

# A discussion of spherulitic crystallization and spherulitic morphology in high polymers

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An outline is given of revisions in our views as to how our phenomenological theory of spherulitic crystallization should be interpreted in specific application to high polymers. Important considerations, not previously taken into account, are (a) reptation and its consequence that diffusivity of a molecule in the melt depends upon its own molecular weight, (b) influence of crystallographic symmetry, and (c) the fact that morphological instability develops differently in polymer lamellae than in polyhedral crystals. Despite complications introduced by reptation, a meaningful averaged diffusion range of segregated molecules,  $\delta$ , can still be derived in many cases and related to scaling of texture in spherulites grown in regime II. However,  $\delta$  does not correlate with lamellar width as previously proposed but has to be identified differently with morphological dimensions. It is pointed out that in polymers neither the occurrence of elongated lamellae nor the growth of spherulites depends uniquely upon local diffusion of segregated species. Rather, consideration of such diffusion explains gradation from very slow growth of open-textured axialites and hedrites at small supercoolings, through growth of compact spherulites of markedly varying texture at larger supercoolings in regime II, to growth of very finely textured spherulites at yet larger supercoolings in regime III (which involves segmental diffusion rather than diffusion of entire molecules). It is shown that a recent claim by Bassett and Vaughan that local diffusion of segregated species is largely irrelevant in spherulitic crystallization is not substantively founded.

**(Keywords: polymer crystallization; morphology; polymer lamellae; spherulites; texture; diffusion)**

## INTRODUCTION

Introduction of a permanganic acid etching technique by Bassett and coworkers<sup>1,2</sup> has recently made it possible to examine representative morphological detail within bulk samples of polyolefin polymers with considerably better resolution than was previously attainable. A conclusion from their studies of polyethylene using this technique<sup>3,4</sup> has been that the widths of lamellar crystals do not correlate with a scaling length  $\delta$  in the way we originally suggested when applying a general phenomenological theory of spherulitic crystallization<sup>5</sup> to the specific case of spherulites in high polymers<sup>6-9</sup>. In this they are unquestionably correct; application of that theory to systems in which crystals are inherently of very thin lamellar habit needs considerable revision of detail in the light of evidence accumulated during the past two decades, as we shall outline later in this communication and detail in forthcoming papers.

However, in a more recent paper on isotactic polystyrene, Bassett and Vaughan<sup>10</sup> have extended their criticism to question on a deeper level the validity and applicability of the physical basis of our phenomenological theory in the context of high polymers. This criticism appears to be based principally upon two contentions. First, they imply that the dominant/subsidiary lamellar construction they observe in axialites and hedrites grown very slowly at elevated temperatures, and which they consider to persist without significant change during the growth of spherulites at lower temperatures, is fundamentally different from 'assumed' structures we sought to interpret. Secondly, they assert that there is no evidence for local diffusion of segregated species having an

influence upon morphological development of polymer crystals within spherulites except perhaps as an unproven possibility during growth at very large supercoolings. They base this view upon having at high temperature (220°C) grown polystyrene hedrites of order 10  $\mu\text{m}$  across, and having noted that these retain essentially regular hexagonal outline even though, by their claim,  $\delta$  under the conditions of growth was two orders of magnitude smaller than the crystals. On the basis of our theory such an inequality in size, if real, would mean that local diffusion should have manifested itself clearly in significant departures from regularly hexagonal habit. If the fact that it did not do so in this case is taken as ruling out the role we ascribed to local diffusion of segregated species in the case of hedrites, and if spherulites are not significantly different from axialites or hedrites, then a more general conclusion regarding local diffusion having little influence on the growth of spherulites might follow. However, as we shall indicate presently, both contentions of Bassett and Vaughan lack validity, the first because of confusion in terminology, and the second because their estimate of  $\delta$  is based partly upon an incorrect and much undervalued choice of diffusion coefficient and partly upon unsupported assumptions about the nature of the segregated species.

## SPHERULITIC TEXTURE

It should be recognized that our original analysis of spherulitic crystallization was restricted to spherulites of relatively compact texture, and explicitly to structures formed under conditions such that  $\delta$  (the characteristic

diffusion range in diffusion fields at leading growth fronts and given by the quotient of diffusion coefficient ( $D$ ) in the melt\* and radial growth rate ( $G$ ) of a spherulite) falls in the 'micron and sub-micron range'<sup>5</sup>. Attention was later given to axialites and hedrites only in the context of discussion how, when  $\delta$  takes such small values, these multilayer aggregates which commonly serve as precursors of spherulites in polymers give way rapidly to characteristic development of compact globular entities *while still at very small size*<sup>8</sup>. This important change in morphology represents an evolution from aggregates of superimposed but slightly fanning lamellae (which show only slight divergence of crystallographic orientation) into spherically radiating arrays of ribbon-like lamellae that become highly elongated in radial growth directions regardless of their native habits. We interpreted this change as reflecting habit modification under the influence of diffusion-controlled growth brought about by segregation at advancing growth fronts of shorter or of stereo-irregular (including branched) molecules. Since the steepness of corresponding concentration gradients would vary inversely<sup>5</sup> with  $\delta$ , the influence of these gradients on the development of spherulites should be stronger, and assert itself sooner, the smaller the value of  $\delta$ . By our original analysis, transition to globular aggregates of radially elongated lamellae should begin in precursor aggregates when the crystals comprising them have reached a size of the same order of magnitude as  $\delta$ . In the case of axialites and hedrites of open texture, such as those recently studied extensively by Bassett and coworkers because they are 'simpler objects' more accessible to examination, corresponding concentration gradients would be very weak. Commonly, the reason is that, although these crystalline aggregates are relatively large, they are in fact still smaller than even larger values of the length  $\delta$ ; in other circumstances the gradients are weak for different reasons not recognized in our original analysis (see later). In any event, local diffusion and the considerations upon which our theory was based are not significant factors in determining their morphology.

