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Banding in Polyethylene and Other Spherulites

H. D. Keith*

Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269

F. J. Padden, Jr.[†]

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

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ABSTRACT: Circumstances leading to twisting crystallographic orientation in banded polymer spherulites are analyzed, both from the standpoint of qualitative morphology and of more quantitative measurement and calculation. Particular attention is paid to linear polyethylene, for which the most extensive information is available, and to α-poly(vinylidene fluoride), which behaves in a closely similar manner. In polymers that exhibit vigorous twisting (band spacings extending down to 10 μm or less), chiral factors of two distinct kinds can be recognized. One is enantiomorphism, and the other is chain tilt (molecular stems in chain-folded crystals not being codirectional with lamellar normals). Quantitative evidence strongly suggests that the latter produces twisting orientation by generating surface forces in lamellae. It is also responsible for formation of dislocations that are isochiral, although these generally contribute relatively little to twisting. Banding in various classes of polymer is reviewed, and it is emphasized that there are several patterns of behavior, most still in need of elucidation; suggestions are made for continuing research.

Introduction

Banding, a term generally used to denote occurrence of a concerted twisting of crystallographic orientation about radii, is a common feature of spherulites crystallized from the melt; it is usually manifested in the first instance by extinction patterns (often circular bands) in polarized light microscopy. Elucidation of its origins (intentional plural) is an intriguing problem of long standing that has so far yielded little to intensive study. Throughout early work (mostly 1890−1930) on monomeric compounds and on minerals in igneous rocks, enantiomorphism and chirality of structure were tantalizingly recurrent themes, although without sufficient consistency to permit clear interpretation;[1] such systems will be commented upon briefly in a later summary. Here we wish to focus attention upon banding in polymer spherulites where, again, there is a puzzling variety of behavior and, despite widespread investigation over four decades, relatively little understanding.

By far the most closely studied polymer, in this respect as in most contexts involving crystallization of chain macromolecules, is polyethylene. Even for this supposedly prototypical material, however, there is as yet no general agreement either as to how crystalline orientation twists or what causes it to do so. There are two leading viewpoints that share common elements, but they are nevertheless very different in emphasis.[2−9] Much of past experimentation has been qualitative in nature and it is our view that, with appeal to more quantitative considerations, one of these two interpretations becomes significantly the more viable. It is the view that accounts for a crucial, but otherwise unexplained, tenet of the other and lends itself more incisively to accounting for occurrence or absence of banding in other polymers.

Our first objective in this paper is to enlarge upon these considerations in the specific context of banding in polyethylene; included will be some elaboration of experimental evidence mentioned, in passing and without detail, in an earlier publication.[3] We shall have occasion to examine in detail the formation and role of giant screw dislocations in polymer lamellae. In general, these discussions will also provide conveniently a conceptual basis for reviewing behavior in other polymers. We shall see that banding does not follow a similar pattern in all of these materials and that it likely poses a more diverse problem than has commonly been suspected. Where possible, we shall indicate seemingly promising areas for continuing research.

Morphological Background

Banding in polymer spherulites betokens a coordinated rotation about radii among chain-folded lamellae that are elongated in radial growth directions and branch at giant screw dislocations.[10,11] As a preliminary to considering behavior in terms of individual lamellae, however, we do well to recall general results of observations by polarized light microscopy, as follows.

(1) Variation of birefringence across a two-dimensional spherulite of an optically uniaxial polymer, such as polyethylene, suggests that at a given location the spread in lamellar orientation around the radius is confined within ±30°; behavior observed by tilting on a universal stage indicates, however, that on the scale resolvable by visible light averaged orientation rotates remarkably smoothly and uniformly with traverse along radii.

(2) Bands of extinction and intervening birefringence appear in regular sequence right at the advancing envelope of a growing spherulite, and in isothermal crystallization their spacing is essentially independent of radius.

(3) Band spacing commonly increases with crystallization temperature, but can vary during growth in response to temperature excursions, up or down; once established, however, a band spacing remains fixed thereafter regardless of temperature (we may ignore barely perceptible changes attributable to thermal expansion or contraction).

(4) Banded growth very rarely persists to the highest range of crystallization temperature (ΔT < 15−20 °C);

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* To whom correspondence should be addressed.

[†] Retired.

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coordination of lamellar orientation in most polymers appears to break down increasingly over a small temperature interval in which extinction bands become "blotchy" and fade out.

