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On morphological instability in polymeric crystallization

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Abstract

Phenomena displaying the behaviour expected when molecular species segregated at the growth front lower the supercooling for continued growth have been observed using linear low-density polyethylene (LLDPE) nucleated on a fibre to form a macroscopic row structure. Initially, a close-packed array of lamellae grows epitaxially from the fibre, with the lamellae too close together for other parallel lamellae to form between them, so that rejected species can only accumulate ahead of the growth envelope. The more-branched molecular sequences rejected in this polymer lower the equilibrium melting temperature and with it the isothermal supercooling. In consequence, the texture coarsens and lamellae become thicker, both for the rows and in adjacent spherulites. During this process the isothermal growth rate declines continuously as the impurity layer develops, but spherulites always grow faster than rows because their more open crystal–melt interfaces give lower concentrations of impurities. The habit of the rows is then prone to change abruptly as spherulitic growth nucleates sporadically at points around the instantaneous growth envelope and grows faster than, and hence ahead of, the remainder of the row. The depth to instability and the average distance between spherulitic nuclei both increase with crystallization temperature but the former only slightly. It is suggested that nucleation occurs where fluctuations have reduced the concentration of segregated species and we found that the internuclear distance scales approximately as the inverse one-third power of the growth rate. No such instability or cellulation is found for spherulites growing adjacent to the rows even though their characteristic microstructure develops from the start, thereby confirming in a particularly clear way that morphological instability is not the cause of spherulitic growth in polymers. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Linear low-density polyethylene; Morphological instability; Segregation

1. Introduction

Morphological instability, which is a well-known phenomenon in the crystallization of binary metallic alloys (see ref. [1] for a recent overview) has not, so far as we are aware, previously been unambiguously identified in polymeric crystallization. Historically, it was the basis of a proposal for the generation of polymer spherulites [2] and although this has proved not to be the case [3,4], with recent confirmation that polymeric spherulites actually form in response to a short-range repulsion, specifically cilia pressure, on branching lamellae [5,6], it is, nevertheless, of particular interest to record and examine the reality of this much-invoked phenomenon and place it in its correct context for polymeric crystallization. When this mechanism was first proposed the evidence offered in support was indirect and consisted of a comparison of lateral textural widths, of single or grouped lamellae, in spherulites with the characteristic length $\delta = D/G$, for radial growth rate G and diffusion coefficient D. It was not possible to show directly that growth first slowed and then became unstable nor that it had changed character with increasing radial distance, but it was assumed that this had happened at dimensions too small to observe. In the present experiments we are able to demonstrate instability directly for the first time in polymers by employing two strategies. The use of macroscopic row structures (alongside spherulites) varies the interface geometry so as to maximize the concentration of segregants, while the use of polyethylene with branches which are excluded from the crystal lattice ensures that there will be strong segregation of species which will produce significant isothermal lowering of supercooling at the growth interface. As anticipated, instability occurs first for rows because their geometry gives a higher concentration of segregants. Instability in spherulites was not observed in these experiments but has since been produced in still more highly branched polyethylene [18].

In our recent research the several advantages of investigating and characterizing polymer morphology using linear as opposed to point nuclei [9] have brought the former into increasing prominence. In particular, a comparison of the two forms of nucleation, which produce row structures and

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spherulites respectively, is informative about the consequences of different geometries at the growing crystal/melt interface. With row structures one begins with a close-packed, parallel array of lamellae, growing epitaxially on, and perpendicular to, the linear nucleus, whose envelope advances approximately as a planar interface. In contrast, for spherulites the crystal/melt interface is more open because dominant lamellae diverge in forming the geometrical skeleton, allowing new lamellae to appear between them to maintain a uniform average density of lamellae with radial distance. In the event that certain molecular species are rejected at the growth front [2], their resulting concentrations and diffusion fields will differ for the two geometries, with predictable consequences for both growth rate and morphology. For high crystallinity polymers, specifically isotactic polypropylene, no such differences have been observed, which must imply that any species which are segregated produce no significant change in supercooling [10], i.e. depression of equilibrium melting point, T_m^0. This will not be true, however, for a material such as linear low-density polyethylene (LLDPE) with its spectrum of branching frequencies, and for this polymer grown on a high-melting polyethylene fibre, we do find phenomena having the properties expected of morphological instability initiated by segregation of rejected species at the growth front. Initially, lamellae grow outwards in uniform transverse array, but their growth rate declines continuously, they become slightly thicker and further apart on average (eventually to a stable separation [11]), and then, at a particular radial distance, the pattern of growth is prone to change abruptly, as growth is nucleated at points around the instantaneous envelope of the row and develops spherulitically in discrete cells. These changes, but not the abrupt discontinuity, also occur in adjacent spherulites nucleated away from the fibre attesting to the presence of segregation but also confirming that spherulites normally grow in polymers without the occurrence of morphological instability and cellulation. This paper presents the novel observations, explains the reasons for ascribing them to morphological instability and then discusses how the patterns scale with relevant variables and the significance of this phenomenon for polymeric crystallization in general.

2. Experimental

2.1. Materials

The polyethylene used was a commercial product of BP Chemicals, reference LL0209AA—a random copolymer with 1-hexene and an average branch content of 21.0 butyl branches per 1000 carbon atoms; $\overline{M}_w = 126\,000$; $\overline{M}_n = 30\,000$. Discs 0.5 cm in diameter and 3 mm in thickness were prepared by melting at 200°C for 3 min in a Mettler FP52 hot stage, then quenching in ice–water. Bundles of Tekmilon fibres, nominally 40 μm in diameter and 3–4 cm long, were sandwiched, for 1 min at 130°C, between two of the pre-prepared discs, during which process the Tekmilon fibres were secured in place by lightly adhering individual ends using a quick-drying adhesive. The resulting fibre/LLDPE composite was mounted between microscope slide and coverslip and replaced in a Mettler hot stage at 130°C for 3 min, then immediately transferred to a second, adjacent Mettler hot stage controlled at the appropriate crystallization temperature. Crystallization was continued for the chosen time after which samples were quenched into ice-water.

