

# PBI/ Ethyl Phosphoric Acid Grafted PBI Blend Membranes for High Temperature Fuel Cells

Phimraphas Ngamsantivongsa, T. Leon Yu, and Hsiu-Li Lin

**Abstract**— in this research polybenzimidazole (PBI) and grafted side chain phosphonate PBI-EPA were synthesized, the polymer structures, grafting percentage and molecular weight were identified by FTIR, NMR spectroscopy TGA (Thermogravimetric Analysis), and GPC (Gel Permeation Chromatography). The various ratios of PBI/PBI-EPA blended membranes were fabricated. The phosphoric acid doping level of blended membranes was increased when the blended weight percentage of PBI-EPA enhanced. Membrane electrode assemblies (MEAs) of PBI/PBI-EPA membranes had a better PEMFC (proton exchange membrane fuel cell) performance more than pure PBI membrane at 160°C.

**Keywords**— grafted side chain phosphonate PBI-EPA, membrane electrode assemblies, polybenzimidazole (PBI), proton exchange membrane fuel cell

## I. INTRODUCTION

**P**OLYMER electrolyte membrane fuel cells (PEMFCs) are one of the striking alternative energy resource systems that can be utilized in many applications such as vehicles, mobile phones, and on-site power generators [1–7]. Compared with liquid electrolyte systems, PEMFCs with proton exchange membranes (PEMs) as the electrolyte have lots of advantages. They are much easier to be handled, sealed, and assembled [8]. High-temperature operated PEMFCs have attracted substantial attention in the last decade due to their wide applicability, the possibility to reduce costs of the existing devices and to make them more environmentally friendly. In order to optimize the fuel cell performances, a lot of work has been focused on the material development. Among the polymers of choice, acid-doped polybenzimidazoles (PBI) seems to offer an optimal combination of properties such as mechanical stability, higher values of conductivity at temperatures up to 200°C [9]. In this study, the syntheses of PBI and PBI grafted with ethyl-benzyl phosphoric acid are discussed. The synthesized polymers have been characterized using Fourier-transform infrared

spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) for chemical structure identifications, thermogravimetric analysis (TGA) for thermal properties, and gel permeation chromatography (GPC) for polymer molecular weights and weight distributions. The results will be discussed and compared.

## II. EXPERIMENTAL

### A. Materials

3,3'-Diaminobenzidine (DAB):  $(\text{H}_2\text{N})_2(\text{C}_6\text{H}_3)_2(\text{NH}_2)_2$ , isophthalic acid (IPA)  $\text{C}_6\text{H}_4(\text{COOH})_2$ , diethyl (2-bromoethyl) phosphonate, lithium hydride (LiH), polyphosphoric acid (PPA), and N,N'-dimethyl acetamide (DMAc) were all chemical reagent grade and purchased from Aldrich Chemical Co.

### B. Synthesis and characterization of PBI

PBI was synthesized from 3,3'-Diaminobenzidine (DAB) and isophthalic acid (IPA). The general synthetic procedure is shown in Fig. 1. Polyphosphoric acid (PPA) (5400 g) was fed into a four-neck flask with reflux condenser at room temperature. The temperature of the flask is raised to 235°C and the PPA in the flask was stirred at 235°C under  $\text{N}_2$  gas till a flow liquid state was observed. The temperature of the flask was kept at 235°C, 286 g (1.336 mole) DAB monomer was then fed slowly into the flask and mixed with the PPA solvent. The temperature of the flask was still kept at 235°C under  $\text{N}_2$  gas for at least 2 h till a homogeneous mixture was obtained. 221.8 g (1.336 mole) of IPA was added into the flask at 235°C and mixed with DAB and PPA. The temperature was then kept at 235°C under  $\text{N}_2$  gas for 48 h for PBI polymerization. The final mixture consists of PBI and PPA. Pour the hot product mixture into a beaker containing a large quantity of distilled water. A fiber-like PBI precipitate product was obtained. Rinse the precipitate several times with distilled water. Cool the precipitate PBI product with liquid nitrogen and then mill the product to powder. The PBI powder was mixed with 2 L 0.5 N NaOH aqueous solution in a beaker and stirred for 4 h to dissolved out the phosphoric acid inside the powder. Filter the precipitate and repeat the above procedure for 3 times with a fresh NaOH aqueous solution. The PBI product was boiled with distilled water for 3 h and then filtered the PBI product. Repeat this procedure for several times till the filtrate with a pH value of around 7~8. The PBI powder was heated at 100~120 °C

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under vacuum for 3 h to remove the residual moisture.

