

# A New Sequence Isomer of AB-Polybenzimidazole for High-Temperature PEM Fuel Cells

Alexander L. Gulledge, Bin Gu, Brian C. Benicewicz

Department of Chemistry and Biochemistry & USC NanoCenter, University of South Carolina, Columbia, South Carolina 29208

Correspondence to: B. C. Benicewicz (E-mail: benice@sc.edu)

Received 18 August 2011; accepted 3 October 2011; published online 28 October 2011

DOI: 10.1002/pola.25034

**ABSTRACT:** A new sequence isomer of AB-polybenzimidazole (AB-PBI) was developed as a candidate for high-temperature polymer electrolyte membrane fuel cells. A diacid monomer, 2,2'-bisbenzimidazole-5,5'-dicarboxylic acid, was synthesized and polymerized with 3,3',4,4'-tetraaminobiphenyl to prepare a polymer that was composed of repeating 2,5-benzimidazole units. In contrast to previously prepared AB-PBI, which contains only head-to-tail benzimidazole sequences, the new polymer also contains head-to-head and tail-to-tail benzimidazole sequences. The polymer was prepared in polyphosphoric acid (PPA) and cast into membranes using the sol-gel PPA process.

Membranes formed from the new AB-PBI were found to be mechanically stronger, possessed higher acid doping levels, and showed improved fuel cell performance, when compared to the previously known AB-PBI. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 50: 306–313, 2012

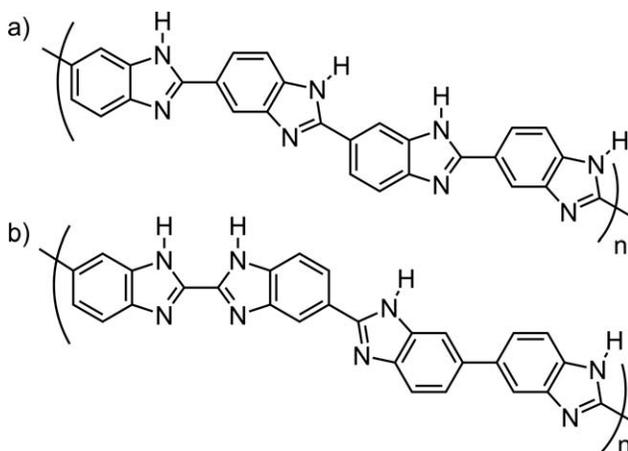
**KEYWORDS:** 2,2'-bisbenzimidazole-5,5'-dicarboxylic acid; AB-PBI; high temperature materials; *i*-AB-PBI; poly(2,5-benzimidazole); polybenzimidazole; polycondensation; polyelectrolytes; polymer electrolyte membrane fuel cells; step growth polymerization

**INTRODUCTION** Polymer electrolyte membrane (PEM) fuel cells have received much attention due to their potential as clean energy conversion devices, which can be used for both mobile and stationary applications.<sup>1</sup> Although PEM fuel cells are excellent candidates for these devices, one problem associated with PEM fuel cells is the availability and development of appropriate materials that would allow manufacturing routes to enable the cost of electricity per kWh to compete with existing technologies.<sup>2</sup> Although several types of materials have been developed for PEM fuel cell operation, only few offer the advantages of higher operational temperatures (>100 °C). Polybenzimidazole (PBI) polymer membranes doped with phosphoric acid (PA) used in PEM fuel cells are capable of operating at temperatures up to 200 °C because they do not require water for proton conduction.<sup>3</sup> The ability of these systems to operate without the presence of water eliminates the need for and cost of external humidification and the related engineering hardware to monitor hydration levels. Moreover, higher operational temperatures provide advantages such as faster electrode kinetics, increased resistance to fuel impurities and simplified water and thermal management.<sup>4</sup>

PBI polymers have been investigated for use as high-temperature PEMs because of their known thermal and chemical stabilities under normal fuel cell operation conditions.<sup>5–7</sup> These membranes showed high proton conductivity (>0.1

S/cm) at elevated temperatures (>110 °C) under low relative humidity conditions and exhibited a high tolerance to fuel impurities (most notably, CO).<sup>8</sup> Previously, we reported a new sol-gel method, termed the polyphosphoric acid (PPA) process, for the preparation of PBI polymer membranes from PPA solutions that resulted in membranes with high levels of PA doping.<sup>9</sup> Membranes prepared from the PPA process showed higher acid doping levels, improved mechanical properties, higher proton conductivities, and overall improved fuel cell performance, when compared to conventionally imbibed PBI membranes.<sup>9</sup> Subsequently, many PBI variants containing a range of structural and functional moieties have been examined to further explore the effects of polymer structure on membrane properties.<sup>10–13</sup>

Among the various PBI polymers developed for high-temperature fuel cell applications, poly(2,5-benzimidazole) (AB-PBI), has been examined by several research groups.<sup>14–18</sup> AB-PBI has been reported as a promising candidate for high-temperature PEM fuel cells and is the simplest known PBI structure prepared from a readily available monomer.<sup>19–21</sup> In addition to the research devoted to homopolymer AB-PBI, substituted,<sup>22</sup> crosslinked,<sup>23</sup> and copolymers containing AB-PBI have also been investigated.<sup>24</sup> AB-PBI membranes that were imbibed with PA typically showed acid doping levels from 2 to 10 mol PA/mol polymer repeat unit and corresponding proton conductivities of ~0.05 S/cm at 180 °C



**FIGURE 1** Chemical structures of (a) poly(2,5-benzimidazole)(AB-PBI) and (b) new isomeric *i*-AB-PBI.

under anhydrous conditions.<sup>25</sup> AB-PBI was prepared using the PPA process and investigated to determine the effects of higher PA doping levels on membrane characteristics compared to the conventional imbibing method of preparation. As previously mentioned, preparation by the PPA process results in films that contain a much higher concentration of PA when compared to imbibed films. In addition to a comparison of AB-PBI preparation methods, a new sequence isomer of AB-PBI, termed *i*-AB-PBI, was synthesized and compared to both in-house AB-PBI using the PPA process and conventional AB-PBI reported in the literature.

