

# On the development of polypropylene spherulites

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The organization of lamellae in developing spherulites of *i*-polypropylene growing from the melt at 155 and 150°C has been investigated in detail using permanganic etching and transmission electron microscopy (TEM). The study forms a link between the simplest development at 160°C, when there is no twinning, and common cross-hatched textures occurring for crystallization down to at least 110°C. Whereas at 160°C growth starts with fan-like splaying of lath-like lamellae, at 155°C and below early objects are quadrites which develop as two families of laths with a common *b*-axis and a mutual orientation of 80°. This orientation relaxes with distance but is still recognizable with microbeam X-rays to sizes >0.2 mm. Randomization in space of the orientation of the growth direction  $a^*$ , and also around this axis, occurs at smaller distances at lower crystallization temperatures. It is inferred that so-called axialites and spherulites are objects which differ in their degree of randomization rather than in kind. The characteristic cross-hatched texture of  $\alpha$ -polypropylene develops differently according to the location in a growing spherulite. Whereas cross-hatching is symmetrical at the centre of a quadrite, in the outer regions radial lamellae dominate. Cross-hatching lamellae form later and are restricted in length to the unfilled space available. As such they are in competition with radial subsidiary lamellae. There is an increasing ratio of transverse to parallel subsidiary lamellae with lower crystallization temperatures. Epitaxy between the two cross-hatching components is observed to occur on the prism faces of lamellae in agreement with molecular mechanisms proposed by Binsbergen and de Lange<sup>5</sup> and Lotz and Wittman<sup>21</sup>.

(Keywords: lamellar organization; *i*-polypropylene;  $\alpha$ -polypropylene)

## INTRODUCTION

The advent of permanganic etching<sup>1,2</sup> has initiated a broad study of lamellar organization in melt-crystallized polymers and its implications for properties. This is an important subject, central to polymer science, because it is the morphology within a sample which commonly determines the degree to which a molecular property (e.g. modulus or strength) is possessed by a macroscopic sample. However, prior to the introduction of permanganic etching (and, for polyethylene, the complementary technique of chlorosulphonation) it was not generally possible to characterize or study representative lamellar organization, which is a principal component of morphology, in bulk material. This is no longer the case. In this laboratory we have developed the technique of etching with a spectrum of reagents based on permanganate and used it to study a broad range of crystalline polymers. In chronological order these comprise linear then branched polyethylene, *i*-polystyrene, *i*-polypropylene, PEEK and *i*-poly(4-methyl pentene-1). All of these polymers possess individual features worth studying. Collectively they yield a general picture, with a single general theme but with individual variations, of the organization and development of textures in melt-crystallized polymers, the distribution of molecular species within these textures, and the implications for properties.

This is the second of our papers reporting on *i*-polypropylene. It concerns the development of the characteristic cross-hatched textures at high crystallization temperatures and finds common ground with melt

growth in other polymers. Other complementary papers dealing with thermal stabilities, growth at lower temperatures and the involvement of the  $\beta$ - or hexagonal phase will follow shortly. Together, these and other papers, either in press or preparation, provide salient detail for the general conclusion drawn in an earlier review<sup>3</sup> that the facts require a new understanding of spherulite growth. In our opinion this can no longer be regarded as driven by segregation of impurities. Segregation can and does occur, more so in polyethylene than in polypropylene or PEEK, but it is a consequence rather than a cause of the splaying and branched morphologies present in spherulites.

We have approached the study of lamellar organization in isotactic polypropylene in the same way that proved advantageous for polyethylenes and isotactic polystyrene. This is to study first objects grown slowly at low supercoolings, partly because these are least complicated, and partly because it is then possible readily to quench crystallization and so to differentiate successive stages of development. Armed with this knowledge one can then more easily unravel the greater complications produced by faster growth. This approach has been particularly helpful for isotactic polypropylene because, as described in our earlier paper<sup>4</sup> and previously by Binsbergen and de Lange<sup>5</sup>, growth at 160°C occurs without twinning. There is no cross-hatching and the pattern of spherulitic development is akin to that of polyethylene and polystyrene, i.e. via splaying and branching of individual dominant lamellae followed by

infilling subsidiary growth. The early stages, first described by Binsbergen and de Lange<sup>5</sup>, are fan-like objects consisting of a bundle of laths splayed about their common *b*-axis to give the fan shape. Deviations about any other axis were quite small, resulting in a lath-like appearance of the whole object when viewed in a direction perpendicular both to the common *b*-axis and the long central axis of the fan<sup>4</sup>. At this stage a two-dimensional architecture of dominant and subsidiary lamellae was already apparent, while early three-dimensional development was observed in rather more mature objects, leading eventually to well-rounded spherulites as observed after long-term crystallization.

#### Scope of the current work

In this paper we report on the additional features introduced by crystallizing at slightly lower temperatures, mostly 155 and 150°C. At these temperatures the occurrence of cross-hatching dramatically alters the morphology, leading to a variety of more or less complicated objects whose development can, nevertheless, be understood by straightforward extension of the dominant/subsidiary pattern. Development of cross-hatching has been observed in this laboratory at all temperatures between 155 and 110°C; the latter is the lowest crystallization temperature so far studied by us.

Phenomena at 155 and 150°C are so similar that the two can usefully be considered together. At these temperatures the early stages of growth give objects which are commonly referred to as quadrites<sup>6,8</sup>. These are quasi two-dimensional arrays of cross-hatched lamellae with an approximately rectangular outline. In these early objects there is no spherical symmetry. Just as in those of other polymers in general, processes of branching and splaying are observed which, if continued, eventually lead to a common radial growth direction. In isotactic polypropylene, however, the geometry of the initial object has legacies which are detectable in the mature spherulites, even though superficially it might seem that a symmetrical condition with all radii equivalent had been achieved.

Subsequent development, beyond the quadrite stage, proceeds predominantly via the establishment of a dense array of outward growing (radial) dominant lamellae with parallel subsidiaries. Locally, the observed morphology falls between two extreme patterns. The first of these is when there are relatively few primary lamellae growing out to fill the available space, as, for example, in the centre of a quadrite. In these circumstances it is possible for a symmetrical cross-hatched network of lamellae to form. The second is when a dense array of outward growing (radial) dominant lamellae with parallel subsidiaries has been established. Any cross-hatching lamellae are confined within narrow regions between radial lamellae, and a relatively small mass of such twinned (tangential) lamellae is formed. The contrast between uniformly cross-hatched centres and peripheral regions with long radial lamellae and short tangential ones has also been observed by means of permanganic etching in the work of Norton and Keller<sup>7</sup>. In our unpublished work we have also shown that there is a corresponding disparity in melting behaviour. In this work systematic use of the technique to study large numbers of three-dimensional objects in different orientations has built up a picture of how the first type of morphology gives way to the second during development.

## EXPERIMENTAL

### Materials and techniques of crystallization

The polypropylene used in crystallization studies throughout this paper is the isotactic polypropylene PP1 in pellet form supplied by PSCC at RAPRA, UK. All experimental specimens referred to have been prepared from this material as received. Its molecular mass has recently been determined (by PSCC) to be  $\bar{M}_n = 4.7 \times 10^4$  and  $\bar{M}_w = 4.2 \times 10^5$ .

