Novel hydrophilic–hydrophobic multiblock copolyimides as proton exchange membranes: Enhancing the proton conductivity

Nanwen Li [a,b], Jia Liu [a], Zhiming Cui [b,c], Suobo Zhang [a,*], Wei Xing [c]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[b] Graduate School of Chinese Academy of Sciences, China
[c] State Key Laboratory of Electroanalytical Chemistry, China

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ABSTRACT

A series of novel multiblock copolymers based on sulfonated copolyimides were developed and evaluated for use as proton exchange membranes (PEMs). In these multiblock copolyimides, the hydrophilic blocks were composed of the sulfonated dianhydride and the sulfonated diamine, with sulfonic acid groups on every aromatic ring (i.e., fully sulfonated). This molecular design was implemented to effectively enhance the proton conductivity. The properties of the multiblock copolyimides with varying IEC values or block lengths were investigated to obtain a better understanding of the relationship between molecular structure and properties of proton exchange membranes. The water uptake and proton conductivity were found to be highly dependent upon their structure. The block copolymers displayed significantly higher proton conductivities, especially at low relative humidity than the random copolymers with a similar IEC. The results indicated that the distribution of sulfonic acid and the length of the blocks play a key role on properties of proton exchange membranes.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted much attention in the last few years as promising power sources for transport, stationary, and portable applications due to their low pollution levels and high conversion efficiency [1–3]. Proton exchange membranes (PEMs), which act as an electrolyte to transport protons from the anode to the cathode, are the key component of PEM fuel cell systems. Among various requirements for PEMs, the most essential property is proton conductivity. The state-of-the-art PEM is perfluorosulfonic acid membranes such as Nafion, because of their superior chemical and electrochemical stabilities, in addition to high proton conductivity with relatively low ion exchange capacity (IEC). However, some specific limitations exist for Nafion membranes including high cost, high gas permeability, and loss of the preferable properties at high temperature ($>80\,°C$) [2,4]. This stimulated many efforts in the development of alternative PEMs.

There has been considerable effort on PEMs based on sulfonated aromatic polymers since they are thermally stable, easy to modify chemically, and inexpensive [5–8]. Generally, sulfonated aromatic polymers can achieve conductivities that are comparable to those of Nafion only with high IECs, resulting in a high water uptake (WU) and the loss of mechanical properties. It is widely recognized that the lower proton conductivity of sulfonated aromatic polymer is attributed to the lack of ion channels and the lower acidity of Ar-SO_3H [9–13]. The model suggested by Kreuer [10] for a sulfonated poly(ether ketone) confirms less pronounced ionic/nonionic separation than that of Nafion, i.e., a morphology with narrower channels than those in Nafion but with highly branched channels and many dead-end channels. Therefore, increasing the hydrophilic/hydrophobic separation to obtain a good microphase separation structure, and thus enhance proton conductivities are desired [14–16].

Various strategies have been pursued to form efficient ionic networks for enhancing the proton conductivity [12,17], include the concentration of the ionic groups on short side chains to increase the hydrophilic–hydrophobic separation [18–24], the incorporation of highly ionic blocks and grafts to favor a microphase separation [25–29], and the use of polymer main chains containing highly hydrophobic fluorinated chains to enhance the hydrophobic–hydrophilic incompatibility [17,25,29]. Among these strategies, the block copolymers is of interest due to their self-organization behaviors which could offer the opportunity for precise control of the membrane morphologies through the manipulation of chemical compositions and relative volumes of the constituent blocks [30,31]. Certain block copolymers based, for example, on sulfonated

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* Corresponding author. Tel.: +86 431 85262118.
E-mail address: sbzhang@ciac.jl.cn (S. Zhang).

polyimide or sulfonated poly(arylene ether sulfone), have been claimed to display higher proton conductivities than the corresponding random copolymers [32–37]. Unfortunately, the so-called hydrophilic blocks of the block copolymers are composed not only of sulfonated but also of unsulfonated (or actually partly sulfonated) aromatic rings, a consequence of their lower hydrophilicity [38,39]. Furthermore, for a given IECs, the partly sulfonated block results in a relatively small volumes of the hydrophobic block, and thus an insufficient hydrophobicity. This in combination with the lower hydrophobicity of the aromatic ring leads to a less pronounced hydrophilic/hydrophobic separation, and thus a low-level microscale organization of the phase-separated nanodomains. The potential advantages of using these materials to enhance the proton conductivity in PEM have therefore not been fully realized. It is important, herein, to design an aromatic ionomer membrane with pronounced hydrophilic–hydrophobic separation, and to subsequently investigate this membrane to completely elucidate the intrinsic effect of the hydrophilic–hydrophobic separation on water uptake and proton transport of the membrane.

The current paper, thus presents a study on novel multiblock-sulfonated polyimides in which the hydrophilic blocks were composed of sulfonated dianhydride and sulfonated diamine monomers, with sulfonic acid groups on every aromatic ring (fully sulfonated), in order to dramatically enhance the hydrophilicity. For a given IEC, the fully sulfonated hydrophilic blocks resulted in the relatively large volumes of the hydrophobic blocks. Such an architectonically novel class of multiblock copolymer was expected to increase the hydrophilic/hydrophobic separation and microphase separation of non-polar and ionic moieties, and thus enhance the proton conductivity. The effect of block lengths water uptake and proton conductivity was studied in detail to further examine the structure–property relationships.

