

On the lamellar morphology of melt-crystallized isotactic polystyrene

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The lamellar morphology of melt-crystallized isotactic polystyrene has been investigated by extending the technique of permanganic etching for electron microscopy. This paper reports on objects grown at 220°C which are comparatively uncomplicated, being aggregates of hexagonal lamellae, with smooth facets and distinguishable internal sectors, organized into axialites. To a first approximation only, hexagonal lamellae splay apart about a common diagonal presenting three characteristic projections in orthogonal directions. These are hexagonal, sheaflike and an array of approximately parallel lamellae. In reality the term axialite is an oversimplification. Splaying is not restricted to a single axis but occurs in three dimensions making these objects incipient spherulites. Polystyrene spherulites grown as low as 180°C the temperature of maximum growth rate are also constructed on the same principles as are spherulites of polyethylene and isotactic polypropylene. These are that a framework is established by individual dominant lamellae which branch and splay apart leaving interstices to be filled by later-crystallizing subsidiary lamellae. There is evidence that subsidiary lamellae contain shorter molecules on average than do dominant lamellae. The dominant/subsidiary construction is not what had been assumed in the Keith and Padden theory of spherulitic growth nor is there evidence of cellulation or local diffusion influencing development even though crystal sizes exceed the Keith and Padden parameter δ by two orders of magnitude. We conclude that polymer spherulites can form independently of the mechanism proposed by Keith and Padden¹⁴. It is suggested that the cause of lamellae splaying apart is a mutual repulsion due to uncrystallized portions of molecules between dominant lamellae.

(Keywords: isotactic polystyrene; spherulites; polymer lamellae; melt-crystallization; permanganic etching)

INTRODUCTION

A fundamental understanding of many important properties of crystalline polymers depends upon an adequate knowledge of their lamellar (and larger-scale) morphologies. For example, the Young's modulus along the chain axis is much less for a series lamellar arrangement than for a parallel one which constrains the soft inter-lamellar regions. Increases to about three orders of magnitude in Young's modulus can be attained by suitably modifying the morphology, usually by drawing to extensions of thirty or more¹. The electric strength of crystalline polymers falls as spherulite size increases because of the changing nature of interspherulite boundaries and the consequent facilitation of breakdown². The number, size and disposition of lamellar crystallites is essential information for calculating thermal conductivities³ and thermal expansion⁴ in semi-crystalline systems. Nevertheless, it remains the case that our morphological knowledge is far from sufficiently detailed and, for melt-crystallized polymers, still rests largely upon the rudimentary information provided by optical microscopy. Development of theoretical understanding of such properties as mentioned above has thus been more or less limited to modelling hypothetical arrangements of equivalent lamellae within two-phase systems.

The primary reason for the lack of detailed morphological knowledge is that this should have been provided by electron microscopy but transmission of electrons through polymers causes radiation damage and

severely limits direct study. The alternative indirect approach of observing polymer surfaces either by scanning microscopy or by replication and transmission microscopy, though very useful, has not generally sufficed to give the necessary information. Scanning microscopy is usually unable to resolve individual lamellae. Replication can resolve lamellae provided the surfaces examined contain the necessary details. This is not always the case but even when it is, one also requires a lack of bias to reveal a representative morphology. Frequently fracture surfaces have been prepared and replicated. These are, in principle, liable to bias because they have been selected by the propagating crack in preference to other routes. For example, detailed work on linear polyethylene has established that fracture surfaces in that polymer tend to be biased (a) because thinner lamellae tend to be under-recorded (and are often seemingly absent) due to the fracture process⁵ and (b) because {200} are the preferential fracture planes⁶. The morphology thus presented in a fracture surface of linear polyethylene tends to over-emphasize thicker and more regular lamellae and is viewed predominantly down *a*, i.e. tangential to spherulites. The important view down the spherulite radius, always *b*, is rarely seen.

A solution to the problem of providing finely detailed and representative surfaces of crystalline polymers enabling transmission microscopy of replicas to resolutions better than 5 nm is permanganic etching^{7,8}. This technique selectively removes $\approx 1 \mu\text{m}$ or less from any surface

of various polyolefines revealing major and minor morphological differences in a systematic way. The opportunities presented by the application of permanganic etching are many. In the first instance it was used to study the lamellar morphologies of linear polyethylene as functions of most readily available crystallization conditions^{6,9-12}. Among the principal conclusions of this work were that melt-crystallized polyethylene is highly lamellar. There is pronounced organization evident in the profiles and disposition of lamellae especially when viewed in the radial (*b* axis) projection. The morphologies develop by the outward growth of individual (dominant) lamellae into the melt creating interstices which are subsequently filled with subsidiary lamellae. The profiles of dominant lamellae vary systematically with the temperature of crystallization and the molecular lengths¹⁰. Moreover, at least for the higher crystallization temperatures, it has been demonstrated that different molecules are placed in dominant and subsidiary lamellae¹¹. In the linear polymers, shorter molecules tend to form subsidiary lamellae, while in lightly branched (linear low density) polyethylenes, it is the more highly-branched species which do so¹³. This is markedly different morphological organization within a melt-crystallized polymer from that which had been anticipated, especially from the theory of Keith and Padden¹⁴.

These authors addressed the problem of organization within spherulites¹⁴, the characteristic products of crystallizing a polymer from its unperturbed melt. They supposed that polymer spherulites consist, as first formed, 'of fibres or fibrils separated to a greater or lesser degree from one another by layers of as yet uncrystallized melt'. Their principal proposal was that such fibrous habits were a consequence of extreme growth promoted by the diffusional segregation of slower-crystallizing or uncrystallizable species. Because of this an otherwise smooth crystal interface would become unstable against cellulation and fibrillation when its lateral dimensions exceeded the parameter $\delta = D/G$ where *D* is the diffusion coefficient of rejected species and *G* is the rate of advance of the growth front. Specifically the diameters of the cells, and thus the widths of the fibres or lamellae contained within them would also be of the order δ in size. Their expectation, therefore, is for ordered arrays of fibres occupying regions or cells of lateral dimensions $\sim \delta$ and separated by 'major accumulations of those impurities which can diffuse freely in the melt'¹⁵.