Herein, we report the synthesis and characterization of a new diacid monomer, 2,2'-bisbenzimidazole-5,5'-dicarboxylic acid (BBDCA), and its AA-BB polymerization with 3,3',4,4'-tetraaminobiphenyl (TAB) to form a new polymer, which constitutionally represents a new sequence isomer of AB-PBI, *i*-AB-PBI. AB-PBI is a polymer with a head-tail repeating benzimidazole sequence. The change in orientation of the benzimidazole groups incorporated into the new sequence isomer introduces two additional types of chemical bonds. In the known AB-PBI, benzimidazole groups of the polymer backbone are linked through benzimidazole-phenyl (2,5) linkages, whereas the new sequence isomer introduces two new linkages, phenyl-phenyl (5,5 linkages), and benzimidazole-benzimidazole (2,2 linkages) in addition to the benzimidazole-phenyl linkage (Fig. 1). Membranes were prepared from the new polymer using the PPA process and investigated to evaluate their proton conductivity and fuel cell performance properties. The properties of the new membranes were compared to both the in-house synthesized AB-PBI prepared by the PPA process and literature data on conventionally imbibed AB-PBI membranes.

## EXPERIMENTAL

### Materials

Methyl-2,2,2-trichloroacemidate (98%) was purchased from Acros Organics and used as received. TAB monomer, TAB (polymer grade, ~97.5%) was donated by Celanese Ventures, GmbH (now, BASF Fuel Cell) and used as received.

PPA (115% concentration) was purchased from Aldrich and used as received. PA (85%) and common solvents (e.g., DMSO, MeOH, EtOH, etc.) were purchased and used as received from Fisher Scientific. Purification of 3,4-diaminobenzoic acid (DABA; 10 g, Acros, 97%) was conducted via recrystallization from water/methanol (480 mL/160 mL) using activated carbon yielding pink/tan crystals after vacuum drying, 75%, m.p. 216.8 °C (Literature,<sup>26</sup> 210–211 °C).

### Polymerization of Poly(2,5-benzimidazole)

Poly(2,5-benzimidazole) (AB-PBI) was prepared using the following method: purified 3,4-diaminobenzoic acid (3 g) and PPA (97 g) were added to a 100-mL reactor. The reactor was equipped with a three-neck reactor head, mechanical stirrer, nitrogen inlet/outlet, and placed into a silicone oil bath with a ramp/soak temperature controller. The polymerization began with an initial temperature of 60 °C and was raised to 140 °C over a period of 1 h. The temperature remained at 140 °C for 2 h to ensure all monomer was dissolved. Once the monomer had dissolved, the temperature was increased stepwise until a final polymerization temperature of 220 °C was obtained. Typically, the polymerization reaction time at 220 °C was between 24 and 36 h, depending on the viscosity of the polymer. The Weissenberg effect was observed during the later stages of the polymerization causing the solution to climb up the stirrer. When this was observed, PA (85%) was added to the reaction mixture to adjust the viscosity of the solution for film casting. Analysis: <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 6.7–7.3 (broad multiplet, aromatics, 3H).

### Preparation of 2,2'-Bisbenzimidazole-5,5'-dicarboxylic acid

To a 1000-mL round bottom flask, purified DABA (10 g, 0.066 mol), and methanol (250 mL) were added. The mixture was then placed into an explosion proof refrigerator and cooled at 10 °C for ~20–30 min. The flask was removed from the refrigerator and methyl-2,2,2-trichloroacemidate (4.1 mL, 0.033 mol) was immediately added dropwise (~5 min) with stirring. After the addition was completed, the reaction flask was placed into a preheated oil bath at a temperature of 50 °C for 24 h. A dark orange precipitate was obtained that was filtered and washed with ethanol several times, during which the product became increasingly lighter in color. The crude product was dried at 120 °C overnight under vacuum.

The light orange crude product described earlier (5.89 g) was dissolved in ~200 mL of heated DMSO, followed by the addition of hot water until the solution became slightly cloudy. A yellow precipitate was obtained on cooling to room temperature, which was filtered and washed with cold ethanol. The product was dried at 220 °C under vacuum to obtain a yellow powder (4.112 g, 69.8% yield). Analysis: FTIR: 1671m, 1625m, 1595w, 1497w, 1312s, 1295s, 1206m, 942m, 769s, 746s, 674m cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 13.98 (s, NH), 12.86 (s, COOH), 8.325 (s, 1H), 8.159 (s, 1H), 7.94–7.63 (m, 2H), 7.63–7.60 (d, 1H, *J* = 8.1). ELEM.

ANAL: Calcd. for  $C_{16}H_{10}N_4O_4$ : C, 59.63; H, 3.13; N, 17.38. Found: C, 59.42; H, 3.23; N, 17.30.

### Polymerization of New Isomeric Poly(2,5-benzimidazole)

In a typical polymerization procedure TAB (1.828 g), PPA (70 g), and BBDCA (2.75 g) were added to a 100-mL reactor. The reactor was then equipped with a three-neck reactor head, a stir rod attached to an overhead stirrer and a nitrogen inlet/outlet. A slow nitrogen flow of approximately one bubble every 2 s was established and monitored with an oil-filled bubbler. The reactor was placed into an oil bath that was regulated using a temperature controller with ramp and soak features. The polymerization used the ramp/soak profile as follows:

An initial temperature of 60 °C was used, and the temperature was raised to 140 °C over a period of 1 h. The temperature remained at 140 °C for 2 h and was then increased to 180 °C over a period of 30 min. The temperature remained at 180 °C for 10 h, and was then increased to 220 °C in a period of 30 min. The reaction remained at 220 °C for the duration of the polymerization. Twenty hours was the typical duration of polymerization for the new sequence isomer (*i*-AB-PBI). At the end of 20 h the solution was very viscous and PA (~15 mL) was back-added to adjust the viscosity. Analysis:  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  6.7–7.3 (broad multiplet, aromatics, 3H), 8.2 (singlet, 1H), 8.5 (multiplet, 2H).

