

# Preparation and Properties of Highly Polyphosphoric-Acid-Doped Polyimide Membranes for Medium Temperature Fuel Cell Applications

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**Abstract:** A series of poly(benzimidazole imide)s (PBII)s have been synthesized by condensation polymerization of biphenyl-4,4'-diyl di(oxo)-4,4'-bis(1,8-naphthalenedicarboxylic anhydride) (BPNDA), (2-(4-aminophenyl)-5-aminobenzimidazole (APABI) and 4,4'-diaminodiphenyl ether (ODA) in *m*-cresol in the presence of benzoic acid and isoquinoline at 180 °C for 20 h. The resulting poly(benzimidazole imide)s showed excellent thermal stability (5% weight loss temperatures  $T_d^5 = 491-547$  °C in air by thermogravimetric analysis). The PBII membranes could be doped with polyphosphoric acid (PPA) at 150 °C and extremely high PPA uptake up to 750 wt% was successfully achieved. Despite the very high doping levels the membranes still maintained relatively high mechanical properties even at high temperatures. The BPNDA-APABI/ODA(1/1) membrane at a doping level of 540%, for example, had a tensile strength of 5.2 MPa and an elongation at break of 140 % at 150 °C, which were much better than the common polybenzimidazole membranes. Moreover, the poly(benzimidazole imide) membranes displayed high proton conductivities (up to 0.2 S/cm) at 0% relative humidity at elevated temperatures due to the high acid doping levels. Fenton's test revealed that these membranes had excellent radical oxidative stability which makes them good candidates for high temperature fuel cell applications.

Keywords: Poly(benzimidazole imide); membrane; PA-doping; proton conductivity

## Introduction

Phosphoric acid (PA)-doped polybenzimidazole (PBI) membranes have been identified to be the most promising polymer electrolyte membranes (PEMs) for medium temperature (120-200 °C) fuel cell applications because of their high proton conductivity at elevated temperatures at low relative humidities or even under completely anhydrous condition [1-6]. The proton conductivity of such membranes is determined by the PA-doping levels, and the higher doping level, the larger proton conductivity. However, too high doping levels often causes excess swelling or even complete loss of mechanical strength of the membranes. From viewpoint of practical applications, it is strongly desired to develop membranes with high PA-doping levels (and thus high proton conductivities), and meanwhile high mechanical strength is maintained [7-9]. In this paper, we report on the synthesis of a series of novel PIs containing benzimidazole groups in the backbones, acid doping, proton conductivity and other properties of the PI membranes. The basic benzimidazole groups is responsible for acid doping, while the PI units are expected to keep the mechanical strength due to the nature of excellent mechanical properties and the weak interactions with acid in comparison with benzimidazole units.

## Experimental

### Materials

4-Bromo-1,8-naphthalenedicarboxylic anhydride was purchased from QuZhou Rainful Chemical Co. Ltd (China) and was purified by recrystallization from chloroform before use. 4,4'-Diaminodiphenyl ether

(ODA) was purchased from TCI. 2-(4-aminophenyl)-5-aminobenzimidazole (APABI) was synthesized according to a literature method [10]. Polyphosphoric acid (PPA, phosphorus pentoxide assay: 80%), phosphorus pentoxide, N,N-dimethylacetamide (DMAc), *m*-cresol, benzoic acid and isoquinoline were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). DMAc was distilled under reduced pressure and stored over 4 Å molecular sieves before use. Other materials were used as received.

#### *Synthesis of biphenyl-4,4'-diyl di(oxo)-4,4'-bis(1,8-naphthalenedicarboxylic anhydride)*

To a 250 mL dry 3-neck flask equipped with a nitrogen inlet and outlet, a condenser and a Dean-Stark trap were added 3.20 g (80 mmol) of sodium hydroxide and 100 mL methanol. The mixture was magnetically stirred at room temperature under nitrogen flow till the solid was completely dissolved. 7.44 g (40 mmol) of DHBP was added to the flask and the mixture was stirred at room temperature for 0.5 h and then heated at reflux for 2 h. The flask was collected to a vacuum pump to remove the solvent (methanol) by evaporation under reduced pressure. After the methanol was completely removed, the flask was allowed to cool to room temperature. 23.268 g (84 mmol) of 4-bromo-1,8-naphthalenedicarboxylic anhydride, 100 mL DMAc and 20 mL toluene were added to the flask and the reaction mixture was heated at 160 °C for 20 h. Most of the solvent (DMAc) was removed by vacuum evaporation and the residual was poured into 300 mL acetone. The solid was collected by filtration, thoroughly washed with acetone and deionized water, and dried at 120 °C for 10 h. 17.22 g yellowish solid was obtained, yield: 74.5%.

