

# Evidence for isothermal lamellar thickening at and behind the growth front as polyethylene crystallizes from the melt

M.I. Abo el Maaty<sup>1</sup>, D.C. Bassett\*

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

Received 1 October 2004

Available online 29 June 2005

## Abstract

The poorly characterized and little understood phenomenon of isothermal lamellar thickening, central to melt crystallization, has been studied morphologically in polyethylene rows, grown around high-melting fibres as linear nuclei revealing that thickening is a function of position within the morphology as well as of elapsed time. In contrast to polyethylene spherulites whose central lamellae are the thickest, in rows the first lamellae to form remain the thinnest because, being close-packed, they have no space into which to thicken. The thickness of lamellae at the growth front increases linearly with the logarithm of elapsed time but, as the thickest lamellae are found at finite radius, thickening must also occur behind the growth front. The data are consistent with a uniform rate of thickening throughout spherulitic polyethylene but melt crystallization must now be envisaged as occurring not at an interface in steady-state condition but at one whose thickness increases asymptotically and where interference will reduce thickening.

© 2005 Elsevier Ltd. All rights reserved.

*Keywords:* Polyethylene lamellae; Isothermal thickening; Melting

## 1. Introduction

Isothermal lamellar thickening is a concept at the heart of polymer crystallization but one which has remained poorly characterized and little understood. It was first proposed by Hoffman and Weeks [1] to explain why melt-grown polyethylene lamellae melt at temperatures well above those at which they crystallized corresponding roughly to a doubling of thickness from that of the secondary nucleus. Their measurements of the X-ray long period of polyethylene, recorded at the crystallization temperature, showed a logarithmic increase with crystallization time of the order of 10 nm per decade of minutes. Questions then arise as to how this is accomplished. Thickening at constant width requires material to be added to a lamella as well as space outside its fold surfaces into which to enlarge. This

would be more easily achieved for a single lamella than a close-packed stack for which the difficulties become progressively more severe the higher the stack and, ultimately, insuperable. Accordingly, thickening will depend upon the local morphology as is found for both polyethylene and  $\alpha$ -polypropylene. It is a function of location as well as of elapsed time.

These and other matters are clarified by the work of this paper which reports observations of how lamellae actually thicken during growth, using linear nucleation of polyethylene to form row structures. It complements our previous work [2,3] which has shown that thickening is a function of radius within the row, accompanying a radial sequence of changing habits with some lamellae failing to propagate [4], thereby providing space for the others to thicken. In addition, the lamellar thickness at the growth front with the melt is shown to increase linearly with the logarithm of crystallization time (at a comparable rate to that measured by X-rays). By itself this would place the thickest lamellae at the outside of rows, which is contrary to experience: thickening must also occur behind the growth front. This is confirmed by the highest melting lamellae lying within the row, at finite radius, in contrast to polyethylene spherulites, which are highest melting at

\* Corresponding author. Tel.: +44 118 378 8540; fax: +44 118 975 0203.

*E-mail address:* [d.c.bassett@rdg.ac.uk](mailto:d.c.bassett@rdg.ac.uk) (D.C. Bassett).

<sup>1</sup> on leave from Physical Science Department, Faculty of Engineering, Mansoura University, Mansoura, Egypt.

their centres. The difference is because neighbouring lamellae constrain thickening adjacent to the nucleating fibre where lamellae are close-packed; such lamellae keep thin and melt first. This is one constraint on thickening; another, as will be discussed in detail, is interference at the growth interface during crystallization.

The implications for kinetic theories of crystallization also include the increasing thickness of lamellae at the growth front for longer crystallization times. This accords with the comments of Frank and Tosi [5] that lamellar thickness will be reduced for finite substrate height but the effect has not previously been recorded.

## 2. Experimental

A particularly favourable means of observing isothermal thickening in situ is the use of linear nucleation to produce cylindrical row structures in polyethylene. Lamellar thicknesses can be observed and measured in these at any desired depth, from the nucleation site to the growth interface, by examination of selected chords of the cylinder produced by controlled etching.