### Polymer Electrolyte Membrane Preparation

Once an appropriate polymer viscosity was obtained, the solution was directly cast at 220 °C onto glass plates for membrane preparation. A heated metal casting blade (120 °C) with a casting thickness of 20 mil (508  $\mu\text{m}$ ) was used. After casting, the glass plates were separated and samples were placed into a humidification chamber maintained at a relative humidity of 55% at 25 °C. The polymer samples were allowed to hydrolyze overnight. Hydrolysis of the PPA to PA induced a sol-to-gel transition that resulted in a gel membrane. The samples were then sealed in 3 mil (76.2  $\mu\text{m}$ ) thick polyethylene bags until testing or membrane electrode assembly (MEA) fabrication.

### Characterization Techniques

FTIR spectra were recorded on a Perkin Elmer Spectrum 100 using an attenuated total reflection diamond cell attachment.  $^1\text{H}$  NMR spectra were recorded using a Varian Mercury 300 spectrometer. Mechanical properties were measured in tension using an Instron 5543A with an extension rate of 5.0 mm/min and were preloaded to 0.1 N at 3 mm/min using a 250 N load cell.

Inherent viscosity (IV) measurements were conducted using a Canon Ubbelohde (size 200) viscometer at a concentration of 0.2 dL/g in methane sulfonic acid (MSA) at 30.0 °C. A small amount of polymer solution was precipitated in water and neutralized with 0.1 N ammonium hydroxide. After thoroughly washing with water, the sample was dried under vacuum overnight at 120 °C and then dissolved in MSA using a mechanical shaker. Recorded IV values are an average of

three separate measurements and were calculated as previously reported.<sup>27</sup>

The PA contents in the membranes were obtained via titration using a Metrohm 716 DMS Titrino automated titrator and a standardized 0.1 M sodium hydroxide solution following procedures reported previously.<sup>28</sup> PA concentrations were expressed as moles of PA per mole of polymer repeat unit.

Ionic conductivities were measured using a quadra-probe alternating current impedance method, which used a Zahner IM6e spectrometer operating in the frequency range of 1 Hz–100 kHz. A rectangular section of the polymer membrane was cut with the dimensions of 3.5  $\times$  7.0  $\text{cm}^2$  and was placed into a glass cell connected to four platinum wire current collectors. Current was supplied to the cell through two outer electrodes, which were set 6.0 cm apart, whereas the potential drop was measured by two inner electrodes that were set 2.0 cm apart. The inner and outer electrodes of the glass cell were positioned on alternating sides of the polymer membrane to obtain through plane bulk measurements of ionic conductivity. A programmable oven was used to house the cell, so that a measure of the temperature dependence of the proton conductivity for the cell could be obtained. Two series of measurements of the conductivity were conducted subsequently. The first series of measurements were conducted from ambient temperature to 180 °C, at intervals of 20 °C, with a 15 min pause at each temperature interval for thermal equilibrium before measurement. The second series of measurements were subsequently conducted in the same manner to obtain the ionic conductivity of the membranes under anhydrous conditions. A Nyquist plot was constructed to fit the experimental curve of the resistance across the frequency range. The conductivities were calculated at different temperatures from the membrane resistance obtained using the following equation:

$$\sigma = \frac{D}{W \times T \times R}$$

where  $\sigma$  is the ionic conductivity,  $R$  is the resistance measured,  $W$  and  $T$  are the width and thickness of the membrane, respectively, and  $D$  is the distance between the two inner electrodes.

### Membrane Electrode Assembly Fabrication and Fuel Cell Testing

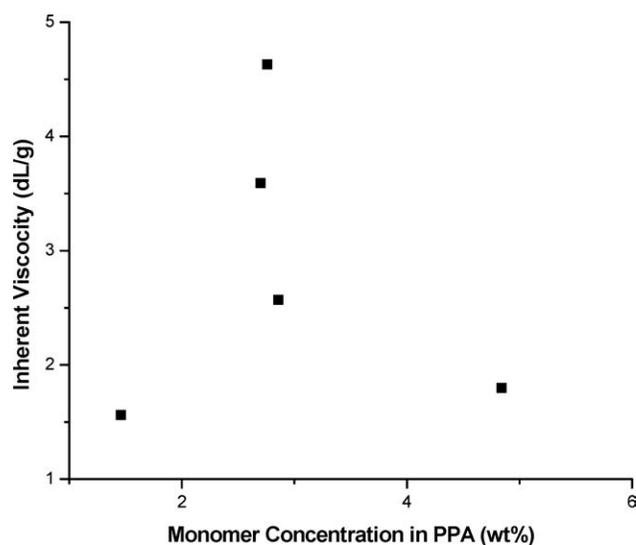
MEA's were fabricated by hot pressing a membrane (~20% compression) sample between two platinum doped carbon electrodes, and were 50  $\text{cm}^2$  in area (45.15  $\text{cm}^2$  active area). Gas diffusion electrodes, with a platinum loading of 1.0 mg/ $\text{cm}^2$ , were obtained from BASF Fuel Cell. A Kapton framework was also incorporated to add stability to the MEA, and to allow handling without damaging the MEA. The MEA was placed into a single-cell fuel cell apparatus for testing. The gas flow plates used were graphite with dual gas channels. Steel endplates were used to clamp the gas flow plates together. Heating pads were attached to the steel plates to regulate and monitor temperature. A commercially available

fuel cell testing station (Fuel Cell Technologies) equipped with mass flow regulators was used to conduct and record measurements. Stoichiometric gases were supplied to the anode and cathode at a stoichiometric of 1.2 and 2.0, respectively, without applied backpressure. Fuel/oxidant studies were performed with hydrogen gas, oxygen gas, and reformate gas, all without humidification. The composition of reformate gas used consisted of ~70% hydrogen, 28% CO<sub>2</sub>, and 2% CO.

