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Synthesis and characterization of novel sulfonated polyimides from 1,4-bis(4-aminophenoxy)-naphthyl-2,7-disulfonic acid

Yuhan Li [a,b], Rizhe Jin [a], Zhiming Cui [a,b], Zhen Wang [a], Wei Xing [a], Xuepeng Qiu [a], Xiangling Ji [a], Lianxun Gao [a,*]

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China*
[b] *Graduate School of Chinese Academy of Sciences, PR China*

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Abstract

A novel sulfonated diamine monomer, 1,4-bis(4-aminophenoxy)-naphthyl-2,7-disulfonic acid (BAPNDS), was synthesized. A series of sulfonated polyimide copolymers were prepared from BAPNDS, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and nonsulfonated diamine 4,4′-diaminodiphenyl ether (ODA). Flexible, transparent, and mechanically strong membranes were obtained. The membranes displayed slightly anisotropic membrane swelling. The dimensional change in thickness direction was larger than that in planar. The novel SPI membranes showed higher conductivity, which was comparable or even higher than Nafion 117. Membranes exhibited methanol permeability from 0.24×10^{-6} to 0.80×10^{-6} cm^2/s at room temperature, which was much lower than that of Nafion (2×10^{-6} cm^2/s). The copolymers were thermally stable up to 340 °C. These preliminary results have proved its potential availability as proton-exchange membrane for PEMFCs or DMFCs.

Keywords: Sulfonated polyimide; Proton conductivity; Degree of sulfonation

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) have attracted much attention because of their high power density and high energy conversion efficiency as well as low pollution levels [1–4]. One of the main components of a PEMFC is proton-exchange membrane (PEM) itself. Hydrated perfluorosulfonic acid membranes, such as DuPont's Nafion membrane, are typically used as the proton-exchange membrane in PEMFCs. However, there are still some drawbacks, such as high cost, low operation temperature, and less echo-friendly [5]. These limitations have stimulated many efforts in the development of alternative membrane materials based on sulfonated aromatic polymers [6–16].

Among these new polymers, sulfonated polyimide (SPI) membranes were shown to be very promising materials for electrochemical applications in terms of proton conductivity, selectivity, stability and cost. Hence, various structures of SPI materials were synthesized and studied [17–39]. For instance, Mercier group first successfully synthesized NTDA-based SPI and tested it in fuel cells [17–20]. Okamoto's group [21–28] has developed two types of SPIs (main-chain type and side-chain type) intending to study systematically the structure–property relationship of SPIs. Watanabe's group has reported sulfonated polyimide copolymers introducing aliphatic segments both in the main and in the side chains, and a stability of more than 5000 h has been achieved in fuel cell [29–32].

We have also developed a kind of binaphthyl type sulfonated polyimide (SPI 1, the chemical structures are shown in Fig. 1), and investigated the relationship between the chemical structure and membrane properties [39]. They showed well microphase-separated structures and higher conductivity.

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* Corresponding author.
E-mail address: lxgao@ciac.jl.cn (L. Gao).

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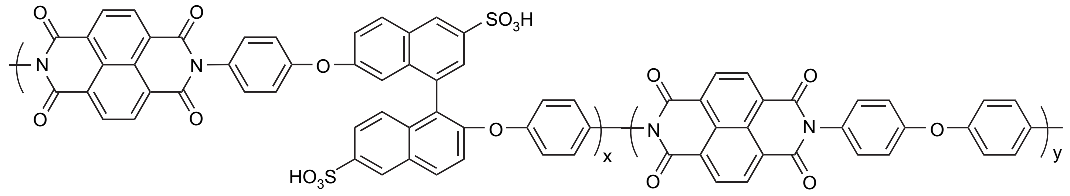
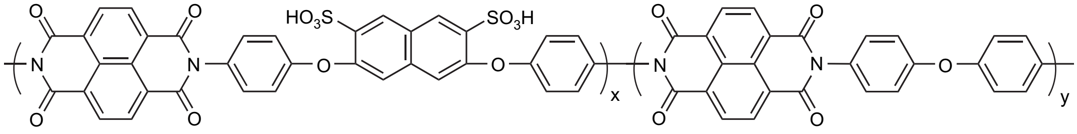


SPI-1: NTDA/BNPNDS-ODA



SPI: NTDA/BAPNDS-ODA

Fig. 1. The chemical structure of binaphthyl polymer (SPI 1) and naphthyl polymer (SPI).

However, unfortunately, these membranes showed poor water stability at higher temperatures because of membranes' excessive swelling. It may be since nonplanar binaphthyl group results in polymer chain easy relaxation and produces large interchain space in which more water molecules can be held.

