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X-RAY DIFFRACTION STUDIES OF IODINE DOPED POLYACETYLENE

P. Robin*, J.P. Pouget**, R. Comès**, H.W. Gibson*** and A.J. Epstein***

*Laboratoire Central de Recherches, Thomson-CSF, Domaine de Corbeville, 91401 Orsay, France

**Laboratoire de Physique des Solides et Laboratoire pour l'utilisation du Rayonnement Electromagnétique, Université Paris-Sud, 91405 Orsay, France

***Xerox Webster Research Center, 800 Phillips, Road-W-114, Webster, New York 14580, U.S.A.

Résumé : Nous présentons une étude, par diffraction des rayons X et du rayonnement synchrotron, du polyacétyle dans ses formes cis et trans, préparé par la méthode de Shirakawa. L'étude d'échantillons lentement et rapidement dopés à l'iode confirme que des régions non dopées subsistent dans $(CH)_x$. Les régions non dopées de $(CH)_x$, initialement cis, semblent s'être isomérisées vers la structure trans $(CH)_x$ durant le processus de dopage.

Abstract : X-ray and synchrotron radiation diffraction study of the structure of cis and trans polyacetylene prepared by the Shirakawa method has been carried out. Studies of rapidly and slowly iodine doped samples confirmed that undoped regions of $(CH)_x$ remain. The undoped regions of the initially cis $(CH)_x$ are shown to isomerize to the trans structure during the doping process.

INTRODUCTION

We report here X-ray diffraction study of iodine doped cis and trans polyacetylene films. These or very similar samples have been well characterized by other physical studies including studies of the fibrillar morphology and the fibril swelling upon doping (1) (2), electric field dependent conductivity studies (3), frequency dependent conductivity studies (4), magnetic susceptibility (5) and an infrared absorption study (6).

EXPERIMENTAL

The polyacetylene films were prepared by the method of Shirakawa (7). They were 60-80 μm thick. Typical diameters of the fibril were approximately 400 to 500 Å. Trans samples were obtained from cis sample by an isomerization conducted at 200 C (refluxing tetralin vapors) for 98 minutes. Iodine doping conditions will be described elsewhere (8).

Experiments were performed with conventional $\text{MoK}\alpha$ (0.707 Å), $\text{CuK}\alpha$ (1.542 Å) X-ray radiations and with higher resolution X-ray synchrotron radiations at the station D 16 of LURE (ORSAY), using a wave length of 1.315 Å.

X-ray data were collected on photographic film fixed on a cylindrical camera with the sample placed at the center of the chamber. During all the exposure the samples were kept under vacuum. X-ray films were read in the equatorial plane of the experimental set-up, using a Joyce Loebler microdensitometer.

RESULTS

Cis samples (Figure 1-a)

d spacings deduced from the position of X-ray reflections shown by undoped cis $(CH)_x$ are given in Table I. They are in good agreement with those found by Baughman et al (9) and by Lieser et al (10).

According to the indexation performed by Baughman et al (9) and by Lieser et al (10), most of the reflections observed have a zero index in the chain direction. As a consequence, the Scherrer formula applied to their width gives transverses coherence length, i.e. perpendicular to the fibril axis. In the present case, the width of the strongest reflections gives a transverse coherence length of about 80 ± 10 Å. This value is about one fifth the average diameter of a fibril. X-ray crystallinity was estimated at about 90 % by comparing the integrated intensity of the weak and broad amorphous ring at ≈ 3.9 Å with that of Debye Scherrer rings of the crystal (see figure 1 a).

Iodine doped cis $(CH)_x$ samples (Figure 1 b)

Three new broad reflections appear upon doping. They correspond to spacings of 7.9 Å, 4.1 Å and 2.9 Å and their width gives a coherence length of 20 ± 5 Å.

In addition the sharp reflections, which were observed in undoped cis samples, remain visible and sharp in iodine doped cis $(CH)_x$ samples. However, they have shifted toward the position they occupy in trans samples : the d spacings reported at 3.65 Å, 2.13 Å and 1.83 Å for cis $(CHI_{0.099})_x$ and at 3.68 Å, 2.12 Å and 1.82 Å for cis $(CHI_{0.143})_x$ in Table I, are close to those observed at 3.72-3.56 Å, 2.12 Å and 1.87-1.79 Å in trans $(CH)_x$ (see Table II). From their width one obtained a coherence length of about 80 ± 10 Å, similar to that found in undoped cis $(CH)_x$.

