CHAPTER 1

Introduction
1.1. HISTORY OF POLYBENZIMIDAZOLE (PBI):

Polybenzimidazoles are a class of thermally and chemically stable aromatic heterocyclic polymer. The concept of polybenzimidazole reported for the first time in a Patent (US Patent 2, 895, 948) in 1959 by Brinker and Robinson. Polybenzimidazole was first synthesized by Marvell and Vogel from Illinois University in 1961 just to obtain the material without any target. But later it was revealed that PBI has marvellous properties like high stability; especially thermally and chemically in drastic conditions. Due to demands of NASA scientists for fire and heat proof material; NASA and Air Force Material Laboratory (AFML) worked on several types of polybenzimidazole to fulfil their requirements and to get extensive properties to manufacture the flake and the fibre. They have explored and synthesized polybenzimidazoles for many good properties like flame retardation property, stable from radiation, excellent mechanical, thermal stabilities and strength retention over wide range of temperatures, toughness, chemically resistance and adhesion characteristics. After the discovery of these properties of the polybenzimidazole; NASA was collaborated with Celanese Company so that they (Celanese) could produce large amounts of PBI which NASA could use as fire resistance jackets and make adhesive foams and fibre for their requirements. In the 1980’s, low molecular weight polybenzimidazoles were marketed under the name of “Celazole” as moulding resins. Then 20 years later, in 1983 Celanese Company marketed polybenzimidazole with meta phenylene linkage, poly[2,2’-(m-phenylene)-5,5’-bibenzimidazole] as “PBI” for the use in wide range of textile fibers. Thereafter, Celanese Company started production of large amount of PBI and they have marketed PBI world-wide. Due to high performance fibres, PBI has been used for several decades for high comfort, non-flammable fabrics and used as flight suits, fireproof clothing and hand gloves for astronauts and pilots. Due to its outstanding fibre, film or membranes formation capability; it has been used in numerous industrial applications. To enhance the properties of PBI, several research groups have made their efforts and the reviews of such have come out in literature.

1.2. SYNTHESIS OF POLYBENZIMIDAZOLES:

After the synthesis of polybenzimidazole by Marvell and Vogel in 1961, the polymerization techniques to make PBI have been explored in different ways. The general synthetic procedure of PBI is the polycondensation reaction of aromatic tetramines (bis-ω-diamines) and aromatic dicarboxylates (acid, ester or amides). Although different types of techniques are available in literature; the most popular and well known technique is solution medium polycondensation using polyphosphoric acid (PPA). Different types of monomers (tetramines and dicarboxylates) which have been used are tabulated in the Table 1.1. This is a representative list of monomers which were used very often, there are several other monomer, are also known in the literature. All the different techniques are carried out at higher heating condition and
under nitrogen atmosphere. These varieties of polycondensation techniques are briefly discussed in the following sections:

**Table 1.1.** Different types of aromatic tetramine and dicarboxylic acid monomers along with their melting points (MP) for the synthesis of polybenzimidazole (PBI).

<table>
<thead>
<tr>
<th>Tetramine Monomer</th>
<th>MP (°C)</th>
<th>Dicarboxylic Monomer</th>
<th>MP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,4,5-Tetraminobenzene</td>
<td>275</td>
<td>HOOC-○-COOH</td>
<td>342</td>
</tr>
<tr>
<td>2,3,6,7-Tetraminonaphthaline</td>
<td>178</td>
<td>Benzene-1,3-(dicarboxylicacid)</td>
<td>&gt;300</td>
</tr>
<tr>
<td>1,2,5,6-Tetraminonaphthaline</td>
<td>—</td>
<td>Benzene-1,4-(dicarboxylicacid)</td>
<td>—</td>
</tr>
<tr>
<td>3,3',4,4'-Tetraminobiphenyl</td>
<td>150</td>
<td>Pyridine-2,5-(dicarboxylicacid)</td>
<td>245</td>
</tr>
<tr>
<td>3,3',4,4'-Tetraminodiphenylether</td>
<td>—</td>
<td>Pyridine-2,6-(dicarboxylicacid)</td>
<td>249</td>
</tr>
<tr>
<td>3,3',4,4'-Tetraminodiphenylsulfide</td>
<td>102</td>
<td>Naphthalene-1,5-(dicarboxylicacid)</td>
<td>—</td>
</tr>
<tr>
<td>3,3',4,4'-Tetraminobenzophenone</td>
<td>174</td>
<td>HOOC-○-COOH</td>
<td>&gt;300</td>
</tr>
<tr>
<td>3,3',4,4'-Tetraminodiphenylsulfone</td>
<td>217</td>
<td>4,4'-Oxybis(benzoicacid)</td>
<td>—</td>
</tr>
<tr>
<td>2,6-bis(3,4-diaminophenyl)-4-phenylpyridine</td>
<td>221</td>
<td>4,4'-Thiobis(benzoicacid)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Benzophenone-4,4'-dicarboxylicacid</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4,4'-(Hexafluoroisopropylidene)bis(benzoicacid)</td>
<td>272</td>
</tr>
</tbody>
</table>
1.2.1. Melt Polymerization:

The melt polymerization technique\textsuperscript{2-4} is mainly carried out between the tetramine and diacid or their ester derivative at higher temperature and under nitrogen atmosphere. This is a two stage process; in the first step equimolecular mixture of tetramine (TAB) and the dicarboxylates [like (isophthalic acid (IPA), diphenyl isophthalate (DPIP) or dimethyl isophthalate (DMIP)] are mixed at 200 °C to 300 °C and in the second step melted and solidified reaction mixture is pulverized at a reduced atmosphere and further increased the temperature to 350-400 °C. The reaction technique and the condition are shown in the Scheme 1.1. The main disadvantage of the two stage melt polymerization is the making of foam due to the formation of phenol or water as a by-product.

\begin{center}
\includegraphics[width=\textwidth]{Scheme1.png}
\end{center}

\textit{Scheme 1.1. Two steps melt polycondensation for polybenzimidazole (PBI) synthesis.}

1.2.2. Solution Polymerization:

In solution polymerization, high boiling solvents such as N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF) were used.\textsuperscript{16-18} But the main drawbacks of these methods are the resulting PBI has low molecular weight as evident from low inherent viscosity (IV) of the polymer solution. The higher molecular weight (MW) can be obtained at higher temperature, but at that temperature (more than 200 °C) the solvents evaporates from the reaction medium and the reaction mixture turns into a melted and solidified product which is quite difficult to remove from the process. Iwakura et al.\textsuperscript{19} reported first time in 1964, the solution polymerization of PBI using PPA, where PPA was used as solvent and as well as catalyst for polyheterocyclization reactions.\textsuperscript{20-22} In this procedure equimolecular tetraamine and the dicarboxylic acid were taken in the polyphosphoric acid (PPA) medium and the reaction mixture was keep under continuous flow of nitrogen gas at 180-210 °C for 24 h. When diamine have counter acid salts then at first tetramines are kept at 140 °C for complete removal of the hydrochloride (HCl)\textsuperscript{6} gas and then add
the equal moles of dicarboxylic acid. The continuous nitrogen flow is required for the removal of by product like water or phenol from the reaction mixture. The main advantages of the PPA medium is high MW PBI can be synthesized and the polymer product can be easily processed from the reaction mixture at the hot condition. The reaction procedure and the condition for PPA based solutions polycondensation of PBI are shown in the Scheme 1.2.

