

# Polybenzimidazoles Based on 3,3'-Diaminobenzidine and Aliphatic Dicarboxylic Acids: Synthesis and Evaluation of Physicochemical Properties Toward Their Applicability as Proton Exchange and Gas Separation Membrane Material

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**ABSTRACT:** A series of aromatic–aliphatic polybenzimidazoles (PBIs) based on 3,3'-diaminobenzidine (DAB) and aliphatic dicarboxylic acid with incremental  $-\text{CH}_2-$  groups were synthesized. Optimization of synthesis parameters and evaluation of physicochemical properties are requisite for PBI applicability as the proton exchange membrane (PEM) and gas separation membrane materials are reported. It was found that though all these PBIs exhibited high thermal, mechanical, and oxidative stability, effect of added flexibility on physical properties is not monotonous. Membranes were prepared by solution casting as well as phase-inversion method. The later types of

membranes exhibited much higher  $\text{H}_3\text{PO}_4$  content than its doping achieved in the solution casted membranes. These PBIs possess low hydrogen and helium permeability than that of conventional PBI. This low permeability, along with their excellent oxidative stability indicated that they can be promising PEM materials. Their  $\text{CO}_2$ -sorption analysis revealed that PBI<sub>6</sub> based on suberic acid possesses appreciable  $\text{CO}_2$  sorption. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1090–1099, 2011

**Key words:** gas permeation; mechanical properties; membranes; oxidative stability; polybenzimidazoles

## INTRODUCTION

Polybenzimidazole (PBI) is a family of heteroatomic polymers, and the most cited member of this family is derived from 3,3'-diaminobenzidine (DAB) and isophthalic acid (IPA), commonly termed as PBI. Owing to its excellent thermochemical and mechanical stability, it is widely explored as the proton exchange membrane (PEM)<sup>1,2</sup> and gas separation membrane material.<sup>2–5</sup> Its application such as ultrafiltration,<sup>6</sup> nanofiltration,<sup>7</sup> and reverse osmosis<sup>8</sup> membrane is also addressed. Uses of PBI in fiber and fabrics, hydrogen sensor, blends, composites with other polymers for making microcellular foam, as a catalyst support in epoxidation of alkenes, nanofiber by electrospinning, aerospace industry, etc., are known.<sup>2,3</sup>

Acid-doped PBIs are widely being explored as the PEM material due to their several advantages such as

high conductivity, good mechanical properties, excellent chemical and thermal stability in the fuel cell environment, low-gas permeability, nearly zero water drag coefficient, high-CO tolerance, and better heat utilization.<sup>1,2</sup> By now, only fully aromatic PBIs are used as PEM material, though several structural variations have been evaluated.<sup>1,2</sup> In the case of Nafion, it is well accepted that the hydrophobic–hydrophilic domain formation enhances proton conductivity; where hydrophilic domains are responsible for the transfer of protons and hydrophobic domains provide morphological stability.<sup>9</sup> In PBIs based on aliphatic dicarboxylic acids, similar kind of domain formation could be anticipated through a chain of hydrophobic  $-\text{CH}_2-$  groups belonging to the dicarboxylic acid moiety.

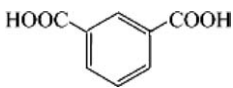
Fully aromatic PBI is known to be highly rigid, possesses poor solvent solubility (thus poor processability) and low gas permeability.<sup>1,2,5,10</sup> These properties could be improved by suitable structural modifications either on monomer level<sup>1–3,11</sup> or on polymer backbone.<sup>1,2,12,13</sup> It could be worth to see the effects of added flexibility through the dicarboxylic acid moiety. PBI derived from some of the aliphatic dicarboxylic acids though are reported<sup>11,14–16</sup>; they were not investigated for physical properties necessary for present developing applications of PBI, especially as PEM and gas separation membrane material. Incorporation of methylene group

Additional Supporting Information may be found in the online version of this article.

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TABLE I  
Details of PBI Synthesis

Polymer abbreviation	Dicarboxylic acid used	Reaction duration		$\eta_{inh}^b$ (dL/g)
		At 170°C	At 200°C	
PBI-I <sup>a</sup>		5 h	12 h	1.4
PBI <sub>2</sub>	HOOC-(CH <sub>2</sub> ) <sub>2</sub> -COOH	4 h	10 h	0.96
PBI <sub>4</sub>	HOOC-(CH <sub>2</sub> ) <sub>4</sub> -COOH	4 h	8 h 30 min	0.99
PBI <sub>5</sub>	HOOC-(CH <sub>2</sub> ) <sub>5</sub> -COOH	1 h 40 min	40 min	2.14
PBI <sub>6</sub>	HOOC-(CH <sub>2</sub> ) <sub>6</sub> -COOH	1 h	1 h 40 min	1.70
PBI <sub>7</sub>	HOOC-(CH <sub>2</sub> ) <sub>7</sub> -COOH	30 min	30 min	2.33
PBI <sub>10</sub>	HOOC-(CH <sub>2</sub> ) <sub>10</sub> -COOH	30 min	20 min	2.49

<sup>a</sup> Ref. 3.

<sup>b</sup> Inherent viscosity using 0.2 g/dL solution in conc. H<sub>2</sub>SO<sub>4</sub> at 35°C.

in PBI via aliphatic dicarboxylic acid is known to decrease chain stiffness while maintaining high-thermal stability<sup>11</sup> as that of solely aromatic PBI. In view of developing applications of PBI as a family of thermochemically and mechanically stable polymers (especially as a membrane material for PEM fuel cell and gas separation), structure-property relationship of PBIs derived from aliphatic dicarboxylic acids needs to be investigated. With this as an objective, this work focuses on synthesis and investigation of requisite characteristics of PBIs derived from DAB and aliphatic dicarboxylic acids. The dicarboxylic acids used possess a linear chain with incremental number of -CH<sub>2</sub>- groups (succinic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and dodecanedioic acid). Synthesis protocol was optimized for individual cases to obtain the polymer with high viscosity. Effects of increasing number of -CH<sub>2</sub>- groups on physicochemical properties (thermal, mechanical, oxidative stability, acid and water uptake, gas permeation, etc.) of formed PBIs are investigated.

