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ScienceDirect
Polymer 48 (2007) 6210–6214
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Water resistant sulfonated polyimides based on 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA) for proton exchange membranes

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Received 5 May 2007; received in revised form 7 July 2007; accepted 10 July 2007
Available online 18 July 2007

Abstract

A series of sulfonated polyimides (SPIs) were synthesized in *m*-cresol from 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA), 4,4′-diaminodiphenylether-2,2-disulfonicacid (ODADS), and 4,4′-diamino-diphenyl ether (ODA) in the presence of triethylamine and benzoic acid. The resulted polyimides showed much better water resistance than the corresponding sulfonated polyimides from 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA) and ODADS, which is contributed to the higher electron density in the carbonyl carbon atoms of BNTDA. Copolyimides S-75 and S-50 maintained their mechanical properties and proton conductivities after aging in water at 100 °C for 800 h. The proton conductivity of these SPIs was 0.0250–0.3565 S/cm at 20 °C and 100% relative humidity (RH), and increased to 0.1149–0.9470 S/cm at 80 °C and 100% RH. The methanol permeability values of these SPIs were in the range of 0.99–2.36 × 10^{-7} cm^2/s, which are much lower than that of Nafion 117 (2 × 10^{-6} cm^2/s).

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Keywords: 4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA); Sulfonated polyimides; Water resistance

1. Introduction

Recently, considerable attentions have been paid to proton exchange membrane fuel cells (PEMFCs) as a clean electric source for automobile, stationary, and portable power applications due to their lower weight, high efficiency, and low poison emission [1–3]. Proton exchange membrane (PEM) is a critical component in PEMFC. Perfluorosulfonate ionomers, such as Nafion, are the state-of-art membrane materials with features of high conductivity and excellent chemical stability [4–6]. However, because of their high cost, low operational temperature below 80 °C, and large gas crossover, many efforts have been made to develop alternative PEMs, especially sulfonated aromatic polymers [7–9].

Sulfonated polyimides have been studied by several groups as potential PEM materials [10–18]. Water resistance (including hydrolytic stability and solubility or swelling in water) of SPIs is an important factor that affects the fuel cell performance since the imide groups are relatively susceptible to decomposition due to the nucleophilic attack by water. The influence of the diamine structures on the hydrolytic stability of SPIs has been well investigated. It is known that SPIs derived from the diamine with higher basicity showed better hydrolytic stability. The separation of sulfonic acid groups from the aminophenyl rings and the introduction of aliphatic segments in both the main and the side chains are effective approaches to enhance the basicity of diamines [10–18]. Watanabe et al. [15,16] prepared SPIs from 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA), 3,3′-bis(sulfopropoxy)-4,4′-diaminobiphenyl (BSPA), and 10-decamethylenediamine (DMDA). Impressively, these SPI membranes showed comparable performance to Nafion in fuel cell at 80 °C and were durable for 5000 h without distinct degradation.

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0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.07.026

By far, most widely used six-membered dianhydride for SPIs is NTDA, except for 4,4′-ketone dinaphthalene 1,1′,8,8′-tetracarboxylic dianhydride (KDNTDA) recently employed by Okamoto et al. [19]. The hydrolysis of imide groups was mainly resulted from the nucleophilic attack of the water molecule on the carbonyl carbon atoms; the dianhydrides with higher electron density in carbonyl carbon atoms should produce polyimides with higher hydrolytic stability. The electron density of the carbonyl carbon atoms can be characterized by their electron affinity (E_a), and the lower the absolute values of E_a is, the higher the electron density is in carbonyl carbon atoms [20]. It has been reported that 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA) has a lower electron affinity, i.e. 3.7790 vs 4.0102 eV, than NTDA [21]. Therefore, in this paper, we present the synthesis of SPIs on the basis of BNTDA, 4,4′-diaminodiphenylether-2,2-disulfonic-acid (ODADS), and 4,4′-diamino-diphenyl ether (ODA). Furthermore, the SPIs based on BNTDA showed enhanced water resistance compared with the corresponding polymers from NTDA.

2. Experimental

2.1. Materials

4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA) [22] and 4,4′-diaminodiphenylether-2,2-disulfonic-acid (ODADS) [12] were prepared according to the reported procedures. The other reagents used in this study were purchased from Shanghai Chemical Reagent Plant. 4,4′-Diamino-diphenyl ether (ODA) was purified by sublimation in vacuum. Triethylamine (Et_3N) and *m*-cresol were used after distillation. Other reagents were of analytical grade and used as received.

2.2. Synthesis of sulfonated polyimides based on BNTDA

A representative polymerization procedure is described as follows: 0.5400 g (1.5 mmol) of ODADS, 0.3004 g (1.5 mmol) of ODA, 0.8040 g (3.0 mmol) of BNTDA, 0.51 g (4.2 mmol) of benzoic acid, 0.36 g (3.6 mmol) of triethylamine, and 15 mL of *m*-cresol were placed in a three-necked, 100 mL round-bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet. The mixture was stirred at room temperature for 10 min and then heated at 80 °C for 2 h and then at 180 °C for 10 h. After cooling to 100 °C, 10 mL *m*-cresol was added to dilute the viscous solution. Then it was poured into 100 mL of ethanol with stirring. The fiberlike precipitate was collected by filtration and extracted with ethanol in a Soxhlet extractor for 24 h, and then dried in vacuum for 4 h to afford powder of sulfonated polyimide with the yield of 95%.

2.3. Membrane preparation and proton exchange

SPI films (in triethylammonium salt form) were prepared by casting their *m*-cresol solution (5%) at 100 °C for 8 h. Then the film was soaked in methanol for 24 h to remove the residual solvent and dried at 120 °C for 8 h in vacuum. The proton exchange was performed by boiling the films in 0.5 mol/L H_2SO_4 for 3 h and then immersing them in 2 mol/L H_2SO_4 at room temperature for 2 weeks. The films in proton form were thoroughly washed with deionized water.

2.4. Measurements

Fourier transform infrared (FT-IR) spectra were determined with a Bio-Red Digilab Division FTS-80 spectrometer. ^1H NMR (tetramethylsilane as an internal standard) spectra were recorded on a Varian Unity spectrometer at 400 Hz. Inherent viscosities were determined at 30 °C with an Ubbelohde viscometer, and the concentration was 0.5 dL/g in *m*-cresol. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min in air. The films were dried at 120 °C or 3 h in vacuum and then balanced at 50% relative humidity for 2 days before measurements. The tensile measurements were carried out on an Instron model 1122 at room temperature at a rate of 5 mm/min. The relative humidity when testing was also 50%.

2.5. Proton conductivity

Proton conductivity of membranes was measured by a four-electrode AC impedance method from 0.1 Hz to 100 KHz, 10 mV ac perturbation and 0.0 V dc rest voltage. Impedance spectra were recorded using a Princeton Applied Research Model 273A Potentiostat (Model 5210 Frequency Response Detector, EG&G PARC, Princeton, NJ). The membranes were fixed in a measuring cell made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in water. The proton conductivity (σ) of the membranes was calculated using the following equation:

$$\sigma = \frac{L}{RA} \tag{1}$$

where L, R, and A denote the distance between the two inner gold wires, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

2.6. Water uptake

Water uptake was measured by immersing an SPI sample into water at 80 °C for 6 h. Then the sample was taken out, wiped with tissue paper very quickly, and weighed on a microbalance. Water uptake was calculated from the following equation:

$$S = (W_s - W_d)/W_d \times 100\% \tag{2}$$

where W_d and W_s are the weights of dry and corresponding water-swollen membranes, respectively.

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