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Banding in spherulites: two recurring topics

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Abstract

Two topics relating to banded polymer spherulites are discussed thoroughly and brought up to date. They are: (a) origins of secondary effects of rhythmic character in thin films and (b) generation of isochiral dislocations and torsions in twisted lamellae. Physical principles of broad applicability are also emphasized. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Banding in polymer spherulites is a topic of long standing that is currently generating renewed interest. This has been stimulated largely by increasing availability of polymers having main-chain chiral structures so that, in the course of crystallization, they involve assembly of helical molecules in *isochiral* conformations which do not lend themselves to neat packing in compact parallel array. This is in sharp contrast with the more familiar crystalline polymers that lack true chirality of chemical structure but are nevertheless chiral in that they assume helical molecular conformations, though in compensating admixture of right- and left-handed units that by alternation are readily capable of such parallel packing. Banded spherulites that evince a twisting of crystalline orientation about the radii are common in both circumstances and, although occurrence is much rarer as yet, polymers of both kinds are also found in the form of isolated twisted crystals having roughly the form of right helicoids. Indeed, looking back to much earlier studies, the same can legitimately be said of spherulites and crystals in many monomeric organic, and some inorganic, compounds that possess chiral structural elements, with the proviso only that we mostly accept individual twisted fibers rather than helicoids. This is, then, a field of study in which, at superficial level, remarkably similar morphology can arise for diverse and seemingly unrelated reasons; not surprisingly, interpretations remain controversial.

Having myself contributed to the subject, on and off for close to 45 years and almost from inception of its extension to polymers, I continue to follow developments with interest. There are published interpretations with which I disagree, and also those who disagree with interpretations I have published with my long-time collaborator Frank J. Padden, Jr. Broadly speaking, this is as it should be, for there is much that is still without explanation or understanding, and science thrives on constructive criticism and dialogue. However, it does not help to allow avoidable reportorial errors, or repetition of demonstrably flawed arguments, to pass unchallenged. In the following I address two specific instances and trust that my comments will be received in the spirit intended. In one case, I am also given an opportunity to clarify a few points from early work that may no longer be clearly appreciated, as well as to record some little-known history of the subject.

2. Rhythmic pattern formation: simulation and reality

Recently, two groups combined to present a mathematical simulation of 'target' (ringed) and spiral spherulitic growths in polymer blends (Kyu et al. [1]). It is a numerical calculation of pattern formation using nonlinear diffusion equations to describe coupled periodicities in compositional and orientational order parameters during outward growth from nucleating centers within thin films. It is not my purpose to comment on this endeavor which accomplished its objective in ways that, qualitatively at least, seem inevitable to me from the initial formulation. I am more concerned with the course followed by the authors in matching their results to an established phenomenology with which I am well acquainted. In particular, they cite as a seemingly significant consequence of their work a reconciliation between a lamellar twisting model attributed to Keller and a 'structural discontinuity' model attributed to

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Keith and Padden. Quite emphatically, no such reconciliation is needed.

Since the widespread recognition of chain folding in the formation of solution-grown polymer crystals, beginning with Keller [2] in late 1957 and reinforced by simultaneous confirmation from Fischer [3] of similar lamellar crystals occurring throughout melt-grown spherulites, there has been no discernible difference in the basic twisted lamellar models of Keith and Padden [4,5], of Price [6], or of Keller [7] (all derived independently in 1958 and published together in 1959 in that order of submission). However, there was a brief period of several months in 1957 during which views held by Keith and Padden [8] were definitely at odds with an earlier model of Keller's [9]; neither of these approaches was really tenable and both were quickly abandoned with the introduction of chain folding. It is difficult to know whether or not Kyu et al. were influenced by this short-lived divergence of interpretation; their references are incomplete and several are inappropriately chosen, bearing little or no relation to the topic allegedly referenced. In any event, special situations, not otherwise encountered in banded spherulites, arise specifically in very thin films and introduce additional periodicities in texture. Discontinuity is too strong a term for this behavior but, if one insists upon using it, it should be noted that the behavior is inevitably a feature common to all twisted lamellar models, and was discussed extensively (though with somewhat different emphasis) both in Keller's paper [7] and in the second of the two contemporaneous papers by Keith and Padden [5].

