

Synthesis and characterization of acid-base polyimides bearing pendant sulfoalkoxy groups for direct methanol fuel cell applications

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ABSTRACT: A series of acid–base polyimides with sulfonic acid groups in the side chains have been prepared, based on a new synthesized sulfonated diamine monomer containing pyridine functional group. The effect of the introduction of pyridine groups into copolymer backbone on the properties of membrane were evaluated through the investigation of membrane parameters. The copolymers produced flexible, tough, and transparent membranes by solvent casting method. All the prepared membranes displayed high thermal stability, great oxidative stability and good mechanical properties. They exhibited appropriate water uptake (15.8–30.2 wt % at 80°C) and remarkable dimensional stability (2.5–6.9% at 80°C). The proton conductivity of SPI-80 was $1.01 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature. Moreover, the methanol permeability of SPI-80 membrane was $1.22 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which was lower than $23.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of Nafion 117. Therefore, these acid-base polyimides materials have a promising prospect for direct methanol fuel cell applications. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42238.

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INTRODUCTION

Direct methanol fuel cells (DMFCs) have attracted considerable attention in the area of portable power devices for their advantages, such as excellent conversion efficiency, high power density, and environmental friendliness.^{1–3} As one of the key components of DMFCs, proton exchange membrane (PEM) acts as an electrolyte for transferring protons as well as providing a barrier to the fuel or oxidant.⁴ At present, perfluorosulfonic acid polymers (PFSA) such as Nafion, Flemion, and Aciplex are the current state-of-the-art PEM materials due to their high proton conductivity, satisfactory chemical stability, and excellent mechanical strength. However, the major drawbacks of PFSA for fuel cell applications are high cost, complicated synthesis procedure, high fuel permeability, and environmental concerns of fluorine.^{5,6} Therefore, it is desirable to develop nonfluorinated materials with low cost and preferable performances.

In recent years, aromatic hydrocarbon polymers have been extensively investigated due to their excellent stabilities and low fuel permeabilities. These sulfonated polymers include sulfonated poly(arylene ether)s (SPAEs),^{7–9} sulfonated polyimides (SPIs),^{10–12} sulfonated polybenzimidazole (SPBI),^{13,14} and sulfonated polyphenylenes (SPP).^{15,16} Among these polymers, SPIs are considered as a competitive candidate for PEM applications owing to their high mechanical strength, high thermal stability,

good film-forming ability, and low fuel permeation. However, chemical stability of SPI membrane is rather poor. The poor chemical stability is caused by the excessive water uptake and the weak hydrolytic of imide moiety in the copolymer backbone.¹⁷ One of the most popular strategies to improve membrane durability is the structural modification of sulfonated diamine.¹⁸ In addition, it is known that SPIs can be classified into main-chain-type and side-chain-type where the sulfonic acid groups are bonded to the polymer backbone.¹⁹ It is found that the side-chain-type SPI membranes have larger water uptake and higher proton conductivities than the main-chain-type SPIs. Moreover, the sulfonic acid groups bearing apart from the backbone tend to improve membrane durability to chemical attacks, such as peroxide radicals and water.²⁰ Watanabe *et al.* reported that aliphatic/aromatic polyimide ionomers were durable for 5000 h without distant degradation.²¹ Okamoto *et al.* synthesized a novel side-chain-type polyimide bearing pendant sulfoalkoxy groups. They claimed that SPI membranes with rigid backbones and relatively flexible side chains exhibited better water membrane stability toward water.^{19,22}

Covalently and ionic crosslinking of polymers have been proved as a viable option to suppress excess fuel permeation and improve the stability of membrane.^{23–25} Ionic crosslinking polymers give a promise to flexible membranes of excellent properties

than covalently crosslinking polymers, which have a tendency to become brittle in a dry state.²⁶ Jang *et al.* reported that acid–base polyimide blends exhibited improved hydrolytic and dimensional stability.²⁷ Zhang *et al.* reported that sulfonated polyimides bearing basic triphenylamine groups exhibited better swelling capacity than those without triphenylamine groups.²⁸ The water stability of acid–base membranes was improved by utilizing the strong intra and inter acid–base interactions through basic triphenylamine functions and sulfonic acid groups. Lei *et al.* synthesized and characterized sulfonated polyimide ionomers by incorporating pyridine groups in the polymer backbone.²⁹ These films exhibited excellent dimensional stabilities and good mechanical properties.

In the present study, a sulfonated diamine monomer, 3-(4-(2,6-bis (4-aminophenyl)pyridin-4-yl)phenoxy)propane-1-sulfonic acid (BAPPS), was synthesized and polymerized to form copolymer containing pyridine groups in copolymer backbones and sulfonic acid groups in the side chains. The interactions between the N-bases and the sulfonic acid groups were expected to induce the formation of ionic crosslinking structure and prevent fuel crossover as well. Simultaneously, the sulfoalkylated side chains induced the formation of chemically stable microstructures resistant to chemical attacks. The properties including inherent viscosity, proton conductivity, thermal stability, dimensional change, and oxidative stability were fully investigated.

EXPERIMENTAL

Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) was purchased from Aldrich Chemical and purified by vacuum sublimation prior to use. 4,4'-diaminodiphenyl ether (ODA, Shanghai 3S reagent) was purified by sublimation. 3-bromopropane sulfonic acid sodium salt was provided by Alfa Aesar (Tianjin, China). Benzoic acid, 4-hydroxybenzaldehyde, and 4-nitroacetophenone were supplied by Sinopharm Chemical Regent (China). Dimethylformamide (DMF), triethylamine (Et₃N), toluene and *m*-cresol were purchased from Tianjin Chemical Reagent Company (China) and purified by distillation under reduced pressure and dehydrated with 4 Å molecular sieves. Potassium carbonate (K₂CO₃) was received from Rionlon (China) and dried under vacuum at 160°C prior to use. All other chemicals were used as received without further purification.

