

Sulfonated Polyimides Containing 1,2,4-Triazole Groups for Proton Exchange Membranes

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Abstract A series of sulfonated polyimide copolymers as novel proton exchange materials were synthesized by the polycondensation of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA), sulfonated diamine based on pyridine group and diamine containing *N*-phenyl-1,2,4-triazole moiety. Flexible, transparent and tough membranes with high thermal stability and good mechanical properties were obtained. They exhibited good stability in boiling water and Fenton's reagent at 80 °C. More interestingly, a nonlinear relationship between proton conductivities of the resulting membranes and the degree of sulfonation (DS) was observed. The membrane with 50% DS exhibited the maximum proton conductivity, which was due to the combinational contributions of sulfonic acid and *N*-phenyl-1,2,4-triazole groups. Thus, the *N*-phenyl-1,2,4-triazole moiety in this study not only can depress water absorption but also increase proton conductivity, especially at low DS.

Keywords: Triazole; Acid-base interaction; Sulfonated polyimide; Proton exchange membrane.

INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) is an attractive energy conversion system for both automobile and stationary applications among the five types fuel cells^[1–3]. The key component of PEMFC is the proton exchange membrane (PEM), which is used to conduct proton and separate gas. The current state-of-the-art PEMs are perfluorinated membranes Nafion^[4, 5], which show excellent performance in fuel cell environment due to their high conductivity and potentially long-term durability. However, their considerable drawbacks with respect to costs and disposal have stimulated extensive research on the investigation of promising non-fluorinated alternatives^[6–9].

Sulfonated polyimides (SPIs) have received considerable attention in the past decades due to their potential application in PEMFCs^[8–12]. Recently, researchers have focused the investigation on the structure-property relationship of SPIs, and some SPIs with reasonably high PEMFC performance were developed^[13–18]. However, to effectively balance the contradiction between high membrane stability and sufficient proton conductivity remains a major challenge^[19]. In order to obtain high conductivity, high DS is needed. Meanwhile much higher DS results in extreme swelling of sulfonated polymer membranes, *i.e.* loss of dimensional and mechanical stability. Various modified PEM materials have been designed to overcome this problem, such as blending polymers^[20, 21], covalently crosslinked ionomer membranes and acid-base blend membranes^[22–28]. Kerres and coworkers have reported that the interactions between the different blend components by van-der-waals forces and hydrogen bridges were too low to sufficiently reduce the swelling degree, while the covalent crosslinks were

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so strong that the membranes became brittle, especially when drying out^[28]. The acid-base interactions, which like ionic crosslinks by base protonation and hydrogen bridges, could reduce the swelling degree markedly and also maintain the flexibility of membranes^[28].

One of the effective strategies for SPI membranes is structural modification of monomers by incorporating *N*-heterocycles to form acid-base interactions between the sulfonic acid group and heterocycles, which can depress membrane swelling and improve membrane stability^[28–30]. As an active group within the domain of polyimide materials^[31], we have presented the pyridine based SPI (Py-SPI) membranes with improved water stability caused by acid-base interactions between sulfonic acid and pyridine groups^[32]. But the proton conductivities of Py-SPI membranes need to be improved. Considering the properties of triazole groups that could facilitate proton transport in PEMs^[33–39], we focus on the enhancement of proton conductivity by involving triazole groups into SPI backbones. As *N*-phenyl-1,2,4-triazole based PEMs have shown potential application for fuel cell^[35], novel SPIs were designed by incorporating *N*-phenyl-1,2,4-triazole moiety in the polymer backbone. Herein, we report the preparation of SPIs by copolymerization of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA), 5-(2,6-bis(4-aminophenyl)pyridin-4-yl)-2-methoxy benzene sulfonic acid (SDAM) and 4-(4-methoxyphenyl)-3,5-bis(3-aminophenyl)-1,2,4-triazole (APT). The effects of *N*-Phenyl-1,2,4-triazole groups on the properties of SPIs are investigated.

EXPERIMENTAL

Materials

NTDA was purchased from Aldrich Chemical Co. and purified by vacuum sublimation. SDAM was prepared according to our previous work^[32]. 4,4'-Diaminodiphenyl ether-2,2'-disulfonic acid (ODADS) was synthesized by the literature method^[12]. All other reagents were purchased from Shanghai Chemical Reagent Plant. Triethylamine (TEA) was dried over sodium followed by distillation. *m*-Cresol was purified by distillation under reduced pressure. Other reagents were of analytical grade and used without further purification.

