Preparation and Properties of Novel Cross-linked Polybenzimidazole Membranes

Nan Xu,[1] Xiaoxia Guo,[1] Jianhua Fang,[1] Hongjie Xu,[1] Ken-ichi Okamoto[2]

[1]School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China. [2]Deapartment of Advanced Materials & Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

Abstract

A series of novel polybenzimidazoles with pendant amino group have been successfully synthesized from 5-aminophthalic acid (APTA), 3,3'-diaminobenzidine (DAB) and dicarboxylic acid co-monomers (isophthalic acid, terephthalic acid and 4,4'-dicarboxydiphenyl ether) in polyphosphoric acid (PPA) at 190 °C for 10 h. The resulting homopolymer and most of the copolymers are well soluble in some organic solvents such as dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc) and 1-methyl-2pyrrolidone (NMP). Cross-linked polybenzimidazole membranes with good mechanical properties were prepared by casting the polymer solutions in DMAc in the presence of an epoxy resin (cross-linker). Phosphoric acid (PA)-doping was performed by immersing the cross-linked polybenzimidazole membranes into PA for a given time. The PA-doped membranes displayed reasonably good mechanical strength and high proton conductivity even at completely anhydrous state (0% relative humidity), making them the promising membrane materials for high temperature proton exchange fuel cell application.

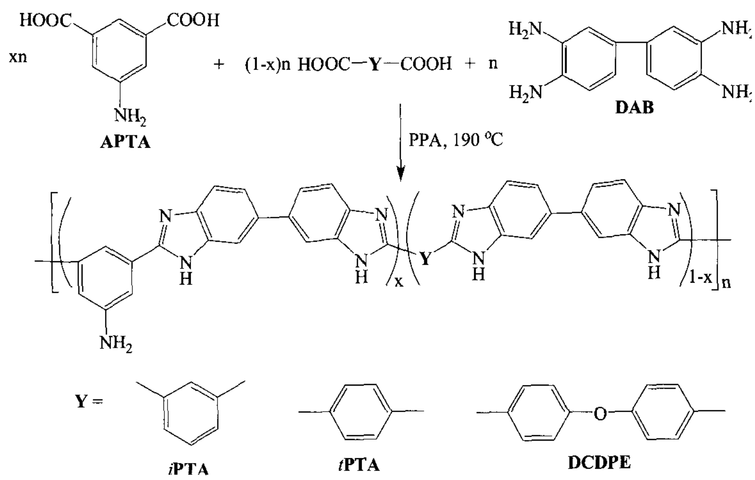
Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are promising power sources for vehicular transportation and for other devices requiring clean, quite and portable power sources. PA-doped polybenzimidazole (PBI) membranes have been identified to be the most promising membrane materials for high temperature (150-200 °C) PEMFC use because of their high proton conductivity at high temperatures and low relative humidity. The commercial PBI, synthesized from isophthalic acid and 3,3'-diaminobenzidine, has been extensively studied in the past decade. However, it only has limit solubility in some organic solvents such as DMAc. Moreover, the PA-doped membranes generally show rather poor mechanical strength at high PA-doping levels. It is strongly desired to develop novel PBIs with good solubility and cross-linkable groups for further cross-linking of the membranes. In this presentation, we report on a new type of PBIs with pendant amino groups and the formation of cross-linked membranes. The PA-doping and proton conductivity of the membranes are also reported.

Results and Discussion

A series of novel PBIs with pendant amino groups were synthesized via condensation polymerization of 5-aminophthalic acid (APTA), 3,3'-diaminobenzidine (DAB) and dicarboxylic acid co-monomers (isophthalic acid, terephthalic acid and 4,4'-dicarboxydiphenyl ether) in polyphosphoric acid (PPA) at 190 °C for 10 h (**Scheme 1**). By controlling the molar ratio between APTA and dicarboxylic acid co-monomers, PBIs with different amino group content were prepared. The homopolymer derived from APTA and DAB displayed good solubility in some organic solvents such as DMAc, NMP and DMSO. The copolymers, however, showed gradually deteriorated solubility in organic solvents with decreasing the content of the pendant amino group. Membranes were prepared by casting the PBI solutions in DMSO at 80 °C for 10 h. Cross-linked membranes were prepared by casting the solution mixtures of PBI and epoxy resin in DMSO at 80 °C for 10 h. PA-doping was performed by immersing the membranes into concentrated phosphoric acid (85%) at room temperature for two days.

Scheme 1 Synthesis of polybenzimidazoles with pendant amino group



The maximum tensile strength (MS), elongation at break (EB), PA uptake and proton conductivity (σ) at 0% relative humidity and 150 °C of the cross-linked and uncross-linked membranes are shown in **Table 1**. It can be seen that cross-linking did not cause significant improvement in mechanical properties. In contrast, for all the membranes EB slightly decreased after cross-linking. However, cross-linking greatly improved the mechanical strength of PA-doped membranes. APTA-DAB, for example, could not undergo PA doping without cross-linking because of its solubility in PA. After cross-linking, the membrane became completely insoluble in PA and the doping treatment could be readily carried out. PA uptake is related to cross-linking density. APTA-DAB showed the lowest PA uptake value because of the highest cross-linking density (the highest content of amino group). With decreasing the cross-linking density, PA uptake tended to increase. The proton conductivity of cross-linked APTA-*i*PTA/DAB(1/1) as function of temperature was measured at 0% relative humidity. It was observed that the conductivity increased with increasing temperature and reasonably high proton conductivity of 0.022 S/cm was obtained at 150 °C. The investigation of proton conductivity of other membranes and other properties such as radical oxidative stability are in progress.

Table 1 Mechanical properties, PA uptake and proton conductivity (σ) at 0% relative humidity and 150 °C of the cross-linked and uncross-linked membranes

PBI	Cross-linking	Maximum Stress (MPa)	Elongation at Break (%)	PA Uptake (wt/wt%)	σ (S/cm)
APTA-DAB	No	53	6.0	Dissolved	
	Yes	61	2.3	79.0	NM
APTA-*i*PTA/DAB(2/1)	No	72	7.0	Dissolved	
	Yes	71	3.0	134	NM
APTA-*i*PTA/DAB(1/1)	No	76	15	Dissolved	
	Yes	58 (7.8)	10 (7.4)	174	0.022
APTA-*i*PTA/DAB(1/2)	No	60	57	Partially Dissov.	
	Yes	61 (13)	20 (23)	165	NM

The data in parenthesis refer to PA-doped membranes. NM: not measured.

Acknowledgment. This work was supported by National Natural Science Foundation of China (No. 20474037)