FTIR analysis of PBI synthesized was carried out by a Perkin Elmer Spectrum 100. KBr pellet method was used.  $^1\text{H}$  NMR spectra of PBI in deuterated  $N,N$ -dimethylformamide (DMF)  $\text{DMF-d}_7$  were recorded on a Bruker 510 spectrometer (1H, 500 MHz). Thermogravimetric analysis (TGA) was performed with a TA TGA Q50 thermogravimetric analyzer (Thermal Analysis Instrument) under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$  and the sample was heated from room temperature to  $800^\circ\text{C}$ . Gel permeation chromatography (GPC) measurement of PBI was conducted by using a Shimadzu GPC equipment, model PU-2080, A 40  $\mu\text{L}$  injection loop was employed with a PBI sample concentration of 0.3 mg/mL. The PBI molecular weight was calibrated with polystyrene standard ( $M_w/M_n < 1.1$ , Aldrich).

### C. Synthesis and characterization of PBI-EPA

The synthetic procedure of PBI-EPA is shown in Fig. 2. 2 g PBI was mixed with 70 g  $N,N'$ -dimethyl acetamide (DMAc) solvent at  $75^\circ\text{C}$  in a four-neck flask with a reflux condenser under  $\text{N}_2$  gas for 6 h till a homogeneous solution was obtained. 0.5 g LiH was added into the PBI/DMAc solution, and the reaction was proceeded at  $75^\circ\text{C}$  for 12 hr. 3.68 g diethyl (2-bromoethyl) phosphonate was then mixed into the solution. The temperature is raised to  $90^\circ\text{C}$  and the reaction was performed at  $90^\circ\text{C}$  for 48 h. Turn off the heater (keep the stirrer on) to cool the mixture to room temperature. Pour the product mixture of procedure into a beaker containing a large quantity of acetone. A dark red brown precipitate was obtained. Filter the mixture solution to obtain the solid precipitate product. Pour the solid product of procedure into acetone solvent to dissolve the un-reacted reactants from the solid product. Filter the mixture to obtain the solid product. Repeat this procedure for three times. Dry the residual solvent at  $100^\circ\text{C}$  under vacuum for 2 h. Mix the product into 100 g 12 M HCl aqueous solution, and stir the mixture at  $60^\circ\text{C}$  for 24 h. Filter the solid powder to obtain PBI-EPA. Mix the PBI-EPA powder into distilled water to remove the HCl from PBI-EPA powder. Repeat this procedure for several times. Evaporate the residual water from the PBI-EPA powder at  $\sim 100^\circ\text{C}$  under vacuum for 2 h.

FTIR analysis of PBI-EPA synthesized was carried out by a Perkin Elmer Spectrum 100. KBr pellet method was used.  $^1\text{H}$  NMR spectra of PBI-EPA in deuterated  $N,N$ -dimethylformamide (DMF)  $\text{DMF-d}_7$  were recorded on a Bruker 510 spectrometer (1H, 500 MHz). Thermogravimetric analysis (TGA) was performed with a TA TGA Q50 thermogravimetric analyzer (Thermal Analysis Instrument) under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$  and the sample was heated from room temperature to  $800^\circ\text{C}$ . Gel permeation chromatography (GPC) measurement of PBI-EPA was conducted by using a Shimadzu GPC equipment, model PU-2080, A 40  $\mu\text{L}$  injection loop was employed with a PBI-EPA sample concentration of 0.3 mg/mL. The PBI-EPA molecular weight was calibrated with polystyrene standard ( $M_w/M_n < 1.1$ , Aldrich).

