

The crystal habit and morphology of polybutylene terephthalate and related copolymers

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The morphology and crystal habit of segmented copolymers of poly(butylene terephthalate) have been investigated. Single crystals have been grown from the melt in thin films of a 73% poly(butylene terephthalate) content copolymer. The crystals exhibit (*hk*0) single crystal electron diffraction patterns which indexes to the alpha crystal form of poly(butylene terephthalate). The lamellae are bounded by (010) faces on the long edges of the crystals and (100) and (1 $\bar{1}$ 0) faces at the crystal tip. The *c* axis of the unit cell (and hence the polymer chain) is normal to the lamellar surface. The preferred growth direction of the crystal is [2 $\bar{1}$ 0]* which is parallel to the projection of the *a* axis on the *a**–*b** plane. The *a* axis is inclined at 26° to the *a**–*b** plane. The [2 $\bar{1}$ 0]* fast growth direction observed for the lamellae also corresponds to the radial growth direction observed in spherulites grown from the melt. The radiation lifetime (100 kV electrons, 23°C) of poly(butylene terephthalate) and poly(butylene terephthalate)–poly(tetramethylene ether glycol) copolymers was measured and found to be 150 C m⁻², independent of copolymer composition.

(Keywords: copolymer; morphology; poly(butylene terephthalate); single crystal; electron microscopy; polyether–polyester)

INTRODUCTION

The crystallization behaviour and crystal structure of poly(butylene terephthalate) (4GT) has been the subject of numerous papers in the recent literature^{1–4}, yet relatively little is known concerning the lamellar morphology and crystal habit of this polymer. This paper, in conjunction with an earlier one⁵, presents new morphological insights into this polymer. To approach this goal the experimental work has been concentrated not on polybutylene terephthalate itself but on a series of segmented copolymers of 4GT with poly(tetramethylene)ether glycol (PTMEG, *M*_n = 1000). Early experiments indicated that, although the samples were copolymers, it was actually easier to grow isolated single crystals of the copolymer than of the homopolymer. This type of behaviour has also been observed in the past for poly(ethylene oxide)–polystyrene block copolymers⁶.

4GT is known to crystallize in two distinct polymorphs, the characterization of which has been the topic of a number of papers^{1,2}. The α form occurs under normal, quiescent crystallization conditions from the melt^{1,2}. The chain conformation is kinked (i.e. not fully extended) with the tetramethylene residue existing in a contracted state. A critical review of the various proposed structures has been presented by Desborough and Hall¹, including a 'best' fit unit cell for the α form with *a* = 0.486 nm, *b* = 0.596 nm, *c* = 1.165 nm, α = 99.7°, β = 116.0°, and γ = 110.8°. The β crystal form occurs through a solid state transformation from the α form due to stress. This transformation is reversible and has been studied by various authors^{1,2,7}. Desborough and Hall¹ have also reviewed the structures proposed for the β form and have

identified the correct unit cell as having dimensions *a* = 0.496 nm, *b* = 0.580 nm, *c* = 1.30 nm, α = 101.9°, β = 120.5° and γ = 105.0°. The polymer chain is completely extended in the β form indicating that the α to β unit cell transformation is due to a change in conformation of the tetramethylene residue and the subsequent shift in the packing of the chains.

The morphology of homopolymer 4GT films cast from solution has been investigated by Roche *et al.*⁴, who found that the α structure forms two distinct types of spherulites. In 'normal' spherulites the arms of the maltese cross extinction pattern, as observed by polarizing optical microscopy, are coincident with the polarizer and analyser directions. In 'abnormal' 4GT spherulites the extinction arms are at 45° to the polarizer and analyser directions. Electron diffraction revealed that in normal spherulites the radial direction of the spherulite corresponded to the [2 $\bar{1}$ 0]* direction (the asterisk denotes a reciprocal lattice direction). In abnormal spherulites the [$\bar{1}$ 11]* direction was radially oriented.

Two types of spherulites (with similar optical properties to the spherulites observed by Roche *et al.*) have also been observed in copolymers of 4GT and PTMEG⁸. Cella has examined 4GT/PTMEG copolymers by electron microscopy and found that the 4GT component crystallizes in the form of highly interconnected lamellae⁹. Wegner *et al.* have developed a stain for 4GT/PTMEG copolymers for electron microscopy based on allyl amine and osmium tetroxide¹⁰. The allyl amine is allowed to diffuse into the amorphous regions of the sample and is subsequently reacted with OsO₄ which acts as a negative stain outlining the 4GT crystals. Lamellae were observed on the order of 10 nm in thickness and many hundreds of nanometers in length.