To prevent membrane excessive swelling, a novel sulfonated diamine bearing naphthyl groups 1,4-bis(4-aminophenoxy)-naphthyl-2,7-disulfonic acid (BAPNDS) was devised. Furthermore, sulfonic acid groups were located at the same side of the main chains. It may be favorable for forming hydrophilic clusters, by which better proton conductivity performance would be achieved. In this article, we report on the preparation of BAPNDS and the corresponding SPI. Through several experiments such as water uptake, proton conductivity, and water stability, the relationship between the chemical structure and membrane properties is discussed.

2. Experimental

2.1. Materials

Naphthalene-2,7-diol, 4-chloronitrobenzene, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) was purchased from Aldrich Chemical Co. All other reagents were purchased from Shanghai Chemical Reagent Plant. NTDA and 4,4′-diaminodiphenyl ether (ODA) were purified by vacuum sublimation prior to use. Triethylamine (Et_3N) and *m*-cresol were purified by distillation under reduced pressure prior to use.

2.2. Synthesis of 1,4-bis(4-aminophenoxy)-naphthyl-2,7-disulfonic acid (BAPNDS)

2.2.1. Synthesis of 2,7-bis(4-nitrophenoxy)naphthalene (BNPN)

A 1 L three-necked round bottom flask containing 48.0 g (0.3 mol) of naphthalene-2,7-diol, 99.2 g (0.63 mol) of 4-chloronitrobenzene, 91.21 g (0.66 mol) of potassium carbonate and 600 mL of *N*,*N*′-dimethylacetamide (DMAc) and 100 mL toluene was fitted with a magnetic stirrer, condenser, nitrogen pad and thermometer. The reaction mixture was heated to reflux (140 °C) for 5 h, the produced water was evaporated as an azeotrope with toluene and collected in the Dean–Stark trap. After cooling to room temperature, the solution mixture was filtered, the filtrate was distilled under reduced pressure and then the mixture was poured into 100 mL water. The solid was filtered off and dried at 60 °C under vacuum. The compound was obtained, 115.0 g of BNPN with a yield of 95%. Mp (DSC): 171.85 °C. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 8.29$ (d, 4H, $J = 7.2$ Hz), 8.21 (d, 2H, $J = 8.7$ Hz), 7.67 (d, 2H, $J = 1.8$ Hz), 7.39 (dd, 2H, $J = 8.7$, 1.8 Hz), 7.24 (d, 4H, $J = 7.2$ Hz). FT-IR (KBr): 3109, 3078, 2837, 2445, 1904, 1611, 1589, 1511, 1486, 1459, 1435, 1339, 1238, 1163, 1109, 961, 874, 845, 777, 748, 686, 637.

2.2.2. Synthesis of 3,6-bis(4-nitrophenoxy)naphthalene-2,7-disulfonic acid (BNPNDS)

To a 250 mL three-necked flask equipped with a mechanical stirring device was charged 40.0 g (0.10 mol) of BNPN. A 100 mL of concentrated sulfuric acid was slowly added with stirring, then heated to 90 °C and kept at this temperature for 4 h. After cooling to room temperature, the mixture was poured into 100 mL of water. The solid was filtered off and was then washed with acetone and dried under vacuum. The crude product was obtained, 74.0 g of BNPNDS with a yield of 98%. Mp (DSC): 276 °C. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 8.42$ (s, 2H), 8.20 (d, 4H, $J = 8.7$ Hz), 7.52 (s, 2H), 7.06 (d, 4H, $J = 8.7$ Hz), 4.85 (broad, 2H). FT-IR (KBr): 3423, 3116, 3079, 2450, 1734, 1627, 1588, 1511, 1489, 1442, 1406, 1348, 1241, 1183, 1167, 1112, 1075, 1015, 872, 852, 749, 720, 651, 615, 516.

2.2.3. Synthesis of 1,4-bis(4-aminophenoxy)-naphthyl-2,7-disulfonic acid (BAPNDS)

56.0 g (0.10 mol) BNPNDS, 0.64 g of Pd/C, 34.0 g of hydrazine hydrate and 500 mL of alcohol were mixed and refluxed for 6 h. And then, the reaction mixture was filtered and the filtrate was cooled to room temperature. The precipitate was filtered off, washed with water and methanol successively, and then dried at 80 °C in vacuo. 22.4 g of product was obtained as white solid with a yield of 40%. Mp (DSC): >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 8.15$ (s, 2H), 6.76 (d, 4H, $J = 8.7$ Hz), 6.57 (d, 4H, $J = 8.7$ Hz), 6.55 (s, 2H), 4.85 (broad, 6H). FT-IR (KBr): 3448, 2612, 1573, 1508, 1445, 1375, 1312, 1247, 1197, 1161, 1070, 1013, 853, 664. Elem. Anal. Calcd.: C, 52.58%; H, 3.61%; N, 5.57%; O, 25.47%; S, 12.76%. Found: C, 51.55%; H, 3.78%; N, 5.32%; S, 13.03%.