## EXPERIMENTAL

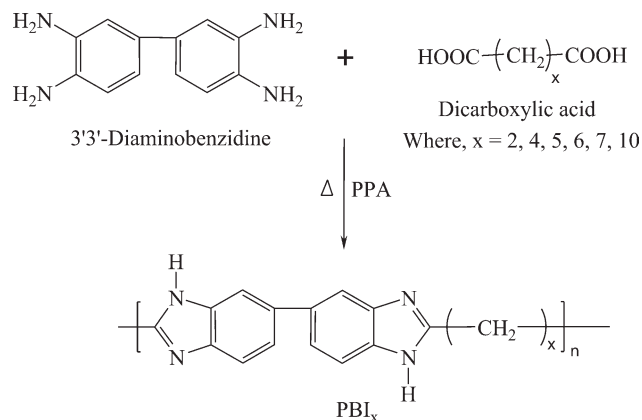
### Materials

DAB, succinic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and dodecanedioic acid were purchased from Aldrich Chemicals. Polyphosphoric acid (PPA) was purchased from Alpha Aesar. Formic acid, conc. H<sub>2</sub>SO<sub>4</sub> (98%), phosphoric acid (88%), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), pyridine, acetic acid, and methanesulfonic acid were purchased from Merck. *N,N*-Dimethylacetamide (DMAc), FeSO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub> (30%) were purchased from Thomos Beaker. All these chemicals and solvents were used without further purification. Pure gases (N<sub>2</sub>, O<sub>2</sub>, He, and H<sub>2</sub>) with a minimum purity of 99.9% were purchased

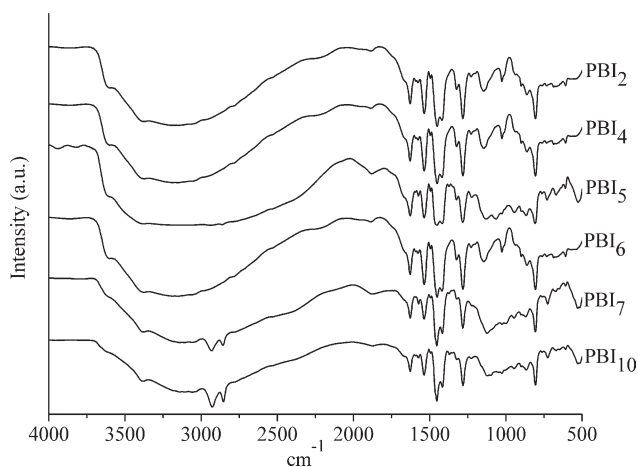
from Inox Air Products; while CO<sub>2</sub> with purity of 99.995% was purchased from Air Liquide.

### Polymer synthesis

PBIs were synthesized by solution polycondensation method using PPA, which acts as both condensation agent as well as polymerization solvent.<sup>1,17</sup> Typically, a three-necked flask equipped with a mechanical stirrer, N<sub>2</sub> inlet, and CaCl<sub>2</sub> drying tube was charged with 300 g of PPA, and the temperature was elevated to 120°C. DAB (10 g, 0.0467 mol) was added, stirred for an hour, and equimolar quantity of the dicarboxylic acid was added. Temperature of the reaction mixture was slowly raised to 170°C and maintained for certain duration as given in Table I, which was dependant on the dicarboxylic acid used. Temperature of the reaction mixture was further raised to 200°C and maintained for certain duration, as given in Table I. After this time, formed viscous solution was poured onto the stirred water. The precipitated polymer was crushed and thoroughly



Scheme 1 Synthesis of PBI based on aliphatic dicarboxylic acid.



**Figure 1** FTIR spectra of polybenzimidazoles.

washed with water, till it was neutral to pH. The polymer was then kept overnight in 10% aqueous  $\text{NaHCO}_3$  to extract the acid left in bulk of the polymer. After removal of aq.  $\text{NaHCO}_3$  by filtration, the polymer was washed with water until the filtrate was neutral to pH. The polymer was further soaked in acetone overnight to extract the water. It was dried in oven at  $60^\circ\text{C}$  for 24 h, followed by vacuum drying at  $100^\circ\text{C}$  for 3 days. Formed PBI was designated as  $\text{PBI}_x$ , where  $x$  denotes the number of  $-\text{CH}_2-$  groups present in the aliphatic dicarboxylic acid used for that PBI synthesis (Scheme 1).

### Methods for physical properties

The solvent solubility was evaluated by stirring 0.1 g of PBI in 10 mL of solvent at ambient for 12 h. In the case of swelling or insolubility, stirring continued for further 12 h at  $80^\circ\text{C}$ , and observations are given in Table I of Supporting Information. The inherent viscosity was determined using Ubbelohde

viscometer with 0.2 g/dL polymer concentration in 98%  $\text{H}_2\text{SO}_4$  at  $35^\circ\text{C}$  (Table I). FTIR spectra of polymers in thin film form ( $\sim 10 \mu\text{m}$ , preparation as given below) were recorded on PerkinElmer-16-PC FTIR spectrophotometer and were as given in Figure 1. The wide-angle X-ray diffraction (WAXD) spectra of polymers in film form were recorded using Rigaku X-ray diffractometer with  $\text{Cu K}\alpha$  radiation in  $2\theta$  range of  $4^\circ$ – $40^\circ$  (as shown in Supporting information Fig. 1). The average  $d$ -spacing ( $d_{\text{sp}}$ ) for the amorphous peak maxima was calculated using Bragg's equation ( $n\lambda = 2d \sin \theta$ , where  $\lambda = 1.5418 \text{ \AA}$ ) as given in Table II. The density ( $\rho$ ) measurement of dry PBI films ( $\sim 120\text{-}\mu\text{m}$  thick) was performed using specific gravity bottle. For this purpose, organic solvent having adequate density and negligible sorption in PBI was selected. The maximum sorption of xylene in PBI films was  $\leq 2 \text{ wt } \%$  for the exposure of 2 h at  $35^\circ\text{C}$ . Because this duration was much higher than that required for the density measurement, xylene was used for the density measurement. Five samples of each PBI were analyzed, and the variation in maximum and minimum density was found to be  $\pm 0.008 \text{ g/cm}^3$ . Thermogravimetric analysis (TGA) was performed on TGA-5000 (TA instruments) under  $\text{N}_2$  atmosphere with a heating rate of  $10^\circ\text{C}/\text{min}$  (Fig. 2). The glass transition temperature ( $T_g$ ) was determined using DSC Q-10 (TA Instruments) under  $\text{N}_2$  atmosphere with a heating rate of  $10^\circ\text{C}/\text{min}$  (Fig. 3). Dynamic mechanical analysis was performed with RSA III (TA Instruments) using film specimens of  $1.4 \times 0.6 \times 0.004\text{-cm}^3$  size at the frequency of 1 Hz under a constant stress in the temperature range of  $-100$  to  $350^\circ\text{C}$ . The heating rate was  $5^\circ\text{C}/\text{min}$ . Variation in  $\tan \delta$  with the temperature is shown in Figure 2 of Supporting information. Tensile tests were performed at the ambient on Linkam TST-350 microtensile testing instrument

