On the lamellar morphology of isotactic polypropylene spherulites

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The lamellar structures within melt-grown spherulites of the monoclinic form of isotactic polypropylene have been studied by transmission electron microscopy following permanganic etching. Spherulites grown at 160°C are composed solely of α laths which develop in the classical radiating branching manner from axialitic precursors. The branching units are not, however, fibres but individual dominant lamellae as previously found for polyethylene and isotactic polystyrene. The theory of instability of planar interfaces of Keith and Padden is not applicable to this textural situation, although local diffusion fields may add an additional structural dimension to spherulites which form quickly at, say, 130°C. Instead, one may possibly look to pressure from compressed cilia as the cause of splaying between adjacent lamellae. Cross-hatching is present in spherulites grown at 155°C and below in the early stages, and thereafter is concentrated in specific locations and subsidiary lamellae. The cross-hatching members are less stable, probably because they are composed of shorter and/or less tactic molecules.

(Keywords: polypropylene; spherulites; permanganic etching; melt-crystallized lamellae; cross-hatching; electron microscopy)

INTRODUCTION

The technique of permanaganic etching[1,2] has made it possible to examine representative lamellar microstructures within the interior of crystalline polymers. In previous research linear polyethylene[3-6] has been studied in detail over most of its accessible crystallization conditions. Linear low density polyethylenes[7] and isotactic polystyrene[8] have also been investigated, especially at their higher crystallization temperatures. A principal concern of these studies has been the organization of lamellae into spherulites and the information and insight this gives into spherulitic growth. This is important as it underlies any fundamental understanding of structure–property relationship in these systems.

Isotactic polypropylene is known to be a complicated system, even by polymeric standards. In the first instance this was suggested by the changing birefringence of its spherulites[9] and the different crystal forms[10]. Subsequently complex twinning of the usual monoclinic form was revealed and interpreted in lamellar objects grown from solution[11]. Certain ambiguities in the inferred twin law have recently been resolved by Lovinger[12] using epitaxial crystallization of thin films on mica. This complex twinning is frequently referred to as cross-hatching because it appears as fibres crossing each other, ideally at an angle of 80.7°, i.e. nearly orthogonally. Such appearances have been familiar ever since isotactic polypropylene became available and are the typical result of crystallization in thin films. Indeed it is difficult to avoid this complex twinning and to grow untwinned lamellae of the monoclinic form. When these have been grown, they have always been lath like, growing out along $\underline{a}$ (or more

probably $\underline{a}^*$) with a propensity to grow branches at 80° to their {001} faces, but initiating at nuclei on the {010} faces of the laths[13].

The consequences of such twinning provide a natural explanation for the changing birefringence of spherulites of monoclinic isotactic polypropylene. The birefringence of parent and twinned daughter crystals will almost cancel because of their near orthogonal orientations. The net birefringence and its sign will, therefore, depend on the relative proportions of twinned and untwinned components. Lamellae with $\underline{a}^*$ along the spherulite radius will give a negative contribution to the birefringence, as is expected of an aliphatic chain tangential to a spherulite, while the twinned component will make a nearly equal positive contribution. The gradual change from positive to negative birefringence for spherulites of the monoclinic form of isotactic polypropylene with increasing crystallization temperature may thus be interpreted in terms of an excess of twinned component at lower temperatures gradually giving way to an excess of untwinned (normal) component[14]. Padden and Keith[14] also associated the nucleation of branches in the prevalent α-phase with the epitaxial deposition of intervening γ-phase related to the segregation of stereoblock molecules of medium and high molecular weight.

Permanganic etching has previously shown that cross-hatched structures are characteristic of the interior of monoclinic (α) polypropylene[1]. Further examination readily shows that the proportion of cross-hatching does vary with crystallization temperature more or less as Padden and Keith had envisaged[14]. Cross-hatching is not, however, uniform in its occurrence and we shall comment in this paper on the location of the twinned component and the molecules it comprises. Most of all we

are concerned to report on the development of spherulites of the monoclinic form. We show that there is a basic pattern common to polyethylene, isotactic polystyrene and isotactic polypropylene of growth occurring via initial individual dominant lamellae growing out into the melt leaving interstices which are filled with subsidiary lamellae. In polypropylene, at appropriate crystallization temperatures, certain but not all of these interstices are favoured locations for cross-hatching to develop. This morphology of dominant and subsidiary lamellae is not that which the Keith and Padden[15] theory of spherulitic growth was formulated to explain. We shall conclude, therefore, that the Keith and Padden theory is not an appropriate description of spherulites which grow at high crystallization temperatures (low super-coolings) even though, as we shall show for spherulites of the α form, these develop in the classical way from individual units via branching to quasi-spherical symmetry. There must, therefore be other mechanisms causing spherulitic growth at high temperatures. It is suggested, as with isotactic polystyrene[8], that a probable candidate for producing the necessary splaying once layers have branched is pressure due to molecular cilia between the initial dominant lamellae. This is not to dismiss the Keith and Padden theory as irrelevant to spherulitic growth but rather to limit its possible application in explaining actual textural dimensions to lower temperatures and more rapid crystallization. There are indications, in polypropylene, that under such conditions an additional textural dimension may arise in ways similar to those envisaged by Keith and Padden[11].

EXPERIMENTAL

It is generally advantageous in studying polymeric crystallization from the melt to study first objects grown at low supercoolings (high temperatures). This is partly because objects are simpler grown in this way and partly for attendant experimental advantages. These include the greater facility for interrupting growth at any stage, the greater ease of quenching so that the objects grown are better demarcated with respect to their surrounding matrix and especially the greater feasibility of being able to distinguish between the molecular composition of the objects grown at temperature and the remainder of the sample by such means as selective extraction by solvents. For polypropylene there is also a particular advantage in studying high temperature crystallization. It is that twinning, leading to cross-hatching, does not occur at 160°C and is only slightly evident at 155°C. This paper, therefore, concentrates on such high temperature objects, mostly those grown at 160°C, and their development into spherulites. To achieve growth at these temperatures in manageable times it is necessary to resort to special procedures of self-seeding to enhance nucleation rates. One can also control the density of nuclei and thus the eventual size of spherulites in the samples. These procedures are described below.