To prepare specimens for electron microscopy, the fibre composite was frozen to a sample holder of a Bright rotary microtome using a proprietary reagent, then its interior was exposed by cutting parallel to the long axis of the fibres with a glass knife, removing successive slices of approximately 10 μm in thickness. An optical microscope, using Nomarski differential interference contrast, was used periodically to assess the progress of the microtoming, until the embedded Tekmilon fibres were on average 50 μm below the exposed surface. Such specimens were etched for 3 h in a 1% w/v solution of potassium permanganate dissolved in 2:1 sulfuric and dry ortho-phosphoric acids.[1] Periodic checks on the progress of the etching were undertaken by arresting the etching process and observing development with the Nomarski optical microscope. Once a reasonable proportion of fibres with epitaxial overgrowths had broken surface, a standard two-stage indirect metal-shadowed carbon replica was made of the etched composite (using cellulose acetate film moistened with acetone) and transferred to grids for examination in the transmission electron microscope.

3. Results

The crystallization procedure described takes advantage of the high melting point of polyethylene fibres with sufficiently extended molecular conformations, which allows their use as nucleants for quiescent polyethylene melts for typical crystallization temperatures below ~130°C. In such cases growth starts epitaxially on the fibre as transverse lamellae sharing a common *c* axis, the chain direction, with the parent to produce a macroscopic row structure or shish-kebab [12]. Fig. 1 shows such an object, crystallized for 15 min at 121.5°C, within a matrix of polymer crystallized on quenching. Contrast this with Fig. 2 showing coarse spherulites and sheaves in the same specimen but grown remote from the fibre. The two cases differ importantly in the geometry of the interfaces with the melt. The lamellae in Fig. 1 are close together—the intervening space is believed to contain molecular cilia by analogy with α-polypropylene

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[1] Independent studies of etching rates on loosely bound Tekmilon fibres reveal through direct observation a chemical attack rate of tens of micrometres per hour.

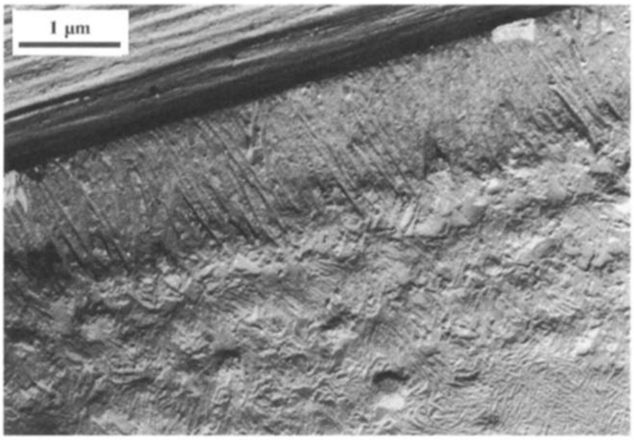

Fig. 1. Uniform transverse lamellar growth of polyethylene nucleated epitaxially on the surface of the high modulus polyethylene fibre at the top of the figure and crystallized for 15 min at 121.5°C. Carbon replica of an etched longitudinal surface.

for which there is a minimum separation, varying with molecular length and crystallization temperature [7,8]—with no room between for other parallel lamellae to form. By contrast, the dominant lamellae in Fig. 2 diverge, leaving space which is already being filled, in some cases, with later-forming lamellae. If, as one expects, there is fractional crystallization with rejection of molecular sequences with too short a branch-free interval, such species will be able to diffuse between dominant lamellae for spherulites but not between the lamellae in the rows at this separation. The concentration of rejected species at the growth fronts will be greater for rows than for spherulites both for this reason and because the growing tips of dominant lamellae are, on average, wider apart in the latter so that less material is rejected, per unit area, in the first place. The growth of rows in LLDPE, therefore, provides particularly favourable circumstances for the concentration of rejected species to rise, leading to a reduction in growth rate and so allowing morphological instability to occur.

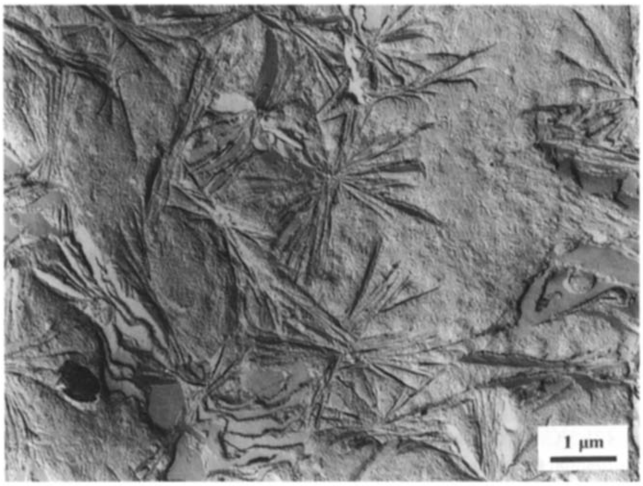

Fig. 2. Coarse spherulites grown away from the fibre in the same specimen as in Fig. 1. Contrast the open packing of lamellae here with the close-packed geometry in the row structure of Fig. 1. Carbon replica of an etched longitudinal surface.

When crystallization is continued for longer times at 121.5°C there is a change of habit, which takes two forms, and is illustrated in Fig. 3. First, while the array stays uniform, there is a coarsening of texture, i.e. fewer lamellae per unit length of fibre, seen in Fig. 3a and Fig. 3b, here associated with deviation from the original perpendicular growth direction and also, as is clearer in later figures, with somewhat thicker lamellae. (This effect has since been quantified by Abo el Maaty [11] who has shown that the interlamellar separation eventually stabilizes to give a constant growth rate). Second, on the perimeter of the row, there is nucleation and then development of faster-growing, essentially spherulitic, forms which are visually prominent both for exposing a range of orientations, especially flat-on lamellae, in otherwise edge-on surroundings and in creating protuberances ahead of the body of the row. Henceforth we refer to these as the product of morphological instability.

