

On row structures, secondary nucleation and continuity in α -polypropylene

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The morphology of row structures in the α form of isotactic polypropylene has been investigated, with lamellar resolution, in a homopolymer and three of its fractions, by transmission electron microscopy following permanganic etching. In longitudinal view, dominant radial lamellae were not always perpendicular to the strain-induced central nucleus with which they shared a common c axis; lamellae parallel to the core increased in number at greater radial distances. The underlying reason is related to novel phenomena observed in transverse sections showing that lattice continuity is not maintained if its loss allows crystallization to occur in otherwise inaccessible regions. If there were lattice continuity, the lathlike habit of α -polypropylene lamellae would lead to gaps developing between neighbouring laths with increasing radial distance. In fact, such gaps are generally filled, frequently by lamellae which are edge-on, *i.e.* parallel to the rows, and rapidly, implying that a loss of continuity is not a significant barrier to growth. Space-filling nucleation increased as the crystallization temperature decreased, leading to finer structures at lower temperatures, but was severely inhibited by a large drop in tacticity in which case the gaps remained largely unfilled. Different mechanisms to effect this infilling have been identified with and without loss of continuity but principally incoherent nucleation; the implications for the properties of melt crystallized polymers in general are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

For the critical assessment of how melt-grown morphologies of polymers are affected by crystallization variables, there are many advantages in examining row structures rather than spherulites¹. The restrictions imposed upon development by the linear nuclei of the former as opposed to the effectively point ones of the latter allow much greater precision both in measurement (*e.g.* of lamellar thicknesses) and in identifying significant changes in lamellar orientation. In the course of a wide-ranging electron microscopic study of lamellar morphologies in polypropylene^{2,3} (undertaken to make measurements of a range of parameters including lamellar thickness, interlamellar separation, cross-hatching frequency, growth rate and maximum curvature as functions of crystallization temperature, molecular length and tacticity using fractionated polymers) we have, accordingly, examined the morphologies of row structures of α -polypropylene in detail. It is also the case that the values measured are identical, in the high crystallinity polymer and within experimental error, to those for spherulites and transcrystalline layers⁴. Besides the intended measurements, two novel features have been documented and explored which form the subject of the present paper. The first is that row structures are much more variable than is generally appreciated with, in α -polypropylene, a proportion of lamellae, increasing with radial distance which are more or less parallel to the central thread rather than perpendicular to it as expected. Secondly, transverse views allow the question of the extent to which

crystallographic continuity is maintained during crystallization to be addressed.

One of the basic problems of crystalline polymers is to describe how the three-dimensional geometry of spherulites develops from an individual lamella. The answer is known, in part, to be that generally there is lamellar and crystallographic continuity from centre to edge and that individual dominant lamellae—those which establish the object's framework—diverge from their neighbours, mostly by the easiest distortion, that of splay. In the early stages of spherulitic growth this results in quasi two-dimensional forms, such as sheaves, hedrites and quadrites, with the axis of splay normal to the fastest or radial growth direction. The basic principle of lamellar and crystallographic continuity has long been attested, *e.g.* by the presence within banded spherulites of regions of opposite twist which occupy complete sectors and has been confirmed by electron microscopy showing continuous dominant lamellae throughout a spherulite. Nevertheless, lattice continuity can make randomization of the radial growth direction, from the early two-dimensional stages, more difficult. If this principle is maintained it will require energetically more costly distortions, for example twisting around the length of a dominant lamella, which does occur but infrequently. With such a distortion, however, a lamella gains the advantage that it can then access areas of space, via splay, that are denied to its neighbours and so aid the attainment of the spherical envelope, with equivalent radii, of a mature spherulite.

In certain circumstances, lamellar and crystallographic continuity appear not to be maintained. These include dominant lamellae within the 'eyes' or central bodies of spherulites which appear to have nucleated at various angles

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to encircling lamellae and many subsidiary and infilling lamellae whose growth directions are typically inclined to those of their parents at large angles of 20° and more. It is probable but has yet to be confirmed that such subsidiary lamellae within spherulites may not be continuous with their parent dominants. Whether or not there are breaks of continuity during growth is difficult to ascertain for spherulites from morphology alone and in the absence of microdiffraction data; in some systems lamellae may bend through $\sim 90^\circ$ in response to the material flux⁵. The question has, however, been resolved positively by the results of this paper using the more restricted geometries imposed by the linear nuclei of row structures in α -polypropylene¹. It is also possible to make inferences about the relative barriers to growth posed by continuity with distortion as opposed to nucleation with loss of continuity.

