PBI Membranes Via the PPA Process

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Kayley Fishel, Guoqing Qian, and Brian C. Benicewicz

10.1 Introduction

Polyphosphoric acid (PPA) has long been used as a polymerization solvent. Its ability to be used at high temperatures and lack of side reactions and tar formation in the presence of organics has proven useful in polymer syntheses that require high temperatures for condensations, ring closure and aromaticity formation [1]. Thermally stable polymers, such as polybenzothiazoles, polyquinazolines, and polybenzimidazoles (PBIs), have all been successfully synthesized in PPA [2, 3]. PBI polymer and fibers have typically been produced through melt/solid polycondensation processes and spun from solutions of DMAc at concentrations over 20 wt% polymer as reported by Celanese and Conciatori et al. [2, 4]. Although the solubility of PBI in PPA would not allow for this high wt % of polymer to be dissolved for fiber production, PBI has sufficient solubility in PPA in order to produce films. For this reason, PPA is used as the polymerization solvent in both the conventional method of film formation and in the PPA process. The methods through which PBI membranes are processed have been found to greatly affect the properties and morphology of the membrane. Differences in acid loading, conductivity, mechanical properties, inherent viscosity and fuel cell performance have been shown to vary depending on the method through which the PBI was synthesized and processed. Two methods of processing have been shown to produce greater conductivity than the conventional imbibing method. Recent reviews by Savinell, Bjerrum, Li, Benicewicz, and Schmidt discuss PBI membranes for fuel cells prepared by many different methods [5–7]. In this review, we will focus on the preparation, properties and fuel cell performance of acid-doped membranes made by a unique sol–gel method termed the PPA process.

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10.2 The Sol–Gel Process

In 2005, Benicewicz et al. (in cooperation with BASF Fuel Cell GmbH) reported a new method for producing PBI films imbibed with phosphoric acid [8]. This process, termed the PPA process, represents a sol–gel process that utilizes PPA as both the polymerization medium and the casting solvent for PBI polymers. In the PPA Process, dicarboxylic acids and tetramines such as 3,3′,4,4′-tetraaminobiphenyl (TAB) (or AB type monomers) are polymerized in PPA between 195 and 220 °C to produce high molecular weight PBI polymers. After polymerization, the PPA solution containing PBI is directly cast onto

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glass plates or other suitable substrates. Since both PBI and PPA are hygroscopic, moisture from the surrounding environment readily hydrolyzes the PPA to phosphoric acid (PA). A sol-to-gel transition can occur which is attributed to the change in the nature of the solvent, i.e., many PBIs show higher solubility in PPA and poorer solubility in phosphoric acid. This process encompasses many favorable attributes. For example, high molecular weight polymer (typically determined through inherent viscosity measurements) can be readily produced using the PPA process. Since the process does not use organic solvents for the polymerization or casting steps, the PPA process eliminates the cost of such solvents, worker exposure, and solvent recovery and disposal costs. Also, separate unit operations for imbibing are not needed as the solvent is transformed into the dopant as part of the process. Mechanical properties of PBI membranes produced through the PPA process also demonstrate greater mechanical properties with greater acid loadings and higher conductivities than membranes formed through other methods [8].

Figure 10.1 provides a summary of the multiple chemical and physical transformations that occur in the PPA Process. Preliminary simulations by Padmanabhan and Kumar of the phase behavior and formation of a physical gel from semiflexible polymer chains provide some insights into the process [9, 10]. Increases in chain stiffness of semiflexible polymer chains will increase chain association in solution and are likely to play a role in the formation of reversible gels with liquid crystalline-like order. Molecular dynamics simulations have also indicated that chain stiffness, depth and rate of the temperature change, and the additional quench provided by the solvent quality (via PPA hydrolysis) result in the transformation of a homogeneous solution into a trapped, three-dimensional network of nematic-like bundles forming a percolated gel as shown in Fig. 10.2. Many of the predictions from these simulations are consistent with the observations made over the past 10–15 years.

10.3 Direct Acid Casting

Researchers at Case Western Reserve University reported a method for casting PBI films directly from acid solutions [11]. This direct acid casting method was performed by initially dissolving PBI in trifluoroacetic acid (TFA). Phosphoric acid was then added to create a single-phase solution which was filtered and cast onto untreated glass plates. The film was heated at 140 °C for 15 min in air. Finally, the film was

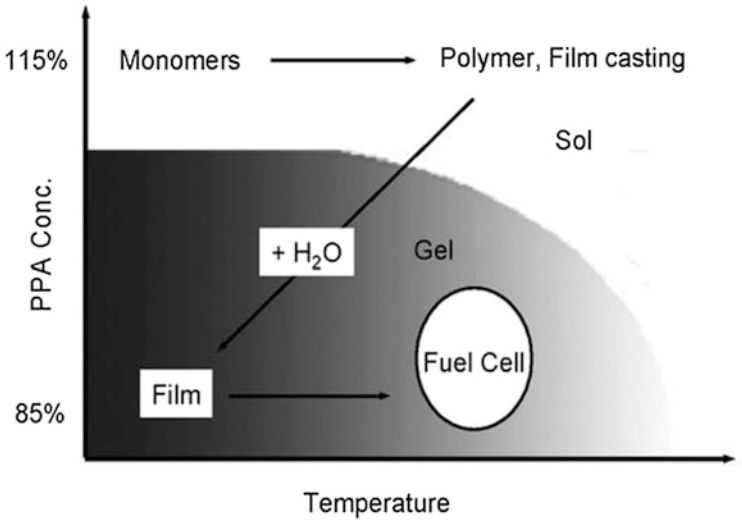

Fig. 10.1 The sol–gel state diagram. Reproduced from [8] with permission of the American Chemical Society

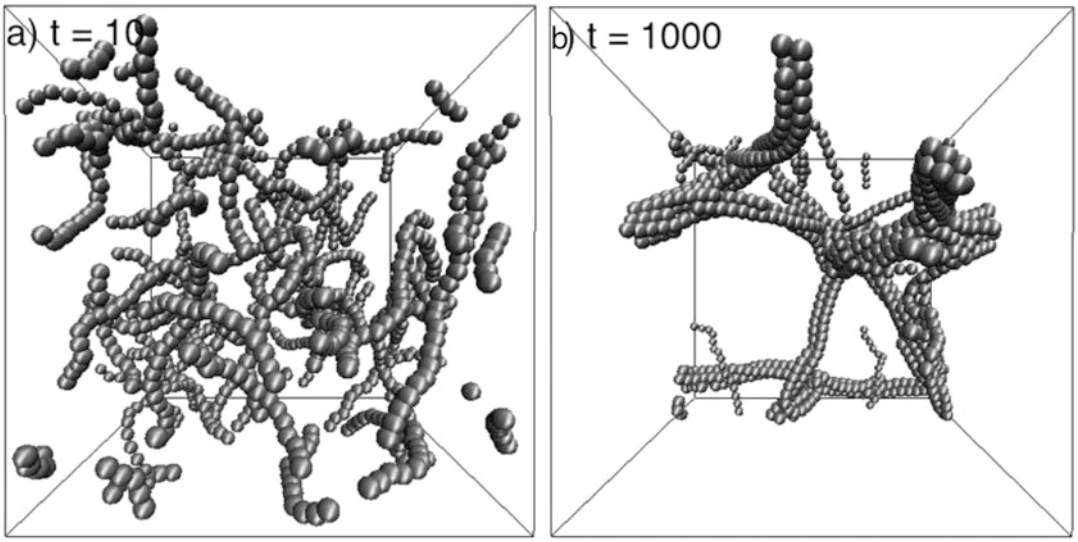

Fig. 10.2 Simulation of (**a**) isotropic homogenous solution of polymer chains and (**b**) dynamically arrested network of nematic-like bundles after thermally quenching the system. Reproduced from [10] with permission of AIP Publishing LLC

removed from the glass plate and heated in a vacuum oven overnight to produce a dry film. Just as PBI prepared through the PPA process exhibits different properties than PBI prepared through the conventional imbibing method, PBI films produced from direct acid casting also display unique properties. It was commonly observed that PBI films prepared through conventional imbibing are tougher and stronger than those prepared by direct acid casting [12]. It was reported that PBI of high inherent viscosity must be used for films cast from TFA to produce films of reasonable strength [12].

10.4 Conductivities and Acid Content

Since the processing method greatly affects the properties of the PBI films, differences in phosphoric acid content and conductivities vary among the PPA process, direct casting, and traditional casting from DMAc even with identical PBI chemistry. When meta-PBI was cast from DMAc and doped in PA baths, conductivities ranged from 0.01 to 0.05 S cm^{-1} [11, 13]. Savinell et al. [11] found that by casting from trifluoroacetic acid rather than DMAc, conductivities for meta-PBI membranes could reach as high as 0.083 S cm^{-1}. This is a significant increase from the traditional casting/imbibing method and demonstrates the influence the processing method has on the membrane properties, such as conductivity. Conductivities for meta-PBI can be significantly increased when membranes are prepared through the PPA process. Perry et al. [13] reported conductivities for meta-PBI membranes made via the PPA process of 0.13 S cm^{-1}. This is nearly a threefold improvement from films cast from DMAc and almost double the conductivity of films cast from trifluoroacetic acid. The PPA process produces membranes that contain more acid than those prepared from conventional imbibing. Acid loadings of 14–26 mol PA per moles polymer repeat unit (PRU) were reported for meta-PBI membranes prepared through the PPA process and 6–10 mol PA per PRU when prepared by conventional DMAc casting and PA imbibing [13]. Additionally, the membranes prepared by the conventionally imbibed technique and PPA process exhibited fundamentally different responses of ionic conductivity on acid doping level.

