Reply to a discussion of spherulitic crystallization and morphology

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The preceding paper, in its discussion of recent studies of lamellar morphologies in melt-crystallized polymers, severely criticizes a previous paper by us. In this reply we reconsider the position but find no reason substantially to modify our previous conclusions. The Keith and Padden rationale is not pertinent to the formation of many polymer spherulites. There is agreement, however, on the ubiquitous branching and splaying of dominant lamellae to form the framework of spherulites. The characteristic internal dimension of spherulites is not the width but the separation of adjacent dominant lamellae.

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The preceding paper by Keith and Padden[1] represents a substantial revision by them of their much earlier theory[2]. In so doing they have recognized the weight of recent observations by electron microscopy concerning representative lamellar organization in melt-crystallized polymers[3–11]. This is now known to be significantly different from the inferences previously made from optical microscopy. They reach a position that is not too different from our own, namely that if the Keith–Padden theory applies it is only to a restricted range of spherulitic morphologies. Any other position is indeed difficult to sustain in the light of the new experimental evidence. Nevertheless Keith and Padden have coupled their revision with extensive criticism of the interpretation of one recent paper[9] concerning isotactic polystyrene in ways that we consider have not represented our position accurately. They have not referred to published work outlining quantitative tests of their scaling hypothesis and its negative conclusions[12] and have seriously and continually represented our position as being different from what it is. It is to prevent these inaccurate representations passing unchallenged into the literature that this reply has to be made.

The introduction of two new techniques of specimen preparation, namely chlorosulphonation of polyethylene[13] and permanganic etching of several polymers[14,15], has created the opportunity of studying the representative lamellar microstructure of melt-crystallized semi-crystalline polymers with the electron microscope. In this laboratory we have taken the opportunity systematically to study first linear[3–8], then branched[16,17], polyethylene followed by isotactic polystyrene[9] and isotactic polypropylene[10]. Our approach has been primarily to inspect the morphology and interpret its features for information on the crystal growth processes that formed them, in a way similar to early work on solution-grown crystals. Almost from the outset our findings have seemed to us to lie outside earlier expectations and predictions but we have, of course, attempted to compare our findings with previous hypotheses, i.e. principally those of Keith and Padden[2]. We have, however, become progressively more convinced that the morphologies we have observed do not accord with their predictions.

The precise predictions of the Keith–Padden theory are, however, few. They propose that fibrillation is a consequence of cellulation due to the segregation of ‘impurities’ (i.e. non-crystallizable or slower-crystallizing species) during growth, by extending the arguments previously advanced by Rutter and Chalmers[18] for metallic alloys. The width of these cells and the ‘fibres’ they create should then be of the order of the characteristic length $\delta = D/G$, where D is the diffusion coefficient of the segregating species and G the radial growth rate. They go on to make the specific suggestion[17] that it will be the width of lamellae comprising a ‘fibre’ that will be of order δ. The thickness of lamellae is not relevant here as this is set by chainfolding.

It is not in question that segregation does occur during spherulitic crystallization of familar systems. Keith and Padden showed this directly for polypropylene by adding radioactive impurity molecules to the melt, and, using autoradiography, observed them to concentrate heavily between spherulites and to a lesser extent along their radii[19]. More recently Calvert[20,21] has added fluorescent species to isotactic polypropylene and studied their location optically. Nevertheless segregation must happen if the composition of crystals differs from the melt and other workers have queried whether segregation is the *cause* of spherulitic development. Magill[22] has observed spherulites developing in systems of very high purity and questioned whether this can be caused by impurities. Keller in 1968 commented[23] that ‘the whole subject is still open ... as far as whether impurity segregation is a necessary or sufficient condition for spherulite growth’.

