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A quantitative electron-microscopic investigation of α-phase lamellae in isotactic polypropylene fractions

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ABSTRACT

Lamellar thicknesses and cross-hatching frequencies in α-isotactic polypropylene have been measured for two series of fractions using linear nucleation to provide large arrays of oriented lamellae in row structures for sampling. One series is of high tacticity polymers differing in molecular mass from $\sim 6 \times 10^4$ to $\sim 8 \times 10^5$, the other has low and high tacticity materials for $\sim 9 \times 10^4$ and $\sim 2 \times 10^5$ masses. These have allowed the differing influences of both molecular mass and tacticity to be evaluated. Lamellar thicknesses increase with molecular mass to $\sim 5 \times 10^5$ then level off. This is consistent with the fold surface increasing its free energy by ~20% for longer molecules as its structure becomes progressively more complex. Except for the lowest fraction, the thickness of cross-hatching lamellae is less than that of its radial neighbours because of differential thickening. The frequency of cross-hatching is greatest for the least tactic fraction but decreases linearly with molecular length. This dependence suggests that chain ends play a key role in initiation probably by laying down the first segment in epitaxial orientation. This suggestion could also account for the reduced thermal stability of spherulite centres and regions of high cross-hatching density where there is competition for chain ends between thickening and cross-hatching. The curvature of lamellae at the very end of a row mirrors the dependence of lamellae thickness with molecular mass and allows cilia pressure, the factor strongly involved in causing the lamellar divergence underlying spherulitic growth, to be estimated as ~100 Pa.

1. Introduction

This paper reports a quantitative study of the lamellar morphology of melt-crystallized isotactic polypropylene as functions of molecular length and tacticity undertaken for two principal reasons. On the one hand, the macroscopic properties of a crystalline polymer depend crucially on its inherently complex physical microstructure so that such knowledge provides a background to tailoring properties of commercial materials. On the other hand, there is the underlying fundamental issue of what additional properties are brought to polymeric crystallization by molecular length beyond those found for small molecules.

Most of our knowledge of the latter has come, logically, from studies of linear polyethylene and its oligomers which are the closest approach to the ideal flexible chain. The key factor is lamellar growth, which for longer molecules is accomplished by chainfolding, driven by the volume free energy reduction on crystallization of the internal molecular stems albeit partly offset by the additional surface contribution, then subject to the common but still mysterious process of isothermal lamellar thickening. For typical fast growth rates (Regime II for polyethylene) surface condition is a secondary issue leading to rough, less-well-ordered surfaces prone to subsequent reorganization. Only for slowest (Regime I for polyethylene) growth is there time for as-grown surfaces to achieve smooth ordering. In linear polyethylene it is the reorganization of rough surfaces towards the preferred smooth ones ({001} to {201} and the associated adoption of S-profiles) which is responsible for banded growth. More generally, as shown for linear-low-density polyethylene, reduction of surface stress drives banding [1].

Study of polypropylene can bring additional knowledge on two counts. First it is the simplest poly(α-olefine) $[CHCR]_n$, with $R = CH_3$, introducing tacticity into the aliphatic chain. We find, as is expected, that less tactic as well as shorter molecules are less able to crystallize and so segregate within the morphology although this is now known not to be the cause of spherulitic growth as was once proposed. Additionally and more importantly, the common α form of the isotactic polymer has a unique cross-hatched twinned

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morphology in which chains change orientation across the twin plane by ~90° creating a distinct lamellar (cross-hatching) population and significantly affecting properties. Thus unlike most other polymers, including the β form of isotactic polypropylene, its spherulites do not have their highest melting point at their centres so that they melt from the outside in. On the contrary, isothermally-crystallized spherulites of α polypropylene melt in their centres before regions at greater radius [2,3]. This is because of the restriction imposed by cross-hatching on isothermal lamellar thickening which in other systems makes the oldest lamellae (at spherulite centres) the thickest and highest melting. There is the potential, therefore, of gaining further understanding of isothermal lamellar thickening and how it is inhibited.