\[
\begin{align*}
\text{Scheme 1.2.} & \quad \text{Solution polymerization process for synthesis of polybenzimidazole (PBI) in polyphosphoric acid (PPA) medium.}
\end{align*}
\]

1.2.3. Use of Catalyst for PBI Synthesis:

In catalytic polymerization technique several research groups have put in their efforts. In this technique 3,3',4,4'-tetrathomobiphenyl (TAB) as well as isophthalic acid as monomer and diphenyl isophthalate, dichlorophenylphosphone, chlorophenylphosphone, triphenyl phosphite, diphenylphosphine oxide, diphenyl chlorophosphate, triphenyl phosphate, dimethoxyphenylphosphine, dibutoxyphenylphosphine, o-phenyl phosphorochloridate, phenyl and dichlorodimethylsilane are used as a catalyst for the production of PBI. By these catalysts, PBI with IV > 0.7dL/g can be easily produced. It has also been demonstrated and reported in the literature that with the increase of catalyst concentration upto 1 wt% the MW gradually increases. The reaction procedure is shown in the Scheme 1.3.

\[
\begin{align*}
\text{Scheme 1.3.} & \quad \text{Catalytic polymerization process for polybenzimidazole (PBI) synthesis.}
\end{align*}
\]
1.3. STRUCTURAL VARIATION OF POLYBENZIMIDAZOLES:

After 1961 synthesis of polybenzimidazoles by Marvell et al. without any specific target, till now several research groups have modified the structure of high temperature resistance PBI. Commercially available PBI has been well explored since 1980 which is mostly used in different advanced fields. PBI has some different unique properties and difficulties that have been discussed in the next few sections. To improve the properties of PBI according to the requirements; scientist have made varieties of PBI. The varieties of PBI include poly[2,2′-(1,4-phenylene)-5,5′-bibenzimidazole] (known as p-PBI), poly(4,4′-diphenylether-5,5′-bibenzimidazole) (OPBI), poly(2,5-benzimidazole) (AB-PBI), pyridine based PBI (Py-PBI), sulfonated PBI, cross-linked and hyperbranched PBI, naphthalene based PBI, fluorinated PBI, N-substituted PBI (N-PBI), meta-para random PBI copolymer, PBI with sulfone or sulfonic acid groups in the backbone and many others. Due to highly rigid rod structure and strong inter-molecular and intra-molecular chain hydrogen bonding; its solubility is poor in common organic solvents. Varieties of PBI have been synthesized to monitor the properties. To improve the solubility of PBIs researchers have incorporated hetero atoms in the polymer main chain or by N-substitution post polymerization with sulfonic or the aliphatic groups. PBIs have acid uptake capability and hence incorporation of hetero atom in the polymer main chain can increase the acid doping level which is useful for fuel cell application. To increase the flexibility; PBI have been modified with main or side chain by incorporation of flexor like para linkage monomer or aliphatic group or bulky group containing hetero atom. Sulfonated acid group containing PBI can play an important role to increasing the water and acid uptake capacity. To improve the membrane quality, especially thermal and mechanical properties, many modifications have been explored. Recently our group has modified PBI with side and the main chain which increases solubility, flexibility and acid doping capability. The classification of PBI as shown in the next following sections is based on main chain repeat unit order, structures.

1.3.1. Polybenzimidazole Block Copolymer:

Monitor and control of extensive properties of PBI modifications have been carried out by changing the crucial structure. It is well known that polymer architecture has an influence on final polymer properties. The block copolymers can change morphology and the properties. In block copolymer (Figure 1.1) can make multiphase separation morphology observed due to the blocky nature and it reflects to the entire properties of the whole polymer. Sulfonic acid group containing PBI can absorb more amount of acid and water. For this reason Mader et al. has produced an alternative segmented block copolymer of PBI with one block part containing the sulfonic acid group. Lee et al. has made block PBI with sulfone containing poly (arylene ether) polymer which shows more acid loading and mechanical properties. Our group has successfully made the meta-para block PBI which shows excellent proton conductivity as well.
as thermomechanical properties (discussed in Chapter 6)\textsuperscript{55}. The multi block copolymer can make hydrophilic and hydrophobic phase separation which can make the entire ionic domain connected. Ng et al.\textsuperscript{56} prepared multi block poly arylene ether and PBI block copolymer, also.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Different types of polybenzimidazole (PBI) block copolymer.}
\end{figure}

\subsection{1.3.2. Polybenzimidazole Random Copolymer:}

It has been well reported and documented that the structural architecture can affect the several properties of polymer. Incorporation of hetero atom to the polymer back bone can change the mechanical, thermal and solubility of PBI polymer.\textsuperscript{35,57,58} To increase the solubility ether linkage can easily be introduced to the PBI backbone by random copolymerization.\textsuperscript{51,59} The incorporation of the hetero atom and bulky group to the polymer back bone increases the flexibility as well as the proton conductivity of the PBI.\textsuperscript{35} The sulfonic acid group containing PBI can alter the proton conductivity and the crucial physical properties as well. Sulfonic acid group can be incorporated into the polymer backbone by random copolymerization by introducing monomers which have the sulfonic acid group and it is the best technique to incorporate the sulfonic acid group in PBI backbone. The fluorine containing PBI\textsuperscript{35,44} shows the excellent thermal and mechanical properties that can be easily prepared by random copolymerization by opting fluorine containing monomers. Recently, our group has done three types random copolymers of PBI (a) meta and para PBI,\textsuperscript{48} (b) pyridine based meta and para PBI\textsuperscript{37} and (c) phenylene containing pyridine based meta and para PBI.\textsuperscript{60} In literature different type PBI have been explored to change the properties of PBI. Some of the representative random PBI copolymers are listed in the Figure 1.2.

\subsection{1.3.3. Polybenzimidazole Homo Polymer:}

Even though PBI shows good proton conductivity, thermal and mechanical stabilities but it has some limitation such as, it is soluble only in highly polar aprotic solvents like DMSO, DMAc and N-methyl pyrrolidone (NMP) etc.\textsuperscript{35,37,46} due to high rigid rod structure. To overcome this limitation, modifications have been done by incorporation of hetero atoms like N, S, O to the main chain or by incorporation of different
groups like hydroxyl, sulfonate, imidazole groups etc. Recently our group has done a series of pyridine based PBI which enhances the solubility as well as proton conductivity. Flexibility of PBI can be increased by introducing para linkage in the synthesized PBI. The glass transition temperature ($T_g$) of $p$-PBI decreased by around 60 °C in comparison to $m$-PBI. Fluorine containing PBI can be prepared by using different monomers which exhibits high thermal and chemical stability when compared to $m$-PBI. Few representative homopolymers are shown in the following Figure 1.3.

![Figure 1.2. Different types of polybenzimidazole (PBI) random copolymer.](image)

![Figure 1.3. Different types of polybenzimidazole (PBI) homo copolymer.](image)

### 1.3.4. N-substituted PBI:

Polybenzimidazole has amine (-NH-) group which is responsible for 'nucleophilic substitution reaction.' The -NH proton can be easily substituted by less reactive hydroxyethyl, sulfalkyl, etc.
cyanooethyl$^{64}$, phenyl$^{65}$, alkyl, alkenyl or aryl$^{66}$ groups. Sansone et al.$^{63-67}$ developed the methods of N-substitution in DMAc or NMP solution. Generally in the beginning PBI is dissolved in solvents and then a strong base like NaH is added for the replacement of hydrogen at higher temperature under inert atmosphere. After that, electrophiles are added to the reaction medium to get the N-substituted PBI.

