

SULFONATED POLYIMIDES CONTAINING PYRIDINE GROUPS AS PROTON EXCHANGE MEMBRANE MATERIALS*

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Abstract A series of sulfonated polyimides (SPIs) containing pyridine groups were prepared by direct polycondensation from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS) and 4-(4-methoxy)phenyl-2,6-bis(4-aminophenyl)pyridine (DAM). The resulting copolymers displayed good solubility in common organic solvents. Flexible, transparent, tough membranes were obtained *via* solution casting. All the films showed high thermal stability with desulfonation temperature over 300°C. They exhibited prominent mechanical properties with Young's modulus around 2.0 GPa. High proton conductivity (0.23 S/cm at 100% RH) was also observed. More importantly, the new materials exhibited low water uptake (30 wt%–75 wt% at 80°C) and improved water stability, which were attributed to the acid-base interaction between sulfonic acid and pyridine functional groups.

Keywords: Sulfonated polyimide; Pyridine; Acid-base interaction; Proton conductivity.

INTRODUCTION

As the increasing demand for clean, efficient and portable energy devices, proton exchange membrane fuel cells (PEMFCs) have been attracting considerable attention as clean electrical power source for vehicles, stationary and portable applications^[1–3]. The key component of fuel cells is the proton exchange membrane (PEM), which is used to conduct proton and separate gas. Nafion is by far the most studied PEM materials with excellent proton conductivity and unsurpassed longevity in a fuel cell environment^[4, 5]. However, there are some demerits including high cost, low proton conductivity at low humidity or high temperatures (> 80°C), and high methanol permeability, which seriously limit their application^[2, 6]. Thus, the development of alternative non-fluorinated materials with low cost and high performance is strongly desired^[7].

Sulfonated polyimides (SPIs) are one of the most promising candidates for fuel cell applications. Many works have been carried out on the structure-property relationship of SPIs^[8–16]. Although some SPIs exhibited excellent fuel cell performance, water stability of SPI is a major remaining challenge. As water molecules are carriers of the protons, high water uptake is needed to ensure high proton conductivity. However, high water uptake may result in membrane swelling, *i.e.* loss of mechanical stability. Introducing *N*-heterocycle into polymer backbone to form acid-base interactions between the sulfonic acid group and heterocyclic pyridine group is an attractive strategy to depress membrane swelling^[17–21]. It was also reported that polyimides

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containing heterocyclic units possess excellent thermal stabilities^[22]. In order to prepare novel processable sulfonated polyimide with enhanced thermal stability and low swelling property, diamine monomer containing pyridine heterocyclic group was introduced. A series pyridine based SPIs were synthesized from NTDA, ODADS and 4-(4-methoxy)phenyl-2,6-bis(4-aminophenyl)pyridine (DAM). Their water uptake, proton conductivity, membrane stability and methanol permeability were investigated.

EXPERIMENTAL

Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) was purchased from Aldrich Chemical Co. All other reagents were purchased from Shanghai Chemical Reagent Plant. NTDA was purified by vacuum sublimation before use. ODADS was synthesized by the literature method^[9]. DAM was synthesized according to the literature method^[23]. Triethylamine (Et₃N) was dried over sodium then distilled. *m*-Cresol was purified by distillation under reduced pressure before use. Other reagents were of analytical grade and used as received.

Preparation of NTDA-ODADS-DAM Based SPI Membranes

Various NTDA-ODADS-DAM based copolyimides were synthesized by the typical method as in our previous work^[19]. Taking the synthesis of SPI-50 as a typical example: To a 50 mL completely dried three-neck flask were added 0.3602 g (1 mmol) of ODADS, 0.3670 g (1 mmol) DAM, 0.5360 g (2 mmol) of NTDA and 0.5190 g of benzoic acid, followed by the addition of 6.0 mL of *m*-cresol, and 0.31 mL of triethylamine. The mixture was stirred at room temperature for 10 min and then heated to 80°C for 4 h and 180°C for 8 h under nitrogen flow. After cooling to 80°C, the solution was poured into 100 mL acetone. The resulting fiber-like precipitate was collected by filtration, washed with acetone, and dried in vacuum at 80°C for 12 h. Yield: 96%. The other SPIs were synthesized by the same method and their yields are 95%–97%.