The observations on polyethylene were substantially different from these predictions. In the first place cellular growth patterns of the suggested type, comprising cells whose boundaries contained accumulated rejected lower mass species between outgrowing fibres, were not found^{6,10-12}. The first system examined⁶ did appear to show organized growth cells, occurring in a very restricted range of conditions, but these had the opposite character from that expected. They consisted rather of individual non-planar dominant lamellae (of higher mass molecules) enclosing columns of melt (of lower mass molecules) which subsequently crystallized as subsidiary lamellae. Subsequent investigations¹⁰⁻¹² of a wide range of growth conditions, always showed the dominant/subsidiary growth pattern. There were no growth cells analogous to those observed in the constitutional supercooling of metals and organic compounds. On the contrary the occurrence of enclosed columns of melt during growth

seemed a secondary consequence of the non-planar lamellar habits of polyethylene rather than a fundamental phenomenon. Moreover, even fibres considered in a generalized sense, namely objects with widths $\sim \delta$ and much greater lengths, were not observed. The specific suggestion¹⁵ that, because of cellulation, lamellar widths would be of order δ was not supported. Measurement of the widths of dominant lamellae gave values increasing from 1 to 7 μm with temperature through the crystallization range¹², very different from large corresponding variations in the parameter δ . It was pointed out¹², furthermore, that the principal and characteristic textural dimension between the locations of segregated species observed within melt-crystallized polyethylene was not the width of lamellae, but the smaller and little varying separation between adjacent dominant layers.

Although the Keith and Padden theory had been applied to polyethylene¹⁵, the observations mostly cited in its support were those on isotactic polystyrene and polypropylene^{15,16}. In view of the difficulties recounted above in relating the observations on polyethylene to this theory, it seemed appropriate to investigate melt-crystallized lamellar morphologies in these two other polyolefines. This paper reports the first results on isotactic polystyrene. The lamellar morphologies will be shown to be comparatively uncomplicated. It is also noteworthy that, for this polymer, Keith¹⁷ reported observations which he interpreted as showing the onset of cellulation at 215°C and dimensions $\approx 10\text{--}20 \mu\text{m}$. We have now investigated growth at a similar high temperature, 220°C, examining crystallization in bulk as well as thin films such as Keith studied¹⁷. It is advantageous to begin to study the morphology of a system at high growth temperatures because of the simpler objects formed and the ease of distinguishing isothermal growth from additional development on quenching. Our subsequent work has, nevertheless, shown that no major modification of the conclusions reached is necessary at least to crystallization temperatures as low as 180°C, the maximum in the growth rate curve. These principal conclusions are:

- (1) that there are no 'fibres' and no indication of incipient instability of planar growth faces even though crystal dimensions greatly exceed the parameter δ .

- (2) mechanisms of splaying and branching exist, independently of fibrillation, which are themselves sufficient to give equivalent radiating branching units capable of generating spherulites.

- (3) that growth occurs with the same dominant/subsidiary pattern identified previously in polyethylene and subsequently in isotactic polypropylene²⁵. The characteristic textural dimension this gives to the crystallized polymer and the distance apart of the sites for segregation is the separation between adjacent dominant sheets.

EXPERIMENTAL

Materials and procedures

The isotactic polystyrene studied was extracted with toluene from polymer purchased from Polymer Laboratories, UK. As such it had average molecular masses, determined by gel permeation chromatography, of $\bar{M}_w = 1.2 \times 10^6$, $\bar{M}_n = 1.3 \times 10^5$. This was moulded into cylindrical specimens, $\approx 1 \text{ cm}$ in diameter and 1–2 mm thick, which were then sealed in oxygen-free nitrogen in

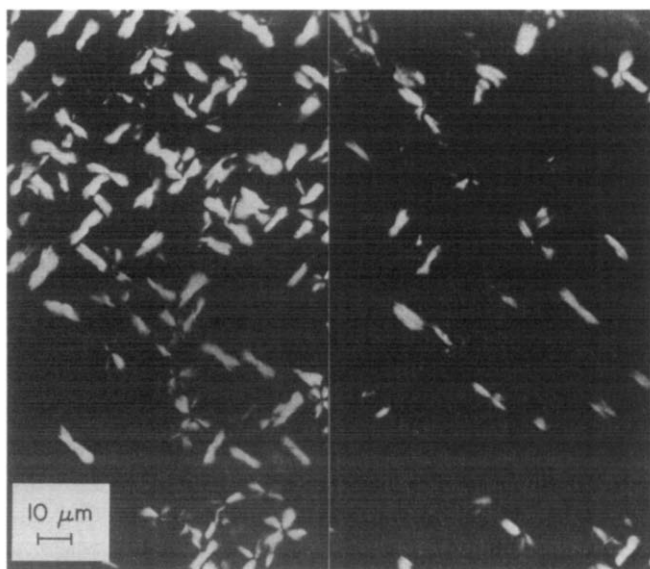


Figure 1 Composite optical micrograph of developing morphologies in isotactic polystyrene crystallized from the melt at 220°C. The left half is of a thin film crystallized for 37 h; the right half is of a thin section cut from bulk material crystallized at 220°C for 24 h. Crossed polars

flat-bottomed glass tubes for crystallization. Initially the samples were deliberately degraded slightly, to achieve a suitable nucleation density, by being held at 258°C for 2.5 h. They were then crystallized for 24 h at 220°C and quenched. The material which had crystallized in this period had average molecular masses of $\bar{M}_m = 6.5 \times 10^5$, $\bar{M}_n = 9.8 \times 10^4$; the remainder (which could be extracted using methylene chloride) had lower parameters, viz: $\bar{M}_m = 4.9 \times 10^5$, $\bar{M}_n = 9.3 \times 10^4$.

