452 *J. Org. Chem.* **1995**, *60*, 452–453

Synthesis of Poly(sulfonium cation) by Oxidative Polymerization of Aryl Alkyl Sulfides

Kimihisa Yamamoto,[†] Eiichi Shouji, Fumiaki Suzuki, Shintaro Kobayashi, and Eishun Tsuchida*

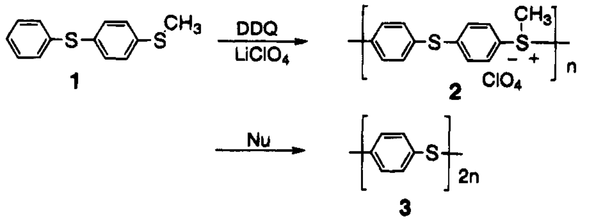
Department of Polymer Chemistry, Waseda University, Tokyo 169, Japan

Received February 9, 1994 (Revised Manuscript Received November 11, 1994)

Aryl alkyl sulfonium salts have been used as photoactive cationic initiators[1] and for the photogeneration of protonic acids in the lithographic resist field.[2] The polymeric sulfonium salts are also of considerable interest for other applications, for example, as alkylation agents[3] and in terms of their synthesis.

The poly(diaryl alkyl sulfonium cation) has been synthesized by the alkylation of poly(arylene sulfides) with alkyl halides in the presence of $AgBF_4$.[4] The efficiency and selectivity of the alkylation were not good because of the insolubility of poly(arylene sulfide), which restricts the formation of the poly(sulfonium cation). A unique application of this chemistry is in the formation of a soluble precursor for the high-performance poly(arylene sulfide) polymer. Recently, we reported[5] that poly(phenylene sulfide) (PPS) was synthesized by the oxidative polymerization of diphenyl disulfide via a cationic mechanism. In this paper, we report an efficient method that yields first the sulfonium compounds and then the poly(arylene sulfide) by the dealkylation of the poly(sulfonium cation) through oxidative polymerization.

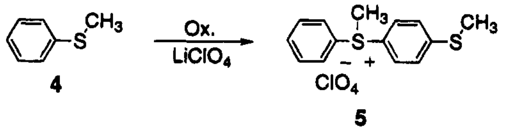
Methyl 4-(phenylthio)phenyl sulfide (**1**) was allowed to react with 2,3-dicyano-5,6-dichloro-4-benzoquinone as an oxidizing agent under acidic conditions at room temperature. During the reaction, 2,3-dichloro-5,6-dicyano-4-hydroquinone precipitated as a reduction product. After 20 h, the polymer **2** was isolated as a white powder with empirical formula $C_{13}H_{11}S_2ClO$ by precipitation from perchloric acid (eq 1).



(1)

The absorption band at 2932 cm^{-1} in the IR spectrum of the resulting polymer is attributed to the vibration of the C–H of the methyl group. The IR spectrum also shows absorption bands at 1120 and 625 cm^{-1} ascribed to the counterion, ClO_4^-. The combination of ^{13}C- and ^{1}H-NMR reveals the formation of poly[methyl[4-(phenylthio)phenyl]sulfonium perchlorate] **2**. The peak attributed to the methyl group of the cation is observed at lower field than that of the neutral compound in ^{1}H- and ^{13}C-NMR spectra, which means that the polymer possesses a positively charged sulfonium cation (electron acceptor). After demethylation in refluxing pyridine, PPS **3** was isolated as a white powder. The IR spectrum of the resulting polymer agreed with that of PPS prepared by a literature method. The molecular weight of the resulting PPS was found to be 9.5 × 10^{3} by means of high temperature GPC (eluent: 1-chloronaphthalene, 1 mL/min, 210 °C).

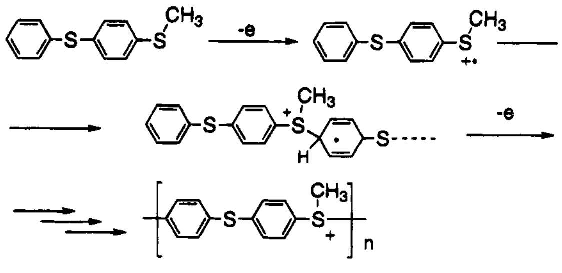
A control experiment for the electrooxidation of alkyl aryl sulfides was carried out in sulfolane in the presence of $LiClO_4$ as a model oxidative coupling reaction. Dimerized methyl [4-(methylthio)phenyl]phenylsulfonium cation **5** was obtained in 88% yield by electrolysis at the oxidation potential of methyl phenyl sulfide (**4**) (1.4 V vs Ag/AgCl, in CH_3CN) (eq 2).



(2)

The oxidation of methyl phenyl sulfide (**4**) through an electron-transfer reaction results in predominant formation of the aryl sulfonium bond. After the demethylation by the conditions described above, the dimerized methyl 4-(phenylthio)phenyl sulfide is produced quantitatively.

The electrooxidative polymerization of methyl 4-(phenylthio)phenyl sulfide also yields the poly(sulfonium cation). On the basis of coulometry, it is estimated that 2 F/mol are required for the polymerization in a stepwise oxidative coupling of methyl phenyl sulfide by an electron-transfer mechanism (eq 3).



