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AN X-RAY INVESTIGATION ON CIS-TRANS POLYACETYLENES

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Résumé - On démontre, en partant de données de diffraction de rayons X que le polyacétylène est formé d'une phase cristalline unique contenant soit l'isomère cis soit l'isomère trans.

Abstract - The formation of cis-trans mixed crystals in polyacetylene is demonstrated by x-ray diffraction data.

Two crystalline modifications of polyacetylene (PA) are described in the literature, corresponding to the all-cis/1-3/ and all-trans/4-8/ polymers respectively. On the contrary, no detailed informations exist about the crystallization of cis-trans copolymers (c,t-PA), though the latters constitute the usual as-synthesized materials. We have therefore investigated a series of c,t-PA with compositions varying continuously from the all-cis to the all-trans, by using wide-angle-x-ray diffraction (WAXS) technique. The composition of the materials was controlled either by change of the polymerization temperature or by appropriate thermal isomerization.

WAXS patterns of c,t-PA show:
- considerable line broadening but no detectable halo typical of an amorphous phase, independent on the composition.
- A unique set of hko reflections with both d spacings and intensity distribution varying continuously with the composition (Fig. 1). An equatorial pseudo-ortho-hexagonal cell with composition dependent parameters, intermediate between those of the all-cis and all-trans respectively (see Tab. 1), fits the experimental values of d (see Fig. 2).
- Two sets of hkI reflections, which agree with the repeat lengths of macromolecular chains with planar conformation in cis and trans configurations respectively. For each set, the intensity decreases and the line broadening increases with the decreasing of the concentration of the related configuration; the 001 reflections only are relatively sharp for all the composition range. On the contrary, both the intensity distribution and the d values are practically independent on the composition within each set of reflections.

The interpretation of WAXS patterns allows to exclude that c,t-PA contain separate crystals of cis-PA and trans-PA, while suggesting
the formation of mixed crystals. A mosaic model is proposed, built up of blocks of chain segments in cis configuration and blocks in trans configuration (schematized in Fig. 3). The mutual arrangement of the blocks is of nematic type while three dimensional order exists within the block, similar to that of the corresponding pure form. The block size is generally relatively large along the direction of the chain axis but the average lateral size decreases when decreasing the concentration of the related configuration.

The model gives calculated intensities for hk0 reflections in good agreement with the experimental ones. A refinement is in progress, by taking into account also the hkl reflections. The details of the structural calculations will be reported elsewhere.

Conclusions
- c,t-PA are almost completely crystalline polymers, the whole crystalline phase being constituted by cis-trans mixed crystals, para-crystalline in character. They are essentially one-phase materials.
- The formation of mixed crystals provides for a continuity in the crystal structure of c,t-PA for the whole composition range. This suggests the cis to trans isomerization to proceed through progressive re-arrangements of the macromolecules within the mixed crystals. In this view, isomerization is to be considered as an intracrystalline process.

Experimental - The isomer content of the samples was determined from IR spectra according to Ref. 9. WAXS patterns of stretched films were recorded by a single crystal AED diffractometer; for unstretched materials a standard step scanning diffractometer was used.

References
Fig. 1. Equatorial (e) and meridional (m) scattering of polyacetylenes with different compositions.

Fig. 2. Unit-cell parameters, calculated density and interplanar spacing of the most intense reflection as a function of the cis content.
### TABLE 1-Crystal data

**All-cis**

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<td>50-60</td>
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<td>31-36</td>
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**All-trans**

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<td>24</td>
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<td>51</td>
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(a) Angle between the plane of the chain and the (010) plane of the crystal (setting angle). (b) Extrapolated by assuming an ortho-hexagonal cell and $\rho_{\text{calc}}=1.165$. (c) From electron diffraction. (d) From x-ray diffraction. (e) From x-ray diffraction and packing calculations.

![Fig. 3. Schematic model of the structure of c,t-PA viewed along the chain axis.](image-url)