On circular crystals of polyethylene*

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Individual lamellae of anabaric polyethylene have been studied after extraction from their matrix. Those formed as a minority component (below the triple point) at 0.3 GPa are circular discs with tapering edges and diameters of tens of micrometres. As recovered, they show an internal microstructure composed of three sets of lines at ~60° to each other. These are a legacy of the hexagonal-to-orthorhombic transition and confirm the anabaric origin.

The discovery of circular habits supersedes earlier observations of elongated crystals, then considered to have formed anabarically, although this attribution raised a problem in that they did not possess the symmetry of the high-pressure phase. In fact, these elongated lamellae are elliptic and closely resemble those formed from the melt at low supercoolings at atmospheric pressure. It is suggested that they would in practice have crystallized in the orthorhombic structure.

The circular habit must make niches available at the highest growth temperatures and thereby raises problems for kinetic theories, which currently predict regime I growth (on planar facets) at low supercoolings. Whereas recent developments have given an explanation of elliptic habits in terms of differences between types of close-packed growth surfaces in the orthorhombic phase, this possibility does not exist for the two-dimensional hexagonal structure of the anabaric phase. The phenomenon seems rather to be a result of surface roughening.

Following crystallization at 0.5 GPa, anabaric lamellae have only been extracted from blends. Those isolated from the interior of a 5% blend with branched polyethylene have a more feathery habit suggestive of incipient spherulitic growth but have still grown as discs of constant shape. It is, therefore, unlikely that segregation of impurities could have caused the perturbation from a circular habit.

(Keywords: polyethylene; crystallization theory; spherulites; high-pressure growth; lamellar habits; melt growth)

INTRODUCTION

Discussion of the implications of curved growth faces observed on polymer lamellae has been a strong stimulus to recent developments in theories of polymeric crystallization. The earliest observations of polymer lamellae revealed habits based on planar faces. These were macroscopic lozenges, squares and hexagons according to the crystal symmetry or degenerate forms that, via microfacetting, could show a range of shapes from macroscopically curved outlines to dendrites[1]. Further investigations showed that lamellae were not always polygonal but, in some systems, could have microscopically rough outlines with no planar facets apparent[2].

Kinetic theories of lamellar growth have been developed assuming polygonal habits. They have considered the nucleation barrier to be surmounted when a new layer is added to a pre-existing planar facet. These theories have proved capable of explaining many observed phenomena, notably changes of kinetic regime according to the relative rates of nucleation of a new layer and its spreading on a planar substrate[3]. According to a simplified explanation, regime I, at low supercoolings, would correspond to faces that remained planar because the nucleation rate i was much less than the spreading rate g between centres a characteristic length L apart. By contrast, surfaces formed under the lower-temperature regime II would be rough because $i \sim g$. A third regime is predicted at temperatures below regime II when L reduces to intermolecular dimensions[4].

Stimulus to the recent development of these theories has come in large measure from the insistence of Sadler: first, that the quantitative enhancement of niches or microfacets, long observed to grow at constant shape, was much less than predicted[5]; secondly, that the outlines of polyethylene monolayers grown under a variety of conditions from solution showed a pronounced curvature, increasing with decreasing supercooling, of what are still termed the $\{2\,0\,0\}$ faces[6]. Such curved faces must be rough, with many niches, and so present no nucleation barrier to growth, thus calling into question the basis of kinetic treatments. Sadler pointed out that surface roughness should be anticipated *a priori* at high crystallization temperatures on arguments first proposed by Burton, Cabrera and Frank[7]. Moreover, models based on rough surfaces and molecular continuity (the roughness-pinning model) could, he proposed, reproduce observations of lamellar thickness and growth rate as an alternative to models based on nucleation[8].

In a recent contribution from this laboratory we have extended the observations of curved habits to melt-grown monolayers of polyethylene[9]. Such lamellae, grown under regime I conditions, were extracted from their quenched matrix and examined in the electron microscope. They showed continuously curved (elliptic)* habits and contained two distinct sectors, one for each growth face,

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implying a degree of regularity in folding and thereby establishing continuity with observations from solution growth.

These observations of curved habits have, nevertheless, been given an explanation by a development in nucleation theory[11]. According to this, the long elliptic facets represent a steady-state profile of stepped {2 0 0} surfaces formed under regime II, whose lengthwise growth along *b* is controlled by microscopic planar {1 1 0} facets growing in regime I. The substrate length *L* of these facets is predicted to be 'within a factor of about two of 21 nm', a dimension so small that it is difficult to be categoric as to whether they are or are not absent from the elliptic crystals examined. In some instances small facets as wide as ~100 nm are clearly present[9]. In this treatment there is no longer any nucleation barrier to form niches on the stepped {2 0 0} faces, but a free-energy barrier is still taken to exist because of lattice strain due to expansion of the lattice to accommodate folds. This would only apply to folding on {2 0 0}, not along {1 1 0} planes. Several quantitative assessments follow from this model, including the early melting of {2 0 0} compared to {1 1 0} sectors, first observed 30 years ago[12]. A value of strain energy in the {2 0 0} sectors of only 1.82 mJ m^{-2} is calculated to be sufficient to account for observations[11].

