Macromolecules 1985, 18, 2374–2379

Polyacetylene Crystal Transformations during Thermal Isomerization

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Received March 12, 1985

ABSTRACT: Thermal isomerization at 100 °C of *cis*-$[CH]_x$ polymerized directly onto gold EM grids has been studied by electron diffraction on aligned bundles of fibrils at −120 °C. Several processes for isomerization are seen. One is the direct local domain conversion of oriented *cis*-$[CH]_x$ crystallites to oriented *trans*-$[CH]_x$ crystallites, which occurs within a few minutes at 100 °C; crystallites of both isomers thus coexist. At the same time there appears a new 1.41-Å meridional reflection that broadens and disappears in ca. 60 min as do all the *cis*-$[CH]_x$ reflections. This intermediate state may be converted to an unoriented *trans*-$[CH]_x$ or via the intermediacy of another transient structure characterized by heretofore unreported new Debye rings at 1.25, 1.78, 2.54, and 4.20 Å. These structural alterations occur in about 12 h at 100 °C. Eventually, after 24 h, all samples show only sharp oriented fiber patterns of the thermodynamically most stable *trans*-$[CH]_x$ crystals. In addition to the observed intermediate structures, the changes in orientation during crystal–crystal transformation are almost unprecedented. A systematic statistical study was made of the effect and ascertained their general occurrence. A mechanism is proposed for these noncooperative transformations. The reorientation is postulated to be due to either melting and recrystallizations nucleated by oriented *trans*-$[CH]_x$ crystallites and promoted by the surface tension on the 20–30-Å microfibrils or annealing-induced segmental reorganization of the $[CH]_x$ chains. None of the 14 different packing structures for *trans*-$[CH]_x$ proposed by Enkelmann et al. is consistent with all the reflections of the intermediate state. Our results are contrary to the X-ray diffraction results of Robin et al. on unoriented samples. It is possible that the $[CH]_x$ polymerized directly onto EM grids has $\bar{M}_n < 1000$, thus isomerizing readily and more completely than the free-standing films of $[CH]_x$ of $\bar{M}_n \sim 11000$. The low $\bar{M}_n$ of our specimens may render possible a variety of isomerization pathways with the participation of transient intermediate structures.

Introduction

The polymerization of acetylene initiated by the Ziegler–Natta catalyst proceeds via cis opening of the C≡C bond and cis insertion into a Ti–C bond.[1] At low temperature the polymer formed has predominantly a cis-transoid structure;[2] $[CH]_x$ obtained at higher polymerization temperatures has increasing amounts of trans structure. Pure *trans*-$[CH]_x$ was formed in polymerization at about 150 °C. It is a common practice to synthesize *cis*-$[CH]_x$ at −78 °C and subsequently isomerize by heating to the thermodynamically more stable trans isomer.[3] The crystal structures of *cis*-$[CH]_x$[4–6] and of *trans*-$[CH]_x$[7–11] have been determined by X-ray and electron diffraction techniques.

Important theoretical distinctions have been proposed for the two isomers of $[CH]_x$.[12] The ground state of *trans*-$[CH]_x$ is doubly degenerate; the two phases on a chain are separated by a moving domain or soliton.[13,14] In *cis*-$[CH]_x$, the formation of bipolarons,[15] not solitons, is favored since cis-transoid and trans-cisoid are not degenerate in energy. Many properties, such as optical, magnetic, and transport, of *cis*- and *trans*-$[CH]_x$ have been interpreted according to the different stability of these defect levels.[12] In light of these experimental and theoretical differences attributed to the electronic excitation of the two isomers, it is important to gain insight into the structural changes that occur during the isomerization of the *cis*-$[CH]_x$ to *trans*-$[CH]_x$.

Robin et al.[16] made a synchrotron radiation diffraction study of the evolution of the structure during in vacuo isomerization at 100 °C of *cis*-$[CH]_x$ film, prepared by the Shirakawa technique comprised of 200–500-Å-diameter fibrils. The measurement was made at ambient temperature; neither the irradiation time nor considerations of radiation damage were given. The authors observed only one set of Debye patterns for all degrees of isomerization. The three most intense equatorial reflections were monitored:[17] {(110) (200)}, (210), and {(310) (020)}. Their *d* spacings changed linearly with % trans from 3.81, 2.87, and 2.21 Å of *cis*-$[CH]_x$ to 3.69, 2.75, and 2.12 Å of *trans*-$[CH]_x$.[18] The results were interpreted to mean that the isomerization occurs homogeneously throughout the polymer and not in isolated or selected crystallite regions. At 100 °C, the cis reflections disappeared after 3 h (>50% trans) and the (002) trans reflection appeared after 1 day of heating (>80% trans). The degree of crystallinity and lattice coherence are said to remain constant throughout isomerization even though the transverse coherence length as deduced from the width of the (110) and (200) reflections was shown to increase from 130 to 181 Å at 50% trans and then decrease to 120 Å upon nearly complete isomerization.