Trans samples (Figure 2 a)

d spacings deduced from the position of X-ray reflections shown by undoped trans $(CH)_x$ are given in Table II. This table and figure 2 a show that the strongest reflection of cis $(CH)_x$ is now splitted in two reflections. This splitting has been already reported by Itô et al (7) and Haberkorn et al (11). Position of X-ray reflections reported in Table II, can be found using the lattice parameters of the structure of trans $(CH)_x$ given by Baughman et al (12). Such is not the case using the lattice parameter of Fincher et al (13) and Shimamura et al (14).

As in the case of cis $(CH)_x$ the transverse coherence length is of 80 ± 10 Å and the crystallinity is estimated at 90 %. Hence neither the degree of crystallinity nor the crystallite size are significantly reduced by the isomerization process(15)

Iodine doped trans $(CH)_x$ samples (Figure 2 b)

As in doped cis $(CH)_x$ samples, three new broad reflections have appeared at 7.9 Å, 4.1 Å and 2.9 Å, with a coherence length of 20 ± 5 Å.

As with doped cis $(CH)_x$ samples, figure 2 b and Table II show that sharp reflections of pure trans $(CH)_x$ remains observable in doped trans $(CH)_x$. However for the latter compound, their position does not shift upon doping. Their width gives a coherence length of about 80 ± 10 Å, similar to that found in undoped trans $(CH)_x$.

In order to estimate the amount of undoped regions in iodine doped trans $(CH)_x$, we have measured the intensity of the sharp diffraction lines in a pure trans $(CH)_x$ and in a slowly doped trans $(CHI_{0.125})_x$ obtained from the same starting film. The ratio of the two quantities shows that about 50 % of trans $(CHI_{0.125})_x$ remains undoped. This implies that the concentration of iodine in doped areas is on average $CHI_{0.25}$. A similar study of the inhomogeneous doping of cis $(CH)_x$ is more difficult because of the shift of sharp reflections of the undoped part of the sample, from their position in pure cis $(CH)_x$.

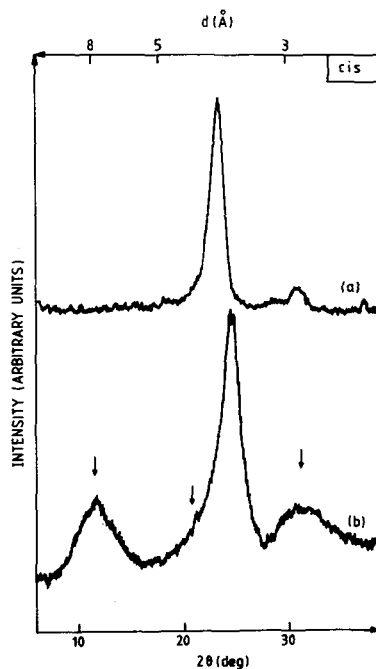


FIGURE 1

Microdensitometer readings from X-ray patterns of (a) cis $(\text{CH})_x$ and (b) slowly doped $(\text{CHI}_{0.099})_x$. Three additional broad reflections are shown by arrows. Note the shift of the sharp reflections upon doping.

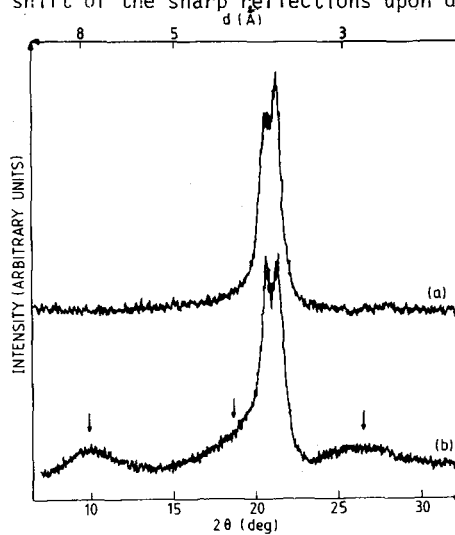


FIGURE 2

Microdensitometer readings from X-ray patterns (a) trans $(\text{CH})_x$ and (b) slowly doped trans $(\text{CHI}_{0.0449})_x$. Three additional broad reflections are shown by arrows. Note the splitting of the strongest reflection both in pure and doped trans $(\text{CH})_x$.

