Polybenzimidazole Bearing Benzimidazolyl Pendants: Synthesis and Proton Conductivity

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Polybenzimidazole (PBI) is a class of polymers with excellent thermal stability but with limited solubility.[1] However, when doped with phosphoric acid (PA), some PBIs exhibit good proton conductivities at temperatures higher than 100 $^{\circ}$C, giving them potential for uses as high-temperature fuel cell proton exchange membranes under anhydrous conditions.[2]

The performance of PBI membranes can be enhanced by raising the doping levels of PA.[3,4] A chemical modification that increases the number of basic nitrogen atoms in the main polymer chain resulted in the increase in the PA doping level and consequently the proton conductivity of the resulting membrane.[5,6] A PBI derivative involving covalently linked phosphonic acid groups has been reported, but the performance of its membrane was not satisfactory.[7] Benicewicz and coworkers have reported a new *in situ* casting method for PBI membranes.[8] Another effort has attempted to increase the doping level of PA using porous PBI membranes,[9] and the doping level of PA was reported to increase with increasing membrane porosity, leading to the increase in the proton conductivity.

PBI derivatives bearing benzimidazolyl (BI) pendants appeared interesting to us because the BI pendants may affect the PA doping level and consequently proton conductivity of the resulting membranes.[10,11] Thus, in this study, a new PBI derivative bearing BI pendants (PBBI) was synthesized, and the proton conductivity behavior of the resulting PBI membranes was compared with that of poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole) (mPBI).

Results and Discussion

5-(1*H*-Benzo[*d*]imidazol-2-yl)isophthalic acid (compound **3**, BIPA) was synthesized as outlined in Scheme 1. Briefly, 3,5-dibromobenzoic acid and 1,2-phenylenediamine underwent a condensation reaction in the presence of polyphosphoric acid to give 2-(3,5-dibromophenyl)-1*H*-benzo[*d*]imidazole (compound **1**). Initially, the dibromide was reacted with CuCN for conversion of the bromine to cyano groups, but a portion of the cyano groups was hydrolyzed to amide groups under these conditions. Therefore, the reaction mixture was hydrolyzed to the dicarboxylic acid form without purification and esterified using ethanol to give compound **2**, which was then hydrolyzed to form dicarboxylic acid **3**. The reactions were simple, and the
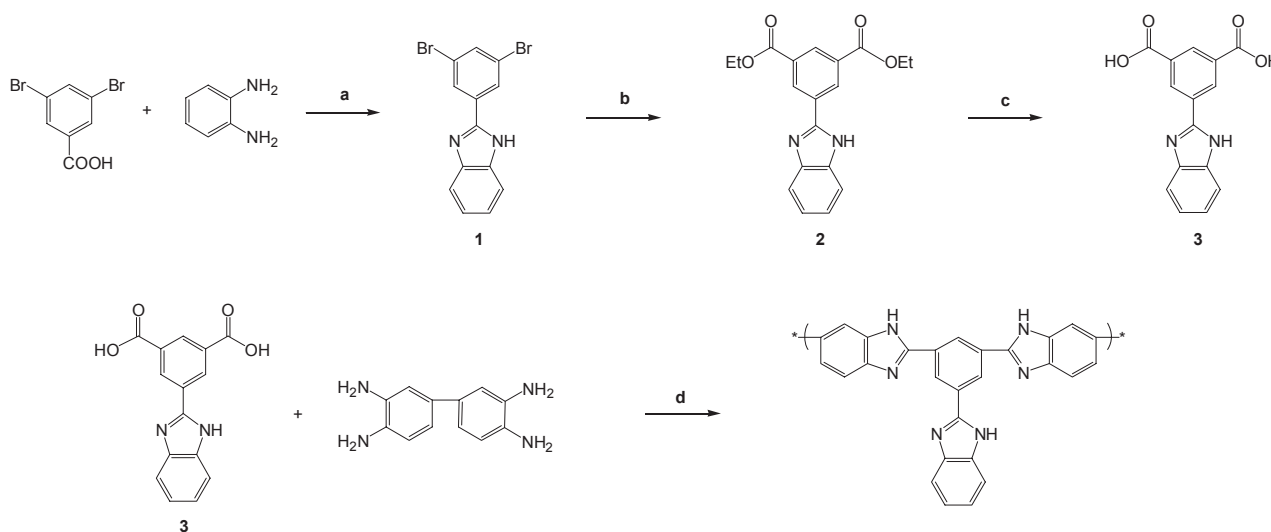
Scheme 1. Synthetic routes to 5-(1*H*-benzo[*d*]imidazol-2-yl)isophthalic acid (BIPA) and PBBI: (a) polyphosphoric acid, 190 $^{\circ}$C, 16 h, (b) i) copper(I) cyanide, DMF, reflux, 2 days; ii) KOH, reflux, 2 days; iii) ethanol, H$_2$SO$_4$, reflux, 2 days, (c) NaOH, H$_2$O, reflux, 6 h, (d) polyphosphoric acid, 230 $^{\circ}$C, 12 h.