This is possible because of the geometry of row structures which comprise lamellae deposited epitaxially on an extended linear nucleus, along which their common chain axis lies; they are distinct from transcrystalline layers in which lamellae grow normal to a nucleating surface with only the growth direction in common. Moreover, in α -polypropylene, lamellae (to which the chain axis, c , is normal and the growth direction, a^* ,⁶) are narrow laths as a consequence of very limited lateral growth. Their continuing development in a row will tend to give it a starlike aspect, in any transverse cross-section, as the laths diverge from the centre at near constant width. Maintained lamellar continuity will not allow the space between the arms of the star to be accessed, except by crablike sideways growth with alternate cross-hatching⁶ and radial steps, unless lamellae twist around their length, then splay. In practice, this intervening space is found generally to be filled, most often with a change of lamellar orientation at its boundaries. The new lamellae are frequently more or less parallel rather than perpendicular to the row, and the variety and range of new orientations adopted suggests that nucleation has probably been incoherent on the sides of the original radial lamellae. But the discontinuous change of orientation demonstrates, in a very clear way, that the maintenance of lamellar continuity will be overridden if adjacent space can thereby be occupied. There can be no general presumption, therefore, that polymer textures develop exclusively with maintained lamellar crystallography; changes are likely to occur in response to particular circumstances and especially the possibility of crystallizing within otherwise inaccessible space. With this knowledge one can gain new insight into both the fundamental growth processes in crystalline polymers and the morphologies which control their properties, not least in fibre-nucleated polypropylene itself⁷.

It should also be borne in mind that row structures are of interest in their own right, being commonly present in isotactic polypropylene and its commercial products so that a knowledge of their internal organization carries wider implications. The stressed melts produced in injection moulding, for example, often contain oriented row structures which confer a marked structural memory effect and may be recovered after repeated melting/crystallization cycles^{8,9}. This is because of the high thermal stability of their cores whose melting points can exceed 200°C , according to the temperature and stress to which they were subjected when formed¹⁰. There is also a growing technology in deliberately creating row structures as a means of self-reinforcement of injected moulded articles^{11,12}.

EXPERIMENTAL

The four isotactic polypropylenes used during this particular investigation, one homopolymer and three of its fractions, were provided and characterized by Borealis Oy of Finland and are listed in Table 1. They have been chosen to allow a comparison of morphologies with molecular weight at constant tacticity (samples A,C,D) and of tacticity at constant molecular weight (samples B,C). Row structures were produced in them by two slightly different methods in films around 0.5 mm thick. The homopolymer and highest average molecular weight material, A, was sheared by hand, between a bottom layer of Kapton sheet and a cover slip made of a sheet of poly(4-methylpentene-1), on a Koffler Hot Bench when the sample had just started to melt. It was then transferred directly to a Mettler Hotstage (FP52) controlled at the appropriate crystallization temperature and operating with a nitrogen atmosphere. Samples were crystallized either at 140°C for 5 min, 130°C for 2 min, or at 115°C for 10 s, after which they were quenched in cold water. The three fractions, B, C and D, were placed, for 1 min, at 200°C in a nitrogen atmosphere, in a Mettler Hotstage (FP800) then quickly transferred to a second Mettler Hotstage (FP52) operating at 140°C with nitrogen in the specimen area. At this stage, glass fibres were pulled through the sample producing nuclei for row structures in their wake. All these samples were crystallized at 140°C for 15 min, this being the most informative temperature according to the results for the homopolymer, before being quenched in cold water.

Two types of section through the row structures were examined, exposing longitudinal and transverse views as sketched in Figure 1. Longitudinal views were revealed by etching down from the appropriate external surface of the sample, transverse views by cutting the structures at right angles to the length of the rows with a microtome and glass knife then etching. The etchant used was a 1% (w/v) solution of potassium permanganate in a mixture of 10:4:1 volumes of concentrated sulfuric acid, orthophosphoric acid and distilled water, respectively^{13,14}. A 2 h period of etching at room temperature was generally sufficient to reveal the

Table 1 Isotactic polypropylenes used during this investigation

Isotactic polypropylene	M_w	M_w/M_n	% mmmm (isotacticity)
A	541000	5.9	91.4
B	91000	2.7	45.7
C	92000	1.9	86.4
D	199000	2.6	88.5

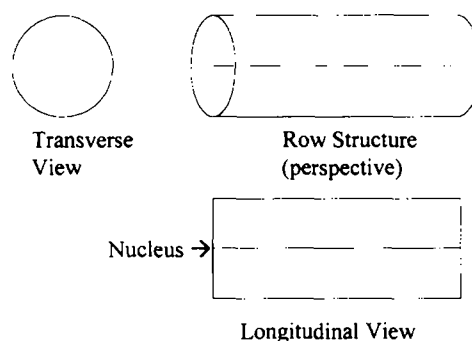


Figure 1 Schematic diagram identifying longitudinal and transverse views of a row structure

