



Synthesis and properties of highly branched star-shaped sulfonated block poly(arylene ether)s as proton exchange membranes

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ABSTRACT

Star-shaped sulfonated block copoly(ether ketone)s exhibit excellent properties for use as proton exchange membranes (PEMs). However, very few investigations of the use of highly branched star-shaped sulfonated block polymers as PEMs have been reported. In this work, two types of highly branched star-shaped sulfonated block poly(arylene ether)s with 6% branching agent were synthesized via direct polycondensation reactions of a trifunctional core (branching agent) with sulfonated 4,4'-difluorobenzophenone, bisphenol fluorene, and 4,4'-difluorodiphenyl sulfone. The properties of a polymer with hydrophilic segments surrounded by hydrophobic segments (P1) and a polymer with hydrophobic segments surrounded by hydrophilic segments (P2) were investigated. The block polymer P1 exhibited better oxidative stability (332 min) and dimensional stability (< 12%) than the highly branched sulfonated random polymer (P3), whereas P2 exhibited higher proton conductivity (0.40 S cm^{-1} at 80°C) and water uptake (59.1% at 80°C) than P3. The highly branched star-shaped sulfonated block poly(arylene ether)s exhibit greater potential than P3 for use as PEMs.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have received worldwide attention because of their potential applications in transportation and in stationary and portable electronics [1,2]. Interest in using PEMFCs as power sources has driven considerable fundamental research in the field of proton-conducting polymers in recent years [3–5]. Although considerable progress has been made in the development of proton exchange membranes (PEMs) in the past decade [6–8], durability and cost are still two major obstacles hindering their widespread application [9]. Perfluoro-sulfonic acid polymers such as Nafion are the most promising proton-conducting polymers from the standpoint of chemical and thermal stability as well as physical and proton-conducting properties [10]. However, their high cost is a major obstacle to their widespread application in PEMFCs and has stimulated extensive research into promising alternatives [4], including sulfonated poly(arylene ether)s [5,11–14]. Sulfonated poly(arylene ether)s possess good thermal stability, appropriate mechanical strength and high proton conductivity. However, most of them are inappropriate for use as PEMs because of their short lifetimes when subjected to a combination of hydrolysis and oxidative degradation [15,16].

Therefore, extensive efforts to improve the durability of these membranes are required.

Cross-linking is an effective method of improving oxidative stability [17]. Various cross-linked PEMs have been reported [17–20]. Na et al. have prepared a series of cross-linked hybrid membranes using a combination of silane cross-linking and thiol-ene click chemistry based on a sulfonated poly(arylene ether ketone); the hybrid membranes exhibited high dimensional stability and high oxidative stability [21]. Chen et al. have reported a series of quinoxaline-based cross-linked membranes with excellent oxidative stability; the elapsed time of the cross-linked membranes in Fenton's reagent was 2–3 times longer than that of the corresponding precursor membranes [22]. However, cross-linked membranes are usually insoluble in common organic solvents and difficult to reprocess.

Compared with cross-linked PEMs, only a few branched PEMs have been reported [16,23–30]. Hay et al. have reported branched poly(arylene ether)s with sulfonic acid groups on the end groups [23]. Ueda et al. have developed a series of sulfonated block copolymers with hydrophilic and hydrophobic segments as arms, which exhibit high oxidative stability [24]. Park et al. have prepared a series of branched sulfonated polymers containing less than 0.4% branching agent using a facile method [25]. Our group has introduced 1,1,1-tris(4-hydroxyphenyl)ethane, 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene and 1,3,5-tris[4-(4-fluorophenyl-sulfonyl)phenyl]benzene as branching agents to synthesize three series of branched nonfluorinated polymers [16,26,27] with

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degrees of branching (DB) of 2%, 4% and 10%, respectively. Wang et al. have also successfully prepared partially fluorinated branched sulfonated poly(ether ether ketone)s with 6.67% branching agent by introducing 1,3,5-tris(4-fluoro benzoyl)benzene as the branching agent [28]. These studies have demonstrated that branched PEMs with good solubility in common organic solvents exhibit improved oxidative stability and proton conductivity and therefore have great potential as PEMs.

Among branched polymers, star-shaped sulfonated block copolymers with hydrophilic and hydrophobic segments as arms are particularly worthy of attention because of the ingenious design of their structure and their excellent properties for use as PEMs. Although many sulfonated block polymers have been prepared for use as PEMs [31–38], no recent studies of star-shaped sulfonated block polymers have been reported. In addition, according to Ueda et al. [24], some shortcomings of star-shaped sulfonated block polymers remain unresolved. First, the DB value of star-shaped sulfonated block copolymers is low (~1%), and higher DB values are associated with better PEM properties. Second, only polymers with hydrophilic segments surrounded by hydrophobic segments have been prepared and investigated. Block polymers with hydrophobic segments surrounded by hydrophilic segments may also have promising properties and should be pursued. Third, the method for preparing star-shaped sulfonated block copolymers must be improved because it is relatively difficult to control the sulfonated position using the post-sulfonation method.

In this study, two types of highly branched star-shaped sulfonated block polymers, a polymer with hydrophilic segments surrounded by hydrophobic segments (P1) and a polymer with hydrophobic segments surrounded by hydrophilic segments (P2), were synthesized via direct polycondensation reactions of a trifunctional core with bisphenol fluorene, sulfonated 4,4'-difluorobenzophenone, and 4,4'-difluorodiphenyl sulfone. The properties of block polymers P1 and P2, including their hydrolysis and oxidative stability, ion-exchange capacity (IEC), proton conductivity, water uptake, thermal stability and swelling ratios, were investigated and compared with those of the random polymer, P3.

