Synthesis of Hyperbranched Aromatic Poly(ether sulfone) with Sulfonyl Chloride Terminal Groups

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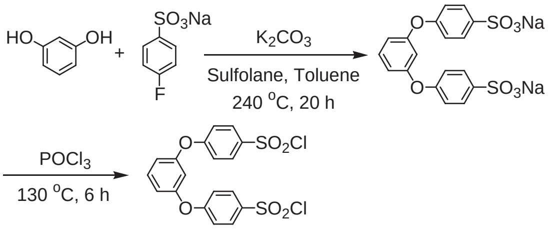
A new hyperbranched aromatic poly(ether sulfone) with sulfonyl chloride terminal groups was prepared by polycondensation of a new AB_2 monomer (**1**), 4,4′-(*m*-phenylenedioxy)-bis(benzenesulfonyl chloride). The polymerization was carried out in nitrobenzene at 120 °C for 3 h in the presence of a catalytic amount of $FeCl_3$, giving the polymer with number-average molecular weights up to 35,700. Furthermore, an ABA block copolymer was prepared from a linear polymer, poly(ether sulfone) with sulfonyl chlorides at both ends and AB_2 monomer **1**.

Recently, proton exchange membranes (PEMs) have attracted much attention due to their great promise for applications such as automotive, stationary, and portable power, where Nafion (DuPont) and sulfonated aromatic polymers such as, poly(ether sulfone)s, poly(ether ketone)s, polyimides, and poly(phenylene ether) containing sulfonic acids have been extensively studied.[1]

Hyperbranched polymers are new interesting materials with their unique properties, such as inherent globular structure, low viscosity, high solubility, and large number of terminal functional groups. There have been many reports on the synthesis and characterization of hyperbranched polymers, and various applications such as blend components, nanoforms, nonlinear optics, and catalysts.[2] Few papers, however, have been published on potential application of hyperbranched polymers to PEMs. Kakimoto et al. reported the synthesis of hyperbranched polymers with sulfonic acid derivatives,[3] where hyperbranched aromatic poly(ether sulfone) having sulfonic acid terminal groups was prepared by polycondensation of 2,6-bis(*p*-sodio sulfophenoxy)benzonitrile using a mixture of phosphorus pentoxide and methanesulfonic acid. The cyano group on phenyl ring, however, deactivates the reactivity of the monomer to electrophilic sulfonylation, and is converted to a carboxylic acid. Thus, more reactive, straightforward AB_2 monomer is required for the application of their hyperbranched polymers to PEMs.

This paper describes the synthesis of hyperbranched aromatic poly(ether sulfone) with sulfonyl chloride terminal groups by polycondensation of a new AB_2 monomer, 4,4′-(*m*-phenylenedioxy)bis(benzenesulfonyl chloride) (**1**) using a catalytic amount of $FeCl_3$. And its application to the synthesis of an ABA block copolymer is described here as well.

The synthetic route for monomer **1** is outlined in Scheme 1. Reaction of resorcinol with sodium *p*-fluorobenzenesulfonate in the presence of potassium carbonate produced 4,4′-(*m*-phenylenedioxy)bis(benzenesulfonicacid disodium salt), which was treated with phosphorus oxychloride to give monomer **1**.[4] The structure of **1** was assigned on the basis of elemental analysis as well as IR and NMR spectroscopy.[4]



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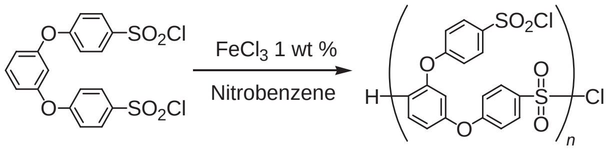
Scheme 1. Synthesis of AB_2 monomer **1**.



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Scheme 2. Synthesis of hyperbranched aromatic poly(ether sulfone) with sulfonyl chloride terminal groups **2**.

