

Nitrophenoxy Groups Containing Polybenzimidazoles as Polymer Electrolytes for Fuel Cells: Synthesis and Characterization

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ABSTRACT: Polybenzimidazoles containing different contents of pendant nitrophenoxy groups were prepared by condensation of 3,3'-diamino-benzidine with a mixture of 3,5-dicarboxyl-4'-nitro diphenyl ether and isophthalic acid (IPA) in different ratios in polyphosphoric acid. The polymers are soluble in polar aprotic solvents, they have inherent viscosities in the range of 0.75–1.10 dL g⁻¹ and they form tough and transparent films on solution casting. They have good thermal stability with initial decomposition temperature ranging from 380 to 416°C in nitrogen, good tensile strength ranging from 56 to 65 MPa and reasonably good oxidative stability. Phosphoric acid uptake of these polymers is low compared

with PBI and membranes doped with phosphoric acid exhibit good proton conductivity in the range of 6.6×10^{-3} to 1.9×10^{-2} S/cm at 25°C and 1.2×10^{-2} to 4.9×10^{-2} S/cm at 175°C, compared with 3.9×10^{-3} S/cm at 25°C and 3.2×10^{-2} S/cm at 175°C for PBI. These membranes are suitable for applications as polymer electrolyte for fuel cell and presumably for gas separation at high temperature. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3282–3292, 2010

Key words: pendant nitrophenoxy group; polybenzimidazoles; synthesis; characterization; proton conductivity; membranes

INTRODUCTION

Aromatic polybenzimidazoles (PBIs) are heterocyclic high-performance polymers having high glass transition temperature, high thermal stability, good flame resistance, excellent chemical resistance, and high mechanical properties¹ offering an attractive combination of chemical, physical, mechanical, and electrochemical properties for various applications. Commercial PBI is a condensation product of IPA and 3,3'-diaminobenzidine, a rigid infusible polymer having poor solvent solubility which comes in the way of development of new applications. Persistent efforts are being made to improve tractability or to modify the properties of PBI by introducing flexibilizing groups or other bulky units in main chain or side chain to suit desired application.

Thus, PBI containing ether group,² azo groups,³ amide groups,⁴ fluorine groups,⁵ pyridine and imidazole groups,⁶ cardo (fluorene) groups,⁷ sulfone linkages,⁸ thioxanthone groups,⁹ aliphatic groups,^{10,11} alicyclic structures,¹² dibenzothiophene and dioxodibenzothiophene units,¹³ adamantane units,¹⁴ benzofurobenzofuran structures,¹⁵ and phenoxaphosphine¹⁶

have been reported. PBIs, containing functional groups such as sulfonic acid, cyano, hydroxy, and nitro groups have also been reported in literature. Sulfonated PBI have been synthesized by condensing sulfonated diacids with 3,3'-diaminobenzidine.^{17–19} Replacing hydrogen from NH group of imidazole ring with a substituent to produce substituted PBI is another route to modify PBI. Thus, PBI containing *N*-phenyl group²⁰ to enhance thermal and oxidative stability, aromatic nitro and cyano groups,²¹ hydroxyl group²² to impart hydrophilicity, *N*-substituted alkyl acid and ester groups²³ for ultrafilters and cation exchange resins and sulfonic acid groups^{24,25} for polymer electrolyte for fuel cells have been documented. PBI containing aromatic nitro group has been studied for nonlinear optical properties.²⁶ Cho et al.²⁷ describe the synthesis of PBI containing nitro groups in which preformed PBI polymer is nitrated with nitric acid to enhance the solvent solubility and miscibility of blends with polyimides. Thus, nitro group plays significant role to modify the properties of PBI. However, a systematic study on the effect of nitro group on the properties of PBI has not been reported. The reported synthetic routes to nitro group containing PBIs are either by nitration or by substitution of N–H groups of preformed high-molecular weight PBI with suitable nitro group containing

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compounds. These polymers are not well-defined polymers as the extent of substitution is difficult to control on a preformed polymer. Thus, synthesis of well-defined PBI using monomer containing nitro group has not been reported.

Presently, PBI is considered to be the promising membrane material of future for high temperature application as polymer electrolyte for proton exchange membrane fuel cells (PEMFCs) and methanol fuel cells (DMFC). However, low solvent solubility and low proton conductivity compared with Nafion, amongst others, are the drawbacks of PBI. To circumvent these shortcomings of commercial PBI, consistent efforts are being made to develop modified PBI with enhanced proton conductivity and high solvent solubility. Incorporation of bulky moiety containing functional groups in side chain capable of interacting with free phosphoric acid may help to enhance solvent solubility due to increased free volume. These polymers may also have enhanced proton conductivity due to increased phosphoric acid uptake. Nitro group is known to enhance solvent solubility of PBI and it is capable of interacting with phosphoric acid via hydrogen bonding. Thus, PBI containing bulky group having nitro group is expected to be a good membrane material for PEMFC. However, well-defined PBI containing pendant nitro group has not been explored for the application as polymer electrolyte for fuel cells.

The present work describes the synthesis and characterization of an aromatic diacid containing a nitro group, namely, 3,5-dicarboxyl, 4'-nitro diphenylether, synthesis of novel PBIs containing pendant nitrophenoxy groups in side chain, their characterization and application as high-temperature proton exchange membranes for fuel cell. These polymers, presumably, may find applications as membrane materials for separation technology also.

EXPERIMENTAL

Materials

3,3'-diamino-benzidine (DAB), isophthalic acid (IPA), 3,5-dimethyl phenol, and 1-chloro-4-nitro benzene were purchased from Aldrich chemicals. IPA was purified by recrystallization from methanol. DAB was recrystallized from water. 3,5-Dicarboxyl-4'-nitro diphenyl ether (NEDA) was synthesized and purified by the procedure described in our earlier reported work.²⁸ *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethyl formamide (DMF) were distilled over calcium hydride. Methanol, ortho phosphoric acid (85%), phosphorus pentoxide and potassium permanganate were purchased from s. d. fine-chem (India), and used without further purification. Polyphosphoric acid (PPA) was prepared by

heating 1 : 1.8 weight ratio of ortho phosphoric acid (85%) and phosphorus pentoxide for 6 h at 100 °C.

Measurements

Elemental analysis was performed on Elementar vario-EL. The IR spectra were recorded on a Perkin Elmer 16 PC FT-IR spectrophotometer. The ¹H-NMR spectra were recorded on Bruker AC-400. The thermo gravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 in N₂ atmosphere at a heating rate of 10 °C min⁻¹. Glass transition temperature (*T*_g) was measured using differential scanning calorimetry (DSC) Q-10 (TA). Solvent solubility was determined by dissolving 4 mg of polymer in 0.5 mL solvent. Inherent viscosity of polymers was determined at 0.5 g/dL concentration at 30 °C in DMAc using an Ubbelohde viscometer. Films were prepared by casting the 2.5 wt % homogeneous solution of the polymer in DMAc on a glass plate and evaporating solvent in a leveled oven at 80 °C for 15 h. Residual solvent (DMAc) in the films was removed by immersing films in boiling water for 6 h and drying the films at 125 °C for 24 h in a vacuum oven. Tensile properties of polymer films were determined on Instron tensile tester series IX using film strip of size 1.5 × 7 cm² at shear rate of 5 mm/min.

