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On variable nucleation geometry and segregation in isotactic polypropylene

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Lamellar thicknesses, cross-hatching frequencies and growth rates have been compared for spherulites, transcrystalline layers and row structures formed from the melt in the α (monoclinic) form of isotactic polypropylene. These three morphologies relate to point, surface and linear nucleation, respectively. The measured quantities are independent of the type of nucleation confirming that morphological statistics compiled from row structures are relevant to general conditions of melt crystallization. This independence also implies that the same supercooling must be effective for growth in the three cases notwithstanding the very different geometries of their crystal/melt interfaces and the consequent locations and concentrations of any fractionated molecular species. With no detectable depression of supercooling at the growth faces the conditions for cellulation to develop do not exist. Segregation of 'impurities' can thus have no influence on the establishment of physical texture in this high crystallinity polymer. © 1997 Elsevier Science Ltd.

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INTRODUCTION

This is the first in a series of papers reporting a quantitative electron microscope study of the lamellar morphology of the α or monoclinic form of isotactic polypropylene and its variation with crystallization temperature and molecular constitution using fractionated materials[1]. Data such as lamellar thickness, interlamellar separation and cross-hatching frequency have been obtained using linear nuclei, referred to as row structures, which have the advantages that all lamellae are equivalent, i.e. all dominant, and parallel, sharing a common c axis, and grow in equivalent environments. However, in order to demonstrate that these data and ensuing conclusions are applicable to melt crystallization of this polymer in general it is necessary to show that such parameters and the growth rate itself are independent of the precise nucleation conditions. This has been achieved by comparing morphologies and growth rates for spherulites, row structures[2–4] and transcrystalline layers[5,6].

In the first instance all three systems were compared for morphology and growth rate at 140°C where the greater lamellar thicknesses and slow crystallization allow the measurements to be made most accurately. The comparison was then extended to lower temperatures both for the morphology of row structures and transcrystalline layers, for which data are more efficiently gathered, and for growth rates of rows and spherulites. The basic finding is that, for the same growth temperature and within the limits of experimental error, there is no difference in growth rate, lamellar thicknesses (of both radial and cross-hatching lamellae) and cross-hatching

frequency, whether nucleation be from a point (spherulites), a line (row structures) or a surface (transcrystalline layers) in this high crystallinity polymer.

This is an important finding which transcends the immediate purpose of the investigation and bears on the pertinence of diffusion fields to melt growth. If it is maintained that segregation of rejected or 'impurity' species causes cellulation[7–9], derived from depression of the local melting point, then one would anticipate differences in growth rate, lamellar thickness and cross-hatching frequency for these three types of nucleation because of corresponding differences in the supercooling produced by the respective geometries of their solid/melt interfaces. As this is not observed, it can be inferred that segregation and cellulation are not significant factors in the growth of this high crystallinity homopolymer. This confirms and reinforces conclusions from other research on the origins of spherulitic growth in polymers.

EXPERIMENTAL

The isotactic polypropylene homopolymer used for this investigation (and also to prepare fractions for subsequent work) was provided by Borealis Oy, Finland and was determined by them to have a mass-average molecular mass of 541 000, a polydispersity of 5.9 and a stereo content of 91.4%, measured as the percentage of mmmm tetrads.

The three different types of morphology studied are shown in the polarizing micrographs of *Figure 1*. Spherulites, *Figure 1a*, are effectively nucleated at a point and their radii can grow in all directions in space. The lamellae in row structures, *Figure 1b*, are nucleated epitaxially upon, and have a common c axis with, their linear nucleus. In α-polypropylene, lamellae, to which the c axis is normal, are thus constrained to grow in