The following explanatory background may prove helpful to students or others new to the field. In Keller's first paper on spherulitic structure in polymers [9], one that more than any other of its time launched the subject of polymer morphology as we now know it, he carefully established conceptual ties with earlier knowledge of spherulitic crystallization in monomeric substances, including that of banding which was known in that context to evidence growth of twisted fibrous crystals. He also recognized at once the major problem facing him in extending this knowledge to polymers, for at that time (1955) it was unthinkable that radial fibrils in polymer spherulites would not comprise axially aligned chains in extended conformation, yet it was clear from birefringence that chain orientations in these spherulites were predominantly tangential. To reconcile these conflicting indications he was obliged, with spherulites such as in polyethylene, to consider fibrils as tightly coiled helices resembling long spiral springs, an assumption that from the standpoint of explaining extinction rings created a serious difficulty, as obvious then as now. At an early stage, however, Keller was fortunate to encounter poly(ethylene terephthalate), a polymer then of no small interest to ICI and in whose spherulites banding generally manifests itself as pronounced zig zags on the Maltese crosses seen between crossed polars. By considering fibrils in this case as loosely wound helices packed radially in phase with one another, he could account for the zig zags in terms of zero amplitude extinction. However, there again was a problem (recognition of which later determined where Padden and I would begin our collaborative work on polymers, as outlined in a recent brief account [10]) in that dense packing of helices would necessitate staggered phasing, leading to averaged principal refractive indices in radial and tangential directions, and hence to nothing but simple unadorned extinction crosses. I was to learn much later from Keller (whom I knew but slightly during the year or so that we overlapped in the Bristol Physics Department since we then applied similar techniques to very different fields of study) that he had indeed been aware of this problem. However, his mentors at ICI (Bunn and Wells, both eminent crystallographers) encouraged him to publish anyway on the grounds that it might draw attention and promote progress in the field. How right they were! I should acknowledge that Point had considered extinction patterns in tilted two-dimensional polyethylene spherulites as early as 1955 [11]. He had in reality hit upon the key factor that later occurred separately to the rest of us, as Keller, Price and I discovered once we met at the Cooperstown conference in August 1958. I no longer have easy access to Point's paper, but seem to recall that it was not easy to translate precisely, that justification for the model chosen was then obscure and that calculated extinction rings were drawn for quite a large tilt and without an accompanying extinction cross (an unfamiliar situation not encountered in practice). Our oversight may be understandable, but some years later we were all chastened upon realizing that Point's contribution had not been properly recognized. To my knowledge, and his great credit, Point never complained.

As for the additional periodicities referred to above, it is sufficient to say that in thin films they arise principally when there are slight, though perceptible, thermal gradients across the films during otherwise nominally isothermal crystallization. Effects are of notably different magnitude, depending on whether the specimens are crystallized on open hot plates (to a degree even when placed on lower plates of closed hot stages) or, in sandwiched form, are brought to crystallization temperature by abrupt immersion in an oil bath. In the presence of slight transverse gradients, radiating fibrils grow not in a planar but in a shallow saucer-like orientation, termed the conical model by Price and Keller; a notable consequence is conversion of closed rings into spirals. Further, since primary nucleation generally occurs at a contacting surface there can be another cause for transverse components of growth near centers of spherulites. Apart from this it is evident that, in sandwiched films of thickness comparable with lamellar width, uniform crystallinity cannot be maintained without the radial flux of lamellae undergoing tightly regulated periodic variation from one ring to the next; there may indeed be an approach to something of this kind, but that it could be very close seems unlikely. Finally, in the case of open-faced films, ringed spherulites develop notably ridged surfaces where edge-on lamellae rise well above lamellae lying in planes close to the substrate. Details on these points are found in Refs. [5, pp. 126–128; 7, pp. 170–171] and need not be elaborated here. However, it would indeed be interesting to know how readily the methods of Kyu et al. can reproduce the various empirical observations made under different circumstances. I note that the center of the spherulite shown in their micrograph (Fig. 2) does not correspond precisely with either accompanying simulation. It might have done so in some cases, but the point is irrelevant since the handedness of a spiral changes with direction of viewing whereas that of a screw does not.

