A Unified Context for Spherulitic Growth in Polymers

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ABSTRACT: The long-standing issue, central to polymer science, of the relevance of cellulation to the formation of spherulites has been resolved by the first demonstration of this phenomenon, in spherulites of a highly branched polyethylene copolymer. The two principal alternative mechanisms proposed for the formation of spherulites are shown to be complementary, with cellulation a secondary process occurring only when segregation reduces growth rate sufficiently. A unified context for polymeric crystallization is thereby achieved in which segregation generally plays a passive rather than an active role in the development of spherulites.

Spherulites and the processes which produce them have long been unsolved major problems of crystal growth.[1] They have assumed particular importance for crystalline polymers such as polyethylene and polypropylene in which they are the characteristic mode of growth from the melt and a principal determinant of properties. In seeking to explain spherulitic growth in such systems, two different views have been taken as to what constitutes the essential problem, namely, whether it is a grouping of lamellae into “fibres”[2] imposed by segregation or a consequence of the divergence of individual dominant lamellae at branch points.[3−6] The work of this paper is able to reconcile these two approaches by demonstrating unambiguously, for the first time, the phenomenon of cellulation in polymer spherulites.[2] This is an additional feature, caused by segregation, superposed on normal spherulites when the concentration of suitable segregants is sufficiently high. We are, accordingly, able to establish when the premises on which the cellulation hypothesis is based are valid and so achieve a unified context for spherulitic growth in polymers in which the respective and complementary roles of the two proposed mechanisms are made clear.

Spherulites, literally little spheres, have been recognized in minerals for at least a century, posing a problem as to how polycrystalline entities, with crystallographically equivalent radii, formed. In 1945 spherulites were reported in polyethylene and have since been recognized as characteristic of quiescent crystallization of macromolecules from their melts.[1] Phenomenologically, they generally develop from a single crystal precursor via repetitive branching and splaying of the direction of fastest growth which thus eventually becomes radial within a spherical envelope. The initially puzzling transverse orientation of molecular chains was understood once it was appreciated that chain-folded lamellar crystals grew radially outward in spherulites.[1] But the nature of the splaying entities and the mutual organization of lamellae in spherulites could not be ascertained with certainty until the advent of systematic studies with the transmission electron microscope.

Prior to this the principal source of information was the polarizing microscope, and extensive studies with it, especially of highly doped melts, led Keith and Padden to the opinion that the essential problem of spherulitic growth was to explain the existence of postulated internal “fibers”. Their proposal[2] was that these resulted from cellulation and fibrillation of an initially planar interface, of presumed close-packed lamellae, growing into the melt because of morphological instability. Any molecular species rejected from the growing crystals, so-called “impurities”, would become concentrated at the growth interface, slow the growth rate, and so render the interface unstable against the formation of protrusions into faster growing conditions. Growth cells and eventually fibers would thus form between whose lateral boundaries impurities would accumulate with cell diameters of approximately the characteristic diffusion length $\delta = D/G$ (D being the diffusion coefficient for the segregants and G the radial growth rate). The space-filling necessary to maintain uniform average density would be achieved by branching of fibers by some small-angle non-crystallographic process.

While fibers undoubtedly exist in special circumstances, e.g., in α-polypropylene grown from minority blends of the isotactic polymer in the atactic form,[7] difficulties arise when it is attempted to extend the concept of cellulation to homopolymers. Although there was and is no direct microscopic evidence that similar fibers exist in normal homopolymers, this was, nevertheless, what was assumed. The predictions then made for the internal organization of such spherulites, specifically of polyethylene,[2] could not be stringently tested for some time because of the unavailability of detail at the lamellar level. But with the advent of systematic electron microscopy of melt-crystallized polymers, based upon the discovery of permanganic etching, the internal lamellar structure of spherulites was established and proved to be very different from the proposed model. There were no fibers in typical melt-crystallized homopolymers, rather the skeleton of spherulites was established by the growth of individual, so-called dominant lamellae, which branched at finite angles, frequently at giant screw dislocations, and mutually diverged.[8,9] Two aspects of this morphology, the crenellated rather than planar interface geometry and the reduced number of lamellae per unit area of interface,

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both implied that segregant concentrations would be too low to instigate morphological instability. This reinforced earlier disquiet that some spherulites grew in highly purified melts so that segregation was not essential to their growth.[10] This is a conclusion reached by others and confirmed by the work of this paper. Nevertheless the claim that internal spherulitic textures are due to segregation and cellulation on the scale of the diffusion fields has continued to be made.[11] The authors have not, however, provided unambiguous textural evidence for cellulation nor, crucially, have they demonstrated the slowing of growth rate which is essential before cellulation can occur and upon which their thesis ultimately rests. This paper is, as far as we are aware, the first in which this evidence is provided, demonstrating that cellulation is a secondary effect which may or may not be present in polymer spherulites, depending on whether segregation produces sufficient depression of growth rate.

