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# Structural and Morphological Study of a Melt-Crystallized Polydiacetylene

**Hajime Tanaka,**[†] **M. A. Gomez,**[‡] **A. E. Tonelli,*** **A. J. Lovinger, D. D. Davis, and M. Thakur**

*AT&T Bell Laboratories, Murray Hill, New Jersey 07974.* *Received July 11, 1988; Revised Manuscript Received October 17, 1988*

ABSTRACT: The melt-crystallized phase of a polydiacetylene, poly(ETCD), whose side-chain substituent is $(CH_2)_4O(C{=}O)NHCH_2CH_3$, has been examined by high-resolution, solid-state $^{13}C$ NMR, X-ray and electron diffraction, and electron microscopy. Compared to the blue and red single-crystal phases of this polymer (obtained by topotactic polymerization), the melt-grown phase has lower crystallinity, shorter $\pi$-electron conjugation length resulting from a less planar backbone conformation, and more extended side chains. These results are consistent with an observed expansion of the unit cell in the *a* direction. Comparison of $^{13}C$ spin–lattice relaxation times indicates greater mobility of both the backbone and side-chain carbon atoms in the melt-grown phase than in its two single-crystal counterparts. Topotactically grown thin films have the *a* axis of the unit cell normal to the substrate and consist of plateletlike crystals in which the molecular backbones are in the lamellar planes. Sharp faceting and easy fracture occur parallel to the backbones, i.e., between hydrogen-bonded sheets. On the other hand, melt-grown films consist of spherulites or lamellar aggregates on edge; in the latter case, the molecular backbones are now perpendicular to the lamellae and preserve the original chain direction of the topotactically polymerized crystals.

## Introduction

Polydiacetylenes (PDA) are highly unusual among synthetic polymers in that they can be obtained as large single crystals from the solid-state, topochemical polymerization[1] of their single-crystal monomers. PDA's have very interesting optical properties[2,3] which are a consequence of their unique backbone chemical structure. They have large nonlinear optical coefficients reflecting their extended $\pi$-electron conjugation lengths. Some PDA's exhibit larger optical nonlinearities than inorganic materials. For these reasons, there have been numerous studies[2–9] of the optical properties and structures of PDA's.

A major structural feature of many PDA's is their thermochromic phase transitions. Recently,[9–11] we have studied the thermochromic phase transition in one such PDA, poly(ETCD) [R = $(CH_2)_4O(C{=}O)NHC_2H_5$] (see Figure 1), by solid-state $^{13}C$ NMR and X-ray and electron diffraction. Preliminary results indicate a deviation from backbone planarity and a conformational change in the side chains of poly(ETCD), resulting in unit cell expansion. From the comparison of the solid-state $^{13}C$ NMR spectra of several PDA's we have found[11] that there are two typical backbone conformations in single-crystal PDA's, one planar and the other nonplanar. The first corresponds to PDA's in their blue phase and the second to those in their red phase. In poly(ETCD), these phases exist below and above ca. 115 °C, respectively,[9,10] The nonplanar, red-phase backbone conformation is likely achieved[10,11] by small rotations (5–10°) of opposite signs about the single $=C-C\equiv$ bonds in each repeat unit. Alternative deformations including distorted bond lengths or valence angles, or the presence of the butatrienic form of backbone conjugation ($-C(R){=}C{=}C{=}C(R)-$), are not consistent[10,11] with the $^{13}C$ NMR evidence.

PDA's exhibit another transition at higher temperatures, the melting transition. Melting is rather unusual in conjugated polymers, because of the high potential barrier hindering rotation about their conjugated multiple bonds. However, because of the entropy available in their large side chains, some PDA's exhibit melting, in contrast to other conjugated systems such as polyacetylene. For the same reason, many PDA's are also soluble in a variety of solvents.

Since PDA's are normally polymerized topotactically from their monomers, their structures after melting are expected to be different. However, there have been no detailed studies yet on melt-crystallized PDA's. It is, therefore, of interest to learn what kind of reordering occurs when PDA's are crystallized from their disordered melts and to study the melting transition of such conjugated polymers. Their reordering from the melt should be related to the inherent macromolecular nature of PDA's while in the case of their solid-state polymerization[1] their ordering is primarily determined by the crystalline arrangement of monomers.

Here, we report a study of the conformations of the backbone and side chains of once-melted poly(ETCD) based on the comparison of high-resolution, solid-state $^{13}C$ NMR spectra and X-ray diffractograms with those obtained from its single-crystal blue and red phases. These results are augmented by use of transmission electron microscopy and diffraction to study the morphology and orientation of PDA crystals both after solid-state polymerization and after growth from the melt.