This explanation is very specific to crystals with orthorhombic or lower symmetries in its reliance upon differences in strain energy between two types of close-packed growth plane. It is interesting, therefore, to consider the examples of curved surfaces in systems of higher symmetry where there is only one type of close-packed growth plane. These have recently been encountered in a study of melt-crystallized poly(4-methylpent-1-ene) in which the familiar square habit progressively changes to circular with increasing crystallization temperature[13]. There are similar reports in the literature for other polymers. It is the purpose of this paper to report the observation of circular lamellae in melt-crystallized polyethylene. They were grown at high pressures, forming as the disordered hexagonal phase[14]. Their existence removes an apparent anomaly from understanding of the crystallization of polyethylene at high pressures. In the context of crystal growth theory for polymers, their crystal symmetry is too high to apply the differential lattice strain model to explain curvature, nor would such thick lamellae be expected to be influenced significantly by lattice strain. It appears rather that these circular lamellae provide an example of curvature due to surface roughening at the growth temperature.

EXPERIMENTAL

The crystals to be discussed formed from linear polyethylene crystallized at moderate pressures. Three grades of Rigidex polyethylene (BP Chemicals Ltd) were used; their molecular masses as determined by gel permeation chromatography are listed in *Table 1*. For reasons to be explained, blends of linear polyethylene with a low-density polyethylene were also examined. This latter grade is denoted LDPE6 (RAPRA, UK) and has a melt index of 200, i.e. very low molecular mass.

Table 1 Molecular masses (10^3 g mol^{-1}) of the three grades of polyethylene used in this work[a]

Polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Rigidex 9 (R9)	9.3	164	17.7
Rigidex 50 (R50)	11.6	67.8	5.9
Rigidex 140-60 (R140-60)	14.2	91.7	6.5

[a] Data supplied by PSCC, RAPRA, Shawbury, Shropshire, UK

It was established in earlier work that, close to the melting point at pressures above ~3 kbar (0.3 GPa), depending on molecular length, linear polyethylene exists as a new phase[15,16], which shows two-dimensional hexagonal packing. Crystallization at 5 kbar usually yields close to 100% of this disordered hexagonal (or anabaric) phase, although when returned to atmospheric pressure the crystals will have transformed to the orthorhombic structure[17]. Chain extension is expected to be constant in this transition and the presence of the typical thick lamellae may be assessed from their high melting point of ~140°C. The proportion of material crystallizing into the anabaric phase falls rapidly near and below the triple point because of kinetic competition with orthorhombic crystallization from the melt[17]. Control of crystallization pressure in the range 2–3 kbar[18,19] thus allows the preparation of samples containing thick, anabaric lamellae, as a dilute suspension (a few per cent) in a matrix of lower-melting polyethylene that crystallized directly as the orthorhombic phase. Such crystallizations were carried out in the high-pressure apparatus described previously[20].

Samples wrapped in aluminium foil were suspended in a silicone-oil-filled pressure chamber subject to a controlled pressure. The temperature of the system was raised above the samples' melting points, maintained for 15 min and then reduced at a rate of ~2 K min^{-1}. This was a satisfactory procedure for pressures of 2–3 kbar (0.2–0.3 GPa) in that it then proved possible to extract the individual thick (anabaric) lamellae as detailed below. But dispersion of such lamellae was difficult to achieve for samples crystallized at 5 kbar, because they then comprise effectively all the specimen. A preliminary solution to this problem has been to prepare a 5% blend of Rigidex 50 with 95% of the branched LDPE6 mixed together while molten.

The dispersed anabaric lamellae have been isolated in the manner described by Bassett *et al.*[9] for melt-crystallized polyethylene. The matrix was dissolved in decalin at 104°C for 20 h. Dissolution of samples with 5–10% hexagonal-phase crystals was facilitated by the use of an ultrasonic disrupter. The residual crystals were then filtered off and redispersed in butanone prior to electron microscopy. Scanning electron microscopy (SEM) of crystals that had settled on the filter membrane was possible following drying and gold coating. Others of the redispersed crystals were collected on carbon support films, metal-shadowed and examined by transmission electron microscopy (TEM).