## RESULTS AND DISCUSSION

### Polymerization of Poly(2,5-benzimidazole)

Poly(2,5-benzimidazole) (AB-PBI) was prepared by polymerizing DABA in PPA. Polymerization conditions for AB-PBI prepared in PPA were experimentally determined. Initial monomer concentrations in PPA were observed to have a direct effect on the molecular weight of the resulting polymer. A study to examine the effect of monomer concentration on polymer IV was conducted through a series of polymerizations to determine the optimal concentration for the formation of high-molecular-weight polymer and is shown in Figure 2. The optimal monomer concentration was ~3 wt % yielding polymer samples with inherent viscosities up to 4.63 dL/g. Attempts below 2 wt % monomer concentration under these polymerization conditions yielded lower molecular weight polymers and unstable films, when the PPA solutions were cast and hydrolyzed. Polymerizations conducted above 3.5 wt % resulted in films with higher rigidity and less favorable mechanical properties. AB-PBI membranes prepared using the PPA process were found to have much higher acid doping levels (22–35 mol PA/mol polymer repeat unit) when compared to conventional imbibing methods (2–10 mol PA/mol polymer repeat unit).<sup>5</sup> However, AB-PBI membranes prepared with elevated PA doping levels (>14 mol PA/mol polymer repeat unit) were found to be unstable at elevated temperatures (>130 °C). The PA level in the



**FIGURE 2** Effect of monomer concentration on IV for the polymerization of DABA in PPA at 220 °C.

membranes was adjusted by soaking the membranes in PA baths with lower PA concentrations than that of the original film. Membrane samples with doping levels of 29.1, 22.7, and 14.5 mol PA/mol polymer repeat unit were obtained. However, the films with lower PA content still did not maintain a gel state at higher temperatures, and therefore, high-temperature anhydrous conductivity and fuel cell performance could not be obtained for AB-PBI membranes with these moderate levels of PA prepared using the PPA process.

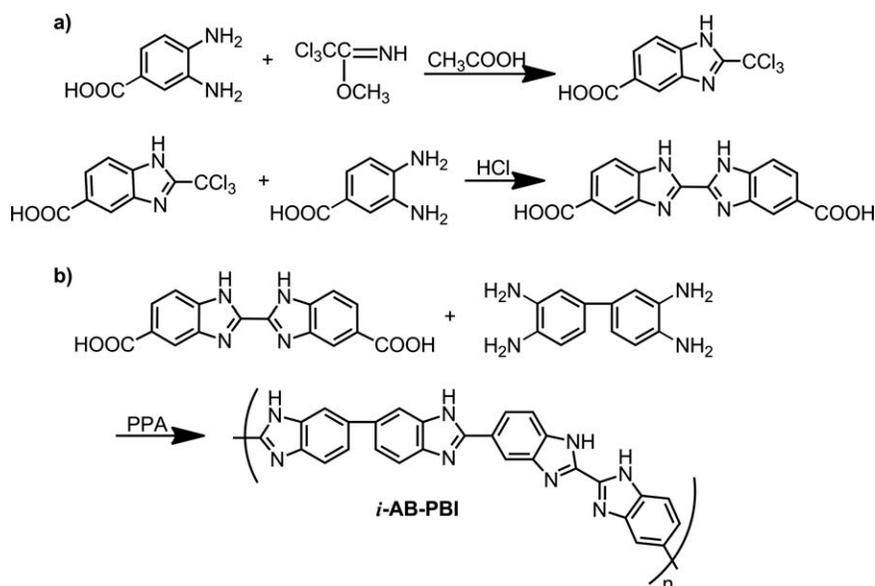
### Synthesis and Purification of

#### 2,2'-Bisbenzimidazole-5,5'-dicarboxylic Acid

Typical synthesis of bisbenzimidazoles involves a reaction between *o*-phenylenediamines with a diacid or diamide in HCl or PPA (PPA).<sup>29</sup> The synthesis of BBDCa has not been previously reported. However, synthesis of 2-substituted benzimidazoles from the reaction of *o*-phenylenediamine with an imidate is well known.<sup>30</sup> Synthesis of BBDCa was achieved by reacting purified DABA and methyl 2,2,2-trichloroacetimidate in a 2:1 stoichiometric ratio, respectively. Synthetic procedures involving 2-trichlorobenzimidazoles are often conducted at room temperature after the exothermic reaction has subsided to avoid unwanted side reactions.<sup>31</sup> Although these types of reactions are typically done at room temperature, an increase in reaction yield of ~10–15% was observed in this work, when the reaction was performed at 50 °C. It is surmised that the exothermic reaction coupled with the increased reaction temperature provided the system with enough energy to induce reaction and ring closure of the intermediate 2-trichloro-5-carboxyl benzimidazole with a second equivalent of DABA. The crude product of this monomer was obtained in yields of 50–60% after 24 h reaction time. The diacid monomer was found to be insoluble in most common organic solvents, but soluble in DMSO and dimethylacetamide. Purification of the diacid monomer was achieved using a mixed solvent recrystallization from DMSO and distilled water. The purified diacid monomer was a yellow colored powder after drying and was typically obtained in yields of ~60–70%. The compound was also determined to be slightly hygroscopic, and therefore, thorough drying was required before polymerization to achieve high-molecular-weight polymer. In addition to standard characterization techniques, FTIR analysis was used to confirm the complete removal of the intermediate after purification by the absence of a peak at ~829 cm<sup>-1</sup>, which correlates to the C–Cl stretch of the intermediate.