2.3. Synthesis of random NTDA–BAPNDS–ODA copolyimides

A synthesis procedure of sulfonated copolyimide is described below using SPI 50 as an example. To a 100 mL completely dried three-necked flask were added 0.5025 g (1 mmol) of BAPNDS, 3.0 mL of *m*-cresol, and 0.35 mL of Et_3N, with stirring under nitrogen flow. After BAPNDS was completely dissolved, 0.2000 g (1 mmol) of ODA, 0.5364 g (2 mmol) of NTDA and 0.5495 g of benzoic acid were added to the flask. The mixture was stirred at room temperature for a few minutes and then heated to 80 °C for 12 h and 180 °C for 12 h. After cooling to 80 °C, the solution was poured into acetone. The resulting fiber-like precipitate was collected by filtration, washed with acetone, and dried in vacuo at 80 °C for 12 h.

2.4. Membrane formation and proton exchange

The SPI membranes were obtained by solution casting using NMP as solvent. The films were dried at 80 °C for 20 h. The membranes were soaked in alcohol at room temperature for 12 h to remove the residual solvent. The proton-exchange treatment in 1 mol/L H_2SO_4 solution at room temperature and the completion of proton exchange was confirmed by ^{1}H NMR measurement judging from the disappearance of the peaks corresponding to triethylamine, followed by washing with deionized water several times.

2.5. Measurements

Fourier transform infrared (FT-IR) spectra were determined with a Bio-Red Digilab Division FTS-80 spectrometer. ^{1}H NMR spectra were recorded on a Varian Unity spectrometer at 300 and 600 Hz with tetramethylsilane as an internal standard. Tandem gel permeation chromatography/light scattering (GPC/LS) was done at 30 °C using an HPLC 515 pump connected to Wyatt Optilab DSP and Wyatt DAWN EOS light scattering detectors. Separations were achieved using HMW 6E columns with 0.1 M LiBr in DMF as eluent and flow rate of 1.0 ml/min. The polymer solutions were filtered through a 0.22 μm PTFE filter prior to injecting into the column. The molecular weight was calibrated with polystyrene standard. Thermogravimetric analyses were obtained at a heating rate of 10 °C/min in nitrogen atmosphere with a Perkin–Elmer TGA-2 thermogravimetric analyzer. The tensile measurements were carried out on an Instron model 1122 at room temperature. Inherent viscosities were determined at 30 °C with an Ubbelodhe viscometer, and the concentration was 0.5 g/dL in NMP.

The ionic-exchange capacity (IEC) was measured by means of a classical titration method. A membrane sample of about 100 mg was soaked in 50 mL of a saturated NaCl solution for 2 days. Released protons were titrated using a 0.1 mol/L NaOH solution.

2.6. Water uptake and dimensional change

Water uptake was measured by immersing an SPI sample into water at 80 °C for 5 h. Then the membrane was taken out, wiped with tissue paper very quickly, and weighed on a microbalance. Water uptake was calculated from the following equation:

$$S = (W_s - W_d)/W_d \times 100\% \tag{1}$$

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

Size change of SPI membrane was investigated by immersing three sheets of samples in water at 80 °C for 5 h. The changes of thickness and diameter were calculated from the following equation:

$$\Delta t = (t - t_s)/t_s$$

$$\Delta l = (l - l_s)/l_s \tag{2}$$

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

2.7. Methanol permeability measurement

A glass diffusion cell was used to obtain the methanol permeability of the SPI membrane. The glass cell was composed of two chambers divided by a membrane sample. One chamber of the cell (V_1) was filled with a 2 M (C_1) methanol solution in distilled water. The other chamber (V_2) was filled with water. A sample (effective area 3.80 cm^2) was clamped between the two chambers. Methanol permeates across the membrane by the concentration difference between the two chambers. The methanol concentration in the receiving chamber as a function of time is given by

$$C_2(t) = \frac{A}{V_2}\frac{DK}{l}C_1(t - t_0) \tag{3}$$

where A (cm^2) is the membrane area, l (cm) the membrane thickness, D the methanol diffusivity, and K the partition coefficient between the membrane and the adjacent solution. The product DK means the membrane permeability (P):

$$P = \frac{C_2(t)}{AC_1(t - t_0)}V_2 l \tag{4}$$

C_2 is measured several times during the permeation experiment and the methanol permeability is obtained from the slope of the straight line. The methanol concentration was measured by using a gas chromatography equipped with a thermal conductivity detector (Shimadzu, GC-2010A, Tokyo, Japan).