With this background we report a fundamental study, using fractionated polymer, of lamellae in melt-crystallized α-isotactic polypropylene, investigating how molecular length and tacticity affect lamellae in both radial and cross-hatched orientations. Lamellar thicknesses and cross-hatching frequencies have been measured, *inter alia*, for a polypropylene homopolymer and fractions thereof as functions of crystallization temperature, molecular length and tacticity. It is shown that, at a given temperature, longer molecules form thicker lamellae, to an asymptotic limit, consistent with a corresponding increase in surface free energy. We now extend previous results which showed that cross-hatching lamellae are thinner than neighbouring radials for higher crystallization temperatures but the difference declines for shorter molecules and disappears for the homopolymer at 115 °C [4]. This equality also applies at all temperatures for fractions below molecular masses of $\sim 6 \times 10^4$.

The results not only provide a unique database of how molecules are distributed within the lamellar morphology but also reflect on molecular mechanisms. Thus the demonstration that the frequency of cross-hatching declines inversely with molecular length suggests that molecular ends are key to its initiation leading in turn to an explanation of the reduced thermal stability of spherulite centres. Moreover, the curvature of lamellae at the very end of a row allows an estimate of cilia pressure which is largely responsible for lamellar divergence and the formation of polymeric spherulites.

2. Materials and experimental

Table 1 lists details of the polypropylene homopolymer used, provided by Borealis Polymers Oy, and fractions separated from it. Those varying in molecular mass, denoted P, Q, R, S, and T, were prepared using a solvent gradient extraction technique at 160 °C with ethylene glycol monobutyl ether as solvent and diethylene glycol monobutyl ether as non-solvent [5]. Also listed in Table 1 are two pairs of fractions, A1, A2 and B1, B2, each differing in tacticity for essentially the same mass. These were prepared similarly but at 125 °C with xylene as solvent and ethylene glycol monoethyl ether as non-solvent. Size exclusion chromatography was used to measure the molecular masses and their polydispersity while the pentad sequences used for the values of isotacticity came from ^{13}C nuclear magnetic resonance spectroscopy.

Table 1
Molecular data for the homopolymer and fractions.

Material	$M_m \times 10^3$	M_m/M_n	%mmmm
Homopolymer	541	5.9	91.4
P	63.5	2.1	83.2
Q	207	1.5	93.6
R	341	2.0	93.6
S	491	2.4	94.4
T	818	2.4	93.0
A1	91	2.7	45.7
A2	92	1.9	86.4
B1	192	2.5	67.7
B2	199	2.6	88.5

The principal experimental results were obtained by transmission electron microscopy of carbon replicas of permanganically-etched samples. Linear nucleation was used to give lamellar arrays aligned in row structures and thereby greatly simplifying the acquisition of lamellar thickness data. Two methods were adopted to this end, the second introduced later for fractions in limited supply.

In both cases, samples were stressed close to their melting point, to generate the linear nuclei, immediately crystallized isothermally in a nitrogen atmosphere on a controlled Mettler FP52 hot stage for the chosen time then finally quenched in cold water. In the first method, two roughened, shaped poly(4-methyl pentene-1) sheets were placed either side of a polypropylene pellet and the whole mounted as a sandwich between two Kapton sheets. This assembly was positioned on a Koffler hot bench where the polypropylene just started to melt, manually compressed using a cork while one poly(4-methyl pentene-1) sheet was slowly and steadily pulled away from the other, then quickly transferred to the hot stage. The presence of row structures is readily confirmed by polarizing optical microscopy. In the second method, glass fibres were laid on a pellet sample and pressed into it, between glass slide and cover slip. After cooling, the ends of the fibres were gathered together with cellulose tape (for easy pulling), the sample was melted at 200 °C in a Mettler FP800 stage for 1 min then crystallized, under nitrogen, in the FP52 hot stage and held in position while the fibres were slowly and steadily pulled through. Row structures were produced in the wake of the fibres.

