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A note on twist-banding in spherulites of poly(3-hydroxybutyrate)

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A mechanism is suggested for twist-banding in spherulites of poly(3-hydroxybutyrate) (PHB), which involves elastic bending of lamellar ribbon crystals caused by chainfolding in different directions on opposite faces of lamellae. This folding behaviour is considered to be a consequence of the stereoregularity of bacterially produced PHB, whose molecules adopt a helical chain form. The model is used to predict values for the band spacing P in terms of crystal elastic moduli, lamellar surface energy density and lamellar thickness. Measured values of P are somewhat larger than predicted, and too small a temperature dependence is predicted at low supercoolings. Reasons for the discrepancies are suggested and discussed. This proposed mechanism for helicoidal twisting could be appropriate for many polymers, in particular for chiral polymers, and in cases where fold staggering does not play a role. © 1997 Elsevier Science Ltd.

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Introduction

The detailed description of the geometry and organization of chainfolded lamellar crystals in polymer spherulites has received much attention. Traditionally, polyethylene has been the subject of most studies[1-5], but recently many other polymers, e.g. polypropylene, have been studied[6-8]. Singfield et al.[9] reported that in the optically active chiral polymer poly(epichlorohydrin) (PECH), optically pure PECH forms banded spherulites, while an equimolar blend of the two chiralities forms non-banded spherulites. They suggested that banding is associated with a stereoselective mechanism or asymmetry operating at the growth front during isothermal crystallization.

The banding observed in spherulites of poly(ethylene terephthalate) (PET), nylon and polyethylene was attributed by Keller[1] to a radially oriented helicoidal twisting of lamellar ribbons, the twisting being caused mainly by the influence of surface stresses arising from the chain folds. Keith and Padden[10] developed this model and proposed that fold staggering causes the chains to be non-orthogonal to the fold surfaces in polyethylene. This creates unequal stresses at opposite fold surfaces, which in turn gives rise to bending moments and to twisting of the lamellae. The feature which determines the direction of twist, the 'chiral factor', is the direction of chain tilt with respect to the lamellar normal.

In view of the large number of crystalline species which form banded spherulites, Singfield et al.[9] point out that there must be a general principal at play involving a necessary level of asymmetry. The element of asymmetry is not essential at the level of the residue, as in PECH. In polyethylene, for example, asymmetry is introduced only at the level of the tertiary (i.e. lamellar) structures.

The present work deals with another chiral polymer which shows banded spherulites, poly(3-hydroxybutyrate) (PHB). The purpose of this note is to propose and discuss a mechanism for twist-banding, where the crystals twist helicoidally by bending elastically in two different planes. This arises due to surface stresses caused by chainfolding in different directions on each face of the lamellae.
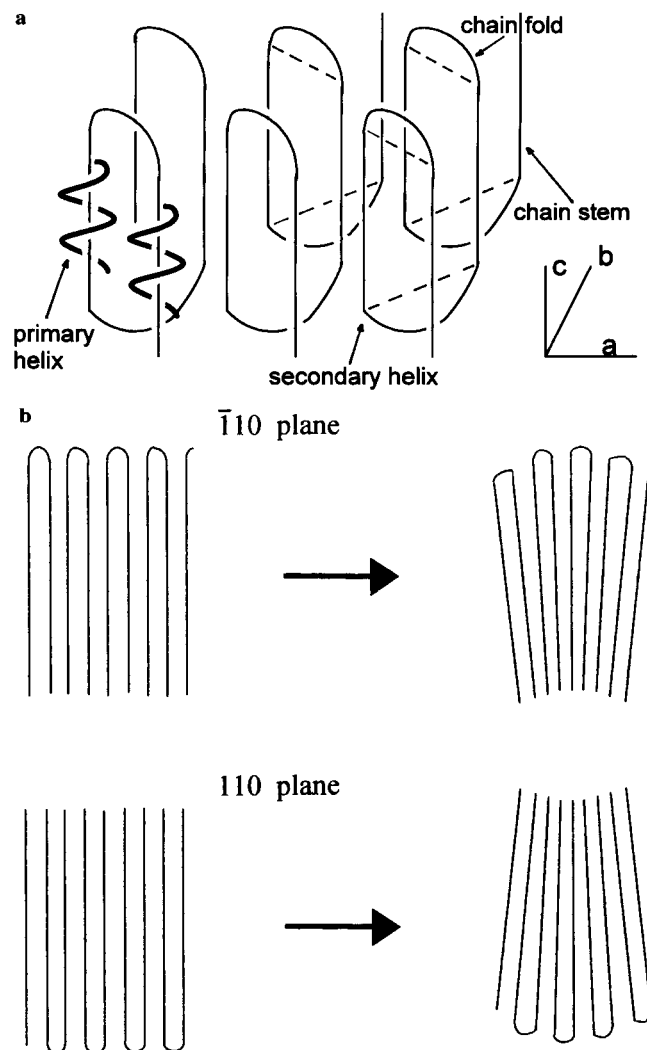
Model and discussion