**TABLE II**  
Physical Properties of Polybenzimidazoles

Polymer	$d_{\text{sp}}^{\text{a}}$ (Å)	$\rho^{\text{b}}$ (g/cc)	TGA <sup>c</sup>				
			$T_w$	IDT	$T_{900}$	$T_g^{\text{d}}$ ( $^\circ\text{C}$ )	$T_\alpha^{\text{e}}$ ( $^\circ\text{C}$ )
PBI-1 <sup>f</sup>	4.05	1.331	147	600	67.0	416	-
PBI <sub>2</sub>	4.29	1.349	218	435	46.5	310	325
PBI <sub>4</sub>	4.33	1.339	141	461	44.4	296	307
PBI <sub>5</sub>	4.57	1.293	172	461	23.8	279	285
PBI <sub>6</sub>	4.48	1.289	153	459	23.1	266	279
PBI <sub>7</sub>	4.43	1.304	132	455	11.4	263	284
PBI <sub>10</sub>	4.39	1.339	137	485	28.8	282	288

<sup>a</sup>  $d$ -Spacing obtained from wide angle X-ray diffraction spectra.

<sup>b</sup> Density measured at  $35^\circ\text{C}$ .

<sup>c</sup> Thermogravimetric analysis, where  $T_w$  is water loss temperature, IDT is the initial decomposition temperature,  $T_{900}$  is char yield at  $900^\circ\text{C}$ .

<sup>d</sup> Glass transition temperature obtained by DSC.

<sup>e</sup> Glass transition temperature obtained by DMA.

<sup>f</sup> Ref. 3.

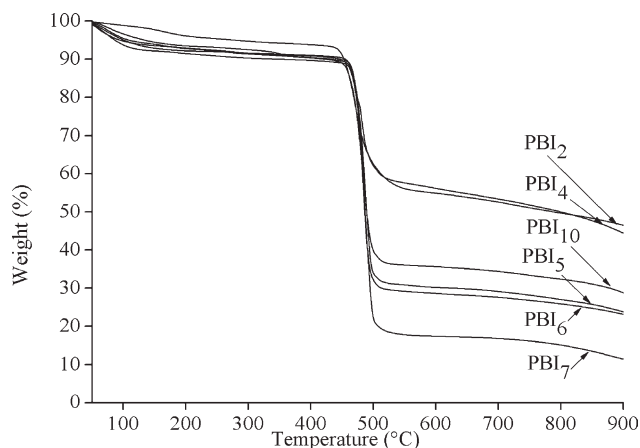


Figure 2 TGA spectra of polybenzimidazoles.

using film samples of  $2 \times 0.6 \times 0.004\text{-cm}^3$  size. Stress-strain curves were obtained with at a speed of  $100 \mu\text{m/s}$ . The mechanical properties are given in Table III, while the representative spectra are given in Supporting information (Fig. 3).

#### Dense membrane preparation by solution casting method and their analyses

These membranes (films) were prepared by solution-casting method using 4% (w/v) PBI solution in formic acid at  $80^\circ\text{C}$  under the flow of  $\text{N}_2$ . Formed film was peeled off, immersed in 5% aqueous  $\text{NaHCO}_3$  solution for 24 h, and then soaked in water at  $60^\circ\text{C}$  for 3 days. Such films were dried in vacuum oven at  $100^\circ\text{C}$  for a week before use for further analyses.

#### Oxidative stability

Fenton test is commonly used to assess stability of the membrane to be used in fuel cell under rigorous oxidative environments.<sup>18</sup> PBI membranes of  $2 \times 1 \times 0.007\text{-cm}^3$  size were dipped in Fenton solution at

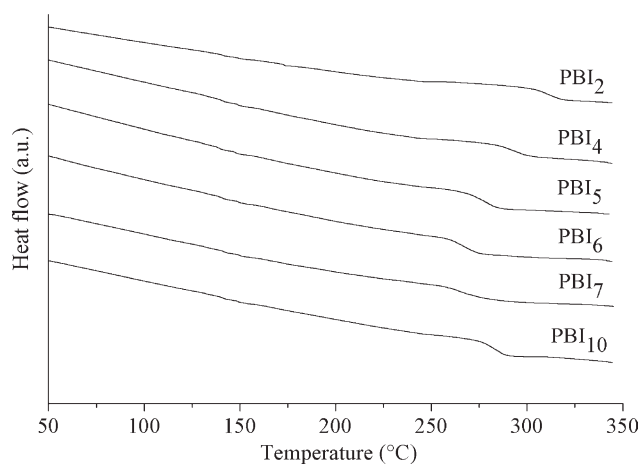


Figure 3 DSC curves of polybenzimidazoles.

