

On the time for fold surfaces to order during the crystallization of polyethylene from the melt and its dependence on molecular parameters

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Received 29 March 2006; received in revised form 7 August 2006; accepted 7 August 2006

Available online 1 September 2006

Abstract

New experiments underpin the interpretation of the basic division in crystallization behaviour of polyethylene in terms of whether or not there is time for the fold surface to order before the next molecular layer is added at the growth front. For typical growth rates, in Régime II, polyethylene lamellae form with disordered {001} fold surfaces then transform, with lamellar thickening and twisting, towards the more-ordered condition found for slower crystallization in Régime I, in which lamellae form with and retain {201} fold surfaces. Several linear and linear-low-density polyethylenes have been used to show that, for the same polymer crystallized alone or in a blend, the growth rate at which the change in initial lamellar condition occurs is reasonably constant thereby supporting the concept of a specific time for surfaces to attain the ordered {201} state. This specific time, in the range from milliseconds to seconds, increases with molecular length, and in linear-low-density polymer, for higher branch contents.

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Keywords: Polyethylene; Fold-surface reorganization; Linear nucleation

1. Introduction

The basic division in the crystallization of polyethylene, long discussed solely in terms of a change in kinetics from Régime II to Régime I [1], corresponds to a change in the nature of the initial fold surface [2], a demonstration, which brings a new context to polymer crystallization. Not only do polyethylene lamellae form with unstable {001} fold surfaces under typical fast crystallization conditions (Régime II) but the origin of banded growth is also indicated to lie in the relief of surface stress present in the initial rough {001} fold surfaces accompanied by the reorganization towards the preferred {201} packing, with isothermal lamellar thickening and the production of S-profiles, viewed down **b**, the growth axis. There is no banding in the linear polymer for slower growth (in Régime I) at

higher temperatures. Here lamellar fold surfaces are stable, retaining their initial $\sim\{201\}$ orientation, inclined to lamellar normals at $\sim 35^\circ$.

The growth rate at which the pattern of behaviour changes, when the initial fold surfaces are {201} rather than {001}, can be converted into a time to add a single 0.5 nm layer of fold stems to the growing surface. Our interpretation of the two behavioural patterns is that only when this time is sufficient will folds come together, employing the strong longitudinal vibrations of the lattice, and optimize their mutual packing, i.e. in {201} surfaces. This is the case at higher temperatures but not for faster growth at lower temperatures. Then fold surfaces will form rough with their precise condition depending on elapsed time, i.e. how long folds have to organize their relative positions and configurations. Accordingly, fold surfaces would be expected to be less disordered at lower supercoolings within Régime II but as the free energy reduction for improved fold packing will be much less than that associated with the crystallization of fold stems, fold surface condition will be subordinate to the latter.

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Our interpretation implies that the time taken for fold surfaces to organize will be a property of the lamella in its environment, especially the time taken by its constituent molecules to explore alternative locations and fold configurations. This time would be expected to be more or less constant for a given polymer, although it could be affected by the lamellar environment because molecules may move from the surface as well as attach to it and also by polydispersity. In particular longer and/or more-branched molecules would be expected to take a longer time to organize than shorter linear ones. Our experiments agree with this expectation and so underpin the concept that a specific time is required for fold surfaces to organize their packing during crystallization.

2. Experimental

Most experiments reported here were carried out, with linear nucleation, on the linear polyethylene homopolymer Sclair 2907 (du Pont, Canada) for which $M_w = 104,000$; $M_n = 11,300$. In part, these used blends of 5 and 20 wt% in Escorene LD100BW (Exxon), a conventional branched low-density polymer with $M_w = 87,000$ and $M_n = 10,000$. These were prepared by melt-mixing, at 160 °C for 30 min under nitrogen flow, in a Winkworth twin z-blade mixer, model IZ. A range of further linear and linear-low-density branched materials, listed in the second column of Table 1, were used either alone or in blends with Escorene in additional experiments to identify the dependence of the changeover growth rate on molecular length and branching ratio using high-melting polyethylene fibres as linear nuclei.