Optical microscopy

The appearance of the sample, prepared as described above, between crossed polars is shown in the right half of *Figure 1*. Many of the objects are sheaflike with an apparent fibrosity of a few μm . Others are less linearly developed but more rounded and circular with corresponding extinction in their images. (Essentially identical appearances, though with more of the rounded ones, result from growth in films $\approx 10 \mu\text{m}$ thick, left half of *Figure 1*.) In all cases the birefringence is positive, i.e. the largest refractive index is (approximately) radial or along the length of a sheaf. There are also hexagonally-shaped objects but these show little or no birefringence and are not readily seen between crossed polars. They are observed in etched surfaces using Nomarski interference contrast optics. *Figure 2* is not of this sample, but of a similar one crystallized at 210°C. It is shown because, by chance, it displays what are diagnostic views of various objects side by side. Object A is sheaflike while B is polyhedral with a sheaflike interior fibrosity. These two types, A and B, are together sufficient to account for nearly all the birefringent objects visible in *Figure 1*.

These samples as crystallized were examined in part by viewing thin microtomed sections optically between crossed polars (*Figure 1*) but mainly following permanganic etching. For this, a stub with a microtomed surface was immersed, usually for 2 h, at room temperature ($\approx 20^\circ\text{C}$) in a 1% solution of potassium permanganate in sulphuric acid to which sufficient water had been added to give the

reagent a brown colour. After subsequent washings, following prescribed procedures⁷, the initially microtomed surface was first examined optically using Nomarski Interference Contrast in reflection (*Figure 2*) and then replicated in two stages. Metal shadow was applied to the first impression and transferred to the second stage carbon replica which was examined by transmission electron microscopy. The appearance of relief in the electron micrographs depends on the orientation at which they are viewed. The correct impression is one of lamellae standing proud of a somewhat pitted matrix.

The smaller object C in *Figure 2*, with a linear substructure, would also be strongly birefringent. Some of the small birefringent areas in *Figure 1* are probably of this kind. In addition D is a symmetrical, smooth-faced hexagon, while E is somewhat more rounded and F has a marked interior structure whose significance will become apparent.

All these views can be derived from different projections of similar entities, namely axialites, geometrically similar to the first polymeric objects so-called, i.e. polyethylene crystallized from concentrated solutions²⁶. They also have points of resemblance to hedrites, a word coined by Geil¹⁸ to describe objects grown from thin molten films and not unrestricted bulk as here. Keith¹⁷ has previously noted similar appearances and interpreted them in terms of objects whose dimensions are $\ll \delta$, a fact which is inconsistent with our measurements as will be demonstrated. The morphological inferences drawn from optical microscopy are substantiated and extended by electron microscopy of etched surfaces.

Electron microscopy

The objects viewed by electron microscopy are the etched intersections of arbitrary planes with crystalline objects embedded in an uncrystallized matrix. There are

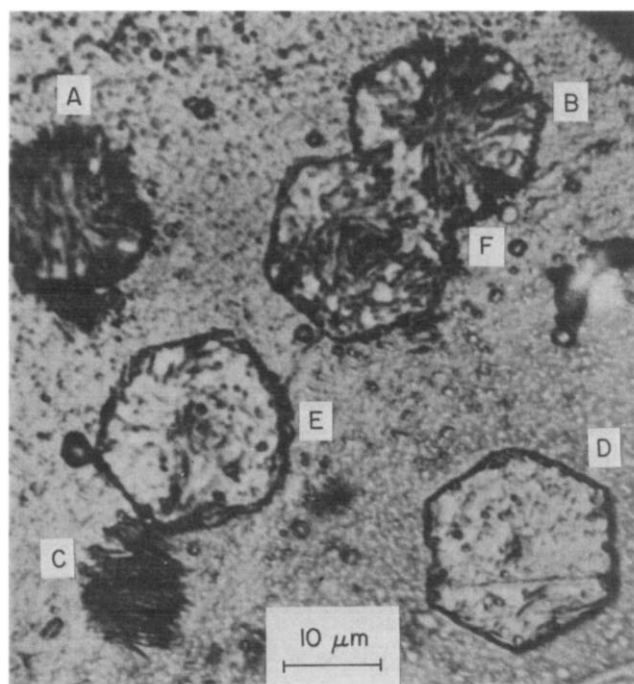


Figure 2 Random views of developing morphologies in isotactic polystyrene crystallized from the melt for 8 h at 210°C. The lettering is identified in the text. Optical micrograph of an etched cut surface seen in reflection by Nomarski Differential Interference Contrast

