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# Synthesis of Oligo(2,3,5,6-tetramethylphenylene selenide)

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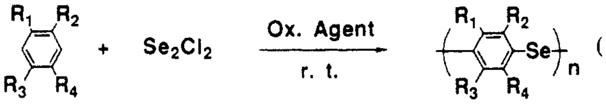
It has been reported that poly(*p*-phenylene sulfide) (PPS) and poly(*p*-phenylene selenide) (PPSe) show high electrical conductivity more than once after doping with acceptor molecules, such as $AsF_5$.[1-3] Much attention is also paid to oligo(phenylene selenide) (OPSe) on the conductivity and photoconductivity, as well as those of PPSe. PPSe is usually prepared from *p*-dichlorobenzene and sodium selenide or the metal salt of *p*-halo-substituted benzeneselenol under high temperature and high pressure, as reported for PPS.[4-6] No paper has been reported on the synthesis of substituted PPSe's having electron-donating substituents, because the polymerization is not feasible through nucleophilic substitution, similar to that for poly(*p*-phenylene sulfide).

Previously, we reported the preparation route of PPS's from diphenyl disulfides through oxidation and electrophilic reaction.[7-10] This paper describes the synthesis of OPSe's with electron-donating substituents through oxidation (eq 1).



(1)

$R_1 = R_2 = R_3 = R_4 = CH_3$ ; durene
$R_1 = R_4 = CH_3$, $R_2 = R_3 = H$; xylene

A typical experiment is as follows. 1,2,4,5-Tetramethylbenzene (durene; 0.025 mol) was dissolved in 25 $cm^3$ of tetrachloroethane. The solution was poured into 25 $cm^3$ of tetrachloroethane containing selenium monochloride (0.01 mol), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (0.01 mol), trifluoromethanesulfonic acid (0.5 mmol), and trifluoroacetic anhydride (0.01 mol). After 40 h, the mixture was filtered to remove elemental selenium. The filtrate was precipitated into methanol (containing 5 vol % of HCl). The precipitate was collected, washed with water and methanol, and dried under vacuum for 10 h.

1,2,4,5-Tetramethylbenzene is allowed to react with selenium monochloride in the presence of an equimolar amount of DDQ (based on $Se_2Cl_2$) under an acidic environment at room temperature and under atmospheric pressure. The color of the solution turns to black from yellow during the polymerization. The formed polymer was isolated as a slight yellow powder with a high melting point (ca. 240 °C) in 57% yield.

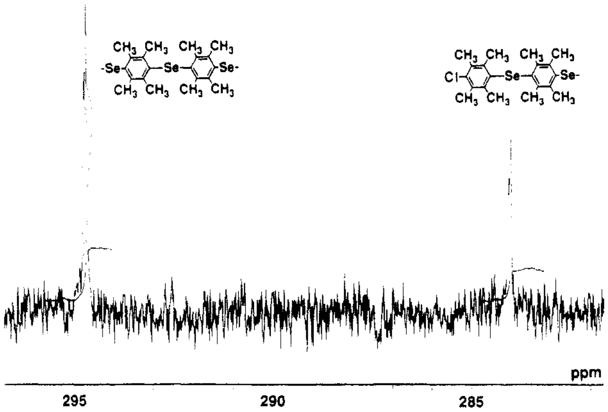


**Figure 1.** $^{77}Se$ NMR spectrum of the formed polymer. The delay period was set to 70 s.

**Table I. Synthesis of Oligoaromatic Selenide by Oxidative Polymerization[a]**

| monomer | yield (%) | mp (°C) |
|---|---|---|
| benzene | 0 | |
| xylene | 8[b] | 174 |
| durene | 57 | 235 |
| *p*-dimethoxybenzene | c | |

[a] [Monomer] = 0.5, [$Se_2Cl_2$] = 0.2, [DDQ] = 0.2, [$CF_3SO_3H$] = 0.01 (mol/L) in $(CHCl_2)_2$. [b] Soluble part of the oligomer. [c] The resulting oligomer was insoluble and cannot be isolated as a pure powder.

The structure of the product was confirmed by spectroscopic and elemental analysis.[11] The elemental analysis shows that the product contains a chloride atom (11.61%). The empirical formula is $C_{10.0}H_{12.4}Se_{0.6}Cl_{0.7}$. The proton at the end of a chain can hardly be detected by $^1H$ NMR measurement because the chloride atom is substituted at the end phenylene ring. Two peaks attributed to methyl protons were observed at 2.2 and 2.3 ppm (integration ratio is 1:3.7). A methylene proton at 3.6 ppm was not detected in the NMR spectrum. This result denies that the monomer units are linked by a selenomethylene bond. It is believed that the peak at 2.2 ppm is ascribed to a methyl group at the meta position of the end phenyl ring. The integration ratio supports the idea that the tetramer and pentamer are produced as a main product. The $^{77}Se$ NMR spectrum also shows two peaks attributed to the phenylene-selenide bond at 284.0 and 294.7 ppm (Figure 1). No peak attributed to diselenide bond has been detected.[12] The assignment of the peaks was based on the gated decoupling experiment.[13] It is suggested that the peak at 284.0 ppm should be assigned to the selenium at the end of the chain. The integration ratio of the peaks also shows a degree of polymerization between 4 and 5. Fragment peaks arising from the phenylene selenide and chlorophenylene selenide structures are observed in the mass spectrum ($m/z$ = 167, 212, 246, 290, 346, 558, 591).