X-ray diffraction studies had been made by Perego et al.[19] on stretched oriented $[CH]_x$ film as a function of isomeric content. The experimental conditions for sample preparation and X-ray measurements were not given. The equatorial pattern displays a unique set of (*hk*0) reflections, as shown for {(110) (200)}, with both interplanar spacing and relative intensity varying monotonically with the composition. On the other hand, there are two sets of (*hkl*) reflections, which correspond to the repeat lengths of the $[CH]_x$ chains and have *d* spacings independent of cis–trans content even though their intensities decrease and lines broaden with decreasing concentration of the cis isomer. These authors proposed that mixed crystals were formed that contain blocks of cis and trans chain segments in a mosaic model of nematic type. The polymer remains a one-phase material during isomerization by an intracrystalline process.

Synchrotron radiation permits rapid recording of X-ray diffraction, requiring only 5 s for each pattern. Heating $[CH]_x$ at 11 °C min^{-1}, Riekel[20] followed the isomerization from 28 to 340 °C in 28 min and found a transition at 150 °C that is the same as that observed by DSC.[3] Isothermal

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Table I
Electron Diffraction of $[\mathrm{CH}]_x$ after 5 min of Isomerization at 100 °C

	cis-$[\mathrm{CH}]_x$[b]			trans-$[\mathrm{CH}]_x$[c]	
obsd reflection d_{obsd},[a] Å	d_c, Å	(*hkl*)	$(d_c - d_{\mathrm{obsd}})/d_c$	d_t, Å	(*hkl*)
3.81 (E)	3.84 (E)	(200)(110)	0.8	3.68 (E)	(200)(110)
2.84 (E)	2.89 (E)	(210)	1.7	2.75 (E)	(210)
2.17 (M)	2.19 (M)	(002)			
1.90 (E)	1.93 (E)	(220)(400)	1.6	1.83 (E)	(220)(400)
1.67 (E)	1.70 (M)	(320)(410)		1.64 (E)	(320)(410)
1.41 (M) new					
1.21 (M)				1.23 (M)	(002)
1.10 (M)	1.12 (M)	(004)			

[a] (E) equatorial; (M) meridional. [b] Reference 4. [c] Reference 7.

measurements at 130 °C showed a continuous shift in reflection position of {(110) (200)}[17] of *cis*-$[\mathrm{CH}]_x$ to {(110) (020)} of *trans*-$[\mathrm{CH}]_x$.[21]

We have extensively studied the crystal structures of $[\mathrm{CH}]_x$, in both the undoped[4,7,21] and doped states[4,22,23] using the electron diffraction technique. In this paper we report the crystal transformation of $[\mathrm{CH}]_x$ during thermal isomerization as observed by electron diffraction.

Experimental Section

Samples were prepared by the previously reported technique[1] of direct polymerization onto 300-mesh uncoated gold grids with a $\mathrm{Ti(OBu)_4/4AlEt_3}$ catalyst solution 7 mM in Ti in toluene. The monomer pressure was about 10 torr, and the polymerization time was about 20 s. The specimens were thoroughly washed in pentane and stored at −78 °C in an evacuated vessel until used. Isomerization was carried out at 100 °C in glass vessels under dynamic vacuum for the time indicated.

Electron micrographs and selected area diffraction (SAD) patterns were obtained on a JEOL 100 CX instrument operated at 100 kV. Some microdiffraction experiments were performed but showed no marked improvement over regular SAD. The microscope was fitted with a customized JEOL cold stage.[24] The grids were transferred from sealed vials to the EM stage by a process taking 15–30 s during which the polymer was exposed to air at ambient temperature. Once placed in the microscope the sample was exposed to the 10^{-7}-torr vacuum for 5 min and then cooled to −120 °C for examination.