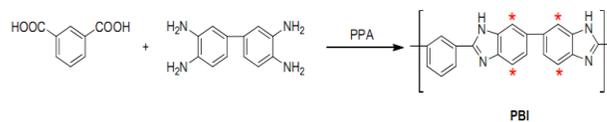


Fig. 1 Synthetic procedure of PBI

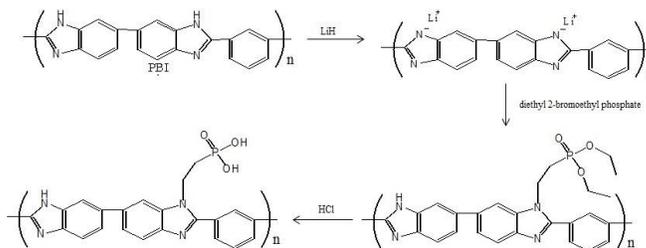


Fig. 2 Synthetic procedure of PBI-EPA

### D. Preparation of PBI and PBI/PBI-EPA membranes

For PBI membrane : PBI (2 g) and  $N,N$ -dimethyl acetamide (DMAc) solvent (35 g) were placed in a bottle and stirred at  $135^\circ\text{C}$  to obtain a homogeneous dilute solution. The solvent was gradually evaporated at  $\sim 100\text{--}120^\circ\text{C}$  using a rotating vacuum evaporator to obtain a  $\sim 15\text{ wt}\%$  PBI / DMAc concentrated solution. The solution was then spread onto a clean flat glass plate. The thickness of the solution was controlled using an adjustable doctor blade. The casted solution was heated stepwise from  $60$  to  $120^\circ\text{C}$  in a convection oven until no DMAc evaporation was noted and then maintaining the temperature for 24 h under vacuum to obtain a PBI membrane with a thickness of  $\sim 70\text{--}80\ \mu\text{m}$ . For PBI/PBI-EPA membrane : PBI and PBI-EPA was mixed with [PBI]/[PBI-EPA] wt ratios of 8/2, 7/3 and 6/4 in DMAc solvent at  $135^\circ\text{C}$  to obtain a homogeneous dilute solution. The solvent was gradually evaporated at  $\sim 100\text{--}120^\circ\text{C}$  using a rotating vacuum evaporator to obtain a  $\sim 15\text{ wt}\%$  PBI/PBI-EPA blend/DMAc concentrated solution. The solution was then spread onto a clean flat glass plate. The thickness of the solution was controlled using an adjustable doctor blade. The casted solution was heated stepwise from  $60$  to  $120^\circ\text{C}$  in a convection oven until no DMAc evaporation was noted and then maintaining the temperature for 24 h under vacuum to obtain a PBI membrane with a thickness of  $\sim 70\text{--}80\ \mu\text{m}$ . For achieving the proton conduction ability of the membrane, the dried films were immersed in PA solution with 85% concentration at  $70^\circ\text{C}$  for 48 h, 12 h, and 6 h. The PA-doped membranes were taken out from the PA solution and then blotted with filter paper.

### E. Acid doping

The membranes ( $1.0 \times 1.0\ \text{cm}^2$ ) were doped with phosphoric acid by immersing the membrane in an 85 wt% phosphoric acid aqueous solution at  $70^\circ\text{C}$  for 6 h, 12 h, and 48 h. The PA content

(wt%) of a membrane is defined as the mass changes of the membrane sample before and after doping:

$$\text{PA content (wt\%)} = (m_A - m_B)/m_B \times 100 \quad (1)$$

where  $m_A$  is the mass of the membrane after the doping and blotting with filter paper and then drying at 110° C for 24h, and  $m_B$  is the mass of the membrane before the doping, respectively[11].