There is, however, one aspect of the erroneous rhythmic crystallization model Padden and I espoused briefly in 1957 that still has significant bearing on ongoing controversy concerning lamellar organization in banded polymer spherulites. The model was never published formally but was previewed briefly in a paper on optical observations of polyethylene spherulites under various conditions of illumination and polarization [8]. Unable to explain periodic absence of birefringence in dark rings when birefringent fibrils *as then conceived* should certainly have been seen, we sought another explanation. All that seemed to offer was a rhythmic crystallization akin to the formation of Liesegang rings well known with crystal growth in gels [12], supposedly giving rise to alternating shells of semicrystalline and essentially amorphous polymer. Strong support for this appeared to come from noting a common behavior of extinction rings at boundaries between spherulites grown at constant temperature. It is obvious that under idealized conditions such boundaries, being loci of points whose radii from fixed centers differ by a constant length, are hyperbolic in films and hyperboloidal in bulk. It follows that, ideally, phases of rotation in uniform twisting about these radii should likewise differ by a constant amount all along a boundary. What we observed in films not only substantiated this but also revealed a marked tendency for extinction rings to join, i.e. to meet in essentially the same phase, and even to become significantly distorted at times in an apparent endeavor to maintain this relationship. Early examples are shown in Fig. 10 of Ref. [5] and Fig. 3 of Ref. [7], and can indeed be seen throughout the literature (see, for instance, Figs. 1 and 2 in a recent paper [13]). Rhythmic crystallization, which depends upon interplay between diffusion in depletion layers around growing crystals and concentration dependence of sporadic nucleation, would certainly be likely to have this property.

The interpretation we ultimately did offer [5], and to which we still subscribe, involves interleaving of lamellae converging upon a boundary at a point where their planes are close to parallel, and to the strong influence such interlocking of orientations would begin to exert in enforcing and maintaining phase-matching so that twisting lamellae from neighboring spherulites would go on meeting periodically in ways that ensure further interleaving. (It is to be noted that, with banded spherulites in monomeric compounds, where radial fibers are often equiaxed in cross-section and do not interdigitate, initial phase-matching, even within rings, commonly deteriorates progressively with increasing radius.) It still appears to need emphasis that, whereas an isolated helicoidal lamella provides an adequate model for calculation of extinction patterns in spherulites, lamellae of such simple form have little reality since they would be incapable of packing together in dense array with uniform phase. Observed phasing of twisting must derive from (undoubtedly complex) interleaving and interlocking of orientation that repeat themselves as twisting lamellae begin to impinge upon one another behind their growth tips and then continue to widen where they can. However, such influence, though apparently effective enough within given ringed spherulites, is not always capable of promoting well-coordinated phasing of rings at boundaries. It does not do so, for example, in closely spaced double-ringed spherulites of aliphatic polyesters; lamellae in these materials are narrow and lath-like whereas in many other polymers they exhibit broader lenticular or polyhedral habits.

3. Chiralities of axial torsion and of stress-induced dislocations in twisted lamellae

Although still without clear understanding on a fine scale, there can be little doubt that growth of twisted crystals in spherulites of optically active materials has its origin in bulk stresses associated with attempted close packing of ill-fitting asymmetrical molecules. A more puzzling problem posed by growth of twisted lamellae in polymers devoid of such optical activity centered upon apparent absence of a credible origin of uncompensated torques capable of producing large torsional strains. This began to yield in the 1980s with recognition that, in several polymers at least, an operative ‘chiral’ factor may well be chain tilt (a circumstance in which normals to growth faces of a lamella are not locally coplanar with fold surfaces). Labaig seems to have been first to suggest this possibility but did not pursue it [14]. Soon thereafter, Bassett and Hodge [15] reported transverse *S*-bending in lamellae within banded polyethylene spherulites, and noted consistent correlation between handedness of twisting and handednesses of both *S*-profile and chain tilt. (All three rotations in a given lamella are of the same hand, provided the latter two are judged as seen along the growth direction — unlike twisting, both reverse hand with direction of viewing). Bassett and Hodge also observed smooth, but curious, transverse variations of chain tilt across *S*-bent lamellae which, together with the bending itself, have been interpreted since very differently by Bassett and by Keith and Padden. This is the origin of an unfortunate and prolonged divergence of views. Bassett and Hodge considered these various effects to derive from isothermal thickening concomitant with crystallization, a

