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Novel Sulfonated Poly(arylene ether): A Proton Conductive Polymer Electrolyte Designed for Fuel Cells

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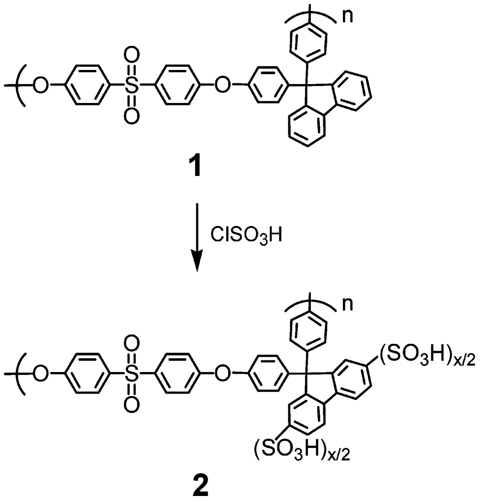
Proton conductive polymers have been attracting more and more attention as an electrolyte material for polymer electrolyte fuel cells (PEFCs)[1] and direct methanol fuel cells (DMFCs).[2] For these applications, the polymer membranes have to meet several demanding requirements: proton conductivity higher than 0.01 S cm^{-1}, long-term stability under humidified and heated conditions, impermeability to hydrogen, methanol, and oxygen.[3] Perfluorinated ionomers such as Nafion with PTFE backbone, fluoroalkyl ether side chains, and sulfonic acid end groups are the most commonly used materials. Although the ionomers show excellent performance under moderate conditions, considerable deterioration in the conductivity and the mechanical strength takes place above the glass transition temperature (ca. 110 °C), which makes them unavailable for the use in high-temperature fuel cells. The high cost and environmental inadaptability of the fluorinated polymers also urge the necessity to develop alternative proton conducting polymers.

One of the effective approaches is acid functionalization of hydrocarbon polymers.[4] Chemically and thermally stable aromatic polymers should serve as a base skeleton for electrolytes. Sulfonated poly(arylene ether)s,[5] poly(arylene ether ether ketone)s,[6] poly(phenylene sulfide)s,[7] polyimides,[8] and acid-doped polybenzimidazoles[6a,9] have been proposed, for example. We have recently found that the introduction of fluorenylbiphenyl groups as a rather bulky hydrophobic component into sulfonated polyimides improves the water affinity at high temperature, resulting in the very high proton conductivity of 1.67 S cm^{-1} at 120 °C.[10] Another important strategy has been proposed that the polyethers with acidic groups on the pendant phenyl groups are more stable to hydrolysis than those with acidic groups directly attached to the main chain.[11] These results prompted us to combine both benefits. In this Communication, we describe the synthesis and properties of novel poly(arylene ether) bearing sulfofluorenyl moieties.

The parent polymer **1** was synthesized by the polycondensation of 9,9-bis(4-hydroxyphenyl)fluorene and bis(4-fluorophenyl)sulfone under nucleophilic substitution conditions (K_2CO_3/DMAc).[12] Polymer **1** is high molecular weight ($M_w = 201\,500$, $M_n = 42\,300$ relative to polystyrene standards measured by GPC) to give a tough film by casting from CH_2Cl_2 solution. Polymer **1** was reacted with chlorosulfonic acid in CH_2Cl_2 to give the title polymer **2** (Scheme 1). Since the product readily precipitates out of the mixture, **2** could be isolated by filtration followed by washing with water. Polymer **2** is soluble in polar organic solvents such as DMSO, DMF, and NMP and was characterized by ^{1}H NMR spectroscopy. The comparison of the spectra between **1** and **2** made it easy to assign the peaks (Figure 1). Although there are some chemical shifts observed between them due to the different solvent used ($CDCl_3$ for **1** and DMSO-d_6 for **2**), two sets of doublet−doublet peaks (1, 2, 3, and 4) ascribed to oxy-1,4-phenylenesulfone and oxy-1,4-phenylenecarbon have the same integration ratio for **1** and **2**, suggesting that the polymer main chain stayed intact throughout the sulfonation reaction.[13] There are remarkable changes in the peaks of fluorenyl groups; peak 6 becomes weaker, and new peaks 9, 10, and 11 well-assigned to 1-sulfo-3,4-disubstituted benzene group appear at 7.63 (s), 7.68 (d), and 7.94 ppm (d) in the spectrum of **2**. The integration ratio of these peaks indicates the introduction of one sulfonic acid group on a fluorenyl group, which corresponds to the ion-exchange capacity of 1.14 mequiv/g. The IR spectrum of **2**, in which a characteristic absorption band of sulfonic acid groups is observed at 1031 cm^{-1} ($\nu_{SO,asym}$), also supports the proposed structure.

