

Synthesis and Membrane Formation of Hyperbranched

Polybenzimidazoles for Fuel Cell Application

Hongjie Xu, Zixing Shi, Xuesong Jiang, Jianhua Fang, Jie Yin

School of Chemistry & Chemical Technology, Shanghai Jiao Tong University, Shanghai
200240, China

Abstract

Various hyperbranched polybenzimidazoles (HBPBIs) were successfully synthesized by condensation polymerization of 1,3,5-benzenetricarboxylic acid (BTA) and 3,3'-diaminobenzidine (DAB) in polyphosphoric acid (PPA) at 190 °C. Different monomer addition manners and molar ratios resulted in different polymers, i.e., simultaneous addition of BTA and DAB with the molar ratio of 1:1 (manner 1) gave carboxyl-terminated HBPBI (HBPBI-1), whereas the addition of BTA portion-wise to DAB solution in PPA with the molar ratio of DAB:BTA = 2:1 (manner 2) yielded amine-terminated HBPBI (HBPBI-2). DAB reacted with BTA in the molar ratio of DAB/BTA = 3/1 yielded hexamine intermediate product which in the next step was allowed to react with various dicarboxylic acid in PPA to give a series of novel amine-terminated HBPBIs. Membranes with good mechanical properties were prepared by solution cast method in the presence of cross-linking reagents (ethylene glycol diglycidyl ether (EGDE) and terephthalaldehyde (TPA)). In comparison with the commercial linear PBI, HBPBI membranes displayed higher phosphoric acid (PA) doping level under the same conditions and higher mechanical strength at similar PA-doping levels. HBPBI membranes with high proton conductivity (0.064 S/cm) at completely anhydrous state (0% relative humidity) and good mechanical properties were successfully developed.