Techniques of crystallization

The rate of homogeneous nucleation of isotactic polypropylene for crystallization from the melt becomes quite low as the crystallization temperature, T_c, increases to 145°C and above; however, the polymer can be induced to form a small number of well spaced nuclei by a self-seeding technique involving slow heating to near its final melting point. When a rapidly crystallized sample (effective $T_c \sim 110°C$) is heated at 2K/min in a hot stage, the last traces of birefringence are observed to disappear at about 169.5°C. Holding it at this temperature for 24 h will allow some recrystallization to take place even at this temperature, resulting in a faint but perceptible birefringence, and on subsequent melting a small d.s.c. peak at ~182°C. However, if heating is continued to still higher temperatures e.g. 175°C, sufficient nuclei remain to initiate immediate growth if the sample is rapidly cooled to say, 150° or 160°C. The number of nuclei formed is very dependent on the maximum temperature attained, and to some extent, on the heating rate, but the final melting point of rapidly crystallized polypropylene heated at 2 K/min is in the region of 177°C. This is not to be confused with the thermodynamic melting point of infinite extended chain polypropylene which is probably about ten degrees higher than this, though there is much controversy on the subject, with various authorities quoting figures between 183°C and 210°C.

We have used two slightly different techniques to produce firstly, specimens in thick films, quenched to produce a transparent matrix, for optical examination of the early stages of growth followed by electron microscopic examination; secondly, bulk specimens for showing the later stages of growth by optical and electron microscopic techniques.

For the first type of specimen, pellets of the isotactic polypropylene PP1, supplied by the Polymer Supply and Characterization Centre, RAPRA, Shawbury, Shrewsbury, were squashed on a Kofler hotbench to a thickness of approximately 45 μm. They were melted in a Mettler hot stage under nitrogen atmosphere first at 190°C for 5 minutes and then 180°C for 1 h; this treatment allows most of the row nuclei, which are abundant in the original pellets, to melt out. Subsequently the samples were quenched on a cold metal surface at room temperature and then reheated. From 120°C to 150°C the heating rate was 10 K/min and from 150°C to 173.5°C it was 2 K/min. Specimens were finally cooled in the hot stage to 160° ±0.1°C as rapidly as the apparatus would allow (40 sec), and crystallized for 20.2 to 20.3 h at this temperature. After crystallization, samples were quenched in an ice-water mixture producing specimens with matrices of varying degrees of transparency, but in all of which the same type of structures could be observed under the optical microscope.

For the bulk crystallized specimens, moulded discs of PP1, 1 mm thick, were sealed in glass tubes under oxygen-free nitrogen, and melted at 210°–213°C for 5 min. This procedure is necessary to melt out row nuclei which could otherwise give rise to misleading objects in the specimen. The tubes were quenched in boiling water, and then placed in the nucleating bath at 155°C. The first batch was heated at 0.2 K/min and specimens transferred at intervals to a bath at 159.5°C, and crystallized for 43 h. The specimen nucleated at 176°C was found to be satisfactory, with well spaced crystal aggregates sufficient in number for further examination and comparison. The second batch was heated at 0.5 K/min and crystallized at 160°C for 9.72 days, the specimen nucleated at 176.6°C showing a small number of large well spaced spherulites.

Comparison of the size of objects formed gives equivalent growth rates for samples prepared by the two

techniques, and gives confidence that significant degradation has not occurred during the higher temperature melting process.

Microscopy

Bulk crystallized specimens were cut open with a glass-knife microtome and etched for 15 minutes with a 0.7% w/v solution of potassium permanganate in 2:1 concentrated sulphuric acid/dry phosphoric acid mixture, with shaking. Thick films were etched in the same mixture for 1 h with vigorous shaking, to remove any uncharacteristic surface regions.

Etched surfaces are conveniently assessed at any stage using Nomarksi Differential Interference Contrast optics in order to ascertain to what extent texture is being revealed. Good textural characterization at the micron level can be obtained in this way. Finer detail requires electron microscopy. Our procedure has been to make two stage replicas of the etched surface and examine the carbon second stage in transmission. Metal shadowing is given at the first stage, i.e. producing negative contrast on the final replica. It is possible to produce the correct appearance of relief, nevertheless, by suitable rotation of the micrographs. This correct appearance is one of lamellae standing proud of their surroundings.

RESULTS

In examining the spherulitic embryos which first form in growth from the melt at 160°C, one notices mostly two types of appearance in the polarizing microscope. The one (*Figure 1a*) is sheaflike, the other (*Figure 1b*) approximates to two parallel lines ~2 μm apart. It is likely and has been confirmed by viewing the same object in different projections on the universal stage, that these are orthogonal views of similar objects, differing by 90° in rotation about their long axes. Other views are also present and, in particular, smaller projections appropriate to looking down the third rectangular axis, i.e. looking down the long axis of the two previous objects, can also be discerned. It is further noteworthy that the sheaflike objects of *Figure 1a* often appear to be twisted slightly about their long axes in that they are imaged clearly at two focal depths. Opposite 'corners' of the sheaf will be at the same level, while adjacent ones will differ. It should not

be assumed, however, that these two levels necessarily correspond to the two lines of *Figure 1b*.

Although these objects are, for polymers, comparatively simple they have initially puzzling signs of birefringence. The two bright lines of *Figure 1b* are optically positive, i.e. their larger refractive index (slow direction) is along their length. In contrast, the sheaves are negative in central regions but reverse sign and become positive at their extremities. The areas of zero birefringence are visible as broad dark bands in *Figure 1a*.