We have determined quantitatively the effect of radiation damage. In SAD mode with a beam current of 8×10^{-9} A (directly calibrated with a Keithley nanovoltmeter) and 0.75-$\mu\mathrm{m}^2$ cross section, the lifetime of diffraction clarity was measured for a *trans*-polyacetylene sample. At −120 °C oriented diffractions were converted to diffuse Debye rings in about 10 s. However, randomly oriented material giving sharp rings maintained sharp diffractions for over 120 s under similar conditions of irradiation. At room temperature, such sharp rings became diffuse within 4–7 s, but oriented arcs became diffuse rings in about 4 s. Therefore, all diffraction patterns were obtained within 1.4 s at −120 °C. Some grids were coated with gold along one edge for reference of *d* spacings. Figure 1 shows the typical aligned bundle of fibrils examined in this work.

Results

The electron diffraction patterns from oriented fibrils of pristine *cis*-$[\mathrm{CH}]_x$ and of completely isomerized *trans*-$[\mathrm{CH}]_x$ can be found properly indexed in Figures 3.10 and 3.17 of ref 12, respectively. In the ensuing description, there will be new reflections that appear during a certain stage of the thermal isomerization. Though the data are insufficient to deduce the structures, for the sake of clarity the reflections will be referred to as *trans-I*, *-II*, and *-III*, in the order of appearance during the crystal transformation. Furthermore, subscripts d of o denote disordered and oriented structures, respectively.

In order to observe structural evolution we elected to isomerize the polymer at an optimal temperature of 100 °C. At higher temperatures the rate of isomerization is too rapid for such investigation. At temperatures well below 100 °C, the process is too slow and one risks side reactions such as autooxidation[25] and oxygen-catalyzed cis–trans isomerization.[26]

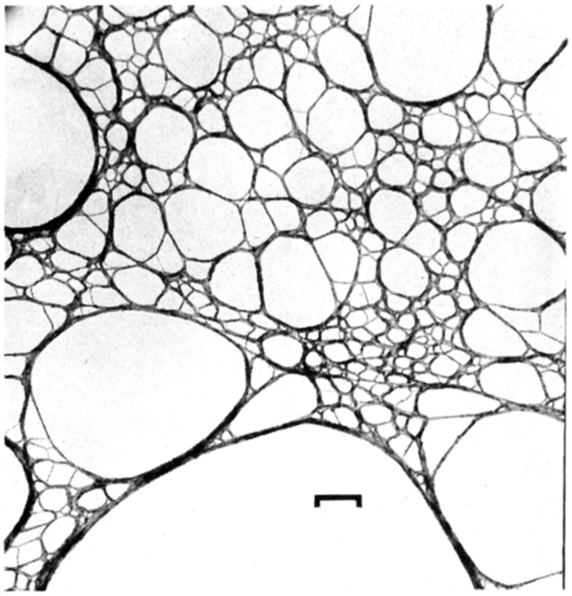

Figure 1. Electron micrograph of aligned bundle of $[\mathrm{CH}]_x$ fibrils polymerized directly onto the gold grid for diffraction studies. Marker is 0.5 μm.

Even very brief isomerization at 100 °C caused pronounced changes. Figure 2 shows the diffraction pattern observed after 20 min of heating. Of central interest are the three intense meridional reflections at 1.10, 1.21, and 1.41 Å. The first one is the (004) reflections of the initial *cis*-$[\mathrm{CH}]_x$ structure, while the second one is the (002) reflection of the final *oriented* trans-transoid structure referred to hereafter as the *trans-III*$_{\mathrm{o}}$-$[\mathrm{CH}]_x$. The third oriented arc is a new reflection not seen previously in either isomer by us or reported in the literature. The 1.41-Å reflection will be denoted as *trans-I*$_{\mathrm{o}}$. All the reflections observed after 5 min of isomerization at 100 °C are summarized in Table I along with those of the initial *cis*- and final *trans-III*$_{\mathrm{o}}$-$[\mathrm{CH}]_x$.

