On fold surface ordering and re-ordering during the crystallization of polyethylene from the melt

M.I. Abo el Maaty[1], D.C. Bassett[*]

J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, P.O. Box 220, Reading RG6 6AF, UK

Abstract

Novel observations of polyethylene crystallizing from the melt as row structures on linear nuclei show that at lower temperatures, when there is banded crystallization, lamellae form first with disordered fold surfaces. Banding itself is associated with the re-ordering of those fold surfaces towards their preferred inclined condition. Lamellae which form initially are close-packed and normal to the row but, at greater radial distance, are separated and develop S-profiles behind the growth front, in conjunction with isothermal lamellar thickening. At the growth front, molecules still add to lamellae whose normals are parallel to the chain axis. A different situation pertains at temperatures $> \sim 127°C$ where the first lamellae to form do so epitaxially with inclined fold surfaces in two orientations symmetrically inclined to the axis of the row. When lamellae widen, this morphology changes to one of planar lamellae normal to the row, which retain inclined fold surfaces. The difference between growth above and below $\sim 127°C$ is due to the development of fold interactions over time, towards the ordering of {201} fold surfaces. For the lower temperatures the rate of radial advance is faster than that of fold-surface ordering with the change, from fold surfaces being initially perpendicular then re-ordered, to being inclined from the start, expected when the relative rates reverse. Banding does not occur when molecules add to lamellae with inclined fold surfaces, only when fold re-ordering occurs within existing lamellae consistent with this process being the cause of banded growth in polyethylene. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Nowadays it is generally accepted that chainfolded lamellae are ubiquitous in melt-crystallized polymers. Nevertheless, how the lamellae present actually form is uncertain in several important aspects. The simplest parameter, lamellar thickness, is often related to that of the secondary nucleus on the growth face by an empirical factor γ [1] which has no theoretical foundation although it is certain that melt-crystallized polyethylene lamellae do thicken isothermally above their initial dimension. This is shown by an increase in the long period with time [2] and, morphologically, by the absence of a residual step — in contrast to solution-grown lamellae — when the crystallization temperature is changed abruptly even though giant screw dislocations formed at the time are liable to remain marking the instantaneous location [3]. The progress

of thickening is seen directly in the work reported in this paper which principally addresses a second aspect, namely the development of chain axis inclination to lamellar normals.

Earlier work showed that, as regards lamellar habit, linear polyethylene crystallized from the melt in one of two ways. For higher crystallization temperatures, depending on molecular length, (in this work $> \sim 127°C$) lamellae are planar or ridged, with fold surfaces near to {201} in the orthorhombic subcell, i.e. with an angle of $\sim 35°$ between the *c*-axis and the lamellar normal [4]. By contrast, dominant lamellae grown at lower temperatures showed S or C profiles when observed down *b*, the growth direction, implying a continuous variation of chain inclination to the local lamellar normal [4]. Here we show that this dichotomy results from different patterns of growth. When planar lamellae with {201} fold-surfaces form, they grow epitaxially from the nucleus so that those molecules adding to a growing lamella attach to one with inclined fold surfaces. By *inclined* we denote that the normal to the fold surfaces and the chain axis, *c*, are not parallel; when they are parallel we describe the fold surfaces as *perpendicular* (to the chain axis). A different situation pertains

* Corresponding author. Tel.: +44-118-931-8540; fax: +44-118-975-0203.
 E-mail address: d.c.bassett@reading.ac.uk (D.C. Bassett).
 [1] On leave from Physical Science Department, Faculty of Engineering, University of Mansoura, Mansoura, Egypt.

for the S-profiled lamellae which are characteristic of banded spherulites [5]. For them, lamellae first form with perpendicular fold surfaces, then develop the S-profiles at greater radial distance as fold surfaces re-organize accompanying isothermal lamellar thickening.