Specimens were prepared in one of two ways. Flat discs of the particular polymer or blend, $\sim 20 \times 30$ mm across and ~ 1 mm thick, were produced 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 removing 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, i.e., parallel to the length of the nucleating fibre and passing through its centre, a specimen containing about seven highly oriented Tekmilon™ polyethylene fibres (Mitsui) within a matrix of the chosen polyethylene was prepared and placed 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 $\sim 40 \mu\text{m}$ below the surface of the disc and approximately parallel to it.

Crystallization adds a more or less concentric cylinder around the nucleating fibre to form a row structure. For specimens used to examine textures looking down the growth axis, in sections parallel to, but outside the fibre (see below) a greater depth of $\sim 60 \mu\text{m}$ 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 $\sim 60 \mu\text{m}$ thick, both prepared as above, otherwise the same procedures were followed.

All crystallized specimens were etched in a 2% w/v potassium permanganate solution in 10:4:1 parts by volume of concentrated sulphuric acid, 85% orthophosphoric acid and distilled water, respectively. All specimens illustrated in this paper were etched as prepared. The etching time was selected according to the particular view required. Four hours were required 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 . Diametral sections were used for the measurement of growth lengths, i.e. distance from the surface of the nucleating fibre and thence growth rates from the linear slopes of these data plotted against elapsed time.

A shorter etching 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 radial 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

Table 1
Characteristics and properties of the polyethylenes used

Type	Name	M_w	M_n	Branch content/ 1000 C atoms	Growth temp. (°C)	G_c ($\mu\text{m min}^{-1}$)	t_c (ms)
Linear	PE 190	18,700	5410	None	119	16.7	1.8
Linear	GA 7260	28,400	6250	None	123	3	10
Linear	Rigidex 140-60	91,700	14,200	None	127	1.0	30
Linear	Sclair 2907	104,000	11,300	None	127	0.35	85
Linear	GX 555-2	149,400	19,770	None	127	0.42	70
Linear	PE 11/26	406,600	87,300	None	>127	<0.01	>3000
LLD	Q	100,000		1.2	122	0.5	60
LLD	Sclair 14B.1	100,000		4.8	120	0.2	150

specimens were coated with gold prior to examination under the scanning electron microscope, SEM. All micrographs have the nucleating fibre and resulting row structure lying horizontal on the page.

3. Results

The principal aim of this paper is to check whether the growth rate, when the change in initial orientation from perpendicular to inclined lamellae (with respect to the nucleating fibre) occurs, is reasonably the same for a given polyethylene alone and in blends and then, given this, to compare the rates and derived times for different polyethylenes. Previous work [2] has shown the coincidence of the change in initial fold surface of the mass of the material, observed within a micron or so of the nucleating fibre, with the Régime transition. The temperatures recorded and listed in Table 1 are used to calculate the growth rate, G_c , of the changeover. However, the comparison

of a homopolymer with its blends is complicated by the presence, in the former, of small regions of inclined lamellae which further investigation has shown to be present close to the nucleating fibre at lower crystallization temperatures [3], consistent, as discussed later, with fractional crystallization of shorter molecules in linear polymers. For Sclair 2907, for example, this occurs as low as 123 °C when the remainder of the sample forms as perpendicular lamellae with {001} fold surfaces. All lamellae only form inclined in this material for crystallization at or above 127 °C [2].

Figs. 1–4 show behaviour within this range, at 125 °C. In Fig. 1a, a section outside the nucleating fibre of a row crystallized for 10 min (growth length $\sim 18 \mu\text{m}$) has in its centre narrow perpendicular lamellae while at top and bottom lamellae are rotated through 90° and are thicker. Detail of the top of this region is in Fig. 1b with S-profile dominant lamellae a few micrometres wide prominent in a background of somewhat thinner subsidiary lamellae. In Fig. 1c, a section above