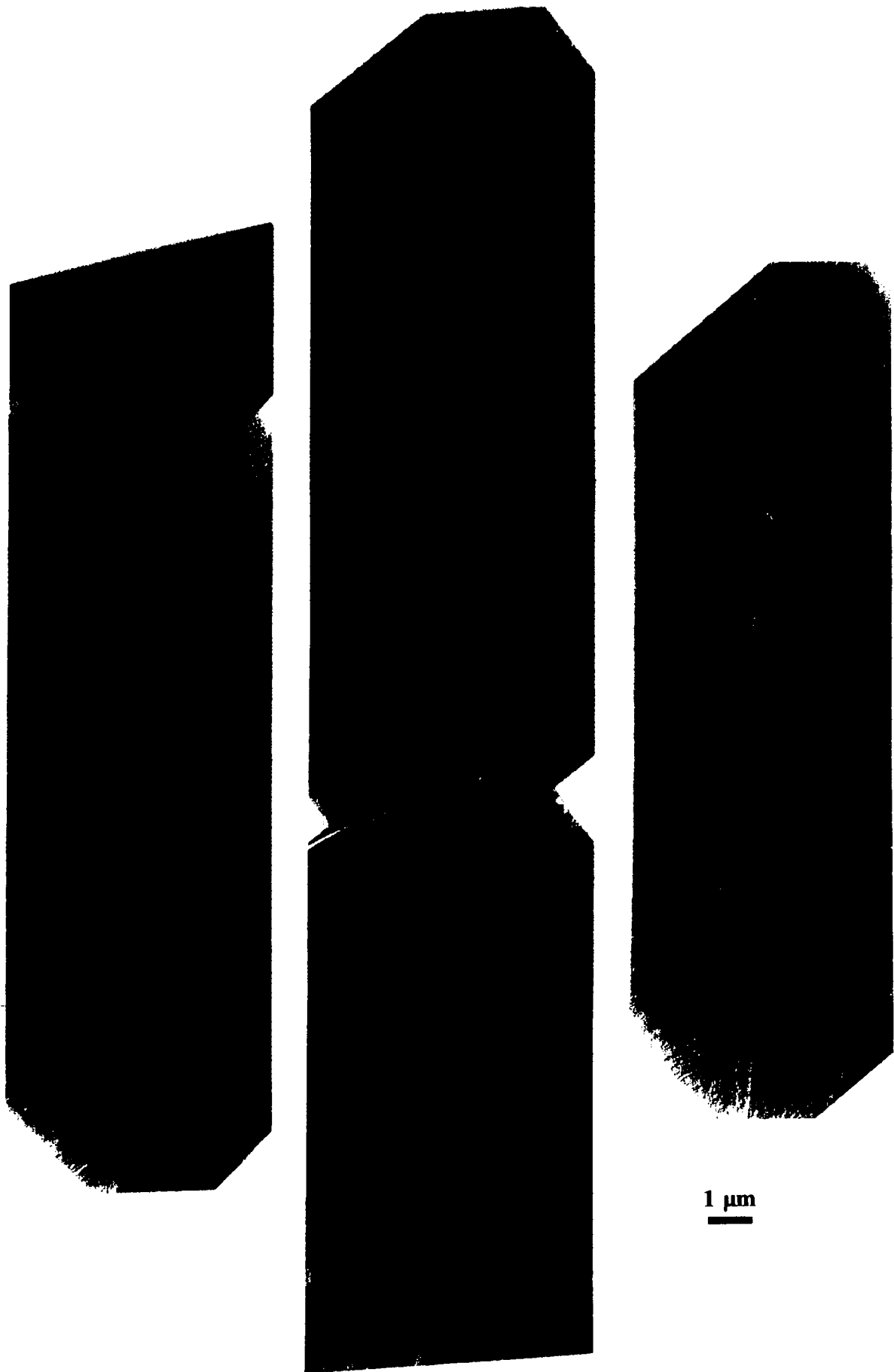


Figure 2 A montage of electron micrographs showing a row, in longitudinal section, within the homopolymer crystallized at 140°C. The locations of the detail shown in *Figure 3* and *Figure 4* are identified by these numbers placed to the side of the respective positions. Carbon replica of an etched surface

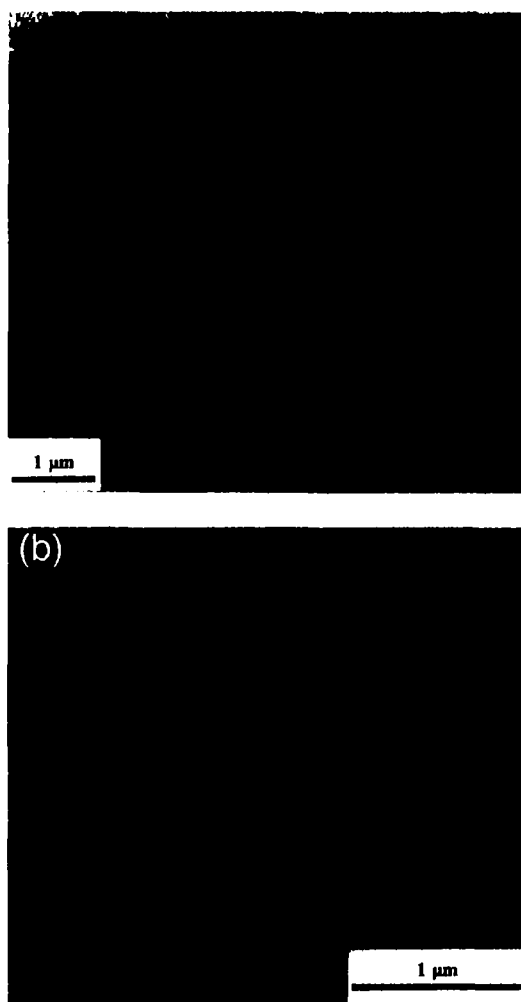


Figure 3 Detail of *Figure 2* illustrating longitudinal sections which include the core of the row. Note the consistent orientation of cross-hatching lamellae in (a), which is well seen below the arrow. In (b), there is a length of double core which has left a step in the etched surface due to the different aspects presented by the cross-hatching lamellae. Carbon replica of an etched surface

surface topography well. Shadowed carbon replicas of the etched surfaces were produced by a standard two-stage process, using cellulose acetate moistened with acetone, for observation in the transmission electron microscope.