10.5 Variations in PBI Chemistry

The properties of the polymer gel film are not only affected by processing and morphology, but also by the chemistry of the PBI polymers. The chemistry of the polymer affects acid doping levels, conductivities, mechanical properties, and the polymer solids content. Many PBI chemistries can be synthesized through the PPA process by varying the chemistry of the monomers and the combination of monomers used. The ability to prepare and process many different PBI chemistries using the PPA process is a great advantage because it is less restricted by polymer solubility issues. The properties of these PBI membranes have been thoroughly studied to evaluate structure–property relationships and ultimately to enhance their properties for use in high-temperature PEM fuel cells.

10.5.1 Para-PBI (p-PBI)

Poly(2,2′-(p-phenylene)5,5′-bibenzimidazole) (para-PBI) exhibits excellent performance when used as a membrane in fuel cells.[5] Para-PBI is prepared through the PPA process using equimolar amounts of terephthalic acid and 3,3′,4,4′-tetraaminobiphenyl in PPA under a nitrogen atmosphere. Unlike Vogel and Marvel's early attempts of preparing p-PBI through a melt process which resulted in low molecular weight polymer (IV=1.0 dL g^{-1}), high molecular weight para-PBI (IVs > 3.0 dL g^{-1}) can be prepared through the PPA process [14, 15]. High molecular weight polymer was achieved after approximately 24 h when polymerized between 195 and 220 °C. This is a significantly more time efficient method than previous work reported by the US Air Force Materials Lab that reported high molecular weight para-PBI could take up to 5 weeks to produce [16]. Extensive studies of para-PBI produced through the PPA process have been conducted. Yu et al. [15] systematically explored the effect of monomer concentration on polymer IV. It was reported that high IVs (~3.0 dL g^{-1}) could be obtained up to approximately 4.5 wt% monomer charges (Fig. 10.3) that could be easily cast into high-quality PA-doped membranes. Monomer charges greater than 4.5 wt% resulted in high solution viscosities, insufficient stirring and early loss of polymer solubility resulting in low IVs and unprocessable solutions. Membranes produced from the lower concentrations exhibited higher levels of acid doping than membranes prepared through direct casting [15]. Since high molecular weight para-PBI is insoluble in organic solvents, it cannot be dissolved and directly cast from organic

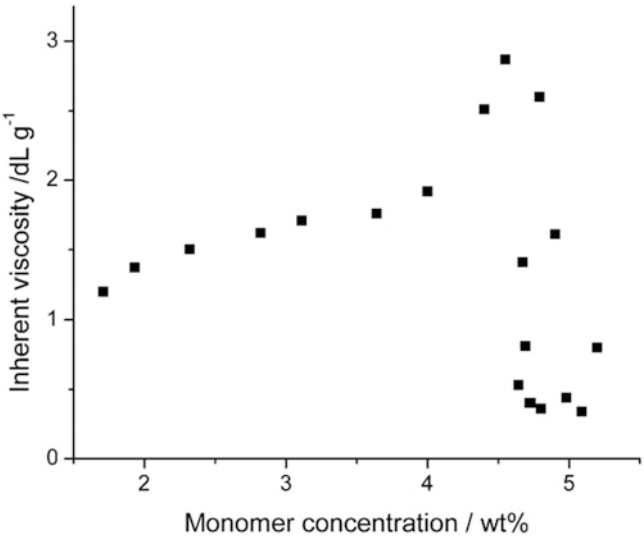

Fig. 10.3 Effect of monomer concentration on inherent viscosity for para-PBI. Reproduced from [15] with permission of John Wiley and Sons

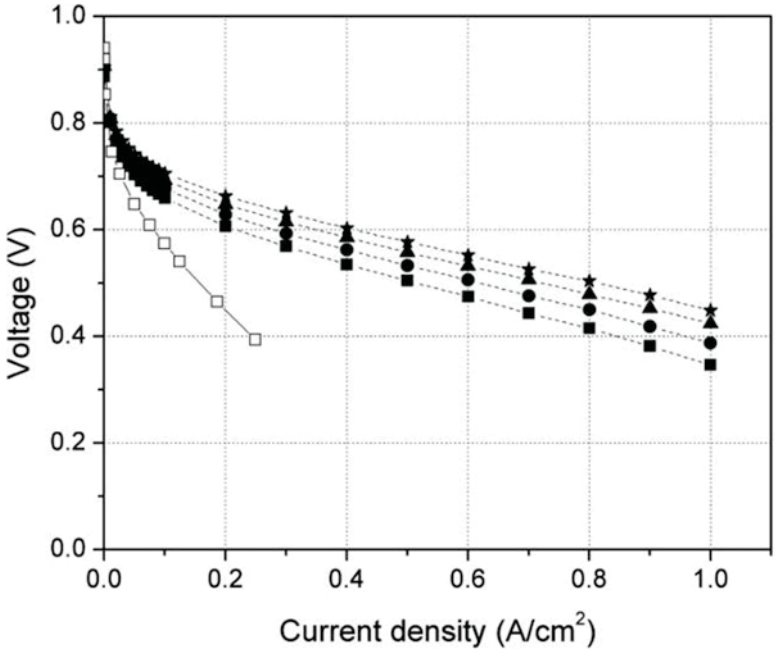

Fig. 10.4 Polarization curves of para-PBI membrane-based fuel cells with hydrogen ($\lambda = 1.2$)/air ($\lambda = 2.00$) at various temperatures at 1 atm. *Squares*: 120 °C, *circles*: 140 °C, *triangles*: 160 °C, *stars*: 180 °C. *Open squares* are data from Wang et al. Electrochim. Acta 1996, 41, 193. Reproduced from [15] with permission from John Wiley and Sons

solvents. Para-PBI membranes prepared by the PPA process contain approximately 30–40 mol of PA/PRU, which are much higher acid doping levels than observed in typical membranes prepared by conventional imbibing (≤13–14 PA/PRU) [15]. The anhydrous conductivity for para-PBI produced from the PPA process is greater than 0.2 S cm^{-1} at 160 °C. When fuel cell performance was evaluated on these membranes at a constant current density of 0.2 A cm^{-2} with hydrogen and air, the voltage was 0.606 V at 120 °C and 0.663 V at 180 °C [15].

Figure 10.4 shows the polarization curves of para-PBI at 120, 140, 160, and 180 °C. Meta-PBI membrane prepared by conventional imbibing is included for comparison. It should be noted that the fuel cell was operated without humidification [15]. At high temperatures para-PBI can also be operated in a fuel cell using gas mixtures other than hydrogen and air. Fuel cells run on reformate gases consisting of varying amounts of hydrogen, carbon monoxide, and carbon dioxide operated reliably even with high concentrations of carbon monoxide, with only slight decreases in voltage. Figure 10.5 shows the polarization curves for para-PBI membrane run on various gas mixtures. Additional testing also demonstrated long-term durability (>1400 h) and very low acid loss rates. Yu et al. [17] reported phosphoric acid loss rates of 3.0 ng cm^{-2} h^{-1} from the cathode and 1.9 ng cm^{-2} h^{-1} from the anode. These results indicate that PA loss from the MEAs is not likely a failure mode under normal operating conditions.

10.5.2 Sulfonated-PBI

A sulfonated version of para-PBI has been produced using the PPA process by reacting equimolar amounts of 3,3′,4,4′-tetraaminobiphenyl and 2-sulfoterephthalic acid in PPA (Fig. 10.6).