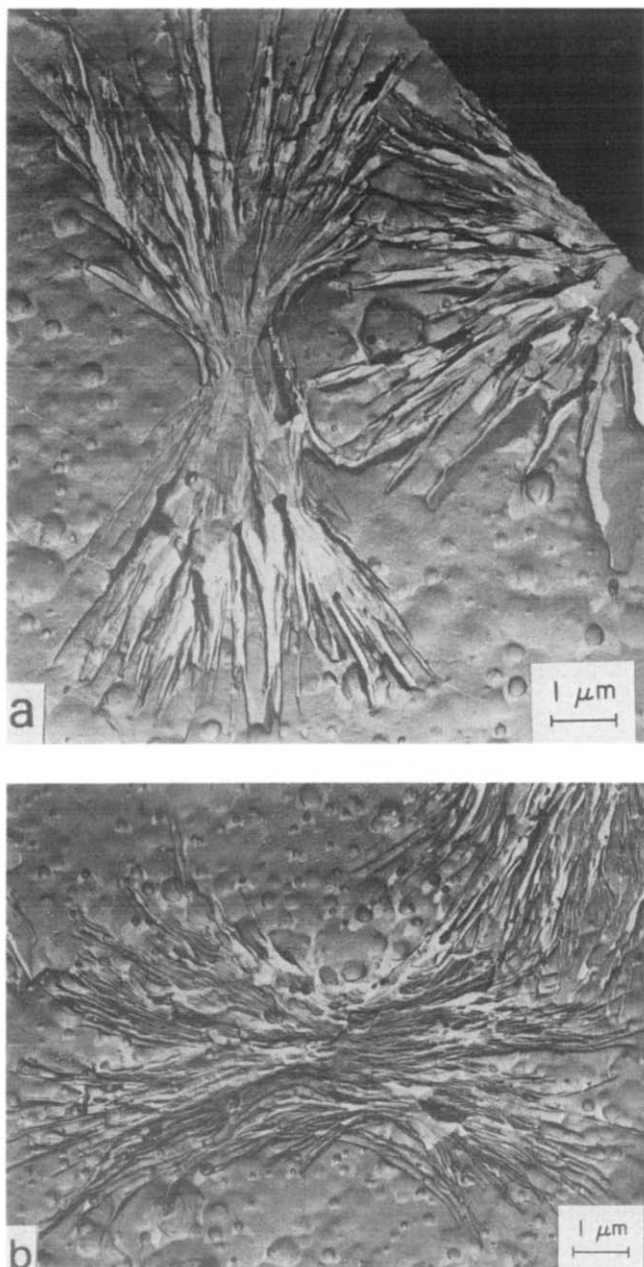


Figure 3 Electron micrographs showing sheaflike objects crystallized in isotactic polystyrene for 24 h at 220°C. Note that the extremities of the sheaves are composed of individual lamellae splaying apart. It is likely that the thinner waist in (a), compared to (b), is due to the cut passing more centrally through the object. Replicas of etched, cut surfaces

again three diagnostic views, equivalent to those seen optically in *Figure 2* for the lower crystallization temperature, but now displaying lamellar detail. One such view is sheaflike (*Figures 3a and b*). This is revealed by observing the lamellar objects from the side, in the planes of their lamellae, whose traces then appear as lines. The lamellae themselves are some 20 nm or so thick and are tightly packed in the centre of the sheaf but splay apart at the edges of the micrograph. Especially important is that, at the outermost edges, one finds individual lamellae, rather uniformly spaced apart and separated by uncrystallized polymer. These are dominant lamellae whose outward growth establishes the bounds and framework of the crystallizing objects. Some microns behind the outer edges one can see that what would, earlier, have been

spaces have become filled with subsidiary lamellae. At the centre of the sheaf one has a stack of lamellae. This is $\approx 1 \mu\text{m}$ deep in *Figure 3a*, but $\approx 3 \mu\text{m}$ in *Figure 3b*. The difference is probably due to the plane revealed in *Figure 3b* being further from the centre of its sheaf than in *Figure 3a*. The centre of *Figure 3b* shows slight differential etching, which is probably to be interpreted as evidence of dominant lamellae being more resistant and thereby being different in nature from subsidiary lamellae. This might reflect their being composed of longer molecules, in accordance with the measured decrease of molecular mass of the residual melt with time. Alternatively it could well also reflect a better internal order due to a longer annealing time after crystallization.

An orthogonal view to *Figures 3a and b* is that of *Figure 4* which presents the hexagonal outline of lamellae viewed approximately normally. One sees here parts of many lamellae sharing a common axis of splay which connects opposite corners of a hexagon and goes from lower left to top right. The most extensive portion of an individual lamella is on the left hand side. This has an internal structure of fine lines normal to the growth faces which subdivides it into sectors. The same phenomenon also occurs for crystallization at 210°C. An apparently similar fine ripple has previously been reported for isotactic polystyrene hexagonal lamellae grown on a mica substrate at 190°C from 10% solution in the atactic polymer¹⁹.

Lines normal to growth faces are found in lamellae of a number of solution-crystallized polymers *after collapse on a sub-strate*^{20,21}. They are a result of lattice distortion due to chainfolding along the growth planes which leads to a shallow dishing of as-grown lamellae. Flattening on a substrate, e.g. in preparation for electron microscopy,

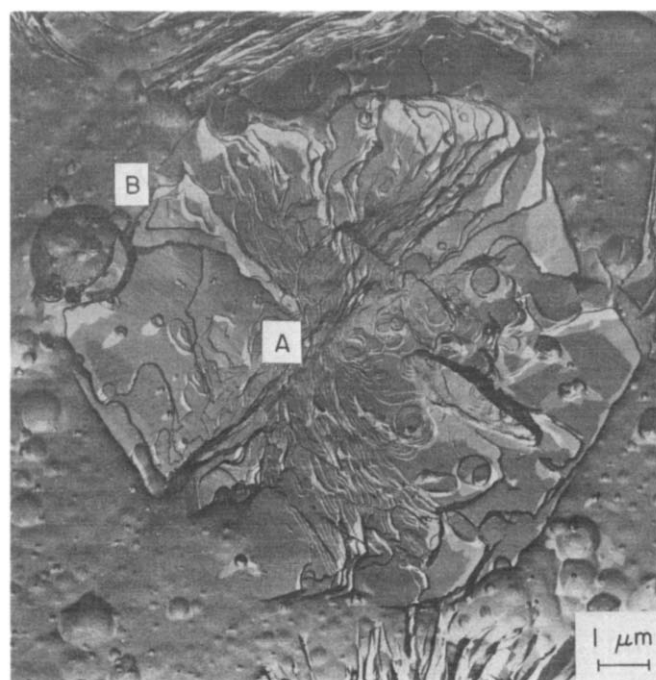


Figure 4 Plan view of hexagonal lamellae in isotactic polystyrene crystallized at 220°C for 24 h. Lamellae splay apart about the diagonal connecting bottom left to top right vertices. A and B identify spiral terraces as discussed in the text. Striations normal to growth faces (e.g. left of A) divide the lamellae into sectors. Electron micrograph of a replica of an etched cut surface

