Synthesis of Hyperbranched Poly(phenylene sulfide) via a Poly(sulfonium cation) Precursor

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Introduction

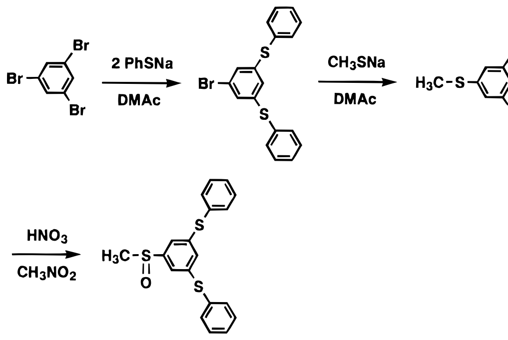
Poly(phenylene sulfide) (PPS) is an excellent engineering plastic which has good chemical and thermal properties (T_g 85 °C, T_m 280 °C). PPS is commercially produced by the polycondensation of *p*-dichlorobenzene and sodium sulfide at high temperatures and pressures. Recently, there have been several reports about new routes to synthesize PPS. Among them, Tsuchida et al. used poly(sulfonium cation) as a precursor to form a high molecular weight PPS under mild reaction conditions.[1,2]

Recently, highly branched molecules, such as dendrimers and hyperbranched polymers, have drawn the attention of various research groups because of their unique physical and chemical characteristics. Generally, these molecules are amorphous and are more soluble in organic solvents compared with their linear isomers. Both divergent[3−10] and convergent[11−13] methods have been developed for the stepwise synthesis of these types of dendrimers. These approaches produce well-defined nanostructures, which can be used as ideal model systems for the study of the relationship between physical properties and molecular size or architecture. We have previously reported the synthesis of polysiloxane dendrons and dendrimers[14,15] and poly(ether ketone) dendrons[16] by either divergent or convergent approaches; however, the syntheses of these well-characterized molecules require numerous steps and it is difficult to scale up the laboratory methods to make large quantities of product. On the other hand, the one-step synthesis of polyphenylenes,[17,18] polyethers,[19,20] polyamide,[21] polyesters,[22−24] polyurethane,[25] and polysilane[26] was investigated as a more convenient route to obtain hyperbranched molecules.

In this paper, we report the synthesis of hyperbranched PPS via a poly(sulfonium cation) starting from an AB_2 type monomer, methyl 3,5-bis(phenylthio)phenyl sulfoxide.

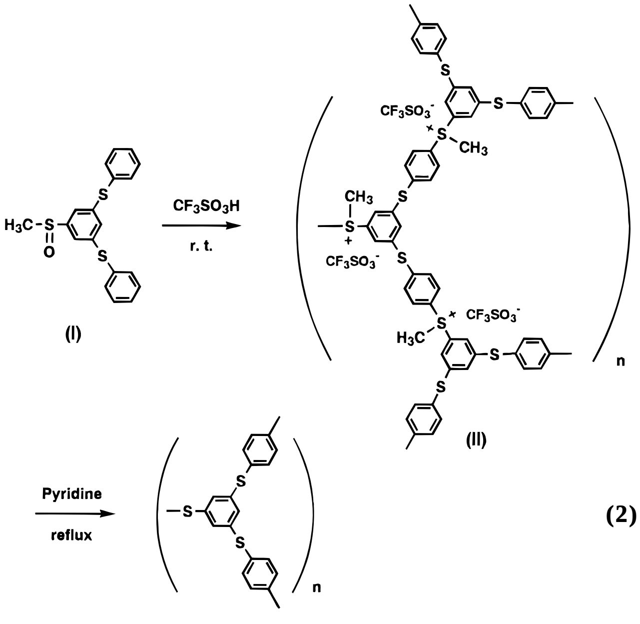
Results and Discussion

Methyl 3,5-bis(phenylthio)phenyl sulfoxide **(I)** was employed as a monomer and was synthesized from 1,3,5-tribromobenzene through nucleophilic substitution, as shown in eq 1. Sodium thiophenoxide (2 equiv) was reacted with 1,3,5-tribromobenzene in *N*,*N*-dimethylacetamide at 150 °C. The resultant 1-bromo-3,5-bis(phenylthio)benzene (yield: 36%) was consequently reacted with 5 equiv of sodium methanethiolate to form 1-(methylthio)-3,5-bis(phenylthio)benzene (yield: 60%), which was then oxidized with nitric acid to form the sulfoxide monomer **(I)** (yield: 60%).[27]



