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NOTE

A NEW SYNTHETIC ROUTE TO POLY(SELENO-1,4-PHENYLENE) FROM SELENOANISOLE

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Key Words: Aryl selenoxide; Polycondensation; Polyelectrolyte; Aryl selenide; Poly(arylene selenide)

INTRODUCTION

Poly(thio-1,4-phenylene) (PPS) is an important engineering plastic and shows high electric conductivity when doped with I_2 or AsF_5 [1-2]. The selenium-containing polyaromatics should also be potentially suitable as a backbone for electroactive polymers because of the increased metallic character and the filled 3d orbitals of the selenium atom [3]. However, the lack of variation in the synthetic route to aryl selenides [4-5] has limited the number of polymers containing selenoarylene repeating units that are presently available. Among them are poly(seleno-1,4-phenylene) (PPSe) [6-7], poly(seleno-4,4'-biphenylene) [8], and poly(seleno-2,5-thienylene) [9]. The selenide bonds in these polymers were produced either from aryl halides and selenium nucleophiles such as sodium selenides and selenophenolates, or from selenium electrophiles such as arylselenenyl halides [10]. Attempts have also been made to find an easy and general method to synthesize diaryl selenides using elemental selenium and aryl donors such as Grignard reagents, aryl diazonium and iodonium salts, and arylbismuthine derivatives (11), but their inherent low conversions have impeded application to polymer synthesis.

On the other hand, we have developed the chemistry to prepare PPS from prepolymers containing alkylsulfoniophenylene units by the dealkylation of the

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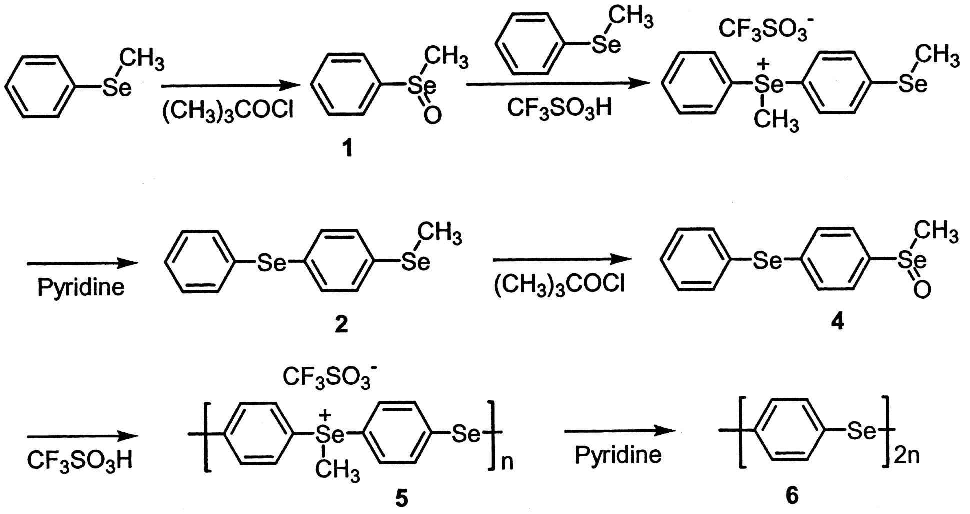
sulfonium moieties using nucleophilic reagents such as pyridine [12]. In particular, we have established that methyl 4-(phenylthio)phenyl sulfoxide undergoes self-polycondensation in CF_3SO_3H under suitable conditions to produce high molecular-weight poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) (PPS^+) in 100% yield [13-14]. The protonated sulfoxide (hydroxyl methyl phenyl sulfonium cation) electrophilically attacks the terminal phenyl ring (Swern reaction of aryl sulfoxides [15]) to exclusively produce linear and high molecular-weight PPS^+. Interestingly, PPS^+ is highly soluble in organic polar solvents [16-17].

We hypothesized that the similar reaction should take place using selenium analogues. Here, we report a convenient method to produce aryl selenides by the Swern condensation of alkyl selenoxides followed by the nucleophilic dealkylation of the resulting selenonium salts, and describe our successful attempts to synthesize PPSe from selenoanisole (Scheme 1). This research may inspire studies on the synthesis of a variety of aromatic polymers containing selenide bonds.