The changes in the intensities of the above-mentioned three reflections with time of isomerization is shown in Figure 3. The (002) reflection of *trans-III*$_{\mathrm{o}}$-$[\mathrm{CH}]_x$ already has significant intensity after 5 min, and it increases steadily with isomerization. At the same time the *cis*-$[\mathrm{CH}]_x$ (004) intensity decreases monotonically; the peak was not observable in microdensitometer scans above the background scattering after 60 min (one can see by the naked eye the remnant in the film negative). The new 1.41-Å reflection is prominent at 5 min but its half-width increases with increasing isomerization; it is not resolved after 60 min at 100 °C. The complete microdensitometer

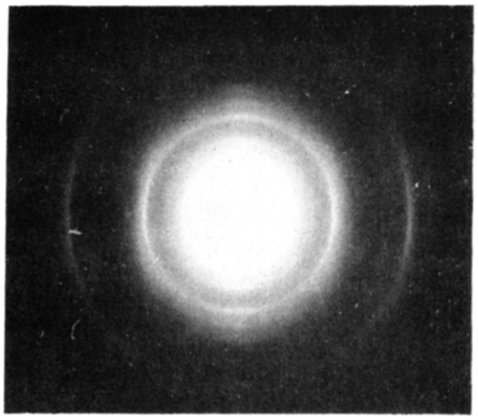

Figure 2. Electron diffraction pattern of $[CH]_x$ isomerized in vacuo for 20 min at 100 °C.

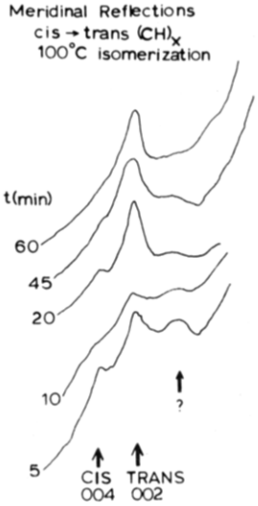

Figure 3. Microdensitometer scans of electron diffraction patterns of a series of $[CH]_x$ samples isomerized at 100 °C for 5, 10, 20, 45, and 60 min.

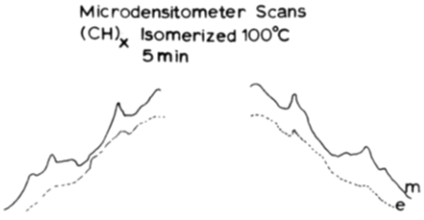

Figure 4. Complete microdenistometer scans of the electron diffraction patterns in Figure 1 showing symmetry and meridional alignment of the outher peaks: (—) meridional; (---) equatorial.

traces for both equatorial and meridional directions are shown in Figure 4, which demonstrates that the three reflections under discussion are indeed all meridional. The deviations of the cis d spacings between those of pristine cis-$[CH]_x$ sample and after 5 min of isomerization at 100 °C are given in column 4 of Table I. They are smaller than the experimental accuracy of ±2%.

Heating of $[CH]_x$ under dynamic vacuum at 100 °C for about 10 h resulted in the electron diffraction pattern as shown in Figure 5 and the d spacings summarized in Table II. There are several important points. First, there is no intensity at 2.19 and 1.10 Å for the (002) and (004) reflections of cis-$[CH]_x$, respectively. Therefore, all the cis crystallites had disappeared in about 1 h at 100 °C. Second, the diffraction patterns are comprised of Debye rings, so initial oriented crystallites become disoriented. They are compared with those of trans-III_o-$[CH]_x$, and the d spacings are in agreement within the ±2% accuracy of electron diffraction (Table II, column 4). Finally, *in about half of the samples examined* there are four new reflections: d = 4.20, 2.54, 1.78, and 1.25 Å. The 4.20-Å reflection is not due to contamination.[27] Reflection for the second order of 4.20 Å would appear at 2.08 Å, coinciding with the (011), (111), and (201) of trans-$[CH]_x$. The other new reflections at 2.54 and 1.25 Å may belong to different orders of the same lattice spacing. In other words some specimens contain reflections from three lattice planes of a new structure denoted as trans-II-$[CH]_x$; the particularly intense innermost pair of rings are shown on the left half of Figure 5 at increased print exposure. The identical diffraction pattern of Figure 5 was obtained when $[CH]_x$ in EM grids was either doped to saturation with iodine vapor and subsequently undoped electrochemically or electrochemically doped with ClO_4^- and undoped for several cycles.[28]

