

Synthesis and Properties of Sulfonated Polyimide/Polybenzimidazole

Cross-linked Membranes

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Abstract: Three anhydride-end-capped sulfonated polyimide oligomers (SPI-*n*) with varied block length ($n = 3, 5, 7$) were synthesized via condensation polymerization of excess 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) with 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS) in *m*-cresol in the presence of benzoic acid and isoquinoline at 180 °C for 20 h. A series of sulfonated polyimide/polybenzimidazole cross-linked membranes were prepared by condensation reaction of the end anhydride groups of the synthesized SPIs with the pendant amino groups of the synthesized polybenzimidazole (H₂N-PBI) in dimethylsulfoxide (DMSO) during the membrane cast process. The ion exchange capacities (IECs) measured by titration method are 0.70, 1.43 and 1.52 meq/g for the cross-linked membranes prepared from SPI-3, SPI-5 and SPI-7, respectively. All the cross-linked membranes could maintain reasonable mechanical strength after being soaked in deionized water at 100 °C for more than two months indicating extremely improved hydrolytic stability. Fenton's test revealed that all the cross-linked membranes displayed significantly better radical oxidative stability than the corresponding SPIs. This is attributed to the presence of highly oxidative-stable PBI component in the cross-linked membranes. The membranes with higher IECs displayed higher proton conductivities. The SPI-7/H₂N-PBI cross-linked membrane displayed the highest proton conductivity among the prepared membranes which is comparable to that of Nafion 112 (measured in deionized water at varied temperatures).

Keywords: Sulfonated polyimide; polybenzimidazole; cross-linking; membrane; proton conductivity; water stability

Introduction

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) have attracted much attention in the past decade because they provide cleaning, quiet and portable power for vehicular transportation and for other applications. One of the key components of a PEMFC is the polymer electrolyte membrane. From viewpoint of practical use, an ideal polymer electrolyte membrane material should satisfy the following requirements: 1) low cost, 2) low resistance (i.e., high proton conductivity) under fuel cell operating conditions, 3) good mechanical strength, preferably with resistance to swelling, 4) long-term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments, 5) low gas (reactant) crossover, and 6) interfacial compatibility with catalyst layers. Among them, proton conductivity and membrane stability are the two most important properties. To achieve high proton conductivity, membranes are generally needed to have high ion exchange capacities (IECs). However, too high IEC often causes excessive swelling or even dissolution in water and thus lose mechanical strength. Cross-linking is a common and effective method to enhance the mechanical properties, to suppress membrane swelling degree and to improve the membrane durability. On the other hand, polybenzimidazoles have been reported to have excellent radical oxidative stability which is very

favorable for PEMFCs [1-3]. In this presentation, we report on the synthesis and properties of a series of cross-linked membranes from anhydride end-capped sulfonated polyimide oligomers and polybenzimidazole with pendant amino groups.

Experimental

Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) was purchased from Multi. Technology Co. Ltd.. 4,4'-Diaminodiphenyl ether (ODA), *m*-cresol, phosphoric acid (PA), dimethylsulfoxide (DMSO), and triethylamine (Et₃N) were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). DMSO and Et₃N were distilled under reduced (for DMSO) or normal (for Et₃N) pressure and dried over 4A molecular sieves before use. Other materials were used as received. 4,4'-Diaminodiphenyl ether-2,2'-disulfonic acid (ODADS) and H₂N-PBI were synthesized according to our previously reported methods [4,5].

Synthesis of anhydride-end-capped sulfonated polyimide oligomers (SPI-n)

A typical procedure is described as follows using the SPI-7 as an example.

To a 100 mL completely dried 3-neck flask were added 1.008 g (2.8 mmol) of ODADS, 18.5 mL *m*-cresol and 1.0 mL Et₃N under nitrogen flow with stirring. After ODADS was completely dissolved, 0.8576 g (3.2 mmol) of NTDA, 0.7808 g (6.4 mmol) of benzoic acid and 0.8256 g (6.4 mmol) of isoquinoline were added. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to room temperature, the solution mixture was poured into 100 mL of acetone with stirring. The yellowish powder precipitate was filtered off, thoroughly washed with acetone and dried in vacuo at 80 °C for 10 h.