Specimens were prepared by squashing individual pellets between slide and cover slip to the appropriate thickness given in the text for each specimen. They were then melted under nitrogen flow in a Mettler FP52 hotstage, generally at 210°C for 1 min, to remove the majority of the row nuclei initially present, quenched on a cold metal surface, and reheated in the hotstage according to the following programme. From 120°C at 10 K min<sup>-1</sup> to 150°C; at 2 K min<sup>-1</sup> to the nucleating temperature (between 173 and 175°C) then cooled as fast as the instrument would allow to the crystallization temperature (generally about 1 min). The growth time was measured from when the instrument stabilized. This procedure of self-seeded nucleation was necessary, as in the earlier study<sup>4</sup>, to give a suitable number of objects. It gives the added advantage of a well-defined uniform age and size. Hotstage work was conducted under nitrogen flow. After the desired crystallization time the specimens were quenched in ice water, with the exception of the 150°C/3 h specimen which contained many impinged spherulites and was, therefore, quenched in boiling water, in an attempt to avoid excessive thermal stresses. Even so, subsequent work showed that this did not make much difference because the effective crystallization temperature for the quenched material must, in all cases, be of the order of 100°C. For specimens crystallized at 155°C for 64 h, a film ca. 0.1 mm thick squashed between cover slips on the hot bench and a moulded disc ca. 1 mm thick were sealed under nitrogen in glass tubes, melted at 210–213°C for 5 min and then treated in silicone oil baths as follows: into bath 1 at 155°C, heated at 0.25 K min<sup>-1</sup> to 176°C, and transferred to bath 2 at 155°C. After crystallization they were quenched in tap water at ca. 20°C.

### Microscopy and X-ray diffraction

Optical microscopy was performed on the film specimens without further modification. Objects were observed:

- Between crossed polars, with a quartz sensitive tint plate used to determine the sign of birefringence.
- In circularly polarized light (crossed polars plus crossed mica quarter-wave plates) to remove the Maltese cross.
- In phase contrast.

For electron microscopy the bulk crystallized specimen was cut open with a glass-knife microtome and etched for 15 min with a 0.7% w/v solution of potassium permanganate in 2:1 concentrated sulphuric acid:dry phosphoric acid mixture with shaking<sup>2</sup>. The thick films were etched for 1 h to remove uncharacteristic surface regions. Two-stage replicas were then prepared, with metal shadowing applied to the first stage replica. An important point which must always be borne in mind when interpreting pictures of polypropylene morphology, is that the shadow direction may highlight one or other of

the two different cross-hatching orientations, leaving the other hardly visible. Realistic presentation of the actual relief has been attempted by displaying the micrographs in a suitable orientation, so that lamellae should appear standing proud of their surroundings.

X-ray diffraction patterns of selected spherulites were obtained using a Norelco Micro Camera with a  $50\ \mu\text{m}$  beam collimator and a specimen to film distance of 15 mm.

## RESULTS AND DISCUSSION

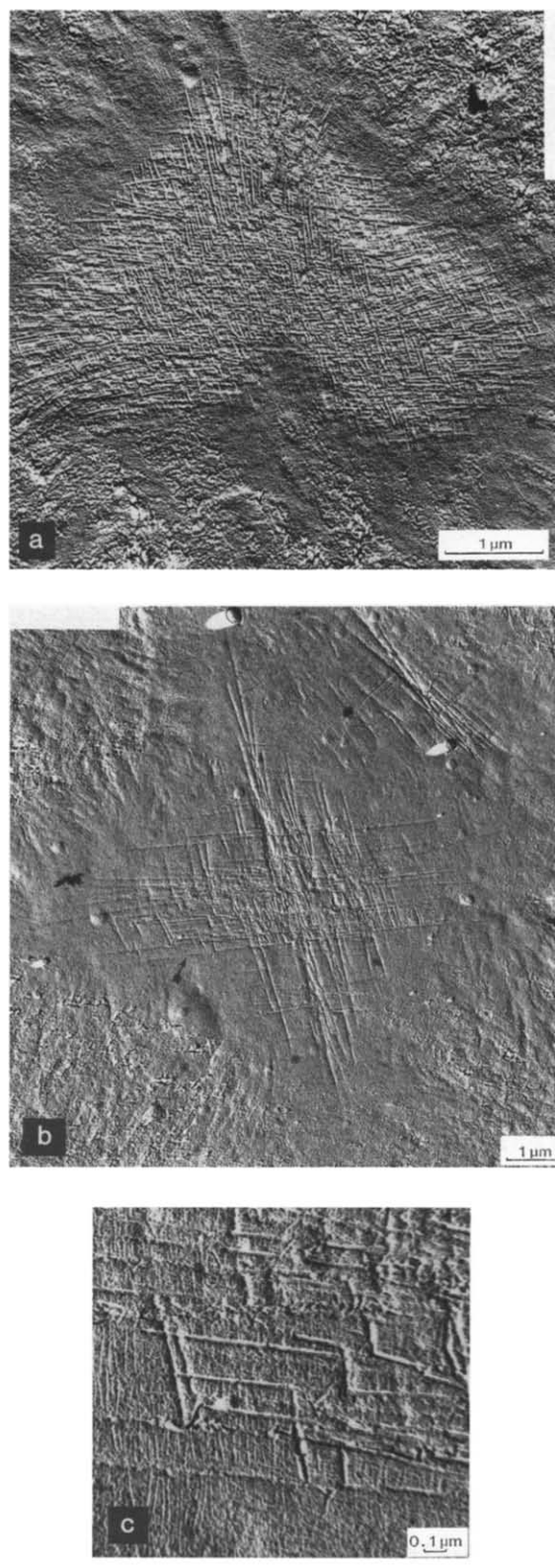
### First stages of growth (quadrites)

Early stages of growth are seen in electron micrographs of quadrites grown at  $150^\circ\text{C}$  for 30 min or at  $155^\circ\text{C}$  for 2 h, such as those shown in *Figure 1*. What is observed in such pictures is, of course, not a complete object but a section (not necessarily a perfect plane section) through it with the lamellar detail brought into relief by the etching. These objects are very thin, so that even in a search through several hundred of them not one was found in which the etched surface plane intersected the whole quadrite for its entire area to be displayed. However, the halo of featureless quenched material surrounding the quadrite often gives a good indication of the shape of the whole object.

The quadrites grown at  $150^\circ\text{C}$  (*Figure 1a*) already show a centre full of dense cross hatching; at the corners the radial lamellae already appear slightly more well-developed than the tangential ones. In this and in that at the corners of the quadrite there is a slight preponderance of outward growing lamellae curving towards the obtuse cross-hatching angle they resemble whole objects grown in molten films at  $143^\circ\text{C}$  by Binsbergen and de Lange<sup>5</sup>. They also show some resemblance to those grown from amyl acetate solution by Houry<sup>8</sup>, but differ in that the solution-grown objects show dense cross-hatching right out to the periphery, apparently with better maintained crystallographic orientation.

In objects grown at  $155^\circ\text{C}$  (*Figure 1b*) the lamellae are rather sparse, and only in the centres is there a resemblance to the cross-hatched morphological pattern typical of lower crystallization temperatures. Beyond this there are found a few outward growing individual lamellae which would have become the precursors of an array of dominant lamellae at a later stage. At  $155^\circ\text{C}$ , in a quadrite of given size, many fewer cross-hatch arms have initiated than in a comparable  $150^\circ\text{C}$  quadrite.