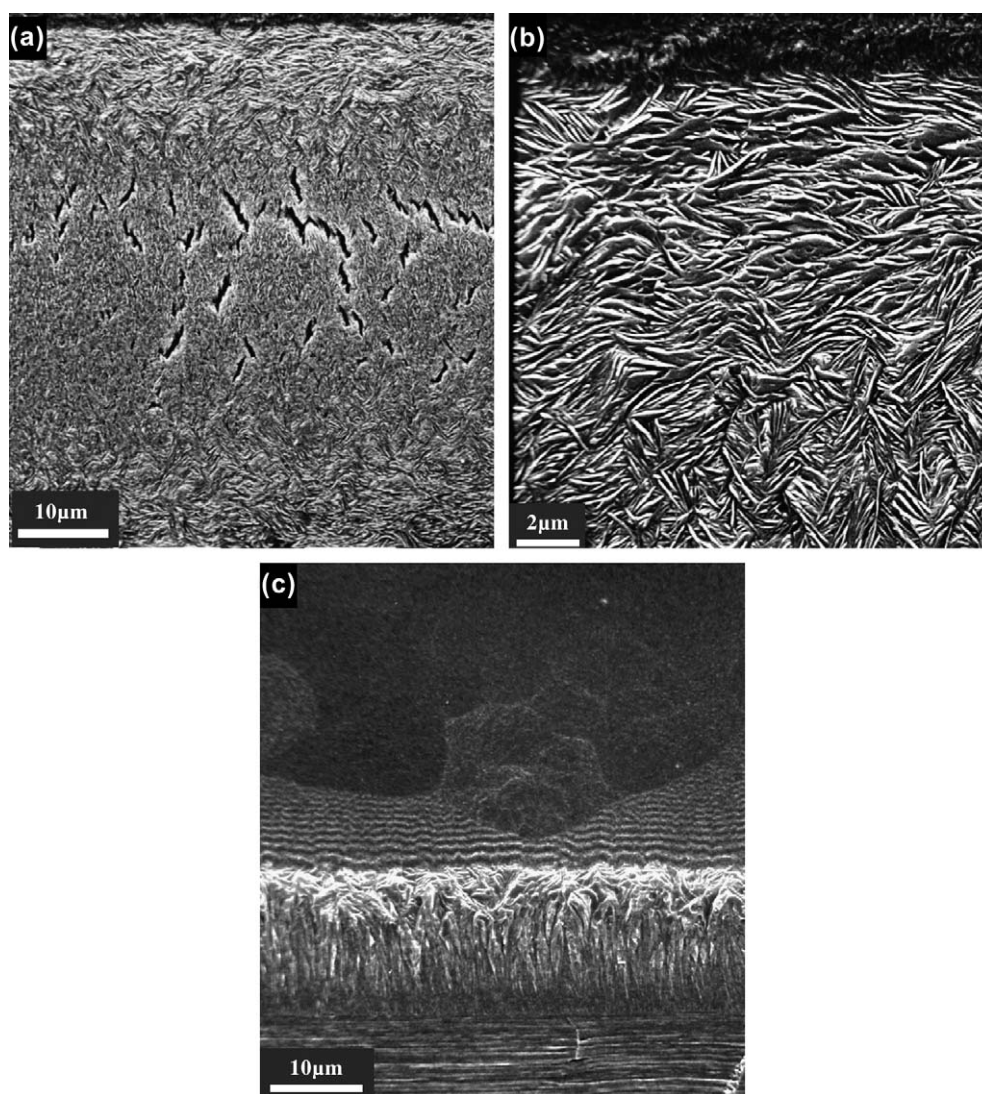


Fig. 1. Details of row structures of Sclair 2907 polyethylene crystallized at 125 °C. (a) An overview of a section through a row crystallized for 10 min. At its centre, the vertical lamellae are perpendicular while, at the upper and lower edges, lamellae have rotated through $\sim 180^\circ$ with the dominants having S-profiles. (b) Latter feature is seen in more detail which shows part of the upper boundary of (a) at higher magnification. (c) A similar row after 9 min growth but in an off-diametral section which shows how the banded texture has developed. Note the rather uniform growth front behind which there is an apparent fibrosity on the scale of $\sim 1 \mu\text{m}$.