Cross-linking and membrane formation

The synthesized SPI oligomers and stoichiometric H₂N-PBI were dissolved in dimethylsulfoxide (DMSO) under nitrogen flow at a total polymer concentration of ~10% (w/v) and then heated at 80 °C for a period of time. The solution mixtures were cast onto glass plates and dried at 80 °C for 10 h. The as-cast membranes were peeled off and further dried in a vacuum oven at 180 °C for 10 h to complete cross-linking reaction.

Proton exchange treatment

The above prepared cross-linked membranes were soaked in methanol at 60 °C for 10 h to remove the residual solvent, and then were immersed into 1.0 M sulfuric acid at room temperature for two days. Finally the obtained membranes were thoroughly washed with deionized water till the rinsed water became neutral followed by drying in vacuo at 120 °C for 20 h.

Measurements

Thermogravimetric analysis (TGA) was performed in nitrogen with a TGA 2050 instrument at a heating rate of 10 °C/min. IEC was measured by the widely used titration method. 0.2 - 0.3 g of dry membranes were cut into small pieces and immersed into saturated sodium chloride salt solution with stirring at room temperature for two days. The membrane sheets were taken out and rinsed with deionized water. The sodium chloride solution and the rinsed water were combined together followed by titration with 0.01 N sodium hydroxide solution using phenolphthalein as an indicator.

Water uptake (WU) measurements were carried out by immersing the membranes (0.2 - 0.3 g per sheet) into deionized water at 80 °C for 5 h. Then the membranes were taken out, wiped with tissue paper, quickly weighed on a microbalance. Water uptake (WU) was calculated from the following equation:

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

where W_d and W_s refer to the weight of dry and wet membranes, respectively.

Proton conductivity (σ) was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) [15]. A sheet of SPI membrane (proton form) and two pairs of blacken platinum plate electrodes were set in a Teflon cell. The cell was placed in either a thermo-controlled humid chamber for measurement at relative humidity (RH) lower than 100% or distilled deionized water for measurement in liquid water. The resistance value was determined from high frequency intercept of the impedance with the real axis. Proton conductivity was calculated from the following equation:

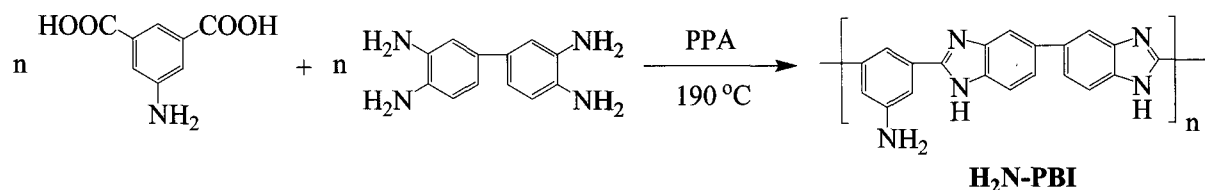
$$\sigma = d / (t_s w_s R) \quad (2)$$

where d is the distance between the two electrodes, t_s and w_s are the thickness and width of the membrane at 70% RH, respectively, and R is the resistance value measured. For measurement in liquid water, the dimensions of fully hydrated membranes were used.