An alternative explanation for spherulitic growth has been proposed in the meantime[4−6,8,9] based upon the observation of constant angles of deviation between successive layers of multilayer crystals at the center of spherulites and the demonstration that adjacent layers of one crystal diverge from each other around a giant screw dislocation, a common branch point within spherulites. This geometry is universal in all the many crystalline polymers we have examined, namely, polyolefines, polyesters, aromatic polyketones, and polyamides. The essential feature which causes spherulitic growth is, accordingly, the deviation of adjacent dominant lamellae at branch points. Provided branch points are distributed in space, as is generally the case, this deviation leads automatically to the development of a spherical envelope.[12] The specific cause of the deviation indicated by the geometry is a short-range repulsive force between adjacent dominant lamellae, operative over distances less than the molecular length. It has been proposed to be generated by the pressure of cilia, i.e., uncrystallized portions of molecules partly attached to the growing lamella. These will tend to occupy space adjacent to a growing lamella and to exert a weak rubbery modulus when compressed.[3] Their effect will be felt during the dynamics of growth and will not necessarily relate simply to the final molecular conformation. Confirmatory evidence for the decisive influence of cilia has recently been provided by studies of the monodisperse *n*-alkane, $C_{294}H_{590}$, which does form spherulites but not when molecules crystallize fully extended, only when they are folded.[13] This agrees with prediction because, to a first approximation, cilia will be absent from the first case but present in the latter, once the first stem is attached.

This positive demonstration of the link between cilia and spherulitic growth in polymers—which can be generalized in terms of an appropriate short-range repulsive force to other systems of comparable geometry—leaves open the question of why morphological instability has not previously been seen to occur in spherulites in typical polymer melts. The reason, as this paper demonstrates, is that the premises assumed are not generally operative. As has been pointed out above, the concentration of segregants is generally lower than had initially been anticipated. There is also another aspect which has recently been identified: the species segregated may not depress the growth rate if, for example, there is negligible change in equilibrium melting temperature and thus of supercooling. Other work[14] has shown that this is the case for α-polypropylene. The identity of growth rate between row structures (in which lamellae are close-packed) and spherulites (in which the texture is more open) carries the implication that if there is segregation in this polymer, it is not affecting the growth rate. In other words, there is no significant depression of growth rate due to segregated species in modern polypropylene homopolymers. For cellulation to be possible there must be sufficient concentration of suitable segregants which do depress the growth rate.

A series of experiments designed to maximize the concentrations of suitable segregants during polymeric growth from the melt has recently been carried out in this laboratory. In so doing both progressive declines in growth rate and corresponding morphological instabilities have been observed. In the first experiments Janimak and Bassett[15] studied the growth of a linear-low-density polyethylene, with 21 butyl branches/1000 C atoms, from linear nuclei, to produce row structures and compared them with spherulites growing freely elsewhere in the same samples. As lamellae are close-packed in row structures, the more-branched molecular sequences which are rejected (because of the exclusion of branches from lamellae) will accumulate ahead of what, to a reasonable approximation, will be a planar growth front. A continual slowing of isothermal growth rate and a progressive coarsening of texture, with modest lamellar thickening, as expected for an isothermally decreasing supercooling, was observed for both rows and free-growing spherulites. Only in the former, however, did this develop further into a form of morphological instability. When the growth rate of rows had declined substantially, spherulites developed sporadically at the row/melt interface—presumably at sites of lower than average impurity concentration—and then grew ahead of it. The fact that free-growing spherulites elsewhere in the sample always grew faster than rows, even though the rates decelerated with radial distance in both cases, is as expected for their more open texture with its lesser concentration of segregants. That the texture of spherulites moved partly through the sequence of changes shown by rows but without leading to morphological instability suggested strongly that, for them and in this polymer, a sufficient concentration of segregants had not been reached. This is a conclusion which the present work confirms and which has led directly to the finding of cellulation in spherulites of still-more-highly-branched polyethylene.

