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On interfering nuclei and their novel kinetics during the crystallization of polyethylene from the melt

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

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

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Abstract

At high temperatures, linear polyethylene crystallizes from the quiescent melt as lamellae with inclined, ~{201}, fold surfaces. Accordingly, when grown on linear nuclei to form row structures, the first lamellae to form do so epitaxially in two orientations symmetrically inclined to the axis of the row. With increasing radial distance, dominant lamellae widen, separate and become normal to the row albeit still with inclined fold surfaces. Isothermal growth rates are constant in both conditions but that for the later one is 3–4 times faster than the initial one. It is suggested that faster growth is a consequence of diminishing interference between secondary nuclei on neighbouring lamellae growing under Regime I conditions. The concept of interfering nuclei, competing for the same molecule, also provides a convincing explanation for previously reported kinetic effects in polyethylene and long *n*-alkanes as well as the presence of faster-growing dominant lamellae in the crystallization of such linear molecules. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Crystallization kinetics; Interfering nuclei

1. Introduction

Theories of polymeric crystallization have long been based on the pioneering work of Turnbull and Fisher [1] in which the rate of nucleation is related to the product of two Boltzmann exponential terms, one for transport to the growth interface, the other involving the excess free energy of the secondary nucleus. More recently, evidence has accumulated showing that transport of linear molecules to the interface is more complex than can be represented in this simple way. First, the crystallization rate of the monodisperse long *n*-alkanes passes through a minimum when there is competition between the formation of two quantized thicknesses [2]. This so-called self-poisoning effect focuses attention on the attachment and detachment of molecules at the interface and the interference, by blocking, of one molecular conformation with another. Second, the extended-chain crystallization of the long *n*-alkanes slows systematically at the onset of branching [3,4] when the number of locations for attachment first multiplies when dominant lamellae start to diverge. Third, in conditions of interfacial instability and cellulation brought about by the segregation of branched molecules in polyethylene, the growth rate of banded crystallization pulsates in phase with the bands due to systematic local changes in the direction of growth linked to segregant concentration and interfacial instability [5]. Although much of this behaviour relates to local changes in isothermal supercooling due to variable segregant concentration, a small effect observed in Sclair 2907 linear polyethylene does suggest that transport is affected to an extent by the branching process in these complex geometries.

These multiple effects can be explained with reference to a new phenomenon, reported in this paper, which occurs in linear polyethylene crystallized as row structures at high temperatures. As reported in the preceding paper [6], the growth from linear nuclei of lamellae with inclined fold surfaces (i.e. with lamellar normals not parallel to *c*, the chain axis) starts with two epitaxially nucleated populations whose planes are symmetrically inclined to the axis of the row. At greater radial distance these two have merged into a single lamellar population normal to the row but still with inclined fold surfaces. Accompanying this change is an increase by 3–4 in linear growth rate. This phenomenon is attributed to interference between crystallization sites, whose loss as lamellae separate gives faster growth. Internuclear interference is an explanation which can readily be generalized to account for previously reported kinetic

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* 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 the Physical Science Department, Faculty of Engineering, University of Manoura, Manoura, Egypt.

