Synthesis and Properties of Sulfonated Poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole]

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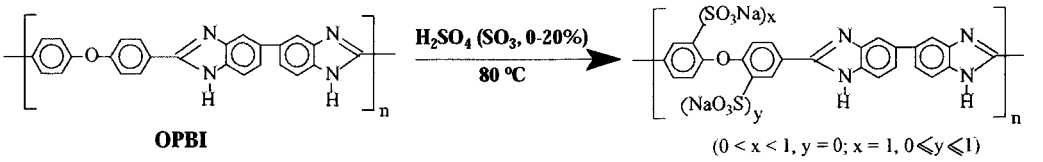
Introduction Polybenzimidazoles (PBIs), known for their excellent thermal stability, high mechanical properties, nonflammability, and good chemical resistance, have attracted much attention in the past decade because of their potential application in polymer electrolyte membrane fuel cells (PEMFCs). In this presentation, a novel sulfonated polybenzimidazole, sulfonated poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole] (SOPBI), were successfully synthesized (Figure 1) and the thermal stability, proton conductivity and radical oxidative stability were investigated.

Scheme Post-sulfonation of OPBI



OPBI (0 < x < 1, y = 0; x = 1, 0⩽y⩽1) **SOPBIs**

Experimental Two approaches, post-sulfonation and direct polymerization, were employed to synthesized SOPBI. For post-sulfonation, poly[2,2'-(p-oxydiphenylene)-5,5'-bibenzimidazole] (OPBI) was sulfonated in concentrated sulfuric acid or fuming sulfuric acid at 80 □. For direct polymerization, 4,4'-dicarboxydiphenyl ether-2,2'-disulfonic acid disodium salt (DCDPEDS) and 3,3'-diaminobenzidine (DABz) were polymerized in polyphosphoric acid (PPA) at 190 □ for 20 h or in phosphorus pentoxide/methanesulfonic acid in the ratio of 1:10 by weight (PPMA) reaction medium at 150 □ for 2-20 h. Proton conductivity was measured by using a four-point-probe electrochemical impedance spectroscopy technique.

Results and Discussion The synthesis of SOPBI was performed via two approaches. One is the post-sulfonation of the parent polymer OPBI using concentrated or fuming sulfuric acid as the sulfonating reagent at 80 □ for a desired time. SOPBIs with the high DS of 154% was obtained with fuming sulfuric acid containing 20% sulfur trioxide at 80 □ for 5 h. No significant polymer degradation was observed in the post-sulfonation processes indicating excellent oxidative stability of OBPI. Another approach is the direct polymerization of DCDPEDS and DABz in PPA at 190 □ or in PPMA at 150 □. However, insoluble gels were also obtained in both reaction mediums because of the occurrence of cross-linking. The SOPBIs prepared by the post-sulfonation method showed good solubility in some organic solvents such as dimethyl sulfoxide (DMSO), high thermal stability, good film forming ability and excellent mechanical properties. Fenton reagent teat revealed that OPBI and the SOPBI (DS = 60%) exhibited much better radical oxidative stability than the commercial PBI. The proton conductivity is strongly dependent on the relative humidity (RH) as well as the DS level. With an increase in RH, the proton conductivity increased rapidly. The SOPBI membrane with high DS (154%) displayed high proton conductivity (0.18 S/cm) in liquid water at 60 □, which is higher than that of Nafion 117 under the same conditions.