### Polymerization of *i*-AB-PBI

The new sequence isomer of AB-PBI, *i*-AB-PBI, was synthesized using the synthetic scheme displayed in Figure 3(b). The synthesis of *i*-AB-PBI is an AA-BB step polymerization and, as defined by the Carother's equation, an exact stoichiometric ratio of BBDCa with TAB was required to achieve high-molecular-weight *i*-AB-PBI. Polymerization conditions for the new sequence isomer were experimentally determined and were conducted over a range of monomer concentrations as shown in Figure 4. A dramatic increase in polymer IV occurred, when monomer concentration was increased from 5 to 6 wt %. The reason for this abrupt

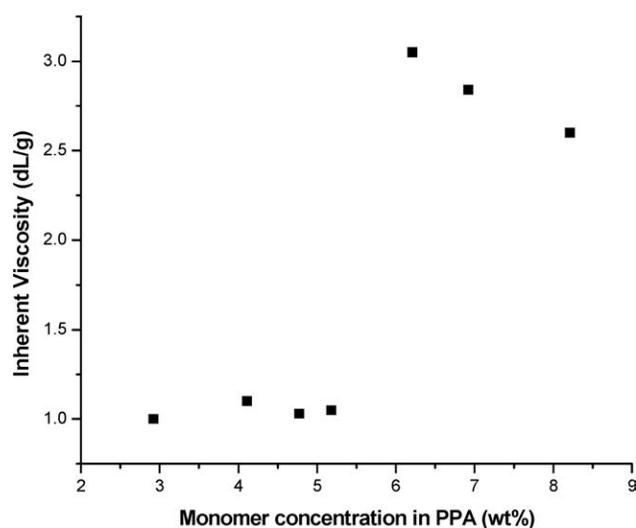


**FIGURE 3** Synthetic scheme for (a) two step synthesis of BBDCa and (b) synthesis of new isomeric *i*-AB-PBI.

change in IV is not completely understood, and this type of behavior has not been observed in our previous and extensive investigations of PBI polymers. Although such abrupt changes in IV could be indicative of a transition to an ordered or liquid crystalline phase, all other observations were not supportive of a liquid crystalline phase. Further increases in monomer concentration led to polymers with slightly lower inherent viscosities, which we attributed to increased solution viscosity and difficulties in stirring during the later stages of the polymerization. Subsequent polymerizations were conducted at 6 wt % monomer concentration to obtain high-molecular-weight polymer.

#### Membrane Formation and Properties

Polymer solutions were directly cast at 220 °C onto heated glass plates (120 °C oven temperature) using a 20 mil (508



**FIGURE 4** Effect of monomer concentration on IV for the new isomeric *i*-AB-PBI at a polymerization temperature of 220 °C.

$\mu\text{m}$ ) casting blade. The solutions then underwent a sol-to-gel transition as the PPA of the membrane hydrolyzed into PA and the system temperature decreased to room temperature. The membrane composition data show that the typical compositions of *i*-AB-PBI membranes prepared using the PPA process are greater than 50% PA and have a polymer content between 7 and 10.5 wt %. Mechanical property evaluations of the *i*-AB-PBI doped membranes typically yielded Young's moduli ranging from 0.9 to 1.6 MPa and tensile strengths between 0.43 and 1.11 MPa. Membrane composition data along with other significant properties for *i*-AB-PBI and the in-house AB-PBI prepared using the sol-gel method are shown in Tables 1 and 2, respectively.

As previously mentioned, the new *i*-AB-PBI contains two additional types of chemical bonds when compared to AB-PBI, benzimidazole–benzimidazole and phenyl–phenyl linkages.  $^1\text{H}$  NMR analysis was conducted for both AB-PBI and the new *i*-AB-PBI. On the basis of chemical structures presented the *i*-AB-PBI spectrum would contain additional peaks, which arise from the C–H bonds in the biphenyl moiety of the polymer. Spectral analysis did in fact show additional peaks at 8.2 and 8.5 ppm, which are consistent with the assignments of the biphenyl moiety in 2,2'-diphenyl-5,5'-bibenzimidazole, a model compound.<sup>32</sup> Preliminary molecular modeling using MOPAC 2009 Semi Empirical PM6 indicated slightly increased chain stiffness for *i*-AB-PBI as compared to AB-PBI. Experimentally, we observed a lower solubility for *i*-AB-PBI in PA at elevated temperatures (130–180 °C), when compared to the known AB-PBI. The lower solubility of the *i*-AB-PBI resulted in films with higher gel stability at higher temperatures, even with higher acid doping levels. Thus, films made with *i*-AB-PBI and doped with high levels of PA were sufficiently stable for conductivity measurements and fuel cell performance evaluations.

**TABLE 1** Characterization Results for *i*-AB-PBI Polymers and Membranes

Sample Number	Monomer Wt%	IV (dL/g)	Mol PA/Mol Polymer Repeat Unit	Anhydrous Conductivity at 180 °C (S/cm)	Membrane Composition (as cast) (wt%)		
					PA	H <sub>2</sub> O	Polymer
1 <sup>a</sup>	2.92	1.0	N/A	N/A	N/A	N/A	N/A
2 <sup>a</sup>	4.11	1.1	N/A	N/A	N/A	N/A	N/A
3 <sup>a</sup>	4.77	1.03	N/A	N/A	N/A	N/A	N/A
4	5.18	1.05	34.76	N/A	55.96	36.37	7.67
5	6.21	3.05	36.52	.202	54.98	37.76	7.26
6	6.92	2.84	24.5	.216	53.92	35.59	10.49
7	8.21	2.60	32.12	.195	54.08	37.90	8.02

<sup>a</sup> Low molecular weight samples were obtained and resulting films were unstable for testing.

