Synthetic Route to Poly(sulfonyl-1,4-phenylenethio-1,4-phenylene) via a Poly(sulfonium cation)

Eishun Tsuchida,* Kimihisa Yamamoto,† and Eiichi Shouji

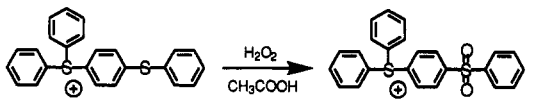
Department of Polymer Chemistry, Waseda University, Tokyo 169, Japan

Received July 27, 1993
Revised Manuscript Received October 25, 1993

Poly(arylene sulfone) (PAS) has received much attention as an amorphous aromatic polymer with a high glass transition temperature.[1] PASs possess excellent properties not only of good thermal resistance, chemical resistance, and high modulus but also of stable electrical properties, such as dielectric relaxation and dielectric loss, over a wide temperature range below T_g, as important characteristics. The amorphous aromatic polymers consist of alternating units of phenyl and functional groups, such as sulfone, ether, sulfide, or alkylidene. Poly(ether sulfone) (PES) and polysulfone (PSF) are well-known as commercially available materials. Poly(sulfonyl-1,4-phenylenethio-1,4-phenylene) (PSPT) has been synthesized by the nucleophilic substitution reaction of 4,4′-dichlorodiphenyl sulfone and sodium sulfide in a polar solvent such as *N*-methylpyrrolidone (NMP), which is a modified Phillip's method for the preparation of PPS at high temperature.[2] The high-temperature conditions cause solvent decomposition and salt contamination.

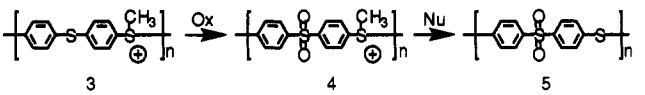
Recently, a new synthetic route to a high molecular weight PPS through the use of a soluble precursor was reported.[3] Poly[methyl-4-(phenylthio)phenylsulfonium trifluoromethanesulfonate], which is constructed of an alternating structure of a sulfide and a sulfonium, is employed as a souble intermediate because the sulfonium bond is easily converted to PPS through demethylation. On the basis of the alternating structure of the poly(sulfonium cation), oxidation of the poly(sulfonium cation) provides formation of a sulfone bond in every other unit of the chain which is protected by the sulfonium bond because the sulfide bond is preferentially oxidized to sulfone. Thus the poly(sulfonium cation) should be employed as an intermediate polymer for the synthesis of PSPT through oxidation. This paper presents a new synthetic route to PSPT by oxidation of the poly(sulfonium cation) under mild conditions.

Diphenyl-4-(phenylthio)phenylsulfonium cation (DPS) is oxidized to a diphenyl-4-phenylsulfonylsulfonium cation (DPSO) in high yield using hydrogen peroxide under acidic conditions.[4] This result indicates that oxidation of the sulfonium bond is suppressed, but the sulfide bond is selectively oxidized to sulfone.



1 2

Oxidation of poly[methyl-4-(phenylthio)phenylsulfonium trifluoromethanesulfonate][5] was done as follows. A three-necked, round-bottom flask (100 mL) with a Teflon-covered magnetic stirring bar, reflux condenser, and thermometer was charged with poly[methyl-4-(phenylthio)phenylsulfonium trifluoromethanesulfonate] (1.0 g, M_w = 21 000 (M_w/M_n = 3.1) as PPS[6]) as a poly(sulfonium cation) (3),trifluoroacetic acid (10 mL), chloroform (10 mL), and hydrogen peroxide 30% (0.9 g) at room temperature. The reaction mixture was stirred, and the temperature was raised to 60 °C. After stirring for 5 h, the mixture was poured into an aqueous sodium chloride (5%) solution (500 mL) and stirred for 2 h, for the demethylation of the sulfonium cation. The precipitate was filtered and washed with water and methanol. The polymer was isolated as a white powder (0.57 g, 87.3%).[7]



3 4 5

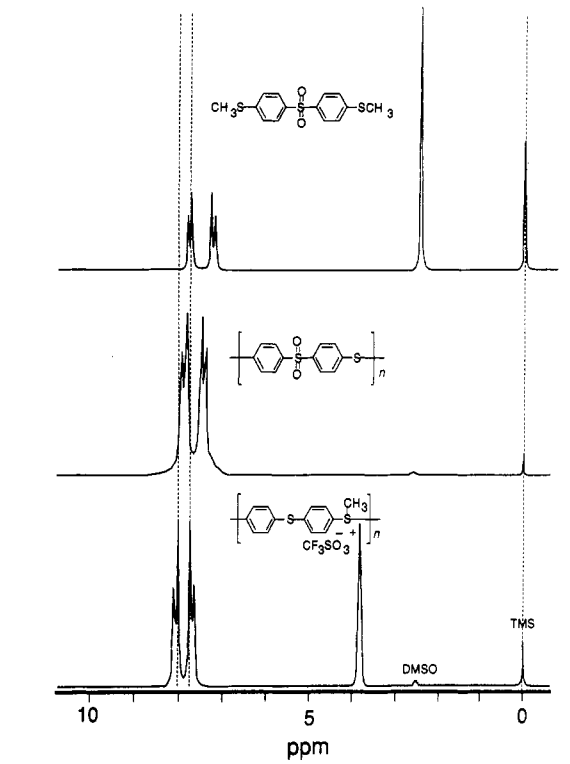


Figure 1. ^{1}H-NMR spectra of the resulting polymer (PSPT), poly(sulfonium cation), and 4,4′-bis(methylthio)diphenyl sulfone (DSO) as a model compound.

