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On the formation of S-profiled lamellae in polyethylene and the genesis of banded spherulites

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Abstract

A study of the habits of individual melt-grown polyethylene crystals has shown how banded spherulites form in this polymer and the essential cause to be the relief of fold surface stress. An initially planar lamella develops a characteristic S-profile over time extending out from central regions. This is a consequence of reducing surface stresses by improving fold packing whose spatial requirements are best met by inclined as opposed to the initial perpendicular fold surfaces. The axis of the S-profile is inclined to *b*, an inclination which introduces the essential asymmetry into the system, and the lamella slightly twisted around the axis of the S. The twist is amplified by the formation of isochiral giant screw dislocations, systematically to one side of the S for a given radius, giving diagonal linkages and each developing lamella a comparatively large increment of twist. The detailed morphology is readily accounted for on this basis as is the restriction of banding to polymers with (eventually) inclined fold surfaces. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Banded spherulites; S-profiled lamellae; Polyethylene

1. Introduction

Banded spherulites are a familiar feature of certain polymeric and non-polymeric systems not least polyethylene, the principal polymer and closest approach to the ideal linear molecule [1–3]. Nevertheless this striking phenomenon has defied explanation since the 19th century. Primary responsibility for this state of affairs has rested with the unavailability of sufficiently detailed textural knowledge so that the precise nature of the problem could not be specified, a situation which has now changed. Systematic observation of how lamellae are arranged within polyethylene and other melt-crystallized polymers is now possible using permanganic etching. An understanding of non-banded spherulitic growth in melt-crystallized polymers has followed [4], with the initial proposals confirmed in substantial detail more recently using monodisperse *n*-alkanes [5–7]. The more complicated problem of banded growth is addressed in this paper.

Concerning spherulitic growth itself, spherulites form from polymeric melts by the advance of diverging dominant lamellae creating a framework which, at least in high crystallinity materials, is filled in later. In the particular case of polyethylene, dominant lamellae are of two principal kinds, distinguishable by their profiles when viewed down *b*, the radial growth direction [8]. At higher crystallization temperatures, $\gtrsim 127\ ^\circ\mathrm{C}$ for the linear polymer, lamellar fold surfaces are approximately $\{201\}$ and spherulites are not banded. A single lamella is usually planar but, for shorter molecules, may have alternating $\{201\}$ fold surfaces in a ridged habit. Lower crystallization temperatures produce banded spherulites whose dominant lamellae have S- or C-shaped profiles viewed down *b*, in which the angle between lamellar normal and the *c* axis changes continuously but with a maximum $\sim 35^\circ$, the same as for a $\{201\}$ surface.

These two different types of dominant lamellae are a consequence of a change in the relative rates of two processes, fold surface ordering and radial advance [9]. The ordering of fold surfaces is not itself a requirement of crystallization of molecular stems because the respective free energies involved are much less for the former. It is both possible and to be expected that lamellae will form with disordered fold surfaces unless there is time for fold packing to order. In terms of texture, ordering of folds brings a change from chains being essentially parallel to lamellar

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normals to one in which they are inclined, commonly at ~35° in {020} planes, i.e. to {201} surfaces as earlier, situations which henceforth we describe as *perpendicular* and *inclined* fold surfaces, respectively. Because crystallization rate declines rapidly with supercooling whereas fold surface ordering is anticipated to vary less, presumably with a negative exponential dependence on absolute temperature, the expectation is that, at higher temperatures, fold surfaces will order faster than growth proceeds. This agrees with observation that, above ~127 °C, fold surfaces of linear polyethylene are inclined from the outset. At lower temperatures lamellae first form with their normals parallel to the *c* axis, then develop S- and C-profiles, with isothermal lamellar thickening, behind the growth front although, at the growth front itself, fold surfaces remain perpendicular to molecular stems [9]. These profiles are the consequence of fold ordering having to occur within the constraints of the existing lamella, an ordering which given its comparatively slower rate will not reach the growing surface.