Monomer Synthesis

Synthesis of 3-nitro-N'-(3-methylbenzoyl) benzohydrazide

A 250 mL three-necked round bottom flask equipped with a dropping funnel was charged with 3-nitrobenzohydrazide (18.12 g, 0.1 mol), THF (100 mL) and cooled to 0 °C. Then 3-nitrobenzoyl chloride (20.40 g, 0.11 mol) in THF (20 mL) was added dropwise through the funnel over 1.5 h, followed by adding Et₃N (15 mL, 0.11 mol) and a small amount of *N,N*-4-dimethylaminopyridine (DMAP). The reaction mixture was stirred for 8 h at 0 °C. The formed white precipitate was collected by filtration, washed with water thoroughly, and treated with 10% sodium bicarbonate solution to remove free acid formed. The product was filtered, washed with water, and dried in vacuum oven at 100 °C to give the pure product (25 g, 76%). ¹H-NMR (400 MHz, DMSO-d₆, δ): 8.90 (s, 2 H), 8.63 (d, 2 H, *J* = 8.0 Hz), 8.51 (d, 2 H, *J* = 8.4 Hz) and 7.96 (t, 2 H, *J* = 8.0 Hz). FTIR (KBr, cm⁻¹): 3094, 1618, 1595, 1544, 1519, 1481, 1428, 1362, 1352, 1305, 1279, 1258, 1091, 1063, 913 and 871.

Synthesis of 4-(4-methoxyphenyl)-3,5-bis(3-nitrophenyl)-1,2,4-triazole (NPT)

The monomer NPT was synthesized by the following method according to the literature^[35]: a 1000 mL three-necked round bottom flask charged with aniline (29.56 g, 0.04 mol), *o*-dichlorobenzene (ODBA) (500 mL) and PCl₃ (3.85 mL, 0.044 mol) was heated at 100 °C for 1 h. Then 3-nitro-*N'*-(3-methylbenzoyl) benzohydrazide (13.21 g, 0.04 mol) was added to the reaction mixture. This solution was heated at 190–200 °C for 12 h, and the ODBA and PCl₃ were distilled out thoroughly. The formed purple crude solid was washed with water carefully and dried at 100 °C in vacuum oven. The crude solid was purified by column chromatography (CH₂Cl₂/CH₃OH, 500:1) to afford the product as white powder (10.50 g, 63%). mp: 250–251 °C. ¹H-NMR (400 MHz, DMSO-d₆, δ): 8.28 (d, 2 H, *J* = 8.4 Hz), 8.25 (s, 2 H), 7.87 (d, 2 H, *J* = 8.0 Hz), 7.72 (t, 2 H, *J* = 8.0 Hz), 7.52 (d, 2 H, *J* = 8.8 Hz), 7.08 (d, 2 H, *J* = 8.8 Hz) and 3.80 (s, 3 H). FTIR (KBr, cm⁻¹): 3453, 3371, 1608, 1588, 1514, 1487, 1464, 1297, 1254, 1171, 1104, 1028, 1019, 1001, 887 and 794.

Synthesis of 4-(4-methoxyphenyl)-3,5-bis(3-aminophenyl)-1,2,4-triazole (APT)

A 500 mL three-necked round bottom flask equipped with a reflux condenser and a dropping funnel was charged with NPT (5.01 g, 0.012 mol), 5% palladium on carbon (0.4 g) and ethanol (300 mL). Then 80% hydrazine hydrate (10 mL) in ethanol (10 mL) was added dropwise through the funnel over a 1.5 h period under nitrogen atmosphere. The reaction mixture was refluxed for 4 h. Then the hot solution was filtered to remove the palladium catalyst. The white acerosc crystal was formed when the filtrate was cooling to room temperature. The pure product was collected by filtration and dried at 80 °C in vacuo (2.50 g, 58%). mp: 252–253 °C. ¹H-NMR (400 MHz, DMSO-d₆, δ): 7.22 (d, 2 H, *J* = 8.8 Hz), 6.96 (d, 2 H, *J* = 8.8 Hz), 6.90 (t, 2 H, *J* = 8.0 Hz), 6.80 (s, 2 H), 6.54 (dd, 2 H, *J* = 8.0, 1.6 Hz), 6.28 (d, 2 H, *J* = 8.0 Hz), 5.20 (s br, 4 H) and 3.77 (s, 3 H). FTIR (KBr, cm⁻¹): 3318, 3206, 1638, 1605, 1590, 1512, 1487, 1466, 1409, 1338, 1297, 1248, 1167, 1103, 1017, 1000, 881 and 842. Elemental analysis: Calculated for C₂₁H₁₉N₅O: C, 70.51%; H, 5.32%; N, 19.59%. Found: C, 70.41%; H, 5.23%; N, 19.88%.

Preparation of NTDA-SDAM-APT and Model Polyimides Based Membranes

Various NTDA-SDAM-APT (SA-SPI) based copolyimides were synthesized by the typical method used in our previous work^[32]. Take the synthesis of SPI-50 as a typical example: A 50 mL well-dried three-necked flask was charged with NTDA (0.5360 g, 2 mmol), SDAM (0.4470 g, 1 mmol), APT (0.3574 g, 1 mmol), benzoic acid (0.5190 g, 4.25 mmol), triethylamine (TEA, 0.31 mL), and *m*-cresol (6.7 mL). The mixture was stirred at room temperature for a few minutes, then stirred at 80 °C for 4 h and 180 °C for another 8 h under nitrogen flow. The resulting solution was poured into acetone after being cooled to 80 °C. The formed fiber-like precipitate was collected by filtration and washed with acetone. The crude products were further purified by Soxhlet extraction with ethanol for 24 h and dried in vacuum at 100 °C for 12 h. Three model polyimides NTDA-ODADS-APT (OA-SPI), NTDA-ODADS-ODA (OO-SPI) and NTDA-ODA-APT (OA-PI) based copolyimides were prepared by the same method mentioned above.