### Membrane Characterization and Fuel Cell Testing

The ionic conductivity data for *i*-AB-PBI are shown in Figure 5 along with the literature data for AB-PBI. At 180 °C under anhydrous conditions, *i*-AB-PBI showed a nearly 10× increase in conductivity, from 0.02 to 0.2 S/cm, when compared to the reported literature on the conventionally imbibed AB-PBI.<sup>25</sup> This is largely due to the stability of *i*-AB-PBI with higher acid doping levels at increased temperatures.

The high conductivity (~0.2 S/cm) for *i*-AB-PBI indicated these membranes would be an excellent candidate for high-temperature PEM fuel cells. Fuel cell performance studies were conducted on *i*-AB-PBI membranes that included polarization curves with hydrogen/air and reformat/air fuel/oxidant combinations over a range of temperatures (120–180 °C). The performance of *i*-AB-PBI in comparison to reported literature of AB-PBI, using hydrogen/oxygen with 1.2:2.0 stoichiometric flows is shown in Figure 6. Significant increases in fuel cell performances for *i*-AB-PBI were observed over a range of temperatures (120–180 °C). At a current density of 0.2 A/cm<sup>2</sup>, a voltage of ~0.65 V was observed with hydrogen and air supplied at 1.2 and 2.0 stoichiometric flows. The polarization curves for the new sequence isomer with hydrogen/air and reformat/air are shown in Figures 7 and 8, respectively. As would be expected, a slight decrease in performance was observed, when the oxidant was changed from pure oxygen to air. The

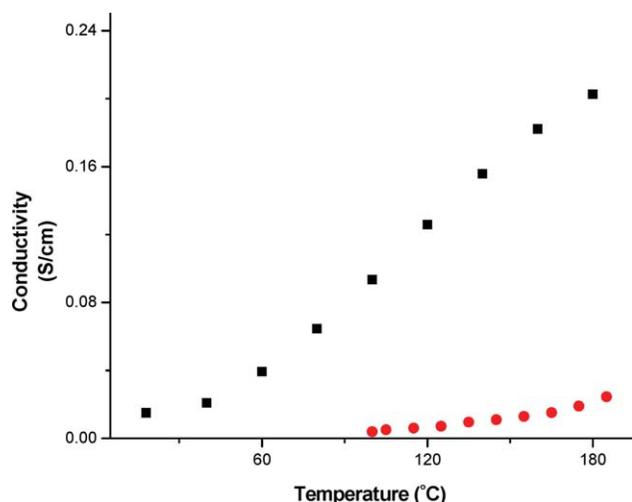
reformat gas used in these polarization studies consisted of ~70% hydrogen, 28% CO<sub>2</sub>, and 2% CO. In the reformat/air polarization curve, it is shown that *i*-AB-PBI membranes maintained high performance at 180 °C, even in the presence of carbon monoxide, a well-known fuel contaminate. At lower temperatures and in the presence of CO (2%), a significant decrease in performance was observed, as would be expected from decreased electrode kinetics and irreversible Pt–CO binding. A lifetime performance study was conducted on *i*-AB-PBI membranes and is shown in Figure 9. An observed break-in period of around 500 h was observed before the cell reached and maintained an average output of 0.65 V. The test was conducted over a period of 3500 h with a relatively constant output voltage of 0.65 V at 0.2 A/cm<sup>2</sup>. Several facility events occurred during the lifetime study of *i*-AB-PBI, which led to uncontrolled shutdowns. However, a full recovery of the cell was observed after normal restart operations. The long (500 h) break-in period for *i*-AB-PBI membranes was attributed to the higher polymer content (~7–10.5%), which introduces a resistance to the transfer of internal PA of the film to the catalytic interface of the electrodes during initial fuel cell operation.

### CONCLUSIONS

AB-PBI membranes were prepared using the PPA process and compared to reported literature on the known conventionally imbibed AB-PBI. A new diacid monomer was

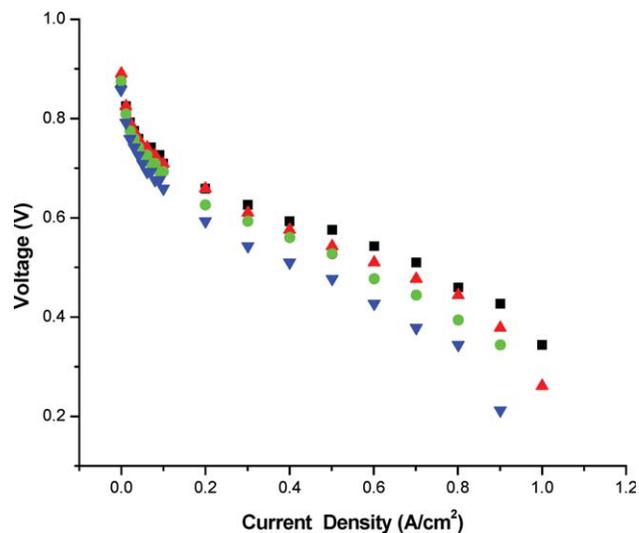
**TABLE 2** Characterization Results for AB-PBI Polymers and Membranes

Sample Number	Monomer wt%	IV (dL/g)	Mol PA/Mol Polymer Repeat Unit	Membrane Composition (as cast) (wt%)		
				PA	H <sub>2</sub> O	Polymer
8	1.46	1.56	35.28	60.22	37.67	2.11
9	2.76	4.63	24.71	62.17	34.36	3.47
10	2.7	3.59	29.07	62.59	34.83	2.58
11	2.86	2.57	31.82	57.27	40.49	2.24
12	4.84	1.8	22.56	73.82	22.25	3.93



**FIGURE 5** Effects of temperature on anhydrous ionic conductivity. (Squares: new isomeric *i*-AB-PBI (Sample 5 from Table 1), circles: reported literature values for AB-PBI.<sup>25</sup>)