Oxidative stability was evaluated by the Fenton test. Three weighed pieces of membranes of 2 cm × 2 cm were immersed in 3% H₂O₂ containing 4 ppm of Fe²⁺ (Mohr's salt, (NH₄)₂Fe(SO₄)₂·6H₂O) at 70 °C. The samples were withdrawn from the solution after 24 h or desired time period, washed thoroughly with distilled water, dried at 120 °C for 6 h and weighed. The Fenton's solution was replaced by freshly prepared solution after every 24 h. Stability was evaluated in terms of weight losses after Fenton test.

To determine the H₃PO₄ uptake, the weighed samples of membranes were immersed in the different molar concentrations of H₃PO₄ for various time intervals at room temperature. For determining the acid uptake by membranes, the membranes after doping for desired time were withdrawn from acid; the adhered phosphoric acid was wiped out by tissue paper and dried at 100 °C under vacuum until an unchanged weight was obtained. The acid uptake in wt % was determined by using the equation,

$$\text{H}_3\text{PO}_4 \text{ uptake [wt\%]} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where, *W*_{dry} is the weight of the dried sample before immersing in H₃PO₄ and *W*_{wet} the weight of the dried doped membrane samples, respectively.

The proton conductivity of H₃PO₄ doped membranes was determined by a two-probe electrochemical impedance spectroscopy (EIS) method using an

impedance analyzer (Autolab PGSTAT 30 with FRA software) recorded between 1 MHz and 0.1 Hz with 10 points per decade at maximum perturbation amplitude of 10 mV. To measure the temperature dependence of the conductivity, the cell was placed in a sealed, tempered, glass vessel, and the temperature recorded in close proximity to the membrane with a K-type thermocouple. Measurements were carried out in a conductivity cell at temperatures ranging from 25 to 175°C without humidification. The conductivity (σ) was calculated by the formula:

$$\sigma = \frac{L}{RA}$$

where, R and L are the measured resistance and thickness and A is cross-sectional area of the membrane, respectively.

Polymer synthesis

Synthesis of PBI based on 3,5-dicarboxyl-4'-nitro diphenyl ether

To a 50 mL three necked round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and a guard tube were added 2.0 g (9.334 mmol) DAB and 80 g of PPA and the mixture was heated to 140°C with stirring under a stream of nitrogen. After the complete dissolution of DAB, 2.830 g (9.334 mmol) of NEDA was added with stirring and the temperature of the reaction mixture was raised to 170°C. The diacid dissolved in 5 h giving a homogeneous solution. The solution was then heated upto 200°C for 4 h. The resulting viscous solution was then cooled and poured into 500 mL water to precipitate the polymer as fiber. The polymer was then filtered, washed repeatedly with water and stirred in 10% aqueous Na₂CO₃ solution overnight to eliminate residual phosphoric acid. The polymer was then washed with water to neutrality and boiled in water for 6 h, three times. The purified polymer was dried at 100°C for 24 h and another 24 h at 150°C. A brown fibrous polymer was obtained in quantitative yield. The inherent viscosity of this polymer at 0.5 g dL⁻¹ concentration, measured in DMAc at 30°C was 0.75 dL g⁻¹.

FT-IR (film, cm⁻¹): 1618 (C=N); 3395 (N-H stretching) 1609 (N-H deformation) 1220 (C-O stretching) 1584, 1498 (aromatic) 1340 and 1510 (—NO₂ stretching)

¹H-NMR [400 MHz, DMSO-d₆, ppm] showed signals of different protons at δ values of 13.16 (s, 2H, H_a); 9.15 (s, 1H, H_b); 8.30 (d, 2H, H_c); 8.24–7.56 (m, 8H, H_{d-f}); 7.31 (d, 2H, H_g).

Elemental analysis, calculated for C₂₆H₁₅N₅O₃: C, 70.11%; H, 3.39%; N, 15.72%. Found: C, 69.11%; H, 3.9%; N, 14.72%.

TABLE I
Inherent Viscosity and Film Nature of PBIs Containing Pendant Nitro-Phenoxy Groups

Polymer code	Diacids used (mole ratio) NEDA: IPA	Inherent viscosity η_{inh} (dL/g)	Film color	Film nature
NPBI	100 : 00	0.75	Pale yellow	Flexible
NPBI-1	90 : 10	0.95	Light brown	Flexible
NPBI-2	70 : 30	1.10	Light brown	Flexible
NPBI-3	50 : 50	0.99	Yellowish	Flexible
NPBI-4	30 : 70	1.40	Yellowish	Flexible
NPBI-5	10 : 90	1.01	Yellowish	Flexible
PBI	00 : 100	1.20	Yellowish	Flexible

NEDA, 3,5-dicarboxyl 4'-nitro diphenyl ether; IPA, isophthalic acid.

Synthesis of copolybenzimidazole NPBI-1 (NEDA : IPA, 90 : 10)

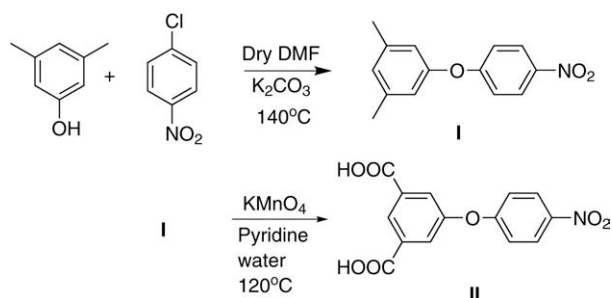
To a 50 mL three-necked round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and a guard tube were added 2.0 g (9.334 mmol) DAB and 20 g of PPA and the mixture was heated at 140°C with stirring under a stream of nitrogen. After the complete dissolution of DAB in PPA, 2.547 g (8.400 mmol) of NEDA and 0.155 g (0.9334 mmol) IPA were added with stirring. Then, the temperature was raised to 170°C, when diacid dissolved in 2 h giving a homogeneous solution. The solution was heated to 200°C and maintained at this temperature for 12 h. The resulting viscous solution was then cooled and poured into 500 mL water to precipitate the polymer as fiber. The polymer was then filtered, washed repeatedly with water and stirred with 10% aqueous Na₂CO₃ solution overnight to eliminate residual phosphoric acid. The polymer was then washed with water to neutrality and boiled in water for 6 h, three times. The purified polymer was dried at 100°C for 24 h and another 24 h at 150°C. A brown fibrous polymer was obtained in quantitative yield. The inherent viscosity of this polymer at 0.5 g dL⁻¹ concentrations, measured in DMAc at 30°C, was 1.12 dL g⁻¹. The ratio of NEDA and IPA in this co-polybenzimidazole is 90 : 10 mol %.

