CHAPTER 3

N-Alkyl Polybenzimidazole: Effect of Alkyl Chain Length

3.1. INTRODUCTION:

Due to large demand of efficient, powerful and eco-friendly source of energy devices, polymer electrolyte membrane fuel cell (PEMFC) has become the one of the most promising candidate for mobile and as well as stationary applications. Although varieties of PEMs are known in the literature, till today the perfluoro sulfonic acid based membrane (Nafion)\(^1\) is mostly used despite of many drawbacks like its high cost and relatively low stability at high temperature etc. As an alternative of Nafion, recently phosphoric acid (PA) doped polybenzimidazole (PBI) membrane\(^2\) has been used and found to be the best alternative because of unique properties such as excellent thermochemical and mechanical stability,\(^3\) high proton conductivity up to 180 °C, zero water osmotic drag coefficient etc.\(^4\) However, one of the major drawbacks of PBI is its poor solubility in common organic solvents. It is soluble in only highly polar solvents like \(N,N\)-dimethyl acetamide (DMAc), \(N,N\)-dimethyl formamide (DMF), \(N\)-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) at higher temperature.\(^5\)\(^6\) Hence, structural modification of the PBI polymer to increase the solubility and processability in common organic solvents and low boiling solvents is one of the key challenges to be addressed for the development of PBI based PEMFC.

Till today many research groups made efforts to produce different types of PBI structure like poly(2,5-benzimidazole) (AB-PBI),\(^10\) sulfonated PBI,\(^11\)\(^13\) hyperbranched polybenzimidazole,\(^14\) crosslinked polybenzimidazole,\(^15\) pyridine based polybenzimidazole\(^16\) N-substituted polybenzimidazole etc.\(^17\)\(^31\) Unfortunately, the solubility and processability of PBI as discussed above are not resolved very satisfactorily. Among various efforts, it has been noticed that substitution on the \(-N\) atoms of the imidazole rings of the PBI backbone by appropriate functionalities resulted better solubility and processability of PBI in common organic solvents. Synthetically, PBI can be modified in two ways either by modification of monomers or substitution (grafting) to the \(-N\) atoms of mother PBI. PBI backbone has highly rigid rod aromatic structure which influences and controls the crucial physical properties of PBI. Upon grafting the PBI chain rigid structure might get affected which in turn may alters the mechanical strength, thermal stability and other physical properties. The chain flexibility which enhances the solubility of polymer can be adjusted by introducing the flexible group\(^32\)\(^33\) in the polymer backbone or by substitution in the \(-N\) atoms with alkyl,\(^30\) alkyl sulfonated\(^34\) or benzene sulfonate\(^54\) groups. However, a careful optimization has to be made between the chain flexibility and thermomechanical stability. Imidazolium hydrogens are acidic in nature; in each repeat unit backbone has two substitutable hydrogen atoms. So, when DMAc solution of PBI treated with alkali hydride like NaH at higher temperature, it forms a polyanion and then one can do substitution reaction with electrophile like \(R-\text{CH}_2-X\).

Earlier, it has been reported that the degree of substitution does not depend on the concentration of alkali hydride and electrophile.\(^23\) However, the effect of electrophile molecular size or other words the effect of alkyl chain length in case the electrophile is alkyl halide on the degree of substitution has not been
studied. PBI has very high glass transition temperature ($T_g > 400 \degree C$) attributing the rigid structure which resulting poor solubility. The very small free volume because of intra and inter hydrogen bonding in PBI are found to be the main reason for high $T_g$ and less solubility. It can be hypothesized that grafting of long alkyl chain in the PBI backbone may decrease the packing density and thereby increase the free volume by disrupting the hydrogen bonding which in turns decrease the $T_g$ and increase the flexibility of PBI. Earlier, in few reports it was observed that $T_g$ can be decrease with grafting, unfortunately no systematic study has been carried out to understand the effect alkyl chain length size on the $T_g$ and other physical properties. Also it will be interesting to analyze the effect of alkyl chain length on the properties of PA doped N-PBI.