TABLE III  
Mechanical Properties of Polybenzimidazoles

Polymer	Tensile strength (MPa)	Modulus (MPa)	% Strain at break
PBI-I	147.7	39.2	36.6
PBI <sub>2</sub>	127.3	30.4	37.2
PBI <sub>4</sub>	102.7	24.4	17.1
PBI <sub>5</sub>	86.0	14.9	21.9
PBI <sub>6</sub>	104.4	22.1	29.9
PBI <sub>7</sub>	79.7	11.8	37.3
PBI <sub>10</sub>	71.7	12.7	19.5

$80^\circ\text{C}$ . Two different concentrations of  $\text{Fe}^{2+}$  (2 or 4 ppm) in 3%  $\text{H}_2\text{O}_2$  solution were used. After 24 and 48 h of dipping, membranes were taken out from the solution, washed thoroughly with water, dried at  $100^\circ\text{C}$ , and weighted. Stability of membranes was evaluated from the weight loss, and the data averaged for three samples is given in Table IV.

#### Water and $\text{H}_3\text{PO}_4$ sorption

Samples of  $2 \times 1 \times 0.0120 \text{ cm}^3$  were used for these analyses gravimetrically at  $35^\circ\text{C}$  as follows.

$$\% \text{ Sorption} = (W_s - W_i) / W_i \times 100 \quad (1)$$

where  $W_s$  is the weight of the membrane after sorption and  $W_i$  the initial weight of the vacuum dried sample. In case of water sorption, samples were dipped in water till constant weight gain (up to 96 h). In case of acid-doping analyses, samples needed to dip in  $\text{H}_3\text{PO}_4$  for 72 h, weighed, and then vacuum dried at  $100^\circ\text{C}$  for a week. Water sorbed along with phosphoric acid was also given as in Table V.

#### Membrane preparation by phase inversion method

The polymerization solution in PPA was cast without isolating the polymer onto a glass substrate in air using a film applicator with a gate thickness of 0.12 mm. It was allowed to cool from polymerization temperature to room temperature in a few minutes.

TABLE IV  
Oxidative Stability of Polybenzimidazoles by Fenton Test

Polymer	Weight loss after 24 h (%)		Weight loss after 48 h (%)	
	2 ppm $\text{Fe}^{+2}$	4 ppm $\text{Fe}^{+2}$	2 ppm $\text{Fe}^{+2}$	4 ppm $\text{Fe}^{+2}$
PBI-I	4.26	9.08	7.00	28.40
PBI <sub>2</sub>	3.13	5.08	5.54	Break
PBI <sub>4</sub>	0.65	0.85	3.06	6.91
PBI <sub>5</sub>	0.68	0.73	0.88	5.10
PBI <sub>6</sub>	0.18	0.29	0.74	0.71
PBI <sub>7</sub>	1.78	4.55	2.78	9.27
PBI <sub>10</sub>	7.58	Break	Break	Break

TABLE V  
Water and H<sub>3</sub>PO<sub>4</sub> Uptake in Polybenzimidazole Membranes

Polymer	Membranes prepared by solution casting method						Membranes prepared by phase inversion method			
	Water uptake		H <sub>3</sub> PO <sub>4</sub> uptake		Water uptake along with H <sub>3</sub> PO <sub>4</sub>		H <sub>3</sub> PO <sub>4</sub> after 6 h		H <sub>3</sub> PO <sub>4</sub> after 21 h	
	wt %	mol/RU	wt %	mol/RU	wt %	mol/RU	wt %	mol/RU	wt %	mol/RU
PBI-I <sup>a</sup>	20.4	3.5	493	15.1	72	12.3	–	–	–	–
PBI <sub>2</sub>	17.8	3.2	89	2.4	39	5.6	775	20.6	692	18.4
PBI <sub>4</sub>	17.1	2.7	108	3.2	28	4.6	940	27.7	704	20.7
PBI <sub>5</sub>	15.8	2.7	116	3.6	26	4.4	861	26.6	646	19.9
PBI <sub>6</sub>	14.2	1.9	116	3.8	6	1.1	882	28.5	696	22.5
PBI <sub>7</sub>	17.5	2.6	111	3.7	20	3.7	1038	35.0	873	29.4
PBI <sub>10</sub>	23.7	4.1	114	4.0	28	5.9	827	31.8	622	23.9

<sup>a</sup> Ref. 3.

Hydrolysis was allowed to proceed under ambient conditions by exposing to the atmosphere (25°C and 52% relative humidity). Extremely, hygroscopic reaction mixture absorbs moisture from the atmosphere and hydrolyzes the PPA to phosphoric acid. Some drain-off of phosphoric acid solution was observed during the hydrolysis process. At the end of 6 and 21 h, membrane samples were removed from the glass surface, water, and phosphoric acid present on the membrane surface was removed and then immersed in 1N NaOH. After 6 days, the concentration of remainder NaOH was determined by titration. The amount of NaOH consumed was correlated with the amount of phosphoric acid present in the membrane, and the data generated for five samples was averaged as given in Table V.

### Gas permeation and CO<sub>2</sub> sorption

Membranes prepared by the solution-casting method were used for these analyses. Pure gas permeability

(He and H<sub>2</sub>) was determined using dense membranes (4.5-cm diameter and ~ 35 ± 5-μm thickness) by the variable volume method as used earlier<sup>3,5,12</sup> at 35°C and upstream pressure of 20 atm. Gas permeability was calculated using following equation.

$$P = N l / (p_1 - p_2) \quad (2)$$

where  $P$  is the permeability coefficient expressed in Barrer,  $p_1$  and  $p_2$  are the feed and permeate side pressure (cm Hg),  $l$  is the membrane thickness (cm), and  $N$  is the steady-state penetrant flux (cm<sup>3</sup> cm<sup>-2</sup> s<sup>-1</sup>). The permeability measurements were repeated for three samples prepared under identical conditions, and the data averaged as given in Table VI. Variation in the permeability measurement was up to 11% for both the gases.