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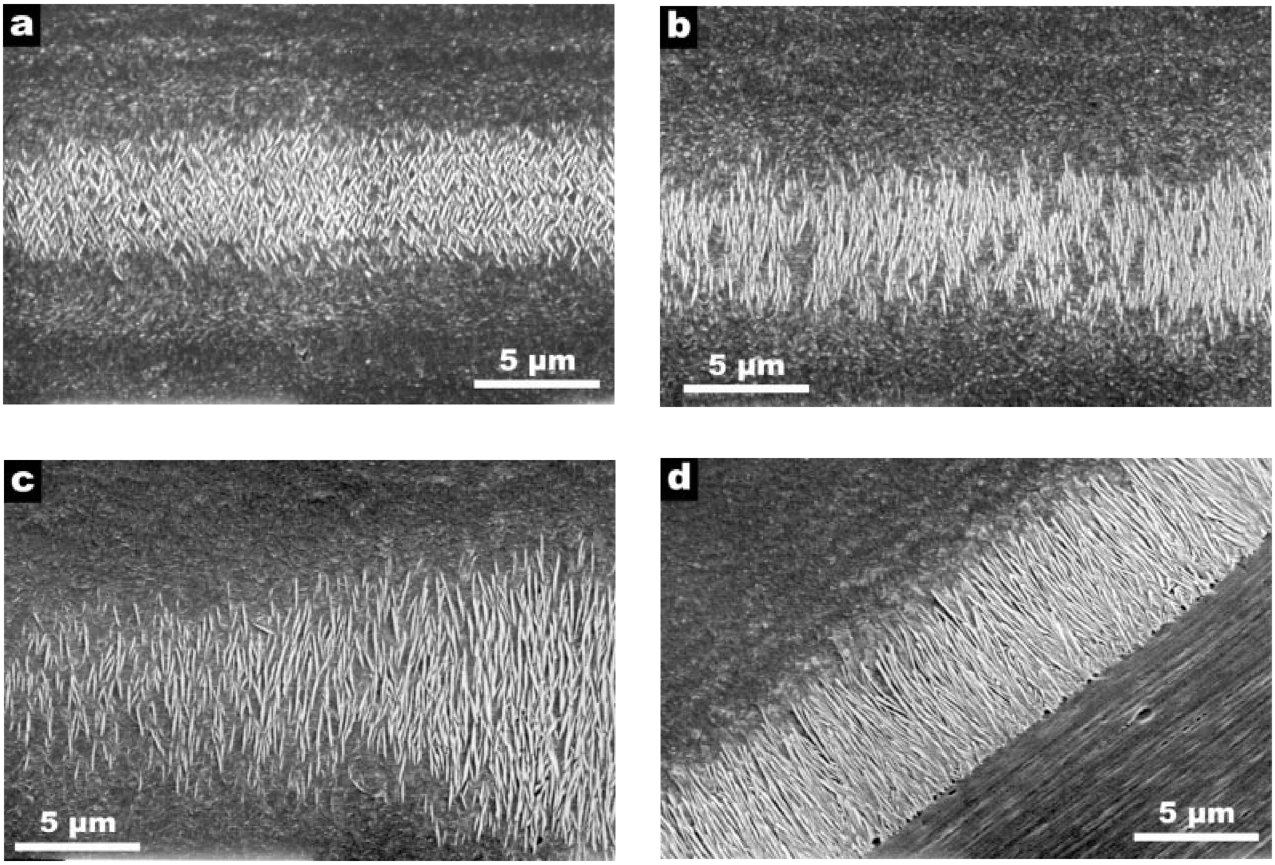

Fig. 1. SEM images of etched row structures grown at 128°C. (a) Radial view after 20 min crystallization showing symmetrically inclined lamellae. (b) Radial view after 40 min crystallization showing that lamellae are predominantly perpendicular to the row, together with some cellulation. (c) After 1 h, the outer edge of the row (extreme left) has dominant lamellae widely separated and perpendicular to the row. Lamellar packing becomes denser deeper into the row, towards the right hand side of this radial view. (d) The corresponding diametral longitudinal view after 1 h showing the change in lamellar packing from an orthogonal perspective.

phenomena in both polyethylene and the long *n*-alkanes as well as the presence of faster-growing dominant lamellae when these linear molecules crystallize from the melt.

2. Experimental

The material (Sclair 2907 linear polyethylene, du Pont, Canada), and all experimental procedures were as detailed in the previous paper [6]. This includes the preparation of samples with Tekmilon™ polyethylene fibres as linear nuclei, crystallization protocols, permanganic etching and subsequent examination by optical and electron microscopy.

The morphologies were viewed in one of three orthogonal directions on specimens prepared appropriately. These employ, first, transverse sections perpendicular to the row; second, diametral longitudinal sections parallel to the row and passing near the centre of the nucleating fibre; or, third, longitudinal sections outside the fibre giving what we term radial views as explained in the previous paper. Measurements of row diameter were obtained, using the scanning electron microscope, SEM, from longitudinal views after quenching and etching, making sure that any non-diametral sections, i.e. with a fibre width markedly less than the nominal 40 μm diameter, were excluded. The numerical data of growth length for each point in the relevant figures, with associated statistical parameters, were obtained from three to five SEM photographs per sample, taking two or three measurements of growth length per photograph, i.e. around ten measurements were taken for each data point. The growth length was measured directly on each photograph, from the fibre surface to a line tangential to the edge of the structure and parallel to the fibre axis.

