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STRUCTURE OF ALKALI-METAL-DOPED POLYACETYLENE

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Abstract The crystal structures of Li, Na, K and Cs doped $(CH)_x$ have been determined by X-ray diffraction and crystal packing analyses. The intercalation model, already proposed for iodine doping, is shown to account for the X-ray data.

INTRODUCTION

Due to the lack of single crystals and the limited number of observable X-ray diffraction lines, the structure of polyacetylene, and especially of doped materials, is not well known. Nevertheless, following the work of FINCHER et al. (1), a consensus in now established for the structure of pristine trans $(CH)_x$. The unit cell is monoclinic with parameters a = 4,24 Å, b = 7,32 Å, c = 2,46 Å and β = 91,5°. The chains lie in the (ac) plane (chain axis along c) and form layers perpendicular to b-axis, with a ABA stacking, like the carbon layers in graphite (2). This structural similarity, reinforced by many others concerning the doping of both materials, led to the proposal of an intercalation model for $(CH)_x$ doped with acceptors : the dopant species would be intercalated between the planes formed by polymer chains. This model, first proposed by BAUGHMAN et al. (3) and confirmed by ourselves in the case of iodine doping (2), can account for the observed X-ray diffraction

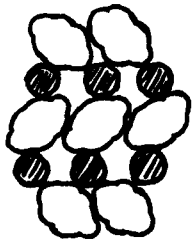

Fig. 1 : Intercalation model

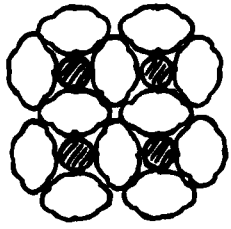

Fig. 2 : Channel model

spectra.

The structure of donor-doped $(CH)_x$, however, is controversial. In the case of sodium we observed diffraction peaks compatible with the intercalation model (2) (fig. 1). On the other hand, BAUGHMAN et al. (4) proposed a quite different model : the polyacetylene chains would form a tetragonal host lattice in which the alkali metal ions would be present in channels (fig. 2). It must be noticed that an amorphous structure was observed with lithium : it was claimed that Li is too small to stabilize the channel structure. In view of these contradictory proposals, we have undertaken a structure study of Li, Na, K and Cs doped $(CH)_x$. Our diffraction data, even for Li, are consistent with the intercalation model.

EXPERIMENTAL

Polyacetylene films were prepared by a modified Shirakawa technique. The apparent density was controlled through the monomer pressure and the thickness of catalyst layer. Experimental conditions were chosen to avoid the formation of dense shiny surface which has been shown to contain a great amount of defects (5) and prevent an homogeneous doping. Polyacetylene films were never in contact with atmosphere and the N doping was carried out in sealed glass vessels.

Doping with sodium and cesium was realized by exposing the films at room temperature to a solution of alkali metal naphtalide complex in THF. Potassium doped $(CH)_x$ was prepared by reaction with tetraphenyl 1, 1, 4, 4, butylene di potassium in THF. After doping

the films were rinsed by internal distillation of THF and dried by cryogenic pumping in liquid nitrogen for one day. In the case of lithium, we used diphenylhexyllithium in cyclohexane : a polar solvent such as THF must be avoided because the cryogenic pumping does not remove the whole THF which is coinserted in the polymer (6). The composition after doping was determined by elementary chemical analysis.

Samples were loaded in an inert atmosphere chamber into Lindeman glas tubes (Ø = 3.5 mm) and sealed for X-ray measurements. X-ray diffraction photographs were obtained in a cylindrical chamber using monochromatic Cu Kα radiation.

RESULTS

Diffraction data were obtained for heavily doped $(CH)_x$ films of composition $(CH\ Li_{0,11})_x$, $(CH\ Na_{0,148})_x$, $(CH\ K_{0,123})_x$ and $(CH\ Cs_{0,101})_x$. All samples, even in the case of lithium contrary to previous allegations, gave a number of diffraction lines (up to 17 peaks in the case of sodium). Some of them correspond to undoped polymer : like intercalated carbon fibers, where diffraction peaks of pristine graphite are always observed, the heart of the polymer fibrils remains probably undoped. An example of photograph in given in fig. 3 for $(CH\ K_{0,123})_x$.

Of particular interest is the first diffraction line observed on the photographs (first ring in fig. 3), which corresponds to the following lattice distances : 4,5 ± 0,1 Å for Li, 5,98 ± 0,05 for Na, 6,15 ± 0,05 Å for K, 6,42 ± 0,05 Å for Cs. These values are very nearly equal (for Li, K and Cs) to the repeat distance along b-axis ((020) peak) expected in an intercalation model (fig. 1) for close packing of host molecules and guest cations, using the ionic diameter of alkali metals. In the case of Na, the value is larger than expected by about 0,6 Å. This could be explained by a partial ionization of sodium (partial charge transfer) leading to a diameter intermediate between ionic and metal diameters. It is worth no-

ticing that sodium has also a particular behavior compared to other alkali metals in graphite intercalation compounds. Finally, the intercalation model allowed us to index the other diffraction peaks and calculation of diffraction intensities gave a rather good agreement with the observed intensities.

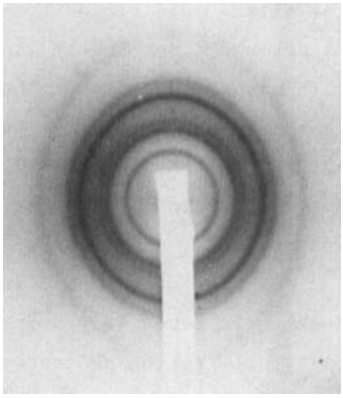

Fig. 3 : X-ray photograph obtained for $(CH\ K_{0,123})_x$

Further comparison with graphite intercalation compounds is useful. Firstly the intercalation model gives distances between alkali metals and nearest-neighbor carbon identical for $(CH)_x$ and graphite compounds. This suggests a similar type of bonding. The diffraction spectra did not give any information on the in-plane intercalant arrangement. If we assume a triangular lattice with metal-metal distance of 4,9-5,0 Å like in graphite compounds, the maximum dopant concentration is 0,25. It must be noticed, in addition, that these metal-metal distances would give commensurate metal and $(CH)_x$ lattices. Another possibility is a honeycoumb lattice which would lead to a maximum dopant level of 0,17. The experimental maximum content is around 0,20.

In conclusion, the intercalation model seems to be relevant for donor as well as for acceptor-doped $(CH)_x$.

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