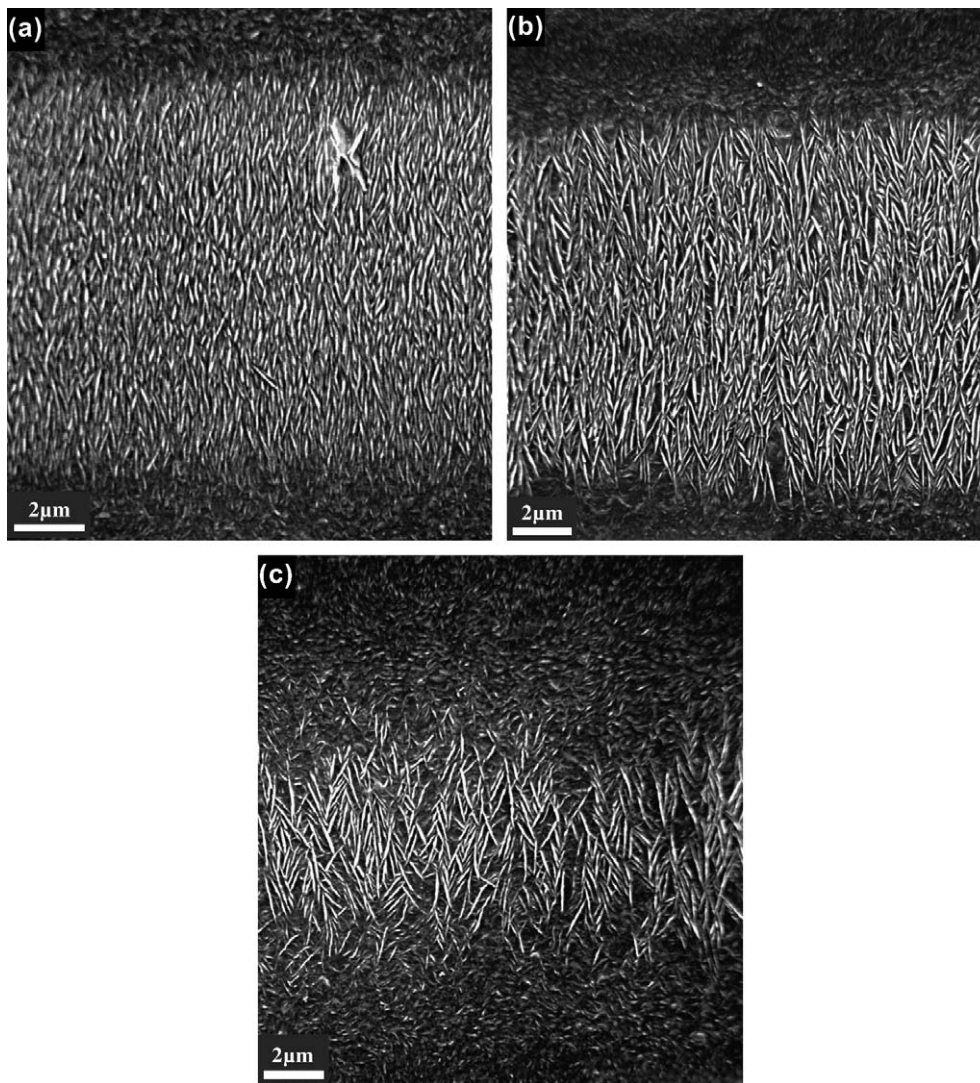


Fig. 2. Developing texture with time. After 1 min, (a) shows that lamellae are still mostly perpendicular but are no longer all equal; the differentiation between dominant and subsidiary lamellae is beginning to appear. This is further developed after 3 min in (b), with inclination to the vertical lamellae present in the outer regions. (c) Shows that, after 4 min, the structure is more rotated and more open where subsidiary lamellae have still to reach the outer section examined.

diametral, after 9 min, reveals a rather uniform growth front behind which are lamellae whose exposed tips lie some microns back. Note also the apparent fibrosity, 1 or more micrometres wide, depending on lamellar orientation, associated with banding.

Lamellar development for short times is shown in Fig. 2, from narrow, mostly perpendicular, lamellae after 1 min, i.e. within the first micron of growth. In Fig. 2a all lamellae are perpendicular after 1 min growth but not all are equal in length and thickness with the developing distinction between dominant and subsidiary lamellae being just evident. The differentiation is much clearer after 3 min (Fig. 2b) with much thicker lamellae in a more open texture with some outer lamellae now inclined to the vertical. After 4 min, Fig. 2c shows that at the outside of the row, which subsidiary lamellae have still to reach, dominant lamellae are more rotated in an open texture.

