

Structural study of the *cis-to-trans* thermal isomerization in polyacetylene

P. Robin

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

J. P. Pouget and R. Comès

Laboratoire de Physique des Solides and Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université Paris-Sud, F-91405 Orsay, France

H. W. Gibson and A. J. Epstein

Xerox Webster Research Center, 800 Phillips, Road-W114, Webster, New York 14580

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We have studied the variations of Debye-Scherrer x-ray synchrotron radiation patterns of polyacetylene with *cis-to-trans* isomerization. At each stage of the isomerization we observe only one series of x-ray lines at positions intermediate between those of pure *cis* and pure *trans* films. In addition, the crystallinity and lateral crystallite size do not change appreciably during isomerization. The observations lead us to conclude that the isomerization process is homogeneous without clustering of *trans* regions within the *cis* host lattice.

Polyacetylene, $(\text{CH})_x$, has been subject to intense theoretical and experimental study due in part to the fact that it is the simplest conjugated polymer.¹ However, despite this simplicity, polyacetylene can be synthesized in either a *cis* or the thermodynamically more stable^{2,3} *trans* isomer (Fig. 1). According to the soliton model,^{4,5} undoped $(\text{CH})_x$ is a semiconductor due to a commensurate Peierls distortion. For the *trans* isomer, the two possible phases of the dimerization of an isolated chain are degenerate in energy [Fig. 1(c)], and a soliton is the boundary between regions of the two phases. Presence of solitons in *trans*- $(\text{CH})_x$ has been confirmed experimentally.¹ The formation of bipolarons,^{6,7} not solitons, is favored from *cis*- $(\text{CH})_x$, since *cis-transoid* [Fig. 1(a)] and *trans-cisoid* [Fig. 1(b)] are not degenerate in en-

ergy. The optical,^{1,8} magnetic,^{1,9} and transport^{1,10} properties of *cis*- and *trans*- $(\text{CH})_x$ differ considerably due to the different stability of these defect levels. Both *cis*- and *trans*-polyacetylene have an increase in their conductivity to metallic levels upon doping with acceptors such as iodine or arsenic pentafluoride.^{1,11} The doping of *cis*-polyacetylene has been shown^{8,12,13} to lead to the isomerization of the *cis* isomer to doped *trans*-polyacetylene. In light of these systematic differences in the electronic excitation of *cis*- and *trans*- $(\text{CH})_x$ it is important to gain insight into the structural changes that occur during the isomerization of the *cis*- $(\text{CH})_x$ to *trans*- $(\text{CH})_x$.

We report here the results of an extensive synchrotron radiation diffraction study of the evolution of the structure of *cis*- $(\text{CH})_x$ to that of *trans*- $(\text{CH})_x$ during isomerization. The results reveal a continuous shift of the initially (*h0l*) *cis* x-ray pattern as a function of degree of isomerization (percent *trans*) with the degree of crystallinity and the lateral coherence remaining constant. This result shows that the isomerization occurs homogeneously throughout the polymer and not in isolated amorphous or selected crystallite regions. Detailed analysis of samples treated for various times at 100 °C reveals the disappearance of the initial *cis* in chain reflections (011), (211), and (020) for samples annealed for greater than 3 h (> 50% *trans*) and the appearance of the (020) *trans* in chain reflection, at $d = 1.23 \text{ \AA}$, for samples annealed greater than 1 day (> 80% *trans*). Similar homogeneous structural transformations are observed^{14,15} for diacetylenes.

