

## On Spherulitic Growth and Cellulation in Polymers. A Unified Context

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**ABSTRACT:** The new, unified, context for crystallization of linear macromolecules from the melt, established by recent work, is expounded. The morphology of spherulites shows that they form because of a short-range force operative at the branch points of dominant lamellae causing them to diverge at non-crystallographic angles  $\sim 20^\circ$ . Work on monodisperse *n*-alkanes has confirmed the identification of this short-range force with the pressure from (transient) cilia during growth. Accordingly, spherulites, like chainfolding, are a direct consequence of molecular length. It is suggested that the tendency to form coarse spherulites even for extended-chain growth at lower temperatures may result from the increasing difference between the lengths of nucleus and molecule. Crystallization on linear nuclei has been used to maximize the concentration of segregants at the growth front and to demonstrate cellulation in undoped polymers for the first time. The behavior of branched polyethylenes differs from the uniform growth of the linear polymer in coarsening and developing a corrugated growth front all the while slowing continuously towards an asymptotic steady state; differences of detail may be useful in distinguishing polymers of different catalytic origin and branch content. Spherulitic growth is also non-linear for these polymers but is always faster than for rows. When there is sufficient segregation spherulites themselves cellulate, increasingly so for higher branch content. Cellulation is thus an uncommon and secondary process which may be superposed on regular spherulitic growth beyond a certain distance. Cell dimensions do not scale with the diffusion length; in so doing the phenomenon displays new physics.

**KEY WORDS** Spherulites / Cellulation / Monodisperse *n*-Alkanes / Melt Crystallization / Linear-Low-Density Polyethylenes /

It is a truism that the characteristic and special properties of polymeric materials are a consequence of their large molecular size which for crystallizable polymers means length. These properties depend strongly upon processing as exemplified by the manufacture of high modulus polyethylenes which arranges molecules so as to approach the inherent properties of the covalent bond in the macroscopic product. Yet the specific contribution of length to the self-organization of macromolecules, *i.e.*, how it affects the way they solidify in comparison to small molecules has not been so clear. Work of the last three years has changed this situation and established a unified context in which apparently competing ideas each has a place.

Chainfolding is central to polymeric self-organization and properties not least because it interrupts the covalent continuity between lamellae to the detriment of mechanical and other properties. Yet the physical insight which came with its discovery did not of itself resolve issues of how and why molecules and lamellae arrange themselves in solid polymers nor is it the only relevant factor. The phenomenon results from molecules being substantially longer than the crystal nucleus so that a molecule has the opportunity of returning to the same lamella in another location. In the meantime (temporarily) uncrystallized portions of molecules are present outside a growing lamella. These are the key to the formation of spherulites which itself is the key to understanding the intrinsic spatial variability of important polymeric properties.

When chainfolding was discovered for solution-grown crystals it was not universally accepted as occurring also in crystallization from the melt nor, indeed, were lamellae. This was in part because of the lack of relevant microstructural information stemming in large measure

from the inability at that time to use the transmission electron microscope with adequate resolution because of radiation damage. Structural models had to be assumed not all of which have turned out to be correct. Nowhere has this been more important than in the organization of spherulites. The introduction of techniques allowing systematic electron microscopic study of melt-crystallized morphologies twenty years ago altered this situation. They showed that spherulites are formed on a skeleton of individual lead or dominant lamellae which grow apart and diverging from their neighbors. Previously it had been commonly assumed that melt-crystallized lamellae grew together in parallel array with some higher order organization into fibrils.

A spherulitic skeleton of individual lamellae has important implications. On the one hand, the growth of separated lamellae gives a clear reason for chainfolding from the melt on the same kinetic basis as for solution-grown lamellae whereas there is no obvious reason why molecules in contacting parallel lamellae should fold. On the other hand, why should adjacent lamellae diverge? This is a major and crucial difference from inorganic materials for which crystallographic continuity is the rule. Moreover, iteration of divergence at branch points distributed in space is sufficient to generate the spherical envelope with equivalent radii which constitutes a mature spherulite.