Other co-polybenzimidazoles of NEDA and IPA in different ratio with DAB were prepared following similar procedure. The feed ratio of monomers, viscosity and film nature of polymers are summarized in Table I.

RESULTS AND DISCUSSION

Monomer synthesis

The synthetic route to aromatic diacid, 3,5-dicarboxyl-4'-nitro diphenyl ether (NEDA), is shown in Scheme 1. It was synthesized in high yield and



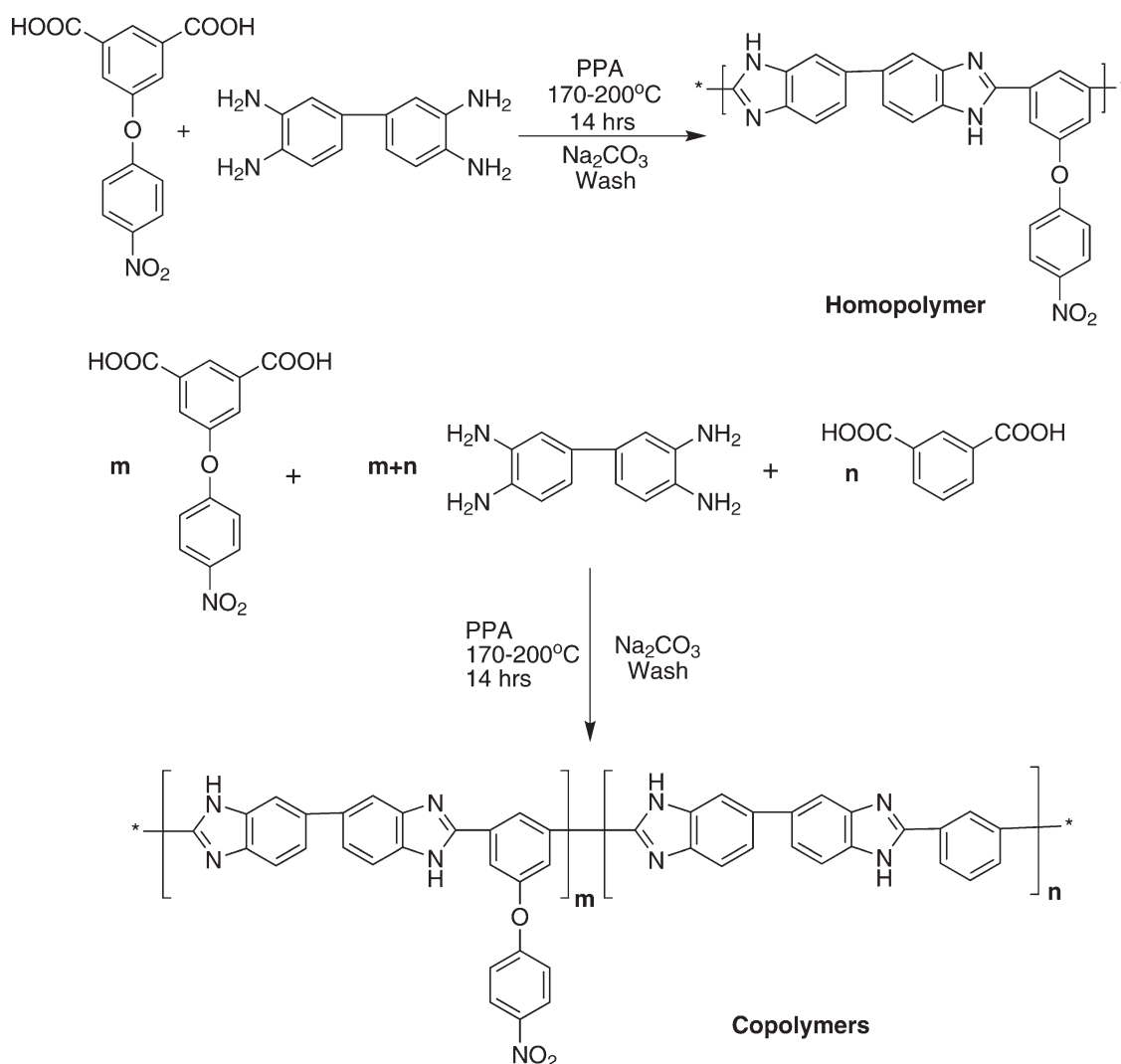
Scheme 1 Synthesis of NEDA.

purity by the procedure detailed in our earlier publication.²⁸

Polymer synthesis and characterization

PBIs are generally synthesized by two methods (i) solid state polymerization at high temperature²⁹ or

(ii) solution polymerization in PPA.³⁰ In the present work, we preferred solution polymerization method in PPA. Homopolymer of NEDA with conventional DAB and copolymers of DAB with a mixture of different mole ratios (90 : 10, 70 : 30, 50 : 50, 30 : 70 and 10 : 90) of NEDA and IPA were synthesized in order to study the effect of pendent nitrophenoxy content on properties of PBIs (Scheme 2). During the synthesis of homopolymer of NEDA, we observed that, heating above 200°C accelerates polymerization reaction forming a rubbery material within half an hour, which stops mechanical stirring. The polymer obtained is insoluble in any solvents including H₂SO₄. To avoid this problem, the polymerization was conducted at 190–200°C for 4 h. Prolonged heating at this temperature also results in polymer insoluble in solvents. Below 190°C, low-molecular weight polymer is obtained. Approximately 12 h stepwise heating is essential to form high-molecular weight homo-polymer. All the co-polymers remain soluble



Scheme 2 Synthesis of nitro groups containing PBI and co-PBIs.