Due to its bacterial origin, the PHB molecule is stereospecific in the R-configuration; in the crystalline state it adopts a right-handed helical form with a two-fold screw axis and repeat period c of 0.596 nm[11]. The molecular chain axis c is perpendicular to the lamellar crystal surfaces, as evidenced by electron diffraction studies of single crystals[12]. Observation of fracture modes suggests that the average direction of chain folding is predominantly along the a-axis in single crystals. Since PHB is highly crystalline, it can be inferred that chain folding at the lamellar surfaces occurs predominantly by adjacent re-entry[13]. Furthermore, the basis of the orthorhombic unit cell contains two 'antiparallel' chains, which implies that the chains fold in a zig-zag fashion alternately at approximately $+45°$ and $-45°$ to the a-axis[14].

Spherulites comprising radially oriented twisting lamellar crystals are formed when PHB is crystallized from the melt. It has been shown by X-ray micro-diffraction that the crystallographic a axis is radial in PHB spherulites, with the b and c axes rotating about this axis[13]. The rotation of these birefringent units as they progress radially causes the well known banded appearance when observed under crossed polars in a polarizing microscope.

In the present work it will be assumed that 'zig-zag' folding also occurs in spherulite lamellar crystals. It shall be proposed here that this type of folding is a consequence of the chiral nature of the PHB molecule. As mentioned, a right-handed helical conformation is thought to occur for PHB chains in the crystals. When a helical chain stem reaches a lamellar surface it folds back adjacently into the crystal. However, it may be energetically favourable during crystal growth if the chain stems and the folds do not remain in the same

plane. A right-handed helix folding over and away from one at the top surface of a lamella would tend to twist or 'zig' to the left; on folding back at the lower surface it would tend to twist in the same sense and thus produce a 'zig-zag'. The opposite sense would be true for a folded left-handed helix. (A simple analogy for demonstrating such behaviour is to take a coiled telephone cord and to fold it back and forth at least twice. The zig-zag folding should become immediately apparent.) This asymmetry imposes a secondary helical structural hierarchy to the chain on the level of the chain stems plus folds. In *Figure 1a* the folding direction on the top surface of a lamella is shown as the [$\bar{1}$10] direction, and on the bottom surface as the [110] direction. The lines indicate the helical coiling of chain stems and folds in a lamella; the primary helical form is also shown schematically. A right-handed primary helix would fold as a left-handed secondary helix, and vice versa.

The tertiary effect of lamellar twisting occurs if the exess energy in the fold causes a stress in the surface directed along the fold direction. This surface stress will cause a bending moment and result in curvature of the lamella (*Figure 1b*). It is simple to envisage that convex curvature on opposite sides of a lamella, in directions at approximately $+$ and $-45°$ to the [100] axis, respectively, results in helicoidal twisting about this axis.