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From the data presented in the literature it is apparent that the α crystal structure of 4GT and related copolymers crystallize in the form of lamellae on the order of 10 nm thick and up to a micron in length. These lamellae are then organized on the supramolecular level into spherulites. The experiments that have been previously presented in the literature have only imaged the lamellae edge-on and hence there is no information as to the width or crystal habit of the lamellae and the relationship of these to the radial directions observed in the different spherulites.

In a previous paper we discussed the morphology of thin films of PTMEG/4GT copolymers crystallized from the melt⁵. Single crystals were observed in copolymers containing 73% and 49% by weight 4GT. WAXS and electron diffraction supported a model of a relatively pure 4GT crystal core with PTMEG (soft segment) and short 4GT sequences being rejected to the lamellar surface and soft segment rich matrix.

In this paper the orientation of the unit cell with respect to the crystal shape is discussed. The fast growth direction of the lamellae is found to correspond to the radial direction observed in 'normal' spherulites of 4GT homopolymer and 4GT/PTMEG copolymers. In addition the radiation lifetime of the copolymers and 4GT homopolymer (subjected to 100 kV electrons) is measured and compared with that of other polymers.

EXPERIMENTAL

Materials

The polyether-polyester segmented copolymer examined was based on poly(tetramethylene)ether glycol ($M_n = 1000$, PTMEG) as the soft segment and poly(butylene terephthalate) (4GT) as the hard segment. The polymer contained 73% by weight 4GT which, due to the oligomeric nature of the soft segment monomer, corresponds to a hard segment mole fraction of 0.93. If a most probable distribution of hard segment lengths is assumed (i.e. a random polymerization) then the average hard segment length is 15 for this composition. This sample was part of a series of polymers ranging in hard segment content from 31% to 81% by weight which were supplied by W. J. Buck of the Du Pont Company. The morphological characterization of the series was reported on in a previous paper⁵. The 4GT homopolymer studied was Valox 315 supplied by the General Electric Company.

Sample preparation

The thin films used for melt crystallization were cast onto carbon coated mica from a 0.075% by weight solution of polymer in 1,1,1,3,3,3-hexafluoro-2-propanol. The carbon coating (5–10 nm) prevented the polymer from adhering to the mica during the subsequent melting and crystallization steps. The mica was dipped into the polymer solution and the excess solution was removed by blotting the edge of the mica with filter paper. The solvent was evaporated rapidly by placing the mica on a hot plate in a hood. If the solvent was not evaporated quickly the films were found to contain holes and thickness variations. The polymer coated mica was then placed in a Mettler FP-2 hot stage that was purged with N_2 . The polymer film was melted and held at 250°C for 5 min and then quenched to the crystallization temperature. The crystallization temperatures (T_c) used were 200°C and 212°C for the 73% hard segment copolymer and the

homopolymer, respectively. The film was held at T_c for 4 h and then cooled rapidly to room temperature. The polymer film with the carbon backing was then floated off the mica using distilled water and picked up on electron microscope grids.

Electron microscopy

Transmission electron microscopy was performed using a JEOL 100CX electron microscope equipped with a scanning transmission attachment. A detailed outline of the microscopy techniques was presented in a previous paper⁵.

The radiation lifetime (τ) of the crystals was evaluated using a Keithley model 602 electrometer which measured the electron beam current on the phosphor screen of the microscope. The screen efficiency had been previously calibrated using a Faraday cup after the method presented by Grubb¹¹.