The work of the last three years has resolved this issue. It has succeeded in confirming previous suggestions that dominant lamellae diverge because of the short-range repulsion of partly-crystallized molecules, *i.e.*, dynamic cilia. In addition it has provided the first demonstration of the phenomenon of cellulation in an undoped polymer. This was a historically important suggestion for the origin of the supposed mesoscale ordering within all polymeric

spherulites. In fact cellulation does not occur for linear polyethylene and highly isotactic polypropylene and has no relevance to the formation of spherulites per se. It is an uncommon secondary process superposed on regular spherulitic growth, beyond a certain distance, in some but not all systems and circumstances. In consequence, the subject has now been unified with different mechanisms placed in context and a firm basis provided for a better understanding of structure/property relations in crystalline polymers.

### THE PROBLEM OF SPHERULITIC GROWTH

Spherulites are the characteristic polycrystalline growth form of synthetic polymers solidified from the melt. They were first recognized<sup>1</sup> as such for branched polyethylene in 1945 although the literature for spherulites in other substances, especially silicate minerals, goes back into the nineteenth century.<sup>2</sup> The name means little sphere corresponding to the envelope of a mature object. Typical development is from a precursor by iterative branching and splaying of equivalent units which eventually become radial, and passes through forms with sheaflike projections prior to the final spherical entity.<sup>2</sup> So-called axialites are immature spherulites which appear at high temperatures allied to a decrease in branching frequency.

Spherulitic growth is, accordingly, that branching and diverging process which, if continued for long enough, will give equivalent radii within a spherical envelope. The essential cause is the repetitive divergence of adjacent units—typically individual lamellae for crystalline polymers—not the nature of the units themselves. Given a distribution of branching points, this produces the requisite polycrystalline objects with crystallographically equivalent radii rather than single crystals.

Following the first systematic electron microscope studies of melt-crystallized polymers, it was proposed,<sup>3-5</sup> on the basis of morphologies such as that of Figure 1, that the origin of lamellar divergence is a mesoscopic short-range repulsive force operative in the region of a branch point. This follows from the linear traces of the lamellae. Because such flexible objects can be made to bend through a right angle in particular circumstances,<sup>6</sup> the linearity demonstrates that they did not grow under stress and that the mutual divergence takes place close to the branch point. A constant repulsive force is suggested by the near-constant angle of divergence and, as the distances involved do not exceed the molecular length, it was proposed<sup>3-5</sup> that the short-range force is due to pressure of dynamic molecular cilia during growth.

This is envisaged in the following way. Until a molecule is able to add completely to a layer, substantial portions will lie outside and adjacent to the fold surfaces. There they will be unable to diffuse away but will occupy space and exert a repulsive pressure, with a weak rubbery modulus, on any competitor for that space. This will be especially pertinent at the start of a new layer when molecules adding to the side surfaces will tend to be in the way of the emerging lamella which will, in effect, repel itself from the mother layer. Adjacent lamellae will, therefore, be forced apart during growth and, given a distribution of branch points in space, iteration will

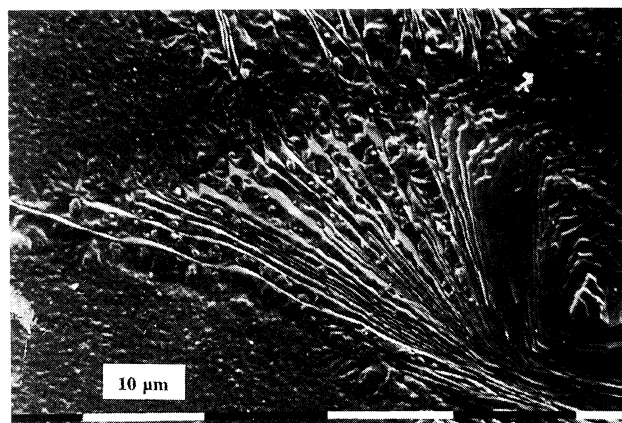


Figure 1. Regular splaying of dominant lamellae in isotactic poly(4-methylpentene-1) crystallized from the melt at 235°C. Replica of etched surface.