The understanding of spherulitic growth proper has benefited from studies of its early stages. It is reasonable to expect, therefore, that insight into the development of banded polyethylene spherulites and their S-profiled dominant lamellae would similarly result from examination of the early stages. Hitherto this has not been possible, largely because of the high nucleation density at relevant temperatures, which both produced small, usually multi-layered, objects and made it difficult to observe them separated and well differentiated within a quenched matrix. These difficulties have now been overcome leading to the observations reported here of individual S-profiled polyethylene lamellae. Their development is shown to be asymmetric producing isochiral screw dislocations, growth around which propagates a consistent sense of twist incrementally at each dislocation. This motif not only accounts for observed morphologies in detail but is also sufficient, by iteration, to lead to the formation of banded spherulites. The observations show that banding in polyethylene is driven by the relief of fold surface stress when fold packing orders to inclined fold surfaces, in agreement with wider experience that banding is confined to systems possessing this property [10].

2. Experimental

Individual melt-grown crystals may be examined by a number of techniques established earlier in this laboratory together with one major addition. The traditional methods are, first, the examination of quenched objects in the interior of a (generally thick) film using permanganic etching of internal surfaces exposed by cutting, followed by replication and transmission electron microscopy (TEM) or, after metal coating, directly at lower resolution by scanning electron microscopy (SEM). Second, individual crystals can be extracted from their quenched matrix, collected on a carbon film or other support and examined directly by TEM or SEM. While both of these methods give informative views of the morphology in the interior of the sample, neither normally allows undamaged specimens to be examined by diffraction TEM in pursuit of internal textural information. In the former case, specimens are usually too thick while in the latter, pervasive cracking indicates that extraction has caused mechanical damage.

The new technique is a compromise designed to allow both morphological and diffraction information to be gained for an undamaged object. To this end, a melt-crystallized film, thin enough for direct transmission at 200 kV, was prepared as follows. Small drops of a solution of the polymer in xylene at concentrations ≤0.3% were cast on carbon-coated slides and the solvent allowed to evaporate. The dry film was melted at 160 °C then crystallized isothermally in a Mettler FP-52 hot-stage, with FP-5 controller, for a sufficient time after which the sample was quenched on ice. Detail was revealed using a 0.7% w/v solution of $KMnO_4$ in a 2:1 mixture of concentrated sulphuric and dry phosphoric acids by allowing drops of etchant to run down the glass slide for a few minutes at room temperature until a suitable crystal was observed, by Nomarski reflection optics, just to break through the etched surface. At this stage etching was stopped by substituting a solution of 2:7 concentrated sulphuric acid to aqueous hydrogen peroxide (100 volumes at 5% v/v), with care taken at all times to retain the polyethylene and carbon films intact. With the procedure complete, the film is allowed to dry before being shadowed with tantalum/tungsten and a support carbon film evaporated on the etched and shadowed surface. When this has been scored, floated off on water and collected on an electron microscope grid, samples are ready for TEM examination at 200 kV using a Philips CM20 analytical electron microscope. Some morphologies and associated diffraction images were recorded directly on plates but, for tilting experiments, the latter were mostly recorded on video using a Gatan model 622-0600 fibre-optic-coupled TV detector.

2.1. Materials

Two linear polyethylenes and one linear-low-density material, whose properties are listed in Table 1, were used to provide examples of lamellae displaying the three types of profile in *b* projection. The commercial Rigidex 140/60 (BP Chemicals Ltd) and an in-house fraction, #14-R1, extracted from it with a solvent, gave crystals with planar and ridged profiles when crystallized at 130 and 129 °C, respectively. Separate S-profiled lamellae were produced in an experimental methyl-branched copolymer, R3, prepared by Ziegler–Natta catalysis and supplied by BP Chemicals Ltd, when crystallized at 120 and 123 °C.

