



Synthesis and characterization of sulfonated poly(arylene ether phosphine oxide)s with fluorenyl groups by direct polymerization for proton exchange membranes

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ABSTRACT

Fluorenyl-containing sulfonated poly(arylene ether phosphine oxide)s (sPAEPO) with various sulfonation degrees were synthesized by direct polycondensation of 9,9-bis(4-hydroxyphenyl) fluorene with sulfonated bis(4-fluorophenyl)phenyl phosphine oxide and bis(4-fluorophenyl)phenyl phosphine oxide. The structure of sPAEPO was confirmed by NMR and IR spectroscopy. The transparent, tough, and flexible membranes of sPAEPO were obtained by solution casting. The thermal properties, ion exchange capacity, water uptake, swelling ratio, proton conductivity, and microstructure were investigated. sPAEPO membranes exhibit excellent overall properties. For example, sPAEPO-100 membrane shows a water uptake of 28.6% and a swelling ratio of 10.5% as well as a proton conductivity of 9.4×10^{-2} S/cm at 80 °C. AFM micrographs illustrated that as the sulfonation degree increases, the phase contrast of images and the connectivity of hydrophilic domains increases. For sPAEPO-100, the hydrophilic domains form the connected and narrow channels of an ionic rich phase, which contributes to high proton conductivity as well as dimensional stability. The sPAEPO membranes are expected to be a promising candidate for fuel cell applications.

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1. Introduction

Nowadays, proton exchange membrane fuel cell (PEMFC) plays an important role in clean power sources. The exploration of PEMFC is becoming more and more intensive during the past three decades due to the advantages such as high energy conversion efficiency, an almost zero emission of pollutants, and low operating temperature. PEMFC converts chemical energy directly into electrical energy and is fit for automotive, stationary, and portable power sources [1]. The proton exchange membrane (PEM) is a key component of PEMFC. Until now, Nafion perfluorinated membrane is the state-of-the-art PEM, but several technical limitations prevent its popularization, including high methanol permeation, low conductivity at low humidity or high temperature, and expensive cost [2]. Therefore, the development of alternative PEM materials with excellent overall properties is still an issue to be addressed.

In recent years, sulfonated aromatic polymers such as sulfonated poly(arylene ether ketone)s, sulfonated poly(arylene ether sulfone)s, sulfonated polyimides, sulfonated polyimidazoles and

their derivatives were extensively investigated as candidate PEM materials, which showed excellent mechanical properties, thermal stability and chemical stability [3–12]. It is well-known that poly(arylene ether phosphine oxide)s are high performance polymers and that the phosphine oxide unit in the polymer backbone could enhance the water retention and adhesive ability with inorganic materials [13,14]. Therefore, the incorporation of phosphine oxide units into PEM materials is of interest [15,16]. However, few studies on PEM containing phosphine oxide moieties could be found. McGrath group reported firstly the synthesis of sulfonated poly(arylene ether phosphine oxide)s in a conference proceeding [17]. Thereafter, our group reported the synthesis and properties of sulfonated poly(phthalazinone ether phosphine oxide)s and sulfonated poly(arylene thioether phosphine oxide)s derived from direct polycondensation [18,19]. On the other hand, fluorenyl-containing sulfonated poly(ether sulfone)s [20–22], and sulfonated poly(ether ketone)s [23,24], and sulfonated poly(ether ketone ketone)s [25,26] have been prepared and showed good comprehensive properties due to the introduction of fluorenyl groups. In this article, both phosphine oxide and fluorenyl moieties were incorporated into the resulting polymers, i.e., fluorenyl-containing sulfonated poly(arylene ether phosphine oxide)s (sPAEPO), in order to prepare the PEM materials with excellent overall properties. A series of fluorenyl-containing sulfonated poly(arylene ether

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phosphine oxide)s was synthesized by direct polycondensation of 9,9-bis(4-hydroxyphenyl) fluorene with various ratios of sulfonated bis(4-fluorophenyl) phenyl phosphine oxide to bis(4-fluorophenyl) phenyl phosphine oxide. The structure of the resultant polymers was confirmed and the properties of sPAEPO membranes were investigated in detail.

2. Experimental

2.1. Materials

9,9-Bis(4-hydroxyphenyl) fluorene (BHF) was purchased from TCI Co. and recrystallized from ethanol/water before use. Cesium carbonate was obtained from Alfa Aesar and used as received. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure prior to use. Phenylphosphonic dichloride, tetrahydrofuran (THF) and toluene were dried and distilled prior to use. 4-Bromofluorobenzene, magnesium, fuming sulfuric acid and other reagents were obtained from commercial sources and used as received. Bis(4-fluorophenyl) phenyl phosphine oxide (BFPPPO) and sulfonated bis(4-fluorophenyl) phenyl phosphine oxide (sBFPPPO) were synthesized according to our previous procedure [18,19].

