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N-substitution of polybenzimidazoles: Synthesis and evaluation of physical properties

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ABSTRACT

Series of *N*-substituted polybenzimidazoles (PBI) were synthesized using selective alkyl groups with varying bulk and flexibility, viz., methyl, *n*-butyl, methylene trimethylsilane and 4-*tert*-butylbenzyl. PBI-I based on 3,3′-diaminobenzidine (DAB) and isophthalic acid and PBI-BuI based on DAB and 5-*tert*-butyl isophthalic acid were chosen for *N*-substitution. Structural characterizations of substituted polymers by FT-IR and ^{1}H NMR revealed elimination of hydrogen bonding. Evaluation of their physical properties revealed that *N*-substitution rendered better solvent solubility in common organic solvents, more open polymer matrix, but reduced thermal properties in comparison to their respective parent PBI. 4-*tert*-butylbenzyl, methylene trimethylsilane or *n*-butyl group substituted polymers were soluble even in chlorinated solvents ($CHCl_3$ and TCE). Substantial variations in gas permeability of inert gases, He and Ar and attractive P_{He}/P_{Ar} selectivity, especially after methyl group substitution depicted potential of these materials for gas separation.

1. Introduction

Aromatic polybenzimidazoles (PBI) are well known for their high thermo-chemical stability and excellent mechanical properties [1–3]. Various members of PBI family are shown to have high degradation temperatures well above 500 °C [1,3,4]. PBI based on isophthalic acid is known to exhibit exceptionally high glass transition temperature of ~416–435 °C [5–8]. Excellent thermal stability of PBI is highly beneficial for their use as a gas separation membrane material, where higher temperatures are involved. At higher temperatures, common polymers usually weaken their capability to discriminate between penetrant molecules. Gas separation applications such as CO_2 separation need a membrane material that is thermally, chemically and mechanically stable at stringent operating conditions in order to maintain its high separation performance. It is said that rigidity of the PBI is responsible for the retention of its permselectivities at high temperature [8]. Though unsubstituted PBI is known to exhibit low gas permeability owing to close chain packing [8–11], it was shown to improve by structural modifications at its acid moiety [9]. Structural modifications of PBI by *N*-substitution using bulky group could be another approach to enhance gas permeability. Moreover, *N*-substitution of PBI is known to improve solvent solubility, which otherwise is poor due to the interchain hydrogen bonding [12,13]. It is reported that *N*-substitution of PBI by an aliphatic [13–15] or aromatic group [16–18] improves solvent solubility. Alkylsulfonated and arylsulfonated derivatives of PBI obtained using 1,3-propane sultone and sodium 4-(bromomethyl)benzenesulfonate as the reagent, respectively, were soluble in water [19,20].

This work presents effects of *N*-substitution of PBI by alkyl groups of varying bulk and flexibility on physical properties. Gas permeability evaluation using inert gases (He and Ar) was also performed to assess effect of the added bulk. Chosen alkyl substituents were methyl, *n*-butyl, 4-*tert*-butylbenzyl and methylene trimethylsilane. It was anticipated that the substitution of these groups on PBI would eliminate the intermolecular hydrogen bonding and simultaneously disrupt the chain packing, which in

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turn would have a profound effect on physical and gas permeation properties. Two PBIs, viz., PBI-I (based on isophthalic acid) and PBI-BuI (based on 5-*tert*-butyl isophthalic acid) were selected for *N*-substitution. PBI-I is well known for its high packing density and low gas permeability [8–10]. PBI-BuI was shown to have lower packing density and higher gas permeability than PBI-I, while retaining high selectivity [9].

2. Experimental

2.1. Material and monomers

3,3′-Diaminobenzidine (DAB), isophthalic acid (IPA), 5-*tert*-butyl isophthalic acid (BuI), sodium hydride (60% dispersion in mineral oil), 4-*tert*-butylbenzyl bromide and (iodomethyl)trimethylsilane were procured from Aldrich Chemicals. Polyphosphoric acid (PPA) was procured from Lancaster. Methyl iodide, *n*-butyl iodide, dry dimethyl sulphoxide (DMSO, moisture content < 0.03%), trifluoroacetic acid (TFA) and conc. H_2SO_4 were procured from S.D. Fine Chemicals. These chemicals (AR grade) were used without further purification.

2.2. PBI synthesis and N-substitution

Polybenzimidazoles based on isophthalic acid (PBI-I) and 5-*tert*-butylisophthalic acid (PBI-BuI) were synthesized as reported earlier [4]. Their *N*-substitution was carried out in dry DMSO by preparing Na salt of PBI, followed by addition of the alkyl halide (Scheme 1). To a three-necked round bottom flask, 160 ml of DMSO, 0.0162 mol of PBI and 0.0341 mol of NaH (2.1 equivalents) were charged under N_2 atmosphere and stirred at ambient for 24 h. The reaction mixture was heated at 80 °C for an hour. At this stage, a deep blood red colour developed and complete dissolution of PBI took place. This solution was allowed to cool to the ambient temperature and 2 M equivalents of an alkyl iodide (methyl iodide, *n*-butyl iodide, 4-*tert*-butylbenzyl bromide or (iodomethyl)trimethylsilane), dissolved in 10 ml of dry DMSO was added in a dropwise manner for a period of 15 min. The reaction mixture was precipitated, which was stirred further at ambient temperature for 12 h. This reaction mixture was slowly poured onto the stirred water. Obtained polymer was washed several times with water and finally with acetone. It was dried in vacuum oven at 80 °C for 3 days.