(3)

Methyl phenyl sulfide shows two oxidation peaks, at 1.4 and 1.9 V, in the cyclic voltammogram. The first oxidation peak potential corresponds to the formation of the cation radical through electron-transfer. The coupled intermediate then undergoes reoxidation accompanied by proton elimination to yield the sulfonium cation. The number of electrons transferred was determined to be 2/monomer by comparison of the peak current of 9,10-diphenylanthracene, which is known to undergo a one-electron transfer process. The latter reaction is also applicable to the formation of poly[methyl(4-phenoxyphenyl)sulfonium perchlorate] (eq 4) through the oxidative coupling of methyl 4-phenoxyphenyl sulfide.

[†] PRESTO investigator, JRDC 1992–1994

(1) (a) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2697. (b) Lin, M. P.; Ikeda, T.; Endo, T. *J. Polym. Sci., Part A, Polym. Chem.* **1992**, *30*, 933. (c) Hamazu, F.; Akashi, S.; Koizumi, T.; Takada, T., Endo, *J. Polym. Sci., Part A, Polym. Chem.* **1993**, *31*, 1023. (d) Dektar, J. L.; Hacker, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 6004.

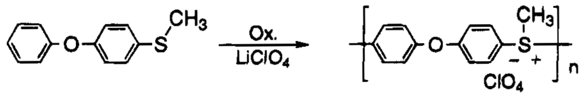
(2) (a) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977. (b) Crivello, J. V.; Lam, J. H. M. *Ibid.* **1980**, *18*, 2677. (c) Hacker, N. P.; Dektar, J. L. *Polym. Mater. Sci. Eng.* **1989**, *61*, 76. (d) Hacker, N. P.; Dektar, J. L.; Leff, D. V.; Macdonald, S. A.; Welsh, K. M. *J. Photopolym. Sci. Technol.* **1991**, *4*, 445.

(3) (a) Badet, B.; Julia, M.; Lefebvre, C. *Bull. Soc. Chim. Fr.* **1984**, 431. (b) Badet, B.; Julia, M.; Munoz, M. R. *Synthesis* **1980**, 926. (c) Wiegand, G. H.; McEwen, W. E. *J. Org. Chem.* **1968**, *33*, 2671.

(4) Beak, P.; Sullivan, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 4450.

(5) Tsuchida, E.; Yamamoto, K.; Jikei, M.; Nishide, H.; *Macromolecules* **1990**, *23*, 931.

0022-3263/95/1960-0452$09.00/0



(4)

Experimental Section

Oxidation of Methyl 4-(Phenylthio)phenyl Sulfide. A 100 mL round-bottom flask with a Teflon-covered magnetic stirring bar was charged with sulfolane (50 mL), methyl 4-(phenylthio)phenyl sulfide (5.80 g, 25 mmol), and trifluoroacetic acid (11.4 g, 0.1 mol). The reaction mixture was stirred for 20 h. During the reaction, 2,3-dichloro-5,6-dicyano-4-hydroquinone precipitated. After the reaction, the reaction mixture was poured into 500 mL of 60% aqueous $HClO_4$ and stirred for 1 h. The precipitate was filtered, washed with ethanol, and dried under vacuum for 20 h. The product was isolated as a white powder (7.85 g, yield 95%): IR (KBr, cm^{-1}) 3086, 3023, 2932, 1568, 1476, 1393, 1120, 1090, 814, 625, 552; ^{1}H-NMR (400 MHz, ppm, DMSO-d_6) 7.61, 7.70, 8.01, 8.10 (phenyl, 8H, AB quartet), 3.79 (s, methyl 3H); ^{13}C-NMR (400 MHz, ppm, HCOOH/$CDCl_3$) 124.6, 131.0, 133.5, 142.3 (phenyl C), 28.1 (methyl C). Anal. Calcd for $C_{13}H_{11}S_2ClO_4$: C, 47.20; H, 3.35; S, 19.38. Found: C, 47.11; H, 3.41; S, 19.45. DSC: mp 228 °C (degradation).

Demethylation of Poly[methyl[4-(phenylthio)phenyl]-sulfonium perchlorate]. 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)phenyl]sulfonium perchlorate](1 g, 3.0 mmol) and pyridine (10 mL). The reaction mixture was stirred for 1 h. (The poly(sulfonium cation) is soluble in pyridine.) Then the temperature was slowly raised to reflux. The reaction was continued for 20 h at reflux temperature. The precipitated polymer was washed with methanol. The polymer was further purified by continuous extraction in a Soxhlet apparatus with ethanol for 5 h and was dried in vacuo for 20 h. The resulting polymer was isolated as a white powder: yield 0.63 g, 96%; IR (KBr, cm^{-1}) 3065, 1574, 1472, 1387, 1094, 1075, 1009, 814, 556, 482; CP/MAS ^{13}C-NMR (100 MHz, ppm) 131.8, 134.4 (phenyl C). Anal. Calcd for C_6H_4S: C, 66.63; H, 3.73; S, 29.64. Found: C, 66.70; H, 3.77; S, 29.55. DSC: T_g, 84 °C; T_c, 125.3 °C; T_m, 280 °C. TGA: $T_{d_{10\%}}$, 520 °C.