By optical microscopy there can be discerned within globular polymer spherulites, particularly within those of coarser texture whether grown in a 'doped' polymer (i.e. one to which a polymeric diluent has been added deliberately) or not, relatively discrete radial units (seemingly of fairly constant lateral dimension if growth has been isothermal) which are clearly not individual lamellae. It remains our view, first, that these are associations of radially elongated lamellae commonly stacked one above the other and, secondly, that, although growth segregated during passage of leading growth fronts may become widely distributed throughout interlamellar regions, there are major accumulations of such species between the stacks. Based upon electron microscopic observation, branching and subsequent splaying of chain-folded lamellar crystals have from the outset been clearly recognized features in development of these structures, the former being considered to involve

both the splitting of such lamellae within their own planes and the generation of new layers at screw dislocations (mechanisms which are closely related)<sup>5,8</sup>. The only significant differences between spherulitic structures as we considered them and as Bassett represents them appear to lie (a) in the emphasis we gave both to general occurrence of lamellae of markedly elongated habit and to commonly observed association of such lamellae in stacks\* and (b) in correlation of  $\delta$  with a meaningful morphological dimension that measures coarseness of texture.

In part, the supposed divergence of viewpoint appears to stem from inadequate definition of the terms 'dominant' and 'subsidiary'<sup>4</sup> as applied to given lamellae within relatively compact textures, and from inconsistent use of the latter term. It is important to distinguish clearly between (a) subsidiary lamellae which, as branches developing from and between dominant lamellae, grow concomitantly with these dominants and usually not far behind them, and (b) 'infilling' lamellae which grow considerably later (often only upon subsequent cooling of specimens) and represent solidification in relatively concentrated form of initially segregated material. This distinction is recognized in Bassett's earlier papers<sup>3,4</sup>, but in Bassett and Vaughan<sup>10</sup> subsidiary lamellae are not distinguished from what were previously called infilling lamellae. Large axialites and hedrites are open-textured and, within them, dominant and subsidiary lamellae are generally well and fairly uniformly separated from one another. Bassett and his coworkers appear to regard spherulitic texture as no more than a uniform compaction of such structures; further, they emphasize the lamellar character of crystals involved without giving adequate attention to other aspects of their habits (their shapes). On the other hand, we view compact spherulitic texture as commonly consisting of recognizable stacks of lamellae (exceptions in which individual lamellae behave as separate units will be noted later). These stacks are formed because, in compact textures, copious growth of subsidiary lamellae follows very closely behind that of dominant lamellae and, for reasons to be considered later, these subsidiary lamellae then tend to remain more tightly clustered around the dominants from which they are derived by repeated branching (including branching of the subsidiary lamellae themselves). This refinement of detail does not represent a departure from what Bassett calls a dominant/subsidiary construction but merely a difference in organization. By confusing subsidiary lamellae with infilling lamellae, indeed by describing the growth of spherulites as involving 'branching and splaying of dominant lamellae followed by *infilling subsidiary growth*'. Bassett and Vaughan have convinced themselves that 'fibres (in the Keith and Padden sense) cannot be identified within polymer spherulites'.

There is abundant evidence to the contrary, regardless of how  $\delta$  relates to the lateral dimensions of fibrous units. Clear examples of fibrous texture have long been known in polymers of low crystallographic symmetry such as

\* Our original analysis preceded introduction of reptation concepts and it was assumed that diffusion in a polymer melt could be characterized, as in simpler liquids, by a single diffusion coefficient. Consequences of diffusivity varying from one molecule to another depending upon molecular weight will be discussed later; by appropriate averaging a diffusion range, having essentially the same morphological significance as the original  $\delta$ , can still be derived in many cases.

\* We commonly called elongated lamellae fibrils and larger units fibres, a usage which preserves correspondence with discrete crystalline fibres in monomeric spherulites. We defined a crystal of fibrous habit *explicitly* as one considerably larger in one dimension than in either of the other two and included an individual ribbon-like lamella as one example<sup>8</sup>; although a broadening of the term, perhaps, this permits common classification of all dendritic crystals formed by similar diffusion mechanisms regardless of whether crystallographic considerations cause them to be more or less equiaxed in cross section or not.

nylons<sup>25</sup>. Within spherulites of coarser texture, early indications from optical microscopy of radially elongated structural units on a scale larger than individual lamellae have also been well supported by subsequent electron microscopic studies on many polymers. As but one example we note the study by scanning electron microscopy of Wingram, Grubb and Keller<sup>11</sup> on polyethylene spherulites from which infilling lamellae had been leached out by selective solvent extraction. In a forthcoming paper we shall show that application of the permanganic etching technique to spherulites in unfractionated polyethylene confirms their observations. However, use of this technique to examine compact structures in circumstances such that infilling lamellae are still present demands careful systematic study of trends which accompany corresponding variations in coarseness of texture as seen by optical microscopy. Bassett appears to extrapolate to such structures on the basis of superficial indications from axialites grown under conditions such that segregated species play a *passive* role in crystallization. Further, to the extent that details were reported, his observations on banded spherulites were made on a fractionated polyethylene ( $M_w = 4.4 \times 10^5$ ;  $M_n = 2.2 \times 10^5$ ) probably containing few short molecules likely to segregate. These approaches are not likely to bring to light important features which (in addition to general occurrence in dominant lamellae of radially elongated habits) are indicative, in our view, of segregated species playing an important *active* role in the evolution of spherulitic texture. We shall indicate presently how we now interpret the nature of this active role.