EXPERIMENTAL

Materials

Commercial reagents of selenopehnol, methyl iodide, *tert*-butyl hypochlorite and deuterated solvents were used as received. The other solvents were purified by distillation prior to use. Selenoanisole was quantitatively obtained by the condensation of selenophenol with methyl iodide in H_2O in the presence of NaOH. Methyl phenyl sulfoxide was prepared by the oxidation of thioanisole with H_2O_2 in the presence of CH_3COOH as previously described (12).



Scheme 1.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Infrared spectra were obtained using a Jasco FT-IR 5300 spectrometer with potassium bromide pellets. Thermogravimetry and differential thermal analysis were performed using a Seiko TG-DTA 220 instrument at a heating rate of 10°C/min under nitrogen at a flow rate of 300 mL/min. A 5 mg sample was used for each thermal analysis. Molecular weight measurement was done by gel permeation chromatography (GPC) at 210°C using a Senshu Kagaku VHT-GPC SSC-7000 system equipped with a UV detector set at 365 nm. 1-Chloronaphthalene was used as an eluent. Calibration was done with polystyrene standards. Elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample. Mass spectra were obtained using a Shimadzu GCMS-QP5050 spectrometer.

Synthesis

Methyl Phenyl Selenoxide (**1**)

Oxidation of selenoanisole to the corresponding selenoxide was accomplished by the previous method (18) with slight modifications as follows: to the solution of selenoanisole (0.17 g, 1.0 mmol) in CH_2Cl_2 (30 mL) was added pyridine (0.08 g, mmol) and methanol (0.16 g, 5.0 mmol). The mixture was kept at 0°C under dry N_2. The solution of *tert*-butyl hypochlorite (0.11 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was slowly added to the mixture which was then stirred for 40 minutes at 0°C. The addition of the solution of NaOH (0.08 g, 2.0 mmol) in H_2O (5 mL) followed by separation of the organic layer and purification by silica-gel column chromatography using $CHCl_3$ as an eluent afforded methyl phenyl selenoxide (**1**) in 80% isolated yield.

IR (KBr, cm^{-1}): 3042, 3000 (aromatic $\nu_{C\text{-}H}$), 1576, 1475, 1436 ($\nu_{C=C}$), 1072 ($\nu_{Se=O}$), 807, 734, 688 ($\delta_{C\text{-}H}$). ^{1}H NMR ($CDCl_3$): $\delta = 2.63$ (3H, s, methyl), 7.49-7.76 (5H, m, phenyl). ^{13}C NMR ($CDCl_3$): $\delta = 36.4$ (methyl), 125.1, 129.1, 130.7, 141.3 (phenyl). Bp: 53-54°C. MS: Calcd. for C_7H_8OSe, 187.10; Found (*m/z*), 188 (M^+).

4-(Phenylseleno)selenoanisole (**2**)

To the mixture of selenoanisole (2.7 g, 16 mmol) and **1** (3.0 g, 16 mmol) was slowly added CF_3SO_3H (4.3 mL) in the dark. The resulting solution was stirred at 20°C for 24 hours. The color of the solution turned from yellow to dark brown. Then, pyridine (50 mL) was added to the solution which was refluxed for 2 hours in the dark. The addition of HCl followed by the extraction with $CHCl_3$, washing with H_2O, dehydration and rotary evaporation afforded 4-(phenylseleno)selenoanisole (**2**) as an orange liquid in 98% isolated yield.

IR (KBr, cm^{-1}): 3026, 2986 (aromatic $\nu_{C\text{-}H}$), 1575, 1478, 1437 ($\nu_{C=C}$), 803, 739, 689 ($\delta_{C\text{-}H}$). ^1H NMR (CD_2Cl_2): $\delta = 2.32$ (3H, s, methyl), 7.21-7.70 (9H, m, phenyl). ^{13}C NMR (CD_2Cl_2): $\delta = 7.21$ (methyl), 126.6, 128.0, 129.3, 130.0, 131.2, 131.8, 132.4, 133.7 (phenyl). Elemental Analysis: Calcd: for $C_{13}H_{12}Se_2$: C, 47.87; H, 3.71. Found: C, 48.01; H, 3.69. MS: Calcd. for $C_{13}H_{12}Se_2$, 326.16; found (*m/z*), 326 (M^+).