Table 1
Polyethylene data

Polyethylene	Source	Branch content	Mm	Mn
Rigidex 140/60	BP chemicals	Linear	54,000	17,000
#14-R1	Fractionated from above	Linear	17,000	10,000
R3	BP chemicals experimental sample	6.25 methyl/1000 C atoms	160,000	50,000

3. Results and discussion

It is convenient to start by illustrating lamellae corresponding to the three different profiles of polyethylene lamellae, projected down the *b* axis [8]. The simplest is that of Fig. 1, for Rigidex 140/60 crystallized for 13 h at 130 °C which is typical of high temperature growth of medium length molecules. To a first approximation the fold surface is a single {201} plane although adjacent layers spiralling around the (etched out) giant screw dislocation are not in contact [11] indicating the presence of a mesoscopically short range repulsion, a major cause of spherulitic growth. Although diffraction contrast reveals that the topography of a single lamella does depart locally from precise planarity, this does not affect the conclusions of the present paper.

A sufficient reduction in molecular length at a given high crystallization temperature tends to introduce alternating {201} facets and a ridged habit [12]. Plan views of such lamellae are illustrated in Fig. 2(a) and (b). That in Fig. 2(b) is an extracted crystal of #14-R1 collected on filter paper. In agreement with earlier reports, the ridges run essentially along the length of a lamella confirming the Miller index. Their origin is likely to be in multiple nucleations of inclined surfaces aided by the higher mobility of the shorter molecules and relatively small inter facet free energy.

The S- and C-profiles, characteristic of dominant lamellae in most samples of linear and branched polyethylene, are shown in Fig. 3(a) although the curvature is not always as pronounced as in this case. Such profiles are seen, for example, within the central ring of a section through a banded spherulite which is a view directly down the *b* axis [13]. What has not previously been shown is how they relate to an individual lamella and how they are propagated. This information is contained in the plan view of a simple lamella in Fig. 3(b). It shows a non-planar entity whose upper centre lies below the level of the etched matrix. The shadow contrast indicates that a central section normal to *b*, which habit and electron diffraction confirm to be the

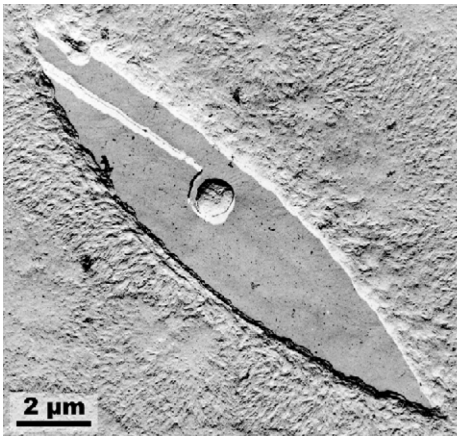

Fig. 1. Planar lamella of R140/60 grown for 13 h at 130 °C.

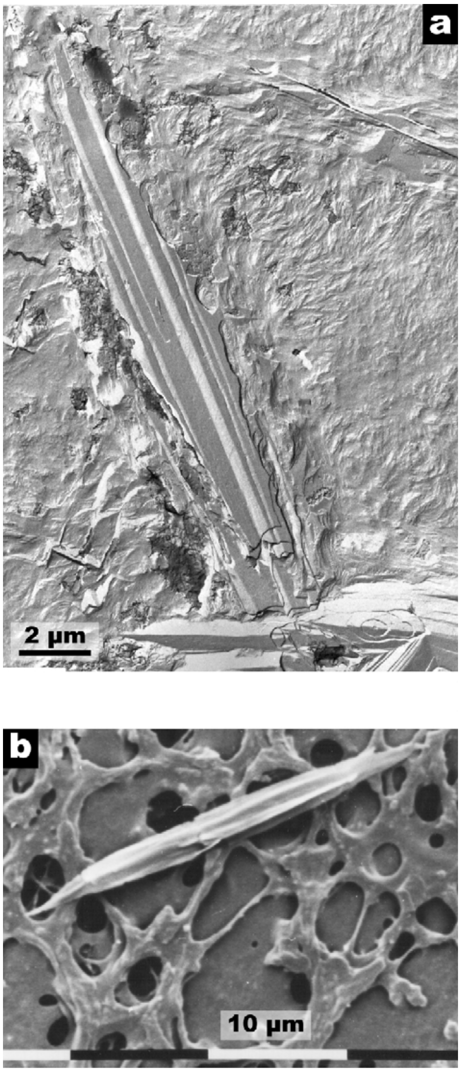

Fig. 2. (a) Surface detail of a ridged lamella of #14-R1 grown at 129 °C for 48 h. (b) An extracted lamella grown under the same conditions as described earlier, sedimented on filter paper.