Keith and Padden themselves cite[19,24] many qualitative changes in optical textures with changing crystallization conditions, which, particularly in its historical context, made a plausible, largely circumstantial, case for their proposal[23]. They did not have then the means to make detailed electron microscopic studies that could establish salient details of spherulitic organization and allow measurement of its dimensions. The best that could then be done for an undoped polymer was to note

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that in polyethylene at 110°C the estimated value of δ was 0.2–0.4 μm, which appeared to be consistent with the fibrosity present[19]. Other such comparisons in blends of isotactic and atactic polystyrene must now be seriously qualified. This is also the case for isotactic polystyrene grown in thin films[26], for reasons we shall discuss presently. Nevertheless, the new electron-microscope techniques and particularly permanganic etching have allowed systematic study of the internal lamellar organization within melt-crystallized polymers. What can be observed and measured with these which is a fair test of Keith and Padden's theory[2]? We have examined the morphologies to seek evidence of cellulation during growth; whether there are textural units that correspond to the claimed 'fibres' of the scale on which there is lateral segregation of impurities; lamellae organized in melt-crystallized polymers and in what circumstances there is organization of groups of lamellae. We have measured lamellar widths[8], the separations between adjacent segregated regions[5], the characteristic separation between adjacent lamellae at the crystal–melt interface and the size of multi-lamellar groupings when they occur[12,27]. This has been done for polyethylene[3–8,26], polystyrene[9,27] and polypropylene[10,28] over a wide range of conditions and compared with the expected variations in the characteristic length δ. In no case that we have studied to date has any textural parameter scaled with δ, or come close to doing so.

In order better to rebut the criticisms made of our work in the previous paper, we now give a brief summary of our current views on spherulitic morphology and how these have developed from experimental findings. The first system we studied, a linear polyethylene fraction $M_m = 26\,000$, $M_m/M_n = 1.3$, crystallized for 20 d at 130.6°C has proved to show the most regular of polyethylene melt-crystallized morphologies[3]. Individual sheets of alternating (201 and $(20\bar{1})$ facets each *ca.* 0.5 μm wide grow out along the *b*-axis with splaying and branching, etc., to form the framework of immature spherulites. These first-forming lamellae were termed dominant while later, infilling growth was said to consist of subsidiary lamellae. Although this texture gave the superfical appearance of cellulation it was recognized that the morphology was really an inverse of cellular development as considered by Keith and Padden[2]. Adjacent individual dominant lamellae enclosed columns of melt enriched with late-crystallizing species rather than *vice versa*. Nevertheless the separation of adjacent regions of subsidiary lamellae was evidently a measure of the lateral distance of segregation of later crystallizing molecules. This was compared with the value of δ, but found to be a million times smaller[3].

The appearance of cellulation soon disappeared for small changes in crystallization conditions[5,6], e.g. by increasing the molecular mass to *ca.* 40 000. It was pointed out that the principal textural dimension was rather that of the separation of adjacent dominant lamellae for all the many growth conditions investigated[6,7]. The width of lamellae instead of scaling with δ, as predicted, showed only a modest decrease with crystallization temperature, remaining within a factor of three of 3 μm.[7] We had thus found nothing to support the Keith and Padden predictions and much that seemed to us indicative that spherulitic growth was not primarily a consequence of segregation of 'impurities'. In particular it was noted that, phenomenologically, adjacent dominant lamellae appeared to repel each other and that this, in association with branching, was sufficient to generate space-filling development leading eventually to mature spherulites.

It was also noteworthy in this work that there was nothing obviously fibrous in the morphologies studied, whereas Keith and Padden's paper[2] starts with the assertion that spherulites are built from 'fibres'. The radial textures that can be detected optically are rather the consequence of chance overlays of wide radial lamellae in the thin specimens observed. Even the pseudofibres seen in the most regular system[3] appeared to derive from a specific reason, lamellar non-planarity, rather than from any more general cause. Whereas in certain systems, such as mixtures of isotactic and atactic polypropylene, there are discrete units visible optically[19] these were only found by us in linear polyethylene when it was co-crystallized with branched polymer[16]. These did give the appearance of discrete radial units optically but, in reality, one was observing aggregations of, say, six lamellae edge on.

It was at this stage that our studies were widened to other polymers to see whether our findings on polyethylene were matched elsewhere. We chose, first, to study isotactic polystyrene, a system offering the advantages of ready quenching and controlled addition of atactic species. One further development of the technique of permanganic etching[9] made this possible and a second[15] created the opportunity of studying the detailed lamellar morphology of melt-crystallized isotactic polypropylene in its monoclinic form[10,11]. Work here in Reading has since proceeded in parallel on these two polymers, which, it should be recalled, are the two that had provided the bulk of the detailed evidence with which Keith and Padden[19,24] had supported their theory. What the electron microscope shows, however, so far provides little or no support for their previous interpretation.