Table 1. Synthesis of hyperbranched polymer **2**

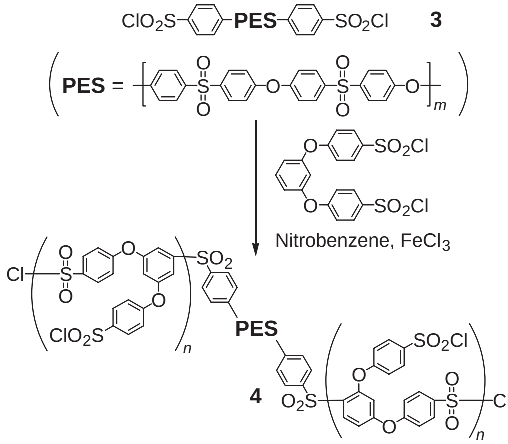
Run	Temperature /°C	Time /h	M_n[a]	M_w/M_n[a]	Yield /%	η_{inh}[b]
1	100	3	13000	1.5	78	0.082
2	110	3	22600	2.0	88	0.115
3	120	3	35700	3.7	85	0.229

[a]Determined by GPC eluted with DMF containing lithium bromide (0.01 mol/L) using polystylene standards. [b]Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

Polycondensation of **1** was carried out in nitrobenzene in the presence of 1 wt % of $FeCl_3$ to **1** (Scheme 2).[5]

The results are summarized in Table 1. The polymerization proceeded smoothly at 120 °C for 3 h, giving hyperbranched polymer **2** with number-average molecular weights up to 35,700, which were determined by GPC using polystyrene standards. These polymers showed typical low solution viscosities around 0.1–0.2 $dL\,g^{-1}$.

The structure of hyperbranched polymer **2** was confirmed by IR and NMR spectroscopy. The IR spectrum of **2** exhibited characteristic absorptions at 1184 and 1369 cm^{-1} due to the SO_2 stretching and at 1223 cm^{-1} due to the C–O–C stretching. All signals of polymer **2** in the ^1H NMR spectrum were well assigned to the corresponding structure of the repeating unit. Polymer **2** is obtained as a light yellow solid, which is soluble in nitrobenzene, tetrahydrofuran, and polar aprotic solvents while insoluble in methanol, ethyl acetate, and acetone. The thermal stability of polymer **2** was examined by thermo-



Scheme 3. Synthesis of ABA block copolymer **4**.

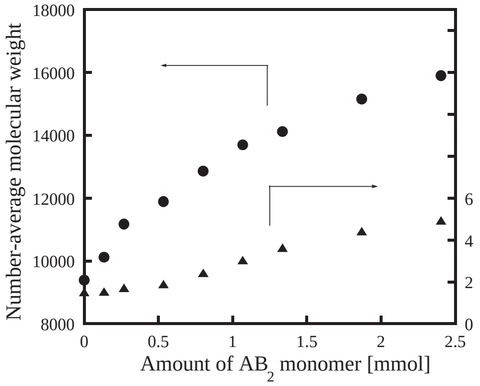


Figure 1. Relationship between the M_n of ABA block copolymers **4** and amount of monomer **1**, where 0.07 mmol of polymer **3** was used.

gravimetry. The 10% weight loss temperature was 320 °C under nitrogen.

The synthesis of a well-defined block copolymers with sulfonated and unsulfonated blocks is important to increase proton conductivity without massive increases in water swelling. Thus, monomer **1** was used for the synthesis of an ABA block copolymer (**4**) consisting of a linear polymer and a hyperbranched polymer (Scheme 3).

The linear polymer, poly(ether sulfone) (**3**) with a number-average molecular weight (M_n) of 9400 was prepared by polycondensation of 4,4′-oxybis(benzenesulfonyl chloride) with diphenyl ether in the presence of a catalytic amount of $FeCl_3$ in nitrobenzene at 110 °C for 4 h. Then, to this polymer solution, the solution of monomer **1** and 1 wt % of $FeCl_3$ in nitrobenzene was added dropwise slowly over 2 h at 110 °C, and stirred at this temperature for 1 h.