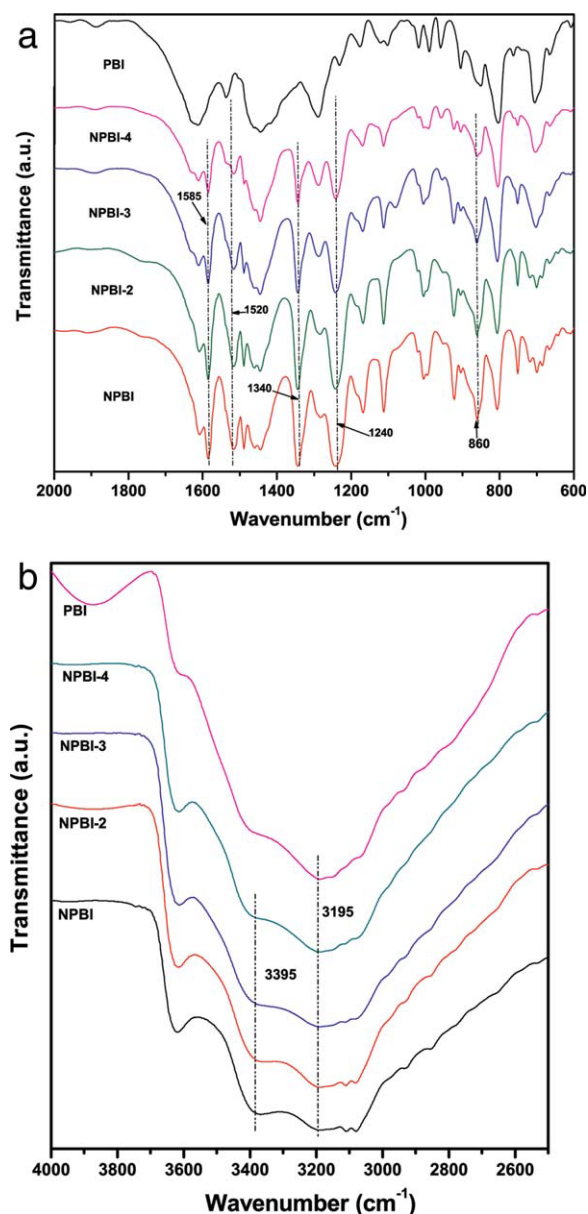


Figure 1 a. FTIR spectra of region 2000–600 cm^{-1} of nitro group containing PBIs compared with PBI. b. FTIR spectrum of nitro group containing PBI and co-PBIs compared with PBI. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in PPA without precipitation forming viscous solutions, which on pouring in hot water form strong thread like structure. All these polymers have film-forming properties and they form transparent, tough film on casting from DMAc solution (Table I).

FT-IR analysis of polymers

The FT-IR spectra of PBI, NPBI, NPBI-2, NPBI-3, and NPBI-4 scanned using thin films, are shown in Figure 1(a). The formation of PBIs was confirmed by the characteristic absorption band at 1610 and 1284 cm^{-1} due to C=N stretching of imidazole ring and

breathing mode of imidazole ring, respectively. For the co-PBIs these values range from 1610–1623 cm^{-1} for C=N stretching of imidazole ring and 1284–1288 cm^{-1} for breathing mode of imidazole ring. The absorption at 1585 cm^{-1} is due to the C–H of phenyl ring in the NEDA which is present only in NPBIs and absent in PBI. Absorption band at 1520 and 1340 cm^{-1} are due to the asymmetrical and symmetrical stretching of free NO_2 groups.

The intensity of band at 1340 and 1520 cm^{-1} [Fig. 1(a)] due to free nitro group decreases with decrease in NEDA in co-PBI series. Band at 860 cm^{-1} corresponds to aromatic C–N stretching vibration of C– NO_2 group. Band due to C–O–C linkage appears at 1240 cm^{-1} , the intensity of which decreases as NEDA content in co-polymer decreases. The absorption due to non hydrogen-bonded and self-associated N–H stretching of imidazole ring is observed at 3395 and 3180 cm^{-1} , respectively. In the case of PBI, the peak intensity due to self-associated H–N \cdots H stretching at 3195 cm^{-1} is higher compared with intensity at 3395 cm^{-1} due to nonhydrogen bonded N–H stretching. In case of copolymers, the intensity of peak of nonhydrogen bonded N–H stretching at 3395 cm^{-1} , in comparison with the peak intensity of self-associated H \cdots N–H stretching at 3195 cm^{-1} , increases systematically with increase in NEDA content in the copolymers [Fig. 1(b)].

The comparison of intensity of peak of nonhydrogen bonded N–H stretching at 3395 cm^{-1} with the intensity of peak of self-associated hydrogen bonded H–N \cdots H at 3195 cm^{-1} in PBI and NPBI clearly indicates that the nonhydrogen bonded free N–H groups are more in NPBI compared with PBI. This clearly shows that the pendant nitro-phenoxy groups disrupt inter-chain self-association between N–H groups in imidazole ring and increase the content of nonhydrogen bonded free N–H groups in NPBIs as compared with PBI.

The presence of benzimidazole groups and free nitro group in the NPBIs was further confirmed by $^1\text{H-NMR}$ spectrum (Fig. 2). The proton at 13.30 δ assigned to hydrogen of N–H group of imidazole ring and the aromatic protons with expected multiples and integration at 7.2–9.2 δ substantiates the formation of PBI with free nitro groups as indicated in Figure 2.

Inherent viscosity

Inherent viscosity was determined in DMAc (0.5 g dL^{-1} concentration at 30°C) using Ubbelohde viscometer. The comparatively high inherent viscosities of these polymers in the range of 0.75–1.4 dL g^{-1} (Table I) indicate that the polymers are of reasonably high molecular weights. All these polymers form tough and flexible films.

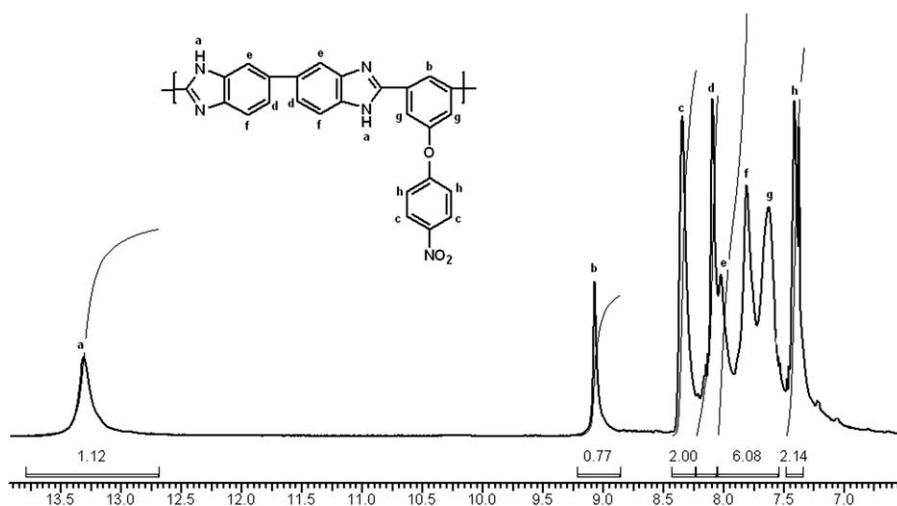


Figure 2 $^1\text{H-NMR}$ spectrum of nitro group containing PBI (NPBI).

Polymer solubility

PBIs, being rigid polymers, are infusible and polymer solubility plays a major role for applications. Solubility behavior of newly synthesized polymers was studied by dissolving 4 mg of polymers in 0.5 mL solvent. Commercial PBI is soluble only in aprotic solvents such as DMAc, after heating at high temperature for several hours in the presence of lithium chloride. The polymers under study displayed good solubility compared with the commercial PBI. They are soluble in polar aprotic solvents such as DMAc, NMP, and DMSO (Table II) at ambient temperature. Copolymers NPBI and NPBI-3 are soluble in DMF at ambient temperature while, NPBI-1 and NPBI-2 are insoluble.

They are readily soluble in strong acids such as H_2SO_4 , trifluoroacetic acid (TFA), formic acid, methane sulfonic acid, etc. However, these polymers are not soluble in common organic solvents such as chloroform, toluene, tetrahydrofuran, dioxane, and

acetic acid due to their polar nature. Low solubility of PBI in solvents is due to rigid structure caused by self-associated hydrogen bonding of N—H groups in imidazole ring. The pendant nitro-phenoxy groups disrupt hydrogen bonding of PBI, as observed in FT-IR spectra, and enhances the solvent solubility.