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50 µm

a

40 µm

100 µm
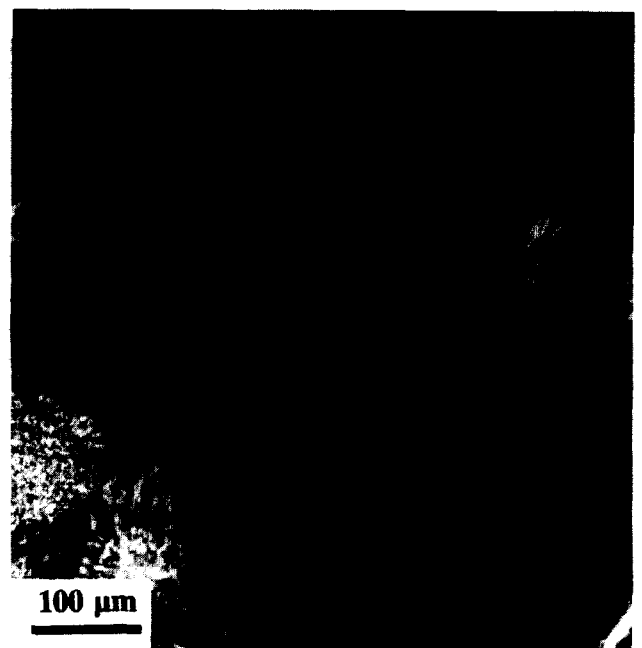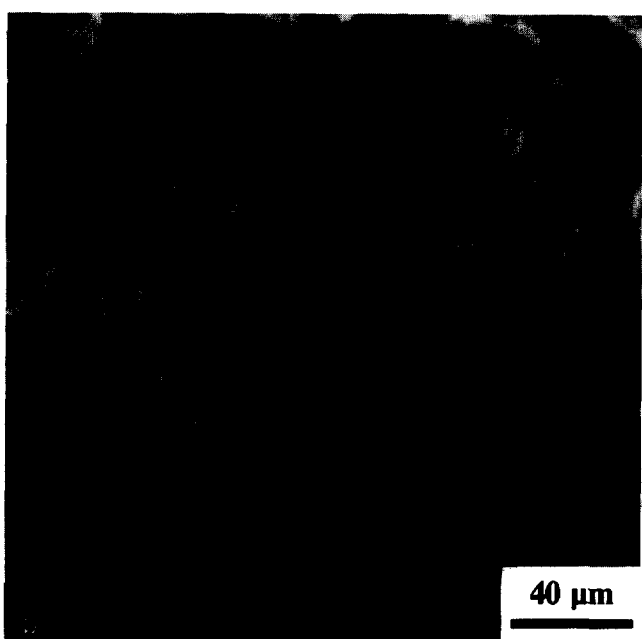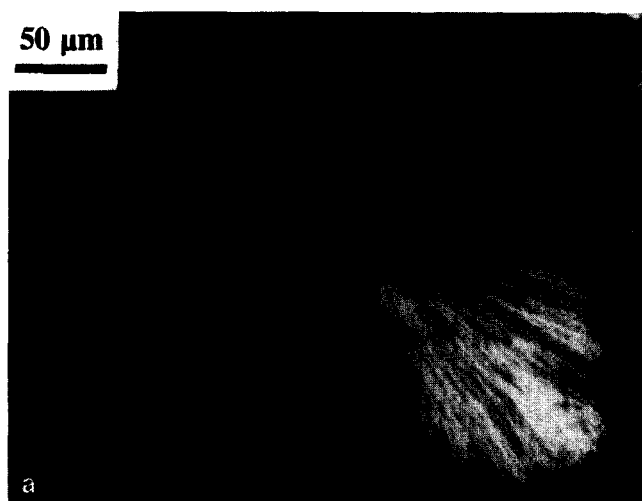
planes normal to the row. There are fewer constraints for transcrystalline layers, *Figure 1c*, which develop because of dense nucleation on a (usually plane) surface to which they then grow perpendicular[5,6]. The normal to the surface is nominally the growth direction (a^* axis[10]) of all lamellae but local deviations of this direction from the normal do occur. The difference from row structures is that there is no overall restriction on the orientation of lamellae around the growth direction. Whereas lamellae in row structures are all parallel to each other because of the common c axis, this is not necessarily the case for those in transcrystalline layers for which only the a^* axis is common.

The three morphologies were produced in the following ways.