As in previous experiments [2,3] polyethylene rows were produced around Tekmilon™ polyethylene fibres as linear nuclei parallel to the sheet specimens, in this case  $\sim 60\ \mu\text{m}$  below the surface. The results reported are for the linear polyethylene Sclair 2907 and the linear-low-density polymer Sclair 14B, both du Pont materials. The former has  $M_w = 104,000$  and  $M_n = 11,300$ . The latter is a film grade polyethylene of density  $0.932\ \text{g cm}^{-3}$  with 4.8 ethyl branches per 1000 C atoms.

To prepare samples, flat discs of the polymer  $\sim 20 \times 30\ \text{mm}$  across, some  $\sim 1\ \text{mm}$ , some  $\sim 60\ \mu\text{m}$  thick, were first prepared by melt pressing, between a clean  $13\ \mu\text{m}$  thick Kapton sheet and a microscope slide, on a Kofler hot-bench at  $150\ ^\circ\text{C}$  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 discs were cut into small squares of  $\sim 5\ \text{mm}$  side which were stored in labelled jars ready to prepare a fibre/polymer composite. To this end, about seven Tekmilon™ fibres were stacked parallel between two films, one  $1\ \text{mm}$  and the other  $60\ \mu\text{m}$  thick, then the whole sandwich placed carefully, with light pressure, on the Kofler hot-bench at  $133\ ^\circ\text{C}$ . The resulting fibre/polymer composite was transferred to the Mettler hot stage at  $133\ ^\circ\text{C}$  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.

All specimens were etched, at room temperature, 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. A few hours etching, monitored with Nomarski interference optics, was

sufficient to bring the outer edges of the rows into the surface of the etched specimen.

Specimens for scanning electron microscopy, SEM, were coated with gold prior to examination and revealed the lamellar character of the row structures in high contrast. Lamellar thicknesses at the growth front, were measured on two-stage carbon replicas of etched surfaces, using transmission electron microscopy, TEM. Particular care was taken to ensure that the lamellae recorded were at the periphery of the row and, by tilting, that their full thickness was measured and not foreshortened.

## 3. Results

Earlier work [2,3] has shown the sequence of habits along the radii of polyethylene rows for the accessible range of crystallization temperatures (encompassing both faster and slower growth, for lower and higher temperatures, respectively) with the thinnest lamellae close-packed by the nucleating fibre. Fig. 1 shows the increase in lamellar thickness with crystallization time at  $128\ ^\circ\text{C}$  for the periphery of two rows formed under slower growth, still with inclined lamellae, imaged by SEM; the change is from 10 min in Fig. 1(a) to 50 min in Fig. 1(b). Measurements of lamellar thickness require the higher resolution of TEM, using replicas of the edge of the row as shown in Fig. 2. Such thickness data are shown in Fig. 3 for the linear polymer. Fig. 3(a) plots these as a function of crystallization time while the data are replotted in Fig. 3(b) against the logarithm of time. The corresponding data for the branched polymer in Fig. 4, plotted against time in Fig. 4(a) and against log time in Fig. 4(b), indicate a slower thickening rate.

As the melting points of polymer lamellae increase with thickness and the thinnest lamellae in rows are by the nucleating fibre, this will also be the region with lowest melting point. Figs. 5 and 6 confirm that this is so. They show the results of heating rows of Sclair 2907, previously crystallized for 100 min at  $128\ ^\circ\text{C}$ , when heated at  $5\ \text{K min}^{-1}$  to the onset of melting then returned to ambient temperature to  $134\ ^\circ\text{C}$ . There has been no melting on heating to  $134\ ^\circ\text{C}$  (Fig. 5) whereas at  $135\ ^\circ\text{C}$  Fig. 6 shows that lamellae closest to the fibre have melted. The zone of melting is seen as a dark band in the centre of the row in Fig. 6(a) which, at the higher magnification of Fig. 6(b), is seen to contain tiny lamellae which no longer have the doubly-inclined orientation of the original (as in Fig. 5(b)), i.e. they have recrystallized on cooling. Beyond this zone, at greater radial distance are unmelted lamellae as is, outside the row, a spherulitic sheaf. Fig. 6(c) and (d) show other views of rows heated to  $135\ ^\circ\text{C}$  which reveal very clearly that the unmelted, i.e. thickest, lamellae lie within the row whose inner and outer portions have melted.

