Synthesis and Properties of Benzimidazole-Containing Sulfonated Copolyimide Membranes

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Abstract

Various benzimidazole-containing sulfonated copolyimides were synthesized by one-pot random condensation polymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), sulfonated diamines, 2-(4-aminophenyl)-5-aminobenzimidazole (APAB) and 9,9-bis(4-aminophenyl)fluorene (BAPF) in *m*-cresol in the presence of benzoic acid and triethylamine at 180 °C for 20 h. The resulting copolyimides showed good solubility in *m*-cresol and/or dimethylsulfoxide (DMSO). Membranes with good mechanical properties were prepared by conventional solution cast method. Thermogravimetric analysis (TGA) measurements revealed that the benzimidazole-containing copolyimides had excellent thermal stability (thermal decomposition temperatures of sulfononic acid group > 350 °C). In comparison with the corresponding benzimidazole-free sulfonated copolyimide membranes, the present benzimidazole-containing sulfonated copolyimide membranes displayed much better radical oxidative stability, which is very favorable for fuel cell applications. Membranes with high proton conductivity, good water stability, excellent radical oxidative stability and low methanol permeability were successfully developed.

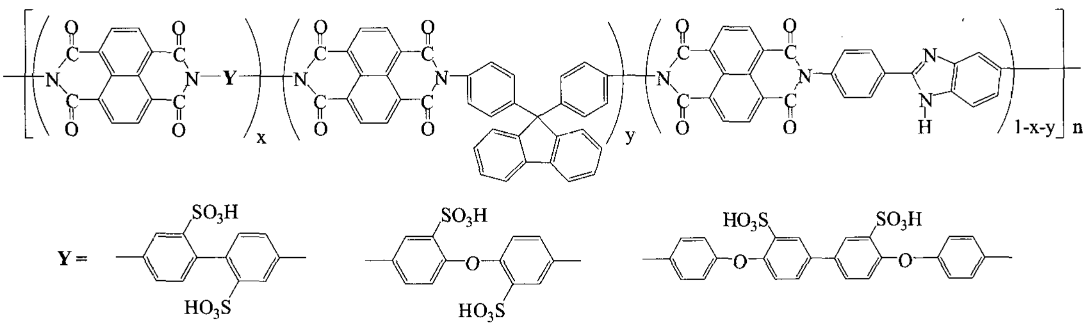
Introduction

Aromatic polyimides, known for their high thermal stability, high mechanical strength and modulus, excellent electric properties, and good chemical resistance, have found wide applications in industry. Recent researches demonstrate that six-membered ring sulfonated polyimides (SPIs) are promising membrane materials for fuel cell application. To achieve high performance fuel cells, membranes are required to have high proton conductivity, good mechanical properties, high water stability (resistance to swelling), minimal reactant (hydrogen, oxygen, methanol, etc.) permeability and good radical oxidative stability. Up to now, the proton conductivity and water stability of sulfonated polymer membranes have been well studied. The relationship between polymer structure and radical oxidative stability has nor been systematically studied yet. In this presentation, we report on the synthesis of various benzimidazole-containing sulfonated polyimides and their proton conductivity, water stability and radical oxidative stability are also investigated.

Results and Discussion

Scheme 1 shows the chemical structure of various benzimidazole-containing sulfonated polyimides. They were synthesized by random copolymerization of NTDA, sulfonated diamines (benzidine-2,2'-disulfonic acid (BDSA), 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS), 4,4'-bis(4-aminophenoxy)-biphenyl-3,3'-disulfonic acid (BAPBDS) and 3,3'-bis(4-sulfophenoxy)benzidine (BSPOB)), 2-(4-aminophenyl)-5-aminobenzimidazole (APAB) and 9,9-bis(4-aminophenyl)fluorene (BAPF) in *m*-cresol in the presence of benzoic acid and triethylamine at 180 °C for 20 h. The resulting copolyimides are well soluble in *m*-cresol and/or DMSO. Membranes with good mechanical properties were prepared by conventional solution cast method. Proton exchange was performed by immersing the membranes into 1.0 N hydrochloric acid for 2 days. The resulting acid form membranes are in ionically cross-linked because of the interaction between the basic imidazole ring of APAB moiety sulfonic acid group. Water stability measurement, however, revealed that ionically cross-linking is not very effective for maintaining highly stable membranes. To further improve the water stability, covalent cross-linking was performed with the membranes by treating them in polyphosphoric acid (PPA) at 180 °C or methanesulfonic acid/phosphorus pentoxide (10/1 by weight) for a certain time. The cross-linking is based on the condensation reaction between sulfonic acid and the activated phenyl rings of BAPF moiety and the resulting cross-linking bond is the very stable sulfonyl group.

Scheme 1 Chemical Structure of Various Benzimidazole-Containing Sulfonated Copolyimides



BDSA ODADS BAPBDS

Thermogravimetric analysis (TGA) measurements revealed that the benzimidazole-containing copolyimides had excellent thermal stability (thermal decomposition temperatures of sulfononic acid group > 350 °C). Figure 1 shows the proton conductivity of various membranes as function of relative humidity (RH) at 60 °C. It can be seen that the conductivity increased rapidly with an increase in RH. Moreover, at high RH the membranes showed reasonably high proton conductivity, which is comparable to or even higher than that of Nafion112. Covalently cross-linked membranes (NTDA-BAPBDS/BAPF/APAB(4/1/1, C) displayed quite similar proton conductivity to that of the corresponding non-covalently cross-linked one in the whole humidity range.

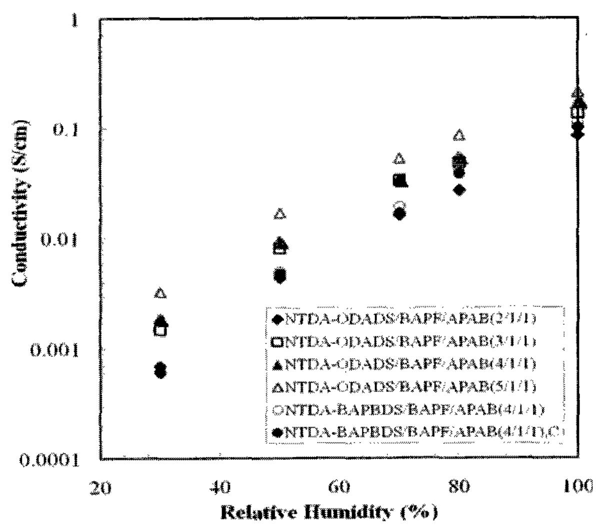


Figure 1 Variation of proton conductivity of various benzimidazole-containing copolyimide membranes at 60 °C.

The radical oxidative stability was investigated by Fenton reagent test (3% H_2O_2 + 3 ppm $FeSO_4$, 80 °C). For the membranes without APAB moiety in their structure, the radical oxidative stability is around 0.5 h. For the membranes containing APAB moiety, however, the radical oxidative stability increased to around 3 h. For the covalently cross-linked NTDA-ODADS/BAPF/APAB(2/1/1), the membrane did not lose mechanical strength or dissolve in the Fenton reagent solution after 10 h test, indicating excellent radical oxidative stability.

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