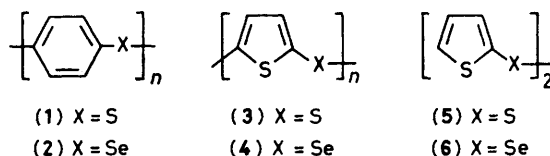


Organic Metals: Conducting Complexes of Poly(2,5-thienylene sulphide) and Poly(2,5-thienylene selenide)

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Exposure of highly purified samples of the new polymers poly(2,5-thienylene selenide) (PTSe) and poly(2,5-thienylene sulphide) (PTS) to arsenic pentafluoride afforded a conducting complex (0.12 S/cm) from PTSe but only a moderately conducting complex (*ca.* 10^{-5} S/cm) from PTS, a result which is in direct contrast to the behaviour of poly(*p*-phenylene selenide) and poly(*p*-phenylene sulphide) upon similar treatment.

Several polyarylene sulphides have been reported to yield highly conducting complexes after exposure to AsF_5 . The most promising among these is the commercially available poly(*p*-phenylene sulphide) (PPS, 1), the conductivity of which can rise to $\sigma > 1$ S/cm after such treatment.¹ Very recently, the closely related polymer poly(*p*-phenylene selenide) (PPSe, 2) has been prepared by two different procedures.^{2,3} After treatment with AsF_5 , PPSe yields a complex of considerably lower conductivity, *i.e.* 10^{-2} – 10^{-3} S/cm for material of excessive selenium composition² and only 8.2×10^{-8} S/cm for stoichiometrically very pure material.³ We now report simple



syntheses of the thiophene analogues poly(2,5-thienylene sulphide) (PTS, 3) and poly(2,5-thienylene selenide) (PTSe, 4), as well as the unexpected electrical behaviour of (3) and (4) after AsF_5 complexation.

Three syntheses of PTS (3) have already been reported. The first, from Cu_2O and 5-chlorothiophene-2-thiol, gave a low-molecular weight product containing 3% chlorine.⁴ The second, from thiophene and SCl_2 in the presence of MgO , gave a higher molecular weight product of low purity.⁴ The third, from Na_2S and 5,5'-dichloro-2,2'-dithienyl sulphide, gave a material for which no properties were given other than thermal stability data.⁵

In our new PTS synthesis, 2,2'-dithienyl disulphide [(5),⁶ prepared by the potassium ferricyanide oxidation of thiophene-2-thiol⁷] was treated with one equiv. of sulphuryl chloride (SO_2Cl_2) in dichloromethane (CH_2Cl_2) at room temperature. The resulting orange sulphenyl chloride solution soon generated HCl with the separation of PTS; the suspension was refluxed overnight to obtain a polymer with the maximum molecular weight. The resulting product, which was extracted with CS_2 and hot dimethylformamide (DMF) to remove a small amount of lower molecular weight material, formed a cream-coloured powder, m.p. 155–157 °C (80% yield), which was shown to be very pure by elemental analysis.

The synthesis of the previously unreported PTSe (4) proceeded in a similar manner. Thus, reaction of 2-thienyl-lithium with selenium, followed by potassium ferricyanide oxidation of the resulting selenolate, gave 2,2'-dithienyl diselenide (6), m.p. 57–59 °C. Treatment of this diselenide with one equiv. of SO_2Cl_2 in CH_2Cl_2 at room temperature gave an orange-red solution of 2-thiopheneselenenyl chloride, which soon began to self-condense with the separation of the polymer. After refluxing overnight, the cream-coloured solid was filtered and extracted with CS_2 followed by hot DMF to give PTSe, m.p. 220–235 °C (87% yield), which again was shown to be of high purity by elemental analysis.

Both PTS (3) and PTSe (4), in the form of powders, were exposed to AsF_5 under identical conditions at 500 mmHg pressure, and the resulting black powders were compressed

into pellets. The final compositions, calculated from weight increases were $\text{PTS}(\text{AsF}_6)_{0.04}$ and $\text{PTSe}(\text{AsF}_6)_{0.50}$, respectively, assuming the dopant species is the AsF_6^- ion. The conductivity of the modified PTS (3) was only 2.6×10^{-6} S/cm, but that of the modified PTSe (4) was 0.12 S/cm, establishing this material as the first example of a conducting poly(arylene selenide) complex.

Thus, in the *p*-phenylene series, the AsF_5 -treated sulphide conducts well and the corresponding selenide conducts poorly, while the exact opposite is true for the corresponding 2,5-thienylene polymers. No explanation for these observations can be given at this time.

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References

- 1 R. R. Chance, L. W. Shacklette, G. G. Miller, D. M. Ivory, J. M. Sowa, R. L. Elsenbaumer, and R. H. Baughman, *J. Chem. Soc., Chem. Commun.*, 1980, 348; J. F. Rabolt, T. C. Clarke, K. K. Kanazawa, J. R. Reynolds, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 1980, 347.
- 2 D. J. Sandman, M. Rubner, and L. Samuelson, *J. Chem. Soc., Chem. Commun.*, 1982, 1133.
- 3 K. Y. Jen, M. V. Lakshmikantham, M. Albeck, M. P. Cava, W. S. Huang, and A. G. MacDiarmid, *J. Polym. Sci.*, in the press.
- 4 E. Jones and I. M. Moodie, *J. Polym. Sci., Polym. Symp.* 1967, 2881.
- 5 M. G. Voronkov, A. K. Khalivllin, V. Z. Annenkova, L. M. Antonik, L. M. Kamkina, E. N. Deryagina, and T. I. Vakul'skaya, *Dokl. Akad. Nauk SSSR*, 1976, **228**, 1341.
- 6 V. Meyer and K. Nevre, *Ber.*, 1887, **20**, 1757.
- 7 E. Jones and I. M. Moodie, 'Organic Synthesis,' vol. 51, ed. R. Breslow, Wiley, New York, 1970, p. 104.