Electrooxidation of Thioanisole. The electrolysis was carried out in a one-compartment cell with 1 cm spacing of working and auxiliary electrodes. The reference electrode was Ag/AgCl. Sulfolane (50 mL) containing methyl phenyl sulfide (3.1 g, 0.5 M), $LiClO_4$ (2.7 g, 0.5 M) as supporting electrolyte was kept at 20 °C under argon atmosphere. The electropolymerization was performed with stirring under controlled potential at 1.7 V(vs Ag/AgCl). After the reaction (coulomb = 2 F/mol), the reaction mixture was poured into 50 mL of 60% aqueous $HClO_4$. The aqueous layer was extracted with dichloromethane (2 × 50 mL). The organic layer was washed with water, dried over anhyd sodium sulfate, and filtered. The product was isolated by recrystallization from diethyl ether (3.8 g, yield 88%): IR (KBr, cm^{-1}) 3009, 2924, 1568, 1476, 1393, 1120, 976, 812, 743, 680, 625; ^{1}H-NMR (400 MHz, ppm, $CDCl_3$) 7.36, 7.58, 763, 7.79, 7.63 (phenyl, 9H, m), 2.46, 3.65 (methyl, 6H, s). Anal. Calcd for $C_{14}H_{15}S_2ClO_4$: C, 48.48; H, 4.36; S, 18.49. Found: C, 48.56; H, 4.45; S, 18.29.

Electrooxidative Polymerization of Methyl 4-(Phenylthio)phenyl Sulfide. Two platinum plates (2 × 5 cm) were set in the electrochemical cell. The reference electrode was Ag/AgCl. Sulfolane (50 mL) containing methyl 4-(phenylthio)phenyl sulfide (5.8 g, 0.5 M), and $LiClO_4$(2.7 g, 0.5 M) as supporting electrolyte, was kept at 20 °C under an argon atmosphere. The preparative electrolysis was carried out at a controlled potential using Nikko Keisoku NPGS-301 potentiogalvanostat. The charge passed was measured by a digital coulometer (Nikko Keisoku NDCM-1). The electropolymerization was performed with stirring under controlled potential at 1.7 V (vs Ag/AgCl). The solution turned from colorless to dark brown. After the reaction (coulomb = 2 F/mol), the reaction mixture was poured into 100 mL of 60% aqueous $HClO_4$. The precipitated polymer was filtered, washed with water, and dried under vacuum (8.1 g, yield 98%): IR (KBr, cm^{-1}) 3086, 3023, 2932, 1568, 1476, 1393, 1120, 1090, 814, 625, 522; ^{1}H-NMR (400 MHz, ppm, DMSO-d_6) 7.61 7.70, 8.01, 8.10 (phenyl, 8H, AB quartet), 3.80 (s, methyl 3H). Anal. Calcd for $C_{13}H_{11}S_2ClO_4$: C, 47.20; H, 3.35; S, 19.38. Found: C, 47.14; H, 3.30; S, 19.49.

Electrooxidative Polymerization of Methyl 4-Phenoxyphenyl Sulfide. Two platinum plates (2 × 5 cm) were set in the electrochemical cell with 1 cm spacing and used as the working and auxiliary electrodes. The reference electrode was Ag/AgCl. Sulfolane (50 mL), containing methyl 4-phenoxyphenyl sulfide (5.4 g, 0.5 M), and $LiClO_4$(2.7 g, 0.5 M) as supporting electrolyte, was kept at 20 °C under argon atmosphere. The preparative electrolysis was carried out at a controlled potential with a Nikko Keisoku NPGS-301 potentiogalvanostat. The charge passed was measured by a digital coulometer (Nikko Keisoku NDCM-1). The electropolymerization was performed with stirring under controlled potential at 1.7 V (vs Ag/AgCl). The solution turned from colorless to dark brown. After the reaction (coulomb = 2 F/mol), the reaction mixture was poured into 100 mL of 60% aqueous $HClO_4$. The precipitated polymer was filtered, washed by water, and dried under vacuum (7.5 g, yield 96%): IR (KBr, cm^{-1}) 3011, 2926, 1576, 1485, 1248, 1143, 1121, 1086, 833, 623; ^{1}H-NMR (400 MHz, ppm, DMSO-d_6) 7.41, 7.52, 8.11, 8.22 (phenyl, 8H, AB quartet), 3.84 (methyl, 3H, s); ^{13}C-NMR (400 MHz, ppm, HCOOH/$CDCl_3$) 120.3,121.4, 132.1, 160.1 (phenyl C), 28.5 (methyl C). Anal. Calcd for $C_{13}H_{11}SO_5Cl$: C, 49.61; H, 3.52; S, 10.19. Found: C, 49.65; H, 3.51; S, 10.32. DSC: mp 234.7 °C (degradation).

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (Nos. 0455523, 05650865, and 0622 6279) from the Ministry of Education Science and Culture.

JO940219U