STRUCTURAL STUDY OF THE CIS-TO-TRANS THERMAL ISOMERIZATION IN POLYACETYLENE

P. Robin*, J.P. Pouget**, R. Comès**, H.W. Gibson*** and A.J. Epstein***

Laboratoire Central de Recherches, Thomson-CSF, Domaine de Corbeville, 91401 Orsay, France**Laboratoire de Physique des Solides and Laboratoire pour l'utilisation du Rayonnement Electromagnétique, Université Paris-Sud, 91405 Orsay, France*****Xerox Webster Research Center, 800 Phillips, Road-W-114, Webster, New York 14580, U.S.A.*

Résumé : Les résultats d'une étude par rayons X de l'isomérisation thermique $cis \rightarrow trans$ dans le polyacétylène sont présentés. Ils montrent que le processus d'isomérisation est homogène, sans formation d'amas de $trans$ dans le réseau hôte cis .

Abstract : An X-ray study of the cis to $trans$ thermal isomerization in polyacetylene is given. It shows that the isomerization process is homogeneous without clustering of $trans$ regions within the cis host lattice.

I - INTRODUCTION

Polyacetylene, $(CH)_x$, has been subject to intense theoretical and experimental studies due in part to the fact that it is the simplest conjugated polymer. Its fibrillar morphology with a great specific area has allowed several technological applications like batteries. Polyacetylene can be synthesized in either a cis or a thermodynamically more stable $trans$ isomer. There are two processes to obtain a $trans$ film. In the first process a cis film is synthesized at $-78^\circ C$ and then annealed at high temperature ($200^\circ C$ during 20 mn for example). In the second process the synthesis is performed at high temperature ($100^\circ C$).

One must notice that from a structural point of view these two processes are not really equivalent. In the first process the crystallisation of the cis form is first performed, then the $trans$ form is obtained later by thermal isomerization. In the second process, on the contrary, the crystallization and the isomerization occur at the same time.

The use of the first process allows a study, step by step, of the isomerization mechanism. A number of experimental and theoretical studies of this process have been reported(1). However, as cis (2) and $trans$ (3)(4) isomers have different crystalline structures, a crystallographic study of partly isomerized films requires special attention. In particular it is not clear if these samples show segregated cis and $trans$ lattices or if the cis and $trans$ forms coexist in a unique lattice. Such a structural analysis is the purpose of the present paper.

II - EXPERIMENTAL CONDITIONS

Polyacetylene was prepared by the Shirakawa technique at $-78^\circ C$ (5). Samples were stored at liquid nitrogen temperature in vacuum until studied. Scanning electron

micrographic studies confirmed a fibrillar morphology with a typical fibril diameter of 500 Å (6). Except to obtain nearly completely converted trans $(CH)_x$, 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 solid NMR analysis (1). X-ray data were collected on photographic films fixed on a cylindrical camera with the sample placed at the center of the chamber. During all the exposures 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 at LURE (Orsay) ($\lambda = 1.34$ Å and $\lambda = 1.25$ Å). Complementary experiments on rolled samples were also performed with the conventional $CuK\alpha$ (1.542 Å) radiation.

III - RESULTS AND DISCUSSION

A preliminary structural study of the cis to trans thermal isomerization mechanism, being under press (7), we shall summarize here only the main results obtained :

- for all degree of isomerization, only one set of Debye Scherrer reflections is observed and not a superposition of cis and trans reflections.

- no noticeable change of the X-ray crystallinity can be detected during the isomerization process. In cis and trans $(CH)_x$ forms (8), as well as for intermediate compositions, the X-ray crystallinity is estimated at about 90 %, a value close to that already reported in earlier studies of cis and trans $(CH)_x$ (9).

- using the Scherrer formula, with (h0l) reflections (see below), a lateral X-ray coherence length of 150 ± 30 Å, independant of the degree of isomerization, is found.

These results mean that the thermal isomerization process is homogeneous within each crystal, in order to keep its integrity. If the process was heterogeneous, i.e with nucleation of trans in a cis matrix, a superposition of the X-ray Debye Scherrer patterns of pure trans $(CH)_x$ should be observed. This is not the case.

We shall now describe more completely the change of the Debye Scherrer pattern upon isomerization.

The Debye Scherrer X-ray pattern observed in cis $(CH)_x$ is identical to those already published in ref (2), (9). Using rolled samples it is easy to separate transverse (h0l) reflections from those containing the chain index k (in the study we choose b as the chain direction). Transverse reflections used during this study are given in table I, with their d spacings. One notices, in particular, that the couples of transverse reflections (200) and (101), (301) and (002), (400) and (202) cannot be separated in cis $(CH)_x$. The reflections (011) at 3.12 Å, (211) at 2.44 Å, as well as the in chain (020) reflection at 2.18 Å, clearly observed in rolled cis $(CH)_x$, have been also followed with the degree of isomerization.