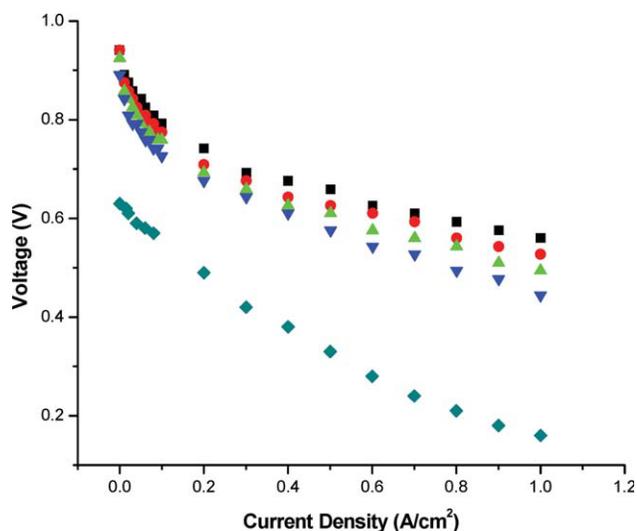
synthesized from an imidate reaction with DABA. Polymerization of this diacid monomer with 3,3'-4,4'-tetraminobiphenyl yielded a new sequence isomer of AB-PBI. Polymerization studies were conducted, which showed an unusual dependence on monomer concentration, but revealed conditions where high IV polymers could be prepared. Membranes prepared from the PPA process exhibited higher levels of PA than typically reported for conventionally imbibed AB-PBI. The membrane mechanical property characterization and proton conductivity measurements indicated that the membranes formed from *i*-AB-PBI were suitable



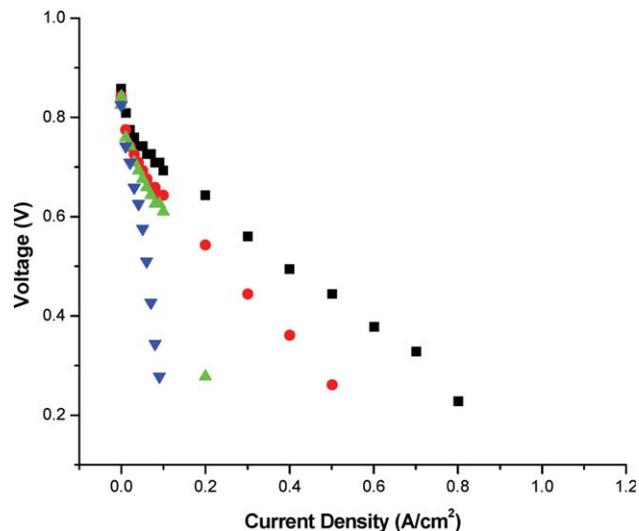
**FIGURE 7** Polarization curves for *i*-AB-PBI membranes with hydrogen/air at 1.2:2.0 stoichiometric flows, respectively. (Squares: 180 °C, triangles: 160 °C, circles: 140 °C, inverted triangles: 120 °C.)

candidates for high-temperature polymer membrane fuel cells.

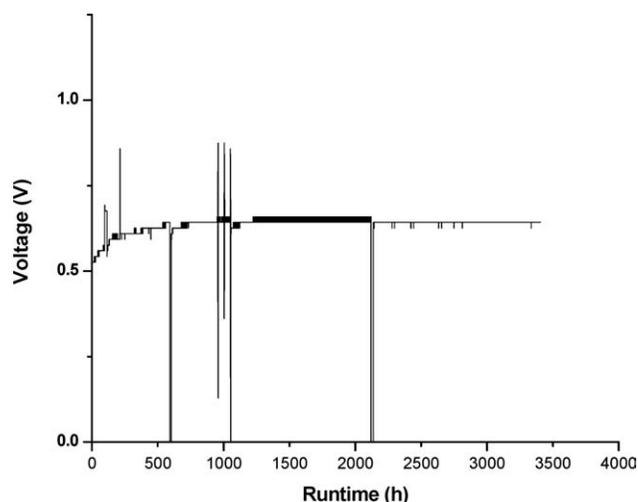
The new sequence isomer, *i*-AB-PBI, was found to be less soluble in PA and mechanically stable at elevated temperatures (120–180 °C) with high PA doping levels (24–35 mol PA/mol polymer repeat unit). The changes in chain sequence are believed to affect chain stiffness, which may contribute to decreased solubility and increased gel stability in PA at high temperatures. Membranes with higher polymer content (~7–10.5 wt %) than those prepared from the traditional



**FIGURE 6** Polarization curves for *i*-AB-PBI membranes with hydrogen/oxygen at 1.2:2.0 stoichiometric flows, respectively. (Squares: 180 °C, circles: 160 °C, triangles: 140 °C, inverted triangles: 120 °C, diamonds: reference data for AB-PBI at 130 °C.<sup>25</sup>)



**FIGURE 8** Polarization curves for *i*-AB-PBI membranes with reformate/air at 1.2:2.0 stoichiometric flows, respectively. (Squares: 180 °C, circles: 160 °C, triangles: 140 °C, inverted triangles: 120 °C; Reformate composition: 70% hydrogen, 28% CO<sub>2</sub>, and 2% CO.)



**FIGURE 9** Long term performance of *i*-AB-PBI membrane fuel cell operated at 180 °C supplied with hydrogen/air at 1.2:2.0 stoichiometric flows respectively. Data collected under 1 atm and deviations were uncontrolled facility events.