Fig. 3 shows this instability in three stages. In Fig. 3a the arrowed region, which has nucleated with a different orientation to its surroundings, widens as it advances, indicating that it has indeed grown faster than neighbouring lamellae. Note that its individual lamellae, which are revealed to be separate at ~1 μm above and to the right of the arrow, have bunched together to give large composite steps in the exposed surface consistent with growth in the presence of impurities. The dotted line marked A–A indicates where average lamellar density along the planar interface has halved from its original value. The position of this line relative to the fibre surface was generally constant, in different specimens, to within a few tens of nm over 100 μm along the fibre. It is, therefore, a useful measure of the changing character of growth with radial distance. It is the basis of data, later in the paper, of the onset of instability used in a preliminary assessment of the nature of the phenomenon. In practice, instability is somewhat more variable in its occurrence, especially for higher crystallization temperatures when growth is slower, presumably because of fluctuations in segregant concentration. In Fig. 3a, for example, it has occurred well before the line A–A, within the early stages of growth; in other cases the situation is reversed. Later figures show that there is greater regularity at lower crystallization temperatures making the criterion more definitive.

Fig. 3b shows a single, more developed, sheaving entity which has grown from a nucleus more or less parallel to, and ~1 μm away from the fibre surface and protrudes a distance similar to the depth of the remainder of the row. Lamellae in it are only slightly curved, indicative of growth at low supercoolings [13]. In Fig. 3c there are several such objects, now presenting a more spherulitic appearance, which provide a fringe to the transverse centre of the row and extend a distance some five times that of uniform growth. Each of these is traceable back to its origin, usually a point, so that a series of origins can readily be identified placed repetitively along the row.

The same sequence of features recurs at lower temperatures, although as growth is then banded, the changes, particularly of orientation, are less conspicuous than in previous figures. Fig. 4 shows the results of 15 min crystallization at 120°C. The texture coarsens with increasing radial distance before giving rise to spherulites nucleated sporadically and a correspondingly non-planar interface. There is little or no banding in the outermost region indicating that, in comparison to the initial conditions, later growth has occurred at reduced supercooling [13]. Another area of this sample, Fig. 5, illustrates comparative development of the row—which parallels that of Fig. 4—with a spherulite which has nucleated to the side of the fibre. This spherulite displays the characteristic dominant/subsidiary microstructural pattern, seen especially clearly at the lower right. Its radius exceeds that of the growth in the row, indicating a faster growth rate even on the worst case assumption that the spherulite nucleated at zero time. But while both show similar coarsening (lamellae are thinner in the interior of the spherulite and thicker to its outside) and loss of banded character, there is an important difference. This is that, unlike the row, there is no discontinuity in growth along the radius of the spherulite such as one might associate with morphological instability. On the contrary, spherulitic growth with its dominant/subsidiary microstructure is continuous from the start and does not depend on the onset of instability which, even for the more favourable case of row crystallization, does not occur until growth has extended to 1 μm or so.

At 118°C, the lowest crystallization temperature chosen for illustration, growth is still uniform after 5 min (Fig. 6a, showing a transverse section), but coarsening, with particularly clear thickening of lamellae, has set in by 15 min (Fig. 6b). The same three stages of growth—uniform transverse lamellae, coarsening, then instability—are, therefore, present at all temperatures although the distance before instability sets in increases slightly with crystallization temperature (Fig. 7). The last quantity is measured as described earlier and along a considerable length of the row which gives a well-defined criterion for the average distance from the fibre; error bars in Fig. 7 refer to the standard errors of the means of the populations. Use of appropriate two-stage crystallization, specifically 15 min at 121.5°C