Formed *N*-substituted PBIs were purified by dissolving in DMAc (except for DMPBI-I, which was dissolved in NMP), centrifugation at 3000 rpm for 3 h (to remove undissolved particles, if any), followed by precipitation in stirred water. The polymer was collected on the Buckner and was soaked in acetone for 5 h. After filtration, the polymer was dried at 80 °C for a week in a vacuum oven. Chemical structures of these polymers along with their abbreviations are given in Scheme 1.

^{1}H NMR analysis of *N*-substituted PBIs was performed using mixture of DMSO-d_6:TFA (1:0.5 v/v) to determine the degree of substitution. These spectra are shown in Fig. 1a and b. The peak assignments are as given below:

DMPBI-I: ^{1}H NMR (DMSO-d_6 + TFA): δ = 7.42–8.48 (10H, aromatic), 3.93 (6H, methyl).

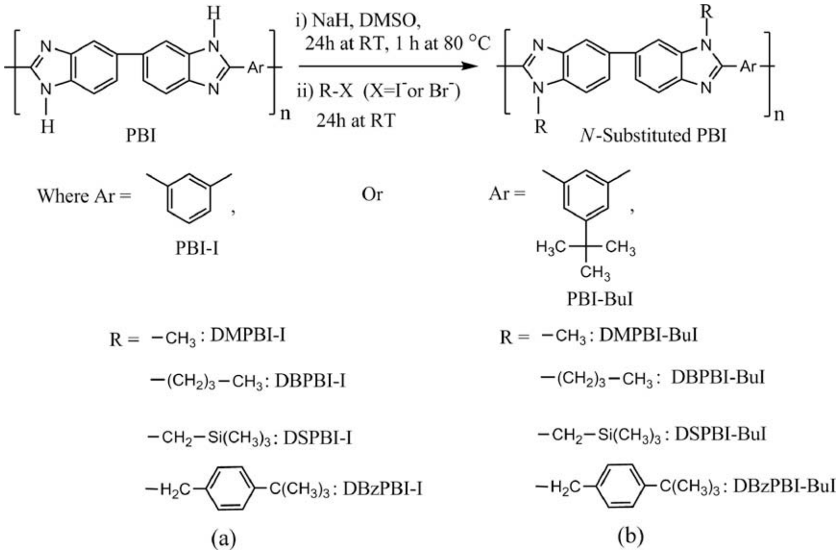
DBPBI-I: ^{1}H NMR (DMSO-d_6 + TFA): δ = 7.72–8.90 (10H, aromatic), 4.63 (4H, methylene), 1.80 (4H, methylene), 1.23 (4H, methylene), 0.74 (6H, methyl).

DSPBI-I: ^{1}H NMR (DMSO-d_6 + TFA): δ = 8.16–9.40 (18H, aromatic), 4.72 (4H, methylene), 0.31 (4.04H, trimethylsilyl).

DBzPBI-I: ^{1}H NMR (DMSO-d_6 + TFA): δ = 6.80–8.60 (18H, aromatic), 5.7 (4H, methylene), 1.03 (18H, *tert*-butyl).

DMPBI-BuI: ^{1}H NMR (DMSO-d_6 + TFA): δ = 7.40–8.71 (9H, aromatic), 4.04 (6H, methyl), 1.47 (9H, *tert*-butyl).

DBPBI-BuI: ^{1}H NMR (DMSO-d_6 + TFA): δ = 7.74–8.96 (9H, aromatic), 4.63 (4H, methylene), 1.8, 1.43, 1.24, 0.73 (23H, methylene, methyl and *tert*-butyl).



Scheme 1. *N*-Substitution of (a) PBI-I and (b) PBI-BuI.