This effect was discovered when Hosier and Bassett[16] investigated the dependence on branch content of the occurrence of instability in rows, for a series of linear-low-density polyethylenes. Instability, which is absent from linear polyethylene, was observed to develop in polyethylene copolymers with 9 and more butyl branches/1000 C atoms with greater effects for broader distributions of branches according to the type of synthesis. In addition, in the most-highly-branched material examined, free-growing spherulites were found to change from the usual circular perimeter to a wavy outline beyond a certain radius, suggesting that they too were exhibiting morphological instability. This is the case and is the subject of the present paper.

The material used is a metallocene-catalyzed polyethylene with 28 ethyl groups/1000 C atoms whose average molecular masses are $\overline{M}_m = 79 \times 10^3$ $\overline{M}_n = 40$

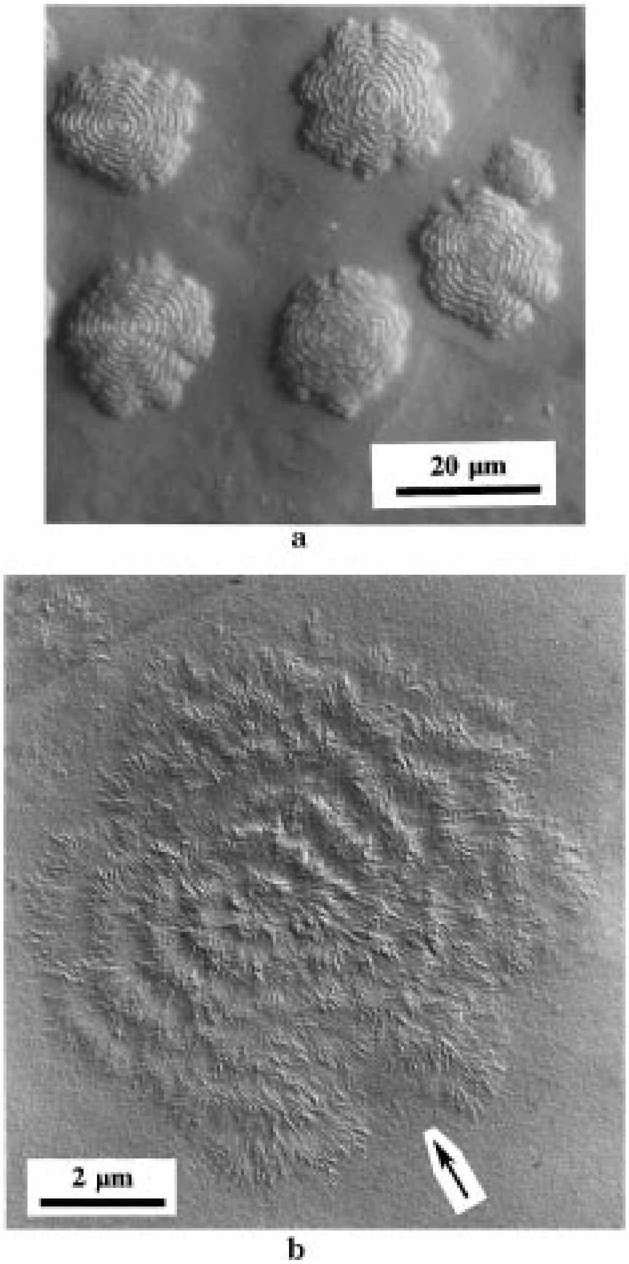

Figure 1. Cellulation developing in the interior of spherulites of branched polyethylene grown from the melt at 95 °C seen (a) using Nomarski reflection optics after 3 h crystallization and then permanganic etching and (b) with lamellar detail in a shadowed carbon surface replica, viewed in the transmission electron microscope, of a similar specimen but crystallized for 1.5 h.

