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Aryl Sulfide Bond Formation Using the Sulfoxide–Acid System for Synthesis of PPS via Poly(sulfonium cation) as a Precursor

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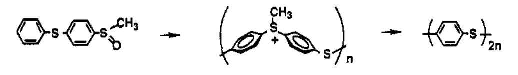
Aryl sulfide bonds have been constructed through a nucleophilic substitution reaction of arylhalides with sodium alkanethiolate accompanied by salt elimination or by the thermolysis of aryl disulfides in the presence of aryl iodides at high temperature.[1–3] Poly(*p*-phenylene sulfide) (PPS), is synthesized by polycondensation of sodium sulfide with *p*-dichlorobenzene in a polar solvent at high temperature and high pressure.[4] The original synthesis of PPS developed by Edmonds and Hill,[4] which was commercialized, gave low molecular weight polymer due to depolymerization by nucleophilic attack of sodium sulfide on the sulfide chain. The polymer subsequently had to be cured in order to develop useful properties even if crosslinking occurs. Until now many workers have consumed much effort to improve the synthesis so that high molecular weight PPS (*ca.* 10^5) can be produced directly.[5] Freidel–Crafts reaction of sulfur and aromatic compounds has been used in attempts to prepare symmetric aryl sulfides with electron-donating substituents, but the electrophilic reaction proceeds along with many side reactions.[6,7]

Recently much effort has been exerted in the development of new synthetic routes to PPS.[8–11] PPS possesses high crystallinity, poor solvent solubility, good thermal stability, chemical resistance, and, when doped, electrical conductivity.[12] These structural properties make PPS a high-performance engineering plastic but also make it difficult to synthesize and characterize.

It is well-known that the insoluble conductive polymers such as polyphenylene and poly(phenylene vinylene) are synthesized by precursor method. On the basis of the electronic structure of the sulfur atom, the poly(phenylsulfonium cation) should be employed as a precursor. We communicate a preliminary successful attempt to synthesize PPS via soluble poly(methyl-(4-phenylthio)phenylsulfonium cation) intermediate (eq 1). The process involves the self-condensation of methyl(*p*-thiophenoxy)phenyl sulfoxide in acid by an electrophilic substitution reaction at room temperature.



(1)

Methyl(*p*-thiophenoxy)phenyl sulfoxide (0.932 g)[13] was polymerized in trifluoromethanesulfonic acid (5 mL) at room temperature for 24 h to produce the polymer quantitatively. The mixture was poured into water to precipitate the polymer as a trifluoromethanesulfonate salt. The resulting polymer (1.425 g) was isolated as a white powder having the empirical formula $C_{13}H_{11}S_2CF_3SO_3$[14] and was soluble in sulfolane, nitrobenzene, dimethyl sulfoxide, pyridine, and formic acid. The methyl group in the resulting polymer was confirmed by the IR spectrum. The IR spectrum of the polymer also shows a strong absorption at 1258, 638 ($\nu_{\mathrm{C-F}}$) and 1161, 1067 cm^{-1} ($\nu_{\mathrm{S=O}}$), which means that the polymer contains trifluoromethanesulfonate as a counteranion. In the 500-MHz COSY ^{1}H–^{13}C NMR spectrum (Figure 1a), methyl groups are observed at 3.78 and 28.93 ppm, respectively, whose shifts are located in a lower field than that of a neutral thiomethyl group. These results support the formation of poly(methy(4-phenylthio)phenylsulfonium cation).

The main structure including the 1,4-phenylene unit was confirmed by the combination of IR and NMR spectra. The absorption attributed to 1,4-phenylene at 816 cm^{-1} indicates a linear polymer structure. Analyses of the polymer by ^{1}H and ^{13}C NMR reveal the presence of AB quartet peaks attributed to phenyl protons and only four peaks[14] attributed to phenyl carbon (Figure 1a).

