

‘Organic Metals’: Polypyrrole, a Stable Synthetic ‘Metallic’ Polymer

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Summary Highly stable, flexible films of polypyrrole with *p*-type conductivities of $100 \Omega^{-1} \text{cm}^{-1}$ have been prepared by electrolytic oxidation of the appropriate pyrrole monomers; similarly prepared films of mixtures of pyrrole and *N*-methylpyrrole have conductivities between 5×10^{-3} and $100 \Omega^{-1} \text{cm}^{-1}$ depending upon the composition.

THE discovery of metallic properties in polymers such as polysulphur nitride, $(\text{SN})_x$,¹ and doped polyacetylene, $(\text{CH})_x$,² has encouraged the search for other polymeric systems with greater chemical stability and plasticity. In 1968 Dall’Olio *et al.*³ reported a value of $8 \Omega^{-1} \text{cm}^{-1}$ for the conductivity of an oxy-pyrrole polymer. We have prepared shiny blue-black flexible films of polypyrrole⁴ which, like $(\text{SN})_x$ and doped $(\text{CH})_x$, show metallic properties. The room temperature conductivity of the present films, measured by four-probe technique is as high as $100 \Omega^{-1} \text{cm}^{-1}$. The films are stable in air and can be heated to 250°C with little effect on their conducting properties. Thermal analysis confirms that the material is thermally inert below 250°C after which the rate of weight loss increases and becomes very rapid above 600°C . The films are prepared by the electrolytic oxidation of pyrrole in acetonitrile solution using a tetraethylammonium tetrafluoroborate electrolyte.⁴ Though the chemical composition of the films depends on the conditions of preparation, a typical composition is $\text{C}_{4.0}\text{N}_{0.87}\text{H}_{3.5}(\text{BF}_4)_{0.25}$ indicating that the pyrrole rings remain intact. This is consistent with polypyrrole being a polymer formed by linking the pyrrole units *via* the α carbon atoms as suggested previously.

The pyrrole units carry a partial positive charge balanced by the BF_4^- ions somewhat akin to the AgBF_4 and AgClO_4 treated polyacetylene films reported by Clarke *et al.*⁶ Raman and reflection i.r. spectra show bands characteristic of pyrroles⁷ confirming the presence of the pyrrole rings in the polymer. The films are less crystalline than pristine polyacetylene. Electron diffraction data show only diffuse rings which correspond to a lattice spacing of 3.4 \AA , close to the value expected if the separation between the pyrrole chains were determined by the thickness of the pyrrole rings. Normally the chains of pyrrole rings are randomly oriented in the plane of the film. However, under certain circumstances the diffraction rings are arced as a result of the preferred orientation of the pyrrole chains. Scanning electron microscopy shows that the polypyrrole, in contrast to both $(\text{SN})_x$ and $(\text{CH})_x$, does not consist of fibres but is a continuous film with a flotation density of 1.48 g cm^{-3} .

The temperature dependence of the four-probe conductivity is weakly activated, decreasing from a value of $100 \Omega^{-1} \text{cm}^{-1}$ at room temperature to $30 \Omega^{-1} \text{cm}^{-1}$ on cooling to -193°C . Thermopower measurements show that the polymer is *p*-type which is consistent with the fact that it is partially oxidized. The room temperature value of the thermopower is $7 \mu\text{V deg}^{-1}$. This small value of the thermopower together with its linear temperature dependence between room temperature and -243°C suggests a metallic nature for the microscopic conductivity.

Corresponding films of poly-*N*-methylpyrrole have also been prepared and they show much lower room temperature conductivities (*ca.* $1 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$). Films prepared by electrolysis of mixtures of pyrrole and *N*-methylpyrrole have conductivities dependent on their composition. Thus

by controlling the relative amounts of the two pyrroles in the electrolytic solution we are able to vary the conductivity of the final film over five orders of magnitude from insulator to 'metallic' material. Systematically varying the conductivity by selecting the copolymer composition is attractive and more readily controllable than the technique used for (SN)_x and (CH)_x where specific conductivities are obtained by limiting the exposure time of the pristine materials to corrosive chemicals, a procedure which does not always achieve uniform doping.

Exposing the metallic polypyrrole to NH₃ gas decreases the room temperature conductivity by a factor of 10. Similar effects have been observed on the treatment of acceptor doped polyacetylene with NH₃. In contrast to

'metallic' polyacetylenes, where NH₃ is believed to react with the carbonium ion sites along the polyacetylene chains,⁸ NH₃ interacts only weakly with polypyrrole and can be readily pumped off restoring the conductivity to the original value. Exposing the insulating poly-*N*-methylpyrrole to bromine vapour causes a permanent increase in its conductivity by a factor of 20.

We believe that these pyrrole polymers represent a significant advance over (SN)_x and chemically doped (CH)_x in the development of stable, practical polymeric 'metals' and semiconductors.

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