#### *Polymerization*

The experimental procedures for the synthesis of poly(benzimidazole imide)s are described below using the copolymer BPNDA-APABI/ODA(4/1, by mole) as an example.

To a 100 mL dry 3-neck flask equipped with a nitrogen inlet and outlet and a condenser were added 1.156 g (2.0 mmol) of BPNDA, 0.3584 g (1.6 mmol) of APABI, 0.0800 g (0.4 mmol) of ODA, 10 mL *m*-cresol, 0.4880 g (2.0 mmol) of benzoic acid and 0.5170 g (2.0 mmol) of isoquinoline. The reaction mixture was magnetically stirred at room temperature for 0.5 h and then heated at 180 °C for 20 h under nitrogen flow. After cooling to room temperature, the highly viscous solution was poured into acetone and the resulting precipitate was collected by filtration, thoroughly washed with acetone and dried under vacuum at 100 °C for 10 h.

#### *Membrane Formation and Acid Doping*

The synthesized poly(benzimidazole imide)s were dissolved in *m*-cresol to form ~10 wt% clear solutions which were subsequently cast onto glass plates and dried at 110 °C for 10 h. The as-cast membranes were immersed in methanol at 50 °C for one day and then dried at 120 °C for 20 h under vacuum to remove any residual solvents. Acid-doping was performed by immersing the dry membranes in PPA at 150 °C for 5 h. The membranes were taken out and washed with 85% PA solution three times (~1 minute each time) to remove the residual PPA on the membrane surfaces. The membranes were blotted with tissue paper and dried at 120 °C for 20 h.

#### *Measurements*

FT-IR spectra of the polymer membranes with thickness of about 10-30 μm were recorded on a Perkin-Elmer Paragon 1000PC spectrometer. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury Plus 400 MHz instrument. Thermogravimetric analysis (TGA) was performed in air with a TGA 2050 instrument at a heating rate of 10 °C/min. The inherent viscosities ( $\eta_{inh}$ ) were measured in DMSO with an Ubbelohde viscometer at 30 °C. Tensile measurements were performed with an Instron 4456 instrument in ambient atmosphere at a crosshead speed of 2 mm/min. 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) [21]. A sheet of membrane (doped with H<sub>3</sub>PO<sub>4</sub>) and two pairs of

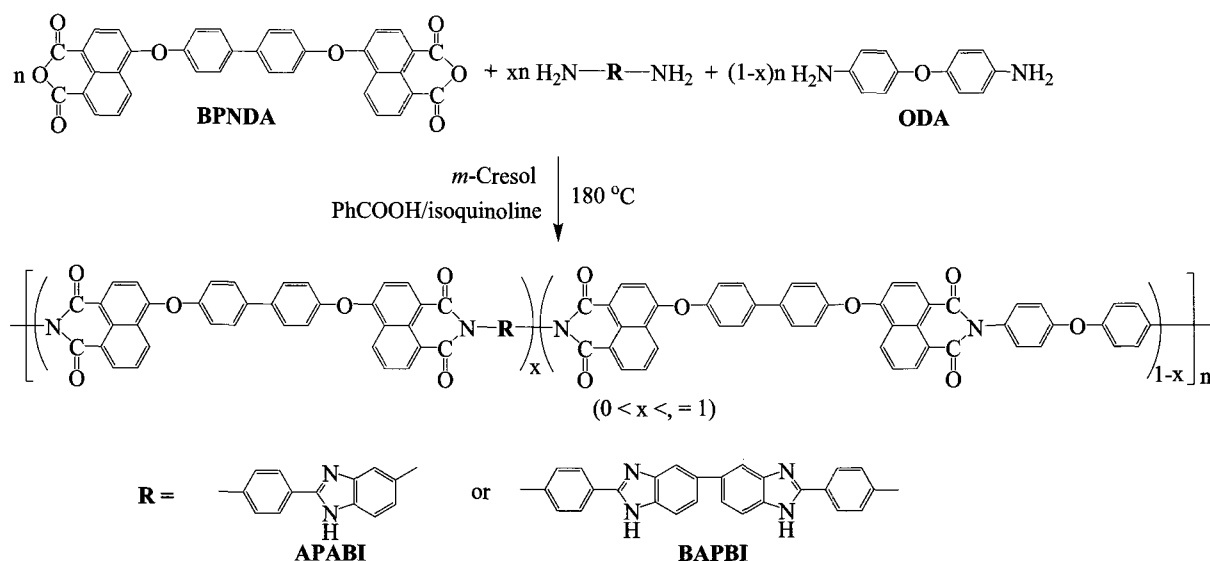
blackened platinum plate electrodes were set in a Teflon cell. The cell was placed in a thermo-controlled chamber which had an inlet and an outlet for continuous nitrogen flow. Before starting the conductivity measurement, the chamber was heated at 170 °C for one day to remove any water vapor so that the relative humidity could reach 0%. After that, the temperatures of the chamber was set at the desired values and kept constant for 30 minutes at each point. 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, and  $R$  is the resistance measured.