Films (TEA salt form) were prepared by casting their *m*-cresol solution (10 wt%) onto glass dishes and dried at 80°C for 24 h. The membranes were soaked in alcohol at room temperature for 10 h to remove the residual solvent. The proton-exchange treatment was carried out in 1 mol/L H₂SO₄ solution at room temperature, and the completion of proton exchange was confirmed from the disappearance of the peaks corresponding to the protons of triethylamine from the ¹H-NMR spectra of the membranes, then the proton form films were washed with deionized water thoroughly.

Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Bio-Red Digilab Division FTS-80 spectrometer. ¹H-NMR spectra was recorded on a Varian Unity spectrometer at 400 Hz with tetramethylsilane as an internal standard. Thermo-gravimetric analyses were obtained at a heating rate of 10 K/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 *m*-cresol.

Ionic-exchange Capacity

The ionic-exchange capacity (IEC) was measured by means of a classical titration method. A membrane sample (about 100 mg) was soaked in 100 mL saturated NaCl solution for 2 days at 30°C. The released protons were titrated using a 0.01 mol/L NaOH solution.

Water Uptake and Dimensional Change

The membranes were first dried in a vacuum oven at 100°C for 12 h. Then the water sorption experiments were carried out by immersing three sheets of films (about 100 mg per sheet) of each polyimide in water at 80°C for 10 h. Then the films were taken out, wiped with tissue paper and quickly weighed on a microbalance. Water uptake (*S*) was calculated from Eq. (1):

$$S = (W_s - W_d)/W_d \times 100\% \quad (1)$$

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

Dimensional change was measured by immersing the round shape samples into deionized water at 80°C for 5 h. The changes of thickness and diameter were calculated from Eq. (2):

$$\begin{aligned}\Delta t_c &= (t - t_s)/t_s \\ \Delta l_c &= (l - l_s)/l_s\end{aligned}\quad (2)$$

where t_s and t are the thickness, l_s and l are the diameter of the membrane before and after soaking treatment, respectively.

Proton Conductivity

Proton conductivity was measured by using an 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 four-point-probe cell with two pairs of platinum plate electrodes pressed with a sample membrane was mounted in a sealed Teflon cell. The distance between two electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. The resistance value associated with the membrane conductivity was determined from high-frequency intercept of the impedance with the real axis. Proton conductivity (σ) was calculated from Eq. (3):

$$\sigma = d/(L_s W_s R) \quad (3)$$

where σ and d denote the proton conductivity and distance between reference electrodes; L_s and W_s are the thickness and width of the membrane, respectively; R is the resistance value measured.

Methanol Permeability Measurements

Methanol permeability of membranes was measured using a liquid permeation cell composed of two compartments, which were separated by a vertical membrane. The membrane was first immersed in water to get the water-swollen sample and then set into the measurement cell (effective area: 3.14 cm²). One compartment of the cell (V_1) was filled with methanol feed solution, and the other compartment (V_2) was filled with distilled water. Methanol permeates across the membrane by the concentration difference between the two compartments. The compartments were stirred continuously during the permeability measurement. The methanol permeability (P_M) can be calculated from Eq. (4):

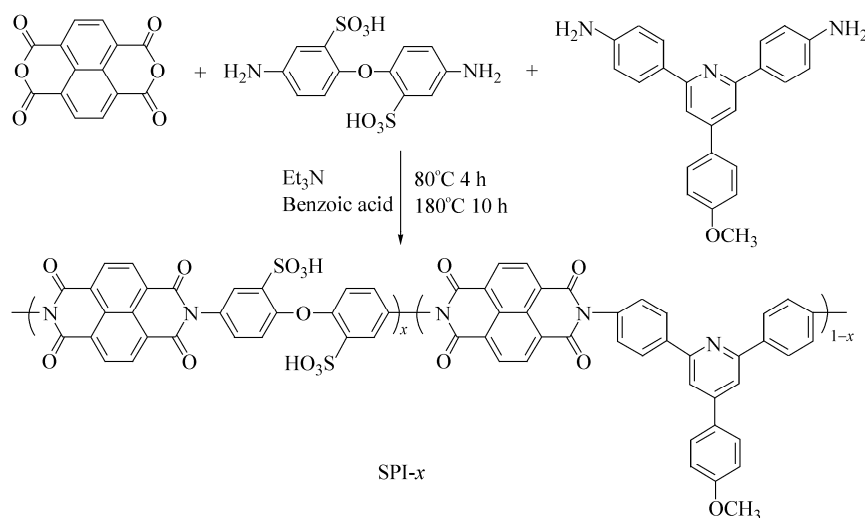
$$P_M = V_2 L k / A c_1 \quad (4)$$

where P_M is the methanol permeability, A and L are the area and thickness of the swollen membrane, respectively; c_1 is the initial and permeated methanol concentration; k is the slope of the straight line of permeated methanol concentration and their corresponding measure-time t . The methanol concentration was measured by using a gas chromatography equipped with a thermal conductivity detector (Shimadzu, GC-2010A, Tokyo, Japan).