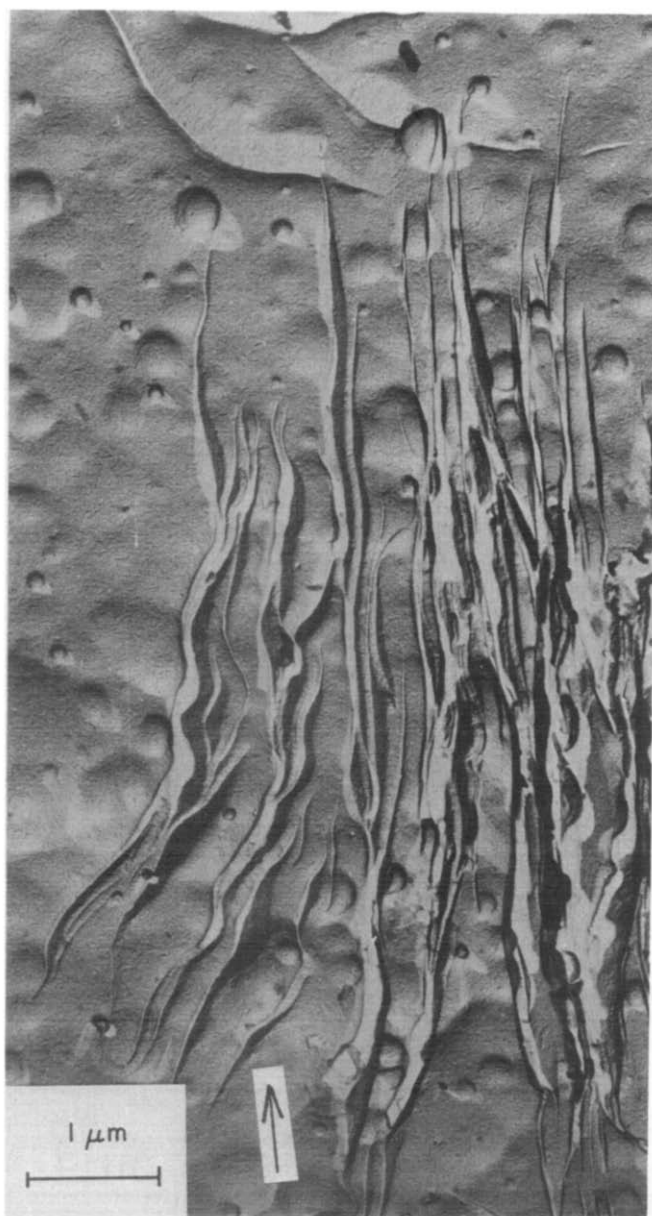


Figure 5 An array of separated and approximately parallel individual lamellae representing organization near the edge of a sheaf in isotactic polystyrene crystallized at 220°C for 24 h (cf Figure 3). Electron micrograph of a replica of an etched, cut surface

causes local shear and rotation of the growth around their normals. As a consequence streaked contrast can then be seen in diffraction imaging^{20,21}. The phenomena seen in polystyrene are not, however, necessarily indicative of ordered folding although they may be. Previous work detected no lattice distortion in association with the ripples in polystyrene¹⁹ in contradistinction to polyoxymethylene²⁰, for instance. One alternative explanation for the ripples could be that they take up excess material when a planar layer becomes dished as at least some lamellae are observed to be (c.f. the discussion of Figure 6). A secondary consequence of rippling could also be the location of screw dislocations at intersector boundaries. One such dislocation exists left of A in Figure 4. A similar siting occurs in melt-⁶ and solution-crystallized^{22,23} polyethylene and has been explained in terms of non-planar growth. A fine ripple would also be one plausible cause, in terms of mistakes during growth,

for screw dislocations at more general sites. There are many such in our samples. One is present at B in Figure 4 which is noteworthy for the etch pit at its centre, itself a further indication of the sensitivity of permanganic etching to crystalline disorder.

Figures 3 and 4 have shown views of two orthogonal sections of equivalent objects. The third orthogonal view will depend appreciably upon where the object is cut open. A cut at either end of a sheaf like those in Figures 3a and b will produce a view such as that in Figure 5. This shows a series of individual lamellae, which would have been growing nearly normal to the page, spaced apart by distances of ≈ 0.25 to $0.5 \mu\text{m}$. (A surface cut across the central region of a sheaf shows lamellae to be continuous in its own centre, but with separated dominant lamellae at the edges.) Evidently the lamellae are approximately planar but some show sinusoidal ripples with a wavelength $\approx 1 \mu\text{m}$. This is most pronounced at the lower left where the average orientation of the lamellae moves some 30° from the vertical on the page. Not only is this in keeping with the earlier suggestion of how ripples might arise, but it also demonstrates in detail that lamellae are splaying apart. The insertion of an 'extra' unit (arrowed) distorts the array accordingly. Phenomenologically this can be explained on the basis of a repulsion between these first forming or dominant lamellae. It also illustrates the point that objects splay in three dimensions and not just the two of an idealized axialite. This conclusion is also exemplified by the comparison of the waist sizes of Figures 3a and 3b, referred to previously.

General views of polystyrene crystallized at 220°C, such as in Figure 6, leave no doubt that the objects formed consist of lamellae radiating and splaying in three dimensions. Although they merit the description 'axialite' as a first approximation, this should not be taken to imply that splaying is about a single axis and certainly not as a basis for supposing that a further, additional, feature of growth needs to be introduced before objects can branch and

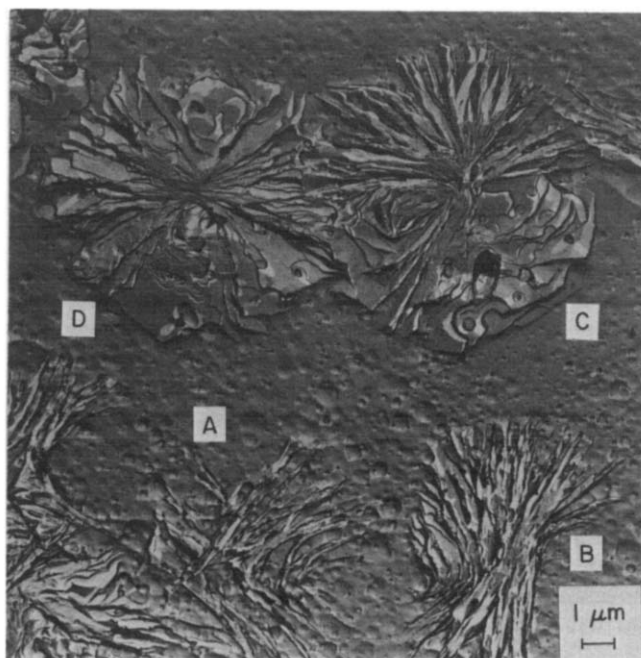


Figure 6 Random views of isotactic polystyrene crystallized at 220°C for 24 h. The four axialites A, B, C and D are all splaying apart in three rather than just two dimensions as discussed in the text. Electron micrograph of a replica of an etched cut surface