#### F. Preparation of MEAs

The Neat PBI, PBI/PBI-EPA blend in different weight ratio membranes were used to prepare MEAs. The catalyst was a carbon supported Pt catalyst (Pt-C, with 40 wt.% Pt, Johnson Matthey) with both Pt loadings of 0.5 mg cm<sup>-2</sup> at anode and cathode. Pt-C/ Py-PBI/ LiCl/ DMAc (19/1/1/4560 by wt) catalyst solution was prepared by ultrasonic disturbing for 5 h. The catalyst solution was ultrasonic spray coated on a carbon paper (SGL, 35BC) and then the solvent of the catalyst layer coated on the carbon paper was evaporated at 80°C for 1 h and then at 120°C for another 1 h under vacuum. The carbon papers coated with catalyst layers were then immersed in distilled water for 20 min and the process was repeated 5 times by changing with a fresh distilled water to remove the LiCl. The carbon papers coated with catalyst layers were then dried under vacuum at 60°C for 1 h to remove residue water. They were then doped with phosphoric acids by dipping in a 10 wt% H<sub>3</sub>PO<sub>4</sub> aqueous solution at room temperature for 24 h and dried in an oven at 110°C for 2 h. Two carbon papers coated with catalyst layers were put on both sides of a membrane then put gaskets with thickness of 200 μm on both side of the MEA, and pressed with a pressure of 25 kgf-cm to obtain a MEA. The active area of each MEA was 3.5x3.5 cm<sup>2</sup>.

#### G. Unit cell PEMFC performance tests

The performances of single cells were tested at 160°C and ambient pressure using a FC 5100 series fuel cell testing system (CHINO Inc., Japan). Both the non-humidified H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air gases were used for fuel cell tests. The non-humidified H<sub>2</sub> and O<sub>2</sub> flow rates were both at 200 mL min<sup>-1</sup>; and the non-humidified H<sub>2</sub> and air gases were at flow rates of 200 mL min<sup>-1</sup> and 1000 mL min<sup>-1</sup>, respectively. The testing cell active area of each MEA was 3.5x3.5 cm<sup>2</sup>. The i-V curves were obtained after the fuel cell was operated for 8 h by measuring the current density  $i$  with step decrement of voltage by an interval of 0.05 V. The duration of each i-V measurement was 30 sec.

### III. RESULTS AND DISCUSSION

#### A. Characterization of PBI and PBI-EPA

The molecular structures of the PBI and PBI-EPA were characterized by FT-IR spectroscopy. FT-IR spectra of PBI, PBI-EPA are shown on Fig. 3 and Fig. 4 respectively. The PBI exhibited characteristic absorption bands at 3450-3250 cm<sup>-1</sup> and 1640 cm<sup>-1</sup>, which were assigned to the stretching vibration of the N-H groups and C=N groups in the imidazole rings. A small shoulder at 3100-3000 cm<sup>-1</sup> from stretching modes of the

aromatic C-H groups, in addition, small peaks at 1036 cm<sup>-1</sup> from the in-plane C-H bending, and the pattern of the oop C-H bending bands in the region 900-675 cm<sup>-1</sup> are also characteristic of the aromatic substitution pattern. The presence of benzimidazole group was, in addition, confirmed by characteristic bands at 1445 cm<sup>-1</sup> due to the in plane deformation of benzimidazole rings. The presence of O=P-OH phosphonic acid at 2725-2525 cm<sup>-1</sup>, 2350-2080 cm<sup>-1</sup> and 1740-1600 cm<sup>-1</sup>. Moreover the P=O stretch appears in the region 1320-1140 cm<sup>-1</sup>.

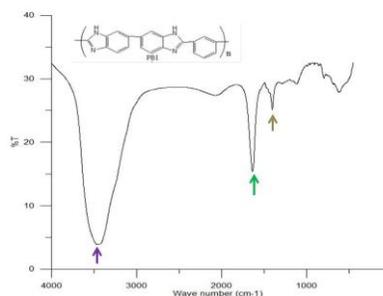


Fig. 3 IR spectra of PBI

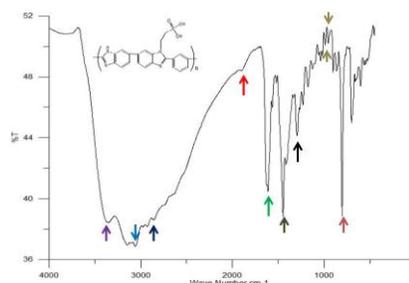
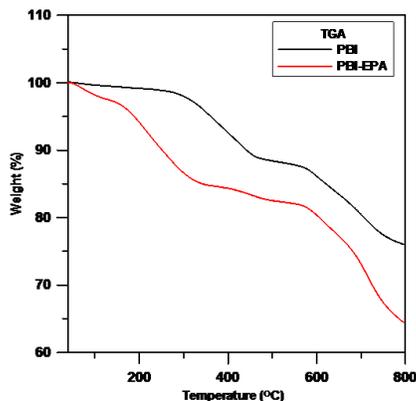