Figure 1 shows the relations between the M_n of resulting ABA block copolymers and the amount of monomer **1**, and the change of molecular weight distribution (M_w/M_n). The M_w/M_n changed from 1.5 to 4.9 with the addition of monomer **1**. And the M_n increased from the M_n of polymer **3** with increasing of amounts of monomer **1**, where the GPC curves kept unimodal features. These results indicate the formation of the desired ABA block polymers. ABA-block copolymers were soluble in nitrobenzene and aprotic solvents at room temperature, and the 10% of weight-loss temperatures were approximately 380 °C.

In summary, new monomer **1** was designed and synthesized. Hyperbranched polymer **2** with number-average molecular weights up to 35,700 was successfully prepared from monomer **1** in the presence of a catalytic amount of $FeCl_3$. Monomer **1** was also applied for the synthesis of ABA block copolymer **4**. Polymer **4** will be applied to PEMs by hydrolysis of its sulfonyl chlorides.

References and Notes

1 M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. McGrath, *Chem. Rev.* **2004**, *104*, 4587.

2 For recent reviews, see: a) S. M. Grayson, J. M. J. Frechet, *Chem. Rev.* **2001**, *101*, 3819. b) M. Jikei, M. A. Kakimoto, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 1293. c) C. Gao, *Prog. Polym. Sci.* **2004**, *29*, 183. d) B. Voit, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2679.

3 a) M. Takeuchi, M. Jikei, M. A. Kakimoto, *Chem. Lett.* **2003**, *32*, 242. b) M. Takeuchi, M. Jikei, M. A. Kakimoto, *High Perform. Polym.* **2003**, *15*, 219.

4 To a 100-mL round bottom flask equipped with a Dean stark apparatus and a reflux condenser was added sodium *P*-fluorobenzenesulfonate (2.9 g, 14 mmol), resorcinol (0.66 g, 6.0 mmol), potassium carbonate (2.5 g, 18 mmol), sulfolane (24 mL), and toluene (20 mL). The reaction mixture was heated to 150 °C for 2 h, then at 240 °C for 20 h, and poured into dichloromethane. The precipitate was dissolved in hydrochloric acid solution. The filtrate was adjusted to pH 10 by adding sodium hydroxide solution. To this solution was added NaCl to precipitate 4,4′-(*m*-phenylenedioxy)bis(benzenesulfonicacid disodium salt). It was recrystallized from ethanol and water. This salt was treated with $POCl_3$ (3 mL) at 130 °C for 6 h. The reaction mixture was poured in ice-water and extracted with dichloromethane. The product was purified using column chromatography (with 3:2 hexane:dichloromethane solvent mixture). Monomer **1** was a viscous liquid. Yield (1.58 g; 57%). IR (NaCl, ν); 1184, 1377 (–SO_2Cl), 1242 (Ar–O–Ar), 1477, 1577 cm^{-1} (Ph–H). ^1H NMR ($CDCl_3$, δ, ppm): 6.89 (s, 1H), 7.02 (d, 2H), 7.15 (d, 4H), 7.51 (t, 1H), 8.03 (d, 4H). Anal. ($C_{18}H_{12}Cl_2O_6S_2$): Calcd: C, 47.07%; H, 2.63%; Found: C, 47.06%; H, 2.79%.

5 A solution of **1** (0.30 g, 0.65 mmol), nitrobenzene (2 mL), and $FeCl_3$ (0.003 g, 0.018 mmol) was stirred at 110 °C for 3 h. The solution was cooled to room temperature, and poured into methanol containing a small amount of concd hydrochloric acid solution. The precipitate was washed with methanol, dried at 80 °C under vacuum. Yield (0.23 g, 88%). IR (KBr, ν); 1184, 1369 (–SO_2Cl), 1223 (Ar–O–Ar), 1473, 1577 cm^{-1} (Ph–H).

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