

Electrical Properties of Polyacetylene Doped with Dihydrogen Hexachloroiridate

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Polyacetylene has been doped from solution (nitromethane) with dihydrogen hexachloroiridate ($\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$) to form an electrically conductive complex.

Polyacetylene can be rendered electrically conductive when exposed to electron-donating or electron-accepting species. Initially, electron acceptors such as I_2 , AsF_5 , and H_2SO_4 were investigated owing to their strong oxidizing ability.^{1,2} More recently, however, it has been reported that transition-metal halides, such as FeCl_3 , also effectively oxidize the π -system of polyacetylene resulting in a highly conductive polymer.³ We have found that transition-metal salts of the third series (*i.e.*, Ir and Os) can be used as dopants for polyacetylene. In this paper, we report on the electrical properties of polyacetylene doped with the transition-metal salt dihydrogen hexachloroiridate ($\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$).

The polyacetylene used was prepared according to the method of Wnek *et al.*⁴ X-Ray diffraction and scanning electron micrograph studies showed that the films as prepared are polycrystalline with a fibrillar morphology.⁵ All doping experiments were carried out on 80–95% *cis*-materials as shown by their i.r. spectra. Doping was accomplished by immersing a polymer film in a solution consisting of 1 g of $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ dissolved in 100 ml of dry nitromethane. The extent of doping was controlled by the exposure time. All manipulations were carried out in an inert atmosphere. Conductivity measurements were made with standard four-point probe techniques.

When polyacetylene, $(\text{CH})_x$, is exposed to a solution of $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ in nitromethane, the electrical conductivity of the polymer increases sharply over seven orders of magnitude to a maximum value of *ca.* 2000 S/m. The electrical conductivity as a function of dopant concentration is shown in Figure 1. It is evident from Figure 1 that there is a distinct transition occurring at the 1–2% dopant level. Thus, at concentrations below this critical concentration (y_c), the conductivity is strongly dependent on the dopant concentration, whereas at

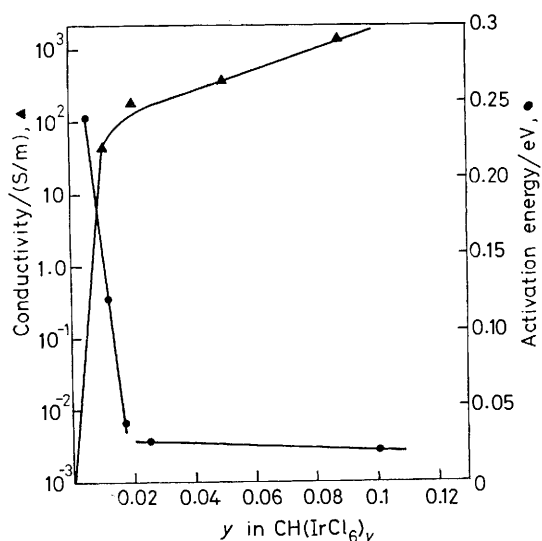


Figure 1. Electrical conductivity and activation energy of polyacetylene as a function of dopant concentration, y , in $\text{CH}(\text{IrCl}_6)_y$.

concentrations above y_c , the conductivity is only weakly dependent on the dopant concentration.

In order to determine the nature of this transition (*i.e.*, whether it is a semiconductor–metal transition), we have examined the temperature dependence of the conductivity of polyacetylene samples doped with various concentrations of the iridium salt. Since the plots of $\log(\text{conductivity})$ vs. $1/T$ give straight line behaviour near room temperature, the

approximate thermal activation energy, E_a , can be determined by the initial slope of the $1/T$ plots. It should be noted, however, that the best fit for the temperature dependence data was obtained for the relationship $\log(\text{resistivity}) \propto T^{-1/2}$.⁶ This behaviour has also been observed in AsF_5 -doped polyacetylene and is attributed to charging energy-limited tunnelling in which charge carriers tunnel between conducting islands as described in the model of Sheng.^{7,8}

The activation energy as a function of dopant concentration is also represented in Figure 1. These data also revealed a transition occurring between $y = 0.01$ and $y = 0.02$. At concentrations below $\text{CH}(\text{IrCl}_6)_{0.01}$, the conductivity is highly activated with the activation energy being strongly dependent on the dopant concentration. At concentrations above $\text{CH}(\text{IrCl}_6)_{0.01}$, on the other hand, the conductivity is only weakly activated, ranging from 0.05 to 0.02 eV. Although this transition implies a change in the transport mechanism such as in a semiconductor-metal transition, the highly doped samples do not exhibit true metallic behaviour as shown by their low conductivities (compared to metals) and the residual activation energy. However, interfibril contacts could play a limiting role in the activation energy at high doping levels.⁹ Similar results have been obtained for iodine-doped polyacetylene, which is believed to be only just on the verge of metallic behaviour.⁹

It has been assumed in the previous discussion that the dopant was present in the polymer as $\text{CH}(\text{IrCl}_6)_y$ (y determined by weight uptake). Elemental analyses, however, revealed that the actual composition of the doped polymer is $\text{CH}(\text{IrCl}_{5-5.5})_y(\text{H}_2\text{O})_w$ [the ratio of w to y was about 7:1 as indicated by the following composition, $\text{CH}(\text{IrCl}_{5.35})_{0.011}(\text{H}_2\text{O})_{0.075}$]. The incorporation of oxygen in the form of coordinated H_2O or as the H_3O^+ ion has been reported for a number of dopants that contain hydrolysable halogen.¹⁰ Therefore, it is possible that the actual doping species may take the form $(\text{H}_3\text{O})_2^+(\text{IrCl}_5\text{OH})^{2-}$, which would be analogous to protonic acid dopants; however, the exact nature of the doping species has yet to be elucidated, and therefore is highly speculative.

The i.r. spectra of polyacetylene lightly doped with the iridium salt revealed the presence of two new bands at 1380

and 900 cm^{-1} . These two additional absorptions have been observed in other lightly doped polyacetylene systems and are characteristic of all dopants.¹¹ At higher dopant concentrations $(\text{CH})_x$ became opaque in the i.r. part of the spectrum.

The use of transition-metal salts of the third series as dopants was also extended to the dihydrogen salt of hexachloro-osmiate ($\text{H}_2\text{OsCl}_6 \cdot 6\text{H}_2\text{O}$). The conductivities thus obtained were comparable to those for polyacetylene films doped with the iridium salt; for example, $\text{CH}(\text{OsCl}_6)_{0.01}$ and $\text{CH}(\text{IrCl}_6)_{0.01}$ both had conductivities of about 70 S/m.

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