The explanation of these observations is suggested by viewing of the same objects in transmission phase contrast (*Figure 2a*). In particular it can be seen in *Figure 2b* that what appeared as two bright lines between crossed polars now gives the impression of a lath. As grown, and observed at 160°C on the hot stage microscope, the objects are indeed laths in this projection and only weakly (positively) birefringent (*Figure 3a*). Most of the birefringence contrast seen at room temperature is formed on cooling from the crystallization temperature. *Figure 3b* shows how the appearance of the area of *Figure 3a* has altered when the sample was cooled from 160°C to 20°C. All objects in the lath projection have increased their birefringence contrast, which was barely visible at the growth temperature. Note particularly that the new contrast giving the appearance of two lines appears *at the edges* of the initial area. What has happened is that the additional growth has nucleated on the surfaces of the lamellae grown at 160°C. One would expect this to develop as in row structures, i.e. with new lamellae growing out normal to the nucleating surface. If these new lamellae have either no preferred orientation about their long axes or, at least, are not oriented specifically with their chain axes along the viewing direction, then the averaged chain axis direction will be along the long axis of the lath and give the observed appearance of positive birefringence. So far as the sheaflike projection is concerned, one may note from *Figures 1a* and *2a* that there appear to be interstices at their outer edges but not in central regions. In this case secondary growth on cooling would occur predominantly at the extremities where, if sufficiently dense, its positive birefringence could offset or overcome the inherent negative birefringence of the sheaf and render the outermost edges positively birefringent.
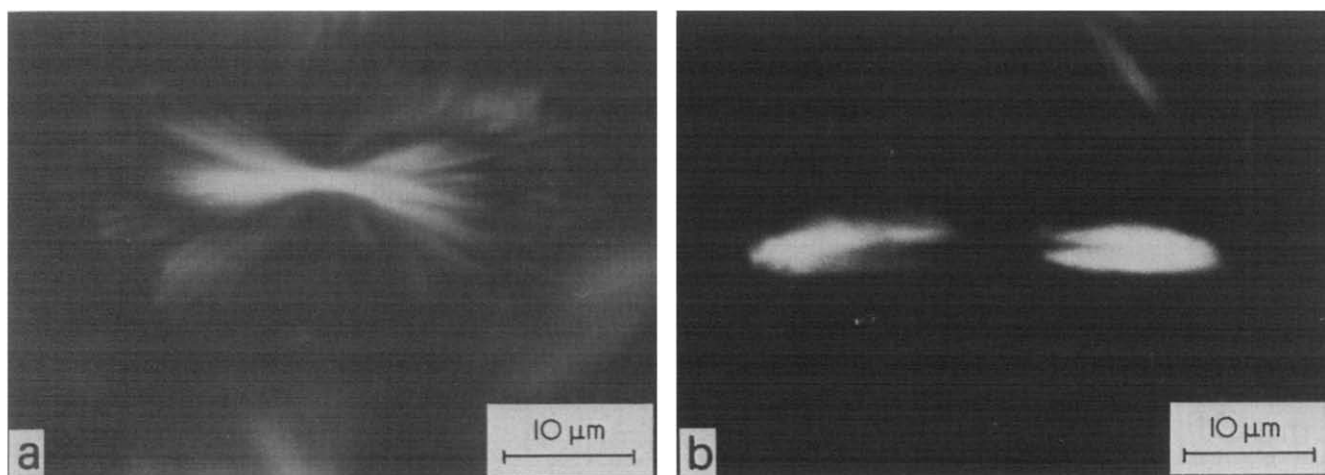
Figure 1 Early stages of spherulitic growth in monoclinic polypropylene after 20.3 h at 160°C, seen between crossed polars; (a) double fan or sheaflike projection, (b) lathlike projection
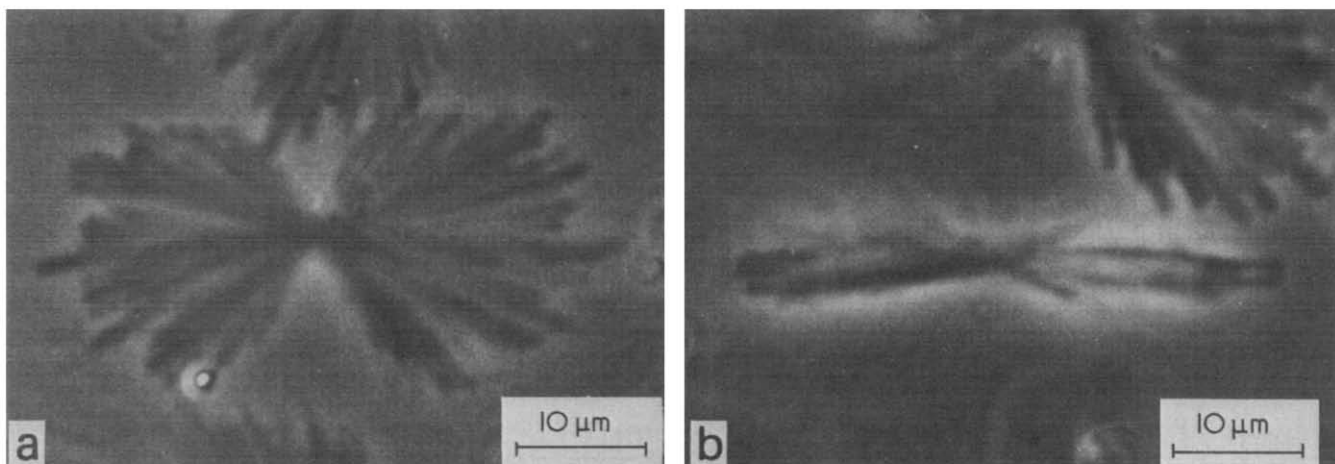
Figure 2 Objects of *Figure 1* seen in optical phase contrast (a) sheaflike projection, (b) lathlike projection.
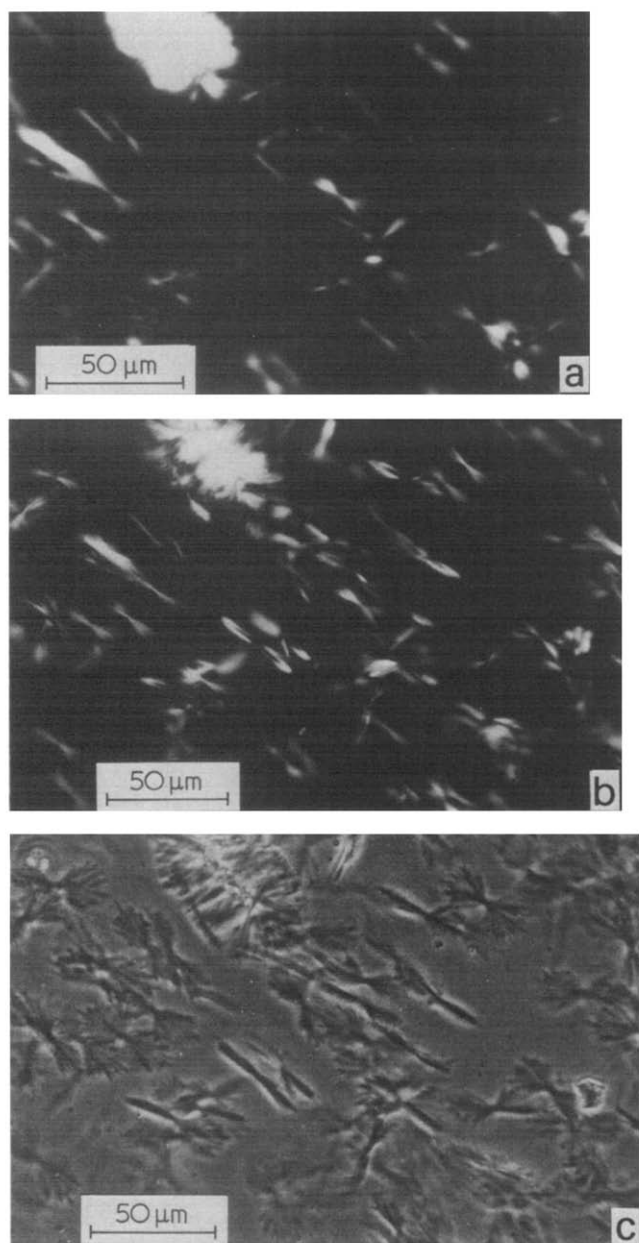