In this Chapter, we have synthesized a series of N-alkyl grafted (ethyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl) polybenzimidazoles. The chemical modification of polybenzimidazole established by $^1$H NMR and FT-IR technique. The thermal stability, mechanical property and the glass transition temperature ($T_g$) are measured by thermogravimetric analyzer (TGA), dynamic mechanical analyzer (DMA), respectively. Efforts have been made to prepare PA doped membranes and all types of essential characterization were carried out to evaluate the potential of these acid doped membranes for their use as PEM in fuel cell. In this present work, our goal is to improve the flexibility and solubility of PBI by grafting alkyl chain in the backbone.

3.2. SYNTHESIS:

3.2.1. PBI Synthesis:

The synthetic procedure (Scheme 3.1) for PBI was similar to our earlier reports. Briefly the process was as follows: equal moles of TAB and IPA were taken into a three neck flask with PPA (115%) and the reaction mixture continuously stirred by mechanical stirrer in nitrogen atmosphere at 190-210 \degree C for 24 h. After completion of the reaction PBI was poured into water, the neutralized by sodium bicarbonate (NaHCO$_3$) and thoroughly washed with water. The PBI was dried in vacuum oven at 120 \degree C for 24 h. The inherent viscosity (IV) of polymer was measured to evaluate the molecular weight of the synthesized polymer. The measured IV of PBI was 1.02 dL/g at 30 \degree C in H$_2$SO$_4$ (98%).

Scheme 3.1. Synthesis of meta polybenzimidazole (m-PBI).
3.2.2. Synthesis of N-Alkyl Substituted PBI:

The different chain lengths (from C₂ to C₁₆) alkyl groups were substituted to the imidazole -NH functional group of the PBI backbone (Scheme 3.2). The reactions were carried out as follows: firstly 250 mL 0.5% (w/v) PBI (4.06 mmol) solution in DMAc solvent was prepared and the solution was filtered through 0.5 μm PTFE membrane. This PBI solution in DMAc was stirred in 500 mL three neck flask for 1 h at 30 °C in nitrogen atmosphere. Then 0.195 g (8.12 mmol) NaH was added and then stirring was continued for another 12 h. The PBI in DMAc solution became red in colour after addition of NaH. Then alkyl halide (8.12 mmol) was added to this solution and reflux at 100 °C for overnight (12 h). Then this solution was poured into ice-water mixture and filtered. The residue was thoroughly washed with water which was light brown colour. The N-substituted PBIs (N-PBIs) were kept in vacuum at 120 °C for 48 h to remove the moisture and other solvents.

3.3. CHARACTERISATION:

All the information about the materials used in this study and solubility test, membrane fabrication method from the synthesized N-PBIs and the experimental methods of all the characterization techniques which include viscosity, spectroscopic characterization by Fourier transform infrared spectroscopy (FT-IR) and proton NMR, X-ray diffraction (WAXD), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA), H₃PO₄ doping level, water uptake, swelling ratio, swelling volume and the proton conductivity measurements for all the N-PBI polymers are discussed in the Chapter 2.

3.4. RESULTS AND DISCUSSION:

3.4.1. FT-IR and ¹H NMR Characterization:

The linear alkyl chains of different chain lengths (C₂-C₁₆) are grafted to the backbone of PBI using reaction conditions as presented in Scheme 3.2. FT-IR and ¹H NMR spectroscopy were used to...
characterize the grafting of alkyl chains in the backbone. The FT-IR spectra of parent PBI and alkyl grafted PBI (N-PBI) membranes are shown in Figure 3.1. PBI is hygroscopic in nature and can absorb moisture up to 5-15% of its weight. The presence of O-H stretching frequency at 3620 cm⁻¹ is confirmed the hygroscopic nature of parent PBI and N-PBIs. Figure 3.1 shows that with increasing alkyl chain length, the intensity of O-H stretching frequency gradually decreases which indicates the hydrophilic nature of alkyl grafted PBI decreases owing to the hydrophobic character of alkyl chain. The broad peak at 3415 cm⁻¹ because of free N-H stretching frequency of benzimidazole is present in N-PBIs with almost negligible intensity indicating that partial alkyl substitution has taken place in imidazole group. The bands at ~2943 cm⁻¹ and ~2865 cm⁻¹ are the C-H stretching frequency of methyl and methylene (near to N atom of benzimidazole) group of long alkyl chain, respectively. A characteristic absorption band near at ~3063 cm⁻¹ is attributing to aromatic C-H stretching frequency. The presence of both imidazole -NH group and long alkyl chain in the N-PBIs indicates that 100% alkyl substitution did not take place and therefore the molecular structure of the N-PBIs is as shown in Scheme 3.2. Hence it becomes necessary to estimate the % of N-alkylation in N-PBIs and we have utilized NMR spectroscopy as described in the following section.