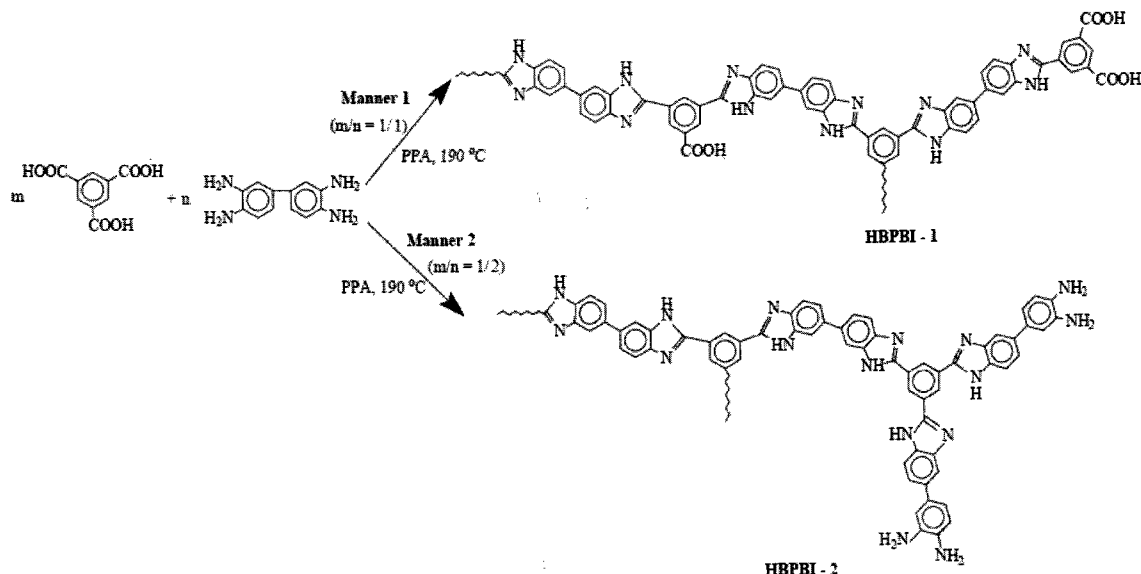
Introduction

Polybenzimidazoles (PBIs), known for their excellent thermal stability, high mechanical properties, nonflammability, and good chemical resistance, have attracted increasing attention in the past decade because of their potential application in polymer electrolyte membrane fuel cells (PEMFCs). However, the poor solubility of PBIs resulting from the highly rigid polymer backbones and the strong interchain hydrogen bonding interaction makes them hard to process. Moreover, phosphoric acid-doped PBI membranes may lose their mechanical strength at high doping levels which are essential for maintaining high proton conductivity. To improve the solubility and to enhance the mechanical strength of PBI membranes, in this study a new class of PBIs, hyperbranched polybenzimidazoles (HBPBIs), have been synthesized via A₂+B₃ approach and their cross-linked membranes have been prepared. The solubility, thermal stability, membrane formation, mechanical properties, phosphoric acid (PA) absorption and proton conductivity have also been investigated.

Results and Discussion

Various HBPBIs have been synthesized via A₂+B₃ approach. Two kinds of trifunctional monomers, 1,3,5-benzenetricarboxylic acid (BTA) and a hexamine in-situ prepared from BTA and 3,3'-diaminobenzidine (DAB) in the molar ratio of DAB/BTA = 3/1 in polyphosphoric acid were used as B₃-type monomers. Accordingly, DAB and a series of dicarboxylic acids (2,2-bis(4-carboxyphenyl)hexafluoropropane (6FA), isophthalic acid (iPTA) and terephthalic acid (tPTA)) were used as A₂-type monomers. Scheme 1 shows the polymerization of BTA

and DAB under different conditions. simultaneous addition of BTA and DAB with the molar ratio of 1:1 (manner 1) gave carboxyl-terminated HBPBI (HBPBI-1), whereas the addition of BTA portion-wise to DAB solution in PPA with the molar ratio of DAB:BTA = 2:1 (manner 2) yielded amine-terminated HBPBI (HBPBI-2). HBPBI-1 and HBPBI-2 were chemically modified by reacting with *o*-diaminobenzene and benzoic acid, respectively. The resulting HBPBIs are generally well soluble in dimethyl sulfoxide (DMSO) and *N,N*-dimethylacetamide (DMAc). Thermogravimetric analysis measurement revealed that HBPBIs generally had high thermal stability (> 450 °C).



Scheme 1 Synthesis of HBPBI-1 and HBPBI-2

HBPBI membranes with good mechanical properties were prepared by solution cast method in the presence of cross-linking reagents (ethylene glycol diglycidyl ether (EGDE) and terephthalaldehyde (TPA)). The HBPBI membranes prepared by cross-linking with TPA showed significantly higher PA uptake under the same conditions and better mechanical properties at similar PA-doping levels than the commercial linear PBI. Figure 1 shows the variation of the proton conductivity of two TPA-cross-linked HBPBI membranes at 0% relative humidity as the function of temperature. It can be seen that the conductivity increases monotonously with increasing temperature and very high proton conductivity of 0.064 S/cm was obtained at 170 °C.

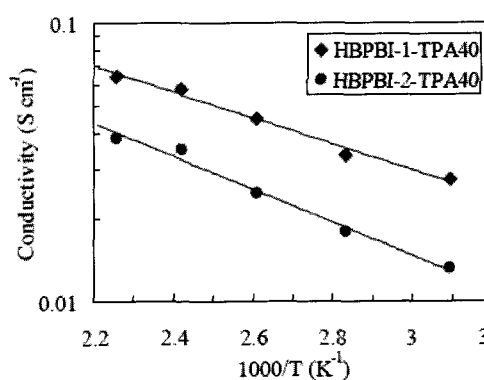


Figure 1 Temperature dependence of proton conductivity of HBPBI membranes at 0% relative humidity.

Acknowledgment. This work was supported by National Natural Science Foundation of China (No. 20474037) and Hi-Tech research and development program of China (2004AA33H010).