Figure 3 Same area of the early stages of melt growth of isotactic polypropylene at 160°C seen (a) between crossed polars at 160°C, (b) between crossed polars after quenching to room temperature and (c) as (b) but in phase contrast
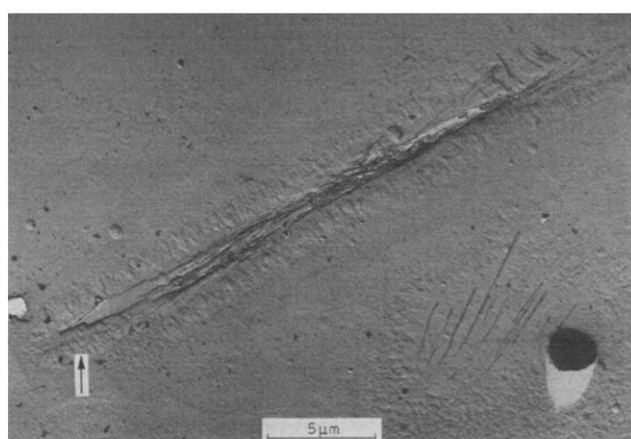

Figure 4 Laths, in the same projection as *Figures 1b* and *2b*, seen in the electron microscope after permanganic etching

These optical observations thus indicate axialites, i.e. lamellae splaying around a common axis. The units of the axialite would be laths of width 1–2 μm. Their thickness is apparently of the same order, according to *Figure 2a*, but one must be cuatious because here we are observing at the limit of resolution of the microscope when broadening of images by diffraction cannot be neglected. Regarding the crystallography of these axialities, one would expect, on the basis of previous studies[12], that the laths would grow along $\underline{a}^*$, and splay about a common $\underline{b}$ axis; $\underline{c}$ would be normal to lamellae.
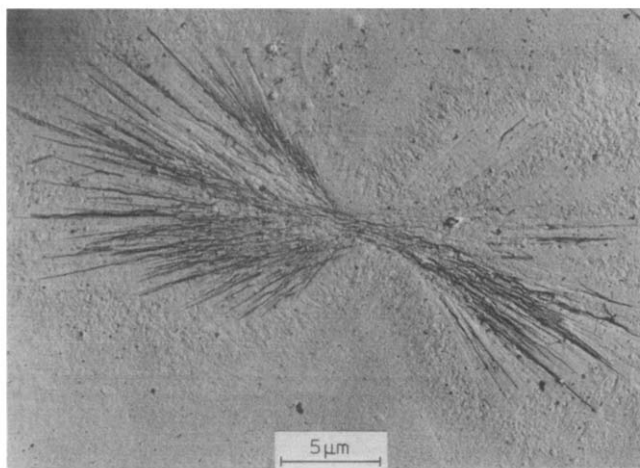
Electron microscopy not only substantiates these inferred morphologies but adds crucial detail. Permanganic etching reveals a surface taken through the interior of the specimen. In such a surface after etching one finds, as expected, many sheaflike views, but clear lath-like appearances are much rarer. This is because to obtain them one must cut through the centre of sheaves as in *Figures 1a* and *2a*. Nevertheless, they do occur; one is shown in *Figure 4*. Even here the alignment is not perfect but one can recognise planar laths at each end, a little under 1 μm wide. In the centre the appearance is rather of having sliced through several laths diverging from a common centre. What is clearly obvious is the envelope of secondary growth extending on all sides for ∼1 μm. It is not certain whether the end of the lath on the left is a true growth face; it could have been broken or attacked during