The ^{1}H-NMR spectrum of the resulting polymer shows the AB quartet peaks at 7.41, 7.52, 7.82, 7.93 ppm, whose pattern indicates the alternating structure of the resulting polymer (Figure 1). These peaks were observed in a higher field than that for the poly(sulfonium cation) (3; 7.7–8.1 ppm). 4,4′-Bis(methylthio)diphenyl sulfone (DSO) was employed as a model compound for comparison with the ^{1}H-NMR spectrum of the resulting polymer. DSO shows the AB quartet peaks (7.1–7.8 ppm) which are also observed in a higher field than that of poly(sulfonium cation). The result is based on the different electron acceptability between the sulfonium bond and the sulfone bond. The resulting polymer exhibited strong bands at 1157 and 1320 cm^{-1} attributed to the sulfone bond but has no band attributed to sulfoxide around 1050 cm^{-1}. The combination of ^{1}H-NMR spectra and IR spectra revealed the alternative structure of the sulfide and sulfone units (Figure 2).

The molecular weight of the obtained PSPT was determined to be M_w = 23 500 (M_w/M_n = 2.4) by means of GPC (eluent: NMP, 1 mL/min, 25 °C), which means

† PRESTO, JRDC Investigator 1992–1994 (Research Institute for Production Development).

0024-9297/93/2226-7389$04.00/0

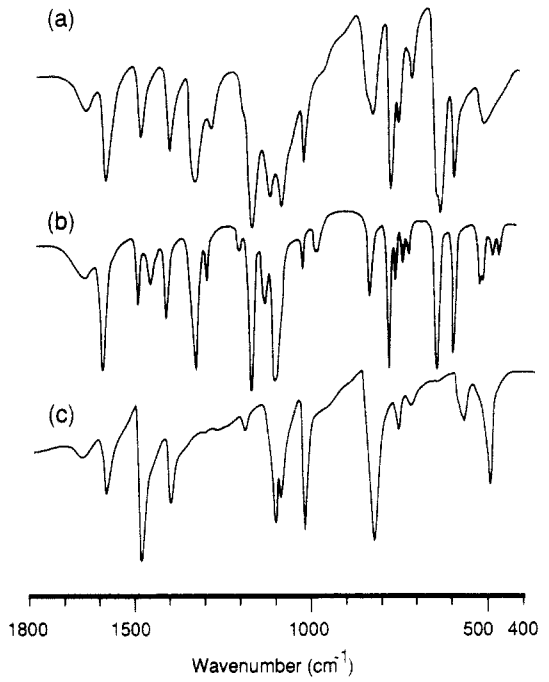


Figure 2. IR spectra of (a) the resulting polymer (PSPT), (b) 4,4′-bis(methylthio)diphenyl sulfone (DSO) as a model compound, and (c) PPS.

that poly(sulfonium cation) was converted to PSPT. The change in molecular weight is considered the result of oxidation from sulfide to sulfone and overpurification of PSPT through reprecipitation. DSC measurement showed the T_g at 215 °C, and TG measurement gave a T_d(10%) at 495 °C.[8] High molecular weight PSPT ($M_w = 1.9 \times 10^5$) is also obtained using a high molecular weight polycation under the same conditions. Poly(sulfonium cation) is available as a soluble precursor for the synthesis of not only PPS but also of PSPT.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Development Scientific Research No. 04555223 and Scientific Research No. 05650865 from the Ministry of Education, Science and Culture, Japan.

References and Notes

(1) (a) Jennings, B. E.; Jones, M. E. B.; Rose, J. B. *J. Polym. Sci., Part C* **1967**, *16*, 715. (b) Johnson, R. E.; Farnham, A. G.; Clendinning, R. A.; Half, W. F.; Merriam, C. N. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2375. (c) Cudby, M. E. A.; Feasey, R. G.; Gaskin, S.; Jones, M. E. B.; Rose, J. B. *J. Polym. Sci., Part C* **1969**, *22*, 747. (d) Newton, A. B.; Rose, J. B. *Polymer* **1972**, *13*, 465. (e) Rose, J. B. *Polymer* **1974**, *15*, 456. (f) Vogel, H. A. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2035. (g) Attwood, T. E.; Barr, D. A.; King, T.; Newton, A. B.; Rose, J. B. *Polymer* **1977**, *18*, 359. (h) Atwood, T. E.; King, T.; Mckenzie, I. D.; Rose, J. B. *Polymer* **1977**, *18*, 365. (i) Attwood, T. E.; King, T.; Leslie, V. J.; Rose, J. B. *Polymer* **1977**, *18*, 369. (j) Tamada, H.; Okita, S.; Kobayashi, K. *Polym. J.* **1993**, *25*, 339.