RESULTS AND DISCUSSION

More than $60\ \mu\text{m}$ of a single row structure (of the homopolymer A crystallized at 140°C) are displayed, with lamellar resolution, in longitudinal section in *Figure 2*, which is a montage of individual micrographs. So far as we are aware, this is the first time in which such a length of row structure in the interior of a melt-crystallized polymer has been displayed with lamellar resolution. Particular aspects of the morphology are discussed below; note, however, both that there is considerable variation in character, nucleation density and outer diameter along the length of the row but that over distances of a few micrometres the lamellar organization is often rather uniform. It does not have the idealized cylindrical symmetry often attributed to row structures. The central core of the row is identifiable throughout, partly as a raised thread in wider regions and partly by the overlying deeply etched canyon in narrower parts.

The anticipated, conventional appearance of a row structure of α -polypropylene is that shown in *Figure 3a*.

Dominant radial lamellae are growing outwards effectively at right angles to the central row nucleus of around $30\ \text{nm}$ width, aligned along the direction in which the sample was sheared. Cross-hatching lamellae, which are twinned with respect to the dominant radials by a rotation of 80° around their antiparallel *b* axes⁶ (which are normal to the page when radial lamellae lie in it edge-on) can be seen clearly throughout this field of view, from core to the outer edges of the row. There are two possible orientations of cross-hatching lamellae in this view, at $\pm 80^\circ$ to the radial lamellae, so that maintained orientation over a distance of a few micrometres (region around the arrow A, top right of *Figure 3a*) and on both sides of the nucleus, implies that the crystallography of the row nucleus is constant over that distance. It is possibly significant that this dimension is roughly that of a fully extended longer molecule in the sample. Note also that radial lamellae, although close-packed, are separated from each other by a well-defined narrow minimum distance of a few nanometres and that areas of cross-hatching lamellae can be seen in these gaps between adjacent radial lamellae. Material between the radial lamellae is thus inherently crystallizable, consistent with its being composed, at least in part, of molecular cilia, *i.e.* uncrystallized portions of molecules already partly attached to lamellae¹⁵; this particular point will be explored in a discussion of such data in subsequent papers^{2,3}.

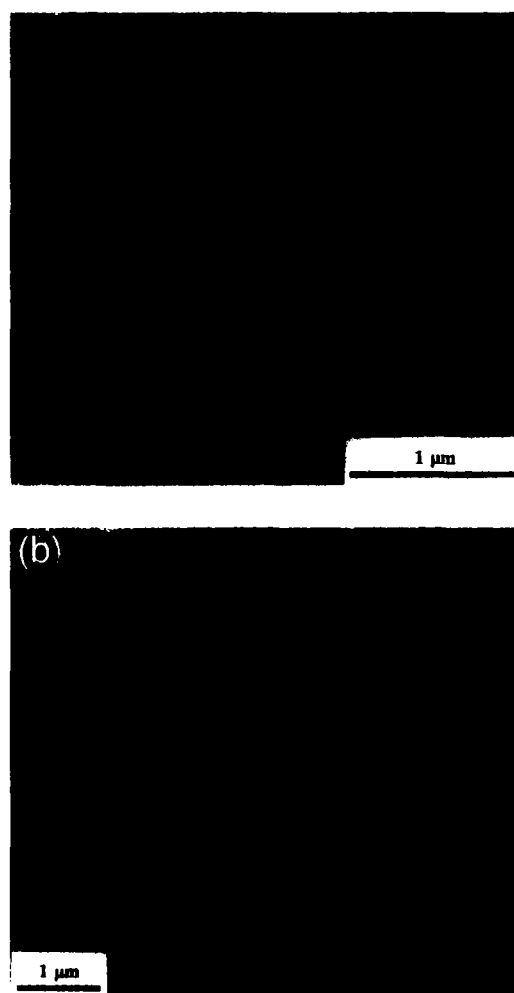


Figure 4 Detail of *Figure 2* illustrating longitudinal sections of narrow portions of the row. (a) The core lies below the etched canyon. (b) The junction between different portions of the row. Carbon replica of an etched surface

Another area of the same row structure, in which a double-cored nucleus can be seen, is shown in *Figure 3b*. Above the core, dominant radial lamellae can be seen growing out, with their *c* axes aligned, but with an alternation of the two ($\pm 80^\circ$) inclinations of the cross-hatching lamellae. Below the core there are two levels related to a change of texture. It is useful at this point to recall that relief in permanganically etched polypropylene surfaces is created, as in polyethylene^{16,17}, by the differential removal of material when etchant penetrates less dense regions, cuts folds and molecules therein and ablates lamellae from their side surfaces. Fold surfaces and less penetrable regions, such as the core in *Figure 3a*, are left standing proud; edge-on lamellae remain at a lower level but one still higher than the quenched matrix whose thinner lamellae and greater disorder allow a faster rate of attack.

