



Highly conductive flexible alkylsulfonated side chains poly(phthalazinone ether ketone)s for proton exchange membranes



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ARTICLE INFO

Article history:

Received 20 December 2017

Received in revised form

13 April 2018

Accepted 13 June 2018

Available online 14 June 2018

Keywords:

Polyethers

PEMs

Alkylsulfonated side chains

ABSTRACT

In this work, a series of long flexible alkylsulfonated side chains poly (phthalazinone ether ketone) (SFG-PPEK-x) are successfully synthesized through polycondensation, demethylation, and sulfobutyl grafting reaction to the polymer backbone. The resulting ionomers could dissolve in polar aprotic solvents, such as DMSO, NMP etc and show excellent film-forming properties. Furthermore, the effect of side chain lengths on the properties of the resulting PEMs, such as proton conductivity, water uptake, and swelling ratio are investigated systematically. The SFG-PPEK-4 membranes (IEC = 1.70 mmol g⁻¹) show the highest proton conductivity in the range of 107 mS cm⁻¹ at 30 °C and 184 mS cm⁻¹ at 80 °C, which is higher than that of Nafion[®] 115. The thermal, mechanical properties and chemical stability of SFG-PPEK-x are discussed, systematically.

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1. Introduction

As a high conversion efficiency and lower environmental cost device, proton exchange membrane fuel cells (PEMFCs) have received great attention for applications in transportation, stationary and electronics [1]. The proton exchange membrane (PEM) is a critical component in PEMFCs. The main function of the PEM is to keep the two electrodes apart and conducts ions from the anode to the cathode [2]. Thus, the PEMs must possess excellent proton conductivity, low gas permeability, low cost and adequate thermal, mechanical and chemical stability. These requirements are essential to guarantee PEMFCs' performance and safe operation [3].

Perfluorosulfonic acid membranes like Dupont's Nafion[®], which possess excellent proton conductivity, high chemical stability and good mechanical properties, have been widely used in PEMFCs. However, some drawbacks like a high production cost and high fuels permeability restrict its large-scale commercial applications [4]. Therefore, demands for alternate membrane materials with lower cost and better properties have increased. Hence, numerous sulfonated aromatic polymers have been reported due to their excellent thermomechanical properties and low fabrication cost. The typical materials used for these PEMs, such as sulfonated

sulfonated poly (arylene ether ketone)s (SPAEEKs) [5,6], sulfonated poly (arylene ether nitrile)s (SPAENs) [7,8], sulfonated polyimides (SPIs) [9,10], sulfonated polybenzimidazoles (SPBIs) [11,12], sulfonated poly (phenylene ether)s (SPPOs) [13] etc., have been investigated during the past two decades. In addition, some inorganic proton-conducting materials such as MOF have also been widely studied [14–17]. The proton conductivities of these materials are high, but the compatibility between organic and inorganic phases while fabricating organic-inorganic hybrid membranes remains to be solved.

SPAEEKs, possessing superior mechanical properties, low production cost and high thermal and thermooxidative stability, have been widely investigated as alternative membrane materials [18]. Most of them contain sulfonic acid groups on the polymer backbone [19–22]. Sufficient conductivities can be achieved only at high degree of sulfonation for these main-chain-type SPAEEKs. An excessive water uptake, which was caused by high degree of sulfonation, will lead to the loss of the dimensional stabilities. Meng et al. found that introduced sulfonic acid groups on the pendant have a positive impact on the proton conductivity of the PEMs [23]. Recently, many side-chain-type SPAEEKs have been synthesized by direct copolymerization of monomers bearing pendant sulfoalkyl groups or chemical grafting the side chains onto polymers backbone. In general, they exhibited comparatively better comprehensive properties than main-chain-type SPAEEKs. Ueda and Higashihara et al. prepared three kinds of poly (phenylene ether)s

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with long alkylsulfonated side chains possessing high thermal stabilities, excellent oxidation resistance, and high mechanical strengths [24]. They also exhibited high proton conductivities than Nafion® 117 under different relative humidity. Zhao and Na et al. prepared SPAEKs containing dual naphthalene and alkylsulfonated side chains [25]. The resulting PEMs showed high proton conductivity. SPAEKs containing a twist phthalazinone moiety possess excellent thermal and mechanical stability, especially excellent solubility in aprotic polar solvents, due to the non-coplanar configuration in polymer's main chain [26,27].

In the present work, a series of long flexible alkylsulfonated side chains poly (phthalazinone ether ketone) (SFG-PPEK-x) were successfully synthesized through polycondensation, demethylation, and sulfobutylation grafting reaction to the polymer backbone. The phthalazinone units were introduced into polymer main chain in order to improve the solubility and thermostability. The effect of chain lengths of pendants on the properties of the resulting PEMs, like proton conductivity, mechanical properties, water uptake, and swelling ratio, were investigated systematically.

2. Experimental

2.1. Materials

1,6-dibromohexane and 1,12-dibromododecane were purchased from Aladdin Industrial Corporation (Shanghai, China). A 1 M amount of BBr₃ and 1,4-Butane sultone (99%) were purchased from Energy Chemical (Chaoyang, China). Toluene (99%), 1,2-dichloroethane (99%), N-methylpyrrolidone (NMP, 99%), dimethyl sulfoxide (DMSO; 99%), and N,N-dimethylacetamide (DMAc; 99%) were purified before used. All other reagents were obtained from National Medicines Corporation of China and were used as received.