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polyimides

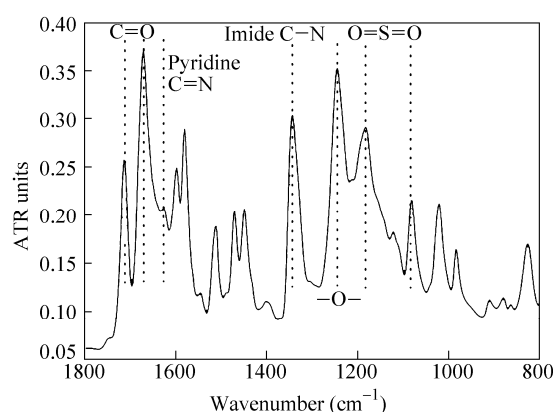
The preparation of resulting SPIs was carried out by a one-step method in *m*-cresol in the presence of triethylamine (TEA) and benzoic acid (catalyst) (Scheme 1). Various SPI-*x* were synthesized by controlling the feeding ratio of ODADS to DAM, where *x* indicated the molar percentage of ODADS and increased gradually from 30 mol% to 70 mol%. The pyridine based SPIs generally show fairly high inherent viscosity (1.14–1.38 dL/g) (Table 1), indicating that high molecular weight polymers are obtained. Their solubility behaviors (TEA salt form) are also listed in Table 1. The derived SPIs show much better solubility than other SPIs^[9, 10]. They are soluble in common organic solvents, such as *m*-cresol, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) and *N*-methyl pyrrolidone (NMP). The heterocycle with bulky pendant group in polymer backbone can lower the packing density of the polymer chain, which is beneficial to enhance the solubility of the polyimides.

**Scheme 1** Synthesis of SPI-*x***Table 1.** Inherent viscosity (η) and solubility behaviors of sulfonated polyimides in TEA salt form

SPI- <i>x</i>	η (dL/g)	Solvents			
		<i>m</i> -Cresol	DMAc	DMSO	NMP
SPI-30	1.14	+	+	+	+
SPI-40	1.17	++	+	+	+
SPI-50	1.16	++	+	+	+
SPI-60	1.38	++	+	+	+
SPI-70	1.38	++	+	+	+

+: soluble at 50°C; ++: soluble at room temperature

The structures of the derived TEA-free films were characterized by FTIR spectra. Figure 1 shows the IR spectrum of SPI-60 as a representative example (only zone region from 800 cm^{-1} to 1800 cm^{-1} is shown for clarity). The corresponding peaks are assigned as following: 1710 and 1668 cm^{-1} : $\nu_{\text{C=O}}$, 1346 cm^{-1} : $\nu_{\text{C-N}}$ imide, 1264 cm^{-1} : $\nu_{\text{O-}}$, 1188 and 1098 cm^{-1} : $\nu_{\text{S=O}}$, 1626 cm^{-1} : $\nu_{\text{C=N}}$ pyridine.

**Fig. 1** FTIR spectrum of SPI-60

Thermal Stability and Mechanical Properties

Thermal stability of the SPIs was investigated by TGA measurements. Figure 2 shows the TGA curves of resulting SPI membranes. All the membranes display three-step degradation. The initial weight loss around

100°C is due to the evaporation of absorbed water in the sample. The second stage weight loss starting from 300°C is attributed to the decomposition of the sulfonic acid groups. The third stage above 550°C is assigned to the degradation of polymer backbone. According to the electron-withdrawing effect of sulfonic acid groups, both the temperature of thermal degradation and residual weight of the membranes decrease with the increase of degree of sulfonation (DS)^[24, 25]. But the resulting membranes still exhibit high thermal stability that all of them maintain residual weight more than 65% above 550°C. The mechanical properties of SPI membranes are important factors affecting membrane performance. As shown in Table 2, all the membranes exhibit excellent mechanical properties with Young's modulus (YM) of 1.89–2.55 GPa, maximum stress (MS) on a scale of 83–161 MPa, and elongation at break (EB) ranging from 30% to 124%.