TABLE I

Spacing between Bragg reflection planes in \AA and intensity (S : strong, M : medium, W : weak, VW : very weak) deduced from position in reciprocal space of Debye Scherrer rings of 90 % cis $(\text{CH})_x$ and slowly doped 90 % cis $(\text{CHI}_{0,099})_x$ and 90 % cis $(\text{CHI}_{0,143})_x$. The symbol \approx in front of 3 distances of doped $(\text{CH})_x$, means that corresponding rings are broad.

Cis $(\text{CH})_x$	Cis $(\text{CH}_{0,099})_x$	Cis $(\text{CH}_{0,143})_x$
$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$
	≈ 7.9 M	≈ 7.85 M
	≈ 4.1 M	≈ 4.1 M
3.81 S	3.65 S	3.68 S
2.87 M	≈ 2.90 M	≈ 2.90 M
2.44 VW	2.23 VW	
2.20 M	2.13 W	2.12 W
2.13 VW	1.83 W	1.82 W
2.00 VW	1.49 VW	
1.90 W	1.32 VW	
1.74 W		
1.65 W		
1.50 VW		
1.36 W		
1.22 W		

TABLE II

Spacing between Bragg reflection planes in \AA , and intensity (S : strong, M : medium, W : weak) deduced from position in the reciprocal space of Debye Scherrer rings of trans $(\text{CH})_x$, slowly doped trans $(\text{CHI}_{0,0499})_x$ and slowly doped trans $(\text{CHI}_{0,125})_x$. The symbol \approx in front of 3 distances of doped $(\text{CH})_x$, means that corresponding rings are broad.

Trans $(\text{CH})_x$	Trans $(\text{CHI}_{0,0499})_x$	Trans $(\text{CHI}_{0,125})_x$
$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$
	≈ 7.9 M	≈ 7.8 M
	≈ 4.1 M	≈ 4.1 M
3.72 S	3.77 S	3.73 S
3.56 S	3.59 S	3.56 S
	≈ 2.9 M	≈ 2.9 M
2.74 W	2.78 W	
2.12 M	2.13 W	2.12 W
2.04 W	2.05 VW	
1.87 W	1.88 W	1.84 W
1.79 W	1.80 W	
1.60 W		
1.56 W		
1.38 W		
1.31 W		
1.23 W		
1.19 W		

Discussion

On the basis of the observation of the first reflections at 7.8 Å, Baughman et al (9) have suggested that iodine species intercalate in sheets between closely packed adjacent planes of polyacetylene ((100) planes using the choice of axis of ref. 9). Here we show evidence of two additional reflections at 4.1 Å and 2.9 Å confirming this periodic ordering, both in doped cis $(CH)_x$ and doped trans $(CH)_x$ (16, 17, 18).

A possible explanation for the inhomogeneous doping of our samples might be due to the very large average diameter (400-500 Å) of the $(CH)_x$ fibrils, which prevent a complete diffusion of iodine inside them during the doping process. At the end of this process, the undoped regions retain their crystallite size (80 ± 10 Å) while the intercalation of iodine reduces the crystallite size of doped regions at about 20 ± 5 Å. This behaviour is consistent with a doping at the periphery of individual fibrils.

In cis iodine doped samples, we observed that lateral spacings corresponding to the undoped regions (sharp reflections of Table I) are very close to that observed in a trans crystalline structure. This suggests that iodine induces an isomerization of the undoped regions of the cis sample. This dopant induced isomerization of the undoped regions may be due to removal of an electron from the pi orbital of the cis enabling easier bond rotation. Alternatively, the crystals which make up the outer layer of fibrils should elongate parallel to the fiber direction upon doping. This stress induces a strain parallel to the chain axis in undoped inner crystal (polymer chain being parallel to the fiber axis (13)). As trans $(CH)_x$ chains are $\approx 10\%$ longer than cis $(CH)_x$ chains, this strain may induce isomerization. Such an effect has been observed for mechanical rolling of cis $(CH)_x$ films (19, 20).

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