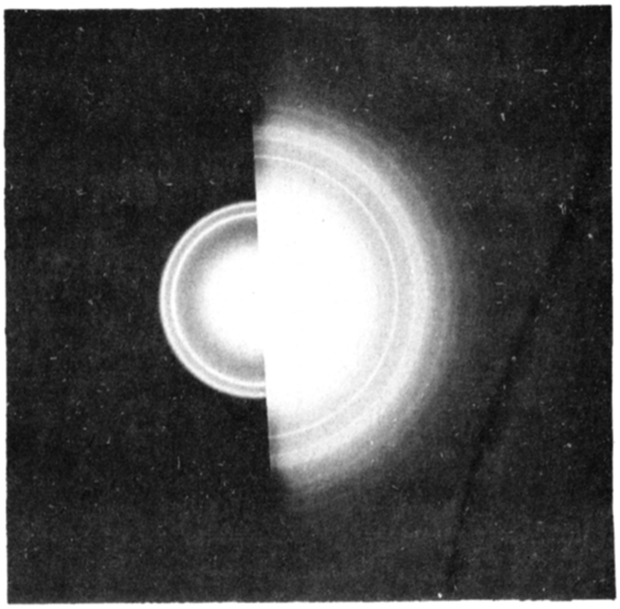

Figure 5. Electron diffraction pattern of $[CH]_x$ isomerized in vacuo at 100 °C for 10 h. The left side shows the intense innermost Debye–Scherrer rings at reduced exposure.

Table II
Electron Diffraction of $[CH]_x$ after 10 h of Isomerization at 100 °C

obsd reflection d_{obsd}, Å	trans-$[CH]_x$ d_t, Å	trans-$[CH]_x$ (hkl)	$(d_{obsd} - d_t)/d_t$
4.20 new			
3.78	3.68	(110)(200)	2.7
2.81	2.75	(210)	2.2
2.54 new			
2.08	2.08	(011)(111)(201)	0
1.90	1.83	(220)(400)	3.8
1.78 new			
1.66	1.64	(130)(230)	1.2
1.25 new			
1.21	1.23	(002)	−1.6

Samples heated for 24 h at 100 °C gave oriented diffraction arcs identical with those given earlier[7,22,23] for trans-$[CH]_x$ isomerized at higher temperatures of 150–180 °C.

Discussion

The effect of heating on the crystal structures of $[CH]_x$ is almost unprecedented. Normally, transformation from one crystalline polymorph to another occurs cooperatively. The reported monotonic changes in d spacings[16] are in indication of an unusual phenomenon. Our results in

Figure 2 and Table I show that the cooperative conversion does occur readily in a very short time, ≤5 min. Oriented *cis*-$[CH]_x$ crystallites transform to the thermodynamically most stable oriented trans-transoid structure

$$cis\text{-}[CH]_x \rightarrow trans\text{-}III_o\text{-}[CH]_x \tag{1}$$

The evidence is unambiguous that there are coexisting *cis*-$[CH]_x$ and *trans*-$[CH]_x$ crystalline domains and they have the same chain axis orientation. This also demonstrates that there is no chain reorientation in this cooperative transformation (1). The presence of crystalline domains of both isomers implies that this isomerization takes place cooperatively in local domains and not uniformly. That is, once isomerization begins, the cis chain in the vicinity of the new trans chains are more likely to convert to the trans conformation than are chains not adjacent to a trans chain. This result is not inconsistent with the interpretation of X-ray results by Perego et al.[19] that polyacetylene has a mosaic structure during isomerization.

In addition to the cooperative process (1), our results showed that there are other pathways for the isomerization, one of which involves the intermediate oriented *trans-I_o*-$[CH]_x$ structure characterized by the previously unreported 1.41-Å *d* spacing. Although this meridional line is somewhat broader than the cis or trans meridional arcs, it is very similar in appearance and curvature to the latter and appears to be a bona fide new meridional reflection rather than the diffuse streak that is seen in the X-ray work of others.[19c] This intermediate structure is present in the isomerizing fiber, which may have a chain-repeat distance longer than that of either the cis or trans chains. In the absence of any other reflections it is impossible to assign the 1.41-Å meridional arc as anything but some (00*l*) reflection. One plausible transformation is that from the cis-transoid structure to trans-cisoid

$$cis\text{-}[CH]_x \text{ (cis-transoid)} \rightarrow trans\text{-}I\text{-}[CH]_x \text{ (trans-cisoid)} \tag{2}$$

This hypothesis is based on the fact that according to the mechanism of polymerization at low temperature the polymer formed has the cis-transoid structure,[1] that trans-cisoid is the necessary intermediate structure for the isomerization, and that there is little or no barrier for the transformation of trans-cisoid to the trans-transoid structure.[29] However, the C–C bond distance in the trans-cisoid has been estimated by several workers to be ≥1.45 Å, which would not give rise to a meridional 1.41-Å reflection. Whatever the mechanism of the process is, there is progressive line broadening during the brief existence of this transient state. This process is probably also responsible for the gradual shift in relative intensity from cis to trans crystallinity, with cis becoming unobservable at about 60 min at 100 °C.