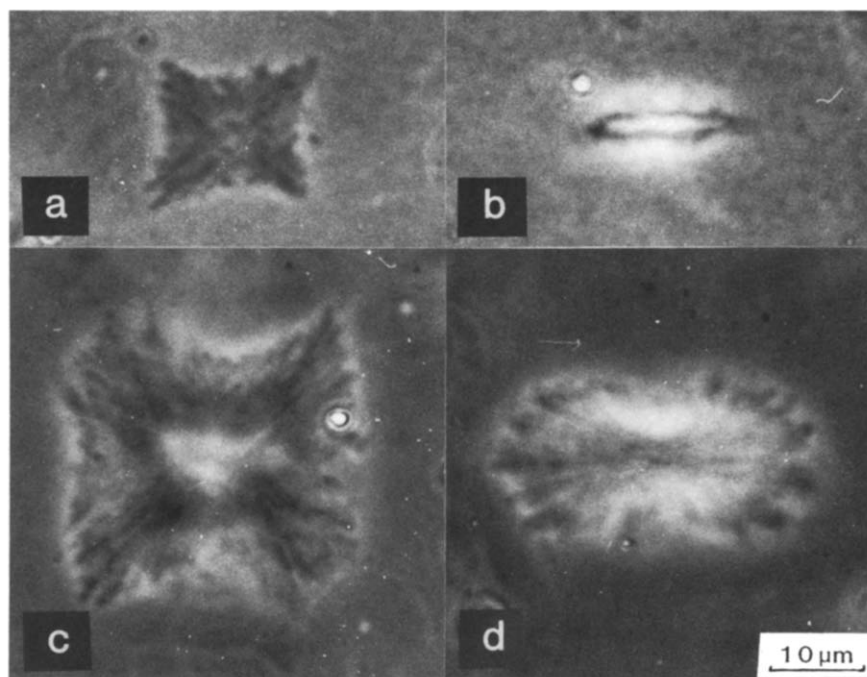
It is worth comment that, in *Figure 1b*, the resolved quadrite lies within a larger, near rectangular region, of distinct texture. Only beyond that is the general quenched matrix apparent. Higher magnification (*Figure 1c*) shows that the distinct texture consists of thin cross-hatching lamellae formed on quenching, lying transverse to the thicker lamellae formed at  $155^\circ\text{C}$ . Evidently reduction in crystallization temperature reduces lamellar thickness, but the more distinct texture implies that below (or above) the etched surface lay hidden portions of the quadrite which have nucleated the cross-hatching lamellae. It is consistent with the thin film observations of Padden and Keith<sup>10</sup> that the secondary lamellae nucleate on the side surface of  $\alpha$ -laths and lie in a different plane. This fact is also central to the epitaxial relationship of side surfaces giving the  $80^\circ\ 40'$  twinning angle characteristic of cross-hatching. Molecular interpretations for such



**Figure 1** Very early stages in growth of polypropylene, viewed down the original twin axis: electron micrographs of etched surfaces. (a) After 30 min at  $150^\circ\text{C}$ ; (b) after 2 h at  $155^\circ\text{C}$ ; (c) detail of arrowed portion in (b) showing fine cross-hatching formed on quenching

epitaxy, on side as opposed to fold surfaces, have been proposed by Binsbergen and de Lange<sup>5</sup> and Lotz and Wittman<sup>21</sup>.

The appearance of complete objects grown for 4 h at  $155^\circ\text{C}$ , this time in optical phase contrast, is strongly dependent on orientation. The object in *Figure 2a* is viewed down the common twin axis of two sets of



**Figure 2** Early objects in polypropylene at 155°C, seen in optical phase contrast. (a) After 4 h, viewed down the original twin axis; (b) transverse view; (c) after 7.5 h, viewed down the original twin axis; (d) transverse view

lamellae, which are diverging at about 80° to each other. A similar object viewed in a perpendicular direction in *Figure 2b* is seen to be very thin in the dimension of the common twin axis. In these early objects it is easy to define the original twin axis and the original object plane normal to it by inspection. These can then be used for reference to different views of much more mature objects, even complete 'spherulites'.

As the objects develop, the four leading groups of lamellae fan out rapidly from each of the four corners. They round out the appearance in the initial object plane (*Figure 2c*), and also begin to spread out of this plane (*Figure 2d*), so that the transverse section appears sheaf-like. In this discussion we use the term fan to describe structures formed by splaying about the *b*-axis. The more traditional term sheaf is used to describe those formed by deviation out of the initial object plane. This has the merit of easily differentiating what are two distinct views of the same object, though the sheaves do not have the cylindrical symmetry of the agricultural object.

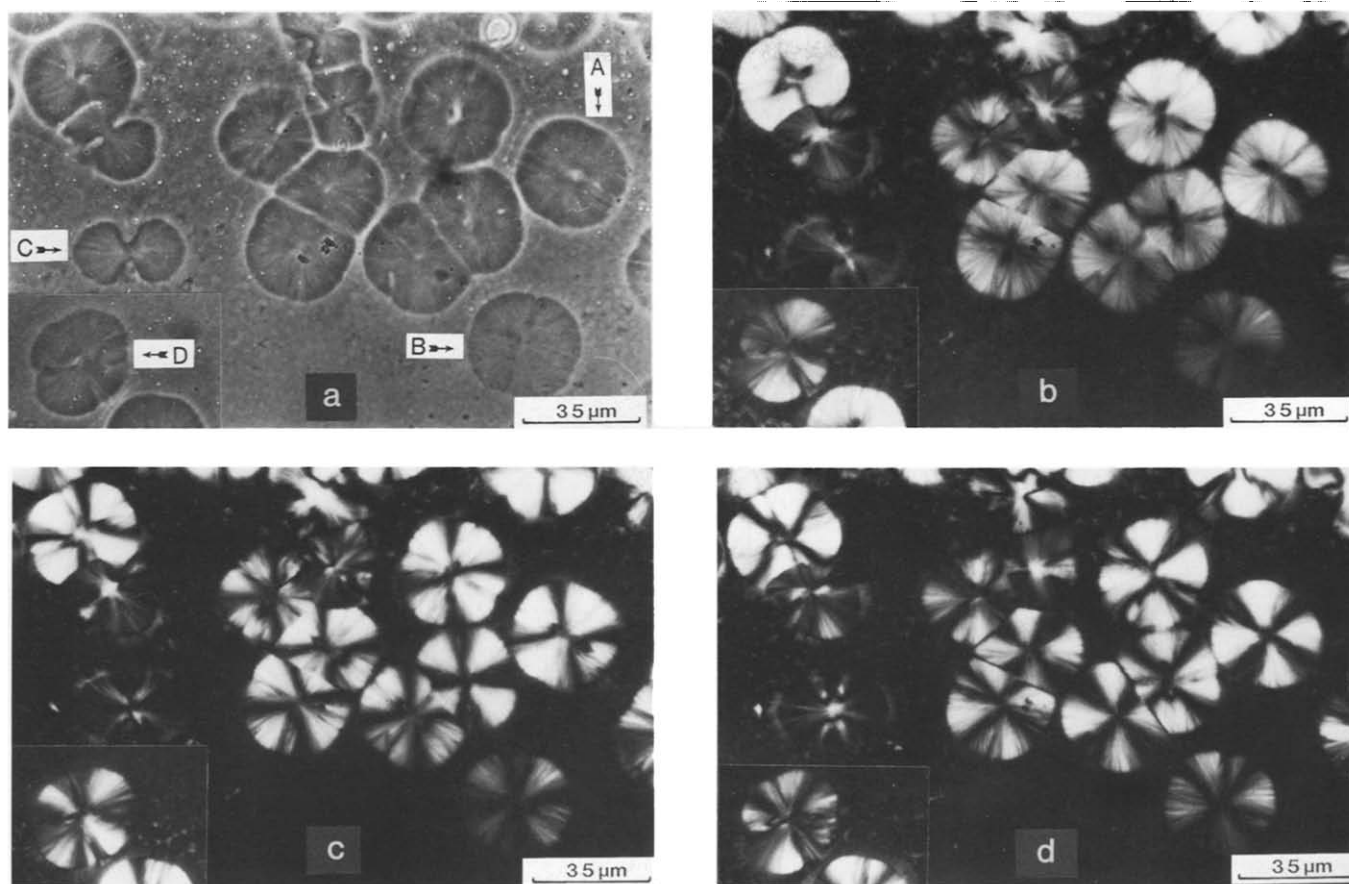
All these quadrites, viewed down the common *b*-axis, display low birefringence because the chain axes of the two sets of lamellae are almost at right angles, in the original object plane. Only in the peripheries of the 155°C objects are individual negatively birefringent strands of material seen where the cross hatching lamellae have yet to develop. These are surrounded by a quenched halo of positively birefringent material, as was previously observed from 160°C (ref. 4). When the quadrites are viewed in a transverse direction, they show strong positive birefringence. It is instructive at this point to contrast these objects with classical melt-grown polymer hedrites as defined by Geil<sup>11</sup>. Many examples of these are shown in his book, where it can be seen that the typical early stages of spherulitic growth in a high symmetry polymer consist of an object which may either appear polygonal with weak birefringence, or else oval or sheaf-