In *Figure 3b*, accordingly, the lower level, at the bottom of the photograph, is similar in height and character to that above the nucleus. The upper level, emanating from the lower of the core's two strands, is different. Not only is there a switch of cross-hatching inclination with respect to the lower region, but these lamellae are no longer edge-on to the page but are somewhat inclined to it, a change of orientation to which the reduced etching of this step can be attributed.



Figure 5 (a) A transverse section of a row of the polypropylene homopolymer grown at 140°C; (b) detail. Carbon replica of an etched surface

Figure 4a shows a length of a narrower portion of the row (whose variable diameter shows that it is not the simple right cylinder commonly assumed). The top surface is raised above the matrix and those lengths of the row shown in *Figure 3*. This is due to a uniform array of flat-on lamellae divided along its centre by a narrow cleft within which edge-on radial lamellae are exposed with the core itself

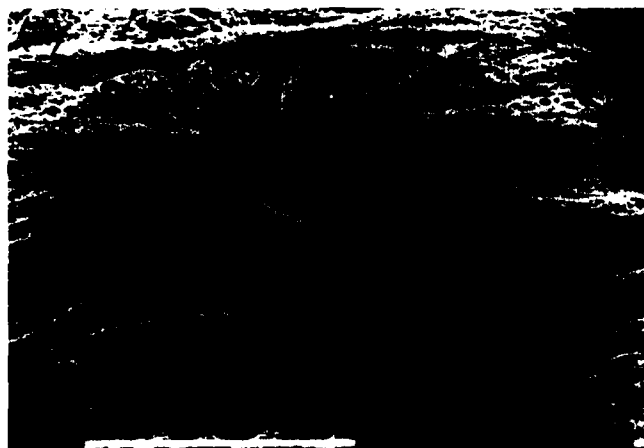


Figure 6 Scanning electron micrographs of etched transverse sections of polypropylene homopolymer tilted at 54° and grown, respectively, at (a) 130°C and (b) 115°C. Note the greater number of laths growing from the core at the lower temperature

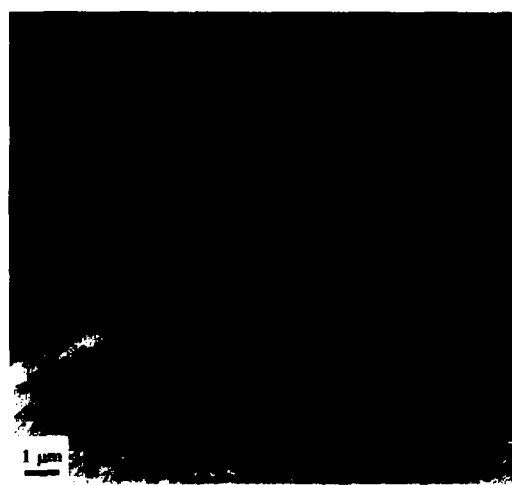


Figure 7 Transverse view of a row structure of polypropylene fraction D crystallized at 140°C illustrating the considerable variation in internal texture. Carbon of an etched surface

presumable lying below them. *Figure 4b*, of a similar area in the centre of the row, shows that the flat-on lamellae, at least those higher on the page than the central defile, are continuous with cross-hatching lamellae in the adjacent area towards the top of the figure. The areas above and below the etched-out row centre in *Figures 4a* and *4b* show few radial lamellae in the plane of the page similar to those of *Figure 3* and appear rather to represent regions in which growth has been predominantly out of the paper. Nevertheless, the projected alignment of the cross-hatching lamellae is not parallel to the row, *i.e.* rotated solely about the *b* axis which will lie in the plane of the paper, showing that the crystallography of both figures differs from the conventional one for row structures and is not adequately described as a common *c* axis with cylindrical symmetry plus, for α -polypropylene, associated cross-hatching. The nature of this changed circumstance becomes clearer with the examination of transverse sections¹⁵.

Low-resolution views of the transverse sections of rows of the homopolymer emphasize the way in which laths diverge as they grow out from the centre. They are separated by regions which have etched more deeply and often appear as near discrete entities with strongly etched boundary regions. It is also clear that laths which, in perpendicular views seem to be at the same level, are in some instances

spaced at intervals along the row when their depth is revealed in the tilted view. Detail of such sections makes it clear that, as in *Figure 5*, lamellae are present in all orientations from flat-on to edge-on and that, from backward extrapolation, many have nucleated at sites remote from the central core.