This distinction is suggested to be due to the development of fold interactions over time moving towards the ordering represented by inclined and specifically {201} fold surfaces. Inclined, planar surfaces are present from the outset when ordering occurs faster than radial advance. When the reverse is true, belated ordering of fold surfaces develops within an existing lamella, in a partly frustrated attempt to attain the {201} free energy minimum, resulting in the S-profiles. This finding strongly supports the contention that it is the re-ordering of fold surfaces within existing lamellae which provides the driving force for spherulitic banding [3,4].

2. Experimental

The material of these experiments was Sclair 2907 (Du Pont, Canada) a linear polyethylene for which $M_w = 104,000$; $M_n = 11,300$ chosen because of its ability to give large banded spherulites. Specimens containing high-melting polyethylene fibres as linear nuclei were prepared in one of two ways. Flat discs of the polymer, $\sim 20 \times 30$ mm^2 across and ~ 1 mm thick, was prepared from the appropriate quantity of pellets by melt pressing, between a clean 13 μm thick Kapton sheet and a microscope slide, on a Kofler hot-bench at 150°C for 5 min. At the end of this time each disc, with the Kapton sheet and the microscope slide, was quenched by placing on a large metal plate. After removal from the microscope slide it was cut into small squares of ~ 5 mm side which were stored in labelled jars ready to prepare a fibre/polymer composite as below.

For the examination of diametral sections, a specimen containing about seven highly oriented Tekmilon™ polyethylene fibres (Mitsui) within a Sclair polyethylene matrix was prepared, between microscope slide and cover slip. Initially the fibres were stacked parallel on a microscope slide to which their ends were lightly adhered with Araldite epoxy resin. This slide was inverted and placed carefully on one of the stored square discs already sitting on a cover slip at 130°C on the Kofler hot bench, applying light pressure to the already-melted disc. The resulting fibre/polymer composite, with microscope slide and cover slip, was then transferred to the Mettler hot stage at 130°C for 5 min before the temperature was lowered to the required crystallization temperature using a Mettler FP90 central processor. The composite specimen was quenched in ice-water mixture after the selected time of crystallization and carefully removed from the slide and cover slip. Nomarski differential interference optical microscopy showed that the fibres were usually embedded ~ 40 μm below the surface of the disc and more or less parallel to it. For specimens used to examine textures looking down the growth axis, a greater depth of

~ 60 μm was used to keep the fibres well away from the specimen surface. In this case the fibres were placed between two discs, one 1 mm thick, the other ~ 60 μm thick, both prepared as above, otherwise the same procedures were followed.

All specimens were etched in a 2% (wt/v) potassium permanganate solution in 10:4:1 parts by volume of concentrated sulphuric acid, 85% orthophosphoric acid and distilled water, respectively. Those specimens used for observations of morphology in planes normal to the nucleating fibre were cut open with a microtome prior to etching; all others were etched as prepared. The etching time was selected according to the particular view required. Four hours was used to expose a diametral section in longitudinal views, i.e. so that the final plane surface of each specimen passed close to the fibre axes. This was readily checked with Nomarski optics which showed the width of fibres to be close to their nominal diameter of 40 μm. A shorter period was used when it was desired to view the rows down the growth direction in planes outside the original fibre. In such cases, it was often possible to observe views at different distances from the fibre simply by moving along the length of the row, taking advantage of any slight inclination of the fibre to the etched surface.

Etched specimens were either coated with gold prior to examination in the scanning electron microscope (SEM) or replicated by a standard two-stage process for transmission electron microscopy (TEM).

3. Results

The nature of the growth of polyethylene around a fibre as nucleus is shown in the transverse section of Fig. 1. The central fibre, which now contains etched craters where density deficient material known to lie along the fibre axis has been removed, is not exactly circular in cross-section and the contour of its perimeter is followed first by the isothermal banded overgrowth then by the much narrower
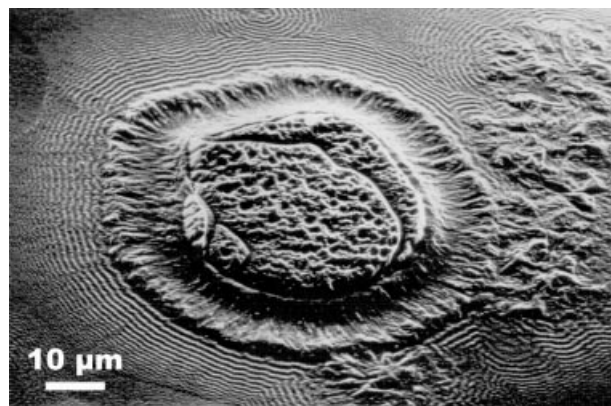