The CO<sub>2</sub> sorption analysis was carried out at varying pressures (up to 20 atm) at 35°C. The gas-solubility apparatus consisted of dual-volume, single-transducer setup based on the pressure-decay

TABLE VI  
Gas permeability ( $P$ )<sup>a</sup>, Selectivity ( $\alpha$ )<sup>b</sup>, and CO<sub>2</sub> Sorption Parameters

Polymer	P(He)	P(H <sub>2</sub> )	$\alpha$ (He/H <sub>2</sub> )	Dual-mode sorption parameters <sup>c</sup>			Solubility coefficient <sup>d</sup>
				$k_D$	$C'_H$	$b$	
PBI <sub>2</sub>	0.13	0.04	3.25	$1.8 \times 10^{-8}$	21.7	0.25	0.90
PBI <sub>4</sub>	0.14	0.06	2.33	0.19	20.2	0.11	0.88
PBI <sub>5</sub>	0.24	0.09	2.66	$6.9 \times 10^{-7}$	16.5	0.19	0.79
PBI <sub>6</sub>	0.35	0.12	2.92	0.17	32.4	0.12	1.32
PBI <sub>7</sub>	0.44	0.25	1.76	$3.6 \times 10^{-6}$	14.9	0.33	0.64
PBI <sub>10</sub>	1.98	0.63	3.14	$5.4 \times 10^{-7}$	14.7	0.25	0.61

<sup>a</sup> Expressed in Barrer (1 Barrer = 10<sup>-10</sup> cm<sup>3</sup> (STP)·cm Hg<sup>-1</sup> cm<sup>-1</sup> s<sup>-1</sup>).

<sup>b</sup> Ratio of pure gas permeability.

<sup>c</sup>  $k_D$  is expressed in cm<sup>3</sup> (STP)·cm<sup>-3</sup> polymer atm<sup>-1</sup>,  $C'_H$  is expressed in cm<sup>3</sup> (STP) cm<sup>-3</sup> polymer, while  $b$  is expressed in atm<sup>-1</sup>.

<sup>d</sup> Solubility coefficient of CO<sub>2</sub> gas at 20 atm expressed in cm<sup>3</sup>(STP)·cm<sup>-3</sup> polymer·atm<sup>-1</sup>.

method,<sup>19</sup> having estimated uncertainty up to 1.7%. The gas sorption in glassy polymers is often described by the dual-mode model<sup>19</sup> as below.

$$S = C/p = k_D + C'_H b / (1 + bp) \quad (3)$$

where  $S$  is the solubility coefficient,  $C$  is the gas concentration in polymer,  $p$  the applied gas pressure,  $k_D$  the Henry's solubility coefficient,  $C'_H$  the Langmuir saturation constant, and  $b$  is the Langmuir affinity constant. These constants were obtained by the nonlinear regression analysis of experimentally determined gas sorption by genetic algorithm, an optimization technique capable of searching global optima.<sup>5</sup>

## RESULTS AND DISCUSSION

### Polymer synthesis

The ratio of DAB:PPA as 1 : 30 and sequential rise in temperature after the addition of the dicarboxylic acid (170°C and then 200°C) was based on our previous investigations of PBI synthesis using aromatic dicarboxylic acid.<sup>3</sup> During this work, the reaction duration at 170°C was 5 h, while the duration at 200°C needed to be varied; depending upon the reactivity of aromatic dicarboxylic acid used. In present cases of aliphatic dicarboxylic acids, even the duration at 170°C needed to be varied on case-to-case basis (Table I). In cases of succinic and adipic acid (PBI<sub>2</sub> and PBI<sub>4</sub>), this duration was 4 h. In other cases with further increase in number of  $-\text{CH}_2-$  groups, a rapid rise in the viscosity of reaction mixture at 170°C led this duration to be reduced till 30 min. After this stage, the reaction temperature was raised to 200°C. Again, in case of succinic and adipic acid, the reaction duration at this temperature was 12 and 10 h, respectively, which needed to be reduced till 20 min with an increase in number  $-\text{CH}_2-$  groups of the dicarboxylic acid used. This observation with general increase in viscosity (Table I) indicated that the reactivity of dicarboxylic acid increased with its number of  $-\text{CH}_2-$  groups. Tsur et al.<sup>11</sup> and Ueda et al.<sup>16</sup> also noted the similar observation on general lowering of reaction time and increase in viscosity of PBI as the number of  $-\text{CH}_2-$  group increased in the dicarboxylic acid used. In all the present cases, reaction duration at both the temperatures was smaller than that required for the synthesis of PBI based on IPA (largely used as PEM material).<sup>3</sup> Two reaction parameters, viz., duration and concentration of monomers, are known to be crucial for PBI synthesis in terms of physical properties of obtained polymer.<sup>3,20</sup>

### Analysis of physical properties

#### Solvent solubility

All PBIs were soluble in conc.  $\text{H}_2\text{SO}_4$  at ambient temperature. PBI<sub>2</sub>, PBI<sub>4</sub>, PBI<sub>5</sub>, and PBI<sub>6</sub> were soluble

in formic acid and methane sulfonic acid at the ambient, whereas PBI<sub>7</sub> and PBI<sub>10</sub> could be dissolved in these solvents only after heating at 80°C for 12 h (Supporting Information Table I). Although all these PBIs were insoluble in solvents like DMF, DMSO, DMAc, and NMP, PBI possessing lower number of methylene groups in their dicarboxylic acid moiety showed swelling.

#### IR spectra

FTIR spectra of these polymers are given in Figure 1. The benzimidazole ring was characterized by the absorption at 1430, 1600, and 1620  $\text{cm}^{-1}$ . These peaks were common in all PBIs investigated. The region 1650–1500  $\text{cm}^{-1}$  is the characteristic of benzimidazoles.<sup>21</sup> These bands are derived from C=C and C=N stretching as well as ring modes, which are characteristic of conjugation between benzene and the imidazole rings. The prominent peaks at 2930–2850  $\text{cm}^{-1}$  in the IR spectrum of PBI<sub>7</sub> and PBI<sub>10</sub> could be ascribed to C–H vibrations in methylene groups of the acid moiety. Iwakura et al.<sup>14</sup> also observed similar two bands at 2950–2850  $\text{cm}^{-1}$  due to stretching of methylene groups. The broad band at  $\sim 3140 \text{ cm}^{-1}$  could be ascribed to the hydrogen bonding of the type  $N\text{--}H\text{--}N$ , while the peak at  $\sim 3400 \text{ cm}^{-1}$  was due to the free nonhydrogen-bonded  $N\text{--}H$  stretching.<sup>3</sup> For all PBIs, the peak at 3610–3590  $\text{cm}^{-1}$  could be attributed to the O–H stretching of absorbed water. Appearance of such peak due to moisture absorbed during sample handling is known and could be removed by heating at 120°C<sup>22</sup> or at 150°C during the scanning.<sup>12</sup>