like with strong birefringence, depending on projection. A classical case of these would be the early stages of isotactic polystyrene spherulites as grown at 200°C (ref. 11) and 220°C (ref. 12), which, in appropriate projections, are displayed either as hexagons of low birefringence or sheaves of high birefringence<sup>12</sup>. However, hedrites and quadrites are totally different kinds of objects. The polystyrene hexagons are weakly birefringent because their molecular chain lies along the line of view, whereas in the polypropylene quadrites two sets of molecular chains lie in the plane of view, almost perpendicular to each other.

#### *Intermediate stages of growth*

Even in the earliest stages, the difference in growth rates between these two temperatures (155°C: 0.7 nm s<sup>-1</sup> and 150°C: 1.7 nm s<sup>-1</sup>) is apparent, from the respective sizes. In subsequent growth another factor becomes evident concerning the change in shape from the quadrite to the fully rounded spherulite. This is, that as compared to an object at 150°C, one at 155°C will have to grow to roughly twice the linear dimension before it attains an equivalent degree of maturity, i.e. a geometrically similar envelope. This renders 155°C objects more suitable for optical microscopy; for study of whole objects under the electron microscope 150°C ones are more suitable.

The situation after 3 h at 150°C is shown in *Figures 3* (optical) and *4* (electron micrographs). Subsequent detail, from electron micrographs of objects in a thicker part of the same specimen, will show that the objects labelled A and B in *Figures 3* and *4* are observed approximately down the original twin axis, with the original object plane in the plane of the film. Object A appears brighter because it is in a thicker part of the film. They have the form of a four-part rosette, whose common tangents give an exscribed shape which is slightly rectangular rather than square in form. Object C is observed in a perpendicular



**Figure 3** Intermediate stage in growth of polypropylene after 3 h at 150°C, seen (a) in optical phase contrast; (b) in circularly polarized light; (c) between crossed polars with extinction directions parallel to sides of picture; and (d) as (c) but polars rotated by 45°. For description of objects A–D see text

direction which gives a sheaf-like section. Object D is one where the axis of one pair of fans lies more or less in the plane of the film and the other is tilted at roughly 45°.

The same kinds of view are found in objects grown in films approximately 0.1 mm thick, which have then been etched and examined by electron microscopy. Many other views have also been examined, but we have selected for special study those objects in which the etched surface passes close to the centre, as well as being in the desired orientation. Electron micrographs of such sections are shown in *Figure 4*.

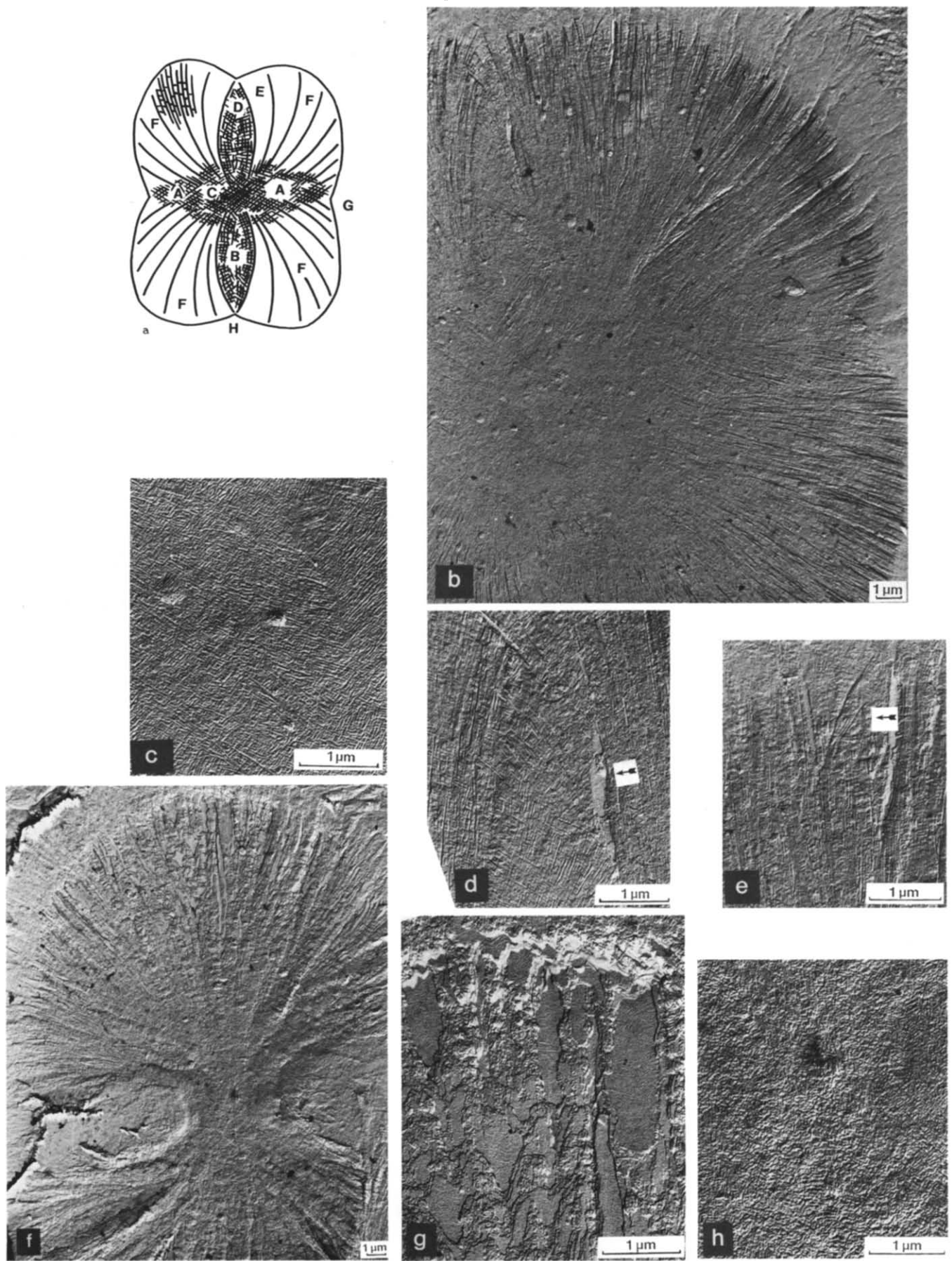
When the original object plane coincides with the etched surface, then the rosette view is displayed. The detailed morphology within the rosettes is too fine to be seen in the picture of the complete object. Therefore the various parts of the rosette are illustrated diagrammatically in *Figure 4a*, with a micrograph of an area containing the centre and one of the four (equivalent) lobes in *Figure 4b*. The two morphological patterns defined earlier can be observed in this view. Fans of dominant lamellae with parallel infilling subsidiaries but with little cross-hatching are observed to radiate within the lobes of the rosette. The centre and the eyes between the fans (Popoff's leaves<sup>13</sup>) are filled with more uniformly cross-hatched material. Note that the lamellar traces are not always straight, but that the majority are slightly curved towards the vertical bisector of the rosette. An enlarged view of the centre in *Figure 4c* shows dense cross-hatching. Although two overall preferred lamellar orientations diverging roughly at the 80° 40' cross-hatching angle can be made out, neither direction predominates. Close examination