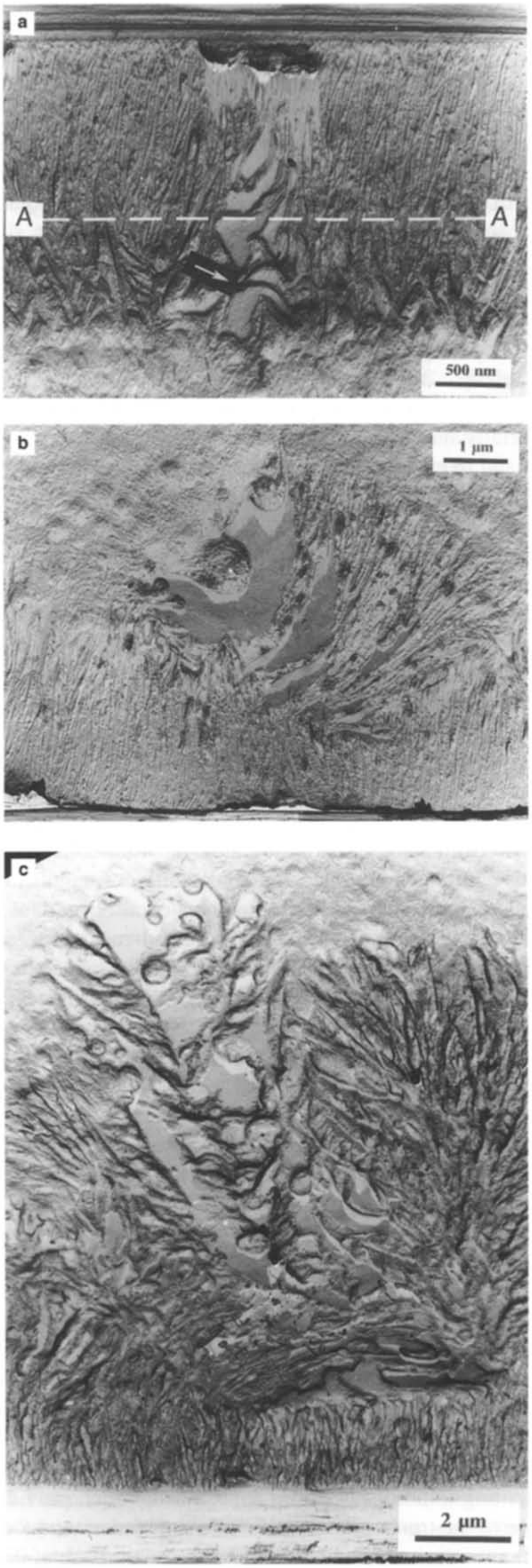

Fig. 3. Stages in the onset of morphological instability formed in different regions after growth of row structures from polyethylene fibres for 30 min at 121.5°C. (a) A single object (arrowed) with flat-on lamellae growing within, but faster than, its surrounding row which has become progressively coarser with increasing radial distance. (b) A later stage when a single sheaving object has grown well ahead of the remainder of the row. (c) Part of a more uniform development whereby several spherulites have nucleated at intervals along the then envelope of the developing row structure. Carbon replicas of etched longitudinal surfaces.

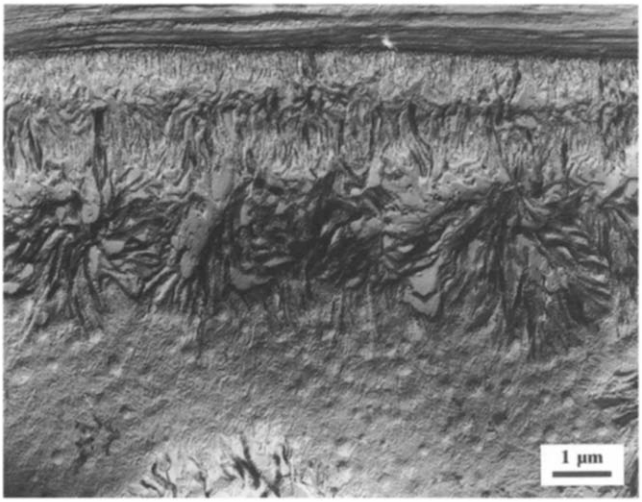

Fig. 4. Progressive habit changes leading to a non-planar interface during the growth of a polyethylene row structure on a macroscopic fibre for 15 min at 120°C. Note that the initial growth is banded. Carbon replica of an etched longitudinal surface.

followed by 15 min at 118°C, as shown in Fig. 8, accentuates the onset of instability and emphasizes the separation of nuclei along the row. In all cases, the altered growth develops from just a few nuclei, each of which can be traced back to an effective point, repetitively located along the fibre direction. This feature allows the projected separation of nuclei to be measured, leading to the numerical data plotted in Fig. 9. These are of average separation along the row, obtained by averaging, typically 10, individual measurements; error bars refer to the standard errors of the means of the populations.

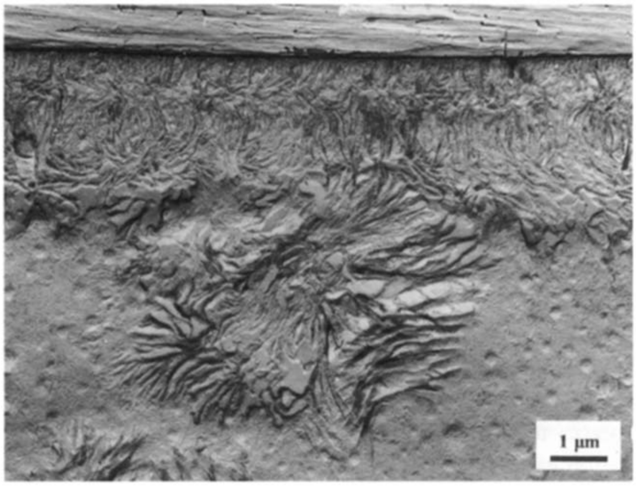

Fig. 5. A comparison of lamellar development in a polyethylene spherulite with that in the adjacent row structure in the sample of Fig. 4. Note that the spherulite has a larger radius than that of the row, that it has the characteristic dominant/subsidiary microstructure from the outset and that both row and spherulite become texturally coarser with increasing radius. Carbon replica of an etched longitudinal surface.

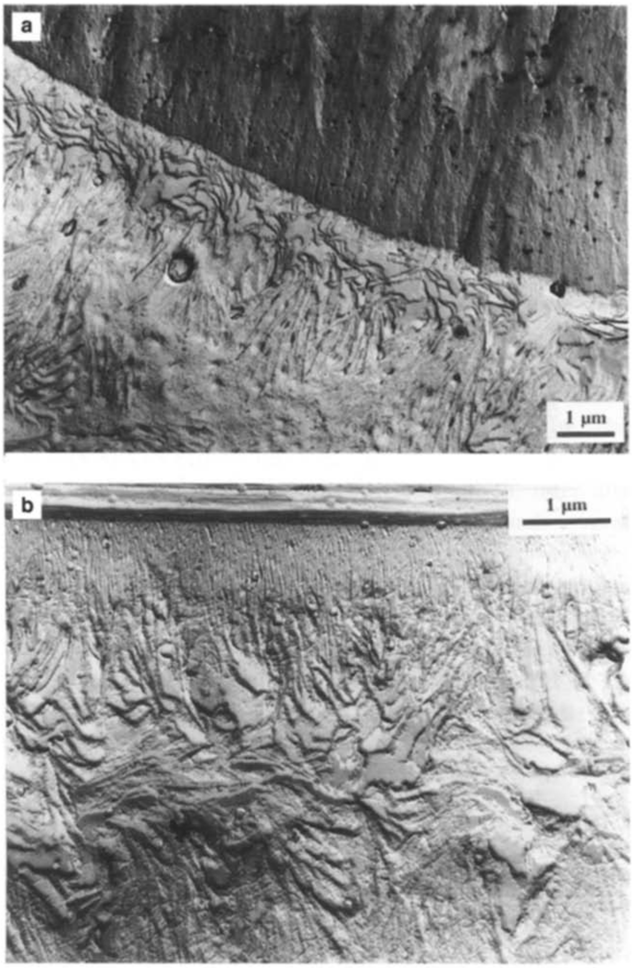

Fig. 6. Development of polyethylene row structures with crystallization time at 118°C. (a) Uniform banded growth, in transverse section, after 5 min. (b) Coarsening, thickening of lamellae and the onset of instability, in longitudinal section, after 15 min. Carbon replicas of etched surfaces.