All the films (in TEA salt form) were prepared by casting the *m*-cresol solution (5 wt%) on the glass plate and dried at 80 °C for 48 h. Then 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 2 mol/L H₂SO₄ solution at room temperature. The proton form films were washed with deionized water thoroughly when the protons exchange completely, and then dried at 80 °C in vacuum for 12 h.

Characterization of Membranes

Measurements

FTIR spectra were determined with a Bio-Red Digilab Division FTS-80 spectrometer. ¹H-NMR spectra were recorded on a Varian Unity spectrometer at 400 Hz with tetramethylsilane as an internal standard. Thermo gravimetric analyses (TGA) 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 0.5 g/dL solutions in *m*-cresol.

Ionic-exchange capacity

The ionic-exchange capacity (IEC) was measured by means of a classical titration method. Three samples of each membrane were dried at 120 °C in a vacuum oven at first. Then the samples (*ca.* 100 mg) were soaked in 100 mL saturated NaCl solution for a week, respectively. The released protons were titrated using 0.01 mol/L NaOH solution. The reported IEC values corresponded to the average of the three samples.

Water uptake

The samples were first dried at 120 °C in a vacuum oven for 12 h. Then the water absorption experiments were carried out by immersing three sheets of films (*ca.* 100 mg per sheet) of each polyimide membrane in water at 80 °C for 5 h. 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 represent the weight of dry and corresponding water-swollen film sheets, respectively. The S values were estimated from the average of the three samples.

Proton conductivity

The proton conductivity of the hydrated membrane was measured using an electrochemical impedance spectroscopy technique (Model 5210 Frequency Response Detector, EG&GPARC, Princeton, NJ) over the frequency range from 100 Hz to 100 kHz. 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 cell was placed in a thermo-controlled chamber in deionized water for measurements. Proton conductivity (σ) was calculated from Eq. (2):

$$\sigma = d / (L_s W_s R) \quad (2)$$

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

Methanol permeability

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 obtain the water-swollen sample and then mounted 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 permeated 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) was calculated from Eq. (3):

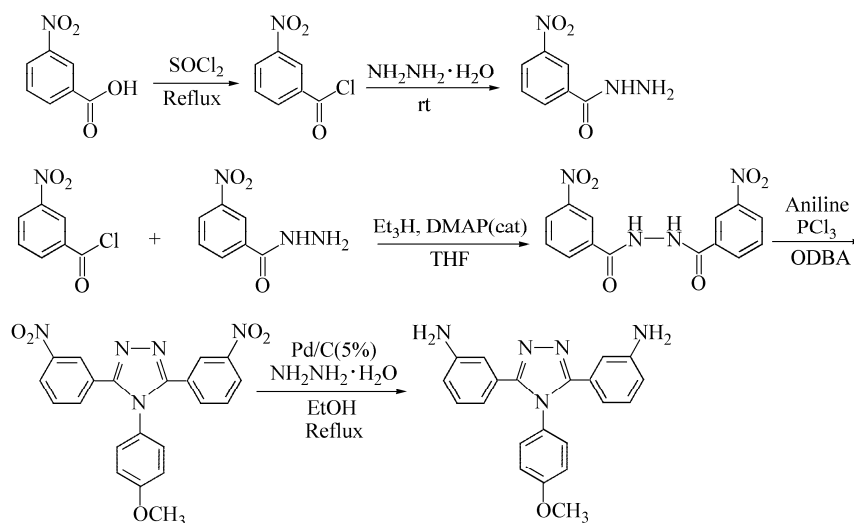
$$P_M = V_2 L k / A C_1 \quad (3)$$

where A and L are the area and thickness of the swollen membrane, respectively; C_1 is the initial 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 a gas chromatography equipped with a thermal conductivity detector (Shimadzu, GC-2010A, Tokyo, Japan).