2.8. Proton conductivity

Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique (Model 5210 Frequency Response Detector, EG&GPARC, Princeton, NJ) over the frequency range from 0.1 Hz to 1 MHz. A sample of the membrane and two pairs of gold plate electrodes were set in a Teflon cell. The distance between two electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Proton conductivity was calculated using the following equation with the value of membrane resistance obtained in the above experiment:

$$\sigma = L/(RS) \tag{5}$$

where σ, L, R, and S denote the proton conductivity, thickness of membranes, the resistance of the membrane and the cross-sectional area of the membrane, respectively.

3. Results and discussion

3.1. Synthesis and characterization of monomer and copolyimides

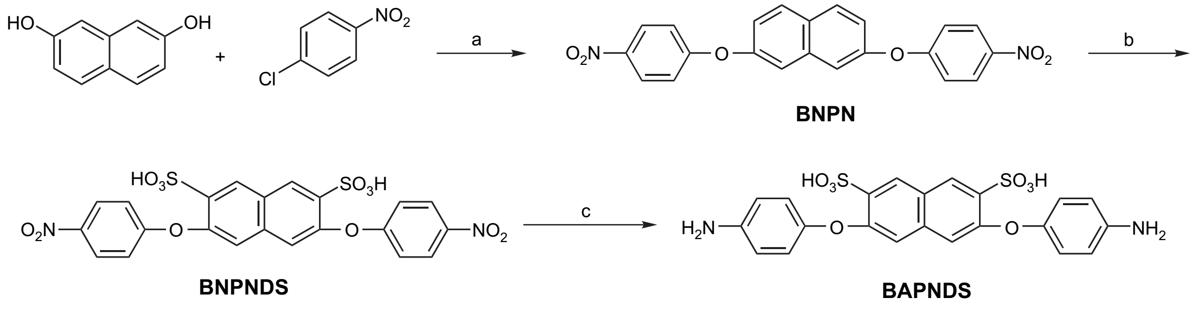
BAPNDS monomer was prepared according to common methods and the synthetic routes are shown in Scheme 1. First, BNPN was synthesized from compound naphthalene-2,7-diol and 4-chloronitrobenzene. Water was generated as the by-product of the reaction and was removed with toluene as an azeotroping agent. Then, BNPN was sulfonated by concentrated sulfuric acid at 90 °C for 4 h. The electrophilic substitution reaction occurred on *ortho* position to ether bond. Finally, BNPNDS was reduced in alcohol using hydrazine monohydrate as the reducing agent and Pd/C as the catalyst to obtain the sulfonated diamine BAPNDS. The chemical structure of the obtained product was characterized by ^{1}H NMR, FT-IR, and elemental analysis.

A series of novel sulfonated copolyimides were synthesized by copolymerization of NTDA, BAPNDS, and common unsulfonated diamine (ODA) in the presence of triethylamine and benzoic acid (Scheme 2). This is a literature method that has been used for the preparation of various six-membered ring polyimides [19]. The obtained copolyimide membranes were proton-exchanged with 1.0 M H_2SO_4 at room temperature and the completion of proton exchange was confirmed by disappearance of the peaks corresponding to triethylamine in ^{1}H NMR spectrum. The IEC values obtained from titration (1.294–2.127 mEq/g) were slightly smaller than the theoretical value (1.289–1.970 mEq/g). The chemical structure of sulfonated polyimide was confirmed by ^{1}H NMR and FT-IR spectroscopy. Fig. 2 shows the ^{1}H NMR spectrum of SPI 60. Aromatic protons were well assigned to the chemical structure of the copolyimide. The integration ratios of the peaks corresponded well to the polymer composition from the feed monomers. Fig. 3 shows the FT-IR spectrum of SPI 60 (proton form). FT-IR: 1714 (C=O, symmetric), 1670 (C=O, asymmetric), 1345 (C–N, symmetric), 1036 (S=O, symmetric), 1120 cm^{-1} (S=O, asymmetric). The resulting SPIs showed excellent solubility. They (triethylamine salt form) can be soluble in common polar solvents, such as (DMAc), *N*-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO). Table 1 shows properties of sulfonated polyimide copolymers.

The molecular weights of the polymers were evaluated by GPC using DMF as the eluent and the data are listed in Table 1. The number molecular weights (M_n) of the sulfonated polymers in the proton form are in the range from 44,630 to 74,330 and the polydispersity indices (M_w/M_n) are between 1.014 and 1.140.