Mader et al. [18] originally investigated this chemistry to see if the addition of a stronger acid group would improve conductivity and therefore the overall fuel cell performance. Inherent viscosity was tested with various monomer charges and it was found that the highest IV, 1.71 dL g^{-1}, was obtained at a monomer charge of 3.61 wt%. Monomer concentrations ranged from 2.48 to 7.39 wt% and IVs ranged from 1.03 to 1.71 dL g^{-1}. The membrane mechanical properties were found to increase with increasing polymer solids concentration. Tensile stress at

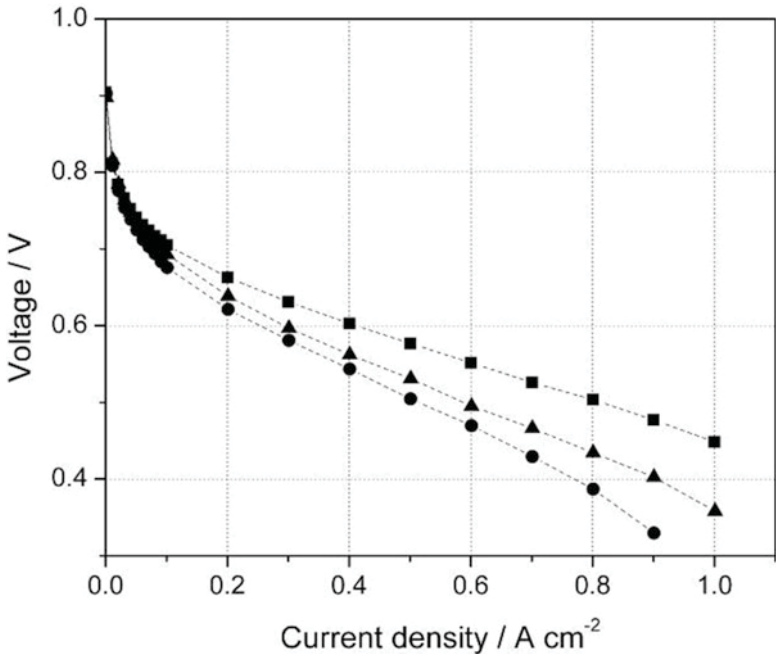

Fig. 10.5 Polarization curves of para-PBI membrane-based fuel cells with various gas mixtures at 180 °C under ambient pressure. (*Squares*: hydrogen/air), (*triangles*: H_2 70 %, CO 1 %, CO_2 balance/air) and *circles*: (H_2 35.8 %, CO 0.2 %, CO_2 11.9 %, N_2 balance/air). Reproduced from [15] with permission John Wiley and Sons

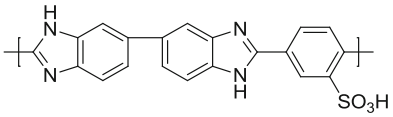

Fig. 10.6 Chemical structure of sulfonated-PBI repeat unit

break reached a maximum of 2.25 MPa and a modulus of 15.1 MPa. The pristine sulfonated-PBI membrane demonstrated high phosphoric acid loadings, 28–53 mol PA/PRU, though an increase in conductivity was not seen when samples contained more than 39 mol PA/PRU (maximum conductivity was approximately 0.32 S cm^{-1}). Fuel cell testing was performed on membranes with the highest IVs (Fig. 10.7). The highest performance was seen in the membrane with the highest level of acid loading, 0.679 V at 160 °C and 0.2 A cm^{-2}. The lowest performance, 0.617 V, was seen with the membrane that had the lowest level of acid loading. These results indicate a correlation between fuel cell performance and acid loading but not fuel cell performance and conductivity directly. Since PBI is known to be both thermally and chemically stable, further studies were performed on sulfonated-PBI doped with sulfuric acid. This was performed by first synthesizing sulfonated-PBI in PPA, casting films and hydrolyzing the PPA to PA, and exchanging the PA under different conditions in concentrated sulfuric acid baths. Conductivities were tested for nearly 500 min from room temperature (~20 °C) to 100 °C and reached 0.54 S cm^{-1} but decreased with time at 100 °C. Acid loadings ranged from approximately 25–50 mol of sulfuric acid/PRU (Table 10.1). These acid loadings were found to be similar to the phosphoric acid loadings in sulfonated-PBI prepared through the PPA process. A comparison of conductivities at various temperatures and over time for these films doped in different sulfuric acid baths can be seen in Fig. 10.8.

10.5.3 AB-PBI and Isomeric AB-PBI (*i*-PBI)

The simplest PBI chemistry is AB-PBI with a repeat unit consisting solely of one 2,5-benzimidazole ring. AB-PBI is synthesized using 3,4-diaminobenzoic acid as the only

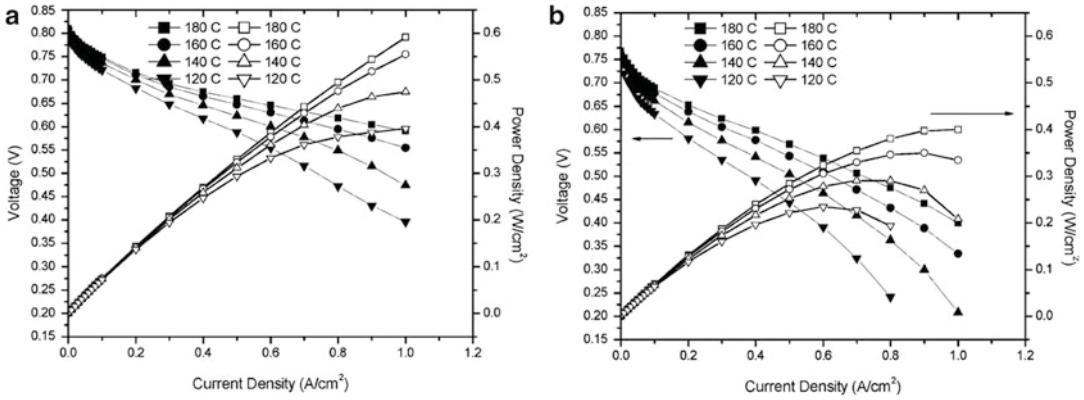

Fig. 10.7 Fuel cell performance of PA-doped sulfonated-PBI (3.13 wt% polymer, IV = 1.67 dL/g, and 28.41 mol PA/PBI): polarization curves (filled symbols) and power density curves (open symbols) with (**a**) hydrogen and oxygen and (**b**) hydrogen and air. Reproduced from [18] with permission of the American Chemical Society

Table 10.1 Acid content, sulfuric and phosphoric acid, in sulfonated polybenzimidazoles. Reproduced from [18] with permission of the American Chemical Society

Film	Polymer contents (g)	Acid loading (mol acid/PRU)
PA-doped s-PBI	0.0413	39.84
30 wt% SA room temp bath	0.0516	25.47
30 wt% SA heated bath	0.0553	30.36
50 wt% SA room temp bath	0.0583	50.49
50 wt% SA heated bath	0.0587	31.48

monomer since it contains both the o-diamine and the carboxylic acid functionality. Because there are no additional phenyl rings or other aromatic rings in the repeat unit as there are in other PBI chemistries, the solubility of AB-PBI in phosphoric acid is greater than most other types of PBIs. In past work, AB-PBI was polymerized through the PPA process and was found to be too soluble in PA to produce a gel membrane that could maintain gel stability at high temperatures, even at high IVs (~10 dL g^{-1}) [19]. This is due to the greater acid loading of the AB-PBI membranes produced from the PPA process (22–35 mol PA/PRU) versus the conventionally imbibed membranes (2–10 mol PA/PRU) [6]. In 2011, Gulledge et al. [20] reported a method of synthesizing a new isomeric version of AB-PBI, also consisting solely of 2,5-benzimidazole repeat units, however, these repeat units were no longer in a strictly head-to-tail arrangement like AB-PBI, but rather contained head-to-head, head-to-tail, and tail-to-tail arrangements. This polymerization was done through the use of a novel monomer, 2,2′-bisbenzimidazole-5,5′-dicarboxylic acid to create an isomeric AB-PBI (*i*-AB-PBI) shown in Fig. 10.9.

This change in sequence introduced new types of bonds. Benzimidazole–benzimidazole and phenyl–phenyl linkages were now part of the backbone along with the benzimidazole–phenyl linkages. Unlike conventional AB-PBI, *i*-AB-PBI was not as soluble in PA, allowing for the formation of gel membranes via the PPA process containing large amounts of PA that maintained gel stability at elevated temperatures (130–180 °C). Polymerizations in PPA up to ~6 wt% yielded IVs >3.0 dL g^{-1} [20]. Isomeric AB-PBI membranes had conductivities of ~0.2 S cm^{-1} at 180 °C which is approximately a tenfold increase in conductivity over AB-PBI prepared by the conventional imbibing method (0.02 S cm^{-1}) [20, 21]. Figure 10.10 shows the conductivity of *i*-AB-PBI at various temperatures. The higher conductivity was largely due to the greater stability of *i*-AB PBI at higher temperatures with

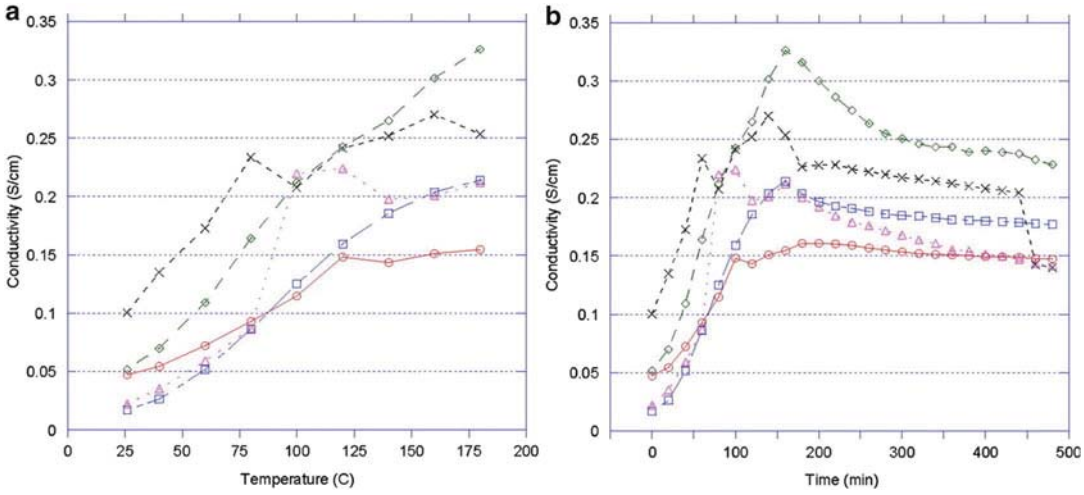

Fig. 10.8 Conductivity as a function of temperature and time (**a**) short-term testing, (**b**) long-term testing. *Red circles*: 30 wt% sulfuric acid bath at room temperature, *blue squares*: 20 wt% heated sulfuric acid bath, *green diamonds*: 50 wt% sulfuric acid bath at room temperature, *black crosses*: 50 wt% heated sulfuric acid bath. Reproduced from [18] with permission of the American Chemical Society