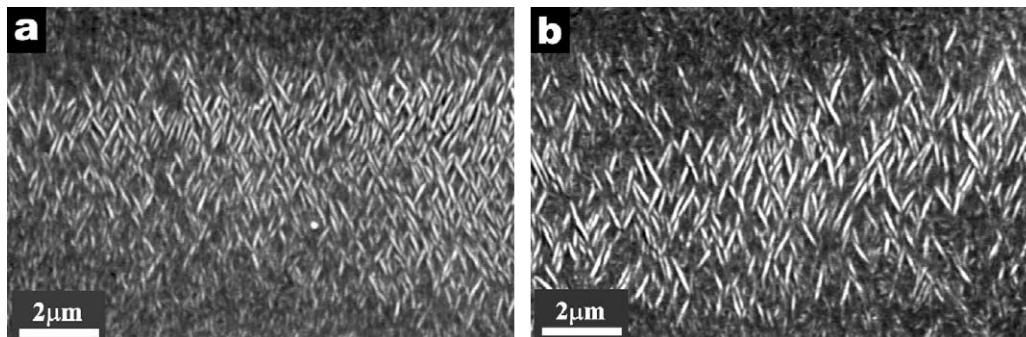


Fig. 1. SEM images of the edges of row structures of Sclair 2907 polyethylene crystallized at 128 °C (a) for 10 min, (b) for 50 min showing that lamellae in the latter are thicker. Under these conditions of slower growth, lamellae are inclined at  $\pm \sim 55^\circ$  to the (horizontal) fibre axis.

#### 4. Discussion

Polymer lamellae form because this is the fastest route for macromolecules to crystallize but, once formed, they are metastable with respect to increased thickness which reduces the surface to volume ratio and thereby the specific Gibbs function or chemical potential. Frank and Tosi [5] showed that, nevertheless, secondary nucleation on an infinite substrate could be expected to yield a well-defined thickness,  $\ell_g^*$ , with individual fold lengths fluctuating around a mean and probably subject to later evening out; a lesser length,  $\ell_g^{**}$ , would result for a substrate of finite height. Solution-grown lamellae do have a well-defined thickness, which does not increase unless and until they are heated well above their growth temperature, commonly by partly melting then recrystallizing at a higher thickness.



Fig. 2. A replica of the outer edge of a row structure of Sclair 2907 crystallized for 30 min at 128 °C and used for TEM measurements of lamellar thickness with the precautions described in the text.

Melt-crystallized polyethylene lamellae are different; they thicken isothermally as they grow, roughly doubling their nucleation thickness, as Hoffman and Weeks [1] first proposed to account for their raised melting temperatures. Such thickening must occur in the solid state because melting is only possible above the crystallization temperature.

Isothermal increases in the X-ray long period of crystallizing polyethylene show a thickness increasing linearly with the logarithm of elapsed time. This was represented in later theory [6] by the factor  $\gamma$ , the ratio of observed thickness at long times,  $\ell$ , to that calculated for secondary nucleation,  $\ell_g^*$ , i.e.

$$\ell = \gamma \ell_g^*$$

with values of  $\gamma$  for polyethylene typically lying in the range 2–2.5. The rate of thickening at atmospheric pressure is  $\sim 10$  nm per decade of minutes with some variability according to molecular length and polydispersity. Thickening is enhanced, but not greatly so, in the hexagonal phase which has been measured, at 5 kbar, to be 28 nm per decade of minutes, only 2.4 times more than for the orthorhombic phase at 1 bar [7].

Although molecules must refold to a longer stem length in a thicker lamella, refolding alone would reduce the lamellar width proportionately. If this does not happen, which is normal, then new molecules must be added to the lamella as it thickens. The implication from Kovacs' work on poly(ethyleneoxide) oligomers was that molecules could be incorporated into lamellae, from the melt, behind the growth front [8]. It is, nevertheless, easier to envisage how an individual lamella might thicken than if it were a member of a stack when space for expansion is likely to be restricted as is access for new molecules.

Such matters have been much clarified since it became possible to examine lamellar morphologies of melt-crystallized polymers systematically with electron microscopes following the introduction of permanganic etching. It has been shown, in particular, that thickening depends upon location in the morphology and is not simply a time-dependent phenomenon.