RESULTS

Figure 1 shows a representative group of anabaric lamellae (of linear polyethylene Rigidex 140-60), which were crystallized from the melt at 2.3 kbar. They are essentially circular with diameters in the range 10–30 μm.

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* We employ the term elliptic in its botanical usage[10]

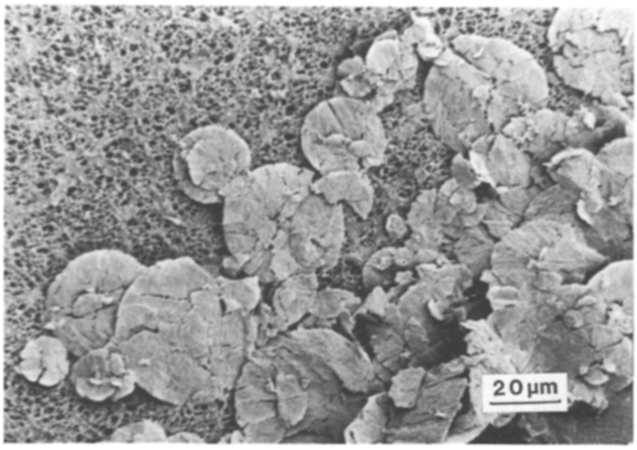

Figure 1 Aggregate of circular lamellae collected on a filter after extraction from their matrix and viewed by SEM. Crystallization pressure 2.3 kbar

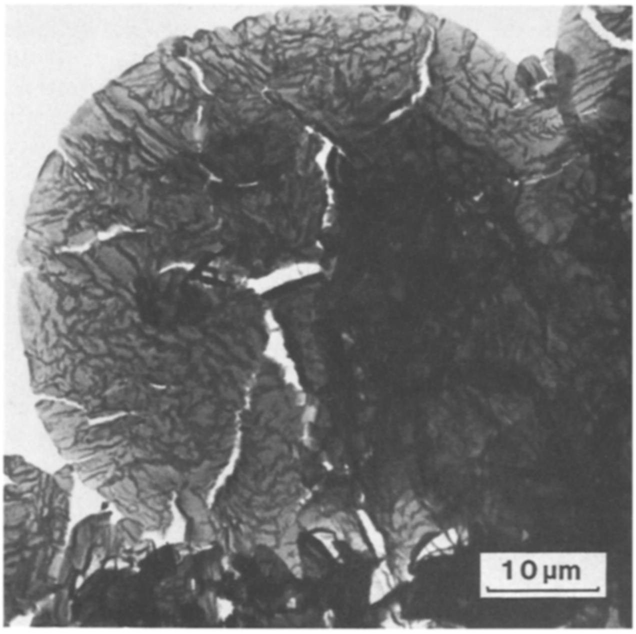

Figure 2 Transmission electron micrograph of an extracted lamella from the same sample as in *Figure 1*. The lighter contrast towards the edge is due to a tapered profile

The majority appear to be monolayers but spiral terraces indicative of giant screw dislocations are also evident (e.g. upper left). The internal structure consists in part of cracks, often linear and sometimes bridged by threads. There are also linear traces, which are seen more clearly in subsequent figures.

Because of their thickness, it is more convenient to study anabaric lamellae using SEM rather than TEM (with 100 kV electrons). Nevertheless, a transmission micrograph of a similar circular crystal is shown in *Figure 2*. This degree of transparency in lamellae some 5000 Å thick is only obtained after holding in the 100 kV electron beam to allow radiation damage to effect a reduction in mass thickness. *Figure 2* confirms the features described in *Figure 1*. It also shows details of the periphery, whose departure from a circle is seen to be small and confined to indentations of less than about 1 µm in depth. The tapered edge profile of anabaric lamellae familiar from replicas[1,17] (cf. *Figure 5*) is detectable as a slight lightening of contrast towards the perimeter, but at this stage of radiation damage the effect is not very marked.

Internal detail is seen to better advantage in *Figure 3*. There are smaller layers, not in contact with their parent, growing in the centre in a manner paralleling observations of polyethylene and other polymers at atmospheric pressure. The linear features are now seen to subdivide the circle into regions and to make angles of approximately 60° with each other. Cracks tend to parallel these lines, in which case they are straight, but can cut across them, in which case they have variable geometry. This latter aspect is prominent in *Figure 4*, where the most striking feature is a spiral terrace of some eight visible turns. Also notable is the corner developed in the basal layer where the outline has developed two planar facets.