#### Chain packing

WAXD analysis indicated that all these PBI are amorphous in nature (Supporting Information Fig. 1). The  $d$ -spacing ( $d_{\text{sp}}$ ) corresponding to the amorphous peak maxima is given in Table II, which varied in a narrow range (4.29–4.57 Å). It is known that the presence of H-bonding in PBI brings chains closer, resulting in efficient chain packing.<sup>2,3</sup> Although the incorporation of aliphatic groups in acid moiety of PBI enhances  $d_{\text{sp}}$  than that of fully aromatic PBI-I (4.05 Å), it is still lower than the common polymers like polysulfone (5.0 Å)<sup>23</sup> and polycarbonate (5.2 Å).<sup>24</sup> The tighter chain packing in present PBIs is further supported by their higher density (Table II), which is closer to the density of common PBI-I (which is reported to be 1.33–1.34 g/cc).<sup>2,3</sup> Although both  $d_{\text{sp}}$  and density (parameters to express chain packing in the polymer matrix) varied in the narrow range, an interesting observation was that as the number of  $-\text{CH}_2-$  groups in acid moiety of PBI increased from PBI<sub>2</sub> to PBI<sub>5</sub>,  $d_{\text{sp}}$  increased,

which again starts falling down as the number of  $-\text{CH}_2-$  groups increased further up to PBI<sub>10</sub>. Almost similar effect was reflected by the variation in the density values (which is in reverse order, i.e., highest density for PBI<sub>2</sub> and PBI<sub>10</sub>, while lowest for middle PBI<sub>5</sub> and PBI<sub>6</sub>). This indicates that the chain packing do not follow the monotonous order of increasing number of  $-\text{CH}_2-$  groups (in acid moiety of PBI), and comparatively more open structure is offered by middle member, PBI<sub>5</sub>, and PBI<sub>6</sub>. Smaller number of  $-\text{CH}_2-$  groups in acid moiety (two or four) may not be effective enough to push chains apart, and the packing is predominantly governed by H-bonding originated from imidazole rings. On the other hand, larger number of  $-\text{CH}_2-$  groups could be able to align themselves effectively to result in a better packing, for which the driving force is again strong H-bonding.

### Thermal analysis

Thermogravimetric analysis shows initial loss till  $\sim 218^\circ\text{C}$  (Fig. 2), attributable to the absorbed water.<sup>3,25</sup> Both IDT and char yield at  $900^\circ\text{C}$  of present polymers were lower than that of common PBI-I based on IPA due to inclusion of flexible  $-\text{CH}_2-$  groups in their acid moiety (Table II). These PBIs exhibited degradation temperature of  $\geq 440^\circ\text{C}$ . This temperature though is lower than that for solely aromatic PBI-I, it is high enough toward their applicability as a fuel cell membrane, which are demonstrated up to  $200^\circ\text{C}$  under ambient pressure.<sup>1,2</sup> Within the series, though IDT varied in a small range, it is little affected by the addition of  $-\text{CH}_2-$  groups in the acid moiety. These results are in accordance with the previous findings of Tsur et al.,<sup>11</sup> who reported marginal variation in IDT from  $460$  to  $480^\circ\text{C}$  by the variation of  $-\text{CH}_2-$  groups in the acid moiety of PBI from two to eight. Frunze et al.<sup>15</sup> has reported that an introduction of the methylene groups in PBI causes practically no lowering of their heat resistance. Kakimoto et al.<sup>26</sup> reported a series of polyamides (which possess H-bonding as like in PBI) with varying number of  $-\text{CH}_2-$  groups in the acid moiety from 4 to 10. Although the degradation temperature was high and varied in a small range ( $380$ – $425^\circ\text{C}$ ), a systematic increase in the degradation temperature was observed. Above findings reveal that in PBI possessing H-bonding, incorporation of flexible  $-\text{CH}_2-$  groups though lead to a small decrease in IDT, it is not necessarily governed by the number of  $-\text{CH}_2-$  groups. This behavior of strong influence of H-bonding in PBI and lower influence of variation in the number of  $-\text{CH}_2-$  groups on IDT of resulting PBI can be taken into advantage to design new polymers with improved properties without seriously affecting their thermal stability.

DSC curves (Fig. 3) showed well-defined glass transition temperature ( $T_g$ ) ranging from  $310$  to  $266^\circ\text{C}$ , as given in Table II. A general lowering in  $T_g$  with increasing number of  $-\text{CH}_2-$  groups in the acid moiety of PBI backbone (with an exception of PBI<sub>10</sub>) was observed. Similar general lowering in  $T_g$  was reported by Tsur et al.<sup>11</sup> for PBI<sub>2</sub>, PBI<sub>4</sub>, and PBI<sub>6</sub> as  $290$ ,  $240$ , and  $235^\circ\text{C}$ , respectively. These values are slightly lower than that of present cases, which could be due to the difference in viscosity (and thus molecular weight). The reduction in  $T_g$  from solely aromatic case (PBI-I,  $416^\circ\text{C}$ ) to the present PBIs with inclusion of aliphatic groups via acid moiety was considerable. Similar observations could be found in the literature report on polyamides. Kakimoto et al.<sup>26</sup> reported considerably higher  $T_g$  for fully aromatic polyamide derived from *m*-phenylene diamine (*m*-PDA) and either iso- or terphthalic acid ( $320$  and  $340^\circ\text{C}$ , respectively); which was reduced to  $127^\circ\text{C}$ – $97^\circ\text{C}$  in polyamides based on *m*-PDA and aliphatic dicarboxylic acids containing 4 to 10  $-\text{CH}_2-$  groups. The lowering in  $T_g$  from fully aromatic to aromatic-aliphatic cases was considerably larger in these polyamides than that of present PBI cases. This could be due to the stronger H-bonding in PBI cases. As could be seen from Table II, for a particular PBI case, the  $T_g$  obtained by DSC is slightly lower than its  $T_g$  determined by DMA (designated as  $T_\alpha$ ). This is in accordance with the observation found in case of other family of polymers, such as polyarylates<sup>27</sup> and PBI.<sup>28</sup> Usually, such difference is attributable to the method of analysis.<sup>28</sup> Within the present series of PBI, variation in  $T_\alpha$  caused by the variation in number of methylene groups is in good agreement with the similar variation seen in  $T_g$  by DSC.