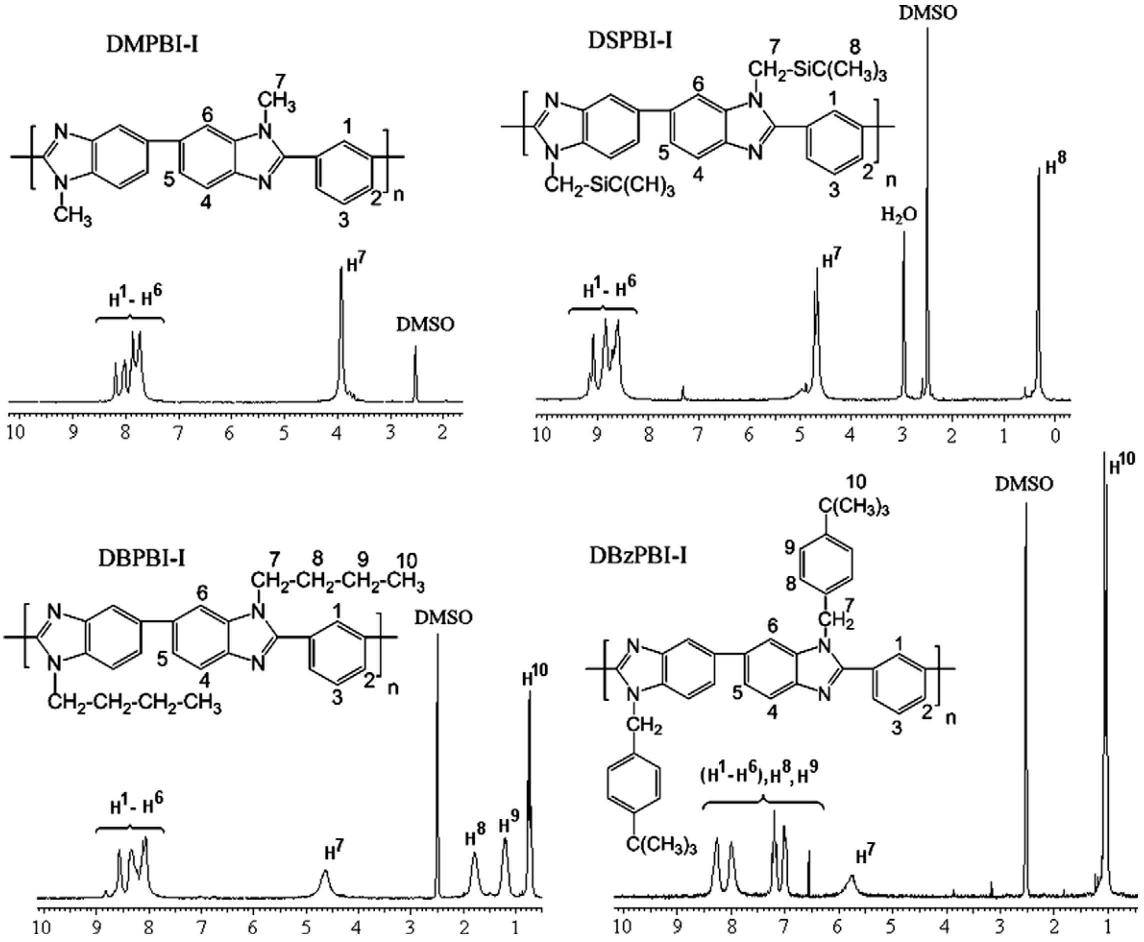


Fig. 1a. ^{1}H NMR spectra of *N*-substituted PBI-I.

DSPBI-BuI: ^{1}H NMR (DMSO-d_6 + TFA): $\delta = 8.14–9.38$ (9H, aromatic), 4.7 (4H, methylene), 1.9 (9H, *tert*-butyl), 0.29 (5H, trimethylsilyl).

DBzPBI-BuI: ^{1}H NMR (DMSO-d_6 + TFA): $\delta = 6.71–8.88$ (17H, aromatic), 5.83 (4H, methylene), 1.14 (27H, *tert*-butyl).

2.3. Film preparation

Films of *N*-substituted polymers were prepared by solution casting method using 3% (w/v) DMAc solution (except for DMPBI-I) at 80 °C for 18 h under dry conditions on a flat glass surface. In case of DMPBI-I, the solvent used was NMP, which was evaporated at 90 °C under N_2 atmosphere. After initial solvent evaporation, formed films were peeled off from the glass surface and were immersed in water at 60 °C for 3 days to extract remaining solvent. They were dried in vacuum oven at 100 °C for a week. Such films were used for FT-IR, density and gas permeability investigations. Though many of the polymers are soluble in low boiling solvents like chloroform (Table 1), in order to maintain consistency, a single type of solvent was chosen so that their gas permeation can be evaluated. It is known that variation in solvent vary the gas permeation property of a polymer [21].

2.4. Characterizations

The solubility of *N*-substituted PBIs in common solvents was determined at the concentration of 2% (w/v) and the observations are given in Table 1. Inherent viscosity (η_{inh}) was determined using 0.2 g/dL polymer solution in conc. H_2SO_4 (98%) at 35 °C. The ^{1}H NMR spectra were recorded on Bruker AC-200 (Fig. 1a and b). FT-IR spectra of polymers in thin film form (~10 μm) were recorded at ambient temperature on a Perkin-Elmer Spectrum-1 spectrometer (Fig. 2). FT-IR spectra of same films at 150 °C were recorded on Perkin-Elmer Spectrum GX spectrophotometer provided with high temperature assembly of Mettler Toledo make with FP90 central processor. Wide angle X-ray diffraction (WAXD) spectra of polymers in film form were recorded using Rigaku X-ray diffractometer (*D*-max 2500) with CuKα radiation (Fig. 3). The density (ρ) measurements were carried out at 35 °C by the floatation method using ~100 μm thick films (except for DSPBI-BuI) using 1,2-dibromobenzene and cyclohexanone mixture. Prior to the density estimation, it was confirmed that the sorption