3. Results

Row structures grown at four temperatures, 127, 128, 129 and 130°C have been examined. Radial views all show the same character in which initial growth, from the surface of the nucleating fibre, has two epitaxially nucleated lamellar populations, symmetrically inclined to the row. As crystallization proceeds, lamellar normals to what are still inclined

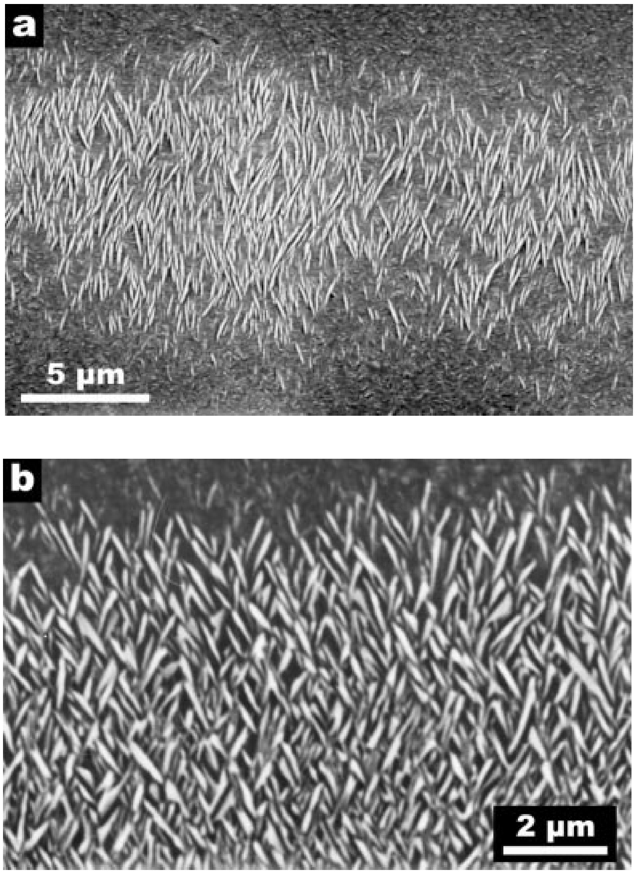

Fig. 2. SEM images of radial views of etched row structures grown at 129°C for intermediate times: (a) a mixed texture of inclined and perpendicular lamellae after 2 h crystallization; (b) in another specimen grown for 3 h, lamellae are still inclined to the outer edge of the row.

fold surfaces, become parallel to the row [6]. Corresponding data of growth length, i.e. diameter outside the nucleating fibre, have been measured on diametral longitudinal sections, as described above, as a function of time for all temperatures save the very slow growth at 130°C for which only the one time, 12 h, was employed.

The basic phenomenon with which this paper is concerned is illustrated in Fig. 1 for growth at 128°C. Fig. 1a and b, for 20 and 40 min crystallization, respectively, shows radial views of similar-sized areas, i.e. of planes near to the edges of their respective rows. Lamellae are inclined to the row in the former, but have become perpendicular in the latter. Fig. 1c, for 1 h crystallization, is a radial view with the row inclined slightly to the plane of the paper so that the progression in morphology from left to right moves farther into the row and reveals the denser packing of lamellae found there after this time. Complementary information is contained in the orthogonal diametral longitudinal view shown in Fig. 1d; this shows the denser packing, due to infilling, nearer to the fibre but is unable to reveal the inclined lamellae as the view is perpendicular to the tilt axis relating the two orientations.

Although the change of lamellar orientation always occurs there is some variability in its precise location and timing. This is illustrated in Fig. 2 for crystallization at 129°C. Fig. 2a, towards the edge of a row after 2 h growth, shows a somewhat mixed texture in which many wider lamellae are inclined to the row, especially in the more sparsely populated regions, but others, tending to be narrower and frequently in clusters within what appear to be cells, are perpendicular to it. On the other hand, all lamellae are inclined to the outer edge of the row in Fig. 2b which was crystallized for 3 h. For very long times such as the 11 h of Fig. 3, not only are all lamellae perpendicular to the row at the outer edges but also a form of cellulation is well developed (Fig. 3a) due, doubtless, to the segregation of shorter molecules which are either slow or unable to crystallize isothermally. The detail of Fig. 3b highlights the difference between areas in which there has been no growth where the segregants will have concentrated and neighbouring regions in which growth has continued with little modification. A deeper section, as in Fig. 3c, shows the earlier and subsequently denser inclined growth in its centre, details of whose changes towards the perpendicular orientation are contained in Fig. 3d.

A different view of cellulation and, particularly, the change of lamellar orientation is in the transverse section of Fig. 4a, also for 11 h crystallization at 129°C. In this instance the etchant has penetrated between the fibre and growth from it exposing lamellar detail as in Fig. 4b. This shows the narrow, inclined lamellae adjacent to the fibre and the much broader perpendicular lamellae farther out.

Fig. 5 shows the results of crystallizing for 12 h at 130°C. For the most part lamellae are still inclined to the outer edge of the row, as seen to the right of Fig. 5a, forming the boundaries of cells in places. All lamellae in the deeper sections of Fig. 5b and 5c are also inclined and illustrate how, within the cells, later, thinner, lamellae have grown between the earlier ones. Not only is the texture at the edges more open but at the instant of quenching, central regions contain lamellae which are much more densely packed, indicating the progressive nature of polymeric crystallization. The nucleating fibre is exposed at the extreme left of Fig. 5c, where the earliest stages of growth are on display: these are inclined lamellae.