Prior to this work, samples similar to those giving the extracted crystals of *Figures 1–4* had been studied in this laboratory either by fracture surface replication or by using permanganic etching[21] prior to electron microscopy. The latter technique applied to the cut surface of a sample provides a representative view of the interior morphology. We have now re-examined such photographs in the knowledge of the existence of circular crystals. One such is shown in *Figure 5*. The central anabaric lamella contains a giant screw dislocation and shows a uniform linear surface striation with a small region of changed

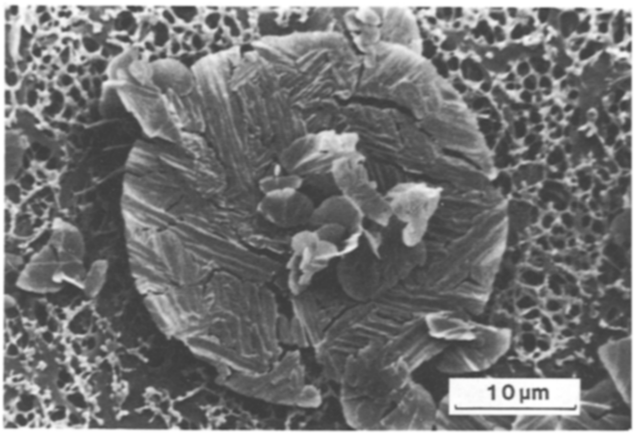

Figure 3 The internal microstructure, consisting of three sets of linear features initially inclined at ~60°, is evidence of the hexagonal-to-orthorhombic transition within the circular lamellae

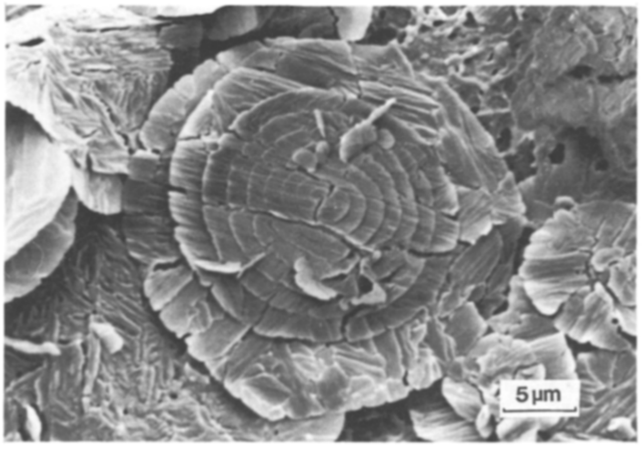

Figure 4 A spiral terrace around a giant screw dislocation in the sample of *Figure 1*

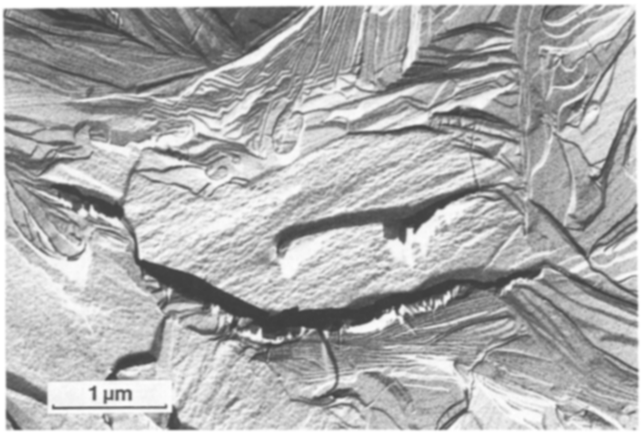

Figure 5 Anabaric lamellae in their surrounding matrix of thin lamellae crystallized directly as the orthorhombic phase. Replica of an etched cut surface of a sample crystallized at 2.3 kbar. Note the giant screw dislocation and the linear texture of the basal surface of the central anabaric lamella. Above and below this are the thin lamellae of the matrix. Their ridged habit indicates crystallization in regime I. At the upper right the parallelism of ridges in the matrix with the linear texture of the anabaric lamella suggests that the lines are along b and that both basal surfaces are of $\{2\,0\,1\}$ type. (Micrograph courtesy of Dr A. M. Freedman)

direction at its extreme left. The lamellar outline appears roughly circular, though it cannot be assumed that this is the original growth surface. Surrounding this on all but the lower left corner are the thinner layers of the matrix. Some of these (upper centre) reveal the ridged orthorhombic habit familiar from crystallization, within regime I, *in vacuo*[22,23].