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Notes
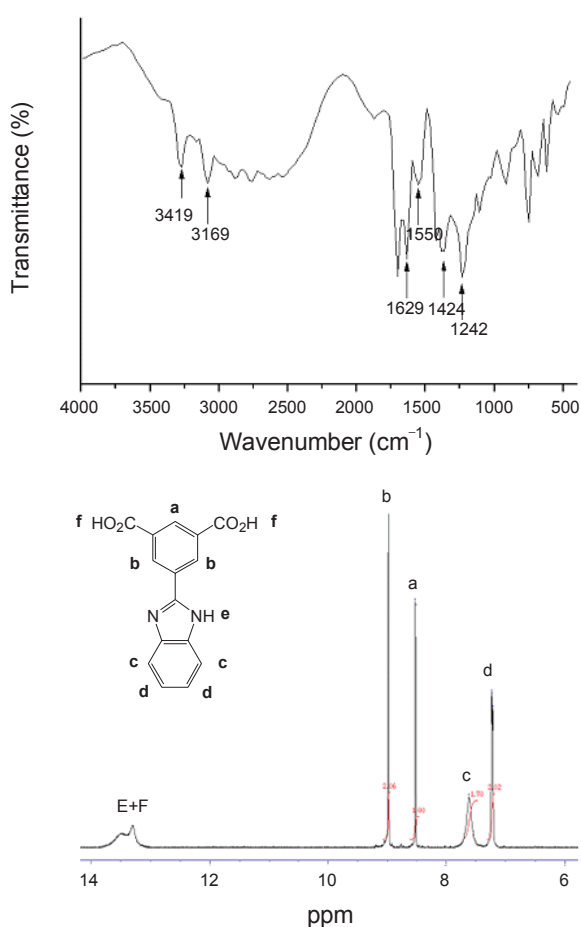
Figure 1. FT-IR (Top) and ^{1}H NMR (DMSO-d_6) (Bottom) spectra of compound **3**.
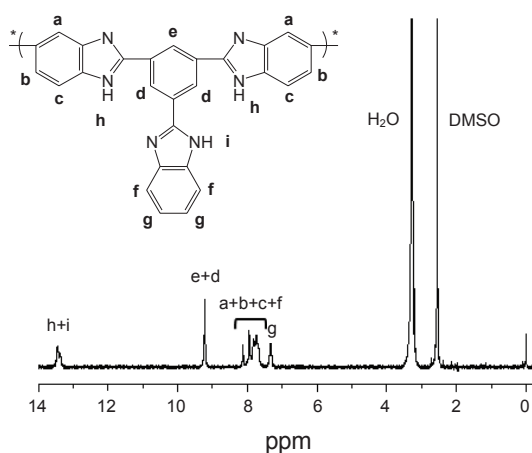
Figure 2. ^{1}H NMR spectrum of PPBI (DMSO-d_6).

overall yield of the three-step synthesis was about 33%.