Prior to electron microscopy a suitable surface, produced if necessary by cutting the outer surface away at liquid nitrogen temperatures with a microtome, was etched. In this work the etchant was a 1% w/v solution of potassium permanganate in a 10:4:1 mixture of concentrated sulphuric acid, orthophosphoric

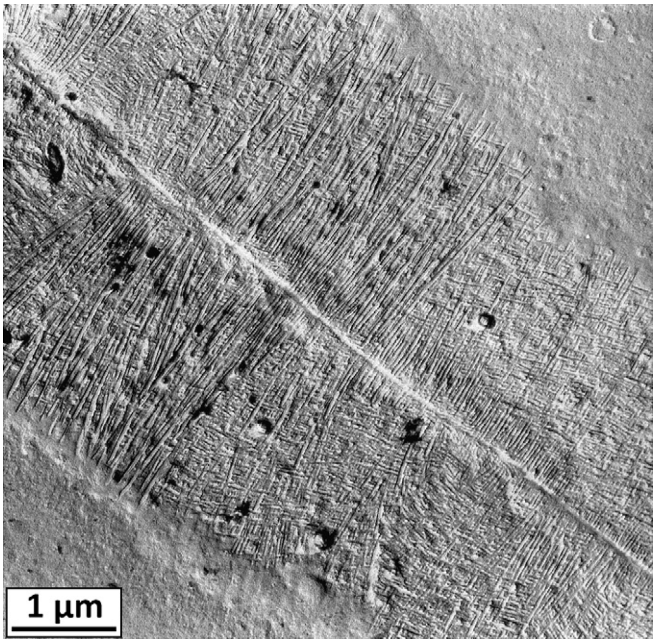

Fig. 1. A longitudinal section of a row of the homopolymer crystallized at 140 °C. In this perspective both radial and cross-hatching lamellae are oriented normal to the image, i.e. correctly presented for thickness measurement.

Table 2
Data for length fractions.

Fraction	Radial lamellar thickness/nm	Cross-hatching lamellar thickness/nm	Frequency of cross-hatching, X_f/μm^{-1}	Minimum radius of curvature for radial lamellae, ρ/μm	Separation of adjacent radial lamellae, Δ/nm
P	15.1 ± 0.25	15.1 ± 0.25	49.78 ± 0.89	1.44 ± 0.12	2.0 ± 0.7
Q	16.7 ± 0.24	15.4 ± 0.22	46.59 ± 1.44	2.04 ± 0.25	3.6 ± 1.0
R	17.9 ± 0.27	16.0 ± 0.25	43.89 ± 1.27	2.91 ± 0.23	3.7 ± 0.9
S	18.5 ± 0.18	16.5 ± 0.32	41.98 ± 1.68	3.02 ± 0.36	4.1 ± 1.0
T	18.3 ± 0.19	16.3 ± 0.20	36.41 ± 1.77	2.86 ± 0.36	4.6 ± 0.6

acid and distilled water; etching was for 2–3 h at room temperature with shaking. Subsequent procedures were as previously published [6]. Fold and {hk0} side surfaces are exposed in this way, the latter being parallel to the molecular length; here they are essentially {0k0}.

Metal-shadowed carbon replicas of these etched surfaces, produced via indirect replication using cellulose acetate, were examined in transmission. Row structures were located and their lamellar thicknesses measured. The methods of preparation tend to produce row structures with their length, i.e. the **c** axis, lying in the plane of the specimen as in Fig. 1. In this case lamellae growing radially in the row are correctly positioned edge-on for their thickness to be measured. As cross-hatching lamellae share a common **b** axis with the radials from which they grow [7] both populations will be edge-on when the **b** axis is normal to the specimen as it is when the linear nucleus is in the specimen surface. Such areas can readily be identified by inspection and show the two populations equally prominently. A check that lamellae are being viewed in the correct orientation is to rotate them, around their traces as axis, using a suitable stage, and confirming that they then show their maximum thickness. The figures cited are the averages of, typically, twenty to fifty measurements computed with their standard errors. Absolute values depend upon the microscope's calibration which was checked against carbon replicas of standard gratings.