shows, moreover, that the obtuse angle of the cross-hatching faces up and down along the long axis of the rosette, which therefore lies parallel to the short side of the original quadrite. This is brought about by the curvature of the dominant lamellae inwards towards the obtuse angle. At first this is surprising, but it is in keeping with the similar observation by Binsbergen and de Lange<sup>5</sup>. It is, however, different from the situation in highly doped materials observed growing on mica by Lovinger<sup>9</sup>, where lamellae tend to curve inwards towards the acute angle.

An enlarged view of the eye in *Figure 4b* is shown in *Figure 4d*. This shows the more evenly cross-hatched texture here. The isolated lamella in the fan bounding the eye (arrowed) with its tilted orientation does not seem to have disturbed the overall structure.

An enlarged view of the fan next to it is given in *Figure 4e*. In this particular region one is looking down the common *b*-axis, and so neither set of lamellae masks the other. The projected shadow direction is from above, so the contrast of the dominant lamellae in the fan is suppressed and the cross-hatching between them is highlighted. This allows one to see that the cross-hatching is restricted to lengths between dominant lamellae.

It has previously been noted, in the fan-like view of objects grown at 160°C where cross-hatching is completely absent, (*Figure 5* in ref. 4) that in some parts of the fan the lamellae are closely packed while in others gaps are found. A similar situation pertains at 150°C for dominant lamellae, but here it causes variations in the amount of cross-hatching lamellae found between the radial ones (*Figure 4e*). Furthermore, at 160°C and at



**Figure 4** The objects in *Figure 3*, seen in the electron microscope after permanganic etching. (a) Line diagram illustrating the structure observed in the rosette view down the original twin axis, with key to structure; A, the cross-hatched regions growing from the acute angle of the central cross-hatching; B, one of the eyes filled with cross-hatched material formed in the obtuse sector. By the letter C, the cross-hatched centre shows the obtuse angle pointing up-and-down. D is the end of an obtuse sector eye, E is a neighbouring fan region and F indicates the four fans, of which the fine structure is shown in the top left corner. G, H are cusps in the rosette. Cross-hatching is not indicated for most of the four fans. (b) Electron micrograph of part of an object seen in the rosette view, corresponding to the centre and upper right part of the diagram, with (c) higher magnification views of the centre and (d, e) of the upper top parts D and E of the rosette. (f) A view perpendicular to the original twin axis with higher magnification views of the edge (g) and of the centre of the object (h)

150°C occasional dominant lamellae branch out from the main system at angles of the order of 40°, as arrowed in *Figure 4e*. However, these are geometrically disfavoured from being able to continue outward growth, and will eventually collide with other lamellae growing radially outwards. These outward-growing lamellae will have advanced further, and will continue, thus maintaining the overall orientation. Nevertheless, occasionally a divergent lamella, perhaps generated at the very tip of a leading lamella, can grow ahead of the lamellae beside it, and introduce a 'defect' into the rosette structure large enough to be clearly visible optically.

A central section with the original twin axis lying horizontally in the plane of the picture, and the original object plane making a vertical intersect, is displayed in *Figure 4f*. It has the same sheaf-like appearance as the object C in *Figure 3a*. Note how the object has developed in relation to the original object plane to grow out in three dimensions. In *Figure 4g*, which is an enlarged view of the end of the object, the lamellae are displayed flat-on, down their *c*-axis, which is to be expected with *a*\* along the outward growth direction and *b* along the original twin axis, both of which are in the plane of the picture. As also observed at 160°C, the rate of splaying about *b* is much greater than about *c*. Closer examination shows that the lamellae away from the long axis of the sheaf are not viewed directly down the *c*-axis. Instead, as new dominant lamellae arise, they are inclined about their *a*\*-axis (growth direction) with respect to the original ones. Where there is sufficient space then new fans can form by splaying about the new *b*-axis, thus allowing three-dimensional development, as also occurs at 160°C (ref. 4). Flat-on lamellae are not observed in this instance in the centre of the object (see the enlarged view in *Figure 4h*). Here what is displayed is not part of a sheaf of parallel lamellae, but a section through densely cross-hatched material with the common *b*-axis in the plane of the film.

This type of view is also frequently observed in polypropylene grown at lower temperatures, but although familiar it remains one of the most difficult views to interpret in fine detail. Two sets of lamellae, both less than 1 μm wide, are seen growing out of the plane of the micrograph. In addition, cross-hatching in the classical projection, down the common *b*-axis, is beginning to develop in the eyes being formed by the closing of the sheaf.

Other views of the objects, such as diagonal sections through the centre and off-centre sections, have also been scrutinized in detail, but these are not shown. Generally, away from the original object plane the dominant lamellae are less densely packed, and greater lengths of cross-hatching are observed.

'Spherulites' grown at 155°C show, in general, little cross-hatching. Small amounts are observed between the radiating lamellae but only if the orientation is correct and it is much less pronounced than at 150°C. There are isolated patches of more extensive cross-hatching. These could be in the centre, in the Popoff's leaves between the fans of the rosette, or in the eyes formed by the closing of the sheaf perpendicular to the original twin axis.