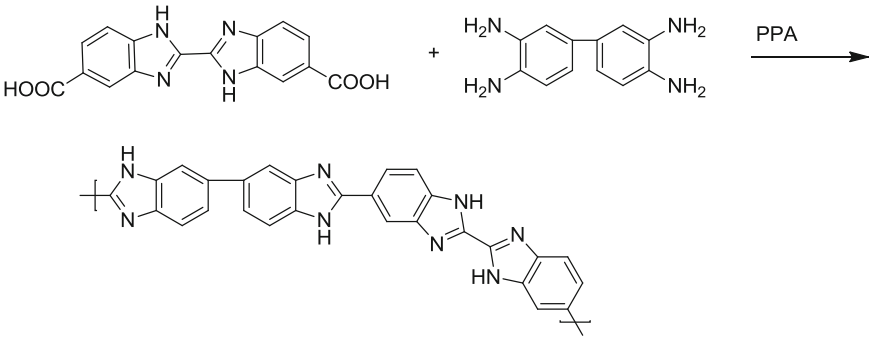

Fig. 10.9 Synthetic scheme for *i*-AB-PBI. Reproduced from [20] with permission of John Wiley and Sons

increased acid doping levels, apparently derived from the sequence isomerism. The high conductivity of these membranes indicated they would be excellent candidates for use in HT-PEM fuel cells. Isomeric AB-PBI membranes displayed much improved fuel cell performance, ~0.65 V when run at 180 °C and 0.2 A cm^{-2}, compared to AB-PBI prepared through conventional imbibing [20]. The fuel cell performance comparison of these two chemistries can be seen in Fig. 10.11. The fuel cell using *i*-AB PBI as the membrane was able to operate for over 3500 h with little decrease in performance further demonstrating the gel stability of this sequence isomer.

10.5.4 Pyridine-Based PBIs

Due to the large affect chemistry has on the properties of PBI membranes, Xiao et al. [22] investigated the properties of PBI membranes that contained a pyridine moiety in the repeat unit rather than a phenyl moiety. Four different PBI homopolymers were synthesized that contained pyridine moieties in the repeat unit. These homopolymers were synthesized by reacting TAB with a pyridine diacid, (3,5-, 2,4-, 2,5-, and 2,6-pyridine dicarboxylic acid). Figure 10.12 shows the repeat unit of each of the four pyridine PBIs. 2,5-Pyridine PBI differs from the other three chemistries in that it is the

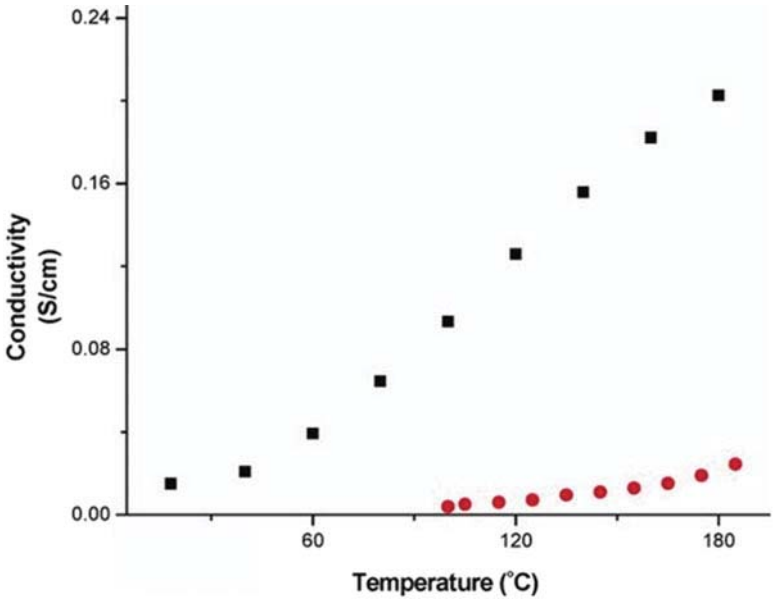

Fig. 10.10 Conductivity of i-AB PBI (*black squares*) and AB-PBI (*red circles*: data from Asensio, J. et al. Fuel Cells 2005, 3, 336–343). Reproduced from [20] with permission of John Wiley and Sons

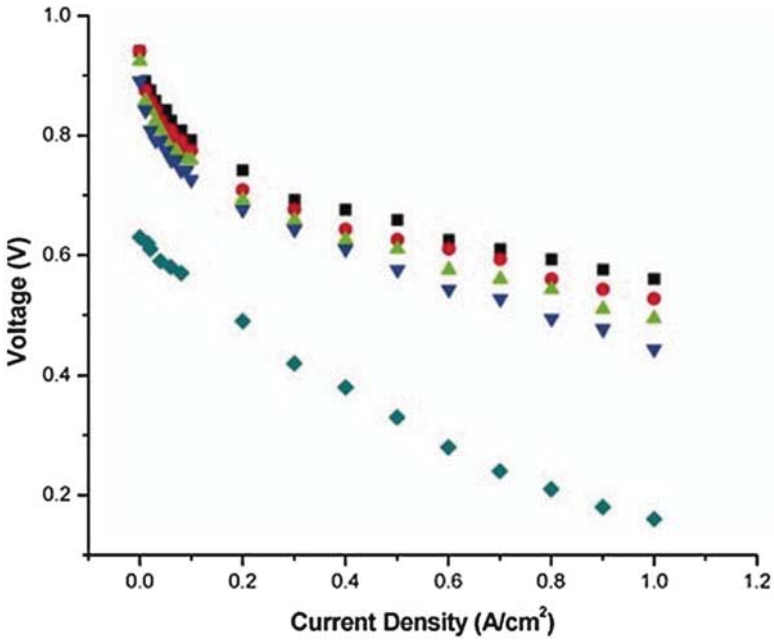

Fig. 10.11 Polarization curves for i-AB-PBI membranes with hydrogen/oxygen at 1.2:2.0 stoichiometric flows, respectively. (*Squares*: 180 °C, *circles*: 160 °C, *triangles*: 140 °C, *inverted triangles*: 120 °C, *diamonds*: reference data for AB-PBI at 130 °C) (Asensio, J. et al. Fuel Cells 2005, 3, 336–343). Reproduced from [20] with permission of John Wiley and Sons

only pyridine PBI in this series that has para-orientation within the backbone. Due to its more rigid nature than the other three pyridine PBI chemistries, it reportedly became more viscous during polymerization than the others after equivalent polymerization times.

All pyridine PBI chemistries achieved IVs $\geq$ 1.0 dL g^{-1}, indicating high molecular weight polymer was obtained from all four homopolymers. Specific IVs are listed in Table 10.2. Mechanically strong membranes of 2,5-pyridine PBI were obtained through the PPA

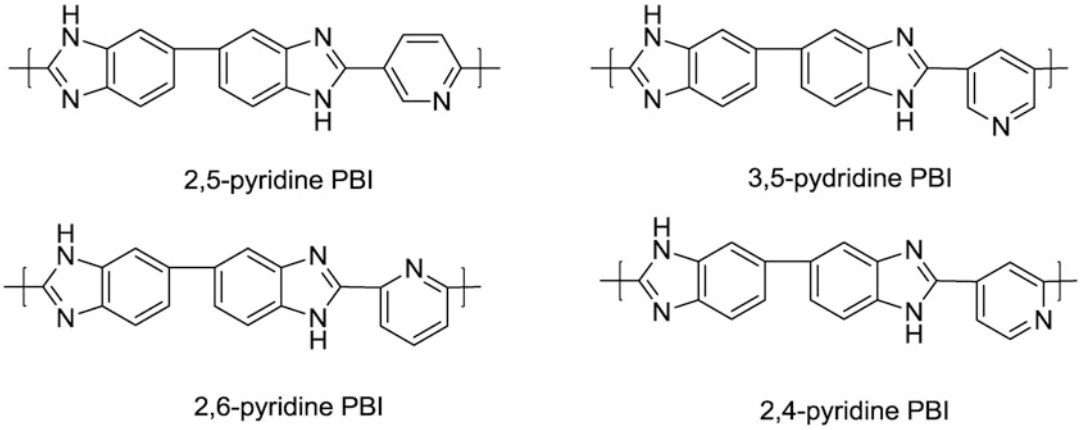

Fig. 10.12 Chemical structure of repeat units for pyridine-based polybenzimidazoles

Table 10.2 Pyridine PBIs and polymerization data where represents final monomer concentration