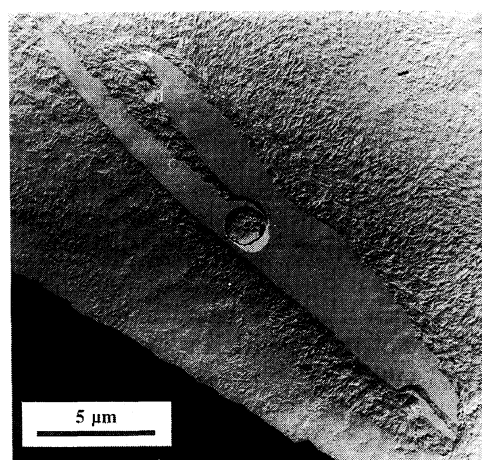


Figure 2. Splaying of successive layers around a screw dislocation in a crystal of linear polyethylene, crystallized from the melt at 127°C, within a quenched matrix. Replica of etched surface.

produce the spherical envelope around equivalent radial units of a mature spherulite. Work on the *n*-alkanes described below has emphasized how close to the branch point these influences are at work.

Unambiguous confirmation of the existence of a mesoscopic short-range force for polymeric growth has come from the geometry of spiral terraces in multilayer crystals within a quenched matrix<sup>7</sup> as shown in Figure 2. The essential point is that the adjacent layers which have developed around the (etched-out) giant screw dislocation are not in contact. Such behavior differs from that found in inorganic materials which may, for example, build up complex and extensive polytypes over many layers but is a feature of polymers. What it shows is that divergence as in Figure 1 is not a nucleation phenomenon but is a distortion of lamellae away from adjacency and crystallographic continuity; this implies the existence of a mesoscopically short-range force. The two layers on the left of Figure 2 both have the *b* axis along their lengths but these two directions no longer coincide in space but are radial to the developing object; this is the essence of spherulitic growth.

It is not a major objection to the role of ciliation that there are circumstances in which inorganic components may form spherulites: these are, in general, both complex,

*e.g.*, ice from aqueous glycerine solution<sup>8</sup> and poorly documented. In this particular case the morphology is also one of diverging units and, as in polymers, has been proposed to be a response to short range pressure.<sup>9</sup> Spherulitic growth of apparently simpler inorganic systems but in complex circumstances poses no inherent contradiction to the concept that the characteristic spherulitic growth of polymers is a consequence of ciliation, *i.e.*, their molecular length.

#### *Monodisperse n-Alkanes*

The monodisperse *n*-alkanes<sup>10</sup> presented the first opportunity for a critical test of the proposed role of ciliation. Earlier X-ray studies<sup>11</sup> had shown that these systems tended to crystallize with the methyl end groups confined to the basal surfaces resulting in quantized thicknesses of the extended-chain length (in projection) or an integral submultiple thereof. There are departures from strict quantization, as would be expected for the small contribution surface packing makes to the total free energy of the system, but it offers a convenient classification of crystallized systems.

For melt growth of alkanes with  $> \sim 200$  C atoms, the kinetics pass through a minimum with increasing supercooling; above this temperature the extended form predominates, below it the once-folded.<sup>12</sup> To the approximation that molecular stems add as units to the crystal there will be no cilia—and hence no spherulites for the extended form—but (transient) cilia of half the molecular length will occur for the once-folded form which should, therefore, form spherulites. This simple prediction is borne out<sup>13,14</sup> for growth close to the kinetic minimum in  $C_{294}H_{590}$ .

The corresponding microstructure changes from diverging dominant lamellae and later-forming subsidiaries, as in polymer spherulites, to extensive parallel arrays of extended-chain lamellae. The change in morphology not only confirms the essential role of ciliation but also demonstrates that, to operate for alkanes, the range of the associated force must be much less than could be inferred for polymers. For cilia no more than several nm long, the implication is that splaying is effected very close to the branch point, so close that molecules partly attached to the lateral growth surface would provide effective repulsion from neighboring basal surfaces.