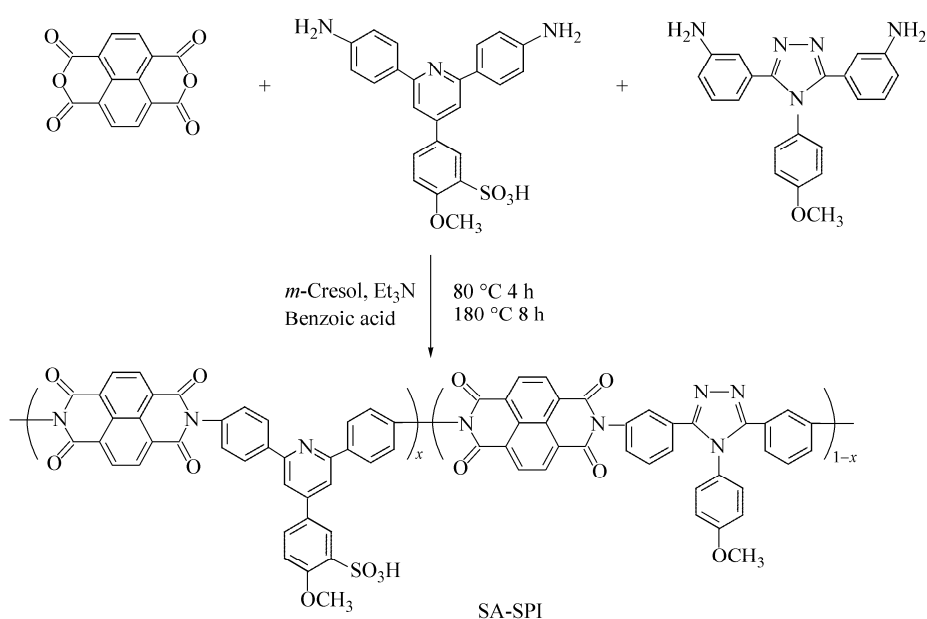
RESULTS AND DISCUSSION

Synthesis and Characterization of the Monomer and Polyimides

Synthesis of monomer APT is outlined in Scheme 1. 3-Nitro-*N'*-(3-methylbenzoyl)benzohydrazide, which was synthesized by the condensation of 3-nitrobenzohydrazide and 3-nitrobenzoylchloride, reacted with aniline in ODBA in the presence of PCl_3 to form NPT. APT was obtained by reduction of nitro groups in NPT with hydrazine hydrate catalyzed by 5 wt% Pd on carbon. Various SA-SPIs were synthesized by controlling the feeding ratio of SDAM to APT, where x (10%–90%) stands for the molar percentage of SDAM (Scheme 2). Their inherent viscosities (in TEA salt form) are in the range of 1.0–1.5 dL/g in *m*-cresol. All of them show good solubility in a broad range of polar solvents, such as *m*-cresol, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidinone (NMP). The structures of the proton form SA-SPI membranes were characterized by FTIR spectroscopy, and SPI-10, 30, 50, 70, 90 were chosen as representative examples. Their IR spectra are shown in Fig. 1(a) (only zoomed region from 1000 to 2000 cm⁻¹ are shown for clarity). The corresponding peaks are assigned as following: 1714 and 1672 cm⁻¹: $\nu_{\text{C=O}}$, 1340 cm⁻¹: $\nu_{\text{C-N}}$ imide, 1188 and 1098 cm⁻¹: $\nu_{\text{S=O}}$, 1623 cm⁻¹: $\nu_{\text{C=N}}$ pyridine, 1510 cm⁻¹: $\nu_{\text{C=N}}$ triazole. The characteristic band of C=N stretching in triazole moiety at 1510 cm⁻¹ (dotted in Fig. 1a) confirms the presence of *N*-phenyl-1,2,4-triazole group in SA-SPI, and the intensity of this peak increases with the decrease of DS from 90 mol% to 10 mol%. In addition, the broad absorption band at around 3070 cm⁻¹ in Fig. 1(b) corresponds to the hydrogen bonding between *N*-phenyl-1,2,4-triazole moieties and sulfonic acid groups.



Scheme 1 Synthesis of the diamine monomer APT



Scheme 2 Synthesis of SA-SPI copolyimides

Thermal stability of SA-SPI based membrane was investigated by TGA measurements. All the resulting membranes display similar TGA behavior. As shown in Fig. 2 with SA-SPI-30 as a representative example, a four-step weight loss (dotted line) can be observed: step (1) is the loss of absorbed water around 100 °C; steps (2) and (3) are the degradation of sulfonic acid groups and triazole groups around 299 °C and 422 °C, respectively; step (4) is the decomposition of polyimide backbones at around 525 °C. According to the TGA data of all the SA-SPI membranes in Table 1, all the membranes presented here exhibited good thermal stability.

