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Growth and morphology of undoped and doped polyacetylene thin films

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Résumé. — Des films très fins de polyacétylène polymérisés sur grille ont été étudiés par microscopie électronique à transmission. Sur les films non dopés, des microfibrilles naissantes ont été mises en évidence. Par ailleurs, les effets dus aux dopages par l'iode, le pentafluorure d'antimoine et le pentachlorure de molybdène, ont été étudiés.

Abstract. — Very thin films were studied by means of transmission electron microscopy. On undoped films, the existence of nascent microfibrils was pointed out. Elsewhere the effects of doping with iodine, SbF₅ and MoCl₅ were studied.

1. Introduction.

At this time a number of works were devoted to the study of physical properties of (CH)_x films both in experimental [1, 2] and theoretical ways [3], however some aspects remain misunderstood. Concerning doping, samples were studied by means of microprobe analysis [4] and scanning electron microscopy [5] which allowed us to observe the modifications of the fibrils when doping; however the dopant distribution inside the fibrils remains unknown. At this time works concerning TEM studies of (CH)_x [6, 8] are devoted to special polyacetylene synthesis. We can also report few earlier studies concerning polyacetylene and doped polyacetylene morphologies, usually effected by scanning electron microscopy [9-11].

The aim of this paper is both to point out the morphology of nascent polyacetylene films and to show the distribution of various dopants in the fibrils.

2. Sample preparation.

Thin (CH)_x films were directly grown onto grids (100 to 400 MESH) fastened on the vertical surfaces of a glass vessel wetted by the Ziegler-Natta catalyst solution, triethylaluminium and tetrabutoxytitanium with a molar ratio Al/Ti = 4, and a 0.4 mole/liter concentration of Ti in pentane solvent. The poly-

merization was performed at -78 °C to favour the *cis* isomer synthesis. We also used a low acetylene pressure of a few Hg centimeters and after a few seconds of polymerization, the remaining monomer was rapidly pumped out in order to stop the fibril growth.

Various dopants were used: iodine both in vapour phase or in pentane solution, MoCl₅ in solution and SbF₅ in vapour phase. After doping the samples were pumped to remove the interfibrillar dopant unfixed (around or inside the fibrils).

The transmission electron microscopy study was performed by means of a JEOL TEMSCAN 200 CX apparatus, working with an acceleration voltage up to 200 000 V, and allowing magnification up to 450 000. By using high definition negative films, we could reach a resolution power as high as 5 Å on amorphous materials. In all cases, we needed to study ultra thin films, in order to observe isolated fibrils. In addition we could only observe the undoped microfibrils when they were not moving (due to electron charge collection as undoped (CH)_x is an insulating material). We must also notice that in some viewgraphs Fresnel's diffraction fringes appear due to the random fibrils orientation.

At last we specify that we never covered the samples with a metallic layer (often used in S.E.M. studies).

3. Experimental results.

3.1 UNDOPED MATERIAL. — The classical morphology of the fibril lattice appears on the figure 1 concerning the undoped material at low magnification. We can observe a number of thin and long fibrils (300 Å diameter, few microns long) appearing like a tangle of strings. At higher magnification we observe nascent ramified microfibrils (30-50 Å diameter) growing along or at the end of a fibril (Figs. 2 and 3). Elsewhere we often observed the existence of a ring at the end of the fibrils (Fig. 2). On the viewgraph 3 we see microfibrillar ramifications, certainly related with the whole morphology of a films (nascent film, figure 8, or usual macroscopic film on which S.E.M. studies exhibit several fibrils fastened together). At last we do not observe significant changes in morphology after sample isomerization.

3.2 DOPED MATERIAL. — The various dopant species were used to correlate the electrical macroscopic properties and the dopant diffusion inside the film with the microscopic intrafibrillar dopant distribution. The aspect depends on the dopant specie, I_2 , SbF_5 , $MoCl_5$ and on the doping process.

The crystallinity of the films before and after doping is unknown. However Robin *et al.* [12] show evidence of a decrease of the crystallinity in the high iodine doped regions of the polyacetylene films.

The figure 4 shows the typical morphology of thin $(CHI_{0.1})_x$ film obtained by vapour phase doping at room temperature. It is not possible to measure directly the doping level of the film deposited onto a grid; however to estimate its order of magnitude we have simultaneously doped a thick film whose weight uptake was measured.

In addition to the morphology of undoped films, the figure 4 exhibits an homogeneous statistical distribution of dark points but of various size up to 25-30 Å. We can reasonably attribute these dots to iodine agregates.

Fig. 2. — Nascent microfibrils.

Fig. 3. — Other kind of growing microfibrils.

Fig. 1. — Whole aspect of thin undoped $(CH)_x$ films.

Fig. 4. — Iodine high doped $(CH)_x$.

The figure 5 exhibits, at a larger magnification, the iodine distribution. An rough evaluation of the iodine concentration may be obtained by the ratio of the volume occupied by the dark dots v compared to the whole volume V . From figure 5, we obtain $\sigma = v/V \approx 10^{-3}$ in contradiction with the evaluated doping level. On the contrary, if we assume that the visible dark dots only correspond to iodine fastened on the visible surface S , we obtain a new ratio $s/S \approx 3 \times 10^{-2}$ more consistent with the estimated doping level. However at this time we cannot really assume if the iodine distribution lies on or inside the fibril. As written above, the apparatus resolution is higher than five angstroms. Consequently we can think that some of the smallest dots are consistent with the I_3 molecules size. But the bigger dots may be aggregates of several iodine atoms or molecules (I_3^- , I_5^-).

The figure 6 exhibits the typical aspect of SbF_5 doped (around five percent) sample. Dopant distribution is strongly inhomogeneous.

Similar behaviour takes place when the film is doped with liquid phase $MoCl_5$. In this case, the figure 7 shows at high magnification an important and local swelling of the fibril. We think that dopant deposits on the fibril surface and then diffuses inside inducing the local swelling and dark regions (Figs. 6, 7, 8).

4. Discussion.

A growth process of the fibrillar morphology has been pointed out, specially by evidencing the microfibrils with diameter about 50 Å. These microfibrils may be the basic unit of the polyacetylene fibril morphology.

The different dopant species and doping processes used in this work always leads to dopant agglomerate of various sizes which produces the fibrils swelling, clearly evidenced with $MoCl_5$. However, in the case

Fig. 6. — Vapour phase SbF_5 high doped $(CH)_x$.

Fig. 7. — Liquid phase $MoCl_5$ high doped polyacetylene.

Fig. 5. — Detailed aspect of the iodine distribution inside the fibril.

Fig. 8. — Detailed viewgraph of the fastened fibrillar structure.

of vapour phase iodine doping, the dopant heaps distribution is much more homogeneous.

At last, as showed on figure 8, an other outcome of the SbF_5 doping is to disclose that each fibril is settled by several elementary fibrils fastened together.

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