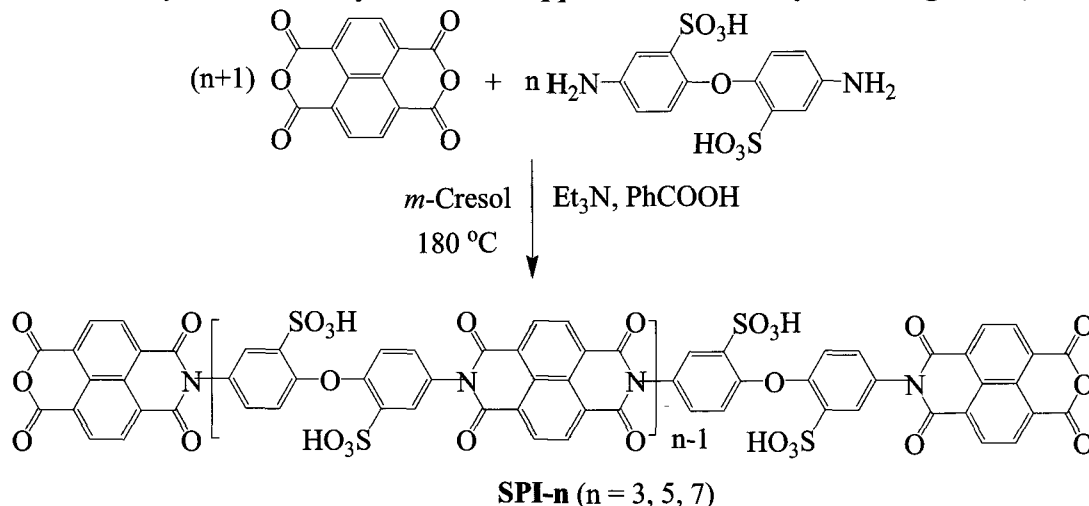
Results and Discussion

The polybenzimidazole with pendant amino groups (H_2N -PBI) was synthesized via condensation polymerization of 5-aminoisophthalic acid and 3,3'-diaminobenzidine (DAB) in polyphosphoric acid at 190 °C for 20 h (Scheme 1). Three anhydride end-capped sulfonated polyimide oligomers (SPI- n) were synthesized via condensation polymerization of excess NTDA with ODADS in *m*-cresol in the presence of benzoic acid and isoquinoline at 180 °C for 20 h. The averaged block length of the SPI oligomers was controlled at 3, 5 and 7 by controlling the molar ratios of NTDA to ODADS at 4:3, 6:5 and 8:7, respectively (Scheme 2).

Scheme 1 Synthesis of the Polybenzimidazole with Pendant Amino Groups (H_2N -PBI)



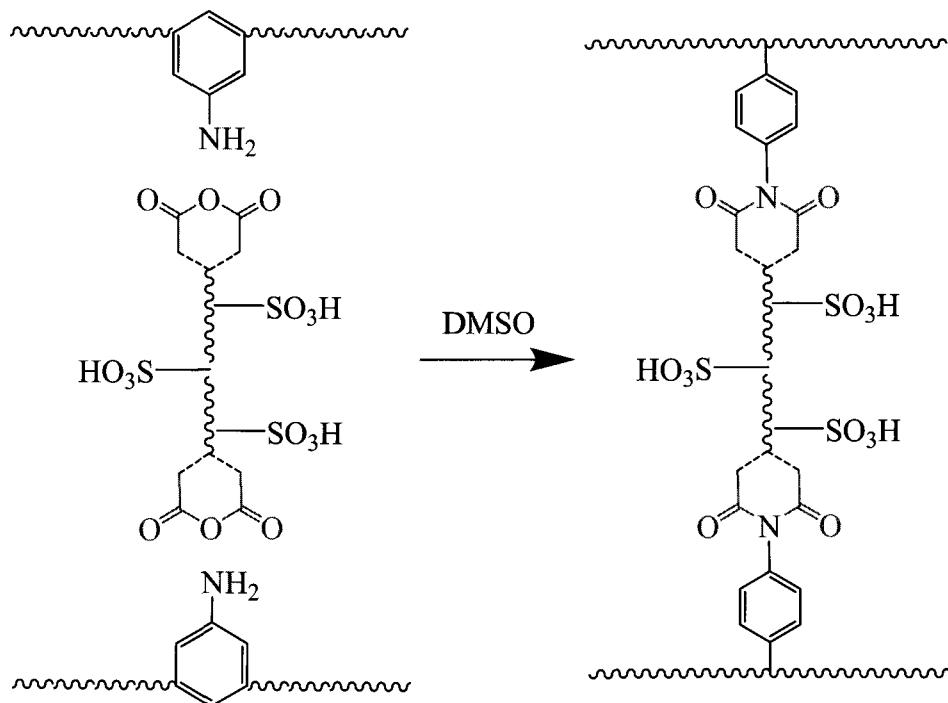
Scheme 2. Synthesis of Anhydride End-Capped Sulfonated Polyimide Oligomers(SPIs)