Measurements

¹H NMR spectroscopic analysis were carried out on a JNM-ECS spectrometer operating at 400 MHz using DMSO-*d*₆ as solvent. FTIR spectra were recorded with a Nicolet NEXUS670 Fourier transform infrared spectrometer using KBr disc. The thermal decomposition behaviors of the sulfonated polyimides were examined by means of thermogravimetry on a Perkin Elmer TG/DTA-6300 instrument. Before analysis, the membranes were dried and kept in the TGA furnace at 120°C under a nitrogen atmosphere for 20 min. After that, films were heated to 800°C at a heating rate of 10°C min⁻¹. The mechanical strength properties of dry films were measured by SHIMADZU Universal Testing Machine AGS-x 5KN at a stretched speed of 2 mm min⁻¹. The inherent viscosity was determined with an Ubbelohde

capillary viscometer using a 0.5 g dL⁻¹ *m*-cresol solution of the prepared copolymer in the Et₃N salt form at 30 ± 0.1°C.

The ion exchange capacity (IEC) values of the membranes were determined by acid–base titration.³⁰ Pieces of the dried, acid-formed membranes were weighed and soaked in saturated NaCl solution for 48 h to undergo an ion-exchange process. The released protons were titrated by 5 mM NaOH solution with phenolphthalein as an indicator. The IEC was calculated from the following formula:

$$\text{IEC} = \frac{\text{consumed NaOH (mL)} \times \text{molarity NaOH}}{\text{weight of dry membrane}} \text{ (mequiv/g)} \quad (1)$$

The reported IEC values were the mean of five measurements, and the standard deviation was ±5%.

Water uptake of membrane was gravimetrically determined from the weight difference between the initial dry and the final humidified sample. The membrane was dried at 120°C under vacuum for 12 h until constant weight. After cooling to room temperature, the dry sample was weighed and then immersed into deionized water at a given temperature for 5 h. Then the film was quickly taken out, excess surface water was wiped with tissue paper, and quickly weighed on a microbalance. The water uptake was calculated from the following equation:

$$\text{Wateruptake(\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

where W_{dry} and W_{wet} are the weights of dry and corresponding water-swollen membranes, respectively.

The dimensional stability of membrane was evaluated from measuring the change of film length by:

$$\text{Swellingratio(\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (3)$$

where L_{dry} and L_{wet} are the length of the dry and wet membranes, respectively. The values of the water uptake and swelling ratio are the mean of five measurements, and the standard deviations were ±6% and ±8%, respectively.

Proton conductivity was measured using a two-probe electrochemical impedance spectroscopy technique over the frequency from 1 Hz to 10⁴ Hz (Autolab PGSTAT 30). Membrane samples were placed tightly between two platinum electrodes of the PTFE clamp and immersed in deionized water as a function of temperature. Prior to measurement, the membranes were fully hydrated in ultrapure water for 48 h. At a given temperature, the samples were equilibrated for at least 30 min before measurement. After each measurement, the ultrapure water was replaced. The proton conductivity performed at desired temperature was calculated by using the following relationship:

$$\sigma = \frac{L}{RW} \quad (4)$$

where σ (S cm⁻¹) represents the proton conductivity, L represents the distance between two electrodes, R represents the membrane ohmic resistance, W and T represent the width and thickness of the measured film. The standard deviations of the conductivity values were less than ±8%.

The methanol permeability coefficient was measured using a home-made diffusion cell with a solution containing 10M methanol on one side and deionized water on the other side as describing in the Ref. [30]. Magnetic stirrers were used in each compartment during the measurement to ensure uniformity. The concentration of methanol was determined by gas chromatograph. The methanol permeability was calculated by the following formula:

$$C_B(t) = \frac{A DK}{V_B L} C_A(t-t_0) \quad (5)$$

where A , L , and V_B are the effective area, the thickness of the membrane and the volume of diffusion reservoir, respectively. C_A and C_B are the methanol concentration in feed and in diffusion reservoir, respectively. DK is the methanol permeability.

The oxidation stability of the fresh membrane was determined by Fenton's test.²⁹ A small piece of membrane sample was soaked in Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80°C. The oxidation stability was evaluated by the residual weight after immersing in Fenton's reagent for 1 h and the time when the membrane started to disappear.

Monomer Synthesis

Synthesis of Sodium 3-(4-(2,6-bis(4-nitrophenyl)pyridin-4-yl)phenoxy)propane-1-sulfonate (BNPPS). To a 100 mL three-necked flask with nitrogen gas inlet and outlet and a Dean-Stark trap fitted reflux condenser, 35 mL of DMF was charged. 4.14 g (10 mmol) of 4-(2,6-bis(4-nitrophenyl)pyridin-4-yl) phenol (BNPP), which was synthesized according to the reported method,³¹ was added with stirring under a nitrogen flow. 2.07 g (15 mmol) of K₂CO₃ was added successively and the mixture was stirred at room temperature for 30 min. Then the reaction mixture was stirred at 135°C while adding 10 mL toluene dropwise to remove the formed water from the system, and maintained at 160°C for 5 h. After cooling to room temperature, 2.25 g (10.0 mmol) of 3-bromopropane sulfonic acid sodium salt was feed to the flask and the reaction was performed at 150°C for 30 h. The resulting reaction mixture was poured into tetrahydrofuran (THF) after cooling to room temperature, the precipitation was filtered and washed with tetrahydrofuran and dried in vacuo at 60°C for 10 h. The obtained crude solid was recrystallized from acetonitrile and water ($V_1 : V_2 = 3 : 2$) to give 4.34 g desired yellow product.