Spherulites

A film of material approaching 0.5 mm in thickness was prepared between a glass microscope slide and glass cover slip then placed for 5 min in a nitrogen atmosphere within a Mettler FP800 Hotstage, controlled at 230°C. The sample was transferred directly from the first Mettler Hotstage to a second (type FP52) in which it was crystallized under nitrogen until quenched on a cold surface such as a metal bench top. The sample used to measure lamellar thickness and cross-hatching frequency was crystallized at 140°C for 8 h.

Transcrystalline layers

A pellet of the homopolymer was squashed on a Koffler Hot Bench, between a glass microscope slide and PTFE (polytetrafluoroethylene) cover slip, at a temperature greater than 180°C to remove all memory of previous growth history, including row structures. Crystallization then proceeded as described for the spherulitic sample above. Two samples were produced, the first crystallized at 140°C for 8 h; the second at 130°C for 30 min, with transcrystalline layers developing from the PTFE sheets.

Row structures

The homopolymer, contained between a bottom layer of Kapton sheet and a cover of a sheet of poly(4-methylpentene-1), was heated on the Koffler Hot Bench until the sample just started to melt and then sheared by moving the cover over the slide. This creates extensional strain along the direction of shear leading to linear nuclei. The sample was transferred immediately to the Mettler FP52 Hotstage and there crystallized under nitrogen. Three samples were prepared at, respectively, 140°C for 5 min, 130°C for 2 min and 115°C for 10 s, after which they were each quenched in cold water.

Electron microscopy

An acidified permanganic etchant[11,12], in this instance a 1% w/v solution of potassium permanganate in 10/4/1 volumes of concentrated sulfuric acid, orthophosphoric acid and distilled water respectively, was used for 2 h

Figure 1 Photomicrographs of (a) spherulites, (b) row strctures, with RR the longest row, and (c) transcrystalline layer viewed between cross polars. The crystallization conditions where, respectively, 140°C for 17 h; 130°C for 2 min and 140°C for 8 h. In (c) AA denotes the transcrystalline layer emanating from the PTFE surface and BB its continuation on quenching after 8 h crystallization

at room temperature to reveal topography beneath the sample surfaces which were originally exposed by cutting. Carbon/metal replicas of the etched surfaces were prepared and observed by transmission electron microscopy. Typical views showing lamellae in the three morphologies are seen in *Figure 2*.

The lamellar thickness was measured both for dominant lamellae and the cross-hatching lamellae between them. Dominant lamellae are radial in spherulites and the cylinders comprising row structures but lie normal to the nucleating surface in transcrystalline layers. For convenience, however, we may describe them all as radial in contradistinction to cross-hatching. In longitudinal views of row structures all radial lamellae are correctly presented for measurement which is not generally the case either for the cross-hatched component[13], which has its **b** axis in common with its radial parent and is inclined to it at 80°, nor for all lamellae in other views and morphologies. The cross-hatched component is correctly presented in diametral sections of rows, i.e. those containing the length of the nucleus, whose selection thereby facilitates measurement. In other circumstances it is always possible, by tilting around the lamellar trace as axis, to ensure that α-polypropylene lamellae are being viewed exactly edge on. All thicknesses were measured on micrographs taken with specimens correctly positioned. *Figure 3* displays the comparative data for the three types of sample as a function of crystallization temperature. The frequency of cross-hatching was also measured (*Figure 4*) from the micrographs as the number of cross-hatching lamellae per micrometer of dominant radial lamella. All measurements were repeated, typically twenty to fifty times and an average value calculated with its corresponding standard error. Growth rate data for spherulites and row structures (*Figure 5*) were gathered by direct observation using the Mettler FP52 Hotstage mounted on a Vickers polarizing microscope. The graticule eyepiece on the microscope allowed the diameter of the spherulite or row structure to be measured as a function of time with three objects being measured simultaneously in a typical run. Average values plus error bars equal to the standard error of their means have been used for each point in the graphs featured in this paper.