2. Experimental

2.1. Materials

1,3,5-Triphenylbenzene, 4,4'-difluorodiphenyl sulfone (DFDS), 4-fluorobenzenesulfonyl chloride, sulfonated 4,4'-difluorobenzophenone (SDFBP) and bisphenol fluorene were purchased from commercial sources and used as received. Before use, toluene was dried using sodium wire, and DMAc was dried using 4 Å molecule sieves. Anhydrous potassium carbonate was dried at 300 °C for 24 h in a furnace before use.

2.2. Measurement

¹H NMR spectra, reported in ppm, were recorded using a Varian 400-Hz NMR instrument with tetramethylsilane (TMS) as the internal standard. The inherent viscosities of ~0.5 g/dL polymer solutions in DMAc were measured using an Ubbelohde viscosity meter at 30 °C. The thermal stability of the polymers was investigated at a heating rate of 10 °C min⁻¹ in the temperature range from 50 °C to 600 °C using a Q50 TGA instrument in a nitrogen environment with a flow of 50 mL min⁻¹. Cross-sectional images of the membranes were obtained using a scanning electron microscope (SEM, SU-70, Hitachi) after freeze-fracturing the membranes in liquid N₂ and then coating them with a thin layer of gold (~10 nm) using a sputter coater, which increased their surface conductivity and thereby improved the resolution and

quality of the SEM images. Tapping-mode atomic force microscope (AFM) images were acquired using a Dimension Icon scanning probe microscope.

2.3. Synthesis of 1,3,5-tris[4-(4-fluorophenylsulfonyl)phenoxy]benzene (B₃)

B₃ was synthesized from 1,3,5-triphenylbenzene and 4-fluorobenzenesulfonyl chloride using the method reported in the literature [23]. A white powder was obtained with an overall yield of 75.9% after purification by recrystallization from acetic acid. The structure of B₃ was confirmed by ¹H NMR. ¹H NMR (CDCl₃, ppm): 8.02–8.08 (m, 12H), 7.78–7.81 (m, 9H), 7.22–7.30 (m, 6H). Mp: 143–144 °C.

2.4. Synthesis of the hydrophilic polymer bP1

Bisphenol fluorene (0.966 g, 2.76 mmol), SDFBP (1.0135 g, 2.40 mmol), B₃ (0.1872 g, 0.24 mmol), potassium carbonate (0.571 g, 4.14 mmol), DMAc (7 mL) and toluene (8 mL) were carefully introduced into a 50 mL three-neck round-bottom flask equipped with a Dean–Stark trap and a condenser under nitrogen protection. The reaction mixture was stirred at 140 °C for 4.0 h. After the removal of toluene, the reaction temperature was increased to 170 °C, and the reaction was continued for 1.5 h. After cooling to room temperature, the mixture was poured slowly into 150 mL of water containing 4 mL of concentrated HCl to precipitate the formed polymer. The precipitates were filtered and washed with water three times to remove any inorganic salts. The fibrous polymer was collected and dried at 110 °C under vacuum for 24 h. ¹H NMR (400 MHz, DMSO, ppm): 8.10 (s, 0.87H), 8.04 (s, 0.26H), 7.89 (t, 1.65H), 7.56 (d, 0.87H), 7.44 (d, 1H), 7.38 (d, 1H), 7.31 (m, 1.26H), 7.12 (m, 1H), 6.91 (d, 1H), 6.8 (d, 0.87H).

2.5. Synthesis of the highly branched sulfonated block polymer P1

Bisphenol fluorene (0.966 g, 2.76 mmol), SDFBP (1.0135 g, 2.40 mmol), B₃ (0.1872 g, 0.24 mmol), and potassium carbonate (0.571 g, 4.14 mmol) were added to a 50 mL three-neck round-bottom flask equipped with a Dean–Stark trap. Then, DMAc (7 mL) and toluene (8 mL) were added to the flask under nitrogen. The reaction mixture was stirred at 140 °C for 4.0 h. After the water was removed, the reaction temperature was increased to 170 °C, and the reaction was continued for 1.5 h. After the mixture had cooled to 120 °C, bisphenol fluorene (0.434 g, 1.24 mmol), DFDS (0.3149 g, 1.24 mmol), potassium carbonate (0.257 g, 1.86 mmol), DMAc (6 mL) and toluene (8 mL) were carefully introduced into the three-neck round-bottom flask. The reaction mixture was again heated to 140 °C for 4.0 h to remove water, and the temperature was then increased to 170 °C. The reaction mixture was maintained at this temperature for 4 h. After cooling to room temperature, the mixture was slowly poured into 200 mL of water containing 5 mL of concentrated HCl to precipitate the formed polymer. The precipitates were filtered and washed with water three times to remove any inorganic salts. The fibrous polymer was collected and dried at 110 °C under vacuum for 24 h. ¹H NMR (400 MHz, DMSO, ppm): 8.11 (s, 0.6H), 8.05 (br, 0.18H), 7.83–7.96 (m, 2.07H), 7.57 (d, 0.6H), 7.46 (d, 1H), 7.39 (d, 1H), 7.34 (d, 1.18H), 7.15 (m, 2H), 7.04 (d, 0.62H), 6.98 (d, 0.62H), 6.93 (d, 1.38H), 6.82 (d, 0.6H).

2.6. Synthesis of the hydrophobic polymer bP2

Bisphenol fluorene (0.56 g, 1.6 mmol), DFDS (0.3149 g, 1.24 mmol), B₃ (0.1872 g, 0.24 mmol), potassium carbonate

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