Fig. 1. Transverse section of Sclair 2907 polyethylene crystallized around a polyethylene fibre for 90 s at 123°C then quenched. Scanning electron micrograph of etched surface.
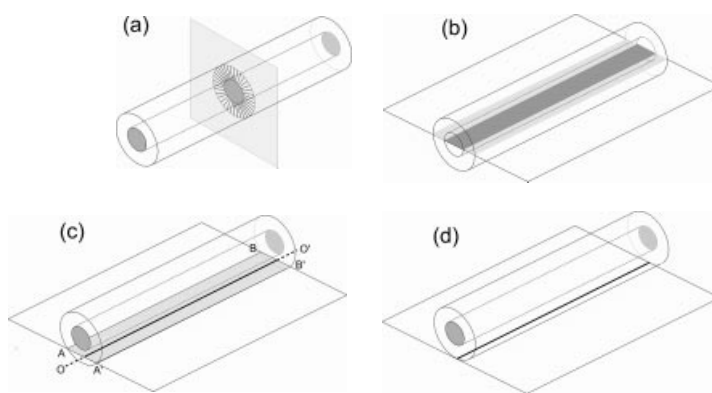
Fig. 2. A sketch of the geometries of etched specimens to illustrate the various views described in the text: (a) transverse section; (b) diametral longitudinal section; (c) general radial view; and (d) radial view of the edge of the row.

bands produced on quenching. It should be mentioned in passing that the symmetry of this and all other transverse sections reveals no evidence of growth being influenced by undue proximity of the outer surface of the specimen. Succeeding figures show other views of various row structures, in two orthogonal directions with the length of the fibre in the plane of the paper as indicated schematically in Fig. 2. The first of these is of diametral longitudinal sections, i.e. when the plane of the image passes through or close to the centre of the fibre; for these growth is also in or near to the plane of the paper. Second, there are views down the growth direction, i.e. of planes parallel to the fibre but external to it and offset from its axis; these views we term *radial* although only along one central longitudinal line, OO$'$ in Fig. 2c will the growth direction, *b*, be precisely normal to the page.

For crystallization at temperatures $< \sim 127°C$, i.e. the conditions commonly pertaining, banded spherulitic growth is characteristic of linear polyethylene [6,3] although a low nucleation density, as prevails in Sclair 2907, is necessary
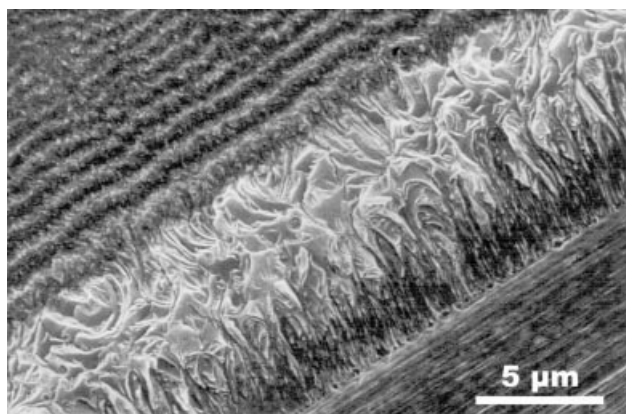
for a well-developed texture to result. Such banded growth is constructed from a framework of dominant lamellae with S-profiles viewed down the *b* axis [4,5]. The origin of the S and its development are brought out especially well in radial views.