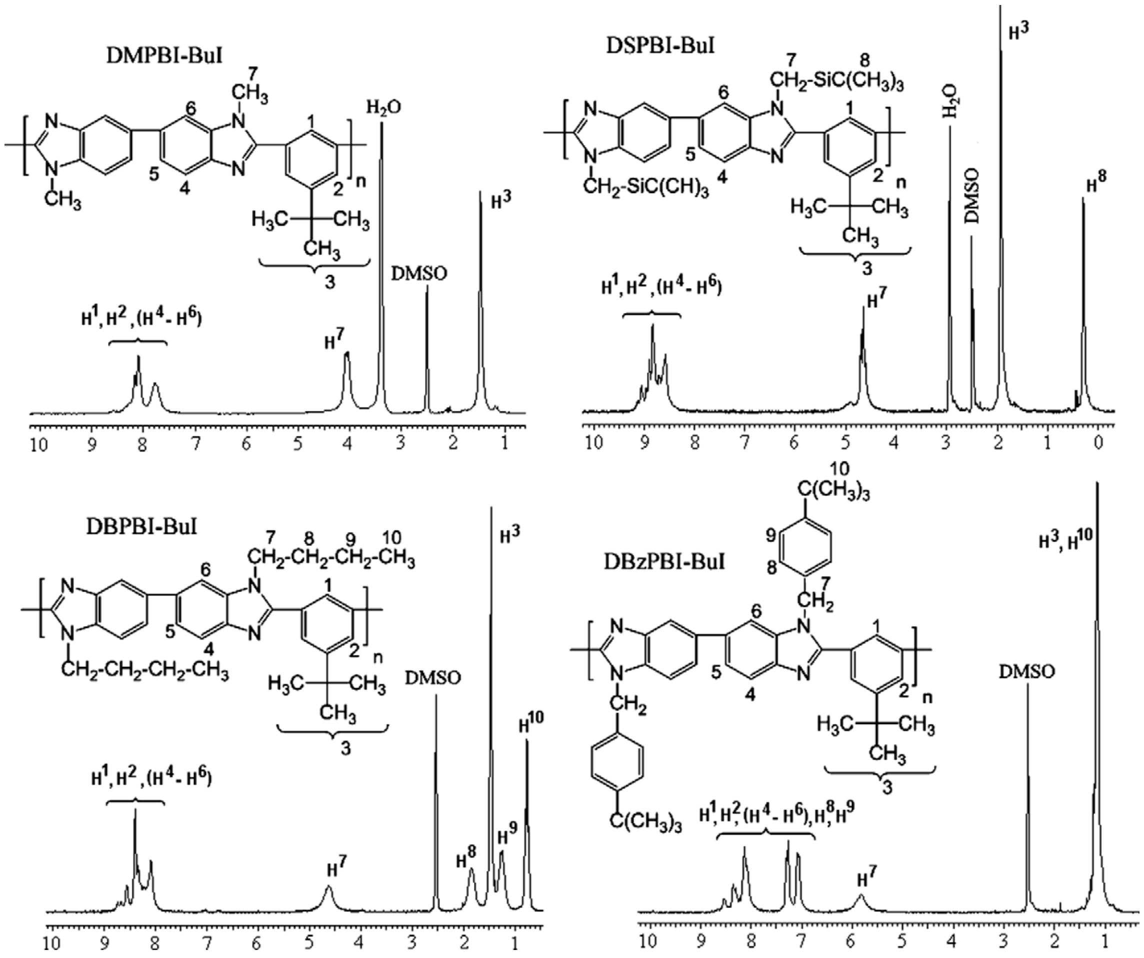


Fig. 1b. ^{1}H NMR spectra of *N*-substituted PBI-BuI.

Table 1
Solubility of *N*-substituted PBI in common solvents.

Solvent	DMF	DMAc	DMSO	NMP	$CHCl_3$	TCE	THF	H_2SO_4	CH_3SO_3H	HCOOH	CF_3COOH
DMPBI-I	–	–	–	++	–	±	–	++	++	++	++
DBPBI-I	±	++	–	++	++	++	±	++	++	++	++
DSPBI-I	±	++	±	++	±	++	–	++	++	++	++
DBzPBI-I	++	++	–	++	++	++	++	++	++	++	++
DMPBI-BuI	++	++	+	++	++	++	–	++	++	++	++
DBPBI-BuI	++	++	–	++	++	++	±	++	++	++	++
DSPBI-BuI	++	++	+	++	++	++	±	++	++	++	++
DBzPBI-BuI	+	+	+	+	++	++	±	++	++	++	++

++: soluble at ambient temperature; +: soluble after heating at 80 °C for 18 h; ±: partially soluble or swelling after heating; –: insoluble after heating.

of these solvents in all *N*-substituted PBI was negligible (<0.7%) for a period of 2 h exposure. DSPBI-BuI was found to have higher uptake of 1,2-dibromobenzene. Thus, a mixture of carbon tetrachloride and decalin in which DSPBI-BuI showed negligible sorption was used as a solvent pair for determination of the polymer density. Measurements were repeated at least with five different film samples of a polymer. The deviation in density measurements for a polymer was found to be ±0.007 g/cm^3. Based on the density determination, fractional free volume [$v_f = (V_{sp} - V_w)/V_{sp}$] and solubility parameter [$\delta = (E_{coh}/V)^{1/2}$] were estimated by group contribution method [22]; where V_{sp} is the specific volume (ratio of repeat unit molecular weight and density), V_w is the van der Waal's volume, E_{coh} is the cohesive energy and V is the molar volume of the polymer. Thermogravimetric analysis (TGA) was performed on

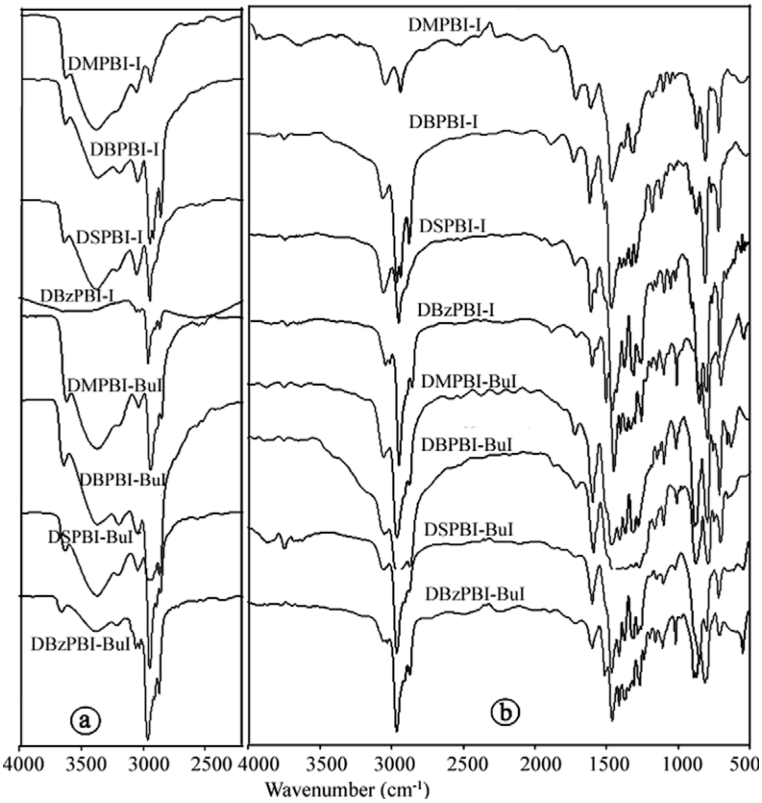


Fig. 2. FT-IR spectra of *N*-substituted polybenzimidazoles at (a) ambient and (b) 150 °C.