#### DIFFUSION OF SEGREGATED MOLECULES

We turn now to the second contention of Bassett and Vaughan regarding comparison of  $\delta$  with crystal sizes in isotactic polystyrene. We note that in estimating  $\delta$  they used a diffusion coefficient taken from the work of Ueno, Otsuka and Kishimoto<sup>12</sup> on sharp fractions of atactic polystyrene, it being assumed, not unreasonably, that tacticity has little influence upon diffusion in the melt. These authors derived diffusion coefficients from melt viscosity by means of the Bueche equation. Their plot of  $\ln D$  vs.  $\ln M$  has a slope close to  $-3.4$  whereas, since the introduction of reptation concepts, it is now well established both theoretically<sup>13</sup> and experimentally<sup>14-16</sup> that  $D$  commonly varies as  $M^{-2}$  or close to it. Recent measurements by different direct techniques<sup>15,16</sup> agree in showing that at a crystallization temperature of 220°C, and for the molecular weight chosen by Bassett and Vaughan to represent segregated species, a more accurate diffusion coefficient would be  $2.1 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ , a value about 30 times larger than they estimated.  $\delta$  would be increased by the same factor. There is also some question concerning the molecular weight selected as representative of segregated species. This was assumed to be the weight-average molecular weight of the *entire* polymer remaining uncrystallized after 24 h at 220°C when, by the reported evidence, relatively little crystallinity had yet developed because of sparse nucleation and very slow growth. In our view, the case presented by Bassett and Vaughan does not justify a conclusion of broad and important implication negating the role of local diffusion of segregated species in polymer crystallization.

In terms of the reptation mechanism, migration of each diffusing molecule is governed by a diffusion coefficient dependent mostly upon its own molecular weight. This introduces a previously unforeseen complication into estimation of a diffusion range  $\delta$ . What is now required is an averaged value that represents the combined influence of all segregated molecules upon crystal growth. In monomeric systems for which diffusion in the melt is characterized by a single diffusion coefficient,  $\delta$  is the distance at which an exponentially decaying concentration of species segregated at an advancing plane interface falls to  $(1/e)$  of its value at that interface<sup>5</sup>. Let us now imagine a hypothetical situation in which polymer molecules segregate at such an interface and diffuse in accordance with  $D_i = kM_i^{-2}$ . Given the molecular weight distribution of segregated polymer, variation in concentration along the normal to the interface can be calculated and an averaged  $\delta$  estimated from its corresponding decay. It will be shown in a forthcoming paper that, with any realistic modelling of the distribution of molecular weights among shorter molecules likely to be segregated by fractionation, concentration profiles approximate exponential form quite closely; the averaged  $\delta$  is close to the value calculated for molecules having the  $z$ -average molecular weight of segregated polymer. In the case of fractionation, therefore, morphological consequences of segregation can be discussed much as in our early work but now in terms of this averaged  $\delta$ . It is to be emphasized, however, that this is a consequence of the fact that molecular weight distributions for fractionated material are inevitably fairly narrow (polydispersity  $< 1.5$ ); for this same reason,  $\delta$  can be estimated with reasonable accuracy knowing the constant of proportionality  $k$ .

With segregation involving stereo-irregular molecules much depends upon their molecular weight distribution. When this is relatively sharp as, for example, when an isotactic polymer is blended with a fractionated sample of its atactic isomer, an averaged  $\delta$  can again be assessed as before. On the other hand, when the distribution is broad concentration profiles depart considerably from exponential form. There would be an accumulation of longer segregated molecules near growth fronts and a more extended diffusion field corresponding to shorter segregated molecules. In general, such a situation cannot be represented adequately by a single parameter; each case requires individual consideration.

#### GENERAL DISCUSSION

An outline in anticipation of later publication of our recent experimental results, and of revisions of interpretation based partly upon them, may help further clarification of areas of agreement and disagreement between Bassett's views and ours.

##### *Theoretical background*

To put our remarks in proper perspective we first offer some pertinent observations concerning our theory of spherulitic crystallization. That analysis was conceived on a general basis applicable in principle to a wide variety of materials both monomeric and polymeric<sup>5</sup>. It was presented in terms more directly applicable to materials of the former kind and specific crystallographic features of given materials were ignored. Arguments were developed

by analogy with cellular crystallization in metals and described in corresponding terminology. Adaptation in modified form of the explanation offered for such crystallization by Rutter and Chalmers<sup>17</sup> appeared to offer a way of reconciling (a) fibrous habits in crystals whose native habits are usually not fibrous (seemingly a sure indication of strongly diffusion-controlled growth) with (b) linear growth kinetics whose temperature dependence apparently indicated nucleation-controlled growth. Such reconciliation depends crucially upon highly localized diffusion of segregated species at growth fronts in a manner similar to that occurring at advancing cellular interfaces in metal crystals. In both cases, segregated species become redistributed in spatially periodic manner within macroscopic confines of the growing solid phase<sup>6,18,19</sup>. On dimensional arguments, it is easily shown that  $\delta$  should play a dominant role in determining the scale of such segregation; this scale is of order  $10^{-2}$  cm in metals but considerably smaller in compact spherulites.