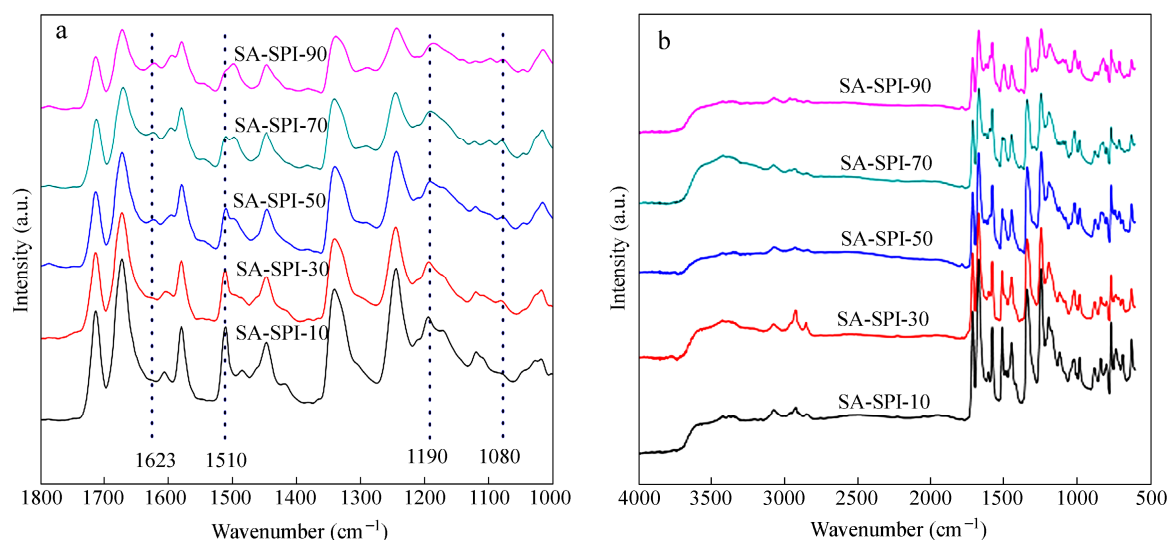


Fig. 1 FTIR spectrum of SA-SPI-10, 30, 50, 70 and 90 (proton form): (a) region from 1000 to 2000 cm^{-1} and (b) region from 500 to 4000 cm^{-1}

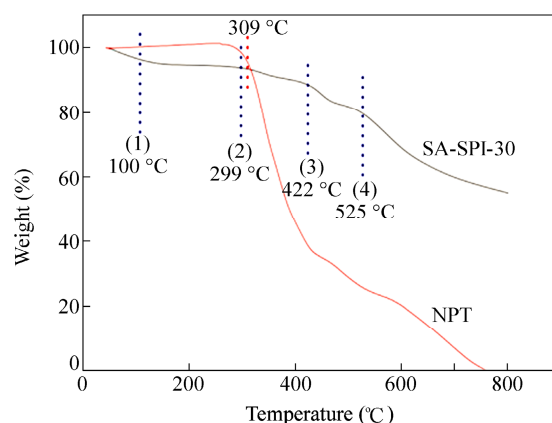


Fig. 2 TGA curve for SA-SPI-30 (proton form) and monomer NPT

Table 1. Thermal properties of SA-SPI membranes

SA-SPI- <i>x</i>	Onset temperature			Residue at fourth step (%)
	Second step (°C)	Third step (°C)	Fourth step (°C)	
SA-SPI-10	299.11	422.06	525.96	77.05
SA-SPI-30	299.42	422.12	524.49	81.09
SA-SPI-50	280.22	416.24	528.62	91.42
SA-SPI-70	290.14	421.19	577.99	84.92
SA-SPI-90	280.06	409.20	522.07	82.78

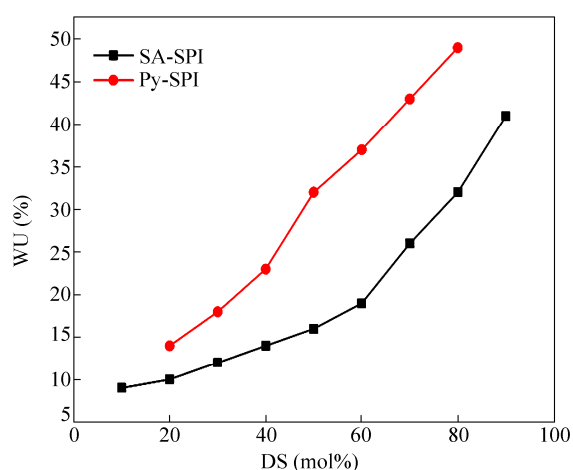
The mechanical properties of the SA-SPI membranes are summarized in Table 2 (SPI-10, 30, 50, 70, 80 as representative examples) as indicated by 0 h soaking time. All the membranes display good mechanical properties with Young's modulus (YM) around 2.0 GPa, maximum strength (MS) on a scale of 75 MPa to 160 MPa, and elongation at break (EB) ranging from 40% to 231%, which are all accrescent with the content of triazole increasing.

Table 2. Mechanical properties of the resulting membranes (SA-SPI-10, 30, 50, 70, 80) before and after aging in boiling water

SA-SPI-x	Soaking time (h)	MS (MPa)	YM (MPa)	EB (%)
SA-SPI-10	0	155	3110	231
	48	119	2795	140
	96	85	1930	84
	200	83	1740	80
SA-SPI-30	0	160	3423	101
	48	110	2057	98
	96	104	2080	98
	200	90	1823	70
SA-SPI-50	0	104	2189	40
	48	83	1737	32
	96	79	2073	28
	200	78	1865	18
SA-SPI-70	0	75	1428	52
	48	80	1592	32
	96	72	1896	32
	200	56	1509	20
SA-SPI-80	0	88	1770	57
	48	82	1639	30
	96	71	1543	22
	200	59	1840	12