## Experimental Section

Poly(ETCD) was obtained by the solid-state polymerization of ETCD [5,7-dodecadiyne-1,12-diol bis(ethylurethane)]. The synthesis of ETCD monomer was performed by the procedure reported in the literature.[7,12] Polymerization was accomplished by irradiation with 50 Mrad of $^{60}Co$ $\gamma$-rays at room temperature. Unreacted monomer was removed by extraction with acetone.

$^{13}C$ NMR spectra were recorded on a Varian XL-200 spectrometer operating at a static magnetic field of 4.7 T. Magic angle sample spinning (MAS) at speeds of ca. 3 kHz was achieved with a Doty Scientific variable-temperature probe, which utilizes a double air bearing design. Once-melted poly(ETCD) films were packed in an aluminum oxide rotor with Kel-F [poly(chlorotrifluoroethylene)] end caps. A 45-kHz radio-frequency field was used for the dipolar decoupling (DD) of protons, with a decoupling period of 200 ms. The optimum cross-polarization (CP) time was found to be 2 ms at room temperature. Spectra were referenced[13] to the resonance of poly(oxymethylene) (POM) (89.1 ppm from TMS) which had been added to the rotor. Spin–lattice relaxation times, $T_1$, were measured for each carbon under the CP condition by application of the pulse sequence developed by Torchia.[14]

A Perkin-Elmer DSC-4 differential scanning calorimeter was used for thermal studies. X-ray diffractograms were recorded

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[†] Permanent address: Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

[‡] Permanent address: Instituto de Plasticos y Caucho, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain.

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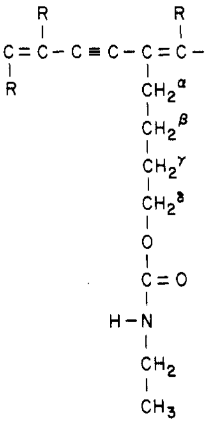

POLY (ETCD)

**Figure 1.** Chemical structure of the polydiacetylene, poly(ETCD).

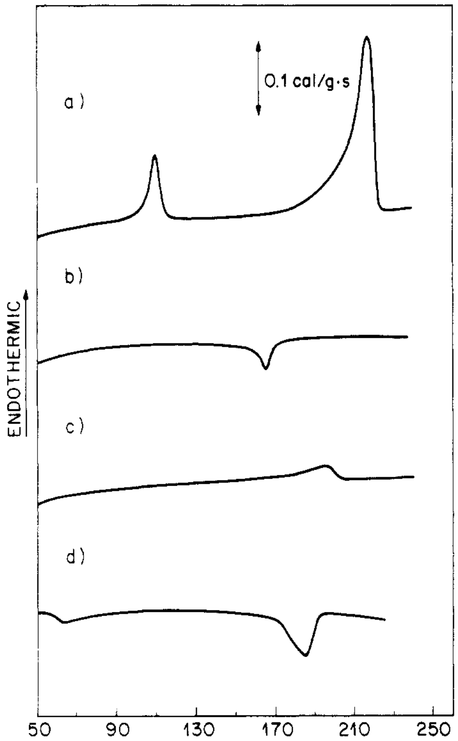

**Figure 2.** DSC scans at 10 °C/min for poly(ETCD). (a) First heating of single crystal. (b) Cooling from the melt. (c) Second heating. (d) Cooling immediately following melting.

on a Rigaku diffractometer in the reflection mode at 1° (2$\theta$) per minute, using Ni-filtered Cu K$\alpha$ radiation. Electron microscopy and diffraction were performed in a JEOL instrument at 100 keV on thin films that had been shadowed with Pt/C, carbon coated, floated off in water, and deposited onto grids in the usual manner.

## Results and Discussion

DSC scans of poly(ETCD) are presented in Figure 2. In the initial heating, two clear transitions are observed, as reported previously. The first is the solid-state (blue-to-red) thermochromic phase transition and the second the melting of the single-crystal red phase. After waiting a short period of time, cooling from the melt shows crystallization around 165 °C with a very small exotherm. Heating the recrystallized sample does not produce a thermochromic phase transition, but instead causes melting at 194 °C, which is approximately 20 °C below the initial single-crystal melting temperature. Not only is the melting temperature of the once-melted sample lower than that of the single crystal, but its heat of fusion is also reduced and the endotherm is very broad. These observations indicate a substantially less ordered structure for the melt-crystallized sample of poly(ETCD). Samples cooled immediately after heating through the thermochromic and melt transitions show that only partial melting occurs (Figure 2d). Crystallization begins at a higher temperature (180 °C), due to the presence of some single crystals, and shows a small exotherm around 65 °C corresponding to the thermochromic transition of the remnant single crystals.