splay in three dimensions, i.e. be potential spherulites. The actual splaying geometries observed can be discussed with respect to rectangular axes with an origin at the centre of a stack of parallel lamellae and one axis, T , along the common lamellar normal. An ideal axialite would be generated by causing lamellae to splay apart around one of the axes originally in the plane of the lamellae. This we term the major axis of splay, M . In polystyrene it is parallel to one set of the $\{11.0\}$ growth faces. It is usual also to observe lesser splay about the minor axis, m , i.e. the second axis lying in the plane of the parallel stack. Although rotation about two perpendicular axes is sufficient to generate all possible orientations of lamellar normals, the additional descriptive convenience of relating a zone of lamellar normals to a single (zone) axis of splay, makes it appropriate to refer also to rotations about the third orthogonal axis T . We may now identify the observed geometries of objects in *Figure 6* in relation to the three axes, M , m and T .

The object of the lower right of *A* has M in the plane of the page, parallel to the linear traces of lamellae, but the increasing curvature of these traces towards the bottom right indicates splay about m normal to the page. Object *B* has M normal to the page. The interesting point here concerns the curved lamellae on its left. As the minor axis m must lie in the page, splay around this would only yield a morphology symmetrical about the waist. The observed skewness may thus be described by an additional rotation around T . The point that the polystyrene objects which grow at 220°C are already geometrically complex with lamellar normals spreading in three, and not just two, dimensions is evidently made. Indeed objects *C* and *D* in *Figure 6*, seen in general, rather than special, positions show that they are already approximating to the condition of having lamellae growing radially outwards in all directions which is the condition of mature spherulites.

The question arises as to how lamellae, which are presumably planar in an unstrained state, can accommodate themselves to the bent, splaying and dished morphologies displayed in *Figure 6* and elsewhere. There are two principal alternatives for individual lamellae to become dished. If molecular inclination is preserved within lamellae (perpendicular for polystyrene) then dishing can only be accomplished with concomitant pleating or fluting of excess material in the same way as is necessary for a sheet of paper. The puckering of lamellae seen in *Figure 5* could be an example of this phenomenon. Alternatively, dished shapes are readily derived by shear parallel to a common molecular axis. (The reverse process occurs in the collapse, without pleating, of hollow pyramidal polyethylene crystals grown from solution²⁴.) If this happens, the change in molecular inclination to lamellar normals should be observable by electron diffraction and related imaging. In a limited number of such observations we have so far always found molecules to be normal to lamellae, i.e. no indication of shear having occurred, although the lamellae selected for examination tend to be among the largest and presumably most planar ones, so the possibility of sheared structures should not yet be ruled out completely. These geometrical difficulties arise if lamellae are bent or curved in two dimensions rather than one. They are much reduced if lamellae are narrow, as they are in isotactic polypropylene²⁵ and as envisaged in general by Keith and Padden¹⁴ among others. However, the lamellae in these—and in other polystyrenes crystal-

lized down to at least 180°C—remain broad but in the regions where geometrical difficulties would be most severe, i.e. normal to the waist of a sheaf, they appear to nucleate on the waist and grow outwards from it: see objects *C* and *D* in *Figure 6*. Similar behaviour is seen in polypropylene²⁵. The suggestion is that lamellae grow out from the waist analogously to petals from the centre of a double flower, like a rose. In this way a single lamella would occupy only a limited angular range with the structure. It could well have pronounced curvature only about one axis and so more readily accommodate itself to its environment.

In the ways just described, polystyrene axialites can develop so as to produce lamellae growing outward along all directions. At lower crystallization temperatures, when the balance between nucleation and growth is more favourable, similar development continues to give the quasispherical envelopes of mature spherulites. Nevertheless, to fill space consistently it is necessary that dominant lamellae should branch. *Figure 7* shows details of how this occurs. In *Figure 7a* one sees that one dominant lamella will branch into two equal daughters at angles $\approx 15^\circ$ (*A* and *A'*); that layers curve away from each other when in close (≈ 50 nm) proximity, *B*; but that lamellae can also be parallel for $\approx 1 \mu\text{m}$ and then suddenly diverge, as at *C*. One needs more information than such a plan view provides to elucidate the details of how branching is initiated. Views through a depth of material are inherently more useful than the examination of surfaces which permanganic etching allows. Nevertheless, in *Figure 7b* (arrowed), one can see lamellae diverging from a line. This suggests that branching is not necessarily associated with giant screw dislocations, with Burgers vector equal to the lamellar thickness. One would expect this lack of association if only because although such dislocations are common in polystyrene—and could, for example, be the origin of the parallel lamellae at *C* in *Figure 7a*—they have not been observed in isotactic polypropylene, a polymer whose spherulites are constructed with frequent branching. The detail of actual branching illustrated in *Figure 7b* has a geometry seemingly more appropriate to classical secondary nucleation.