(2) Edmonds, J. T., Jr.; Hill, H. W., Jr. U.S. Patent 3354129, 1967; *Chem. Abstr.* **1968**, *68*, 13598. Campbell, R. W.; Edmonds, J. T., Jr. U.S. Patent 4038259, 1976; *Chem. Abstr.* **1977**, *87*, 854v. Hill, H. W., Jr. *Ind. Eng. Chem., Prod. Res. Dev.* **1979**, *18*, 252.

(3) Yamamoto, K.; Shouji, E.; Nishide, H.; Tsuchida, E. *J. Am. Chem. Soc.* **1993**, *115*, 5819.

(4) Uneyama, K.; Torii, S. *J. Org. Chem.* **1972**, *37*, 367.

(5) A 100-mL round-bottom flask with a Teflon-covered magnetic stirring bar was charged with methyl-4-(phenylthio)phenyl sulfoxide (3 g, 12 mmol). The flask was cooled to 0 °C. Trifluoromethanesulfonic acid (40 mL) was added at 0 °C, and the solution was stirred. The temperature increased slowly to room temperature in 30 min. The reaction was continued for 5 h at room temperature. Thereafter, the reaction was quenched by pouring the solution into ice water, washing the product with water, and drying under vacuum at room temperature for 20 h. Yield: 4.59 g (100%). IR (KBr, cm^{-1}) 3086, 3023, 2932 (ν_{CH}), 1570, 1478, 1423 (ν_{C-C}), 1258, 638 (ν_{CF}), 1160, 1067 (ν_{S-O}), 815 (ν_{CH}). ^{1}H-NMR is shown in Figure 1. ^{1}H-NMR (DMSO-d_6, 90 MHz): δ 7.75, 7.80, 8.01, 8.16 (phenyl, 8H, AB quartet); 3.82 (methyl, 3H). ^{13}C-NMR (DCOOD, 90 MHz): δ 125.4, 131.6, 133.8, 143.3 (phenyl C); 28.93 (methyl C). Anal. Calcd for $C_{14}H_{11}S_3F_3O_3$: C, 44.20; H, 2.91; S, 25.28. Found: C, 44.15; H, 2.85; S, 25.35.

(6) PPS was obtained by demethylation of poly(sulfonium cation) (3) as follows. The molecular weight was measured using high-temperature GPC (eluent: α-chloronaphthalene, 1 mL/min). A 200-mL three-necked, round-bottom flask equipped with a Teflon-covered magnetic stirring bar, reflux condenser, thermometer, and N_2 gas inlet was charged with poly[methyl-4-(phenylthio)phenylsulfonium trifluoromethanesulfonate] (1 g) and pyridine (10 mL). The reaction mixture was stirred at room temperature. The poly(sulfonium cation) is soluble in pyridine. The reaction mixture became slightly pale yellow. After a few minutes, the reaction mixture formed a white suspension. The reaction was continued for 1 h at room temperature, and then the temperature was slowly raised to reflux. The reaction was continued for 18 h at reflux temperature. Thereafter, the reaction was quenched by cooling the solution down to room temperature and then pouring it into methanol (10% HCl). The precipitate was washed with methanol. The polymer was purified by continuous extraction in a Soxhlet apparatus with ethanol for 2 h and was dried in vacuo at 60 °C for 20 h. The resulting polymer was isolated as a white powder. Yield: 0.54 g, 98%. IR (KBr, cm^{-1}): 3065, 1572, 1472, 1387, 1091, 1074, 1009, 810, 554, 481. CP/MAS ^{13}C-NMR (400 MHz): δ 132.1, 134.3 (phenyl C). Anal. Calcd for C_6H_4S: C, 66.63; H, 3.73; S, 29.64. Found: C, 66.72; H, 3.66; S, 29.58.

(7) IR (KBr, cm^{-1}): 3065, 1572, 1473, 1391, 1319, 1157, 1072, 1010, 821, 763, 621, 583. ^{1}H-NMR (DMSO-d_6, 90 MHz): δ 7.41, 7.52, 7.82, 7.93 (phenyl H, AB quartet). ^{13}C-NMR (DMSO-d_6, 90 MHz): δ 127.9, 131.0, 138.9, 140.2 (phenyl C). Anal. Calcd for $C_{12}H_8S_2O_2$: C, 58.0; H, 3.25; S, 25.8. Found: C, 58.3; H, 3.20; S, 26.0.

(8) DSC measurement was done using a Seiko SSC220/DSC120, and TG measurement was done using a Seiko SSC220/TG-DTA220.