(5) In crystallization at fixed supercooling band spacing in a given polymer almost invariably decreases with increasing molecular weight (see later discussion for detail). In comparing different polymers, however, there is no simple correlation between relative rates of radial growth and corresponding band spacings; spacings in the range 1−10 μm are found both with very rapid growth (1−250 μm/s) in polyethylene and with very slow growth (10^{-4}−10^{-2} μm/s) in α-PVF$_2$, whereas bands with large spacings (∼100 μm) appear at ∼1.5 μm/s in poly(ethylene oxide) and at 0.1 μm/s in β-polypropylene.

(6) In linear polyethylene, with which we shall be much concerned in the following, banded spherulites are formed over a wide range of conditions, band spacings ranging from about 0.75 μm in polymer rapidly quenched to room temperature to about 7 μm with crystallization at temperatures up to near 125 °C. (Data for films about 15 μm thick, crystallized isothermally between 105 and 123 °C, and close to isothermally between 95 and 105 °C, will be shown later in Figures 2 and 3.) Throughout this smooth variation, from deep in Regime III to within about 3 °C of transition from Regime II to Regime I, spherulitic texture as revealed by light microscopy appears quite compact even as seen immediately behind growth fronts.[3,12,13] However, there is much continuing crystallization behind these fronts and, in specimens examined ultimately at room temperature, assessment of lamellar organization, and particularly of stages in the development of that organization, presents a formidable challenge to the electron microscopist.

Extinction patterns in banded spherulites can be accounted for satisfactorily by considering indicatrices spiralling uniformly along radii.[12,14] The simplest model consistent with this is one in which a typical lamella in isolation is considered to be a twisted ribbon (a right helicoid) and it has often been so represented in the literature. There are valid aspects of this model but, without deeper consideration and major qualification, it cannot apply directly to lamellae within a mature banded spherulite; relatively wide helicoidal ribbons of like hand, parallel and in phase, simply cannot be brought together and packed closely enough. Accordingly, there have developed two approaches to interpreting banded structure: one[3,12] emphasizes smooth twisting of leading lamellae near their growth tips, band spacing and coordination in phasing both deriving from "locking in" of orientation as these widening crystals interleave progressively; the other[2,6−9] emphasizes a twisting described as "quasidiscontinuous" ("lamellae with little or no twisting for about a third of a band spacing followed by a region in which more abrupt changes in orientation occur"[7]). Let us elaborate each in turn using polyethylene as exemplar, but recognizing that much of the discussion has wider implications.

On the first of these views leading lamellae twist smoothly back from growth tips while they are still relatively narrow. When their widening shoulders impinge upon one another (obliquely with planes at small incidence), these lamellae become mutually transfixed by continuing interpenetrating growth. This has consequences, not only that on a local scale their nearly parallel orientations become permanently locked within a squat cellular texture but also that subsequent growth of subsidiary lamellae sandwiched between them is closely constrained in like orientation. [SEM micrographs of oncoming growth fronts in coarse aggregates grown from solution convey some impression of such a cellular texture though without torsion about growth directions—see Figure 1 of ref 15.] In this interpretation, then, interleaving of smoothly twisted tips of leading lamellae establishes a three-dimensional "template" that limits lamellar orientation in most subsequent crystal growth, whether individually twisted or not, and leads to an averaged orientation that twists in a manner consistent with observation. On a finer scale, however, resulting lamellar organization is compact, quite complex and difficult to decipher, a confusing aspect being that late growth of subsidiary lamellae may contribute isolated crystals in a manner suggestive of segmented or discontinuous twisting.[3]

The alternative interpretation places prime emphasis upon quasidiscontinuous changes in orientation as new, essentially untwisted, lamellae are generated at isochiral screw dislocations and splay (diverge) sharply away from parent lamellae.[2,7] Relatively large divergences (some claimed to approach 60°) are attributed to a short-range repulsion or pressure between lamellae that derives from uncrystallized cilia or other amorphous polymer in areas of contact between them. Such marked splaying, though not universal, is known in branching of isolated lamellae grown in polymers at relatively small supercooling,[16] but it is not a common occurrence in compact banded textures where densely stacked lamellae are found even close to growth fronts.[13]

Both interpretations can draw limited support from qualitative observation by electron microscopy; nevertheless, it is our view that evidence from this source alone is, and for some time is likely to remain, indecisive. Much of it is indirect, being inferred from features clearly observable only in specimens crystallized at higher temperatures such that whatever twisting there may be is poorly coordinated and structure is likely modified considerably by lamellar thickening. Examinations of more compact spherulites with smaller band spacings have not produced much clarification and, to the extent that neighboring lamellae at the same radial distance are oblique to one another, one cannot then distinguish easily between (i) their having come together that way as they widened or (ii) their having originally diverged abruptly after branching. We need to adopt a more analytical approach and, where possible, pay close attention to quantitative evidence. Three interwoven topics are particularly relevant. Framed as questions they are as follows: what could cause smooth twisting in lamellae and by how much?; how are giant screw dislocations generated, and why under some circumstances are they isochiral?; is a model of quasidiscontinuous twisting based primarily upon such dislocations really viable when, as in polyethylene, band spacings vary continuously down to ∼1 μm?