The pendant amino groups of the H_2N -PBI can react with the end anhydride groups to form cross-linking network (Scheme 3). The molar ratio of the pendant amino groups to the end anhydride

groups was controlled at 1:1. To fabricate the cross-linked membranes, the H₂N-PBI and SPI oligomers were allowed to slightly pre-cross-linked in DMSO at 80 °C and underwent further cross-linking reactions during the process of cast. The cross-linking was completed by drying the membranes under vacuum at 180 °C. The occurrence of cross-linking was confirmed by the complete insolubility of the membranes in organic solvents such as DMSO.

Scheme 3 Cross-linking Reactions between the NH₂-PBI and the SPIs



Thermogravimetric analysis (TGA) revealed that the decomposition of sulfonic acid groups started from ~300 °C indicating good thermal stability of the cross-linked membranes. The IECs, tensile properties, water uptake (WU), hydrolytic stability, proton conductivity and radical oxidative stability of the cross-linked membranes are shown in **Table 1**. The cross-linked membranes showed relatively good mechanical properties (tensile strength = 55-80 MPa, elongation at break = 5-19%). The ion exchange capacities (IECs) of the cross-linked membranes measured by titration are significantly lower than the theoretical ones because of the strong acid-base interaction of which part of protons could hardly undergo ion exchange in saturated sodium chloride solution. The membranes with higher IECs showed larger water uptake values. It's interesting that the cross-linked membranes showed anisotropic swelling behaviors, i.e. the dimensional changes in 'in-plane' direction were rather small (~5%), whereas the dimensional changes in 'through-plane' direction were relatively large (12-20%). Fenton's test (test conditions: 3% H₂O₂ + 3 ppm FeSO₄, 80 °C) revealed that the cross-linked membranes could maintain their forms after immersing in Fenton's reagent for 70-80 min which is significantly longer than the pure ODADS-based SPI membranes (~30 min). This should be attributed to the excellent radical oxidative stability of the H₂N-PBI. The variations of proton conductivity of the cross-linked membranes as a function of relative humidity (RH) at 60 °C and temperature in deionized water were investigated and the results are shown in Figures 1 and 2, respectively. It can be seen that the proton conductivity increased with increasing RH and temperature. Moreover, the membranes with higher IECs tend to have higher proton conductivity. At high relative humidities and temperatures, the cross-linked membrane prepared from H₂N-PBI and the SPI oligomer of block length = 7 showed reasonably high proton conductivities which are comparable to that of Nafion 112.

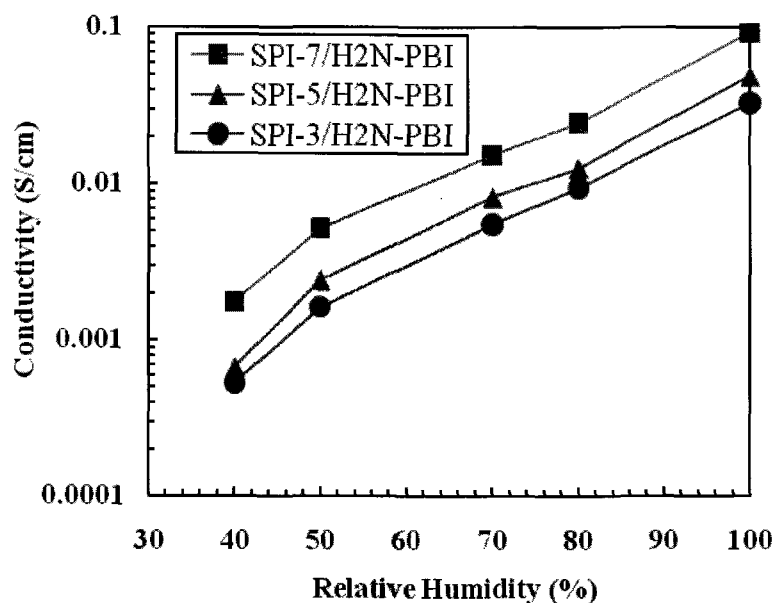


Figure 1. Proton conductivity of the cross-linked SPI-*n*/H₂N-PBI membranes as a function of relative humidity at 60 °C.

