CHAPTER 7

Summary & Conclusions

Conclusion
7.1. SUMMARY:

Thesis entitled “Synthesis and Studies of Novel Polybenzimidazoles with Improved Properties for Proton Exchange Membrane” describes the synthesis and characterization of several structurally different polybenzimidazole from conventional 3,3',4,4'-tetraaminobiphenyl (TAB) and unconventional 2,6-bis(3',4'-diaminophenyl)-4-phenylpyridine (Py-TAB) tetraamines monomers. We have carried out the structural variation of PBI by (a) post polymerization to synthesize N-alkyl substituted PBIs, (b) by tetraamine and diacid monomer structure variation to synthesize a series of pyridine based PBI (Py-PBIs), (c) a series of meta and para random Py-PBI copolymers and (d) the meta-para PBI block copolymers by using ammine and acid terminated PBI oligomers. The synthesized PBIs are fully characterized and proton exchange membranes are fabricated from these polymers which are finally examined for their potential as PEM. The thesis consists of seven chapters. The summary of the contents of each chapter is given below.

CHAPTER 1:

This Chapter 1 described a brief introduction of various types of polybenzimidazoles (PBIs) types of polymers, history of PBI, describes their different synthetic procedure of preparation, different types PBI, brief discussion on physical and chemical properties. This chapter also discussed common and advanced application for membrane formation and phosphoric acid (PA) doped polybenzimidazole in high temperature polymer electrolyte membrane fuel cell (HT-PEMFC). A brief introduction about fuel cell, types of fuel cells and challenges involved in PEM fuel cell research were also included. Finally the aims of the current work were presented.

CHAPTER 2:

Chapter 2 described the details of materials which were used for all the working chapters and the details of experimental procedures, instrumentation techniques for characterization and properties evaluation of the synthesized different types of PBIs.

CHAPTER 3:

Despite the presence of bulk literature on polybenzimidazole (PBI), unavailability of readily soluble and processable PBI remains as the tallest challenge for the end-use. N-alkyl PBIs (N-PBIs) were synthesized by grafting the alkyl chain in the imidazole backbone to resolve this key constrain. The chain length of substituted alkyl groups was varied to evaluate the influence of chain size on the structures and properties of N-PBIs. Significant enhancement of solubility of N-PBIs compared to parent PBI in formic acid offered the opportunity to fabricate the homogeneous mechanically tough membranes with minimal
efforts. The substituted long alkyl chains pushes apart the PBI chains and hence increases the face-to-face packing distance by breaking the self-association between the chains; resulted into less rigid highly soluble N-PBIs. Alkyl chain length dependent weight loss at ~300 °C, presence of two glass transition temperatures and peculiar deep rubbery modulus in storage modulus vs. temperature plots resembled the copolymer molecular structure of N-PBIs. Hydrophobic character of alkyl chains and loosely packed structure of N-PBIs facilitated decrease in water uptake and swelling of the N-PBI membranes compared to parent PBI membrane. The temperature dependent proton conductivity of PA loaded N-PBIs membranes were found to be satisfactory.

CHAPTER 4:

Tetraamine 2,6-bis(3′,4′-diaminophenyl)-4-phenylpyridine (Py-TAB) was found to be an efficient, readily accessible, inexpensive monomer for synthesizing pyridine bridge polybenzimidazoles (Py-PBIs). The Py-TAB monomer replaced the frequently and conventionally used 3,3′,4,4′-tetraaminobiphenyl (TAB) monomer for synthesizing polybenzimidazoles (PBIs) structure. Py-TAB monomer showed wider scope for synthesis of PBIs with various dicarboxylic acids. Py-PBIs displayed superior solubility in low boiling solvent and hence eliminated the processability issues of PBIs which often restricted the large scale use. Comparable and in some instances superior thermal, mechanical and oxidative stability of Py-PBI proved that the Py-TAB is the most attractive alternative tetraamine monomer to TAB for synthesis of PBIs. The membranes obtained from Py-PBIs displayed significantly lower water uptake and swelling than the conventional PBIs due to the presence of bulky Py-TAB monomer. The presence of pyridine moiety in Py-PBIs helped to load larger amount of phosphoric acid (PA) compare to conventional PBIs. The proton conductivity of PA doped Py-PBI membranes were higher than the conventional PBI membranes owing to the higher PA loading and the complex bulky structure. Photophysical studies demonstrated the complexity of Py-PBIs structure. In summary, 3-fold objectives, namely, (I) alternative tetraamine monomer, (II) soluble PBI, and (III) higher proton conducting PBI based PEM, were achieved in this study.