![Figure 3.1. FT-IR spectra of N-substituted Polybenzimidazoles (N-PBI) (A), magnified portion in the region 2500 to 3725 cm⁻¹ (B). All spectra recorded from the thin films (~40 μm).](image)

The representative ¹H NMR spectra of N-PBIs along with peak assignments and chemical structures are shown in Figure 3.2. The NMR signal matches perfectly as expected from the chemical structure. The characteristic aromatic C-H protons are appearing at δ ~7.5-9.5 ppm for all the N-PBI.
Signals at $\delta \sim 4.47$ ppm (denoted as g) for the methylene protons attached to imidazolium nitrogen atom. The other alkyl chain proton signals are appeared at $\delta \sim 1.72$, 1.04 and 0.7 ppm for h, i and j as denoted, respectively. The signals h, i for methylene groups and j for methyl group of alkyl chains. A careful analysis and comparison of methylene (4.47 ppm) and aromatic protons signals suggests partial N-alkylation. We estimated % of N-alkylation of N-PBIs from the $^1$H NMR peaks integral ratio (Table 3.1) which alters from 40% to 65% depending on the size of alkyl chain length. The % of N-alkylation are obtained from the $^1$H NMR peaks integral ratio of -NCH$_2$ ($\delta$ 4.47 ppm) and all aromatic hydrogens ($\delta$ 7.5-9.5). Higher % of N-alkylation observed in case of larger chain may be due to the better electrophilic character of long chain alkyl halides. The above estimation and the complicated aromatic protons peak patterns of N-PBIs compared to PBI ascribes the N-PBIs structure as shown in Scheme 3.2 which resembles the copolymer structure.

**Figure 3.2.** $^1$H NMR spectra of few representative N-substituted PBI along with parent PBI. DMSO-$d_6$ is used as NMR solvent.

3.4.2. Solubility Test:

The solubility of parent PBI and N-PBIs are checked in several common organic solvents like DMAc, NMP, DCM, THF, formic acid (FA), chloroform etc. and the solubility chart is shown in Table 3.1. It is clearly evident from the solubility chart (Table 3.1) that the PBI and N-PBIs are highly soluble in DMAc and NMP. Interestingly, N-PBIs show very high solubility in formic acid (FA) whereas parent PBI is partially soluble. This enhanced solubility of N-PBI is because after alkyl substitution the PBI backbone becomes less rigid (as seen from the $T_g$ data in the later section) by increasing their face-to-face packing distances.
N-substituted PBI (N-PBI)  |  Chapter 3

Table 3.1. Solubility of N-substituted PBI in different organic solvents and % of N-alkylation.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% of N-alkylation&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DMAc</th>
<th>NMP</th>
<th>FA</th>
<th>CH₂Cl₂</th>
<th>CHCl₃</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI</td>
<td>–</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PBI–C₂</td>
<td>42.25</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PBI–C₅</td>
<td>46.25</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PBI–C₆</td>
<td>50.25</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PBI–C₇</td>
<td>57.75</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PBI–C₁₀</td>
<td>60.75</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PBI–C₁₂</td>
<td>65.00</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PBI–C₁₄</td>
<td>63.50</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

++ : Soluble at ambient temperature; + : Partial solubility; - : Insoluble even after heating; solubility was carried out up to 3% (w/v) concentration.

<sup>a</sup> Estimated from the <sup>1</sup>H NMR peaks integral ratio of -NCH₂ (δ 4.47 ppm) and aromatic hydrogens.

Figure 3.3. Photographs of membranes casting from (A) DMAc, (B) formic acid solution of PBI and (C) DMAc, (D) formic acid of C₁₄ N-PBI samples.