Polymer	Monomer purity	η_{inh}/ dL g^{-1}	Polymerization concentration (%)
2,5-PPBI	As received	0.5	4–18
	Recrystallized	2.5–3.1	
3,5-PPBI	As received	0.6	4–20
	Recrystallized	1.3–1.9	
2,4-PPBI	As received	0.3	~7
	Recrystallized	1.0	
2,6-PPBI	As received	0.2	~7
	Recrystallized	1.3	

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process when cast from a 4.5 wt% polymer solution [22]. Acid doping levels were found to be 15–25 mol PA/PRU which is much higher than acid loadings in PBI membranes made via the conventional imbibing method. In comparison, 3,5-pyridine PBI membranes exhibited significantly different properties than 2,5-pyridine PBI membranes. Although, 3,5-pyridine PBI attained an IV of 1.8 dL g^{-1}, mechanically stable membranes could not be produced via the PPA process. After casting and hydrolysis, the solution remained a viscous solution rather undergoing gelation and film formation. The polymerization studies examined a wide range of monomer charges (5–20 wt%), but the high solubility of 3,5-pyridine PBI prevented film formation at all polymer loadings [22]. 2,4-pyridine PBI membranes were found to be mechanically weak, therefore, further characterization of membrane properties was not performed. Mechanically stable membranes of 2,6-pyridine PBI were produced through the PPA process and acid doping levels of the membranes were found to be between 8 and 10 mol PA/PRU with polymer contents between 15 and 20 wt%. Conductivities of both 2,5-pyridine PBI and 2,6-pyridine PBI were tested under anhydrous conditions from 20 to 210 °C (Fig. 10.13) and 2,5-pyridine PBI (~0.2 S cm^{-1}) was found to have almost twice the conductivity of 2,6-pyridine PBI (~0.1 S cm^{-1}) from 160 to 210 °C [22]. The higher conductivity of the 2,5-pyridine PBI membranes was attributed to the significantly higher acid loading than the 2,6-pyridine PBI membranes and to its para-orientation. These results contribute to our general understanding that demonstrate significant effects of polymer design such as chain stiffness, functional group incorporation, and orientation on the properties of PBI membranes.

10.5.5 Meta-PBI

Meta-PBI, poly(2,2′-(m-phenylene)5,5′-bibenzimidazole), has gained great attention since

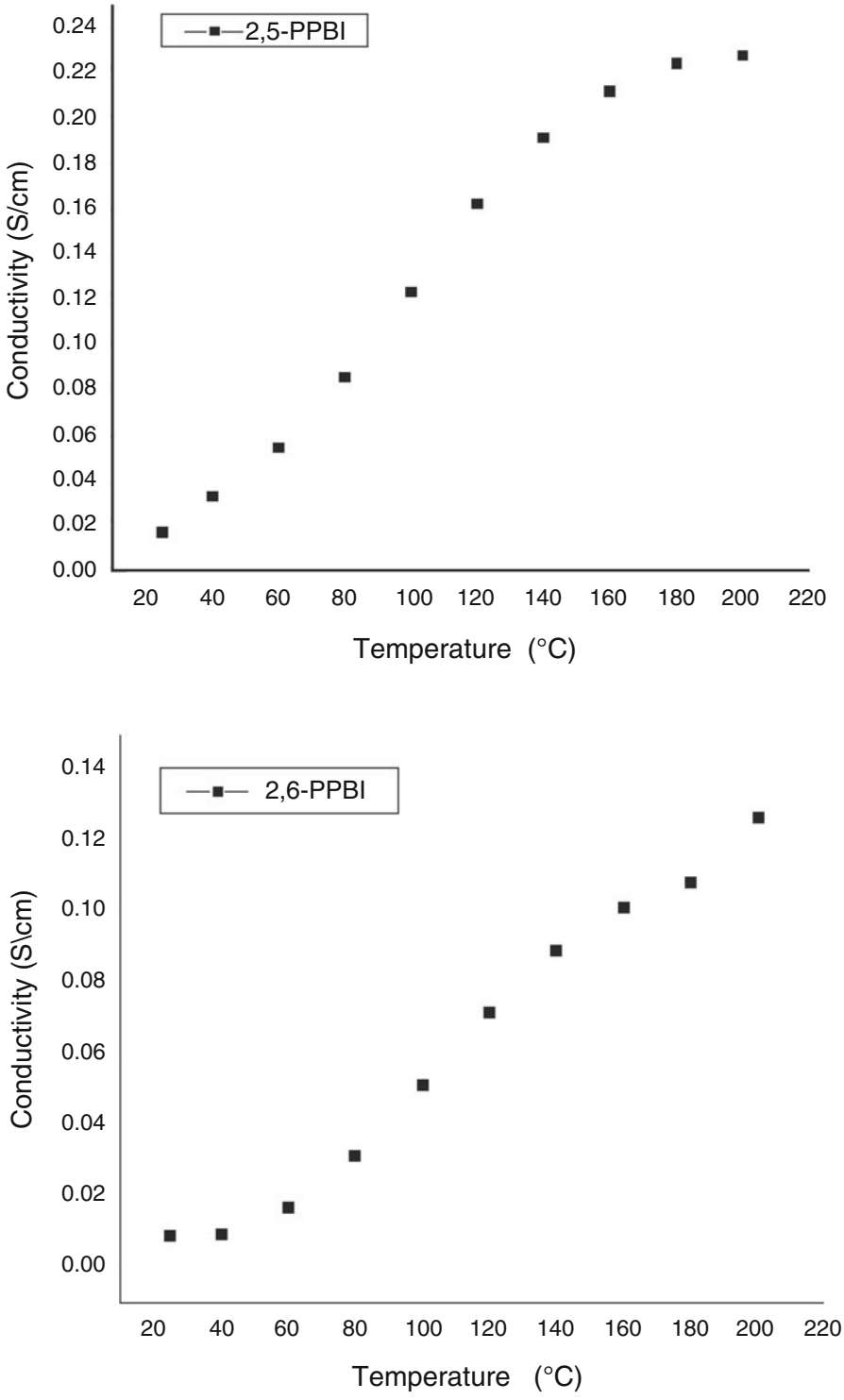


Fig. 10.13 Conductivities of phosphoric acid doped pyridine polybenzimidazoles. Reproduced from [22] with permission of John Wiley and Sons

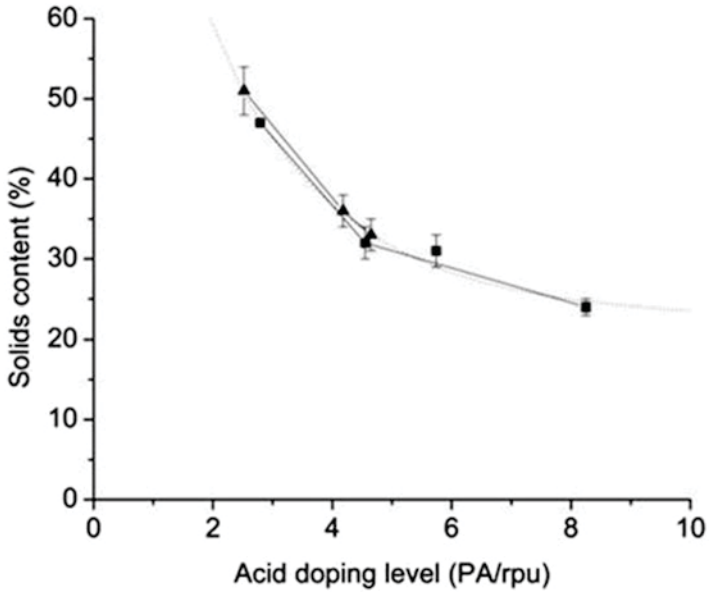


Fig. 10.14 Relationship of solids content and acid doping levels of heat-treated phosphoric acid imbibed meta-PBI prepared by *squares*: sol–gel process, *triangles*: conventional imbibing. Reproduced from [13] with permission of John Wiley and Sons

Wainright et al. [23] showed that meta-PBI films doped with phosphoric acid can be used in fuel cells operating at 100–200 °C. Since meta-PBI can be prepared by both the conventional imbibing method and the PPA processes, many studies have been performed on comparing meta-PBI membranes prepared by both processes. Meta-PBI prepared by the PPA process produces membranes with higher levels of acid doping, i.e., 14–26 mol PA/PRU versus 6–10 mol PA/PRU by conventional imbibing [5, 6]. Due to the higher acid doping levels in membranes prepared by the PPA process, it is no surprise that these membranes displayed higher conductivities than those prepared by conventional imbibing, i.e., 0.13 S cm^{-1} at 160 °C and 0.04–0.05 S cm^{-1} at 150 °C, respectively [5, 6]. Perry et al. [13] recently conducted carefully controlled comparisons of membranes produced by each process. Membranes with similar solid contents were prepared by each method and treated using acid baths and heat treatments to assess acid uptake. Figure 10.14 shows that membranes prepared by the sol–gel process were able to take up more acid while still retaining mechanical integrity. Additionally, at similar acid doping levels, membranes prepared by the PPA process consistently demonstrated higher conductivities than membranes prepared by conventional imbibing (Fig. 10.15). Interestingly, the fundamental dependence of ionic conductivity and acid doping level was different for the membranes made by the two processes, pointing to potentially important contributions of the membrane morphology on proton mobilities.