3. Results

The lamella is the principal building block of melt-crystallized polymer morphology and its thickness one of the easiest parameters to measure. The common method is via small angle X-ray scattering, SAXS, but there the interpretation is generally oversimplified based on a two or three phase model of stacked lamellae leading to a single averaged value. Different populations of lamellae and/or systematic variations in lamellar thickness in what in reality are more complex morphologies are rarely, if ever, identified. By contrast, microscopy has the advantage of revealing lamellar thickness directly and shows that lamellae differ according to their position in the morphology with, for example, spherulites constructed on a framework of dominant lamellae filled later with subsidiary ones. The two populations thicken differently on heating probably implying different thicknesses [8]. However, gathering sufficient data is normally both complex and tedious encountering problems of locating lamellae correctly oriented for measurement and avoiding bias in selection. These difficulties are greatly eased by linear nucleation. Here, in row structures of α-isotactic polypropylene the two populations of radial and cross-hatching lamellae are readily observed edge-on (Fig. 1). Adjacent lamellae are not in contact, at least away from the nucleus, i.e. they are not in stacks but their thicknesses and other features can be measured directly to provide substantial bodies of data on whole populations. The measurements made include lamellar thicknesses, the frequency of cross-hatching, the minimum radius of curvature of lamellae located at the ends of rows and the separation of adjacent lamellae for four crystallization temperatures, 100, 115, 130 and 140 °C. The highest of these proved most informative on morphological detail and was chosen for a detailed comparison of the changes with molecular mass and tacticity.

3.1. Effects of molecular length

We have previously shown, for the homopolymer, that not only do lamellar thicknesses fall as expected with crystallization temperature but also that radial lamellae are thicker than their cross-hatched twins when grown above 115 °C [4]. Comparable thickness and other data for fractions P through T, differing in molecular mass, are listed in Table 2 and used for the graphs described below. In Fig. 2 lamellar thicknesses, ℓ, are plotted for both populations as a function of molecular mass after crystallization for 5 min at 140 °C. Note that radial lamellae are thicker than their cross-hatching neighbours except for the lowest fraction, P. The differential thickness between the two populations increases from zero reaching a maximum ∼2 nm asymptotically roughly simultaneously with the respective thicknesses attaining their maximum values. At the same time, as Fig. 3 shows, the frequency of cross-hatching, X_f, measured along radial lamellae in row structures, decreases linearly with molecular length from ∼50 to ∼36 per micron.

At the ends of a row, lamellae no longer grow normal to the linear nucleus but curve away from it. The last lamella is the most curved; its associated radius of curvature, ρ, was derived from measurements of the angle φ between two tangents to its outer surface (with respect to the centre of curvature) across a chord of length d using

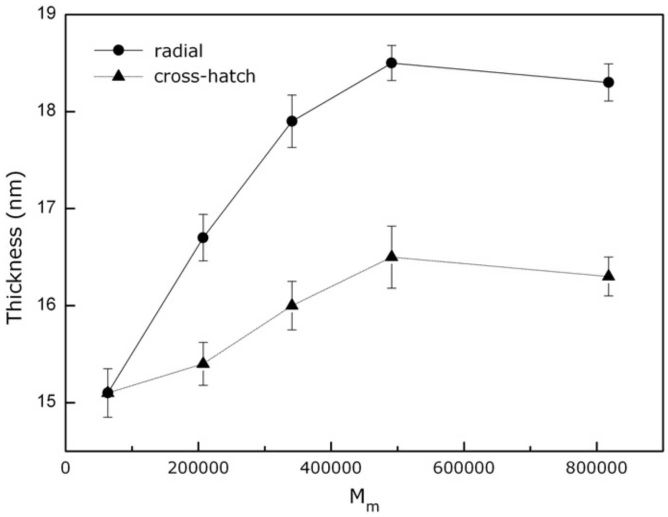

Fig. 2. Lamellar thickness as a function of molecular mass for crystallization at 140 °C; upper curve radial lamellae, lower curve cross-hatching lamellae.