## Results and Discussion

The benzimidazole-containing polyimides were synthesized by condensation polymerization of BPNDA, APABI and ODA in *m*-cresol in the presence of benzoic acid and isoquinoline at 190 °C for 20 h (Scheme 1). APABI is the benzimidazole group-containing diamine monomer. APABI was synthesized according to a literature method [1]. ODA is a common diamine which was used in this study as a comonomer to regulate the benzimidazole group content in the polymers. The new naphthalenic dianhydride monomer, BPNDA, was synthesized via the reaction of 4-bromo-1,8-naphthalenedicarboxylic anhydride and 4,4'-dihydroxybiphenyl in DMAc in the presence of sodium hydroxide at 160 °C at a yield of 75%. The chemical structures of the synthesized monomers (BPNDA and APABI) were characterized by <sup>1</sup>H NMR and FT-IR spectra. It should be noted that replacing BPNDA with the commercial naphthalenic dianhydride monomer, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), which has been widely used for the synthesis of various sulfonated polyimides resulted in insoluble precipitate during polymerization processes, and therefore NTDA could not be used for synthesizing the benzimidazole-containing polyimides.



**Scheme 1.** Synthesis of various benzimidazole group-containing polyimides.

The polyimides synthesized in this study are soluble in *m*-cresol and NMP but insoluble in other organic solvents such as DMSO and DMAc (Table 1). The reduced viscosities of these polymers are in

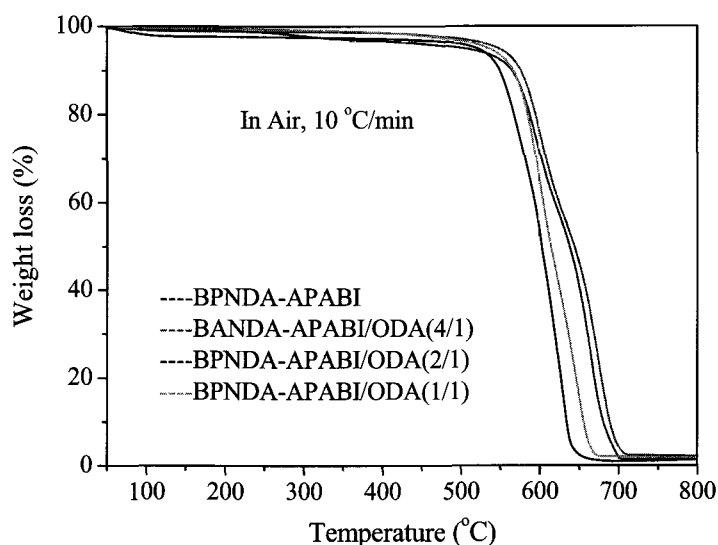
the range of 0.33-0.88 dL/g in *m*-cresol at 0.5 g/dL at 30 °C. Transparent and tough membranes were fabricated by solution cast method. The tensile strength of the membranes is in the range of 81-123 MPa indicating that high molecular weight polyimides have been successfully synthesized.

Table 1 Reduced viscosity ( $\eta$ ), PPA uptake, tensile strength and elongation at break (EB) of the membranes

Membrane	$\eta^a$ (dL/g)	PPA Uptake (wt%)	MS (MPa)	EB (%)
BPNDA-APABI	0.33	0	81	12
BPNDA-APABI/ODA(4/1)	0.55	780	4.4 (1.5)	41 (43)
BPNDA-APABI/ODA(2/1)	0.74	610	6.5	18
BPNDA-APABI/ODA(1/1)	0.88	550	7.8	25
BPNDA-BAPBI/ODA(1/1)	0.70	510	28 (5.2)	30 (140)
Commercial PBI*	-	430	9.8 (3.3)	25 (103)
		410 (H <sub>3</sub> PO <sub>4</sub> )	7.8-8.2	80-96

<sup>a</sup> Measured in *m*-cresol at 0.5 g/dL at 30 °C. The data in parenthesis were obtained at 150 °C