The context of the observations is set by diametral longitudinal views such as that of Fig. 3 and the kinetics derived therefrom. The latter have been published previously [7] and show that, for the growth of Sclair 2907 at 123°C, the averaged rotation around the radius in banded growth is 90° by 30 s and 180° for 60 s crystallization corresponding to growth lengths of some 4 and 8 μm, respectively. It is also noticeable in Fig. 3 that isothermal thickening has occurred from the first close-packed and thin lamellae nucleated on the fibre to the separated and substantially thicker lamellae in a more open texture at the edge of the row where growth was quenched. Such information allows a judicious choice of crystallization times prior to preparing samples giving radial views.

In radial views such as Fig. 4, what one sees depends upon the location of the etched surface relative to the row structure. Longer etching times move this surface towards the fibre nucleus, making a greater chord in the cross-section of the row. In all radial views, the outer edge of the row corresponds to the full crystallization time with inner locations showing the morphology initially formed at shorter times plus any later development. In the limit of very narrow intersected widths, one sees the quenched edge of the row. Elsewhere, because of the imprecise geometry of the fibre cross-section it is not generally possible to derive from the measured width either the precise location of the surface within the row or the corresponding crystallization times. It is possible, nevertheless, to identify when the etched surface reaches the nucleating fibre — unlike the comparable situation in spherulites — while the nature of the changes within the morphology are themselves most informative. They show that the first lamellae to form are planar and normal to the fibre axis; the S-profile develops with radial distance accompanying isothermal lamellar thickening.

Fig. 3. Diametral longitudinal section of Sclair 2907 polyethylene crystallized around a polyethylene fibre, at lower right, for 80 s at 123°C then quenched showing the change from initial close packing of perpendicular lamellae to the more open texture of thicker, curved dominant lamellae associated with banded growth. Scanning electron micrograph of etched surface.
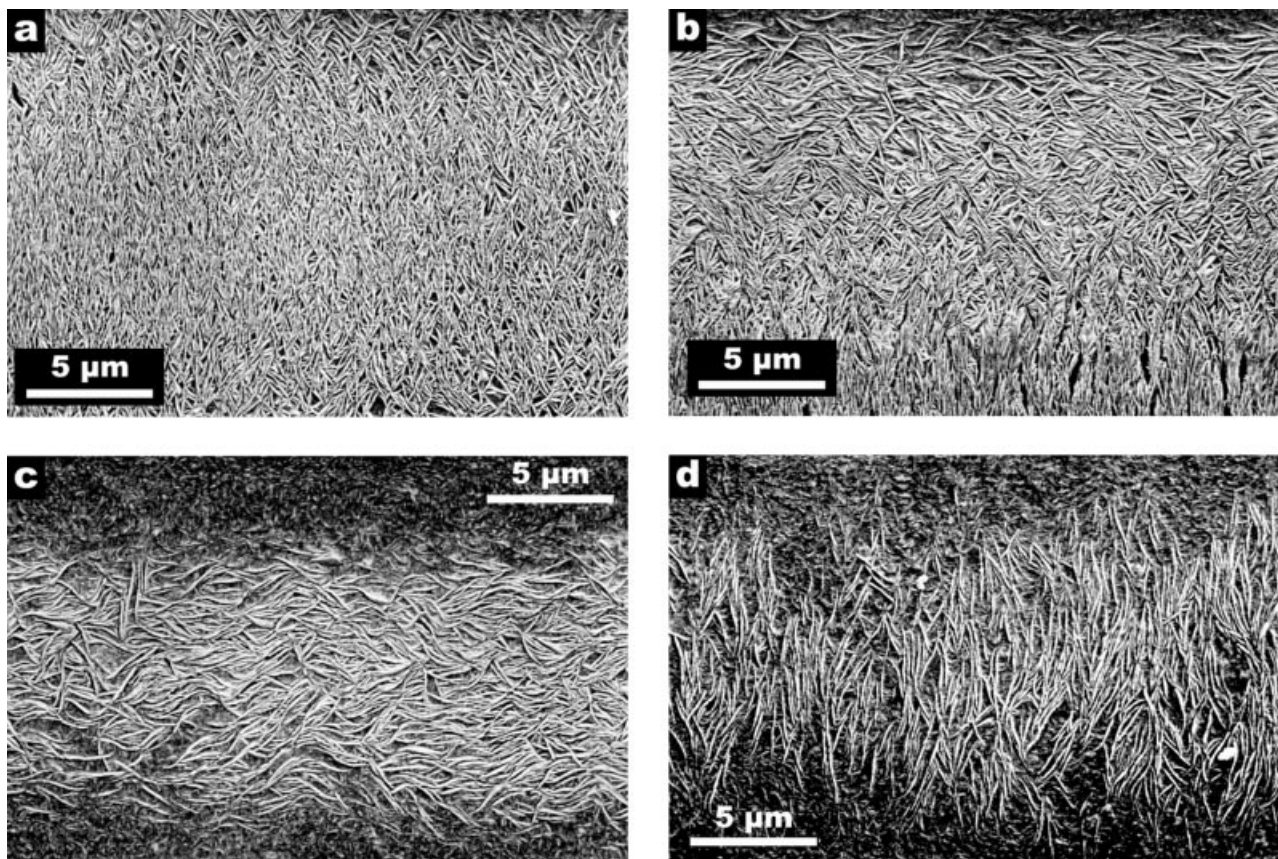
Fig. 4. Radial views of Sclair 2907 polyethylene crystallized around a polyethylene fibre at 123°C within a quenched matrix. Scanning electron micrographs of etched surfaces. (a) A section near to the fibre after 25 s crystallization showing denser central growth with perpendicular lamellae giving way to more open textures at top and bottom with slightly curved dominants. (b) Half a deeper section after 40 s crystallization shows the progression from close-packed perpendicular lamella at the bottom to S-profiled dominants, along the fibre axis, at the top. (c) A section far from the fibre after 40 s crystallization has S-profiled dominant lamellae aligned approximately along the fibre axis. (d) The outer edge of a row after 70 s crystallization shows that the dominant lamellae are still perpendicular at the growing edge so that molecules do not add to a lamella with inclined fold surfaces.