Experimental results (Table II, Figure 5) suggest that *trans-I*-$[CH]_x$ isomerizes via

$$trans\text{-}I\text{-}[CH]_x \rightarrow trans\text{-}II_d\text{-}[CH]_x \tag{3}$$

$$trans\text{-}I\text{-}[CH]_x \rightarrow trans\text{-}III_d\text{-}[CH]_x \tag{4}$$

leading to two different disoriented *trans* structures. The *trans-II_d*-$[CH]_x$ is the new structure first observed in this work, whereas *trans-III_d*-$[CH]_x$ is just the disoriented form of the most stable trans-transoid. Postulation of the two pathways 3 and 4 is necessary because only approximately half the samples examined exhibit the four new reflections (vide supra).

Table III
Statistics of Change in Orientation during Thermal Isomerization of $[CH]_x$ at 100 °C

		% of total^b		
time^a	no. of specimens	arcs only	arcs and rings	rings only
5 min	10	0	10	90
5–60 min	35	46	34	20
12 h	10	0	40	60
24 h	10	80	20	0

^{a}Time of heating at 100 °C. ^{b}% for each time of heating, i.e., 5 min, 60 min, etc.

An unexpected behavior is that all the specimens after 24 h at 100 °C or shorter time at higher temperatures exhibit cleanly oriented fiber diffraction patterns. In fact, the arcs of *trans*-$[CH]_x$ are always more oriented than the initial *cis*-$[CH]_x$. Therefore we must have the orientation of *trans-III_d*-$[CH]_x$

$$trans\text{-}III_d\text{-}[CH]_x \rightarrow trans\text{-}III_o\text{-}[CH]_x \tag{5}$$

In the case of *trans-II_d*-$[CH]_x$, its further transformation can proceed directly

$$trans\text{-}II_d\text{-}[CH]_x \rightarrow trans\text{-}III_o\text{-}[CH]_x \tag{6}$$

or more likely it goes through the *trans-III_d*-$[CH]_x$

$$trans\text{-}II_d\text{-}[CH]_x \rightarrow trans\text{-}III_\alpha\text{-}[CH]_x \tag{7}$$

and then process (5). The observation raises two puzzling questions: how does the disoriented crystallite become oriented again, and why does the degree of order increase with isomerization?

Because the observed effect is so unexpected we tried to obtain some statistics of the unusual phenomenon. Instead of selecting and reporting "typical" micrographs, we have made some effort to statistically quantify the change in degree of orientation in the course of isomerization. A large ensemble of grids and grid squares was therefore observed. Diffraction patterns photographed were classified according to whether only Debye rings, rings superimposed on arcs, or only clean fiber arcs were observed. Thirty-five samples were isomerized for 5–60 min and examined; 10 samples each were isomerized for 12 and 24 h and diffraction patterns photographed. The statistical results are given in Table III.

This systematic statistical study reveals that the initial *cis*-$[CH]_x$ samples show very few oriented fibrils. In other words, our reports on electron diffraction of *cis*-$[CH]_x$[4] had emphasized the oriented fiber pattern but ignored the unoriented Debye rings. Furthermore, the specimens used in the previous studies were subjected to standing at room temperature for unknown lengths of time, whereas the *cis*-$[CH]_x$ of this work was kept at low temperature except for the 15–30 s during transfer (vide supra). The present diffraction photographs were all taken from single bundles of fibrils as in Figure 1, which are supposed to produce oriented fiber patterns. Now we must state that during polymerization, crystallization of the cis-transoid chains results only infrequently in oriented fibril aggregates but more often in unoriented fibril bundles. The latter may acquire orientation upon standing at room temperature. Consequently, we have to add to cooperative transition of oriented *cis*-$[CH]_x$ to oriented *trans*-$[CH]_x$ of reaction 1

$$cis_d\text{-}[CH]_x \rightarrow trans\text{-}III_d\text{-}[CH]_x \tag{8}$$

However, the fact that heating for only a few minutes at 100 °C makes it easy to find clearly oriented fibers requires a postulate of the following transformations

$$cis_d\text{-}[CH]_x \rightarrow cis_o\text{-}[CH]_x \tag{9}$$

$$cis_d\text{-}[CH]_x \rightarrow trans\text{-}III_o\text{-}[CH]_x \tag{10}$$

For longer heating of 12 h, the extent of orientation becomes lower regardless of whether the double inner rings