The appearance of the objects in polarized light, shown in *Figures 3b-d*, tallies well with what is observed under the electron microscope. The peculiar and characteristic birefringence of α-polypropylene was noted long ago, both in quadrites<sup>8</sup> and spherulites<sup>14</sup>. For a guide see *Table 1*, but for a more detailed derivation of the effect of cross-hatching on the birefringence of polypropylene spherulites the reader is referred to the work by Binsbergen and de Lange<sup>5</sup>. Objects observed down the original twin axis (rosette view, A and B) are like negative spherulites. This is as expected when a weakly cross-hatched system is viewed down the common *b*-axis. The eyes and centres have lower birefringence, because their two sets of cross-hatching lamellae have their chain axes

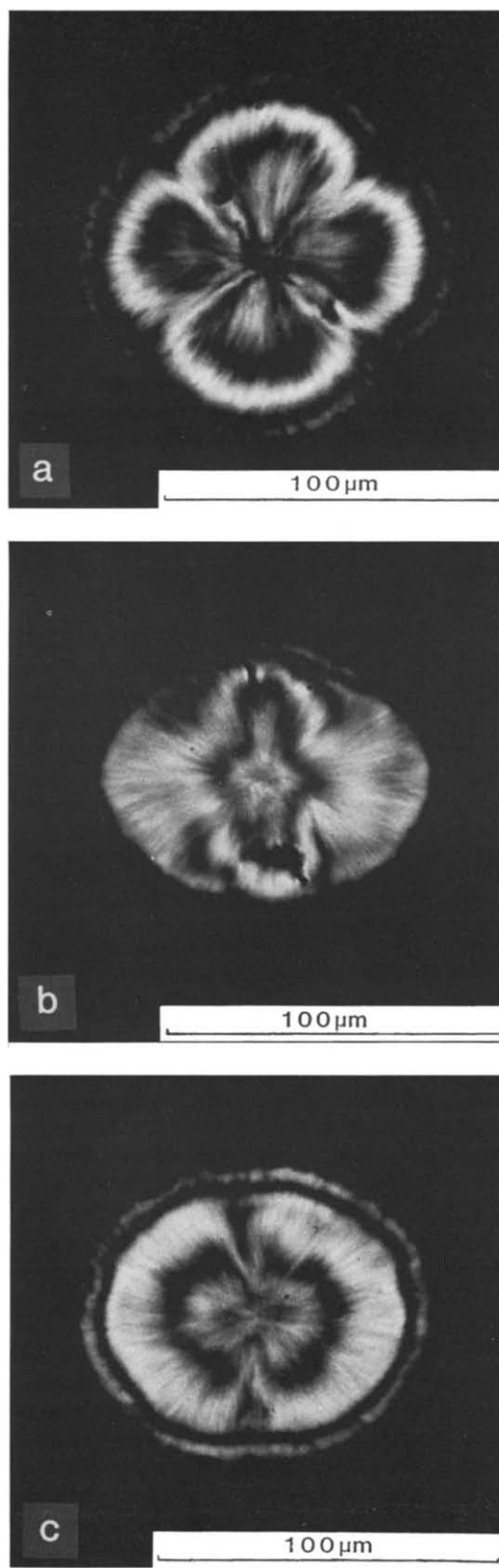
**Table 1** Cross-hatching and birefringence. This table gives a key to the birefringence of α-polypropylene spherulites, in principal orientations. Spherulite radii are presented, either as viewed lying in the plane of the film (grown in thin films or diametral sections) or emerging directly towards the observer (as in off-diametral sections). Because of alternation of generations of radial and tangential lamellae, in normal isothermal growth there will always be an excess of radials, but as *T<sub>c</sub>* decreases, the proportions become more equal. Symbol *F* refers to Mass of tangentials/Mass of radials. Centres and quadrites are treated as viewed, either in the original object plane, or along any axis perpendicular to it. The sign of birefringence +ve means that the slow direction (high refractive index) lies along the radius of the spherulite, -ve that it is perpendicular to it. Subscript *r* refers to crystallographic axes in the radial population. For a more comprehensive introduction to birefringence of spherulites, see reference 19

Type of material	Direction of view	Sign of birefringence
Spherulite radii Dense radials $\mathcal{F} \ll 0.5$ negative spherulite	Radius in-plane, down $b_r$ Radius in-plane, down $c_r$ Radius emerging, down $a_r^*$	strong -ve weak +ve very strong; slow $\parallel c_r$
Spherulite radii Not so dense radials $\mathcal{F} \approx 0.5$ mixed spherulite	Radius in-plane, down $b_r$ Radius in-plane, down $c_r$ Radius emerging, down $a_r^*$	medium -ve medium +ve strong slow $\parallel c_r$
Spherulite radii More open radials $0.5 \ll \mathcal{F} < 1$ positive spherulite	Radius in-plane, down $b_r$ Radius in-plane, down $c_r$ Radius emerging, down $a_r^*$	weak -ve strong +ve slow $\parallel c_r$
Spherulite radii Equal cross-hatching (doped materials)	Radius in-plane, down $b_r$ Radius in-plane, down $c_r$ Radius emerging, down $a_r^*$	very weak -ve strong +ve slow $\parallel c_r$
Spherulite radii Sparse radials Excess cross-hatching (quenched borders)	Radius in-plane, down $b_r$ Radius in-plane, down $c_r$ Radius emerging, down $a_r^*$	weak +ve strong +ve slow $\parallel c_r$ for $\mathcal{F} < 6$
Centres and quadrites	Down common <i>b</i> -axis	very weak, slow $\parallel$ obtuse bisector
Equal cross-hatching	Any direction in <i>a</i> *- <i>c</i> plane, with <i>b</i> in the plane of view	very strong slow $\perp$ to <i>b</i> -axis

almost at right angles. The object C mostly shows little birefringence because along the major axis the dominant lamellae are viewed down  $c$ . However, in the centre the much greater cross-hatching gives rise to strong birefringence with the slow direction parallel to the long axis of the sheaf. With polars crossed parallel to the eyes of the rosette, as with object A in *Figure 3d*, then the appearance is indeed similar to the classical Maltese cross spherulite pattern. However, when they are rotated by  $45^\circ$  as in *Figure 3c*, the split cross pattern seen here is displayed. The classical picture of a spherulite is obviously far too simple to describe these objects.

It is possible to observe corresponding birefringence effects in whole objects, provided that the surrounding matrix is quenched fast enough to produce a microspherulitic structure of low overall birefringence, and that the objects are well enough spaced not to overlap with each other. Such a condition has been realized in a film ca. 0.1 mm thick, crystallized at  $155^\circ\text{C}$  for 17 h. Objects in definitive orientations, as seen in circularly polarized light, are shown in *Figure 5*. Note that in monochrome the lightest colour is the first order white; higher orders of birefringence colour, in the inner parts of the objects, appear grey, with the first order red separating the two orders appearing very dark grey. In *Figure 5a* the original object (quadrite) lies in the plane of the film. The object is rosette shaped, with four distinct lobes. Again, the birefringence rosette must not be confused with the Maltese cross shown by classical spherulites under linearly polarized light. Two objects with their original twin axes in the plane of the film are shown in *Figures 5b* and *c*. They appear brighter than the rosette view, but this is due to the predominance of first-order white and yellow, rather than higher order colours. In *Figure 5b* two lobes of the rosette are lying up and down along the axis of view and the other two perpendicular to it. In *Figure 5c* they are positioned diagonally. All the objects are surrounded by a positively birefringent halo due to quenched material. They also contain small blemishes, due to non-isotropic thermal contraction on quenching.