Klaehn et al.$^{46}$ recently prepared the alkenyl organosilane (with -CH$_2$SiMe$_2$R where R = methyl, vinyl, allyl, hexyl, phenyl, and decyl) substituted PBI which are more and easily soluble in common organic solvents. Pu et al.$^{50}$ have made methyl and ethyl substituted PBI which improves the solubility and conductivity as well as decreases the glass transition ($T_g$). The general procedure of N-substitution of PBI is shown in the next chapter (Chapter 3). We have studied a series of N-alkyl (ethyl to hexadecyl)$^{45}$ substituted PBI which enhances the solubility in low boiling solvent like formic acid (FA) and decrease the rigidity and thermal stability (Chapter 3). Few representatives N-substituted PBI presented in the Figure 1.4.

\[\text{Figure 1.4. Different types of N-substituted polybenzimidazole (N-PBI) polymer.}\]

### 1.3.5. Pyridine Based PBI:

Pyridine dicarboxylic acid containing PBIs have been synthesized by different groups.$^{35-37}$ The polar pyridine ring containing (Figure 1.5) polybenzimidazole was first introduced Kalistus et al.$^{68}$ by incorporation of meta and para connection to the polymer main chain. The incorporation of extra hetero nitrogen atom to the polymer backbone changes the physical along with chemical properties. Xiao et
al.,\textsuperscript{21,36} proved that extra nitrogen atom containing pyridine group changes the solubility and the acid doping level with increase in the chemical stability. Recently our group has developed the pyridine ring containing PBI which shows high thermal stability. Our group\textsuperscript{35} has recently reported a series of pyridine ring containing phenylene group which increases flexibility, chemical stability, acid doping level in addition to proton conductivity.

\[ \text{Figure 1.5. Different types of pyridine based polybenzimidazole (Py-PBI) polymer.} \]

1.3.6. Cross-linked PBI:

In literature,\textsuperscript{39-42} cross-linked or hyperbranched PBIs are synthesized to increase thermal, chemical and mechanical stability. Generally three types of cross-links happen in case of PBI and these are:

(i) Covalent cross-linking: This happens when a covalent chemical bond is formed among polymer.

(ii) Ionic cross-linking: This takes place when the polymer chains are interacting by electrostatic or hydrogen bonding. This type generally observed in acid-base blend or acid-blend ionomers.

(iii) Mixed ionic-covalent cross-linking: This occurs when a mixture of the above two are found.

Kim et al.\textsuperscript{69} demonstrated that cross-linked PBI by 3-phenyl-3,4-dihydro-6-tert-butyl-2H-1,3-benzoxazine (pBUa) in DMAc at 220 °C shows high proton conductivity (0.12 S cm\textsuperscript{-1}) at 150 °C under anhydrous conditions. Aili et al.\textsuperscript{70} prepared cross-linked PBI by post-treatment with divinylsulfone which are more stable chemically as well as mechanically when compared to linear PBI. Han et al.\textsuperscript{71} obtained cross-linked PBI membranes by using 4,4'-diglycidyl(3,3',5,5'-tetramethylbiphenyl)epoxy resin (TMBP) as an cross-linker at 160 °C. They showed that the resulting PBI is chemically, mechanically stable with increase proton conductivity and decreased swelling in H\textsubscript{3}PO\textsubscript{4}. Luo et al.\textsuperscript{72} have prepared cross-linked PBI via a Diels-Alder reaction between vinylbenzyl functionalized PBI (PBI-VB) and α,α'-difurfuryloxy-p-xylene (DFX). They have shown the crosslinked PBI membrane improved mechanical strength, chemical stability as well as higher H\textsubscript{3}PO\textsubscript{4} retention ability. Fang's\textsuperscript{42,73} group made the hyperbranched PBI by using tetramine benzidine and benzene tricarboxylic acid which have more tensile strength in the region 4.1-4.9
GPa comparable to PBI membranes. Sheratte reported a cross-linked PBI and they have also obtained mechanically and chemically stable PBI. Few representative Cross-linked PBI structures are shown in Figure 1.6.

![Cross-linked PBI structures](image)

**Figure 1.6. Different types of cross-linked polybenzimidazole (PBI) polymer.**

### 1.4. PHYSICAL PROPERTIES OF POLYBENZIMIDAZOLE:

Polybenzimidazole (PBI) is an amorphous aromatic heterocyclic polymer which has a highly rigid rod structure. It has strong tendency to form intra and inter molecular hydrogen bonding through the imine (\(-\text{N}=\)) and amine (\(-\text{NH}^-\)) group which are represent in the imidazole group of the polymer main chain.\(^{58,75-77}\) Due to highly rigid rod structure it shows high thermal, mechanical and chemically, radiative stability.\(^{6-8}\) Due to these excellent properties it has numerous applications in different areas like chemical, aerospace, electrical industries, as a membrane and the most recent one is as a polymer electrolyte membrane (PEM) for application in the fuel cell. PBI has proton donor and acceptor side and for this reason it can consume acid via hydrogen bonding. The acid doped membranes are used as PEM in fuel cell.\(^{35,45}\) Due to highly rigid rod structure, PBIs are soluble only in few highly polar aprotic solvents like DMAc, DMF, dimethyl sulfoxide (DMSO), NMP.\(^{35,37,45}\) PBI shows higher glass transition temperature (\(T_g\)) around 400 °C.\(^{2,35}\) The PBI are absorbs light and very active as fluorescence molecules due to presence of non-bonding electron in the imidazole ring. Generally PBI shows only one absorption peak in DMAc dilute solution for \(\pi \rightarrow \pi^-\) transition with certain conformation in the chain.\(^{10,75,77}\) But recently, we have observed that at room temperature phenylated pyridine ring containing PBI (Py-PBIs)\(^{35}\) are showing two different absorption peaks due to the two different conformation of the phenyl group in the polymer chain. The absorption spectra in DMAc solution of PBI polymers shows distinct \(\pi \rightarrow \pi^-\) transition at 344 and 394 nm for meta (\(m\)}
The emission spectra of PBI in DMAc solution shows two distinct fluorescence bands at 398 and 416 nm which are due to $^1L_0$ state in the benzimidazole ring of PBI assigned to the 0 - 0 and 0 - 1 transitions from the excited state. Recently, our group has demonstrated that PBI forms aggregated structure in the solution like DMAc and formic acid. Literature also discussed the formation of gels of PBI in an appropriate concentration in different solvents.