In a related progression of another row, Fig. 5d suggests how the change of lamellar orientation is effected. Here, all along the tapering section of the row, the outer edges have lamellae in perpendicular orientation. Moreover, on the left-hand side, cellulation, bounded by inclined lamellae, is evident. Here the location is nearer to the edge of the row than on the right of the figure where the cells have often been filled and with lamellae which are perpendicular to the row. It appears that here not only is the change from inclined to perpendicular lamellae starting to occur after 12 h crystallization at 130°C but also that this may be accomplished by the preferential advance of later-forming lamellae in the more propitious orientation.

Diametral longitudinal views are not well suited to reveal

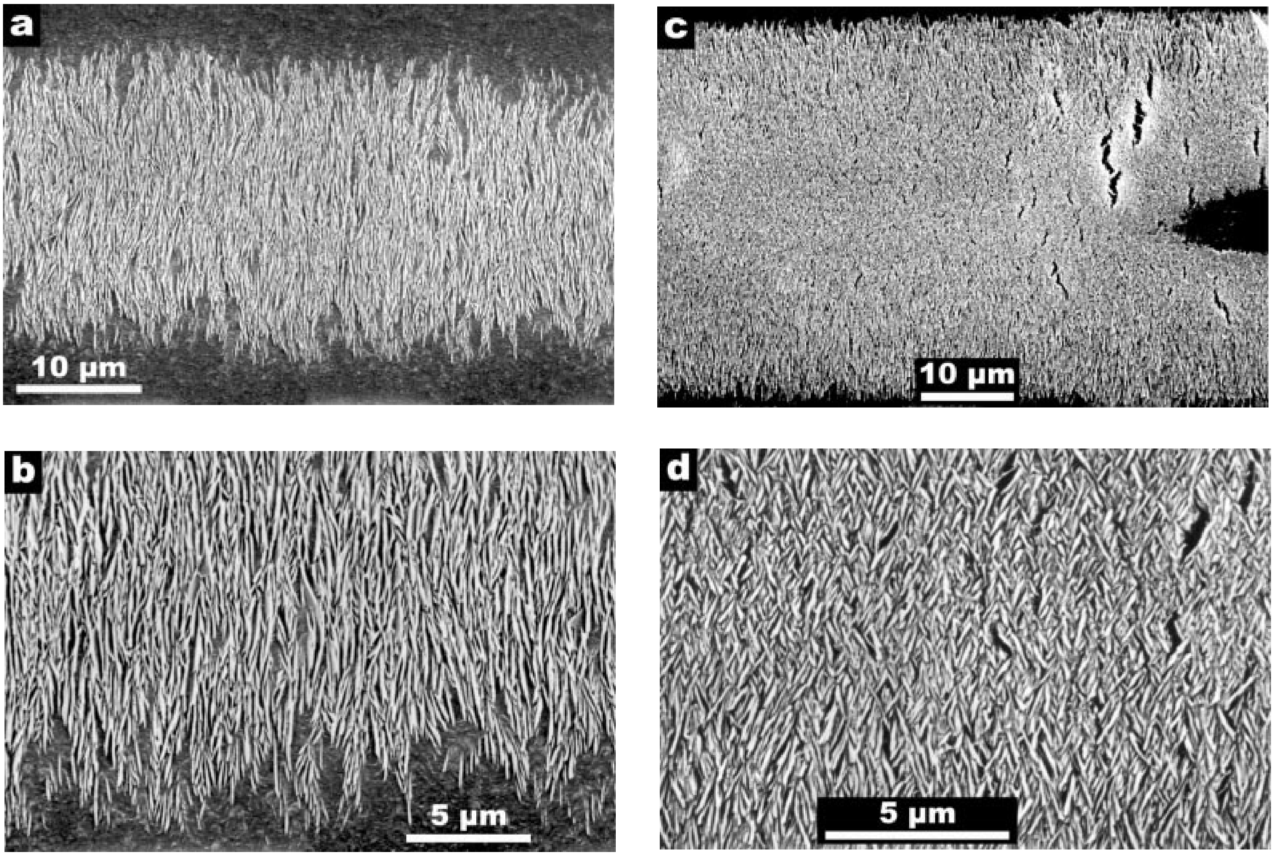

Fig. 3. SEM images of radial views of etched row structures grown at 129°C for long times: (a) a row formed after 11 h has dominant lamellae essentially perpendicular to it and has developed a degree of cellulation visible especially at the outer edges; (b) detail of the above to show the lamellar texture; (c) a deep radial view of a row revealing the change form incline to perpendicular lamellar orientation; (d) detail of the central region of (c).

such changes in morphology. At these resolutions, they tend to show essentially just the traces of radial lamellae. They may show the denser earlier packing (Fig. 6a) but the overall impression is of a continuously advancing texture with no sudden change to mark the change from inclined to perpendicular lamellae. What is evident, however, is that the kinetics increase with radial distance. In Fig. 6, for example, the row of (b) is more than twice as wide as that in (a) for less than half the crystallization time.