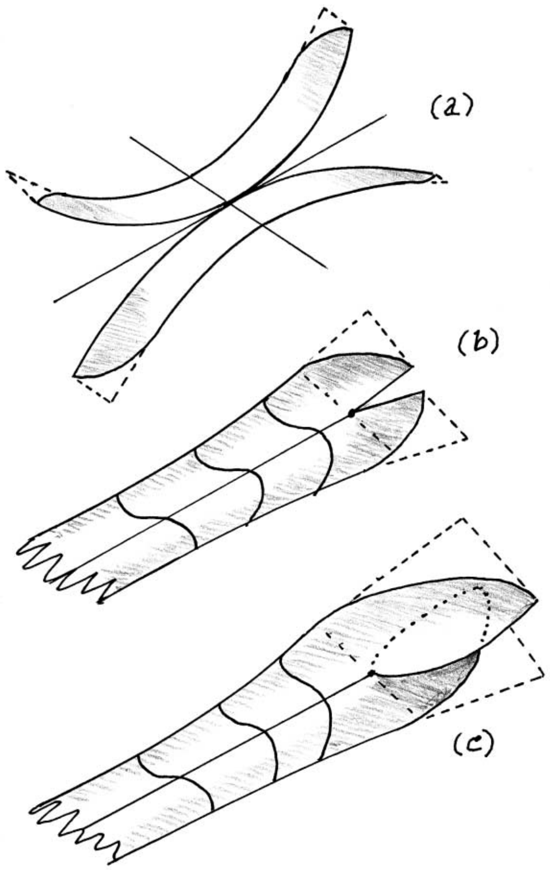

Fig. 1. Illustrating the Keith–Padden argument for generation of S-bending and twisting in elongated lamellae as modified by Toda et al. [23] to include splitting and splaying along central axes: (a) bent half-crystals brought together forming; (b) *S*-bent lamella with twisted tip split near end; (c) generation of screw dislocation in continuing growth.

view recently reaffirmed by Bassett in a claim that it is reordering of fold surfaces in flat crystals initially without chain tilt that causes *S*-bending and 'drives' banding [16] (however, as for banding, see below). Keith and Padden, on the other hand, interpreted *S*-bending as a mechanical response to surface forces of a specific kind, viz to bending moments attributable to degrees of overcrowding being significantly different in opposite fold surfaces as a consequence of a growth asymmetry introduced by already extant chain tilt [17,18]. They argued that associated bending moments about transverse axes would give rise to twisting of correct (observed) handedness, an inference supported by modeling experiments; also that, being immersed in highly viscous media and mutually interleaved, bent and twisted lamellae retain *S*-profiles and torsions even though subsequent rearrangement of folds could relax stresses and encourage adjustment of local tilt angles.