We first drew a parallel between redistribution of segregated species at the spherical boundary of a mature globular spherulite and that at a (macroscopically plane) cellular interface of a metal crystal. We used the term cellular to describe likely patterns of segregation in the spherulite case even though their periodicity cannot possibly be as regular as in unidirectionally solidified metals. The 'cells' must constantly subdivide since  $\delta$  is constant while the macroscopic spherical interface expands (subdivision of these cells is directly related to low-angle branching of fibrous units). The process by which such a growth regime is initiated at the outset of spherulitic growth we chose to describe as 'cellulation and fibrillation'\* although it is, in fact, a manifestation of morphological instability and pronounced dendritic development which, under conditions of small  $\delta$ , would be expected to begin in small polyhedral crystals when they have attained a size of order  $\delta$ <sup>22</sup>. We recognize that use of the term 'cellulation and fibrillation' may have contributed to later confusion, even though in the context of real crystals we never applied it to growth faces having smooth simple profiles over distances significantly longer than  $\delta$ . Despite a periodic redistribution of segregated species that can be regarded as having irregular cellular character, what we represent as occurring in spherulitic crystallization is not, in a strict literal sense, true cellulation as the term is used conventionally by crystal growers. There are many fundamental differences† and some revision of terminology is in order.

With these clarifications, our theory appears applicable to monomeric spherulites in much the way we originally

described. We note only one additional point; we do not claim to have identified a unique cause of fibrous habits in such spherulites, some materials such as hydroquinone having fibrous habits whether crystallized spherulitically or not. Rather, we believe we have explained why fibrous habits arise quite generally in spherulites even when these are not native habits of the crystals involved and, in either event, we suggest that lateral dimensions of the fibres are closely related to  $\delta$ . We also believe we have explained how many monomeric materials crystallize spherulitically in a consistent way under the conditions we analysed whereas under other conditions they crystallize in more conventional habits. Application of the theory to polymer spherulites is necessarily different and in our early work we did not recognize how considerable are the differences caused by chain folding and the thin lamellar crystal habits that result. In outline, we now interpret the morphology of melt-crystallized polymers as follows.

#### Patterns of segregation in polymer spherulites

First, we note that occurrence of native crystal habits in the form of ribbon-like lamellae is much more common in high polymers than was recognized in early work. In general, regularly polygonal lamellae occur only in polymers in which unit cells exhibit 3-, 4- or 6-fold rotational symmetry about chain axes (it is in these polymers that hedrites are formed at high crystallization temperatures). Crystals of lower symmetry often adopt ribbon-like habits because of much faster growth along one unique axis than along any other (in this case crystallization at high temperatures gives rise to axialites). Well known examples are to be found in  $\alpha$ -polypropylene<sup>24</sup>, nylons<sup>25</sup> and polyesters<sup>26</sup>. Even in polyethylene, which is orthorhombic but not far from hexagonal and whose optical character is very close to uniaxial, native habits in crystals grown slowly from paraffinic solvents or from the melt are highly elongated<sup>9,27</sup>. (Much confusion arose in early thinking because of the common use of xylene as a solvent for growing crystals of this prototypical polymer; crystals formed at faster rates in this way are rhombs whose growth is faster along the  $a$  than along the  $b$  axis, the reverse of what is observed in crystallization from the melt.) Such polymer crystals therefore adopt fibrous habits for reasons of their own and, in combination with the ubiquitous properties of branching and splaying, this alone is sufficient for spherulitic growth to occur sooner or later, quite apart from any considerations we have discussed. However, spherulitic crystallization in polymers of high crystallographic symmetry calls for further examination and, in any event, an important

\* Reasons for this choice rather than description in terms of morphological instability *per se* will be apparent from a discussion by Frank<sup>20</sup> of the uncertain state of emerging theories of morphological instability prior to the seminal work of Mullins and Sekerka<sup>21</sup>, work which was published almost simultaneously with our paper.

† Cellulation in metal crystals is characterized by: (a) very small supercoolings at growing interfaces; (b) growth rates governed by interface attachment kinetics and determined by impressed thermal gradients such that heat flows from melt to solid; (c) morphological instability caused by constitutional supercooling within localized diffusion layers; and (d) an opposing stabilizing influence provided by interfacial energy. Corresponding behaviour in spherulitic growth is characterized by: (i) relatively large supercoolings at interfaces; (ii) growth apparently controlled by surface nucleation in the absence of appreciable thermal gradients; (iii) morphological instability induced by

steep concentration gradients (within diffusion layers) which nevertheless represent only modest modulation of an already large driving force for crystallization (such modulation may, and commonly does, manifest itself in terms of constitutional changes in already extant supercooling, but not necessarily); (iv) a stabilizing influence generally provided by the spreading of surface layers on normally faceted crystals; and (v) insensitivity with respect to the direction of whatever very small thermal gradients may be present. We note that (iii) and (iv) have the consequence that interfacial energy is not involved significantly as a stabilizing influence on morphology in this case. Additional interfacial energy associated with the edges of incomplete surface layers on curved growth faces has already been provided during the nucleation of these layers. Calvert's criticism of our neglect of interfacial energy<sup>23</sup> is based upon his having overlooked this point in particular and the distinctions we have just noted in general.

general question remains as to what controls scaling of texture and its well known variation with crystallization temperature and melt viscosity (molecular weight)<sup>6</sup>. In the context of high polymers, it is in relation to such concerns that our theory has its more meaningful implications.