Yield: 78%. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.66 (d, 4H, J = 8.8 Hz, H₁), 8.48 (s, 2H, H₃), 8.40 (d, 4H, J = 8.4 Hz, H₂), 8.11 (d, 2H, J = 8.8 Hz, H₄), 7.14 (2H, J = 8.4 Hz, H₅), 4.19 (t, 2H, J = 6.4 Hz, H₆), 2.58 (t, 2H, J = 6.8 Hz, H₈), 2.05 (m, 2H, J = 7.2 Hz, H₇).

Synthesis of 3-(4-(2,6-bis(4-aminophenyl)pyridin-4-yl)phenoxy)propane-1-sulfonic acid (BAPPS). In a 500 mL three-necked round-bottomed flask equipped with a reflux condenser and a dropping funnel. A suspension of BNPPS (3.1 g, 5.6 mmol), palladium on carbon 10% (0.2 g), water (200 mL) and ethanol (100 mL) were charged. Then 80% hydrazine hydrate (8 mL) in water (20 mL) was added dropwise through the funnel over a 5 h period under nitrogen atmosphere. The mixture was refluxed for 30 h and filtered while hot. After cooling to room

temperature, the mixture was filtered into 10 mL concentrated hydrochloric acid solution. The red precipitate was filtered and washed with acetone carefully. The crude product was recrystallized from water and dried at 60°C in vacuo to give 1.1 g of the pure product.

Yield: 42%. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.01 (d, 4H, J = 8.4 Hz, H₁), 7.90 (d, 2H, J = 8.8 Hz, H₄), 7.76 (s, 2H, H₃), 7.07 (d, 2H, J = 8.8 Hz, H₅), 6.68 (4H, J = 8.4 Hz, H₂), 5.42 (s, 4H, H₉), 4.16 (t, 2H, J = 6.8 Hz, H₆), 2.61 (t, 2H, J = 7.2 Hz, H₈), 2.05 (m, 2H, J = 7.2 Hz, H₇).

Synthesis of Random BAPPS-ODA-NTDA Polyimides. A typical synthetic procedure, illustrated by the preparation of SPI-80 copolymer ($x = 80$: BAPPS/ODA = 80/20), is conducted as follows. 0.4096 g (0.8 mmol) of BAPPS, 0.0400 g (0.2 mmol) of ODA were combined in a 25 mL completely dried three-neck flask and stirred magnetically under nitrogen flow. Then 6 mL of *m*-cresol and 0.27 mL of triethylamine were added into the flask. After BAPPS and ODA were completely dissolved, 0.2682 g (1 mmol) of NTDA and 0.27 g of benzoic acid were added to the flask. With stirring, the reaction mixture was kept at 80°C for 4 h and at 180°C for 20 h. After cooling to 80°C, an additional 10 mL of *m*-cresol was added to dilute the highly viscous solution, which was then poured into 100 mL of acetone. The precipitate thus formed was collected by filtration and washed with acetone and water. The dark brown product dried in vacuum at 80°C for 20 h to give product with 97% yield.

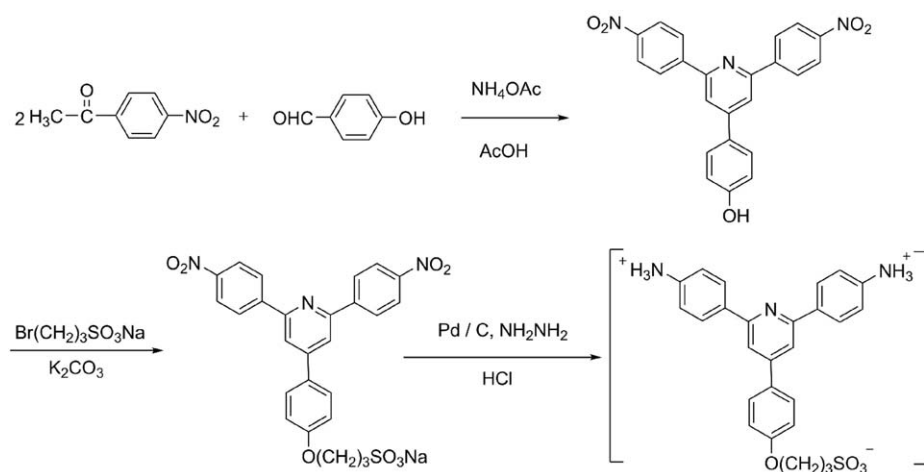
Membrane Formation and Proton Exchange

The resulting polyimides (in triethylammonium salt form) were dissolved in *m*-cresol to form 5 wt % solutions at 80°C overnight. Then the solution was filtered and casted directly onto clean glass plate. The membrane was dried at 120°C for 10 h and peeled from the glass plate by immersing them in water. The as-cast film was soaked in methanol at 60°C for 1 h to remove the residual *m*-cresol, followed by the proton exchange treatment in 1.0N hydrochloric acid at room temperature for 48 h successively. The hydrogen form film was thoroughly washed with deionized water and then dried in vacuum at 120°C for 24 h. The thickness of the resulting membranes was in the range of 30–80 μ m.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Monomers and Polyimides

As shown in Scheme 1, the monomer of BAPPS was synthesized via three-step reactions. First, BNPP was synthesized using a modified Chichibabin reaction according to the reported method.³¹ Then BNPP reacted with 3-bromopropane sulfonic acid sodium salt in the presence of K₂CO₃ to give the intermediate compound BNPPS. BNPPS was reduced in ethanol/water solution in the presence of Pd/C hydrazine hydrate system to give the sulfonated diamine monomer BAPPS. The structure of the desired product was characterized by ¹H NMR spectroscopy in DMSO-*d*₆. Triethylamine was used to liberate the protons of amine groups. As shown in Figure 2, the spectrum confirms the proposed structure of BAPPS.