To this likely familiar, but necessary, background must be added to the roles of giant screw dislocations, which are the principal agents in lamellar branching. As found in conjunction with lenticular crystals and banding in polyethylene, these are preponderantly isochiral with the same hand as lamellar twisting, as was originally noted independently by Bassett et al. [19,20] and by Keith et al. [21]. Unlike screw dislocations with modest Burgers vectors ($\mathbf{b} \approx 5$ Å) but considerable strain energies as encountered in metal plasticity, giant screws ($\mathbf{b} \approx 100$ Å) in chain-folded lamellae are primarily topological features of relatively small energy produced only along advancing growth faces, generally at reentrant sites; moreover, it is evident that, without causing severe local disruption of crystalline order, they can neither undergo appreciable lateral movement (glide) nor can they be produced by mechanical deformation [22]. It is a simple matter to show, by the rules of conventional dislocation geometry, that a torsion of π within a band spacing (S) of 5 μm could be achieved in a lamella of thickness 150 Å (b) by longitunal rows 2 μm (w) apart of isochiral dislocations only if the average radial spacing (ρ) between dislocations were ≈100 Å (and even less for smaller band spacings — the formula is $\rho \approx bS/\pi w$). (Distributed more or less uniformly across the lamella the corresponding average spacing would be ≈ 0.15 μm). Similar estimates were made many years ago by Schultz and Kinloch [23] and, in view of repulsive interactions between even these dislocations at such small spacings, and especially of the relative paucity of dislocations in electron micrographs of etched sections of banded polyethylene spherulites, it is inescapable that some potent additional influence is absolutely essential to account for most observed banding. We have already summarized the model of Keith and Padden. Drawing upon an earlier observation of what, in an ultramicrotomed stained specimen, seemed to be large and fairly abrupt changes in lamellar orientation along radii [24], Bassett has for some years interpreted banding in terms of an assumed large splaying (divergence) of relatively flat lamellae at isochiral dislocations attributed to 'cilia pressure', viz compression within contacting irregular fold surfaces that are tightly sandwiched between initially adjacent lamellae around dislocation cores [20,25]. Neither model is without some merit and both may well contribute in practice although, as judged by quantitative consideration of geometrical constraints throughout the wide range of observed behavior, nothing like equally [18].

The point I now wish to address arose in a recent paper by Toda, Arita and Hikosaka [26] on poly-(vinylidene fluoride) (PVDF) which, as far as chain tilt and banding are concerned, behaves in a manner closely similar to polyethylene. Following an approach developed earlier by Toda and Keller [27], they elaborated upon the model used by Keith and Padden in arriving at their interpretation of lamellar twisting, *but in such a way as to predict generation of screw dislocations of hand opposite to that of twisting*. This got my attention since, if valid, it would seriously threaten an otherwise promising explanation of most available experimental evidence relating to polyethylene and PVDF. If, on the other hand, their proposed mechanism is invalid it should be challenged. Apart from the immediate

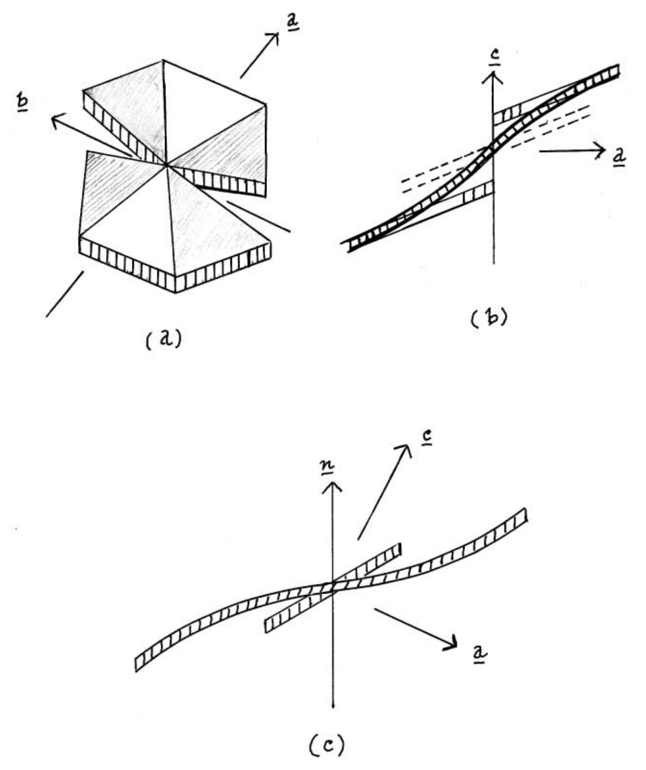

Fig. 2. Generation of chair distortion in truncated lozenge crystal of polyethylene (after Toda and Keller); (a) half-tents sharing same molecular orientation but brought together in opposite alignment; (b) molecular reorientation upon forcing conjunction along central seam (see text); (c) chair form realized by relaxation of stresses in cross-sections through center and near ends of seam.

context, it is of some concern in that the origin of giant screw dislocations in polymer crystals (other than by agency of foreign nucleating particles) remains a significant challenge to understanding polymer morphology in general.