RESULTS AND DISCUSSION

The primary result of this paper is that, for this high crystallinity polypropylene, lamellar thickness, radial growth rate and cross-hatching frequency are independent of the precise way in which growth was initiated. In terms of growth rate this is not a new conclusion; the agreement between the growth rate for spherulites and row structures has been noted by previous authors[14,15] and, indeed, is in line with the simple observation that row structures of the α form may often be seen to end in hemispherical caps whose radius equals that of the
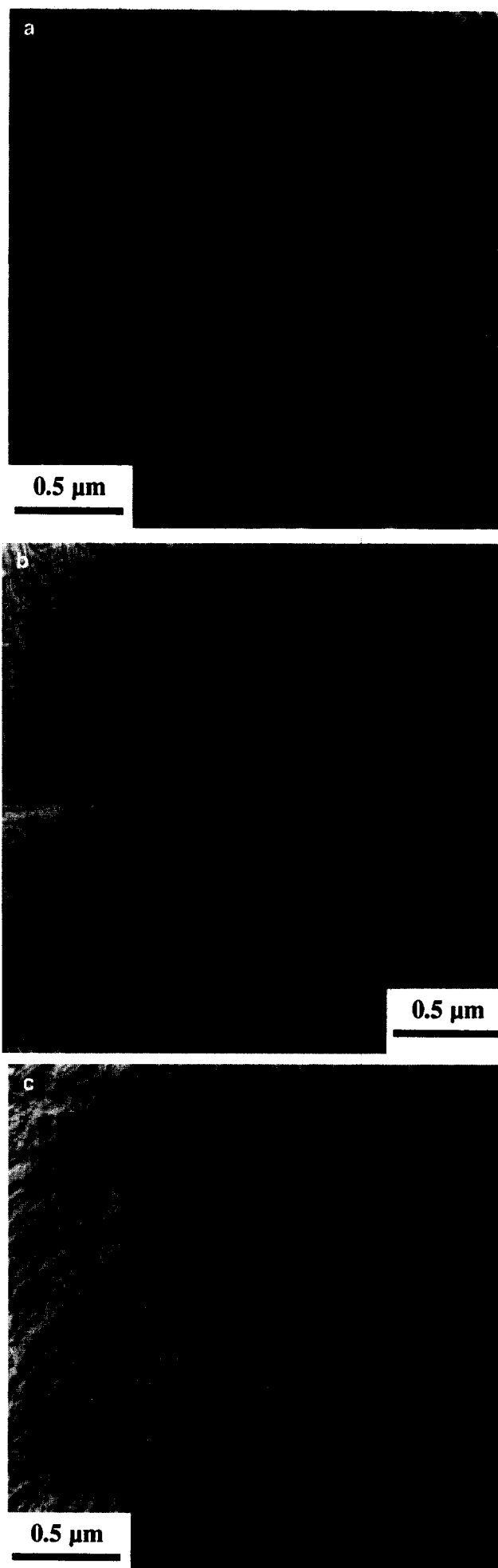

Figure 2 Electron micrographs of replicas showing radial and cross-hatching lamellae in the three systems revealed by permanganic etching. All samples were crystallized at 140°C for, respectively, 8 h, 5 min and 8 h. Note the change of some 45° in the radial direction in the spherulite of (a) in contrast to the parallelism in the transcrystalline layer across the central portion of (c). The separation between dominant lamellae is much less in the row structure of (b) than in the other two systems

row[1,4]. The same identity has previously been found in comparisons of the growth rates of transcrystalline layers and spherulites[16,17]. We note in passing that our values of growth rate are consistent with those of previous
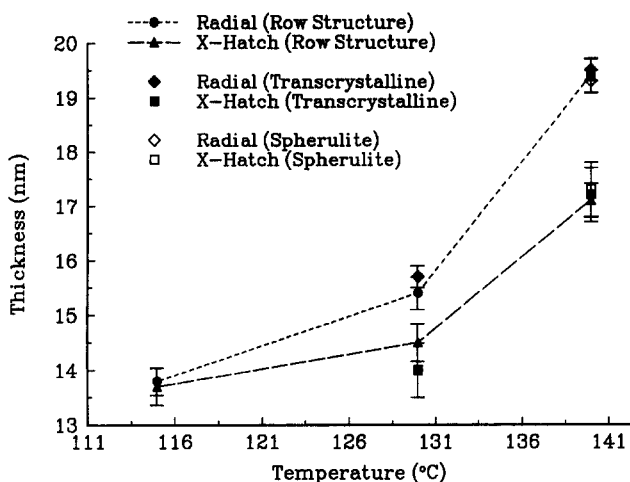

