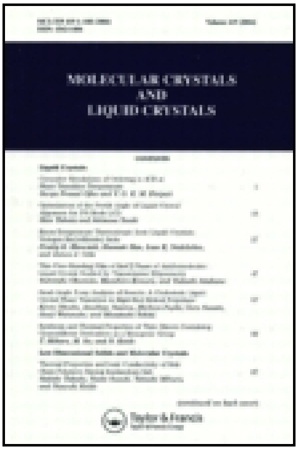

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Properties of Well-Aligned Polyacetylene Obtained with a Shear Proceure

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PROPERTIES OF WELL-ALIGNED POLYACETYLENE OBTAINED WITH A SHEAR PROCEDURE

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We have developed a procedure to polymerize acetylene under shear conditions and graphoepitaxially in a couette type arrangement. With this procedure $(CH)_n$ is obtained in the form of thin films consisting of highly aligned fibers. Electron diffraction patterns evidence that the polymer chain axis is oriented parallel to the fiber direction in the $(CH)_n$ film plane. From striations appearing perpendicular to the fiber during e-beam irradiation, from staining experiments and from dark field imaging in strong reflections of the fiber pattern it is concluded, that the $(CH)_n$ fibers consist of lamellae with a periodicity of about 110 Å.

INTRODUCTION

A large number of publications dealing with the interesting physical and chemical properties of polyacetylene have appeared in recent years[1].

The electrical transport properties in $(CH)_n$ have been discussed in a variety of models, two of which, the soliton picture[2] and the metallic droplet model[3] still are matter of controversies. Although the structural and especially the morphological details of the $(CH)_n$-films may be decisive for the transport properties, these aspects in most discussions usually are neglected. One reason is, perhaps, because relatively little is really known about polyacetylene morphology.

SYNTHESIS OF ORIENTED POLYACETYLENE

In order to fulfill the requirement still apparent for better defined material, and to investigate the morphology and structural details of $(CH)_n$-films let us try to transfer the method of polymerization under shear flow to the polyacetylene system. Details regarding the synthesis procedure have already been reported earlier[4]. In the following we will refer to trans $(CH)_n$ only, since our workup procedure includes isomerization of the samples into the trans isomer.

In a first set of experiments we used a rotor speed of 3000 rpm. Examination of $(CH)_n$-films obtained under these conditions with a scanning electron microscope shows the films to consist mainly of parallel running strings (Fig. 1).

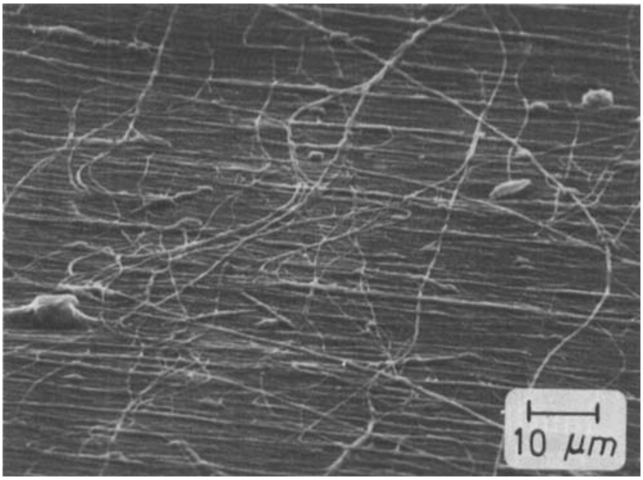

FIGURE 1 Scanning electron micrograph of parallel oriented $(CH)_n$ obtained with "low" rotor speeds. Magnification: x 970

Electron diffraction experiments with this material resulted in diffraction patterns typical for trans-modification-II $(CH)_n$[5]. The reason, why we do not call the $(CH)_n$-specimen "fibers", but strings, is, that we found no indication for a preferential orientation of the polymer chain axis parallel to the long axis of these specimen. In addition, this material exhibits only very weak optical dichroism[6].

In another experiment with rotor speed 4000 rpm we obtained a material which consisted of polyacetylene of the type described above, but also of highly oriented $(CH)_n$-fibers. Electron diffraction patterns obtained with very small diffraction apertures such that the diameter of the diffracting area was in the order of 0.1 µm demonstrate that these fibers consist of a new modification of trans-polyacetylene, which in an earlier publication was called trans-modification I [5]. This modification differs from the "usual" trans-modification (II) in the lack of symmetry elements and in unexpectedly large d-spacings along the chain direction. From the position of the 002-reflections relative to the fiber it is evidenced, that in the trans-modification I polyacetylene the chain axis is oriented parallel to the fiber axis in the $(CH)_n$-film plane (Fig. 2).