High relief in *Figure 5*, to be called ridges for convenience, results when lamellae are flat-on in the page. Polymer has been removed faster elsewhere because of the greater rate of attack experienced by other lamellar orientations. Note that the core is difficult to identify in a transverse section because its response to etching is similar to that of the surrounding flat-on lamellae. The row itself has an almost circular perimeter except for the section at 8 o'clock in *Figure 5a*. Diametrically opposite, at 2 o'clock, an equivalent sector stands proud and has evidently been filled by nucleation away from the core. Had this second sector not been filled, the row would have had a pronounced waist with a diameter similar to the narrow portions of *Figure 2* and of *Figure 4*. The cause of the reduced diameter is that, in this case, there has been no discontinuity in crystallography, with nucleation of differently oriented lamellae able to grow directly into the intervening space. Instead, this space has been entered, of necessity slowly, only by the sideways extension of the adjacent ridges, by the

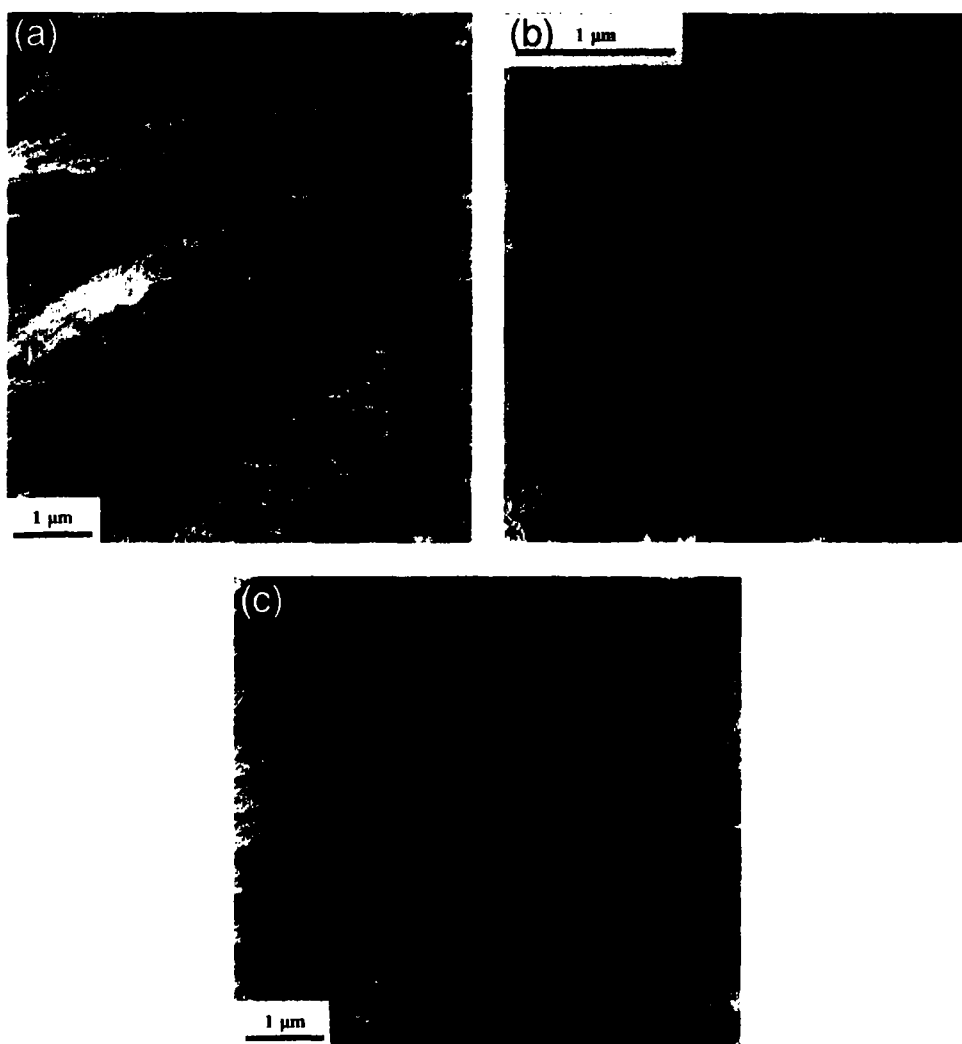


Figure 8 Detail of *Figure 7*. Note in (a) the filled sector of edge-on lamellae at 7 o'clock, in (b) (which is rotated anticlockwise by around 55° from the orientation of *Figure 7*) the abrupt 90° change in chain axis orientation going across the figure from left to right and, in (c), which is of an infilled sector, the different orientations of lamellae reaching the bottom of the micrograph

alternation of radial and cross-hatched sections mentioned above. Individual lamellae with this topography are, indeed, visible in the ridges at 9 and 10 o'clock, e.g. below A in *Figure 5b*. With this geometry, each cross-hatched component will have its growth velocity directed out of the page so that the total (projected) diameter will be decreased according to its relative time delay.

Other examples of filled sectors are, first, at 6 o'clock where fold surfaces, though parallel to the radius of the ridge to the immediate left, are rotated around that direction to be inclined to the page and appear to have started from the ridge to the right. Second, an area of edge-on lamellae growing out from the neighbouring ridge is seen well between 10 and 11 o'clock in both *Figure 5a* and *5b*. Note that in all such cases, when infilling growth between ridges is in a direction close to radial, there is little or no reduction in the final diameter; this must imply that nucleation, with discontinuous crystallography, has occurred without significant delay even at this comparatively high growth temperature.