Our researches have shown similar basic development of spherulitic organization in both these isotactic polymers to that previously found in polyethylene. Although as yet only one paper on each polymer has been published, several others concerning what is now a large corpus of research are in advanced preparation. It has, however, been possible to herald these new findings and to begin to discuss their implications in a review[12] contemporary with our first paper on polystyrene. This represents the fullest published statement of our position and also includes considerable data and measurements on polystyrene crystallized down to 180°C, including tests for scaling. Keith and Padden have not referred to this review in the preceding paper[1] and have even stated that tests of correspondence between 'scaling of texture... and reliable quantitative assessments of δ have not been made'. On the contrary many such tests have been made[12,27] and we believe them to be reliable. The review[12] also illustrates how the appearance of discrete fibres optically in polystyrene is an additional phenomenon found in blends with the atactic polymer, but here too no measurements show scaling with δ.

In our paper on isotactic polystyrene[9] we drew several conclusions. One, which Keith and Padden accept in the preceding paper[1], is that the characteristic textural dimension in spherulites is the width between adjacent dominant lamellae. This is at variance with the principal prediction of their 1963 theory[2], which was that it would be the width of lamellae that would reflect cellulation and scale with the length δ.[19] There are no other quantitative predictions of the 1963 theory, but it is possible to compare observed morphologies qualitatively with those Keith and Padden had expected. We concluded that there are no 'fibres', no indication of incipient instability of planar growth fronts and that there was no indication of cellulation having been involved in the formation of the objects. It is with these statements that Keith and Padden take issue[1], but in attempting to counter our views, they have started with an inaccuracy.

They claim, wrongly, that we believe no polymer systems contain fibres, and go on to cite nylons as an example where they occur. On the contrary, we expressed no opinion on systems we have not investigated. For polystyrene crystallized at 180°C and above, to which our paper[9] solely referred, then we believe our statement to be true. Indeed, subsequent work[29] on polystyrene fully supports our contention. Melt-crystallized morphologies found in homopolymers are based on a framework of individual lamellae. *Figure 1* shows how these splay apart at the very start of a spherulite. Similar features have been observed for crystallization as low as 130°C. We have explained carefully[9] why lamellae whose width substantially exceeds their thickness cannot be regarded as 'fibres' for reasons we believe are sound.

It is, however, a common observation that from doped melts, optically discrete 'fibres' grow. In our work on isotactic polystyrene[27,29] we have found that this only occurs from heavily doped melts, e.g. 1:1 atactic/isotactic blends. Under such conditions aggregates of, say, six lamellae grow as a group. It is when such groups are seen sideways on in a thin specimen that one sees the appearance of 'fibres'. One of our major criticisms of the Keith and Padden approach is that they have generalized from such observations to their premise that polymer spherulites consist of 'radiating arrays of fine crystalline fibres'[2]; in polystyrene we have not found this to be the case. The optical appearance of discrete fibres results as a direct consequence of the same dominant/subsidiary growth mechanism described previously. When the melt separating dominant lamellae contains a non-crystallizable component that is unable to diffuse away from the advancing interface, the resulting morphology has to be one of alternating crystalline and non-crystalline regions. For the polystyrene studied the isotactic melt component crystallizes around the established dominant lamellae, leaving the atactic material between the resulting fibres. This is in agreement with previous observations on polyethylene[16,17] and subsequent work on polypropylene[28]. Measurements of scaling on such aggregates in polystyrene also differ from Keith and Padden's predictions.