Perkin-Elmer TGA-7 in a N_2 atmosphere with a heating rate of 10 °C/min (Fig. 4). The glass transition temperature (T_g) was recorded on DSC Q-10 (TA instruments) in N_2 atmosphere with a heating rate of 10 °C/min. Physical properties thus determined are summarized in Table 2.

2.5. Gas permeability

Permeability measurements using pure gases, viz., He and Ar were carried out by standard variable volume method [23] at upstream gas pressure of 20 atm at 35 °C, while maintaining permeate side at the atmospheric pressure. Membrane samples of 7.5 cm diameter and 25–30 μm thickness were used. The permeability was determined using the following equation:

$$P = \frac{Nl}{p_2 - p_1}$$

where P is the permeability coefficient expressed in Barrer, p_1 and p_2 are the permeate side and feed side pressure (cm Hg), respectively, l is the membrane thickness (cm) and N is the steady-state flux (cm^3/s). Permeation measurements were repeated with at least four different membrane samples prepared under identical conditions and the data averaged as given in Table 2. The variation in permeability measurement was up to ±10% for these gases. The ideal selectivity, P_{He}/P_{Ar} was calculated by taking ratio of pure gas permeability.

3. Results and discussion

3.1. Synthesis, ^{1}H NMR and FT-IR characterization

A synthetic route to the *N*-substitution of chosen PBIs is given in Scheme 1. Both, PBI-I and PBI-BuI reacted with NaH, developing a deep blood red colour to the reaction mixture. This indicated generation of the anion. In order to ensure completion of Na-salt formation, this homogeneous solution was further heated at 80 °C for an hour. Then temperature of the reaction mixture was lowered to the ambient. Alkyl halide (2 M equivalents) was added over a period of 15 min and was stirred further for 24 h. Addition of the reaction mixture onto the stirred water offered a pale yellow precipitate in all cases, except for the cases of *n*-butyl substitution of both PBIs, where a sticky light brown mass was obtained. After purification and drying, the yield was found to be almost quantitative for all *N*-substituted PBIs.

^{1}H NMR spectra (Fig. 1a and b) of all *N*-substituted PBI showed disappearance of imidazole N—H protons that appeared at $\delta \sim 13.3$ ppm in cases of unsubstituted PBIs [4,24]. The disappearance of this peak as well as the integration of peaks for the protons belonging to the added alkyl group indicated quantitative *N*-substitution, except for the case of methylene trimethylsilane substitution. In this case, though the disappearance of peak at $\delta \sim 13.3$ ppm was noted, the integration for trimethyl silyl group was less than as expected. This observation was noted for both the

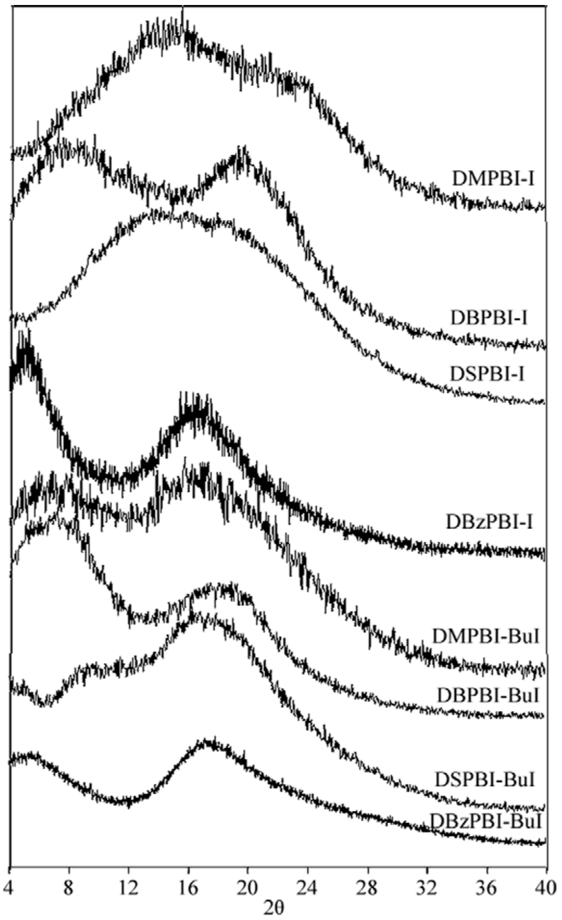


Fig. 3. WAXD spectra of *N*-substituted polybenzimidazoles.

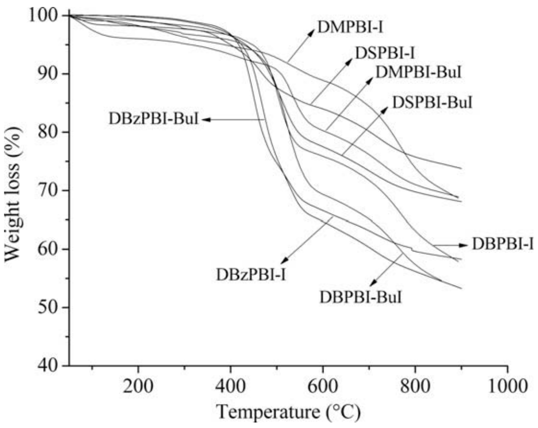


Fig. 4. TGA spectra of *N*-substituted polybenzimidazoles.

cases, viz., DSPBI-I and DSPBI-BuI and needs further investigations. Except for the 4-*tert*-butylbenzyl substitution, all *N*-substituted PBIs showed a peak at δ 3.93 to 4.72 ppm for methyl or methylene group attached to the nitrogen of the imidazole ring. In the case of 4-*tert*-butylbenzyl substitution, appearance of methylene protons shifted to further downfield (~5.7–5.83 ppm) due to deshielding effect of the adjacent phenyl ring.