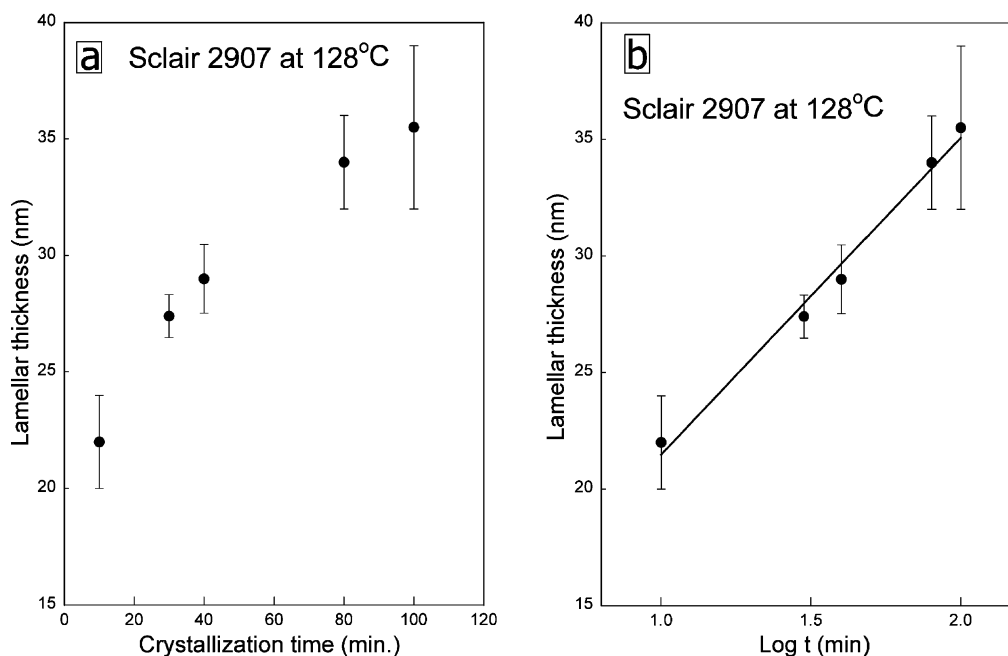


Fig. 3. Lamellar thickness of Sclair 2907 crystallized at 128 °C plotted (a) against time and (b) against log time.

The earliest morphological observations bearing on lamellar thickening were consistent with it being solely a function of initial thickness and elapsed time. When a polyethylene spherulite melts, it does so from the outside in [9], as is to be expected if the oldest lamellae are the highest melting. Similarly, subsidiary lamellae melt first in spherulites of poly(4-methylpentene-1), being thinner than the older enclosing dominants, then recrystallize isothermally increasing their thickness linearly with log time [10]. By contrast, cross-hatched spherulites of the  $\alpha$  form of *i*-

polypropylene, have lower-melting centres while the polyethylene rows of our investigations have the thinnest lamellae adjacent to the nucleating fibre. These observations show that lamellar thickening also depends upon its morphological context and illustrate the effects of physical constraints on the thickening process.

Solid state thickening presumably occurs via the strong longitudinal vibrations and torsional oscillations typical of polymers as they approach their melting point. At lower temperatures the inability of the vibrations to overcome the