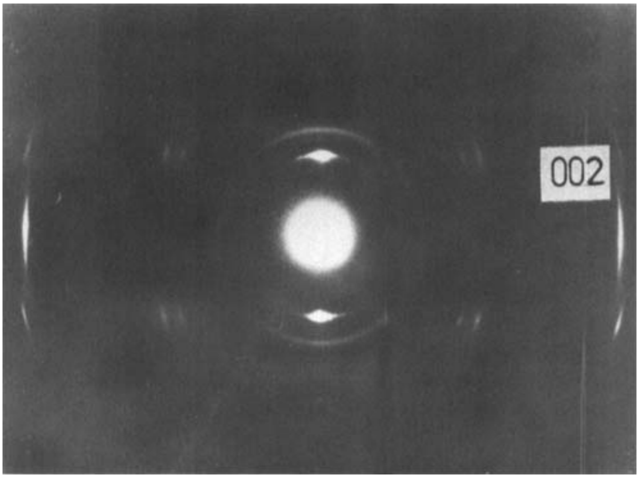

FIGURE 2 Electron diffraction pattern of fibers of trans-modification I polyacetylene. Diffracting sample area diameter: ~ 0.1 µm (c=chain direction).

A breakthrough towards highly aligned polyacetylene bare from matrix material was achieved with a sort of "graphoepitaxial" growth of $(CH)_n$. "Graphoepitaxy" was introduced by Flanders and co-workers for the description of oriented growth of silicon on artificial surface patterns in amorphous substrates[7].

In our case the artificial surface pattern consists of concentric grooves on the inner surface of the stator. The Couette type apparatus with 3000 rpm rotor speed was used since the shear flow seems to be necessary to precipitate the polyacetylene onto the stator surface.

The polyacetylene films prepared with this technique are shown in Figure 3. The scanning electron micrograph clearly shows this material to be highly oriented. The film is only about 200 Å thick, since it appears, that only the $(CH)_n$ layers adhering directly to the substrate are well aligned. The thicker the film grows, the less orientation occurs in additional layers.

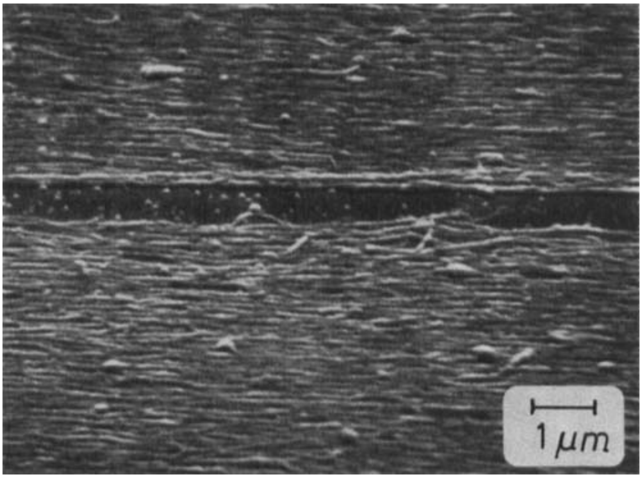

FIGURE 3 Scanning electron micrograph of graphoepitaxially grown $(CH)_n$ (trans-modification II), Magnification: x 9200

An even better impression of the material can be gained from the transmission electron micrograph with a higher magnification shown in Figure 4. The degree of orientation in these films becomes evident, when one examines the electron diffraction pattern obtained with this material shown in Figure 5. For this diffraction experiment a relatively large diffraction aperture, such that the diameter of the diffracting sample area was about 50 μm, could be chosen.

