDA-BSPOB/*m*BAPPS(9/1) could maintain film form after being soaked in deionized water at 100 °C for more than 2000 h indicating unusually high water stability. The other two TrMPD-containing polyimide membranes did not show so good water stability as NTDA-BSPOB/*m*BAPPS(9/1). Such a water stability difference is likely because the nonsulfonated diamine moiety *m*BAPPS is fairly flexible and the central sulfonyl linkage is a strong polar group which may enhance the interchain interaction and allow regular packing of the polymer chains. In contrast, TrMPD moiety is highly rigid and the rotation of imido ring along C-N bond axis is strictly prohibited due to the steric effect of the three methyl groups. This results in relatively loose packing of the polymer chains. For NTDA-BSPOB/TrMPD(2/1), the regularity of chain packing was broken due to the considerable fraction of

Table II Water uptake, water stability, and dimensional changes of the sulfonated copolyimide membranes.

Polyimide ^a	IEC [meq/g]	Water uptake [g/100g polymer]	Water stability		Dimensional changes [%]		Ref.
			T [°C]	T [h]	ΔL	ΔA	
NTDA-BSPOB/ <i>m</i> BAPPS(9/1)	2.40	160	100	>2000	150	7	g
NTDA-BSPOB/TrMPD(9/1)	2.49	143	100	600	110	32	g
NTDA-BSPOB/TrMPD(2/1)	2.10	72 ^b	80	>720	22 ^e	32 ^e	g
NTDA-BAPBDS	2.63	107 ^b	100	1000	16 ^f	15 ^f	16
NTDA-3,3'-BSPB	2.89	250 ^c	100	700	180 ^f	11 ^f	16
NTDA-2,2'-BSPB	2.89	222 ^c	100	2500	220 ^f	0 ^f	16
NTDA-DAPPS	2.09	105 ^c	80	200	12 ^f	15 ^f	14,16
NTDA-BDSA/Ar(NH ₂) ₂	0.56-1.86	13.5-46.5 ^d	80	200	-	-	8

^aBAPBDS, 3,3'-BSPB, 2,2'-BSPB, and ODADS refer to 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid, 3,3'-bis(3-sulfopropoxy)benzidine, 2,2'-bis(3-sulfopropoxy)benzidine, and 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid, respectively.

^b80 °C; ^c50 °C; ^d25 °C; ^emeasured at 80 °C; ^fmeasured at room temperature.

-: not available from the literature. T: Temperature, t: Time. g: This study.

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

Membrane	Soaking Treatment Conditions	Tensile Strength (MPa)	Elongation (%)	Ref.
NTDA-BSPOB/ <i>m</i> BAPPS(9/1)	No Treatment	80	2.5	This study
	25 °C, 6 h	27	7.5	This study
	100 °C, 12 h	14	6.5	This study
	100 °C, 100 h	12	2.7	This study
NTDA-BAPBDS	No Treatment	54	58	16
	100 °C, 10 min	31	109	16
	100 °C, 10 h	22	64	16
NTDA-ODADS/ODA(1/1)	No Treatment	103	102	16
	100 °C, 3 h	32	46	16
NTDA-BAPFDS/ODA(2/1) ^a	No Treatment	65	39	16
	100 °C, 10 min	18	25	16
	100 °C, 30 min	12	11	16
	100 °C, 2 h	-	-	16
NTDA-BDSA/ODA(1/1)	100 °C, 10 min	-	-	13

^aBAPFDS and ODA refer to 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid and 4,4-diaminodiphenyl ether, respectively.

-: could not be measured because the membrane became brittle.

TrMPD moiety. The dimensional change measurements revealed that NTDA-BSPOB/*m*BAPPS(9/1) had much stronger anisotropic property than NTDA-BSPOB/TrMPD(9/1), whereas for NTDA-BSPOB/TrMPD(2/1) the size changes along thickness direction and planar direction were almost identical.

It should be noted that the water stability of all the BSPOB-based polyimide membranes is in high level that is much better than that of BDSA-based ones reported in the literature [8] although the former had much larger IECs and water uptakes. We have previously reported that the poor water stability of BDSA-based polyimide membranes is due to the low basicity of BDSA moiety that accelerates the hydrolysis of imido rings [12, 13]. It is obvious that BSPOB has higher basicity than BDSA judging from the electron donating effect of the phenoxy groups. This should be a reason that BSPOB-based polyimide membranes had much better water stability than BDSA-based ones. Another important structural difference between BSPOB- and BDSA-based polyimides is that the sulfonic acid groups of the former is not directly attached to the backbone but separated by a phenoxy spacer. Thus BSPOB-based polyimides are noted as side-chain type polymers, and accordingly BDSA-based polyimides are noted as main-chain type polymers. Since the sulfonic acid group is highly hydrophilic, whereas the polymer backbone is hydrophobic, the side chains tend to form "ion-rich" domains, while the polymer backbones form hydrophobic domains, i.e., the side-chain type polyimides are easier to form microphase-separated structure. The hydrophobic domains are favorable for enhancing the water resistance of the membranes. In contrast, main-chain type polymers could not form such microphase-separated structure. This should be another important reason that BSPOB-based polyimide membranes had much better water stability than BDSA-based ones.