We agree with Bassett that scaling of texture, and hence that of the redistribution of segregated species, is governed primarily by an average separation between dominant lamellae. By this term we mean those lamellae that lead the advance of macroscopic growth fronts, even if but slightly in the case of compact textures (where dominance in this sense may well be a property that is transient in any given lamella). The significant question is: what controls this separation? In axialites and hedrites it is certainly not  $\delta$  (nor would that be expected) but, rather, the frequency with which growing dominant lamellae form branches and the extent to which branches then splay apart.\* In more compact spherulitic textures, however, we believe there is a significant influence of the diffusion of segregated species at growth fronts and that under a wide range of conditions the separation between dominant lamellae is then related to  $\delta$ .

In detail, however, such an influence could be manifested in several ways depending upon whether lamellae in a given spherulite are inherently narrow or inherently broad. As already mentioned, differences in growth rate along those crystallographic directions which in spherulites become oriented radially or tangentially reflect symmetry of the unit cell. Pronounced anisotropy in growth rate can thus exert a strong influence upon lamellar habits within a spherulite quite apart from any superimposed influence of concentration gradients within diffusion layers. Broadly, we may distinguish three cases in which: (a) lamellae are inherently very narrow ribbons and their widths under given conditions of growth are significantly smaller than  $\delta$ , (b) lamellae are inherently ribbon-like and under given conditions of growth their widths are significantly larger than  $\delta$ , and (c) lamellae would normally be highly symmetrical (square, rhombic

or hexagonal) in shape but, for reasons to be discussed presently (anisotropic growth under the influence of diffusion among them), they nevertheless assume radially elongated habits when formed within compact spherulites.† Reviewing present knowledge of spherulitic structure in various polymers it appears that all three situations are encountered in practice. Some polymers exhibit more than one type of behaviour, either as a result of polymorphism or, in polymers of low crystallographic symmetry<sup>32</sup>, possibly because anisotropy of growth rate along different crystallographic directions may be acutely sensitive to changes in crystallization temperature. The contrasting spherulitic morphologies of  $\alpha$ - and  $\beta$ -polypropylene<sup>33,34</sup> highlight the marked degree to which crystallographic considerations can influence structure on a larger scale.

Our present view is that, in spherulites whose structures are as classified in (a)–(c) above (and under conditions whose limits will be noted presently), redistribution of segregated species occurs in ways which can be summarized as follows. When the distribution of molecular weights among segregated molecules is such that a meaningful averaged  $\delta$  can still be recognized (see earlier) this length governs the average separation between dominant lamellae. It can be related to a periodicity which is often discernible by optical microscopy at finely scalloped envelopes of growing spherulites, a periodicity which must also be reflected in texture developed within the spherulites. Whether or not discrete accumulations of segregated species easily recognizable by microscopy are likely to be found within this texture, however, will depend upon how much material is segregated during crystallization and the degree to which subsidiary lamellae cluster around their parent dominant lamellae. On the scale of individual lamellae there is considerable disorder but, to the extent that segregation is recognizably discrete, we suspect in case (a) above that it takes an irregular (see above) 'cellular' form much as we implied in our early papers; however, within each 'cell' of more or less equiaxed cross section and of a 'width' given roughly by  $\delta$  there should be found clusters of many narrow lamellae (see, for example, Figure 5 of ref. 25). In cases (b) and (c) we believe that broader lamellae are arranged in stacks whose average thickness is closely related to  $\delta$  and that major

\* Neither of these characteristics has been explained satisfactorily. It is known empirically that branching occurs much more frequently during growth at larger supercoolings, apparently increasing rapidly in the case of polyethylene at temperatures close to that at which a transition occurs between regime I and regime II kinetics<sup>28</sup>. In the case of branching which involves spiral growth at screw dislocations such behaviour is readily explicable (see later in text). However, it is less clear how dislocations form from time to time in crystals which, like those found in axialites and hedrites grown very slowly at high temperatures, have well defined growth faces of simple and seemingly smooth profile. Other lamellar branching mechanisms are now recognized, particularly in lamellae grown at relatively high temperatures<sup>29,30</sup>, but as yet their origin also remains to be established. Marked splaying apart of adjacent lamellae seems to depend upon availability of space to accommodate it and to occur in aggregates of open texture which grow very slowly so that highly localized diffusion fields do not exist. It is observed in abrupt and pronounced form when branching occurs in axialites and hedrites, whether grown slowly from the melt or from solution. On the other hand, splaying is relatively slight in compact spherulites formed during more rapid growth. Radially directed concentration gradients may then exert greater influence upon growth directions and more widely splaying branches would in any event soon impinge upon their neighbours. However, other factors also seem to be involved, particularly in the case of subsidiary lamellae which remain closely stacked with their parent dominant lamellae. Closely adjacent overlapping lamellae produced by rapid growth are generally considered to be connected by tie molecules formed in some way during the growth of one crystal by incorporation of fringing chains emerging from the surface of an existing neighbour. Progressive 'stitching' of this kind may in many cases frustrate the tendency to splay, whatever its origin.