the etching process. However, underlying this (arrowed) is a second layer only just revealed and protected since the lamella above it is intact, which shows a growth face after etching appearing nearly normal to the length of the lath i.e. approximately {100} if our inferred crystallography is correct.
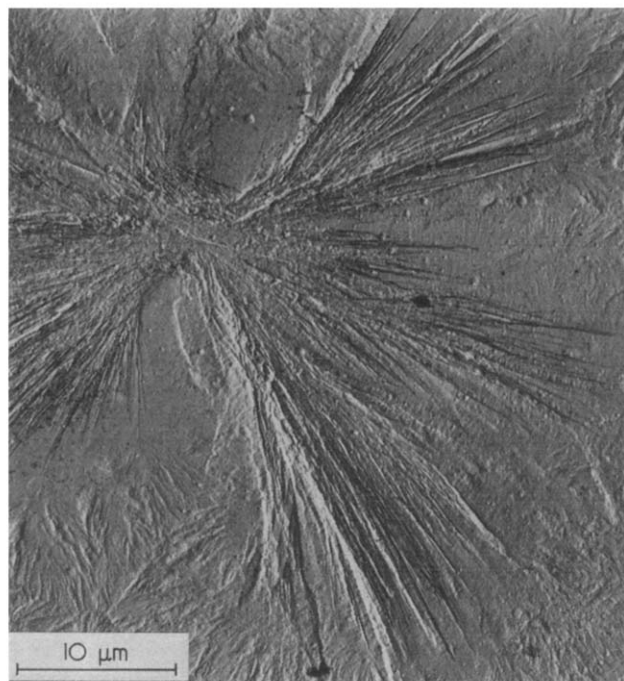
In the lower right hand corner of *Figure 4* one sees the extremity of a sheaf, showing a very important feature, namely that in these regions one has an assembly of more or less equally spaced individual dominant lamellae. A more comprehensive view of another sheaf is shown in *Figure 5*. The advancing regular arrays of dominant lamellae are again most striking. Behind them, by as much as 10 μm, the interstices they have created have been filled by further lamellae. Around the entire sheaf and within every unfilled interstice, one observes the envelope of secondary growth formed on cooling.

Even at these early stages, when the growing objects approximate to two-dimensional axialites, there is still clear evidence of development in the third dimension. It is that often one finds exposed in an etched surface only the opposite extremities of fans or sheaves. These extremities evidently lie in a plane normal to the axis of splay but at a higher (or lower) level than do the central regions.

If these axialites are allowed to grow for longer times they develop into spherulites. A section though an object grown for roughly twice as long as the previous axialites is illustrated in *Figure 6*. One sees the central region of a splaying object which has almost developed the well known feature of 'eyes' or Popoff[16] leaves by encirclement from opposite ends. Two features are worth special comment. One is that what are, in effect, later sheaves have grown out from the central area of the original sheaf. It is these later sheaves which are enclosing the central eyes. This can be seen more clearly in *Figure 7*, which is an enlargement of the central area. The second feature which also requires higher magnification (*Figure 8*) to be identified, is that, at the edges, laths show various orientations about their lengths. For an ideal axialite, they would all be identical (edge-on in this perspective). In fact, flat-on views are also present. Such variation facilitates the attainment of a three dimensional envelope, appropriate to a mature spherulite. Such is seen after 9.72 days growth in *Figure 9*. Notice in this that radial lamellar orientation has now been achieved but the initial sheaf and central eyes formed in achieving this form are still

Figure 6 After 43 h growth at 159.5°C, a sheaf is in process of enclosing central eyes. Etched surface
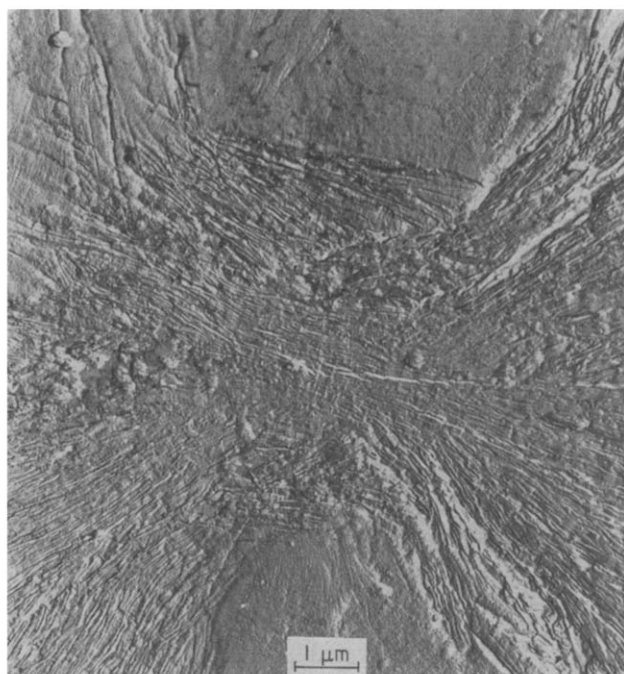
Figure 7 Detail of *Figure 6* illustrating later nucleation on and growth from the central region of the early sheaf

visible. Other objects sometimes show more elliptical outlines which reflect lesser growth times normal to the sheaf than along it. We have, nevertheless, grown objects at 160°C which are essentially spherulites in the strict sense of that term, in that lamellae are growing radially outwards along the same crystallographic direction, presumably a^{*}[12]. They have done so through the classical construction of continued splaying and branching. However, the objects which splay and branch are not multilamellar fibres as has previously been assumed, but individual dominant lamellae.