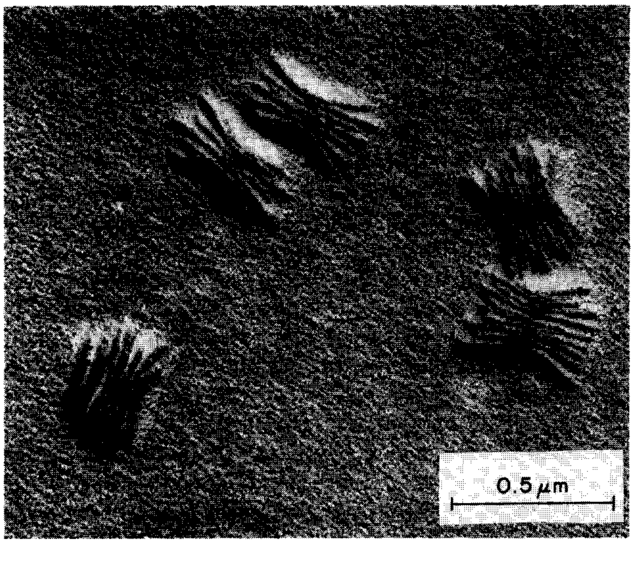

Figure 1 The centres of incipient isotactic polystyrene spherulites formed by isothermal crystallization from the melt at 190°C. Surface replica of a permanganically etched surface, exposing the interior of the sample

A second major criticism is that Keith and Padden express here their old belief that lamellae in spherulites are narrow while those in axialites are wide[26]. We have searched in a 'careful systematic study' for this effect in isotactic polystyrene but have found no evidence for it. This belief in the narrowness of lamellae within spherulites appears to be the origin of various of their comments to the effect that we are extrapolating from axialites to spherulites, i.e. from objects with wide lamellae to others with narrow ones. Perhaps this is the reason for Keith and Padden's current emphasis[1] on globular, i.e. 'proper', spherulites. We do not believe this distinction to be valid or the constant criticism sustainable. Neither have we made any extrapolation nor had need to do so, having explored a full range of relevant textures ourselves directly. This is not to say that all the lamellae in all spherulites are wide, and indeed examination of large spherulites crystallized at 162°C in isotactic polystyrene[29] reveals a morphology that appears to consist of radially elongated lamellar units. However, even here the lamellar widths greatly exceed the value of δ. The belief in the narrowing of lamellae once crystal dimensions exceeded δ seemed at one time to be supported by work by Keith. He published[26] photographs of four different lamellar objects of isotactic polystyrene grown in thin films at 215°C and interpreted them as successive stages in fibrillation of an initially hexagonal habit. Because of the difficulties of trying to reconcile this interpretation with our very different findings we have attempted to repeat Keith's observations. We have been able to reproduce the several lamellar shapes he reported but, by studying the progressive development of individual objects growing on a microscope hot stage, we have established that they grow at constant shape[29]; we are thus unable to support Keith's earlier interpretation. None of our careful and extensive series of experiments on isotactic polystyrene crystallized at temperatures from 130°C to 230°C has supported the hypothesis that lamellae are substantially reduced in width once conditions to grow 'globular spherulites' pertain. We cannot, therefore, accept Keith and Padden's criticism that our conclusions are based on study of inapt conditions, i.e. where 'impurities' play a passive rather than an active role. Nor is there truth in the claim that we neglected crystal habits. It is simply that we have searched for changes in them but found little substantial alteration with changing growth conditions. In polyethylene there were significant changes in habit and two papers[6,7] were devoted to their discussion. There is no comparable phenomenon in polystyrene.

The persistent theme of much of Keith and Padden's argument that we have been looking at inappropriate types of objects adequately to test their hypothesis is, fundamentally, a corollary of how far their point of view has changed. In 1963, a 'theory of spherulitic crystallization' was offered[2], with the expectation that it would apply when $\delta < 10\,\mu$m, but expressed very positively in the awareness that the mechanism appeared to have wide relevance. Now the one quantitative earlier prediction is acknowledged to be wrong[1] and there is a search for conditions in which segregation of impurity molecules can be shown to affect texture with the proviso that at least in polyethylene, the system they were studying, the relevant range is 'quite narrow'. They also state that 'branching and splaying' are 'ubiquitous' and that the spherulitic growth can occur 'quite apart from any considerations we have discussed', This is a point of view close to our own although we do not couple branching and splaying necessarily with constituent 'fibres' for spherulites to form. We have also quite explicitly kept open the possibility that molecular segregation might apply under specific conditions[9,12], indeed it would be surprising if such a characteristic length as δ failed to reveal its presence in the morphology in some circumstances. Our position is that, in general, the explanation of melt-crystallized textures in polymers lies outside the Keith–Padden theory.