### Mechanical properties

The tensile properties of present PBIs are summarized in Table III, whereas representative stress-strain curve are shown in Figure 3 of Supporting Information. It could be seen that the tensile strength and modulus show a general decrease with increase in the number of  $-\text{CH}_2-$  groups in PBI. The mechanical strength of fully aromatic PBI-I based on DAB and IPA was also evaluated. Its tensile strength is  $147.7$  MPa, and modulus is  $39.2$  MPa. The tensile strength for this polymer is reported to be  $60$ – $70$  MPa for the dry sample,<sup>2</sup> whereas Lobato et al. reported it to be  $60$ – $120$  MPa, depending on the molecular weight of PBI.<sup>29</sup> In the present series, PBI<sub>2</sub> exhibited higher tensile strength ( $127.3$  MPa) and modulus ( $30.4$  MPa), which are slightly lower than the respective properties of PBI-I evaluated. The tensile strength and Young's modulus decreased, while elongation increased with increasing number of methylene groups in PBI. This could be ascribed to

the increased flexibility in PBI backbone, as also supported by a general decrease in  $T_g$  with increasing number of  $-\text{CH}_2-$  groups. Similar results of decrease in tensile strength and Young's modulus, while increase in elongation by an increase in number of methylene groups in polyesters, were reported by Nagata et al.<sup>30</sup> The high-Young's modulus for all the present PBIs would be attributable to the strong H-bonding present in these polymers.

### Evaluation towards PBI applicability as PEM material

For applicability of present PBIs as a PEM material, investigations on some crucial properties such as oxidative stability, acid ( $\text{H}_3\text{PO}_4$ ), and water uptake and barrier properties (transport of  $\text{H}_2$  and  $\text{O}_2$ ) are necessary. Following section deals with these investigations.

#### Oxidative stability

During the operation of fuel cells, hydroxyl ( $\bullet\text{OH}$ ) and hydroperoxy ( $\bullet\text{OOH}$ ) radicals are generated, leading to degradation of membrane.<sup>18</sup> It was also opined that Fenton test is still the most useful method to evaluate the chemical oxidation degradation of PEM. This method rely on observing changes in the membrane by using a solution in which the  $\bullet\text{OH}$  and  $\bullet\text{OOH}$  radicals are produced by the decomposition of  $\text{H}_2\text{O}_2$  catalyzed by  $\text{Fe}^{2+}$ . Oxidative stability of present PBIs was evaluated after exposing membrane samples to Fenton reagent (3%  $\text{H}_2\text{O}_2$  and 2 or 4 ppm  $\text{Fe}^{2+}$ ) for 24 and 48 h. The results are summarized in Table IV. Except for PBI-I, weight loss for all the PBIs is lower than 10% after 24 and 48 h and for both the concentrations of  $\text{Fe}^{2+}$ . PBI-I was also evaluated, because it has been well investigated toward its stability to Fenton's reagent. Nearly, 10% weight loss of PBI-I with Fenton's reagent was reported.<sup>29,31</sup> Present series of aromatic-aliphatic PBIs showed better oxidative stability than PBI-I, as could be seen from Table IV. Within the series, PBI<sub>2</sub> and PBI<sub>10</sub> (extreme end cases) showed lesser stability than the other cases. PBI<sub>6</sub> exhibited excellent oxidative stability than any other PBI investigated. The films of PBI<sub>4</sub>, PBI<sub>5</sub>, PBI<sub>6</sub>, and PBI<sub>7</sub> were strong and remained tough even after treatment for 48 h and 4 ppm of  $\text{Fe}^{2+}$ . These findings suggest that incorporation of  $-\text{CH}_2-$  groups (aliphatic nature) via acid moiety in PBI could be acceptable toward their applicability as PEM materials, provided other properties such as acid-doping level are appropriate.

#### Water and acid sorption

For these evaluations, initially, membranes were prepared by solution-casting method using formic acid

solution of these PBIs, as given in the Experimental section. The  $\text{NaHCO}_3$  treatment was adopted to extract the formic acid remaining after the solvent evaporation. This was followed by the water treatment at 60°C for 3 days to ensure the removal of the formed salt (sodium formate), if at all remaining in the membrane matrix. These precautions were taken to ensure that the use of formic acid as the casting solvent should not interfere with the  $\text{H}_3\text{PO}_4$  doping in the later stage. Table V shows that the water as well as  $\text{H}_3\text{PO}_4$  uptake levels in all present PBIs is lesser than that of PBI-I. This could be due to the presence of  $-\text{CH}_2-$  groups, responsible for hydrophobicity. Because of this observed smaller doping capacity, it was decided to make membranes by the phase-inversion method. The PBI-I membranes made by phase-inversion method are known to exhibit high- $\text{H}_3\text{PO}_4$  content of the order of 20–40 mol/repeat unit than that of membrane prepared by the solution-casting method.<sup>1,17,32</sup> By adopting phase-inversion method in present cases, use of formic acid as the solvent and the tedious posttreatment could be avoided. As could be seen from Table V, membranes casted from polymerization solution offered much higher doping level than the membranes prepared by solution-casting method. Exposure of membranes for 6 h to the ambient offered 20–35 mol/RU of  $\text{H}_3\text{PO}_4$  in their matrix, which lowered down to some extent as the time of exposure increased to 21 h. The  $\text{H}_3\text{PO}_4$  content at this stage was  $\sim$  18–24 mol/RU for various PBIs. These values are several times higher than that of membrane prepared by solution-casting method and are comparable with the literature data.<sup>17,32</sup> Thus, these values could be sufficient enough for investigations toward their applicability as the PEM. Although, other aspects, such as membrane thickness and mechanical integrity under operating conditions, require further investigations and need membrane preparation protocol to be further optimized.