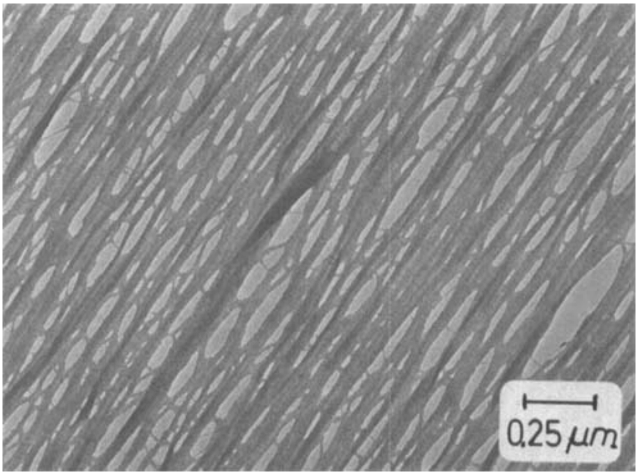

FIGURE 4 Transmission electron micrograph of graphoepitaxially grown $(CH)_n$ (trans-modification II), Magnification: x 40600

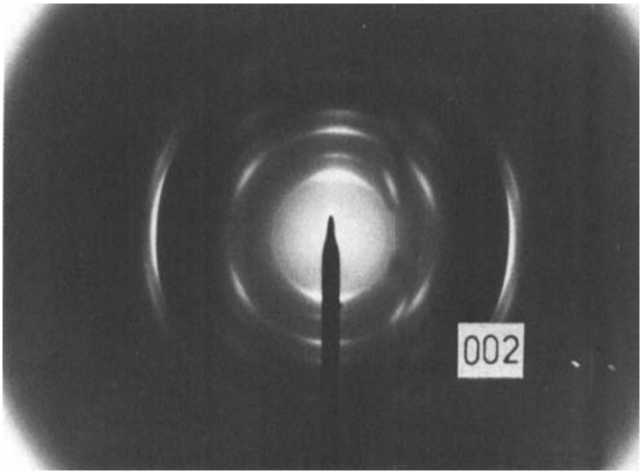

FIGURE 5 Electron diffraction pattern of graphoepitaxially grown $(CH)_n$, (trans-mod. II). Diffracting sample area diameter: 50 µm (c=chain direction).

From the orientation of the pattern and especially the 002-reflections with respect to the fibers, it is evidenced that the polymer chain axis is oriented parallel to the polymer fiber axis. Thus the graphoepitaxially grown $(CH)_n$ consists of real fibers and the diffraction pattern is a real fiber pattern. The unit cell parameters derived from the diffraction pattern are identical to those obtained for unoriented trans-modification II polyacetylene[5].

MORPHOLOGY OF ORIENTED $(CH)_n$

When examining the graphoepitaxially grown $(CH)_n$-films in the electron microscope, most surprisingly, well defined striations perpendicular to the fiber axis appear, which best can be observed with an unshadowed self-supporting film as shown in Figure 6. It turns out, that the striations appear especially quickly when low accelerating voltages are used. The effect clearly is a radiation damage effect. With the striations appearing in the bright field image, they are

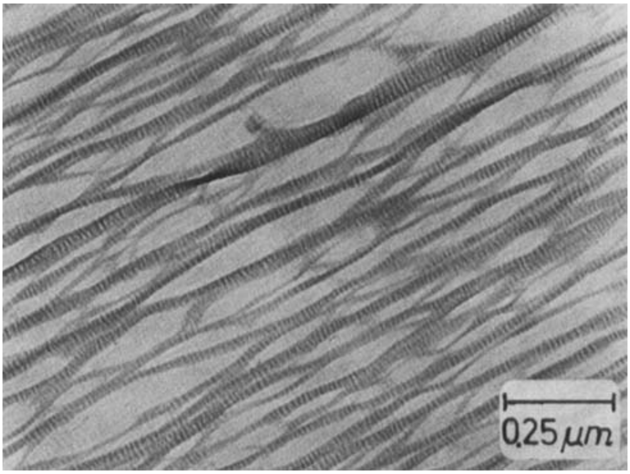

FIGURE 6 Transmission electron micrograph of e-beam damaged $(CH)_n$-fiber exhibiting striations perpendicular to the fiber direction. Magnification: x 64700

due to absorption contrast. Such radiation damage effects are well known in polymers: Absorption contrast in lamellar morphologies for example maybe increased or inverted by crosslinking or scission reactions taking place in either the amorphous or crystalline domains. This can give rise to severe dimensional changes of the samples as has been brilliantly demonstrated for polyethylene single crystals by D.T. Grubb[8]. Thus, the kind of morphology visualized by radiation damage does not necessarily represent the morphology of the undamaged sample, but presumably is a derivative of it. If the striations found trace back to a lamellar morphology in the undamaged $(CH)_n$ fiber, it should be possible to visualize the lamellae also by staining experiments.