2.2. Polycondensation

Fluorenyl-containing poly(arylene ether phosphine oxide) and sPAEPO with various sulfonation degrees were prepared by the following procedure. The synthetic process of homopolymer sPAEPO-100 was described as a representative example. 1.0512 g (0.003 mol) of BHF, 1.2409 g (0.003 mol) of sBFPPPO, 8 mL NMP, 9 mL toluene, and 1.0752 g (0.0033 mol) cesium carbonate were added into a three-necked flask equipped with a mechanical stirrer, a Dean–Stark trap, and a nitrogen inlet/outlet. The reaction mixture was stirred at room temperature under nitrogen protection for 30 min to dissolve the reactants and heated to reflux at 160 °C for 4 h to dehydrate completely via azeotropic distillation. After toluene was distilled thoroughly, the reaction mixture was heated to 190 °C and held for 48 h until the solution became very viscous. Thereafter, the brown mixture was cooled to 110 °C and diluted with 2 mL NMP and poured into deionized water with vigorous stirring to produce the fibre-like polymer. The polymer was washed with hot water several times to remove the inorganic salts and dried *in vacuo* at 100 °C for 48 h. The polymer was nominated as sPAEPO-100, where “100” is the molar percentage of sBFPPPO in the entire dihalide monomers.

Yield: 96%. ¹H NMR (DMSO-*d*₆, ppm): 7.94–7.84 (3H), 7.82–7.75 (2H), 7.58–7.39 (8H), 7.39–7.31 (2H), 7.31–7.21 (2H), 7.16–7.07 (4H), 7.05–6.99 (4H), 6.99–6.90 (4H). ¹³C NMR (DMSO-*d*₆, ppm): 161.717, 155.436, 152.085, 150.153 (d, *J*_{CP} = 10.4 Hz), 143.268, 141.090, 135.466 (d, *J*_{CP} = 10.8 Hz), 134.847 (d, *J*_{CP} = 101.8 Hz), 133.254 (d, *J*_{CP} = 9.9 Hz), 131.106, 130.736, 130.113 (d, *J*_{CP} = 14.5 Hz), 129.968 (d, *J*_{CP} = 9.9 Hz), 129.716, 129.508, 128.542 (d, *J*_{CP} = 107.0 Hz), 127.648, 122.259, 121.347, 119.452 (d, *J*_{CP} = 11.8 Hz), 65.585.

2.3. Membrane preparation

A series of salt form membranes was prepared by dissolving sPAEPO in NMP and casting the solutions on dust-free glass plates. The solutions were dried in an oven without disturbance at 70 °C for 36 h. After cooling to room temperature, the glass plates were immersed in deionized water, the yellow, transparent, and tough membranes peeled off. The acidification procedure was performed by immersing the salt form membranes in 1 M HCl for 48 h, followed by rinsing with deionized water. The acid form membranes were dried under vacuum at 100 °C for 24 h.

2.4. Characterization and measurements

The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III plus spectrometer (400 MHz) with deuterated dimethyl sulfoxide (DMSO-*d*₆) as the solvent and tetramethylsilane (TMS) as the internal standard. The acid form membranes with thickness of around 6 μm were used as the sample of FT-IR measurements. The FT-IR spectra of the membranes were performed on a Bruker Equinox-55 Fourier transform spectrometer. Intrinsic viscosities were measured using an Ubbelohde viscometer in NMP solution of polymer at 30 °C. Digital instrument (DI) NanoScope III under tapping mode was used to observe the morphology of sPAEPO membranes. A silicon cantilever (a force constant of 40 N/m and a resonant frequency of 300 kHz) with an etched conical tip (a radius of curvature less than 10 nm, a tip height of 25 μm, and a full tip cone angle less than 30°) was used for scan.

Thermogravimetric analysis (TGA) was conducted on a Q5000 IR TA instrument in a nitrogen atmosphere. The samples were preheated at 150 °C for 30 min to remove the moisture at a heating rate of 20 °C/min. The differential thermal analysis (DSC) was carried out on a PE Pyris-1 differential scanning calorimeter. The samples were preheated to 150 °C for 30 min under nitrogen protection to remove the absorbed water, then cooled to 90 °C at a rate of 5 °C/min and heated from 90 to 350 °C at a heating rate of 10 °C/min.

The titration method was employed to determine the ion exchange capacity (IEC) of sPAEPO membranes. The membranes in the acid form were soaked in saturated NaCl solutions for 48 h to liberate the H⁺ via ion exchange. The free H⁺ was titrated by 0.01 M NaOH solution with phenolphthalein as an indicator. The IEC value was calculated by the following equation:

$$\text{IEC} = \frac{N_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}} \times 100\%$$

where *N*_{NaOH}, *V*_{NaOH}, and *W*_{dry} are the concentration, the consumed volume of NaOH solution, and the dry weight of acid form membranes, respectively.

The acid form membranes were dried under vacuum at 100 °C for 24 h, then measured the weight and length. Subsequently, the membranes were kept in deionized water at the given temperature for 24 h, taken out and wiped dry with tissue paper. The weight and length of the wet membranes were measured immediately. The water uptake and swelling ratio were calculated according to the following equations:

$$\text{water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

$$\text{swelling ratio} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\%$$

where *W*_{dry} and *L*_{dry} are the weight and length of the dry membranes, *W*_{wet} and *L*_{wet} are the weight and length of the wet membranes, respectively.

The proton conductivity of the membranes was measured by Autolab PGSTAT 302 (Eco Chemie, Netherlands) apparatus with AC current amplitude of 0.1 mA over frequency ranging from 1 MHz to 100 Hz. The measurement of the proton conductivity followed a reported procedure [18]. The membranes (20 mm × 8 mm) were clamped in the moulds. Before measurement, the acid form membranes in the moulds were rinsed with ultrapure water several times and immersed in ultrapure water for 24 h in order to hydrate completely. The longitudinal conductivity (σ) of the membranes was determined by the following equation:

$$\sigma = \frac{L}{RWd}$$

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