Based on these ideas, it is instructive to attempt to predict the magnitude of the twisting periodicity (or band spacing) P from other properties of the polymer, using simple elasticity theory. Consider the elastic bending of a plate of thickness t and elastic modulus E to a radius of curvature R. The work done W per unit area is given by[15]

$$W = \frac{Et^3}{24R^2} \qquad (1)$$

Now assume that the fold energy is entirely responsible for the bending and furthermore equate this to the lamellar surface energy density σ.

By considering the two bending processes inclined to the radial direction, it is fairly straightforward to show that the pitch of the helicoidal ribbon P is related to the radii of curvature R by

$$P = 4\pi R \sin\theta \cos\theta \qquad (2)$$

where θ is the angle between the fold direction and the helicoidal axis or radial direction. From the unit cell of PHB, this angle can be calculated to be $64°$ (not $45°$, which was loosely used for the sake of argument previously). Combining equations (1) and (2) gives the following relationship for the pitch P:

$$P = \left(\frac{2}{3}\right)^{1/2} \pi \sin\theta \cos\theta \left(\frac{E}{\sigma}\right)^{1/2} t^{3/2} \qquad (3)$$

The maximum strain involved in the proposed bending mechanism (ϵ_{max}) is given by

$$\epsilon_{max} = \frac{t}{2R} = (2\pi \sin\theta \cos\theta)\frac{t}{P} \qquad (4)$$

For $t = 7$ nm and $P = 10\,\mu$m (typical measured values), one obtains $\epsilon_{max} = 0.0017$, which is a value well within the elastic limit of a typical crystal. It is, therefore, not necessary to invoke defect structures (such as dislocations) or plastic deformation in order to explain twist-banding in spherulites.

The predicted range of band spacings P can be estimated by inserting literature values for E, σ and t into equation (3), as follows. Nicholson *et al.*[16] have presented the stiffness matrix for the PHB crystalline phase, obtained from molecular modelling. The modulus relevant to pure bending at $64°$ to the a axis can be calculated from the values of the stiffness constants given in ref. 16, from which one obtains $E = 6.1$ GPa. However, the molecular modelling effectively calculates stiffnesses at very low temperatures; at elevated temperatures the modulus would be lower. The fold surface energy has been otained by Barham *et al.*[13] to be 38 mJ m^{-2}, and the lamellar thicknesses lie in the range 6–9 nm. Inserting these values into equation (3) predicts twist periodicities of the order of $0.3\,\mu$m.

Experimentally measured twist periods are much larger than this; they lie approximately in the range 7–$100\,\mu$m (see *Figure 2*; adapted from ref. 13). A slope of $3/2$ on a log–log plot is indeed obtained at large supercoolings, possibly reflecting the $t^{3/2}$ behaviour in
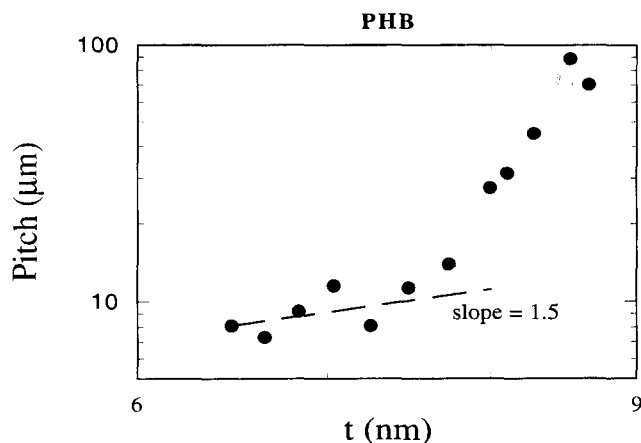

Figure 1 (a) Proposed chain folding in PHB lamellar ribbons showing (schematically) primary right-handed helical molecular chains together with secondary left-handed helical stems and folds. The diagram shows the case where circumferential cracks may occur, i.e. the axis of the secondary helix is circumferential not radial (*a* is the radial direction). (b) Schematic diagram showing lamellar bending in two different planes

Figure 2 Band spacing P versus lamellar thickness t for PHB (adapted from ref. 13)

Figure 3 Band spacing P versus supercooling ΔT for PET (adapted from ref. 1)

equation (3), but at low supercoolings the experimental slope is much greater than this.