RESULTS AND DISCUSSION

Melt crystallized thin films of the 73% 4GT content copolymer crystallized at 200°C were observed to contain single crystal lamellae (see *Figure 1*). Electron diffraction patterns obtained from the crystals indexed to the α form of 4GT. By monitoring the decay of the diffraction spots as a function of electron dose the radiation lifetime was measured. *Figure 2* is a plot of the (100) intensity versus time (at a dose rate of $5 \text{ C m}^{-2} \text{ s}^{-1}$) from a 73% hard segment crystal. The decay curve can be fitted with a single exponential and a decay time, τ , extracted. τ can then be related to a characteristic dose, D^* , where $D^* = (\tau) \times (\text{dose rate})$. D^* is the dose required to reduce the intensity of the diffracted beam to 1/e of its original value. The data presented in *Figure 2* gives a value for D^* of 150 C m^{-2} . Under similar conditions polyethylene has a D^* of about 60 C m^{-2} .¹² It should be noted that radiation damage lifetimes are sometimes quoted as the dose to complete damage as opposed to the exponential time constant. The dose to complete damage for 4GT is about 300 C m^{-2} (while the corresponding value for polyethylene is about 100 C m^{-2}).¹² While it was not possible to grow isolated single crystals of the 4GT



Figure 1 BF TEM micrograph of a thin, melt crystallized film of a 73% hard segment PTMEG/4TG copolymer. Many single crystal lamellae are observed growing throughout the film

homopolymer (all attempts resulted in overlapped and overgrown crystals such that the crystal boundaries and habit could not be distinguished) regions of 4GT crystals could be found that were sufficiently large for selected area diffraction allowing the measurement of the homopolymer radiation lifetime. While Figure 2 presents data for a 73% 4GT crystal, radiation lifetimes were also measured for a 49% 4GT copolymer and 4GT homopolymer. All the lifetimes measured were equal within experimental error and not dependent on copolymer composition which supports the model presented in a previous paper of a relatively pure 4GT crystal core with the PTEMG rejected to the fold surfaces⁵. Had significant amounts of the soft segment been incorporated in the crystal, the associated lattice distortions would have likely caused the copolymer crystals to be damaged more readily than the homopolymer, contrary to the observed data.

Figure 3 is a composite Figure of the bright field image formed by increasing the current in the intermediate lens (which defocuses the diffraction pattern forming a bright field image from the central, unscattered beam) with the normal focused electron diffraction pattern. This Figure shows the correct orientation of the lateral faces of the crystal relative to the diffraction pattern. When the

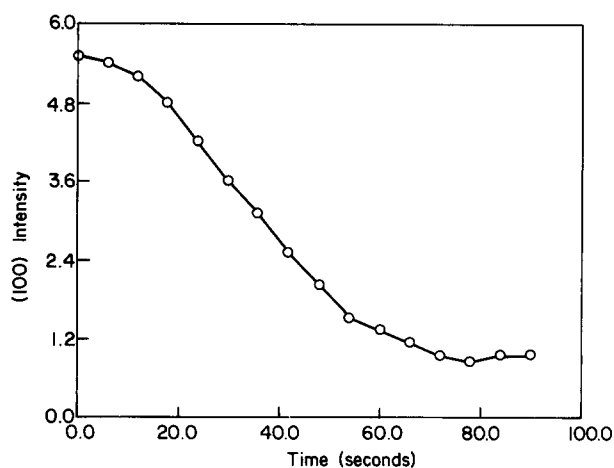


Figure 2 Plot of the (100) diffracted intensity versus time at a dose rate of $5 \text{ C m}^{-2} \text{ s}^{-1}$ (100 kV electrons, room temperature). $D^* = 150 \text{ C m}^{-2}$

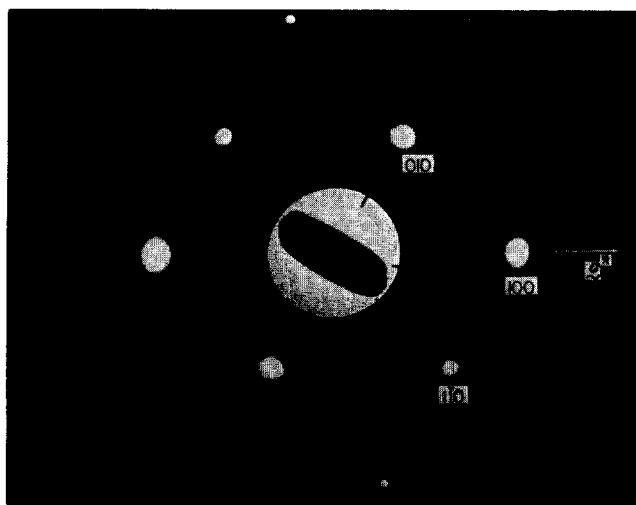


Figure 3 Composite figure of the bright field image formed from the central spot (000) in the electron diffraction pattern by defocusing the intermediate lens and the focused selected area diffraction pattern. The image is shown in the correct orientation with the diffraction pattern