(discussed in the WAXD section) which helps to decrease the self-association between the chains. FA is a low boiling solvent and hence one can readily remove the solvents to cast the film from the polymer solution. Earlier, we have observed that certain type of PBI structure like [poly(4,4ʹ-diphenylether-5,5ʹ-bibenzimidazole)], an ether linkage present in the polymer backbone, forms very transparent homogeneous films when films were made from FA solution. Therefore the solubility in FA helps easy processability. Table 3.1 clearly shows that N-PBIs have very high solubility compared to parent PBI which makes these modified PBI as easily processable material when FA is used as processing medium. Figure
3.3 compares the photographs of PBI and N-PBI membranes obtained from DMAc and FA. It is very clear from photographs that the N-PBI membranes obtained from FA are very much homogeneous and transparent compared to all other membranes. Also, parent PBI membrane from FA is mechanically weak owing to its low solubility as evident from the photographs. Therefore it can be summarized that N-substitution with alkyl group in the PBI backbone enhances the processability and solubility of rigid PBI.

3.4.3. Structural Prediction of N-PBIs:

3.4.3.1. Thermal Study:

The thermal stability of N-PBI samples obtained from TG-DTA studies under nitrogen atmosphere are presented in Figure 3.4. It is known that approximately 5-15% weight loss occurs for PBI due to its hygroscopic nature at 100 °C. We observed here from TGA that with increasing alkyl chain length the initial weight loss due to hygroscopic nature decreases indicating that N-PBIs are less hydrophilic than PBI, which is also observed from FT-IR studies presented in earlier section. Although N-PBIs are found to be less thermally stable compared to parent PBI, however all the samples show first major degradation above ~300 °C, indicating good and enough thermal stability for the use as thermally stable processable materials.

![TGA curves of N-PBI under N₂ atmosphere. Samples are separated in two figure for the clarity.](image)

**Figure 3.4.** TGA curves of N-PBI under N₂ atmosphere. Samples are separated in two figure for the clarity.

All the N-PBIs samples display weight losses in three stages; first one is at ~100 °C due to absorb moisture, the second weight loss is at ~300 °C followed by third weight loss at ~510 °C owing to the degradation of PBI backbone (Figure 3.4A & B). Parent PBI does not exhibit second weight loss at ~300 °C. This attributes that at ~300 °C, the grafted alkyl chains are knocked out form the PBI backbone. The extent of this weight loss for N-PBI samples increases with increasing alkyl chain length attributing the
fact that this weight loss is associated with N-substituted PBI backbone. Hence the second weight loss is
due to degradation of grafted alkyl chains. The degradation behaviour of N-PBIs also predicts the partial
grafting of alkyl group in the polymer backbone and copolymer type molecular structure as discussed in
the previous section from NMR results.