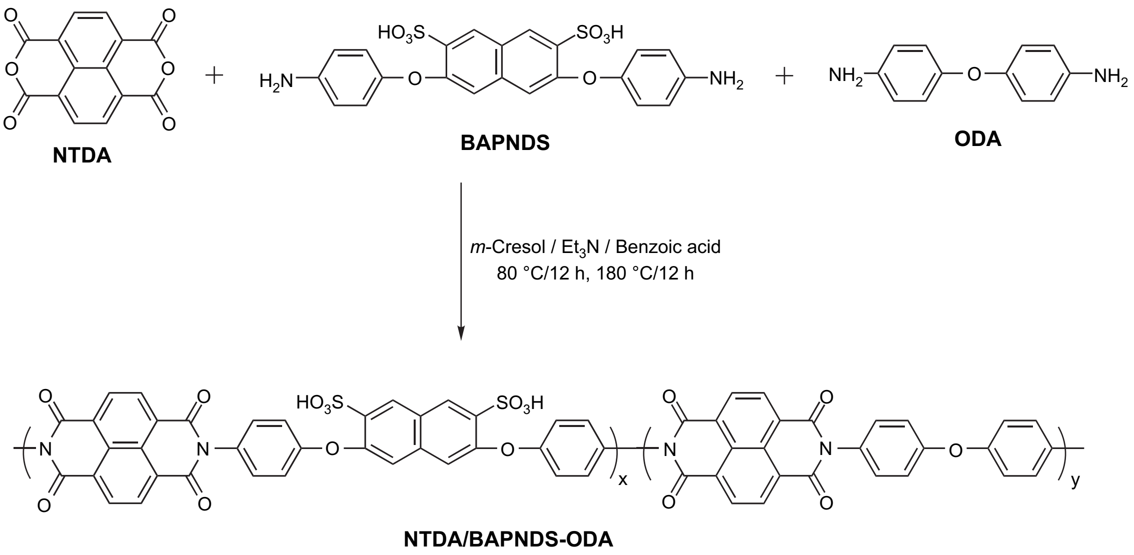
3.2. Water uptake and dimensional change

The water uptake of the sulfonated polyimide films was evaluated and is given in Table 2 and Fig. 4. Generally, higher IEC shows higher water uptake, because the introduction of sulfonic acid group makes the polymer membranes hydrophilic. As expected, water uptake increases with increase in the amount of sulfonyl group. SPI 40–SPI 70 exhibited an increase in water uptake from 8.32 to 44.36%. Fig. 4 shows the



a: K_2CO_3, DMAc, 140 °C; b: H_2SO_4, 90 °C; c: $NH_2NH_2H_2O$, Pd/C, EtOH, reflux.

Scheme 1. Synthesis of monomer BAPNDS.



Scheme 2. Synthesis of naphthyl sulfonated polyimides (SPI).

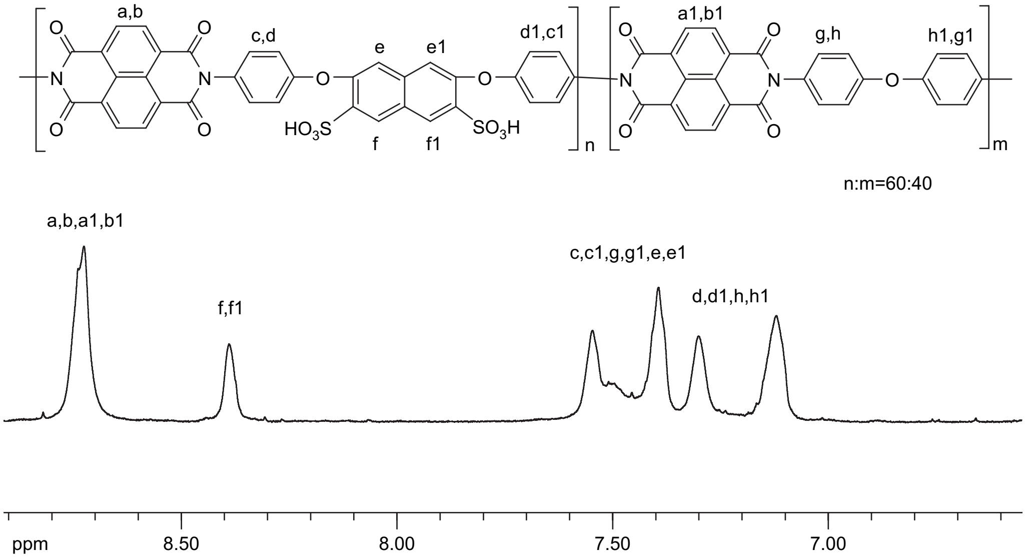


Fig. 2. Aromatic part of ^{1}H NMR spectra of SPI 60.

water uptake of naphthyl polymers (SPI) and binaphthyl polymers (SPI 1), they had different water uptake behavior. In addition, the difference of water uptake values between SPI and SPI 1 membranes became much large with increasing sulfonated diamine content. For binaphthyl polymers (SPI 1), nonplanar binaphthyl group results in polymer chain easy relaxation and produces large interchain space, so more water molecules were held. In the case of naphthyl polymer (SPI), the ionic channels were relatively narrow, thus the water molecules might be localized in a limited area, which were favorable of decrease membrane swelling. It proved that reasonable water uptake and membrane swelling can be controlled by the changes in the chemical structure. The SPI membranes displayed slightly anisotropic membrane swelling. The dimensional change in thickness direction was larger than that in planar. The ratios of $\Delta t/\Delta l$ were in the range of 1.8–3, indicating the more significant anisotropic membrane swelling.