The linear configuration and symmetric structure of BSPOB moiety should also be an important factor responsible for the high water stability of NTDA-BSPOB/*m*BAPPS(9/1) membrane. This is

because linear configuration and symmetric structure of moieties of polyimides generally allow regular chain packing of the polymers. An example is 3-(2',4'-diaminophenoxy)propane sulfonic acid (DAPPS), a side-chain type diamine monomer reported in the literature [15]. It had nonlinear configuration and thus the related sulfonated polyimide NTDA-DAPPS showed only moderate water stability. On the contrary, 2,2'-(3-sulfopropoxy)benzidine (2,2'-BSPB) [15] have linear configuration and symmetric structure, and therefore NTDA-2,2'-BSPB displayed the highest water stability among the sulfonated polyimide membranes reported so far. As shown in Table II, NTDA-BSPOB/*m*BAPPS(9/1) showed comparable water stability to NTDA-2,2'-BSPB.

It is interesting to compare the water stability of NTDA-BSPOB/*m*BAPPS(9/1) and NTDA-BAPBDS. BSPOB and BAPBDS are isomers to each other. NTDA-BAPBDS belongs to main-chain type polymer and has been reported to have fairly high performance (high proton conductivity and high water stability) [17]. The present NTDA-BSPOB/*m*BAPPS(9/1) copolyimide membrane showed even much better water stability than NTDA-BAPBDS. This is likely attributed to the microphase-separated structure and regular packing of polymer backbones of NTDA-BSPOB/*m*BAPPS(9/1). NTDA-BAPBDS did not have microphase-separated structure and the dimensional changes are isotropic.

The water stability of the sulfonated polyimide membranes was also examined by tensile strength measurements. As shown in Table III, 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 100 h indicating excellent water stability. In contrast, for NTDA-BDSA/ODA(1/1), here ODA refers to 4,4-diaminodiphenyl ether, the tensile measurement

Table IV Methanol permeability, proton conductivity and their ratios of sulfonated polymer membranes.

Membrane	P_M (10^{-6} cm ² /s)		σ (S/cm)	$\Phi = \sigma / P_M$ (10^4 S·cm ⁻³ s)	Ref.
	30 °C	50 °C			
NTDA-BSPPOB/ <i>m</i> BAPPS(9/1)	1.73	2.67	0.18	10	This study
Nafion 117	2.21	3.32	0.11	4.8	16

could not be performed because the membrane became highly brittle after being soaked in deionized water at 100 °C for only 10 minutes [13].

3.4 Methanol permeability

Methanol crossover is a big problem often associated with direct methanol fuel cells (DMFCs). The methanol permeability of NTDA-BSPPOB/*m*BAPPS(9/1) at a methanol concentrations in feed of ~10 wt% at 30 and 50 °C is shown in Table IV. For comparison purpose, the data for Nafion 117 are also listed in this Table. It is obvious that NTDA-BSPPOB/*m*BAPPS(9/1) had significantly lower methanol permeability and higher ratio of proton conductivity to methanol permeability than Nafion 117 indicating better performance of the former.

4. Conclusions

A novel side-chain type sulfonated diamine monomer BSPPOB and the related polyimides were synthesized. The resulting sulfonated copolyimides showed fairly high thermal stability. In the whole humidity range, NTDA-BSPPOB/TrMPD(9/1) did not show significant reduction in proton conductivity decrease as temperature increased up to 160 °C. NTDA-BSPPOB/*m*BAPPS(9/1) copolyimide membrane displayed unusually high water stability as well as high proton conductivity, i.e., it did not lose mechanical strength even after being soaked in deionized water at 100 °C for more than 2000 h, while its proton conductivity was 0.18 S/cm in liquid water at 25 °C which is higher than that of Nafion 117. This copolyimide membrane also showed significantly lower methanol permeability than Nafion 117 indicating excellent performance.

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References

- [1] O. Savadogo, *J. New Mat. Electrochem. Systems*, **1**, 47 (1998).
- [2] M. Rikukawa and K. Sanui, *Prog. Polym. Sci.*, **25**, 1463 (2000).
- [3] J. Kerres, W. Cui, S. Reichle, *J. Polym. Sci.: Part A: Polym. Chem.*, **34**, 2421 (1996).
- [4] F. Wang, M. Hickner, Y.S. Kim, T. A. Zawodzinski, J. E. McGrath, *J. Membr. Sci.*, **197**, 231 (2002).
- [5] Schmeller, A.; Ritter, H.; Ledjeff, K.; Nolte, R.; Thorwirth, R. *EP 0574791 A2*, 1993.
- [6] Bailey, C.; Williams, D. J.; Karasz, F. E.; Macknight,

W. J. *Polymer*, **28**, 1009 (1987).

[7] Miyatake, K.; Fukushima, K.; Takeoka, S.; Tsuchida, E. *Chem. Mater.* **11**, 1171 (1999).

[8] Genies, C.; Mercier, R.; Sillion, B.; Petiaud, R.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer*, **42**, 5097 (2001).

[9] Faure, S.; Mercier, R.; Aldebert, P.; Pineri, M.; Sillion, B. *French Pat.* 9605707, 1996.

[10] Zhang, Y.; Litt, M.; Savinell, R. F.; Wainright, J. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **40** (2), 480 (1999).

[11] Kim, H.; Litt, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **42** (2), 486 (2001).

[12] Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules*, **35**, 6707 (2002)

[13] J. Fang, X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *Macromolecules*, **35**, 9022 (2002).

[14] Y. Yin, J. Fang, H. Kita, K. Okamoto, *Chem. Lett.*, **32**, 328 (2003).

[15] Y. Yin, J. Fang, Y. Cui, K. Tanaka, H. Kita, K. Okamoto, *Polymer*, **44**, 4509 (2003).

[16] K. Okamoto, *J. Photopolym. Sci. Technol.*, **16**, 247 (2003).

[17] T. Watari, X. Guo, J. Fang, K. Tanaka, H. Kita, K. Okamoto, *J. Membr. Sci.* (in press).

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