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Poly(arylene ether sulfone) proton exchange membranes with flexible acid side chains

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ABSTRACT

New monomers containing two or four pendent methoxyphenyl groups were synthesized by bromination of bis(4-fluorophenyl)sulfone, followed by Suzuki coupling with 4-methoxybenzeneboronic acid. Copoly(arylene ether sulfone)s containing methoxyphenyl groups (2-MPAES-*xx* and 4-MPAES-*xx*) based on the corresponding monomers were prepared by aromatic nucleophilic substitution (SNAr) polycondensation. After demethylation of the methoxy group to the reactive hydroxyl group, the respective side chain-type sulfonated copolymers (2-SPAES-*xx* and 4-SPAES-*xx*) were obtained by sulfobutylation. Flexible and tough membranes having good mechanical strength were obtained by solution casting of all copolymers. The sulfonated copolymers with two or four pendent sulfobutoxyphenyl groups had high proton conductivities in the range of 0.108–0.258 S/cm for 2-SPAES-*xx* and 0.135–0.194 S/cm for 4-SPAES-*xx* at 80 °C, respectively. The methanol permeabilities of these membranes were in the range of 1.59×10^{-7}–4.69×10^{-7} cm^2/s, which is much lower than Nafion® (15.5×10^{-7} cm^2/s). 2-SPAES-*xx* and 4-SPAES-*xx* display comparatively better balance between proton conductivity and water swelling than the analogous poly(arylene ether sulfone)s containing pendent sulfophenyl groups. A combination of high proton conductivities, low water uptake, and low methanol permeabilities for some of the obtained copolymers indicated that they have some of the requisite properties for proton exchange membranes in fuel cell applications.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been widely investigated for automotive, stationary, and portable power devices because of their high efficiency, high power density, quiet operation and low emissions levels [1–4]. As one of the key components of PEMFCs, the proton exchange membrane (PEM) acts as a separator for the reactants, a catalyst support, and provides ionic pathways for proton transport. Currently, perfluorosulfonic acid (PFSA) polymers, such as Nafion® (DuPont), are commercialized PEMs normally utilized in PEMFC and direct methanol fuel cells (DMFC) because of their excellent chemical stability and high proton conductivity. However, their well-recognized drawbacks, such as a limited operating temperature range up to 80 °C due to dehydration, high methanol/fuel gas diffusion, and environmental recyclability, has led to intensive research efforts in developing hydrocarbon-based proton conducting polymers as alternative materials having high conductivity, higher operating temperature, and lower methanol/fuel gas diffusion [5–7]. The most widely reported aromatic PEMs include sulfonated derivatives of poly(arylene ether ketone)s [8–10], poly(arylene ether sulfone)s [11,12], poly(arylene sulfide sulfone)s [13,14], poly(arylene ether)s [15,16], and polyimides [17,18]. Generally, the randomly distributed sulfonic acid groups in these polymers are located on the main chain, and the rigid polyaromatic backbone prevents continuous ionic domain clustering from occurring to form distinct phase-separated structures [19]. As a result, these sulfonated polymers only attain suitable conductivities comparable with Nafion, at much higher ion exchange capacities (IEC) and high water contents, which consequently lead to large dimensional variations and poor mechanical properties. The balance between dimensional stability and proton conductivity of aromatic PEMs are crucial issues that require improvement through careful structural design.

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As is well-known, Nafion exhibits high proton conductivity at low IEC values due to ion-rich channels that formed by phase separation between the hydrophilic sulfonic acid groups, which are strongly acidic and the highly hydrophobic domains [20,21]. Inspired by the chemical structure of Nafion® bearing flexible pendant hydrophilic sulfonic acid groups attached to the hydrophobic perfluorinated backbone, aromatic PEMs tailored with pendant sulfoalkyl groups have been developed, which generally exhibited a comparatively better balance between proton conductivity and water dimensional swelling than PEMs with sulfonic acid groups attached directly onto the aromatic chain [22–34]. These side-chain-type PEMs have been prepared by the direct copolymerization method or by chemical grafting the pendants onto polymers. Compared to the direct copolymerization method, the chemical grafting method avoids the need to prepare sulfonated monomers and offers an easier route to introduce locally and densely populated sulfonated structures into the aromatic polymer backbone. Karlsson and Jannasch [22], Hvilsted and coworkers [25], Na and coworkers [26,27], and Zhang and coworkers [28,29] reported sulfonated aromatic PEMs containing one or two pendant sulfoalkyl groups in each hydrophilic unit by the chemical grafting method. The highest conductivity of 0.179 S/cm was obtained for these copolymers (IEC = 1.82 mequiv./g) under a hydrated state at 80 °C, which is higher than that of Nafion117 (0.146 S/cm) [26]. In our previous work, we reported fluorene-based poly(arylene ether sulfone)s containing locally and densely populated flexible butylsulfonic acid pendant units [35]. The results indicated that these side-chain-type sulfonated polymers displayed advantageous proton conductivities with relatively low water contents.

In this article, we present a study of poly(arylene ether sulfone) copolymers containing two or four pendent butylsulfonic groups prepared by the chemical grafting method. Poly(arylene ether sulfone) copolymers containing methoxy groups were first prepared based on two novel bis(fluorophenyl) sulfone monomers, and then the methoxy groups were converted to reactive hydroxyl groups, which reacted with 1,4-butanesultone resulting in sulfonated copolymers bearing sulfobutoxyphenyl side chains. The copolymers were characterized in detail, and the membrane properties of this new series of PEMs with flexible side chains are investigated and compared with previously reported analogous poly(arylene ether sulfone)s containing the inflexible pendant sulfophenyl groups. In addition, the effects of the amount of pendent groups on the properties of these PEMs are discussed.