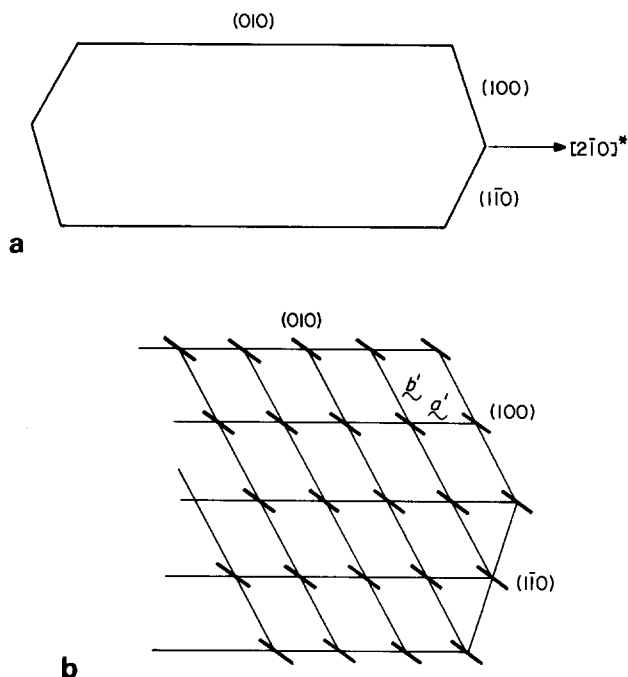


Figure 4 (a) Schematic showing the observed crystal habit for poly(butylene terephthalate); (b) schematic indicating the projection of the a^*-b^* plane of the unit cell on the crystal

intermediate lens is strengthened, in addition to the central spot becoming a bright field image, each of the diffracted beams forms the corresponding (hkl) dark field image. Each of the dark field images is in correct orientation with respect to the bright field image¹³⁻¹⁵. Due to the large range of optical densities present on the negative of the defocused diffraction pattern it was easier, for illustrative purposes, to construct the composite diffraction pattern shown in Figure 3 using the defocused central beam and the focused diffraction pattern. From the arrangement of the crystal faces with the indexed diffraction pattern the crystal habit can be established. Figure 4a is a schematic of a 4GT crystal and indicates the crystal planes defining the shape of the crystal. It is interesting to note that the two faces defining the tip of the crystal are not equivalent. The long edges of the lamellae are parallel to the (010) planes which are close to the $[2\bar{1}0]^*$ reciprocal lattice direction. This corresponds to the radial growth direction in 'normal' spherulites of 4GT.⁴

The strong (hk0) electron diffraction patterns obtained from crystals normal to the electron beam indicates that the surface of the lamella coincides with the a^*-b^* plane of the reciprocal lattice. By definition this means the c axis of the real lattice and hence the polymer chains are normal to the lamellar surface. Since the α form unit cell for 4GT is triclinic the a^*-b^* plane does not correspond to the $a-b$ plane. Figure 4b is a projection of the $a-b$ plane, indicated as $a'-b'$, onto the a^*-b^* plane (and hence the plane of the lamella). The heavy bars at the vertices of the unit cell projection correspond to the position of the polymer chains. The preferred growth direction $[2\bar{1}0]^*$ is parallel to the projection of the a axis onto the a^*-b^* plane. The a axis is inclined at 26° to the a^*-b^* plane as shown in Figure 5. The fact that the c axis is observed to be normal to the crystal surface may be because the crystallization is occurring in a thin film on a substrate and hence the polymer chains are somewhat constrained. It is not

known whether 4GT exhibits chains tilted with respect to the lamellar normal in the bulk.