FT-IR analysis showed peaks at ~3300 and ~3600 cm^{-1} (Fig. 2a). The nature of these peaks was different than the broad peaks appeared at 2400–3500 cm^{-1} for unsubstituted PBI, attributable to N—H stretching [4,7,25]. In case of substituted PBI, the peak appearing at ~3300 cm^{-1} could be attributed to the sorbed moisture, which could be assigned to hydrogen bonding of the type N- - -H—O—H, between imidazole '*N*' and water molecules. Intensity of this peak within a series of particular *N*-substituted PBI decreased in an order of substituent as: methyl > *n*-butyl ≈ methylene trimethylsilane > 4-*tert*-butylbenzyl. This trend followed the order of increased number of carbon atoms, which could be correlated to the increased order of hydrophobicity. The presence of water was also supported by a peak at ~3600 cm^{-1}, observed for all the polymers, attributable to the O—H stretching of absorbed water. Though films used for FT-IR analysis were vacuum dried, these peaks could have been originated because of moisture absorbed during handling or storage. Thus, these samples were scanned at 150 °C. It was found that peaks at 3300 and 3600 cm^{-1} were disappeared completely due to removal of moisture upon heating (Fig. 2b) for all the substituted PBIs. Absence of peak for N—H stretching confirmed that almost all the N—H sites of a PBI were substituted by the respective alkyl group. Peaks appearing in the range of 2800–2900 cm^{-1} were ascribed to the C—H stretching of methylene or methyl group. Intensity of these peaks was least for the methyl substitution cases (DMPBI-I and DMPBI-BuI) and was increased as the number of methyl or methylene groups in the particular substituent increased. The benzimidazole ring was characterized by the absorption at 1430, 1600, and 1620 cm^{-1} in all PBIs investigated [7].

3.2. Solvent solubility and viscosity

Elimination of intermolecular hydrogen bonding by *N*-substitution is anticipated to improve the solubility of resulting PBIs. It is known that dissolution of the PBI in organic solvents is sluggish due to intermolecular hydrogen bonding [12,13]. Solvent solubility of the present polymers was as shown in Table 1. These *N*-substituted PBIs were easily soluble at the ambient temperature in HCOOH, CF_3COOH, CH_3SO_3H and H_2SO_4. The methyl group substitution on PBI-I (DMPBI-I) did not show significant improvement in solubility, as it dissolved only in NMP and acidic solvents. On the other hand, DMPBI-BuI was soluble in all solvents used, except in THF. This enhanced solubility than that for DMPBI-I was attributed to the presence of *tert*-butyl group on the acid moiety in the repeat unit of DMPBI-BuI. The substitution of 4-*tert*-butylbenzyl, methylene trimethylsilane or *n*-butyl group on PBI-I and PBI-BuI rendered solubility even in chlorinated solvents ($CHCl_3$ and TCE). Thus, in general, *N*-substitution of PBI-I and PBI-BuI improved solvent solubility. Similar observations are reported in the literature. *N*-substitution of polybenzimidazole with organosilane derivatives [24] and by $-(CH_2)_{12}O(C{=}O)CH_2CPh_3$ group [14] imparted solubility in solvents such as $CHCl_3$, THF, etc. Pu and Liu [13] reported

Table 2
Physical properties of *N*-substituted PBI.

Polymer	η_{inh} (dL/g)	d_{sp} (Å)	ρ (g/cm^3)	υ_{f} (cm^3/cm^3)	T_g (°C)	TGA analysis		Permeation property		
						IDT[a] (°C)	W_{900}[b] (%)	P_{He}[c]	P_{Ar}[c]	$P_{\mathrm{He}}/P_{\mathrm{Ar}}$[d]
DMPBI-I	1.2	3.74	1.279	0.317	341	480	67.9	3.11	0.009	345
DBPBI-I	1.1	4.44	1.168	0.330	233	420	57.9	6.63	0.17	39
DSPBI-I	1.1	5.72	1.214	–	294	375	73	6.43	0.15	42.9
DBzPBI-I	0.9	5.34	1.131	0.344	239	330	58	17.96	0.83	21.6
DMPBI-BuI	1.4	5.22	1.196	0.325	361	500	68.4	11.76	0.37	31.8
DBPBI-BuI	1.2	4.67	1.124	0.332	270	440	54.6	21.26	1.29	16.5
DSPBI-BuI	1.3	5.02	1.146	–	324	404	68	26.64	1.70	15.7
DBzPBI-BuI	1.0	5.22	1.097	0.348	261	370	53	38.28	3.24	11.8

[a] Initial decomposition temperature.
[b] Char yield at 900 °C.
[c] Pure gas permeability expressed in Barrer [1 Barrer = 10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cm Hg^{-1}].
[d] Permselectivity, a ratio of pure gas permeability.

improved solubility with an increase in alkyl chain length and alkylation degree of PBI in DMAc and NMP.