2. Experimental

2.1. Materials

4,4′-Difluorodiphenyl sulfone (DFDPS), N-bromosuccinimide (NBS), 4-methoxybenzeneboronic acid, tetrakis(triphenylphosphine) palladium (0), and 1,4-butanesultone were purchased from Sigma–Aldrich Ltd. 4,4′-(Hexafluoroisopropylidene) diphenol (6F-BPA) was purchased from Alfa aesar and recrystallized with toluene. All other solvents and reagents (obtained from Sigma–Aldrich) were reagent grade and were used as received.

2.2. 3,3′-Dibromo-4,4′-difluorodiphenyl sulfone (DBDFDPS) and 3,3′,5,5′-Tetrabromo-4,4′-difluorodiphenyl sulfone (TBDFDPS)

3,3′-Dibromo-4,4′-difluorodiphenyl sulfone (mp: 158–160 °C) and 3,3′,5,5′-tetrabromo-4,4′-difluorodiphenyl sulfone (mp: 180–182 °C) were synthesized according to the method reported in our preceding studies [36].

2.3. 3,3′-Di(4′′-methoxyphenyl)-4,4′-difluorodiphenyl sulfone (DMDFDPS)

To a 1 L three-necked round-bottom flask, equipped with a reflux condenser, mechanical stirrer, and nitrogen inlet, 41.20 g (0.1 mol) of DBDFDPS, 31.91 g (0.21 mol) of 4-methoxybenzeneboronic acid, and 300 mL of toluene were charged. The solid was completely dissolved at 50 °C with stirring. 300 mL of 10 wt% aqueous sodium carbonate solution and 2.00 g (0.0017 mol) of tetrakis(triphenylphosphine) palladium(0) were carefully added into the solution. The reaction mixture was heated at 110 °C for 10 h, and then the solvent was evaporated to obtain a solid. Crude product was recrystallized from toluene/dimethylformamide (DMF) (2:1) twice to afford 39.65 g of pure white crystalline 3,3′-di(4′′-methoxyphenyl)-4,4′-difluorodiphenyl sulfone. Yield: 85%, mp: 174–176 °C. ^{1}H NMR (300 MHz, DMSO-d_6; ppm): 8.13 (d, J = 7.2, 2H, H-4), 8.07 (m, 2H, H-3), 7.52–7.58 (m, 6H, H-2, H-5), 7.08 (d, J = 8.8, 4H, H-1), 3.81 (s, 6H, $-OCH_3$).

2.4. 3,3′,5,5′-Tetra(4′′-methoxyphenyl)-4,4′-difluorodiphenyl sulfone (TMDFDPS)

Using similar methodology to the di(4-methoxy)phenyl analog above, the monomer with four pendent 4-methoxyphenyl groups, 3,3′,5,5′-tetra(4′′-methoxyphenyl)-4,4′-difluorodiphenyl sulfone was prepared from 3,3′,5,5′-tetrabromo-4,4′-difluorodiphenyl sulfone (TBDFDPS) by reaction with 4.4 mol equiv. 4-methoxybenzeneboronic acid at 115 °C for 24 h. The purified product was obtained by recrystallization from DMF twice. Yield: 71%, mp: 280–282 °C. ^{1}H NMR (300 MHz, $CDCl_3$; ppm): 7.93 (m, 4H, H-3), 7.47–7.51 (m, 8H, H-2), 6.98–7.02 (m, 8H, H-1), 3.87 (s, 12H, $-OCH_3$).

2.5. Synthesis of poly(arylene ether sulfone)s containing methoxy groups (MPAES-xx)

A typical synthetic procedure, illustrated by the preparation of 2-MPAES-60 copolymer (xx = 60: DMDFDPS/DFDPS = 60/40), is described as follows. 2.799 g (6 mmol) DMDFDPS, 1.017 g (4 mmol) DFDPS, 3.362 g (10 mmol) 6F-BPA, 1.656 g (12 mmol) K_2CO_3, 20 mL N-methylpyrrolidone (NMP) and 10 mL toluene were added into a 100 mL round-bottomed flask which was equipped with a Dean-Stark trap, condenser, a mechanical stirrer, and gas adapter. The reaction mixture was refluxed at 140 °C for 4 h to remove water. After removal of toluene and water, the reaction temperature was raised to 155 °C. After 5–8 h, 8 mL of NMP was added to the mixture to reduce the solution viscosity. The solution was poured into 500 mL deionized water with vigorous stirring. The resulting fibrous copolymer was washed several times with deionized water and dried at 100 °C under vacuum for 10 h.

2.6. Conversion of methoxy (MPAES-xx) to hydroxyl group (HPAES-xx)

The methoxy-containing copolymers were converted into hydroxyl functionalities according to the method reported in the preceding studies [32,35]. Typically, 4.0 g 2-MPAES-60 was dissolved into 100 mL CH_3Cl in a 100 mL three-neck flask equipped with a mechanical stirrer and a nitrogen inlet. After the temperature was cooled down to 0 °C (ice bath), an excess (3 mL) BBr_3 dissolved in 25 mL CH_3Cl was added dropwise. The reaction mixture was stirred at room temperature for an additional 6 h under nitrogen. Then, the resulting copolymer (2-HPAES-60) was filtered, washed with boiling water, recovered and then dried under vacuum at 100 °C for 24 h.