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Fluorenyl-containing sulfonated poly(aryl ether ether ketone ketone)s (SPFEEKK) for fuel cell applications[☆]

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Abstract

A series of fluorenyl-containing sulfonated poly(aryl ether ether ketone ketone)s (SPFEEKK) were synthesized via aromatic nucleophilic substitution polymerization. The sulfonation content (SC) was controlled by the feed ratios of sulfonated and nonsulfonated monomers. Flexible and strong membranes in the sulfonic acid form were obtained from cast membranes in the sodium salt forms by treatment with acid. The thermal properties, water uptake, swelling ratio, water state, oxidative stability, proton conductivity and methanol permeability were investigated. All the polymers had proton conductivities greater than 1×10^{-2} S/cm at room temperature, and the conductivity values of *m*-SPFEEKK-80 and *p*-SPFEEKK-80 were up to 1.86×10^{-1} and 1.78×10^{-1} S/cm at 100 °C. This series of polymers also possessed good dimensional stability in water and low methanol crossover.

Keywords: Fuel cell; Proton exchange membrane; Sulfonation; Poly(ether ketone)s; Polymerization

1. Introduction

Proton exchange membrane fuel cells (PEMFC)s are promising clean power sources for automotive and portable applications [1,2]. Nafion®, which is comprised of a perfluorosulfonic acid structure, is the principal material used as the polymeric electrolyte in PEMFC systems because of its excellent chemical and mechanical stabilities, and high proton conductivity. However, high cost, low operation temperature and high methanol crossover of Nafion and other similar perfluorinated membranes have limited their widespread commercial application in PEMFC. Currently, there is much research on developing non-perfluorinated polymers with better performance and lower cost as alternative proton exchange membrane (PEM) materials [3–6]. Aromatic polymers with sulfonic acid groups are regarded as promising materials for PEMs because of their high thermal and chemical stability. Sulfonated derivatives of poly(ether ether ketone) (SPEEK) [7–11], poly(ether sulfone) (SPES) [12–14], polyimide (SPI) [15–17], poly(arylene ether) [18,19] and poly(phenylquinoxaline) [20] are among those being investigated as potential PEMs. However, further work is required in designing polymeric structures to obtain improvements in hot water dimensional stability and methanol resistance for materials with good proton conductivities.

Aromatic poly(ether ketone)s (PEKs) are well known as high performance thermoplastics for their overall combination of chemical, physical and mechanical properties [21,22]. As an important commercial polymer of the PEK family, aromatic poly(ether ether ketone ketone) (PEEKK) containing rigid ketone linkages show high glass transition temperature, excellent thermal stability and high strength modulus. For their relatively rigid backbones, PEEKK polymers even with bulky pendants showed improved solvent-resistant properties compared with their analogous PEEK polymers [23,24]. From the molecular design viewpoint, the incorporation of long and

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regular ether ether ketone ketone moieties should increase the relative length of nonsulfonated hydrophobic segments and make the hydrophilic segments well dispersed, thereby possibly improving the mechanical properties, and methanol and hot water stability. Most recently, Guiver and co-workers [25] and Na and co-workers [26,27] developed several series of sulfonated polymers comprising ether ether ketone ketone backbones, and several of them have exhibited attractive properties such as good mechanical properties and dimensional stability in water.

The introduction of fluorenyl groups into aromatic polymer chains would enhance the T_g and free volume, improve the solubility but maintain high thermal stability. Recently, sulfonated polyimides [28–30], sulfonated poly(ether sulfone)s [14] and sulfonated PEEKs [31] containing fluorenyl groups that exhibited good thermal and oxidative stability as well as high proton conductivity at elevated temperature were reported.

In order to investigate the effect of polymer structure on their properties and enhance the performance of PEEKK-type polymers, a new series of sulfonated aromatic polymers comprising rigid PEEKK backbones (associated with hot-water stability and low methanol permeability) and bulky pendant fluorenyl groups (associated with free volume, and thereby water uptake and proton conductivity) were prepared by the direct polymerization of sulfonated monomer. The properties relevant to fuel cells were investigated, including thermal and oxidative stability, water uptake, water state, swelling ratio and proton conductivity as well as methanol permeability.