Twisting under the Action of Surface Forces: Qualitative

Lamellae in most banded spherulites exhibit chain tilt; that is, chain folding in which molecular stems are oblique to lamellar normals. Excepting the special cases of two polymers which exist in enantiomeric forms and for which information is yet lacking, chain tilt is a factor in all instances involving band spacings less than 10 μm, including α-poly(vinylidene fluoride)[17] [α-PVF$_2$] despite mistaken suggestions to the contrary (see later).

Of these, all but two involve unit cells of low symmetry (mono- or triclinic) such that chain tilts $\sim$20−40° are mandated even if fold surfaces have indices (001); a significant consequence is that oblique chain packing enhances space for accommodation of possibly disordered chain folds within surface layers. Having orthorhombic unit cells, the other two polymers, polyethylene (PE) and α-PVF$_2$, are not similarly constrained by crystallography; among all polymers involved, however, they lead in terms of volume expansion upon melting ($\sim$17% in PE, $\sim$14.3% in α-PVF$_2$) and, doubtless in consequence,[18] both invariably exhibit chain tilts ($\sim$35° in PE, $\sim$25° in α-PVF$_2$) when crystallized from melt under conditions of present interest. Fold surfaces approximate (201) in PE and (102) in α-PVF$_2$ but need not necessarily be confined to low-index planes. Much attention[18] has been given in recent years to density mismatch across fold “surfaces” and to disordered molecular packing within what are really surface layers comprising irregular folds, loose loops, cilia, etc.; in both theory and experiment, this is particularly true of PE, the exemplar to which we now return. It is, or course, obvious that disorder will tend to increase with molecular weight and with growth rate.

We have pointed out that fold surfaces which are considerably disordered (at least prior to onset of any lamellar thickening that might occur) are probably congested to the point of being under substantial compressive stress.[3] The reason is that availability of space would allow greater disorder to develop in fold surfaces very close to the edge of a growing lamella than could subsequently be tolerated within the body of the crystal. Kinetics of growth may therefore involve, or possibly depend upon, relaxation of transient states of disorder. In any event, surface layers behind the growth front could easily be compressed at or close to the physical limit. Such surface stresses would be of small consequence in the absence of chain tilt, except perhaps that unmatched fluctuations might cause wrinkling in otherwise flat crystals. In sharp contrast, chain tilt by $\sim$35° about the **b** axis in PE lamellae ensures that normals to operative growth faces, {110} and {200}, are both inclined (by about 18 and 35°, respectively) to (201) planes and, consequently, that opposite fold surfaces develop under circumstances that are geometrically quite disparate. We postulated that stresses in opposite fold surfaces reflect this disparity, thereby giving rise to bending moments in growing lamellae. In the context of spherulites we developed arguments showing how in various ways curved lamellar profiles and twisting about radii could follow. Initially a promising hypothesis prompted by Bassett and Hodge’s report of S-bending and its correlation with twisting,[19] this approach is now well supported by direct confirmation of disparate structure at opposite fold surfaces and of related bent growth in lamellae.[5] It is further supported by an all but universal correlation, in (nonhelical) polymers other than PE, between occurrence or absence of chain tilt and occurrence or absence of banding (the sole exception, the ferroelectric polymer γ-PVF$_2$, is a special case—see later).

In our supporting experiments with PE[5] two other significant observations were made: first, that lamellae growing in fairly intimate contact with a substrate or with one another tend to display marked asymmetry in rates of transverse (widening) growth; second, that giant screw dislocations generated in twisted lamellae are predominantly isochiral, their handedness matching that of the twist which, in turn, is governed by direction of chain tilt. A consequence of the first is that whereas isolated lamelae tend to widen symmetrically, develop S-shaped transverse profiles, and twist helicoidally, packets of closely stacked lamellae (evidence for which is to be found in work by Norton and Keller[20]) tend to develop asymmetrically, exhibit C-shaped profiles, and twist more strongly to resemble augers of large pitch. (An auger is a boring tool that except for its pointed end resembles a spiral staircase.) Isochiral dislocations would make positive contributions to twisting although, without consistent amplification through marked splaying, not sufficient to account for more than a modest fraction of the overall torsions observed (see later).