10.5.6 Dihydroxy-PBI

Previous literature [24] on rigid-rod polymers containing nitrogen heterocycles reported strong hydrogen bonds with polymers containing hydroxyl groups. Yu et al. [25] investigated dihydroxy-PBI (2OH-PBI) prepared from 2,5-dihydroxyterephthalic acid and TAB. The chemical structure, membrane properties, and fuel cell performance were all evaluated. During polymerization, solutions were reportedly viscous for monomer charges of ~3 wt% which is lower than many other PBIs. It was also observed that 2OH-PBI powders would not fully dissolve in sulfuric acid for IV testing [25]. Small molecule studies were conducted which indicated that the high solution viscosity and insolubility in sulfuric acid resulted from intermolecular

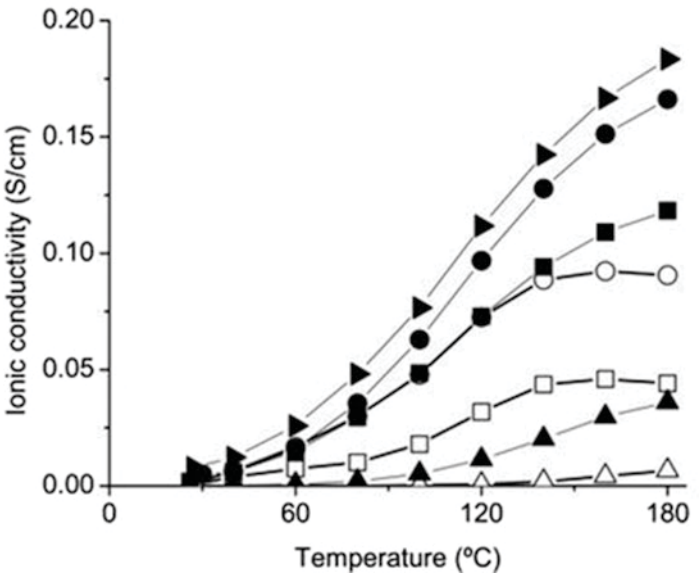


Fig. 10.15 Ionic conductivities for heat-treated PA-doped meta-PBI at various acid doping levels (averages) conventionally imbibed membranes (*open triangles*: 3, *open square*: 4, *open circle*: 5) and sol–gel membranes (*filled triangle*: 3, *filled square*: 5, *filled circle*: 6, *filled sideways triangle*: 8) moles PA/mol of polymer repeat units. Reproduced from [13] with permission of John Wiley and Sons

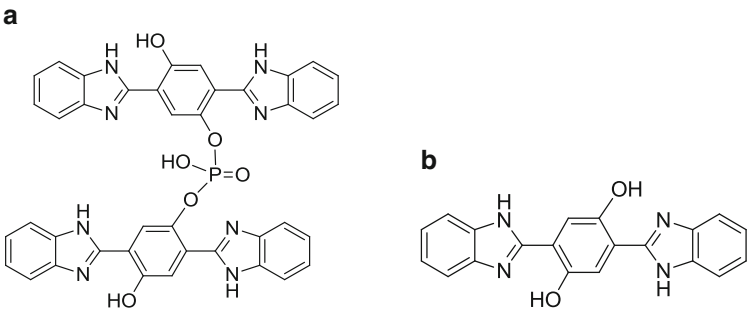


Fig. 10.16 (**a**) Phosphate bridge in small molecule 2OH-PBI study. (**b**) Model compound 2,5-bis (2-benzimidazolyl) hydroquinone. Reproduced from [25] with permission of the American Chemical Society

phosphate bridges as shown in Fig. 10.16a [26]. The model compound, 2,5-bis (2-benzimidazolyl)hydroquinone (Fig. 10.16b), was heated in PPA for 13 h and FTIR was used to confirm the formation of phosphate bridges.

Acid doping levels of the 2OH-PBI membranes were determined to be ~28 mol PA/PRU and the proton conductivity reached 0.43 S cm^{-1} at 180 °C which is even higher than that of para-PBI (0.35 S cm^{-1}) [25]. The 2OH-PBI membranes exhibited higher conductivities than para-PBI at all temperatures (Fig. 10.17) and also higher conductivities when the PA doping levels were adjusted to identical levels. Suarez et al. [27] conducted more detailed NMR experiments on 2OH-PBI membranes that showed lower proton diffusion for the 2OH-PBI membranes, indicating that enhanced proton transport could be due to a Grotthuss or structural diffusion mechanism, with likely participation of the phosphate groups. Due to the high conductivity found in 2OH-PBI membranes, fuel cell testing was performed. Fuel cell testing using hydrogen ($\lambda = 1.2$)/air ($\lambda = 2.0$) at 160 °C produced a voltage of 0.642 V at 0.2 A cm^{-2} which was found to be very close to that of para-PBI when operated under the same conditions (~0.64 V), showing that while a good conductivity is important for fuel cell performance, other factors can effect cell performance [25]. When testing on Pt alloy cathode catalysts, the 2OH-PBI membranes showed improved performance, exhibiting 0.69 V at 0.2 A cm^{-2}.

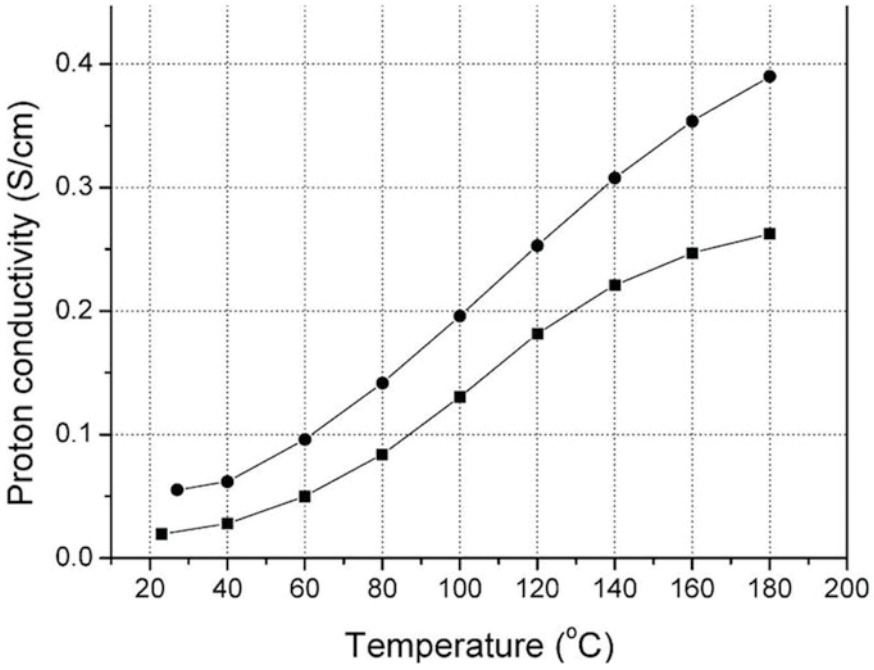


Fig. 10.17 Proton conductivities of phosphoric acid doped 2OH-PBI (*circles*) and para-PBI (*squares*) membranes. Reproduced from [25] with permission of the American Chemical Society

10.6 Copolymers Through the PPA Process

In the previous section, various homopolymer analogs of PBI prepared through the PPA process were reviewed to show the effects of chemical structure on membrane properties. The properties of various PBI derivatives are summarized in Table 10.3. Since it is commonly observed that copolymers can have characteristics of both their homopolymers, it is interesting to study the effects of copolymerization on PBI membrane properties. Countless random copolymers can be made through the PPA process by varying the combinations of diacids or tetramines. A few that have been previously studied through the PPA process are reported below.

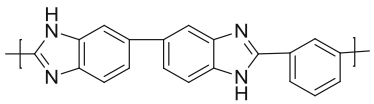
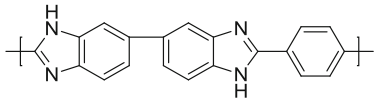
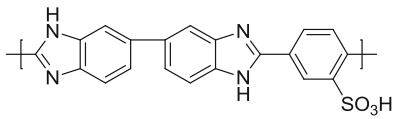
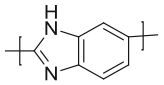
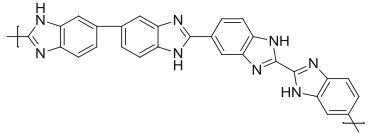
10.6.1 Sulfonated Para-PBI

A random copolymer series of sulfonated and para-PBI was synthesized by Mader et al. [28] by varying the ratios of 2-sulfoterephthalic acid and terephthalic acid for polymerization. Sulfo/para-PBI ratios of 75/25, 50/50, and 25/75 were compared to the homopolymers of sulfonated-PBI and para-PBI. Polymer IVs decreased with increasing sulfonated content of the copolymers. Conductivities of the random copolymers 75/25, 50/50, and 25/75 sulfonated-to-para all demonstrated high conductivities at 180 °C, 0.157 S cm^{-1}, 0.148 S cm^{-1}, and 0.291 S cm^{-1}, respectively [28]. The increase in conductivity with greater para-character was attributed to the greater acid loadings. Fuel cell performance was evaluated for all three variations and showed better performance with increasing amounts of para-character, however, all of the copolymers had lower fuel cell performance than the para homopolymer [28].