† A special case, intermediate between (a) and (b), in which  $\delta$  is closely related to lamellar width (implying also the presence of stacks roughly  $\delta$  in overall thickness) is also possible. In globular spherulites, however, it would be an unusual occurrence probably achieved in a given polymer only in a very narrow range of crystallization temperature (generally,  $\delta$  is strongly temperature dependent). Among the reasons for our early proposal that  $\delta$  might correlate quite generally with lamellar width (except in  $\alpha$ -polypropylene whose curiously branched morphology was even then recognized as exotic) was direct observation of a qualitative correlation of this kind *over a wide range of crystallization temperature* in the special case of polymer spherulites grown in films thin enough for phase contrast optical microscopy or electron microscopy<sup>9</sup>. As is now evident, however, this comes about for a relatively trivial reason. During crystallization under these conditions segregated species must diffuse away essentially within the same plane as that in which growing lamellae spread along a substrate. Segregation is then constrained to follow a pattern representing a two-dimensional analogue of behaviour in monomeric spherulites so that, provided the lamellae are not inherently too narrow, a correlation between  $\delta$  and observed lamellar width would inevitably follow. Observed dependence upon growth conditions of radial periodicity in banded spherulites also pointed strongly but misleadingly toward generality of such a correlation<sup>29</sup>; such dependence has now been explained in other ways<sup>31</sup>.

accumulation of segregated species occurs between the stacks. On a local scale, the stacks are either roughly parallel as in spherulites of polyethylene (a situation closely analogous to formation of elongated cells in metals<sup>18</sup>) or they may form cross-hatched structures exhibiting a cellular character geometrically unlike either the elongated or hexagonal cells commonly observed in metal crystals (see *Figure 1*).

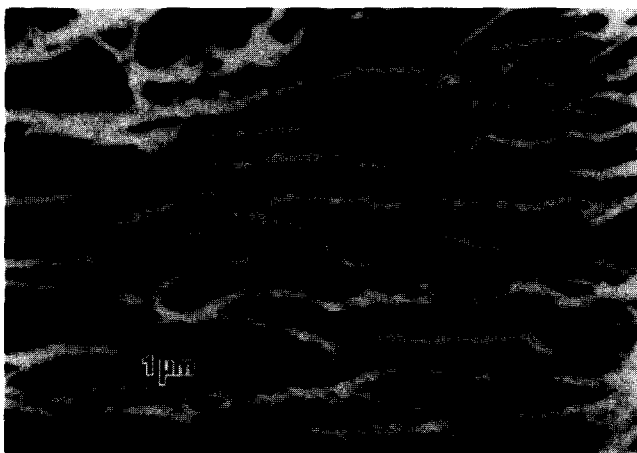
Thus far, tests of correspondence between scaling of texture in structures of these known kinds and reliable quantitative assessments of  $\delta$  have not been made; much further work is required. The sole exception is unfractionated linear polyethylene where our recent experiments<sup>29</sup> have revealed the presence of locally parallel stacks of lamellae whose spacing agrees with a calculated  $\delta$  to well within an order of magnitude. However, we point out that this correlation obtains only when crystallization occurs within regime II, which in this particular polymer is restricted to an unusually narrow range of crystallization temperature because of a temperature coefficient of spherulitic growth rate that is exceptionally large. Not unexpectedly, limits to the correlation are set as follows. On one hand,  $\delta$  attains a value equal to the thickness of a single lamellae ( $\sim 0.02 \mu\text{m}$ ) when crystallization temperature falls to a value close to the regime II–III transition. On the other hand, during growth at higher temperatures near the regime I–II transition (where  $\delta$  is  $\sim 2 \mu\text{m}$  and axialitic growth begins) structure becomes so open-textured that a few widely spaced dominant lamellae then cause relatively little segregation and corresponding diffusion fields are too extended to have significant influence upon scaling of texture. We emphasize, however, that while the temperature range over which  $\delta$  correlates significantly with texture is quite narrow in polyethylene ( $\delta$  changes in this polymer by three orders of magnitude over a range of about  $7^\circ\text{C}$ ) similar behaviour would be considerably more protracted in other polymers.

This quantitatively detailed study of only one polymer as yet represents limited evidence. However, we remind the reader of our extensive early experiments<sup>6,8</sup> indicating that, quite generally, changes in texture as gauged by optical microscopy correlate qualitatively with  $\delta$  (in some

instances *D* and *G* were varied independently)\*; that there is significant meaning to this behaviour we have no doubt. Coarseness of texture as revealed by optical microscopy is related partly to the sizes of discrete radial units and partly to local correlations in crystallographic orientation between neighbouring units. As regards detail, however, it is evident from foregoing discussion that spherulitic morphology in high polymers is likely to show wide variation in structural organization depending (a) upon the amount and molecular weight distribution of species segregated under given conditions of growth, and (b) upon the crystallographic symmetry of crystals involved. Apart from occurrence in many cases of recognizable accumulation of segregated species in concentrated form, there will generally be some interlamellar segregation on a finer scale as well, particularly of longer segregated molecules which have smaller diffusive mobilities. Textures formed in fractions of medium or high molecular weight or during crystallization at large supercoolings (in regime III) fall mostly outside the scope of present consideration and we shall return to this topic presently.

#### *Morphological instability and habit modification in polymer lamellae*

Growing polymer crystals, other than those having inherently acicular habits because of low crystallographic symmetry, maintain regularly polygonal shapes so long as surface nucleation occurs at the same average rate on crystallographically equivalent growth faces and so long as growth is slow enough for new surface layers to spread to completion relatively rapidly. In order that morphological instability can manifest itself (i.e. that systematic departures from regular shapes bounded by smooth surface profiles can evolve), two conditions must be met. Rates of surface nucleation at favoured sites (usually protuberant apices<sup>35</sup>) must (a) appreciably outstrip rates of nucleation elsewhere and (b) outstrip the spreading of layers to such a degree that uneven surface profiles can develop. In the context of growth from the melt there are two important implications, one being that crystallization obviously must occur under conditions such that regime II kinetics are followed. The second is that concentrations of species segregated at growth fronts must be appreciably smaller near sites of faster surface nucleation than elsewhere. This requires the existence of gradients which are steep enough in relation to crystal size for adequate differences in concentration to be maintained *despite* the fact that local differences in growth rate tend to even out the differences in concentration<sup>35</sup>. For crystals other than thin lamellae (those of polyhedral form that grow in three dimensions) Cahn's analysis of corresponding behaviour has shown that onset of instability is to be expected when crystals attain a size of order  $\delta^{22}$ . We had ourselves arrived at a similar conclusion on the basis of more intuitive dimensional arguments but had also considered that, without further qualification, the same criterion would apply to polymer crystals as well. Observation of crystals grown in very thin