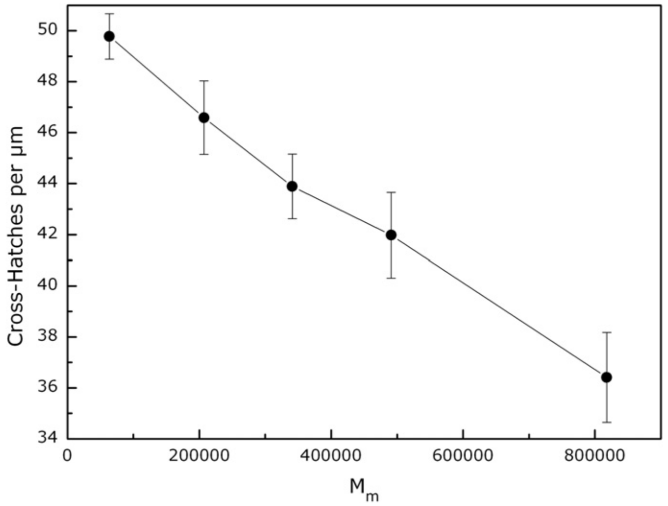

Fig. 3. Cross-hatching frequency as a function of molecular mass for crystallization at 140 °C.

$$\rho = d/2\cos(\varphi/2)$$

Results of minimum radii for many lamellae are plotted in Fig. 4a as a function of molecular mass. The levelling off for higher fractions mirrors that for lamellar thickness in Fig. 2. Elasticity theory predicts that the radius of curvature of elastically bent lamellae – and the strains here are <1%, i.e. within the expected elastic limit – should vary linearly with the cube of lamellar thickness [9]. Fig. 4b is such a plot for all data at all temperatures, for all nine fractions against lamellar thickness; it is linear.

3.2. Effects of tacticity

The two fraction pairs used in the same experiments at 140 °C allow supplementary comparisons of the effect of tacticity, (i.e. %mmmm), at the same molecular length with pair A being almost half as long as pair B. The experimental data for these four materials are listed in Table 3.

Fig. 5 shows that radial lamellae are thicker than their cross-hatched counterparts for three of the four fractions and that radial lamellae are thinner for A1 than the others. However, this sample with 46% tacticity has the highest frequency of cross-hatching (Fig. 6), measured for all nine fractions. There is no corresponding increase for fraction B1 with a tacticity of 68% which shows the same frequency as its partner, B2. The minimum radii of curvature reflect the lamellar thickness in the same way found previously (Fig. 4a).

4. Discussion

4.1. Morphology

The morphology of the rows is one in which radial lamellae appear close-packed or nearly so in contact with the nucleus then separate from 2 to 5 nm (Tables 2 and 3) increasing with molecular length. This recalls similar features found in polyethylene rows where the initial thin, contacting lamellae at the surface of the nucleus thicken and separate with radial distance, the necessary space being provided by others which fail to propagate [10]. The separation there eventually increases to beyond the length of the constituent molecules when intermolecular interference is avoided and the radial growth rate changes from one constant rate to a faster one. Such large interlamellar separations are not observed here except for fraction A1 where distances ∼1 µm are found at row edges, a feature very likely related to fractional crystallization. Elsewhere fewer lamellae are found at the outer edges of rows, as in Fig. 1, although their mutual separation is still much less than molecular lengths; this could well change at greater radius.

