

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 XeOF₄, XeF₂, or IF₅ causes it to be doped to the metallic regime.

BOTH IF₅ and XeOF₄ have been shown to form intercalation compounds with graphite.¹ More recent experiments on the intercalation of XeOF₄ into highly oriented pyrolytic graphite (HOPG)² have shown striking parallels between the series of intercalation compounds C_{8n}XeOF₄ and C_{8n}AsF₅ (*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 AsF₅³ 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 (10³ 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 XeOF₄, XeF₂, and IF₅.

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 XeOF₄ or IF₅ 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 (CCl₄ slush). The vapour pressures of XeOF₄⁷ and IF₅⁸ at the latter temperature are *ca.* 1.5 and 0.4 Torr, respectively.

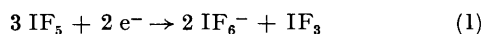
Polyacetylene film spontaneously inflamed on contact with *liquid* XeOF₄. Hence, all doping experiments using XeOF₄ involved exposure to the vapour only. For samples of (CH)_x about 0.06 mm thick, the resistance dropped within seconds of initial exposure to XeOF₄ from > 2 × 10⁷ Ω to 10⁵ Ω and after 1 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 stoichiometry of [CH(XeOF₄)_{0.025}]_x assuming the weight uptake is due to XeOF₄ only. The conductivity corresponds to that of a [CH(AsF₅)_{0.025}]_x sample of similar composition.³ Polyacetylene films doped with XeOF₄ show the typical golden colour observed with other dopants.

Preliminary experiments involving XeF₂ 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_{0.90}(XeF₂)_{0.045}F_{0.36}]_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.

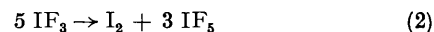
The changes in resistivity of (CH)_x exposed to IF₅ are even more striking. Immediately upon exposure the resistance drops from > 2 × 10⁷ Ω to several hundred ohms. The lowest resistance observed for a 0.12 mm thick film doped with IF₅ was 1.7 Ω after four hours, corresponding

to a conductivity of $150 \Omega^{-1} \text{cm}^{-1}$. 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 $(\text{CH})_x$ and IF_5 underwent reaction. In two different experiments the $(\text{CH})_x$ 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 $(\text{CH})_x$ 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 $[\text{CH}(\text{IF}_{5.27})_{0.091}]_x$ and $[\text{CH}(\text{IF}_{5.63})_{0.096}]_x$. The composition of these materials bears a striking resemblance to that of $(\text{CH})_x$ doped with AsF_5 where compositions from analytical data ranging from $[\text{CH}(\text{AsF}_5)_{0.1}]_x$ to $[\text{CH}(\text{AsF}_6)_{0.1}]_x$ with a variety of intermediate values have been obtained.⁹ The primary reaction between $(\text{CH})_x$ and IF_5 might possibly be analogous to one of the reactions proposed between $(\text{CH})_x$ and AsF_5 where partial reduction of the MF_y species¹⁰ with concomitant oxidation of $(\text{CH})_x$ occurs [*e.g.* equation (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,



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 $(\text{CH})_x$.

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