Syntheses and Characterization of Sulfonated Poly(arylene ether sulfone) Containing Naphthyl Moiety as Pendent Groups for Proton Exchange Membranes

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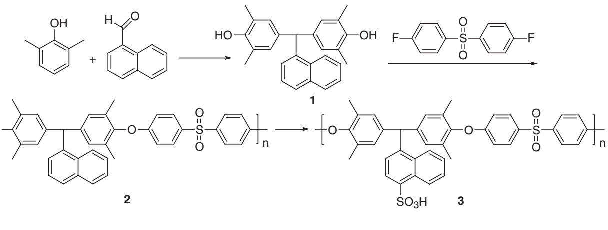
Novel poly(arylene ether sulfone) with sulfonic acid groups attached onto pendent naphthyl rings was successfully synthesized by the nucleophilic displacement of aromatic dihalides with bisphenols in aprotic solvent, followed by sulfonation with chlorosulfonic acid. The sulfonation took place only on the pendent naphthyl rings due to the specially designed molecular structure. The sulfonated polymers are soluble in common organic solvents and can be readily cast into tough and smooth films. The films of the side-chain-type polymer showed good thermal and oxidation stabilities.

Proton exchange membranes have attracted considerable attention because they are key-components in polymer electrolyte membrane fuel cells (PEMFCs), which are promising environmentally friendly and efficient power sources for a wide range of different applications.[1] Nafion is typically used as the polymer electrolyte in PEMFC because of its excellent chemical and mechanical stabilities as well as high proton conductivity. However, it suffers from several shortcomings among which their high cost presents a major obstacle for widespread application in fuel cells. As a result, considerable efforts have been devoted to the development of nonfluorinated PEM materials with excellent comprehensive properties. Recently, it has been reported by several research groups that polymer electrolytes containing sulfonic acid groups on the pendent side chains exhibit decent dimensional and thermal stabilities as well as good durability.[2–10] In this regard, we present here a kind of novel poly(arylene ether sulfone) with sulfonic acid groups attached to pendent naphthyl rings.

As depicted in Scheme 1, polymer **2** was prepared by two-step polycondensation. To a 25 mL three-neck round bottom flask equipped with a Dean–Stark trap and condenser under nitrogen protection, bis(4-fluorophenyl) sulfone (0.254 g, 1.0 mmol), **1** (0.382 g, 1.0 mmol), potassium carbonate (0.208 g, 1.5 mmol), DMAc (2.0 mL), and toluene (5.0 mL) were carefully introduced. The reaction mixture was first heated at 140–150 °C for 3.0 h to remove the water produced. The toluene was then distilled off by increasing the temperature up to 170 °C (oil bath temperature). The reaction mixture was kept at this temperature for 8 h. After it was cooled, the resulting viscous mixture was diluted with 5 mL DMAc and poured slowly into 100 mL methanol containing 2 mL of concentrated HCl to precipitate out the formed polymer. The obtained polymer **2** was washed with water and methanol. After drying, the polymer was dissolved in 50 mL of chloroform and filtered through a sintered glass funnel. The filtrate was concentrated to about 6 mL, and then added slowly dropwise into 100 mL of methanol with stirring to precipitate out the final polymers. The inherent viscosity of the polymer was 0.34 dl g^{-1}. The structure of the polymer was confirmed by ^{1}H NMR spectra; (Figure 1: ^{1}H NMR (CDCl$_3$): δ 2.00 (s, 12H), 6.16 (s, 1H), 6.80–6.84 (m, 8H), 6.98–7.00 (d, 1H), 7.38–7.48 (m, 3H), 7.76–7.82 (m, 5H), 7.86–7.89 (d, 1H), 7.98–8.01 (d, 1H).



Scheme 1. Synthesis of sulfonated polymer **3**.

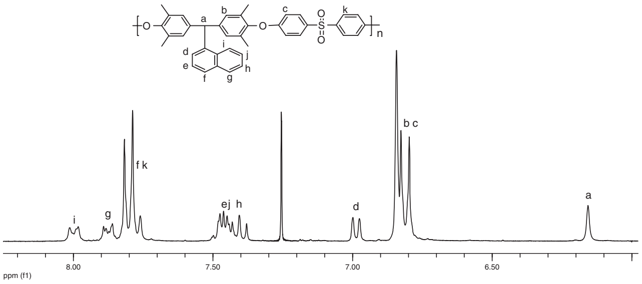


Figure 1. ^{1}H NMR of polymer **2**.

Polymer **2** was sulfonated with chlorosulfonic acid. A typical example for the praperation of polymer **3** is as follows: To a solution of 1.00 mmol of polymer **2** in 100 mL of methylene chloride, 6 mL of 1 M chlorosulfonic acid in methylene chloride was added dropwise at room temperature. The mixture was stirred vigorously for 4 h until the pale brown products precipitated out from the solution. The precipitates were collected by filtration and washed with hexane three times and redissolved in 20 mL of DMAc. To the solution was added 40 mL of 3 wt % aqueous potassium hydroxide solution. After 6 h reaction, the mixture was acidified with 100 mL of 5 vol % hydrochloric acid. The aqueous solution was dialyzed for 2 days. The sulfonated product was recovered by evaporation of water. The product was characterized by ^{1}H NMR spectroscopy (Figure 2) and inherent viscosity was 0.89 dl g^{-1}.