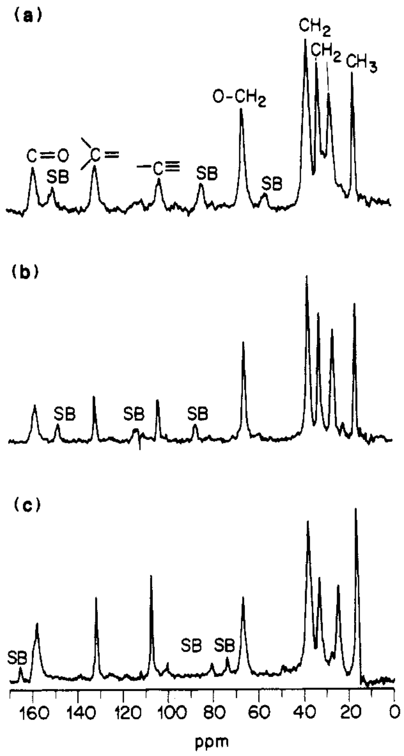

**Figure 3.** CP MAS/DD $^{13}$C NMR spectra of (a) once-melted, (b) single-crystal red-phase,[9,10] and (c) single-crystal blue-phase[9,10] poly(ETCD).

**Table I**
**$^{13}$C Chemical Shifts of Poly(ETCD): δ ($^{13}$C, ppm, versus TMS)**

| ETCD | C=O | >C= | —C≡ | $\alpha$-CH$_2$ | $\beta$-, $\gamma$-CH$_2$ |
|---|---|---|---|---|---|
| blue | 157.5 | 131.6 | 107.4 | 37.3 | 24.5 |
| red | 158.3 | 132.0 | 103.6 | 37.8 | 26.4 |
| melt | 158.1 | 130.8 | 102.5 | 37.3 | 27.2 |

The sample color of single-crystal poly(ETCD) changes from blue to red at the thermochromic phase transition and then from red to yellow upon melting. Both color changes reflect a reduction in the effective $\pi$-electron conjugation length along the poly(ETCD) backbone. Through crystallization during cooling, the color changes from yellow in the melt to red in the solid, and further cooling results in no color change. The color change at the melting point is thought to be related to the increase in backbone nonplanarity: Theoretical calculations[15] suggest that rotation about the backbone single bonds (=C—C≡) is relatively facile (ca. 2 kcal/mol barrier), and only minor rotations (5–10°) away from planarity may be sufficient to produce the color changes accompanying both the thermochromic and melt transitions.

Figure 3 presents the solid-state CP MAS/DD $^{13}$C NMR spectra of the once-melted sample and red and blue phases of the single-crystal powder of poly(ETCD). There are significant differences in the chemical shifts of the back-

**Table II**
**Spin-Lattice Relaxation Times ($^{13}C$) of Poly(ETCD)**

| carbon | $T_1$ ($^{13}C$), s<br>blue, 23 °C ↑[a] | red, 110 °C ↓[a] | melt crystallized, 23 °C |
|---|---|---|---|
| C=O(↓) | 137 | | 12 |
| C=O (↑) | 116 | 47 | |
| >C= | 153 | 25 | 15 |
| —C≡ | 172 | 30 | 36 |
| δ-$CH_2$ | 11 (22%), 110 (78%) | 6 | 3 |
| α-$CH_2$ | 9 (34%), 103 (66%) | 8 | 5 |
| ε-$CH_2$ | 9 (15%), 108 (85%) | 6 | 3 |
| β-, γ-$CH_2$ | 2 (9%), 97 (91%) | 4 | 5 |
| $CH_3$ | 2 (81%), 14 (19%) | 6 | 1.5 |

[a] ↑ indicates observations made during heating and ↓ corresponds to results obtained on cooling.

bone —C≡ and of the β- and γ-$CH_2$ carbons of the side-chain alkyl group among these three samples. Table I summarizes the chemical shifts of the three poly(ETCD) samples. The chemical shift of —C≡ is furthest downfield for the blue phase, intermediate for the red phase, and most upfield for the once-melted sample. This suggests that the π-electron conjugation length along the backbone is decreasing in the same order, because of a change in the planarity of the backbone conformation.[10,11]

Allegra et al.[16] suggested two alternate models for the flexibility of soluble PDA's in solution: in model 1 only twisting and bending fluctuations away from the planar, trans blue-phase conformation were allowed, while occasional ±90° roations away from the trans conformation about the —C≡C— bonds were permitted in model 2. Our $^{13}C$ NMR results are compatible with model 1 for both the red and melt-recrystallized phases of poly(ETCD) but do not support the existence of model 2 structures to any significant degree in the disordered, melt-recrystallized phase.