A brief summary of early growth at  $130^\circ\text{C}$  follows, prior to fuller publication. A film ca.  $10\ \mu\text{m}$  thick crystallized at this temperature for 2 min following enhanced nucleation, and then quenched, is shown in *Figure 6a* as seen in circularly polarized light and *Figure 6b* as seen between crossed polars with a mica quarter-wave plate. In general, these objects can be thought of as wheel-like with the original twin axis being the axle of the wheel, the radiating primary lamellae form the spokes of the wheel with cross-hatching, much more extensive than at  $150^\circ\text{C}$ , filling the gaps. (It is generally the case that cross-hatched subsidiary lamellae melt somewhat below the primary radials which contain them<sup>4</sup>. A full account of this phenomenon will be published elsewhere<sup>18</sup>.) The appearance looking down the original twin axis is like that of a spherulite section with mixed positive and negative birefringence. Viewed perpendicular to the original twin axis the objects appear highly birefringent and elliptical in cross-section, with the slow direction along the major axis of the ellipse. Their mixed birefringence as viewed down the original twin axis is due to the much greater cross-hatching, approximating not-so-dense radials in *Table 1*, and the fact that the radiating lamellae do not stay in well defined fans. Instead,



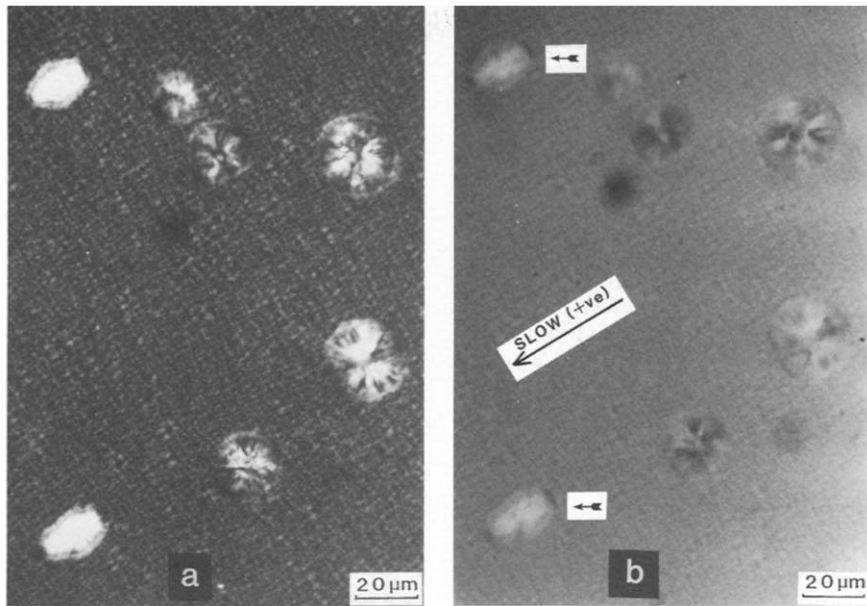
**Figure 5** Spherulites of polypropylene after growth for 17 h at  $155^\circ\text{C}$ , seen in circularly polarized light. (a) As viewed down the original twin axis and (b), (c) two transverse views perpendicular to this axis

numerous sub-fans are formed with rotation about  $a^*$ , and effective randomization of the  $b$  and  $c$ -axes.

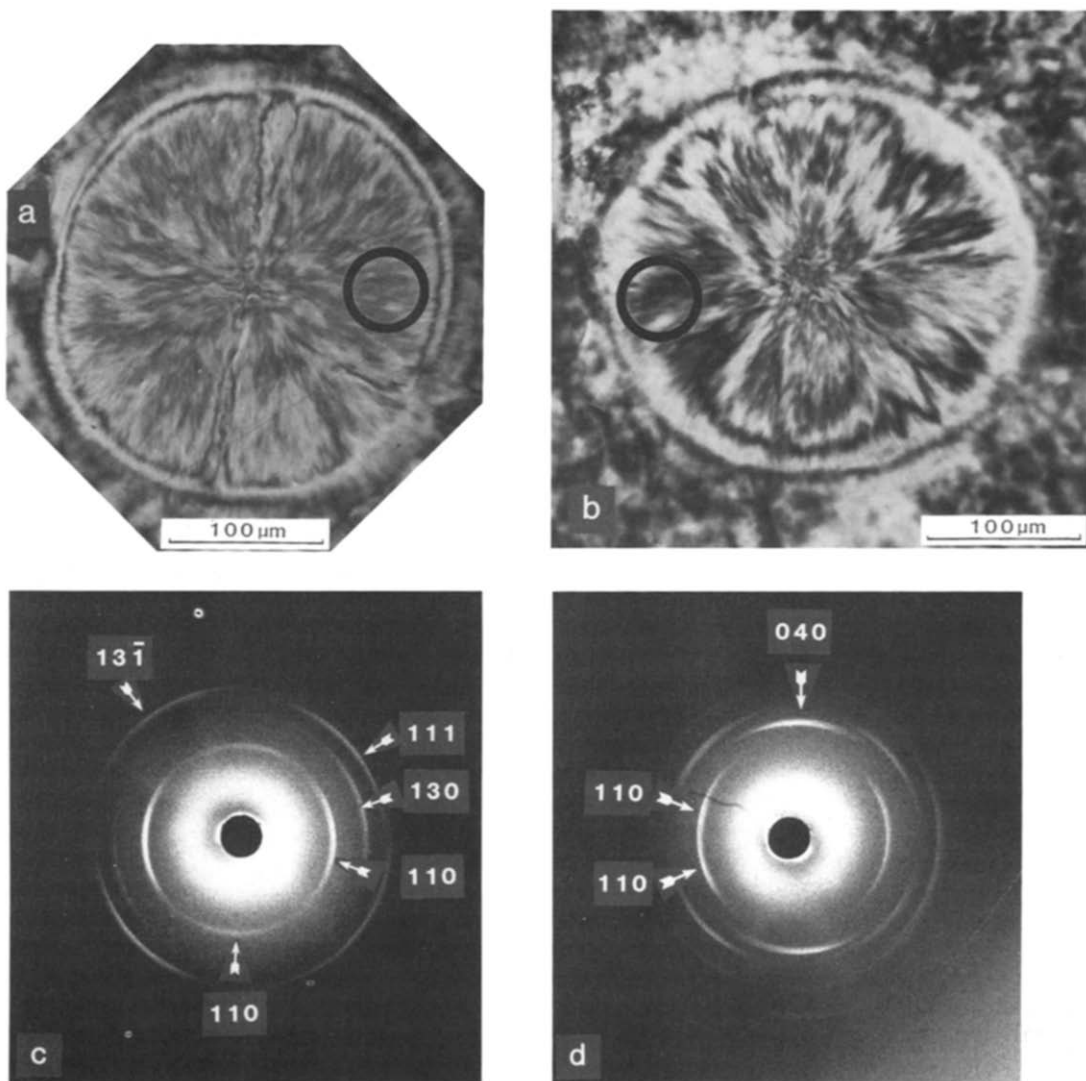
#### More advanced stages of growth

The orientation of the original quadrite persists in considerable measure to very large dimensions. *Figure 7*





**Figure 6** Early spherulites in polypropylene after 2 min growth at 130°C: (a) in circularly polarized light and (b) between crossed polars with a mica quarter-wave plate. Arrowed objects are viewed perpendicular to the original twin axis



**Figure 7** Thick spherulite sections of  $\alpha$ -polypropylene after 64 h growth at 155°C: (a) viewed down the original twin axis; (b) perpendicular to the original twin axis; (c) microbeam X-ray of the detailed area in picture (a); and (d) the same for picture b

shows two objects exceeding 200  $\mu\text{m}$  in diameter and the microbeam X-ray patterns from their extremities. These objects were grown for 64 h at 155°C in a  $\approx 0.1$  mm thick film, which will eventually have restricted their growth so that they are effectively thick central sections. For the object in *Figure 7a*, the shape and internal structure indicate that it is being viewed down a direction close to that of the original twin axis, i.e. it is an enlarged rosette. Its diffraction pattern (*Figure 7c*) shows two sets of 110 arcs (the innermost reflections). The stronger pair is centred about the radial direction. These derive from radial dominant lamellae with about  $\pm 30^\circ$  spread of orientation. The weaker second set, at  $\approx 80^\circ$  to the first, is due to the cross-hatched component, which for this growth temperature has much less mass. The  $80^\circ$  relation is in the same sense as that derived previously, i.e. with the obtuse angle facing the long axis of the rosette; 12.30/06.30 in *Figure 7a*. The 040 reflection is absent from *Figure 7c* as would be expected if the twin axis *b* is essentially normal to the photograph.