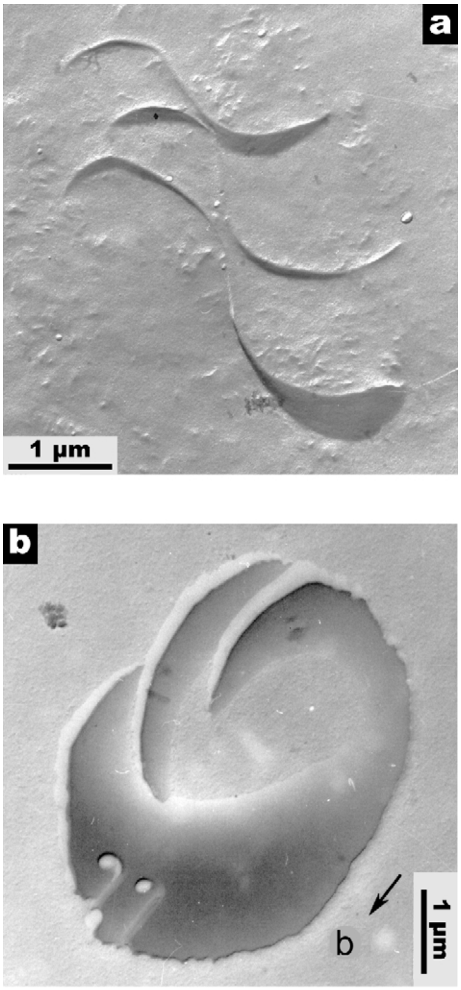

Fig. 3. (a) S- and C-profiles in R3 lamellae crystallized at 120 °C for 1 min. (b) An individual lamella of R3 copolymer crystallized at 123 °C for 35 min showing a central S-profile, asymmetrically placed screw dislocations and new layers diverging therefrom.

longest dimension, will have an S-profile in central regions with one or two C's in cross-section at the top where two diverging layers have developed strongly. These are topographically associated with one or two giant screw dislocation for which a clockwise turn lowers the spiral terrace by one layer. Two other screw dislocations, whose cores have been etched away, are at the lower end of the crystal but these are of opposite chirality in that a clockwise turn raises the level of the embryonic spiral terrace. The new developing layers at either end of the basal lamella are mutually rotated around the common *b* axis, contributing an overall twist around *b* to the growing system, which is propagated by, and increased discontinuously at, each screw dislocation. These features are a systematic feature of S-profiled polyethylene crystals.

The overall twist shows the system to be asymmetric and related, as will be shown in more detail below, to the asymmetry of the S-profile. To describe this succinctly an appropriate terminology needs to be introduced: for a sheet with an S-profile in cross-section and no curvature in the orthogonal direction, it is convenient to refer to the latter as the axis of the S and to the former as the plane of the S. When polyethylene lamellae are viewed in *b* projection they show an S-profile but it does not follow that the axis of the S is parallel to the *b* axis. On the contrary Fig. 3(b) shows that this is not the case. Here the axis of the S, judged by the matrix material lying above it, is inclined some 20° to the *b* axis. This most important observation reveals how the asymmetric habit develops in a crystallographically symmetric system. In combination with the previous demonstration of a one-to-one correlation of the sense of the S-profile with that of banding in the spherulites (with increasing radius, the S rotates in the direction of the outward normals to its concave surfaces [13]) the link is made from the asymmetric habit of the initial S-profiled crystal to the sense of banding in the consequent spherulite.