Formation of the sulfonium cation was also demonstrated by the control experiment in which methyl(4-phenylthio)phenylsulfonium cation was isolated quantitatively as a stable salt by the reaction of methylphenyl sulfoxide with thioanisole in acidic environments (eqs 2 and 3).[15] The sulfonium cation was identified by 2D ^{1}H–^{1}H NMR and 2D ^{1}H–^{13}C NMR (Figure 1b).[16] The demethylation proceeds quantitatively in pyridine (eq 4). The predominant unsymmetric aryl sulfide formation using the sulfoxide–acid system through an electrophilic substitution reaction is confirmed in the reaction with diphenyl ether, diphenyl sulfide, and naphthalene. Computational calculation of the methyldiphenylsulfonium cation by the PM3[17] method indicates

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† PRESTO, JRDC Investigator, 1992–1994.

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[13] Methyl(*p*-thiophenoxy)phenyl sulfide is synthesized by the reaction of methylphenylsulfoxide with thioanisole in a 98% yield in methanesulfonic acid. The corresponding sulfoxide is prepared by the oxidation of the thioanisole with nitric acid (20%) in nitromethane. The monomer is purified to 99.9% purity by recrystallization in ether. Methyl(*p*-thiophenoxy)phenyl sulfoxide: MS (*m/e*) 248, 232, 217, 184, 108; ^{13}C NMR (CDCl$_3$, 500 MHz) δ 124.5, 128.5, 129.7, 133.0, 133.5, 141.5, 144.3 (phenyl C), 46.0 (methyl C); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.30–7.57 (phenyl, 9H, m), 2.67 (methyl, 3H); IR (KBr, cm^{-1}) 3061, 2919 ($\nu_{\mathrm{C-H}}$), 1576, 1476, 1439 ($\nu_{\mathrm{C=C}}$), 1051 ($\nu_{\mathrm{S=O}}$), 816 ($\delta_{\mathrm{C-H}}$), 750, 639. Anal. Calcd for $C_{13}H_{12}S_2O$: C, 62.87; H, 4.87; S, 25.82. Found: C, 62.89; H, 3.91; S, 25.72.

[14] Spectroscopic data: IR (KBr, cm^{-1}) 3086, 3023, 2932 ($\nu_{\mathrm{C-H}}$), 1570, 1478, 1422 ($\nu_{\mathrm{C=C}}$), 1258, 638 ($\nu_{\mathrm{C-F}}$), 1161, 1067 ($\nu_{\mathrm{S=O}}$), 816 ($\delta_{\mathrm{C-H}}$); ^{1}H NMR (DCOOD, 500 MHz) δ 7.76, 7.77, 7.96, 7.98 (phenyl, 8H, AB quartet), 3.78 (methyl, 3H); ^{13}C NMR (DCOOD, 500 MHz) δ 125.43, 131.59, 133.76, 143.23 (phenyl C), 28.93 (methyl C). Anal. Calcd for $(C_{14}H_{11}S_3F_3O_3)_n$: C, 44.18; H, 2.92; S, 25.30; F, 15.00. Found: C, 44.10; H, 2.73; S, 25.11; F, 14.9.

[15] A typical procedure is as follows. Methylphenyl sulfoxide (14.0 g) was dissolved in thioanisole (12.4 g). The mixture was added to methanesulfonic acid (57.6 g) in a closed vessel maintained at 20 °C under a dry argon atmosphere for 10 h. After the reaction, the mixture was poured into perchloric acid (70 wt %) to isolate the cation as a stable perchlorate salt. 34.5 g of the cation was yielded. Methyl(4-phenylthio)phenylsulfonium perchlorate: ^{13}C NMR (CDCl$_3$, 500 MHz) δ 119.7, 126.4, 127.2, 129.5, 130.2, 131.4, 134.6, 148.9 (phenyl C), 14.6, 28.4 (methyl C); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.36, 7.58, 7.63, 7.79, 7.63 (phenyl, 9H, m), 2.45, 3.65 (methyl, 6H); IR (KBr, cm^{-1}) 3003, 2920 ($\nu_{\mathrm{C-H}}$), 1088 ($\nu_{\mathrm{C-Cl}}$), 816 ($\delta_{\mathrm{C-H}}$). Anal. Calcd for $C_{14}H_{15}S_2ClO_4$: C, 48.48; H, 4.36; S, 18.49; Cl, 10.22. Found: C, 48.32; H, 4.40; S, 13.34; Cl, 10.01.