The FT-IR spectrum of BIPA showed C=N and C=C stretching bands for the benzimidazolyl moiety at 1629, 1550, and 1424 cm^{-1} (Fig. 1, Top). A breathing mode band of the benzimidazole was observed at 1242 cm^{-1} and the free N-H and hydrogen-bonded N-H stretching bands clearly observed at 3419 and 3169 cm^{-1}, respectively. In the ^{1}H NMR spectrum (Fig. 1, Bottom), a proton resonance observed at 13.45 - 13.23 ppm corresponded to the benzimidazolyl ring N-H proton and another resonance peak at 13.69 - 13.45 ppm corresponded to the -COOH group. Thus, the above spectral data clearly indicated that the isolated compound had the expected chemical structure of BIPA.

BIPA and 3,3-diaminobiphenyl underwent a polycondensation reaction in the presence of polyphosphoric acid to produce PBBI. The FT-IR spectrum of PBBI showed free N-H and hydrogen-bonded N-H stretching peaks at 3400 and 3200 cm^{-1}, respectively. In the ^{1}H NMR spectrum, proton resonance peaks at 13.45 - 13.37 ppm were due to the N-H bond in the BI rings and all peaks in the range of 9.22 - 7.34 ppm corresponded to protons in the aromatic rings (Fig. 2). These results supported the conclusion that PBBI had been successfully synthesized. For comparison with PBBI, a well-known PBI (mPBI) was also synthesized from 3,3-diaminobiphenyl and isophthalic acid, according to the published procedure.[13]

The Mark-Houwink expression was used to calculate the molecular weight of the polymers from the intrinsic viscosity measurements. The intrinsic viscosity of PBBI (0.788 dL/g) was slightly smaller than mPBI (1.12 dL/g) and, thus, the weight-average molecular weight of PBBI (187,000) was calculated to be slightly smaller than mPBI (221,000). The reduced molecular weight of PBBI, relative to mPBI, probably resulted from a reduced condensation rate due to the higher monomer molecular weight of BIPA, compared to isophthalic acid.[5] As previously reported, mPBI was only slightly soluble in aprotic polar solvents such as DMSO, NMP, and DMAc, but its solubility was enhanced in the presence of LiCl (2 wt %).[10] On the other hand, PBBI was slightly less soluble in the aprotic polar solvents than mPBI.

PA-doped PBBI and mPBI membranes were obtained by immersing the polymer membranes in aqueous PA solutions.[14] When doped in 60 wt % PA solution, the resulting PBBI membranes were very sticky. On the other hand, when doped in 40 wt % PA solution, the PBBI membranes were less sticky. The PA doping levels in mPBI and PBBI membranes, prepared by soaking in a 40% PA solution, were estimated to be 8.5 and 37.2 mol PA/polymer repeat unit, respectively. The PA doping level of mPBI here was in good agreement with the reported values obtained under similar experimental conditions.[15] These data indicated that the average doping levels of the BI unit in these mPBI and PBBI membranes were 4.3 and 12.4 moles of PA, respectively, since the repeat unit of mPBI and PBBI has two and three BI moieties, respectively. In other words, the PA doping level of the PBBI membrane was about 3 times higher than the mPBI membrane.

PBIs prepared from either higher molecular weight monomers or more basic monomers have been reported to have higher PA doping levels.[5] mPBI was prepared from 3,3'-diaminobenzidine and isophthalic acid, while PBBI was synthesized from 3,3'-diaminobenzidine and BIPA, with the only difference in the reactants being whether isophthalic acid or BIPA was used. The molecular weight difference between isophthalic acid and BIPA is 116 g/mol. Carollo *et al*. reported that the PA doping level of a PBI derivative synthesized from 3,3'-diaminobenzidine and 2,6-naphtylic acid was 10.4 mol PA/repeat unit while

Table 1. Proton conductivities of PA-doped mPBI and PBBI membranes under anhydrous conditions

		mPBI		PBBI	
Doping level (mol PA/BI)		2.2	4.3	2.2	12.3
Proton Conductivity (mS/cm)	at 90 °C	9.8	64	0.021	62
	at 100 °C	11	74	0.025	71
	at 110 °C		91		
	at 120 °C		98		

that of mPBI was 4.5 mol PA/repeat unit.[5] In their work, the difference in the monomer molecular weights was only 50 g/mol, and each repeat unit had two BI moieties, meaning that the doping level of each BI moiety was increased from 2.3 moles to 5.2 moles of PA. This analysis suggested that the significant increase in the doping level of PBBI, compared to mPBI, mainly derived from the increase in the monomer molecular weight.