The final salient feature of Fig. 3(b) is the systematic, asymmetric locations of the screw dislocations which lie to the left of the S at the top of the figure and to the right at the bottom. As a consequence the connections to outward growth, which occurs via the new lamellae arising from these dislocations, will be in consistent diagonal directions rather than directly along the radial *b* axis. There are parallels here with the asymmetric distributions of dislocations noted by others [14]. Diagonal linking makes the texture what has been described earlier as 'multiply connected' [13], a feature which is liable to develop further complexities based on the evident lamellar divergence.

More precise information on the topography of the S-profiled lamella emerges from Fig. 4 which shows two diffraction images related by a rotation around the *b* axis. Shadow contrast once again reveals a more or less cylindrical surface with an S-profile in cross-section and an axis at $\sim 20°$ to the *b* axis. The interval across the S, i.e. between crest and trough, is ~ 1 μm. The continuous dark fringe identifies locations where the operative reflection, here the $\{110\}$ plane roughly perpendicular to the fringe, is parallel to the electron beam; other reflections are rotated far from parallelism. In what is typical behaviour, comparison of the two images shows that a rotation of 5°, from 25 to 30°, around the *b* axis advances the fringe ~ 1 μm equivalent to a band period of $\sim 180/5 = 36$ μm if twist were uniform, much greater than the actual band period. This illustrates the earlier established fact that banding does not involve uniform twisting of lamellae [15], large increments of twist being inserted at screw dislocations, as in Fig. 3(b).

A further important deduction from the shape and movement of the fringe which moves little in the centre of the lamella but advances ~ 1 μm towards the outside on rotation, is that the S-profile is more pronounced in the centre, i.e. the oldest part of the crystal which has had the longest time to adopt the S-profile. This shows that fold surface inclination develops within an individual lamella which itself becomes moderately twisted in the process.

Some indication of the complexity of textural connections leading to banded spherulites may be gained from

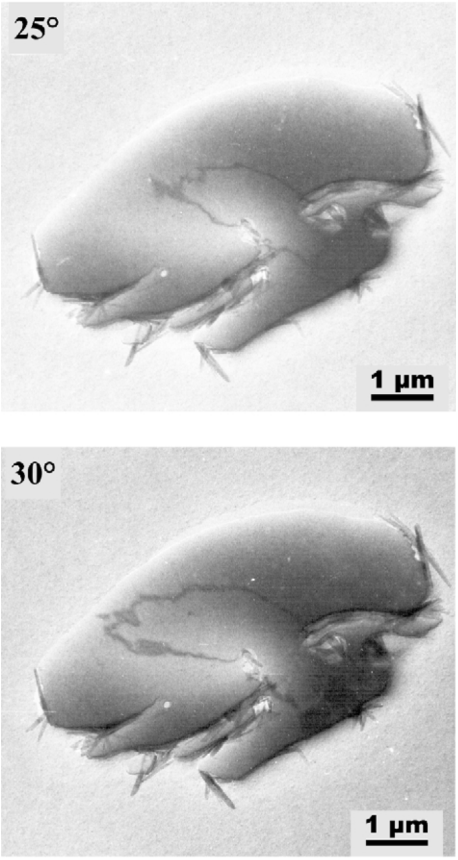

Fig. 4. TEM micrographs of a lamella of R3 copolymer crystallized at 123 °C for 5 min showing Bragg diffraction fringes. The lamella had been rotated about its long axis by 25° for the left-hand image and by 30° on the right.

Fig. 5. Fig. 5(a) shows a portion of an S-profiled lamella within which the cores of at least four screw dislocations have been etched out. These are all isochiral and have generated new downward curving layers demarcated from the parent along {200} planes. While all of these have advanced towards the lower right corner of the figure that at the upper right is also proceeding in the opposite direction, demonstrating that both growth directions may develop. In practice backwards growth in a dense system such as a spherulite may be inhibited by both geometry and material supply.

Further iteration of such branching and growth leads to such complicated objects as those of Fig. 5(b). Splitting of layers, topographically equivalent to the generation of a screw dislocation is visible in several places. In others dislocation cores have been etched away. Once a lamella has split, the separate portions diverge markedly but are liable to meet again at a distance because of the adoption of an S-profile. Much if not all of this conforms to a pattern whereby lamellae tend to adjust until their fold surfaces become inclined, with their normals at ~35° to the *c* axis, in the centre and outsides of the S-profile. Once a lamella has divided the new portion also behaves in this way and essentially independent of its parent as would be expected of a response to the torsional stresses in the system.

