

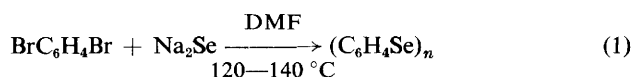
Poly(*p*-phenylene selenide): Structure Control in a Precursor to a Conducting Polymer

Daniel J. Sandman,* Michael Rubner, and Lynne Samuelson

GTE Laboratories, Inc., 40 Sylvan Road, Waltham, MA 02254, U.S.A.

Poly(*p*-phenylene selenide), synthesized for the first time from *p*-dibromobenzene and a new sodium selenide reagent, has a crystal structure isomorphous to its sulphur analogue and is rendered conducting by arsenic pentafluoride.

The thermoplastic poly(*p*-phenylene sulphide) (PPS) has received considerable recent attention as an example of a polymer without a continuous conjugated carbon π -system which becomes highly conducting on exposure to strong oxidants.¹ In spite of the current interest in PPS, its selenium analogue has not been reported to date although an attempt along these lines has been noted.² Our recent successful use of new alkali metal chalcogenide reagents for the preparation of both new and previously known aromatic chalcogen materials^{3,4} encouraged us to attempt the synthesis of poly(*p*-phenylene selenide) (PPSe), and we now report our initial results on the chemical, physical, and electrical properties of PPSe.



As shown in equation (1), *p*-dibromobenzene reacts with sodium selenide prepared *in situ* directly from its elements in *N,N*-dimethylformamide (DMF), avoiding the use of liquid ammonia, for 20 h to give PPSe as a light-yellow powder in 80% yield after removal of low molecular weight material with warm tetrahydrofuran (THF). These experimental conditions are significantly milder than those used⁵ for PPS synthesis, probably because of an $S_{\text{RN}}1$ ⁶ mechanism in the

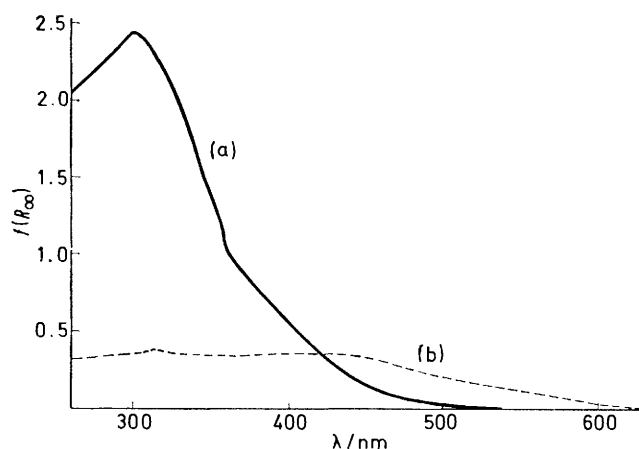


Figure 1. Diffuse reflectance spectrum of PPSe (a) and (b) ammonia-compensated AsF_5 -exposed PPSe. Both samples are 1% by weight dispersed in NaCl.

present work. The yellow powder which darkens at 200 °C and melts at *ca.* 220 °C, was found to have a compositional range $\text{C}_{6.0}\text{H}_{3.9-4.2}\text{Se}_{1.06-1.15}\text{Br}_{0.015}$ by elemental analysis. The

percentage of bromine suggests a molecular weight of 10 000. Between 4000 and 600 cm^{-1} , the i.r. spectrum of PPSe is superimposable on that reported^{1c,e} for PPS; the band at 550 cm^{-1} in PPS shifts to 500 cm^{-1} in PPSe and the 475 cm^{-1} band is unchanged. The electronic spectrum of PPSe, given in Figure 1, exhibits a maximum at 300 nm and a slight shift to lower energies compared with phenyl selenide,⁷ with the tail into the visible accounting for the yellow colour.

X-Ray diffraction of just-prepared PPSe powder reveals partial crystallinity, and a structure isomorphous to that reported⁸ for PPS and poly(phenylene oxide) is indicated by the strong resemblance of the X-ray data to those reported^{1d,e} for PPS. A strong peak is observed at $2\theta = 20.2^\circ$, analogous to that at 21.0° in PPS, with the shift to larger d -spacings manifesting the increased van der Waals' radius of selenium vs. sulphur. We tentatively assign the orthorhombic unit cell $a = 8.7$, $b = 5.7$, $c = 10.5$ Å, $U = 520$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.98$ g cm^{-3} . This observed expansion of the unit cell in going from PPS to PPSe is in quantitative agreement with analogous expansions in the tetrachalcogeno-tetracenes⁹ and -fulvalenes.¹⁰

The observed density of PPSe samples prepared either as described above or from *p*-dichlorobenzene falls in the range 2.05–2.15 g cm^{-3} , exceeding the theoretical density, an unusual observation in partially crystalline polymers. The presence of selenium in an excess of stoichiometry revealed by the elemental analysis suggests the presence of diselenide linkages in the noncrystalline regions of PPSe which would enhance the density. The presence of weak i.r. absorption near 290 cm^{-1} in all PPSe samples is consistent with this suggestion.¹¹

Exposure of PPSe powder to AsF_5 (100 Torr) for 5 h at 40 °C turns the yellow material green and finally black and results in a weight increase of 40–45%. Exposure of a sample to moist air reverses these colour changes to give a yellow–orange solid. The observed room temperature conductivity of the compacted black material is 10^{-2} – 10^{-3} (ohm cm)⁻¹. Like PPS rendered conducting by AsF_5 ,¹ the PPSe material is crystallographically amorphous, exhibits i.r. absorptions at 705 and 395 cm^{-1} , suggestive of AsF_6^- , and is compensated by ammonia to a yellow–orange solid. The solid state spectrum of the latter (Figure 1) is consistent with dibenzselenophen⁷ formation induced by AsF_5 crosslinking¹ of PPSe.

Exposure of PPSe to sodium naphthalenide in THF leads to extensive decomposition of the polymer, analogous to PPS.¹ While PPS is rendered conducting on exposure to NO^+PF_6^- ,^{1d} PPSe is extensively decomposed by this reagent.

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