1.4.1. Solubility:

The solubility of PBIs are restricted to only few highly polar aprotic solvents and few strong organic, inorganic acids due to presence of highly rigid rod structure for imidazole ring and formation of strong inter and intra hydrogen bonding. It is soluble only in DMAc, DMF, DMSO, NMP solvents which are highly polar and aprotic solvents. PBI are soluble in sulfuric acid ($H_2SO_4$), methane sulfonic acid ($CH_3SO_3H$), formic acid (FA) and in phosphoric acid ($H_3PO_4$). Recently, solubility in ionic liquid medium has been reported and fabrication of membrane from this solution was discussed. The solubility of PBI polymer depends upon the structure and still now many modifications have been found to increase solubility. N-substituted alkylated organosilane PBIs are soluble in organic medium. Recently, we have explored a series of N-alkylated PBI which are soluble in low boiling solvent like FA. Incorporation of hetero atom like N, S, O to the polymer main chain increases the solubility as well the flexibility. Recently we reported that phenylene pyridine ring incorporation to the PBI main chain increases the d-spacing of inter molecular chain distance and for this reason the solvents molecules goes to the inside of the polymer chain and hence the solubility increases. The other modification whereby incorporation of different groups to the polymer chain increases the solubility and processability such as the nitro, silane, hexafluoroisopropylidene, etc.

1.4.2. Viscosity and Molecular Weight:

The solubility of PBI is restricted to few solvents and hence most of the viscosity measurements are done extensively in DMAc, CH$_3$SO$_3$H, H$_2$SO$_4$. The viscosity of PBI depends upon the solvents due to the orientation of polymer chain in solution. According to the nature of solvent and the interaction between solvent and PBI, the dynamic radius of chains can alter and this affect the resulting viscosity. Most often viscosity measurement carried in conc. H$_2$SO$_4$ (96-98%) medium. Marvel had shown that the viscosity is 2 to 3 times more in FA and H$_2$SO$_4$ medium in comparison to DMSO. The inherent viscosity (IV) depends upon the moisture, temperature, solvent and the polymer character. The molecular weight (MW) can be calculated from the viscosity. Kozima et al. studied the molecular weight of OPBI in DMAc by light scattering and intrinsic viscometric study. Kozima also studied the molecular weight of OPBI in FA with the help of Mark-Houwink equation ([η] = $KM_0^a$) where ‘a’ and ‘k’ are the constant and
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depend on the character of polymer backbone and solvent. Recently our group has made an effort to measure the MW of PBI with the help of iso-ionic dilution method and by applying Mark-Houwink equation in formic acid in case of OPBI. The other well known technique to calculate the MW is by applying end group analysis with the help of $^1$H NMR analysis. This method can be applied in case of oligomeric PBI species. Several group have utilized gel permeable chromatography (GPC) and light scattering technique to measure the MW. However, the poor solubility and tendency to form aggregates, interferes these measurements and hence often the measured MW by these methods are found to be overestimated. All these measurement are carried out at 60-70 °C in presence of LiCl in the PBI in DMAc/DMSO solution.

1.4.3. Thermal Properties:

PBI is an ideal candidate as a high performance polymer owing to its high thermal stability. Marvel et al. at first experienced that at higher temperature PBI are stable and hence it can be used as a fire retardant material. To determine the thermal stability thermogravimetric analyzer (TGA) is the most reliable instrument and used very often to determine the PBI thermal stability. Literature reports conclude that PBI polymers are stable upto 600 °C under nitrogen (Figure 1.7) atmosphere and beyond this temperature degradation of PBIs backbone start with the release of carbon dioxide. The initial weight loss happens upto 5 wt% below 150 °C due to the loss of loosely bounded water molecules. It is well reported in literature that PBIs are hygroscopic in nature and it absorbs moisture from the atmosphere. The exceptionally high thermal stability of PBI polymers are mainly due to the following reasons:

(A) Strong inter and intra molecular hydrogen bonding.
(B) High extend of conjugation via imidazole ring to whole polymer chain.
(C) Highly rigid rod structure.
(D) “Bond healing” capabilities.

The thermal stability is less in an oxidative condition compared to inert atmosphere. The hetero atom containing -O- and -SO$_2$- linkage reduces the thermal stability of PBI due to the increase in flexibility and unsymmetrical structure. The introduction of methyl group into the imidazole ring of PBI causes the thermal stability to decrease. Recently we have studied a series of N-alkyl substituted PBIs and observed that with increase of alkyl chain length, the thermal stability gradually decreases. Our group has observed that the thermal stability of p-PBI is more than the m-PBI due to the presence of more symmetrical nature of para phenylene linkage in p-PBI.

PBIs are amorphous, thermo plastic in nature and they show high $T_g$ in between 350-450 °C. The $T_g$ can well be monitored by differential scanning calorimeter (DSC) and dynamical mechanical analysis (DMA) techniques. The $T_g$ truly depends on the internal chemical structure of the PBI chain. The crystallinity can be increase by introduce the hetero atoms like S, N, O, F etc. to the polymer
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The \( T_g \) also depends on the symmetrical nature of the polymer backbone. Recently, our group has demonstrated that the \( T_g \) of \( m \)-PBI (420 °C) is more than \( p \)-PBI (361 °C) owing to para phenylene linkage presence in the \( p \)-PBI chain which is more symmetrical in nature.\(^\text{48}\) Menczel observed that \( T_g \) of \( m \)-PBI by DSC and DMA that the \( T_g \) of the \( m \)-PBI polymer is 387 °C and calculated the \( \beta \)-relaxation at 290 °C associated with loss of water while the \( \gamma \)-transition at 20 °C which is not similar and he assign \( \delta \)-transition at 90 °C due to the rotation of the \( m \)-phenylene ring. Recently we have demonstrated the \( T_g \) gradually decreases with the increase in the alkyl chain length in imidazole ring due to the incorporating flexible alkyl chain.\(^\text{93}\) We have also demonstrated the incorporation of the extra nitrogen atom to the PBI backbone increases thermal transition temperature.\(^\text{35}\)

![Figure 1.7. Thermal stability of polybenzimidazole (PBI) polymer (adapted from reference 91a).](image)

1.4.4. Mechanical Properties:

PBIs has a highly rigid rod structure and has strong hydrogen bond formation tendency because of the presence of imine (-N=) and amine (-NH-) groups which helps in forming close packed structures and resulting in good mechanical stability (Figure 1.8).\(^\text{58,75-77}\) The mechanical strength of PBI is one of key parameters for application in fuel cell. The acid loaded PBI membranes show low mechanical properties which is not good for fuel cell. Below 2 moles of phosphoric acid (PA) loaded membrane decreases the cohesion force of PBI chains due to interaction of PA and imidazole group of PBI chains.\(^\text{94}\) If more acid loading in the PBI chain happens it further decreases the intermolecular interaction of PBI and hence the mechanical stability decreases. From DMAC casted membranes which have acid doping level, \(~5-6\text{ mole/repeat unit}\) is the optimum acid loading to maintain good mechanical stability.\(^\text{95}\) The mechanical stability depends on the internal chemical structure of PBI.\(^\text{31,37,38,43,96}\) To improve the mechanical stability of the PBI membranes researchers have made cross-linked and hyperbranched PBI.\(^\text{69,73}\) Li et al. made the
crosslinked PBI via p-xylene connection between the PBI chain molecules which shows 21-23 MPa more tensile in strength when compared to the parent PBI. The molecular weight of polymer also controls the mechanical stability of PBI, for example, from 20000 to 55000 gmol\(^{-1}\) the tensile strength increases from 4 to 12 MPa of acid doped PBI membranes.