To this point the growth lengths, i.e. the distance from the surface of the nucleating fibre, measured in diametral sections, show a linear plot against time (Fig. 3) indicating a constant

isothermal growth rate. For longer times the plot falls away, by some 4 standard errors in the region of 5 min before recovering at the 6 min; the difference at 5 min, therefore, appears significant. Fig. 4 shows that the 6 min growth corresponds to the outermost lamellae having become parallel to the row. Spaces separate dominant lamellae in Fig. 4a whereas these have become filled by subsidiary lamellae in Fig. 4b. After 8 min bunches of lamellae at the edge of the row have rotated more, beyond parallel orientation, with an organization consistent with the fibrosity of Fig. 1c.

All observations for crystallization times ≥ 1 min at 125 °C have been in line with previous reports that initial lamellae of this polyethylene form inclined lamellae only at temperatures ≥ 127 °C. However, at times less than 1 min additional features are found within the first micron or so of growth although this does not affect the major pattern. In the central region of the deep section of Fig. 5a, after 50 s growth, besides the perpendicular lamellae (lying vertically) are areas where inclined lamellae are prominent, although at the edge, as views

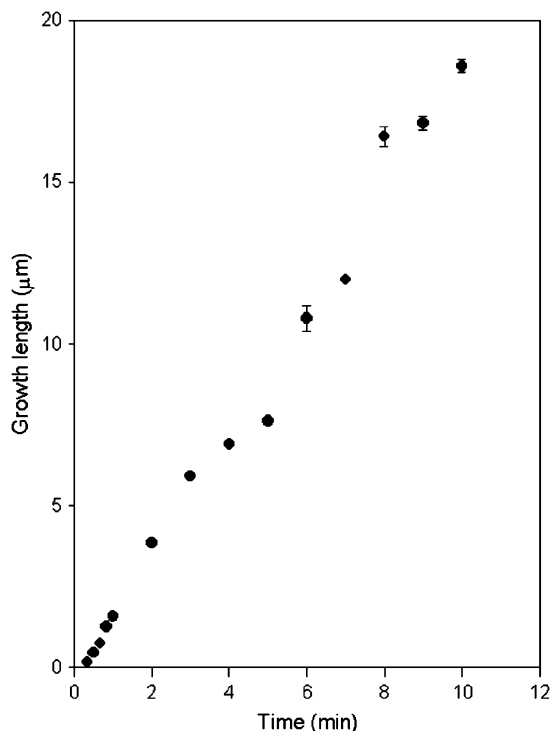


Fig. 3. A plot of growth length against time for Sclair 2907 at 125 °C.

from a different perspective confirm, perpendicular lamellae predominate. The existence of a limited area of inclined lamellae close to the nucleating fibre is confirmed by Fig. 5b for which the growth length, after 40 s, is $\sim 0.75 \mu\text{m}$. Even so, the contact with the fibre, visible to the right, here has a mixture of small lamellae in which both perpendicular and some inclined lamellar orientations are present with some inclined lamellae persisting to the edges of the row. As is considered in Section 4, such sensitivity of lamellar inclination is to be expected for internal fractional crystallization and for the known complexity of the growth process. This general behaviour with

phenomena similar to those of Figs. 1–5 is also found for Rigidex 140-60 [3] which attains $\sim 5 \mu\text{m}$ in the first minute of growth at 125 °C, i.e. growing roughly twice as fast.

These findings do, however, complicate the comparison of the initial fold surface orientation for the homopolymer and its blends. Whereas in the homopolymer epitaxial growth and the homogeneity beyond $\sim 1 \mu\text{m}$ radial distance allow a reliable assessment from inspection beyond the nucleating surface, blend morphology is more complicated [3]. For these there is no practicable alternative to examine the fibre surface and to seek to identify a condition when all lamellae form perpendicular to the nucleating fibre with no isolated pockets of inclined lamellae. This is effective in allowing the comparison to be made and shows that the measured changeover rate is more or less constant for a given polyethylene but has the disadvantage that avoiding such isolated pockets depresses the measured crystallization temperature (by $\sim 3 \text{ K}$ in Sclair 2907) below that applicable to the majority of the material. The apparent changeover growth rate for the homopolymer will, therefore, be too fast and the corresponding time for fold surfaces to organize too low although adjustment is easily made with the knowledge of the variation of growth rate with temperature.