Fig. 4 IR spectra of PBI-EPA

#### B. Thermal gravimetric analyses (TGA)

The thermooxidative stability of PBI and PBI-EPA was studied with TGA in N<sub>2</sub>, as shown in Fig. 5. The pure PBI displayed high thermooxidative stability (stable up to 500°C). TGA curve showed two steps degradation. A relatively wt. loss started at about 50°C and continued till 160°C. The weight loss below 200°C is due to the evaporation of moisture. After first weight loss stage, the polymer remained stable until the temperature of 580°C, the second degradation step started where weight loss curves of these three polymers were similar over this temperature range, which suggests that the weight loss primarily resulted from the decomposition of the PBI imidazole groups. However, at about 200°C and continued until a temperature of 580°C the TGA curve showed larger weight losses for the PBI-EPA which can be attributed to the decompositions of functional groups grafted to PBI main chains.


 Fig. 5 TGA thermograms of PBI and PBI-EPA in  $N_2$ 

### C. Gel permeation chromatography (GPC)

The achievement of PBI and PBI-EPA were also verified via gel permeation chromatography. The absolute weight of PBI and PBI-EPA were not measured due to the lack of an absolute molecular weight detector in our high temperature GPC system. However, the determination of relative molecular weights was conducted by comparing PBI and PBI-EPA with the PS standards as shown in Fig. 6. The relative molecular weights are summarized in Table I.

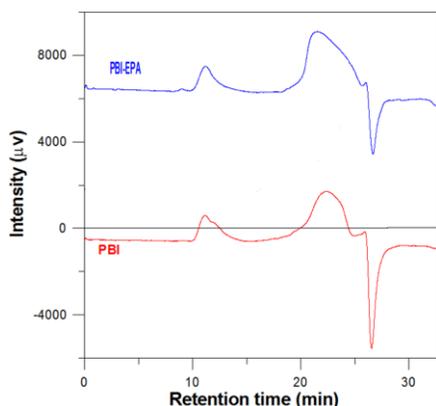


Fig. 6 GPC of PBI and PBI-EPA

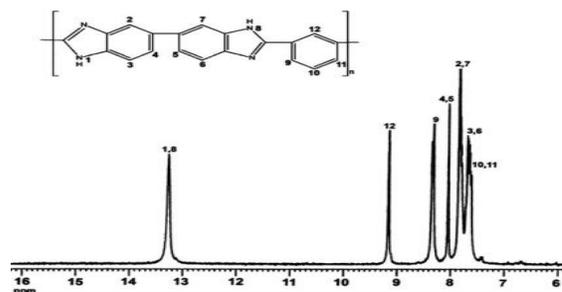
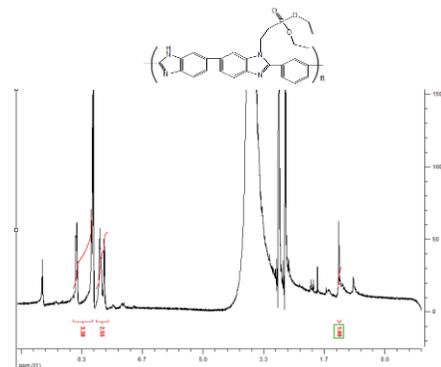
TABLE I  
RELATIVE MOLECULAR WEIGHTS FOR PBI AND PBI-EPA CALIBRATED USING  
PS STANDARD

Polymer	Retention time (minute)	$M_w$	$M_n$	PDI
PBI	22.41	$1.65 \times 10^5$	$7.32 \times 10^4$	2.25
PBI-EPA	21.39	$1.40 \times 10^5$	$7.1 \times 10^4$	1.97