Thermal stability

The thermal behavior of the nitro group containing PBIs and the conventional PBI was analyzed by TGA at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere. Incorporation of pendant nitrophenoxy groups in PBI is expected to disrupt rigid structure of PBI by weakening self-association of inter-chain NH groups resulting in overall reduction in thermal stability. IR spectra show free NH groups in NPBIs [Fig. 1(b)]. Incorporation of even 10 mol % of nitrophenoxy groups in IPA-based PBI disrupts regular rigid structure and self-associated hydrogen bonding

TABLE II
Solubility Behavior of PBIs Containing Pendant Nitro-phenoxy Groups

Polymer code	Solvents								
	TFA	MSA	HCOOH	H_2SO_4	DMF	DMSO	DMAc	NMP	THF
NPBI	++	++	+	++	+	++	++	++	--
NPBI-1	++	++	++	++	--	++	++	++	--
NPBI-2	++	++	++	++	--	++	++	++	--
NPBI-3	++	++	++	++	+	+	++	++	--
NPBI-4	+	++	++	++	++	++	++	++	--
NPBI-5	++	++	++	++	++	++	++	++	--
PBI	++	+	++	++	+	+	+	+	--

+, Soluble at room temperature; +, soluble on heating, and --, insoluble on heating.

TFA, trifluoro acetic acid; H_2SO_4 , Conc. sulfuric acid; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethyl acetamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone; THF, tetrahydrofuran; HCOOH, formic acid; MSA, methanesulfonic acid; NEDA, 3,5-dicarboxyl-4'-nitro diphenyl ether; IPA: isophthalic acid.

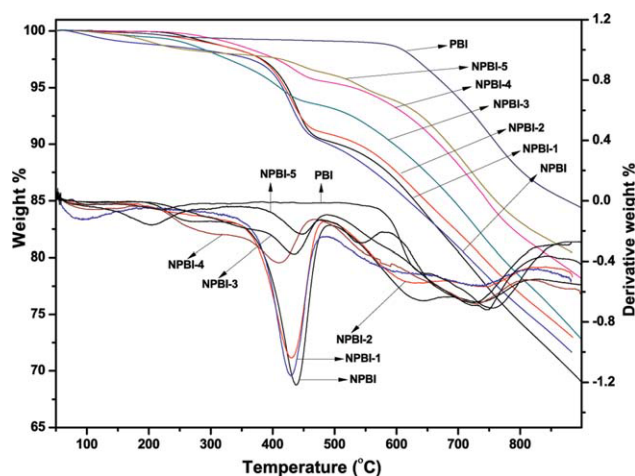


Figure 3 TGA thermograms of nitro group containing PBIs compared with PBI in N_2 at heating rate $10^\circ\text{C min}^{-1}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of PBI which has a significant effect on the thermal stability of PBI. Thus, IDT of PBI is 603°C , whereas IDT of NPBI-5 is 416°C . The IDT of the nitro group containing PBIs vary in the range of $380\text{--}415^\circ\text{C}$.

About 2–3% weight loss observed upto 300°C for NPBIs is, probably, due to loss of absorbed moisture. All the nitro group containing PBIs exhibited a two-step degradation pattern (Fig. 3; Table III). The first step of degradation, observed between 300 and 400°C , was due to the decomposition of nitro groups.³¹ The percentage weight loss in the region $300\text{--}400^\circ\text{C}$ increases with increase in nitro group content in the polymer indicating the weight loss, probably, is due to the loss of nitro groups. The second step decomposition occurring at $520\text{--}620^\circ\text{C}$ is due to the decomposition of polymer main chain. Low values of IDT ($380\text{--}415^\circ\text{C}$), T_5 ($410\text{--}550^\circ\text{C}$) and T_{10} ($500\text{--}680^\circ\text{C}$) compared with PBI indicate that the nitro phenoxy group lowers overall thermal stability of PBI. However, thermal stability of these polymers is high enough for the applications as polymer electrolyte membranes for fuel cell or membrane for separation at high temperature.

Glass transition temperature

PBI, due to rigid structure, show high glass transition temperature. Incorporation of flexible groups in side chain is expected to lower T_g . NEDA-based PBIs were subjected to DSC analysis in nitrogen atmosphere at heating rate of 20°C/min to determine glass transition temperature and the DSC thermograms of these polymers are shown in Figure 4. T_g of all these polymers could not be detected in DSC curves. The curves in Figure 7 clearly show the exothermic reaction occurring above 300°C , probably

due to decomposition of nitro group, which may be interfering the detection of T_g .²⁷ It appears that the T_g of nitro group containing PBI is not below 300°C , which is sufficiently high for applications in polymer electrolyte for fuel cells or membranes for separation technology at high temperature. Thus, these polymers have sufficiently high thermal stability suitable for high temperature applications.

Mechanical properties

Polymer membranes for application as polymer electrolyte for fuel cell or separation technology are expected to have good mechanical strength. Commercial PBI has superior mechanical properties due to rigid structure and any structural change is expected to affect mechanical properties. Commercial PBI has meta substituted phenyl rings in the main chain whereas, NEDA-based PBI also has meta substituted phenyl ring in main chain and in addition, nitrophenoxy pendant group attached to the phenyl ring. The flexible bulky pendant group is expected to affect the mechanical properties of PBI. In the present study, it was observed that the pendant nitrophenoxy groups lower the overall mechanical strength of PBI. Thus, tensile stress and modulus of NPBI are 62 and 2950 MPa compared with 151 and 3770 MPa, respectively for PBI (Table IV). Tensile stress and modulus of all copolymers vary in the range of $55\text{--}65$ MPa and $2000\text{--}2600$ MPa, respectively. The comparison of tensile properties of PBI and NPBI-5 (Fig. 5) reveals that the addition of even 10 mol % of NEDA to IPA has a significant effect on mechanical properties of PBI. Thus, the tensile

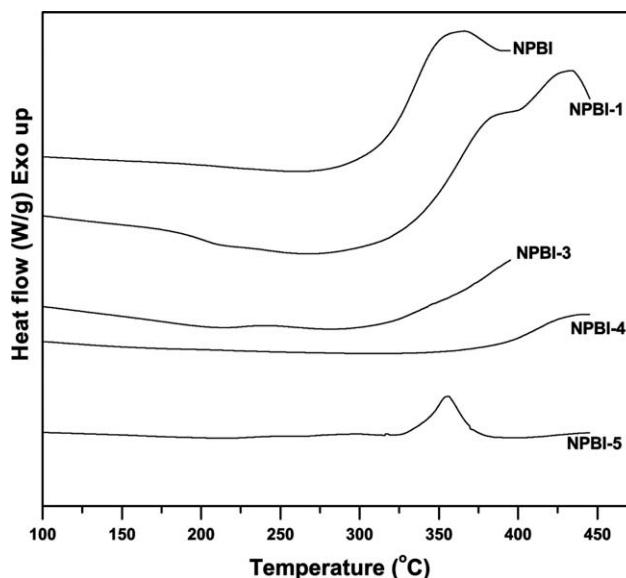


Figure 4 DSC thermograms of nitro group containing PBI and co-PBIs in N_2 at heating rate of $10^\circ\text{C min}^{-1}$.