A central observation is that growth rates decline with time. It has not been possible to measure this quantity directly in this instance because the change in the diameter of rows is too small for precise in situ measurement with an optical microscope. But the conclusion follows from the data of Fig. 10 showing the change in overall diameter (of the homogeneous part of a row) as a function of growth time. A comparison of values, using the shortest growth times and excluding all small objects and those nearing impingement, shows that spherulites always grow faster than rows at the same temperature (Fig. 11) even though this procedure tends to underestimate spherulitic growth rates because of the assumptions that they started to grow at zero time and that they are being observed in diametral section. This differs from the common experience in high crystallinity polymers that growth rate is both independent of radial distance and the same for rows as for spherulites [10] because of the influence of molecules segregated at the growth front and their different distributions and concentrations in the two cases.

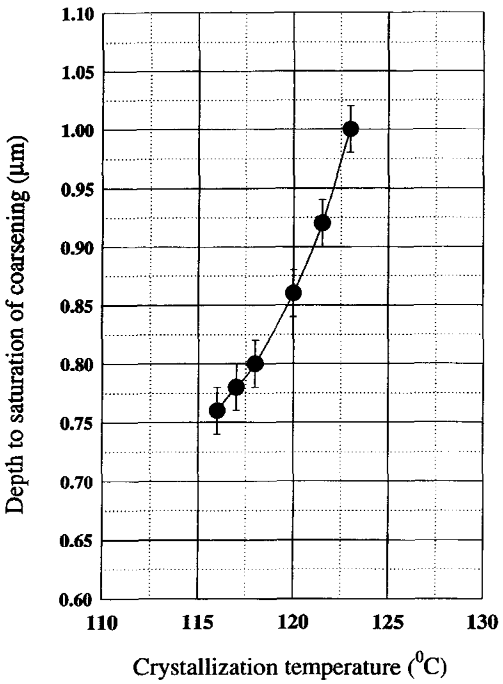

Fig. 7. Variation of the depth of the near-planar interface, to the onset of morphological instability (doubled coarsening), as a function of crystallization temperature.

4. Discussion

The extent of fractional crystallization and segregation in a typical homopolymer such as polyethylene or polypropylene is a decreasing function of crystallization temperature and may well be negligible at temperatures used in commercial processing. Even when these processes do occur it is a moot point whether they will cause sufficient depression of the local equilibrium melting temperature, T_m^0, at the growth interface significantly to affect the continuing growth rate. Segregation of molecular masses of, say, 5000 will have little effect on a melt of linear polyethylene. However, in copolymers whose branches are excluded from the crystal lattice, not only will there be rejection of molecular sequences whose interbranch lengths are too short for crystallization but they will certainly lower T_m^0 and with it

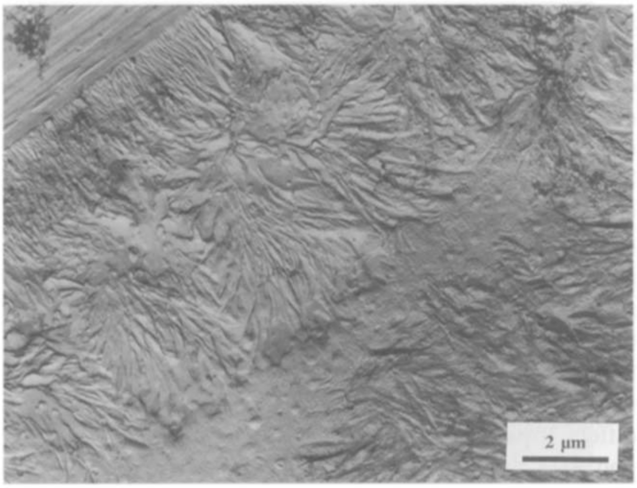

Fig. 8. Development of the sites where spherulites have nucleated during the onset of morphological instability by crystallizing for 15 min at 118°C after 15 min at 121.5°C. Note the repetitive nucleation along the row. Carbon replica of an etched longitudinal surface.

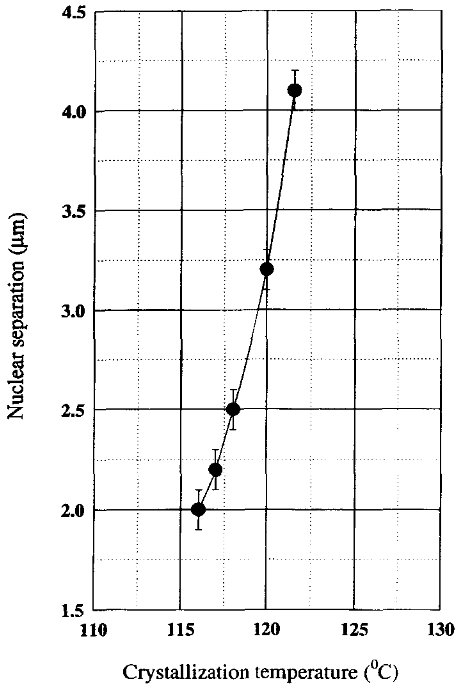

Fig. 9. Average projected separation of nuclei of morphological instability as a function of crystallization temperature.