Quantitative data are presented in Fig. 7 which shows (together with previously published data for 123°C) average growth lengths, outside the row, as functions of crystallization time for the three temperatures 127, 128 and 129°C. In every case the early and late stages can be fitted to two straight lines whose slopes are the respective constant radial growth rates. These growth rates and their ratios are listed in Table 1 for the three temperatures. It is not suggested that there is necessarily a sharp change of growth rate at a particular stage rather that, as the somewhat variable transitional morphology suggests, a more continuous change takes place between two well-defined growth conditions and rates.

4. Discussion

The phenomenon reported here is quite novel. It is that for high temperature crystallization of polyethylene there is an increase in isothermal linear growth rate of row structures with radial distance, in conjunction with a change in lamellar orientation to the row. This is not only interesting in itself but also has important wider implications both for other previously unexplained kinetic behaviour principally in the long *n*-alkanes and the formation of dominant lamellae when long molecules crystallize. Spherulitic crystallization of the same polymer under the same conditions does not show the effect but gives large objects with continuous ridged dominant lamellae [7] and no equivalent change of lamellar orientation. The difference derives from the initial constraints which linear nucleation imposes upon crystallization, as will become clear as the discussion proceeds. Moreover, previous kinetic data for the same polymer [5] — reproduced here in Fig. 7 — show that the effect does not occur for row structures giving banded growth at lower temperatures when, except for a systematic small oscillation in phase with the bands, the isothermal growth rate is constant. The evidence points to this striking new phenomenon being a consequence of interference between adjacent

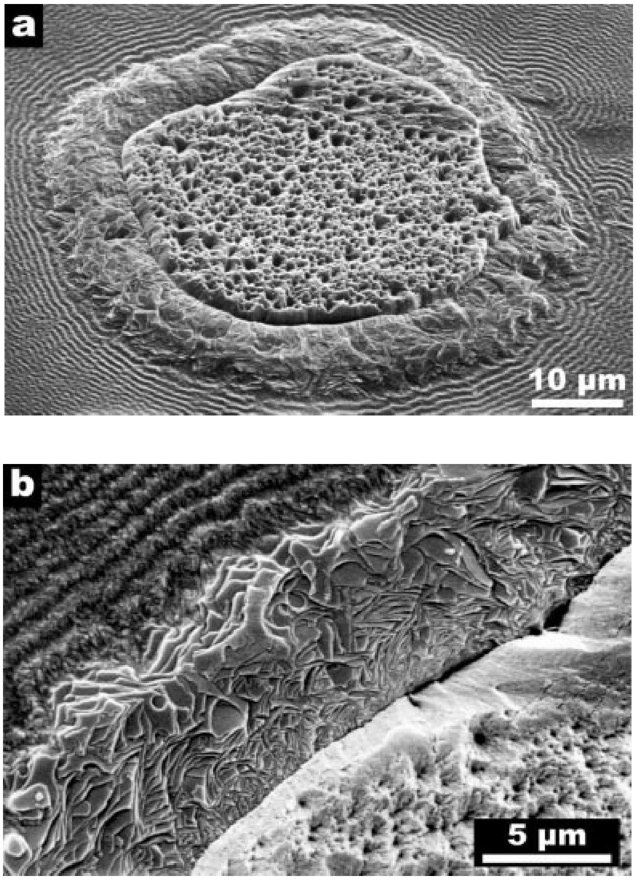

Fig. 4. SEM images of an etched transverse section of a row grown around a polyethylene fibre nucleus for 11 h at 129°C. The section has been tilted for enhanced contrast: (a) the whole row in perspective; (b) detail which, in the etched gap at the edge of the fibre reveals inclined lamellae which, at greater radial distance give way to wide perpendicular lamellae.

Table 1
Growth rate data

Temperature (°C)	Initial rate (μm min^{-1})	Final rate (μm min^{-1})	Ratio
127	0.09	0.31±0.01	3.4
128	0.07±0.008	0.19±0.02	2.8±0.6
129	(6.0±0.84) 10^{-3}	0.026±0.025	4.4±1.1

sites of secondary nucleation. As such, it provides an informative further instance of how crystallization kinetics are influenced by the nature of the instantaneous crystal/melt interface and gives greater insight into the wider molecular processes of self-organization of linear molecules.