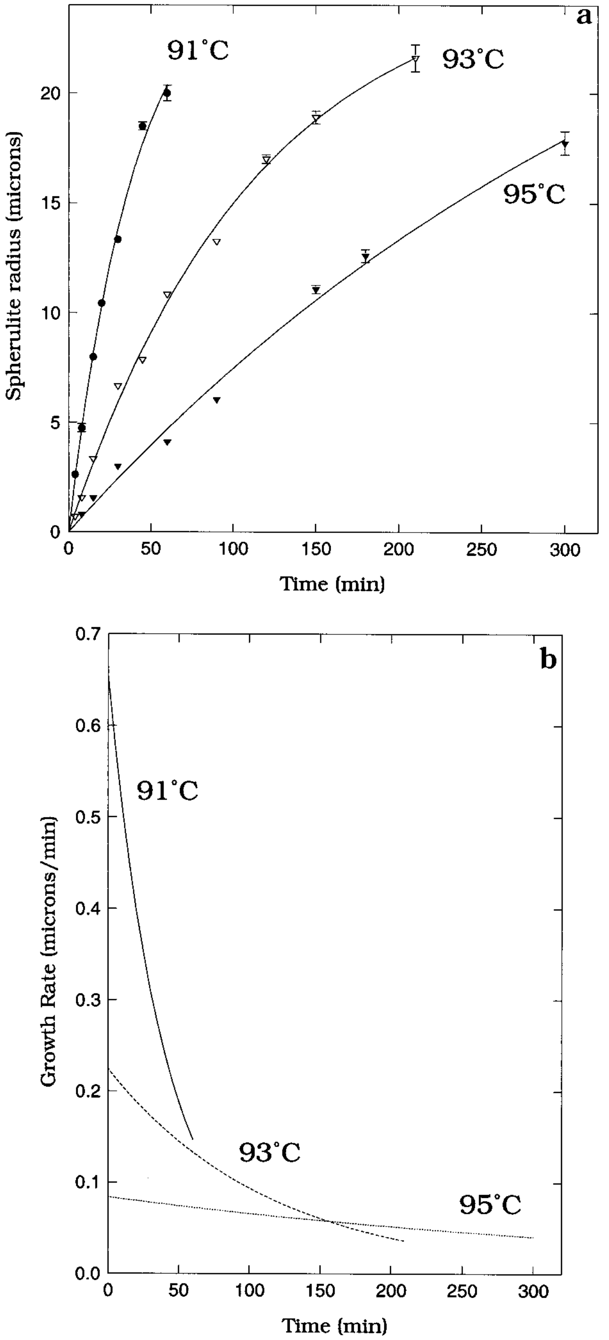

Figure 2. (a) Maximum radii of spherulites of branched polyethylene as functions of time for three growth temperatures. (b) Corresponding isothermal growth rates obtained as the derivatives of the fitted curves in part a.

× 10^3 which was kindly supplied by Dr. P. Jääskeläinen of Borealis Oy, Finland. The appearance of spherulites of this polymer after isothermal crystallization (at 95 °C, as ~1 mm thick specimens in a Mettler FP 82 hot stage) and permanganic etching, is shown in Figure 1 both optically, using Nomarski reflection imaging, and with the higher resolution of the transmission electron microscope, via two-stage replication. Cellulation, visible as the onset of discontinuities of the internal banding, starts within the body of the spherulites at radial distances of a few microns, the average figure increasing from 3 to 6 μm as the isothermal crystallization temperature rises from 91 to 95 °C. In consequence perimeters do not remain circular but become wavy with the development of protuberances. Certain regions, as arrowed in Figure 1b, where segregants will have accumulated, show no evidence of crystallization. At greater radial distances these soon lead to the development of separated fibers very much as proposed by Keith and Padden in their original paper.[2] [A qualitatively similar effect reported in 1984 in the early electron microscopic examinations of spherulitic textures in polypropylene, using an earlier generation material, is in good accord with the present observations and was almost certainly correctly ascribed to morphological instability.[4] The feature is generally absent from modern polypropylenes.]

The associated growth rate data are presented first in Figure 2a as the primary observations of maximum radius, *r*, as a function of crystallization time, *t* (with error bars representing the standard errors of the populations, shown if they extend beyond the symbols). The fitted curves have the form

$$r = R[1 - \exp(-bt)]$$

whose derivatives are the growth rates shown in Figure 2b. These may be written as

$$G = G_0 \exp(-bt)$$

and fall continuously, with the growth rate reducing in the same proportion for each additional increment of time. Although the growth rate of individual objects would be expected to accelerate at the onset of instability (such an acceleration, within individual spherulites, has now been observed), this phenomenon is likely to be smoothed out in the averaged values of Figure 2a. Nevertheless, at 95 °C, the experimental points do drop below the fitted curve around the onset of instability at ~90 min and then rise above it, in an appropriate manner. Steady-state growth, which has not occurred before impingement in the present experiments, has been found in further studies[17] at distances well beyond the onset of cellulation, effectively when the growth rate and diffusion rate of the segregants are matched.