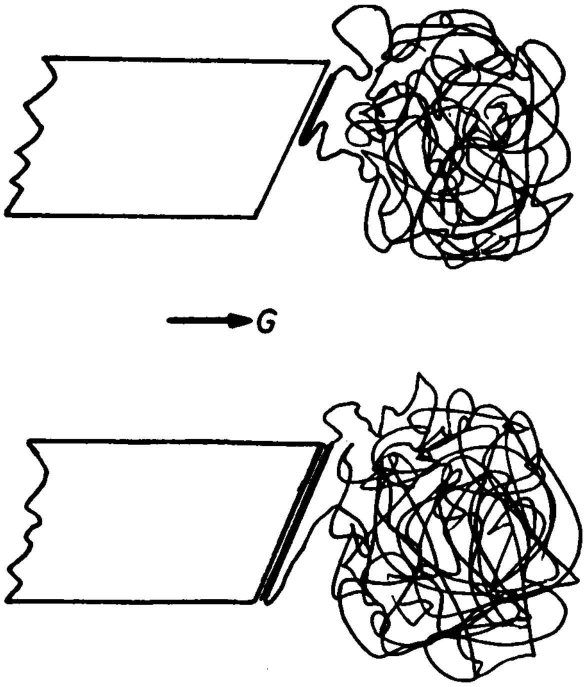

Figure 1. Schematic representation of a growing lamella encountering a coiled molecule directly in its path, indicating how obliquity of a tilted growth face influences attachment of a folding chain, favoring tighter and more compact loops at the fold surface intersected at an obtuse angle. (The argument is discussed in more quantitative terms in Appendix 1 of ref 3.)

A major difficulty in all consideration of mechanism associated with polymer crystallization is ignorance about chain dynamics at and near a growth face. Our presumption of greater congestion and larger stress in fold surfaces laid down at acute-angled edges of tilted growth faces was in the first instance dictated by empiricism, and the rationale we proposed was tentative.[3] A key element (Figure 1) is that, in such a tilted face, approach of the point of attachment of a crystallizing chain toward the obtuse-angled edge involves reptation of a loop along or close to the surface. Resistance to that reptation then militates strongly in favor of the ensuing fold being relatively tight and neatly packed; at the acute-angled edge, on the other hand, attachment is likely, if anything, to introduce more and looser loops into the fold surface than would be the case without chain tilt. We are still persuaded that there is substantial merit to this interpretation. In summary, our view is that when chain tilt introduces obliquity between the plane of a lamella and the normal to a growth face, and attachment of crystallizing chains at that face is appreciably encumbered as, for example, by frictional resistance to reptation, bending moments will develop along the advancing edge of the lamella so as to produce convexity of the fold surface making a protuberant acute angle with the growth face.[3] Because of the prominence of {110} facets near growth tips of PE lamellae moments will have comparable axial and transverse components (the latter contributing most to twisting) and, although these moments might gradually relax after passage of a growth front, bends or twists are likely to persist when lamellae are constrained within spherulites. (Although developed by considering behavior in PE, we suggest that these inferences may be widely applicable and may possibly become an important general consideration in polymer crystallization.)

Twisting under the Action of Surface Forces: Quantitative

We have limited information upon which to quantitate the model to which these concepts lead. Nevertheless, we can profitably explore limits of feasibility and derive approximate functional relationships for experimental test. Considering a lamella as a cantilever consisting of a core of thickness t flanked by surface layers, thickness Δt, in which disparate compressive stresses $\sigma_+ = \sigma + \delta$ and $\sigma_- = (\sigma - \delta) > 0$ cause bending with curvature $1/\rho$, we derive the relation $\Delta\sigma\Delta t = Et^2/6\rho$, where $\Delta\sigma = \sigma_+ - \sigma_-$ and E is Young's modulus of the core. The difference between strains in the surface layers can be written $\Delta\epsilon = \Delta\sigma/E = t^2/6\rho\Delta t$, assuming that values of E in congested surface layers and in the core are commensurate. They are unlikely to differ much from one another or from the value 4 GPa $\approx 4 \times 10^{10}$ dyn cm^{-2} derived indirectly for crystals loaded transversely to chain axes and also typical for glassy organic polymers.[21] (Throughout the following, we shall adopt other nominal values for PE crystals as follows: $\Delta t = 15$ Å (a deliberately conservative underestimate); $\sigma_e = 100$ erg cm^{-2}; $\Delta H = 3 \times 10^9$ erg cm^{-3}; $T_m° = 145$ °C). In an attempt to assess how large $\Delta\epsilon$ might be, we have chosen observation by Bassett *et al.*[22] of marked curvature ($\rho \approx 1$ μm) in S-bent lamellae crystallized at 128.1 °C in linear polyethylene of high molecular weight and modest polydispersity, $M_w = 440\,000$, $M_n = 220\,000$; congestion in fold surfaces in such a case is likely to have been close to the tolerable maximum. Further, since the total crystal thickness ($t + 2\Delta t$) of 220 Å estimated from their micrograph (Figure 5 of ref 22) agrees very closely with a long period measured in very early stages of crystallization of PE at 128.8 °C by Barham and Keller[23] using synchrotron radiation, we are confident that thickening had not intervened. With $t = 190$ Å, $\rho = 1$ μm we then find $\Delta\epsilon_{\max} = 0.04$, but note that this value may be inflated by what could be appreciable underestimation of Δt. However, any error involved becomes irrelevant when, assuming the same values of E, $\Delta\epsilon_{\max}$, and Δt to apply in a lamella crystallized at about 107 °C and having a core thickness of 100 Å, we now estimate a corresponding value for ρ. The result is 0.28 μm, and this significantly reduced magnitude will presently assume some importance. On physical grounds, there is no reason to think that either Δt or $\Delta\epsilon$ could be appreciably reduced when crystallization occurs at large supercooling (deep in Regime III); our estimation, therefore, relies entirely upon well-established variation in crystal thickness, and fictions in enumerating $\Delta\epsilon_{\max}$ are inconsequential.