After *N*-substitution, the inherent viscosity (Table 2) was found to be lowered than that of respective parent PBIs. It was 1.4 dL/g for PBI-I and 1.5 dL/g for PBI-BuI. The lowering in viscosity could be ascribed to the elimination of hydrogen bonding interactions after the *N*-alkylation. Substitution by the methyl group showed highest viscosity among the respective PBI series, while 4-*tert*-butybenzyl substitution showed the lowest viscosity. This indicated that the substituent size and its flexibility also play a role in governing viscosity of substituted polymer, though the starting PBI was same for different substituents.

The density was lowered after the *N*-substitution of PBI-I or PBI-BuI. This could be attributed to the two simultaneous effects, viz., disruption of close chain packing due to the elimination of hydrogen bonding and an addition of bulk of substituent group, which would further push the polymer chains away from each other. It could also be seen from Table 2 that the extent of decrease in density for either PBI-I or PBI-BuI substitution was largest for the 4-*tert*-butylbenzyl as a substituent in comparison to the other substituent cases. It was observed that the effect of *N*-substitution in decreasing the density was more prominent for the initially dense packed PBI-I (decrease by 4–15%) than for the PBI-BuI (decrease by 0.3–8%), which was already loosely packed. The density of PBI-I (1.33 g/cm^3) was higher than PBI-BuI (1.19 g/cm^3) indicating that chains are closely packed in earlier case [4].

3.3. Packing density parameters

Chain packing density is commonly represented by the *d*-spacing (d_{sp}) determined by WAXD analysis and/or fractional free volume (υ_{f}) determined by semi-empirical method using experimentally measured density [4,22,26]. PBI-I is known to have closely packed structure as revealed by its low d_{sp} (4.05 Å) and υ_{f} (0.3096 cm^3/cm^3) [9]. *N*-substitution of PBI with alkyl groups of varying bulk would lead to variation in these packing density parameters. WAXD analysis indicated amorphous nature of these substituted polymers (Fig. 3). In many cases, more than one amorphous peaks were present, indicating that more than one type of chain packing arrangements co-exist in the polymer matrix. The d_{sp} corresponding to only the higher 2θ values are given in Table 2, since these domains would govern the penetrant diffusion properties. *N*-substitution in the case of PBI-I increased the d_{sp} of resulting polymers in the order of substituents as methyl < *n*-butyl < 4-*tert*-butylbenzyl < methylene trimethylsilane. However, *N*-substitution in the case of PBI-BuI did not show any such trend with respect to the nature of substituent group. This could be due to the initial more open structure of unsubstituted PBI-BuI (d_{sp} 4.69 Å) than for PBI-I (d_{sp} 4.04 Å) [9]. It is known that though both d_{sp} and υ_{f} are used as indices of the degree of ‘openness’ of the matrix, sometimes d_{sp} has limitations since it measures only the distance between the centres of masses of neighbouring chains [27].

In case of PBI-I substitution, fractional free volume (υ_{f}) was increased in the order of bulk of the substituent (methyl < *n*-butyl < 4-*tert*-butylbenzyl). The υ_{f} for methylene trimethylsilane substituted PBIs could not be calculated due to unavailability of the van der Waal’s volume of $\text{—Si(CH}_3)_3$ group. Conversely, high initial υ_{f} of PBI-BuI (0.339 cm^3/cm^3, [9]) was lowered by methyl (υ_{f} = 0.325 cm^3/cm^3) or *n*-butyl (υ_{f} = 0.332 cm^3/cm^3) substitution, indicating bulk of these groups could have been accommodated in the available free space of PBI-BuI matrix. Such cases of decreased υ_{f} by substitution of small alkyl groups like methyl is known in the cases of dimethylpolysulfone [28], dimethylpolyarylate [29], etc. Wilks et al. [30] observed that in case of rigid poly(norbornene) backbone, number of large free-volume elements decreased as the length of flexible aliphatic side chain increased. The bulky 4-*tert*-butylbenzyl substitution on PBI-BuI led to increased υ_{f}.

3.4. Gas permeability

In order to assess the effect of substitution, two gases (He and Ar) were chosen for permeability determination. Owing to non-interacting nature, their sorption in the polymer matrix is anticipated to be negligible. Thus, observed variation in permeation properties can be directly correlated to the variation in bulk size of substituents. The permeability coefficients and ideal selectivity (the ratio of pure gas permeability) for substituted PBIs are given in Table 2. It was seen that He permeability in a given polymer was higher than Ar permeability, owing to size of penetrant molecule. Within a series of either PBI-I or PBI-BuI, substitution by methyl group showed least permeability for a particular penetrant (He or Ar), while 4-*tert*-butylbenzyl substitution led to the highest permeability. Size of the substituent group which affects the chain packing density in polymer matrix would be responsible for this variation in permeability. It would be worth to compare van der Waal's volume (V_w [22]) of the substituent group. The same for methyl group is 13.67 cm^3/mol where as for *n*-butyl and 4-*tert*-butylbenzyl V_w is 44.36 and 97.89 cm^3/mol, respectively. V_w for methylene trimethylsilane was unavailable hence could not be compared. It was observed that the effect of *n*-butyl and methylene trimethylsilane substitution on permeation was more or less similar in magnitude as seen from Table 2. For different substituents present on either PBI-I or PBI-BuI, the selectivity (P_{He}/P_{Ar}) followed almost a reverse order than that followed for the permeability variations. It is said that a trade off exists between permselectivity and permeability in polymeric membranes [27].