3.4.3.2. Thermo-mechanical Studies:
The effect of alkyl substitution on the glass transition temperature ($T_g$) and the mechanical
properties of the PBI are studied using DMA both in the sub-ambient temperature (-120 °C to 100 °C) as
well as in the higher temperature (100-450 °C). DMA data for both the temperature ranges are shown in
Figures 3.5 and 3.6. It is known that the peaks appeared in the loss modulus ($E''$) and tan δ plot
corresponds to the thermal transitions of the polymer. Parent PBI exhibits a transition at -78 °C (from $E''$
plot) [-71 °C from tan δ plot] which corresponds to the rotation of the m-phenylene ring. This transition
can be called as δ transition and it shifts towards higher temperature with increasing size of alkyl chain
length in case of N-PBIs (Figure 3.5, Figure 3.6 and Table 3.2). This indicates that the substituted alkyl
group interferes the m-phenylene ring rotation resulting the δ transition shift. Parent PBI also displays a
transition at ~30 °C which is known as γ transition, but this transition is absent in N-PBI (Figure 3.5). The
δ transition and $T_g$ values obtained from loss modulus ($E''$) and tan δ plots are listed in Table 3.2. The
parent PBI shows only one $T_g$ at 350 °C (tan δ, inset of Figure 3.6) which is in agreement with previous
results. DMA studies exhibit peculiar thermomechanical properties for N-PBI samples. The decrease in $T_g$
value compared to parent PBI is expected as flexible alkyl groups are incorporated in the PBI backbone; $T_g$
value of N-PBIs decreases with increasing alkyl chain length up to C7 (Table 3.2). We observed two distinct
$T_g$’s from C8 substitution onwards for all N-PBI (Table 3.2, Figure 3.5 and Figure 3.6); in which one $T_g$ ($T_{g1}$
<300 °C) appears much below than the parent PBI $T_g$ (~350 °C) and other $T_g$ ($T_{g2}$) appears quite close to
$T_g$ of parent PBI. It also must be noted that $T_{g1}$ decreases with increasing alkyl chain length; however $T_{g2}$
remains almost unaltered with size of alkyl chain length. The presence of two $T_g$’s and variation of one $T_g$
with altering the chemical structures clearly attributes the copolymer structure of the N-PBI backbone. The
lower $T_g$ ($T_{g1}$) is the segmental motion of the PBI backbone in which N-substitution has taken place with
the alkyl chain and the higher $T_g$ ($T_{g2}$) is the segmental motion of the unsubstituted PBI backbone. The
alteration in $T_{g1}$ with increasing alkyl chain length is due to the increase alkyl size and this result again
confirms that $T_{g1}$ is the N-PBI $T_g$. The other $T_g$ ($T_{g2}$) does not display the variation much since this is the $T_g$
for unsubstituted PBI, whatever little variation is observed that is because of the effect of $T_{g1}$. So the above
discussion clearly attributed the copolymer nature of N-PBI which consists of alkyl substituted and
unsubstituted PBI chains. Our above DMA results are also tally with our TGA observation. The overall
decrease of $T_g$ drives the enhanced solubility of N-PBIs.
Figure 3.5. Temperature dependent (-120 to 100 °C) plots of mechanical properties obtained from DMA of N-PBI samples; (A & D) storage modulus (E'), (B & E) loss modulus (E'') and (C & F) tan δ. Samples are separated into two figures for the clarity of presentation.
Figure 3.6. Temperature dependent (100-450 °C) plots of mechanical properties obtained from DMA of N-PBI samples: (A & D) storage modulus (E'), (B & E) loss modulus (E'') and (C & F) tan δ. Inset of (C) is the magnified tan δ plot of parent PBI. Samples are separated into two figures for the clarity of presentation.
**Table 3.2.** Various thermal transitions data of N-PBI films obtained from DMA study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g (^{\circ}C)$ from $E''$</th>
<th>$T_g (^{\circ}C)$ from Tan $\delta$</th>
<th>$\delta (^{\circ}C)$ from $E''$</th>
<th>$\delta (^{\circ}C)$ from Tan $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI</td>
<td>327</td>
<td>350</td>
<td>−78</td>
<td>−71</td>
</tr>
<tr>
<td>$C_5$</td>
<td>320</td>
<td>341</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>$C_6$</td>
<td>297</td>
<td>324</td>
<td>−62</td>
<td>−58</td>
</tr>
<tr>
<td>$C_7$</td>
<td>275</td>
<td>309</td>
<td>−54</td>
<td>−55</td>
</tr>
<tr>
<td>$C_8$</td>
<td>279, 361</td>
<td>315</td>
<td>−57</td>
<td>−55</td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>240, 366</td>
<td>278, 343</td>
<td>−55</td>
<td>−54</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>225, 353</td>
<td>264, 340</td>
<td>−41</td>
<td>−32</td>
</tr>
<tr>
<td>$C_{14}$</td>
<td>215, 359</td>
<td>258, 335</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>$C_{16}$</td>
<td>220, 359</td>
<td>270, 330</td>
<td>−36</td>
<td>−27</td>
</tr>
</tbody>
</table>