The IR spectrum of the product is similar to that of poly(2,3,5,6-tetramethylphenylene sulfide) obtained by oxidative polymerization of durene and sulfur monochloride. The number-average molecular weight of the resulting OPSe is ca. 1000, which was measured by GPC calibrated with polystyrene standards. These results indicate that the product is identified as oligo(2,3,5,6-tetramethylphenylene selenide) substituted by a chloride group at the end of the chain.

The reaction proceeds efficiently in dichloromethane and tetrachloroethane which have low donor numbers and are able to dissolve the resulting oligomer. Basic solvents, such as dimethylformamide and *N*-methyl-2-pyrrolidone, retard the polymerization. It is believed that the polymerization proceeds via cationic species generated by oxidative reaction, similar to that of *p*-xylene with sulfur monochloride.[14] However, side reactions, such as the formation of the elementary selenium and the chlorination at the end of the chain, are feasible to occur during the polymerization because of the greater instability of $Se_2Cl_2$ compared to $S_2Cl_2$.

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Oligomerization of aromatics with selenium monochloride can be applied for the formation of oligo(arylene selenide)s. *p*-Xylene with $Se_2Cl_2$ is oxidatively reacted to yield the corresponding linear oligomer (Table I). Benzene was not reacted to oligo(*p*-phenylene selenide) because of its low reactivity for an electrophilic reaction. It is also possible to use *p*-dimethoxybenzene as a monomer. However, it is difficult to separate the resulting oligomer from byproducts.[15] Aromatics having electron-donating groups are suitable for the oligomerization. Though substituted aromatic selenium oligomer has been prepared and studied with electron-withdrawing substituents, this method results in the formation of the oligomer with electron-donating ones. The cyclic voltammogram of the oligomer was measured in dichloromethane containing 0.1 M of tetra-*n*-butylammonium tetrafluoroborate (TBABFl$_4$). Oligo(2,3,5,6-teramethylphenylene selenide) possesses a redox potential (*p*-type dope–dedoping) at 1.5 V,[16] whose electroactivity is believed to expand the potential application. Further electrical properties of the oligomers will be reported in the near future.

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(11) IR (KBr): 2920, 2850 ($\nu_{CH}$), 1582, 1570, 1450 ($\nu_{C=C}$), 883, 870, 805, 758 ($\delta_{CH}$), 1390, 1061, 1050, 1038, 980, 458, 432. $^1$H NMR (CDCl$_3$): $\delta$ 2.20, 2.33 (s, methyl), 6.90 (s, phenyl). $^{13}$C NMR (CDCl$_3$): $\delta$ 18.48, 21.60 (methyl), 132.59, 134.25, 135.50, 138.23 (phenyl). $^{77}$Se NMR (CDCl$_3$): $\delta$ 284.00, 294.67. MS (*m*/*z*): 424, 212. Anal. Calcd for $(C_{10}H_{12}Se)_n$: C, 56.88; H, 5.73; Se, 37.39. Found: C, 59.18; H, 6.16; Se, 22.14; Cl, 11.61.

(12) Gated decoupling experiments were carried out in order to permit quantitative work. The delay period was 70 s. The integration ratio for 284.0 to 294.7 (ppm) is 3.4:1.9.

(13) It is reported that chemical shifts of diphenyl selenide and diphenyl diselenide are 402 and 464 ppm, respectively. However, the spectrum of the oligomer shows two peaks whose space is about 10 ppm, and no peak is detected in the region of low magnetic field. If a diselenide bond existed in the oligomer, the peak would appear between ca. 330 and 370 ppm.

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(15) IR (KBr): 2920, 2850 ($\nu_{CH}$), 1480, 1460, 1430 ($\nu_{C=C}$), 1202, 1020 ($\nu_{COC}$), 850, 755 ($\delta_{CH}$), 1360, 1285, 1180, 1060. This spectrum is almost consistent with that of the corresponding PPS derivative.

(16) The potential of the reference electrode (Ag/AgCl) was adjusted by using a ferrocene/ferrocenium redox couple to be 0.42 V in dichloromethane.