So far we have taken advantage of the fact that at moderate pressures anabaric lamellae can be prepared as a small percentage of the sample. Most studies of anabaric polyethylene have, however, been made at 5 kbar, where all but the shortest molecules crystallize in this form[20,24]. Unless one can interrupt crystallization by quenching, which is difficult to achieve, one then cannot obtain anabaric lamellae dispersed in a matrix. As one means of addressing this problem we have crystallized dilute blends of linear with branched polyethylene. The matrix of branched molecules is then readily extracted. *Figures 6* and *7* are of anabaric lamellae isolated in this way. They show lamellae that are still planar (*Figure 7*) but now display a markedly indented periphery. This shows two periodicities, the coarser at 2–3 μm giving a rosette appearance and the finer, at a little under 1 μm, adding a fringe to this profile. Internal lines are still present. Sometimes these can be parallel to the faces of the exscribed hexagon (e.g. bottom of the upper left lamella in *Figure 6*); in other places they extend radially to the growth tips. In this latter instance the lines are continuous from the centre of a lamella, or very close to it, demonstrating the stability of the growth profile with lamellar size.

DISCUSSION

The remarkable circular crystal habit reported here has implications for the understanding of high-pressure crystallization of polyethylene, for kinetic theories and for spherulitic growth. We shall discuss these aspects in turn.

Concerning high-pressure (anabaric) crystallization, the first point to make is that the circular habit has not previously been identified, although in the experiments just described, we have found it to be universal. The resolution of this paradox probably lies in the restricted information given by the various techniques used to examine the product. As such, it is a cautionary tale of how partial our morphological information can be.

The first[25] and most widely used technique of viewing anabaric (so-called chain-extended) polyethylene has been replication of fracture surfaces. Because fracture occurs preferentially in $\{2\,0\,0\}$ planes[22], fracture surfaces sample the cross-sections of lamellae. The chain axis c lies in them and is visible as the direction of a characteristic striation[25]. Lateral habits are very rarely evident but have been seen in lamellar fragments dispersed following degradation with nitric acid[26]. General views of the morphology have become available following the introduction of permanganic etching prior to electron microscopy[21]. Etching of cut surfaces reveals random views, including, for the first time, the fine structure of the basal surfaces[1,27]. This shows linear traces (*Figure 5*) presumed to be parallel to the orthorhombic b axis, which is the common direction if the anabaric phase transforms to orthorhombic with $\{2\,0\,1\}$ surfaces[1]. While crystals grown at the usual

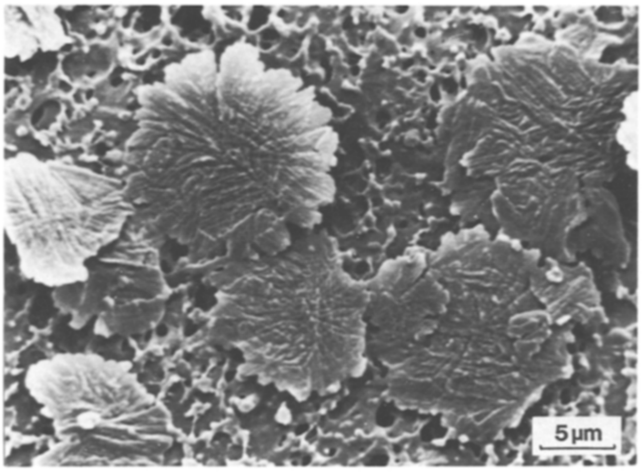

Figure 6 SEM photograph of linear polyethylene lamellae crystallized at 5 kbar as a 5:95 blend with branched polyethylene after extraction and collection on a filter. Note the lines extending to near the centre of the upper left lamella revealing the continuity of habit during growth

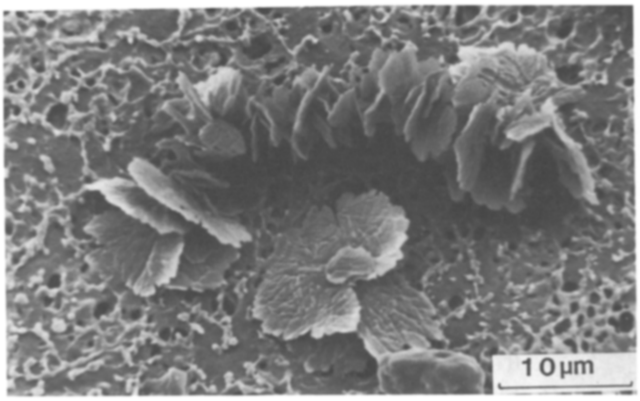

Figure 7 The same sample as in *Figure 6* showing the planarity of the individual lamellae

0.5 GPa (5 kbar) show much evidence of lateral impingement, circular habits should have been found, especially in the dilute dispersions of anabaric lamellae grown at lower pressures as in the present work. One reason why this has not been recognized is probably the limited amount of work on this type of specimen. A second is the small chance of achieving the precise orientation needed to reveal the whole, or a sufficiently large, portion of a lamella to display the curved edge. Although with hindsight such views do seem to be present (see, for example, figure 7.13 in ref. 1) there has also been a presumption in favour of other elongated habits from optical studies in the diamond anvil cell.