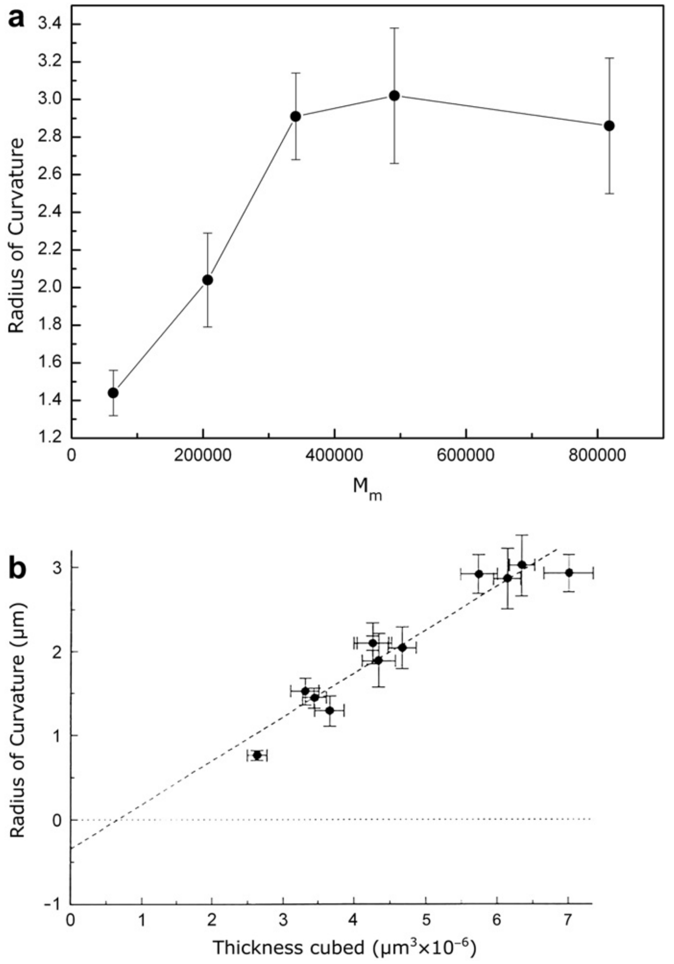

Fig. 4. (a) Minimum radii of curvature of radial lamellae at row ends as a function of molecular mass for crystallization at 140 °C. (b) Minimum radii of curvature for all crystallization temperatures plotted against the cube of lamellar thickness.

4.2. Lamellar thickness

The lamellar thickness of melt-crystallized polymers varies according to the thickness of the secondary nucleus, ℓ, and time unlike solution grown lamellae for which there is no time dependence. Both variables affect the data of Fig. 2. Time dependence has to be the cause of the lower thicknesses of cross-hatching lamellae in Fig. 2 because both they and the radials will have the same secondary nuclear thickness. Moreover, both populations have been measured across the width of the rows, i.e. for lamellae formed for all elapsed times. The only difference between populations, therefore, is the time delay in nucleating what are daughter lamellae of the radials plus any slower thickening rate consequent upon the more congested lamellar environment in which cross-hatching lamellae form. When the thicknesses are equal, for the shortest fraction, P, thickening will be essentially complete as will be most likely for shorter molecules with their reduced entanglements. The equality at lower crystallization temperatures is most likely due to the decline of thickening rate with temperature.

Table 3
Data for tactic fraction pairs.

Fraction	Radial lamellar thickness/nm	Cross-hatching lamellar thickness/nm	Frequency of cross-hatching, X_f/μm^{-1}	Minimum radius of curvature for radial lamellae, ρ/μm	Separation of adjacent radial lamellae, Δ/nm
A1	14.9 ± 0.30	14.6 ± 0.36	45.7 ± 2.63	1.5 ± 0. 16	2.0 ± 1.0
A2	16.3 ± 0.29	15.1 ± 0.20	49.5 ± 1.45	1.9 ± 0. 32	2.6 ± 0.9
B1	16.2 ± 0.28	14.8 ± 0.35	45.5 ± 1.95	2.1 ± 0.25	2.9 ± 0.8
B2	16.2 ± 0.33	24.8 ± 0.39	45.0 ± 1.86	2.1 ± 0.25	3.3 ± 0.8

To account for the thicknesses of both types of lamellae levelling off with molecular length at constant crystallization temperature one must look elsewhere. Indeed as thickening would be greater for shorter molecules, being less entangled, this would have the opposite effect to that observed. The size of the nucleus has, therefore, to be the pertinent factor. As is well-known

$$\ell = 2\sigma_e/\Delta T + \delta\ell$$

where ΔT is the supercooling, a factor which is not only insensitive to molecular length in this range but would also increase isothermally with molecular length and so depress thickness, the opposite of what is required. Accordingly it is to σ_e, the surface free energy, to which we must look as the cause of the levelling off in Fig. 2. It is indeed very plausible that this would increase to an asymptotic limit as the fold surface becomes more complex and rougher with longer molecules and, as is observed, should apply to both radial and cross-hatching lamellae. The proportional increase should be roughly equal to the ratio of lamellar thicknesses, i.e. 18/15 from Table 2 and Fig. 2 which is a 20% increase.