The proton conductivity of PA-doped mPBI membranes (4.3 mol PA/BI) under anhydrous conditions at 90 °C and 100 °C was measured to be 0.064 and 0.074 S/cm, respectively, and was in good agreement with the reported values in the literature.[15] And, as expected, the proton conductivity increased with increasing temperature (Table 1). On the other hand, the proton conductivities of PA-doped PBBI membranes (12.3 mol PA/BI) at 90 °C and 100 °C were measured to be 0.062 and 0.071 S/cm, respectively, under identical conditions, showing clearly that the proton conductivities of these different membranes were very similar to each other, even though the PA doping level of PBBI membranes was almost three times higher than in the mPBI membranes.

Next, mPBI and PBBI membranes were prepared with the same PA doping levels (2.2 mol PA/BI). The proton conductivities of mPBI measured under anhydrous conditions at 90 and 100 °C were found to be 9.8 and 11 mS/cm, respectively, while those of PBBI membranes under the same conditions were 0.021 and 0.025 mS/cm, respectively. Thus, it appeared that the proton conductivity of PBBI membranes was significantly lower than that of mPBI membranes at the same doping level.

Ma *et al.* proposed that proton conduction occurs mainly *via* the PA-PA chain and PA-water pathways, depending on the water content when the PA doping level is higher than 4 moles PA per repeat unit of mPBI (in other words, 2 moles PA/BI).[16] Similarly, the proton conductivity of the current mPBI membranes with doping level of 2.2 moles PA/BI can be assumed to occur mainly *via* the PA-PA chain under anhydrous conditions. And then a similar proton conductivity should have been obtained in the above experiment. The observed lower conductivity suggested that the BI pendants played an important role in reducing the proton conductivity of the PBBI membranes. However, the understanding on proton conduction in PBBI membranes requires more extensive experimentation beyond the scope of this research.

Conclusions

A new PBI polymer derivative, PBBI, which corresponds to the BI pendant-containing mPBI, was successfully synthesized. The presence of the BI pendants significantly increased the PA

doping level of the polymer membranes, compared to mPBI. However, the increased PA doping level of PBBI membranes did not lead to enhancement of proton conductivity of the membranes. Rather, the proton conductivity of PBBI membranes was much lower than that of mPBI membranes at the same PA doping level under anhydrous conditions. The lowered proton conductivity of PBBI membranes was attributed to the presence of BI pendants, but the role of the BI pendants remained to be studied.

Experimental Section

Materials. 3,3'-Diaminobenzidine (99%), isophthalic acid (99%), polyphosphoric acid (115%), lithium chloride (99%), *N,N*-dimethylacetamide (DMAc, 99%), 3,5-dibromobenzoic acid (97%), 1,2-phenylenediamine and copper(I) cyanide (99%) were purchased from Sigma-Aldrich, and used without further purification.

