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Synthesis of novel sulfonated polybenzimidazole and preparation of cross-linked membranes for fuel cell application

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Abstract

A novel sulfonated polybenzimidazole, sulfonated poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (SOPBI), was successfully prepared by post-sulfonation reaction of the parent polymer, poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (OPBI), using concentrated and fuming sulfuric acid as the sulfonating reagent at 80 °C, and the degree of sulfonation (DS) could be regulated by controlling the reaction conditions. No significant polymer degradation was observed in the post-sulfonation processes. Direct polymerization of 4,4′-dicarboxydiphenyl ether-2,2′-disulfonic acid disodium salt (DCDPEDS) and 3,3′-diaminobenzidine (DABz), however, resulted in insoluble gels either in polyphosphoric acid (PPA) or in phosphorus pentoxide/methanesulfonic acid (PPMA) in a ratio of 1:10 by weight reaction medium. The SOPBIs prepared by the post-sulfonation method showed good solubility in dimethyl sulfoxide (DMSO), high thermal stability, good film forming ability and excellent mechanical properties. Cross-linked SOPBI membranes were successfully prepared by thermal treatment of phosphoric acid-doped SOPBI membranes at 180 °C in vacuo for 20 h and the resulting cross-linked membranes showed much improved water stability and radical oxidative stability in comparison with the corresponding uncross-linked ones, while the proton conductivity did not change largely. Highly proton conductive (150 mS cm^{-1}, 120 °C in water) and water stable SOPBI membrane was developed.

Keywords: Sulfonated polybenzimidazole; Synthesis; Cross-linking

1. Introduction

Polybenzimidazoles (PBIs) have attracted much attention in the past decade because of their potential important application in polymer electrolyte membrane fuel cells (PEMFCs) [1–16]. One of the most important features of phosphoric acid-doped PBI membranes is that at high doping levels (>300%) they show high proton conductivities even in completely anhydrous state and the conductivity increases with an increase in temperature up to 200 °C, which make them the most promising membrane materials for medium temperature (150–200 °C) PEMFC application. This is quite different from the case of sulfonated polymer membranes whose proton conductivity strongly depends on the dissociation of sulfonic acid and the amount of water molecules (carrier) for proton transport leading to drastic reduction in proton conductivity as the relative humidity decreases to low levels (<30%). The proton conductivity of phosphoric acid-doped PBI membranes is closely dependent on the doping level and higher doping level generally results in larger proton conductivity. The widely studied PBIs for PEMFC use are poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (a commercial PBI) and poly(2,5-benzimidazole) (ABPBI). Recently sulfonated polybenzimidazoles (SPBIs) have attracted particular attention and it has been reported that phosphoric acid-doped SPBI membranes generally showed higher proton conductivities than the corresponding phosphoric acid-doped non-sulfonated PBI membranes [10–18]. The synthesis of SPBIs can be

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achieved by three approaches. The first approach is chemical modification of the commercial PBI with lithium hydride followed by reaction with sulfonating reagents such as 4-bromomethylbenzene sulfonic acid sodium salt [10] and alkanesultone [11]. The second approach is direct polymerization from the sulfonated dicarboxylic acid monomers [12–14]. The third approach is post-sulfonation of PBI or ABPBI by heat treatment of sulfuric acid-doped membranes at high temperatures (450–475 °C) [15–18]. Direct polymerization method can give SPBIs with exactly desired structure and precisely controlled degree of sulfonation, but almost all the sulfonated monomers are not commercially available and needed to be synthesized. Post-sulfonation method is quite simple, however, it is reported that cross-linked and/or fragile membranes with low degree of sulfonation were often obtained because of the too high reaction temperature which is essential for sulfonation due to the rather low reactivity of both the commercial PBI and ABPBI. If the reactivity of PBIs is enhanced, sulfonation reaction might be carried out under relatively mild conditions. Incorporation of activated phenyl rings into PBI structure is expected to be an efficient way to achieve this goal. In this paper, we report on the synthesis and properties of a new sulfonated polybenzimidazole, sulfonated poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (SOPBI), via both direct polymerization method and post-sulfonation method. A new and facile cross-linking method is also proposed to prepare cross-linked sulfonated polybenzimidazole membranes.