Let us now estimate strain energies to confirm that they fall within credible limits. Apportioning $\Delta\epsilon_{\max}$ as $\epsilon_+ = 0.05$ and $\epsilon_- = 0.01$, say, we find energy ($E\epsilon^2/2$ per unit volume) in both surface layers combined to be $\approx$4 erg cm^{-2}, that is, per unit area *of crystal*. Inclusion of roughly estimated strain energy in the core (tension and bending) increases this value by 25% in thicker crystals and almost doubles it in thin (<100 Å). Either way, the result is modest in comparison with $2\sigma_e \approx 200$ erg cm^{-2} or with the "excess" free energy, $\geq$15 erg/cm^2 of crystal, that is available to drive crystal growth. As before, numerical fictions are largely irrelevant to the essential physical argument. In fact, choice of an almost certainly low value for Δt has likely magnified our estimates of strain energy.

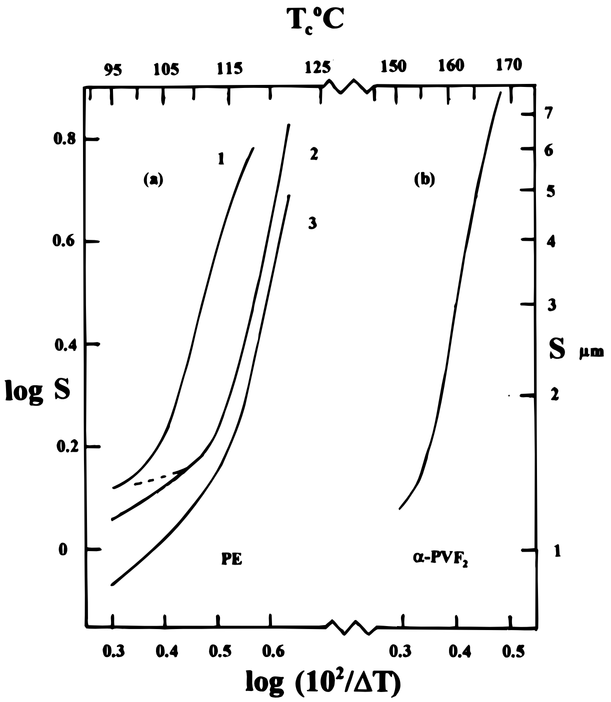

Figure 2. log−log plots of band spacing S against ($1/\Delta T$): (a) for various linear polyethylenes (identified in text); (b) for α-poly(vinylidene fluoride).

For variation of band spacing with crystallization temperature we argue as follows. Taking curvature ($1/\rho$) as a measure of "effective torque" τ producing twist and, assuming constant E and Δt, we write $\tau \sim \Delta\epsilon/t^2$. We now put $\Delta\epsilon = f\Delta\epsilon_{\max}$, where f, a function of crystallization temperature and molecular weight, represents difference between strains in surface layers as a fraction of a maximum or saturation value $\Delta\epsilon_{\max}$. As ΔT increases from zero, f is expected to increase, perhaps slowly at first, then increasingly until close to saturation at $f = 1$; a functional dependence of form $f \sim \Delta T^n$, $n > 1$ would seem a reasonable approximation until f approaches unity. We relate band spacing to torque by $S \sim 1/\tau$ assuming that, when crystallization temperature increases, texture becoming more open and twisting becoming less vigorous may offset one another and validate such a reciprocity, at least as an approximation through the range of rapid variation in S. Thus, since $t \sim (1/\Delta T)$,[11] we suggest $S \sim 1/\tau \sim t^2/f$, implying $S \sim (1/\Delta T)^2(1/\Delta T)^n$, that is, $\log S \sim (n + 2)\log(1/\Delta T)$, a relation readily amenable to experimental test.