4.3. Cross-hatching

Cross-hatching is due to epitaxy on {010} i.e. the long side surfaces of the lathlike radial lamellae [11]. According to Lotz and Wittmann [12] it is a consequence of a single loss of the alternation of helical hand in successive layers of the crystal structure. Here, however, we discuss the implications of the linear decrease in cross-hatching frequency, X_f, with molecular length, L, shown in Fig. 3. This dependence suggests that chain ends, whose concentration is $2/L$, are involved in a key way. Quite probably a cross-hatching lamella would begin to be laid down at a chain end. Although it is usual in polymeric crystallization to make the simplest *a priori* assumption that all monomers have equal probability of initiating secondary nucleation here, for the first time, we have experimental information suggesting the contrary. This is a significant inference which is plausible for two reasons. First, chain ends are freer to explore alternative sites and conformations in initiating epitaxy. Second, the involvement of chain ends suggests consistent interpretations of why thickening of radial lamellae is suppressed in regions of cross-hatching, the reduced proportion of cross-hatching lamellae at greater radial distance in spherulites and the associated variation of melting point [2,3].

Chain ends are necessarily involved in thickening behind the growth front at constant width, a process which requires new material to be brought into lamellae either by reeling in from the melt further lengths of partly crystallized molecules or by inserting chain ends into stem vacancies created as chain ends are pulled through the lamella to increase the fold length. Other more complex processes involving e.g. double vacancies and the insertion of a loop of chain are inherently less likely. For a chain end to enter a lamella will bring competition for chain ends between thickening and the initiation of a new cross-hatching lamella. The outcome will be less thickening when there is profuse cross-hatching on the one hand and greater thickening where there is less cross-hatching on the other. This is precisely what is observed in α-isotactic polypropylene spherulites and accords with the variation in melting points.

As to why the degree of cross-hatching varies with radial distance, one may note that the observed small separation between radial lamellae away from the nucleus is too small to accommodate another. Molecules in the confined intervening space will have correspondingly distorted conformations with chain segments preponderantly parallel to the surfaces of the radial lamellae. This is close to the 80° rotation of **c** axes required for epitaxial nucleation of a cross-hatching lamella on a side surface [7] and must increase

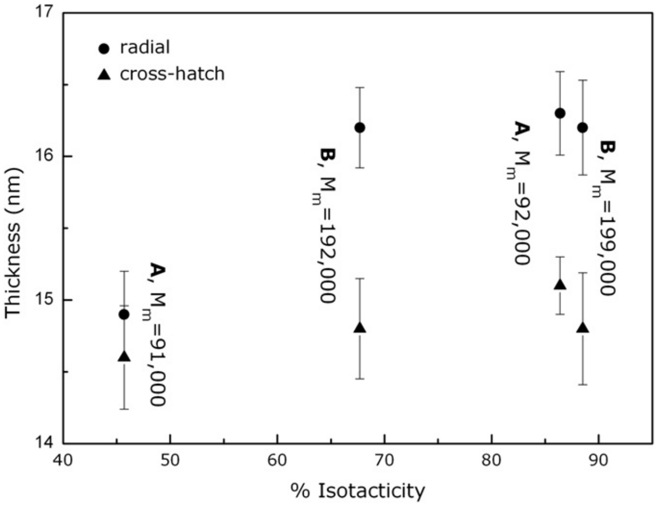

Fig. 5. Lamellar thickness as a function of tacticity for crystallization at 140 °C. Upper points radial lamellae; lower points cross-hatching lamellae.

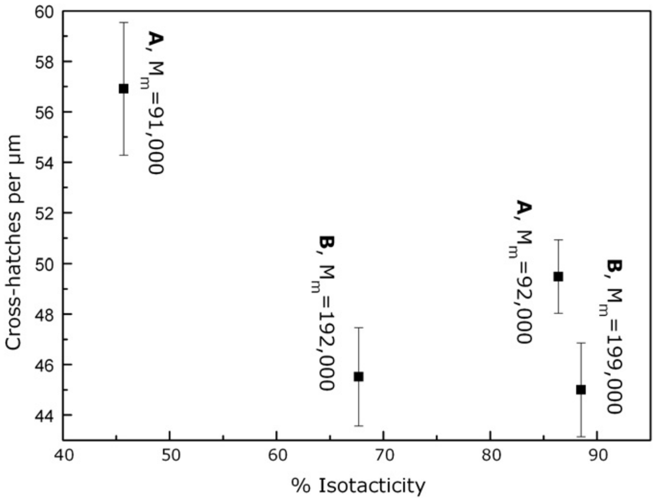

Fig. 6. Cross-hatching frequency as a function of tacticity for crystallization at 140 °C.