The sequence is illustrated in the four photographs in Fig. 4. Fig. 4a is a surface a little above the fibre for 25 s crystallization at 123°C, a time approaching the first 90° rotation of the banded growth. Dominant lamellae at the outside of the row, at the top and bottom of the micrograph, are weakly S-profiled, ~1 μm wide and in an open texture. This contrasts with the centre of the figure where lamellae are narrower, thinner and planar even though the close packing and normal alignment to the fibre axis present at the fibre surface have been modified to a degree. The latter feature is better preserved in Fig. 4b which shows the upper half of a row after 40 s growth. The thin, narrow lamellae at the bottom of the figure, normal to the fibre axis, give way progressively, with a dominant/subsidiary architecture, until at the top there is a full 90° rotation of thicker, wider lamellae in a more open texture with more-pronounced S-profiles. The outer regions of another row, also crystallized for 40 s, in Fig. 4c, contain S-profiled dominant lamellae and narrower infilling lamellae in an open texture. These observations leave no doubt that the S-profiles of dominant lamellae characteristic of banded crystallization of polyethylene develop with radial distance in association with isothermal

lamellar thickening. However, Fig. 4d, a row crystallized for 70 s at 123°C, shows that lamellae are still predominantly planar and ~2 μm wide at the outside of the row. It follows that the development of non-planarity in banded growth is ongoing as crystallization proceeds but occurs behind, not at, the interface with the melt.