For poly(PTS-12), with side chains R = $(CH_2)_4OSO_2C_6H_4CH_3$, solid-state $^{13}C$ NMR spectra have been reported[17] for both single-crystal (blue) and solution-crystallized samples. In this case, the backbone —C≡ resonance of the solution-crystallized poly(PTS-12) sample shows a chemical shift close to that observed here for melt-crystallized poly(ETCD). This observation is not unexpected since both samples are reordered from a disordered state and are expected to lose memory[18] of their single-crystal monomer structures.

The chemical shifts of the β and γ side-chain carbons are furthest downfield in the once-melted sample, intermediate in the red phase, and most upfield in the blue phase. As discussed previously,[10] a comparison of the solid-state $^{13}C$ NMR chemical shifts of the methylene carbons in model compounds and polymers with chemical structures similar to the side chains in poly(ETCD), and whose solid-state conformations are known from X-ray diffraction studies, suggests that the progressive downfield shift of the side chain β- and γ-$CH_2$ carbon resonances in poly(ETCD), as it is transformed from the blue to the red and finally to the melt-crystallized phase, reflects the progressive extension of the alkyl portion of the side chains.

Note that the chemical shifts of the C=O carbons are very similar among the three samples, indicating a substantial retention of side-chain hydrogen bonding. In the melt-crystallized sample, however, the side-chain hydrogen bonds may not be exclusively intra-chain as in the blue and red phases of the single-crystal samples.

Table II presents the spin-lattice relaxation times, $T_1$, for each carbon in the three poly(ETCD) samples. As noted previously[10] in the blue phase, there are two separate populations of side-chain $CH_2$ and $CH_3$ carbons relaxing at different rates, with the relative amounts of each given in parentheses in Table II. This is possibly a reflection of two distinct modes of side-chain packing in the blue-phase crystals. The $T_1$'s observed for the once-melted sample are similar to those measured for the single-crystal red-phase material, both being much reduced compared to the $T_1$'s found for the more rigid blue phase. The only significant difference is for the side-chain C=O carbon whose $T_1$ is only 12 s in the melt-crystallized sample and 47 s in the red-phase crystals. This suggests that the hydrogen-bonding network in the melt-grown crystals may be more mobile than in the red phase, even though the alkyl portions of the side chains in both phases appear to possess comparable mobilities.

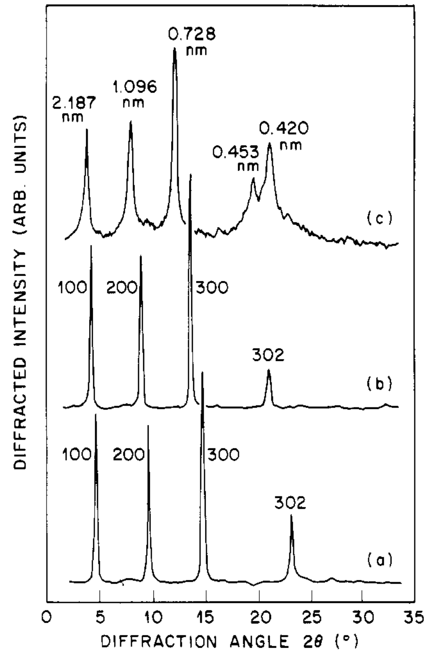

**Figure 4.** X-ray diffractograms of (a) single-crystal blue-phase at 25 °C, (b) single-crystal red-phase at 140 °C, and (c) once-melted poly(ETCD) at room temperature.

X-ray diffractograms for the three poly(ETCD) samples are presented in Figure 4. In all of these samples, the three strongest reflections are identified as successive orders of *h*00, indicating that the *a** axis is aligned close to normal to the plane of the thin-film specimens. The fourth reflection is tentatively identified as 302 on the basis of the published unit cell parameters of Chance et al.[8] However, this plane is inclined by ~45° with respect to the *bc* plane. Therefore, if this identification is correct, the crystals must be present in more than one orientation. It should be kept in mind that these unit-cell parameters[8] have been questioned[19,20] and that a full crystal-structure analysis has not been published.