#### Gas permeation and $\text{CO}_2$ sorption analysis

In a PEM fuel cell, fuel crossover from either electrode side to the other results in "chemical short circuiting," and to minimize this, the membrane should have sufficient barrier properties for gases used, especially toward  $\text{H}_2$  and  $\text{O}_2$ .<sup>2,33</sup> In the present cases, the permeability of  $\text{O}_2$  and  $\text{CO}_2$  in all PBIs was very low (less than 0.01 Barrer) and could not be measured accurately using the present set up based on variable volume method (which could have been useful to judge the selectivity performance of other gases, especially  $\text{CO}_2/\text{H}_2$  in these PBIs). Thus, the permeability of  $\text{H}_2$  and He was evaluated to have primary assessment of permeation properties of these PBIs. The permeability values of both the gases



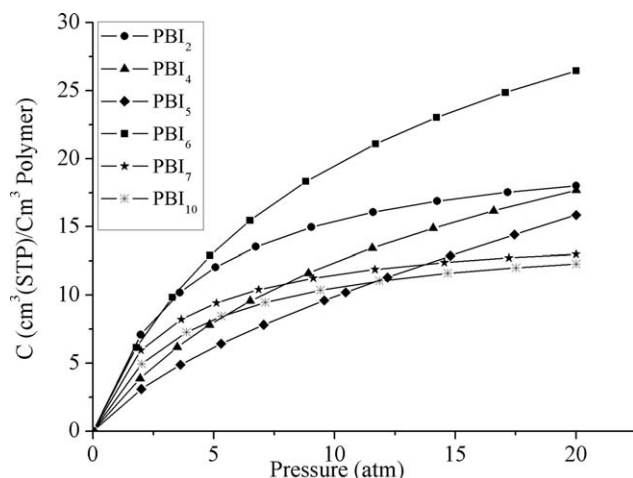


Figure 4 Sorption isotherm of polybenzimidazoles.

in all PBIs are given in Table VI. These values are much lower than those for common glassy polymers like polysulfone<sup>23</sup> and polycarbonate.<sup>24</sup> With an exception of PBI<sub>10</sub>, both gas permeability values are lower or comparable than that of PBI-I, which is reported to be 1.05 Barrer for He and 0.09–3.9 Barrer for H<sub>2</sub>.<sup>5,10</sup> The overall low O<sub>2</sub> and H<sub>2</sub> permeability indicates that these materials could be used as PEM materials. As the number of  $-\text{CH}_2-$  groups in PBI backbone increased, gas permeability also found to be increased. This behavior could be correlated to the added flexibility with the number of  $-\text{CH}_2-$  groups in the chain backbone. Because this elevation in permeability is not prominent enough, it could be inferred that the H-bonding is more influential in controlling permeability of these PBIs than the added flexibility. Interestingly, He/H<sub>2</sub> selectivity for some of these PBIs (especially PBI<sub>2</sub> and PBI<sub>10</sub>) is considerably higher (3.25 and 3.14) than that of usual glassy polymers reported for gas permeability, such as polyarylates and polysulfone (He/H<sub>2</sub>  $\approx$  1–1.2).<sup>23,34</sup> The only polymer known to have high-He/H<sub>2</sub> selectivity is Nafion under extremely dry conditions, which is reported to be 5.8<sup>33</sup> and 4.4 Barrer.<sup>35</sup> This unusual high selectivity for glassy PBIs could be useful in the separation of these two gases.

Although the permeability of present polymers was low, it was thought to investigate CO<sub>2</sub> sorption in these PBIs, because amine functionality is known to act as a fixed carrier for CO<sub>2</sub>, which leads to higher CO<sub>2</sub> permeation rate and comparatively higher selectivities.<sup>36</sup> Recently, we also observed that N-substitution of PBI by appropriate group leads to significant enhancement in the gas permeability.<sup>12</sup> CO<sub>2</sub> sorption isotherms in present PBIs at 35°C are given in Figure 4. The typical dual-mode nature attributable to the glassy nature of these polymers was noted. The sorption parameters are given in Table VI, where  $k_D$ , the Henry's solubility coefficient (representing gas–polymer interactions in

rubbery mode), was found to be low, owing to the high-glass transition temperature of these polymers. The  $C'_H$ , the Langmuir saturation constant (representing sorption in microvoids in glassy state), is also lower than that for common glassy polymers due to close chain packing of these polymers as explained earlier, where presence of microvoids is anticipated to be lower. In a whole series, PBI<sub>6</sub> exhibited the highest  $C'_H$  (which could be correlated to its lowest density in the series) and highest solubility parameter at 20 atm applied pressure. This indicated that this polymer could be a good candidate for gas permeability investigations after systematic structural modifications.

## CONCLUSIONS

PBI based on DAB and aliphatic dicarboxylic acid could be synthesized within much shorter duration than that of solely aromatic PBI-I based on IPA (PBI-I). This duration decreased with increasing number of  $-\text{CH}_2-$  groups in dicarboxylic acid used. All PBIs exhibited good solution viscosity, appreciable thermal properties, were amorphous in nature, and were soluble in acidic solvents. Stress–strain curve showed that these PBIs exhibited comparable mechanical strength as that of fully aromatic PBI-I (derived from IPA and commonly used as PEM material). PBI<sub>4</sub>, PBI<sub>5</sub>, PBI<sub>6</sub>, and PBI<sub>7</sub> showed better oxidative stability with Fenton's reagent than that of PBI-I, and most of them remained tough after the test. Membranes prepared by phase-inversion method showed H<sub>3</sub>PO<sub>4</sub> content of 20–32 mol/RU for 6 h and 18–24 mol/RU for 21 h exposure to the atmosphere. These values were much higher than for the membranes prepared by solution-casting method. This series of PBI possesses lower gas permeability than that of PBI-I. Above investigations on requisite physicochemical properties indicated that some of these PBI could be used as PEM materials for fuel cell. The He/H<sub>2</sub> selectivity for some of the PBIs investigated was unusually higher than that of common glassy polymers used for gas separation. PBI<sub>6</sub> possesses appreciable CO<sub>2</sub> sorption. These investigations suggest that middle members of this series, especially PBI<sub>6</sub>, could be useful in the area of gas separation, possibly after appropriate modifications to improve permeability. All above results offer primary promises of applying these aromatic–aliphatic PBIs as PEM and gas separation membrane material.

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