The overall change, from a initial slow process to a faster one, is in general accord with a basic tenet of crystal growth in that faster crystallization ultimately prevails simply because it occurs ahead of the competition. In the present case the final, faster state is one of widely separated dominant lamellae growing normal to the row — see Fig. 1b and c, for example. In this condition, lamellae are too far apart for a single molecule to be simultaneously attached to more than one: there can be no interlamellar interference. Nor, for Regime I growth [8,9] (in which individual secondary nuclei are well separated along the lateral growth surface of a lamella, with each added layer of molecular stems being completed before the next is initiated) will there be intralamellar interference between competing secondary nuclei on the same growth face. By contrast, in the early stage of growth, while there would still be no intralamellar interference this would not be the case for interlamellar interference which would be anticipated to occur. Geometry alone will bring adjacent dominant lamellae into close contact if they are differently inclined to the row. In such circumstances a single molecule may attach to more than one lamella at the same time, consequently, the exploration of more possible conformations during attachment will increase the time taken to add a long molecule permanently to the crystal.

The suggestion that active nucleation sites may attract and compete for the addition of the same molecule is not, in itself, a new idea having been proposed, e.g. for the generation of interlamellar links [10]. However, that such interference should delay the kinetics of attachment, though seemingly a logical consequence, does not appear to have been considered explicitly. The suggested mechanism should, in principle, also apply to Regime II growth [8,9] but to less effect. This would follow because of the occurrence of intralamellar interference with many secondary nuclei then present close together on one lamella; the effect of interlamellar interference, from nuclei on neighbouring lamellae, would, under these conditions, be substantially diluted.

Interference between nuclei on adjacent lamellae will be expected to arise most strongly at the outset of growth when lamellae are thin and close-packed. It will be progressively ameliorated as dominant lamellae separate and contacts reduce but so long as lamellae grow with different orientations, at some stage — if not originally then as they widen — they must come close enough to allow their respective secondary nuclei to compete for a given molecule. On the other hand, an array of lamellae all growing parallel will adopt that mutual separation which allows the fastest growth, i.e. beyond that where interlamellar interference operates. Qualitatively, this is what is observed.

If one pursues this reasoning, the ratio of final to initial growth rates might be anticipated to increase with temperature because the number of conformational options will be greater for thicker lamellae making the initial rate the more depressed. While the limited data of Table 1 do appear to support this hypothesis, in fact they are insufficient to yield a statistically significant conclusion.

It is also likely that interlamellar interference might affect other concurrent molecular processes, such as isothermal lamellar thickening and fold surface ordering. A priori, one would expect that they, too, would be liable to be slowed compared to their values for an isolated lamella for essentially the same reasons. In the case of fold surface ordering this could result in lesser inclinations being