Scheme 1. Synthesis of the sulfonated diamine monomer (BAPPS).

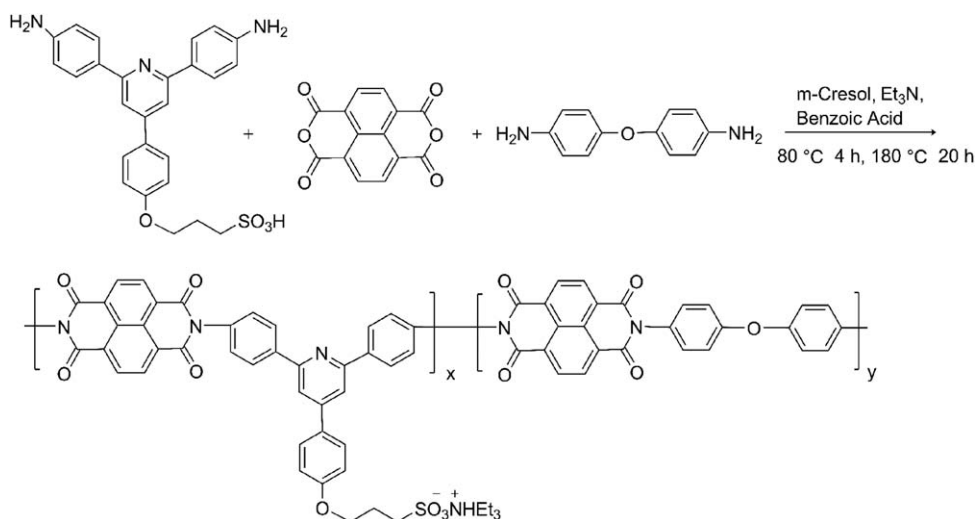
A series of polyimides were synthesized through one pot polycondensation of BAPPS, ODA, and NTDA using *m*-cresol as the solvent in the presence of Et_3N . Benzoic acid was added as a catalyst (Scheme 2). Common nonsulfonated diamine ODA was introduced to provide suitable IEC. The copolymers were denoted as SPI-*x*, where *x* was the molar fraction of BAPPS in the feed and increased from 40 to 80 mol %. The solubility behavior of the polyimide (Et_3N salt form) was studied and the results are summarized in Table I. With increasing IEC, polyimides tended to dissolve in aprotic organic solvents like *m*-cresol, *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO). The heterocycle with alkoxy linkage in polymer backbone can disorder the symmetry of the main chain and reduce the interaction between polymer chains, which are beneficial to improve the solubility of the polymers. The obtained polymers could use NMP as the solvent during the membrane preparation, which is a less toxic solvent than *m*-cresol. The viscosity values were in the range from 1.01 to 1.35 dL g^{-1} (Table II). These results confirmed that high molecular weight copolymers were obtained. The resulting

membranes (Et_3N salt form) were converted to the proton form with 1.00N HCl at room temperature for 48 h.

The FTIR spectra of salt-form SPIs are shown in Figure 1. The peaks around 1713 cm^{-1} (symmetric C=O), 1634 cm^{-1} (asymmetric C=O) and 1344 cm^{-1} (C–N) were attributed to the naphthalenic imide rings. The absorption band appeared at 1540 cm^{-1} was the characteristic one of pyridine rings. The bands at 1038 and 1124 cm^{-1} were assigned to the symmetric and asymmetric O=S=O stretching vibration of sulfonic acid groups. ^1H NMR spectra of copolymers in the triethylammonium salt form were run to confirm the structure of the polymer. Taking SPI-50 as example, all H-signals were assigned to the protons. The integration ratio of these peaks agreed with the structure (Figure 2).

Thermal and Mechanical Properties

The thermal stability of membranes in proton form was studied by TGA under nitrogen atmosphere, and the result of SPI-80 is shown in Figure 3. The membrane showed a two-step degradation pattern. The first step starting from 300°C was caused by



Scheme 2. Synthesis of sulfonated copolyimides.

Table I. Solubility of Sulfonated Polyimides

Polyimides	<i>m</i> -cresol	DMSO	NMP	DMAc	Ethanol	Water
SPI-40	++	+	+	±	–	–
SPI-50	++	++	++	±	–	–
SPI-60	++	++	++	+	–	–
SPI-70	++	++	++	+	–	–
SPI-80	++	++	++	++	–	–

++: Soluble at room temperature; +: Soluble at heated temperature; ±: Partially soluble; –: not soluble.

the loss of sulfoalkoxy groups from SPI-80, implying initial degradation of membrane. The second step around 530°C was attributed to the degradation of the main chain of copolymer. SPI-40, 50, 60, and 70 exhibited similar degradation pattern with that of SPI-80 (data not shown). Table II gives the 10% weight loss temperature ($T_{d10\%}$) of the obtained membranes. Both the decomposition temperature and residual weight of the membranes decreased with increasing of IEC. All of the membranes maintained residual weight more than 60% above 700°C. This result revealed that the obtained ionic crosslinking membranes exhibited good thermal stabilities for DMFC applications.

The mechanical properties of dry SPI-*x* membranes were measured and the results are summarized in Table III. The membranes demonstrated a tensile strength of 31.2–45.1 Mpa, a Young's modulus of 1.23–1.92 Gpa, and an elongation at break of 22.6–77.9%. The pendent sulfoalkoxy groups functioned as a plasticizer for membrane, thus leading to the enhancement of membrane ductility. These results indicated that the side-chain type SPIs films were strong and tough enough for potential use in PEMs.