The disarmingly facile argument of Toda et al. amounts to assumption that in the Keith and Padden model, when bent strips are imagined to be flattened and joined to simulate a stressed lamella, a slit may develop along the central axis as 'growth' proceeds. This is represented in Figs. 1a and b, which differ slightly from their Figs. 2c–d [26] in that I emphasize that imaginary strips (dashed outlines) really represent a lamella that narrows to a leading tip. What Toda et al., propose in effect is that giant dislocations in real lamellae are formed in this way on axis at growth tips, and were this to happen as sketched in the figure the dislocations would indeed be of hand opposite to that of torsion, as is clear from Fig. 1c. However, following the above general observations concerning giant screw dislocations in polymers, it is not surprising that in practice they seem never to arise at, and very rarely close to, such tips;[1] instead, they are generated perceptibly, usually well, to one or other side of central axes leading back from growth tips, and apparently by a totally different mechanism. This prevalence of off-axis locations is evident in many electron micrographs of crystals in both polyethylene [19,27,28] and of PVDF [26]. Indeed, Toda et al. appear to recognize this circumstance by their representation of rows of dislocations *along the sides* of PVDF lamellae in their Figs. 1b and 2g. Significantly, in these figures they also drew dislocations which are isochiral with lamellar torsion, a choice they support by reference to the earlier paper by Toda and Keller. However, in arriving at a claim that dislocations should be isochiral with torsion, Toda and Keller had employed essentially the same mechanism as that by which, in their recent critique, Toda et al. have derived the opposite result. I contend that, when properly pursued, the original analysis of Toda and Keller would in fact predict the same opposition of handedness that is now attributed incorrectly to the Keith–Padden model. The following may clarify a potentially confusing situation.

Toda and Keller were exploring parallels between S-bending in banding and seemingly similar distortions in truncated lozenge crystals of polyethylene in chair form [27], which is an alternative to the more symmetrical tent form, nonplanarity in both cases being a consequence of interaction between folds. They envisaged a chair as a combination of two half-tents, one facing up and one down, initially joined only at their peaks as in Fig. 2a, and then brought into conjunction at a seam parallel to the **b** axis. From obvious geometrical considerations they concluded that right-handed dislocations could be produced along the seam in the +**b** direction and, correspondingly, that left-handed dislocations could arise along −**b**. As already indicated, we may doubt these conclusions, but certainly not question the proposed assignments of handedness. Where they definitely erred, in my opinion, was in assessing likely torsions along the **b** axis. In Fig. 2b we see a view facing along +**b**, first by dashed lines of a central section through the contacting peaks of as yet undistorted half-tents in opposed (ultimately chair) orientation; light full lines then show corresponding initial sections at some distance outward along ±**b**. Joining the halves together (full heavy lines) would then, in this view, induce on axis an anticlockwise rotation of molecular orientation that begins as zero at the center but increases progressively outward along ±**b**. In effect, we would have created left-handed torsion about +**b** and right-handed torsion torsion about −**b**, in both cases *contrary to handedness of putative dislocations in the same locales*.

Transverse profiles are more difficult to judge. Toda and Keller considered the principal departure from planarity to be as shown by heavy full lines in Fig. 2b. However, to realize chair form completely we must remember that interactions at folds have produced upward convexity in the left half-tent and upward concavity in the right half-tent in Fig. 2a. Relaxation of these stresses across central sections would favor a situation as represented in Fig. 2c where,

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[1] Shear stresses in the body of an *S*-bent lamella are communicated to its growing tip as a rotation (torsion) and in the immediate neighborhood of that tip would themselves be small.

somewhat arbitrarily, I have drawn the central section of the resulting chair (at the origin of axes) parallel to the original **ab** plane. This seems to me to correspond more closely to the chair form shown in Fig. 5a of Ref. [27]. (I suspect that Toda and Keller mistook a clockwise net rotation of molecular orientation at the center of their simulated chair as indicative of right-handed twisting along the direction of viewing (+**b**); their Fig. 7a suggests this.) We note, as did Toda and Keller, that the relation between profile and chain tilt in chair crystals is likely the reverse of that originally reported by Bassett and Hodge and invoked in the Keith and Padden interpretation of *S*-bending and banding. This is not problematic; stresses due to substantial disorder in fold surfaces in the case of rapid crystallization from melt presumably overwhelm weaker interfold interactions as encountered in chair crystals grown slowly from solution.