#### *Quantitative Ciliation*

The simple correlation between the occurrence of spherulites with characteristic microstructure and chain-folding and its absence for extended chain growth only holds to the approximation that molecules add to the crystal as integral stems. Our studies of *n*-alkanes such as  $C_{98}H_{196}$ , which only crystallize in extended-chain form, show that it begins to fail progressively as crystallization temperature is lowered.<sup>15</sup> A kind of spherulite ensues but with a texture consisting of wide sectors of the same orientation—much coarser than the equivalent radii of the classic spherulite but becoming finer at lower temperatures. Such objects also show repetitive divergence of adjacent dominant lamellae (with a parallel lamellar substructure appropriate to the coarseness) indicating that they, too, have been subject to a short-

range repulsive force. Our working hypothesis has been that this is likely to be a response to transient cilia deriving from the excess of molecular length over that of the relevant nucleus. The latest preliminary results, which show that lamellar divergence increases as crystallization temperature is lowered, and is greater for longer cilia, support this proposal.

Ciliation is an interesting and physically sensible idea on several grounds. First, it is in agreement with the previous inference that the formation of polymeric spherulites is, like chainfolding, a consequence of molecular length. Second, the small dimensions involved—two orders of magnitude less for alkanes than for polymers—show that the interaction is localized very close to the branch point so that cilia from molecules attaching to the lateral surfaces will be within range of the developing new layer and be able to exert an effective repulsive force upon it. Third it is in accord with theoretical concepts embodied in Hoffman's theory of extended-chain growth<sup>16</sup>—whose predicted linear kinetics are fitted by our data—and the fold surface structures modelled by Higgs.<sup>17</sup> It needs, however, to be made more quantitative.

Quantification is likely to result from the study of binary blends of *n*-alkanes following significant preliminary results. Preliminary work in this laboratory<sup>18</sup> has shown that when a 95:5 blend of  $C_{162}$  with  $C_{246}$  is crystallized, finer spherulites are produced than for the pure host and the kinetics stay linear but are much slowed. This is in accord with expectation for the introduction of cilia due, respectively, to the excess length of the longer molecule and consequent hindering of attachment to the growth surface. On the other hand a 95:5 blend of  $C_{162}$  with  $C_{122}$  crystallized above the melting point of the shorter *n*-alkane has kinetics which are both slower and have become non-linear as would be expected for cellulation due to segregation of the shorter molecules as discussed below.

## CELLULATION

The phenomenon of cellulation is one in which molecules rejected at the growth interface accumulate there, affect the growth kinetics and give the resulting solid a texture in which rejected species are concentrated between cells. It is well known for binary metallic alloys and has been proposed to exist also for crystalline polymers in general.<sup>19</sup> Only recently, however, has it been unambiguously observed for an undoped polymer.<sup>20–22</sup> It is an unusual phenomenon which may be superposed on regular spherulitic growth if appropriate conditions are met. The required conditions are that rejected species are of a kind able to slow the growth rate significantly, most likely by lowering the local equilibrium melting temperature and with it the isothermal supercooling, and that their concentration is sufficiently high.

Study of the phenomenon is facilitated if row structures grown from linear nuclei are studied in preference to spherulites. This is because for them the concentration of rejected species at the interface is maximized there being insufficient space between growing lamellae to accommodate segregants so that they can only accumu-

late ahead of the advancing row. In spherulites, by contrast, space is created by lamellar divergence into which segregants will diffuse and reduce their concentration at the interface.

#### Row Structures

Row structures<sup>23-25</sup> are generally met with in conditions when a linear nucleus has been created by application of applied stress or flow from which lamellae have crystallized epitaxially and transversely. Similar morphologies can be obtained in polyethylene without stress by using the new advanced polyethylene fibers whose high melting point,  $\sim 150^{\circ}\text{C}$ , allows their immersion in molten polymer to nucleate crystallization at temperatures of  $\sim 130^{\circ}\text{C}$  and below.