The diamond anvil cell[28] permits optical and X-ray studies of systems at high pressure. It was first used in an earlier version to study the solidification of polyethylene by Jackson, Hsu and Brasch[29]. Anabaric crystallization was observed to occur as cigar-shaped objects, which, it has since been confirmed, are also views of lamellar cross-sections, i.e. with molecules lying in the plane of the cell. While this orientation is at least in part introduced by compressing the sample into the cell, one would also expect to see flat-on lamellae, despite their inherently low contrast, especially for crystallization over long times when any memory of initial strain will have been lost. This is the case but the crystals that have resulted have been elongated, appearing more or less diamond-shaped within the cell[1,30,31]. It has been correctly concluded from X-ray studies (though the poor photographic reproduction in the journal does not allow the reasoning to be confirmed) that, in the orthorhombic state, the b axis is that of the long axis of the crystal[31,32].

These observations have presented a puzzle, which the present paper can resolve. It is that the elongated habit has lower symmetry that the two-dimensional hexagonal cell of the anabaric phase[14]. The habit of a hexagonal layer must have hexagonal symmetry, i.e. whether the faces are planar or curved, their normals must be invariant to a six-fold rotation. This is a considerable difficulty, being based on symmetry, for which there seemed no obvious solution. Now the observations of this paper suggest a simple resolution of the problem. It is that the elongated crystals observed previously formed not as the anabaric phase but as the orthorhombic. The circular lamellae are of anabaric polyethylene and their habit does not conflict with symmetry criteria because it is invariant against a six-fold rotation.

This interpretation is strongly suggested by the results of recent work on isolated melt-grown crystals of orthorhombic polyethylene[9]. The habit of lamellae formed at high crystallization temperatures (regime I) at atmospheric pressure is elliptic, a description we have borrowed from botanical usage[10]. They are elongated along the b axis with a biconvex outline. They have been studied after extraction from their surrounding (and lower-melting) matrix by selective dissolution. The same technique lends itself to extraction of the high-melting anabaric lamellae, provided they are sufficiently isolated. The first illustration of a monolayer extracted in this way from polyethylene crystallized at high pressure showed a lamella with an elliptic habit, but with a lower aspect ratio (length/breadth) than for those grown at atmospheric pressure[33]. In contrast, our observations reported above have shown only circular habits. There is thus a dichotomy in observed habits. One is closely similar to the known habit of lamellae crystallized with the orthorhombic structure. The other is novel and, for reasons to be discussed below, evidently formed initially as the anabaric phase.

The evidence that the circular lamellae are the anabaric component of the sample comes in the first instance from knowledge of the parent sample. This has the divided melting endotherm and the two-component morphology used in the original demonstration that the thick crystals produced at high pressure result from a first-order transition from the melt to the then unknown high-pressure phase[15,16,18,19]. The 'cigar-shaped' bodies seen optically are characteristically striated in fracture surfaces or, in the more general views allowed by permanganic etching of cut surfaces, appear as in *Figure 5*. The extracted circular crystals have the same order of thicknesses and lateral dimensions as this previously identified anabaric component. Although this formal argument needs to be put, there is no reason to doubt that the extraction procedure is yielding substantially unaltered lamellae. There is no evidence that the circularity is an artefact; that would also be inconsistent with the work on the orthorhombic elliptic crystals whose habit has been shown to be unchanged by the same extraction procedure[9].

Corroborative evidence can be found in the interior of the circular lamellae, specifically in the three sets of linear traces therein. Such traces are a phenomenon discovered with the application of permanganic etching to anabaric polyethylene[1,27]. It was inferred, from parallel overgrowths (cf. *Figure 5*) and other features, that after the hexagonal-to-orthorhombic transition the basal surfaces of lamellae tend also to be $\{2\,0\,1\}$[1,27], the typical fold surface of polyethylene crystallized from the melt at atmospheric pressure[22,34]. It is known, from extinction directions observed optically between crossed polars, that in the anabaric phase molecules are normal to lamellae[1]. To achieve $\{2\,0\,1\}$ basal surfaces, the hexagonal-to-orthorhombic transition would involve shear displacements of $\{2\,0\,0\}$ planes in the c direction. If this were inhomogeneous, such that successive $\{2\,0\,0\}$ planes were not uniformly displaced, linear traces parallel to b would occur on the basal surfaces. The known observations are consistent with this interpretation. There would be three sets of lines, aligned at approximately 60° to each other, because the orthorhombic b axis can be aligned parallel to any of the three hexagonal axes (x, y, u) of the anabaric phase. The precise value of the near 60° angle will depend on the constraints of the transformation in a similar way to a previous discussion[35].