In Figure 7 the transmission electron micrograph of graphoepitaxially grown $(CH)_n$ stained with OsO_4 is shown.

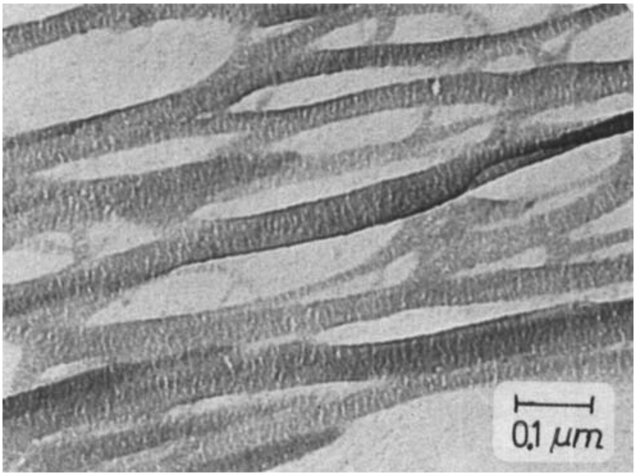

FIGURE 7 Transmission electron micrograph of OsO_4 stained $(CH)_n$-fibers. Magnification: x 112000

The absorption contrast is not as pronounced as in the beam damaged case, but especially at very thin parts of the fibers a periodicity of light and dark striations perpendicular to the fiber axis can be observed. This is clear evidence for the following picture:

The fibers in graphoepitaxially grown polyacetylene consist of lamellae which are packed after each other like salami slices. This results in the sequence of crystalline and amorphous regions which outline in the TEM as striations perpendicular to the fiber. A long period of the order of 110 Å can be derived from TEM-micrographs of stained $(CH)_n$.

Another substantiation of the lamellar morphology of the polyacetylene fibers are dark field images taken in 002- or other strong reflections as shown in Figure 8. The light areas contributing to the 002-reflection are crystalline domains. Clearly, these domains do not extend over long distances along the fiber direction as one might have expected for the case of extended chain polyacetylene crystals. The thickness of the crystalline domains derived from the dark field image coincide reasonably well with the domain dimensions derived from the staining experiments.

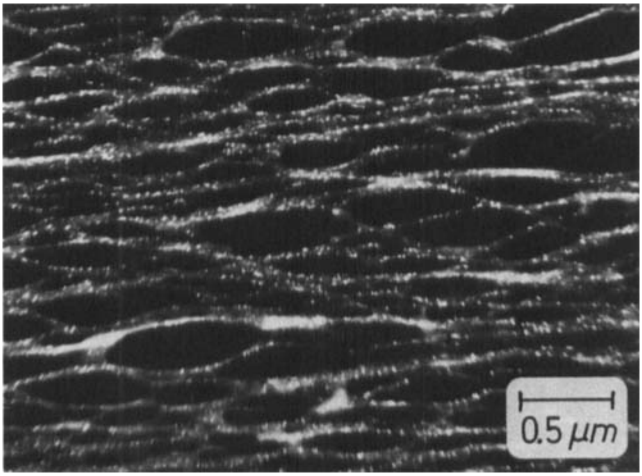

FIGURE 8 Transmission electron dark field image im 002-reflection of fibrous $(CH)_n$ - trans-modification II. Magnification: x 27900

CONCLUSIONS

With our shear flow procedure and with the help of graphoepitaxy three types of polyacetylene could be obtained:

1. Polyacetylene films consisting of parallel running strings of trans-modification II, with no preferential orientation of the polymer chain axis.
2. Polyacetylene films consisting of highly oriented fibers of trans-modification I, embedded in a matrix of unoriented $(CH)_n$.
3. Trans-modification II - polyacetylene, which is highly oriented by a sort of graphoepitaxial growth with well defined polymer chain direction parallel to the fiber axis.

Radiation damage and staining experiments as well as dark field transmission electron microscopy indicate that polyacetylene fibers have a lamellar morphology. Our conclusion for unoriented polyacetylene is, that it presumably consists of polymer lamellae too, which may be packed in a random fashion.

The lamellar morphology implies $(CH)_n$ to be inhomogeneous, namely to consist at least of two phases: the amorphous and the crystalline phase. This should be considered when discussing the electronic transport properties of polyacetylene.

ACKNOWLEDGEMENT

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