2.2. Synthesis of sodium 6-bromohexylsulfonate (6-Br-HS) and sodium 12-bromododecylsulfonate (12-Br-DS)

6-Br-HS and sodium 12-Br-DS were synthesized according to the literature procedure in reference 7,28 [7,28].

2.3. Synthesis of monomer

4-(3-methoxy-4-hydroxyphenyl)-phthalazin-1-one (MO-DPHZ) was synthesized according to the report procedure [29]. Yield: 46%. ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.76 (s, 1H), 9.40 (s, 1H), 8.33 (dd, 1H), 7.97–7.75 (m, 3H), 7.18–6.84 (m, 3H), 3.82 (s, 3H). ESI-MS (*m/z*), 267.25 [M]⁺, calculated: 267.27.

2.4. Synthesis of poly(phthalazinone ether ketone) containing methoxy groups (PPEK-Me)

The synthetic procedure for PPEK-Me is described as follows. 4,4'-Difluorobenzophenone (2.1821 g, 10.0 mmol), MO-DHPZ (2.6827 g, 10.0 mmol), K₂CO₃ (4.1463 g, 30.0 mmol), DMAc (26 mL), and toluene (25 mL) were added into a 100 mL three-necked flask at room temperature (r.t.). The reaction mixture was heated to 140 °C. After dehydration for 3 h, the toluene was released slowly, then the system was heated to 155 °C and reacted for 16 h to complete the polymer chain growth. The resulting mixture was precipitated into deionized water (DIW) and washed with DIW.

2.5. Synthesis of poly(phthalazinone ether ketone) containing –OH groups (PPEK-OH)

PPEK-Me (1.0 g) was dissolved in 20 mL of CHCl₃ in a 100 mL, three-neck flask. BBr₃ (2.0 mL) was diluted with CHCl₃ (31.4 mL) and the resulting solution was added dropwise to the PPEK-Me solution at r.t. After 12 h, the resulting polymer (PPEK-OH) was filtered and washed with DIW. Yield: 95%.

2.6. Synthesis of poly(phthalazinone ether ketone) functionalized with flexible sulfoalkyl groups (SFG-PPEK-x)

The synthetic procedure for SFG-PPEK-4 is described as follows: PPEK-OH (0.56 g, 1.3 mmol) were dissolved in 15 mL of DMSO, and NaH (0.104 g, 2.6 mmol) was added to the solution. The mixture were stirred for 30 min. Then 1,4-butane sultone (0.27 mL, 2.6 mmol) were added dropwise and the mixture was heated to 100 °C for another 24 h. The reaction system was terminated by 300 mL of anhydrous acetone and precipitating polymer solid. The polymer (SFG-PPEK-4) was washed by acetone/water and dried at 100 °C for 24 h. Yield: 93%.

Other polymers with flexible sulfoalkyl groups were synthesized by the same method described above. The resulted polymers are denoted by SFG-PPEK-x, where x represents the number of carbon atoms in the flexible sulfoalkyl groups.

2.7. Membrane preparation

SFG-PPEK-x was dissolved in DMSO to form a 5 wt% solution. The solution was casted on glass petri dish and dried at 60 °C. After the DMSO was evaporated, the membrane was peeled off and immersed in 1 M H₂SO₄ solution for 24 h, and then in DIW for 48 h. The dry membranes were obtained by drying at 80 °C for 12 h under vacuum.

2.8. Characterization

¹H NMR spectra were recorded using the Bruker 500 MHz NMR spectrometer with deuterated chloroform and DMSO-*d*₆ as the solvent, and tetramethylsilane (TMS) as the internal standard. FT-IR spectra were obtained with a NEXUS EURO FT-IR spectrometer (Thermo Nicolet Corporation, USA). The intrinsic viscosities were determined in CHCl₃ at 30 °C with a polymer concentration of 0.5 g dL⁻¹ with an Ubbelohde capillary viscometer. Tensile measurements were conducted with an Instron-1211 at a speed of 2 mm min⁻¹ at ambient conditions (at 30 °C and 50% relative humidity). The samples were dried at 100 °C in vacuum for 12 h before test. The thermal analysis (TGA) was performed to estimate the thermal stability of the polymer membranes by using a TG209F1 (NETZSCH, Germany) with the controlled heating rate of 10 °C min⁻¹ from 30 to 800 °C under nitrogen atmosphere. All the specimens were dried in vacuum at 100 °C for 24 h before the measurement. The small-angle X-ray scattering (SAXS) characterization was performed at r.t. on a Bruker Nanostart small-angle X-ray scattering system equipped with a Siemens X-ray generator operated at 40 kV. The experiment was conducted on dried samples under vacuum. Tapping mode atomic force microscope (AFM) images were taken in air by using a Agilent PicoPlusII Instruments.

2.9. Water uptake (WU) and swelling ratio (SR)

The SFG-PPEK-x membranes were dried under vacuum until a constant weight, and their weight (*W*_{dry}), length (*L*_{dry}) and thickness (*T*_{dry}) were recorded. Then they were wetted in the DIW at r.t. and 80 °C for 24 h. The membranes were brought out and wiped

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