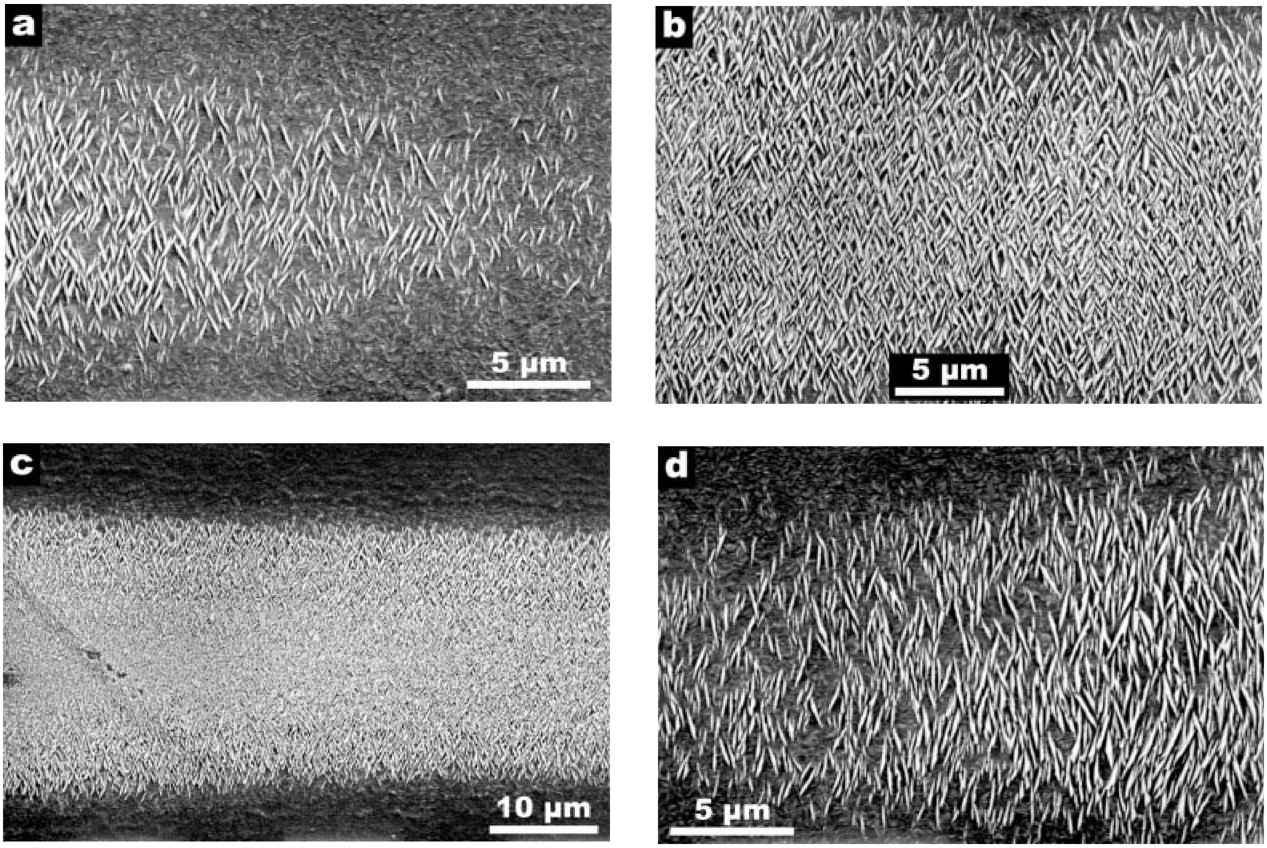

Fig. 5. SEM images of radial views of an etched row structure grown for 12 h at 130°C: (a) a rather open texture of inclined lamellae towards the outer edge of the row; (b) a deeper section brings out the more dense packing in the central regions; (c) at the outer edge of the row, lamellae are both inclined and widely separated; (d) an outer region showing the first appearance of perpendicular lamellae which have formed preferentially between the network of incline lamellae.

achieved in the earliest stages of growth, adjacent to the fibre, provided the rate of ordering is reduced more than that of radial growth. There is some suggestion that this may be the case in Fig. 5d of the previous paper.

There are several other known kinetic and morphological circumstances for which the concept of internuclear interference can provide an explanation. The first of these is the recently reported, but unexplained, temporary slowing in the growth of extended-chain long *n*-alkanes at the onset of branching [3,4]. In those circumstances of Regime I crystallization, the growth rate will be reduced so long as there is interlamellar competition between nuclei. This must be the case at and near a branch point but once adjacent dominant lamellae diverge and separate sufficiently, the growth rate will revert to the previously existing pattern of behaviour. The formation of the dominant lamellae which are observed to be present in what are parallel stacks of *n*-alkane lamellae [11] would be a logical consequence of internuclear interference. This follows simply because a smooth interface, with all lamellae in phase, would be unstable against perturbations which took one lamella ahead of its neighbours, over which it would then have a competitive advantage and grow faster.

The presence of dominant lamellae in spherulitic growth of crystalline polymers would follow for the same reason, thereby providing an a posteriori justification for treating the radial spherulitic growth rate as equal to that of a single lamella.

A third circumstance concerns the recently reported pulsation of growth rate in banded growth of polyethylene rows [5]. Whereas, for linear-low-density polyethylene, this phenomenon has been explained in terms of repetitive reductions in segregant concentration when lamellar orientation rotates, for the linear polymer, the temporary loss of interlamellar interference would be expected to cause a concomitant temporary speeding up of growth rate of the kind observed.

In total, the increased growth rate observed as interlamellar interference between secondary nuclei declines has revealed that this phenomenon, which has not previously been taken explicitly into account in kinetic theories of polymeric crystallization, can provide explanations for diverse, previously unexplained, phenomena and so advance the fundamental understanding of the molecular processes occurring as polymers crystallize.

