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Synthesis and properties of novel side-chain-sulfonated polyimides from bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone

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Abstract

A novel side-chain-sulfonated aromatic diamine of bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone (BAPSBPS) was synthesized. Sulfonated copolyimides were synthesized by random and sequenced block copolymerization of 1,4,5,8-naphthalene tetracarboxylic dianhydride, BAPSBPS and nonsulfonated diamine. They displayed good solubility in common aprotic solvents and high desulfonation temperature of 350 °C, suggesting the high stability of sulfonic acid groups. The reduced viscosity was in the range of 0.4–1.8 dl/g at 0.5 g/dl and 35 °C. Flexible and tough membranes with reasonably high mechanical strength were prepared. They showed anisotropic membrane swelling with larger swelling in thickness than in plane. They displayed reasonably high proton conductivity (σ), taking their lower ion exchanging capacity (IEC) into account. For example, the membrane with IEC of 1.54 mequiv/g showed σ values of 81 and 11 mS/cm in water and 70% RH, respectively, at 60 °C.

Keywords: Sulfonated polyimide; Polymer electrolyte membrane; Proton conductivity

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been developed as promising alternative energy supplies for mobile and stationary applications. The most important part of fuel cell is polymer electrolyte membrane (PEM) [1–4]. Up to date, the commercially available PEMs for PEFCs are perfluorosulfonic acid membranes, such as DuPont's Nafion membrane, which have high proton conductivity and excellent chemical stability. However, high cost, high methanol permeability and lower operating temperature below 80 °C limit their industrial applications. This stimulated many efforts in the development of alternative PEMs.

In recent years, many kinds of sulfonated aromatic polymers have been developed. Sulfonated polyimides (SPIs) with six-membered imide rings have been studied as one of the promising candidates for fuel cell applications because of their low methanol permeability, excellent thermal and chemical stabilities [1,4–20]. Some SPIs showed both relatively high proton conductivity and relatively high water stability. One example is main-chain-type SPIs derived from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), 4,4′-bis(4-aminophenoxy)biphenyl-3,3′-disulfonic acid (BAPBDS) and nonsulfonated diamine such as 4,4′-bis(4-aminophenoxy)biphenyl (BAPB) [9,10,13]. The relatively high water stability of the BAPBDS-based SPI membranes was attributed to the flexible structure and the higher basicity of BAPBDS due to the absence of electron-withdrawing substitution on amino phenyl groups [9]. Another example is side-chain-type SPIs derived from NTDA, 2,2′- or 3,3′-bis(3-sulfopropoxy)benzidine (2,2′- or 3,3′-BSPB), and nonsulfonated diamine [11–13,16]. The relatively high water stability of the BSPB-based SPIs was attributed to the higher basicity of BSPB and the microphase-separated structure composed of hydrophilic side chain domains and hydrophobic polyimide main chain domains. These suggest that a sulfonated diamine with high basicity of diamine, high flexibility and sulfonated pendant groups lead to favorable SPIs for fuel cell applications.

Based on this consideration, in this study, a novel sulfonated aromatic diamine of bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone (BAPSBPS) has been developed. BAPSBPS has flexible structure due to the sulfone and ether linkages and sulfonic acid groups bonded to the aromatic side chain. This paper reports on synthesis and characterization of BAPSBPS and BAPBDS-based SPIs together with the

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preliminary results about membrane properties such as proton conductivity.

2. Experimental

2.1. Materials

4,4′-Dichlorodiphenyl sulfone (DCDPS) and aluminum chloride were purchased from Aldrich and used as received. Butyllithium (1.6 M in hexane) and thionyl chloride were purchased from Wako and used as received. NTDA (Aldrich) and *p*-aminophenol (*p*-AP, Wako) were purified by vacuum sublimation before use. Benzene and tetrahydrofuran (THF) were purchased from Wako and were distilled over anhydrous P_2O_5 and sodium, respectively. Triethylamine (TEA), sulfuric acid (95%), fuming sulfuric acid (60%), *m*-cresol, dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl acetamide (DMAc), *N*,*N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP) were purchased from Wako and used as received. BAPB, 1,3-bis(4-aminophenoxy)benzene (1,3-BAPBz) and 1,4-bis(4-aminophenoxy) benzene (1,4-BAPBz) were purchased from Wako and recrystallized from ethanol before use. Ultra-pure water was obtained from a Millipore Mill-Q purification system.