4-(Phenylthio)selenoanisole (**3**)

CF_3SO_3H (4.3 mL) was slowly added in the dark to the mixture of selenoanisole (2.7 g, 16 mmol) and methyl phenyl sulfoxide (2.2 g, 16 mmol). The resulting solution was stirred at 20°C for 24 hours. Then, pyridine (50 mL) was added to the solution which was refluxed for 2 hours in the dark. The addition of HCl followed by the extraction with $CHCl_3$, washing with H_2O, dehydration and rotary evaporation afforded 4-(phenylthio)selenoanisole (**3**) in 91% isolated yield.

IR (KBr, cm^{-1}): 3057, 2919 (aromatic $\nu_{C\text{-}H}$), 1580, 1476, 1437 ($\nu_{C=C}$), 810, 744, 677 ($\delta_{C\text{-}H}$). ^1H NMR (CD_2Cl_2): $\delta = 2.25$ (3H, s, methyl), 7.01-7.40 (9H, m, phenyl). ^{13}C NMR (CD_2Cl_2): $\delta = 10.6$ (methyl), 126.6, 129.0, 129.8, 130.5, 131.2, 134.4, 135.4, 138.7 (phenyl). Elemental Analysis: Calcd. for $C_{13}H_{12}SSe$: C, 55.91; H, 4.33. Found, C, 55.98; H, 4.19. MS: Calcd. for $C_{13}H_{12}SSe$, 279.27; found (*m/z*), 279 (M^+).

Methyl 4-(phenylseleno)phenyl selenoxide (**4**)

Oxidation of **2** to the corresponding selenoxide **4** was accomplished by the oxidation with *tert*-butyl hypochlorite as follows. To the solution of **2** (1.5 g, 4.6 mmol) in CH_3OH (4.6 mL) and CH_2Cl_2 (4.6 mL) maintained at 0°C under dry N_2 was slowly added *tert*-butyl hypochlorite (1.0 g, 9.2 mmol) which was stirred for 1 hour at 0°C in the dark. During the reaction, the solution turned from yellow to colorless. The addition of CH_2Cl_2 (4.6 mL) and the saturated aqueous solution of $NaHCO_3$ (9.2 mL) followed by the extraction with $CHCl_3$, washing with H_2O, dehydration and rotary evaporation afforded **4** as a colorless liquid in 80% isolated yield.

IR (KBr, cm^{-1}): 3046, 3022 (aromatic $\nu_{C\text{-}H}$), 1560, 1444, 1436 ($\nu_{C=C}$), 1065 ($\nu_{Se=O}$), 815, 734, 613 ($\delta_{C\text{-}H}$). ^1H NMR (CD_2Cl_2): $\delta = 2.56$ (3H, s, methyl), 7.46-7.77 (9H, m, phenyl). ^{13}C NMR (CD_2Cl_2): $\delta = 37.6$ (methyl), 125.8, 126.0, 126.3, 129.0, 130.5, 131.4, 132.7, 142.9 (phenyl). Elemental Analysis: Calcd. for $C_{13}H_{12}OSe_2$: C, 45.63; H, 3.54. Found: C, 45.70; H, 3.64. MS: Calcd. for $C_{13}H_{12}OSe_2$, 342.16; Found: (*m/z*), 342 (M^+).

Poly(methylselenonio-1,4-phenyleneseleno-1,4-phenylene triflate) (**5**)

To the monomer **4** (1.0 g, 2.9 mmol), CF_3SO_3H (0.4 mL) at r.t. in the dark was slowly added. The resulting solution was stirred for 48 hours. During the polymerization, the solution turned from light yellow to dark brown. The resulting viscous solution was then poured into diethyl ether in the dark to precipitate the product which was collected by filtration, washed with diethyl ether and H_2O, and dried under vacuum to give poly(methylselenonio-1,4-phenyleneseleno-1,4-phenylene triflate) (**5**) as a white powder in 80% yield.

