

'Organic Metals.' Reaction of FeCl₃ with Polyacetylene, (CH)_x, and Poly-(*p*-phenylene), (*p*-C₆H₄)_x

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Summary Films of the polymer semiconductor polyacetylene, (CH)_x, and powders of the polymer semiconductor poly-(*p*-phenylene), (*p*-C₆H₄)_x, when treated with FeCl₃ (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 Fe³⁺ to Fe²⁺, as evidenced by Mössbauer spectroscopy.

It has been shown that the polymer semiconductors polyacetylene, (CH)_x, and poly-(*p*-phenylene), (*p*-C₆H₄)_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*-C₆H₄)_x into organic metals; namely, the transition-metal halides.

The reaction of FeCl₃, dissolved in rigorously dried nitromethane, with (CH)_x occurs within a few minutes at room temperature. The excess of FeCl₃ 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 FeCl₃ 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 $[\text{CH}(\text{FeCl}_3)_{0.12}]_x$. Room temperature Mössbauer spectra show a doublet with quadrupole splitting of E_Q $2.38 \pm 0.10 \text{ mm s}^{-1}$ and an isomer shift of $1.15 \pm 0.10 \text{ mm s}^{-1}$, 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 counteranions.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 cations⁵ 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 $[\text{CH}_{1.05}(\text{FeCl}_{3.65})_{0.11}]_x$ 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 $(\text{CH})_x$ doped with different amounts of FeCl_3 are listed in the Table.

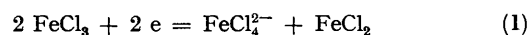
TABLE. Room-temperature conductivity of $[\text{CH}(\text{FeCl}_3)_y]_x$ and $[p\text{-C}_6\text{H}_4(\text{FeCl}_3)_y]_x$.

Compound	Conductivity ^a ($\text{ohm}^{-1} \text{ cm}^{-1}$)
$[\text{CH}(\text{FeCl}_3)_{0.10}]_x$ ^{b,c}	7.8×10^2
$[\text{CH}(\text{FeCl}_3)_{0.08}]_x$ ^{b,c}	4.6×10^2
$[p\text{-C}_6\text{H}_4(\text{FeCl}_3)_{0.157}]_x$ ^{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 $(p\text{-C}_6\text{H}_4)_x$ and convert the non-conductive poly- $(p\text{-phenylene})$ powder into a black conductive material. The reaction is more complex than in the case of polyacetylene. The Mössbauer spectrum of heavily doped poly- $(p\text{-phenylene})$ 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 $(p\text{-C}_6\text{H}_4)_x$ doped to the metallic level show the disappearance of all peaks characteristic of undoped $(p\text{-C}_6\text{H}_4)_x$ 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 $(\text{CH})_x$ and $(p\text{-C}_6\text{H}_4)_x$ 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).



The reaction of FeCl_3 with $(\text{CH})_x$ and $(p\text{-C}_6\text{H}_4)_x$ 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 $\text{C}_n^{\delta+}(\text{FeCl}_3)^{\delta-}$.

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