The advantages of studying row structures to characterize polymer morphology are many,<sup>26</sup> in addition to that cited above, because of their uniform orientation. In essence they allow the properties of lamellae to be assessed in a known environment, as part of a constrained parallel array, instead of in isolation. Not only does this give a straightforward means of positioning lamellae correctly for measuring their thickness, but it allows departures from uniformity to be revealed unambiguously. Cellulation is one example of the advantages of this approach. Others have been the measurement of interlamellar separations as functions of crystallization variables in  $\alpha$ -polypropylene; the measurement of cilia pressure from radii of curvature of elastically bent lamellae at the ends of rows and the demonstration that crystallographic continuity is broken in polymeric growth when this allows crystallization to reach into otherwise inaccessible regions.<sup>27</sup> Of especial note is the continued uniform, close-packed lamellar growth of rows of linear polyethylene and highly isotactic polypropylene, at the same isothermal rates as spherulites notwithstanding their quite different interface structures, which shows that cellulation does not occur for these modern homopolymers.<sup>28</sup> Any segregation which does occur is passive rather than active, of molecules which do not slow the kinetics, and so fails to establish the essential condition to render a smooth envelope unstable.

In homopolymers such as linear polyethylene and isotactic polypropylene, the transverse lamellae in a row structure continue to grow out from the nucleus indefinitely. The first experiments which demonstrated the quite different behavior of linear-low-density polyethylene were those of Janimak and Bassett.<sup>20</sup> They showed that the initial constrained parallel lamellar array went through a series of morphological changes with increasing radial distance, accompanied by a declining radial growth rate, culminating in instability and irregular development. Significant differences were found<sup>29</sup> between linear-low-density polyethylenes of different catalytic origin in further investigations, metallocene materials being morphologically more regular than Ziegler-Natta ones. However, at high temperatures, when the segregant concentration fell below a critical value, Ziegler-Natta materials behaved like metallocene ones with the morphology and kinetics moving smoothly towards a steady state.<sup>30</sup>

The situation is encapsulated by Figure 3 which shows a row structure of a Ziegler-Natta-catalyzed poly-

ethylene, with 9.7 butyl branches per 1000 C atoms, quenched after being crystallized at  $122^{\circ}\text{C}$  for 30 min on a cylindrical Tekmilon advanced polyethylene fiber (Mitsui) as nucleus. What started out as a uniform array of close-packed lamellae nucleated on the fiber at the top of the picture has, over a few microns radial distance, developed a corrugated envelope. The new interface has protrusions growing ahead into the melt which are essentially spherulitic in character, *i.e.*, built of separated, diverging lamellae. To reach this stage the row has passed through a characteristic sequence of changes. The initial narrow separation between adjacent lamellae has widened allowing the growth direction to deviate from the radial together with a modest increase in lamellar thickness. This is common to all materials, leading to a corrugated outer profile. Only Ziegler-Natta polymers, at sufficiently high initial growth rates, have so far been observed to go further and develop spherulitic protrusions separating segregant-rich regions.

The cause of this novel behavior, quite different from that of the linear polymer, is the branch content of the segregated molecules. Ethyl and longer branches are excluded from polyethylene crystals; those portions of molecules with branches which are too close together cannot crystallize and will be rejected causing the local equilibrium melting temperature to fall. In other words the isothermal supercooling decreases and with it the growth rate but lamellar thickness will tend to increase if branch positioning allows. The crystal habit also tends to move from non-planar towards planar forms normally found for growth at higher temperatures for the same reason. None of this applies to linear polyethylene for which segregated molecules are merely short but insufficiently so to depress the growth rate enough for the planar envelope to become unstable. Instability only occurs when it is possible to achieve a lateral variation in growth rate large enough for protrusions to be able to grow sufficiently faster than adjacent regions (where segregants will tend to accumulate). In linear polyethylene and modern polypropylene homopolymers any segregants do not have this effect and are unable to stimulate instability; their role is merely passive although their presence may well affect subsequent properties such as stress-cracking resistance.