That such a relation is in fact followed fairly well throughout the anticipated range in linear PE has been pointed out[3] (without detail and, unfortunately, in confused form because of insertion in printing of a correction without removal of the original typographical error). In Figure 2a we show plots for various polyeth-

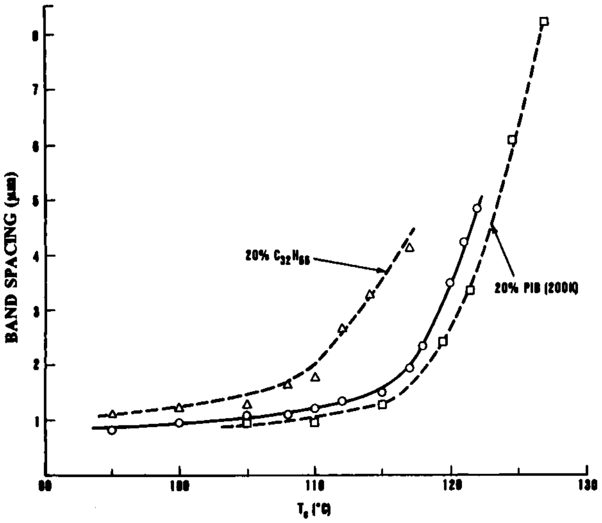

Figure 3. Band spacing as a function of crystallization temperature for (full curve) a linear polyethylene fraction (NBS SRM 1484; $M_w = 119\,600$, $M_n = 100\,500$) and (dashed curves) for the same polymer blended with 20 wt % of n-$C_{32}H_{66}$ and of a polyisobutylene of molecular weight 200 000.

ylenes from which values of $(n + 2)$ can be read directly as slopes. These are representations (using $T_m° = 145$ °C) of curves originally plotted as S vs T_c; Figure 3 is an example which also serves to indicate the quality of data typically obtained in our experiments. (It is convenient here to depart from convention by relegating commonplace experimental detail to an appendix.) The numbered curves in Figure 2a were obtained using linear PE polymers as follows: (1) NBS SRM 1483, $M_w = 32\,100$, $M_n = 28\,900$; (3) NBS SRM 1484, $M_w = 119\,600$, $M_n = 100\,500$; (2) a 1/1 blend of (1) and (3) having $M_w = 75\,800$, $M_n = 44\,900$. Except for slight divergence (dotted) at low T_c, curve (2) also represents within experimental error data for Du Pont Sclair 2907 polymer, $M_w = 72\,000$, $M_n = 19\,500$ (average of two determinations) and, in addition, it also comes very close to representing a 1/1 blend of (3) with NBS SRM 1482 ($M_w = 13\,600$, $M_n = 11\,400$) having $M_w = 66\,600$, $M_n = 20\,500$. When $S \geq 1.6$ μm, slopes for (1), (2), and (3) average 3.55, 4.15, and 4.35, respectively; however, slopes decrease rapidly when $S < 1.6$ μm. (That variation of S begins to slow down dramatically at lower (nominal) values of T_c is real and scarcely surprising; the trend is soon exaggerated, however, by inability to achieve isothermal conditions.) It is a simple matter to reproduce the steeper slopes and even the sigmoid shapes of the upper curves in Figure 2a by adopting appropriate and quite credible assumptions about f as a function of T_c, although this would for the moment seem unprofitable. We have, however, gone quite far toward establishing credibility for our interpretation, including its potential for extension to small band spacings ≤ 1 μm.