3.3. Proton conductivity and methanol permeability

Conductivity of the sulfonated polyimides with different sulfonated degrees was measured against increasing temperature and is given in Table 2 and Fig. 5. Proton conductivities of these copolyimides are strongly dependent on their IEC and water uptake, membranes with higher IEC and larger water uptake tend to have higher proton conductivities. For example, membranes with degrees of sulfonation of 50, 60 and 70% exhibit conductivities at 30 °C of 0.0836, 0.1320 and 0.1720 S/cm, respectively. For comparison purpose, the conductivity data of binaphthyl type polyimide membrane (SPI-1-70) and Nafion 117 are also shown in Fig. 5. It can be seen that for all the polyimide membranes the proton conductivities increased with increasing the temperature, which is a typical behavior as has been observed for Nafion 117 and many other sulfonated polymer membranes. Naphthyl type sulfonated

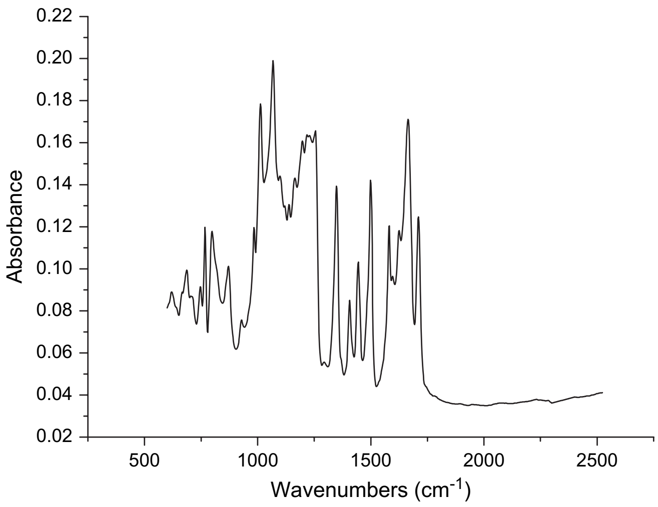


Fig. 3. FT-IR spectrum of naphthyl polymer SPI 60.

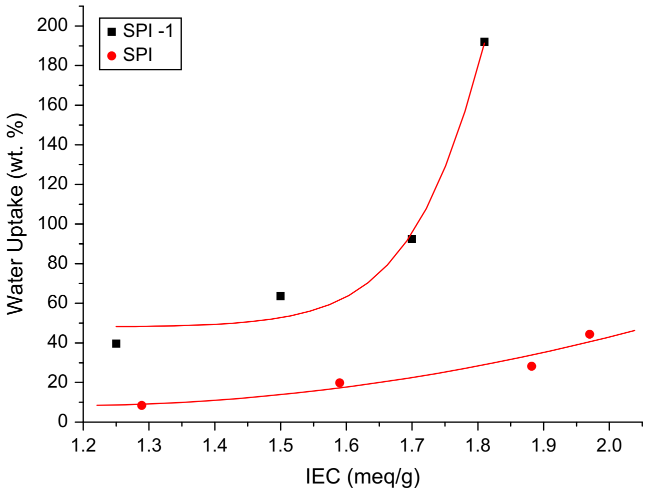


Fig. 4. Plots of water uptake for binaphthyl polymer (SPI 1) and naphthyl polymer (SPI) as a function of IEC.

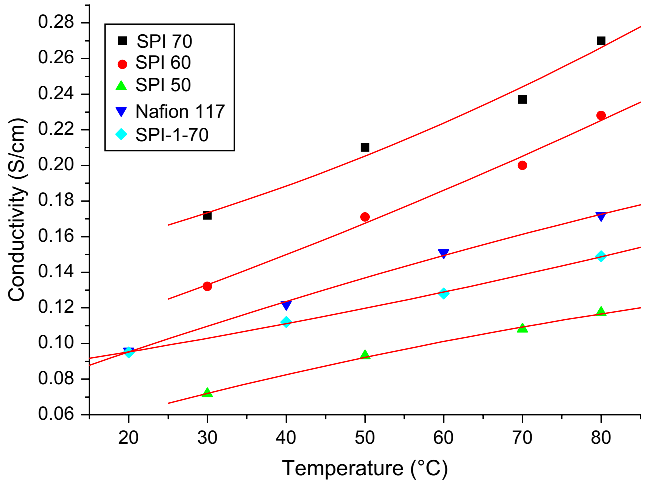


Fig. 5. Proton conductivity SPI-1-70 (a) and SPI (b) as a function of temperature. (a) SPI-1-70: sulfonated degree is 70% of binaphthyl polymer (IEC = 1.81, WU = 192). (b) SPI: naphthyl polymers, for example, SPI 60: sulfonated degree is 60% of naphthyl polymer (IEC = 1.88, WU = 28.21).

