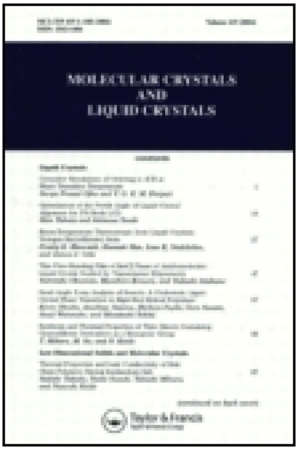

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X-Ray Investigation on Highly Oriented Polyacetylene

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X-RAY INVESTIGATION ON HIGHLY ORIENTED POLYACETYLENE

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Abstract The crystal structure of polyacetylene has been investigated by X-ray analysis on highly oriented polymers at various cis-trans content. A mosaic-like cis-trans mixed crystal model is proposed which fits the experimental X-ray data.

INTRODUCTION

Films of polyacetylene (PA) have been prepared in our Laboratories, which can be stretched to obtain highly oriented large ribbons (HOPA).[1] This material has been identified by an excellent X-ray fiber pattern, not reported so far in the literature. The availability of these new X-ray data prompted us to undertake a crystal structure determination of all-trans- and all-cis-PA as well as of the cis-trans copolymers (c,t-PA) which constitute the usual as-synthesized materials. Preliminary results have been previously presented.[2] This paper briefly reports the conclusive results of the work; a detailed paper on this subject will be published elsewhere.[3]

EXPERIMENTAL

Stretched samples (draw ratio ca. 7) with trans content in the range 15-100% have been examined. The cis to trans ratio was controlled by appropriate thermal isomerization under stress. The X-ray experiments were accomplished by a Single-crystal Siemens AED diffractometer with CuK$_{\bar{\alpha}}$ radiation on specimens 0.2-0.5 mm thick, formed by stretched strips clamped together. Both θ-scan and ζ-scan at constant ζ (along the layer line in the fiber pattern) were performed. Intensities were measured by integration over θ-scan.

RESULTS AND DISCUSSION

As previously reported[2], the main features of the X-ray fiber pattern of HOPA at different cis-trans content can be summarized as in the following.

The equatorial pattern constantly displays a unique set of (hk0) reflections with both interplanar spacing and relative intensity varying continuously with the composition.

On the contrary, two sets of (hkl) reflections are observed for any composition, corresponding to the repeat lengths of cis and trans planar chain conformations respectively. For both sets the intensity decreases and the line broadening increases when decreasing the concentration of the related configuration. The 'trans' reflections significantly shift their angular positions when going from the all-trans to the cis-rich zone. The set of cis reflections is practically invariant in this respect.

(00l) reflections with l even are only observed. Broad peaks appearing on the meridian, close to the angular positions expected for odd orders of (00l) are really streaks perpendicular to the chain axis and not Bragg's reflections. For this reason, the experimental evidence for the presence of the (00l) reflection in the electron diffraction pattern of a partially oriented trans-PA, as claimed in the literature,[4] has to be regarded as doubtful.

On the basis of the above experimental data, a mosaic-like cis-trans mixed crystal model was proposed,[2] based on three-dimensionally ordered blocks of cis and three-dimensionally ordered blocks of trans chain segments, arranged in a nematic way. The mixed crystals are characterized by an orthogonal equatorial cell with values of the unit cell parameters continuously increasing going from the all-trans to the all-cis polymer. The average block size perpendicular to the chain axis decreases by decreasing the concentration of the related configuration. On the contrary, the coherence length parallel to the chain axis doesn't vary dramatically with respect to the pure forms, at least for the cis blocks, as suggested by the invariance of the 'cis' (002) reflection in terms of both interplanar spacing, d, and line width, B, over the composition range (Figure 1). The increase of B, together with the slight decrease of d observed for the 'trans' (002) as a function of the overall trans content (Figure 1), could arise from disorder rather than from size effects. In fact, conformational distortions are required in trans sequences at the junction with cis segments in order to parallel the chain axes of the two segments within the mixed crystals (Figure 2). The chain model, reported in Figure 2, characterized by alternate distortions of +5 and -5° with respect to the regular conformation, has been assumed as a possible conformation of the cis-trans junctions.

