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Synthesis of Poly(arylene sulfide) via Poly(sulfonium cation) through Electrophilic Substitution Reaction of Methyl Phenyl Sulfide with Antimony Pentachloride

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Poly(phenylene ether sulfide)(PPES) was synthesized via poly(sulfonium cation) by electrophilic substitution of the chloro methyl phenyl sulfonium cation as an active species. Methylphenyl sulfide derivatives were chlorinated by electrophilic attack of antimony pentachloride to yield chloro methyl phenyl sulfonium antimony hexachloride. The electrophilic substitution of the cation with the phenyl ring of monomer or oligomer resulted in formation of poly(methyl-4-phenoxyphenyl sulfonium antimony hexachloride) with a by-product of hydrochloric acid. By demethylation of the resulting poly (sulfonium cation), PPES was obtained under mild conditions (Mw = 24000, Tm = 177 °C).

Poly(arylene sulfide)(PAS) deserves much attention as a high performance, excellent engineering plastic that has advantageous chemical, thermal and physical properties.[1,2] Commercially available PAS is synthesized by a nucleophilic aromatic substitution reaction with arylharide and sodium sulfide at high temperature and pressure.[3,4] So many PASs are insoluble in many common solvents at r.t., and the poor solvent soublility makes it difficult to obtain high molecular PAS at r.t..

Sulfur exists in a tetravalent state as a sulfonium cation with a positive charge. The positive charge plays an important role in the solubility. Recently, we have reported a new synthetic route to high molecular weight poly(phenylene sulfide)(PPS) via poly(sulfonium cation) as a soluble precursor.[5] Using the poly(sulfonium cation), synthetic difficulties such as solvent solubility can be overcame to synthesize PAS under mild conditions. Alkyl aryl chloro sulfonium cation was prepared using antimony pentachloride and can act as an electrophile in a substitution reaction with an aromatic compound.[6] In this paper, we report that methyl-4-(phenylthio)phenyl sulfide reacts with antimony pentachloride and is polymerized to poly(phenylene ether sulfide)(PPES) via a poly(sulfonium cation) through the electrophilic reaction of chloro methyl phenyl sulfonium cation. The control experiment for the formation of sulfonium compounds was carried out using thioanisole(1) (12.4 g,0.1 mol). Under lower temperature at -60 °C and in the presence of antimony pentachloride, chloro methyl phenyl sulfonium antimony hexachloride(2) was formed accompanied by antimony trichloride as a by-product of this reaction. Increasing the reaction temperature, the electrophilic couplingreaction of chloro methyl phenyl sulfonium cation with thioanisole was accompanied by an equimolar amount of hydrogen chloride. Methyl-4-(methylthio)phenyl phenyl sulfonium antimony hexachloride (3)(27.4

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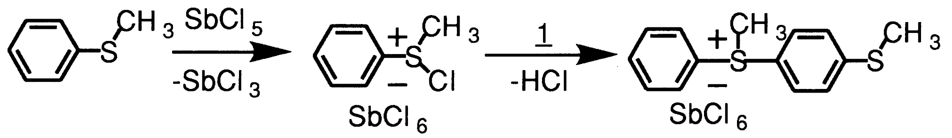

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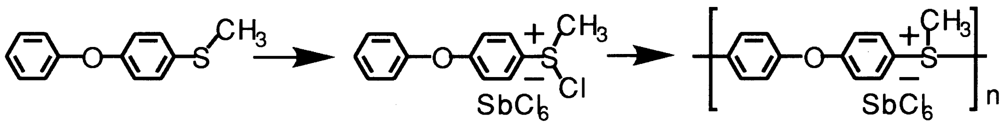
g, yield 94%) was isolated as a stable salt having the empirical formula, $C_{14}H_{15}S_2SbCl_6$. The ^{1}H-NMR showed two peaks at 3.58 and 2.52 ppm attributed to methyl groups and 7.5 - 7.9 ppm attributed to phenyl protons. The former peak(3.58 ppm) is assigned to methyl protons binding the sulfonium cation because the peak was observed at a lower field than that of the neutral methyl group due to the positive charge. NMR and IR spectra revealed the formation of the cation. Formation of ortho substituted dimer was not confirmed by means of the ^{1}H-NMR whose spectrum is clearly assigned to the para substituted one.

The polymerization of methyl-4-(phenoxy)phenyl sulfide was carried out in dichloromethane in the presence of antimony pentachloride.



