Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/he

Soluble sulfonated polybenzothiazoles derived from 3,3′-disulfonate-4,4′-dicarboxylbiphenyl for proton exchange membranes

Gang Wang, Guyu Xiao, Deyue Yan**

College of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

ARTICLE INFO

Article history:
Received 4 October 2011
Received in revised form
28 November 2011
Accepted 4 December 2011
Available online 29 December 2011

Keywords:
Polybenzothiazole
Proton exchange membrane
Soluble
Sulfonated

ABSTRACT

Two series of sulfonated polybenzothiazoles were synthesized by polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride and 3,3′-disulfonate-4,4′-dicarboxylbiphenyl with 4,4′-dicarboxylbiphenyl or 2,2-bis(4-carboxyphenyl) hexafluoropropane, which were termed as sPBT-DP and sPBT-BP, respectively. The first series is insoluble in common polar solvents because of its rigid structure. In contrast, the sPBT-BP series are soluble in DMSO and NMP, due to the flexible hexafluoroisopropylidene moieties in the backbone. Thus they could be cast into homogeneous membrane and evaluated as proton exchange membranes. The studies illustrated that they showed high thermal and oxidative stability as well as excellent mechanical properties. Moreover, they exhibited high proton conductivity and outstanding dimensional stability. For example, sPBT-BP57.5 displayed a proton conductivity of 0.094 S/cm and an in-plane swelling of 9.7% as well as a through-plane swelling of 35% at 80 °C. The sPBT-BP ionomers are a promising material for proton exchange membranes.

Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) attracted much concern in recent years. Proton exchange membranes (PEMs) are one of the key components of PEMFCs. Up to now, the perfluorinated Nafion is still the widely used PEMs. However, the drawbacks such as low operating temperature, high methanol permeability, and high cost limited its applications [1]. Therefore, a variety of non-fluorinated aromatic polymers with high thermal stability, excellent mechanical properties and high chemical stability have been employed as the matrix of PEMs [1–7]. These aromatic polymers include poly(arylene ether)s [8–12], poly(arylene thioether)s [13–16], polyimides [17–19], poly(phthalazinone ether)s [20–22], polyphosphazenes [23,24], polybenzimidazoles [7,25–28], polybenzoxazoles [29], and their derivatives [11,30–35]. Many aromatic PEMs exhibited excellent properties.

Polybenzothiazoles are a kind of high performance polymers and thus are regarded as a promising matrix for PEMs [36]. However, only a few of sulfonated polybenzothiazoles (sPBT) were synthesized till now. Furthermore, they were initially designed to be used as structural materials, which displayed low molecular weight or poor solubility [37,38]. On the other hand, sulfonated polybenzothiazoles exhibit no softening or glass transition before thermal degradation because they possess rigid structure and strong intermolecular

* *Corresponding authors*. Tel.: +86 21 54742664; fax: +86 21 54741297.
E-mail addresses: gyxiao@sjtu.edu.cn (G. Xiao), dyyan@sjtu.edu.cn (D. Yan).
0360-3199/$ – see front matter Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2011.12.022

interactions, similar to polybenzothiazoles [36]. Hence sPBT could not form homogeneous membrane by extrusion or blow molding, and the sPBT membranes could only be achieved by casting polymer solution [38]. This demands that sulfonated polybenzothiazoles exhibit high molecular weight as well as good solubility. The previous sPBT could not be utilized as the PEM materials because of low molecular weight or poor solubility [37,38]. Our group developed highly soluble sPBT with high molecular weight for the first time by incorporating the bulky pendent group or flexible linkage into the backbone, which displayed excellent overall properties as PEMs [38]. Their sulfonic acid groups are derived from the monomer of bis(3-sulfonate-4-carboxyphenyl) sulfone (BSCPS). In addition to this article, PEMs based on sulfonated polybenzothiazoles have not been found at present.

In this paper, two series of sPBT were prepared by polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and 3,3′-disulfonate-4,4′-dicarboxylbiphenyl (SCBP) with 4,4′-dicarboxylbiphenyl (DCBP) or 2,2-bis(4-carboxyphenyl) hexafluoropropane (6FA), respectively. The first series was expressed as sPBT-DPxx, while the other series was denoted as sPBT-BPxx, where "xx" is the molar percent ratio of sulfonated monomer in the feed. The effect of the flexible hexafluoroisopropylidene moieties on the solubility of sPBT was explored by comparative study. The structure of these sPBT was analyzed, and the properties of the corresponding membranes, such as the solubility, water uptake, swelling, oxidative stability, mechanical properties, and proton conductivity, were investigated in detail. In addition, their properties were compared with those of sPBT derived from the monomer of BSCPS.