2. Experimental

2.1. Materials

1,4-Bis(4-fluorobenzoyl)benzene (1,4-BFBB, Jilin University, China) and 1,3-bis(4-fluorobenzoyl)benzene (1,3-BFBB, Sigma–Aldrich Ltd.) were recrystallized from 1,2-dichlorobenzene and ethanol, respectively. *N*,*N*-Dimethylacetamide (DMAc), anhydrous potassium carbonate and toluene were obtained from Sigma–Aldrich Ltd., and used as received. 4,4′-(9-Fluorenylidene)diphenol (FDP) was obtained from Sigma–Aldrich Ltd., and recrystallized from toluene before use. All other solvents were used as received.

2.2. Synthesis of 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (S-BFBB)

The sulfonated monomer, 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene, was synthesized following a reported synthetic procedure [32,33].

FTIR (powder, cm^{-1}): 1659 (C=O), 1093, 1040 (S=O).
^{1}H NMR: (DMSO-d_6): 8.15 (dd, $J = 6.8$ Hz, 2.0 Hz, 1 H), 7.89 (s, 2 H), 7.88–7.84 (m, 1 H), 7.39 (t, $J = 8.4$ Hz, 1 H).
^{13}C NMR: (DMSO-d_6): 193.83, 161.40 ($J = 257.9$ Hz), 140.07 ($J = 17.6$ Hz), 133.19 ($J = 9.1$ Hz), 131.90, 130.73, 130.08, 116.72 ($J = 23.7$ Hz).

2.3. Synthesis of sulfonated poly(aryl ether ether ketone ketone)s in salt form (SPFEEKK-Na)

All the polymers were prepared by polycondensation via typical high-temperature nucleophilic substitution reaction conditions [34,35]. SPFEEKK from 1,4-bis(4-fluorobenzoyl)benzene with sulfonation content (SC) = 1.0 (*p*-SPFEEKK-50) is given as a representative example: 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (1.05 g, 2 mmol), 1,4-bis(4-fluorobenzoyl) benzene (0.65 g, 2 mmol), 4,4′-(9-fluorenylidene)diphenol (1.40 g, 4 mmol), anhydrous K_2CO_3 (0.72 g, 5.2 mmol), toluene (12 mL) and DMAc (12 mL were added into a 100-mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and a Dean-Stark trap. The system was allowed to reflux for 3–4 h to remove the water from the reaction system by the azeotropic distillation of toluene. The reaction mixture was then heated to 170–180 °C. Another 5 mL of DMAc were added into the viscous reaction mixture after 12 h at this temperature. The polymerization was complete after a further 3–4 h. The resulting viscous polymer solution was then poured into ethanol. The polymer was thoroughly washed with hot deionized water to remove the salts and solvents, and dried at 100 °C for 48 h.

2.4. Preparation of sulfonated poly(ether ether ketone ketone)s in acid form (SPFEEKK-H)

An amount of 1.0 g polymer in the sodium salt form was dissolved in 20 mL of DMAc and filtered. The filtered solution was poured onto a glass plate and dried at 50 °C under a constant purge of nitrogen for about one week. The film was removed from the plate by immersing it in water until it released. The resulting flexible membrane in sodium form was dried in a vacuum oven at 120 °C for 48 h.

SPFEEKK-H membranes were prepared by immersing SPFEEKK-Na membranes in 2N H_2SO_4 for 48 h at room temperature, and then in deionized water for 24 h, during which time the wash water was changed several times. The thickness of all membrane films was in the range of 60–80 μm.

2.5. Measurements

2.5.1. FTIR and NMR

FTIR spectra of SPFEEKK-Na samples were measured on a Nicolet 520 Fourier transform spectrometer, and a diamond cell was used as a support for the thin films of SPFEEKK-Na polymers and for S-BFBB monomer powder. The thin films for the FTIR measurements were cast from DMAc polymer solution. ^{1}H and ^{13}C NMR spectra of S-BFBB monomer and SPFEEKK-Na polymers were obtained on a Varian Unity Inova NMR spectrometer operating at frequencies of 399.95 MHz for ^{1}H and 100.575 MHz for ^{13}C. Deuterated dimethylsulfoxide (DMSO-d_6) was selected as the solvent and the DMSO signals at 2.50 ppm (^{1}H NMR) and 39.51 ppm (^{13}C NMR) were used as the chemical shift references.