There are a number of reasons which might be causing these discrepancies. Firstly, the assumption that all the surface free energy (measured calorimetrically) produces lamellar bending could be too simplistic; non-adjacent or disordered chain folding could 'dilute' the bending effect considerably, and lead to much larger band periodicities. Secondly, bulk material properties for E and σ were used in the comparison with the model, whereas periodicities P were measured in thin films. In thin films, the twist periods are of the same order of magnitude as the sample thickness. Conceivably, the top and bottom surface constraints 'flatten out' the lamellar twist in thin films. It would be desirable to have measurements of banding at different crystallization temperatures using bulk samples, but this is much more problematical to achieve experimentally as samples have to be sectioned or etched for light or electron microscopy.

Finally, the question arises as to whether the twisting mechanism proposed above could be applicable to other polymers. Since P is usually measured as a function of crystallization temperature T_c, whereas values of lamellar thicknesses are not normally known, it is desirable to obtain an expression relating P and T_c. Simple theory relates the lamellar thickness t to the supercooling (according to the well known Thompson equation[17]), where

$$t = \frac{2\sigma T_m^0}{\Delta h_0 \Delta T} \qquad (5)$$

σ is the lamellar surface energy density, T_m^0 the equilibrium melting temperature, Δh_0 the enthalpy of melting, and $\Delta T = T_m^0 - T_c$ is the supercooling.

From equations (3) and (5) it follows that one expects P to vary as

$$P \propto \Delta T^{-3/2} \qquad (6)$$

if all other parameters are regarded as constant.

One may now compare the above model with the results of Keller[1] on PET. His results for P versus ΔT give a good straight line power law fit with a slope of -1.6 (*Figure 3*), which agrees satisfactorily with equation (6). One is, however, unable to assess whether the model
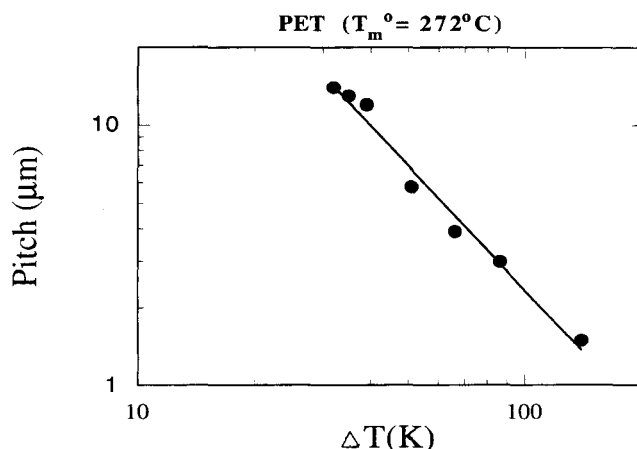
predicts realistic absolute values of P, as one does not know for PET the values of all the constants in equations (3) and (5).

Conclusion

In this paper it has been proposed that the twist-banding in PHB spherulites is due to elastic bending of radially oriented lamellar ribbons, where the folding directions on opposite faces of the lamellae are approximately orthogonal and inclined to the radial direction, leading to the formation of helicoidally twisting lamellae. The banding periodicity predicted by the model is, however, somewhat smaller than observed experimentally and the dependence on lamellar thickness is not correct for the lowest supercoolings. The model predicts the correct temperature dependence of banding periodicity for PET samples. It seems possible that the proposed mechanism could apply much more generally than just for the case of PHB, in particular where chiral molecules are involved and where fold staggering does not play a role. More experimental results on chiral polymers and in particular on bulk specimens are required in oder to test the model further.

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