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A 100 mL round-bottom flask with a Teflon-covered magnetic stirring bar was charged with methyl-4-(phenoxy) phenyl sulfide (2.0 g, 9.25 mmol) and dichloromethane (10 mL). The flask was cooled to -60 ^{o}C. Antimony pentachloride (5.55 g, 18.5 mmol) with dichloromethane (10 mL) was added for a 10 min period and the solution was stirred for 1 h. The temperature increased slowly to room temperature in 1 h. The reaction solution changed from dark orange (-60 ^{o}C) to dark green (r.t.) and the evolution of hydrogen chloride was observed. The reaction was continued for 20 h at room temperature. After that the reaction was quenched by pouring the solution into ethanol, and the poly(sulfonium cation) was quantitatively isolated as a pale yellow resin having the empirical formula, $C_{14}H_{11}OSSbCl_6$ (4.9 g, 96%). The ^{1}H-NMR also shows that the integral ratio of methyl protons to aryl protons is 3(s, 3.80 ppm) : 8 (AB quartet, 7.4, 7.47, 8.14, 8.21 ppm)(Fig.1). The ^{1}H-NMR spectrum shows that the polycation constructed alternative para linked structure of sulfide and sulfonium cation because a formation of ortho-linkage disturb the symmetrical split of AB quartet. The typical absorption band attributed to the C-H out-of-plane vibration of the 1, 4-phenylene structure was observed at 833 cm^{-1}. The IR spectrum showed that the resulting polymer contained a methyl group (2926 cm^{-1}). $SbCl_6^-$ has no band in the region between 4000 and 400 cm^{-1}. These spectroscopic data revealed the formation of poly(methyl-4-(phenoxy)phenyl sulfonium antimony hexachloride).$^{7)}$

To convert to PPES(7) from the poly(sulfonium cation)(6), the demethylation was carried out using pyridine as a nucleophile. Poly(sulfonium cation) (6) was dissolved in pyridine as nucleophile(Nu) with refluxing at 110 ^{o}C for 10 h. The reaction was quenched by cooling the solution down to room temperature and then pouring it into 10% HCl methanol. The precipitate was washed with methanol and with refluxing methanol for 2 h.

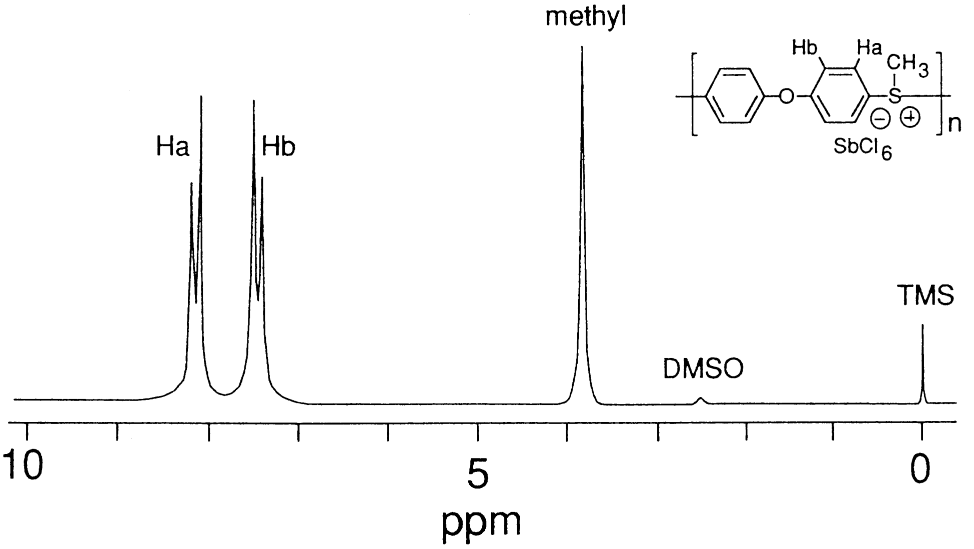


Fig.1. ^{1}H-NMR spectrum of poly(methyl-4-(phenoxy)phenyl sulfonium antimony hexsachloride), in DMSO (25 °C).