the chance of a chain end being suitably oriented so to do. Additionally, the random conformations surrounding a dominant radial lamella growing out into the melt will have a lesser probability of initiating cross-hatching.

4.4. Cilia pressure

The divergence of individual dominant lamellae which causes spherulitic growth is due to cilia pressure supplemented, for faster growth, by the poor packing of rough fold surfaces. Cilia are those uncrystallized portions of molecules partly attached to the growing lamella which by occupying space adjacent to the basal surface deny it to a neighbouring lamella effectively by a short-range repulsive pressure. The magnitude of this pressure may be estimated from the curvature of the outermost lamella at the end of a row where it is from the one side only. From elasticity theory [9], a thin plate of thickness ℓ adopts a radius of curvature ρ in response to a bending moment M per unit width (normal to the curvature) where

$$M = E\ell^3/12\rho$$

and E is the Young's modulus. This leads, using the slope of Fig. 4b, $5.2 \times 10^{17}\ \mathrm{m}^{-2}$, and estimating $E \sim 1$ GPa, to

$$M \sim 1.6 \times 10^{-10}\ \mathrm{N}$$

Equating this to

$$M \sim 1/2PW^2$$

where W is the length of the bent radial lamella, here $\sim 2\ \mu\mathrm{m}$, and assuming cilia pressure, P, is constant across the length of the lamella as is reasonable for separations much smaller than the molecular length, gives

$$P \sim 100\ \mathrm{Pa}.$$

5. Conclusions

1. The thickness of α-isotactic polypropylene lamellae crystallized isothermally increases with molecular mass (length) before levelling off above $\sim 5 \times 10^6$ mass. The rise is consistent with increases ~20% in surface free energy of rougher and more complex surfaces.
2. Radial lamellae are generally thicker than their cross-hatching neighbours because of differential isothermal thickening but are the same for the lowest fraction of 63,500 mass when thickening is essentially complete.
3. The frequency of cross-hatching decreases linearly with molecular length. This dependence points to the key influence of chain ends probably because one attaches to a lamella to initiate cross-hatching. Competition for chain ends between cross-hatching and isothermal lamellar thickening provides explanations for the lower melting point of spherulite centres in α-isotactic polypropylene and less cross-hatching at greater radial distance.
4. It is suggested that confined molecular conformations, such as between adjacent radial lamellae, increase the probability of initiating cross-hatching.
5. The curvature of lamellae at the end of a row gives an estimate for cilia pressure of ~100 Pa.

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References

[1] Bassett DC. Polymer 2007;48:3384–7.
[2] Weng J, Olley RH, Bassett DC, Jääskeläinen P. J Macromol Sci Phys 2002;B41:891–908.
[3] Weng J, Olley RH, Bassett DC, Jääskeläinen P. J Polym Sci B Polym Phys 2003;41:2342–54.
[4] White HM, Bassett DC. Polymer 1997;38:5515–20.
[5] Paukkeri R, Lehtinen A. Polymer 1993;34:4083–8.
[6] Olley RH, Bassett DC. Polymer 1982;23:1707–10.
[7] Lovinger AJ. J Polym Sci 1983;21:97–110.
[8] Bassett DC, Patel D. Polymer 1994;35:1855–62.
[9] Cottrell AH. The mechanical properties of matter. New York: Wiley; 1964. p. 125.
[10] Abo el Maaty MI, Bassett DC. 2001;42:4965–71.
[11] Padden FJ, Keith HD. J Appl Phys 1966;37:4013.
[12] Lotz B, Wittmann JC. J Polym Sci B Polym Phys 1986;24:1541–58.