Water Uptake (WU), Methanol Permeability, Water and Oxidative Stability

The SA-SPI films exhibit low WU values ranging from 9% to 41% at 80 °C with the increase of DS from 10 mol% to 90 mol% as shown in Fig. 3. The SA-SPI membranes show lower WU than the Py-SPI membranes do as a resulting of only replacing the ODA moiety of Py-SPIs by APT group^[31], which suggests that the *N*-phenyl-1,2,4-triazole group should contribute to the depression of water absorption. Methanol permeabilities of the SA-SPI membranes are listed in Table 3. The SA-SPI films exhibit P_M within a range of $(0.80\text{--}5.80) \times 10^{-7} \text{ cm}^2/\text{s}$ at room temperature, which are about one order of magnitude lower than that of Nafion membranes ($2.6 \times 10^{-6} \text{ cm}^2/\text{s}$) under the same condition.

**Fig. 3** Water uptake of SA-SPI and Py-SPI membranes at 80 °C

The water resistance of SA-SPI membrane was tested by measuring mechanical properties of the samples aged in boiling water. As shown in Table 2, only SA-SPI-90 becomes brittle and all the other membranes still maintain high mechanical stability with YM still higher than 1.5 GPa, MS in a range of 56 MPa to 90 MPa and EB ranging from 12% to 80% after aging 200 h. Further experiments reveal that all the resulting membranes are

tough enough until by immersing the films in water at 80 °C for longer than 2000 h except for SA-SPI-90 as shown in Table 3. As water absorption is depressed by the acid-base interaction between sulfonic acid and *N*-phenyl-1,2,4-triazole groups, water stability can be improved.

Table 3. Water and oxidative stability at 80 °C and methanol permeability (P_M) of SA-SPI membranes

SA-SPI- <i>x</i>	Thickness (μm)	Water stability	Oxidative stability	P_M ($10^{-7}\text{cm}^2/\text{s}$)
SA-SPI-10	33	> 2500 h	280 h	0.80
SA-SPI-30	40	> 2500 h	140 h	1.02
SA-SPI-50	38	> 2000 h	55 h	1.20
SA-SPI-70	36	> 2000 h	15 h	3.23
SA-SPI-90	35	900 h	11 h	5.80

The oxidative stability of SA-SPI membrane was evaluated by measuring the lasting time of the films until their breakage under bending gently after immersing in Fenton's reagent (30×10^{-6} FeSO₄ in 30% H₂O₂) at 80 °C. The SA-SPI membranes show enhanced oxidative stability, and the representative data of SPI-10, 30, 50, 70, 90 are shown in Table 3. The lasting time increases from 12 h to 280 h with the increase of the content of triazole moiety, which is much longer than that of other SPIs^[11, 17]. Consequently, the incorporation of APT groups in SA-SPIs enhances the oxidative stability, and a similar result was also reported by other group^[35].

IEC and Proton Conductivity

IEC values and proton conductivity are key parameters for PEM. The experimental IEC values of various SA-SPI membranes are curved as a function of DS as shown in Fig. 4. Here, an interesting observation is that the experimental IEC values of SA-SPI membranes are not in good accordance with the calculated data. Namely, the calculated data show a linear increase with the increase of DS, however, we observe a knee point at DS around 50% for the experimental IEC. From this value, the IEC decreases rapidly with the increase of DS up to 80%. Then a large increase of IEC is observed when the DS increases from 80% to 90%. As shown in Fig. 5, the proton conductivities of SA-SPI membranes at 80 °C display a peak value at 50% DS, which is consistent with the IEC behavior. According to the data in Table 4, the proton conductivities of SA-SPI membranes increase with the increase of temperature, and they all exhibit the peak value at 50% DS at the same temperature level. We propose that the *N*-phenyl-1,2,4-triazole groups in SPI backbone would play an important role in influencing the nonlinear changes of IEC and proton conductivity.

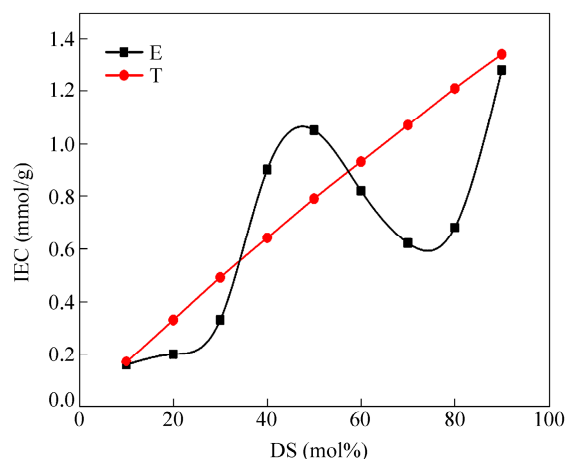


Fig. 4 IEC values of SA-SPI membranes at different DS (E: Experimental IEC and T: Theoretical IEC)