Figure 6 shows a higher magnification bright field and a (010) dark field pair of micrographs of the same crystal. The most prominent feature is that the crystal appears to be divided up into strips parallel to the (010) direction. As indicated in a previous paper⁵, the crystal has split into these strips on cooling from the relatively high crystallization temperature (200°C) due to the large thermal

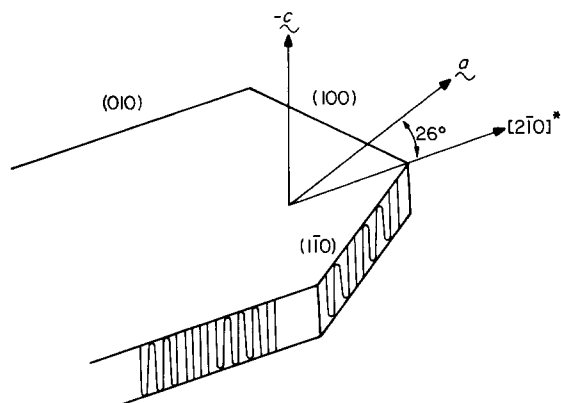


Figure 5 Schematic showing the reciprocal lattice relationship with the observed crystal habit and fast growth direction ($[210]^*$) of the lamella

contraction of the amorphous matrix relative to the crystal.

The clearly evident crystallographic faces of the crystal in Figure 6 would lead to the expectation of sectorization defined by the crystal faces. No clear sectorization is observable in the dark field image though there is a change in the orientation of the diffracting regions near the crystal tips. The fact that the cracks propagate parallel to the (010) planes indicates that the mechanical strength is relatively poor in this direction. Indeed, the (010) planes have the largest d -spacing and the greatest separation between molecules in the $(hk0)$ projection of the unit cell.

There appears to be no significant change in the crack behaviour near the crystal tip as the crack crosses the region where a sector boundary should occur and the folding would be expected to change from along the (010) planes to along either the (100) or $(1\bar{1}0)$ planes. This along with the fact that these crystals were actually grown from the melt (and not from solution as with most polymer single crystals) would argue for somewhat disordered folding.

Figure 7 is a bright field electron micrograph and associated diffraction pattern from a 73% by weight 4GT copolymer film crystallized at $T_c = 170^\circ\text{C}$ ($\Delta T \cong 45^\circ\text{C}$). Spherulites are clearly visible and the inset electron diffraction pattern indicates the radial direction is

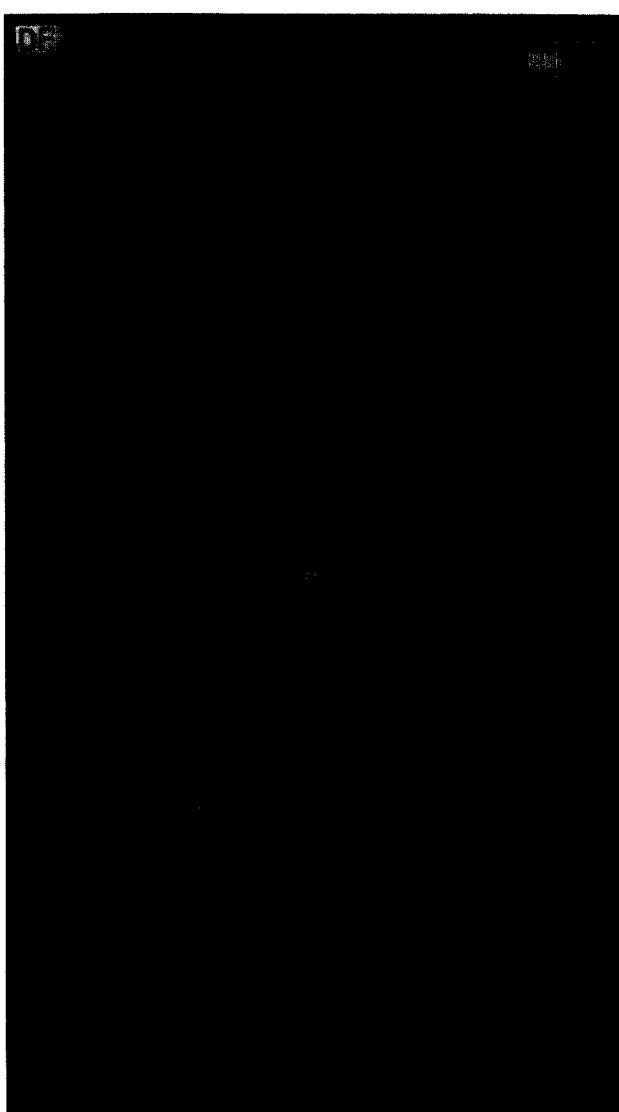


Figure 6 Bright field-(010)DF pair of micrographs of the same crystal. Note that the crystal shows many cracks parallel to the (010) planes