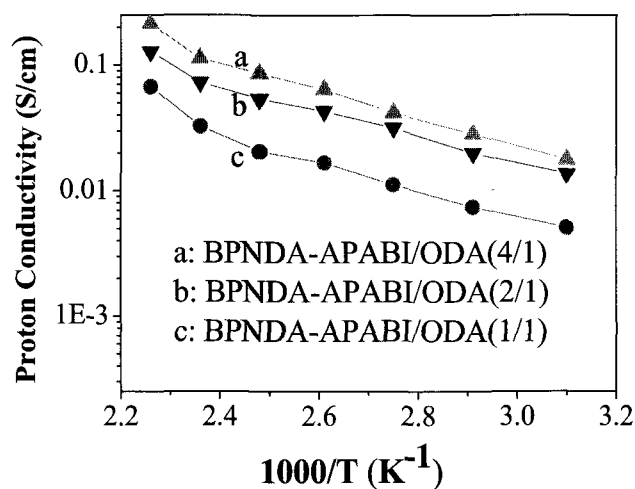
The thermal stability of the PBIs was investigated by TGA in air at a heating rate of 10 °C/min (**Figure 1**). The 5% weight loss temperatures ( $T_d^5$ ) are in the range of 491-547 °C indicating excellent thermal stability of the polymers.



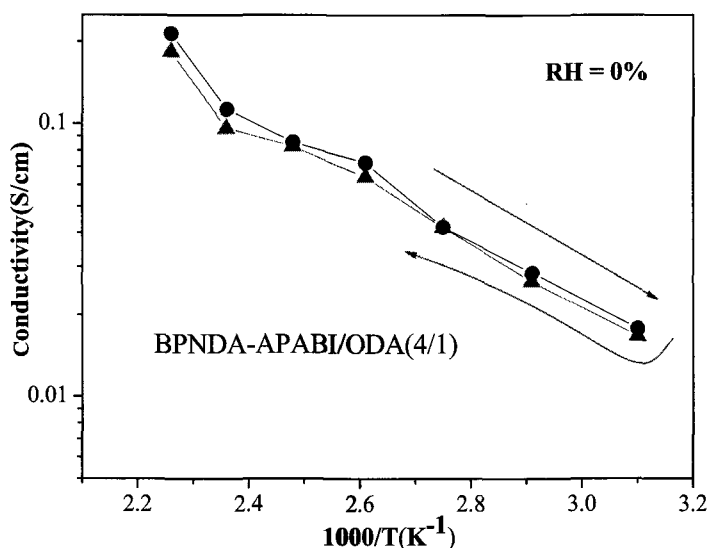
**Figure 1.** TGA curves of the synthesized poly(benzimidazole imides).

The acid-doping was performed by immersing the membranes into PPA at 150 °C for 5 h. As shown in Table 1, all the membranes had extremely high PPA uptake (430-700 wt%) due to the strong acid-base (PPA-benzimidazole groups) interaction. Moreover, the membranes with higher benzimidazole content tended to have higher PPA uptake. PPA-doping caused large decreases in tensile strength because of the plasticization effect of PPA. However, all the PPA-doped membranes could still maintain reasonably high mechanical strength. BPNDA-APABI/ODA(1/1), for example, had tensile strength of 28 and 5.2 MPa and elongation at break of 30% and 140% at room temperature and 150 °C, respectively, which is much superior to the commercial polybenzimidazole membrane. In fact, at high

temperatures (e.g. 150 °C), the commercial polybenzimidazole membrane completely lost mechanical strength at high acid doping levels [3].



**Figure 2.** Variation of proton conductivity of PPA-doped polyimide membranes as a function of temperature at 0% relative humidity.



**Figure 3.** Variation of proton conductivity of the BPNDA-APABI/ODA(4/1) membrane as a function of temperature at 0% relative humidity on both heating run and cooling run.

The proton conductivity was measured at 0% relative humidity at different temperatures. As shown in **Figure 2**, the membranes generally displayed high proton conductivities because of the high PA doping levels. Moreover, it can be seen that the conductivity increased with an increase in temperature and at the same temperature the membranes with higher doping levels displayed higher proton conductivities. High proton conductivity up to 0.2 S/cm was successfully achieved with the membrane BPNDA-APABI/ODA(4/1) at 170 °C. **Figure 3** shows the variation of proton conductivity of the BPNDA-APABI/ODA(4/1) membrane as a function of temperature at 0% relative humidity on both

heating run and cooling run. It can be seen that the conductivity data obtained in the heating run are close to those in the cooling run. This indicates that the hysteresis is insignificant.

### Conclusions

A new naphthalenic dianhydride monomer, BPNDA, and a series of BPNDA-based poly(benzimidazole imide)s have been successfully synthesized. The synthesized poly(benzimidazole imide)s displayed excellent thermal stability in air. The poly(benzimidazole imide)s membranes with good mechanical properties were prepared by solution cast method. They showed very high PPA uptake and thus high proton conductivities even at 0% relative humidity, while high mechanical strength was maintained which is very favorable for use in high temperature PEMFCs.

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