As the poly(ETCD) sample is heated from the blue to the red phase (Figure 4b), there is a clear expansion[20] of the *a* axis (from 1.82 nm at 25 °C to 1.88 nm at 140 °C). The reflections remain as sharp as originally observed, and there is no increase in the (minimal) diffuse background, indicating retention of single-crystal character. These results are consistent with our $^{13}C$ NMR evidence (described above) which showed preservation of hydrogen bonding and extension of the side chains. As is discussed later, the side chains are expected to be aligned close to the *a* axis which undergoes the observed expansion. The temperature dependence of this expansion is seen in Figure 5 for the 100, 200, 300, and 302 reflections. For all of these,

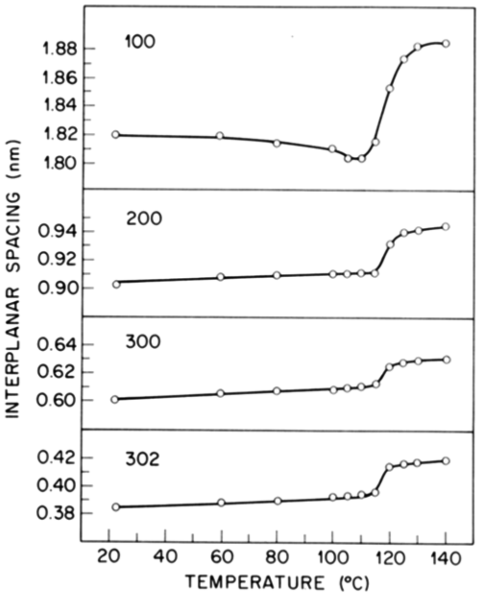

**Figure 5.** Temperature dependence of the interplanar spacings in single-crystal poly(ETCD).

the transition is clearly seen to be localized between 110 and 120 °C. The very small initial reduction in the $d_{100}$ spacing is not significant, since it is inconsistent with the behavior of its higher order counterparts; at low $2\theta$ angles small angular differences have a disproportionately large effect on the corresponding values of the *d* spacing.

Heating poly(ETCD) to its melting point leads to the diffractogram of Figure 4c after cooling to ambient temperature. The three strongest reflections still correspond to 100, 200, and 300, but now of a further expanded lattice ($a = 2.19$ nm). The *d* spacing of the reflection tentatively assigned to 302 is also increased (to 0.453 nm), but in addition, a new broad peak is seen at 0.420 nm; this may imply a reduction in symmetry. The lattice expansion observed is in agreement with our $^{13}C$ NMR results, which show an increased downfield shift of side-chain carbon resonances ($\beta$ and $\gamma$) as the material is transformed from the red to the melt-crystallized phase. The major difference between these two phases lies in the loss of the single-crystal character of the specimen (Figure 6a) and its replacement by a spherulitic morphology typical of polymers (Figure 6b). These spherulites were nucleated as the temperature was reduced from above the melting point to 130 °C and grew rapidly at that temperature; because of profuse nucleation, their ultimate sizes were generally less than 40 $\mu$m. The highly reduced crystallite sizes and the semicrystalline nature of these melt-grown spherulites are clearly reflected in the increased peak width and diffuse background of their diffractogram (Figure 4c).

Single crystals of poly(ETCD), such as those seen in Figure 6a, have also been examined in greater detail by transmission electron microscopy and diffraction. Typical morphologies consist of large (many micrometers), thin (down to ca. 5-nm) platelets with sharp facets parallel to one direction (see Figure 7a). From the corresponding electron-diffraction pattern (Figure 7b), this direction is identified as the *b* axis of the unit cell,[8] i.e., as the molecular backbone. This unusual orientation, in which the macromolecular chains are parallel to the lamellar surfaces, has also been found in other topochemically polymerized polydiacetylene single crystals.[21,22] The transverse lamellar direction corresponds to $c^*$ (all reflections are of the $0kl$ type), and thus the lamellar normal is the *a* axis. Since a full crystal-structure analysis has not been reported in the literature,[8,19,20] the three-dimensional molecular ori-