A salient feature of systems which may cellulate is their non-linear kinetics with growth rates decreasing from the initial value as segregation proceeds. This stands in sharp contrast to the familiar linear growth of spherulites in homopolymers. The extent by which the growth rate is depressed depends on the local segregant concentration which, in turn, depends upon the nature of the crystal/melt interface. It is generally the case that spherulites grow faster than rows in the same sample which is a consequence of their more open structure within which the same amount of segregant produces a lower concentration at the interface. The spherulite at the bottom of Figure 3, whose radius is larger than that of the row above, illustrates the point.

When the first experiments only found cellulation and associated morphological instability for rows but not for adjacent spherulites, research turned to investigate more branched polymers. A metallocene polyethylene, with 28 ethyl branches per 1000 C atoms, revealed cellulation in

an undoped polymer spherulite for what is believed to be the first time.<sup>21</sup> Figure 4 shows how crystallization for 1 h at 95°C gives a circular perimeter but for 1.5 h a corrugated one with segregated, *i.e.*, uncrystallizable molecules concentrated between the fingers of crystalline polymer.

This change in morphology with time demonstrates clearly that cellulation is superposed on regular spherulitic growth after a given time, when segregants have slowed growth sufficiently to allow the spherical envelope to become unstable against fluctuations. The greater the segregant concentration, the greater will be the fluctuations around the mean with associated variations in local growth rate. Laggards and leaders will ensue which, when they differ sufficiently in growth rate to achieve stability, create fingers of crystalline material separated by regions of high segregant concentration.

The demonstration of cellulation needs to be followed by further study leading to fuller understanding of the underlying science. This has already begun with surprising results. The historic discussion of cellulation in polymers<sup>19</sup> cannot apply to the new observations because they all involve growth rates decreasing towards a steady state contrary to the old assumption that they would recover to the initial values once cellulation had set in. Physically this means that growth actually takes place within the segregant or 'impurity' layer rather

than beyond it as was then assumed. One might well have expected, nevertheless, that the characteristic dimensions of cellulation, namely the distance to its onset and the cell width would scale with the diffusion length,  $\delta = \text{Diffusion coefficient}/\text{Growth rate}$  which is not so.

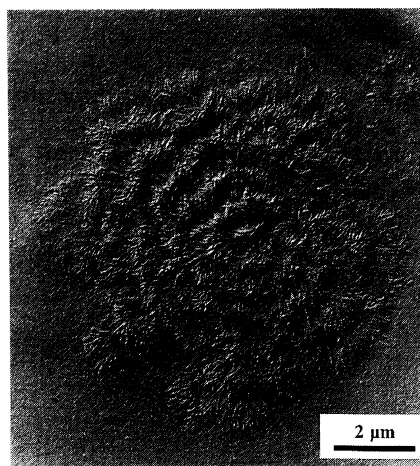
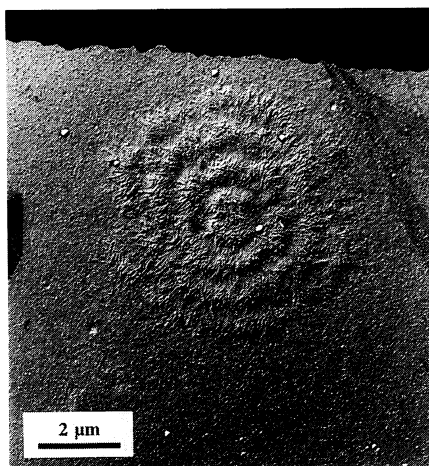
Investigations<sup>22</sup> of a series of metallocene-catalyzed polyethylenes, with average ethyl branch contents ranging from 14 to 37 per 1000 C atoms, showed that the distances to instability and cell width both decreased with increasing branch content but were insensitive to substantial changes in growth rate for only 2 K change in crystallization temperature, *i.e.*, when the diffusion coefficient would remain essentially constant. In all cases the growth rate declined asymptotically towards a steady state and the cellulated morphologies became increasingly similar to those postulated to be present in all polymer spherulites the sooner cellulation set in.