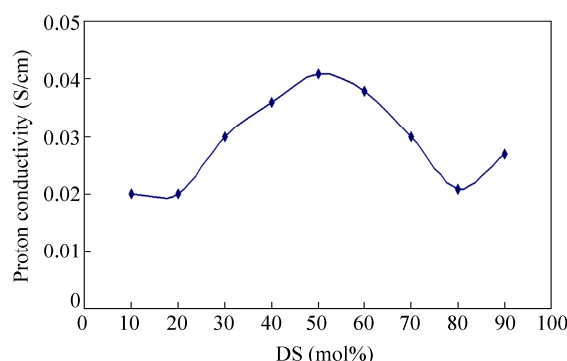
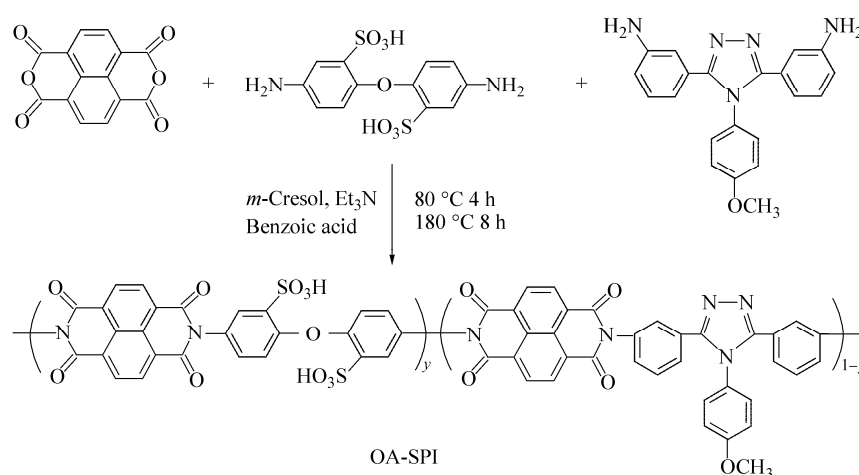


Fig. 5 Proton conductivities of SA-SPI membranes with various DS at 80 °C

Table 4. Proton conductivities of SA-SPI membranes with various DS at different temperatures

SA-SPI-x	Proton conductivity (σ , S/cm)			
	20 °C	40 °C	60 °C	80 °C
SA-SPI-10	0.0043	0.0061	0.008	0.02
SA-SPI-20	0.0045	0.0063	0.0081	0.02
SA-SPI-30	0.0047	0.0069	0.0083	0.03
SA-SPI-40	0.009	0.012	0.016	0.036
SA-SPI-50	0.0098	0.015	0.020	0.041
SA-SPI-60	0.0086	0.013	0.019	0.038
SA-SPI-70	0.0063	0.011	0.015	0.03
SA-SPI-80	0.0071	0.0096	0.017	0.021
SA-SPI-90	0.009	0.014	0.022	0.027

Model SPIs (OA-SPIs) were prepared from polycondensation of NTDA, ODADS and APT with DS ranging from 10% to 90% (Scheme 3) to confirm the above results. The OA-SPI membranes also display a nonlinear IEC trendline with a peak at about 33% DS as shown in Fig. 6. Then, the IEC increases in terms of normal change tendency above 40% DS. The proton conductivities of OA-SPI membranes experience a similar function of DS in Fig. 7. An interesting observation for the SA-SPI and OA-SPI membranes is that SA-SPI films exhibit the peak values of experimental IEC and proton conductivity at around 50% DS, corresponding to a 1:1 molar ratio of sulfonic acid and triazole groups; and the OA-SPI films show knee points of experimental IEC and proton conductivity at around 33% DS, indicating also a 1:1 molar ratio of sulfonic acid and triazole groups.



Scheme 3 Synthesis of OA-SPI copolyimides

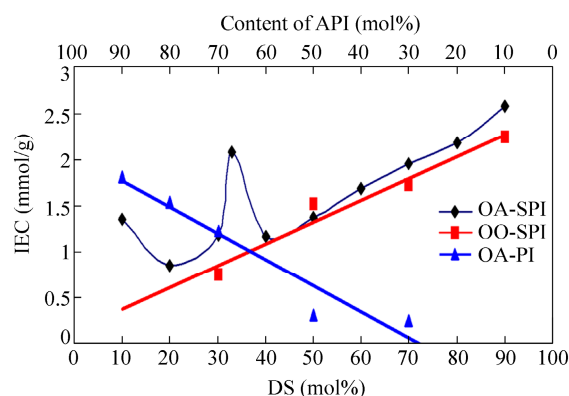


Fig. 6 Experimental IEC values of OA-SPI and OO-SPI membranes with various DS and experimental IEC values of OA-PIs with different contents of APT