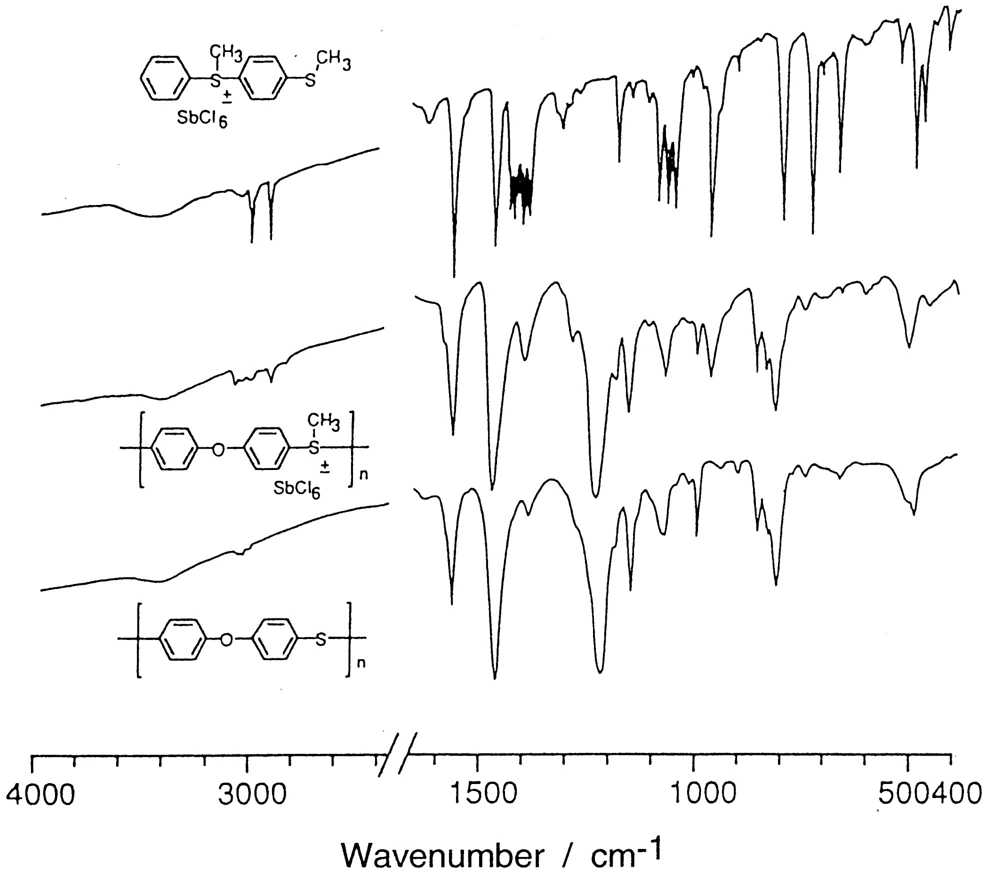
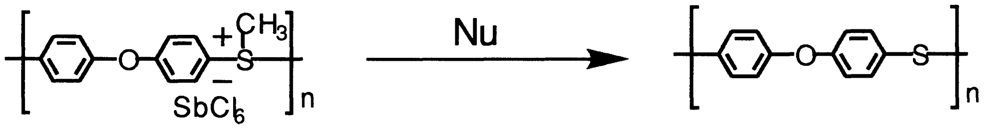


Fig.2. IR spectrum of PPES, poly(sulfonium antimonate) and methyl-4-(methylthio)phenyl phenyl sulfonium antimony hexachloride.



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The absorption attributed to the methyl group disappeared in the polymer. The resulting polymer also showed a band attributed to the C-H out-of-plane vibration of the 1,4-phenylene structure at 827 cm^{-1} and to an ether bond at 1240, 1087 cm^{-1}.8) The molecular weight of the polymer was determined to be Mw: 2.4 x 10^{4} by high temperature GPC. DSC measurement show PPES have Tg= 83 ^{o}C, Tc= 136 ^{o}C, Tm= 177 ^{o}C. PPES is crystalline polymer like PPS. Termogravimetry analysis show PPES has $Td_{10\%}$ = 515 ^{o}C and this value suggest that PPES is stable polymer under high temperature. PPES insoluble in any common solvent under r.t., but swelling in hot chloroform and soluble in hot DMSO. These character show PPES have thermo-stable character and chemical resistance properties at r.t. This polymerization provides a high molecular weight poly(arylene sulfide) at room temperature.

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7) IR (KBr, cm^{-1}) 3011, 2926, 1576, 1485, 1248, 1082, 833; ^{1}H-NMR is showed in Fig.1. ^{13}C-NMR(CDCl3 / HCOOH, 90MHz, ppm) δ 120.8, 121.5, 132.1, 160.2 (phenyl C); δ 28.4 (methyl C). Anal. Found: C, 28.2 ; H, 1.99; S, 5.72; Sb, 21.6; Cl, 39.4%. Calcd for $C_{13}H_{11}OSSbCl_6$: C, 28.4 ; H, 2.02; S, 5.83; Sb, 22.2; Cl, 38.7%.
8) IR (KBr, cm^{-1}) 3011, 1582, 1483, 1240, 1165, 1097, 1010, 868, 827; ^{1}H-NMR (DMSO-d_6, 90MHz, ppm) δ 7.0, 7.3 (phenyl, 8H, AB quartet). Anal. Found: C, 72.6 ; H, 4.01; S, 16.3%. Calcd for $C_{12}H_8OS$: C, 72.0; H, 4.03; S, 16.0%.

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