TABLE III
Thermal Properties of PBIs Containing Pendant Nitro-phenoxy Groups Compared with PBI

Polymer code	IDT (°C)	SDT (°C)	T_5 (°C)	T_{10} (°C)	T_{max}^1 (°C)	T_{max}^2 (°C)	Residue (wt %)
NPBI	400	577	424	501	440	635	67
NPBI-1	394	560	418	530	430	685	73
NPBI-2	402	546	420	500	431	732	71
NPBI-3	385	582	419	589	410	726	74
NPBI-4	380	614	526	671	430	744	79
NPBI-5	416	527	548	680	542	721	80
PBI	603	–	679	760	751	–	84.5

IDT, initial decomposition temperature due to NO₂ group; SDT, second decomposition temperature due to decomposition of polymer backbone T_5 , T_{10} : Temperature at which 5%, 10% weight loss of polymer takes place; T_{max}^1 , T_{max}^2 , temperatures at which maximum weight loss of polymer takes place in the first- and second-step decomposition, respectively.

strength and modulus of NPBI-5 are 65 and 2160 MPa compared with 151 and 3770 MPa for PBI, whereas the %elongation of NPBI-5 is 24.65% compared with 6.28% for PBI. The flexible pendant nitro-phenoxy groups disrupt rigid polymer structure by the disruption self-association of –NH– groups between inter-chains as observed in FT-IR spectral analysis which reduces tensile stress and modulus. The presence of small percent, i.e. 10–20 mol % of thinly and randomly distributed flexible nitro-phenoxy groups in PBI, (NPBI-5& NPBI-4) helps slipping of polymer chains past each other resulting in observed increase in elongation. However, higher content of nitrophenoxy groups resists such movement due to close distribution and elongation decreases for polymers containing high content of nitro-phenoxy groups.

Though, PBI containing pendent nitro-phenoxy groups has low tensile strength and modulus compared with commercial PBI, the observed strength is good enough for applications as membrane materials for polymer electrolytes for fuel cells or separation technology.

TABLE IV
Mechanical Properties of PBIs Containing Pendant Nitro-Phenoxy Groups Compared with PBI

Polymer code	Tensile stress (MPa)	Modulus (MPa)	Toughness (MPa)	Elongation at break (%)
NPBI	62	2950	3.26	3.64
NPBI-1	61	2500	5.03	5.21
NPBI-2	57	2585	2.69	3.29
NPBI-3	63	2575	6.22	6.15
NPBI-4	56	2070	12.05	12.03
NPBI-5	65	2160	29.9	24.65
PBI	151	3770	5.77	6.28

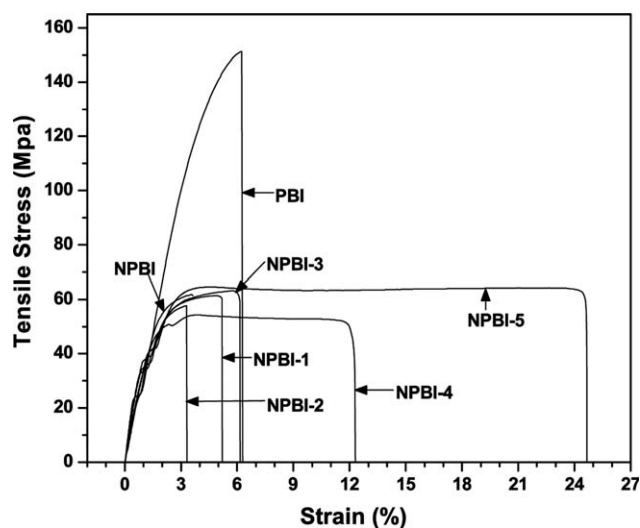


Figure 5 Tensile stress versus strain graph of nitro-phenoxy group containing PBI and co-PBIs compared with PBI.

Oxidative stability

A good polymer electrolyte is desired to have long lifetime at operational conditions of fuel cells. Proton exchange membrane is subjected to strongly oxidizing and reducing environment in the presence of platinum catalyst and they generally undergo degradation at operational condition of fuel cells, which reduces the life time of fuel cell stack. Membrane based on PBI is known to undergo degradation by ·OH or ·OOH radicals formed by the decomposition of H₂O₂ generated at cathode during operational conditions of fuel cells.³² Crosslinking³³ is reported to enhance the oxidative stability of PBI. Experimentally, oxidative stability of PBI membrane is evaluated by Fenton test. Membranes of PBIs containing nitrophenoxy groups, along with PBI were evaluated for oxidative stability by Fenton test as described in the Experimental and Results and Discussion sections are depicted in Figure 6. The membrane samples of NPBI, NPBI-1, and NPBI-3 showed 9–10% weight loss after 72 h in Fenton reagent test compared with 14% weight loss for PBI membrane indicating nitrophenoxy groups enhance oxidative stability to some extent. The samples were still very strong and tough indicating good oxidative stability of these membranes.

Doping study

The doping level of phosphoric acid in PBI has a profound effect on proton conductivity. Proton conductivity increases with increase in doping level. The doping level of PBI depends on the concentration of the phosphoric acid and the time and temperature of doping. The acid uptake property of a