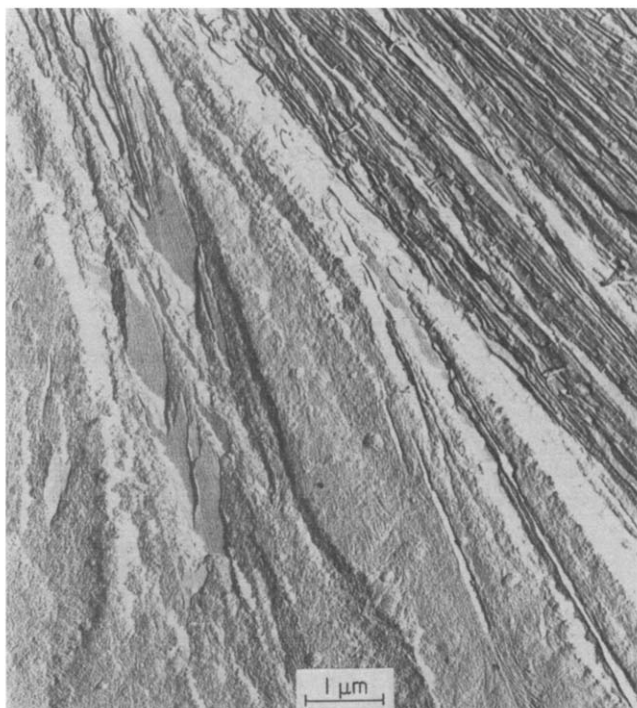We now briefly outline results of crystallization at

Figure 5 Sheaflike or double fan appearance, as in *Figures 1a* and *2a*, after permanganic etching. Electron micrograph

Figure 8 Detail of *Figure 6* showing the variation in lath orientation in peripheral areas
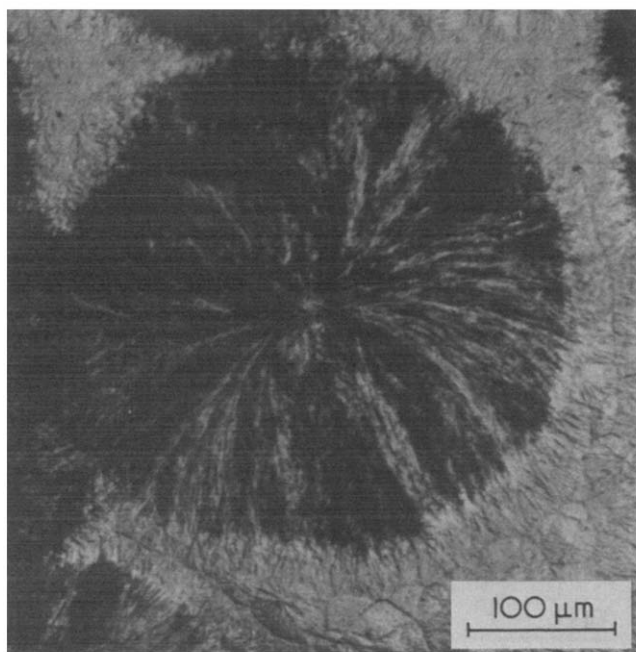

Figure 9 One-time sheaflike object has become a mature spherulite after 9.72 h growth at 160°C. Nomarski interference contrast optics, etched surface

lower temperatures which are relevant to the role of twinned lamellae and cross-hatching. The development of spherulites becomes more complicated under these conditions and fuller results will be published elsewhere.

Essential details are that at 155°C and below, the early object is no longer the double fan or axialite described above for growth at 160°C, but consists of two sets of lamellae inclined at approximately 80° to each other. The appearance is similar to that of solution-grown objects observed by Khoury[11] and it may be inferred that the two sets of lamellae are also twinned with a common *b* axis.

However, in more mature objects, sheaves of radial lamellae have developed. Dense cross-hatching is evident at their centres but this feature is virtually absent at the edges of sheaves. Apart from the very early stages, it is observed at 155°C and below that spherulites still develop from radiating individual dominant lamellae. In 155°C-grown material the morphology away from spherulite centres is still quite similar to 160°C-grown but for growth temperatures of 150°C and below increasing amounts of cross-hatching rather than parallel subsidiary lamellae fill the gaps. These cross-hatching lamellae are less stable than the radial laths. They are preferentially removed in permanganic etching and they have a lower melting point. Indeed it is possible to convert an initially positively birefringent spherulite grown at 115°C with an excess of cross-hatching into a negatively birefringent one simply by heating at 163°C and melting the cross-hatching lamellae out. They do not then reform in the twinned orientation on holding indefinitely at 155°C, but are replaced by parallel lamellae.

A further illustration of the selective locations of cross-hatching is provided by *Figure 10*. It shows a section through a spherulite grown at 150°C. The point of interest is that one has a prominent sheaf (with some cross-hatching visible in and retricted to regions between radial lamellae) with the remainder of the cross-section densely and finely cross-hatched throughout. In many instances the cross-hatched region can be seen to have nucleated and grown away from the sides of the sheaf. It is this difference which the etching is revealing in making the sheaf so prominent. It is also quite characteristic that such regions, including eyes, between developing sheaves are profusely cross-hatched in contrast to the sheaves themselves.

Further work has shown that these objects are in fact built up from two sets of sheaves at approximately 80° to each other, derived from the two sets of lamellae in the original object. The elliptical appearance of the object shown results from a section being taken through one of the sheaves but diagonally to the other.

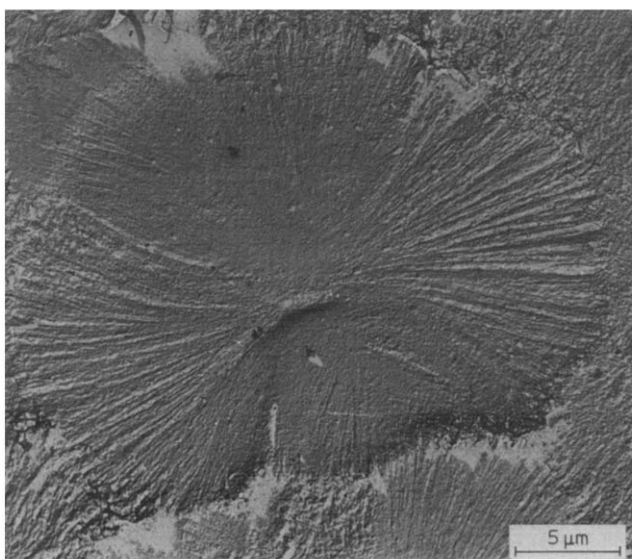Finally, when spherulitic growth is sufficiently fast, as at

Figure 10 An isotactic polypropylene spherulite crystallized at 150°C for 3 h. Cross-hatching is mostly present in lateral regions surrounding the sheaf of radial lamellae but may also be discerned as subsidiary lamellae between them. Etched surface

130°C, one sees what appears to be another textural dimension superposed on the prevailing pattern of dominant radial and subsidiary cross-hatching lamellae. It may be that this is a dimension of a kind relevant to the Keith and Padden theory. Certainly the appearance is strikingly similar to those obtained by crystallization of binary eutectic alloys of organic compounds under conditions of constitutional supercooling[17] (*Figure 11*).

