

Synthesis and properties of novel sulfonated polyimides from a dianhydride monomer biphenyl-4,4'-diyl-di(oxo)-4,4'-bis(1,8-naphthalenedicarboxylic anhydride)

Sen Yuan, Weizheng Fan, Xiaoxia Guo, Jianhua Fang*

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University

Introduction

Polymer electrolyte membrane (PEM) which functions as an electrode separator, a proton conductor and an electronic insulator is one of the key components of a fuel cell. From viewpoint of practical use, a PEM must have high proton conductivity, good mechanical strength, low swelling ratio and long-term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments. In the past decade, a great number of sulfonated polymers have developed as possible PEMs for fuel cells such as sulfonated poly(ether sulfone)s (SPESs), sulfonated poly(ether ether ketone)s (SPEEKs), sulfonated polyphenylenes (SPPs) and sulfonated polyimides (SPIs). Among them, the SPIs have been identified to be one of the most promising PEMs because of their high mechanical strength and modulus, high thermal stability, excellent electric properties, good film-forming ability and structural variety. However, previous studies have mainly focused on the SPIs derived from a commercial naphthalenic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and various sulfonated diamines. Only a few studies dealing with the SPIs derived from different naphthalenic dianhydride monomers have been reported [1,2]. To further study the structure-property, in this presentation we report on the synthesis and characterization of a new naphthalenic dianhydride monomer, biphenyl-4,4'-diyl-di(oxo)-4,4'-bis(1,8-naphthalenedicarboxylic anhydride) (BPNDA), and a series of SPIs based on this dianhydride monomer. The properties such as proton conductivity, chemical stability and mechanical properties of the SPI membranes are also investigated.

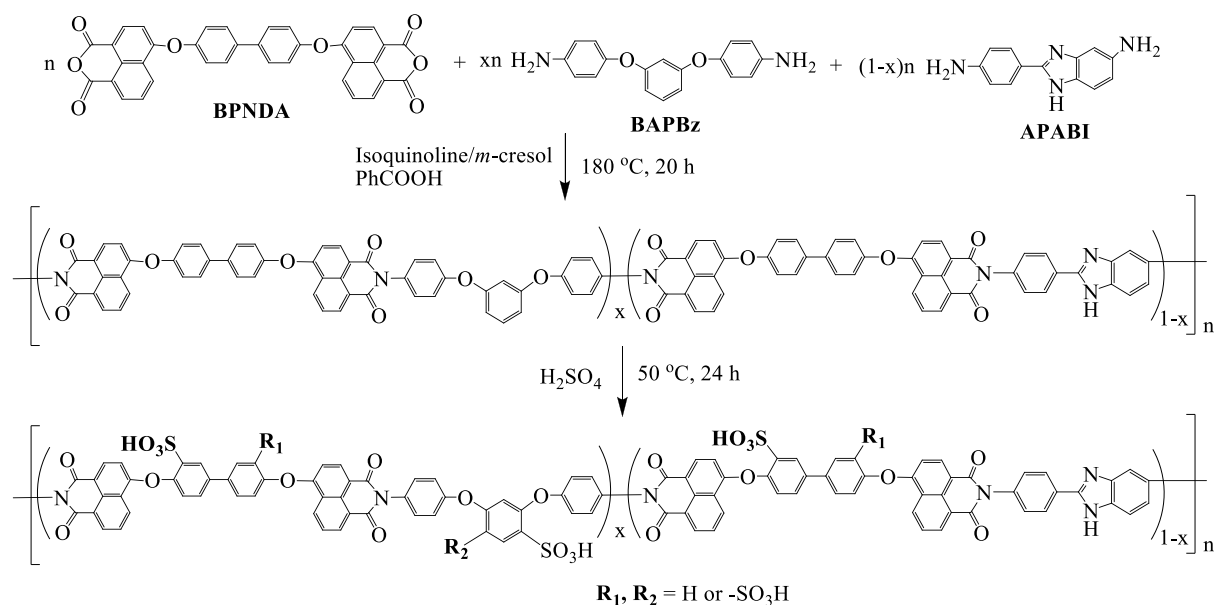
Experimental

The BPNDA was synthesized by the reaction of 4-bromo-1,8-naphthalenedicarboxylic anhydride and 4,4'-dihydroxybiphenyl with in N,N-dimethylacetamide in the presence of anhydrous K₂CO₃ at 150 °C for 20 h at a yield of 75%. A series of copolyimides were synthesized by condensation polymerization of the BPNDA with 1,3-bis(4-aminophenoxy)benzene (BAPBz) and 2-(4-aminophenyl)-5-aminobenzimidazole (APABI) in *m*-cresol in the presence of benzoic acid and isoquinoline at 180 °C for 20 h. The resulting copolyimides were post-sulfonated in concentrated sulfuric acid at 50 °C for 24 h. Membranes were prepared by solution cast method. Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) at varied relative humidities and temperatures.