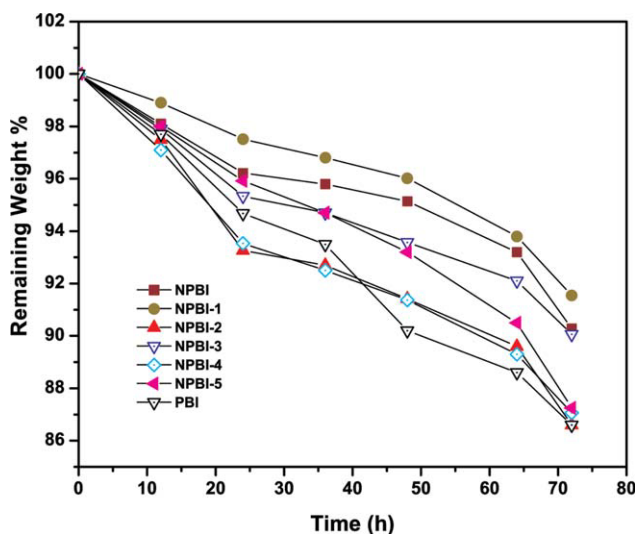


Figure 6 Oxidative stability expressed as remaining wt % in Fenton's test of nitro group containing PBI and co-PBIs compared with PBI. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymer depends on the structure of the polymer also. The acid uptake capacity of newly synthesized polymers was determined by doping membranes of NPBIs and commercial PBI for comparison in 2–14 molar H_3PO_4 solutions for 24 h at room temperature. The time-dependent doping study of NPBIs and PBI was conducted in 85% H_3PO_4 at room temperature for 36 h to study the effect of time on doping level. The doping level is expressed as the wt % of H_3PO_4 of the polymer or copolymers. Compared with PBI, NPBIs show low acid uptake (wt %) in all the concentrations of acid as shown in Figure 7(a). The acid uptake is slow upto 8 M H_3PO_4 solution in comparison with PBI, although a steady increase in acid uptake with increase in concentration is observed. In fact, the acid uptake in NPBI, should have been faster than that for PBI, because of the expected enhancement of free volume due to bulky nitro-phenoxy group in side chain and the presence of high content of basic free non-bonded N–H groups, which should facilitate the diffusion of phosphoric acid into matrix faster compared with rigid PBI. However, the phosphoric acid uptake upto 8M is slow compared with PBI [Fig. 7(a)]. Upto 8M phosphoric acid, the percent of water (v/v) is more than that of phosphoric acid and it appears, that the nitro group being hydrophobic in nature does not support uptake of acid fast from the acid solution of low concentration. However, acid uptake is faster above 10 molar acid solution [Fig. 7(a)], because above 10 molar solution content of phosphoric acid is more than water. Thus, phosphoric acid uptake of NPBI in 12 and 14 molar phosphoric acid increases faster

and acid uptake of NPBI is 268 wt % compared with 250 wt % for PBI in 14 molar phosphoric acid after 24 h.

This is further substantiated by the time-dependent acid uptake study in 85% H_3PO_4 solution [Fig. 7(b)]. In the case of PBI, a steady increase in acid uptake with time upto 24–27 h and saturation thereafter is observed, whereas acid uptake in NPBIs is comparatively fast, and saturation point is reached within 12–15 h. This is, probably, due to the nature of N–H group bonding in these polymers. The rigidity of PBI, due to the presence of high self-associated H–N...H hydrogen bonding between inter-chain imidazole groups, resists penetration of phosphoric

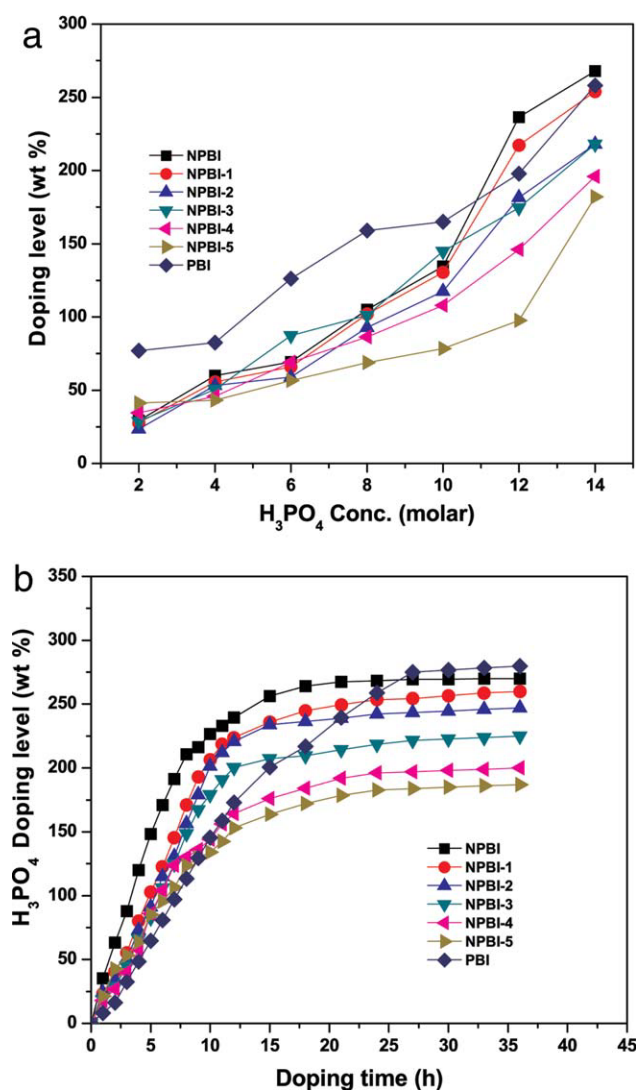


Figure 7 a. Doping level of phosphoric acid (wt %) in polymers as a function of the H_3PO_4 concentration for nitro group containing PBI and co-PBIs compared with PBI. b. Time-dependant doping level of nitro-phenoxy group containing PBI and co-PBIs compared with PBI in 85% H_3PO_4 at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

acid into polymer matrix, whereas NPBIs, having more un-bonded free N–H groups compared with PBI, as evidenced by the IR-study, give access for easy penetration of phosphoric acid in polymer matrix. Thus, acid uptake in copolymers increases with increase in NEDA content in polymer. Interestingly, the membranes of NPBIs have good strength and flexibility suitable for the preparation of PEM even after high acid uptake. After confirming the stability of membranes of NPBIs in 85% phosphoric acid, the membranes for the proton conductivity study were doped with 85% phosphoric acid for 24 h.

Proton conductivity

Proton conductivity of NPBI and copolymers, NPBI-1-5, doped with 85% phosphoric acid for 24 h and PBI doped for 36 h, was determined by AC impedance method at different temperatures in the range of 25–175°C as described in the Experimental section. As expected, proton conductivity of all polymer membranes increases with increase in temperature (Fig. 8). In case of PBI, proton conductivity increases from 3.9×10^{-3} S/cm at 25°C to 3.3×10^{-2} S/cm at 175°C, whereas the proton conductivity of NPBI membrane is 6.8×10^{-3} S/cm at 25°C and 4.6×10^{-2} S/cm at 175°C (Fig. 10). High proton conductivity of NPBI is, probably, due to high phosphoric acid doping level. Though, apparently it appears that the doping level of NPBI (260 wt %) is low compared with the doping level of PBI (270 wt %), the doping level in mole/repeat unit for PBI is 8.5 mol compared with NPBI 11.8 mol/repeat unit (Table V), because the molecular weight of repeat unit of PBI

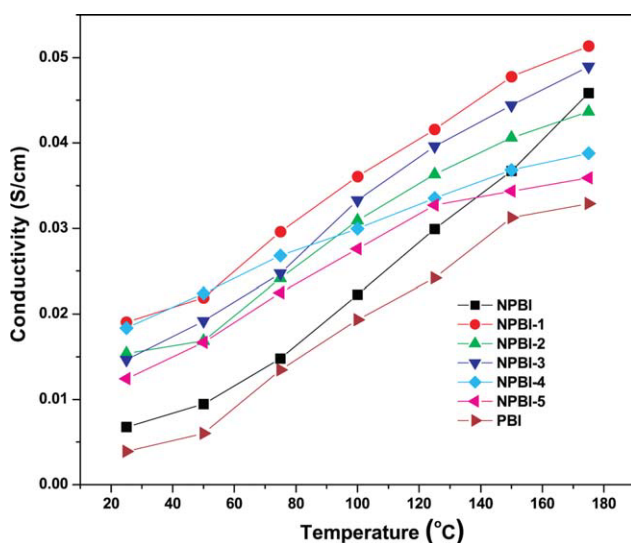


Figure 8 Proton conductivities of nitro-phenoxy group containing PBI and co-PBIs compared with PBI at different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Proton Conductivity and Doping Level of PBI and NPBIs at 25 and 175°C