IR (KBr, cm^{-1}): 2900 (methyl $\nu_{C\text{-}H}$), 1563, 1477, 1421 ($\nu_{C=C}$), 1255, 640 ($\nu_{C\text{-}F}$), 1164, 1031 (ν_{SO3}), 803 ($\delta_{C\text{-}H}$). ^1H NMR (acetone-d_6): $\delta = 3.81$ (3H, s, methyl), 7.87 (4H, d, phenyl), 8.27 (4H, d, phenyl). Elemental Analysis: Calcd. for $C_{14}H_{11}F_3O_3SSe_2$: C, 35.46; H, 2.34. Found: C, 35.98; H, 2.25.

Poly(seleno-1,4-phenylene) (**6**)

The polyselenonium **5** (0.5 g) was dissolved in pyridine (50 mL) which was refluxed in the dark for 5 hours. After cooling, the resulting suspension was poured into CH_3OH (500 mL) to precipitate the product which was washed with H2O and CH_3OH and dried under vacuum to give poly(seleno-1,4-phenylene) (**6**) in 98% yield as a pale brown powder.

IR (KBr, cm^{-1}): 3055 (aromatic $\nu_{C\text{-}H}$), 1563, 1473, 1379 ($\nu_{C=C}$), 811, 740, 688 ($\delta_{C\text{-}H}$). Elemental Analysis: Calcd. for C_6H_4Se: C, 46.48; H, 2.60; Se, 50.92. Found: C, 46.90; H, 2.00; Se, 51.1.

RESULTS AND DISCUSSION

Methyl phenyl selenoxide (**1**) is inactive in the acid-induced electrophilic polymerization, because the protonation of the selenoxide significantly lowers the electron density of the phenyl carbons. The experimental behavior is supported by the PM3 semi-empirical MO calculation, where the carbon net charges of the hydroxyl methyl phenyl selenonium cation are more cationic and less susceptible to electrophilic substitution reaction than those of the parent compound **1** (Figure 1). On the other hand, the carbon net charges of the selenonium cation derived from **4** is less cationic, which suggests that **4** could undergo self-polycondensation in CF_3SO_3H to produce **5**.

In order to prepare the monomer **4**, selenoanisole was coupled by the oxidation and Swern condensation strategies (Scheme 1). A model reaction was carried out to ensure the reactivity of selenoanisole in the electrophilic substitution using methyl phenyl sulfoxide. Superacidification of the sulfoxide in the presence of selenoanisole followed by the treatment with pyridine effected the high yielding conversion to produce **3** (see Experimental section), which prompted us to examine the condensation of selenoxides.

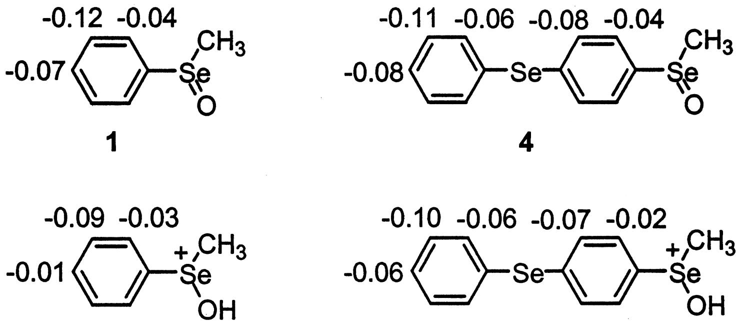


Figure 1. Carbon net charges of selenoxides **1** and **4** and the corresponding hydroxyselenonium cations.