IEC, Water Uptake, and Dimension Change

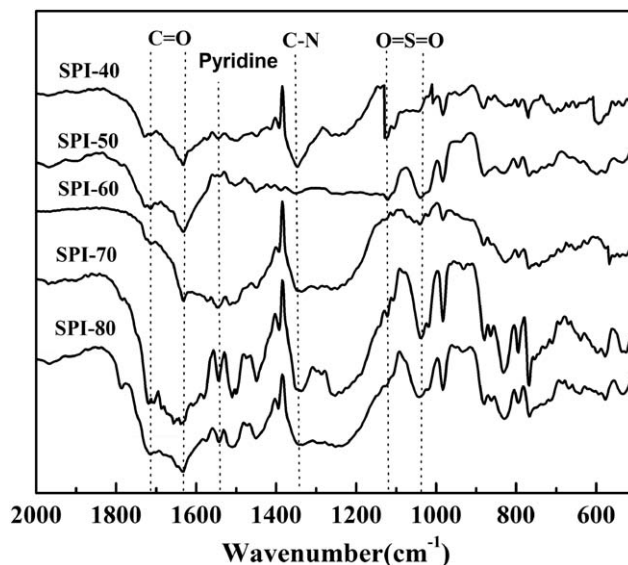
IEC is an important factor to affect many properties of ionomer membranes like proton conductivity and water uptake. The IEC values of membranes obtained by theoretical calculation and titration experiment are compiled in Table II. It is noted that the experimental values were generally much smaller than the theoretical values. This observation implied the formation of an

Table II. Basic Properties of SPI-*x* Membranes

Polymer	η_r (dL g ⁻¹)	IEC (meq g ⁻¹)		$T_{d10\%}$ (°C)
		Theoretical	Titration	
SPI-40	1.35	0.74	0.40	500
SPI-50	1.17	0.88	0.47	518
SPI-60	1.22	1.00	0.49	438
SPI-70	1.19	1.12	0.71	406
SPI-80	1.01	1.23	0.74	428

η_r , the viscosity of the copolyimides measured by Ubbelohde capillary viscometer at 30 ± 0.1°C.

$T_{d10\%}$, the temperature of 10% weight loss of polymers measured by TGA.

**Figure 1.** FTIR spectra of SPI-*x* membranes (salt form).

acid-base complex between the high basicity of the pyridine groups and the sulfonic acid groups. The acid–base interactions (inter or intraionic crosslinking) reduced the contents of free sulfonic acid groups. As a result, the sulfonic acid protons of the copolymer are partly exchanged.

Water uptake of PEM has meaningful effect on the proton conductivity, dimensional stability, and mechanical strength. Figure 4 shows the temperature dependence of water uptakes of obtained SPI-*x* membranes. Clearly, the water uptake increased with IEC and enhanced very slowly with temperature. The water uptake of SPI-*x* membranes with calculated IEC of 0.40–0.74 meq g⁻¹ varied from 15% to 30% at 80°C (Table IV). SPI-80 membrane (IEC 0.74 meq g⁻¹) showed a high water uptake of 26.52%, while the water uptake of NTDA-ODADS-DATPA (3 : 7) (IEC 0.89 meq g⁻¹) was 18% at room temperature.²⁸ The relatively higher water uptake suggested that the sulfoalkylated side chains widened the inter-chain separations and increased the free volume for absorbing water molecules. Swelling ratio of the SPI membranes at six different temperatures namely, 30, 40, 50, 60, 70, and 80°C is shown in Figure 5. Similar to the water uptake, the swelling ratio of membranes increased with IEC values and temperatures. All the membranes exhibited swelling ratio with 2.48–6.94% at 80°C. The water uptake and swelling ratio of SPI-*x* membranes were attributed to the introduction of the pendent sulfoalkylated chains and basic pyridine rings into copolymer backbone. The interaction between the flexible sulfoalkylated grafting and *N*-bases play an important role for the IECs, water uptake and dimensional change of membranes.

Proton Conductivity and Methanol Permeability

The proton transport behavior of membranes was measured under fully hydrated condition using impedance diagrams, and the results at different temperature are presented in Table IV and Figure 6. As indicated, the proton conductivities of the SPI-*x* membranes increased slightly with elevating temperatures.