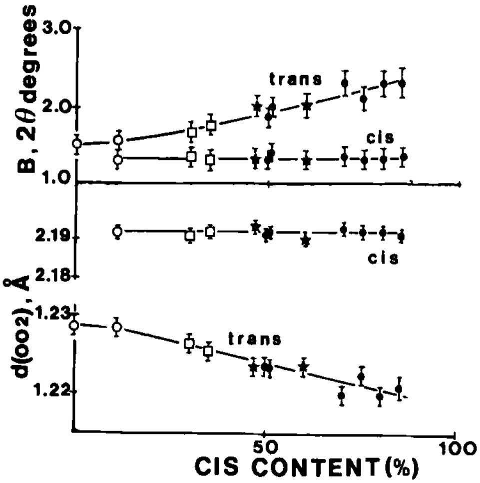


FIGURE 1 Interplanar spacing, d, and line width, B, of 'trans' and 'cis' (002) reflections as a function of the cis content.

Calculation of the intensities diffracted by the mixed crystal model was performed, including the limiting compositions of the all-trans and all-cis-PA. Because the pattern of an all-cis polymer was not available, the structure of the pure cis form was tested by using (hkl) and (hk2) reflections measured on a cis-rich sample. Both cis-transoid and trans-cisoid models were considered. The geometrical parameters of the 'regular' chain models used are reported in Figure 3. A bond alternation corresponding to $u_0 = 0.04$ Å was assumed for the trans conformation, according to the results of Nutation-NMR studies,[5] and kept constant throughout the calculations. In fact, there is no practical possibility to derive u_0 directly from X-ray analysis because no reflection, apart from (001) and (101) (not detected

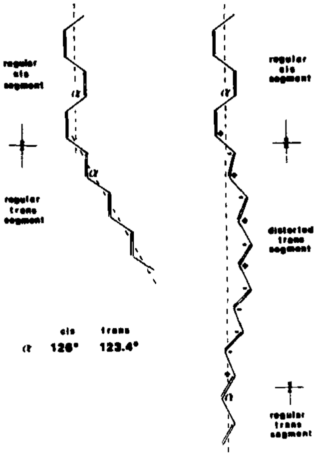
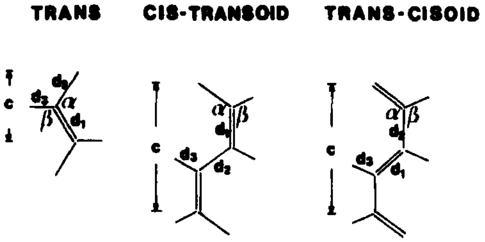


FIGURE 2 Regular and distorted conformations at the cis-trans junction. (+) and (–) refer to enlarged and reduced bond angles with respect to the regular conformation.



	TRANS	CIS-TRANSOID	TRANS-CISOID
c	2.457	4.384	4.384 Å
d_1	1.355	1.34	1.34 Å
d_2	1.435	1.45	1.45 Å
d_3	1.09	1.09	1.09 Å
α	123.4	126.0	123.6°
β	119.2	115.0	114.0°

FIGURE 3 Geometrical parameters of the chain models used for the calculations.

in our patterns), is significantly sensitive to small variation of this parameter.

For this reason, the approaches of Chien et. al.[4] and Fincher et. al.[6] who derived $u_0 = 0.03$ Å for trans-PA, seem to us questionable. Moreover, the conclusion of the former authors for an in-phase alternation (space group $P2_1/a$) is opposite to that of the latters who proposed an out-of-phase alternation (space group $P2_1/n$).

The absence of both (001) and (101), which would be visible on the basis of the corresponding calculated intensities for $P2_1/a$ and $P2_1/n$ space groups respectively, suggests the orthorhombic Pnam space group as more appropriate. In this case, the lattice symmetry requires a disordered packing with a statistical occupancy of short and long bonds in the crystal site, which means that short-range in-phase and short-range out-of-phase alternations are statistically present in the lattice. On the other hand, this assumption appears reasonable if one considers that the presence of defects inducing phase-shift in the bond alternation within the chain prevents by itself the possibility of establishing long-range in-phase or out-of-phase ordered packing.