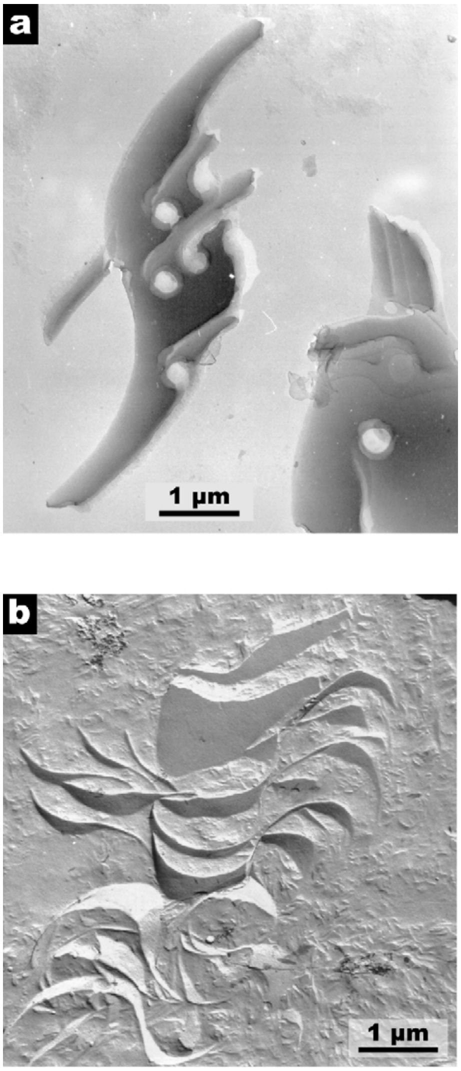

Fig. 5. (a) An individual lamella of R3 copolymer crystallized at 123 °C for 35 min. (b) Complex textures in R3 copolymer crystallized at 120 °C for 1 min.

3.1. Phenomenology

S-profiled lamellae are not simple sheets with a uniform S in all cross-sections perpendicular to the *b* axis. Their departures from this condition are informative both on how they form and how iteration will lead to banded polyethylene spherulites. The salient points are first that the profile is not uniform but is more non-planar in the central, older part of the lamella. The depression in Fig. 3(b) and the trough in Fig. 4 are deeper in the centre of their respective lamellae. Second, the axis of the S is not parallel to *b*, but inclined at ~20° to it. This implies inter alia that the centre of an S is not a {201} plane but some nearby one such as, approximately, {412} or {613}. Third, the lamella has an overall modest twist but less than required to give the band period. Fourth, the asymmetry of the axis of the S is linked to an asymmetric distribution of screw dislocations, which are isochiral for a given radius and generate diagonal linkages. Fifth, new portions of lamellae inserted at a screw dislocation diverge rapidly and tend to achieve their own S-profile, with the cross-section related in phase to the parent. In this way increments of overall twist are inserted at each dislocation. It is now necessary to relate these findings to the perceived problem of spherulitic banding.

3.2. Banded spherulites

The literature of banded spherulites is profuse, extending beyond polymers, with optical banding generally related to a uniform average twisting around the radius, as shown by tilting in the polarizing microscope [1] and by X-ray diffraction [16]. Although rhythmic growth has also been observed in particular circumstances [17], the concern of this paper is to address the more general problem and relate the overall twist to lamellar growth mechanisms.

Chainfolded lamellae grow radially in polymer spherulites, a finding which in its day provided an immediate solution to the previously puzzling tangential, or near-tangential, chain axis orientation for spherulites in general. However, for banded spherulites in particular, packing considerations rule out uniform lamellar twisting around the radius [18] as the underlying microstructure. Not until the advent of techniques allowing systematic electron microscopy with lamellar resolution, despite radiation damage, did it become clear how lamellae were arranged within polymer spherulites. In non-polymeric systems comparable information is still lacking.