Selenoanisole was oxidized to **1** using several oxidants such as H_2O_2, *N*-chlorosuccinimide, $NaIO_4$, HNO_3, and *tert*-butyl hypochlorite [18]. Among these, *tert*-butyl hypochlorite most efficiently gave the selenoxide without the formation of undesired by-products such as selenone. The selenide dimer **2** was obtained easily by the condensation of selenoanisole and **1** in CF_3SO_3H followed by the treatment of the resulting selenonium cation with pyridine. The oxidation of **2** to the monomer **4** was also accomplished using *tert*-butyl hypochlorite. Polymerization of **4** was carried out in CF_3SO_3H at room temperature to produce the polyselenonium **5** as a white powder which was soluble in polar organic solvents such as acetone and acetonitrile. A homogeneous and transparent film could be prepared by casting the solution. The structure of the polymer was confirmed by ^1H (Figure 2(c)) and IR spectra (Figure 3(a)) and elemental analysis. The doublet signals at 7.87 and 8.27 ppm and a singlet peak at 3.81 ppm in the ^1H NMR spectrum were assigned to the methylselenonio-1,4-phenyleneseleno-1,4-phenylene unit that provided good support for the linear structure. The end selenophenyl groups of the polymer chain were not detected in the ^1H NMR spectra, which indicated the high molecular weight (*vide infra*). The ^1H NMR spectra (Figure 2) revealed that the $CH_3Se(O)$- atoms in **4** are deshielded by 0.24 ppm compared to the CH_3Se- atoms in **2**. The magnitude of the deshielding is even larger for the selenonio group. In fact, a deshielding effect of 1.25 ppm was observed for the methyl protons in **5** relative to those in **4** revealing the stronger electron-withdrawing character of the selenonio group, which rationalized that polymerization did not proceed from **1**.

We previously reported that the superacidified reaction of aromatics with a selenic acid led to the formation of polyselenonium (19). Poly(phenylselenonio-1,4-phenyleneseleno-1,4-phenylene triflate) was thus obtained by the polycondensation of diphenyl selenide and benzeneselenic acid in CF_3SO_3H. However, the triphenylselenonio group was inactive to nucleophiles, and could not be converted to a diphenylseleno group even by treating with refluxing NaOH aqueous solution or pyridine, in contrast to the methyldiphenylselenonio group. On the other hand, the polymer **5** was easily converted to PPSe (**6**) by the nucleophilic demethylation

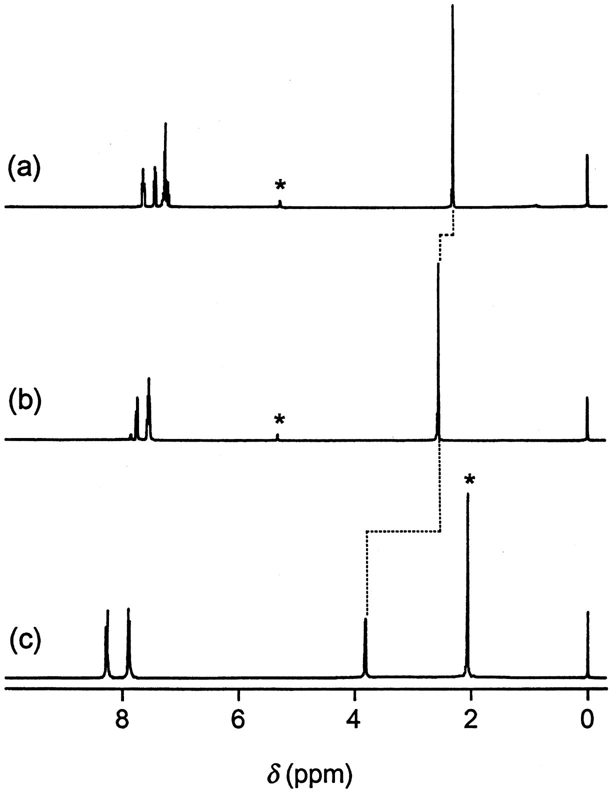


Figure 2. ^{1}H NMR spectra of (a) **2** in CD_2Cl_2, (b) **4** in CD_2Cl_2 and (c) **5** in acetone-d_6. Residual proton signals in the deuterated solvents are shown with asterisks.

of the selenonio group using pyridine. The product was a pale brown powder which was insoluble in any solvent at room temperature. The molecular weight was determined by GPC using 1-chloronaphthalene at 210°C as eluent to be M_n = 5300 and M_w = 7800. IR spectrum of the product was almost superimposable on that reported for PPS (Figure 3(a)); the disappearance of peaks near 2900, 1260, and 640 cm^{-1} ascribed to the stretchings of methyl, sulfonate, and trifluoromethyl groups in **5**, respectively, established the conversion to **6** upon the treatment with pyridine. Although a further characterization was impeded by the lack of solubility of the product, the IR spectrum and the elemental analysis clearly indicate that the demethylation went essentially to completion.