It is worth pointing out that the three sets of lines are internal evidence of single-crystal orientation within the circular lamellae when in the anabaric phase. The precise orientation of the lines has not yet been confirmed by electron diffraction, because the crystals are too thick to transmit 100 kV electrons in their undamaged state. Nevertheless, there is a strong presumption that they are along b, from their parallelism to the known b direction of ridged habits in the adjoining matrix (*Figure 5*)[22].

As a final comment on the crystallographic orientation within anabaric lamellae, it would follow that an elliptic lamella, grown in the orthorhombic structure and then annealed into the anabaric phase, would have one of the hexagonal axes x, y or u along its length. This agrees with an earlier conclusion[31] (although for the reasons cited it is difficult to confirm the argument). However, the converse, that lamellae formed anabarically would be 'needle-like' with a hexagonal axis along their length, would clearly not be true. They would then be circular and could not show this feature.

Competitive growth

We now address the question of how elliptic orthorhombic crystals grow at pressures below the orthorhombic/hexagonal/melt triple point. We base this on the concept of kinetic competition between crystallization from the melt alternatively into orthorhombic or hexagonal (anabaric) phases. This was an essential step in demonstrating that the then unexplained phenomena of high-pressure crystallization were due to the intervention of a predicted new phase[16,17]. In the isobaric crystallization of tolerably sharp fractions (polydispersity 1.13) it was found that, over a 5 K interval of supercooling, the product of crystallization from the melt changed from all anabaric to all orthorhombic[19]. These conditions lie below the triple point. The suggested explanation is that the supercooling of the orthorhombic phase with respect to the melt is increased but that of the now metastable anabaric phase is decreased until their respective crystallization rates become comparable. It follows that if one wishes to crystallize polyethylene to a particular proportion of anabaric phase then there is only one condition available, with no choice, at least for a given molecular weight. Crystallization then occurs at a particular rate, appropriate to the supercoolings of the two competing phases. There is no possibility of crystallizing more slowly while retaining the same conversion rate. An isobaric increase of crystallization temperature would simply increase the anabaric fraction[19]. Conversely, crystallization on cooling, i.e. with progressively increasing supercoolings, will increase the orthorhombic fraction. One has, therefore, virtually no control over the rate of supercooling under which anabaric lamellae grow as a small proportion of the sample. The timescale is of the order of 1 h and the orthorhombic supercooling approximately 10 K[19]. One would thus expect the orthorhombic component to have formed in regime I (by comparison with the 17 K supercooling of the regime I/II transition at 1 bar)[3]. The ridged habits visible in *Figure 5* confirm that the matrix did indeed crystallize in regime I[22,23].

The situation is different for crystallization in the gasketed diamond anvil cell. For isothermal crystallization this will approximate closely to constant-volume conditions[14], because nearly all the impressed force is supported by the metal gasket. Even for crystallization on cooling, a choice of gasketing material such as Inconel, with a low coefficient of expansion, will not change matters very significantly. It follows that, during crystallization, sample pressure will fall to maintain the volume constant. For isothermal conditions supercooling will thus decrease (as the melting point falls) and growth rates will slow. With suitable choice of initial conditions, one can indeed observe crystallization rates to slow down and decrease eventually to zero. The fall in pressure will mitigate against anabaric crystallization while the fall in supercooling will reduce nucleation rates and produce larger crystals. It is in just these circumstances, namely crystallization for many hours below the triple point with a small anabaric population, that we have observed large elongated (we would now infer elliptic) crystals develop[30].

This scenario is, we believe, sufficient to account for the occurrence of circular anabaric and elliptic orthorhombic lamellae for crystallization when both phases compete to crystallize in the diamond anvil cell below the triple point. Only circular anabaric crystals would result for isobaric growth but conditions will move towards those giving elliptic crystals when pressure falls as crystallization proceeds. This explanation can go further and account for the seemingly anomalous crystallization kinetics reported for studies with the diamond anvil cell.

Data now exist showing that polymer lamellae normally show a linear increase of dimensions with time whether growing from solution or melt. The principal exception has appeared to be studies with the diamond anvil cell in which lamellar size has been reported to increase not linearly but as the square root of elapsed time[36]. If true, this would undermine the position we have always adopted, namely that anabaric crystallization is a valuable model for polymeric crystallization, differing from other systems only in the properties of the anabaric phase[24].