Polyacetylene was prepared by the Shirakawa technique² at $-78 \text{ }^\circ\text{C}$. Samples were stored at $-80 \text{ }^\circ\text{C}$ in vacuum until physical studies commenced. Scanning electron micrographic studies¹⁶ confirmed a fibrillar

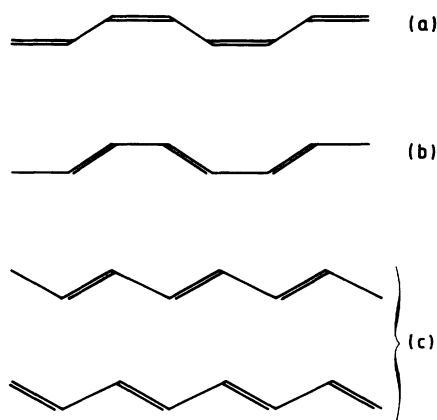


FIG. 1. Different structures of a $(\text{CH})_x$ chain: (a) *cis-transoid*; (b) *trans-cisoid*; (c) *trans-transoid*.

morphology with a typical fibril diameter of 500 Å. Unless otherwise noted, the isomerizations were carried out at 100°C in an evacuated glass tube. The ratio of *cis*-to-*trans* isomer in a given film was determined through extensive correlated infrared and NMR analysis.¹⁷ 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. In order to have limited exposure time at ambient temperature, data were obtained with the x-ray synchrotron radiation at the station D-16 of Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), Orsay. During this experiment the wavelength was chosen at 1.34 Å. X-ray films were read in the equatorial plane of the experimental setup, using a Joyce Loebble microdensitometer.

The x-ray patterns for *cis*-^{1,13,18} and *trans*-^{1,13,19} polyacetylene have been reported by various authors. The x-ray patterns are composed of Debye-Scherrer rings. Such an isotropic distribution of the diffracted intensity corresponds to the random orientation of polyacetylene fibrils¹⁶ with respect to the x-ray beam. The diameter of the ring was converted into Bragg angle θ_0 by use of the Bragg relationship $\lambda = 2d \sin \theta_0$, where λ is the wavelength of the incident radiation and d is the spacing between diffracting planes. The angular width at half height of the ring $\Delta_E(2\theta)$ was always found larger than the experimental resolution $\Delta_R(2\theta)$. The intrinsic broadening $\Delta_I(2\theta)$, due to the finite size L , of the crystalline areas which contribute to Bragg reflections was obtained after a Gaussian correction. The coherence length L was thus deduced from the Scherrer formula $L = 0.9/(\cos \theta_0) \Delta_I(2\theta)$.

The x-ray crystallinity of both *cis*- and *trans*-(CH)₂ and the intermediate compositions is estimated at about 90%. The amorphous content of the polymer film does not increase with isomerization.

In this study we observe only one set of Debye-Scherrer patterns for all degrees of isomerization. We follow quantitatively the position and width of the three strongest reflections as a function of isomerization. By referring to the indexing scheme of Baughman *et al.*¹⁸ for *cis* sample (Table I) these reflections are at 3.81 Å [(101) and (200)], 2.87 Å (201), 2.20 Å [(301), (002), and (020)]. Note that, except for the last one, these reflections do not include the in-chain direction.²⁰ Using the Scherrer formula these reflections give a transverse coherence length of 150 ± 30 Å independent of the degree of isomerization (Fig. 2).

Figure 3 presents the evolution of the d spacing of the three strongest reflections as a function of *trans* content. Only a single Debye-Scherrer pattern is present at each intermediate position in the isomerization and not a superposition of *cis* and *trans* patterns. This result demonstrates that the isomerization proceeds homogeneously throughout the poly-

TABLE I. Spacing between Bragg reflection planes in Å and intensity (S: strong; M: medium; W: weak; VW: very weak) for *cis*-(CH)_x. The indexation of these reflections is done according to the structure of Baughman *et al.* (Ref. 18) with b along the chain axis. Only spacings corresponding to the ($h0l$) reflections and to the three (hkl) with $k \neq 0$ reflections (+) clearly observed on stretched samples are indexed.

| d (Å) | hkl | Intensity |
|---------|----------------------------------|-----------|
| 3.81 | { 101 200 | S |
| 3.12 | 011 ⁺ | W |
| 2.87 | 201 | M |
| 2.44 | 211 ⁺ | VW |
| 2.20 | { 301 002 020 ⁺ | M |
| 2.18 | 020 ⁺ | M |
| 2.13 | 102 | VW |
| 2.00 | | VW |
| 1.90 | { 202 400 | W |
| 1.74 | | W |
| 1.65 | 302 | W |
| 1.50 | | VW |
| 1.36 | | W |
| 1.22 | | W |

acetylene crystal. It is not consistent with the heterogeneous growth of isolated *trans* regions. The structural results for *cis*-to-*trans* isomerization of polyacetylene are thus similar to the homogeneous polymerization of diacetylenes.^{14,15}