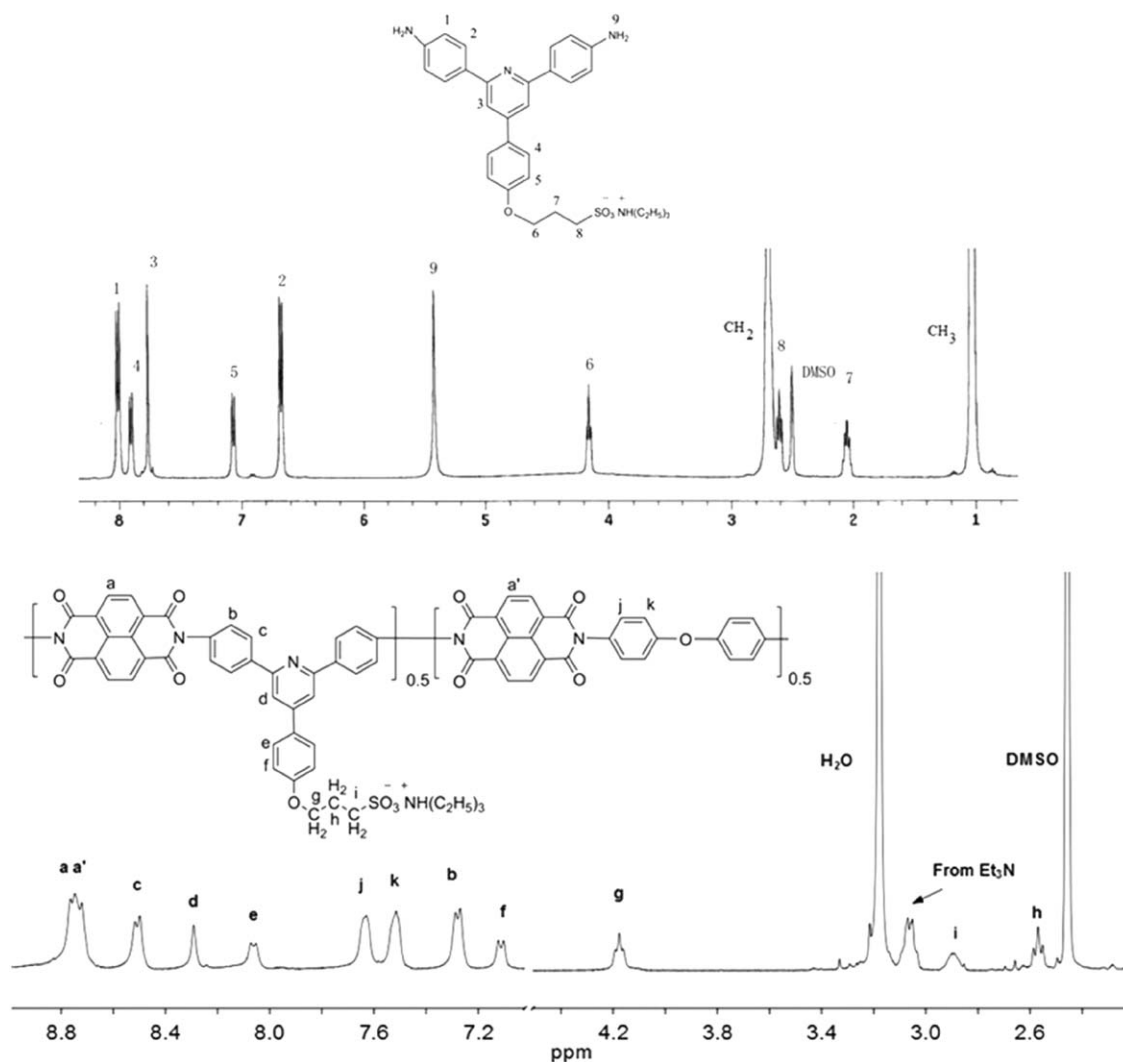


Figure 2. ^1H NMR spectra of BAPPS and SPI-50, respectively.

For example, the proton conductivity of SPI-50 increased from 3.9 mS cm^{-1} at 30°C to 7.8 mS cm^{-1} at 80°C . The low proton conductivity was attributed to the low IEC and acid–base inter-

actions. However, the proton conductivity of SPI-60 with IEC 0.49 meq g^{-1} was 9.4 mS cm^{-1} , which was higher than that of NTDA-SADM-ODA (7 : 3) (8.6 mS cm^{-1}) with IEC 0.489 meq g^{-1} under the same condition.²⁹ The relatively high proton conductivity could be attributed to the higher water uptake and the flexible pendent sulfonated aliphatic chains.

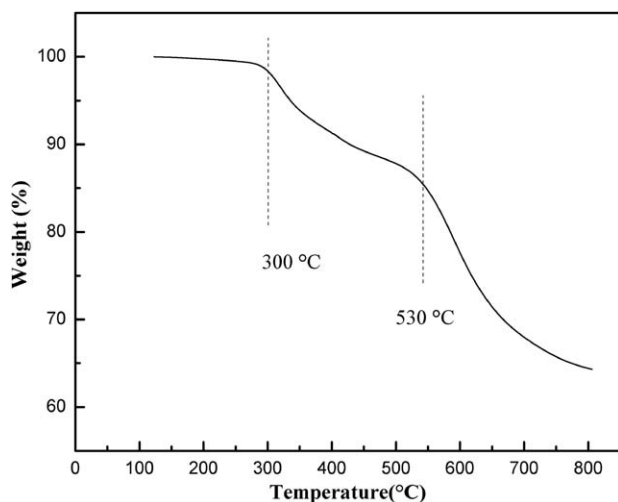


Figure 3. TGA curve of SPI-80 membrane (proton form).

Table III. Mechanical and Oxidation Stability of SPI-*x* Membranes

Polymer	Tensile strength (MPa)	Maximum elongation (%)	Young's modulus (GPa)	Oxidative stability	
				RW (%) ^a	<i>t</i> (h) ^b
SPI-40	39.2	77.9	1.92	100	18
SPI-50	39.7	49.5	1.23	99	16
SPI-60	38.6	75.4	1.72	98	15
SPI-70	45.1	39.9	1.43	97	11
SPI-80	31.2	22.6	1.48	95	10

^a Remaining weight after treating in Fenton's Reagent for 1 h.

^b Disappearance time of membranes in Fenton's Reagent.