2. Experiment

2.1. Materials

2,5-Diamino-1,4-benzenedithiol dihydrochloride (DABDT) was purchased from TCI. 2,2-Bis(4-carboxyphenyl) hexafluoropropane (6FA) and 4,4′-dimethylbiphenyl were bought from Acros Organics. 4,4′-Dicarboxylbiphenyl (DCBP) was obtained from Sigma–Aldrich. Phosphorous pentoxide, polyphosphoric acid (PPA, 81%), methane sulfonic acid (MSA), and other chemicals were purchased from Shanghai Chemical Reagents Company. All the commercial reagents were used without further purification. 3,3′-Disulfonate-4,4′-dicarboxylbiphenyl (SCBP) was prepared according to our previous report [26].

2.2. Synthesis of polymers

As a typical procedure, the preparation of sPBT-BP65 was depicted as follows. The preparation was performed in a 100 mL three-necked round bottom flask equipped with a nitrogen inlet/outlet and a mechanical stirrer. DABDT (0.45 g, 1.8352 mmol) was dissolved in deaerated PPA (12.4 g). The mixture was stirred at room temperature for 12 h and then held at 70 °C for 24 h until the evolution of hydrogen chloride ceased. After cooling to room temperature, SCBP (0.4915 g, 1.1011 mmol) and 6FA (0.2879 g, 0.7340 mmol) were added to the clear reaction system and stirred at 100 °C for 8 h. Subsequently, an additional phosphorus pentoxide (3.8 g) was added, the mixture was heated as follows: 120 °C for 3 h, 150 °C for 3 h, 170 °C for 3 h, 190 °C for 12 h, and 210 °C for 12 h. The viscous mixture was cooled to 140 °C and poured into deionized water to give dark-green fibrous polymer. The product was washed with deionized water several times to remove residual acid, and then soaked in 5% $NaCO_3$ for 48 h. Finally, the product was washed until achieving a neutral pH and dried in vacuum at 100 °C for 24 h.

Yield: 94%. ^{1}H NMR (DMSO-d_6): 8.97, 8.90, 8.81, 8.37, 8.31, 7.91, 7.63. FT-IR (film, cm^{-1}): 1492, 1402, 1314, 965 cm^{-1} (vibration of benzothiazole rings), 738 cm^{-1} (deformation of benzothiazole rings), 1095, 1018, and 632 cm^{-1} (sulfonate).

2.3. Preparation of membranes

The membrane was prepared by casting polymer solutions in DMSO (6 wt%) onto dust-free glass plate and drying at 70 °C for 48 h. After cooling to room temperature, the glass plate was immersed in deionized water, the salt form membrane then peeled off. Subsequently, it was converted into the acid form membrane by soaking in 1 M HCl for 48 h. The acid form membrane was washed with deionized water several times to remove the residual acid.

2.4. Measurements

^{1}H NMR spectra were recorded on a Varian MERCURY plus 400 MHz spectrometer, using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS) as internal standard. FT-IR spectra were obtained from Bruker Equinox-55 Fourier Transform infrared spectrometer. Gel permeation chromatography (GPC) was performed on a PE 200 apparatus equipped with a mixed 5 μm PS column (range of pore sizes: 1×10^5, 1×10^4, and 1×10^3 Å) and a refractive index detector, using DMF with 0.05 mol/L LiBr as an eluant.

Ion exchange capacity (IEC) was determined by titration. The membrane was immersed in the saturated NaCl solution for 48 h to liberate the H^+ into the solution. The IEC was determined by titrating with 0.01 M NaOH, using phenolphthalein as indicator.

Thermogravimetric analysis (TGA) was run on a TGA 2050 instrument in the air. The acid form samples were preheated at 150 °C for 30 min to remove the moisture. TGA traces were recorded in the range of 200–700 °C at 20 °C/min. The differential thermal analysis was conducted on a PE Pyris-1 differential scanning calorimeter (DSC). The acid form samples were also preheated at 150 °C for 30 min for dehydration under nitrogen. After cooling to 90 °C, DSC curves were recorded over the temperature range of 90–350 °C at a heating rate of 10 °C/min.

The water uptake and swelling of membranes were determined by measuring the change of the weight, length, and thickness from the dry to wet state. The membranes (6 cm × 6 cm × 40 ~ 50 μm) were dried *in vacuo* at 100 °C for 48 h. The weight (W_{dry}), length (l_{dry}) and thickness (t_{dry}) of dry membranes were measured. Thereafter, the membranes were immersed in deionized water at a given temperature for 24 h, then taken out and wiped dry. The weight (W_{wet}), length (l_{wet}) and thickness (t_{wet}) of wet membranes were measured. The

Download English Version:

https://daneshyari.com/en/article/1271537

Download Persian Version:

https://daneshyari.com/article/1271537

Daneshyari.com