Results and Discussion

We have previously reported that the incorporation of benzimidazole groups into polyimide main chain could significantly improve the radical oxidative stability of the SPI membranes [3]. However, the hydrolytic stability of the SPI membranes decreased when NTDA was used as the dianhydride monomer. The hydrolytic mechanism involves the attack of water molecules to the carbonyl carbon atoms and more positive the carbonyl carbon, the faster hydrolytic rate. As a result, it is expected that the SPIs derived from the dianhydride monomers with lower electron affinity will have higher

hydrolytic stability. In this presentation, a new dianhydride BPNDA with lower electron affinity was synthesized to replace NTDA. As shown in Scheme 1, first a series of copolyimides are synthesized by random copolymerization of BPNDA, BAPBz, and a benzimidazole-containing diamine APABI. The diamine molar ratio was controlled at BAPBz/APABI = 2/1, 1/1, 1/2 and 1/3, and the resulting copolyimides are denoted as PI-2/1, PI-1/1, PI-1/2 and PI-1/3, respectively. Then the prepared copolyimides were post-sulfonated using concentrated sulfuric acid as the sulfonating reagent at 50 °C for 24 h. Accordingly the resulting sulfonated polymers are denoted as SPI-2/1, SPI-1/1, SPI-1/2 and SPI-1/3, respectively. The formation of polyimide structure and the successful sulfonation are confirmed by the FT-IR spectra (not shown).



Scheme 1. Synthesis of BPNDA-based PIs and SPIs.

Table 1. Reduced viscosity, solubility and tensile properties of the synthesized PIs and SPIs

Polymer	η^a (dL/g)	Solubility ^b				Tensile strength(Mpa)	Elongation at break(%)
		<i>m</i> -Cresol	DMSO	DMAc	NMP		
PI-2/1	0.31	+	-	+/-	+	79	42.8
PI-1/1	0.55	+	-	+/-	+	82	19.4
PI-1/2	0.58	+	-	+/-	+	84	18.1
PI-1/3	0.42	+	-	+/-	+	95	27.5
SPI-2/1	1.72	-(+)	+	+	+	50	14.8
SPI-1/1	1.71	-(+)	+	+	+	70	31.1
SPI-1/2	1.90	-(+)	+	+	+	69	44.8
SPI-1/3	1.65	-(+)	+	+	+	83	20.4

Keys: “+” – soluble on heating; “+/-” – partially soluble on heating; “-” – insoluble on heating.

^a PIs – measured in *m*-Cresol at 30 °C; SPIs – measured in DMSO at 30 °C.

^b The data in the parenthesis refer to the polymers in their triethylamine salt form.

The viscosity, solubility and tensile properties of the synthesized PIs and SPIs are listed in Table 1. The reduced viscosities of the nonsulfonated PIs are in the range 0.31-0.58 dL/g in *m*-cresol at 30 °C. After sulfonation the reduced viscosity increased to 1.65-1.90 dL/g under the same conditions due to the presence of ionic groups of the SPIs. The PIs are well soluble in *m*-cresol and

1-methyl-2-pyrrolidone (NMP) but insoluble in DMSO. The SPIs in their triethylammonium salt form are well soluble in all the tested solvents (*m*-cresol, DMSO, DMAc and NMP) indicating that the solubility was improved after sulfonation. From Table 1, it can also be seen that the PI membranes show high tensile strength ranging from 79-95 MPa indicating that high molecular weight polymers have been successfully synthesized. After sulfonation, the tensile strength decreased to some extent but is still high (50-83 MPa). It's well known that polyimides are generally unstable (hydrolyze) in concentrated sulfuric acid. The reasonably high tensile strength of the SPI membranes in this study suggests that no serious polymer degradation occurred during the process of post sulfonation. This is likely attributed to the high stability of the PIs resulting from the low electron affinity BPANDA moiety which greatly suppressed the hydrolysis of the imide rings.

The ion exchange capacity (IEC), water uptake (WU), swelling ratio, and proton conductivity (σ) in water at 60 °C of the SPI membranes are shown in Table 2. It can be seen that the IEC values are in the range 2.81-1.63 meq/g and decreases with an increase in the BAPBI content in the copolyimides. Note that the benzimidazole groups of the BAPBI moiety have basicity which can react with the sulfonic acid groups to form ionic cross-linking. The SPII-2/1 is soluble in deionized water at 80 °C due to its very high IEC. The SPI-1/1 and SPI-1/2 became insoluble in hot water due to decreased IECs but the swelling ratios are still very large. To suppress membranes swelling, the SPI-2/1, SPI-1/1 and SPI-1/2 are further covalently cross-linked by treating in polyphosphoric acid at 180 °C for 14 h, and the the resulting membranes are denoted as CSPI-2/1, CPI-1/1 and CSPI-1/2, respectively. The IEC, WU, swelling ratio and are also listed in Table 2 for comparison. It can be seen that the covalent cross-linking caused slight decreases in IEC but significant reduction in WU and membrane swelling. All the membranes except SPI-1/3 show high proton conductivity comparable to that of Nafion (0.11 S/cm).