Transverse sections of rows of the homopolymer formed isothermally at temperatures down to 115°C have also been examined. At lower temperatures, the growth is faster and will allow less relaxation of the imposed strain on the linear nucleus before lamellae form; also, cross-hatching is more frequent. In addition, there appears to be a concomitant

increase in the efficacy of infilling growth indicated by the progressive disappearance of significant gaps between ridges. The principal change of character resulting is, however, an increase in the number of laths emanating from the central nucleus with decreasing crystallization temperature: 130°C in *Figure 6a*, 115°C in *Figure 6b*. The increase in their number at lower growth temperatures is an indication of increased nucleation density around the row nucleus.

The remainder of the investigation has concerned a comparative study of the effects of molecular length and stereoregularity on row structures formed at 140°C, using fractions B, C and D of *Table 1*. The transverse view of a row of fraction D, shown in *Figure 7* and in detail in *Figure 8*, displays particularly clearly various ways in which sectors between ridges are filled in. The 7 o'clock sector of *Figure 8a* contains edge-on lamellae, up to 5 μm long, all of which can be traced back to a point close to the right hand edge of the photograph. Immediately above this, at X, is a continuous lamella with alternate radial and cross-hatched orientations. Another is present below Y in *Figure 8b* which illustrates the 90° change of chain axis orientation between the flat-on radial lamellae to the left and the extensive cross-hatched infill to the right. *Figure 8c* shows the range of orientations adopted by the infilling lamellae nucleated on the ridge, R, to the right, which changes from edge-on to flat-on across the width of the infilled sector.

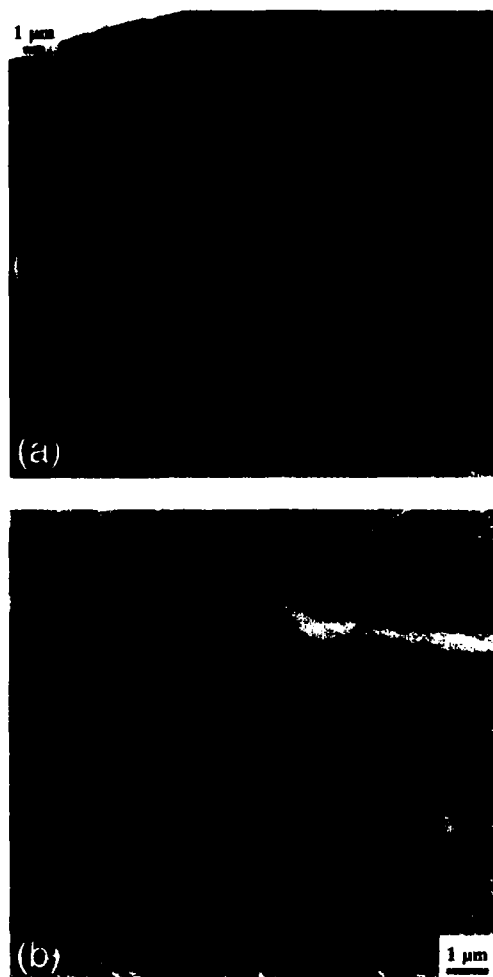


Figure 9 (a) Transverse view of a row structure of fraction C crystallized at 140°C; (b) detail. Note how on the right-hand side, lateral space has been accessed by nucleation on radial lamellae, beside A in (a), and from radial lamellae twisted around their length, both by splaying, below B, and by progressive cross-hatching, above C. Carbon replica of an etched surface

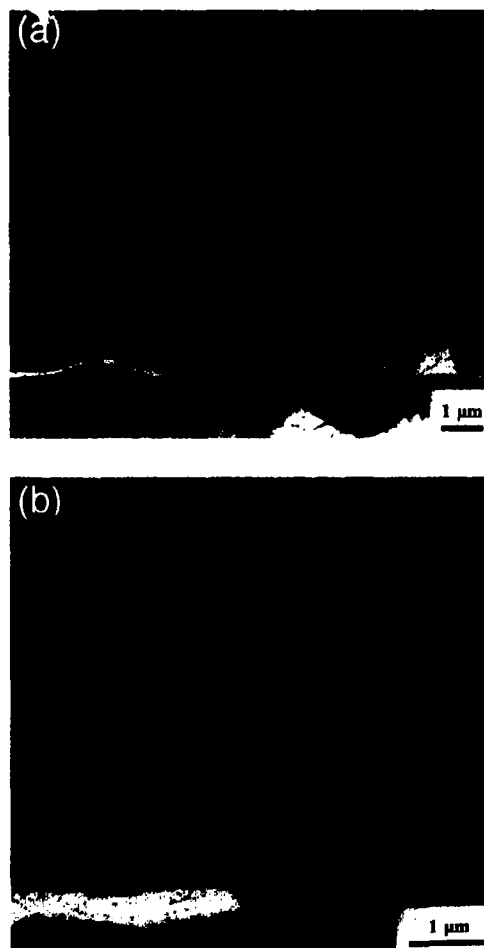


Figure 10 (a) Transverse view of a row structure of the low tacticity fraction B crystallized at 140°C; (b) detail. Note the copious cross-hatching but the very limited (arrowed) infilling between the separated lobes. Carbon replica of an etched surface

Still another mechanism is present in the row of fraction C shown in *Figure 9a* and specifically the detail of *Figure 9b*. This is at 4 o'clock where, along the ridge mid way between B and C, the radial lamellae have rotated about the radius to become edge-on, thereby enabling their associated cross-hatching to fill the space immediately below. Certain lamellae in this area show alternate cross-hatched and radial components. To the left of A in *Figure 9a*, cross-hatched lamellae, coming from a radial lamella whose plane is nearly parallel to the row, have filled an entire sector between ridges. All these features show that the opportunity to fill space is taken and taken rapidly by whatever means are locally available.