A second large object, this time in transverse view, is shown in *Figure 7b*. In this case we expect the *b*-axis to be vertical in the initial quadrite. This is also the case for the outer region used for the microbeam photograph of *Figure 7d*. What this shows is approximately a single crystal texture viewed down the chain axis, consistent with the foregoing discussion and the low birefringence contrast. A recent study<sup>20</sup> of low molecular weight polypropylene shows a similar maintenance of orientation in large objects grown at 155°C. This gives rise to a variety of birefringence patterns and corresponding X-ray diffractograms.

X-ray patterns obtained similarly by other authors, but for objects grown at 150°C (ref. 5) and below (ref. 14), show increasingly more of the character of a rotation diagram around  $a^*$ . This indicates that randomization of the *b* and *c* axes occurs in a shorter space, the lower the temperature.

This trait is not unfamiliar in polymers. Classic spherulites, i.e. spheres with equivalent radial units, are more closely approached at lower crystallization temperatures than at higher temperatures. However, in *Figure 7* we see objects grown to much greater dimensions than is usual at low supercoolings. We may use them to make a general point about the relative significance of forms grown at high and low supercoolings, and specifically the relation between axialites and spherulites.

The term axialite was first used to describe multilayer polyethylene crystals grown from solution, which to a first approximation consisted of layers splaying about a common axis<sup>15</sup>. Somewhat similar objects, observed for high symmetry polymers growing in films from the melt, were termed hedrites<sup>11</sup> because in different perspectives they displayed either regular polygonal or splaying habits. In previous studies of melt growth of *i*-polystyrene and *i*-polypropylene at 160°C, the objects formed consisted, to a first approximation, of assemblages of splaying lamellae, so that geometrically they were axialites. The continuity with spherulitic growth, both at longer times and at lower temperatures, has, however, been stressed. In this paper, the objects formed at 150 and 155°C also consist, to a first approximation, of assemblages splaying about an axis (fans), but with the added factor of cross-hatching. To a second approximation (which also holds for all other polymer

axialites we have studied) splaying develops in three dimensions as the original axis (pair of axes for cross-hatched polypropylene) branches into a cone of directions. In our previous work we have described the early axialitic stages of melt growth as immature spherulites. We recognized that they possessed means of branching and splaying in three dimensions, which with sufficient continuation must lead to growth along all radii. We drew no essential distinction between axialites and spherulites, nor do we now with further experience of several polymer systems.

This is in contrast with the view of Keith<sup>12</sup>, who claimed that axialites consist of equiaxed lamellae, in contrast to elongated lamellae present in spherulites, into which axialites would change beyond a characteristic size. This point was never shown explicitly, but inferred from the shapes of different polystyrene crystals interpreted as though they formed a time sequence. Such an interpretation must now be regarded as very doubtful. Experiments in this laboratory have reproduced the lamellar habits reported by Keith, but they show that growth occurs at constant shape. The same holds true for *i*-poly(4-methyl pentene-1). Indeed Keith now also recognizes that radial extension in polystyrene spherulites is largely brought about through screw dislocations<sup>16</sup>. If there are also changes of habit, they have yet to be found.

What our paper can contribute to the debate is to show how quadrites develop into large objects in polypropylene, through what are effectively crossed axialites. These shown in *Figure 7* have reached the stage of growing along  $a^*$  in all directions in space. They are not yet spherical, because of the relatively slow deviation out of the plane of the quadrite, but are well on the way to becoming so. The principal difference of the objects in *Figure 7* from classic spherulites is, however, that there is incomplete randomization around the radial direction, in that the quadrite orientation is still recognizable, albeit much broadened. This slowness in randomization both around the growth direction and out of the plane of the initial object is, we suggest, the main difference of an axialite as opposed to a spherulite. Yet there is continuity to lower crystallization temperatures, through what are usually described as coarse-textured spherulites, towards classic appearances at high supercoolings. We make the further point that randomization will be facilitated by the increasing occurrence of screw dislocations, as also will finer textures. It may well be, therefore, that the difference in optical appearance between coarse-textured 'axialites' and finer-textured 'spherulites' reported, e.g. in polyethylene<sup>17</sup>, is due to increased branching in thinner lamellae very probably via screw dislocations. We infer no difference in kind between axialites and spherulites, only of degree.

#### *Summary of differences between growth temperatures*

The differences in morphology observed between objects grown at 155°C and 150°C (and lower) can be summarized as follows:

- (i) Lamellae formed at 155°C are, as is to be expected, somewhat thicker; this point has not, however, been investigated in any detail in the current work.
- (ii) Cross-hatching is more abundant in material crystallized at 150°C, but the effect of this is not sufficient to modify the general form or structure of the spherulite.

(iii) Especially at 155°C, the fans from the original quadrite maintain their integrity, even in very large spherulites. At 130°C rapid randomization of the *b* and *c* axes occurs.

(iv) The rate of divergence in space of fans and sheaves of lamellae is lower, the higher the temperature. As a result both the twin fans which form the rosettes and the sheaf of the transverse section can, at 155°C, grow two to three times as big as at 150°C before they close to form a rounded object. At 130°C the objects round out very rapidly indeed.

## CONCLUSIONS

At 150 and 155°C, just as at 160°C, polypropylene spherulites develop by outward growth of radiating dominant lamellae. This is coming to be recognized as a general method of spherulite development in polymers<sup>3</sup>.

In polymer spherulite growth in general, including polypropylene at 160°C, the space between the dominant lamellae is filled in by more or less parallel subsidiaries. With polypropylene at 155°C and even more so at 150°C, the space is beginning to be filled by transverse twinned lamellae. However at these temperatures the generation of parallel subsidiaries is still sufficiently faster than the twinning rate to be the predominant factor determining local morphology.

In spaces where an array of dominant lamellae has not yet been formed, the local morphology follows the cross-hatched pattern characteristic of  $\alpha$ -polypropylene.

The orientation of the radiating dominant lamellae, even in a large spherulite, is closely related to that of the lamellae in the initial object from which the spherulite was formed. Lamellar orientation is far from random over the surface of a spherulite. Simple geometrical considerations are adequate to account for this. However this has

important consequences regarding the precise definition of a spherulite.

The initial development of spherulites at 130°C can be more clearly understood in the light of higher temperature observations, but more observations need to be reported<sup>18</sup> to provide a detailed picture.

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