CHAPTER 5:

In our effort to promote 2,6-bis(3,4-diaminophenyl)-4-phenylpyridine (Py-TAB) as an alternative tetraamine monomer to conventionally used 3,3′,4,4′-tetraaminobiphenyl (TAB) for synthesizing readily processable pyridine bridged polybenzimidazoles (Py-PBIs), two series of random copolymers (PBI-co-Py-PBI) were synthesized by polymerizing Py-TAB and TAB with isophthalic acid (IPA), and terephthalic acid (TPA) to produce meta (mPBI-co-mPy-PBI) and para (pPBI-co-pPy-PBI) connected copolymers, respectively. For the first time in the PBIs literature, copolymers were synthesized by varying the relative compositions of tetraamines (TAB and Py-TAB) in the polymerization feed with a single dicarboxylic acid
(DCA) instead of traditionally used method where two DCAs with variable compositions are polymerized with single tetraamine. The solubility and hence the processability of the copolymers were improved significantly upon introduction of Py-PBI in the copolymer chain. The detailed characterizations of both meta and para series copolymers compellingly established that thermal, chemical and mechanical stabilities can be easily modulated as per the need by altering the relative compositions of PBI and Py-PBI. The phosphoric acid (PA) loading of copolymers were increased gradually with increasing Py-PBI content in the copolymer chain since bulky pyridine moiety facilitated the absorption of PA. The presence of pyridine functionality and larger PA loading caused the higher proton conductivity of PA doped copolymer membranes and the conductivity at 160 °C steadily increased with increasing Py-PBI. In summary, two age-old notions in the PBI chemistry, namely, (1) copolymers can be prepared only by altering DCAs compositions and (2) PBIs properties can be tuned only by DCAs structure, were replaced in this study by synthesizing copolymers from TAB and Py-TAB with different DCAs.

CHAPTER 6:

A series of meta-polybenzimidazole-block-para-polybenzimidazole (m-PBI-b-p-PBI), diblock copolymers of PBI, were synthesized with various structural motifs and block lengths by condensing the diamine terminated meta PBI and acid terminated para PBI oligomers. NMR studies and existence of two $T_g$'s, obtained from DMA results, unequivocally confirmed the formation of diblock copolymer structure through the current polymerization methodology. Appropriates and careful selection of oligomers chain length enabled us to tailor the block length of diblock copolymers and also to make varieties of structural motifs. Increasingly distinct $T_g$ peaks obtained from DMA studies with higher block length of diblock structure attributed the decrease in phase mixing between the meta and para PBI blocks which in turn resulted into naophase segregated domains. The diblock structure and the block length did not display any significant trend on the phosphoric acid loading of membrane obtained from these diblock copolymers. The proton conductivities of H$_3$PO$_4$ doped diblock copolymer membranes were found to be increasing substantially with increasing block length because of the nanophase separation and thereby less morphological barrier within the block and hence better conductivity in the same block. The structural varieties also influenced the phase separation and proton conductivity. In comparison to meta-para random copolymers, the current meta-para diblock copolymers were found to be more suitable for PBI based PEM.
7.2. CONCLUSIONS:

From the above discussion in the Chapter 3 to 6 on the topic “Synthesis and Studies of Novel Polybenzimidazoles with Improved Properties for Proton Exchange Membrane," the following conclusions are drawn:

1. A series of N-alkyl substituted polybenzimidazole has been synthesized and their properties are studied.

2. The storage modulus and water uptake and swelling volume of the N-PBIs gradually decreases with increasing of alkyl chain length.

3. We have synthesized 2,6-bis(3,4-diaminophenyl)-4-phenylpyridine (Py-TAB) as an alternative tetraamine monomer to conventionally used 3,3',4,4'-tetraaminobiphenyl (TAB) for synthesizing readily processable pyridine bridged polybenzimidazoles (Py-PBIs) which is cost effective, readily available and easy to synthesis.

4. We have synthesized a series of pyridine based polybenzimidazole (Py-PBIs) which shows the greater thermal and chemical stability and more soluble in low boiling solvent formic acid (FA) and proton conductivity than the conventional polybenzimidazole.

5. All the Py-PBIs can be an alternative to the PBI for the use in fuel cell.

6. Py-TAB and TAB are used to synthesize readily processable meta and para series pyridine bridged polybenzimidazoles random copolymers (PBI-co-Py-PBI)

7. Both meta and para series random copolymer are mechanically and chemically stable than normal PBI.

8. The phosphoric acid (PA) loading increases with increasing in both meta and para series random copolymers (PBI-co-Py-PBI) with increasing the Py-TAB contents.

9. Both meta and para series polybenzimidazoles random copolymers (PBI-co-Py-PBI) are more proton conducting than the normal PBI which can be used in high temperature polymer electrolyte membrane fuel cell (HT-PEMFC).

10. Acid and diamine terminated PBI oligomers can be easily synthesized by changing the mole ratio of tetramines and diacids monomer.

11. The proton conductivity of the block copolymer displayed dependency on block length due to the nanophase segregation of individual blocks.
7.3. SCOPE OF FUTURE WORK:

The present thesis has addressed three important aspects of polybenzimidazoles random copolymerization, block copolymerization and monomer structure variation. We believe the findings of this thesis will have great impact on the future development of polybenzimidazole (PBI) chemistry in general, especially the use of PBI in PEMFC application. The thesis put forward and establish novel concept in the PBI chemistry research. The potential and scope of future work of this thesis are enormous. Few of these are listed below

1. Structure variation of PBI by post polymerization technique can be developed.
2. Pyridine based different structured PBIs have enough potentially enough to be used in PEMFC.
3. Efforts can be made to make new PBI structure using Py-TAB.
4. The Py-PBIs show higher proton conductivity compare to the conventional m-PBI, efforts should be made to study more details.
5. Synthesis of block copolymers from Py-PBI can be tried.
6. More systematic efforts must be made to understand the usefulness of newly synthesized Py-PBIs.
7. Varieties of block copolymer can be made using the methods established in this thesis.
8. Finally, all these newly developed PBIs can be tested as PEM in working fuel cell so that the potential of these polymers are explored.