

## CHAPTER VII

### CONCLUSIONS AND RECOMMENDATIONS

The present work was originally focused on the non-aqueous polymer membrane preparations for the use of polymer electrolyte membrane for fuel cells (PEMFCs) via (i) a copolymers of acrylic acid and 4-vinylimidazole, which consists of proton donor and acceptor, respectively, including temperature dependency and structural relationships, (ii) a SPEEK blended with Poly (AA-co-4VIm), and (iii) a polyamide functionalized with imidazoles.

In the case of (i) (Chapter III and IV), acrylic acid and 4-vinylimidazole were copolymerized and prepared in the membrane form. With homogeneous transparent films, a series of copolymers showed fairly good degradation temperature ( $T_d$ ) above 230 °C and glass transition temperature ( $T_g$ ) values at 105–177 °C. All the membranes exhibited the proton conductivity at  $10^{-2}$  S/cm whereas the membrane with high imidazole content showed a significant increase in conductivity at the temperature above 80 °C.

We further studied the mechanism of the proton conductivity via imidazole and carboxylic acid groups by using temperature dependent and simultaneous analyses, such as WAXD-DSC, FTIR, including the simulation based on the molecular modeling (Chapter IV). It is important to note that the proton transfer mechanism is occurred by a strong hydrogen bonding network between the carboxylic acid and the 4-vinylimidazole group. During heating, the proton transport was accelerated along the imidazole-rich copolymer membranes via the weakening in the hydrogen bond network. In addition, the carboxylic acid-rich copolymer membranes were changed to be planar non-cyclic anhydrides with splitting water molecules above 150 °C. WAXD patterns showed that temperature motivated the change in packing structure. The changes of WAXD patterns were further quantitatively analyzed by using radial distribution function (RDF). At temperature between 20 and 200 °C, the intermolecular distance in the copolymers expanded discontinuously at a temperature corresponding to their glass transition temperatures.

(ii) With a good candidate for high temperature PEMFC, SPEEK<sup>®</sup> possesses good mechanical properties, high chemical resistance, cheap price and thermal stability. Poly (AA-co-4VIm) was blended with sulfonated polyether ether ketone for improving the thermal and mechanical properties of copolymer itself (Chapter V). The homogeneous blend films were confirmed from SEM images. The proton conductivity of Poly (AA-co-4VIm)/SPEEK increased in all copolymer blend membranes.

(iii) Aza-methylene phenol obtained from the ring opening benzoxazine monomer was applied as a spacer molecule to provide the functionalization with adenine and polyamide (Chapter VI). Adenine was used as a proton transferring part whereas 1, 10-diaminodecane was used as reactive amine groups. Finally, an appropriate spacer of aza-methylene phenol derivatives was successfully coupled with adenine via tosylation. This novel polyamide material is demonstrated to achieve high efficiency proton transferring polymer membrane in PEMFC system.