Further reinforcement can be discerned in the above behavior, as follows. Horizontal displacement between curves in Figure 2a represents influence of molecular weight in the same direction as we consistently found in unpublished early work with many linear PEs, fractions and whole polymer. In this case, however, overlap between curves for Sclair polymer and the 1/1 blends of NBS fractions seems clearly to focus attention upon M_w rather than M_n, that is, upon dominance of longer chains in generating twist. Blending linear PE with other diluents in modest amounts provides additional evidence suggesting sensitivity of S to molecular mobility in the melt. For example, Figure 3 shows results in the case of NBS SRM 1484 ((3) above) blended with n-$C_{32}H_{66}$ and with a polyisobutylene fraction of molecular weight 200 000. The oligomeric diluent increases S and shifts the rising curve by about 5 °C toward lower T_c even though DSC melting point is reduced by 2.5 °C only; the second diluent tightens an already close banding and extends its measurable range to 127 °C. (Although the latter diluent is incompatible with PE it can by coprecipitation be incorporated homogeneously in mixed melt long enough to permit crystallization without detectable sign of accompanying separation; blended at the same concentration in less viscous NBS SRM 1483 ((1) above) it rapidly becomes separated in minute droplets that are engulfed within growing spherulites without perceptible influence upon S.) In additional experiments, blending at 5% concentration with each of various atactic polypropylenes, which separate relatively slowly from PE in mixed melt, we have found interesting variation with molecular weight of diluent; S at given T_c (≈120 °C) is decreased by diluent of higher molecular weight whereas it is *increased* by diluent of lower molecular weight (<10 000). The latter result is particularly significant in that it suggests stronger response to molecular mobility of crystallizing chains than to segregation of amorphous polymer between lamellae. Prompted by expectation that concentration of short branches in amorphous regions would enhance congestion at fold surfaces even at relatively high crystallization temperatures, we have studied banding in several linear low-density PEs having DSC melting points ≈125 °C. When $T_c = 95$ °C, values of S fall in the range 0.75–1.0 μm, but increase only to about 2.5 μm at $T_c \approx 120$ °C; behavior is somewhat erratic but the result is clear, although analysis as in Figure 2a is prevented by inaccessibility of $T_m°$. The extreme case of tight banding produced in hydrogenated polybutadiene during exceptionally slow and nonlinear radial growth (~0.1 Å s^{-1}), which we have noted elsewhere,[3] is an extension of this trend. (Anticipating a later topic, we note that the curve of average slope 5.1 in Figure 2b is drawn using Lovinger's data[24] for S vs T_c in α-PVF_2 and an extrapolated melting point 200.9 °C;[25] a close analogy with PE in terms of chain tilt about radii has clearly been reflected in similar banding behavior.)

Previously, we discussed how moderate helicoidal twisting could arise near the tips of symmetrical S-bent lamellae despite compensation between opposing transverse components of bending moment.[3] It was obvious, however, that asymmetrical lamellae (those that widen by growth predominantly on one side) in which there is inevitably an imbalance between these components would twist more readily and throughout their lengths in auger-like forms. In spherulites, moreover, these lamellae would be strongly stretched along their axes, for it is to be remembered that volume shrinkage is concomitant with solidification and places growing lamellae under considerable radial tension. [In films of aliphatic polyesters of moderate molecular weight we have seen examples of such radial tension causing cavitation (instantaneous production of many small bubbles) in melt trapped after growing spherulites achieve mutual contact—see Figure 5.] Now knowing that growth with an asymmetrical habit commonly occurs in closely stacked lamellae,[4,5] we believe that much of the banding observed in more compact PE spherulites involves lamellae in the form of stretched auger-like spirals. Several appealing corollaries follow from this view: first, it would account for a waviness of profile seen along radii in thin banded films;[2,26] second, such lamellae should exhibit relatively flat or slightly C-bent profiles in cross-sections normal to radii, as is indeed observed;[2] and lastly, it lends support to use of $(1/\rho)$ as a measure of τ, and also to reasonable expectation that spacings as small as 1 μm or less can be accounted for.

It should perhaps be emphasized that prediction of approximately linear dependence of log S upon log$(1/\Delta T)$ with slope in the neighborhood of 4 has been based upon a specific mechanical interpretation of twisting. There is no reason to expect universal applicability; indeed, significant departures from such behavior may well indicate twisting attributable to different stimuli (see later).

Giant Screw Dislocations

It has long been recognized in PE crystals of rhombic and truncated rhombic habit, particularly those that develop dendritically during rapid growth from dilute solution, that giant screw dislocations almost invariably arise at re-entrant corners on roughened growth faces.[26,28,29] Axial displacements were originally considered to involve staggered molecular folding but it is now evident that lamellar curvature could also contribute, with the difference, however, that whereas staggered folding does not necessitate *reorientation* of chain stems, lamellar curvature does. It was also noted in early experiments on PE dendrites (recently repeated and confirmed by us) that dislocations of both right and left hands appear widely distributed and in profusion, sometimes in rows with alternating hands and, moreover, that dislocations of like hand are never found closer together than 0.25 μm and, indeed, very seldom closer than 0.5 μm. The latter limits also appear to hold for PE lamellae crystallized from melt.[8]