The banded crystallization characteristic of polyethylene at lower temperatures gives way at ~127°C to textures in which lamellae have well-defined planar fold surfaces, close to {201} planes of the orthorhombic subcell, i.e. with molecules inclined at ~35° to lamellar normals. Fig. 5a and b show two radial views of such textures grown at 129°C. The first of these, after 3 h growth, shows lamellae everywhere inclined to the fibre axis. The overall texture coarsens towards the edge of the row where lamellae are thicker and more separated. On the other hand, after 11 h growth, in Fig. 5b lamellae are essentially normal to the row while the corrugated outer edge reveals a form of cellulation. In fact, as Fig. 6a makes clear, notwithstanding the lamellar orientation, molecules within them are inclined to the normals (being parallel to the arrowed striations): lamellae have retained their inclined character but changed their
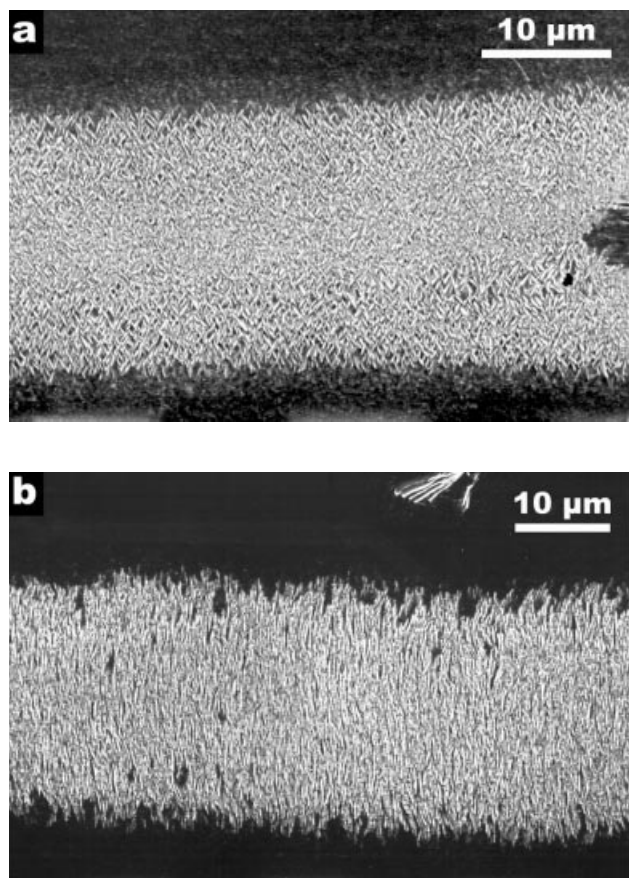
Fig. 5. (a) A row grown at 129°C for 3 h has inclined lamellae throughout with denser packing at the centre of the section. Scanning electron micrograph of etched surface. (b) After 11 h growth at 129°C lamellae grow with their planes normal showing to the row. Scanning electron micrograph of etched surface.
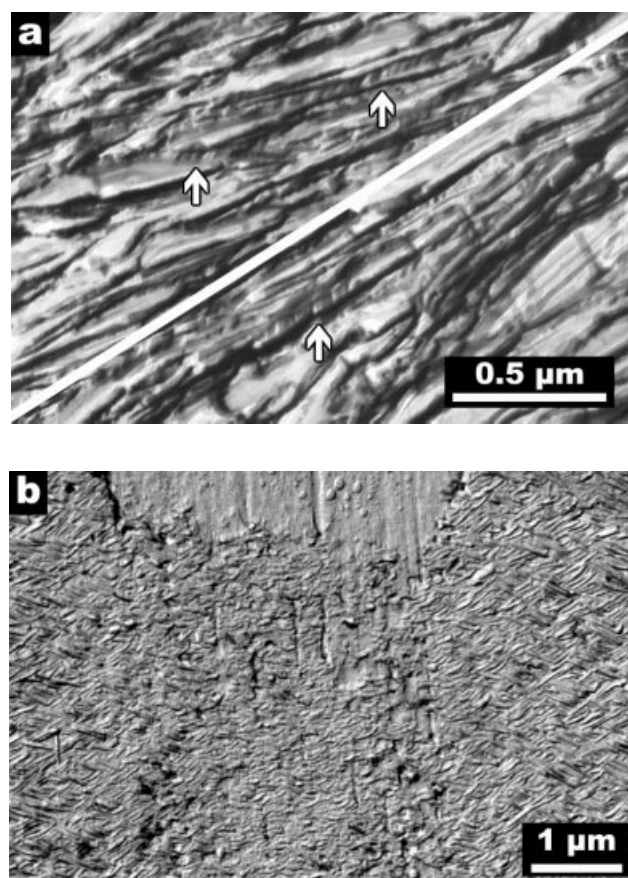