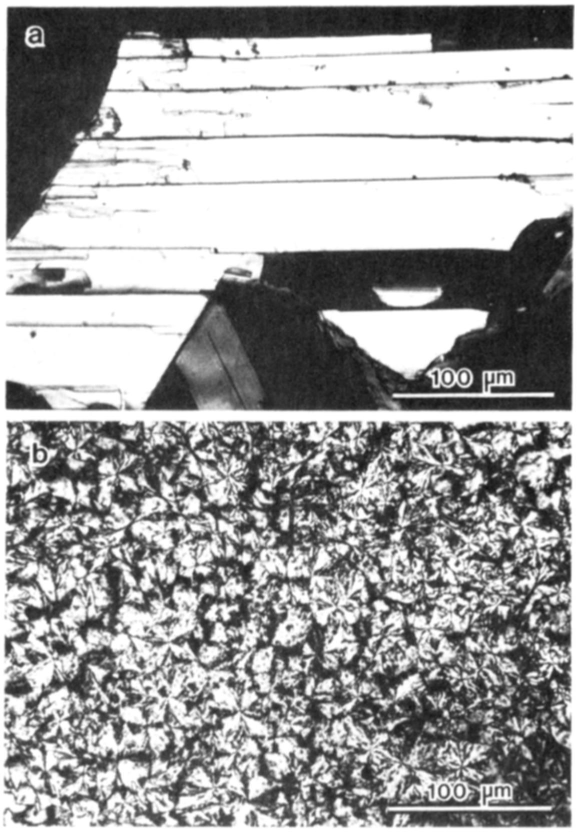

**Figure 6.** Optical micrographs of poly(ETCD) (a) single crystals and (b) melt-grown spherulites.

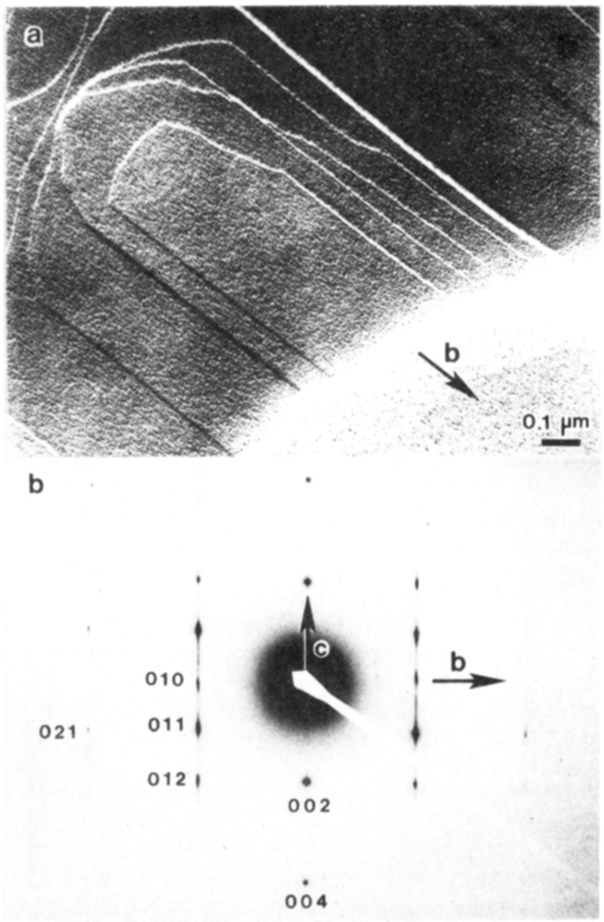

**Figure 7.** (a) Transmission electron micrograph and (b) electron-diffraction pattern of poly(ETCD) single crystals in the blue phase ($T = 25$ °C).

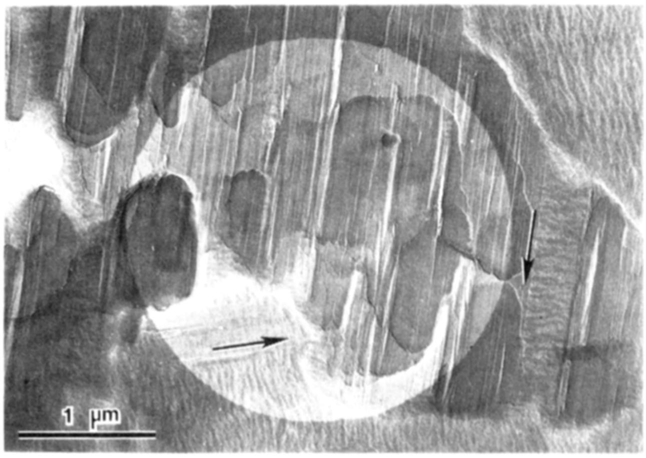

**Figure 8.** Transmission electron micrograph showing the mutual orientation of poly(ETCD) crystals grown by solid-state polymerization, followed by partial melting and rapid cooling to ambient. The remnants of the topotactically polymerized crystals are distinguished by their profuse fracture in the backbone direction (arrows), while the melt-crystallized lamellae are seen to have grown in the perpendicular direction. The circular area is an image of the selector aperture used for diffraction.