**Figure 3.7.** Temperature dependent (first and second heating scans) plots of mechanical properties obtained from DMA of $C_{14}$ and $C_{16}$ N-PBI samples; (A) storage modulus ($E'$), (B) loss modulus ($E''$) and (C) tan $\delta$. Inset of (C) is the magnified second heating scan plot of $C_{14}$ and $C_{16}$ samples.
It is interesting to notice that very unusual storage modulus vs temperature dependence in case N-PBI (Figure 3.6A and Figure 3.5A). Storage modulus decreases with increasing temperature as expected, but once the $T_g$ range is crossed the rubber modulus increases sharply with increasing
temperature. This deep rubbery modulus is quite uncommon and very interesting. This kind of observation was observed earlier in case of PVDF/PMMA blend where deep rubbery modulus is explained as the result of non-equilibrium crystalline states of PVDF.\textsuperscript{41} But in the current system, no crystallization is observed since all PBI and N-PBI are amorphous in nature (discussed in later section). It is also noticed that (Figure 3.6) the deepness of rubbery modulus increases with increasing size of the alkyl chain length. We believe this deep rubbery modulus may be the result of following; as we increase the temperature the N-PBI shows the \( T_{g1} \) (N-substituted chains) at \(<300 \, ^\circ\text{C} \) (onset of deep is \(<300 \, ^\circ\text{C} \)), after that with increasing temperature the N-substituted part degrades; as seen in TGA studies where at \(~300 \, ^\circ\text{C} \) a major weight loss is observed and which varies with alkyl chain length size; and then only unsubstituted PBI exists which has \( T_g \) beyond \( 350 \, ^\circ\text{C} \) (\( T_{g2} \)). To display its \( T_g \) (\( T_{g2} \)), the unsubstituted PBI gains the modulus and exhibits its \( T_g \), therefore we observed the deep rubbery modulus. To confirm our argument that these deep is due to the degradation of N-substituted part, we have carried out DMA experiments (second heating) with the N-PBI samples which are already scanned in DMA from 100 \, ^\circ\text{C} \) to 400 \, ^\circ\text{C} \) and displayed the deep rubbery modulus. In the second heating scan in DMA (Figure 3.7) we observe no such deep in rubbery modulus and the second heating scan is exactly similar to parent PBI indicating that our claim of degradation of N-substitution is indeed correct. To prove it further we have recorded IR spectra of PBI and N-PBI samples after DMA scan and annealing at 400 \, ^\circ\text{C} \); and results are shown in Figure 3.8. It is clear that the parent PBI does not show any significant changes in the spectrum; however N-PBI spectra after annealing display a peak around \(~2235 \, \text{cm}^{-1} \) which corresponds to -C≡N vibration resulting from the degradation of imidazole group; attributing that N-substituted part are degrading after heating at 400 \, ^\circ\text{C} \).

3.4.3.3. X-ray Study:

The wide angle X-ray diffraction (WAXD) patterns of the parent PBI and representative N-PBI samples are presented in Figure 3.9. Absence of any sharp peak in all the samples suggests the amorphous nature of all N-PBIs. It is known in the literature that PBI is amorphous in nature and our results indicate that substitution did not alter the amorphous nature of the PBI. Earlier several authors\textsuperscript{42-44} pointed out two broad peaks at around \(~25 \) and 11° 2\( \theta \) for the PBI. These peaks are correspondence to \( d \)-spacing 3.64 and 7.29 Å, respectively. The first \( d \)-spacing is the characteristic of the planes formed by face to face packing of PBI chain and the latter is due to the length of one repeat unit. Figure 3.8 clearly shows that in case of N-PBI samples the peak corresponding to 7.29 Å \( d \)-spacing does not alter with increasing alkyl length chain length. However \( d \)-spacing for face to face packing increases with increasing alkyl chain length size and reaches to maximum value at 4.38 Å (\( 2\theta = 20.25^\circ \)) for C\textsubscript{16} sample. These observations clearly attributes that with increasing alkyl chain length size the distance between the PBI chains are increasing and as a result the self-association between the PBI chains decreases with increasing alkyl
length. Therefore, substituted alkyl chains in the PBI backbone pushes the PBI chains apart and hence decrease the self-association between the chains. This hinted that the N-PBIs are less tightly packed. Earlier similar observation has been reported in the literature on N substitution of PBI. The increase d-spacing of face-to-face packing also helps to increase the solubility of N-PBIs.