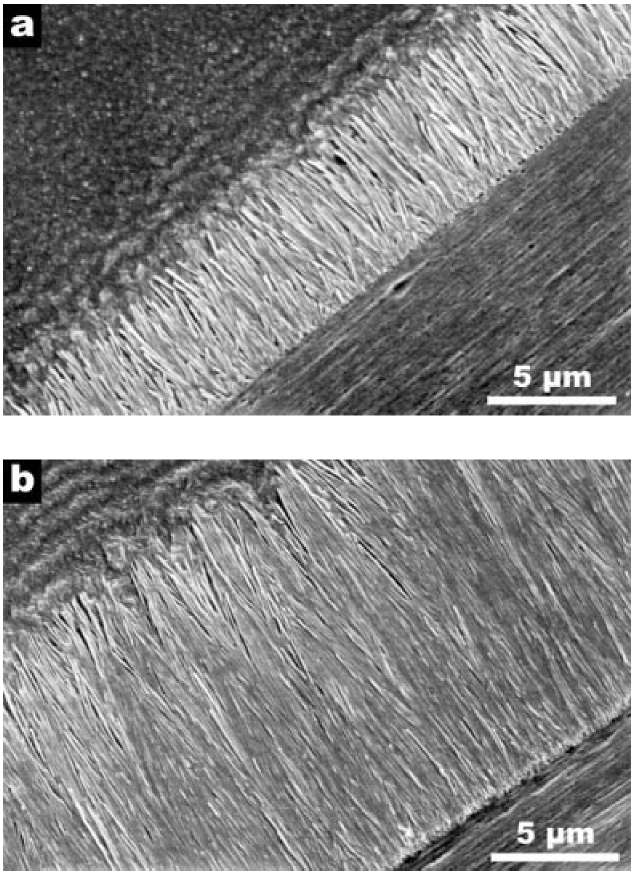

Fig. 6. A comparison of two diametral longitudinal sections grown at 129°C for different times to demonstrate the increase in radial growth rate: (a) 6 h; (b) 11 h.

5. Conclusions

1. At 127°C and above, polyethylene crystallizes as lamellae with inclined fold surfaces.
2. When grown from oriented fibres as linear nuclei to form row structures, lamellae form initially, after epitaxial nucleation, as two symmetrical orientations equally inclined to the axis of the row. At further radial distance, dominant lamellae are wider and well separated, still with inclined fold surfaces, but with their planes now normal to the row.
3. In this final condition, when there can be no interlamellar interference between nuclei, the growth rate is 3–4 times faster than the initial value. In the early stages of growth, interlamellar interference between secondary nuclei on adjacent lamellae would be expected, with a consequent slower growth rate. The reduction in rate would be greatest at the start of growth but then gradually decrease to zero when all lamellae grow separated and parallel.

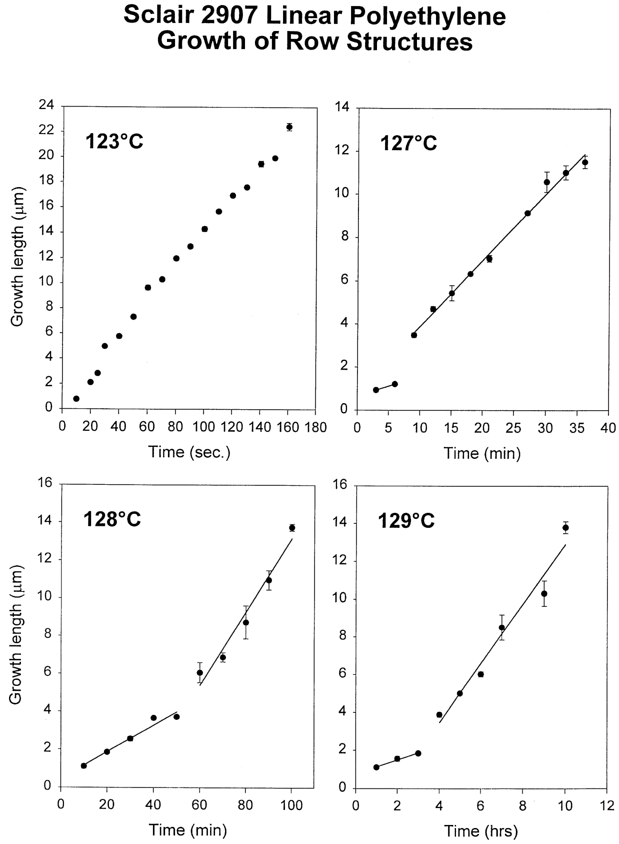

Fig. 7. Plots of radial growth length, beyond the nucleating fibre, as functions of time for the stated temperatures. While the banded growth at 123°C is substantially linear, at 127°C and above there are well-defined slower initial and faster final modes of growth.

4. The concept of interfering nuclei also provides a convincing explanation for previously reported kinetic effects in polyethylene and long *n*-alkanes as well as the occurrence of faster-growing dominant lamellae in the crystallization of such linear molecules.

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