Fig. 6. Transmission electron micrographs of carbon replicas of etched surfaces. (a) The microstructure of two portions of a row, grown at 128°C for 80 min, with lamellae normal to the row shows, from the direction of the *c*-axis striations, that fold surfaces are inclined. (b) Detail of the contact area with the fibre, similar to that at the right of Fig. 5a, demonstrating that lamellae grow with inclined fold surfaces from the outset.

orientation. In contrast to the changing habits in banded growth, at high growth temperatures inclined lamellae are present from the outset. Fig. 6b, shows this where the etched surface reveals the nucleating fibre. The details of these high temperature effects and a concomitant change in growth kinetics are the subject of Ref. [8].

4. Discussion

The phenomena revealed in this paper lie at the heart of polymeric crystallization from the melt. In certain instances they may have previously been glimpsed or inferred but, for crystallization from linear nuclei, they are displayed in real space, clearly, unambiguously and systematically. Isothermal lamellar thickening develops with time and radial distance but, in this paper, the concomitant changes in lamellar habits are the main interest. For banded growth of polyethylene, S-profiles develop with radial distance, in conjunction with isothermal lamellar thickening and a more open texture. At high crystallization temperatures, there is no banding and lamellae with inclined fold surfaces begin to

grow epitaxially on the nucleating fibre, sharing a common *c*-axis direction. Although such chevron type lamellar growth on row structures at high temperature is familiar from previous studies [9,10], its replacement as lamellae widen by lamellae with inclined surfaces lying normal to the row has, so far as we are aware, not been previously recorded.

These phenomena are an inherent consequence of chainfolded crystallization of long molecules. Chainfolding itself occurs because it is the fastest mode of growth available to linear macromolecules but, as folds cost energy, it leaves the system in a metastable state with respect to thicker lamellae and fewer folds. Given sufficient molecular mobility, more stable lamellae may, in principle, be reached by isothermal thickening. Folds themselves, constituting only a small part of the molecules, are unlikely to exert a strong influence on the initial crystal habit especially for rapid growth at high supercoolings, which is driven by large differences of free energy. It is likely, and has long been presumed, that the stem length first laid down will be variable [11,12] and that folds will be sufficiently separated, in rough fold

surfaces,[2] so as not to interact strongly. However, the strong translational movement of chains within the crystal will, over time, tend to remedy this situation, remove gross roughness and promote optimum packing of folds with a lowering of free energy.

So far this scenario can be expected to apply to all crystalline polymers. What is particular to melt-grown polyethylene is that the preferred packing of folds is inclined reflecting their spatial requirements combined with a tight packing (low cross-sectional area) of fold stems. For the crystallization temperatures of our experiments the preferred inclination is in {201} surfaces [4]. Lesser inclinations of higher free energy — as known for solution growth [14] — could represent other metastable minima, adopted either temporarily in transit towards {201} surfaces or when re-organization is restricted. In consequence, the ordering of fold surfaces also tends, in polyethylene, to change their inclination. It is this factor, unusual in polymers, which underlies the various non-planar geometries and provides the driving force for banding in this polymer.

How far optimum, inclined packing can be achieved will differ according as the time required to achieve it is more or less than the time to add an additional layer of fold stems to a lamella. If it is less then each molecular layer will have adopted inclined packing before the next is deposited and lamellae will grow out from the nucleus with ordered fold surfaces. On the other hand, when the next layer of stems adds before the previous one has organized its folds, then ordering will have to proceed within the more demanding confines of an existing lamella. The oldest, central region of an isolated lamella will order first and the adoption of a small portion of inclined surface in this location will naturally tend to produce an S because of connectivity to the remainder of the lamella. Such a shape change will be less easy to adopt in a close-packed stack of lamellae than in an open texture and one would anticipate that the process would be easier and speedier once the dominant lamellae have separated, at greater radial distance, as they are observed to do.