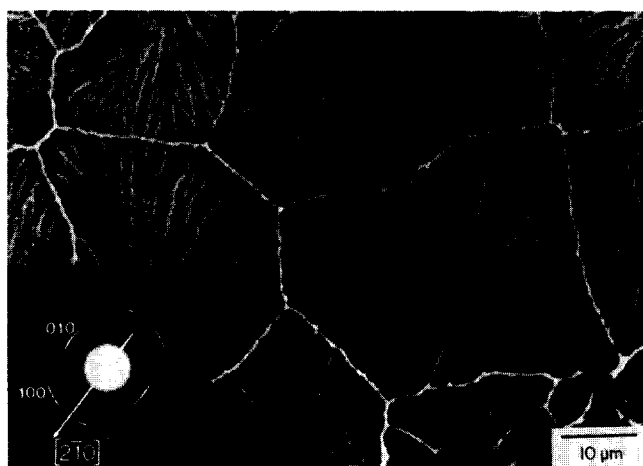


Figure 7 Bright field micrograph and associated electron diffraction pattern (taken from circled area) of a 73% hard segment film crystallized at 170°C ($\Delta T \cong 45^\circ\text{C}$). The electron diffraction pattern indicates that the radial direction in the spherulite is parallel to the $[2\bar{1}0]^*$ reciprocal lattice direction

approximately $[2\bar{1}0]^*$ agreeing with the previous results on 4GT homopolymer⁴ and with the fast growth direction of the single lamellae. These spherulites correspond to the 'normal' spherulites observed by Roche *et al.* in 4GT homopolymer⁴.

It is generally believed that spherulitic crystallization from the melt involves the formation of a radiating array of highly elongated or lath-shaped lamellar crystals. In polyethylene at high crystallization temperatures both from solution^{16,17} and from the melt¹⁸ distinct faceting does not appear to occur with the crystals exhibiting a lenticular habit with pointed tips and curved growth faces. Alternative explanations have been discussed for the formation of the curved crystal faces involving either changes in the relative growth rates of the facets during isothermal crystallization¹⁹ or the occurrence of a crystal roughening transition²⁰. The tendency of the 4GT copolymer crystals to show faceting indicates that the relative growth rates of the (010), (100) and $(1\bar{1}0)$ faces are similar and that the rates appear to be approximately constant with time (or that any crystal roughening transition for this system is above the experimental crystallization temperature). At larger undercoolings the 4GT copolymers exhibit a spherulitic morphology and hence the crystal habit would be expected to change to a more fibrillar or lath-shaped one at these temperatures. Whether this change in habit occurs gradually as the undercooling increases due to progressive decrease in the ratio of $G_{(010)}$ (growth rate of the crystal normal to the (010) planes) to $G_{(100)}$ and $G_{(1\bar{1}0)}$ or due to a different mechanism such as a transition to dendritic growth is an area for further work.

CONCLUSIONS

Single crystals of a segmented copolymer of PTMEG/4GT (containing 73% by weight hard segment) have been grown in thin films from the melt. The room temperature radiation lifetime (for 100 kV electrons) has been measured for 4GT and PTMEG/4GT copolymers and D^* , the radiation lifetime for 100 kV electrons, was found to be 150 C m^{-2} , independent of copolymer composition

further supporting the model of a relatively pure 4GT crystal core, with the PTMEG and short 4GT sequences being rejected to the fold surface and surrounding matrix. The crystals show distinct faceting with the faces being bounded by (010), (100) and $(1\bar{1}0)$ planes. The long axis of the lamella (the fast growth direction) is parallel to the (010) planes, which corresponds to the $[2\bar{1}0]^*$ reciprocal lattice direction. This direction is equivalent to a projection of the q axis on to the lamellar surface (the q axis is actually directed out of the plane of the lamellar surface at 26°). The fast growth direction of the crystal is parallel to the radial direction observed in spherulites of both PTMEG/4GT copolymers and 4GT homopolymer.

Selected area electron diffraction indicates that the c axis and hence the polymer chains are normal to the crystal surface. The fact that lamellar single crystals are formed with the chain perpendicular to the thin dimension of the lamella indicates that chain folding must be occurring. The degree of regularity in the folding is not clear with the distinct faceting observed supporting a model with preferential fold planes while the lack of distinct sectorization argues for disorder.

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