In order to quantify the isomerization process we construct a simple model for the evolution of the *cis* to the *trans* structure as a linear variation of the lattice parameters with *trans* content. We use only the transverse lattice parameters because the in-chain re-

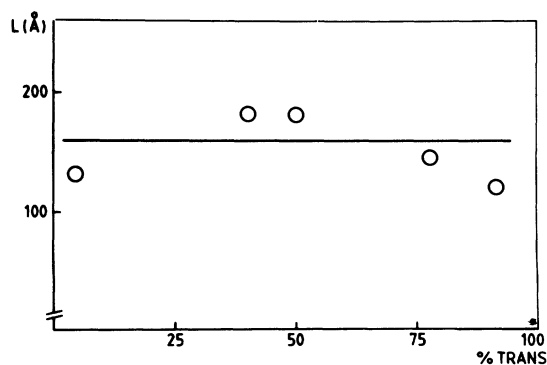


FIG. 2. Transverse coherence length deduced from the width of the (101) and (200) reflections as a function of isomerization.

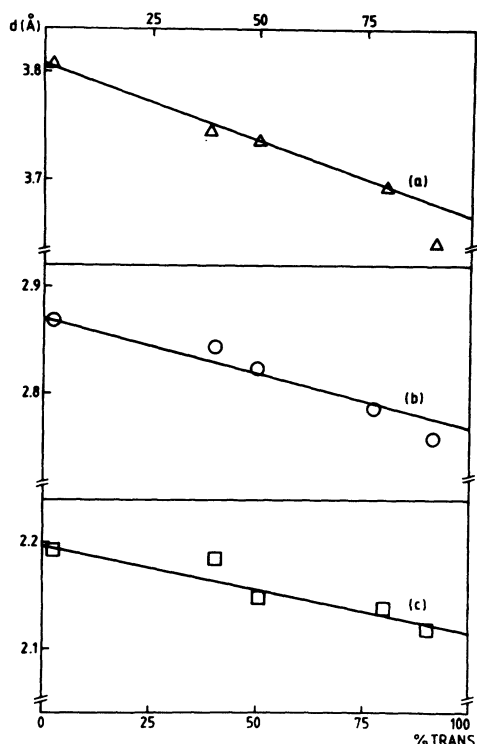


FIG. 3. Variation of the d spacing corresponding to the three strongest reflections as a function of isomerization. Symbols (a) Δ for (101) and (200); (b) \circ for (201); and (c) \square for (301) and (002) are the experimental data and straight lines results of the calculation described in the text.

flections disappear for mixed isomer compositions. This may be due to several effects including the large difference between the *cis* and *trans* in-chain periodicity [4.38 Å and 2.26 Å, deduced from the observation of (020) reflections in *cis*- and *trans*-(CH)_x, respectively]. Thus, for a polymer chain composed of random segments of *cis* and *trans*, there is no long-range coherence along the individual chain. In addition, there will be no coherence among the neighboring chains.²⁰

The model is summarized by the following:

$$a(x) = a_{cis} - x(a_{cis} - a_{trans}) ,$$

$$c(x) = c_{cis} - x(c_{cis} - c_{trans}) ,$$

where x is the *trans* content in *cis* film, a_{cis} and c_{cis} are given by the structure of Braughman *et al.*,¹⁸ 7.61 and 4.39 Å, respectively; while a_{trans} and c_{trans} are given by the structure of Fincher *et al.*¹⁹ 7.32 and 4.24 Å, respectively.