**Figure 1** Scanning electron micrograph of a lamellar aggregate in polyethylene crystallized from a 6% solution in *p*-xylene and dried by exchanging the solvent with liquid carbon dioxide which was then removed at its critical point. Although cross-hatched cellular textures of this kind have not yet been reported in polymers crystallized from the melt, they may well be formed in certain cases (see text)

\*In the case of isotactic polystyrene spherulites grown at lower temperatures, when the temperature coefficient of growth rate is positive, we pointed out that correlation of observed texture with  $\delta$  implied what then seemed an inordinately large activation energy for diffusion in this polymer ( $> 30 \text{ kcal mole}^{-1}$ ); we note that reliable recent data have yielded a value  $39.7 \text{ kcal mole}^{-1}$ .<sup>15,16</sup>

films of melt appeared to bear this out<sup>8</sup> but, as pointed out in an earlier footnote, crystallization in such circumstances is exceptional in that segregated species are largely confined to the plane of growth. In the more general case of a polymer crystal growing within bulk melt other considerations enter as follows.

It is in fact doubtful if an isolated monolayer polymer crystal growing in bulk melt would ever exhibit morphological instability, provided that it remains free of screw dislocations. While the general arguments just outlined should apply in principle, it is clear that any incipient instability would be very 'weak'. What little material would be segregated by so thin a crystal could diffuse away freely in three dimensions from growing edges; very small differences between concentrations at apices and at midpoints of growth faces might then remain ineffectual. With overlapping lamellae in a stack of thickness  $\delta$ , however, more significant concentration gradients would develop in the plane of growth, particularly if there are other stacks above and below it within a compact spherulitic structure. Morphological instability in the sense of sensitivity with respect to radially directed dendritic development of crystals at growth fronts in compact spherulites is not in doubt; further, lamellae in a given stack will all tend to respond similarly to local concentration gradients. Nevertheless, the important question remains as to how lamellae in precursor aggregates, regularly polygonal lamellae in particular, evolve into such compact structures.

Our recent experiments<sup>29</sup> indicate that the key factor is formation of screw dislocations. Although of major consequence in many respects, dislocations in most crystals represent only minor structural disorder. In a growing polymer lamella, however, formation of a screw dislocation and the spiral overgrowth that ensues completely disrupt the normal pattern of growth. In place of a single layer of regular symmetrical outline they give rise to a number of more irregularly shaped lamellae in a multilayer aggregate, an aggregate which may nevertheless preserve the same overall outline as the original parent crystal would have done had the dislocation not been formed. Generally, a number of dislocations will be formed as the aggregate continues to grow and these contribute to ongoing fragmentation (splitting in earlier terminology) of lamellae within the aggregate. This, indeed, is the case with the hedrites reported by Bassett and Vaughan and is typical behaviour. Such generation of many smaller and irregularly shaped component layers within aggregates that still retain regular outlines overall marks an important step toward development of morphological instability in precursor aggregates. However, such instability in a full sense is realized only when outwardly directed dendritic growth begins and the aggregates lose their geometrically regular outlines.

Continued branching, in which screw dislocations again play a major role, is the vital factor causing this further development. By increasing the number of crystals that contribute to segregation and at the same time making texture more compact, branching increases outwardly directed concentration gradients and makes them more effective in their influence upon crystal habits. Increased frequency of branching at lower temperatures obviously enhanced this tendency. In hedritic precursors of polystyrene spherulites, our experiments show that the

fibrillation we originally emphasized as being a major consequence of 'cellulation' (morphological instability) does not begin abruptly at some well-defined early stage of growth. It takes time for outwardly directed concentration gradients to become established. As they build up, however, irregularly shaped component layers and new layers formed at screw dislocations (which are naturally considerably smaller than parent crystals) begin to show increasingly marked anisotropy of growth, as evidenced by outwardly directed apices advancing more rapidly than other crystallographically equivalent apices. Evidence will be presented elsewhere, but the overall effect is that lamellae soon begin to develop radially elongated habits. At this stage the aggregates often develop finely scalloped outlines, mostly because spiral overgrowths commonly show a progressive rotation of orientation in successive layers in a manner akin to that previously noted in polyethylene crystals by Keller<sup>36</sup>. These misalignments cause a progressive divergence of growth directions within medial planes which, together with splaying, contributes to development of the radiating orientation characteristic of globular spherulites. (Disorder built into crystals at reentrant corners, our original interpretation of how divergence of orientation is caused within medial planes<sup>8</sup>, also plays a small but relatively insignificant role.) Aggregates grown at lower temperatures develop globular form quite rapidly but, even then, the structural organization that is characteristic of more mature spherulites develops progressively as the pattern of segregation gradually settles into a (statistically) steady state.\*

An important general aspect of such behaviour is that compactness of texture appears to develop quite rapidly in a narrow range of crystallization temperature which marks a relatively sharp division between conditions under which large axialites or hedrites are formed and those under which typical spherulitic growth occurs. The fact that in the case of polyethylene this division coincides with the regime I-II kinetic transition<sup>28</sup> is highly suggestive. Regime II kinetics imply appreciable roughening of growth fronts on a fine scale, and it is known that reentrant corners between microfacets are sites where screw dislocations are readily formed<sup>9</sup>. We suggest that when microfacetting occurs there is cooperative behaviour; increased frequency of branching at dislocations would steepen concentration gradients at growth fronts, and steeper gradients in turn would promote increased microfacetting at curved fronts near growth tips and thus favour generation of yet more dislocations. This we believe is how compactness and formation of discrete stacks of elongated lamellae are achieved in structures formed at crystallization temperatures which have been reduced into the range in which characteristic spherulitic growth begins.