It was shown that polymer spherulites typically form with dominant/subsidiary architecture resulting from the initial growth of individual, branching and diverging dominant lamellae forming a framework from which later-forming subsidiary lamellae grow. The repeated divergence is the underlying cause of spherulitic growth. However, although dominant lamellae of polyethylene banded spherulites have S- or C-profiles viewed down *b*, whose sense is uniquely related to that of the banding [13], other aspects of the lamellar habit have not been reported earlier. A principal problem has been the introduction of asymmetry into an otherwise symmetric, orthorhombic lamella. The suggestion was made [16,19] that this could result from molecular deposition on the prism faces of lamellae with inclined fold surfaces although it has now been made clear that banding does not result in these circumstances [9].

It has long seemed to us, on the contrary, that the cause of the S-profiles is delayed fold ordering, an extension of an idea first propounded in connection with the ridged and hollow pyramidal habits of solution grown polyethylene lamellae [20], as has recently been confirmed by direct observation [9]. This does not, however, of itself resolve the question of the origin of the asymmetry. The observation, reported here, that the axis of the S is inclined to the growth direction now shows how asymmetry is introduced. That there should, in principle, be some inclination is to be expected because of the lack of crystallographic ordering of fold surfaces. This is, for example, the cause of the misorientation of bilayers used to produce moiré patterns and to identify subcell distortions due to chainfolding [21,22] but such misalignment would be expected to be small. The actual deviation of ~20° seems too large and consistent to arise solely in this manner. It is suggested later that the elastic energy of the nucleating S may also be pertinent.

Phenomenologically, lamellar twisting is associated with the relief of surface stress in disordered fold surfaces when inclined surfaces are adopted in conjunction with an S-profile, of increasing amplitude, and lamellar thickening. There is no banding in linear polyethylene at 127 °C and higher temperatures when folds order before the next molecular layer is added [9]; they can then be expected to adjust their relative positions accordingly and approach optimum packing. The situation which accompanies banding is different in that folds are, presumably, placed haphazardly and somewhat loosely [23] because crystallization of stems is the driving process with folds themselves contributing little to the overall fall in free energy. When, later, longitudinal molecular vibrations bring them into proximity their lateral positions will be largely fixed, with only minor adjustments possible. The associated surface stress may be partly alleviated by twisting in that, if it occurs at constant length, outer regions of the lamella will be extended. In practice banding only appears to occur when the stress is sufficiently high eventually to produce inclined fold surfaces. Twisting is likely to be a more effective relief when the stress is concentrated along the two parallel strips at the crest and trough of an S where the surface is still locally {001}. The time dependence of fold ordering within an existing lamella will naturally lead to an S-profile developing because, as fold surfaces incline first in the central older part, lamellar continuity will produce opposite inclinations at either side, i.e. inclined surfaces in the centre of the S, opposite inclination at both outsides with stressed regions between. It should also be noted that such changes of lamellar shape can only occur given sufficient free space, in agreement with observation that lamellae must have a finite separation before the S-profile develops [9]. C-profiles, as the example at the top of Fig. 3(b) reveals, derive from appropriate cross-sections of branching lamellae.

The generation of the S-profile in the centre of a lamella will create an additional torque around the axis of the S. This may be seen by considering the extra side-surfaces created when folds stagger. While staggering in the plane of the S will reduce the free energy because {201} are the preferred basal surfaces for both polyethylene and *n*-alkane lamellae, topographical continuity along the axis of the initially limited S will produce excess surface and thus stresses—which are a derivative of the free energy—facilitating the propagation of the non-planar region. When the S-profile nucleates in the centre of a lamella, the associated elastic energy of external areas along the axis of the S will make a significant positive contribution to the free energy of nucleation. Its minimization is possibly the reason for the substantial inclination of the axis of the S to the *b* axis and why inclined surfaces depart from the preferred {201} orientation; once an S has nucleated its rigidity will ensure that its direction will not change. The total twist in an S-profiled lamella is insufficient of itself to give the observed band period. It is the amplification of this twist by the formation of isochiral screw dislocations and the growth of new lamellae on them by which this greater lamellar rotation is accomplished.