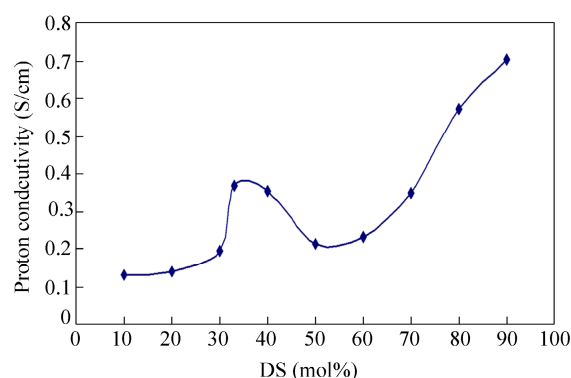
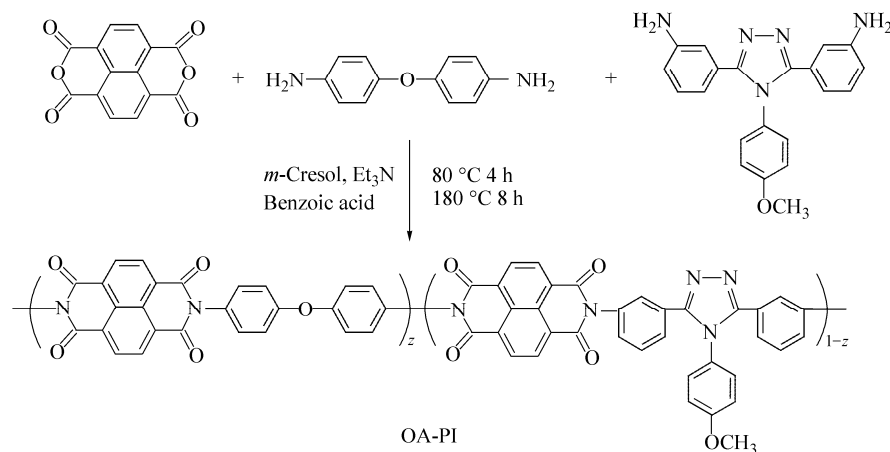


Fig. 7 Proton conductivities of OA-SPI with various DS at 80 °C

To further investigate the nonlinear behaviors of IEC and proton conductivity, sulfonated polyimides OO-SPIs, whose structure were free of APT, were prepared from NTDA, ODADS and ODA^[12]. Non-sulfonated polyimides OA-PIs were also synthesized by condensation of NTDA, ODA and APT (Scheme 4). As shown in Fig. 6, a comparison of IEC values of OA-SPIs, OO-SPIs and OA-PIs exhibits that the IEC values of OA-PI membranes increase as the content of APT increasing, suggesting that the *N*-phenyl-1,2,4-triazole groups have been protonated during proton exchange process. On the other hand, the IEC values of OO-SPIs membranes increase with DS in same trend to that reported in literature^[12]. These two curves intersect at a point where the DS of OO-SPIs is *ca.* 33% and the content of APT for OA-PIs is around 66%. Thus, the maximum experimental IEC values of OA-SPIs and SA-SPIs appeared at around 33% and 50% DS, respectively, are most probably due to the joint contribution of APT moiety and sulfonic acid groups in the polymer backbone.

Compared with Py-SPI membranes, the SA-SPI membranes display higher proton conductivities by only replacing the ODA moiety of Py-SPIs with APT group, especially at relatively low DS. For example, proton conductivity of Py-SPI-80 (theoretical IEC 1.303 mmol/g) is 0.018 S/cm at 80 °C (100% RH)^[32], while the proton conductivities of SA-SPI-80 (theoretical IEC 1.21 mmol/g) and SA-SPI-50 (theoretical IEC 0.79 mmol/g) are 0.021 S/cm and 0.041 S/cm at 80 °C (100% RH), respectively. The IEC behaviors of OA-PI membranes can explain this phenomenon. As shown in Fig. 6, the IEC values of OA-PI membranes increase as the content of APT increasing, suggesting that the *N*-phenyl-1,2,4-triazole groups have been protonated during proton exchange process. Thus, the contribution of total IEC value of SA-SPI membrane can be from two aspects: sulfonic acid groups and the protonated *N*-phenyl-1,2,4-triazole groups. Compared with Py-SPI membranes at the same DS level^[32], the SA-SPI membranes show higher experimental IEC values, especially at relatively low DS. With the increase of IEC values, the proton conductivities of SA-SPI membranes increase. In brief, the

N-phenyl-1,2,4-triazole groups can be protonated and functioned as ion exchange sites, which lead to the increase of proton conductivity.



Scheme 4 Synthesis of OA-PI copolyimides

CONCLUSIONS

A series of SA-SPIs with different DS were prepared by copolymerization of NTDA, SDAM and the new diamine monomer containing *N*-phenyl-1,2,4-triazole group (APT). Flexible, transparent and tough membranes were obtained by solution casting. The resulting membranes displayed not only good solubility and high membrane stability but also enhanced proton conductivity. We found that the *N*-phenyl-1,2,4-triazole groups in SPIs could be protonated and functioned as ion exchange sites, which led to the peak values of IEC and proton conductivity at relative low DS. With controlling the balance of APT and sulfonated parts, SPI membranes with good membrane stability and sufficient proton conductivity can be prepared. Thus, the results presented herein would provide a new strategy for the design of novel SPIs for PEM application.

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