Recognizing, as Keith and Padden now do, that 'spherulitic growth can occur anyway for other reasons' what can one learn from an examination of melt-crystallized morphologies on their own merits? The pattern that has presented itself from the outset of our research is of the splaying and branching of individual dominant lamellae (*Figure 1*). In polystyrene this occurs throughout the crystallization range and must surely be taken as the principal contributor to spherulitic texture. To emphasize this point, in our previous paper[9] we drew attention to the fact that even at the highest crystallization temperatures we had investigated, our crystal dimensions were more than the length δ calculated in the traditional way, i.e. the prevailing conditions were those in which Keith and Padden had expected cellulation and fibrillation. In their one significant criticism of this paper, Keith and Padden suggest[1] that the diffusion coefficient should nowadays be calculated on the basis of reptation. For the one temperature (220°C) at which we had made the comparison this would move δ beyond the crystal sizes studied. Obviously one needs to use the correct diffusion coefficient, but it is not obvious *a priori* that reptation is a valid mechanism for such long molecules as we crystallized. Even if, for the sake of argument, we accepted the point, the criticism would have little weight. This is because the same pattern persists down through the crystallization range and, on either basis of calculation, δ soon becomes much less than lamellar widths. For example, reducing the crystallization temperature to 200°C produces structures intermediate between the axialites seen at 220°C and globular spherulites. Nevertheless hexagonal growth faces can still be observed, with dimensions greater than 2.4 μm. This is a factor *ca.* 20 greater than the value of δ, when this parameter is estimated as proposed by Keith and Padden[1].

In another comment, Keith and Padden[1] criticize us for not making a distinction between subsidiary and infilling lamellae and claim that we have somehow forgotten to carry this concept forward from earlier work. Had we done so, they conclude, we must have recognized the presence of 'fibres' in isotactic polystyrene. This is totally erroneous for various reasons. First, a distinction between shades of later growth has no value unless there is evidence for its occurrence in the morphology. Secondly, if the separation of adjacent dominant lamellae sets a textural periodicity – as they admit – then that remains, irrespective of how later crystallization occurs. Only if there is evidence of additional ordering is it useful to adopt corresponding language. Thirdly, even if one recognizes clusters of lamellae associated with a given dominant lamella, how is it supposed that this later-forming cluster could have influenced the separation of the adjacent dominants? Nor is it enough to claim that this cluster size is of order δ for a small range of conditions. It is probably always possible to select conditions in which the slowly varying inter-dominant gap approximates to the more rapidly varying δ. One would need a systematic and predictable pattern on which to base the measurement before an attempted validation of the Keith–Padden hypothesis would be plausible. Finally, the proffered distinction between subsidiary and infilling lamellae is too facile: the situation is often much more complex. In suitable circumstances (e.g. Figure 5.5 of ref. 25) at least three types of later-growing lamellae have been identified at specific locations within the morphology. Related situations are by no means uncommon and show much of interest. For their discussion they require much more subtle consideration than a mere subsidiary/infilling distinction would allow. Furthermore, such patterns have yet to be recognized in polystyrene.

Our emphasis on the branching and splaying of individual dominant lamellae is to be regarded as a basic pattern – itself adequate geometrically to produce mature spherulites – on which others may be superposed. It should certainly not be taken that we recognize no other relevant ordering. On the contrary, we have constantly sought to identify groupings of several dominant lamellae, which, from work especially on thin-film specimens (e.g. Figure 2.6 in ref. 25), had previously often been observed. Of the three polyolefines studied in this laboratory only isotactic polypropylene shows such an effect clearly. The similarity of this morphology to cellular growth of eutectic alloys has been noted[12] and, more recently, preliminary measurements have been made of how the cross section of these 'cells' changes with crystallization conditions. These measurements have not, however, shown a scaling with δ.

In making this reply we feel it important to end on a positive note. There seem to us to be two important points. One is that there is agreement on the need, at least in many circumstances, for a new theory of spherulitic growth for polymers over and above the rationale offered by Keith and Padden. The other, and much more substantial, is to emphasize that permanganic etching and other techniques have opened up many important opportunities to establish, at least on the scale of observation by electron microscopy, what really is the structure of melt-crystallized polymers. The work is demonstrably demanding and its interpretation not easy, but at least now, nearly thirty years after the discovery of polymer single crystals, it can be done.

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