# Organic Metals: Poly-(*p*-phenylene Sulphide) Hexafluoroarsenate

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*Summary* Electrically conducting p-type films, wires, and powders (*ca.* 1 $\Omega^{-1}$ $cm^{-1}$) have been prepared by the $AsF_5$ oxidation of poly-*p*-phenylene sulphide, the first melt- and solution-processible polymeric precursor to a conducting polymer.

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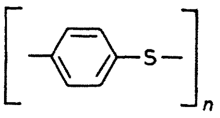
ALTHOUGH certain polymers such as $(SN)_x$ and its derivatives,[1,2] doped polyacetylene,[3,4] and doped poly-*p*-phenylene[5] exhibit high electrical conductivity, they do not possess the processing characteristics desirable in a polymeric metal. Electrochemically prepared polypyrrole,[6,7] though remarkably stable, is not melt- or solution-processible. We describe here the first conducting polymer prepared by oxidation of a highly crystalline melt- and solution-processible polymer: poly-*p*-phenylene sulphide (PPS).



(PPS)

Reaction of purified $AsF_5$ gas with poly-*p*-phenylene sulphide in the form of commercially available powder, film, or fibre (Ryton)† produced a blue-black material with a conductivity of *ca.* 1 $\Omega^{-1}$ cm$^{-1}$ at room temperature. The reaction with $AsF_5$ is slow relative to the corresponding reaction with $(CH)_x$ and was allowed to proceed for 4 days with 250 Torr of $AsF_5$, using a stainless steel vacuum line and reaction vessel. Under these conditions, the uptake of $AsF_5$ measured by weight increase corresponded to *ca.* 1 $AsF_5$ molecule per phenylene sulphide group. During the reaction, the transparent, colourless poly-*p*-phenylene sulphide became blue-green and finally blue-black. The oxidized films are opaque in the i.r. region which is typical of a metal; however, i.r. peaks at 705 and 400 cm$^{-1}$ in lightly doped samples indicate the presence of $AsF_6^-$ ions suggesting that oxidation of the polymer takes place *via* the reaction (1). A similar mechanism[8] has been shown to take place in $AsF_5$-doping of $(CH)_x$ and poly-*p*-phenylene, where we have also observed $AsF_6^-$ in the i.r. spectrum.

$$2e + 3AsF_5 \rightarrow 2AsF_6^- + AsF_3 \qquad (1)$$

Pristine PPS is highly crystalline, with phenylene sulphide chains passing through the centre and edge of the orthorhombic unit cell.[9] The planes of the successive phenylene rings are not flat but alternate at ±45° to the (100) plane. In view of this orthogonal arrangement of successive phenylene groups, it is remarkable that partial oxidation leads to sufficient delocalization to give rise to electronic conductivity. Even if the geometry of the chain changes on reaction in order to facilitate delocalization, it is necessary to consider the possibility that d-orbitals on the sulphur may be involved. *X*-Ray diffraction studies show a considerable loss of order on exposure to $AsF_5$, the strong 110 and 111 peaks of pristine PPS are replaced by a broad absorption covering both regions.

Oxidation of biaxially stretched films of PPS leads to anisotropic optical and electrical properties consistent with the chain orientation in the starting polymer. This result is in accord with the expectation that the disruption of crystallinity on doping does not seriously distort the parallel orientation of the PPS chains.

Films of $(PPS)^+(AsF_6)^-_{0\cdot9}$ prepared from biaxially oriented 25 $\mu$m thick PPS film have a flotation density of 1·78 g/cm$^3$ compared to 1·39 g/cm$^3$ for the pristine film. At these high doping levels, these films are quite brittle. On heating to 300 °C, these films slowly lose weight and decrease in conductivity. Unlike pristine PPS, these oxidized films do not melt even on heating to 900 °C by which temperature they have become graphitized. The conductivity of the films decreases with temperature, showing a $T^{1/4}$ dependence. Room temperature thermopower measurements confirm that the polymer is p-type (50 $\mu$V deg$^{-1}$), consistent with partial oxidation of the polymer by the $AsF_5$. Exposure to air causes deterioration in the conductivity although the shiny black appearance of the films does not change. Attempts to make the films n-type by doping with sodium naphthalide were not successful.

Powders of poly-*m*-phenylene and poly-*m,p*-phenylene sulphide (random mix of *m* and *p* isomers) also react with $AsF_5$ to give black conducting solids.

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