Scheme 1. Synthesis of Polymer 2



The degree of sulfonation (*x* in Scheme 1) could be controlled by simply changing the amount of chlorosulfonic acid used in the reaction because the reaction is so fast that the sulfonation proceeds before the product precipitates out. When an equimolar amount of chlorosulfonic acid to the repeating unit was applied, polymer **2** ($x = 0.56$, ion-exchange capacity of 0.92 mequiv/g) was obtained. In our series of experiments, polymers **2** with *x* up to 1.28 were prepared without substituting sulfonic acid groups on the main chain.

Polymer **2** gives a transparent, tough, and flexible film by casting from DMAc solution. The stability of the polymer **2** ($x = 0.71$, ion-exchange capacity of 1.14 mequiv/g) has been investigated under both dry and wet conditions. TG/DTA analyses under a dry nitrogen atmosphere showed two step weight losses: the first one from 50 to 180 °C due to the desorption of water molecules and the second one above 250 °C due to the degradation (loss of sulfonic acid groups). The high thermal stability is comparable to that of other sulfonated hydrocarbon polymers or perfluorinated iono-

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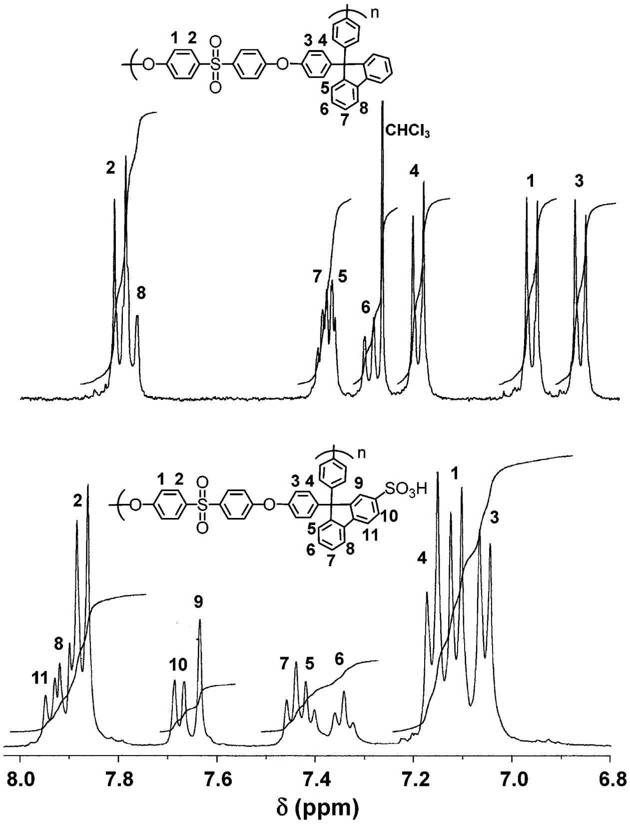

Figure 1. ^{1}H NMR spectra of polymers **1** (upper) and **2** ($x = 1$) (bottom).

mers.[4] No thermal transition such as glass transition or melting was observed below the decomposition temperature.

The hydrolytic stability was evaluated by treating the membrane sample at 140 °C and 100% RH for 24 h as an accelerated testing. The membrane did not display any changes in appearance (color, flexibility, and toughness). Since there were not any changes observed in ^{1}H NMR and IR spectra, it is assumed that the sulfonic acid groups are intact during the treatment. GPC profiles measured with DMF containing 0.01 M LiBr as the solvent also stay the same as that of the pristine polymer, indicating that there is no practical hydrolytic degradation occurred. The membrane was subjected to stability test (oxidative stability) against Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C. It took 40 min before the dissolution of the membrane commenced. After 1 h treatment, the membrane still retains its flexibility although the molecular weight is lowered to about one-third of the original as indicated by GPC analyses.

Proton conductivity of the polymer **2** ($x = 0.71$) membrane was measured at 100% RH and compared with Nafion 112 (ion-exchange capacity of 0.91 mequiv/g) in Figure 2. At the temperatures below 100 °C, both membranes show almost the same conductivity of 0.1–0.2 S cm^{-1}. The activation energy for the proton conduction estimated from the slope is to be 21 kJ mol^{-1}, implying that both share the similar conduction mechanism involving hydronium ions. While Nafion 112 loses the conductivity at 140 °C down to 60% of the value at 100 °C, the conductivity keeps increasing even above 100 °C for polymer **2**. This is the similar behavior observed for the sulfonated polyimide with fluorenyl moieties to have water confinement effect at high temperatures.[10] Polymer **2** ($x = 1.28$, ion-exchange capacity of 1.92 mequiv/g) with more sulfonic acid groups shows higher proton conductivity at low temperatures; however, the conductivity decreases at 100 °C. High concentration of sulfonic acid groups seems to diminish the water confinement effect. It would be because increasing sulfonic acid groups results in lowering the π–π interaction among aromatic polymer chains so that they lose structural stiffness and water holding capability.