Table 2. Ion exchange capacity (IEC), Water Uptake (WU), swelling ratio, and proton conductivity (σ) of the cross-linked and uncross-linked SPI membranes

Polymer	IEC (meq/g)	WU ^a (wt%)	Swelling ratio ^b (%)		σ^c (S/cm)
			ΔL (in-plane)	ΔT (through-plane)	
SPI-2/1	2.81	–	NM	NM	NM
SPI-1/1	2.35	113	32.5	30.8	0.15
SPI-1/2	2.10	105	26.7	25.9	0.14
SPI-1/3	1.63	48	9.3	10.9	0.058
CSPI-2/1	2.68	128	38.4	37.1	0.26
CSPI-1/1	2.08	80	15.5	16.4	0.10
CSPI-1/2	2.01	75	15.1	15.5	0.093

“–”: dissolved in water. NM: not measured. ^a At 80 °C. ^b At 80 °C. ^c In water at 60 °C.

The results of the radical oxidative stability and the water stability of the polyimide membranes are summarized in Table 3. To evaluate the oxidative stability, all the membranes are immersed in 3% hydrogen peroxide containing 3 ppm ferrous sulfate at 80 °C and the radical oxidative stability is characterized by the elapsed time when the membranes starts to break into pieces (τ_1) or to dissolve (τ_2). It can be seen that for the covalently uncross-linked membranes, the values of τ_1 increases in the order: SPI-2/1 < SPI-1/1 < SPI-1/2 < SPI-1/3, which follows the increases in the BAPBI content. It should be noted that the SPII-2/1 membranes had a very short τ_1 , because it was soluble in water at 80

°C. The SPII-1/3 membrane with the highest content of benzimidazole groups shows the longest τ_1 value which is superior to that of common SPI membranes. For the covalently cross-linked membranes, both the CSPII-1/1 and CSPII-1/2 display about four times longer τ_1 value than the uncross-linked ones. This indicates that the synergic action of the incorporation of benzimidazole groups into polymer main chain and the covalent cross-linking caused significant improvement in the radical oxidative stability of the SPI membranes.

Table 3. Radical oxidative stability of various SPI membranes by Fenton's test in 3% H₂O₂ containing 3 ppm FeSO₄ at 80 °C and water stability at 140 °C

Membrane	IEC (meq/g)	τ_1^a (min)	τ_2^b (min)	Weight loss at 140 °C (%)
SPI-2/1	2.81	1	1	100 (1 day)
SPI-1/1	2.35	38	48	100 (1 day)
SPI-1/2	2.15	42	54	100 (1 day)
SPI-1/3	1.53	182	210	NM
CSPI-2/1	2.68	25	42	NM
CSPI-1/1	2.08	125	140	7.9 (5 days)
CSPI-1/2	2.01	185	208	6.1 (5 days)

^a Elapsed time when the membranes started to dissolve.

^b Elapsed time when the membranes started to break into pieces.

To evaluate the water stability, all the membranes are soaked in deionized water at 140 °C for 5 days in an autoclave and the water stability is characterized by the weight loss of the membranes. It was found that the SPI-1/1 and SPI-1/2 membranes dissolved in water for 1 day indicating poor water stability. However, the CSPII-1/1 and CSPII-1/2 membranes did not dissolve in water even after 5 days soaking and the weight loss values are only 7.9% for the CSPI-1/1 and 6.1% for the CSPI-1/2. This indicates that the covalent cross-linking treatment is very effective to enhance the water stability. Moreover, the employment of BPNDAs instead of the widely used NTDA as the dianhydride monomer is really very effective to suppress the hydrolysis of imide rings.

Conclusions

A new dianhydride monomer BPNDAs and a series of BPNDAs-based copolyimides have been successfully synthesized. Post-sulfonation did not cause serious degradation of polymer main chains. The covalently cross-linked SPI membranes showed decreased water uptake and swelling ratio, greatly enhanced radical oxidative stability and water stability. The employment of BPNDAs instead of NTDA as the dianhydride monomer is very effective to suppress the hydrolysis of imide rings.

Acknowledgement

This work was supported by Shanghai Municipal Natural Science Foundation (Grant No. 08ZR1410300) and the Jiangsu Key Laboratory for Design and Manufacture of Micro-Nano Biomedical Instruments (Grant No. JSNBI201002).

[1] Yan, J.; Liu, C.; Wang, Z.; Xing, W.; Ding, M., *Polymer*, **48**, 6210-6214(2007).

[2] Wei, H. Fang, X., *Polymer*, **52**, 2735-2739(2011).

[3] Zhang, G.; Guo, X.; Fang, J.; Chen, K.; Okamoto, K. *J. Membr. Sci.*, **326**, 708-713(2009).