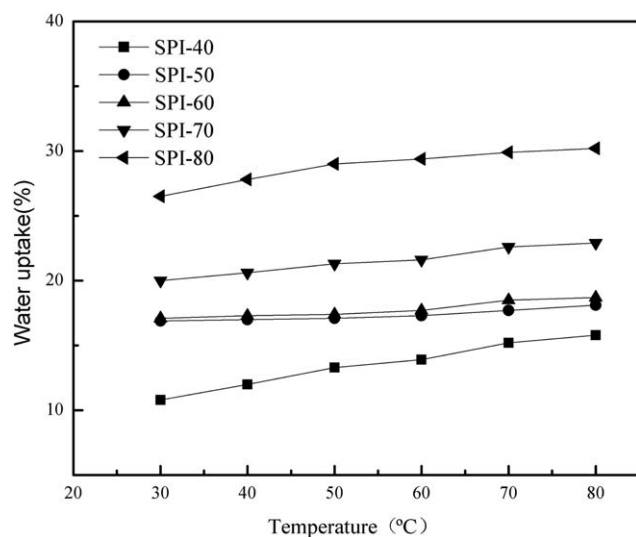


Figure 4. Water uptake of SPI-x membranes at different temperatures.

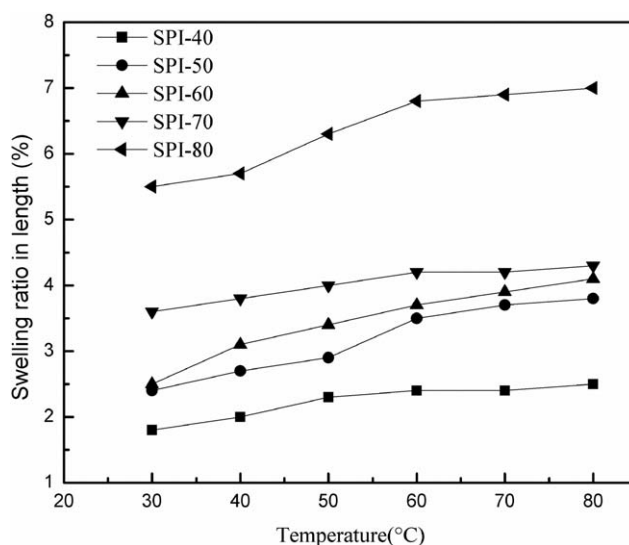


Figure 5. Swelling ratio of SPI-x membranes at different temperatures.

Methanol crossover from the anode to the cathode will restrict the potential applications of the membranes in DMFCs. The methanol transport behavior of SPI-x membranes and Nafion 117 were investigated and the results are summarized in Table IV. The methanol permeability values of SPI-x membranes at room temperature were in the range of $0.33\text{--}1.22 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which were much lower than that of Nafion 117 ($23.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) measured at the same condition. The methanol permeability increased with IEC, which was attributed to the increased contents of sulfonic acid groups and water uptake. Moreover, the increased flexible sulfoalkylated chains will widen the interchain separations and increase the trend of methanol crossover. Selectivity (the ratio of proton conductivity to methanol permeability coefficient) is a combined factor to evaluate DMFC performances. The resulting SPI membranes displayed higher selectivity than Nafion 117 (Table IV).

Oxidative Stability of Membranes

Previous research has demonstrated that oxygen, hydroxide, peroxide attack the polymer backbone resulting in the degradation of membrane. Oxidative stability is one of the important parameters of aromatic PEMs, which determines their durability under harsh conditions. The oxidative stability of all the mem-

branes was evaluated by the residual weight after the typical aging test and the completely dissolved time in Fenton's Reagent at 80°C . As presented in Table III, the oxidation stability of these samples decreased with an increasing of IEC. Except for SPI-80, the weight of all sample membranes was above 97% after treating in Fenton's Reagent at 80°C for 1 h. All the resulting membranes stayed integrated in Fenton's Reagent for over 10 h at 80°C , which indicated that these films exhibited good stability in oxidative resistance.

CONCLUSIONS

In this study, a series of sulfonated polyimides containing pyridine rings and sulfoalkylated side chains have been prepared as proton conductive materials. The resulting membranes exhibited excellent dimensional and thermal stability. The introduction of pyridine rings into copolymer backbone induced ionic crosslinked structure, which resisted polymer swelling in water and increased the mechanical stability of the membranes. The flexible sulfoalkylated side chains induced the formation of chemically stable microstructures resistant to chemical attacks. Furthermore, the copolymers presented low methanol permeability, which suggested potential feasibility of PEM materials for DMFC applications.

Table IV. Water Uptake, Swelling Ratio in Length and Proton Conductivity, and Methanol Permeability of SPI-x Membranes

Polymer	Water uptake (%)		Swelling ratio in length (%)		Proton conductivity (mS cm^{-1})		Methanol permeability ($\text{cm}^2 \text{ s}^{-1}$) $\times 10^{-7}$	Selectivity (Ss cm^{-3}) $\times 10^4$
	30°C	80°C	30°C	80°C	30°C	80°C	30°C	
SPI-40	10.76	15.82	1.82	2.48	3.2	5.2	0.33	9.70
SPI-50	16.89	18.14	2.40	3.83	3.9	7.8	0.69	5.65
SPI-60	17.09	18.73	2.52	4.11	4.8	9.4	0.83	5.78
SPI-70	20.0	22.90	3.63	4.29	5.1	10.0	0.92	5.54
SPI-80	26.52	30.20	5.47	6.94	10.1	13.4	1.22	8.28
Nafion 117	19.34	29.23	13.8	20.14	47.9	150.7	23.8	2.01

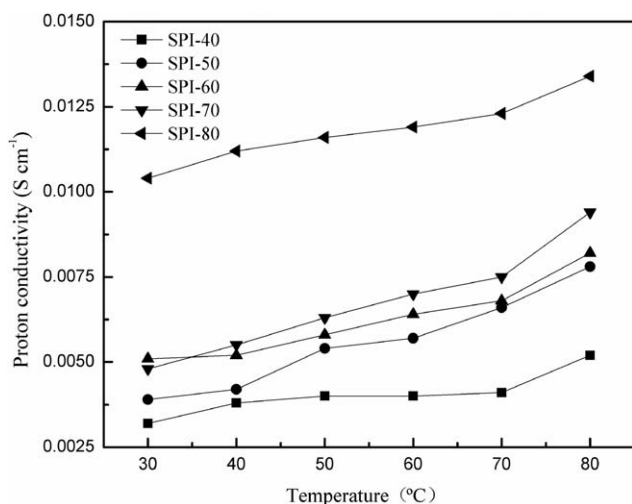


Figure 6. Proton conductivity of SPI-x membranes as function of temperature under 100% RH.