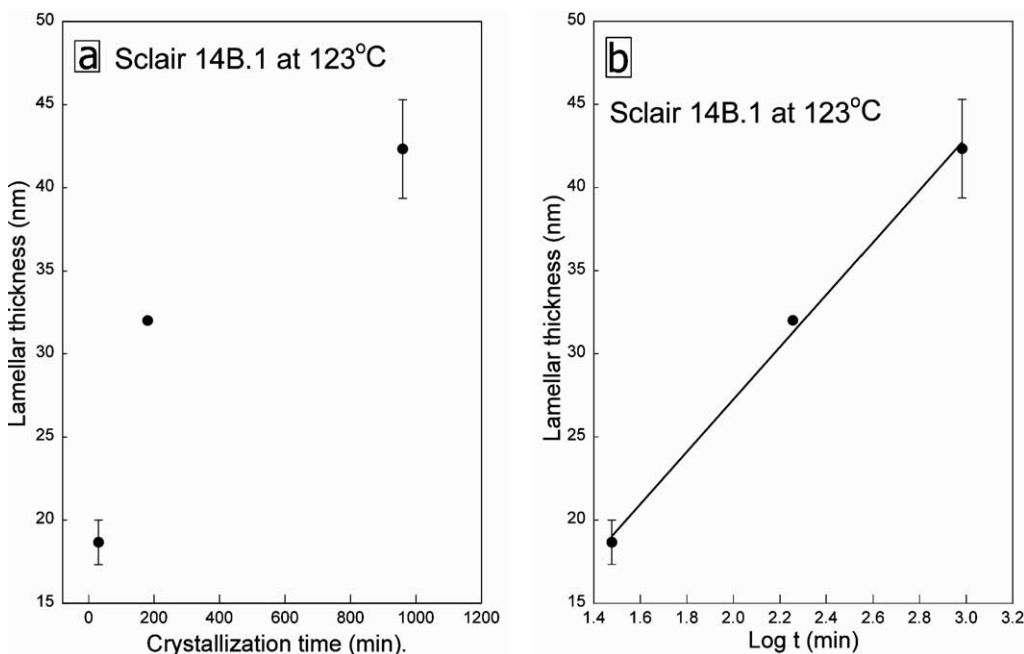


Fig. 4. Lamellar thickness of Sclair 14B crystallized at 123 °C plotted (a) against time and (b) against log time.

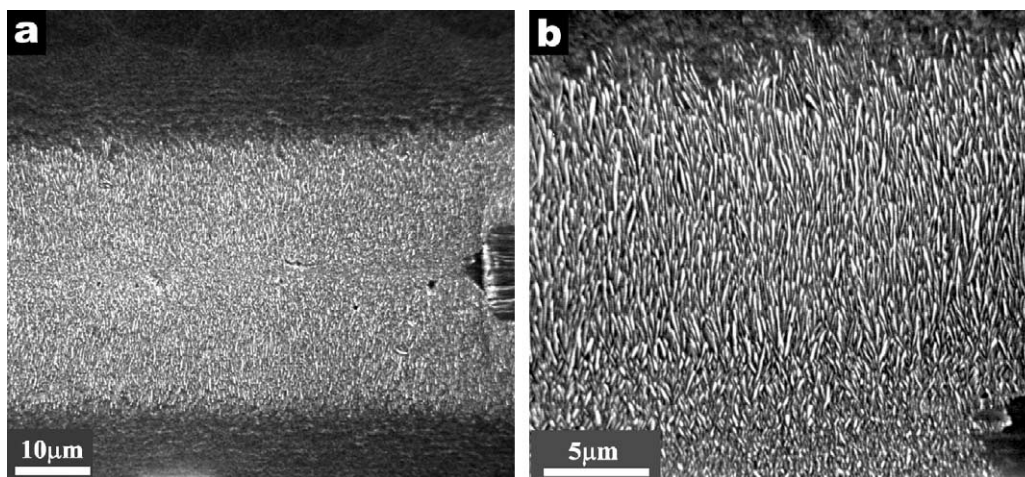


Fig. 5. A row structure of Sclair 2907 polyethylene crystallized for 1 h at 128 °C, heated at 5 K min<sup>-1</sup> to 134 °C then cooled; (a) overall view, (b) detail. The lamellae retain their original morphology with no sign of melting.