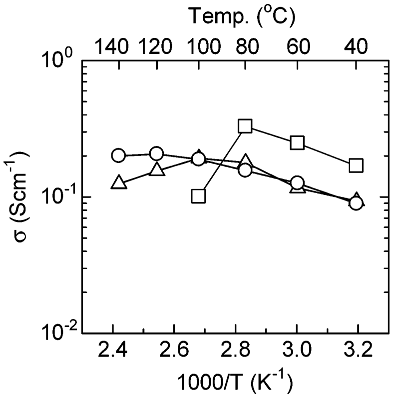

Figure 2. Temperature dependence of the proton conductivity of polymers **2** (circle, $x = 0.71$) (square, $x = 1.28$) and Nafion 112 (triangle).

In conclusion, we have synthesized a poly(arylene ether) containing sulfofluorenyl groups. The new polymer electrolyte with acid function at the end of bulky substituents affords a good film which endures severe hydrolytic and oxidative treatments. Better proton conducting properties than those of perfluorinated ionomer membrane were confirmed at 100% RH. These preliminary results have proved its potential availability as an electrolyte for high-temperature PEFCs.

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Supporting Information Available: Experimental details of proton conductivity measurement and the TG/DTA thermogram. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Appleby, A. J.; Foulkes, F. R. *Fuel Cell Handbook*; Van Nostrand Reinhold: New York, 1989. (b) Gottesfeld, S.; Zawodzinski, T. A. *Adv. Electrochem. Sci. Eng.* **1997**, *5*, 195. (c) Steele, B. C. H.; Heinzel, A. *Nature (London)* **2001**, *414*, 345. (d) Carratte, L.; Friedrich, K. A.; Stimming, U. *Fuel Cells* **2001**, *1*, 5.

(2) (a) Wasmus, S.; Kuver, A. *J. Electroanal. Chem.* **1999**, *461*, 14. (b) Hogarth, M. *Prospects of The Direct Methanol Fuel Cells*; CRC Press: Boca Raton, FL, 2003. (c) Aricò, A. S.; Srinivasan, S.; Antonucci, V. *Fuel Cells* **2001**, *1*, 133. (d) Schulz, T.; Zhou, S.; Sundmacher, K. *Chem. Eng. Technol.* **2001**, *24*, 12. (e) Nichols, R. J. *J. Sci. Ind. Res.* **2003**, *62*, 97.

(3) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.

(4) Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463.

(5) (a) Cabbaso, I.; Yuan, Y.; Mittelsteadt, C. US Patent 5989742, 1999. (b) Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J.; Zawodzinski, T. A.; McGrath, J. E. *Macromol. Symp.* **2001**, *175*, 387.

(6) (a) Jones, D. J.; Rozière, J. *J. Membr. Sci.* **2001**, *185*, 41. (b) Kobayashi, T.; Rikukawa, M.; Sanui, K.; Ogata, N. *Solid State Ionics* **1998**, *106*, 219.
(7) (a) Hruszka, P.; Jurga, J.; Brycki, B. *Polymer* **1992**, *33*, 248. (b) Miyatake, K.; Iyotani, H.; Yamamoto, K.; Tsuchida, E. *Macromolecules* **1996**, *29*, 6969. (c) Miyatake, K.; Shouji, E.; Yamamoto, K.; Tsuchida, E. *Macromolecules* **1997**, *30*, 2941.
(8) (a) Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer* **2001**, *42*, 359. (b) Zhang, Y.; Litt, M. H.; Savinell, R. F.; Wainright, J. S. *Polym. Prepr.* **2000**, *41*, 1561. (c) Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules* **2002**, *35*, 9022.
(9) (a) Wainright, J. S.; Wang, J.-T.; Weng, D.; Savinell, R. F.; Litt, M. *J. Electrochem. Soc.* **1995**, *142*, L121. (b) Xing, B.; Savadogo, O. *J. New Mater. Electrochem. Syst.* **1999**, *2*, 95.
(10) Miyatake, K.; Zhou, H.; Uchida, H.; Watanabe, M. *Chem. Commun.* **2003**, 368.
(11) (a) Miyatake, K.; Oyaizu, K.; Tsuchida, E.; Hay, A. S. *Macromolecules* **2001**, *34*, 2065. (b) Miyatake, K.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3211. (c) Miyatake, K.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3770.
(12) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 358.
(13) A similar example has been reported. See: Shaikh, A.-A.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 496.

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