1.4.5. Oxidative Stability:

In fuel cell application one of the most important parameters is the chemical stability of the membranes at drastic chemical environment. The oxidative stability (Figure 1.9) of PBI membranes has been extensively studied by the application of Fenton’s solution technique which is made from 3% H\(_2\)O\(_2\) solution in water containing the Fe\(^{2+}\) ion. Gaudiana and Conley\(^{101}\) show that in Fenton’s test, the produced hydroxyl (OH\(^{•}\)) and hydroperoxyl (OOH\(^{•}\)) radical attack the PBI weakest part, the nitrogen atom of imidazole ring in the polymer chain. The FT-IR study also has been studied to know the degradation procedure. Musto et al.\(^{102}\) shown that two new absorption peaks are formed which indicate that the degradation of PBI has taken place and the stretching vibrations of the product or intermediate of the polymer are identified. The oxidative stability depends on the chemical structure of the PBI backbone. The wt% loss varies during Fenton’s test and it can show 10-40 wt% degradation. The cross-linked PBI shows high oxidative stability rather than the mother PBI which is well reported in literature.\(^{71,97,103}\) To improve the chemical stability in drastic chemical condition, composite membranes of PBI have been reported.\(^{104-106}\)

Recently our group has demonstrated that the amine functionalized silica nano particle enhances oxidative stability in case of OPBI polymer.\(^{104}\) The hetero atom F containing PBI polymers are chemically more stable than the normal PBI.\(^{103,107}\) Our group has recently reported that hetero nitrogen atom can also improve the chemical oxidative stability.\(^{35}\)
1.4.6. Photophysical Properties:

PBI shows absorption (Figure 1.10A) and fluorescence (Figure 1.10B) properties both in solution and solid state. In literature, photophysical studies have been extensively studied to understand inter and intra molecular interaction with a particular solvent and the chain conformation, aggregation and gelation properties. Till now only very few reports have explored the chain conformation of PBI in solution due to the solubility problem of PBIs. The absorption as well as the emission depend on the internal structure of PBI and the solvents. PBI shows two different absorption peak at 340 nm and 440 nm due to $\pi-\pi^*$ and $n-\pi^*$ transition of imidazole moiety, respectively in N,N-dimethyl acetamide (DMAc) solution. Recently, Sannigrahi et al. observed that absorption spectra of PBI in DMAc solution shows distinct $\pi \rightarrow \pi^*$ transition at 344 and 394 nm for meta ($m$) and para ($p$) PBI, respectively due to enhancement of the conjugation of $p$-phenylene linkage into the polymer backbone. Recently, our group has demonstrated that the absorption maxima of PBI alters due to the different chemical environment of PBI backbone structure.

**Figure 1.9.** Thermochemical stability (Fenton test) of polybenzimidazole (adapted from reference 106).

**Figure 1.10.** (A) Absorption and (B) fluorescence emission spectra of meta ($m$)-para ($p$) random copolymers of PBI in DMAc solution (concentration is $2 \times 10^{-5}$ M) (adapted from reference 48).
PBI is fluorescence active and the quantum yield is also high (>0.5). The emission spectra of PBI also depends on the polymer backbone structure and the solvent. The emission spectra are obtained in both solution and solid state condition. The emission spectra of PBI in DMAc solution shows two distinct fluorescence bands at 398 and 416 nm due to \( \text{L}_b \) state in the benzimidazole ring assigned to the 0-0 and 0-1 transitions from the excited state. Recently, our group has demonstrated that PBIs are showing the aggregation properties in the solution like PBI in DMAc and OPBI in FA and the aggregation properties depends on the excitation wavelength.

### 1.4.7. Solution Properties:

Due to limitation of solubility of PBI, the solution properties have not been thoroughly investigated in literature. But few literatures, reported by us and others indicate that different solvents and different structures of PBI show the aggregation, gel and polyelectrolyte nature at varied concentration and temperature. From the solution properties we can understand the conformation and structural behavior of PBI chain easily. The following sections will briefly discuss the solutions properties:

#### 1.4.7.1. Aggregation Properties:

Aggregation in solution can happen due to covalent, hydrogen bonding, electrostatic attraction or Van der Waals force, hydrophobic and hydrophilic interaction of the polymer chains. The aggregation depends on solubility, concentration, polymer backbone structure, molecular weight, solvent and the temperature. Ogata et al. have studied the aggregation behaviour of polystyrene-\( b \)-poly(ethylene/butylene)-\( b \)-polystyrene triblock and Nuopponen et al. have studied poly(\( N \)-isopropylacrylamide-\( b \)-styrenes) diblock copolymer. They have tried to explore the aggregation behaviour of copolymer as it depends on solvent polarity. They have also explored the connection between solvent polarity and aggregation behaviour of the copolymer by comparing the aggregations in several solvents. PBI has one major problem which is solubility and due this the aggregation properties have not been explored much. Generally, the solubility decreases with increasing the molecular weight (MW). Kojima et al. have studied the aggregation of PBI and concluded that the overlapping of PBI chains as the cause of aggregation. Recently our group has explored the aggregation of PBI in DMAc by using viscosity, steady state and time dependent fluorescence techniques and our study revealed that the concentration dependent PBI chains make orientation from compact coil to an extended helical rod like structure. Our group has also demonstrated the aggregation behavior of poly(4,4'-diphenylether-5,5'-bibenzimidazole) (OPBI) in polar aprotic DMAc and protic FA solvents which depends on the polymer concentration and solution temperature. This study reveals that the swelling of OPBI happens in case of aprotic solvent but not in protic solvent. The temperature study shows the aggregation destabilizes when temperature is increased and the aggregation behavior is dependent on the solvent character as shown in Figure 1.11.
1.4.7.2. Gel Properties:

Polymer solutions and gels have great importance in bio and other applications. Gel formation can happen either physically or chemically, depending on the reversible or irreversible nature of the gel. Factors affecting gel formation include temperature, solvent polarity, polymer backbone structure, concentration, and MW. Chemical gel formation occurs due to the covalent bond of the polymer chain, interchain cross-linking, or hyperbranched polymer chains.

**Figure 1.11.** Schematic representation of the aggregation behavior of OPBI in DMAC and FA solvent with increasing concentration. Also, the stability of aggregated structures upon heating is shown (adapted from reference 159c).
Physical gel formation can happen due to the weak interaction with solvents and polymer chain hydrogen bonding, Van der Waals force or by electrostatic attraction of charged species of polymer backbone structure. The main attraction of the gel formation study reveals that (i) the crystal structure and morphology, (ii) the mechanism of gel formation and gel kinetics and (iii) the relation between structure and thermal study in order to understand several physical properties of the gel. Our group has demonstrated experimentally the formation of thermoreversible gel of PBI in H₃PO₄ and FA. The nature and the structure of the gel vary depending on the PBI structure and the solvent. The formation of PBI gel is found to be very attractive alternative to fabricates proton conducting membrane as described in Figure 1.12.

**Figure 1.12.** Thermoreversible gelation of polybenzimidazole (PBI) in phosphoric acid (PA) (adapted from reference 79).

