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SULFONATED POLY(ARYLENE ETHER BENZIMIDAZOLE) COPOLYMERS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

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Introduction

Polybenzimidazoles have been largely studied as candidates for proton exchange membrane (PEM) fuel cells.[1,2] The basic nature of the imidazole ring promotes interactions with strong acids such as HBr, H_2SO_4, and H_2PO_3.[3,4] In particular, PBI can incorporate significant amounts of phosphoric acid even from dilute aqueous solutions.[5]

Hergenrother et al. previously reported the synthesis of poly(arylene ether benzimidazole)s from a novel benzimidazole bisphenol.[6] The resulting copolymers displayed high unoriented thin-film tensile properties. Our group has shown the direct synthesis of novel sulfonated poly(arylene ether)s from sulfonated monomers. This direct copolymerization method leads to increased acidity of the proton-conducting sites, precise control of the ion exchange capacity, and improved thermal and mechanical stability.[7] Direct copolymerization of sulfonated PBIs has not been extensively studied. Asensio et al. prepared a sulfonated PBI using 5-sulfoisophthalic acid. Herein, we report the synthesis and characterization of disulfonated poly(arylene ether sulfone benzimidazole) copolymers.

Experimental

The synthesis of S-DCDPS[8,9,10] and HPBI[6] were previously reported. The direct synthesis of a disulfonated poly(arylene ether benzimidazole) with 50 mol % disulfonation is discussed. DCDPS (2.000 g, 7 mmol), SDCDPS (3.4210 g, 7 mmol), and HPBI (5.8286 g, 14 mmol) were introduced to a 250-mL, three neck flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and a nitrogen inlet/outlet. Potassium carbonate (2.21 g) and 75 mL of NMP were added to the reaction flask to afford a 15% (w/v) solid concentration. Toluene (40 mL) was added to the flask as an azeotroping agent. The Dean-Stark trap was filled with toluene and the reaction mixture was heated to 140 °C to dehydrate the system. After 4 h at 140 °C, the Dean-Stark trap was emptied and the oil bath temperature was heated to 190 °C for 20 h. The resulting viscous solution was diluted with DMAc, cooled to room temperature, and precipitated into an excess of deionized water. The precipitated copolymer was collected by filtration and the resulting white, fibrous copolymer was dried under vacuum at 120 °C for at least 24 h. Membranes were prepared by dissolving the copolymers in N,N-dimethylacetamide, filtering, and then casting the solution directly onto glass plates. The solvent was evaporated under nitrogen flow at 40 °C and the membranes were dried at 120 °C for 12 hours. All of the copolymer membranes were converted to the sulfonic acid form using dilute sulfuric acid.

Results and Discussion

The sulfonated copolymers were prepared by direct copolymerization (Figure 1). The benzimidazole bisphenol was chosen to study the effect of the incorporation of benzimidazole units on the properties of the resulting copolymers. The degree of disulfonation (or ion exchange capacity) was easily controlled by varying the ratio of SDCDPS to DCDPS in the copolymerization. The high molecular weight copolymers (intrinsic viscosities ranging from 1.9 to 2.7 dL/g) were analyzed by ^1H NMR, infrared spectroscopy, and thermogravimetric analysis (TGA).

^1H NMR was used to identify the molecular structure of the sulfonated copolymers and evaluate the degree of disulfonation. The degree of disulfonation was determined from the ratio of a peak in the sulfonated region to one in both the sulfonated and unsulfonated regions. The calculated values match well with the feed ratios indicating that the incorporation of the sulfonated comonomer was quantitative.

Standardized FT-IR spectra allowed for determination of the functional groups in the copolymers. The spectra displayed the characteristic benzimidazole adsorption bands as well as those associated with the sulfonic acid groups. The symmetric and asymmetric stretches of the sulfonic acid groups appeared at 1030 and 1097 cm^{-1}, respectively. The intensities of the peaks at 1030 and 1097 cm^{-1} increased with the degree of disulfonation.

The disulfonated copolymers were investigated by TGA in both their salt and acidified forms. The membranes were analyzed between 30 and 800 °C at a heating rate of 10 °C / min in air. A two-step degradation profile was observed for all sulfonated copolymers.

The influence of the benzimidazole moiety on the copolymer properties (water uptake, proton conductivity, etc.) will be discussed at the meeting.

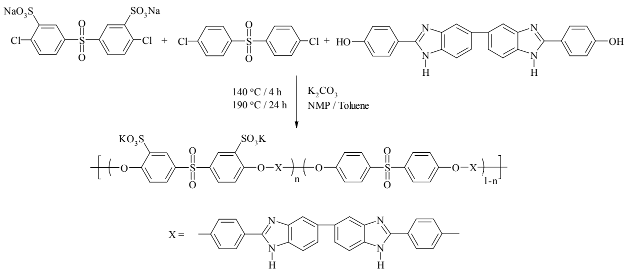

Figure 1. Synthesis of Sulfonated Poly(arylene ether sulfone benzimidazole) Copolymers

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