Tables 2–4 list growth rates for lamellae grown at temperatures in the changeover region for a series of linear and linear-low-density polyethylenes. Measurements of both inclined and perpendicular lamellae, bracketing the changeover condition, are given for cellulated blends [3]. Limited data for pockets of inclined lamellae in homopolymers are included where possible. The changeover growth rates G_c (in $\mu\text{m min}^{-1}$) and times t_c (in ms) to add a single 0.5 nm thick layer of fold stems to the growing {110} surface are calculated using the following formula

$$t_c = 300/G_c.$$

The values of G_c and t_c in Table 1 are the preferred estimates being representative of the great majority of the several

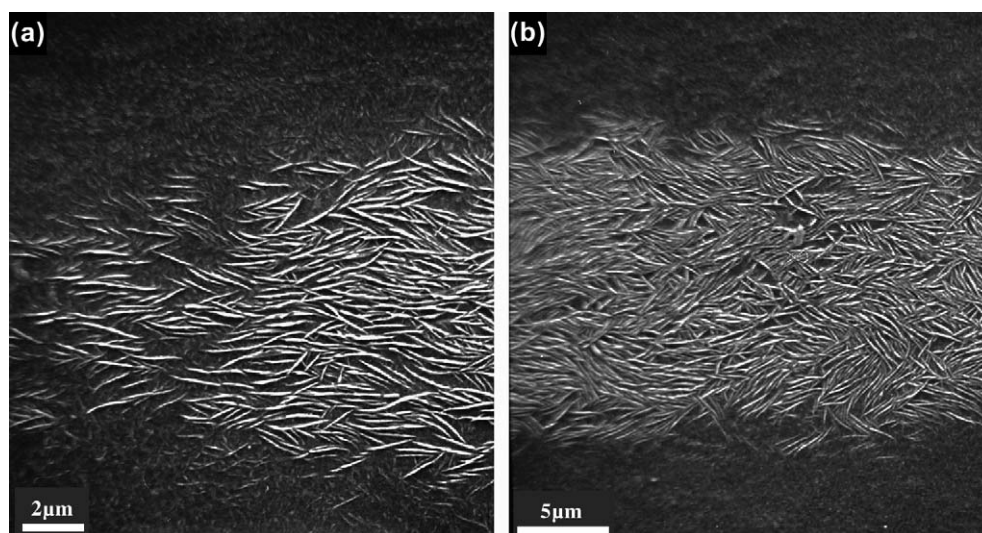


Fig. 4. The dip in Fig. 3 after 6 min at 125 °C occurs when, (a), the plane of the outermost lamellae has rotated through $\sim 90^\circ$. The fibrosity present in such a region with dominant lamellae parallel to the fibre after 6 min growth at 125 °C is shown in (b) when subsidiary lamellae have essentially filled the intervening spaces.

