'Organic Metals.' Reaction of $FeCl_3$ with Polyacetylene, $(CH)_x$, and Poly-(*p*-phenylene), $(p\text{-}C_6H_4)_x$

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Summary Films of the polymer semiconductor polyacetylene, $(CH)_x$, and powders of the polymer semiconductor poly-(*p*-phenylene), $(p\text{-}C_6H_4)_x$, when treated with $FeCl_3$ (dissolved in dry nitromethane), are converted into organic metals which exhibit high p-type conductivity due to the oxidation of the π-system of the polymers, with the concomitant complete reduction of Fe^{3+} to Fe^{2+}, as evidenced by Mössbauer spectroscopy.

It has been shown that the polymer semiconductors polyacetylene, $(CH)_x$, and poly-(*p*-phenylene), $(p\text{-}C_6H_4)_x$, can be doped with electron-donating or electron-accepting species to give materials which exhibit n- or p-type conductivity at semiconductor or metallic levels, dependent on the concentration of the dopant. To date, three general classes of acceptor-type (p-type) dopants have been established for $(CH)_x$ *i.e.* protonic acids,[1] main group halides,[2] and halogens.[3] We report a new class of p-type dopants which convert $(CH)_x$ and $(p\text{-}C_6H_4)_x$ into organic metals; namely, the transition-metal halides.

The reaction of $FeCl_3$, dissolved in rigorously dried nitromethane, with $(CH)_x$ occurs within a few minutes at room temperature. The excess of $FeCl_3$ was washed off the film with pure nitromethane. The resultant films were golden and underwent a slow change in conductivity and appearance upon exposure to air.

The i.r. spectra of polyacetylene lightly doped with $FeCl_3$ show the two expected new bands at ν 1370 and *ca.* 900 cm^{-1}, characteristic of all dopants.[4] On the addition of further dopant, $(CH)_x$ became opaque to the i.r. spectrum. *X*-Ray diffraction patterns show a significant increase in the inter-chain distance, from 3·8 Å in undoped $(CH)_x$ to *ca.* 7·9 Å in the heavily doped film of composition $[CH(FeCl_3)_{0\cdot12}]_x$. Room temperature Mössbauer spectra show a doublet with quadrupole splitting of E_q 2·38 ± 0·10 mm s^{-1} and an isomer shift of 1·15 ± 0·10 mm s^{-1}, characteristic of Fe^{2+} high-spin complexes. The most common high-spin Fe^{2+} halide complex is $FeCl_4^{2-}$ which is known to be stabilized by large countercations.[5] The quadrupole splitting and the isomer shift characteristic of $FeCl_4^{2-}$ vary with the size of the counterion. The value reported herein is in the range of the values observed for large cations[5] which is consistent with the polymeric nature of the polycarbonium cation. We can, therefore, conclude that $FeCl_4^{2-}$ is the dopant species in the highly conductive polymer. Further support for this conclusion is given by the elemental analysis which shows the empirical formula $[CH_{1\cdot05}(FeCl_{3\cdot65})_{0\cdot11}]_x$ for the film doped to saturation. Lack of nitrogen in the elemental analysis indicates that no neutral solvent molecules are incorporated into the sample.

The room temperature conductivity values for $(CH)_x$ doped with different amounts of $FeCl_3$ are listed in the Table.

TABLE. Room-temperature conductivity of $[CH(FeCl_3)_y]_x$ and $[p\text{-}C_6H_4(FeCl_3)_y]_x$.

Compound	Conductivity[a] (ohm^{-1} cm^{-1})
$[CH(FeCl_3)_{0\cdot10}]_x$[b,c]	7·8 × 10^2
$[CH(FeCl_3)_{0\cdot08}]_x$[b,c]	4·6 × 10^2
$[p\text{-}C_6H_4(FeCl_3)_{0\cdot157}]_x$[d,e]	0·31

[a] Measured by the pressure-contact 4-probe method. [b] Measured on films. [c] Composition determined by mass uptake. [d] Measured on pressed pellets. [e] Composition determined by elemental analysis.

Similar reactions with dopants occur in the case of $(p\text{-}C_6H_4)_x$ and convert the non-conductive poly-(*p*-phenylene) powder into a black conductive material. The reaction is more complex than in the case of polyacetylene. The Mössbauer spectrum of heavily doped poly-(*p*-phenylene) shows the existence of high-spin Fe^{2+} ions in two distinct chemical forms with different Mössbauer parameters; the parameters of the main species are, however, similar to those of polyacetylene doped with $FeCl_3$. Chemical analysis shows an Fe to Cl ratio of 1:3. *X*-Ray diffraction studies of $(p\text{-}C_6H_4)_x$ doped to the metallic level show the disappearance of all peaks characteristic of undoped $(p\text{-}C_6H_4)_x$ and the absence of new peaks, which indicates a large crystalline disorganization in the doped material, as previously reported with AsF_5 as the dopant.[6]

The results obtained for $(CH)_x$ and $(p\text{-}C_6H_4)_x$ unequivocally show that the complete reduction of Fe^{3+} to Fe^{2+} and the concomitant oxidation of the π-system of the polymers occur, possibly as in a reaction of type (1).

$$2\,FeCl_3 + 2\,e = FeCl_4^{2-} + FeCl_2 \qquad (1)$$

The reaction of $FeCl_3$ with $(CH)_x$ and $(p\text{-}C_6H_4)_x$ is significantly different from the reaction observed in the case of graphite,[7] since in the latter case $FeCl_3$ retains its coordination and only a partial charge-transfer occurs to give $C_n^{\delta+}(FeCl_3)^{\delta-}$.

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