The Role of AsF$_3$ in Modifying the Electrical Properties of Polyacetylene, (CH)$_x$

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Summary In contrast to previous results we present evidence that AsF$_3$ reacts with polyacetylene to oxidize the (CH)$_x$ chains, in analogy with other acceptors, and to form AsF$_3^{-}$ anions, which intercalate between the polyolefinic cation chains.

Three principal mechanisms may be considered for the reaction of AsF$_3$ with (CH)$_x$ leading to the dramatic increase in electrical conductivity which spans the range from insulator to metal depending upon the extent of AsF$_3$ uptake. These mechanisms are summarized in reactions (1)–(3).

1. (CH)$_x$ + AsF$_3$ $\rightarrow$ (CH)$_x$$^+$ + (AsF$_3$)$^-$
2. (CH)$_x$ + AsF$_3$ $\rightarrow$ (CH)$_x$$^+$ + AsF$_3$$^-$
3. 2(CH)$_x$ + 3AsF$_3$ $\rightarrow$ 2(CH)$_x$$^+$ + 2AsF$_3$$^-$ + AsF$_3$

Elemental analysis and photoelectron spectroscopy have provided evidence which has been interpreted in terms of reaction (1) or (2) in which the AsF$_3$ 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 demonstrated by Bartlett et al. for AsF$_3$-graphite intercalation compounds. Preliminary X-ray absorption data for AsF$_3$ treated (CH)$_x$ are presented in the Figure, details

FIGURE. X-Ray absorption spectrum of AsF$_3$ treated (CH)$_x$. 
of which will be published elsewhere.5 The Figure shows As $K$-edge absorption data for polycetylene containing ca. 10 atom % of As; similar absorption data for AsF$_3$ gas are also shown for comparison. The 1.5 eV shift between the AsF$_3$ peak in doped polycetylene occurs in the same position as the peak identified by Bartlett et al. as AsF$_3$ in graphite. Detailed calculations of the various excitonic transitions in AsF$_6$, AsF$_5$, and AsF$_4$ 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 As$^{+5}$ exciton features are consistent with our observation that AsF$_3$ vapour is only weakly bonded to (CH)$_n$ and may be removed by pumping.7 The presence of AsF$_3^-$ in the AsF$_3$ treated (CH)$_n$ 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 AsF$_3^-$.

Thus our model involves intercalation of AsF$_3^-$ ions between the (CH)$_n$ chains in a similar manner to that described by Hsu et al.8 for iodine treated (CH)$_n$. 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 AsF$_3^-$. Despite this increase in unit cell volume, scanning electron microscopy shows that the dimensions of individual fibres of (CH)$_n$ do not change on treatment with AsF$_3$. Although polycetylene 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 AsF$_3^-$ which could be accommodated in a monolayer around the outside of the 200 Å fibres would correspond to a composition CH(AsF$_3$/As$_2$). The observation of significantly higher doping levels is consistent with the intercalation model presented above.

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