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REFERENCES

- Ahmed, M.; Dincer, I. *Int. J. Energy Res.* **2011**, *35*, 1213.
- Neburchilov, V.; Martin, J.; Wang, H. J.; Zhang, J. J. *J. Power Sources* **2007**, *169*, 221.
- Kamarudin, S. K.; Achmad, F.; Daud, W. R. W. *Int. J. Hydrogen Energy* **2009**, *34*, 6902.
- Jiang, Z. Q.; Zhao, X. S.; Fu, Y. Z.; Manthiram, A. *J. Mater. Chem.* **2012**, *22*, 24862.
- Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587.
- Laberty-Robert, C.; Vallé, K.; Pereira, F.; Sanchez, C. *Chem. Soc. Rev.* **2011**, *40*, 961.
- Zhou, W. H.; Xiao, J. C.; Chen, Y. W.; Zeng, R.; Xiao, S. Q.; He, X. H.; Li, F.; Song, C. S. *J. Appl. Polym. Sci.* **2010**, *117*, 1436.
- Zhang, Y.; Wan, Y.; Zhao, C.; Shao, K.; Zhang, G.; Li, H.; Lin, H.; Na, H. *Polymer* **2009**, *50*, 4471.
- Lee, H.-F.; Wang, P.-H.; Huang, Y.-C.; Su, W.-H.; Gopal, R.; Lee, C. C.; Holdcroft, S.; Huang, W.-X. *J. Polym. Sci. Part A: Polym. Chem.* **2014**, *52*, 2579.
- Chen, G. F.; Pei, X. L.; Wei, H. B.; Xu, L. B.; Fang, X. Z. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/app.41501.
- Wei, H.; Chen, G.; Cao, L.; Zhang, Q.; Yan, Q.; Fang, X. *J. Mater. Chem. A* **2013**, *1*, 10412.
- Yasuda, T.; Nakamura, S.-I.; Honda, Y.; Kinugawa, K.; Lee, S.-Y.; Watanabe, M. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1783.
- Aili, D.; Li, Q. F.; Christensen, E.; Jensen, J. O.; Bjerrum, N. B. *Polym. Int.* **2011**, *60*, 1201.
- Maity, S.; Jana, T. *Macromolecules* **2013**, *46*, 6814.
- Seesukphronrarak, S.; Ohira, A. *Chem. Comm.* **2009**, *31*, 4744.
- Si, K.; Wycisk, R.; Dong, D.; Cooper, K.; Rodgers, M.; Brooker, P.; Slattery, D.; Litt, M. *Macromolecules* **2012**, *46*, 422.
- Li, N. W.; Cui, Z. M.; Zhang, S. B.; Li, S. H. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 2820.
- Fang, J. H.; Guo, X. X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K.-I. *Macromolecules* **2002**, *35*, 9022.
- Hu, Z. X.; Yin, Y.; Okamoto, K.-I.; Moriyama, Y.; Morikawa, A. *J. Membr. Sci.* **2009**, *329*, 146.
- Yin, Y.; Fang, J. H.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K.-I. *J. Mater. Chem.* **2004**, *14*, 1062.
- Asano, N.; Aoki, M.; Suzuki, S.; Miyatake, K.; Uchida, H.; Watanabe, M. *J. Am. Chem. Soc.* **2006**, *128*, 1762.
- Yin, Y.; Du, Q.; Qin, Y.; Zhou, Y.; Okamoto, K.-I. *J. Membr. Sci.* **2011**, *367*, 211.
- Maranesi, B.; Hou, H.; Poini, R.; Sgreccia, E.; Alberti, G.; Naraducci, R.; Knauth, P.; Di Vona, M. L. *Fuel Cells* **2013**, *13*, 107.
- Luo, H.; Vaivars, G.; Mathe, M. *Int. J. Hydrogen Energy* **2012**, *37*, 6148.
- Wang, J.; Zhao, C. J.; Zhang, G.; Zhang, Y.; Ni, J.; Ma, W. J.; Na, H. *J. Membr. Sci.* **2010**, *363*, 112.
- Li, W.; Manthiram, A.; Guiver, M. D. *J. Membr. Sci.* **2010**, *362*, 289.
- Jang, W. B.; Sundar, S.; Choi, S.; Shul, Y.-G.; Han, H. *J. Membr. Sci.* **2006**, *280*, 321.
- Zhang, F.; Li, N.; Cui, Z.; Zhang, S.; Li, S. *J. Membr. Sci.* **2008**, *314*, 24.
- Lei, R.; Kang, C.; Huang, Y.; Li, Y.; Wang, X.; Jin, R.; Qiu, X.; Ji, X.; Xing, W.; Gao, L. *J. Appl. Polym. Sci.* **2009**, *114*, 3190.
- Guo, W.; Li, X.; Wang, H.; Pang, J.; Wang, G.; Jiang, Z.; Zhang, S. *J. Membr. Sci.* **2013**, *444*, 259.
- Tamami, B.; Yeganeh, H. *Polymer* **2001**, *42*, 415.