Instability sets in at 95 °C at an average radial distance of 6 μm, when the growth rate has fallen by some 18% from its initial value. At 91 and 93 °C the equivalent values of 3 and 4 μm correspond to growth rate reductions of 11 and 16%, respectively. The average cell widths so produced, obtained by dividing the perimeter by the number of protuberances, increase slightly with temperature, from 4 to 6 μm over the range. If the cell width is to scale exactly with the characteristic diffusion length, $\delta = D/G$, with all other factors remaining constant, then the two sets of data in conjunction show that D must increase by a factor of ~5 over the 4 K interval, a value which, *a priori*, does not seem unreasonable in view of the increased segregation which will occur at the higher temperatures. But, at the same time, exact scaling may well not be appropriate.

The sequence of changes which this work and its immediate predecessors[15,16] have shown is entirely in accord with expectations for morphological instability.[2] As spherulites increase in diameter they will encounter a progressively increasing concentration of more-highly-branched molecules segregated at the growth front. In consequence, the growth rate continually declines and there are concomitant textural changes. Coarsening with a degree of isothermal thickening occurs first, with the latter indicative of lowered isothermal supercooling, leading finally to instability. Previous work[15] identified this phenomenon for rows, the present work now does so for spherulites but in a more-highly-branched polymer. That instability develops in polymers of lower branch contents for rows than for spherulites is as expected for their respective interface profiles, which are close-packed for rows and more open for spherulites, and consequent concentrations of segregants. All relevant behavior has thus been demonstrated to occur in a controlled and expected manner, so confirming the earlier conclusions that, for cellulation to occur, concentrations of segregants must be high enough to give a sufficient depression of growth rate. This is in accord with the great majority of evidence and opinion that cellulation is neither present in nor the prime cause of spherulitic growth in polymers.[3,18] It does occur in the exceptional circumstances cited and no doubt also in the highly doped melts studied by Keith and Padden.[7]

The unified understanding of spherulitic growth in polymers now gained may be summarized as follows. Spherulitic growth generally occurs in the absence of cellulation because of the divergence of adjacent individual dominant lamellae, itself a demonstrable consequence, according to recent work, of cilia pressure.[13] When morphological instability does occur, it requires the presence of two factors. First, there must be segregation so that a layer of rejected species accumulates at the growth front. Second, this layer must cause the growth rate to slow sufficiently. Once these conditions are met, then a protuberance which advances through the impurity layer into conditions allowing faster growth will have gained a competitive advantage; if this is sustained, then it renders the interface unstable. Regarding segregation, the situation in linear polyethylene, for which most quantitative work has been done, is that it occurs to a degree, especially at higher growth temperatures,[19,20] but that its extent decreases as crystallization temperatures fall and may be close to zero for temperatures used in commercial operations. However, as the equilibrium melting point is insensitive to molecular length in the range of typical segregants in the linear polymer, one would not anticipate a significant reduction in growth rate even when there is segregation. This is in accord with the common observation that polyethylene spherulites increase their radii linearly with time. As far as we are aware, our recent measurements on branched polyethylenes in this and the immediately preceding work are the first time that growth rate has been observed to slow as the impurity layer builds up. Moreover, when branched molecules accumulate, one expects that they will lower the equilibrium melting temperature in their region of melt and with it the isothermal supercooling at the interface, leading directly to a fall in growth rate. That instability is absent for linear polyethylenes and only sets in when the branch content reaches high levels of ~28/1000 C atoms for spherulites and rather less for the close-packed geometries of rows points firmly to the conclusion, in agreement with other work, on α-polypropylene,[14] that the segregation which occurs within modern commercial homopolymers causes a negligible effect on growth rate. Segregation as an active influence on texture in crystalline polymers is thus a scarce and atypical phenomenon. Its general role is a passive one in which fractional crystallization tends to place particular species systematically in different, previously created, locations within spherulitic textures with marked consequences for properties.

This first demonstration of cellulation leading to "fibrillation" in polymer spherulites confirms that morphological instability is not itself the cause of spherulitic growth but is an additional phenomenon which may be superposed on spherulitic texture when conditions produce exceptionally heavy segregation which reduces the growth rate sufficiently. The two alternative explanations previously offered for spherulitic growth, namely, cellulation and lamellar divergence due to cilia pressure, are thus seen to be complementary and are now, for the first time, set in a unified context within polymer science.

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