2. Experimental

2.1. Materials

3,3′-Diaminobenzidine (DABz) was purchased from Acros Organics and used without further purification. 4,4′-Dicarboxydiphenyl ether (DCDPE) was kindly supplied by Peakchem (Shanghai) and vacuum dried at 80 °C prior to use. Methanesulfonic acid (MSA), phosphorus pentoxide, polyphosphoric acid (PPA), fuming sulfuric acid, 96% concentrated sulfuric acid, dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) were purchased from SCRC. DMSO, NMP, DMAc and DMF were distilled under reduced pressure and dried over 4A molecular sieves before use. Other materials were used as received. Poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (OPBI) was synthesized by condensation polymerization of DCDPE and DABz in PPMA at 140 °C for 160 min with total monomer concentration of 10 wt% [19].

2.2. Post-sulfonation

To a 100 mL dry flask were added 1.0 g of OPBI and 10 mL of 96 wt% concentrated sulfuric acid or fuming sulfuric acid containing 10% or 20% sulfur trioxide. The mixture was magnetically stirred and slowly heated to 80 °C and kept at this temperature for a given time. The homogeneous solution was slowly poured into ice water and the resulting fiber-like precipitate was soaked in 5% sodium bicarbonate solution at room temperature for two days. The solid was collected by filtration, thoroughly washed with deionized water and dried in vacuo at 150 °C for 10 h.

2.3. Synthesis of 4,4′-dicarboxydiphenyl ether-2,2′-disulfonic acid disodium salt (DCDPEDS)

To a 100 mL dry three-neck flask were added 5.16 g (20.0 mmol) of DCDPE and 20 mL of fuming sulfuric acid (30% SO_3). The reaction mixture was stirred at 80 °C for 12 h. Upon cooling to room temperature, the mixture was poured into crushed ice. Sodium chloride was added to salt out the product. The resulting precipitate was filtered off, washed with saturated sodium chloride solution and dried in vacuo. The crude product was added to 200 mL of DMSO with stirring and the insoluble solid was filtered off. The filtrate was distilled under reduced pressure and the residual was thoroughly washed with acetone and dried in vacuo at 120 °C for 20 h. A white solid weighing 5.75 g was obtained, yield: 62%. ^{1}H NMR (DMSO-d_6):$\delta = 13.02$ (2H, −COOH), 8.371 (s, 2H), 7.885 (d, 2H), 6.809 (d, 2H). Melting point: 250 °C (DSC, no decomposition peak was observed up to 350 °C).

2.4. Polymerization

Two procedures were employed for polymerization of DCDPEDS and DABz and the experimental details are described as follows using the homopolymer as an example.

Procedure 1. To a 100 mL dry three-neck flask were added 0.6428 g (3.0 mmol) of DABz, 1.386 g (3.0 mmol) of DCDPEDS and 20 mL of PPMA under nitrogen flow. The reaction mixture was magnetically stirred and slowly heated to 140 °C for 20 h. Upon cooling, the gel-like mixture was transferred to ice water with stirring and the precipitate was filtered off. The solid was soaked in 5% sodium bicarbonate solution for two days, then filtered, thoroughly washed with deionized water and dried in vacuo at 120 °C for 10 h.

Procedure 2. To a 100 mL dry three-neck flask equipped with a mechanical stirring device were added 25 g of PPA and 5.5 g of phosphorus pentoxide under nitrogen flow. The mixture was heated and stirred until phosphorus pentoxide was completely dissolved. After cooling to room temperature, 0.6428 g (3.0 mmol) of DABz and 1.386 g (3.0 mmol) of DCDPEDS were added to the reaction flask. The reaction mixture was stirred and heated at 150 °C for 4 h and 190 °C for 20 h, respectively. Upon cooling, the gel-like mixture was transferred to ice water with stirring and the precipitate was filtered off. The solid was soaked in 5% sodium bicarbonate solution for two days, then filtered, thoroughly washed with deionized water and dried in vacuo at 120 °C for 10 h.

2.5. Membrane formation

Polymer solution of 5–10 wt% in DMSO was cast onto glass plates and dried in an air oven at 80 °C for 5 h. The films were peeled off from glass plate and dried in vacuo at 120 °C