We have returned to this problem after an interval principally because of the interest in the profile of the edge of a melt-crystallized lamella engendered by Sadler's proposals. In his theoretical models a lamella can only advance when all stem lengths out to the periphery are complete, i.e. the profile would be rectangular[6]. It is well known that, on the contrary, the edge profile of anabaric lamellae is tapered. We have investigated tapering and its time dependence in a parallel investigation. Other work in the laboratory has examined the quantitative reduction in growth rates in the diamond anvil cell as crystallization proceeds. This has confirmed that the apparent departure from linear growth rates is an artefact of the concomitant continuously falling pressure[37]. In summary, the position now established is that elliptic lamellae are orthorhombic while anabaric lamellae are circular (at least when formed at ~0.3 GPa). Furthermore, our contention that anabaric crystallization of polyethylene is a valid model for polymeric crystallization in general has been strengthened.

Implications for kinetic theories

The ingenious explanation of Hoffman and Miller[11] whereby curved surfaces of the elliptic habit, with their concomitant niches at the molecular level, can be accommodated within an extended kinetic theory does not appear capable of accounting for a circular habit, not at least without further modification. The reason is that the present extension depends upon contrasts between different close-packed growth planes, i.e. $\{1\ 1\ 0\}$ and $\{2\ 0\ 0\}$ in orthorhombic polyethylene. One set, $\{1\ 1\ 0\}$, is assumed to grow in regime I and have no strain energy, while the other, $\{2\ 0\ 0\}$, has strain energy and grows in regime II. As no system with symmetry higher than orthorhombic can differentiate between different close-packed planes, we do not yet have the basis of a kinetic explanation for curvature in tetragonal or hexagonal polymer structures.

It is also pertinent to enquire whether curvature in such high-symmetry systems has the same origin as that of elliptic habits in orthorhombic polyethylene. The latter has been quantitatively accounted for on the basis that it is the dynamic profile of incomplete $\{2\ 0\ 0\}$ strips resulting from the constraints of $\{1\ 1\ 0\}$ surfaces growing at the tips of the lamellae[38]. The former may, on the other hand, indicate surface melting, as cited by Sadler[5], following BCF theory[7]. The prediction is that singularities in the polar plot of surface free energy would disappear at temperatures towards the melting point as surfaces became molecularly rough because of the associated gain in entropy and reduction of Gibbs function.

This topic is wider than polymer physics but it could well be that polymers show examples of this phenomenon. Thus recent work[13] has shown that poly(4-methylpent-1-ene) with an equilibrium melting temperature of 272°C grows from the melt as square lamellae at 225°C but changes progressively, via rounding of the corners, to a circular habit for growth at 242°C[13]. According to existing kinetic theory[11], curved surfaces would have to grow in regime II, i.e. at temperatures lower than for regime I. In our examples these show that rounding increases with crystallization temperature. Moreover, anabaric polyethylene forms at low supercoolings, lower below the triple point than those applicable for the orthorhombic crystallization with which it is competing. *A priori*, therefore, the expectation would favour high-temperature or regime I kinetics, at least until the question can be decided experimentally. These are intriguing possibilities for kinetic theories to address.

Implications for spherulitic growth

The relevance of the present observations to spherulitic growth concerns *Figures 6* and *7* and the reasons for the habit change as compared to earlier figures. What these show is, apparently, the degeneration of the circular habit into 'fibrous' units, thereby inviting comparison with observations of Keith[39]. He published micrographs of four different polystyrene crystals grown in thin films from the melt and inferred that somewhat similar changes occurred as a function of crystal size because of lateral segregation of non-crystallizing species. Attempts to reproduce these phenomena in polystyrene in this laboratory have shown, on the contrary, that the different outlines persisted from the earliest observations and were not a function of size. This is also true of the present observations on anabaric polyethylene, which, with the continuity of internal lines from centre to growth tip, support the view that such habit changes are not a consequence of impurities segregated by crystallization. One must also note that the diffusion conditions are very different. Not only is our system very dilute (a 5% blend) by comparison with a homopolymer blend but growth is occurring in bulk and not in a thin film. The concentration gradients of rejected species will, therefore, be small. They will also be greatest perpendicular to the discs rather than in their planes. We may confidently conclude, therefore, that these departures from a circular habit are not caused by segregation of 'impurities'.

CONCLUSIONS

The principal conclusion of this paper is that circular lamellae are characteristic of high-pressure (anabaric) crystallization of polyethylene at ~0.3 GPa. Earlier and then paradoxical observations of elongated crystals now appear to be a consequence of growth as the orthorhombic phase.

It is also noted that (a) the circular habit probably represents a surface roughening/melting phenomenon whose occurrence in a high-symmetry polymer is a further challenge for kinetic theory and (b) changes in habit suggestive of incipient fibrosity and spherulitic growth observed in dilute blends at 0.5 GPa cannot be attributed to impurity segregation.

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