Figure 3 The lamellar thickness of all samples plotted against crystallization temperature showing that there is no significant difference with the type of nucleation. Note that radial lamellae are thicker than their cross-hatched neighbours except at the lowest crystallization temperature
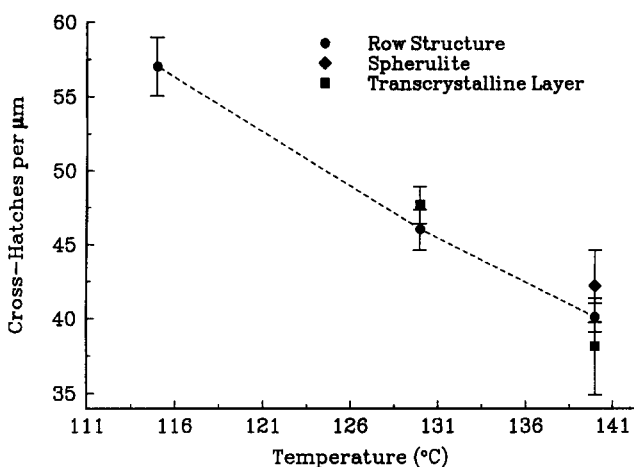

Figure 4 The frequency of cross-hatching is independent of nucleation conditions but increases as crystallization temperature falls
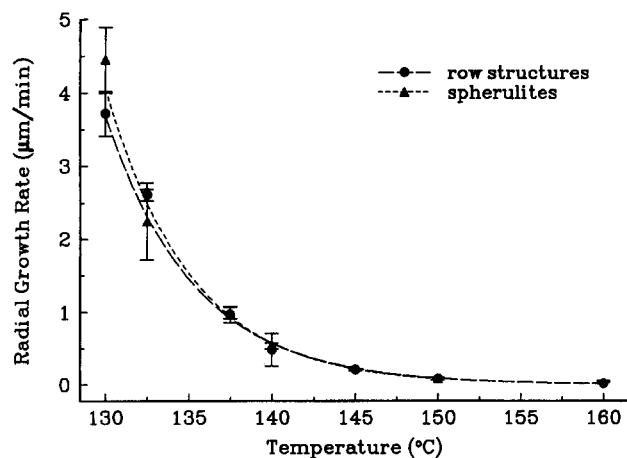

Figure 5 Growth rate data as a function of crystallization temperature for spherulites and row structures of α-polypropylene

workers[4]. The immediate aim of our investigation, that of validating the extensive data to be published shortly, as being of general relevance to melt growth is thereby achieved. Detailed points of interest within the data, such as the difference in thickness between radial and cross-hatching lamellae and its temperature variation, also the dependence of cross-hatching frequency on temperature, are more appropriately dealt with in the wider context of fractionated polymer in these future publications.

The principal point we wish to discuss here is the implication of this independence of morphology and growth parameters from the geometry of nucleation on the proposal that segregation of rejected species has a major influence, via cellulation, on the morphology of melt-grown polymers[7-9]. The rationale offered for expecting cellulation to occur is that species rejected at the growth front will accumulate at the crystal/melt interface where, by reducing the effective supercooling, because of depression of the local equilibrium melting point, they render a planar interface unstable against the development of protuberances which penetrate into or through the impurity layer into regions of higher supercooling and faster growth[7]. Cellulation results if the protuberances persist, leaving impurities concentrated between them. The width of cells, which is predicted to scale with the characteristic length of the diffusion field for segregated 'impurities', $\delta = D/G$, where D is a diffusion coefficient and G the rate of radial advance of the interface with the melt[7], is claimed to correspond to textural differences in melt-crystallized polymers[7-9].