### D. $^1H$ NMR analyses

The formation of PBI polymer was confirmed by the  $^1H$ -NMR spectra as shown in Fig. 7 and Fig. 8. In this NMR spectrum, the imidazole proton peak (-NH) was observed at 13.3 ppm, and all the aromatic protons were at 7–10 ppm. The composition of the C, H, and N in the PBI structure was analyzed by elemental analysis. The theoretical percentages of C, H, and N of the polymer are, respectively, 77.92, 3.9, and 18.18. The peaks at  $\delta = 2.7$  and 2.9 ppm were observed, which was attributed to the DMF solvent. The characteristic peak for

the aromatic proton of O-CH<sub>2</sub>-CH<sub>3</sub> of the grafted EPA was observed at  $\delta = 1.5$  ppm. The EPA grafting conversion ratio for PBI-EPA determined by  $^1H$  NMR were 12.2%.


 Fig. 7  $^1H$ -NMR spectra of PBI

 Fig. 8  $^1H$ -NMR spectra of PBI-EPA

### E. Phosphoric acid doping levels of membranes

The PA content and swelling of the neat PBI, PBI/PBI-EPA (ratio 8/2 and 7/3 by wt) blend membranes are summarized in Table II. The PA content of the membranes increased with time.

TABLE II  
PA CONTENT OF PBI AND PBI-EPA

Sample	Time (h)	PA content (wt.%)
Neat PBI	48	297.44
Neat PBI	12	289.58
Neat PBI	6	204.17
PBI/PBI-EPA (8/2)	48	350.00
PBI/PBI-EPA (8/2)	12	307.58
PBI/PBI-EPA (8/2)	6	278.46
PBI/PBI-EPA (7/3)	48	302.44
PBI/PBI-EPA (7/3)	12	294.59
PBI/PBI-EPA (7/3)	6	252.17

### F. PEMFC performance of MEAs

Fig. 9 shows the polarization curves of PBI and PBI/PBI-EPA (ratio 8/2 and 7/3 by wt) blend membranes MEA tests. The highest power densities observed for PBI/PBI-EPA

(ratio 8/2 by wt) with PA content 350% (at 48 h  $H_3PO_4$  doping time).

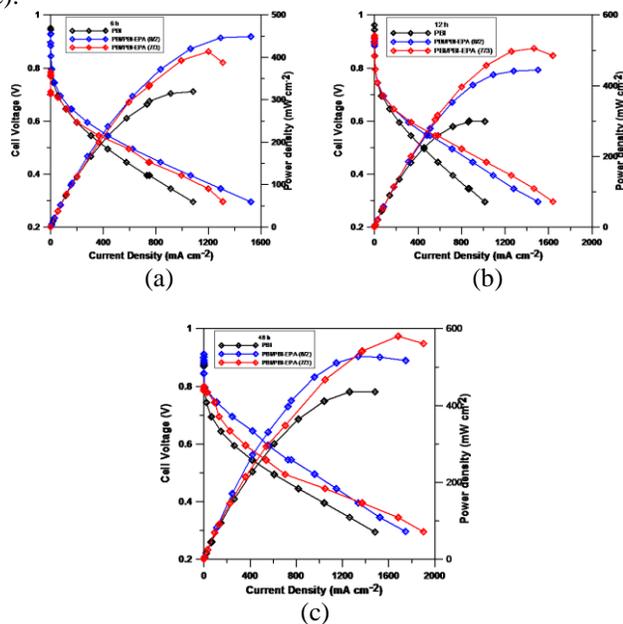


Fig. 9 Polarization curves of PBI and PBI/PBI-EPA (ratio 8/2 and 7/3 by wt) blend membranes from fuel cell tests at 160°C (a) at 6 h  $H_3PO_4$  doping time; (b) at 12 h  $H_3PO_4$  doping time; (c) at 48 h  $H_3PO_4$  doping time

#### IV. CONCLUSION

PBI and PBI-EPA were synthesized via the condensation polymerization. The proton exchange reactions between PBI and the side chain functional group were confirmed by FT-IR and NMR spectrum. Decomposition of the polymers starting above 200°C was shown by thermogravimetric analysis. The addition of EPA can significantly enhance fuel cell performance.

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