[16] Before the calculation the structure was optimized. LUMO energy (eV): trityl cation, –6.30.

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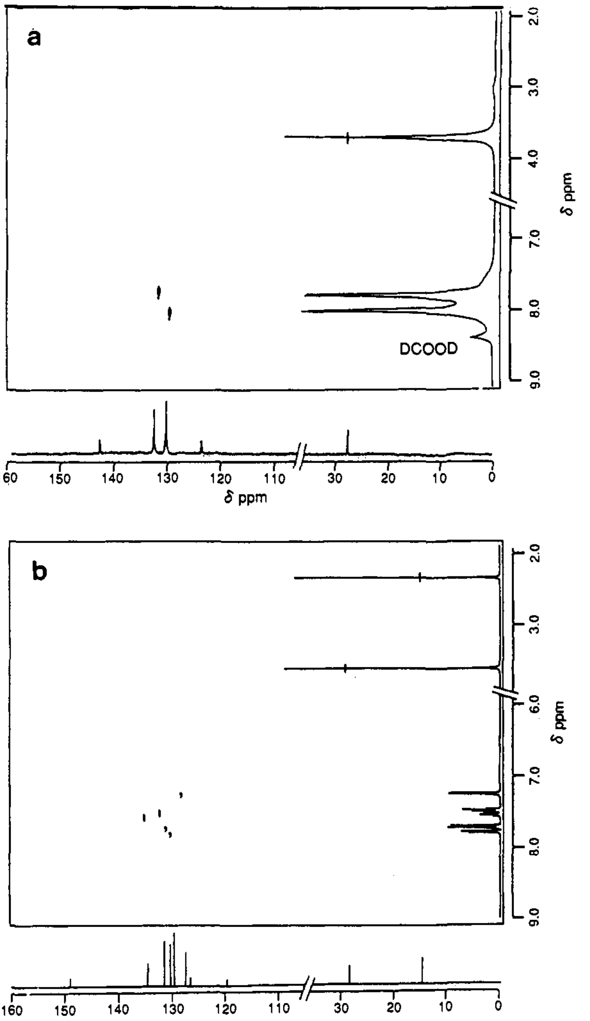
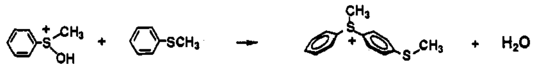


Figure 1. Two-dimensional ^{1}H–^{13}C NMR spectrum of the presursor polymer (a) and methyl(4-phenylthio)phenylsulfonium cation (b).

(2)



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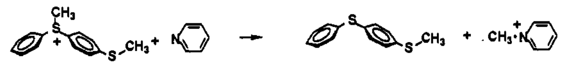

(4)

that the cation possesses a higher LUMO energy level than that of trityl cation (LUMO = –6.30 eV). This also suggests that the cation exists more stably than the trityl cation and can be isolated as a salt.

The polymerization is influenced by the acidity of the mixture. Methyl(p-thiophenoxy)phenyl sulfoxide was polymerized to yield the polysulfonium cation in the presence of phosphorus pentoxide. The polymerization was accelerated by dehydration using phosphorus pentoxide. The sulfoxide bond is polarized as $S^{+}O^{-}$ due to the presence of the d empty orbital. Attack on the negatively charged oxygen atom is facilitated by electrophiles. The activated sulfoxide is well-known for use as an electrophile (Swern method).[18] The polymerization of the sulfoxide compound is initiated via the sulfonium cation as an active species by the protonation on the oxygen of the sulfoxide bond (eq 2). The active species electrophilically substitutes on the benzene ring to eliminate water.