polyimide (SPI 70) displayed the highest proton conductivity among these membranes due to the highest IEC. However, it should be noted that although naphthyl type sulfonated polyimide SPI 60 (IEC = 1.882) and binaphthyl type sulfonated polyimide SPI-1-70 (IEC = 1.81) had similar IEC, the former showed higher proton conductivities than latter. Furthermore, SPI 60 displayed much lower water uptake than SPI-1-70. It showed a different trend from water uptake. This might be related to substitution position of the sulfonic acid groups. Sulfonic acid groups located at the same side of the main chains will be favorable for forming hydrophilic clusters, thus better proton conductivity performance would be achieved.

Polymer membranes exhibited methanol permeability at 20 °C of 2.4×10^{-7} to 8×10^{-7} cm^2/s depending on the degree of sulfonation. These values are around one order of magnitude lower than that of Nafion membranes (2×10^{-6} cm^2/s) at the same temperature. The proton conductivity and methanol permeability ratio φ ($\varphi = \sigma/P_M$) at 20 °C was 19×10^4

Table 1
Properties of naphthyl sulfonated polyimide copolymers

SPI X	Theoretical IEC (mEq/g)	Experimental IEC (mEq/g)	η_{inh}[a] (dL/g)	$M_n \times 10^{-4}$	$M_w \times 10^4$	M_w/M_n	Dimensional change	
							Δt	Δl
SPI 40	1.294	1.289	1.322	7.433	7.537	1.014	0.09	0.03
SPI 50	1.673	1.590	1.386	4.439	5.060	1.140	0.09	0.03
SPI 60	1.911	1.882	1.087	4.463	4.822	1.081	0.12	0.05
SPI 70	2.127	1.970	0.887	4.600	4.952	1.077	0.14	0.08

[a] Triethylamine salt form.

Table 2
IEC, water uptake (WU), proton conductivity and methanol permeability of naphthyl SPIs

Membrane	IEC (mEq/g)	WU (wt%)	Proton conductivity (S/cm)				P_M (10^{-6} cm^2/s)	Φ (10^4 S s/cm^3)
			30 °C	50 °C	70 °C	80 °C		
SPI 40	1.289	8.32	0.0717	0.093	0.108	0.117	0.24	27.96
SPI 50	1.590	19.83	0.0836	0.117	0.123	0.138	0.38	21.18
SPI 60	1.882	28.21	0.1320	0.160	0.194	0.228	0.51	23.00
SPI 70	1.970	44.36	0.1720	0.210	0.237	0.270	0.80	19.80

to 27 × 10^4 S s/cm^3, which was about 4–5 times larger than that of Nafion 117. These characteristics reduce the hydrodynamic solvent transport, which may help reduce the problems associated with water and methanol crossover for direct methanol fuel cells.

3.4. Thermal stability and mechanical properties

Thermal stability of the sulfonated polyimides was investigated by TGA measurement. The onset temperature for the second and the third degradation steps is given in Table 3, and the thermograms are shown in Fig. 6. All the sulfonated polyimide films exhibited three-step degradation patterns. The initial weight loss around 100 °C is due to the absorbed water in the membrane. The second step of degradation around 340 °C corresponds to the degradation of sulfonic acid groups. The third step indicates the decomposition of the polyimide backbone (around 550 °C). The TGA curve clearly indicates that this polyimide has fairly good thermal stability.

It is essential for electrolyte membranes to retain the mechanical strength under humidified conditions in light of membrane electrode assembly (MEA) to be used in fuel cells. To evaluate the mechanical properties of membranes under wet conditions, membranes were immersed in liquid water at room temperature. After one day of equilibration, the tensile properties of these membranes were measured and are depicted in Table 4. The membrane initial Young's modulus is from 1.128 (SPI 40) to 0.9578 GPa (SPI 70). The maximum tensile stress at break was from 80.556 (SPI 40) to 36.218 MPa (SPI 70). These results showed that the SPI membrane was tough enough at high moisture conditions, which is favorable for practical application in PEMFCs or DMFCs.