Besides bulk of the substituent, nature of PBI used for *N*-substitution also had a significant effect on permeability. For example, He and Ar permeability in DBzPBI-I was 5.8 and 92 times higher than that of DMPBI-I, respectively. On the other hand, He and Ar permeability in DBzPBI-BuI was just 3.3 and 8.8 times higher than that of DMPBI-BuI, respectively. In other words, substitution effects to improve permeability were more prominent in case of PBI-I, than in the case of PBI-BuI substitution. This could be attributed to the initial open bulk of PBI-BuI than that of PBI-I. In later case, the chain packing density (either expressed in terms of v_f or d_{sp}) was higher than that of PBI-BuI [9]. Therefore, bulk of the added substituent have more pronounced effect on initial densely packed structure of PBI-I. In other words, PBI used for substitution also has its own effect in governing permeation properties, though the substituent group is the same. This fact would provide additional dimension for structural variation while aiming their application as the gas separation membrane materials.

It would be worth to compare the permeability of *N*-substituted PBI with their parent PBIs. He permeability for parent PBIs viz., PBI-I and PBI-BuI was 1.05 and 10.1, respectively [9]. Ar permeability in PBI-I was not measured, while its permeability in PBI-BuI was 0.16 Barrers [9]. In the cases of *N*-substitution of PBI-I by substituents studied, He permeability was increased by 3–17 times. In case of *N*-substitution of PBI-BuI by these substituents, increase in He permeability was by 1.2–3.8 times.

These initial explorations based on inert gas (He and Ar) permeability measurement suggested the promises of *N*-substitution towards improving permeation properties. This is depicted by certain examples from the present study. The P_{He}/P_{Ar} selectivity for DMPBI-I was 345, which is highly attractive, though the He permeability for this polymer is 3.11 Barrer. On the other hand, *n*-butyl and methylene trimethylsilane group substitution, especially on PBI-I exhibited appreciable combination of permeability and selectivity. This indicates a need for detailed investigation on gas sorption, diffusion, permeability and respective selectivity elucidations for commercially useful gases such as H_2, N_2, O_2, CH_4, CO_2, etc.; where not only the diffusion but sorption characteristics also play a crucial role in governing gas permeation properties.

3.5. Thermal properties

An introduction of flexible group led to lowering in T_g, as was evident from the comparison of T_g of *N*-substituted PBI-I with that of unsubstituted PBI-I (∼416–435 °C) [5–9]. This decrease in T_g could also be correlated to the elimination of hydrogen bonding after the *N*-substitution. It has been reported for PBI blends with polyimide that the hydrogen bonding is one of the important factors which influences T_g of the blends [31]. Nakamura et al. [32] reported an increase in T_g of polyhydroxy-styrene derivatives with increasing mole fraction of hydroxystyrene due to hydrogen bonding through hydroxyl groups. In present cases, an extent of decrease in T_g by methyl group was lesser than by the any other substituent, which could be correlated to the flexibility in these added groups. It was observed that *N*-substitution of PBI-BuI with a particular alkyl group showed higher T_g than for its substitution on PBI-I. Thus, it could be inferred that PBI-BuI could have higher T_g than that of PBI-I. During our earlier work also, T_g of PBI-BuI could not be detected even after repeated cycles of heating and cooling [9].

The initial decomposition temperature (IDT) of PBI-I and PBI-BuI were 600 and 525 °C, respectively [9]. Thermal stability after *N*-substitution was found to be decreased (Fig. 4), as evident from the lowering in initial decomposition temperature of substituted PBIs as given in Table 2. The methyl substituted PBI showed highest thermal stability, whereas, 4-*tert*-butylbenzyl substituted PBI showed the lowest thermal stability in a series. This decrease in thermal stability could be attributed to the addition of flexible alkyl group, susceptible for degradation. It is reported that *N*-substitution of polyamide-imide by alkyl groups (methyl, ethyl and *n*-butyl) led to a small decrease in thermal stability [33]. On the other hand, Chen et al. reported significant deterioration of thermal stability of poly(*p*-phenylene) after alkylation with isopropyl and isoamyl groups [34]. The IDT of poly(*p*-phenylene) was 650 °C while alkylated poly(*p*-phenylene) showed IDT of 174 °C. This decrease was attributed to the presence of alkyl groups which are well known as susceptible to elevated temperatures. Elimination of hydrogen bonding after the *N*-substitution leading to lowering in intermolecular attractions could also be another reason for lowering thermal properties. The char yields for all these *N*-substituted PBIs were high (45–73%).

4. Conclusions

N-Substituted PBIs were obtained with quantitative yield and degree of substitution. The spectral analysis by ^{1}H NMR and FT-IR indicated elimination of hydrogen bonding. All these polymers were amorphous in nature, as indicated by WAXD analysis, though they exhibited more than one type of chain packing arrangements. Bulk and flexibility of the added substituent had its own effects on physical properties of resulting *N*-substituted PBIs. Substitution by 4-*tert*-butyl benzyl group showed higher fractional free volume than that by methyl or *n*-butyl group substitution. Solvent solubility was enhanced in comparison to parent PBI cases, which were soluble only in DMAc or NMP. Some of the *N*-substituted PBIs were soluble even in chlorinated solvents. The T_g by methyl group substitution was highest in the series, while the same by 4-*tert*-butyl benzyl group was the lowest in the series based on either PBI-I or PBI-BuI. Thermal stability as revealed by TGA was reduced, as anticipated. These variations in properties in comparison to the parent PBI was due to both, an elimination of hydrogen bonding and addition of alkyl groups. The gas permeability was improved to a greater extent by 4-*tert*-butylbenzyl substitution than by methyl group substitution, while the ideal selectivity followed the reverse order. DMPBI-I showed high PHe/PAr selectivity of 345, while permeation characteristics of other substituted PBIs were also attractive and depicted that *N*-substitution can be a promising approach to improve gas permeation properties of PBI.

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