### 1.5. APPLICATION OF PBI:

Since the discovery of polybenzimidazole by Vogel in 1960, numerous applications of PBI have been explored in several technologically important areas owing to its high thermal, chemical, mechanical stability and inflammable nature. PBIs is used in aerospace, aircraft, electrical, textile and chemical industries. It is being used in the air force as a fire proof jacket due to high thermal stability. Due to its good membrane forming property, these membranes have been used in reverse osmosis, gas permeation and water desalination. Most recently, as an advanced application, acid doped PBI membrane has been used in the fuel cell as a polymer electrolyte membrane (PEM). The following sections will discuss in details the applications of the PBI:

#### 1.5.1. Conventional Application:

1.5.1.1. **Structural Engineering Materials:**

PBI is used in structural engineering application like aerospace, aircraft and electrical engineering industries because of thermo-mechanical and chemical stabilities.
1.5.1.2. Insulating Material Applications:

PBI can resist heat conduction and act as an insulator. Hence PBI is used as fire proof jacket and the material in aircraft and aerospace at lower and higher temperatures. PBI is not electrically conducting and therefore can be used as good electrical insulator, especially it is being use in cable and wire covers for electrical purpose.\textsuperscript{10,13,119,120}

1.5.1.3. Adhesive Materials:

PBIs are used as adhesive materials from the last decade in industry and aerospace. PBI adhesive shears tress at 550 °C and at room temperature is 2500 and 3000 psi, respectively. For this reason PBI can be used in airspace at higher and lower temperature as adhesive due to retard the atmospheric solar orientation. PBI is also used as a cryogenic adhesive materials at various temperatures.\textsuperscript{10,11,13}

1.5.1.4. Fiber Materials:

PBI polymer forms good fibre which is mechanically, chemically and thermally stable.\textsuperscript{10-13} Due to fibre formation property it is used in different industries like textile, electrical, aeronautical and chemical. The thermal stability is as high as 300 °C and at that temperature it shrinks upto 3% and it does not form smoke and melt at above 500 °C only.\textsuperscript{10-13} It does not form any kind of smoke or flame and has the capability to maintain mechanical stability constantly at higher temperature, resists form chemicals, stable at high humidity condition etc.,\textsuperscript{150,151} hence PBI is found to be an important material for use as fibre.

1.5.1.5. PBI Membranes:

PBI polymers have excellent capability to form membranes which are highly stable mechanically, chemically and thermally.\textsuperscript{6,10,121,122} The PBI membranes are used as semipermeable membranes for reverse osmosis, nano filtration and some medical applications. PBI membranes are used as ion exchange membrane for both cation and anion like phosphate, arsenate, arsenite, sulphate, chromate, phosphate, cupper etc.\textsuperscript{121,122,123-125} PBI has proton donor and proton accepter site because of the presence of imidazole ring which chelate the different ions and make hydrogen bond with the electrolyte. PBI membrane can be made as porous in nature and used as gas separator membrane.\textsuperscript{126} Recently, acid doped PBI membranes are being used in the high temperature polymer electrolyte membrane fuel cell application as a polyelectrolyte membrane.\textsuperscript{34-36} Wang et al.\textsuperscript{127} fabricated PBI hollow fibre membranes for nanofiltration by chemically modified crosslinker using $p$-xylene dichloride. The next section discusses in detail about the application of acid doped PBI membrane in the fuel cell.
1.5.2. Advanced Application:

1.5.2.1. Fuel Cell:

Fuel cell (Figure 1.13) is an electrochemical energy conversion device which converts chemical energy to electrical energy. Sir William Grove first introduced the concept of a fuel cell in 1839, after that now fuel cell is the most promising technology for power source. But it was first commercialized and demonstrated by NASA in the 1960’s with the usage of fuel cells on the Gemini and Apollo space flights. As electrical power source device in stationary or mobile purpose; fuel cell is the most dedicated and the most eco-friendly device due to the formation of water as a product. A fuel cell consists of positively charged anode electrode, negatively charged cathode electrode, electrolyte and external load. In anode electrode surface oxidation and cathode surface reduction of the fuels takes place in between two electrode, electrolytes used for separation of the fuels and also passes it ions. The fuel cell (Figure 1.13) can be divided depending upon the type of electrolyte is used in the cell. Different types of fuel cells are known and these fuel cells electrolytes, operating temperature and the catalyst are shown in the Table 1.2.

Table 1.2. An Overview of different types of Fuel Cells. (Adapted from google image).

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Common Electrolyte</th>
<th>Operating Temperature</th>
<th>Typical Stack Size</th>
<th>Efficiency</th>
<th>Applications</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte Membrane (PEM)</td>
<td>Perfluorosulfonic acid</td>
<td>50-100°C</td>
<td>1-10 kW</td>
<td>60%</td>
<td>Backup power, Portable power, Distributed generation, Specialty vehicles</td>
<td>Solid electrolyte reduces corrosion and electrolyte management problems, Low temperature, Quick start-up</td>
<td>Expensive catalysts, Sensitive to fuel impurities, Low temperature, Low energy density</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>Aqueous solution of potassium hydroxide, soaked in a matrix</td>
<td>90-100°C</td>
<td>10-100 kW</td>
<td>60%</td>
<td>Military, Space,</td>
<td>Cathode reaction faster in alkaline electrolyte, leads to high performance, Low cost components</td>
<td>Sensitive to CO2 in fuel and air, Electrolyte management</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>Phosphoric acid soaked in a matrix</td>
<td>150-200°C</td>
<td>400 kW, 100 kW module</td>
<td>40%</td>
<td>Distributed generation</td>
<td>Higher temperature enables CHP, Increased tolerance to fuel impurities</td>
<td>Pt catalyst, Low start up time, Low current and power</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Solution of lithium, sodium, and/or potassium carbonate, soaked in a matrix</td>
<td>600-700°C</td>
<td>300 kW, 2 MW module</td>
<td>45-50%</td>
<td>Electric utility, Distributed generation</td>
<td>High efficiency, Fuel flexibility, Can use a variety of catalysts, Suitable for CHP</td>
<td>High temperature corrosion and breakdown of cell components, Long start up time, Low power density</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Yttria stabilized zirconia</td>
<td>700-1000°C</td>
<td>1 kW, 2 MW</td>
<td>60%</td>
<td>Auxiliary power, Electric utility, Distributed generation</td>
<td>High efficiency, Fuel flexibility, Can use a variety of catalysts, Solid electrolyte, Suitable for CHP &amp; CHP</td>
<td>High temperature corrosion and breakdown of cell components, Long start up time, Low power density</td>
</tr>
</tbody>
</table>

For More Information

1.5.2.2. Proton Exchange Membrane Fuel Cell:

Polymer electrolyte membrane fuel cell is the most promising and dedicated electrochemical device for stationary as well as the mobile purposes due to its simplicity, low cost, long lasting, small size, high efficient, low as well as high operating temperature and for being pollution free among all the other type fuel cell.\textsuperscript{133-139} The main construction of the fuel cell is by the two electrode, cathode and anode and a polymer electrolyte membrane which is placed in between the electrodes. In cathode side reduction happens where oxygen fuel is used and anode side oxidation happens where hydrogen fuel is used. The electrodes have platinum surface for the oxidation and the reduction. The protons move from the anode side to the cathode side via the polymer electrolyte membranes. The produced electrons are passed through the external circuit and there loads are applied. The all reaction of hydrogen PEM fuel cell is as follows:

\[
\text{Cell Reactions} \\
\text{Anode: } \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \\
\text{Cathode: } \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \\
\text{Overall reaction: } \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Electrical Energy} + \text{Heat}
\]