Segregation then appears to influence structural organization in the ways we have indicated throughout a substantial range of supercooling. However, detailed interpretation cannot yet be offered concerning

\* We note that significant radial concentration gradients develop in polystyrene ( $M_w = 4.76 \times 10^5$ ;  $M_n = 1.15 \times 10^5$ ) hedrites of size  $\sim 10 \mu\text{m}$  only at temperatures below  $210^\circ\text{C}$ ; also that, for reasons which should be obvious from the discussion, small aggregates grown in bulk melt which serve as precursors of spherulites show significant morphological changes only when appreciably larger than  $\delta$  in size, commonly by about an order of magnitude.

spherulitic crystallization either (a) in sharply fractionated polymers of medium or high molecular weight, which contain few components likely to segregate during solidification (at least for the usual reasons), or (b) at large supercoolings (regime III), when little segregation of entire molecules may occur even in unfractionated polymer and calculated values of  $\delta$  may become commensurate with the thickness of an individual lamella as is the case with polyethylene<sup>29</sup>. Under these various conditions crystal growth would again be expected to be strongly influenced by diffusion, but not of entire molecules so much as of molecular segments. One might think in terms of intramolecular segregation (formation of long loops at chain folds) or of segregation of entangled chains<sup>6</sup>, but ultimately an appeal to inherent 'disorder' seems necessary. Until the nature and specific influence of the disorder become better understood, interpretation along these lines can scarcely be illuminating. It is clear, however, that insofar as texture varies with crystallization conditions in regime III it would tend to become finer as either the molecular weight of the polymer is increased or as growth becomes faster.

## CONCLUSIONS

Spherulitic crystallization in high polymers has been discussed with emphasis both upon recent criticism of our early interpretations of behaviour in these materials in terms of a general phenomenological theory, and upon revision and extension of those interpretations in the light of new knowledge. As Bassett and coworkers have correctly pointed out, our scaling parameter  $\delta$  does not correlate with lamellar width in the way we originally supposed; nevertheless, we still contend that it does determine scaling of textures grown over a wide range of crystallization conditions, although in ways that in detail depend upon crystallographic symmetry of the particular polymer involved. It has been emphasized that more recent criticisms by Bassett and Vaughan of the physical basis of our theory, specifically of the structural model we chose to analyse and of the prominence we gave to the role of diffusion in influencing crystal habits and determining scaling of texture, are not substantively founded. Our present assessment of (a) applicability of the theory to spherulitic crystallization in polymers and of limits to that applicability, and (b) Bassett's divergent views, may be summarized as follows.

(a) Considerations that underlie our phenomenological theory of spherulitic crystallization are less directly applicable to polymers than to monomeric materials. They do not provide a unique explanation for occurrence of fibrous crystals in either case but are crucially important only in those situations where crystals would otherwise have more compact habits. However, applicability to polymers is limited even further. In many cases, when crystal habits are inherently acicular, spherulitic growth could occur anyway for other reasons. At root, these reasons have their origin in molecular disorder that must inevitably arise during crystallization from viscous macromolecular melts<sup>37</sup>, disorder that is further exacerbated by growth of very thin lamellae which not only branch with appreciable lattice misalignments at screw dislocations because of large Burgers vectors but also splay, warp and sometimes twist. Our theory nevertheless has the considerable merit of explaining quite

generally why characteristic spherulitic growth occurs in regime II whereas at high temperatures crystallization gives rise to large axialites or hedrites, distinctly different morphological forms. Development of mature spherulitic structure represents a gradual, though spatially confined, evolution from small axialitic or hedritic precursors. Over a substantial range of crystallization conditions the theory also offers a general explanation for observed systematic variations in coarseness of mature spherulitic texture; further, with revised interpretation, it appears to carry this understanding to finer levels of detail, although many implications remain to be critically tested by quantitative experiment. Finally, to the degree that it does apply to high polymers, our theory highlights commonality of understanding with respect to simpler materials in terms of general principles of crystal growth.

(b) Discussions of spherulitic crystallization in polymers as published in Bassett's papers appear to us, on the other hand, to have significant shortcomings. Apparently, it is assumed that segregated species mostly play an entirely passive role in such crystallization; given that the concentration gradients involved must be much steeper than is commonly the case in diffusion-controlled crystal growth, this seems remarkable. Strong emphasis is given to the obviously lamellar character of polymer crystals while other important aspects of the habits, and the variety of habits, they assume in spherulites are all but completely neglected. (This may reflect generalization from a limited sampling represented by three polyolefins, one of which (polypropylene in its  $\alpha$ -modification) has a unique morphology based upon self-epitaxy, while lamellae in the others, although highly elongated, are nevertheless inherently quite broad (polyethylene) or else very broad (polystyrene).) Lastly, no explanation is offered for the variations in coarseness of texture that constitute the principal evidence in support of our analysis.

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