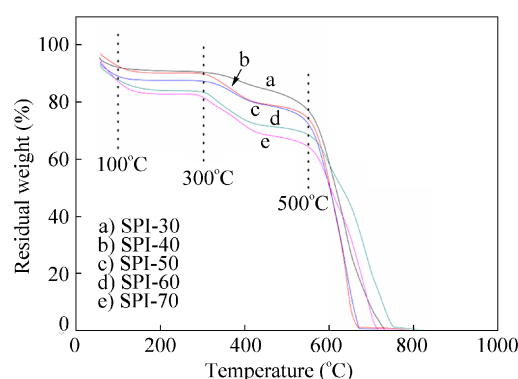


Fig. 2 TGA curves of resulting SPI membranes

Table 2. Mechanical properties of the resulting membranes

SPI- <i>x</i>	Young's modulus (GPa)	Maximum stress (MPa)	Elongation at break (%)
SPI-30	1.89	83.62	47.88
SPI-40	2.34	126.86	89.83
SPI-50	2.37	128.83	31.39
SPI-60	2.55	160.57	30.73
SPI-70	2.26	158.08	123.51

Ionic-exchange Capacity (IEC), Water Uptake (WU) and Dimensional Change

Membrane swelling is a critical issue for membrane electrode assembly (MEA) stability in fuel cells, and it generally trends with IEC and WU. IEC, WU and dimensional change of the resulting SPI membranes are shown in Table 3. It is noted that all the membranes display much lower experimental IEC values than theoretical ones, which are consistent with our previous work^[19]. We have proved that the lower IEC values were attributed to the acid-base interaction between sulfonic acid group and pyridine ring by reducing the content of free sulfuric acid groups^[19]. What's more, all the NTDA-ODADS-DAM based SPI membranes (calculated IEC 1.01–2.36 mequiv/g) show low WU values from 30% to 75% at 80°C, while the WU value of NTDA-ODADS-ODA (1/1) (calculated IEC 1.95 mequiv/g) is 87% at 80°C^[19]. The relatively low WU values

Table 3. IEC, WU and dimensional change of SPI membranes at 80°C

SPI- <i>x</i>	IEC (mequiv/g)		WU (%)	Dimensional change	
	<i>T</i>	<i>E</i>		Δt_c	Δl_c
SPI-30	1.01	0.55	30.08	0.059	0.055
SPI-40	1.34	0.83	34.91	0.074	0.066
SPI-50	1.68	1.05	51.65	0.10	0.082
SPI-60	2.02	1.36	64.71	0.15	0.085
SPI-70	2.36	1.49	75.66	0.21	0.10

E: experimental IEC; *T*: theoretical IEC

suggest that the acid-base interaction can contribute to the depression of water absorption. Low dimensional change is also obtained (Table 3). The dimensional change of membrane with low DS (< 60 mol%) is below 0.1 both in thickness and planar direction. Both of the low WU and dimensional change are caused by the acid-base interaction, thus, the membrane swelling is depressed.

Proton Conductivity and Methanol Permeability

The proton conductivities of the resulting membranes with various DS at 100% RH are plotted as a function of temperature as shown in Fig. 3. For comparison, the conductivity of Nafion 117 was also analyzed under the same condition. All the membranes display increased proton conductivities with increasing temperature. For example, the proton conductivities of SPI-70 increase from 0.10 S/cm at 20°C to 0.23 S/cm at 80°C, which are larger than those of Nafion 117 under the same experimental condition. In addition, the proton conductivities increase obviously as DS increase, which is a typical behavior of sulfonated polyimide membranes. Comparing with Nafion 117, membranes with low DS exhibited lower proton conductivity, which is attributed to the limited microphase separation and lower acidity than those of the perfluorinated ionomers.

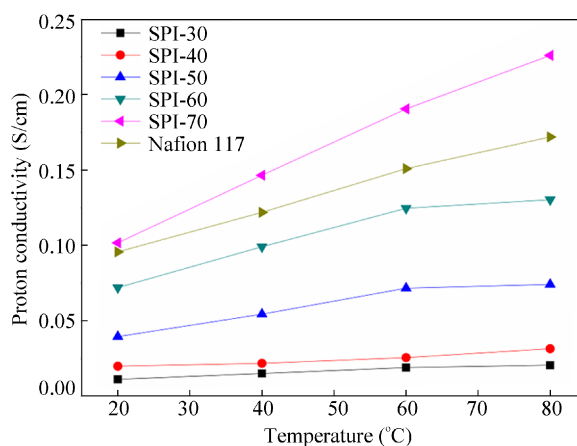


Fig. 3 Proton conductivities of SPI membranes with various DS and Nafion 117 as a function of temperature at 100% RH