We have monitored the d-spacing of face-to-face packing as a function of temperature for both parent PBI and N-PBI (C_{14} as a representative) and data are shown in Figure 3.10. Both the cases the d-spacing increase (2θ decreases) with increasing temperature indicating the increase in distance between the PBI chains. However in case of parent PBI a significant peak broadening is observed which is not observed in case of C_{14} N-PBI. This attributes that in case of N-PBI, part of the polymer chain has already been separated apart by the long alkyl chain.

In earlier section, we have concluded that the N-PBI samples have copolymer structure, in which one part is N-PBI and other part is unsubstituted PBI, and the N-PBI part degrades upon annealing at 400 °C. Figure 3.11 data reconfirms our claims. The WAXD pattern of N-PBI (C_{14}) samples recorded at room temperature after annealing at 400 °C for 30 min is similar with the parent PBI, indicating that the N-PBI structure is indeed a copolymer in nature and degradable at 400 °C.

![Figure 3.11](image.jpg)

**Figure 3.11.** WAXD patterns of PBI, C_{14} samples and C_{14} sample after annealing at 400 °C for 30 min.

### 3.4.4. Studies of Crucial PEM Membrane Properties of N-PBIs:

#### 3.4.4.1. Water Uptake, Swelling Ratio and Volume:

It is well known that PBI is hydrophilic and moisture sensitive. Even at room temperature PBI can absorb water up to 15 wt% when dipped into deionized water for several days. This may be due to
hydrogen bonding formation between two nitrogen atoms of amine and imine groups.\textsuperscript{45,46} In the imidazole moiety there are two nitrogen atoms one is proton accepter and one is proton donor and these nitrogen atoms undergo hydrogen bonding readily with H\textsubscript{2}O molecule. Figure 3.12 displays that the water absorption capacity gradually decreases with increasing size of the alkyl chain length. In our earlier sections (FT-IR and TGA study), we have seen the exactly similar observation where we demonstrated that the hydrophobic alkyl chain grafting onto the PBI backbone decreases the hydrophilic nature of N-PBI. In the polymer backbone there are two parts, one is nitrogen containing polybenzimidazole which is hygroscopic in nature and another is polymer chain grafted with hydrophobic long alkyl chain. All polymers have the same hydrophilic part but due to different alkyl chain length which is hydrophobic, the hydrophilic nature of whole polymer backbone governed by the size of alkyl length. With increase of alkyl chain length the hydrophobic nature of N-PBI increases resulting lower water absorption by N-PBI. Also since % of N-alkylation increases with increasing alkyl chain length (Table 3.1) hence more hydrophobic character of N-PBIs is expected. Figure 3.13 represents the swelling ratio (SR) and volume (SV) data as a function of number of alkyl carbon atoms substituted in N-PBI. Both SR and SV alter significantly after grafting with the alkyl substitution and decreases with increasing size of alkyl chain length. This is primarily due to the increase hydrophobic nature of N-PBI. Also, we have noticed using X-ray studies that molecular packing (density) decreases with increasing alkyl length, which in turns creates more voids between the chains in case of N-PBI compared to parent PBI. Hence N-PBI has very little chance to swell further upon absorbing water. Therefore it can be concluded that our water uptake and swelling studies data are in agreement with our other results.

![Figure 3.12. Water uptake of N-PBI samples.](image)
3.4.4.2. Acid Doping Level:

It is well known that mechanical properties become poorer for PA doped PBI membrane at high acid doping level although it exhibit higher proton conductivity. Proton conduction occurs in PA doped PBI polymer membranes is because of the presence of amine (\(-\text{NH}-\)) and imine (\(-\text{N}=\)) groups which are act as proton donor and proton acceptor, respectively. The amount of acid PBI can consume dictates proton conductivity of the doped PBI and it depends on the concentration of acid and also water uptake capacity of PBI.

Figure 3.13. (A) Swelling ratio and (B) swelling volume in water of N-PBI samples.