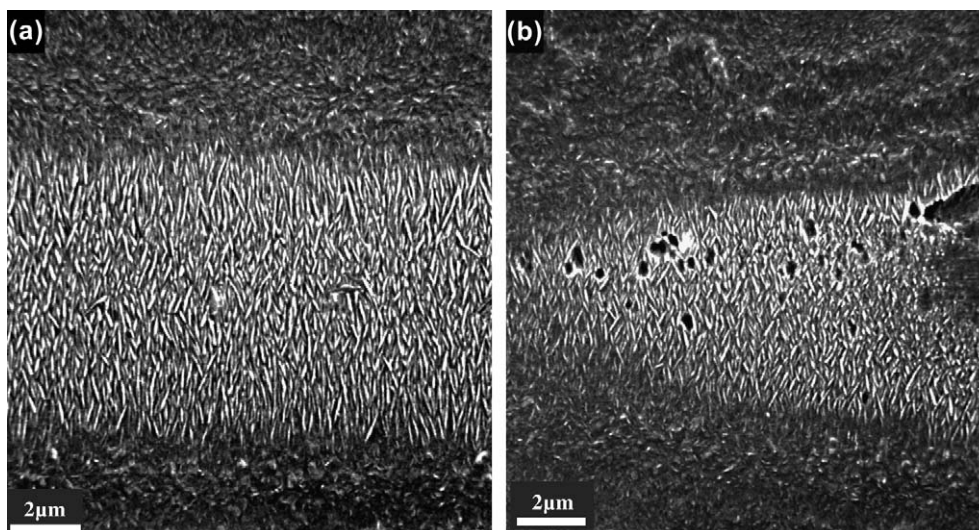


Fig. 5. Reveals conditions within 1 μm of the nucleating fibre at 125 $^{\circ}\text{C}$. After 50 s, (a) shows a few, smaller, inclined lamellae within a predominantly perpendicular matrix. After 40 s, (b) shows more extensive coverage of inclined lamellae but in the contact zone with the fibre, on the extreme right, the smallest lamellae appear to be almost all perpendicular.

materials. They do rely, however, on the validity of a specific ordering time based on the comparisons in later tables. Thus, Table 2 confirms the near equality of these two quantities in Sclair 2907 and its blends as do Table 3 for the linear-low-density polymer Q and Table 4 for the more-highly-branched Sclair 14B.1. The collected data show that the time for fold surfaces to reorganize increases with molecular length and branch content.

Table 2
Data for Sclair 2907 and its blends

Sclair 2907 (%)	Growth temp. ($^{\circ}\text{C}$)	Growth rate ($\mu\text{m min}^{-1}$)		G_c ($\mu\text{m min}^{-1}$)	t_c (ms)
		Inclined lamellae	Perpendicular lamellae		
5	113	4.7	—	~ 4.7	6.4
	115	2	—		
20	118	—	13.7	3.5–6.8	4.4–8.6
	119	~ 3.5	6.8		
100	123	~ 7	14	3.7–7	4.3–8.1
	124	~ 2	3.7		

Table 3
Data for polymer Q and its blends

Polymer Q (%)	Growth temp. ($^{\circ}\text{C}$)	Growth rate ($\mu\text{m min}^{-1}$)		G_c ($\mu\text{m min}^{-1}$)	t_c (ms)
		Inclined lamellae	Perpendicular lamellae		
5	111	None	2.64	0.25–1.0	30–120
	113	~ 1	2.15		
	115	0.25	1.08		
100	121	None	3	~ 0.5	~ 60
	122	~ 0.5	1.25		
	123	~ 0.25	0.5		

Table 4
Data for Sclair 14B.1

Growth temp. ($^{\circ}\text{C}$)	Growth rate ($\mu\text{m min}^{-1}$)		G_c ($\mu\text{m min}^{-1}$)	t_c (ms)
	Inclined lamellae	Perpendicular lamellae		
118	None	1.8	~ 0.2	~ 150
119	None	0.5		
120	0.2	0.35		

4. Discussion

The first experiments using linear nucleation [2] were all made on Sclair 2907 polyethylene crystallized either at 123 $^{\circ}\text{C}$ or in the range 127–130 $^{\circ}\text{C}$. In the latter range fold surfaces were observed always to be inclined, i.e. ordered,² in agreement with earlier work showing the presence of $\sim \{201\}$ fold surfaces for lamellae grown at these temperatures [7]. At 123 $^{\circ}\text{C}$, the lowest temperature at which the banded row structures could readily be grown isothermally free from the interference of adjacent spherulitic crystallization, the familiar texture of S-profiled dominants associated with banding [7], was shown to develop from lamellae initially perpendicular to the nucleating fibre, i.e. with $\{001\}$ fold surfaces. This behaviour accords well with the concept of a specific time being required for fold surfaces to order. But this would be expected to be a molecular property, depending on the exploration of alternative positions and configurations of folds via the longitudinal chain motions linked to isothermal lamellar thickening. This prediction can be tested if lamellae are formed by different routes, e.g., in blends and then show the same changeover growth rate.

The data in Tables 2–4 underpin this concept but a single time to order is an over-simplified concept; some inherent

² This is not to imply that fold placements are ordered within the surfaces.

variability must be expected for various reasons including differing lamellar environments and the irregular placement of folds in fold surfaces. Polydispersity will also be a factor with the variation in the transition temperature from Régime II to Régime I, measured [1] as ~ 4 K for a change in molecular mass from 2×10^4 to 8×10^4 . We have shown previously [3] that different lamellar populations in the same sample can be either perpendicular or inclined to the nucleating fibre according to their different growth rates. The scope for such differentiation will increase as the changeover growth rate is approached; those populations, which grow more slowly than their relevant value will form inclined lamellae. Populations of segregated shorter molecules, which grow faster and order more quickly (Table 1) will tend to appear at lower temperatures than the rest of the sample in line with our experimental findings.