The lamellar organization of these objects, grown in melt-crystallized polystyrene at 220°C, is thus describable in terms of two major constructional principles for dominant lamellae. The essential features are that dominant lamellae splay apart and that they branch. In addition three dimensional development is facilitated by nucleation of additional lamellae at the waists of the initial sheaving habits. As has been pointed out above, their regular splaying apart suggests that dominant lamellae experience a mutual repulsive force at small separations. The origin of such a force remains to be established but may well be found in the cilia or uncrystallized portions of molecules protruding from fold surfaces. At interlamellar separations less than the diameters of randomly coiled molecules, the conformation of cilia will be compressed. In consequence there will be reductions in entropy and possibly increases in internal energy from altered *trans-gauche* ratios and distorted bond angles. All these factors will contribute to a repulsive force equal in magnitude to the gradient of chemical potential. It is noteworthy that these melt-crystallized morphologies parallel those observed long ago for growth from concentrated solutions²⁶ and that essentially the

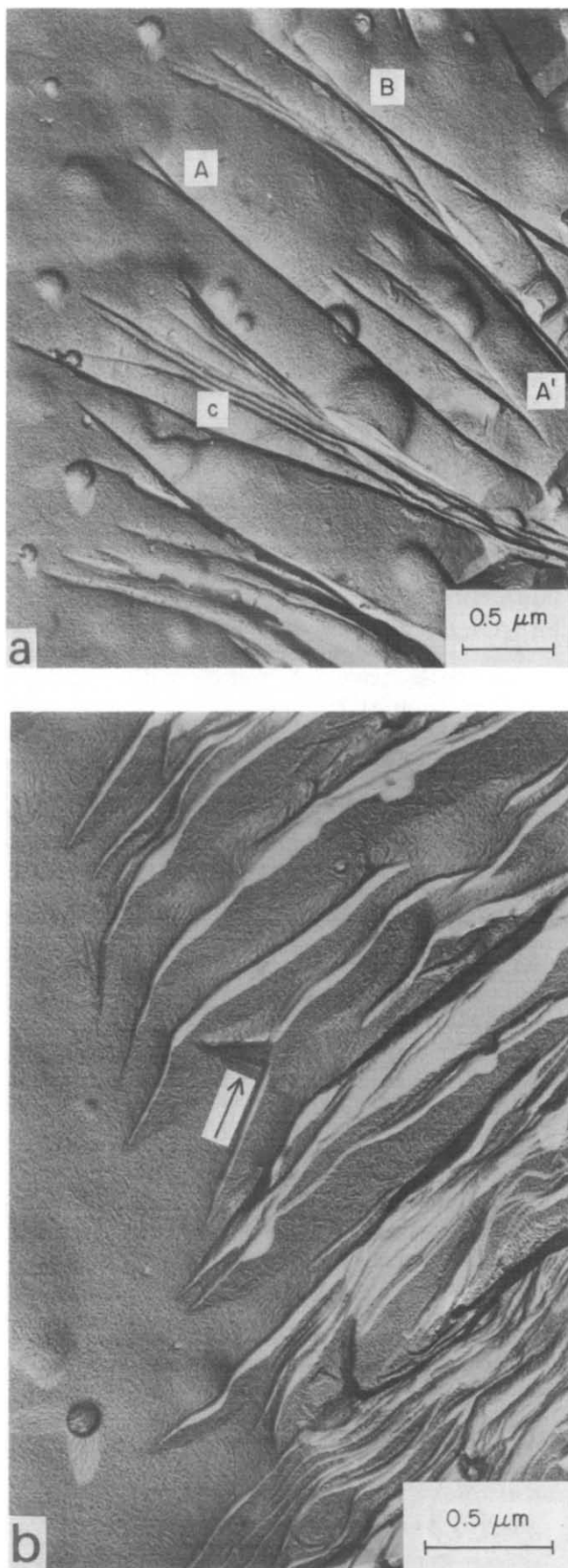


Figure 7 Detail of lamellae splaying apart and branching in isotactic polystyrene crystallized at 220°C for 24 h. *Figure 7a* shows the traces of lamellae only, with details identified for discussion in the text, while a more general view of branching lamellae is presented in *Figure 7b*. Electron micrographs of replicas of etched cut surfaces

same molecular origin was proposed then for their habit development.

Although these first polystyrene morphologies to be studied by permanganic etching have been grown at a comparatively high temperature, to simplify the experimental situation, further work has established that the same constructional principles apply to objects formed at lower temperatures, down to at least 180°C which is the temperature of maximum growth rate. At these temperatures the objects which form would be described as spherulitic according to all the various criteria which are in use. They then grow with a quasispherical envelope and, although they usually show evidence of sheaflike precursors, have developed far enough for lamellae everywhere to be growing radially outwards. The potential of developing into a spherical aggregate is inherent in splaying and branching microstructure and, in our own view, it is the presence of such microstructure which is sufficient to merit the description spherulitic. Sheaflike forms would then be immature spherulites and e.g., in isotactic polypropylene can be shown to become spherical given sufficient time to grow²⁵. Other workers²⁷ have reserved their use of spherulitic to objects which have attained spherical symmetry. This difference is semantic, with no physical significance.

The point we wish to make is that the microstructures we have observed at 220°C are also found at least in some mature polystyrene spherulites, namely those which grew at or above the temperature of maximum growth rate, 180°C. Moreover, this dominant/subsidiary pattern, with splaying of the dominant lamellae, also occurs in polyethylene^{6,10-12} and isotactic polypropylene²⁵. We have, therefore, an organization of some generality which gives spherulites a texture with a characteristic dimension of the separation between adjacent dominant lamellae. We have also shown that dominant lamellae differ in molecular composition from subsidiary lamellae. In linear polyethylene¹¹ and, to a lesser extent, in polystyrene they contain longer molecules, on average. (A numerical comparison between the two polymers must take into account the greater average length of the polystyrene molecules and the thinner lamellae into which they crystallize in assessing the lengths of segregated molecules.) In linear low density polyethylenes dominant lamellae include the least-branched molecular species, which tend also to be the longer ones¹³. Evidently molecular segregation is involved in the growth of the spherulites we have examined but the organization and scale of the textures observed are different from those predicted by Keith and Padden¹⁴. Before considering these differences and their implications it is necessary to consider whether, in fact, the Keith and Padden mechanism should apply under the circumstances examined. There are two reasons for supposing that it should.