When this proposal was first put forward it was widely believed that lamellae would crystallize from the melt so that their adjacent growth faces would effectively constitute a planar surface. The appreciation that this is not so and that spherulites are built on a skeleton of individual branching and diverging dominant lamellae undermines the credibility of the proposed role of cellulation[18,19]. In reality, spherulites form with a crenellated interface with the melt[18,20] and, because the quantity of polymer actually crystallizing as the geometrical skeleton is being created is small in comparison to the volume between adjacent lamellae, the concentration of rejected species must be reduced, typically by an order of magnitude initially, below that which would occur for a planar interface. Not only, therefore, is the geometry different from the model proposed but also the concentrations of 'impurity' are much less than had been supposed. The present measurements reinforce the weight of these objections to the cellulation hypothesis and indeed to segregated species having any significant effect in establishing the physical texture of melt-crystallized (spherulitic) morphologies in a high crystallinity polymer[7-9].

That the different lamellar arrangements studied here produce no measurable differences in growth rate, lamellar thicknesses or cross-hatching frequency, all of which vary with growth temperature (*Figures 3, 4* and *5*) and with molecular length[1], must imply that growth conditions are effectively equivalent with the same supercooling operative for the three types of nuclei. This equivalence does not, however, extend to the corresponding diffusion fields even though their length scales are generally much greater than the separation of adjacent lamellae.

This follows from the different geometries of the melt/

solid interfaces. Whereas that for spherulites is open-textured, with adjacent dominant lamellae diverging to separations of $\sim 1\,\mu$m, i.e. of the order of the molecular length before new lamellae to intervene, that of row structures is equivalent to a plane. (The comparison between the two is well shown in Figures 1 and 2 of ref. 21.) For the latter, lamellae grow outward in close proximity with insufficient room between them for other parallel lamellae to form. As *Figure 2b* shows the interlamellar separation in row structures is only a few nm; for this sample the mean value and its standard error are 3.9 ± 1 nm. We know from the presence of small cross-hatching lamellae in α-polypropylene rows that material in the gap between radial lamellae is capable of crystallizing and also that it does not diffuse away. It has accordingly been suggested[21] that, at least in part, interlamellar material comprises molecular cilia, i.e. the uncrystallized portions of molecules already partly attached to lamellae. Support for this view is provided by the manner in which this small dimension varies consistently with crystallization temperature and molecular parameters[1]. If material rejected at the growing interfaces cannot access interlamellar space, it will have no alternative but to accumulate ahead of the interface as it would for a plane. The situation would change little even on the doubtful scenario that segregated polymer is able to penetrate between radial lamellae because, in contrast to spherulites, the interlamellar volume is small. One may cite the invariance of cross-hatching frequency, which is particularly sensitive to molecular length[1], as showing a lack of segregation at the cross-hatching sites, which lie between radial lamellae, consistent with the absence of segregated polymer in these regions. Row structures unlike spherulites are, therefore, close to the original model hypothesized for cellulation to occur. In consequence, the concentration of rejected species will be considerably greater for row structures than for spherulites. The factor will initially be inversely proportional to the average separation of adjacent dominant lamellae in the two cases, i.e. one order of magnitude or more. It will increase if and when impurities segregate between dominant lamellae in spherulites diluting their concentration in contrast to their steady accumulation as row structures crystallize.

The essential point is that if the concentration for spherulites is supposed to be sufficient to depress the supercooling and thence growth rate, as is required for cellulation to occur, the effect must be considerably larger for row structures and of intermediate value for transcrystalline layers. That there is no such effect in practice, even though the constant growth rate confirms that steady state conditions are operative, implies that insofar as there is fractional crystallization, the species segregated do not cause significant changes in equilibrium melting point. With no change in supercooling, the mechanism proposed for cellulation cannot operate.