DISCUSSION

The principal point we wish to discuss is the implication of the morphologies found in spherulites of monoclinic isotactic polypropylene grown at 160°C. This polypropylene system confirms the trend found previously for polyethylene[3,6,7] and isotactic polystyrene[8], showing particularly clearly that the problem of spherulitic growth is not what had previously been assumed. It had been thought that the problem was one of accounting for the splaying and branching growth of fibres. Keith and Padden[15] specifically addressed the problem of the instability of a planar interface to fibrillation caused by the accumulation there of uncrystallizable or slower-growing molecular species. What we now know, from study of these polyolefins, is that the problem is, instead, one of accounting for the splaying and branching growth of individual dominant lamellae. Subsequent growth, which can lead to a seemingly fibrous texture, is shown to be a secondary phenomenon, occurring after the essential spherulitic geometry has been established.

The first spherulitic system to be examined in detail was linear polyethylene of 2.6×10^4 molecular mass, crystallized at 130°C. This gave the most regular morphology found in polyethylene, consisting of individual ridged $\{201\}$ dominant sheets ~ 3 μm wide and separated by ~ 0.5 μm. Because these sheets are non-planar, they come into contact and create small volumes which have the appearance of growth cells. These were not
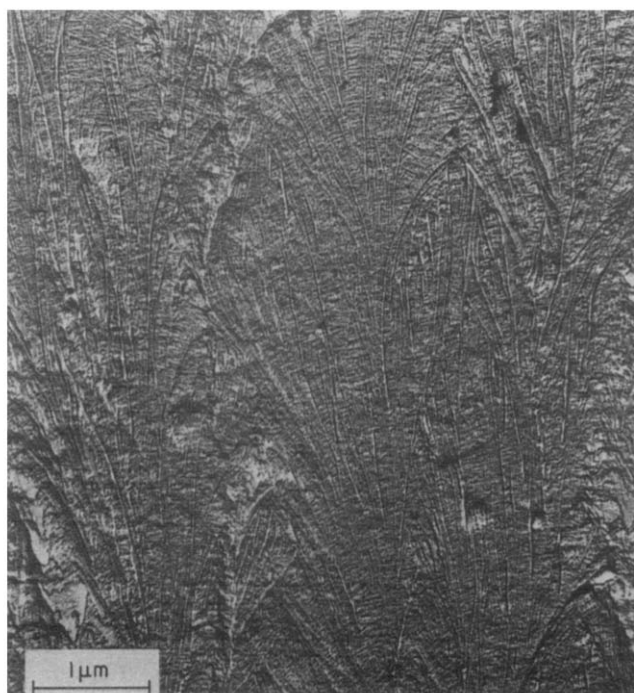
Figure 11 Interior morphology of monoclinic isotactic polypropylene crystallized at 130°C, with a morphology apparently also influenced by constitutional supercooling

growth cells of the type envisaged by Keith and Padden[15], namely fibrous rods and connected sheets of boundary regions but the inverse, i.e. connected sheets of polymer surrounding columns of melt. It was therefore, suggested that the growth problem might still be a local diffusion one with a corresponding change of boundary conditions[3].

Examination of other polyethylene morphologies[4-6] established that, for most growth conditions, the dominant sheets were S-shaped in tangential cross-sections and cross-connected in ways which have not been fully elucidated. They are still non-planar and are still suggestive of growth cells despite it being clearly shown that the width of sheets did not vary with the parameter δ as had been predicted[6]. Instead, it was pointed out[6] that the important dimension in giving a texture to spherulites was the separation of adjacent dominant sheets.

This conclusion has been reinforced by examination of isotactic polystyrene morphologies[8]. For this polymer growth temperatures above ~ 203°C give early objects which are, to a first approximation, axialites. In one perspective they are indistinguishable from similar aspects in polypropylene (*Figure 5*). In the orthogonal view, however, instead of laths as in polypropylene one has hexagonal lamellae which splay about a diagonal connecting opposite corners. Polystyrene has shown, as polypropylene now confirms, that in these systems with planar lamellae (and molecules normal to them) the internal textural dimensions given to spherulites are those of the repetitive separation of arrays of more or less equally spaced individual dominant lamellae. The non-planarity of polyethylene lamellae has, in this instance, proved an initially confusing complication though doubtless it will, in time, reveal salient aspects of melt crystallization. Polystyrene, however, does not show, at least for growth temperatures down to 180°C, any clear limitation of lamellar width. The axialite approximation breaks down for these lower crystallization temperatures and prolonged growth, as it also does for polypropylene, but the wide lamellae give the resulting spherulites characteristic substructures different from the radial fibres present in classic spherulites although optically the textures have much in common. In polypropylene where, as always, lamellar widths are narrow, this complication does not arise and the issue is presented most clearly. In this system, classic spherulites can form so slowly (at growth rates $\sim 10^{-8}$ cm s^{-1}) that there can be no question of a local diffusion field (due to enhanced 'impurity' concentrations) on the necessary micron scale. One must look instead for mechanisms which cause individual dominant lamellae consistently to branch and to splay apart. It may be that, at lower temperatures with faster growth, constitutional supercooling and local diffusion fields may impose an additional dimension on spherulitic textures, as *Figure 11* suggests has happened, but this can no longer be regarded as the primary mechanism of spherulitic growth.