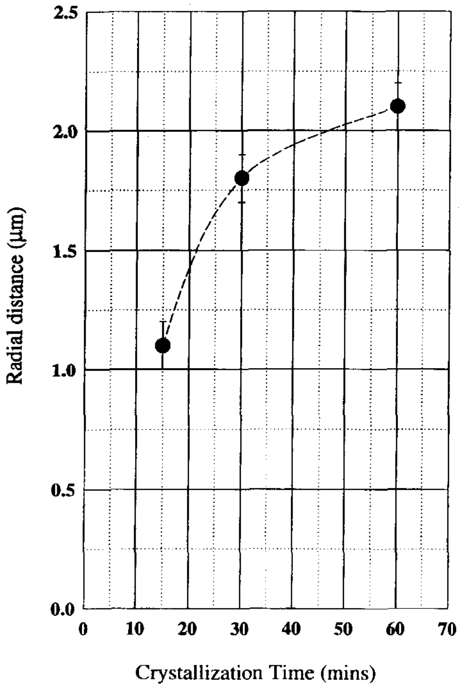

Fig. 10. The radial distance grown in a polyethylene row structure at 121.5°C as a function of crystallization time.

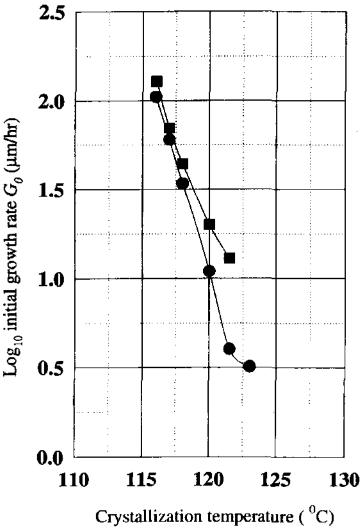

Fig. 11. The logarithms of initial growth rates for rows (circles) and spherulites (squares) as functions of crystallization temperature.

the isothermal supercooling for growth. This is the situation in our experiments.

The expected consequences of a build up of rejected species at the growth front are as follows. First, the growth rate is liable to fall as transport of crystallizable molecules to the growth sites is impeded (but only if this is the rate-controlling step) and will do so if the supercooling for isothermal growth is lowered because of a reduction in the effective equilibrium melting point, T_m^o. Neither of these factors pertains to the growth of rows of α-polypropylene of high stereoregularity [10] but at least the second is operative for LLDPE rows when more-branched molecules accumulate ahead of the growth front. Second, once the supercooling for growth is reduced, lamellae will tend to become thicker, provided there is room physically to accommodate them and isothermal lamellar thickening is not unduly suppressed. This latter factor is, however, liable to inhibit any thickening for polymers with minimum crystallizable inter-branch lengths. Coarsening, that is a reduced number of lamellae crossing unit length of interface, is characteristic of spherulites grown at lower supercoolings [2], but will also be favoured for a further reason; namely that when lamellae become further apart they will encounter a reduced concentration of rejected species and so sustain a higher growth rate. Instability will occur when the tips of any protuberances which form are able both to crystallize faster than neighbouring regions and to sustain their competitive advantage.

All these anticipated effects are observed in our experiments. Growth starts as parallel arrays, seen in longitudinal view most simply in Fig. 1, in which lamellar traces are normal to the fibre or nearly so. A departure from precise normality, as occurs here, is indicative of the c axis becoming inclined to lamellar normals in response to developing interactions between folds allowing them a greater separation [13]. Similar behaviour has been reported previously in the lamellar component formed during the hot compaction of Tenfor (now Certran) melt-spun polyethylene fibres [14] but its observation requires that the b axis, the radial growth direction, deviates to some extent from parallelism with the sample plane. Given that the 40 μm diameter fibre nuclei are immersed in the sample, this is likely quite often to be the case in our experiments. Such oblique habits are found at lower supercoolings, but with falling growth temperatures one anticipates a change to banded growth of the row akin to that of the corresponding spherulites formed in quiescent conditions. Cooperative banding, which rotates the lamellar normals from their initial orientation parallel to the fibre axis (Fig. 6a) progressively around the growth direction, is indeed found for growth at 120°C (Fig. 5) and below. This also reproduces effects reported earlier [12] for growth on compacted fibres of linear polyethylene which, inter alia, have confirmed the cooperative nature of such overall twisting.

The initial growth of rows, being one of close-packed lamellae with too little space between them for other parallel lamellae to form, is a good approximation to the advance of a planar interface in that any species rejected at the growth envelope can only accumulate ahead of it. The growth envelope itself will be wide and effectively plane for the experimental geometry employed in this work and the broad lamellae typical of polyethylene. Moreover, for LLDPE there will be considerable fractional crystallization, especially at higher temperatures when only the longer inter-branch lengths are able to crystallize into the thicker lamellae formed under those conditions. Growth of LLDPE on a fibre is thus a particularly favourable system on which to explore the consequences of the accumulation of rejected species on morphology.

There is confirmation of the presence of a considerable impurity layer in our experiments first in the changes of lamellar habit to those appropriate to lower supercooling, including increased thickness, and second in the slowing of the growth rates with radial distance from the fibre and in coarsening. The first two factors are clear evidence for the depression of equilibrium melting point as growth proceeds. Although this is contrary to normal experience with rows and spherulites, it is expected to occur during the establishment of a layer of rejected molecules at the growth front. It has previously been supposed [2] that spherulites grow at constant rate because a steady state has been established with fibrous protrusions penetrating through the impurity layer of equilibrium width $\delta = D/G$ (where D is the diffusion coefficient of rejected species and G the steady state radial growth rate), then continuing to grow in conditions of little or no depression of supercooling, although this was never shown explicitly. In the present experiments it is clear that no such steady state is attained but that the concentration of segregated species at the growth front is still increasing as evidenced, for example, by the continuous decline in the growth rate. This observation is in agreement with estimates of δ for our polymer, over the range 116–123°C, which are from 0.2 to 10 μm using literature data for diffusion and the initial growth rate, and higher as growth slows. We can be very confident, therefore, that our present observations are of morphologies resulting from growth moving into a developing impurity layer, of increasing concentration, and not of a steady state situation. (The conditions under which a steady state operates have since been established [11].) In consequence, as the supercooling declines, the overall texture will coarsen and the lamellar thickness will tend to increase continuously with distance in accordance with established trends for polyethylene crystallization [15] and in agreement with our observations.