In the first place, Keith and Padden¹⁵ themselves consider that their theory applies to an isotactic polymer of mass 41.7×10^3 crystallizing at 200°C a temperature within our range of experiments. Moreover, observations by Keith¹⁷ of polystyrene grown at 215°C (which we have reproduced but on whose interpretation we differ) have been claimed as substantiation by him of the general criterion that the Keith and Padden mechanism applies once crystal dimensions exceed $\delta = D/G$. Our second point is that this condition holds in our experiments. The parameter D , it is quite clear from the context of

cellulation¹⁴, should be the centre-of-mass diffusion coefficient for non-crystallizing molecules. These molecules have a mass-average mass of 4.9×10^5 from our measurements. Comparison with results of Ueno, Otsuka and Kishimoto²⁸ for atactic polymer suggests a value for D of $4 \times 10^{-4} \mu\text{m}^2 \text{min}^{-1}$ at 220°C and this molecular mass. Our measured value of G is $(4.7 \pm 0.3) \times 10^{-3} \mu\text{m} \text{min}^{-1}$ whence $\delta = 0.08 \mu\text{m}$, some two orders of magnitude less than the lateral dimensions of our lamellar crystals. We are thus forced to conclude that, as formulated, the Keith and Padden theory¹⁴ should have applied to our observations.

The predictions of this theory¹⁴⁻¹⁶ are, as stated earlier, of a textural organization derived from cellulation leading to fibres separated by segregated polymers at lateral distances of order $\delta = D/G$. Our findings differ from these expectations firstly in the lack of evidence for cellulation. By analogy with cellulation in metals and organic materials subject to constitutional supercooling one would have anticipated an organization with cells probably in hexagonal array (thereby minimizing boundary energies). Nothing of the sort has been seen in our experiments even though the parameter δ is very much less than crystal dimensions. There is no array of anything save individual dominant lamellae. It would not, however, be appropriate to regard one dominant lamella either as occupying one growth cell or as constituting an individual fibre in Keith and Padden's terminology. On the first point a cell would be expected to be bounded by relatively narrow 'major accumulations of impurities'¹⁵ (i.e. in this context, of shorter molecules). This is the opposite of our findings in polystyrene, polyethylene and polypropylene, of separate dominant lamellae immersed in substantially greater volumes of only moderately 'impure' melt. Concerning the second point, although Keith and Padden¹⁵ stress that it is the width of lamellae which should be set by δ , with lamellar thicknesses determined by chainfolding, it is implicit in their discussion that all lateral dimensions of fibres must be roughly the same and, specifically, that the distances between the locations of segregated species parallel to lamellar thicknesses must also be comparable to δ . If this were not so and this distance were much less than δ , the concentration gradients between adjacent dominant lamellae would greatly exceed those along lamellar widths. They would then dominate steady state diffusion and make it difficult to establish δ as the dimension of fibrillation along lamellar widths. In consequence one would not generally expect a single lamella to qualify as a 'fibre' unless its thickness and its width were both of order δ in size. Not only, therefore, are we unable to identify any fibres (in the Keith and Padden sense) in our morphologies but also the dimension δ does not appear to be the approximate width of any identifiable units in our specimens.

Nevertheless, one might well expect on general grounds, that at sufficiently low crystallization temperatures local diffusion fields should influence crystal growth and habits. There are, indeed, progressive changes in habit which occur as the crystallization temperature is reduced below 180°C , the lower limit of the observations reported here. Perhaps these, and changes reported for isotactic polypropylene²⁵, are a consequence of diffusion-controlled habits, though this remains to be established. The scale at which any change might be anticipated is likely again to be of order (diffusion coefficient/growth

rate) purely on dimensional arguments. But there are good reasons for not using the centre-of-mass diffusion coefficient if the system is one of separate dominant lamellae growing outwards, especially in undoped melts. Possibly a segmental diffusion coefficient would be more appropriate. This, however, is taking us beyond the evidence provided in this paper.

The observations of representative lamellar morphologies within melt-crystallized polymers which permanganic etching now allows us to make with the electron microscope extend our knowledge well beyond the previous resolution imposed by being restricted to optical microscopy. In earlier studies Keith¹⁷ noted that objects similar to *Figure 1* consisted of layers which 'for reasons which are far from clear, these splay and give rise to aggregates which appear sheaf-like when viewed edge-on'. He went on to conjecture that 'further growth to sizes considerably larger than δ usually leads to spherulites presumably because individual layers respond to rejected impurities by breaking up into lamellar fibres'. It is this presumption of breaking up and fibrillation which our experiments have failed to support. The distinction which Keith¹⁷ draws between axialites (comprising broad lamellae but $< \delta$ in size) and spherulites (comprising narrow lamellae $\sim \delta$ in width) is not one substantiated in our experiments. Our experience is, on the contrary, that there is a basic construction (also found in polyethylene and isotactic polypropylene) by which both axialites and spherulites develop. It is by the branching and splaying growth of individual dominant lamellae followed by infilling subsidiary growth. The cause of splaying has been suggested^{25,26} to be pressure from uncrystallized molecular portions of cilia confined between lamellae.

In further work, our studies of isotactic polystyrene have been extended to lower crystallization temperatures, varying molecular weights and to melts heavily doped with atactic polymers. These will be reported elsewhere. The conclusions we draw at this stage are as follows:

(1) that, in the range of our observations, melt-crystallized isotactic polystyrene is lamellar.

(2) Larger scale objects (axialites and spherulites) are constructed from a framework of individual dominant lamellae which splay apart and branch. Subsequently subsidiary lamellae (probably composed of shorter molecules) fill the interstices between dominant lamellae.

(3) It is not possible to identify 'fibres' or cellular habits in the observed microstructure. The Keith and Padden interpretation of spherulitic textures in terms of 'fibres' is thus not supported in these circumstances even though the condition that lamellar widths should greatly exceed their parameter δ is met.

(4) The characteristic textural dimension and the predominant interval between areas of segregated shorter molecules in melt-crystallized polystyrene is the separation between adjacent dominant lamellae.

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