Polymer code	Doping level H ₃ PO ₄ (wt %)	Doping level H ₃ PO ₄ (mol/repeat unit)	σ_{\max} (S cm ⁻¹) at 25°C	σ_{\max} (S cm ⁻¹) at 175°C
NPBI	260	11.8	6.8×10^{-3}	4.6×10^{-2}
NPBI-1	250	11.0	1.9×10^{-2}	5.1×10^{-2}
NPBI-2	240	9.9	1.5×10^{-2}	4.4×10^{-2}
NPBI-3	220	8.5	1.5×10^{-2}	4.9×10^{-2}
NPBI-4	190	6.8	1.8×10^{-2}	3.9×10^{-2}
NPBI-5	180	5.9	1.2×10^{-2}	3.6×10^{-2}
PBI	270	8.5	3.9×10^{-3}	3.3×10^{-2}

in PBI is 308, whereas that of NPBI is 445. Doping level in moles/repeat unit for homo and copolymers was calculated on the basis of feed mole ratio of monomers for the polymers. Thus, free phosphoric acid after bonding with imidazole groups is more in NPBI compared with PBI, which explains observed high proton conductivity in NPBI. It appears that the structure and composition of the polymers also have some effect on the observed high proton conductivity. Thus, all copolymers (NPBIs) show high proton conductivity, although doping level (wt %) of these polymers is low compared with PBI (Table V). It was observed that these polymers, on doping, exhibit elastomeric nature, which probably facilitates proton conduction. Thus, incorporation of nitrophenoxy groups in PBI enhances proton conductivity significantly.

CONCLUSIONS

Novel homo PBI and co-PBIs with varying contents of pendant nitrophenoxy groups were successfully synthesized by condensing a mixture of NEDA and IPA in different ratios with 3,3'-diaminobenzidine in PPA. The PBIs containing nitrophenoxy groups have good solubility in polar aprotic solvents and they form tough and transparent membranes on solution casting. They have high thermal stability, good mechanical strength, and good oxidative stability, and the membranes of these polymers on doping with phosphoric acid exhibit high proton conductivity suitable for application as membrane materials for PEMFCs at high temperature.

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References

- Buckley, A.; Steutz, D. E.; Serad, G. A. *Encyclopedia*, 2nd ed.; 1988; Vol. 11, p 572.

2. Hergenrother, P. M.; Smith, J. G.; Connell, J. W. *Polymer* 1993, 34, 856.
3. Srinivasan, P. R.; Srinivasan, M.; Mahadevan, V. *J Polym Sci Part A-1: Polym Chem* 1982, 20, 1145.
4. Iwakura, Y.; Uno, K.; Imai, Y.; Fukui, M. *Die Makromol Chem* 1964, 77, 41.
5. Chuang, S.-W.; Lien-Chung Hsu, S. *J Polym Sci Part A: Polym Chem* 2006, 44, 4508.
6. Xiao, L.; Zhang, H.; Jana, T.; Scanlon, E.; Chen, R.; Choe, E.-W.; Ramanathan, L. S.; Yu, S.; Benicewicz, B. C. *Fuel Cells* 2005, 5, 287.
7. Srinivasan, P. R.; Mahadevan, V.; Srinivasan, M. *J Polym Sci Part A-1: Polym Chem* 1982, 20, 3095.
8. Lakshmi Narayan, T. V.; Marvel, C. S. *J Polym Sci Part A-1: Polym Chem* 1967, 5, 1113.
9. Ashok Reddy, T.; Srinivasan, M. *J Polym Sci Part A-1: Polym Chem* 1988, 26, 1051.
10. Varma, I. K.; Veena, S. M. *J Polym Sci Part A-1: Polym Chem* 1976, 14, 973.
11. Varma, I. K.; Veena, S. M. *J Macromol Sci Chem* 1977, 11, 845.
12. Inoue, S.; Imai, Y.; Uno, K.; Iwakura, Y. *Die Makromol Chem* 1966, 95, 236.
13. Srinivasan, P. R.; Mahadevan, V.; Srinivasan, M. *Polymer* 1981, 22, 1290.
14. Moon, S.; Schwartz, A. L.; Hecht, J. K. *J Polym Sci Part A-1: Polym Chem* 1970, 8, 3665.
15. Pourabas, B.; Banihashemi, A. *Polym Int* 2002, 51, 1086.
16. Sato, M.; Yokoyama, M. *J Polym Sci Part A-1: Polym Chem* 1981, 19, 591.
17. Uno, K.; Niime, K.; Iwata, Y.; Toda, F.; Iwakura, Y. *J Polym Sci Polym Chem Ed* 1977, 15, 1309.
18. Qing, S.; Huang, W.; Yan, D. *J Polym Sci Part A: Polym Chem* 2005, 43, 4363.
19. Asensio, J. A.; Borros, S.; Pedro, G.-R. *J Polym Sci Part A: Polym Chem* 2002, 40, 3703.
20. Thaddeus, E. Helminiak. US Patent 4377546, March 22, 1983.
21. Sansone, M. J.; Kwiatek, M. S. Hoechst Celanese Corp. European patent, 385687, 5 September 1990.
22. Trischler, F. D. US Patent 3578644, 11 May 1971.
23. Sansone, M. J. Hoechst Celanese Corp. US Patent 4814400, 21 March 1989.
24. Jouanneau, J.; Mercier, R.; Gonon, L.; Gebel, G. *Macromolecules* 2007, 40, 983.
25. Glipa, X.; El Haddad, M.; Jones, D. J.; Roziere, J. *Solid State Ionics* 1997, 97, 323.
26. Choe, E. W.; Randolph, N. J. Celanese Corp. US Patent 4579915, 1 April 1986.
27. Cho, J.; Park, M. S.; Choi, J. H.; Ji, B. C.; Han, S. S.; Lyoo, W. S. *J Polym Sci Part B: Polym Phys* 2001, 39, 1778.
28. Kulkarni, M.; Potrekar, R.; Kulkarni, R. A.; Vernekar, S. P. *J Polym Sci Part A: Polym Chem* 2008, 46, 5776.
29. Chung, T. S. *J Macromol Sci-Rev Macromol Chem Phys* 1997, 37, 277.
30. Vogel, H. A.; Marvel, C. S. *J Polym Science: Part-A* 1961, 50, 511.
31. Teng, Y.-H.; Kaminski, G. A.; Zhang, Z.-B.; Sharma, A.; Mohanty, D. K. *Polymer* 2006, 47, 4004.
32. Gourdoupi, N.; Andreopoulou, A. K.; Deimede, V.; Kallitsis, K. *J Chem Mater* 2003, 15, 5044.
33. Li, Q.; Pan, C.; Jensen, J. O.; Noye, P.; Bjerrum, N. J. *Chem Mater* 2007, 19, 350.