What is unexpected, to an extent, is the manner in which this gradual change in a more or less uniform array of lamellae gives way to sudden morphological instability. At all crystallization temperatures and at a distance of only a few μm, the comprehensive transverse lamellar growth is superseded by development in what is essentially a spherulitic manner from discrete centres, as for example in Fig. 3c. Instead of certain pre-existing lamellae developing and extending ahead, there is a discontinuity in crystallography along the radius shown by lamellae no longer having a common projected orientation; now some are flat-on in the page. It appears that new entities have been nucleated sporadically in space once growth has slowed to a low value. Unlike the case of polypropylene row structures where nucleation with a change of crystallography is required to fill space [4,16], no reason for its occurrence is self-evident. If one notes, however, that the differential rate of crystallization, below the initial value, increases as growth rate slows, the conditions under which we find morphological instability are indeed those of high probability. It is no surprise that spherulites then develop from the perimeter of the row because the conditions for maximum growth, i.e. least segregant concentration, will occur at separate points and spherulites grow from point nuclei in polymeric melts. Moreover, spherulites grow faster than rows, as confirmed experimentally, because impurities will diffuse away laterally—and thereby further depress the growth rate of competing development in adjacent portions of the rows—so that they will maintain their advantage and the change of habit will be stable. As the initially surprising discontinuity of orientation involves additional surface free energy terms of only a very few mJ m^{-2}, small in comparison to the free energy of crystallization, changes of orientation should be anticipated. Once instability has happened in the manner observed, each nucleus is able to crystallize, without competition, within its own growth cell. (By growth cells we mean those space-filling volumes centred on the nuclei and normal to the initial near-planar interface.) In these circumstances it will grow faster than is possible for the unmodified rows, because the open, crenellated interface and lateral diffusion both reduce the concentration of segregated impurities. The change in habit will thus be stable and persist.

The small size of the spherulitic nuclei, which are much smaller than the internuclear distance or cell width, shows that cell dimensions are set before significant modified growth has occurred and caused additional segregation. This rules out the possibility that internuclear separation could be a measure of the scale of a lateral diffusion field because, prior to the onset of instability, there would be no systematic lateral variation of impurity concentration for a growth envelope which was effectively plane.

The data of Figs 7 and 9 show, respectively, the average distances just prior to instability setting in and projected cell widths, both as functions of temperature. Note first that the distances from the fibre surface at which spherulitic growth is initiated are not only much less than the estimated values of δ, as discussed above, but also that their value is nearly constant, showing only a small increase with temperature. This suggests that the condition for instability may well be just that the amount of rejected species has reached a sufficiently high value. For a given volume, the amount rejected by the total growth will be proportional to the distance from the interface, less that lost by diffusion, a quantity which will increase only slightly with temperature. Moreover, as growth prior to instability appears uniform across the width of the front, the onset of cellulation has no obvious antecedent except for fluctuations in this concentration, presumably occurring where it is least. In this respect one expects that in a time t an initial excess concentration will spread to a width of $\sim\sqrt{2Dt}$ and that for a height h beyond the fibre interface, $t \sim h/2G_0$, with G_0 the initial growth rate. One might anticipate, therefore, that concentration variations separated by less than $\sim\sqrt{hD/G_0}$ will have decayed over this timescale. In practice, with h, taken to be the depth at which instability sets in, and D varying little over the range of experimentation, this would give

$$L \propto \sim G_0^{-1/2}$$

or more properly,

$$\log L = -\tfrac{1}{2}\log G_0 + \text{const.}$$

where L is the mean internuclear separation. The experimental data are plotted in Fig. 12 using values for G_0 estimated for both rows (circles) and spherulites (squares) by dividing whole dimensions by the crystallization time, yielding respective slopes of -0.22 and -0.31. The latter will be the better estimate because both growth rates will be identical at zero time but that for spherulites will suffer less reduction as segregation proceeds. It will, however, still be low both for this last factor and also if there is a non-zero induction time for spherulites to nucleate. With so many uncertainties involved, too much should not be read into the precise slope, but -0.31 is close to the value of $-1/3$ for the weak convection limit observed for morphological instability in other circumstances [17]. What is quite clear is that the internuclear separation does not depend on δ, the diffusion length which scales approximately as $1/G$ over a small temperature range; nor should it as diffusion is not involved in its establishment.

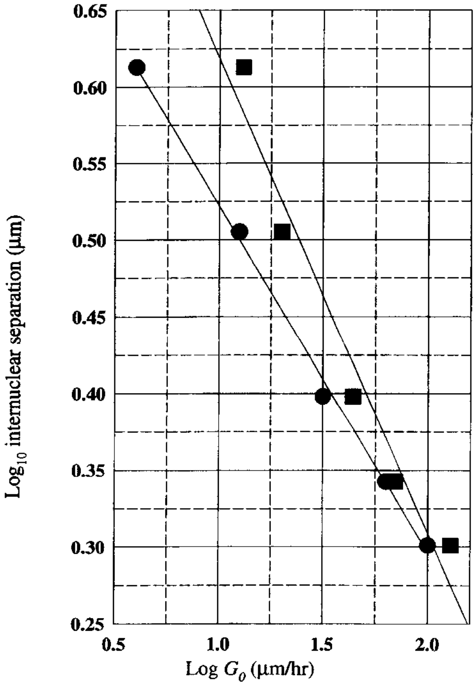

Fig. 12. Logarithmic plots of internuclear separation against initial growth rate for rows (circles) and spherulites (squares).