Table 3
Thermal property of naphthyl SPI films

SPI X	Onset temperature (°C)		
	Two steps	Three steps	Residue (%)
SPI 40	344.93	570.43	67.524
SPI 50	347.65	593.57	67.483
SPI 60	340.56	563.21	65.532
SPI 70	350.70	513.42	64.449

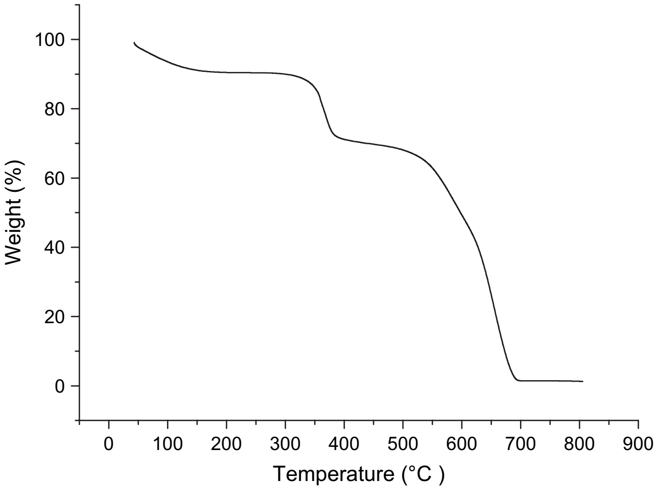


Fig. 6. Thermogram of naphthyl polymer SPI 60.

Table 4
Mechanical properties of SPI membranes

SPI X	Young's modulus (GPa)	Maximum of stress (MPa)	Elongation at break (%)
SPI 40	1.128	80.556	122.310
SPI 50	0.9597	62.652	247.13
SPI 60	1.0392	39.660	232.10
SPI 70	0.9578	36.218	138.69

3.5. Membrane stability

The stability test toward water of the polyimide membranes was performed by immersing the membranes into distilled water at 100 °C and characterized by the elapsed time until the hydrated membranes lost mechanical properties. The criterion for the judgment of the loss of mechanical properties is that the membrane sheet starts breaking into pieces under boiling. Table 5 lists the IEC, water uptake, and the water stability of the polyimide membranes. Usually water stability of polymer membranes is strongly dependent on the water uptake. Membranes with lower water uptake should have better water stability. Naphthyl SPI displayed better water stability than binaphthyl SPI with the same nonsulfonated diamine moiety (ODA) and similar IEC. The naphthyl SPI also displayed better water stability than other main-chain type sulfonated polyimide, for example, NTDA–BAPFDS/ODA (1/1) and NTDA–ODADS/ODA (1/1) [22]. Compared to side-chain type sulfonated polyimide [25,29], our SPI membranes showed rather poor water stability. The results suggest that the substitution position of the sulfonic acid groups had significant influence on the membrane stability. The longer the distance between the sulfonic acid group and the amine group, the better the water stability of the resulting SPI.

The stability of the copolyimides to oxidation was also investigated by immersing the membranes (the size of each sheet: 1.0 × 1.0 cm^2) into Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at 30 °C. The oxidative stability of the membranes was characterized by the expended time that the membranes started to become a little brittle (the membrane was broken when it was lightly bent). As listed in Table 5, the oxidation stabilities of these membranes are comparable to that of some sulfonated polyimides with the sulfonic acid

Table 5
IEC, water uptake and water stability of SPI membranes

Membrane	IEC (mEq/g)	WU (wt%)	Thickness (μm)	Water stability		Oxidation stability	
				Temperature (°C)	Time (h)	Temperature (°C)	Time (h)
SPI 40	1.289	8.32	50	100	500	30	17
SPI 50	1.590	19.83	57	100	320	30	15
SPI 60	1.882	28.21	57	100	300	30	13
SPI 70	1.970	44.36	45	100	240	30	10

groups directly bonded to the polymer backbone [21,22]. The SPI membrane exhibited higher proton conductivity and lower methanol permeability compared with the Nafion 117 membrane, but their membrane stability did not reach the stringent membrane criteria for practical applications yet. Therefore, we will focus on the development of high performance membrane materials with long-term durability under hydrolysis and free radical attacks in future work.

4. Conclusions

A series of novel SPIs were prepared from NTDA, BAPNDS, and common nonsulfonated diamines. Tough and transparent membranes were obtained from solution casting. The novel SPIs displayed good solubility in common polar solvents and high thermal stability of the sulfonic acid groups up to 350 °C. They showed high proton conductivities in liquid water, for example, SPI 70 showed conductivity values of 0.27 S/cm at 80 °C, which has higher proton conductivity than Nafion 117. Naphthyl SPI membranes displayed lower water uptake values than binaphthyl SPIs and exhibited smaller dimensional changes. The dimensional change was clearly anisotropic, with much larger swelling degree in thickness direction than that in plane. The SPI exhibited good mechanical properties before and after the treatment in water at 100 °C for 240–500 h, and this indicated higher flexibility and robustness in both dry and hydrated states. These electrolyte properties (thermal stability, mechanical strength, and proton conductivity) seem promising for the application to PEMFCs and DMFCs.

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