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Synthesis and characterization of sulfonated polybenzimidazoles containing 4-phenyl phthalazinone groups for proton exchange membrane

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ABSTRACT

A novel series of sulfonated 4-phenyl phthalazinone-based polybenzimidazoles (SPPBIs) were synthesized by solution polycondensation of 3,3′-diaminobenzidine (DAB), 4-(4-(4-(4-carboxyphenoxy)phenyl)-1-oxophthalazin-2(1H)-yl) benzoic acid (CPPBC) and 5-sulfoisophthalic acid monosodium salt (SIPN) in polyphosphoric acid (PPA). Their chemical structures were characterized by NMR, FT-IR and wide angle X-ray diffraction (WAXD). The inherent viscosities in 98 wt.% H_2SO_4 were in the range of 1.49–1.78 dL/g. The SPPBIs exhibited good solubility in polar aprotic organic solvents, such as *N*-methyl-2-pyrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO). The membranes were prepared by solution casting technique using DMSO as solvent. The SPPBI polymers showed excellent thermal stability, and their membranes displayed low water uptake, low swelling ratio, good mechanical properties and excellent resistance to oxidation. The SPPBI membranes had unexpected low methanol permeability (5.46×10^{-10}– 1.27×10^{-9} cm^2/s). They exhibited high conductivities in the range of 4.8×10^{-3} S/cm to 1.3×10^{-2} S/cm at 80 °C and from 2.3×10^{-3} S/cm to 8.5×10^{-3} S/cm at 20 °C.

1. Introduction

As clean and efficient energy conversion devices, proton exchange membrane fuel cells (PEMFCs) have attracted increasing attention recently [1,2]. Proton exchange membrane (PEM), which determines the performance of a PEMFC system, is one of the key elements. Over the past decade, much research has focused on perfluorosulfonic acid type membranes, such as DuPont's Nafion® or similar polymers [3,4]. However, their high cost, environmental inadaptability and susceptibility to catalyst poisoning by impurities such as CO have limited their application. In recent years, many efforts have been focused on the development of new cheaper PEMs to substitute the perfluoropolymers and to improve the performance of PEMFC. Aromatic polymers such as polyimide [5,6], poly(ether sulfone) [7,8], and poly(ether ketone) [9] have been widely investigated as PEM candidate materials because of their excellent thermal and chemical stability.

Polybenzimidazole (PBI), particularly known for its high chemical and thermal stability, has attracted considerable attention over recent years, particularly since the landmark study by Wainright et al. of the acid doped PBI membranes as promising high temperature PEMFC candidates [10]. A notable feature of PBIs is their excellent thermal and oxidation stability, as well as good stability in the presence of acid and base. Such properties satisfy the requirements of PEM in fuel cells [11,12]. To obtain the ionic group containing PBI, sulfonated PBIs are developed by post-sulfonation, grafting and direct polycondensation method [13]. The direct polycondensation method displays the advantages to design the polymer structure and to control the sulfonation degree. The strong acid–base interactions and the rigid backbones of sulfonated PBIs make them hardly soluble in organic solvents. Meanwhile, the interactions between SO_3^- and NH of benzimidazole ring impede the proton conduction via sulfonic acid group. Therefore, most sulfonated PBIs present comparatively relatively low proton conductivity at the level of 10^{-4}–10^{-3} S/cm even at 100% relative humidity which is too low to meet the lowest requirement (10^{-2} S/cm) for practical use [14,15].

4-Phenyl phthalazinone has a twisted and noncoplanar structure, which can cumber the close packing of chains, reduce the regularity of the main chain, and increase the free space between the molecular

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chains. We have developed a series of aromatic polymers containing 4-phenyl phthalazinone moieties, which have good solubility and excellent thermal properties [16–20]. Moreover, the sulfonated aromatic polymers containing phthalazinone groups have been prepared [21–23]. They exhibited excellent thermal stability and good solubility, and their membranes showed low methanol permeability and high proton conductivity. Recently, we have found that introduction of phthalazinone moiety could improve the solubility of PBI and facilitate proton transfer [24,25].

As a part of our continuing research on the synthesis of proton conducting aromatic heterocyclic polymers, the synthesis of SPPBI from 4-(4-(4-(4-carboxyphenoxy)phenyl)-1-oxophthalazin-2(1H)-yl) benzoic acid (CPPBC), 5-sulfoisophthalic acid monosodium salt (SIPN) and 3,3′-diaminobenzidine (DAB) monomers was addressed in this work. In varying the ratio CPPBC/SIPN monomers, different SPPBIs were prepared as random copolymers. The relationship between polymer structure and the enhancement of properties was investigated.

2. Experimental details

2.1. Materials

5-Sulfoisophthalic acid monosodium salt (SIPN) and 3,3′-diaminobenzidine (DAB) were purchased from Sigma-Aldrich Co., Inc. and used as received. 4-(4-(4-(4-Carboxyphenoxy)phenyl)-1-oxophthalazin-2(1H)-yl)benzoic acid (CPPBC) was synthesized according to the method reported previously [26]. Polyphosphoric acid (PPA, 116%) was prepared by heating 1:1.8 weight ratio of orthophosphoric acid (85%) and phosphorus pentaoxide for 6 h at 100 °C. All other solvents and chemicals were obtained from commercial sources and used as received.

