

The Role of AsF₅ in Modifying the Electrical Properties of Polyacetylene, (CH)_x

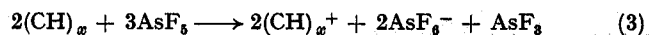
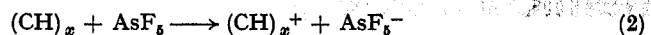
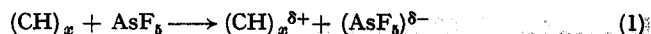
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Summary In contrast to previous results we present evidence that AsF₅ reacts with polyacetylene to oxidize the (CH)_x chains, in analogy with other acceptors, and to form AsF₆⁻ anions, which intercalate between the polyolefinic cation chains.

demonstrated by Bartlett *et al.*⁴ for AsF₅-graphite intercalation compounds. Preliminary X-ray absorption data for AsF₅ treated (CH)_x are presented in the Figure, details

THREE principal mechanisms may be considered for the reaction of AsF₅ with (CH)_x leading to the dramatic increase in electrical conductivity¹ which spans the range from insulator to metal depending upon the extent of AsF₅ uptake. These mechanisms are summarized in reactions (1)–(3).



Elemental analysis² and photoelectron spectroscopy³ have provided evidence which has been interpreted in terms of reaction (1) or (2) in which the AsF₅ unit remains intact.

In this communication we present X-ray absorption, *i.r.*, and other evidence for the third mechanism summarized in reaction (3). This mechanism is closely analogous to that

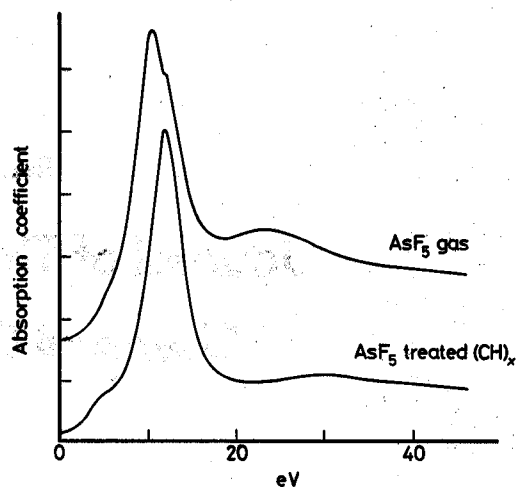


FIGURE. X-Ray absorption spectrum of AsF₅ treated (CH)_x.

of which will be published elsewhere.⁵ The Figure shows As K-edge absorption data for polyacetylene containing ca. 10 atom % of As; similar absorption data for AsF₅ gas are also shown for comparison. The 1.4 eV shift between the AsF₅ gas and the arsenic species in (CH)_x is identical to that reported for AsF₆⁻ in graphite. In addition, the shoulder located 0.7 eV below the AsF₆⁻ peak in doped polyacetylene occurs in the same position as the peak identified by Bartlett *et al.* as AsF₃. Detailed calculations of the various excitonic transitions in AsF₅, AsF₃, and AsF₆⁻ have been performed and will be published elsewhere.⁶ The calculations suggest a core level structure broadened by core hole lifetime and instrumental broadening which may complicate the simple interpretation given here. The relatively weaker As³⁺ excitonic features are consistent with our observation that AsF₃ vapour is only weakly bonded to (CH)_x and may be removed by pumping.⁷ The presence of AsF₆⁻ in the AsF₅ treated (CH)_x has been confirmed by i.r. transmission on thin films and also by reflection studies on thicker films. Both sets of data show strong peaks at 696 and 393 cm⁻¹ characteristic of AsF₆⁻.

Thus our model involves intercalation of AsF₆⁻ ions between the (CH)_x chains in a similar manner to that described by Hsu *et al.*⁸ for iodine treated (CH)_x. The

separation of the (100) planes increases from 7.60 to 8.83 Å on intercalation⁹ indicating a van der Waals diameter of 4.98 Å for AsF₆⁻. Despite this increase in unit cell volume, scanning electron microscopy shows that the dimensions of individual fibres of (CH)_x do not change on treatment with AsF₅. Although polyacetylene films have been shown to have a flotation density close to theoretical,¹⁰ it must be assumed that the individual fibres are not single crystals but contain significant voids to allow the observed unit cell expansion without exhibiting macroscopic changes in dimensions. Electron diffraction studies confirm that the fibres are not single crystals. Simple calculation shows that the maximum AsF₆⁻ which could be accommodated in a monolayer around the outside of the 200 Å fibres would correspond to a composition CH(AsF₆)_{0.02}. The observation of significantly higher doping levels is consistent with the intercalation model presented above.

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