10.6.2 Segmented Block AB-Para-PBI

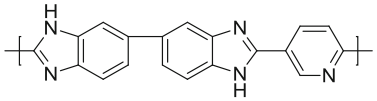
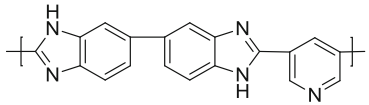
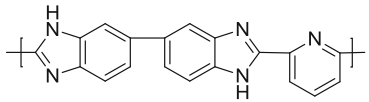
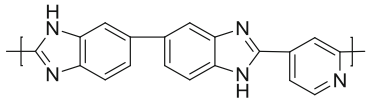
As previously mentioned, AB-PBI forms unstable gels when prepared by the PPA process due

Table 10.3 Properties of various chemistries of PBI prepared through the PPA process

PBI chemistry	Structure of polymer repeat unit	Monomer charges (wt %) Tested via PPA process	Inherent viscosity ranges (dL g^{-1})	Approximate membrane acid loading (mols PA/mol PRU)	Conductivity (S cm^{-1}) at 180 °C	Ref.
Meta-PBI		2–12	0.8–2.3	14–26	0.13	6
Para-PBI		1–5	0.3–2.9	30–40	0.25	15
Sulfonated-PBI		2.48–7.4	1.03–1.71	28–53	0.33	18
AB-PBI		N/A	≤10.0	22–35	N/A	19
i-AB-PBI		2.9–8.2	1.0–3.1	24–37	0.2	20

(continued)

Table 10.3 (continued)

PBI chemistry	Structure of polymer repeat unit	Monomer charges (wt %) Tested via PPA process	Inherent viscosity ranges (dL g^{-1})	Approximate membrane acid loading (mols PA/mol PRU)	Conductivity (S cm^{-1}) at 180 °C	Ref.
2,5-pyridine PBI		4–18[a]	0.8–3.1	15–25	0.22	22
3,5-pyridine PBI		4–20[a]	0.6–3.1	N/A	N/A	22
2,6-pyridine PBI		~7[a]	0.2–1.3	8–10	0.1	22
2,4-pyridine PBI		~7[a]	0.3–1.00	N/A	N/A	22

N/A = film was too unstable to test

[a]Polymer concentration

to its higher solubility than many other PBIs and the high PA content of the membranes produced by the PPA process. One way to stabilize membranes is copolymerization using another polymer system that exhibits lower solubility in PA. Yu et al. [19] attempted to improve the PA stability of AB-PBI membranes by preparing segmented block (sb) copolymers with para-PBI. This was done by setting up two separate pre-polymerizations, one for each homopolymer, and then combining them for the final polymerization step. Various mole ratios of para-PBI to AB-PBI were evaluated, i.e., 90/10, 75/25, 50/50, 25/75, and 10/90. Proton conductivities of all copolymers showed a similar proton conductivity to that of para-PBI (~0.25 S cm^{-1}) at 160 °C with the exception of the 10/90 ratio (0.15 S cm^{-1}) [19]. This was attributed to its lower acid doping level (~17 mol PA/mol 2-benzimidazoles) than the other copolymer membranes (~19–24 mol PA/mol 2-benzimidazoles) [19]. Since the AB-PBI membrane is not stable when prepared through the PPA process, it cannot be used as a baseline for comparison, however, all of the copolymer membrane conductivities demonstrated greater acid doping levels and conductivities ~20 times higher than AB-PBI membranes prepared by the conventional imbibing method [19]. Polymers containing 90/10, 75/25, 50/50, and 25/75 para-to-AB compositions were evaluated in fuel cells. The 10/90 membrane was not durable at high temperatures and therefore not used in fuel cell testing. The 90/10, 75/25, and 50/50 membranes showed similar fuel cell performances while the 25/75 membrane showed lower fuel cell performance. This could be due to the lower conductivity and the lower gel stability at high temperatures from the higher AB content in the copolymer [19].

10.6.3 Dihydroxy Para-PBI

Along with the homopolymers of 2OH-PBI, Yu et al. [25] synthesized a copolymer series of 2OH-PBI with para-PBI. Compositions of 75/25, 50/50, and 25/75 2OH-to-para were all made at ~3 wt% monomer charges and compared to the respective homopolymers. Acid doping levels of the three copolymers were found to be approximately equivalent (~21–23 mol PA/PRU) and all were found to have similar conductivities at 160 °C (0.27–0.33 S cm^{-1}) [25]. No particular trend was detected in the room temperature mechanical properties, however, all compositions of the 2OH-para-PBI copolymer membranes showed they were sufficiently stable for MEA fabrication and fuel cell testing.

10.7 Membrane Electrode Assemblies and Fuel Cell Testing

Membrane electrode assemblies (MEA) were fabricated by hot-pressing a piece of PPA-processed PBI membrane between the two Pt/C electrodes, typically using 1 mg Pt cm^{-2} on each electrode. The electrodes for fuel cells based on PPA-processed PBI membranes are usually PTFE-bound electrodes. In the PTFE-bound electrode, the Pt/C catalyst particles are bound by a hydrophobic PTFE network, which is commonly cast onto the gas diffusion layer. The PTFE network provides the channel for gas transportation and water removal; the electrons are conducted through the carbon black network while proton transport is dependent on the phosphoric acid in the catalyst layer. The MEAs are assembled into a single-cell fuel cell testing hardware using graphite gas flow plates with serpentine gas channels. Stainless steel end plates with attached heaters were used to clamp the graphite flow plates. The fuel cell performance evaluations were usually performed at high temperatures (120 °C up to 200 °C), and gases were supplied to both electrodes were without external humidification and under ambient pressure. These PPA-processed PBI membranes showed excellent high-temperature performance in fuel cells. The polarization curves of p-PBI membranes at various temperatures are shown in Fig. 10.4 with the comparison to conventionally imbibed membranes [15]. These membranes also showed exceptionally high tolerance to typical

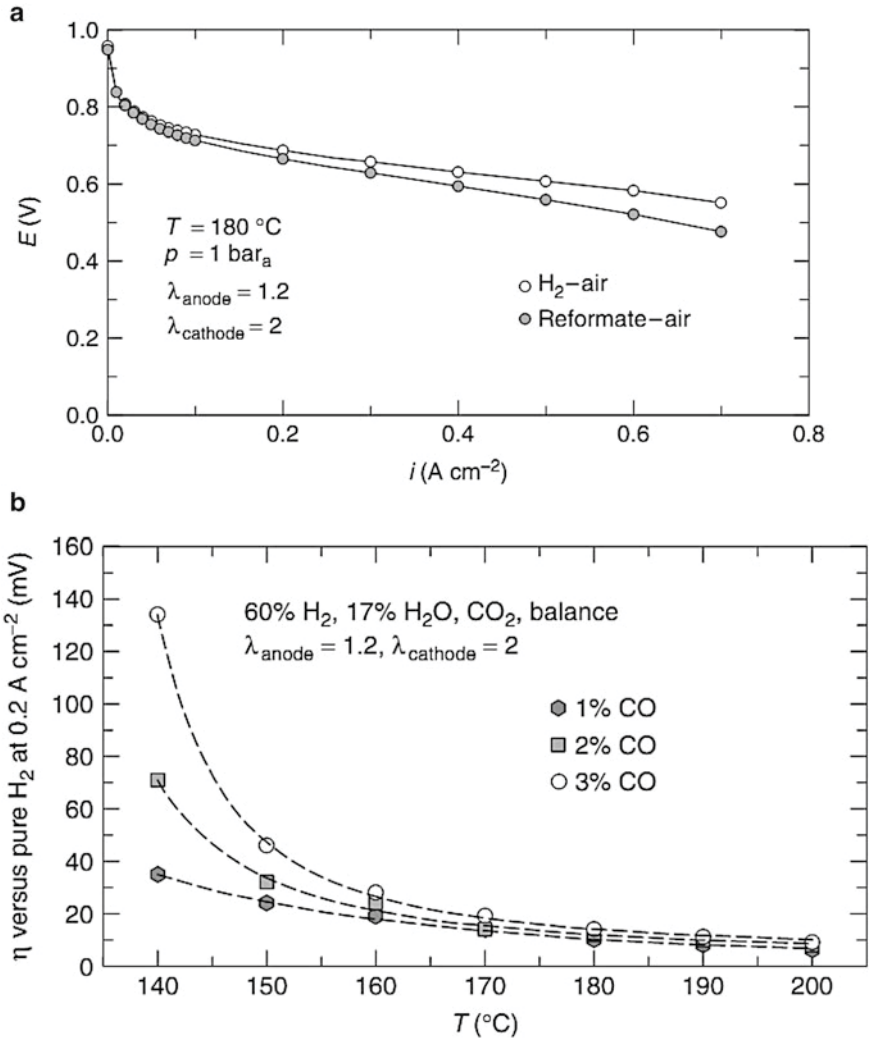


Fig. 10.18 Celtec-P1000 MEA performance and degradation (single-cell data, 50 cm^2, 1.7 mg cm^{-2} total Pt loading). (**a**) H_2–air and reformate–air polarization curves at 180 °C, 1 bara, stoichiometry 1.2/2, reformate composition 70 % H_2, 2 % CO, balance CO_2 (nonhumidified gases). (**b**) anode overpotential versus pure hydrogen operation as a function of temperature and CO partial pressure. Base reformate contains 60 % H_2, 17 % H_2O, balance CO_2 and the CO concentration as shown in the figure. Anode stoichiometry 1.2, 1 bara (anode Pt loading is 1 mg cm^{-2}). Reproduced from [31] with permission of The Electrochemical Society