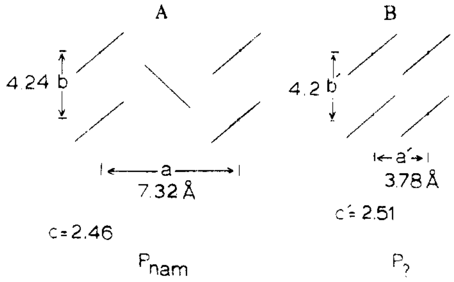

Figure 6. Speculative schematic of crystal packing of polyacetylene chains viewed along the *c* axis: (A) fully isomerized *trans-III*-$[CH]_x$; (B) proposed structure of *trans-II*-$[CH]_x$.

and other new reflections are present or not. However, upon further heating there is a high degree of orientation with clean arcs. For isomerization times greater than 1 day at 100 °C we have seen from aligned bundles of fibrils only oriented fiber diffractions previously assigned to the trans crystal structure of polyacetylene.[7] In our work the fully isomerized *trans*-$[CH]_x$ always displays the highest degree of orientation.

We believe that the observed change in orientation during isomerization is due to either partial melting and recrystallization or annealing of crystallites with segmental reorganization of polymer chains. The driving force toward the final highly oriented state is probably the surface tension on the microfibrils of 20–30 Å, which is the ultimate morphological entity of the $[CH]_x$ fibrils of 200–300-Å diameter.[12] Those oriented *trans*-$[CH]_x$ crystallites produced early during the isomerization by cooperative process 1 can act as nucleation centers for the formation of *trans*-III_0-$[CH]_x$ in reactions 5–7. The *trans-I*, *-II*, *-III*$_d$ are kinetic intermediates. Their lifetimes are short, from minutes to hours at 100 °C, and they would not be observable during high-temperature isomerizations.

The second intermediate structure *trans-II*-$[CH]_x$ is characterized by four new reflections. This information is, however, far from sufficient to solve its structure. Indeed even the dozen reflections of *trans*-$[CH]_x$ are inadequate to resolve all structural ambiguities. What follows is our speculation of that isomerization pathway involving this intermediate.

The appearance of a reflection at 4.2 Å indicates what is probably a breakdown of the glide planes of the *Pnam* space group, i.e., in *Pnam* (*h*00), (0*k*0), (00*l*) reflections are of zero intensity for *hkl* odd because of the screw axes along the **a**, **b**, or **c** space directions. The single observation of an (equatorial) 4.2-Å spacing demands that the *d* spacing be either (010) or (100), i.e., either the **b** or **a** unit-cell length (maximal planar spacings). Figure 6A shows the chain-end view of stacking of $[CH]_x$ chains in trans (or cis) polyacetylene. The **b** length of 4.24 Å is very close to that of the new *d* spacing, suggesting, with minimal rearrangement, that the trans **b** spacing is conserved and that the **ab** face-centered polymer chain "flips" and the **a** *d*-spacing collapses. This model is consistent with, though not strictly determined by, the reflections in Table II. If the 4.2-Å reflection is assigned to (010) then the (020) would be assignable within our error limits to be under the trans 2.08-Å line. The new 2.54- and 1.25-Å reflections could be (001) and (002), respectively. Because it is not possible to separate the reflections of *trans-III* crystallites from those of the *trans-II* structure, one cannot use the general (*hkl*) reflection to corroborate the hypothetical unit cell. Interestingly, if the (001) and (002) assignments are correct, then the mirror plane dividing the chain direction of the *Pnam* unit cell is lost. The 2.54-Å chain axis repeat distance is very close to that of the usual trans-transoid structure so that loss of the mirror plane indicates a stronger alternation of bond length[9] between single and double bonds than is seen in the final trans structure.

The observation of the diffraction patterns seen in Figure 5 in other $[CH]_x$ samples that have been fully doped with iodine vapor or with ClO_4^- electrochemically and subsequently electrochemically undoped indicates that the *trans-II* transitional state is not a peculiar artifact of oxidation during 100 °C isomerization but is one stage of the isomerization process.