2.2. Monomer synthesis

2.2.1. 2,2′-Dicarboxy-4,4′-dichlorodiphenyl sulfone (*I*)

To a fully dried 500 ml 4-neck flask, which was equipped with a pressure-equilibrium drop funnel, a magnetic stirrer, a N_2 inlet/outlet and a thermometer, 11.5 g (40 mmol) of DCDPS and 200 ml of THF were charged under N_2 flow. After the solution was cooled to −60 °C by ethanol-dry ice bath, 53 ml (84 mmol) of BuLi solution was added at a rate to keep the inner temperature below −55 °C. After the addition, the reaction mixture was maintained at this temperature for 2 h. Then, the reaction solution was cooled to −70 °C and dry CO_2 gas was bubbled through a pipe at the rate to keep the inner temperature below −50 °C. When CO_2 gas escaped, the inflow rate was turned down and kept for about 3 h. Then, 80 ml of 10% NaOH solution was added and two phases appeared, which were separated. The organic layer was extracted twice with 40 ml of 10% NaOH solution. The aqueous solutions were collected and acidified with 20% HCl solution. White precipitate appeared and was filtrated and dried to get 12.8 g of compound **I**. After being washed with 100 ml of chloroform, 10.7 g of pure product **I** was obtained (yield: 71%). FT-IR (KBr; cm^{-1}): 1722 (C=O, carboxylic acid), 1329 (S=O, asymmetric, sulfone), 1156 (S=O, symmetric, sulfone). ^1H NMR (270 MHz; DMSO-*d*6; ppm): 8.06 (d, 2H), 7.80–7.86 (m, 4H).

2.2.2. 2,2′-Dichlorocarbonyl-4,4′-dichlorodiphenyl sulfone (*II*)

To a fully dried 100 ml flask, 15.0 g (40 mmol) of compound **I** and 60 ml of SO_2Cl were charged. The mixture was heated to reflux for 8 h. After the exceed SO_2Cl was distilled, the residue was recrystallized from 1,2-dichloroethane. 14.0 g of product **II** was obtained (yield: 85%). FT-IR (KBr; cm^{-1}): 1788 (C=O), 1334 (S=O, asymmetric, sulfone), 1160 (S=O, symmetric, sulfone). ^1H NMR (270 MHz; $CDCl_3$; ppm): 8.18 (d, 2H), 7.85 (d, 2H), 7.75 (dd, 2H).

2.2.3. 2,2′-Dibenzoyl-4,4′-dichlorodiphenyl sulfone (*III*)

To a fully dried 300 ml 3-necked flask, 10.3 g (25 mmol) of compound **II** and 225 ml of benzene were charged. The temperature was raised to 35 °C until the solid was dissolved completely, and then, 7.34 g (55 mmol) of $AlCl_3$ was added part by part. After the addition, the reaction mixture was kept at 35 °C for 20 h, and then poured into a large amount of ice water containing 10 ml of 10% HCl solution. The resulting solid was filtrated to get about a half of the product. The filtrate was separated to two phases, and the organic phase was evaporated to get another half of the product. The two parts of product were combined and recrystallized from acetonitrile, 10.5 g of **III** was obtained (yield: 85%). FT-IR (KBr; cm^{-1}): 1676 (C=O, aromatic ketone), 1332 (S=O, asymmetric, sulfone), 1158 (S=O, symmetric, sulfone). ^1H NMR (270 MHz; $CDCl_3$; ppm): 8.05 (d, 2H), 7.78 (m, 4H), 7.55–7.65 (m, 4H), 7.42–7.50 (m, 4H), 7.25 (d, 2H).

2.2.4. Bis[4-dichloro-2-(3-sulfobenzoyl)] phenyl sulfone, disodium salt (*IV*)

9.75 g (19.8 mmol) of compound **III** was added to a 100 ml flask. At room temperature, 9.8 ml of concentrated sulfuric acid was added slowly. After the solid was dissolved, 9.8 ml of fuming sulfuric acid was added. Then, the mixture was slowly heated to 75 °C and kept at this temperature for 12 h. Cooled to room temperature, the mixture was poured into 450 ml of ice water, and 120 g of NaCl was added into the solution to produce precipitate of the product. The solid was filtrated and redissolved in 450 ml of water and neutralized to the pH of 6–7 with 10% NaOH solution. 100 g of NaCl was added to salt out the product **IV**. The precipitate was filtrated and dried, and then added into 100 ml of DMSO. After the undissolved part was filtrated off, the filtrate was distilled under vacuum, and the residue was washed by acetone, and dried at 60 °C under vacuum for 8 h to get 13.7 g of product **IV** (yield: 99%). FT-IR (KBr; cm^{-1}): 1677 (C=O, aromatic ketone), 1330 (S=O, asymmetric, sulfone), 1164 (S=O, symmetric, sulfone), 1198 (S=O, sulfonate), 1037 (S=O, sulfonate). ^1H NMR (270 MHz; DMSO-*d*6; ppm): 8.07 (s, 2H), 7.90–8.04 (m, 6H), 7.85 (d, 2H), 7.73 (d, 2H), 7.62 (t, 2H).

2.2.5. Bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone (BAPSBPS, *V*)

To a 200 ml 4-neck flask, which was equipped with a magnetic stirrer, a Dean–Stark trap mounted a condenser and a N_2 inlet/outlet, 2.36 g (21.6 mmol) of *p*-AP, 2.99 g (21.6 mmol) of K_2CO_3, 5.60 g (9 mmol) of compound **IV**, 70 ml of NMP and 35 ml of toluene were added under N_2 flow. While the solution was refluxed for 4 h at 140 °C, the produced water was removed with toluene as azeotrope. Then, the