(I)

(1)



(I)

(II)

(III)

(2)

Self-polycondensation of **I** was carried out in CF_3SO_3H at 25 °C to form the poly(sulfonium cation) **(II)**.[28] Trifluoromethanesulfonic acid acts not only as the solvent but also as the reagent for protonation of the sulfoxide in the polymerization reaction. After precipitation in water, a red powder was isolated. The resulting poly(sulfonium cation) **(II)** was soluble in polar solvents such as sulfolane, nitromethane, and acetone, but insoluble in hexane. In the IR spectrum of the resulting polymer, new absorption peaks attributed to the trifluoromethanesulfonate anion appeared at 1273, 1260, 1157, 1030, and 639 cm^{-1}, while the absorption attributed to the sulfoxide group at 1059 cm^{-1} disappeared. In the ^{1}H NMR spectrum, there was a peak at 3.82 ppm which is attributed to a methyl group substituted at the sulfonium cation.[29] However, small peaks were also observed between 2.2 and 3.7 ppm. The broad peak from 2.6 to 2.2 ppm is attributed to thiomethyl groups, and the small peaks between 3.7 and 3.2 ppm are attributed to different methyl groups connected to the sulfonium cation because of its low magnetic field.

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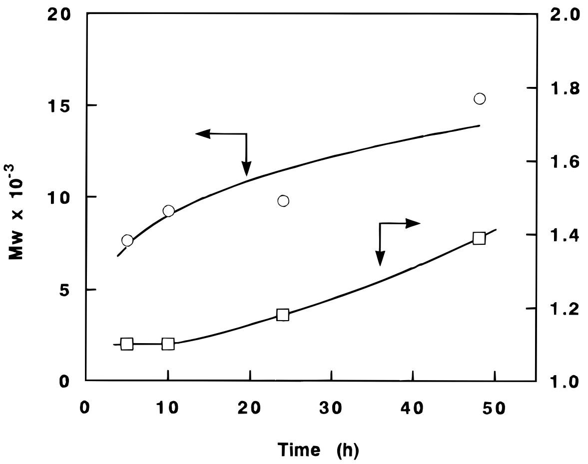

Figure 1. Time dependence of M_w (○) and M_w/M_n (□) of the hyperbranched PPS **(III)** on the reaction time of the self-polycondensation of **I**.

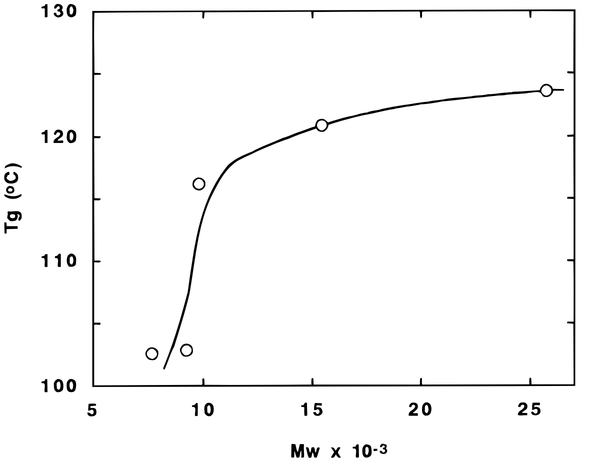

Figure 2. Glass transition temperature of the hyperbranched PPS **(III)** determined by DSC. The heating rate of the measurements was 10 °C min^{-1}.

From the integration ratio of the peaks, the percentages of the protons associated with the peaks at 3.82, 3.7−3.2, and 2.6−2.2 ppm were determined to be 64%, 21%, and 15%, respectively.