Some comment is required on possible mechanisms of branching and splaying. By splaying we mean deviation of adjacent lamellae from their ideal natural crystallographic orientations. Lamellae which should initially be parallel would diverge, and those which crystallographically (because of twinning etc.) should initially be inclined at a given angle would show a greater or possibly lesser divergence. Branching is the creation of a new lamella. Parent and daughter lamellae may, in principle,

be inclined at any angle. If this angle is zero or nearly so—which would be the case for small angle non-crystallographic branching[15] because of the decreasing probability of nucleation with increasing misorientation – then one needs splaying in addition to branching to generate spherulites (in which all radii are crystallographically equivalent). However, repetitive branching at a finite angle would be sufficient by itself to generate spherulitic geometries.

Details of the observed morphologies in polypropylene indicate splaying as well as branching but precise details of branching are difficult to identify, especially in the arbitrary cross-sections involved in permanganic etching. Leading lamellae diverge at angles of 10–20°, or sometimes over 30°. This would not be expected for small angle non-crystallographic branching and, if such angles apply at the birth of a daughter lamella then generation by twinning would be a serious possibility. Alternatively, it is possible that the initial branching angle could be small but increase over a small distance (perhaps a fraction of 1 μm) because of localized forces giving splaying. This latter situation certainly appears to hold for isotactic polystyrene[8].

The origin of such splaying forces could well be cilia of uncrystallized molecular ends or long loops, attached to a lamella. If present in sufficient concentration they could promote nucleation of a new lamella[18]. However, if they were not incorporated within a second lamella they would generate a repulsive force if compressed. In the first instance this would be due to loss of configurational entropy but at high compressions could also involve higher energy states through changes in the *trans–gauche* ratio and angular distortions. Such a mechanism would only apply when lamellar separations are much less than molecular lengths, i.e. $\ll 1$ μm. Essentially the same proposal was made many years ago to account for the splaying of solution-grown axialities of polyethylene[19].

Pressure from cilia would be expected to cause splaying apart of successive layers of a spiral terrace generated by screw dislocation. These are a common feature of isotactic polystyrene and hexagonal polypropylene[1], though not apparently of monoclinic polypropylene. Moreover, such pressure would be expected to lead to three-dimensional development from initially two-dimensional splaying axialites. Pressure will always produce a response, though its magnitude will depend on the flexural rigidity involved. In the case of monoclinic polypropylene laths, the easiest mode of bending, would be expected to be about the *b* axis. Other deformations will be less but they should still occur. A similar case in favour of the observed axialitic splaying can be made for isotactic polystyrene[8] and polyethylene (for which non-planarity must be taken into account). In the case of multilayer axialites as in polystyrene[8], if contact between successive layers is a line of finite length, then splaying about the line would be of greater extent than splaying of layers beyond the ends of the line—but both will occur giving the familiar degeneration of the two-dimensional splaying axialites into three-dimensionally splaying morphologies[19].

The problem of understanding cross-hatching in monoclinic polypropylene is one of long standing. Khoury[11] made the reasonable supposition that there was an epitaxial relationship between parent and twin. Later Padden and Keith[14] detected the triclinic γ-phase at the origin of the twin i.e. {010} faces of laths of the α (monoclinic) phase but found it absent in the middle of laths. They, therefore, postulated that it was epitaxy of γ on α which initiated the formation of an α twin and thence cross-hatching. Drawing upon results of Turner–Jones[10] they also suggested that the formation of the intervening γ phase was related to the segregation of medium and high mass stereoblock molecules.

This supposition is not in conflict with our findings. Indeed the maximum temperature at which we have observed the formation of cross-hatching, 155°C, agrees with earlier findings[20] that this is near the upper limit of the stability range of γ-phase. Moreover, our observation that profuse cross-hatching starts at the edges of, and to a lesser extent within, α sheaves is support for the link between segregated polymer and cross-hatching. Furthermore, the central region of cross-hatching at the centre of spherulites of radiating α filaments is a feature previously noted by Padden and Keith[9]. Permanganic etching is, however, able to add something to this picture, because of its preferential attack upon the cross-hatching members. In our experience, permanganic etching will discriminate very sensitively between textural nuances so we would regard the differential attack between twin and parent laths as indicating a real structural difference. This is also indicated by the thermal behaviour in which cross-hatching members melt before the parent laths. Moreover, the subsequent behaviour that cross-hatching does not reform at 155°C—though it did initiate the spherulite—is suggestive of a difference in the molecular composition of cross-hatch material between the central nucleus and later growth. Very possibly higher mass molecules would be involved in forming the nucleus, with shorter molecules contributing to later development. There is evidently much to learn by a detailed study of the location and constitution of cross-hatching members and correlation with other work on the distribution of impurities in crystallizing polypropylene[21,22].

CONCLUSIONS

This paper has shown:

(1) That intricate fine structure (cross-hatching) in spherulites of monoclinic polypropylene can be studied in detail by permanganic etching.

(2) That at 160°C, spherulites composed entirely of α laths develop in the classical manner by radiating and branching growth. The radiating and branching units are not, however, multilamellar fibres but individual dominant lamellae. This confirms the behaviour found previously for polyethylene and for isotactic polystyrene.

(3) This developing texture is different from that traditionally believed to occur. Its explanation requires a theory of branching and splaying of individual dominant lamellae, not of the instability of a planar crystal interface as considered by Keith and Padden[15]. It is suggested that the probable cause of splaying is pressure from compressed cilia between adjacent lamellae.

(4) These spherulites form much too slowly to be influenced by the scale of local diffusion fields related to segregation of slower-crystallizing species. At sufficiently low temperatures (e.g. 130°C) there is evidence that local diffusion (constitutional super-cooling) may impose an additional textural dimension on spherulites.

(5) When cross-hatching does occur at 155°C and below it does not occur uniformly, but is concentrated in specific locations and in subsidiary lamellae. Cross-hatching laths are less stable and probably consist of shorter and/or less tactic molecules.

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