Enkelmann et al.[30] proposed 14 different packing models for *trans*-$[CH]_x$. We have calculated the predicted *d* spacing and intensities for all these models to find out whether any of them may correspond with the *trans-II*-$[CH]_x$ intermediate. We found only one of these structures predicts significant intensity near each of the new spacings observed in this work (Table II). This pseudomonoclinic structure with $\mathbf{a} = 3.59$ Å, $\mathbf{b} = 6.65$ Å, $\mathbf{c} = 2.44$ Å, $\delta = 144°$ predicts spacings of 4.15 Å (001), 2.59 Å (021), 1.76 Å (022), and 1.27 Å (023). All other predicted reflections of significant intensity on this model fall within ±2% of the final trans-*III* reflections except for intense lines at 6.65 Å (010) and 3.325 Å (020). One of these latter lines, *but not both*, could be eliminated by an extinction rule forbidding intensity for *k* even or odd. But the fact that neither line is observed eliminates this structure from consideration as an intermediate structure. However, this conclusion should be tempered by the fact that electron diffraction has the shortcoming of high background inelastic scatterings, which can make it difficult to observe weak reflections.

Two questions now remain: why were the intermediate structures and change in orientation during isomerization not observed by other electron diffraction investigators, and what are the reasons that our results are in total disagreement with the X-ray results of Robin et al.?[16] The first one is simple to answer; other workers had not investigated the isomerization process with electron diffraction. For X-ray studies it is customarily to use stretched oriented specimens and some of the transformations mentioned above could have happened during these manipulations, sometimes at elevated temperatures. Also electron diffraction is an unaveraged local probe that can detect discrete oriented patterns in the surrounding of unoriented materials.

Perhaps most important is that our $[CH]_x$ polymerized directly onto EM grids are very different from those prepared by the normal procedure.[2] We have studied the kinetics of acetylene polymerization very thoroughly.[1] Furthermore, we have developed radiotagging techniques to determine the number-average molecular weight, $\bar{M}_n$, of $[CH]_x$.[31] As a result we were able to synthesize and characterize $[CH]_x$ with $\bar{M}_n$ from 400 to 920 000.[32] Unfortunately, the amount of $[CH]_x$ on the EM grid, <100 ng as determined by electrochemical techniques,[33] was too small for direct $\bar{M}_n$ determination. But on the basis of the kinetics, the conditions used to polymerize acetylene directly onto the EM grids should produce polymers with $\bar{M}_n$ probably <1000. This is to be compared with the free-standing films of $[CH]_x$ obtained with the procedure of Ito et al.,[2] which have $\bar{M}_n \sim 11\,000$.[31b] Thermal isomerization of the latter material proceeds initially at a rapid rate and low activation, but the process becomes progressively more difficult and requires greater activation energy as the trans content increases.[3] In contrast, the very low $\bar{M}_n$ $[CH]_x$ isomerized very rapidly to completion with an activation energy of only about 12 kcal mol^{-1}.[32] When the thermal isomerization of *cis*-$[CH]_x$ prepared with the normal procedure is followed by infrared spectroscopy,[19] one finds a cis content of about 40% after heating at 100 °C for 1 h but that subsequent reduction of cis content is slow. A comparison of rate of isomerization had been made on low $\bar{M}_n$ and 11 000 $\bar{M}_n$ polyacetylenes;[32] the isomerization at 150 °C is nearly complete in 30 min while the latter has 25% cis content after 270 min. It is possible that the transformations reported here occur only for low $\bar{M}_n$ polyacetylene and under the precise conditions of this work. However, it must be realized that in X-ray diffraction the structure is averaged over a large specimen. Therefore, small amounts of intermediate structure may escape observation. Certainly, changes in orientation will not be revealed in wide-angle X-ray diffraction study of unoriented specimens. Also our sample had minimal exposure to air and room temperature, and our observations were done at −120 °C and 10^{-6} torr. In the work of Robin et al.[16,17] no error bounds are reported, so the confidence level on the small monotonic decrease of *d* spacing is uncertain.

Conclusion

The process of crystal transformation in the thermal isomerization of *cis*-$[CH]_x$ is very complicated. At the simplest level there is local conversion of oriented *cis*-$[CH]_x$ crystallites to oriented *trans*-$[CH]_x$ crystallites. In addition there are processes involving two or more transient intermediate structures. The unexpected phenomenon is that these transformations involve appreciable disorientation of the crystals followed by reorientation by either melting and recrystallization or annealing reorganization. The effect is so unusual that we have made a systematic statistical study to ascertain its general occurrence.

Acknowledgment. This work was supported in part by grants from NSF and ONR. We are most grateful to Professor E. L. Thomas for helpful discussions, advice on electron microscopy and diffraction, and critical comments on the manuscript.

Registry No. *cis*-Polyacetylene (homopolymer), 25768-70-1.

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