The picture of crystallization which emerges from this work and previous applications of linear nucleation is one in which molecular stems crystallize with the associated folds having to accommodate to this situation as best they can. More disordered, rougher fold surfaces will form for faster growth, at higher supercoolings, with the energetic cost of greater surface area and too-close fold contacts always capable of being offset by longer stems, i.e., thicker lamellae. Reduction in the concomitant surface stress is the driving force for twisting. Nevertheless, once attached, fold stems will experience the strong longitudinal vibrations of the lattice which will allow the inherent roughness of {001} fold surfaces to ameliorate over time as molecular motions explore alternative conformations and possibly fold placements, the latter more so for shorter molecules, and move the system to lower free energy and less-stressed conditions. However, {001} surfaces are unstable and will encompass a range of possible natures depending on how far they have progressed towards a more-ordered condition; the {201} surfaces characteristic of Régime I growth make stable, well-defined lamellae from the outset. There is no evidence of residual stress³ such as that which might result from asymmetric attachment of stems to inclined lamellae [4,5] and one may safely infer that any such stress has relaxed. In general fold surfaces of polyethylene grown from solution or slowly from the melt are inclined, rather than perpendicular to, the chain axis [6] reflecting the system's preference for greater inter-fold separations than a uniform {001} surface⁴ allows. In a similar way, {001} surfaces grown more slowly, at higher temperatures, will be less rough, being subject to more vigorous longitudinal vibrations for longer and, therefore, correspondingly of reduced surface free energy approaching more nearly to the ordered {201} condition. This will reduce the potential loss of free energy on twisting in agreement with the observed greater banding period.

The changeover times listed in Table 1 are in general accord with expectation but for the reasons cited above, too much should not be read into them: the limited information available on the nature of the materials does not begin to approach the subtlety of the crystallization process. It is not immediately clear, for example, why Sclair 2907 and Rigidex 140-60 which have similar molecular averages (Table 1) should differ by a factor of two in crystallization rate and corresponding times. Nevertheless, ~ 50 ms can be taken as a representative figure for the changeover times of these rather typical linear polyethylenes. The value falls to 10 ms for the shorter linear polyethylene GA 7260 and to 1.8 ms for PE 190 behaviour to be expected for increasingly short molecules with their greater mobility and proportion of chain-ends, both factors favouring fold surface ordering. Conversely, molecules whose branches are excluded from the lattice would be expected to order more slowly but, at the same time, exclusion implies selectivity for longer inter-branch sequences so that the branch content of molecules in lamellae will fall below the average for the sample. The closeness of the 60 ms figure for polymer Q to those of the linear Sclair 2907 and Rigidex 140-60 accords with this but the figure for the more-highly-branched Sclair 14B.1 increases, as expected, to 150 ms. Much the longest changeover time is found for the linear polyethylene 11/26. Possibly here the significant factor is the high number average molecular mass perhaps pointing to the enabling influence of shorter molecules on molecular and fold surface readjustment. Better-defined systems than homopolymers are required for more definite interpretation, nevertheless, the underpinning of the concept of a characteristic time to order fold surfaces during polymeric crystallization is a significant advance and an important factor for the understanding of macromolecular behaviour.

5. Conclusions

The main conclusions of this paper are:

1. There is a characteristic time for fold surfaces to order during polymeric crystallization.
2. This time typically falls in the range from milliseconds to seconds, increasing for longer and/or more-branched molecules.

Acknowledgement

MI Abo el Maaty is indebted to The Royal Society for a Developing World Study Fellowship.

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³ The absence of residual stress is indicated both by geometry ([8], Fig. 2) and by dark-field microscopy ([9], Fig. 4).

⁴ Uniform {001} surfaces are known in lamellae of solution-crystallized short polyethylene molecules [10,11] when the stress of too-close folds is presumably mitigated by the presence of chain-ends.

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