Doping of $(CH)_x$ Films to the Metallic State with Xenon Fluorides and Iodine Pentafluoride

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Summary Conductivity measurements have shown that exposure of *cis*-rich $(CH)_x$ film to the vapour of $XeOF_4$, XeF_2, or IF_5 causes it to be doped to the metallic regime.

BOTH IF_5 and $XeOF_4$ have been shown to form intercalation compounds with graphite.[1] More recent experiments on the intercalation of $XeOF_4$ into highly oriented pyrolytic graphite (HOPG)[2] have shown striking parallels between the series of intercalation compounds $C_{8n}XeOF_4$ and $C_{8n}AsF_5$ (n = stage), although the exact nature of the intercalated species is still uncertain. Both series of compounds show substantial increases in their a-plane electrical conductivities over that of graphite. The changes in electrical conductivity of polyacetylene films, $(CH)_x$, upon doping with AsF_5[3] are even more dramatic than those in graphite, increasing the conductivity by *ca.* 12 orders of magnitude from the semiconductor regime (10^{-9} Ω^{-1} cm^{-1}) in *cis*-$(CH)_x$ to the metallic regime (10^3 Ω^{-1} cm^{-1}). Baughman has suggested that doped polyacetylene forms layered structures analogous to those for intercalated graphite.[4] The close correspondence between these systems has prompted us to dope $(CH)_x$ with $XeOF_4$, XeF_2, and IF_5.

The polyacetylene used had a *cis* content of approximately 67% as determined by i.r. intensity measurements.[5] Samples were cemented with Electrodag to two Pt electrodes in an all-Kel-F reactor,[6] or pressed into a 4-point jig in a similar reactor. Additional samples of $(CH)_x$ were kept in close proximity to the electrodes for parallel weight-uptake measurements. The resistance of the films was measured by either the two-point or four-point method as doping progressed. The $(CH)_x$ was exposed to constant vapour pressures of $XeOF_4$ or IF_5 by maintaining a reservoir of these at a fixed temperature. Best results were obtained by keeping the Kel-F reactor at about -15 °C and the dopants at -23 °C (CCl_4 slush). The vapour pressures of $XeOF_4$[7] and IF_5[8] at the latter temperature are *ca.* 1·5 and 0·4 Torr, respectively.

Polyacetylene film spontaneously inflamed on contact with *liquid* $XeOF_4$. Hence, all doping experiments using $XeOF_4$ involved exposure to the vapour only. For samples of $(CH)_x$ about 0·06 mm thick, the resistance dropped within seconds of initial exposure to $XeOF_4$ from $> 2 \times 10^7$ Ω to 10^5 Ω and after 1 h exposure to 130 Ω. Another sample attained a constant resistance of 12 Ω after 10 h. Upon pumping of the sample the resistance rose to 17 Ω. The corresponding conductivity of the film is 50 Ω^{-1} cm^{-1}. Parallel weight measurements indicated a stoicheiometry of $[CH(XeOF_4)_{0\cdot025}]_x$ assuming the weight uptake is due to $XeOF_4$ only. The conductivity corresponds to that of a $[CH(AsF_5)_y]_x$ sample of similar composition.[3] Polyacetylene films doped with $XeOF_4$ show the typical golden colour observed with other dopants.

Preliminary experiments involving XeF_2 gave a maximum conductivity of 70 Ω^{-1} cm^{-1} which, however, decreased rapidly upon pumping to $<10^{-4}$ Ω^{-1} cm^{-1} to give a final light blue product of empirical composition $[CH_{0\cdot90}(XeF_2)_{0\cdot045}F_{0\cdot36}]_x$. Since the ratio of Xe : F in the product is 1 : 10 it is apparent that significant fluorination of the $(CH)_x$ had occurred.

The changes in resistivity of $(CH)_x$ exposed to IF_5 are even more striking. Immediately upon exposure the resistance drops from $>2 \times 10^7$ Ω to several hundred ohms. The lowest resistance observed for a 0·12 mm thick film doped with IF_5 was 1·7 Ω after four hours, corresponding

to a conductivity of $150\ \Omega^{-1}\ cm^{-1}$. Polyacetylene films doped with IF_5 exhibit a metallic blue colour somewhat similar to that of HOPG intercalated with AsF_5 or $XeOF_4$.

The increase in weight of the reaction vessel after doping was used to calculate the molar ratio in which $(CH)_x$ and IF_5 underwent reaction. In two different experiments the $(CH)_x$ to IF_5 ratios were 1·00 : 0·10 and 1·00 : 0·094, respectively. These ratios do not, however, give the true composition of the doped $(CH)_x$ since free iodine could be observed in the reaction vessel after doping. After pumping for several hours to remove the free iodine, elemental analyses for C, H, I, and F gave compositions of $[CH(IF_{5\cdot27})_{0\cdot091}]_x$ and $[CH(IF_{5\cdot63})_{0\cdot096}]_x$. The composition of these materials bears a striking resemblance to that of $(CH)_x$ doped with AsF_5 where compositions from analytical data ranging from $[CH(AsF_5)_{0\cdot1}]_x$ to $[CH(AsF_6)_{0\cdot1}]_x$ with a variety of intermediate values have been obtained.[9] The primary reaction between $(CH)_x$ and IF_5 might possibly be analogous to one of the reactions proposed between $(CH)_x$ and AsF_5 where partial reduction of the MF_y species[10] with concomitant oxidation of $(CH)_x$ occurs [*e.g.* equation (1)].

$$3\ IF_5 + 2\ e^- \rightarrow 2\ IF_6^- + IF_3 \qquad (1)$$

The energetically most favoured decomposition reaction for the thermodynamically unstable IF_3 is given in equation (2).[11] If this occurs to give free iodine the doped polymer,

$$5\ IF_3 \rightarrow I_2 + 3\ IF_5 \qquad (2)$$

therefore, contains both IF_6^- and IF_5, the latter species possibly existing in the form of a weak complex. The IF value intermediate between 5 and 6 in the final product is therefore understandable. This would be basically analogous to the case of C_8AsF_6 which is proposed to consist of a mixture of AsF_6^-, AsF_5, and AsF_3.[12] Upon pumping, the conductivity of the IF_5-doped material decreases gradually. Since such samples retain their fluorine content, it appears that the iodine fluoride dopant gradually fluorinates the $(CH)_x$.

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