entation is not immediately obtainable from these results. It is possible that a portion of the increase in the *a*-axis dimension observed[20] as poly(ETCD) is transformed from its blue to red to melt-recrystallized phases is a result of changes in the angle of orientation between the side chains and the *a* axis. However, by analogy with another polydiacetylene (TCDU)[5,6] which has a very similar chemical structure $[R = (CH_2)_4O(C{=}O)NHC_6H_5]$, we would expect the hydrogen-bonded sheets to lie near the *ab* plane, with the side chains extending close to the *a* axis of the unit cell. In this manner, the hydrogen-bonded sheets should be nearly perpendicular to the lamellae; this would explain the sharp faceting and easy cleavage parallel to the *b* axis (backbone direction). We should also note that the thinnest observed lamellar steps were ca. 5 nm (based upon lengths of Pt shadows), implying that they consist of only three layers of hydrogen-bonded sheets. Finally, a distinct disorder is seen in these polydiacetylenes, as evidenced by the presence of streaks parallel to $c^*$ and superimposed on the 01*l* and 02*l* reflections. This, in conjugation with the fact that the 00*l* reflections are sharp and unsteaked, implies that the hydrogen-bonded sheets are misplaced with respect to each other parallel to the backbone direction. The misplacement might also involve different inclinations of side chains to the backbone direction. Similar evidence for packing disorder has also been found in other polydiacetylenes.[22]

A better understanding of the mutual relationships in poly(ETCD) obtained by solid-state polymerization or melt crystallization can be generated by partial melting of topochemically polymerized single crystals. Heating these to just above their melting point, and then quickly cooling to ambient temperature leads to growth of typical polymeric lamellae in epitaxial relationship with the original, solid-state polymerized crystals. This is seen in Figure 8, where a number of regions of thin melt-grown lamellae are arranged perpendicularly to the characteristic fracture surfaces of the topotactically grown crystals (as discussed above and also in ref 21, these fracture surfaces are parallel to the main-chain *b* axis, which is indicated by arrows in Figure 8). At higher magnifications (Figure 9) the melt-crystallized lamellae are seen to have thicknesses in the 40–50-nm range, which is higher than that of typical polymeric crystals, but still indicative of chain-folded crystals in edge-on orientation. The accompanying electron-diffraction pattern shows a reflection at 0.240 nm, corresponding to 020. The disposition of this reflection demonstrates that the macromolecular chains (*b* axis) are oriented perpendicularly to the lamellar surfaces. Thus, the backbone direction in both the topotactically polymerized crystals and the melt-grown lamellae remains the same in these specimens.

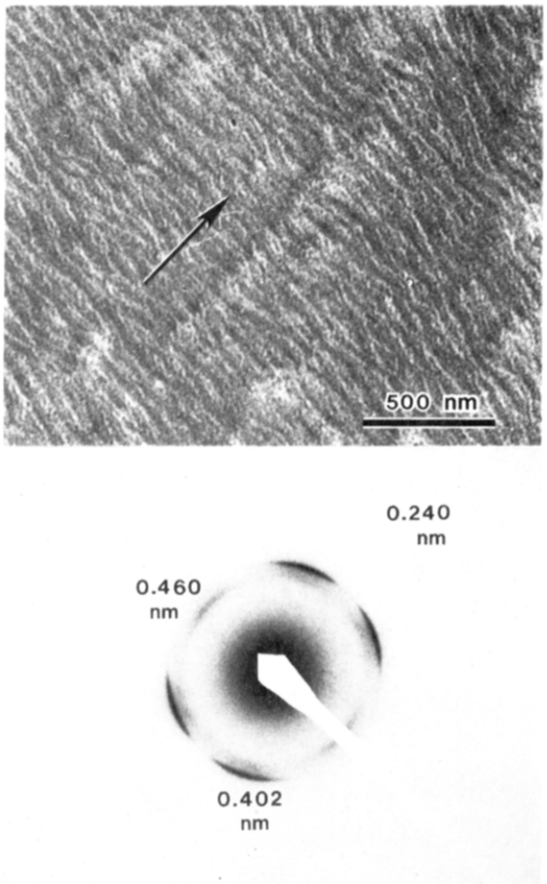

**Figure 9.** Transmission electron micrograph and corresponding diffraction pattern from melt-grown lamellae such as those in Figure 8. The arrow indicates the chain-axis direction.