The evidence so far is that cellulation begins, in conditions of high segregation, when an approximately constant amount of material has accumulated. This could, perhaps, indicate the need for fluctuations to reach a certain value. Moreover, direct observation of how a spherulitic envelope advances<sup>31</sup> reveals that the growth of individual radial fibrils slows to the extent that they are then overtaken by other, less affected ones, from the rear and that volumes of concentrated segregants are avoided.

When first introduced to polymer science cellulation was proposed as the origin of spherulitic growth<sup>19</sup> although direct supporting evidence has never been forthcoming. With the benefit of detailed microstructural knowledge it is now apparent that it is branching which is the essence of spherulitic growth not the nature of the branching unit and, moreover, branching at finite angles, not the supposed low-angle non-crystallographic phenomenon then assumed. Later papers<sup>32</sup> claim instead to have identified microstructural detail within the complexities of polyethylene banded spherulites which scales with the diffusion length, indicative of cellulation. This is an unjustified claim because of doubtful interpretation and reasoning. The average separation of dominant lamellae is not a measure of cell width; it is a product of branching



**Figure 3.** The development of cellulation within a row of linear-low-density polyethylene (9.7 butyl branches/1000 C atoms; Ziegler–Natta catalysis) crystallized on an oriented fiber at 122°C for 30 min showing progressive coarsening, thicker lamellae and spherulitic protrusions extending into the quenched melt. Replica of etched surface.



**Figure 4.** Spherulitic morphologies produced in a metallocene-catalyzed polyethylene with 28 ethyl branches per 1000 C atoms, isothermal crystallization at 95°C. Regular banded growth, on the left, is present after 1 h whereas, on the right, cellulation had set in after 1.5 h. Replicas of etched surfaces.

angle with inter-branch distance. The former increases with supercooling,<sup>6</sup> the latter decreases; the decrease of their product is a consequence of the increased frequency of branching as the texture becomes finer. Nor can the inter-dominant spacing logically be attributed<sup>32</sup> to segregants rejected by the later-crystallizing subsidiary lamellae.

The claim to have identified microstructural evidence of cellulation in linear polyethylene also conflicts with abundant evidence, including that cited above, to the contrary. It is now quite evident that the cause of spherulitic growth is repetitive branching of adjacent dominant lamellae at finite angles akin to former understanding<sup>33</sup> before the role of dominant lamellae was known. Whether or not there is cellulation is irrelevant to the formation of spherulites but it does affect the pattern of distribution of rejected species which will itself affect mechanical and other pertinent properties.

### CONCLUSIONS

Recent work has established a new and unified context for crystallization of linear macromolecules from the melt:

1. The morphology of spherulites shows that they form because of a short-range force operative at the branch points of dominant lamellae causing them to diverge at non-crystallographic angles  $\sim 20^\circ$ . Work on monodisperse *n*-alkanes has confirmed the identification of this short-range force with the pressure from (transient) cilia present during growth.

2. Crystallization on linear nuclei has been used to maximize the concentration of segregants at the growth front and to demonstrate cellulation in undoped polymers for the first time. The behavior of branched polyethylenes differs from the uniform growth of the linear polymer in coarsening and developing a corrugated growth front, all the while slowing continuously towards an asymptotic steady state. Greater instability has been observed for Ziegler–Natta polyethylenes than for metallocene-catalyzed materials, a feature which may have a use in the characterization of branching statistics. Spherulitic growth is also non-linear for these polymers but is always faster than for rows because of the more open interface with the melt.

3. Spherulites themselves cellulate when there is sufficient segregation, increasingly so for higher branch content. Cellulation is an uncommon secondary process which may be superposed on regular spherulitic growth beyond a certain distance. Both the radius to the onset of cellulation and the cell width are effectively independent of growth velocity so that neither scales with the diffusion length. Cellulation, therefore, displays new physics different from previous discussions.

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