The same situation almost certainly recurs in other high crystallinity systems such as linear polyethylene. However, cellulation has recently been observed in the lower crystallinity system of linear low density polyethylene[22], for which exclusion of branches from the crystal lattice imposes not only a high degree of segregation but also of species which do lower the local equilibrium melting point. As anticipated in the above discussion, in this system growth rates do fall with

increasing radial distance while the rates are higher for spherulites than for rows. Nevertheless, the phenomenon has only been observed for row structures and not for spherulites growing alongside showing that, in special circumstances, cellulation can influence morphological development in polymers, but providing yet further confirmation that it is not responsible for the physical texture associated with their *spherulitic* growth.

The mechanism by which polymer spherulites do form has recently been confirmed to be the divergence of adjacent dominant lamellae at representative branch points as they are pushed apart by cilia pressure. Further papers in this series will derive quantitative estimates of cilia pressure and average cilium length as functions of molecular length and growth temperature from measurements of the morphology of α-polypropylene row structures.

CONCLUSIONS

The first of the two principal conclusions from this work is that morphological data on lamellar thickness, cross-hatching frequency and growth rate are independent of the precise method of nucleation in polypropylene of high crystallinity. This validates the relevance of such statistics when compiled more efficiently from row structures to melt growth in general.

The second is that it follows from this same independence from nucleation conditions that there is negligible change of supercooling at the growth front in all cases, notwithstanding the inherently different distributions and concentrations of postulated segregated molecular species. Cellulation can, therefore, have no influence on the development of physical texture, including spherulites, in this high crystallinity polymer.

ACKNOWLDEGEMENTS

REFERENCES

1. White, H. M., Lamellae and their Organization in Melt-Crystallized Isotactic Polypropylene, Ph.D. thesis, University of Reading, 1995.
2. Kargin, V. A. and Andrianova, G. P., *Doklady Akad.*, 1962, **146**, 1337.
3. Binsbergen, F. L., *Nature*, 1966, **211**, 516.
4. Karger-Kocsis J. (ed.), *Polypropylene Structure, Blends and Composites I: Structure and Morphology*. Chapman & Hall, London, 1995.
5. Fitchmun, D. and Newman, S., *Polymer Letters*, 1969, **7**, 301.
6. Gray, D. R., *Polymer Letters*, 1974, **12**, 509.
7. Keith, H. D. and Padden, F. J., *J. Appl. Phys.*, 1963, **34**, 2409.
8. Keith, H. D. and Padden, F. J., *J. Polymer Sci.*, 1987, **25**, 229.
9. Keith, H. D. and Padden, F. J., *J. Polymer Sci.*, 1987, **25**, 2371.
10. Lovinger, A. J., *J. Polym. Sci., Polym. Sci. Edn.*, 1983, **21**, 97.
11. Olley, R. H., Hodge, A. M. and Bassett, D. C., *J. Polym. Sci. Phys. Edn.*, 1979, **17**, 627.
12. Olley, R. H. and Bassett, D. C., *Polymer*, 1982, **23**, 1707.
13. Khoury, F., *J. Res. Nat. Bur. Std.*, 1966, **70A**, 29.

14. Varga, J., *Angew. Mak. Chemie*, 1983, **112**, 191.
15. Sukhanova, T. E., Lednicky, L., Urban, J., Bakliagina, Y. G., Mikhailov, G. M. and Kudryavtsev, V. V., *J. Mat. Sci.*, 1995, **30**, 2201.
16. Avella, M., Volpe, G. D., Martuscelli, E. and Ramio, M., *Polym. Eng. Sci.*, 1992, **32**, 376.
17. Thomason, J. L. and Van Rooyen, A. A., *J. Mat. Sci.*, 1992, **27**, 889.

18. Bassett, D. C., *C.R.C. Crit. Rev.*, 1984, **12**, 97.
19. Olley, R. H. and Bassett, D. C., *Polymer*, 1989, **30**, 399.
20. Bassett, D. C., *Phil. Trans. R. Soc. Lond. A*, 1994, **348**, 29.
21. Monks, A. W., White, H. M. and Bassett, D. C., *Polymer*, 1996, **37**, 5933.
22. Janimak, J. J. and Bassett, D. C., To be submitted to *Macromolecules*.