A new feature enters with fraction B. It is that there is little or no infilling between the radial laths, which have remained discrete but now appear as lobes around the core (*Figure 10a*), although a closer examination shows the apparent beginnings of space-filling growth to the right of the lobe seen in detail in *Figure 10b*. There is copious cross-hatching (*Figure 10b*)—15% more than for fraction C of the same molecular length but higher tacticity^{2,3}—but infilling nucleation between the lobes has been severely retarded. Although the effective supercooling will be a little less with lower tacticity, no such effect has been observed for large changes in supercooling in our other experiments. Rather, we have a clear difference between the nucleation process involved in cross-hatching on the one hand, which is not inhibited by low tacticity, and nucleation on the core and between laths, on the other hand, both of which are depressed.

SUMMARY

Row structures of α -polypropylene are not cylindrically symmetrical objects but possess consistent character and crystallography over some micrometres, a distance comparable with the length of a molecule. The number of lamellae nucleated from the core in transverse view increases with supercooling and declines with tacticity. Such characteristics are potentially useful to inform on the conditions in which row structures have grown in other polypropylene samples such as the recently developed two-dimensional compactions^{18,19}.

The presence of lamellae parallel to the core at greater radial distances in row structures of α -polypropylene derives from the occurrence of space-filling nucleation in this polymer. It has been shown above that crystallization laterally adjacent to existing lamellae may be achieved in α -polypropylene in several ways. Normally, lamellae grow radially outwards, with cross-hatching developing epitaxially from their lateral surfaces and a tendency to splay apart should conditions allow. This is the mechanism by which quadrites develop in the early stages of spherulitic growth²⁰ and sheaves at higher temperatures when cross-hatching does not form²¹, but for rows it would mean that spaces would tend to develop between laths with increasing radius and be liable to be left unfilled. There are only two feasible means by which such space can be filled if there is lattice continuity, both of which have been identified within our morphologies. They are, firstly, alternate sideways steps of cross-hatching and radial components, associated with a reduced (projected) radius because of the changes in growth direction (*Figure 5*). Secondly, radial lamellae may rotate about their length²⁰ whence cross-hatching may access laterally adjacent areas especially at greater radial distances

which reduce the required rotational strain (*Figure 9b*). The prevalent mechanism in these experiments, however, is for lattice continuity to be broken with nucleation of new growth, of changed lattice orientation, at the surfaces of existing lamellae. While statistics of how nucleation varies with angle inform on the relative free energies involved, here so many different orientations are observed that, while twinning is always potentially the cause of a sharp change of lattice orientation, the responsibility seems much more likely to be that of incoherent secondary nucleation. Such a conclusion would also be consistent with observations in polyethylene¹⁵ and poly(4-methylpentene-1)⁵, respectively, in which subsidiary lamellae are inclined at large angles, sometimes around 90°, to their parent dominants. Incoherent secondary nucleation seems to be the alternative way these polymers principally adopt to achieve lateral growth in the absence of the possibility of appropriate twinning which cross-hatching offers to α -polypropylene. The angular distribution is not of maximum probability at zero angle, for which the term non-crystallographic branching was first used²² but, in practice, is clearly weighted to larger angles because of the advantages of gaining greater access to still molten volumes.

Discontinuous changes in lattice orientation between neighbouring lamellae, now demonstrated unambiguously for row structures, can be confidently expected to occur in other circumstances in melt-crystallized polymers. Their presence will affect the properties. For example, those such as birefringence of spherulites which reflect molecular orientation will be reduced below that calculated for strictly maintained crystallography. Another is that the mechanical yield is likely to be affected when subsidiary lamellae have different orientations to neighbouring dominants so that the applied stresses are resolved differently along the respective crystallographic axes in the two cases leading to the activation of different failure mechanisms. This may well be one reason why subsidiary lamellae in polyethylene spherulites have been found to fail in tension before neighbouring dominants²³ because, in the failure zones, they alone would be subject to high shear stresses for chain slip.

This paper, therefore, has explored the microstructure of row structures of α -polypropylene for the first time with lamellar resolution, and revealed that they are both more complex and more informative than previously appreciated. In particular, there is a proportion of lamellae, increasing with radial distance, which is more or less parallel rather than perpendicular to the core. This has a variety of causes of which the most common appears to be incoherent secondary nucleation. The demonstration that lamellae and their crystal lattice are not necessarily continuous is our major conclusion. Although continuity is the norm, it may be overridden, here and elsewhere, if this allows crystallization to occur in otherwise inaccessible regions. This is an important recognition with implications across the whole of structure/property relationships in melt-crystallized, spherulitic polymers.

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