As shown in Table 4, the pyridine based SPI membranes exhibit methanol permeability at room temperature from $0.88 \times 10^{-7} \text{ cm}^2/\text{s}$ to $3.19 \times 10^{-7} \text{ cm}^2/\text{s}$, which are about one order of magnitude lower than that of Nafion membranes ($2.6 \times 10^{-6} \text{ cm}^2/\text{s}$)^[26]. The ratios of σ to P_M , $\phi = \sigma/P_M$, are also listed in Table 4. The ratio ϕ is an effective parameter to evaluate the membrane performance in a fuel cell system. The resulting SPI membranes displayed much higher ϕ values than Nafion 117. These properties are useful to enhance the fuel cell performance.

Table 4. Proton conductivities and methanol permeability of SPI-x membranes

SPI-x	Proton conductivity (S/cm)				$P_M \times 10^7$ (cm^2/s)	$\phi \times 10^{-4}$ (S/cm^3)
	20°C	40°C	60°C	80°C		
SPI-30	0.0113	0.0152	0.0192	0.0207	0.88	12.84
SPI-40	0.0200	0.0219	0.057	0.0316	1.53	13.07
SPI-50	0.0396	0.0545	0.0717	0.0742	1.99	19.90
SPI-60	0.0721	0.0992	0.125	0.130	2.08	34.66
SPI-70	0.102	0.147	0.191	0.226	3.19	31.91
Nafion 117	0.0958	0.122	0.151	0.172	26	3.68

Membrane Stability

The stability test of pyridine based SPI membranes toward water was carried out by immersing the membranes into de-ionized water at 80°C as shown in Table 5. By only replacing the ODA moiety of NTDA-ODADS-ODA based membrane by DAM, water stability of the resulting membranes was improved significantly, which suggested the contribution of pyridine groups to the depression of membrane swelling. For example, the NTDA-ODADS-ODA (1/1) based membrane (IEC 1.95 mequiv/g) can only maintain 25 h in de-ionized water at 80°C^[9], while the water stability of the pyridine based SPI-50 (IEC 1.68 mequiv/g) and SPI-60 (IEC 2.02 mequiv/g) membranes can achieve 130 h and 80 h under the same condition, respectively. Although the acid-base interaction between sulfonic acid and pyridine group could depress membrane swelling in some extent, water stability of the resulting membranes is still poorer than that of other side-chain-type SPI membranes^[13, 14, 19]. The unfavorable effect of the main-chain-type ODADS with poor basicity, which is more hypersensitive to be attacked by water, is the main reason for the poor water stability.

Table 5. Water and oxidative stability of the resulting membranes

SPI-x	Thickness (μm)	Water stability ^a	Oxidative stability ^b
SPI-30	30	> 200 h	33 h
SPI-40	50	180 h	32 h
SPI-50	43	130 h	30 h
SPI-60	52	80 h	25 h
SPI-70	60	56 h	20 h

^a Test at 80°C; ^b Test at 30°C

The oxidative stability of SPI membranes was also investigated by immersing the samples into Fenton's reagent (30×10^{-6} FeSO₄ in 30% H₂O₂) at 30°C. The oxidative stability was characterized by the expended time that the membranes started to dissolve as shown in Table 5. Since the oxidative species such as HO· and HOO· accompany some water molecules when reacting to the substances, the oxidative stability of SPI-x is improved as decreasing in the sulfonation degree. The oxidation stabilities of all the resulting membranes are comparable to that of the main-chain-type SPIs^[9, 10]. Comparing with Nafion 117, which have excellent water and oxidative stability according to their hydrophobic perfluorinated backbones^[27], the water and oxidative stability of the resulting SPI membranes need to be improved. Further investigation is in progress.

CONCLUSIONS

A series of novel SPIs containing pyridine groups were prepared from NTDA, ODADS and DAM. The novel SPIs displayed good solubility in common organic solvents. The resulting membranes exhibited high thermal stability and excellent mechanical properties by the introduction of pyridine groups. All the membranes showed low methanol permeability and high proton conductivity, resulting in high ϕ values, which were much higher than those of Nafion 117. According to the acid-base interaction between sulfonic acid and pyridine group, water stability of the pyridine based membrane was improved in some extent. Thus, the results presented herein would provide a new strategy for the designing of novel SPIs for PEM application.

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