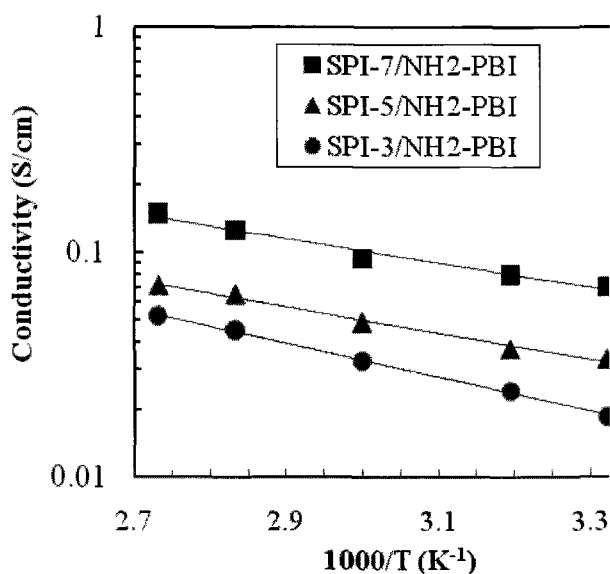


Figure 2. Proton conductivity of the cross-linked SPI-*n*/H₂N-PBI membranes as a function of temperature in deionized water.

Table 1 IECs, tensile properties, water uptake (WU), hydrolytic stability, proton conductivity and radical oxidative stability of the cross-linked membranes

Membrane	IEC ^a (meq/g)	Stress (MPa)	Strain (%)	WU ^b (wt%)	σ ^c (S/cm)	Hydrolytic Stability ^d	τ ₁ ^e (min)	τ ₂ ^e (min)
SPI-3/H ₂ N-PBI	0.75 (0.70)	80	19	36	0.033	>2 months	80	200
SPI-5/H ₂ N-PBI	1.56 (1.43)	56	4.5	38	0.049	>2 months	80	140
SPI-7/H ₂ N-PBI	1.99 (1.52)	55	7.7	70	0.092	>2 months	70	120
NTDA-ODADS/ODA(1/1)	1.95	NM	NM	87	0.012	0.5 h	30	40

^aThe data in parenthesis refer to the experimental values measured by titration method. ^bMeasured at 80 °C. ^cMeasured in deionized water at 60 °C. ^dMeasured at 100 °C. ^eτ₁ and τ₂ refer to the elapsed time

when the membranes started to break into pieces and completely dissolved, respectively (Fenton's test conditions: 3% H₂O₂ + 3 ppm FeSO₄, 80 °C).

Conclusions

A series of cross-linked membranes with relatively good mechanical strength have been successfully prepared by reacting the end anhydride groups of the SPI oligomers with the pendant amino groups of the polybenzimidazole. All the prepared cross-linked membranes displayed extremely improved hydrolytic stability in comparison with the corresponding non-cross-linked ones. The radical oxidative stability was also significantly improved due the introduction of polybenzimidazole component. The cross-linked SPI-7/NH₂-PBI membrane displayed the best performance which has promising applications in fuel cells.

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They exhibit higher glass transition temperatures and superior thermal and thermo-oxidative stability associating with higher decomposition temperatures than the conventional polymers. Incorporation of phthalazinone and sulfone into the PAEP backbone is more effective than meta-ether linkage in improving their organic solubility while maintaining good thermal stability. These attracting properties make the resulting copolymers good candidates for processable and high-performance polymeric materials.

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