The propagation of the asymmetric profile to a succeeding lamella is achieved via isochiral dislocations. Their consistent and asymmetric placement suggests an origin in yielding to the twisting stress in the lamella in regions where a displacement by the layer thickness gives comparatively small shear strain. The corresponding locations will be at equal distance from the axis of the S, hence their asymmetric sitting and isochirality. In this way, the asymmetry introduced in the inclination of the axis of S is perpetuated. Moreover, when the lamella does dislocate, the reduction in width will decrease the torsional rigidity, which varies as the fourth power of width [24], with a greater response to the torque and an effective increment of twist given to a new layer. This constitutes an amplification of the twist in the parent lamella, which will lower the overall band period accordingly.

The sequence of events described is a motif, internal to the lamella—as in an unrelated system, poly(vinylidene fluoride) [25]—whose iteration will lead to banding. While the generality of the observations to systems other than polyethylene and their detailed interpretation to some extent remain to be established,[2] their origin in the relief of surface stress appears well-founded. It is noteworthy, for example, that a ready explanation is provided of why banding in polymers is restricted to systems with inclined fold surfaces [11] because these are those with the highest stress in perpendicular fold surfaces. Moreover, the central role of relieving surface stress is endorsed by the latest results from this laboratory [27] which show that when stress is introduced into previously unstressed fold surfaces of polyethylene lamellae, by bringing excluded branches into a previously ordered fold surface, twisting growth is only then initiated. Furthermore, that the monodisperse *n*-alkane $C_{294}H_{590}$ gives banded spherulites on rapid, and so rather disordered, crystallization of the once-folded form [5,6] fits readily into the same scenario. In general, while relief of basal surface stress is a concept, which would appear capable of wide application, how asymmetry is introduced in a particular case needs to be established. In chainfolded systems, the irregularity of fold placements breaks the link with strict subcell crystallography introducing an asymmetry, which may then propagate in a way similar to that demonstrated for polyethylene.

The familiar observation that band period decreases with crystallization temperature [17] is also to be expected from the earlier discussion although a precise calculation will encounter significant difficulties. It will depend, inter alia, on the frequency of branching and the increment of twist then inserted. The former is a function of yield stress the latter of the compliance while both depend upon the magnitude of the internal stress. Thinner lamellae will have a lower yield stress and a higher compliance, both factors favouring a shorter band period at lower crystallization temperatures. An additional consideration is the common observation that the curvature of the S-profile is less for lower crystallization temperatures and most copolymers than for the linear polymer grown at high temperatures implying less relief of internal stress. This may be connected to the varying constraints on isothermal lamellar thickening known to accompany the formation of the S-profile. Thickening accelerates for higher temperatures but is hindered by the excluded branches of most copolymers. For methyl-branched polyethylenes, as here, it may be that the increased lattice dimensions are an advantage facilitating the high curvatures recorded.

4. Conclusions

This paper has shown how banded spherulites of polyethylene develop from an individual crystal.

1. An initially planar lamella develops a characteristic S-profile over time extending out from central regions. This is a consequence of reducing surface stresses by improving fold packing whose spatial requirements are best met by inclined as opposed to the initial perpendicular fold surfaces.
2. The axis of the S-profile is inclined to *b*, an inclination which introduces the essential asymmetry into the system, and the lamella slightly twisted around the axis of the S.
3. The twist is amplified by the formation of isochiral giant screw dislocations, systematically to one side of the S for a given radius, giving diagonal linkages and each developing lamella a comparatively large increment of twist.
4. The detailed morphology is readily accounted for on this basis as is the general restriction of banding to polymers with (eventually) inclined fold surfaces.

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[2] A recent explanation offered for twisting in poly(vinylidene fluoride) [26] reports similar morphologies to those of this paper, particularly the asymmetric distribution of growth pyramids and the inclination of the axis of twist to the growth direction.

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