4.1. Morphological instability in context

The phenomena of morphological instability we have observed are not the norm in polymer crystallization, indeed they are rather rare. We have not previously encountered them in extensive studies of shish-kebab growth in several polymers including high-density polyethylene and a range of polypropylenes [7,8]. Their observation has required the optimization of both geometry and polymer to increase the concentration of segregated species, i.e. the high fractional crystallization of LLDPE and close-packing of lamellae in rows. They do not occur in rows of high crystallinity materials because, it has been argued [10], any molecules segregated cause negligible depression of the equilibrium melting point. They are not present in LLDPE spherulites growing alongside rows which have become unstable for two connected reasons. First the geometries of the respective interfaces differ, as shown in Figs 1 and 2. Second, the more open interface of the growing spherulite dilutes the concentration of rejected species both because of its geometry and because there are fewer lamellae crystallizing per unit area. In our system the concentrations at which instability might eventually occur within spherulites have evidently not been reached. Later experiments with a still more highly branched polyethylene [18], when the concentration of rejected species will have increased further, have shown morphological instability in spherulites giving textures much as hypothesized by Keith and Padden [2] for homopolymers.

The same considerations lay behind previous comments [19] that morphological instability could not be the cause of spherulitic growth. Others have pointed out that spherulites form in very pure polymeric systems where the concentrations of species rejected for molecular structure must be too low for the proposed mechanism to operate [20]. What the results of this paper confirm is that the patterns of morphological instability of a planar interface in a binary metal alloy [21] do not carry over simply to polymers, in part because there is no initially planar interface to become unstable. When the suggestion was first made, however, it was commonly believed that the growing faces of adjacent lamellae solidifying from the melt would effectively constitute a planar interface, a conjecture on which the Keith and Padden proposal [2] was based. But the advent of systematic transmission electron microscopy of melt-crystallized polymers showed that this was not the case. In reality, spherulites are built on a skeleton of individual (dominant) lamellae diverging to separations of ~1 μm, i.e. of typical molecular lengths, for all crystallization temperatures, as demonstrated in detail by recent electron microscope studies [22,23]. Previous observations to this effect, in thin films and fracture surfaces [24], had somehow been considered untypical and disregarded.

As generally encountered, therefore, fractional crystallization and segregation in polymeric systems are passive rather than active in relation to spherulitic growth. Segregated species do have effects on properties [4] but only because of their locations within already established spherulitic geometries; they do not create those geometries. Where these processes do play an active role is in the coarsening of texture and increase of lamellar thickness due to the depression of equilibrium melting temperature and growth rate. As is demonstrated in Fig. 5 these occur in spherulites of LLDPE as well as in rows. Similar effects have also been observed in separated blends of polypropylene in branched polyethylene whereby the polypropylene texture coarsens in going across the phase boundary into a polyethylene-rich region of lower supercooling [25]. Coarsening is, therefore, a feature of some general consequence to texture and related properties in crystalline polymers but, as was discussed above, it is additional to the original proposal [2] for the effects of segregation in which protuberances were supposed to have penetrated through the impurity layer and to be growing with negligible depression of supercooling.

The electron microscope studies which highlighted the inadequacies of the cellulation hypothesis as the cause of spherulitic growth in polymers also revealed that adjacent dominant lamellae in spherulites tend to diverge at constant angles to their neighbours [19,26]. This prompted a suggestion that a constant short-range repulsive force was responsible, for which the likeliest candidate was the pressure of uncrystallized portions of molecules already partly attached to the growing crystal which we describe as cilia. Although successive studies have reinforced the basis for this proposal [4] it was not until the recent availability of the monodisperse long-chain paraffins, or polyethylene oligomers, that a definitive test could be made. It has now been shown that spherulites, with characteristic dominant/subsidiary microstructure, do form in these pure materials but only when there is molecular folding, not when extended-chain lamellae form from the melt [5,6]. As chainfolding implies cilia, even if only transiently, when one fold stem is attached to the lamella with the rest of the molecule in the melt, this is a straightforward confirmation of the validity of the proposal that spherulites form essentially because their dominant lamellae are pushed apart at branch points by cilia pressure. It should be noted that this proposal is qualitatively consistent with all the observations of this paper and that cilia pressure has now been measured to be equivalent to a weak rubbery modulus [7,8].

5. Conclusions

The principal conclusions of this work are:

1. The use of fibres as linear nuclei for the crystallization of linear low-density polyethylene allows the observation of novel phenomena due to segregation of molecular species at the growth front of macroscopic row structures.
2. Initially, lamellae grow epitaxially from the fibre in close-packed array, too close together for others to form between them, so that rejected species can only accumulate ahead of the growth envelope. The more-branched molecular sequences rejected at the growth front in this polymer lower the equilibrium melting temperature and with it the isothermal supercooling for continued growth.
3. The lowering of supercooling with increasing radial distance is attested by several factors: the physical texture becoming coarser and lamellae thicker, the change in lamellar habit and the continuous decline of the isothermal growth rates.
4. Spherulites of this branched polyethylene always grow faster than rows because their more open crystal–melt interfaces give lower concentrations of impurities.
5. The depth at which instability sets in and the average distance between spherulitic nuclei both increase with crystallization temperature, the former only slightly. It is suggested that nucleation occurs where fluctuations have reduced the concentration of segregated species and found that the internuclear distance scales approximately as the inverse one-third power of the initial growth rate.
6. No such instability or cellulation is found for spherulites growing adjacent to the rows even though their characteristic dominant/subsidiary microstructure is present from the outset, thereby confirming in a particularly clear way that morphological instability is not the cause of spherulitic growth in polymers.

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