1.5.2.3. Requirement for Proton Exchange Membrane:

To get the efficient and high-performance PEMFC, the polymer membranes should satisfy following requirements:\textsuperscript{135,138,139}

(a) High proton conductivity
(b) High mechanical stability
Introduction

Chapter 1

1.5.2.4. Reputed Proton Exchange Membranes:

The efficiency of a fuel cell largely depends on polymer electrolyte membranes, which needs to be economical, long lasting and high performance.\(^{20,133,138,140}\) The polymer electrolyte membranes are the highly charged species which can carry the ions through the membranes in between the two electrodes. Till now many membranes have been explored, but among all the membranes perfluoro sulfonated acid membrane commonly known as the Nafion (Figure 1.14) is most prominent since it was first marketed in 1966 by the USA based DuPont and Dow company.\(^{138,140}\) Nafion are easily available, has high proton conductive efficiency, and is thermally, chemically and mechanically stable. It can work upto 80 °C for 50,000 hours\(^ {137,138,141}\) and conductivity shown at this temperature 10\(^{-2}\) S.cm\(^{-1}\). But the major drawbacks of the Nafion is that it can work upto only 100 °C and does not work beyond this temperature due to dehydration at this temperature, is high in cost, need continuous humidity.\(^ {137,138,141}\) So as an alternative to Nafion many polymers have come to the market as polymer electrolyte membranes and these are polystyrene sulfonic acids,\(^ {142}\) sulfonated polyimides,\(^ {143}\) sulfonated poly(ether ketone)s,\(^ {144,145}\) sulfonated poly(arylene ether sulfone)s,\(^ {146}\) sulfonated poly(phenylene sulfide),\(^ {133}\) sulfonated polyphosphazenes,\(^ {147,148}\) acid doped polybenzimidazoles\(^ {35,45,55,58}\) etc. In the following Figure 1.15 few representative proton exchange membranes molecular structures are shown.

![Figure 1.14. The chemical structures of perfluorosulfonic acid based PEM (adapted from reference 132).](image-url)
As discussed above, there is a need for proton conductivity membranes which can operate at higher temperatures so that the process associated with Nafion can be avoided. Although there are many ion conducting polymer are reported in the literature (some of them are shown in Figure 1.15), however each of them have many disadvantages. To solve this problem PA doped PBI based PEM membrane has been considered.
been developed. Membrane formation capability of polybenzimidazole is one of the most important parameter of PBI and which has been utilized very successfully in advanced applications like PEM fuel cell and osmosis. PBI form stable and strong hydrogen bond with protic solvents due to presence of imidazole ring which has proton donor amine (-NH-) and proton acceptor imine (-N=) bond.\textsuperscript{94,128,182,183} The acid doped PBI can act as a polymer electrolyte membrane is first reported by Savinell.

The acid doped PBI especially PA doped PBI is found to be very efficient polymer electrolyte membrane for use in fuel cell. The PA doping level of the PBIs vary from 3-20 moles per repeat unit. The mechanical stability of PBI gradually decreases with the increasing acid doping level.\textsuperscript{149,150,151} The mechanical stability decreases due to acid molecules which go to the inside of polymer chains and form hydrogen bonding between acid and imidazole ring. The proton conductivity of PBI increases with the increase of acid doping level. But mechanical stability decreases which is not favourable and the excess acid leach out from the membrane, so the cell voltage decreases. For one PBI repeat unit 4 moles PA can be consumed via hydrogen bonding which is called bonded acid and the excess acid is known as the free acid. The free acids normally come out from the membrane. In order to maintain the mechanical as well as the acid doping level several many efforts have been made. The acid doping level depends on the time, acid concentration, temperature, molecular weight and the internal structure of PBI. The acid doped PBI is the most promising polymer electrolyte membrane due to the properties like mechanical stability, high proton conductivity upto 200 °C, low cost, almost zero water drag coefficient, chemically stable etc.\textsuperscript{151,152} Wainright\textsuperscript{94,151} reported that, the acid doped PBI (IV = 0.6 dL/g) shows proton conductivity of 2.5×10⁻² Scm⁻¹ with 5 moles PA per repeating unit at 150 °C. The proton conductivity of PBI membranes increases with the increase in temperature. The proton conductivity of acid doped PBI depends upon the water molecules associated. Two types of proton conduction mechanism of PA doped PBI is suggested and these are: (i) Grothuss mechanics\textsuperscript{153} which shows the phosphoric acid and the imidazole ring via hydrogen bonding and (ii) Vehicle mechanism\textsuperscript{150} which proposes that the water molecules associated with acid and imidazole

![Figure 1.16. Proton transfer process (A) acid- PBI- acid (B) acid- water-acid PBI (adapted from reference 190b).](image-url)
ring via hydrogen bonding which sometimes called diffusion mechanism. Savagado shows that proton conductivity of PBI depends on the acid types and the trends is as follows $\text{H}_3\text{PO}_4 > \text{HClO}_4 > \text{HNO}_3 > \text{HCl}$. Kawahara et al. show that PA making a strong hydrogen bonding with imidazole ring which is proved by the FT-R spectra. The acid doped membrane swells after acid loading and hence decreases the gas permeability. The Figure 1.16 shows the mechanisms of proton transfer in case of acid doped PBI.

**1.5.2.6. Phosphoric Acid Doped PBI Membranes Fabrication Methods:**

Different approaches have been developed for the fabrication of acid doped PBI membranes till today. We have tried to summarize most of these methods in detail in the following section:

(i) **Sol-gel process:** Sol-gel process is one popular method for fabrication of the membranes. This process was first introduced by Xiao et al. as an in situ process. In this process membrane fabrication is carried out from the reaction mixture of PBI in polyphosphoric acid (PPA). The hot reaction mixture (~200 °C) is poured into the petridis and the membrane cast by doctor knives. In this method the membranes are thicker in comparison to the imbibing process. The PPA gets hydrolysed by atmospheric moisture (>50%) to form the PA loaded membrane. In this method more amounts of acid is consumed in comparison to the imbibing process. A schematic diagram of this is shown in Figure 1.17. This process can produce PA doped membrane with very high PA loading and hence very proton conduction. However, there are several limitation to this method as well.

![Figure 1.17. Fabrication of PA doped PBI membrane by PPA process (adapted from reference 21).](image)

(ii) **Imbibing process:** Savinell et al. first developed acid doped PBI membranes which is popularly called as imbibing method. In this method PBI is dissolved into the DMAc solvent with lithium chloride (LiCl) as a stabilizer at higher temperature. Then the solution is poured into petridis to fabricate the
membrane at a particular temperature. Then the fabricated membrane is boiled and soaked into deionized water to remove the LiCl and trace amount of the solvent. Then the dried membrane is soaked into the PA for few days and it is then removed from the acid. This process is good for proton conductivity and mechanical stability due to control of the acid doping level of the membranes. In this method the acid loading varies from 5 to 16 moles per repeat unit.\textsuperscript{158} However, this method is very tedious and time consuming and moreover owing to the low PA loading, the proton conductivity is not high enough to get efficient fuel cell.