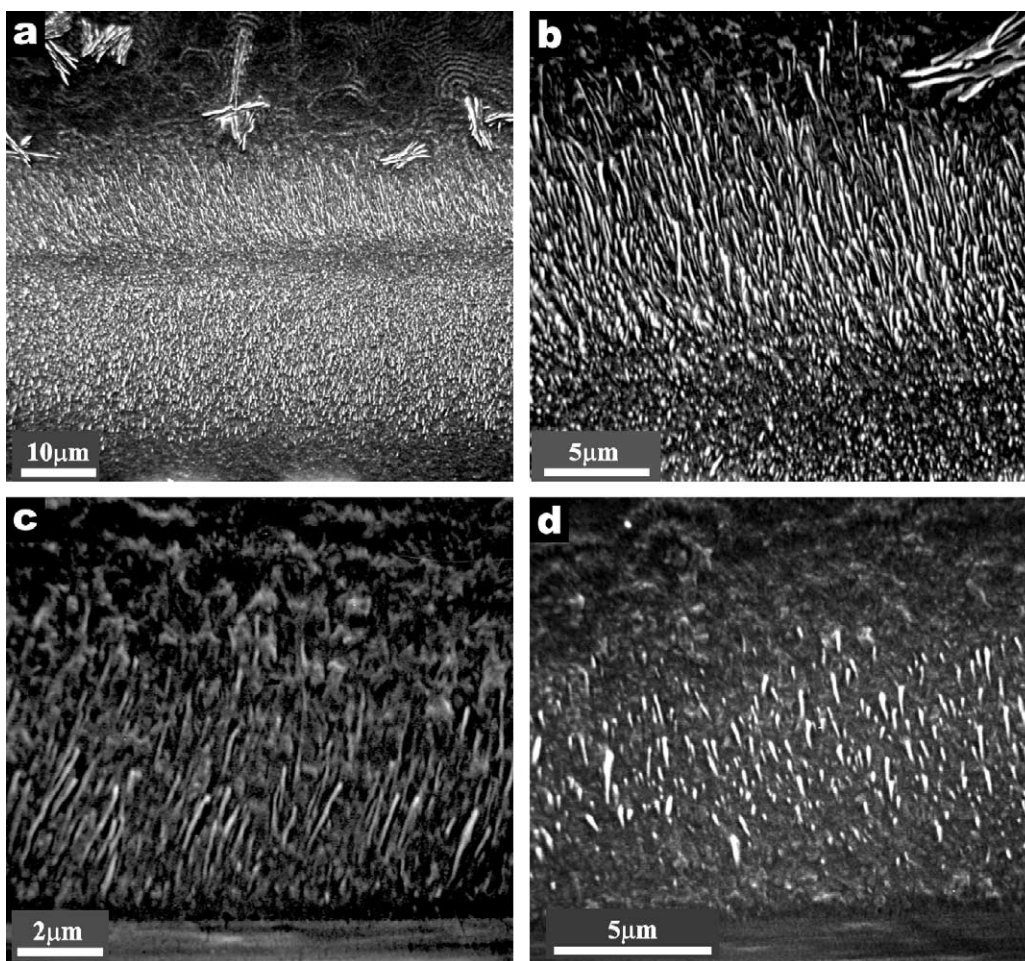


Fig. 6. Row structures of Sclair 2907 polyethylene crystallized for 1 h at 128 °C, heated at 5 K min<sup>-1</sup> to 135 °C then cooled. A central dark zone of melting is seen in the overall view of one row (a) which, in detail (b), consists of melted and recrystallized polymer. Lamellae at greater radial distance have not melted nor has the spherulitic sheaf beyond the row. In the different perspectives of (c) and (d) it is clear that lamellae adjacent to the nucleating fibre and those to the outside have melted while the highest melting (and thickest) lamellae are retained, unmelted, within the row.

energy barrier to thickening is probably why solution-grown lamellae, unlike their melt-grown counterparts, do not thicken at their (lower) growth temperatures. Thickening offers a means whereby a lamella cannot merely reduce its surface to volume ratio but also attain a more ordered, lower energy, surface. In faster-grown polyethylene, with initial {001} fold surfaces, this leads to the adoption of S profiles as fold surface normals incline to molecules, increasing the area per fold, and accompanying twisted growth [2]. There is no twisting in slower-grown linear polyethylene [3] as in Fig. 1, for which fold surfaces remain {201} but the situation alters for the linear-low-density polymer. Here, thickening brings twisting once the initial {201} fold surfaces become stressed as excluded branches are brought into surface regions [11].

Morphological evidence illuminates two constraints on thickening. First, if lamellae are packed close together in a stack, there is no intervening space into which any one lamella can thicken although, in principle, two adjacent lamellae could mutually transform to one of twice the thickness. Our observations on polyethylene rows have shown that thickening of an initially close-packed lamellar array is a function of radius and occurs when some have failed to propagate, so creating space for the remainder to occupy. At their origin, close-packed lamellae have no space to thicken and retain their initial thickness until the requisite space has been created.