2.2. Instrumentation

FT-IR spectra were recorded on a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer. ^{1}H NMR spectra were measured at 400 MHz with a Bruker spectrometer at an operating temperature of 25 °C using H_2SO_4-d_6 as solvent. Inherent viscosities of the polymers were measured by Ubbelohde capillary viscometer at 25 °C using 98% concentrated sulfuric acid as solvent. Solubility behavior of the salt form SPPBIs was studied by dissolving 4 mg polymer sample in 0.5 mL solvent. Thermogravimetric analysis (TGA) of the polymers was performed on a METTLER TGA/SDTA851 thermogravimetric analysis instrument under nitrogen atmosphere at a heating rate of 10 °C/min from 100 to 800 °C. Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Rigaku D/max 2400 automatic X-ray diffractometer with Ni-filtered Cu Ka radiation (40 V, 100 mA).

2.3. Polymer synthesis

A series of sulfonated polybenzimidazoles containing 4-phenyl phthalazinone moiety with different sulfonation degrees (SD) were synthesized by polycondensation of DAB with a mixture of CPPBC and SIPN in different molar ratios in PPA, respectively. The sulfonated polybenzimidazoles are denoted as SPPBI-xx, where “xx” refers to the sulfonation degree. For example, the copolymer labeled as SPPBI-20 indicates that its sulfonation degree is 20%. All the polymers were prepared in the similar procedure. Thus, a typical synthetic procedure of SPPBI-20 is given as an example: 1.2840 g (6 mmol) of DAB, 2.1988 g (4.8 mmol) of CPPBC, 0.3216 g (1.2 mmol) of SIPN and 27 mL of PPA were charged into a 100 mL three-necked round-bottom flask equipped with a mechanical stirring device, a nitrogen inlet and an outlet. The mixture was heated to 160 °C for 8 h and then to 190 °C for another 7 h. The resultant hot solution was poured into deionized water to precipitate the polymer. The yellow fiber-like precipitate was filtered off and washed with boiling water for several times until neutral. The obtained polymer was soaked in 5 wt.% sodium bicarbonate solution for 24 h, washed with deionized water until neutral, and then dried in vacuum oven for 12 h at 100 °C.

2.4. Membrane preparation and characterization

A series of sulfonated polybenzimidazole membranes were prepared by solution casting method. Powdered form of SPPBI (5 wt.%) was dissolved in dimethyl sulfoxide (DMSO, 95 wt.%) to give a homogeneous and viscous solution, from which membranes were cast onto dust-free glass slide using a doctor blade. The samples were kept overnight in an oven at 60 °C to remove the solvent. The dry membranes were removed from their support by immersion in water, and the recovered membranes were treated in 1 M HCl at room temperature for 24 h to ensure complete conversion to the acid form, and then washed by deionized water to remove free HCl. They were dried again under vacuum at 100 °C to remove residual HCl and the last traces of solvent.

The ion-exchange capacities (IEC) of the SPPBI membranes were measured by the classical titration method. A dry membrane sample of about 0.2 g was immersed in 40 mL of 1.0 M NaCl solution for 48 h. The released proton concentration was then titrated with 0.02 mol/L NaOH solution using phenolphthalein as indicator. IEC values can be calculated by the following equation:

$$\mathrm{IEC} = \frac{VNaOH \times CNaOH}{W_{dry}}$$

where W is the weight of the membrane, and V_{NaOH} and C_{NaOH} are the volume and the molar concentration of the NaOH used in titration, respectively.

Meanwhile, the theoretical value of IEC was calculated using the following equation:

$$\mathrm{IEC}^{\mathrm{T}} = \frac{1000 \times SD}{M}$$

where SD is the theoretical sulfonation degree of the polymer, and M is the molecular weight of the repeat unit.

The membranes were dried in vacuum oven at 100 °C for 48 h. The weight (W_{dry}) and length (L_{dry}) of the dry membranes were measured. Water uptake was tested by immersing the dry SPPBI membranes in deionized water for 48 h at 25 °C and 80 °C, respectively. Then, the membranes were taken out, wiped dry, and weighed immediately. The weight (W_{wet}) and length (L_{wet}) of the wet membranes were measured. The water uptake (WU) and the swelling ratio were calculated by the following equations:

$$\mathrm{WU}(\%) = \frac{Wwet - Wdry}{Wdry} \times 100\%$$

where W_{dry} and W_{wet} are the weights of the dry and the wet membranes, respectively.

$$\text{Swelling ratio} = \frac{Lwet - Ldry}{Ldry} \times 100\%$$

where L_{dry} and L_{wet} are the length of the dry and the wet membrane, respectively.

The proton conductivity (σ) was measured by using an electrochemical impedance spectroscopy technique. The tested membrane was sandwiched between two electrodes, and the resistance of the