AB-PBI (~3 wt %) were obtained using the PPA process. The increased solids content of the *i*-AB-PBI films resulted in membranes that were more mechanically robust when compared to the in-house AB-PBI films prepared using the PPA process. Fuel cell performance evaluations were conducted using *i*-AB-PBI membranes and an output voltage of 0.65 V at 0.2 A/cm<sup>2</sup> for hydrogen/air at an operational temperature of 180 °C was observed. The new *i*-AB-PBI is reported as a promising candidate for high-temperature PEM fuel cell devices. Further development of copolymers containing *i*-AB-PBI prepared from the PPA process are being investigated.

The authors acknowledge the work of Vitaly Rassolov for conducting model simulations on the AB-PBI and *i*-AB-PBI polymers. BASF Fuel Cell Inc. is especially recognized for financial and technical support of this research.

## REFERENCES AND NOTES

- 1 Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345–352.
- 2 Steele, B. C. H.; *J. Mater. Sci.* **2001**, *36*, 1053–1068.
- 3 Jayakody, J. R. P.; Chung, S. H.; Duintino, L.; Zhang, H.; Xiao, L.; Benicewicz, B. C.; Greenbaum, S. G. *J. Electrochem. Soc.* **2007**, *154*, B242–B246.
- 4 Jannasch, P.; *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 96–102.
- 5 Mader, J.; Xiao, L.; Schmidt, T. J.; Benicewicz, B. C.; *Adv. Polym. Sci.* **2008**, *216*, 63–124.
- 6 Yu, S.; Xiao, L.; Benicewicz, B. C. *Fuel Cells* **2008**, *3–4*, 165–174.
- 7 Shogbon, C.; Brousseau, J.; Zhang, H.; Benicewicz, B. C.; Akpalu, Y. *Macromolecules* **2006**, *39*, 9409–9418.

- 8 Yu, S.; Zhang, H.; Xiao, L.; Choe, E. W.; Benicewicz, B. C. *Fuel Cells* **2009**, *4*, 318–324.
- 9 Xiao, L.; Zhang, H.; Scanlon, E.; Ramanathan, S. L.; Choe, E. W.; Rogers, D.; Apple, T.; Benicewicz, B. C. *Chem. Mater.* **2005**, *17*, 5328–5333.
- 10 Xiao, L.; Zhang, H.; Jana, T.; Scanlon, E.; Chen, R.; Choe, E. W.; Ramanathan, L. S.; Yu, S.; Benicewicz, B. C. *Fuel Cells* **2005**, *2*, 287–295.
- 11 Yu, S.; Benicewicz, B. C. *Macromolecules* **2009**, *42*, 8640–8648.
- 12 Kang, S.; Zhang, C.; Xiao, G.; Yan, D.; Sun, G. *J. Membr. Sci.* **2009**, *334*, 91–100.
- 13 Quan, G.; Benicewicz, B. C. *J. Polym. Sci. Part A* **2009**, *47*, 4064–4073.
- 14 Ong, A.; Jung, G.; Wu, C.; Yan, W. *J. Hydrogen Energy* **2010**, *35*, 7866–7873.
- 15 Wannek, C.; Lehnert, W.; Mergel, J. *J. Power Sources* **2009**, *192*, 258–266.
- 16 Hyoung-Juhn, K.; Sung, C.; Sung, J.; Yeong, C.; Ju-Yong, K.; Hae-Kwon, Y.; Ho-Jin, K.; Kyoung, H. *Macromol Rapid Commun* **2004**, *25*, 894–897.
- 17 Zheng, H.; Petrik, L.; Mathe, M.; *J. Hydrogen Energy* **2010**, *35*, 3745–3750.
- 18 Wippermann, K.; Wannek, C.; Oetjen, H.; Lehnert, W. *J. Power Sources* **2010**, *195*, 2806–2809.
- 19 Asensio, J. A.; Borros, S.; Gomez-Romero, P. *J. Electrochem. Soc.* **2004**, *151*, A304–A310.
- 20 Gomez-Romero, P.; Chojak, M.; Cuentas-Gallegos, K.; Asensio, J. A.; Kulesza, P. J.; Casan-Pastor, N.; Lira-Cantu, M. *J. Electrochem. Commun.* **2003**, *5*, 149–153.
- 21 Asensio, J. A.; Borros, S.; Gomez-Romero, P. *J. Electrochem. Commun.* **2003**, *5*, 967–972.
- 22 Kumbharkar, S.; Kharul, U. *J. Membr. Sci.* **2010**, *360*, 418–425.
- 23 Sung-Kon, K.; Tae-Ho, K.; Taeyun, K.; Jong-Chan, L. *J. Membr. Sci.* **2011**, *373*, 80–88.
- 24 Yang, J.; He, R.; Che, Q.; Gao, X.; Shi, L. *Polym. Int.* **2010**, *59*, 1695–1700.
- 25 Aseino, J. A.; Gomez-Romero, P. *Fuel Cells* **2005**, *3*, 336–343.
- 26 Dictionary of Organic Compounds, 4th ed.; Harris, G.; Pollock, J. R. A.; Stevens, R., Eds.; Oxford University Press: New York, New York, **1965**; Vol. 2.
- 27 Mader J. A.; Benicewicz B. C. *Macromolecules* **2010**, *43*, 6706–6715.
- 28 Mader J. A.; Benicewicz B. C. *Fuel Cells* **2011**, *11*, 212–221.
- 29 Berrada, M.; Anbaoui, Z.; Lajrhed, N.; Berrada, M.; Knouzi, N.; Vaultier, M.; Sekiguchi, H.; Carriere, F. *Chem. Mater.* **1997**, *9*, 1989–1993.
- 30 Holan, G.; Samuel, E. L.; Ennis, B. C.; Hinde, R. W. *J. Chem. Soc. C* **1967**, *1*, 20–25.
- 31 Grimmett, R.; Imidazole and Benzimidazole Synthesis; Academic Press: London, **1997**, p 79.
- 32 Ryan, M. T.; Helminiak, T. E.; *Polym. Prepr.* **1973**, *14*, 1317–1320.