The conversion of the polyselenonium salt **5** to the selenophenylene chain **6** is also reflected in the drastic increase in the stability against thermolysis. Figure 3(b) shows the TGA curves of **5** and **6**. Polymer **5** was easily decomposed upon heating due to the weaker selenonio linkages. In contrast, polymer **6** showed the onset of decomposition near 351°C without darkening followed by a small amount of weight loss ($T_{d10\%}$ = 453°C). The thermal stability of **6** was even higher than that of the previously reported PPSe prepared by the condensation of *p*-dibro-

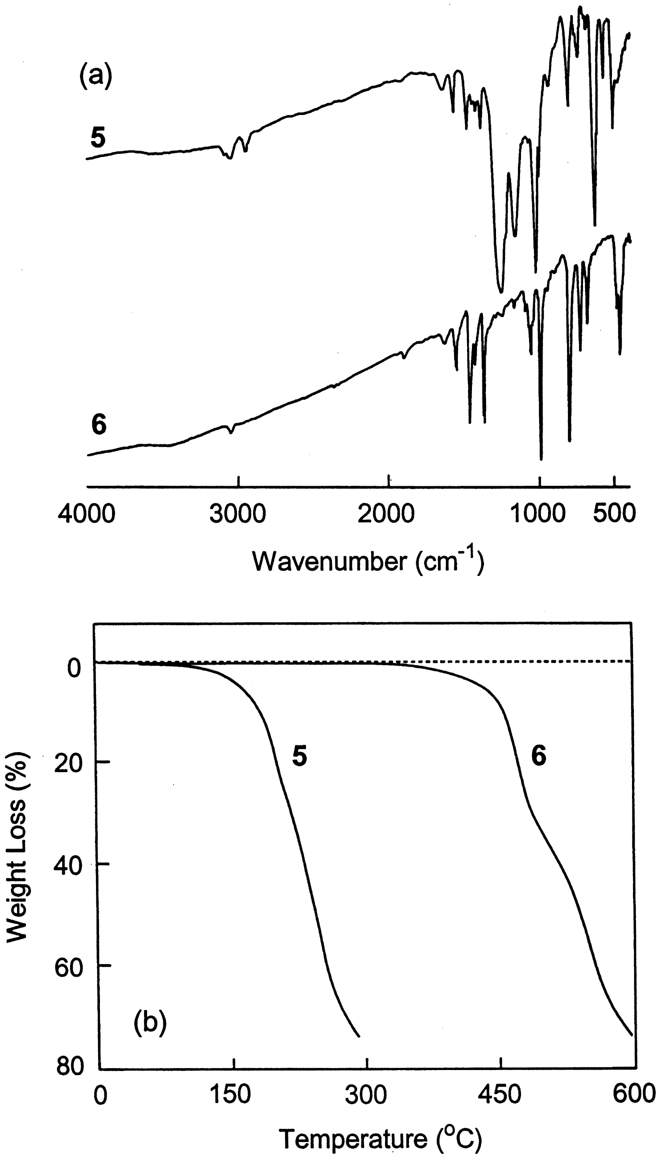


Figure 3. IR spectra (a) and TGA curves (b) of **5** and **6**.

mobenzene and sodium selenide [7], which darkened above 200°C due probably to the terminal bromo groups. While PPSe was reported to be partly crystalline [6-7], polymer **6** showed no X-ray diffraction peak and the DTA analysis showed no endothermic transition before the decomposition, revealing that it is amorphous. This is reminiscent of the formation of amorphous PPS by the polymerization at temperatures much lower than the T_g of the polymer [12-13]. Further characterization of **6** including the annealing behavior and electric conductivity upon doping is the subject of our continuous research.

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