

## SHORT COMMUNICATION

## Synthesis and Characterization of Partially Fluorinated Poly(arylene ether) Containing Sulfluorenyl Groups for Proton Exchange Membranes

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As the key component of proton exchange membranes fuel cell (PEMFC), PEM plays an important role in fuel cells. Nafion is typically used as the polymer electrolyte in PEMFC because of their excellent chemical and mechanical stabilities as well as high proton conductivity. However, it suffers from several shortcomings among which the high cost presents a major obstacle for widespread application in fuel cell. As a result, considerable efforts have been devoted into the development of nonfluorinated or partially-fluorinated PEM materials with excellent comprehensive properties. Recently, it has been reported by several research groups that the polymer electrolytes containing fluorenyl groups show high proton conductivity and good durability.<sup>1–3</sup> The most exciting report is that the membranes containing fluorenyl groups prepared by Miyatake retain their strength, flexibility and high molecular weight with an acceptable decline of proton conductivity after 10000h in fuel cell operation condition.<sup>4</sup> In our previous papers,<sup>5</sup> we have reported the synthesis of partially fluorinated polyaromatics with hindered and bulky groups which allowed position-directed sulfonation. These polymers are more stable to hydrolysis and oxidation than nonfluorinated polymers.<sup>6</sup> In this article, we report the synthesis of partially fluorinated poly(arylene ether)s containing sulfluorenyl groups.

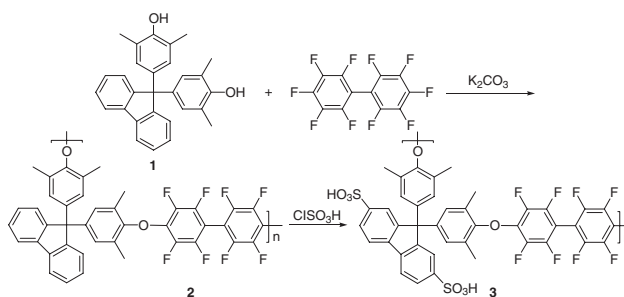
## EXPERIMENTAL

## Synthesis of Polymer 2

To a 25 mL three necked round bottom flask, equipped with a thermometer and a nitrogen inlet, 0.406 g (1.0 mmol) 1, 0.334 g (1.0 mmol) decafluorobiphenyl, 0.208 g (1.5 mmol) anhydrous potassium carbonate, 6–8 mL of DMAc were carefully introduced. The reaction mixture was heated at 120 °C for 4–6 h. When the solution viscosity had apparently increased, the resulting viscous mixture was diluted with 3 mL of DMAc and poured slowly into 100 mL of methanol containing 1.0 mL of concentrated hydrochloric acid with stirring to precipitate the formed polymer. The crude polymer was filtered off and washed with water and methanol continuously, followed by dissolving in 50 mL of chloroform. The solution was filtered to remove inorganic salts. The filtrate was concentrated to about 5 mL and dropped slowly into 100 mL of methanol with stirring to precipitate the final polymer. Pure white polymer (0.65 g, 92.86% yield) in white color was obtained after dried under vacuum at 120 °C for 10 h. <sup>1</sup>H NMR (400 MHz): δ (ppm) 2.14 (s, 12H), 6.84 (s, 4H), 7.26–7.42 (m, 6H), 7.76 (d, 2H).

## Synthesis of Sulfonated Polymer 3

To the solution of 1.0 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



Scheme 1. Synthetic route of sulfonated polymer 3.

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 % potassium hydroxide aqueous solution. After 6 h reaction, the mixture was acidified with 100 mL of 5 vol % hydrochloric acid. The aqueous solution was dialyzed for 2 d. The sulfonated product was recovered by evaporation of water. The product was characterized by <sup>1</sup>H NMR spectroscopy (Figure 1).

## Preparation of Polymer Film

Polymer films were prepared as follows: 0.6 g of sulfonated polymer sample was dissolved in 10 mL DMAc followed by filtration. The filtrate was poured onto glass slides and dried at 60 °C to remove the solvent. The polymer film was further dried at 50 °C under vacuum about 6 h, then at 120 °C under vacuum for 24 h.

## RESULTS AND DISCUSSION

Partially fluorinated polymer 2 belongs to a family of poly(arylene ether)s. The polymers are usually synthesized by the nucleophilic aromatic substitution of aryl halides with phenoxides. However, the reaction is finished in short time and only gel particles that are insoluble in chloroform are obtained. The results can be assumed that decafluorobiphenyl and monomer 1 are so reactive that the side reactions such as branching and crosslinking occurred in this conditions. In our procedure, the reaction was conducted in DMAc in the presence of K<sub>2</sub>CO<sub>3</sub> at 120 °C for 4–6 h. High molecular weight polymer ( $M_n = 46400$ ,  $M_w = 96300$ ) was obtained. Polymer 2 was sulfonated using chlorosulfonic acid in methylene chloride to give sulfonated polymer 3. As depicted in Figure 1, the peaks of polymer 2 at 2.14 ppm(s) and 6.84 ppm(s) were still found in those of sulfonated polymer 3 at 2.12 ppm(s) and 6.81 ppm(s) and the two sets of peaks had the same integration ratio for polymer 2 and sulfonated polymer 3 suggesting that the polymer main chain stayed intact throughout the sulfonation