The structural differences between the as-polymerized single crystals and the crystals obtained from the melt are attributed to the topochemical polymerization. The original monomer crystal structure has a dominating effect on the final structure of PDA's, as originally discussed by Wegner.[18] Residual memory of monomer single crystal structure is one of the characteristics which distinguish PDA's among polymers. This feature is likely to be most important in PDA's which have hydrogen bonding between side chains.

The single-crystal structures of PDA's may not be their lowest free-energy states. However, the potential barrier opposing the transformation of the single-crystal structure to the melt-crystallized may be too high to permit this transformation to occur in the solid state without disruption of the hydrogen bonding. Our observation that the solution-crystallized sample of poly(PTS-12), whose side chains are not capable of hydrogen bonding, has a structure similar to melt-crystallized poly(ETCD) suggests that hydrogen bonding is not a necessary condition for producing a PDA structure from a disordered phase that is distinct from the as-polymerized structure.

Through utilization of high-resolution, solid-state $^{13}C$ NMR spectroscopy, X-ray diffraction, and electron microscopic techniques, we have demonstrated that, once the as-polymerized single crystals of PDA are disordered by

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melting, crystallization does not reproduce the original single-crystal structure. The crystals obtained from disordered phases are characterized by less planar backbones and more extended side chains compared to the PDA structures found in their as-polymerized single crystals. The unit cell is expanded in the *a* direction, and the resulting morphology consists of spherulites or lamellar aggregates (the latter preserving the backbone orientation of the original single crystals).

**Registry No.** Poly(ETCD) [R = $(CH_2)_4O(CO)NHC_2H_5$] (homopolymer), 63809-82-5; poly(ETCD) [R = $(CH_2)_4O(CO)NHC_2H_5$] (SRU), 83441-81-0.

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# Some Ideas Concerning the Elasticity of Biopolymer Networks

**P. G. Higgs* and R. C. Ball**

*Cavendish Laboratory, Madingley Road, Cambridge, CB3 OHE, U.K.*

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ABSTRACT: We consider a network composed of flexible chains which may increase their length by pulling more chain from a compact source. This models the partial unwinding under strain of the helical junction zones which exist in many biopolymer systems. (We draw on the ideas of Nishinari et al. but reach completely different conclusions.) Following the assumptions of the standard affine deformation theory of Gaussian networks, we show that this network will be intrinsically unstable at extension ratios of $\lambda \geq 2.3$, where complete unwinding of the junction zones will occur. We find that low functionality junctions in this network are relatively unstable and that there will be a tendency for certain chains to collapse completely, leading to the formation of a reduced number of junction zones of high effective functionality. We investigate the effects of extended inflexible junction zones on the network elasticity. It is found that the junction zones must be large in comparison to the length of the connecting flexible chains before any substantial difference in the modulus occurs from that of a purely Gaussian network with simple cross-links.

## 1. Introduction

The properties of natural rubbers and networks of flexible synthetic polymers can be explained to a large degree by the familiar phantom network theory, which considers Gaussian chains interacting only at their end points. There are, however, many types of polymer networks for which the ideas of completely flexible chains and permanent covalent cross-links are clearly inappropriate. In this paper we attempt to explain some of the properties of physical networks formed from polypeptide and polysaccharide biopolymers. Although these two classes of polymers are entirely different in their molecular structure, the mechanisms of aggregation by hydrogen bond formation which occur in these molecules result in network structures which have a marked similarity.

The formation of extended helical junction zones is common in these systems. For example, gelatin is a gel formed when denatured collagen (a structural protein found widely in animal tissue) partially re-forms its triple helical structure. The polysaccharides agarose and carrageenan (both derived from seaweed) are thought to form double helices, whilst the alginates are thought to form extended junction zones through the influence of cations such as $Ca^{2+}$ (the so-called egg-box model). These structures are discussed in the review by Clark and Ross-Murphy.[2]

For our purposes, we will treat all these structures as assemblies of rods (representing the ordered junction zones) with flexible chains connecting them. To produce the simplest theory we will follow the assumptions of the standard phantom network model. In particular, we neglect the enthalpies of bending and stretching of chain segments and only consider the contribution to the free energy of the enthalpy of hydrogen bond formation and the entropy of the chains. A model by Doi and Kuzuu[3] for networks of rigid rods neglects entropy and focuses on the bending enthalpy. This model predicts an extremely low modulus for small deformations, followed by a rapid increase in stress as the strain becomes large enough to cause significant numbers of rods to bend. This behavior is not observed in biopolymer gels. McEvoy et al.[4] have found that both gelatin and agarose gels show almost linear

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