2. Experimental

2.1. Materials

4,4′-Diamino-3,3′-dimethyldphenylmethane (DMMDA) was purchased from Aldrich and used as received. 4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) [41] and 6,6′-disulfonic acid-4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (SBTDA) [42] were prepared according to the method previously reported. All other reagents were obtained from commercial sources and used as received.

2.2. Monomer and polymer syntheses

2.2.1. Synthesis of 3,3′-dimethyl-4,4′-methylenedianiline-6,6′-disulfonic acid (DMMDADS)

To a 100 mL three-necked flask equipped with a mechanical stirring device was charged with 2.26 g (10 mmol) of 4,4′-diamino-3,3′-dimethyldphenylmethane (DMMDA). The flask was cooled in an ice bath, and then 1.7 mL of concentrated sulfonic acid (95%) was slowly added with stirring. After DMMDA was completely dissolved, 3.5 mL fuming (SO_3 60%) sulfonic acid was slowly added to the flask. The reaction mixture was stirred at 0 °C for 2 h and then slowly heated to 60 °C and kept at this temperature for additional 2 h. After cooling to room temperature, the slurry solution was carefully poured into 20 g of crushed ice. The resulting white precipitate was filtered off and then redissolved in a sodium hydroxide solution. The basic solution was filtered, and the filtrate was acidified with concentrated hydrochloric acid. The solid was filtered off, washed with water and methanol successively, and dried at 80 °C in vacuum. Then 3.05 g of white product was

obtained (yield: 85%); ^{1}H NMR (DMSO-d_6; Et$_3$N was added for dissolution in DMSO): 7.10 (2H, s), 6.66 (2H, s), 4.48 (2H, s), 4.28 (4H, –NH$_2$), 1.87 (6H, s). ^{13}C NMR: 144.4 (2C, Ar), 143.5 (2C, Ar), 133.9 (2C, Ar), 129.6 (2C, Ar), 122.6 (2C, Ar), 113.2 (2C, Ar), 32.5 (1C, –CH$_2$–), 18.1 (2C, –CH$_3$).

2.2.2. Synthesis of random sulfonated copolyimides

A typical procedure for the random copolymerization is as follows (2.69–r). To a 100 mL completely dried three-necked flask were added 0.5 mmol of DMMDADS, 8 mL of m-cresol, and 1.2 mmol of triethylamine successively under nitrogen flow with stirring. After DMMDADS was completely dissolved, 0.5 mmol of SBTDA, 0.5 mmol of BTDA, 0.5 mmol of DMMDA, 1.2 mmol of triethylamine and 2 mmol benzoic acid were added. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to 80 °C, additional 5 mL of m-cresol was added to dilute the highly viscous solution, and then the solution was poured into 200 mL acetone. The precipitate was filtered off, washed with acetone thoroughly, and dried in vacuum oven for 12 h at 150 °C.

2.2.3. Synthesis of block-sulfonated copolyimides

A typical procedure for the block polymerization is as follows [39,40]. In one flask, the diamine-terminated oligomers were prepared by the reaction of DMMDADS and SBTDA in the presence of triethylamine in m-cresol (8 mL) at 80 °C for 4 h and 180 °C for 18 h. In another flask, the dianhydride-terminated oligomers were prepared from BTDA and an excess of DMMDA in m-cresol (8 mL) at 80 °C for 4 h and 180 °C for 18 h. Benzoic acid and the two mixtures containing each oligomer were mixed and copolymerized at 180 °C for 24 h. After cooling to 80 °C, the solution was poured into a large of acetone. The precipitate was filtered off, washed with acetone thoroughly, and dried in vacuum oven at 150 °C for 12 h.

2.3. Membrane preparation and proton exchange

A series of tough, ductile copolymer membranes were prepared with a controlled thickness of 40–50 μm. The polymers with triethylammonium salt form were dissolved in DMSO to form 8–10% solution at 80 °C. The solution was filtered and cast onto glass plates at 120 °C for 12 h. The as-obtained membranes were dried in vacuum at 150 °C for 12 h to remove the residual solvent, and then treated with 1.0 N sulfonic acid at room temperature for 4 days for proton exchange. The proton-exchanged membranes were thoroughly washed with de-ionized water and then dried in vacuum at 100 °C for 10 h.

2.4. Polymer characterization

2.4.1. Measurements

^{1}H NMR spectra were measured at 300 MHz on an AV300 spectrometer. FT-IR spectra were obtained with a Bio-Rad Digilab Division FTS-80 FT-IR spectrometer. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. Molecular weight was measured with gel permeation chromatography (GPC) equipped with two Shodex KF-805 columns and a Jasco 805 UV detector (270 nm) with DMF containing 0.01 M LiBr as eluent. Molecular weight was calibrated with standard polystyrene samples. Ion exchange capacity (IEC) of the membrane was determined by titration. In the titration method, the membranes in the H$^+$ form were immersed in a 1 M NaCl solution for 24 h to liberate the H$^+$ ions (the H$^+$ ions in the membrane were replaced by Na$^+$ ions). The H$^+$ ions in solution were then titrated with 0.01 M NaOH using phenolphthalein as an indicator.