reformate impurities such as carbon monoxide (CO) and hydrogen sulfide (H_2S) in fuel cell performance tests. Schmidt et al. [29] reported the CO tolerance and fuel cell performances of Celtec-P 1000 (p-PBI membrane prepared by the PPA process) with up to 3 % CO in the fuel stream feed. These studies examined the anode overpotentials resulting from different CO containing steam reformates (reformate composition was 60 % H_2, 17 % H_2O, 1–3 % CO, balance CO_2) versus the same reformate without CO contamination at various operational temperatures. At a typical operational temperature range of 170–180 °C, only very small overpotential changes were observed when the CO partial pressure was changed. This can be seen in Fig. 10.18. Qian et al. [30] also reported that the fuel cell performance at 180 °C was mainly related to the hydrogen gas content, and was less dependent on the CO content in the feed

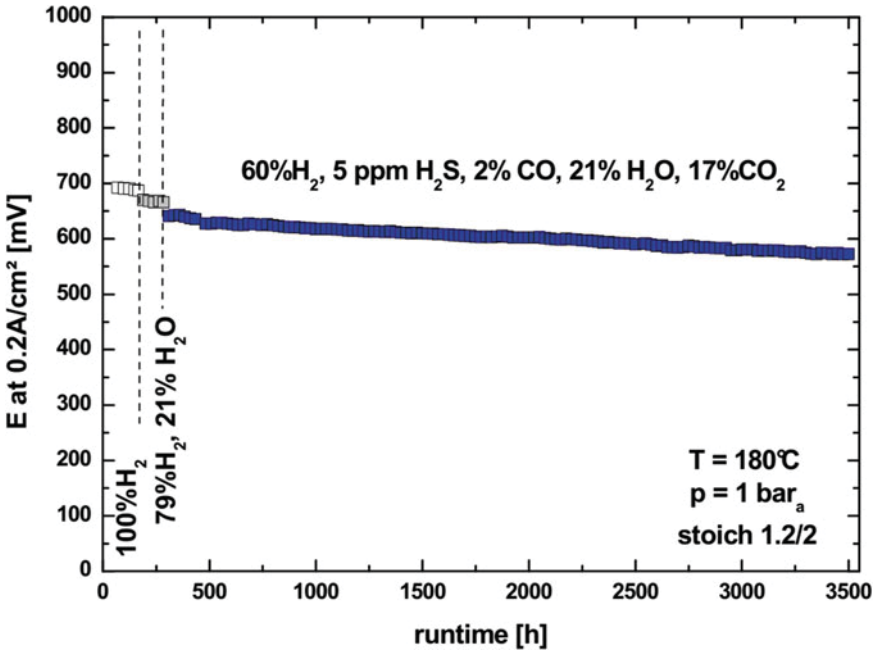


Fig. 10.19 Durability of a Celtec®-P Series 1000 MEA at 180 °C, 1 bara using realistic reformate as denoted. Reproduced from [31] with permission of The Electrochemical Society

gases. The hydrogen dilution effect was the main factor affecting fuel cell performance, and CO poisoning showed smaller effects on fuel cell performance compared to hydrogen dilution at 160 or 180 °C. As the operational temperature of the fuel cell decreased, the sensitivity to the presence of CO dramatically increased. CO poisoning became the dominant factor for fuel cell performance decreases at 140 °C. At 120 °C, the fuel cell voltage quickly dropped to 0 V when the feed gases changed from pure hydrogen to reformate with CO content at 2000 ppm or higher. However, this decrease in fuel cell performance was reversible and the fuel cell performance immediately recovered when the feed gas was changed back to pure hydrogen.

The exceptionally high hydrogen sulfide tolerance of PPA-processed membranes was also demonstrated. Celtec-P 1000 testing at 180 °C using humidified reformate with 2 % CO and 5 ppm H_2S showed an average voltage drop of approximately 17 μV h^{-1} during a 3500 h test, demonstrating high tolerance to sulfur impurities and no additional anode degradation compared to pure reactants at 180 °C [31]. This durability can be seen in Fig. 10.19. Qian et al. [30] reported the nearly full recovery of fuel cell performance after 24 h operation with 25 ppm H_2S in the anode gas at the temperature range of 120–180 °C.

The long-term durability of PPA-processed membranes is an important and commercially relevant issue. The constant current operation at 0.2 A cm^{-2}, 160 °C using dry hydrogen and air is shown in Fig. 10.20 [29]. The performance degradation rate under these conditions was –6 μV h^{-1} over more than a 2-year period. The low fuel cell performance degradation rates were also observed in a cell operated with constant current at 0.4 A cm^{-2}. Aili et al. [32] reported that the long-term durability of conventionally imbibed PBI membranes is highly dependent on the current loads. The fuel cell performance degradation rates were 6 μV h^{-1} and 308 μV h^{-1} at current densities of 0.2 and 0.6 A cm^{-2}, respectively. The PPA-processed PBI membranes demonstrated a much lower performance degradation rate at high current operation, 18 μV h^{-1} at 0.6 A cm^{-2}. Yu et al. [17] reported the

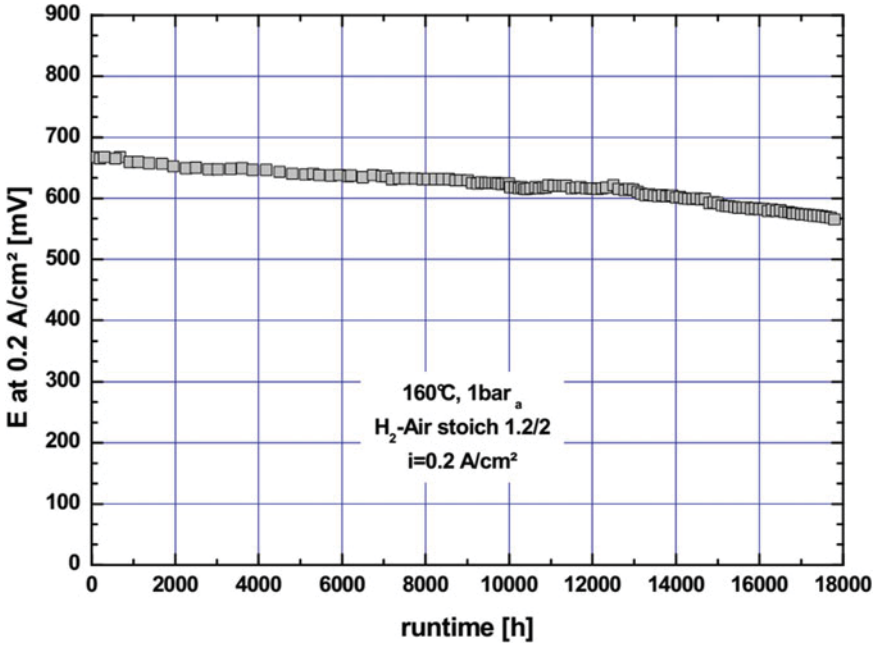


Fig. 10.20 Durability of a Celtec-P-1000 MEA at 160 °C, 1 bara using pure hydrogen and air with stoichiometries of 1.2 and 2, respectively. Reproduced from [31] with permission of The Electrochemical Society

phosphoric acid evaporative loss through the gas exhaust was extremely low. Qian et al. [33] analyzed the phosphoric acid loss from the MEA at the different stages of cell assembly, initial heat-up, and cell operation. The phosphoric acid evaporative loss was not the main pathway of phosphoric acid loss from the MEAs, and a significant amount of phosphoric acid was found in the micropores of the graphite flow plates, which illustrates that the stability of the materials employed as bipolar plates is a key property for long-term operation and durability of PPA-processed membranes in high-temperature PEM fuel cell applications [33, 34].

10.8 Conclusions

The PPA process is a simple, straightforward method for directly preparing high molecular weight polymers and PA-doped PBI membranes with relatively few process steps. There are many advantages of the process that are commercially attractive and early work has shown that the process can be scaled up to reliably produce high-quality membranes. The PPA process also allows for the investigation of different monomers and polymers, which has formed the basis for understanding structure–property relationships. Modeling and simulation studies have provided interesting insights and promise to provide an even more thorough understanding of the process and structure. Many PBI chemistries have shown high performance in operating fuel cells and can be reliably operated for extended periods of time. More detailed studies have shown that the evaporative PA loss from the membranes is typically low, with the data suggesting that extrapolated lifetimes should be many years and other degradation modes may eventually be the limiting factors. Continued development of membranes produced by this process is still being pursued with a focus on addressing the issues of longer term durability and possible failure modes, new devices, and improved manufacturability.

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