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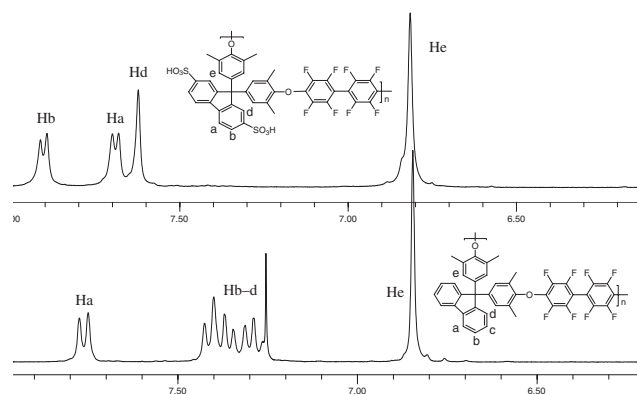


Figure 1.  $^1\text{H}$  NMR of polymer 2 and sulfonated polymer 3.

reaction. There were remarkable changes in the peaks of fluorenyl groups. The peaks of polymer 2 at 7.26–7.42 ppm and 7.76 ppm disappeared and the peaks of sulfonated polymer 3d were observed at 7.62 ppm(s), 7.69 ppm(d), and 7.90 ppm(d). The integration ratio of these peaks of sulfonated polymer 3 indicated the introduction of two sulfonic acid groups only at (2,7)-position on a fluorenyl group. The result was further confirmed by the IEC value. The experimental IEC value (2.29 meq/g) of sulfonated polymer 3 is good accordance with the calculated value (2.32 meq/g).

Parent polymer 2 has a high  $T_g$  of 270.6 °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 ionic nature. Parent polymer 2 is a thermal stable polymer with 5% weight loss temperature of about 420 °C. Sharp weight loss from 400 to 450 °C is ascribed to the decomposition of polymer main chain. Polymer 3 was preheated from 50 to 240 °C and then TGA experiment was run from 50 to 600 °C at a heating rate of 10 °C/min under nitrogen. The weight loss from 250 to 350 is attributed to the loss of sulfonic groups.

Polymer 3 was very soluble in polar organic solvents and could be cast into tough and smooth films. Water uptake of the membrane was measured by immersing the vacuum dried membrane samples into deionized water for 12 h at 80 °C. The films were taken out, wiped with tissue paper to remove the excess of water on the film surface, and quickly weighted on a microbalance. The result was shown in Table I. The proton conductivities of the membrane from polymer 3 in acidic form were measured at different temperature and 100% relative humidity (Figure 2). The membrane exhibited higher proton conductivity than that of Nafion 117 (0.039 S/cm) at 80 °C.

The stability of the sulfonated polymer 3 to oxidation was investigated by immersing the membranes into Fenton's reagent (3 ppm  $\text{FeSO}_4$  in 3%  $\text{H}_2\text{O}_2$ ) at 80 °C. The oxidative stability of the membrane was characterized by the expended time that the membranes started to break into pieces (Table I). The membrane exhibited higher oxidative stability than those reported in the literatures.<sup>1,3</sup> The hydrolytic stability was also investigated by treating membrane in boiling water for more than 8 d. There was not any change observed in both the membrane's shape and appearance, implying that no hydrolysis occurred during the treatment.

In summary, Partially fluorinated poly(arylene ether) containing sulfofluorenyl groups was successfully synthesized and characterized by  $^1\text{H}$  NMR spectroscopy. The sulfonation took place only at (2,7)-position on fluorenyl groups. The sulfonated polymer 3 is highly soluble in common

Table I. Properties of sulfonated polymer 3

Sample	Water Uptake (%)	Conductivity (S/cm)	$T^1$ (min)
Sulfonated polymer 3	80.7	$5.7 \times 10^{-2}$	75

$T^1$  refer to the elapsed time that the membranes started to break into pieces.

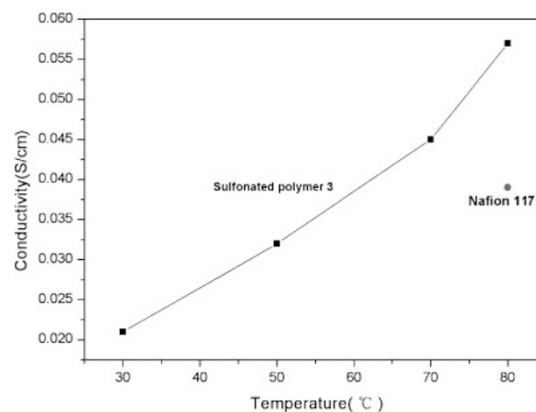


Figure 2. Proton conductivities of sulfonated polymer 3 and Nafion 117.

organic solvent and can be readily cast into tough and smooth films from solutions. The films exhibited greater water uptake and higher proton conductivity than Nafion 117. The thermal decomposition temperatures of the sulfonated polymer is higher than 250 °C without detectable  $T_g$ . The as-made polymer electrolyte films exhibited excellent hydrolytic and oxidative stability.

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## REFERENCES

1. Y. Chikashige, Y. Chikyu, K. Miyatake, and M. Watanabe, *Macromolecules*, **38**, 7121 (2005).
2. X. Y. Shang, S. H. Tian, L. H. Kong, and Y. Z. Meng, *J. Membr. Sci.*, **266**, 94 (2005).
3. X. Y. Shang, X. H. Li, M. Xiao, and Y. Z. Meng, *Polymer*, **47**, 3807 (2006).
4. K. Miyatake, Y. Chikashige, E. Higuchi, and M. Watanabe, *J. Am. Chem. Soc.*, **129**, 3879 (2007).
5. L. Wang, Y. Z. Meng, S. J. Wang, X. Y. Shang, L. Li, and A. S. Hay, *Macromolecules*, **37**, 3151 (2004).
6. L. Wang, Y. Z. Meng, S. J. Wang, and A. S. Hay, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 1779 (2004).