Poly(sulfonium cation) **(II)** was converted into the hyperbranched PPS **(III)** by refluxing in pyridine. A white powder was isolated after the demethylation reaction of **II**.[30] In the IR spectrum of the resulting polymer, the absorption peaks attributed to the trifluoromethanesulfonate anion disappeared, and in the ^{1}H NMR spectrum, the peaks at 3.82 and 3.7−3.2 ppm which were caused by the methyl groups attached to the sulfonium cation disappeared. These results indicate that demethylation of the methyl groups attached to the sulfonium cation in **II** proceeded efficiently to form the hyperbranched PPS **(III)**. However, small peaks at 2.5−1.9 ppm attributed to thiomethyl end groups remained in the ^{1}H NMR spectrum of the resulting polymer. The integration ratio of methyl protons to phenyl protons was larger than the expected value for the methyl group located at a focal point. This observation indicates that **III** contains other thiomethyl end groups.

With increasing reaction time for the formation of poly(sulfonium cation) **(II)**, the molecular weight of the resulting polymer **(III)**[31] also increased, as shown in Figure 1. Gelation was not observed in the reaction times considered (maximum 144 h). The highest M_w and its M_w/M_n of the resulting polymer were 25 700 and 1.45, respectively. The degree of polymerization for the polymer was about 80 based on the monomer unit **(I)**.

The hyperbranched PPS **(III)** is soluble in many organic solvents, such as chloroform and DMF at 25 °C, while the linear PPS is almost insoluble in any organic solvents. In addition, although linear PPS is crystalline, the hyperbranched PPS **(III)** was amorphous, similar to other hyperbranched polymers. The glass transition temperature, determined by DSC, is plotted against the M_w of **III** in Figure 2. T_g values increased from 102 to 124 °C in proportion to the molecular weight of **III**. All the T_g values were higher than that of linear PPS (85 °C). It is reported that T_g values of hyperbranched polymers are almost the same as those of linear polymers if their structures are the same.[32] In this case, we assume that some chain rotations are restricted by the hyperbranched structure in comparison with a linear PPS.

References and Notes

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(27) IR (neat, cm^{-1}): 3056, 2996, 1558, 1477, 1439, 1414, 1402, 1059, 955, 855, 793, 747, 691. ^{1}H-NMR ($CDCl_3$, δ_{ppm}): 7.55−7.20, 7.15−6.95 (m, 13H, phenyl), 2.65 (s, 3H, methyl). ^{13}C-

NMR ($CDCl_3$, δ_{ppm}): 147.79, 141.02, 133.38, 132.40, 130.40, 129.80, 128.77, 120.81, 43.94.

(28) Yield: 91%. IR (KBr, cm^{-1}): 3056, 2924, 1555, 1476, 1397, 1273, 1260, 1157, 1030, 820, 795, 750, 639. ^{1}H-NMR (CD_3NO_2, δ_{ppm}): 7.76, 7.35 (broad, phenyl), 3.82, 3.65, 3.36, 3.27, 2.6−2.2 (methyl). ^{13}C-NMR ($CDCl_3$, δ_{ppm}): 144.89, 137−129, 128.29, 126.14, 123.47, 120.93, 118.38, 29.70, 29.65, 29.35, 15.36. Anal. Calcd for $(C_{20}H_{14}F_3O_3S_4)_n$: C, 49.27; H, 2.89. Found: C, 53.21; H, 3.20.

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(30) Yield: 95%. IR (KBr, cm^{-1}): 3019, 2926, 1551, 1475, 1397, 1215, 851, 818, 756, 669. ^{1}H-NMR ($CDCl_3$, δ_{ppm}): 7.65, 7.57, 7.23, 6.95, 6.90, 6.58 (broad, phenyl), 2.46, 2.31, 2.17, 2.10, 1.94 (methyl). ^{13}C-NMR ($CDCl_3$, δ_{ppm}): 140.13, 139.56, 133.08, 132.79, 132.52, 129.53, 129.46, 128.38, 128.18, 15.58. Anal. Calcd for $(C_{18}H_{11}S_3)_n$: C, 66.84; H, 3.43. Found: C, 63.39; H, 3.64.

(31) Absolute molecular weight was calculated by GPC with a light scattering detector. The specific refractive increment of **III** was determined to be 0.339 mL g^{-1}.

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