Calculation of the (hk0) reflections was performed for compositions ranging from 20 to 100% trans with 10% step. The occupancy of the crystal site was assumed according to the corresponding overall content of the two configurations. A decreasing fraction of distorted trans segments was considered for the 20-60% trans range. The cis-transoid model was used for the cis configuration.

The best fit was obtained for a setting angle $\Phi = 51°$ in all cases. Similar values have been reported in literature for all-cis- and all-trans-PA from X-ray powder diffraction and packing calculations[7,8] or X-ray fiber diffraction of partially oriented trans-PA.[6]

Figure 4 shows the comparison between experimental and calculated intensities of (hk0) reflections for c,t-PA including all-trans.

The agreement is generally good, as indicated by the reliability factor R, though systematic discrepancies relative to reflections with h+k = 2n+1 are evident. This strongly suggests the presence of lattice defects. In fact, by assuming that the general x,y,z position of the lattice is replaced statistically

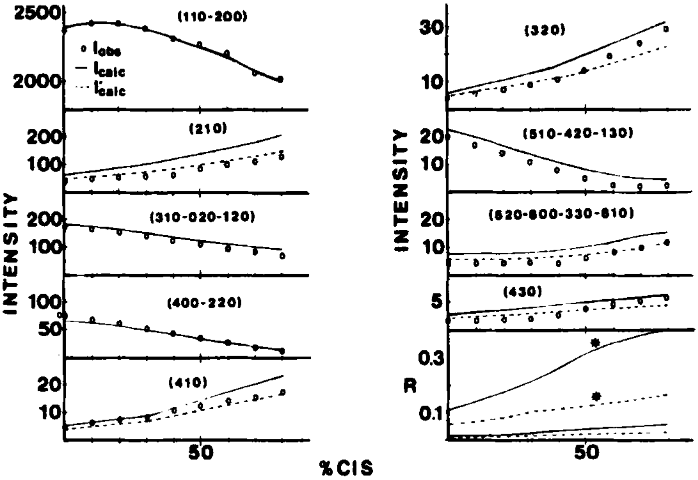


FIGURE 4 Observed and calculated intensities of (hk0) reflections and reliability factor, R, for c,t-PA. Calculated values in the presence of lattice defects (dashed curves); R factor not including the (110)-(200) reflection (starred curves).

by 8% (c,t-PA) and 6% (trans-PA) of -x,y,-z positions, the systematic discrepancies disappear with a significant improvement of the R factor (Figure 4). This type of lattice defect could reasonably be the consequence of intermolecular cross-links and/or molecular motions occurring during the isomerization process.

Figure 5 reports the results concerning (hkl) reflections for the pure forms, having assumed the Pnam space group in both cases.

A very good agreement is obtained in the case of all-trans. Moreover, the cis-transoid model works significantly better than the trans-cisoid for the all-cis structure.

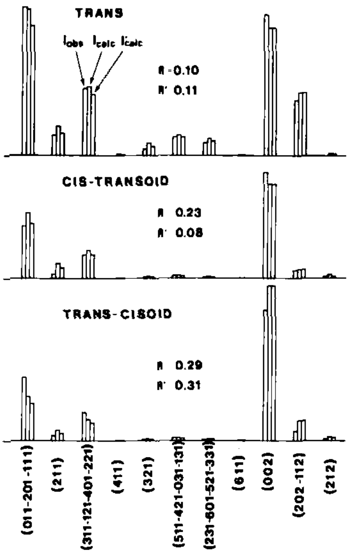


FIGURE 5 Observed and calculated intensities of (hkl) and (hk2) reflections for all-trans and all-cis-PA. I'_{calc} refers to calculated intensities in the presence of lattice defects.

CONCLUSIONS

The structure of c,t-PA is built up of cis-trans mixed crystals with both intra- and inter-molecular block-type distribution of cis and trans units. This suggests the cis to trans thermal isomerization to proceed through progressive rearrangements within the mixed crystals with a non purely random mechanism.

X-ray analysis of highly oriented polyacetylene has given no direct information about the existence and magnitude of bond alternation in trans-PA. If bond alternation is assumed to be present, according to other experimental evidences (Nutation-NMR), a disordered crystal packing (in-phase and out-of-phase alternations statistically present in the lattice) seems to be preferred for trans-PA.

The cis-transoid configuration fits X-ray data better than the trans-cisoid.

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