A different explanation must apply to the reduced thickening at the centres of  $\alpha$ -polypropylene spherulites whose texture is quite open with two sets of nearly orthogonal lamellae [12]. Their fold surfaces do not touch but there is mutual contact on the growth surfaces, which will affect refolding and so delay thickening. The importance of unrestricted growth surfaces for thickening is supported by the thickening data of Fig. 3(b). The increase of some 13 nm per decade of minutes at 128 °C measured at the growth front for this polyethylene of  $10^5$  mass is similar to the total increase measured by X-rays on various polyethylenes previously: the comparison per decade of minutes, is 7.7 nm for a fraction of  $2.4 \times 10^5$  mass at 128.8 °C, 10.5 for Marlex 50 at 128.2 °C [1], 7.8 for Rigidex 2 at 130 °C [7], and 6.5 for annealed, cold-drawn fibres of linear polyethylene at 130 °C [13]. If, as is the case, the highest melting, i.e. thickest lamellae are those in the centre then their thickness must also increase no less than that at the growth front. Only when, as in polyethylene rows, the highest melting lamellae are at finite radial distance from the nucleus, is this not so. For spherulitic polyethylene, the numerical evidence is consistent with the thickening rate being constant throughout. The effect of thickening at the growth front, where molecules have greatest freedom to refold, is to increase the total thickness. Any restriction at the growth front, as in  $\alpha$ -polypropylene, would, therefore, be particularly effective in retaining lamellar thinness.

Effective restrictions are likely to be those which slow radial advance, i.e. too close an approach of neighbours.

Polyethylene lamellae grow fastest when in parallel array separated by more than molecular lengths, so avoiding both physical contact and internuclear interference (when one molecule can add to two lamellae simultaneously, thereby delaying crystallization [3]). Once growth has slowed other, more favourably placed and/or oriented, i.e. faster growing lamellae are able to overtake the former and become dominant in their turn. Thickening is likely to be similarly affected and greatest for a single lamella growing in unrestricted melt but prone to reduction when lamellae approach within molecular lengths. The additional factor of excluded branches affects linear-low-density polyethylenes. The exclusion process itself will reduce both growth and thickening rates [11]; the fact that thickening is continuous (Fig. 4) attests to the variation in the distribution of branches and the consequent fractional crystallization which occurs.

The occurrence of thickening of the growth surface is a significant new finding and one which accords with Frank and Tosi's observation [4] that lamellar thickness would be reduced for a finite substrate because of the extra surface energy of overhanging stems and protruding folds. In consequence, melt crystallization must now be envisaged as occurring not at an interface in steady-state condition but at one whose thickness steadily increases with the logarithm of elapsed time.

## 5. Conclusions

1. Isothermal lamellar thickening during the crystallization of polymers from the melt is a function not only of elapsed time but also of location within the morphology.
2. In contrast to polyethylene spherulites whose central lamellae are the thickest, in rows the first lamellae to form remain the thinnest because, being close-packed, they have no space into which to thicken.
3. The thickness of lamellae at the growth front increases linearly with the logarithm of elapsed time but, as the thickest lamellae are found at finite radius, thickening must also occur behind the growth front.
4. The data are consistent with a uniform rate of thickening throughout spherulitic polyethylene but melt crystallization must now be envisaged as occurring not at an interface in steady-state condition but at one whose thickness increases asymptotically.
5. Interference with crystallization on this interface will also reduce thickening.

## Acknowledgements

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

**References**

- [1] Hoffman JD, Weeks JJ. *J Chem Phys* 1965;42:4301.
- [2] Abo el Maaty MI, Bassett DC. *Polymer* 2001;42:4957.
- [3] Abo el Maaty MI, Bassett DC. *Polymer* 2001;42:4965.
- [4] Abo el Maaty MI. *Polym J* 1999;31:778.
- [5] Frank FC, Tosi M. *Proc R Soc A* 1961;263:263–323.
- [6] Hoffman JD. *IEC* 1966;58:41.
- [7] Bassett DC, Carder DR. *Polymer* 1973;14:387.
- [8] Kovacs AJ, Gonthier A, Straupe C. *J Polym Sci C* 1975;50:283.
- [9] Wunderlich B, Melillo L. *Makromol Chem* 1968;118:250.
- [10] Bassett DC, Patel D. *Polymer* 1994;35:1855.
- [11] Abo el Maaty MI, Bassett DC. *Polymer* 2002;44:6541.
- [12] Weng J, Olley RH, Bassett DC, Jääskeläinen P. *J Macromol Sci Phys B* 2002;41:891.
- [13] Fischer EW, Schmidt GF. *Angew Chem* 1962;74:551.