Highly Conducting Charge-transfer Complexes of a Processible Polymer: Poly(*p*-Phenylene Sulphide)

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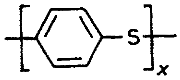
Summary We report the synthesis of highly conducting derivatives of poly(*p*-phenylene sulphide), the first such organic polymer without a continuous system of overlapping carbon π-orbitals, as well as the first melt-processible polymer which can be doped to high conductivity

THERE is now a large and rapidly growing interest in conducting derivatives of organic polymers. The merger of conventional polymer properties with the electronic properties of metals and semiconductors has enormous potential for both fundamental research and commercial applications. In both cases, and in particular for high-volume commercial applications, polymer processibility is a very important consideration. None of the polymers in the previously reported conducting systems [polyacetylene,[1] poly(*p*-phenylene),[2] and polypyrole[3]] is either melt- or solution-processible. We report here a new conducting system based on a melt-processible polymer, poly(*p*-phenylene sulphide) (**1**). Inclusion of the chalcogen in the backbone marks a significant departure from previous systems, all of which contain a continuous system of overlapping carbon π-orbitals.



(1)

Poly(*p*-phenylene sulphide), PPS, is a commercially available polymer which has a variety of uses as a thermoplastic. The material used here was obtained from Phillips Petroleum Company in the form of 0·025 mm films, 0·025 mm diameter fibres, and a highly crystalline powder. The reported conductivity for the undoped material is about 10^{-16} S cm^{-1}.

When PPS is exposed to AsF_5, a strong electron acceptor, the conductivity increases by as much as 16 orders of magnitude to $\sigma = ca.$ 1 S cm^{-1}. This σ is about 1000 times lower than that obtained for polyacetylene or poly(*p*-phenylene) doped with AsF_5. As in the other systems,[1-3] the thermoelectric power is positive, indicating mobile hole-like charge carriers. The conductivity can be controlled by varying the dopant concentration or by adding a compensating agent such as dimethylamine. Preliminary experiments indicate that PPS can be doped to high conductivity by exposure to the vapour of potassium (an electron donor) at elevated temperature, although attempts to dope PPS in potassium naphthalide solutions have been unsuccessful.

The temperature dependence of σ for AsF_5-doped PPS is illustrated in the Figure as $\log \sigma$ *vs.* T^{-1}. For heavily doped samples (near 1 : 1 ratio of AsF_5 to C_6H_4S) σ is activated with an activation energy (E_a) of *ca.* 0·06 eV near room temperature. E_a increases to *ca.* 0·5 eV for the most lightly doped sample in the Figure. A similar variation in E_a with doping level is observed for polyacetylene[1] and, to a lesser extent, for poly(*p*-phenylene).[2] Actually, better linearity is obtained, particularly for the heavily-doped samples, if log σ *vs.* $T^{-1/2}$ is plotted. This behaviour is consistent with trap-modulated, metallic conductivity in one dimension,[4] but has also been observed for highly conducting particles embedded in an insulating matrix.[5]

On exposure to AsF_5, the transparent PPS film turns blue and eventually glossy blue-black owing to a broad absorption beginning around 20,000 cm^{-1} and continuing down to about 2000 cm^{-1}. Below 2000 cm^{-1}, doping produces a background absorption which is significantly less than the maximum absorption in the near i.r., allowing polymer peaks characteristic of PPS, as well as a peak at 705 cm^{-1} due to AsF_6^-, to be observable in the spectral region below 2000 cm^{-1}. Heavily doped samples of polyacetylene, poly(*p*-phenylene), and polypyrole all show free-electron-like absorption down to at least 200 cm^{-1}. Thus, the PPS data indicate an apparent gap in the i.r. spectrum, even for heavily doped samples. This observation is roughly consistent with the temperature dependence of σ and suggests an intrinsic origin for the lower conductivity observed in doped PPS compared to other systems.[1,2]

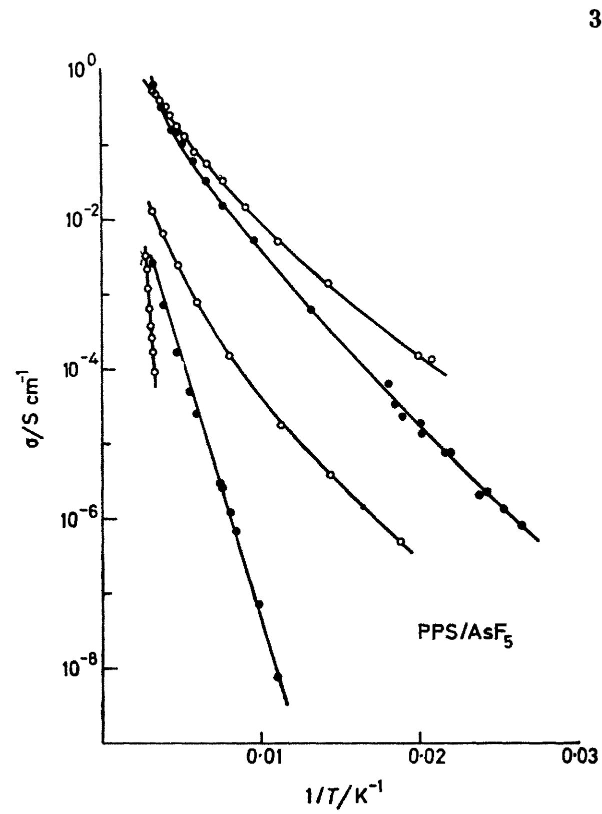


FIGURE. Electrical conductivity of AsF_5-doped PPS *vs.* reciprocal temperature. Data shown are for compacted powders of PPS at various doping levels. Doping level decreases in going from curves on the right to those on the left.

The conductivity of AsF_5-doped PPS is quite stable under high-vacuum conditions and under dry O_2. However, rapid deterioration of σ occurs on exposure to water vapour.

Preliminary experiments on poly(*m*-phenylene sulphide) and poly(*p*-phenylene oxide) indicate that these polymers can also be doped with AsF_5 to yield high conductivities ($>10^{-3}$ S cm^{-1}). Consequently, PPS is the first of an important new family of conductors involving phenyl chalcogen polymers and copolymers.

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