Figures 1 and 2 show ^{1}H NMR of polymer **2** and sulfonated polymer **3**. The peaks (a, b, c, d, g, h, i, j, and k) of polymer **2** were still found in those peaks of sulfonated polymer **3** and the peaks had the same integration ratio for polymer **2** and sulfonated polymer **3** suggesting that the polymer main chain stayed intact throughout the sulfonation reaction. There were remarkable changes in the peaks of naphthyl rings. The peaks (f and e) of polymer **2** disappeared and a peak of 8.95 ppm was observed in sulfonated polymer **3**. The integration ratio of

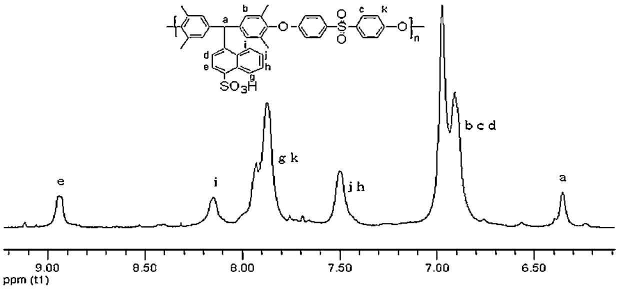


Figure 2. ^{1}H NMR of sulfonated polymer **3**.

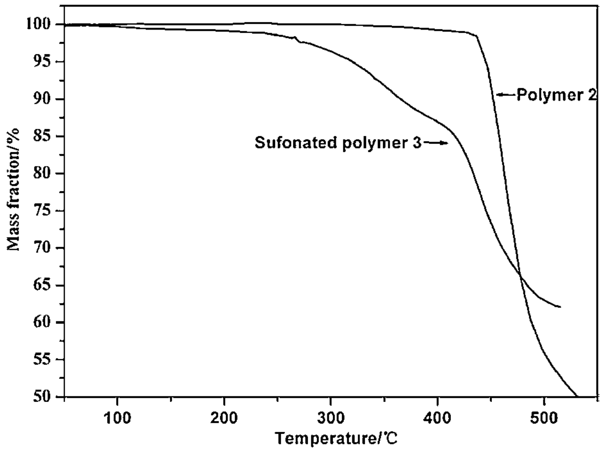


Figure 3. TGA curves of polymer **2** and sulfonated polymer **3**.

these peaks of sulfonated polymer **3** indicated the introduction of one sulfonic acid group only at the 4-position on a naphthyl ring. Ion exchange capacity of polymer **3** is 1.48 mequiv g^{-1} obtained by calculating.

The thermal properties of polymers were investigated using DSC and thermogravimetric analysis (TGA). Parent polymer **2** has a high T_g of 273 °C, while no T_g was detectable for sulfonated polymers **3** before their thermal decomposition. The T_g of sulfonated polymer **3** is much higher than that of parent polymer **2** because of the ionomeric nature. Figure 3 shows the TGA spectra of polymer **2** and sulfonated polymer **3**. Parent polymer **2** is a thermally stable polymer with 5% weight loss temperature of about 445 °C. Sharp weight loss from 440 to 500 °C is ascribed to the decomposition of polymer main chain. Polymer **3** was preheated from 50 to 240 °C and then TGA was run from 50 to 600 °C at a heating rate of 10 °C min^{-1} under nitrogen. Two weight loss stages are attributed to the loss of sulfonic groups and the degradation of polymer main chain.

Polymer **3** was very soluble in polar organic solvents such as *N*,*N*-dimethylacetamide, dimethylformamide, dimethyl sulfoxide, and could be cast into tough and smooth films. The water uptake and proton conductivity of the membrane from polymer **3** in acidic form were measured (Table 1). The membrane exhibited high proton conductivity (3.2×10^{-2} S cm^{-1}).

Table 1. Properties of sulfonated polymer **3**

T/°C	Water uptake /%	Conductivity^a /S cm^{-1}	t^b/min
30	38	2.1×10^{-2}	ND^c
80	45	3.2×10^{-2}	55

^{a}The conductivity was measured at the relative humidity of 100%. ^{b}Refer to the elapsed time that the membranes started to break into pieces. ^{c}Not detected.

The stability of the sulfonated polymer **3** to oxidation was investigated by immersing the membranes into Fenton's reagent (2 ppm $FeSO_4$ in 3% H_2O_2) at 80 °C. The oxidative stability of the membrane was characterized by the expended time that the membrane started to break into pieces. The membrane exhibited good oxidative stability. The hydrolytic stability was also investigated by treating membrane in boiling water for more than 7 days. There was not any change observed in both the membrane's shape and appearance, implying that no hydrolysis occurred during the treatment.

In conlusion, poly(arylene ether sulfone) with sulfonic acid groups attached onto pendent naphthyl rings was successfully synthesized. The films were prepared by casting from solution and exhibited high proton conductivity and good oxidative stability. The films can be potentially used as a proton-exchange membrane for polymer electrolyte membrane fuel cell.

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