Figure 3.14. Phosphoric acid (PA) doping level of N-PBI samples; (A) PA loading vs PA concentration and (B) PA loading vs. number of carbon atom in alkyl chain.
As expected we can see from Figure 3.14 that PA loading of N-PBI membranes increases with increasing acid concentration. It may be noted that there is no definite trend of PA loading of N-PBI with the size of alkyl chain length (Figure 3.14A). To understand it more thoroughly we have plotted PA loading as a function of number of carbon atoms (Figure 3.14B). It has been observed that N-PBI membranes consume the maximum acid when the alkyl chain length is 6-12. We observe a maximum in Figure 3.14B plot and then gradual decrease. Hence among all N-PBI, when the alkyl chain length between 6 and 12, the PA loading is maximum. This could be explained as follows; when alkyl chain length increases the swelling ratio, water uptake, etc. decreases rapidly up to C₆ (as discussed in the previous section) then all these parameters saturate with increasing number of carbon atoms in the alkyl chain, therefore C₆-C₁₂ N-PBI can consume more acids.

### 3.4.4.3. Proton Conductivity Study:

Proton conductivities as a function of temperature from room temperature to 160 °C of all the PA doped N-PBI samples are measured. The proton conductivity data shown here are measured from PA doped N-PBI samples which are doped with 60% PA for seven days. As mention in the experimental section the conductivity data shown here is the second heating scan data. Figure 3.15 shows the plots of proton conductivity against the temperature. As expected in all the cases conductivity increases with increasing temperature and at 160 °C the conductivity of N-PBI samples in the order of ~10⁻² S/cm. Infact, it can be seen that there is no such definite trend of conductivity with alkyl chain length despite the fact that there PA loading is different. Hence it can be said that all N-PBI samples exhibit similar conducting behaviour. The PA loading largely depends on the molecular packing which need not necessarily alter the proton conductivity behaviour.

![Figure 3.15. Proton conductivity against temperature plots of N-PBI membranes.](image1)

![Figure 3.16. Arrhenius plots for the proton conduction of N-PBI samples.](image2)
Proton conductivity data plotted against temperature using the following Arrhenius type equation (3.1) and presented in Figure 3.16.

\[
\ln(\sigma T) = \ln(\sigma_o) - \frac{E_a}{RT} \tag{3.1}
\]

Where \(\sigma\) is proton conductivity of the PA doped membrane (S cm\(^{-1}\)), \(T\) is temperature (K), \(\sigma_o\) is the pre-exponential factor (S K\(^{-1}\) cm\(^{-1}\)), \(E_a\) is the proton conducting activation energy (KJ/mol) and \(R\) is the ideal gas constant (J mol\(^{-1}\) K\(^{-1}\)). All the plots fit well and suggesting Grotthuss mechanism. As it can be seen that; although their conductivity is almost identical, but the calculated \(E_a\) value depends on the size of the alkyl length. The \(E_a\) value exhibits a decreasing trend as length increases indicating the conductivity path depends on the size of the N-substitution alkyl chain length.

3.5. CONCLUSION:

N-alkyl polybenzimidazoles (N-PBI) of variable alkyl chain lengths are prepared and characterized thoroughly to elucidate the effect of alkyl chain length on the structure and properties of N-PBI. The enhanced solubility of N-PBIs in low boiling solvents like formic acid makes these PBI derivatives as readily processable materials and form homogeneous transparent membranes. TGA and in depth DMA studies suggest the copolymer nature of the N-PBIs chain structure in which one part is substituted PBI and other part is unsubstituted PBI. During the first heating scan in DMA in case of N-PBI samples an unusual deep rubbery modulus in the temperature dependent storage modulus plot is observed owing to the copolymer structure of the N-PBI chains. XRD study shows that the d spacing of face-to-face packing of the amorphous N-PBI chains increases with increasing alkyl chain length. Temperature dependent XRD study reconfirms the copolymer nature of N-PBI chains. N-PBI membranes have significantly lower water uptake, swelling ratio and volume compared to parent PBI. The PA doping level increases with increasing acid concentration and it reaches to maximum when alkyl chain length is 6-12. The conductivities of PA doped NPBI membranes at higher temperature are comparable with the parent PBI. In summary, a series of new PBI derivatives have been developed which are easily processable and possess all the essential characteristics to be an efficient polymer electrolyte membrane (PEM).
REFERENCES:


(33) Qian, G.; Smith, D. W.; Benicewicz, B. C. *Polymer* 2009, 50, 3911.


