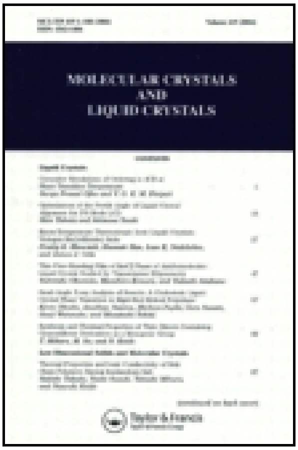

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Doped Polyacetylenes and Graphite Intercalation Compounds

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To cite this article: Denis Billaud & Dominique Begin (1985): Doped Polyacetylenes and Graphite Intercalation Compounds, Molecular Crystals and Liquid Crystals, 117:1, 103-106

To link to this article: http://dx.doi.org/10.1080/00268948508074605

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 103-106
0026-8941/85/1174-0103/$10.00/0

Printed in the United States of America

DOPED POLYACETYLENES AND GRAPHITE INTERCALATION COMPOUNDS

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Abstract Doped polyacetylenes and intercalated graphites are compared. Mechanisms of doping of both materials are related to the intercalation potentials and to the nature of the dopants. Inhomogeneity of doping in $(CH)_x$ and existence of stages of intercalation is discussed.

INTRODUCTION

Doped polyacetylenes and intercalated graphites are frequently compared. However, if certain analogies exist concerning the techniques of doping or the nature of the intercalants, many differences have to be pointed out : dimensionality, cristallinity ; some points, like the formation of stages upon intercalation of electroacceptors into polyacetylene, remain to be checked carrefully. This paper will discuss on some of these aspects.

Electrical Conductivity

In plane conductivity of semimetallic graphite (HOPG) increases upon intercalation with electroacceptors from ca 25.10^3 S/cm to ca 5.10^5 S/cm whereas the anisotropy ratio σ / σ_0 changes concomitantly from ca 10^3 to ca 10^6 ; thus the 2D-character of graphite is largely enhanced after p-type intercalation.

Starting polyacetylenes exist in two isomeric configurations: cis and trans. Due to the fibrillar morphology of PA, the actual 1D-conductivity is difficult to measure. However, bulk measurements indicate that the conductivity changes, after doping, from ca 10^{-9} S/cm for the cis form or ca 10^{-5} S/cm for the trans form, up to ca 10^3 S/cm. Moreover, depending on the dopant concentration, various conduction regimes have been observed and a semiconductor-metal transition occurs at a doping level close to 1 %.

Intercalation Potentials

As seen in electrochemical oxidation curves, the potential edges of p-intercalation are ca 3,2 and ca 4,4 volts vs Li/Li^+ for polyacetylene and graphite respectively [1,2,3]. It means that the intercalation is easier to obtain in polyacetylene than in graphite and therefore a larger number of chemical species is able to be intercalated in polyacetylene than in graphite.

Mechanism of Intercalation

Intercalation can be obtained by chemical or electrochemical ways. Depending on the oxidizing power of the dopant, the mechanism of intercalation can be different in $(CH)_x$ and graphite.

For example, in the case of chemical HNO_3 doping it is assumed that NO_2^+ is the oxidizing species of $(CH)_x$ and graphite :

$$2\ HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_2O$$

The positive charge of the macrocations formed is compensated by the negative charge of NO_3^-. The formula of the doped $(CH)_x$ can be written $|(CH)^+(NO_3^-)_y|_x$ compared to the intercalation compound $C_{5n}HNO_3$ where the NO_3 groups are placed to form two adjacent layers between the sheets of carbon [4,5].

Contrary to HNO_3, $FeCl_3$ reacts differently with $(CH)_x$ and graphite. Thus, $(CH)_x$ is directly oxidized with $FeCl_3$ dissolved in CH_3NO_2 as follows [6] :

$$\begin{array}{lcl} 2xyFeCl_3 + xye^- & \rightarrow & xyFeCl_2 + xyFeCl_4^- \\ (CH)_x & \rightarrow & |(CH)^{y+}|_x + xye^- \\ \hline (CH)_x + 2xyFeCl_3 & \rightarrow & |(CH)^{y+}(FeCl_4^-)_y|_x + xyFeCl_2 \end{array}$$

Existence of extra chlorine is needed to get $FeCl_3$ intercalation into graphite. The intercalation compound obtained has the admitted formula $C_{6n}(FeCl_3)$ where the $FeCl_3$ intercalated layers have the same structure as in bulk $FeCl_3$ [7].

Anions X^- ($X^- = PF_6^-$, AsF_6^-, ClO_4^-) can be introduced into $(CH)_x$ and graphite by electrochemical ways using their lithium salts dissolved in selected solvents, nitromethane CH_3NO_2 for example [2,8]. The richest compounds obtained have the formulae $|CH(X)_{0.06}|_x$ and $C(X)_{0.04}(CH_3NO_2)_{0.08}$. It appears that X^- anions intercalated into graphite are solvated and that the interchain space in $(CH)_x$ is not so filled than the interlayers of graphite. Moreover, the potential-charge curves in the case of $(CH)_x$ shows only one doping plateau contrary to what is observed during the intercalation into graphite where the different plateaux are characteristic of the existence of various stages of intercalation [9].

Morphology and Structure

$(CH)_x$ films prepared by Ito's method [10] are made of a mat of randomly oriented fibrils the diameter of which varying from 500 to 1000 Å. The X-ray crystallinity is generally in the range 75-90 % for both cis and trans isomers which have the 2D-Pgg space group (a = 7.6 Å, b = 4.4 Å for cis-$(CH)_x$; a = 7.4 Å, b = 4.1 Å for trans $(CH)_x$).

Cis-$(CH)_x$ belongs to the 3D-orthorhombic space group Pnam whereas trans-$(CH)_x$ has a monoclinic symmetry with the following groups $P2_{1/b}$ or $P2_{1/n}$ depending on the phase of the bond alternation on the two chains of the unit cell [11]. It has been shown that intercalation of electrodonors or electroacceptors into graphite proceeds via formation of well defined stages [12].

The existence of several stages has been evidenced in $(CH)_x$ doped with alkali metals [13]. The situation is not so clear in the case of p-doping of $(CH)_x$. It has been recently suggested that iodine doping of $(CH)_x$ can lead to the formation of stage 3 and stage 1 compounds depending on the dopant concentration [14]. But the discovery by using diffraction techniques of various stages in other $(CH)_x$ doped with ClO_4^-, $FeCl_4^-$ failed up to now [15]. The latter compounds, when lightly doped, present a mixture of highly doped and undoped trans-$(CH)_x$ parts. In highly doped regions, the dopant is introduced between the chains of $(CH)_x$. The interchain distance is increased according to the size of the dopant[15,16] like in graphite. However, because of the different natures of the intercalants, the comparison between the interplanar distances in graphite and the interchain distances in $(CH)_x$ is not possible.

CONCLUSIONS

Identical chemical or electrochemical techniques are used for intercalation into $(CH)_x$ and graphite. However, if the mechanisms of oxidation of both materials are comparable, the nature of doped materials shows many differences due to the lack of long range crystallinity in $(CH)_x$ and the existence of two $(CH)_x$ isomers ; the evidence of stages of intercalation in p-doped $(CH)_x$ remains to be checked and needs further studies effected on homogeneously doped and highly crystallized materials. The highest doping levels are different in $(CH)_x$ and graphite and in the latter case, the solvation of anions leeds to more filled interlayer spaces. Low temperature measurements are needed to check if the ordering of the intercalated layer occurs in $(CH)_x$ as it was noticed in graphite.

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