Upon annealing, the transverse (h0l) reflections shift continuously with the degree of isomerization. The evolution of three of them : the couples of reflections (200) and (101), (301) and (002) as well as the single (201) reflection, has already been reported in reference (7). Using all the reflections indexed in table I, it is then possible to obtain a and c lateral parameters as a function of the amount of trans (figure 1) assuming an orthorhombic lattice (14). Two regimes can be clearly observed :

- below 80 % trans, a and c transverse parameters follow, within experimental errors, the linear laws :

$$a(x) = a_{cis} - x(a_{cis} - a'_{trans}), \quad c(x) = c_{cis} - x(c_{cis} - c'_{trans})$$

where x is the trans content in cis film, $a_{cis} = 7.61 \text{ \AA}$ and $c_{cis} = 4.39 \text{ \AA}$ are the parameters of the cis structure (2), while a_{trans} and c_{trans} are close to lattice parameters given in reference (4) for trans $(CH)_x$ ($7.32 \text{ \AA}$ and $4.24 \text{ \AA}$ respectively).

- above 80 % a slight increase of the parameter a and a more rapid decrease of the parameter c , with respect to the previous linear laws, is observed. In nearly completely isomerized samples ($\approx 98 \%$ trans) the lattice parameters found, $a_{trans} = 7.46 \pm 0.02 \text{ \AA}$ and $c_{trans} = 4.08 \pm 0.02 \text{ \AA}$, are very different from those of reference (4) but they agree with those reported in an earlier study of trans $(CH)_x$ (3). Table I shows that in our trans $(CH)_x$, the (h0l) reflections can be separated. In particular the splitting between (200) and (101) reflections can be observed, as in data shown in references (5) and (9). Such an effect cannot be obtained with lattice parameters of reference (4). Finally, the unit cell that we found is more compact than that of reference (4). Conditions under which two different crystalline forms of trans $(CH)_x$ can be obtained need further studies, due to the large number of experimental and theoretical works devoted to trans $(CH)_x$.

The (011) and (211) reflections of cis $(CH)_x$ are no longer observable for samples annealed for more than 3 hours at 100°C ($\approx 50 \%$ trans). A similar observation can be done with the (020) in chain reflection. Within experimental error, the cis chain parameter b ($4.36 \pm 0.02 \text{ \AA}$) deduced from the position of these reflections, does not change with x . Preliminary experiments performed on rolled samples seem to show that the (020) reflection disappears by broadening toward the large Bragg angles. This might indicate that in chain Bragg reflections transform into diffuse sheets perpendicular to the chain axis, as expected by a loss of lateral correlations between cis units. The sharp (020) reflection of trans $(CH)_x$ at $1.23 \text{ \AA}$ begins to be observed for samples annealed for more than 1 day at 100°C ($\approx 80 \%$ trans). It is interesting to remark that this reflection is observed at about the same value of x at which the a and c lateral parameters present a different law of evolution as a function of the trans content (figure 1). The vanishing of in chain reflections, for mixed isomer composition, may be due to the large difference between the cis and trans periodicities ($4.38 \text{ \AA}$ and $4.92 \text{ \AA}$ for 4 CH units, respectively) : for a polymer chain composed of random segments of cis and trans, there is no long range coherence along the individual chain (disorder of 2nd kind according to Guinier (10)).

IV - CONCLUSION

X-ray results obtained in this study show that the thermal isomerization process in $(CH)_x$ is homogeneous, without clustering of trans in a cis matrix. From the structural point of view, this recalls the homogeneous polymerization of diacetylenes (11) (12). A continuous change of the transverse parameters a and c , defining an average structure, is observed with the degree of isomerization (13). However, contrary to diacetylene, a common in chain periodicity b cannot be obtained for mixed crystal, due to the very different cis and trans periodicities. Study of the distribution of cis and trans units along b , with the degree of isomerization, needs further works.

Structural results demonstrate that individual polyacetylene chains are restrained within an overall lattice structure. This must be taken into account in any model of isomerization. For example, in order to keep the direction of the chain, at least two simultaneous rotation of bonds must occur, which implies that the isomerization kinetics are at least of second order. This makes a substantial difference with diacetylenes, which show 1st order polymerization kinetics (11).

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FIGURE 1

Variation of the transverse parameters a and c as a function of isomerization.

CIS		TRANS
3.81 Å	{ (2,0,0) (1,0,1)	3.72 Å 3.56 Å
2.87 Å	(2,0,1)	2.74 Å
2.20 Å	{ (3,0,1) (0,0,2)	2.12 Å 2.04 Å
1.90 Å	{ (4,0,0) (2,0,2)	1.87 Å 1.79 Å
1.65 Å	(3,0,2)	1.56 Å

Table I Some d spacings between reflection planes containing the chain axis b, for cis and trans (CH)_x. These selected spacings have been followed during the isomerization process.

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- (14) From the observation of (h0l) reflections alone it is not possible to deduce that the lattice is orthorhombic. References (2) and (4) give an orthorhombic or quasi orthorhombic lattice for cis and trans (CH)_x, while reference (3), in better agreement with our results on trans (CH)_x, does not discard a monoclinic unit cell.