(iii) **Gel process:** Gel process is the easiest process to fabricate the acid loaded PBI membrane. In this process a reversible gel is formed at a particular concentration and temperature. In this process the polymers are dissolved into the PA medium at higher temperature (~180 °C) for 1 to 2 hours. Then the gel solution of the polymer poured into the petridis and the membrane casting takes place. In this process the acid doping level of the PA doped membranes are high and the mechanical properties also high.\textsuperscript{159} Recently, our lab has developed this gel method which consumes 40 mole PA per repeat unit. The overall gel formation method is shown in the Figure 1.18. Till now in the literature, the highest PA loading is reported using this gel process. Among several advantages this process can offer, one of the major drawback of this is that the process is highly dependent on the PBI backbone structure and its solubility.

![Figure 1.18. Thermoreversible gelation of polybenzimidazole (PBI) in phosphoric acid (PA) (adapted from reference 190c).](image)

(iv) **Porogen process:** Porogen process is beneficial over other process for developing acid doped membranes. In the process the porogens like diphthalate (e.g., dimethyl, diethyl, dibutyl and diphenyl, as well as triphenyl phosphate) are mixed with the polymer solution at variable temperature. The well mixture solution is then casted onto the petridis and then the solvent is evaporated at a particular temperature according to the solvent boiling point. The dried membranes are boiled at high temperature with organic
solvent or water to remove porogens from the membrane. After removing the porogens, there is a formation of micro porosity in the membrane and then the membranes are soaked into the PA.\textsuperscript{160} This method (Figure 1.19) has advantages that the loaded acid does not come out of the membranes so easily.

**Figure 1.19. Fabrication of PA doped PBI membrane by porous PBI process.**

(v) **Nanocomposite and blend membranes:** Polymer nanocomposites are two component mixtures which contain nano size filler in the polymer matrix and nano filler tare embedded to the polymer matrix. Recently, nano composites is a very attractive field for research due to the hi-performance and energy application to industrial as well as daily life.\textsuperscript{104-106,161-167} The nano fillers are nano in size and highly affect the polymer backbone due to the interaction between polymer matrix and the nanofillers for their fictional groups presence. Till now various nano fillers have come to the market like carbon nanotube,\textsuperscript{134,135} graphene,\textsuperscript{138} chemically modified silica particles,\textsuperscript{105,166} clay,\textsuperscript{104,165} fullerene\textsuperscript{131,162} etc. Among all, carbon nanotube, graphene and chemically modified silica have been great attraction due to high energy and performance applications. The polymer properties change hugely by adding small amount of the nano materials to the polymer matrix which does not disturb the polymer backbone and the processability of the polymer. A small amount of the nano filler changes the polymer properties like performances such as increased strength and heat resistance, decreased gas permeability and flammability, increased biodegradability of biodegradable polymers, mechanical properties, increase thermal and oxidative stability and acid loading capacity as well as proton conductivity. Nano fillers affect the polymer properties due to properties of nano fillers, such as, (i) low percolation threshold, (ii) arising a low volume fraction due to particle-particle correlation (orientation and position), (iii) extensive interfacial area (communication between matrix and filler) per volume of particles, (iv) short distances between the particles and (v) comparable size scales among the rigid nanoparticles inclusion. According to the dimension of nano fillers can be divided into three different types: (i) one dimension (i.e., clay), (ii) two dimension (i.e., carbon nanotube, graphene) and (iii) three dimension (i.e., silica). Recently, several PBI nanocomposite membrane have been made by using different type nano fillers.\textsuperscript{156,168-172} Silicotungstic acid\textsuperscript{169} and
phosphotungstic acid increases the phosphoric acid doping level as well as the proton conductivity and the mechanical stability. Carbon nanotube and graphene have also increased the several properties of PBI. Our group demonstrated that the ammine modified silica particle and the montmorillonite (Scheme 1.4 and Scheme 1.5) can improve several important properties of the OPBI. The multiwall carbon nanotubes (MWNTs) nanofillers in OPBI nanocomposites containing 0.1-1 wt% are synthesized by Shao et al.

 Scheme 1.4. Schematic representation of OPBI nanocomposites preparation with amine modified silica nanoparticles (AMS) by solution blending process (adapted from reference 105).

 Scheme 1.5. Schematic representation of OPBI nanocomposite with the organoclay (adapted from reference 104).
PBI has a good capability to form a blend due to the presence of both proton donor (-NH-) and proton acceptor (-N=) hydrogen bonding sites which interact with other polymer functional groups. PBI blends are extensively studied for their increasing processability, thermal stability, proton conductivity, mechanical properties etc. Different type blends have been prepared like polyimides (PI), polyamide-imide (PAI), polyyarylate (PAR), high-modulus aramide (HMA), Poly(ether-imide), poly(4-vinylpyridine) (PVP), sulfonated poly sulfone, aromatic polyethers. Our group has demonstrated the formation of PBI with variation of fluorinated polymer like poly(vinylidene fluoride) (PVDF) polymer, polystyrene (Figure 1.20) and PVDF-HFP. Several other polymers like sulfonated polymers, PVT are blended with PBI to improve the properties (Figure 1.21). We have observed significant enhancement in proton conduction upon blending. Our group has recognized that presence of hydrophobic PVDF polymer with PBI which decreases the water uptake but increases the acid loading which affects proton conductivity.

**Figure 1.20.** Formation of core (polystyrene)-shell (polybenzimidazole) nanoparticles. (adapted from reference 173b).

**Figure 1.21.** Schematic representation of blend formation with polybenzimidazole (PBI) and poly(1-vinyl-1,2,4-triazole) (PVT) (adapted from reference 179).
1.6. AIMS OF THE THESIS:

From the above discussion in this chapter, we can convincingly conclude the importance of PBI polymer in the different applications and most recently, especially in the field of PEM for fuel cell. Till now more than 5800 articles, patents and reviews have been published on PBI polymer which confirms the importance of PBI polymer. Despite of large number of literature known to us; till several problems and difficulties like solubility, flexibility and the proton conductivity are not addressed up to the satisfaction. Therefore we have explored the structurally different types of PBIs to tackle the above problems. Therefore the primary aim of this thesis is develop of new PBI structural varieties to solve the problems which are limiting the use of PBI. In Chapter 3 we have attempted to derivatize the PBI by attaching long alkyl chain with an aim that the synthesized PBI will be soluble and hence easily processable. Since most of the reported PBIs are synthesized from only one type of tetramine monomer called TAB, we aims to replace this with a new, easily synthesizable, alternative, efficient tetramine monomer called Py-TAB in Chapter 4. We also aim to prepare the PBI from this new Py-TAB in a way that the new PBI must be soluble, easily processable and should have better proton conductivity behaviour when doped with acid. We have noticed that, almost all the copolymers reported in the literature are made by altering the mole ratio of two dicarboxylic acids with a tetramine. Since we have successful in finding a new tetramine in Chapter 4, hence in Chapter 5, we aim to made new copolymer of PBI where tetramine mole fraction alters with a fixed dicarboxylic acid. This allows us to control the several important properties of PBI copolymer. In Chapter 6 we aim to prepare block copolymer of PBI with three different structures and alter the block length. We also aim to study the effect of these block length on the properties especially conducting properties of doped PBI membranes. The aims and objectives of each chapter of this thesis are explained in more details at the end of the introductory part of the individual chapters.
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