One possible reason for dominant lamellae becoming separated is that while lamellae will nucleate on the fibre in all orientations, those that are oriented with *b*, the fastest growth direction, radial will lead all others and so become an array of separated lamellae. Another, related to the interference between competing nuclei, is discussed in Ref. [8]. However, for present purposes the precise cause of separation is not unduly important: it is sufficient that it occurs. The change of profile to an S must take place behind the growth front because fold surface re-organization will remain slower than growth. Growth itself continues to occur on perpendicular lamellae, as is illustrated in the outer edge of the row in Fig. 4d. This observation carries

the important information that, in banded growth, molecules do not add to lamellae with inclined fold surfaces as has sometimes been assumed [15,16]. On the contrary, it is the re-ordering of fold surfaces which is believed to drive the banding [3,4].

At high temperatures the epitaxial growth of lamellae with ordered fold surfaces, in both {201} orientations, is to be expected when ordering is faster than radial growth. However, the presence of lamellae in the two orientations means that, at least as they widen, they must eventually interfere with each other geometrically. That the outcome is a parallel array of lamellae normal to the row, with retained {201} surfaces, is reasonable but that this change is also accompanied by a substantial increase in kinetics, by factors ~4, is remarkable and the subject of Ref. [8]. It is further evidence of the kind accumulating recently [7,17–19], showing that the addition of long molecules to a crystal is more complex than is considered in current theories.

In their different ways, row structures grown both at low and high temperatures have been shown to change their lamellar habits with radial distance. This new observation needs to be incorporated into the interpretation of row structures encountered in other situations, not least those formed under conditions of flow or applied stress. So-called shish-kebabs generated in this way usually have lamellae transverse to the row [20] although from solution and from the melt at high temperatures, hollow pyramids [21] or inclined growth with the appearance of chevrons [9,10] are found, respectively. To retain the latter habit, it is now clear that lamellae must be small and/or grown from linear nuclei placed sufficiently close together, a factor which increases with elongational stress [20,10]. On the other hand, from widely spaced linear nuclei, the resulting well-developed lamellae will become perpendicular to the row at high temperatures whereas S-profiles may be expected at lower crystallization temperatures. However, whether non-planar profiles develop in practice also depends upon the applied stress: under isothermal conditions where S-profiles appear at low shear rates, or chevrons at higher temperatures, both give way to planar, transverse lamellae at higher shear rates. It appears, therefore, that fold surface ordering is hindered by the application of elongational stress which produces the linear nuclei in such experiments [10]. As the local morphology of row structures is so sensitive to the environment in which they form, it follows that, in principle, it can yield detailed information on the local conditions under which crystallization actually occurred.

5. Conclusions

The principal conclusions of this study of crystallization of polyethylene in row structures formed on linear nuclei are:

When there is banded crystallization, lamellae first form with disordered perpendicular fold surfaces.
Banded crystallization is associated with re-ordering of

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[2] Inherently rough fold surfaces will be expected to make a contribution to the splaying of dominant lamellae which is the essence of spherulitic growth, in accord with recent work on the long *n*-alkanes [13].

perpendicular fold surfaces towards the preferred inclined, more ordered, condition.

Lamellae which form initially are normal to the row and close-packed. At greater radial distance, dominant lamellae are separated and develop S-profiles behind the growth front, in conjunction with isothermal lamellar thickening. At the growth front, molecules add to lamellae whose normals are parallel to the chain axis.

At temperatures $> \sim 127°C$ the first lamellae to form do so epitaxially, with inclined fold surfaces in both orientations to the row. At greater radial distance, wider lamellae, still with inclined fold surfaces, are perpendicular to the row.

This dichotomy of behaviour stems from the development of fold interactions over time; the change from re-ordering of perpendicular fold surfaces for rapid growth to the ordering of inclined surfaces for slow growth is expected when fold-surface ordering becomes faster than the rate of radial advance.

Banding does not occur when molecules add to lamellae whose fold surfaces are already ordered, only when fold re-ordering occurs within existing lamellae consistent with the latter being the cause of banding in polyethylene.

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