5-(1*H*-benzo[*d*]imidazol-2-yl)isophthalic acid (BIPA) (3). 3,5-Dibromobenzoic acid (10 g, 35.7 mmol) and 1,2-phenylenediamine (3.9 g, 35.7 mmol) were added to 200 mL of polyphosphoric acid in a round bottom flask at 120 °C, stirred for 16 h at 190 °C, cooled to room temperature, neutralized with aqueous NaOH, washed with 1 N NaOH, then with water, and dried in an oven at 80 °C to give 2-(3,5-dibromophenyl)-1*H*-benzo[*d*]imidazole (compound **1**, 80% yield) as a white solid. A solution of compound **1** (10 g, 28.4 mmol) and copper(I) cyanide (10 g, 113.6 mmol) in 200 mL of DMF was refluxed for 2 days, followed by the addition of 500 mL of water. The resulting solid was dissolved in aqueous KOH solution (6.4 g, 113.6 mmol) and refluxed for 2 days, after which it was acidified with aqueous 4 N HCl and concentrated under reduced pressure, to give a crude dicarboxylic acid. A solution of the crude dicarboxylic acid and sulfuric acid (15 mL) in 250 mL of ethanol was refluxed for 16 h, neutralized with aqueous 2 N NaOH, and extracted with ethyl acetate. The organic layer was concentrated under reduced pressure and purified by column chromatography (SiO$_2$, dichloromethane/toluene/ethyl acetate = 4:4:1) to give diethyl ester **2** as a white powder (45% yield). A solution of compound **2** (3.1 g, 9.16 mmol) and KOH (2.0 g, 36.6 mmol) in 300 mL of ethanol and 20 mL of water was refluxed for 6 h, and concentrated under reduced pressure. The residue was dissolved in water (10 mL), acidified to pH 1 with aqueous 1 N HCl. The resulting solid was washed with water and dried to give dicarboxylic acid **3** as a white solid (2.4 g, 92% yield). ¹H NMR (DMSO-d_6, δ) 13.69-13.45 (2H, br s), 13.45-13.23 (br s, 1H), 9.01 (d, 2H, *J* = 1.60 Hz), 8.55 (t, 1H, *J* = 1.58 Hz), 7.64 (s, 2H), 7.31-7.19 (m, 2H); ¹³C NMR (DMSO-d_6, δ) 166.69, 149.94, 132.61, 131.57, 131.32, 131.13.

Poly(2,2'-(3-benzimidazole-1,5-phenylene)-5,5'-bibenzimidazole) (PBBI). 3,3'-Diaminobenzidine (0.642 g, 3 mmol) was added to polyphosphoric acid at 160 °C, heated for 2 h, followed by the addition of BIPA (0.846 g, 3 mmol). The reaction temperature was increased to 230 °C, and the reaction was allowed to proceed for 12 h. During this polymerization, the reaction mixture became more viscous and dark brown after which it was poured in small portions into water, neutralized with aqueous KOH, rinsed with water several times until pH neutral. The

polymer (PBBI) taken was dried overnight in a oven at 110 °C.

Poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole) (mPBI). For comparison with PBBI, mPBI was also synthesized following a published procedure.[13]

Preparation of PA-doped membranes. PBBI (2.0 wt %) and lithium chloride (2.0 wt %) were dissolved in DMAc, oxygen removed by bubbling with nitrogen, and the resulting solution sealed and maintained at 200 °C for 10 h, after which the homogeneous solution was spread onto a glass petri dish and dried overnight in a vacuum oven at 120 °C. The petri dish was then immersed in water to detach the membrane, which was boiled in water for 2 days to remove residual solvent and lithium chloride and stored in deionized water. Both PBBI and mPBI membranes were dried under vacuum at 105 °C for 24 h, weighed, immersed in aqueous PA solutions for 4 days, and dried under reduced pressure for 2 days. The membranes were then weighed and any weight increase after doping assumed to be due to absorbed PA.

Measurements of polymer molecular weight. Polymer molecular weights were determined in terms of intrinsic viscosity using an Ubbelohde viscometer. Briefly, from solutions of mPBI (0.4 g/dL and 0.6 g/dL) and PBBI (0.4 g/dL and 0.6 g/dL) prepared in 96% sulfuric acid, the flow times of the solutions and the solvent were measured, and the respective intrinsic viscosities (η_{int}) were calculated.[12] The weight-average molecular weights (M_ws) were then estimated using the Mark-Houwink-Sakurada expression.[13]

Measurements of proton conductivity. A four-point probe system was constructed to measure the ionic conductivity of the polymer membranes. The membranes were introduced into the conductivity cell, stabilized at 90 °C or 100 °C, and the impedance spectrum of the cell measured with a BT-512 Bekk Tech Membrane Conductivity Test System, equipped with a Keithley 2400 Source Meter, from which the AC conductivities of the polymer membranes were calculated. The proton conductivities were calculated using the following formula

where δ, L, R, and A represents the proton conductivity, distance between the two electrodes, resistance, and test area, respectively ($A = TW$, T: thickness; W: width of the membrane):

$$\delta = \frac{L}{R \times A}$$

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