The d spacing corresponding to a (hkl) reflection in an orthorhombic lattice is

$$d = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2} .$$

This equation is evaluated for the strong reflections studied and the results are plotted as the solid lines in Fig. 3. It is seen that there is a very good agreement with experiments for each of the three reflections up to 80% *trans*. Above this value the degenerate (101) and (200) reflections and the degenerate (301) and (002) reflections begin to split while the (201) reflection shifts somewhat from its position calculated by the solid line. The splitting is clearly observed for samples annealed more than 3 days at 100 °C (~90% *trans*). In samples annealed 20 minutes at 200 °C (~95% *trans*) all the reflections can be indexed with the parameters $a'_{trans} = 7.41$ Å and $c'_{trans} = 4.08$ Å previously given by Baughman *et al.*²¹ These parameters are quite different from those of Fincher *et al.*¹⁹

The maintenance of degree of crystallinity and crystallite size during isomerization becomes a critical test of models for the isomerization mechanism. These results demonstrate that individual polyacetylene chains are restrained within an overall lattice structure. Hence, models^{22,23} based upon isolated chains are unrealistic. The constrained polyacetylene chain is unable to rotate large sections because it is blocked by the host lattice. Each bond rotation which occurs during isomerization must happen at the same time as a counter-rotation of a nearby bond on the same chain. The necessity of two simultaneous processes implies that the isomerization kinetics are at least second order. This latter conclusion was confirmed by a detailed NMR and infrared study.¹⁷ This situation differs from the polymerization of diacetylene which shows first-order kinetics.²⁴ In the latter case this is enabled by the rotation of individual monomers.

The evidence for homogeneous isomerization makes it possible to rationalize other experimental results for partially isomerized polyacetylene. For example, the dc conductivity at room temperature increases slowly from that of *cis*-(CH)_x ($10^{-9} \Omega^{-1} \text{cm}^{-1}$) to that of *trans*-(CH)_x ($10^{-5} \Omega^{-1} \text{cm}^{-1}$) with isomerization. At ~50% *trans* (above the percolation threshold) the conductivity remains near that of the *cis* isomer. The usual three-dimensional hopping model cannot explain this. A model of intersoliton-soliton electron hopping has been proposed by Kivelson²⁵ and successfully applied to ~100% *trans*-(CH)_x.¹⁰ This model requires a mobile neutral soliton to diffuse along a *trans*-(CH)_x chain. At intermediate isomerization values the solitons are confined by random *cis* segments, and charge transport must therefore be via a less efficient mechanism. In agreement with this picture is the observation of a broad ESR line for intermediate isomerization values,²⁶ indicative of solitons confined between *cis* segments.

The studies of x-ray patterns are in agreement with the NMR and infrared studies^{2,17} of the isomerization

mechanism. There is an initial rapid evolution of the crystal lattice structure during the first two hours of annealing at 100 °C. This corresponds to achieving approximately 50% *trans*. Further isomerization proceeds more slowly, requiring approximately 72 h to reach ~90% *trans*. This result suggests that at least two processes¹⁷ participate in the *cis*-to-*trans* isomerization.

A similar retention of the crystallite size and degree of crystallinity was noted¹³ for the undoped regions of *cis*-(CH)_x after exposure to iodine vapor. In that case it was reported¹³ that for (CHI_{~0.10})_x derived from slow gas phase doping²⁷ of *cis*-(CH)_x, about one-half of the polymer volume remained undoped and the undoped regions retained their crystallite size but were transformed to the undoped *trans* structure. The 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 the fibrils should elongate parallel to the fiber direction upon doping. This stress induces a strain parallel to the chain axis in the un-

doped inner crystals (polymer chain axis being parallel to the fiber axis¹⁹). As *trans*-(CH)_x chains are ~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.²⁸

Summarizing, we have carried out an extensive x-ray diffraction study of the changes in the crystal structure that occur in polyacetylene upon isomerization from *cis*-to-*trans* isomer. The isomerization process is found to proceed homogeneously throughout the system with no degradation of crystallite size and crystallinity. A simple model of linear shift of transverse lattice parameter with *trans* content is shown to give a good fit of the data. The results of the homogeneous isomerization process are consistent with infrared and NMR studies and provide a basis for understanding transport and magnetic phenomena in partly isomerized samples.

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