In summary, chair crystals have little relevance to banding in polyethylene or PVDF. Anticipation of close analogy between such crystals, on one hand, and *S*-bent lamellae in banded spherulites, on the other, seems to have been illusory, though sufficiently plausible to have enticed Toda and Keller to a false conclusion. That conclusion and its translation into the paper by Toda et al. has clouded the fundamental issues. In particular, the claim [27, p. 341] to have 'ensured the validity of the original Bassett model' is mistaken. In the context of banding in these polymers there seems to be general agreement upon phenomenology regarding correlated handedness of chain tilt, *S*-bending, isochiral dislocations and lamellar torsion; attention should now focus upon thoughtful interpretation.

In that regard, Bassett and his collaborators have evinced little attention to quantitative concerns, and geometrical problems inherent in reconciling the 'cilia-pressure' model with observation, outlined elsewhere [18], have evoked no direct response. The recent paper already mentioned [16] may indicate a significant change of position but, if so, in a direction that seems retrograde. A valid case can be made with polyethylene and PVDF for absence of chain tilt in very minute crystals or within very thin layers (a few molecular stems thick) laid down epitaxially on orienting substrates. In these circumstances, cumulative interactions between folds have not yet forced adoption of stress-relieving chain tilt as must occur, for example, in tent or chair crystals or in habits with (201) fold surfaces such as lenticular crystals, axialites or spherulites. To deny such chain tilt as an existing condition throughout addition of molecules to growth faces in banded spherulites, as now mooted, is a serious break with long-accepted thinking seemingly well founded inter alia upon early experiments by Keller and Bassett, both separately and in collaboration. Moreover, experiments in which polyethylene lamellae having, or in the act of developing, opposite chain tilts are produced in dense but random admixture by nucleation on oriented fibers, although interesting, do not come close to simulating typical situations at the advancing envelopes of banded spherulites, even if quenching does lead via much initial confusion (see Fig. 3 of Ref. [16]) to a tightly banded structure.

In closing this commentary, an important concern remains about how giant screw dislocations really are generated in lamellae and what affects their chirality in given circumstances. Accompanying shears in chain directions could be accommodated mostly by staggered folding, but only in a manner that would be highly coordinated over many stems. Such behavior can scarcely be ascribed credibly to random fluctuations in molecular folding. A possible mechanism has been proposed that concentrates attention on surface reentrants (lacunae) which occur on growth faces some distance from protuberant growth tips through temporary pile-up of spreading layers. Under certain conditions, perpetuating slit defects could result that would permit 'nondestructive' shear under the action of even modest bending moments. If produced as Keith and Padden have suggested, these moments would be of consistent sign along a growth face and hence would produce dislocations of consistent handedness. This is as yet speculative but would seem to fit what is known of isochiral dislocations as they are found in polyethylene and PVDF; further details are given in Appendix 2 of Ref. [18]. One of the objectives of that paper was to emphasize that there are several different causes of banding in polymers; sound understanding of its occurrence in the two polymers dealt with here would be a significant step forward, but still leave much yet to be discovered.

4. Summary

Recent publication of misleading assertions concerning topics that predate current electronic methods for dissemination and retrieval of scientific information have prompted reflection upon, and clarification of, the issues involved. These include secondary effects in banding of spherulites in thin films, means by which cooperatively twisting orientation is achieved among radiating lamellae and generation of isochiral dislocations. There are timely lessons concerning the physics of lamellar crystal growth and organization that needed emphasis. The new technology seems to have discouraged careful reading and thoughtful appraisal of more dated subject matter.

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