The demethylation of poly(methyl(4-phenylthio)phenylsulfonium cation) was carried out in pyridine by refluxing for 5 h. The precursor polymer (1.425 g) is completely soluble in the mixture at room temperature before the reaction. The white insoluble powder (0.81 g) precipitated during time passage. N-Methylpyridinium trifluoromethanesulfonate salt was isolated quantitatively in the reaction mixture. The resulting polymer[19] has the empirical formula of C_6H_4S and shows the same IR spectrum and CP/MAS ^{13}C NMR spectra of commercially available PPS Ryton V-1 (virgin polymer produced by the Phillips method). No absorption bands of methyl, sulfone, and sulfoxide bonds are detected in the IR spectrum. The two-center energy calculated by the PM3 method indicates that the $H_3C–S^{+}<$ bond (–14.8 eV) is the most cleavable one in the diphenylmethylsulfonium cation ($Ph–S^{+}$, 15.9 eV).[20]

The resulting polymer is dominated by the 1,4-phenylene structure with a strong IR absorption band at 810 cm^{-1}, which is characteristic of the C–H out-of-plane bending. The weight-average molecular weight is determined to be over $M_w = 2 \times 10^5$ by high-temperature GPC[21] in α-chloronaphthalene as an eluent.

The polymerization not only enables PPS formation but also efficient synthesis of poly(arylene sulfide) with high crystallinity. The precursor method also efficiently provides poly(oxyphenylene sulfide)[22] with $M_w = 4 \times 10^4$.

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[19] Spectroscopic data MS (m/e) 756, 648, 540, 434, 326, 218, 110; IR (KBr, cm^{-1}) 3065 (ν_{C-H}), 1572, 1472, 1387 ($\nu_{C=C}$), 810 (δ_{C-H}), 1091, 1074, 1009, 554, 482; CP-MAS ^{13}C NMR δ 132.1, 134.3 (phenyl C). Anal. Calcd for C_6H_4S: C, 66.63; H, 3.73; S, 29.65. Found: C, 66.80; H, 3.63; S, 29.61. Glass transition temperature (T_g) is 96 °C $T_m = 260$ °C. $M_w = 2.4 \times 10^5$ The M_w of the Ryton V-1 is determined to be 1.8×10^4.

[20] The bond strength can be estimated by the two-center energy (eV).

[21] The molecular weight of polymer was measured using high-temperature GPC (Senshu Scientific Co. Ltd., SSC VHT-7000) with 1-chloronaphthalene as an eluent. Shoudex GPC columns (AT-80M/s) were used for the analysis. The operating temperature was 210 °C with a flow rate of 1.0 mL/min of 1-chloronaphthalene. The detector was a UV–vis spectrophotometer (Senshu Scientific Co. Ltd., S-3750, 354 nm). A well-defined polystyrene-substituted pyrene group was used as a standard sample.

[22] Poly(thio-1,4-phenyleneoxy-1,4-phenylene): MS (m/e); CP-MAS ^{13}C NMR (400 MHz) δ 121.4, 129.6, 131.7, 156.8 (phenyl C); ^{1}H NMR ($(CD_3)_2SO$, 140 °C) δ 7.0, 7.3 (phenyl); IR (KBr, cm^{-1}) 3032 (ν_{C-H}), 1580, 1481 ($\nu_{C=C}$), 1236, 1082 (ν_{C-O-C}), 826 (δ_{C-H}). Anal. Calcd for $C_{12}H_8SO$: C, 71.97; H, 4.03; S, 16.01. Found: C, 70.06; H, 3.98; S, 16.0. $T_g = 86$ °C. $T_m = 185$ °C.