There are insights to be gained from attempting to assess energetics in these various circumstances. As a basis for comparison, let us estimate elastic strain energy in a sheet 100 Å thick having a conventional screw dislocation of modest Burgers vector $b = 5$ Å running perpendicularly through it; assuming a shear modulus 10^{10} dyn cm^{-2}, conventional formulae yield a result no less than 3×10^{-11} erg. We note that such strain energy would increase as b^2, which is why dislocations of like hand strongly repel one another and why we emphasize the essentially topological character of giant dislocations having $b \geq 100$ Å. Shears accomplished by changes in staggered folding are not without expenditure of energy, however, since in effect they increase surface area at a cost of about 10 erg cm^{-2}. For example, modified staggering in an area 0.3 μm by 0.3 μm, sufficient to produce vertical displacement of one edge by 100 Å, would require about 5×10^{-12} erg, while accomplishing the same result through curvature would require approximately 7×10^{-12} erg ($Et^3/24\rho^2$ cm^{-2}). These comparable values are intermediate between but widely separated from (i) kT at crystallization temperature ($\sim 5.5 \times 10^{-14}$ erg) and (ii) excess free energy available from growth of this small area of lamella ($\sim 1.3 \times 10^{-8}$ erg). A giant dislocation, therefore, has abundant free energy to draw upon for its formation, but there has to be cooperativeness on a scale involving many degrees of freedom. Most likely, this derives from a shuffling toward conformations acceptable for crystallization among molecules partly adsorbed at growth faces, a process sensitive to molecular weight and subject to vagaries of chain statistics.

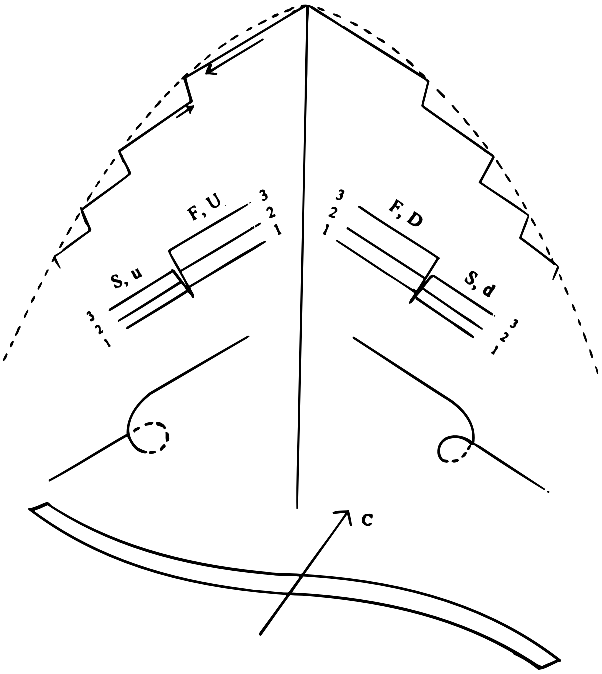

Figure 4. Schematic representation in plane view and elevation (seen along growth direction) of a symmetrical S-bent polyethylene lamella in which chain tilt would result in right-handed twisting. Bunching of spreading layers produces re-entrant corners around which "shears" and subsequent overlapping growth generate embryonic giant screw dislocations as shown; note that in this case dislocations so initiated would be right-handed on either side of the lamella (see Appendix 2 for a fuller discussion).

In polyhedral crystals grown from solution, chain tilt (differently directed in each sector) seems to have little effect since there has been no perceived indication of dislocations of given hand being concentrated in particular sectors. In these nonplanar crystals most dislocations are generated near major boundaries between {110} and {200} sectors[26] whereas, in PE lamellae crystallized from melt at temperatures such that banding occurs (125 °C and below), dislocations are produced along{110} faces that meet at terminations of **b** axes in elongated crystals having essentially uniform chain tilt throughout.[4,5,8] It is in these latter circumstances that dislocations are found to be isochiral, with hand given by direction of chain tilt (away from lamellar normal) about the growth direction. (In this regard our earlier observations[5] are now strongly supported by experiments of Toda and Keller.[8]) Given bending moments based upon chain tilt as we propose it is demonstrated in Figure 4 how this selectivity may come about. This we believe to be the correct interpretation, and Toda and Keller concur in some such possibility.[8] On our model, an implied distinction between a vital role of chain tilt in crystallization from melt and its seeming irrelevance in crystallization from dilute solution would appear to have its origin in markedly different molecular mobilities near and on growth fronts. Nevertheless, the distinction may not be completely sharp; isochiral dislocations have been reported by Organ and Keller[30] in PE crystals grown from dilute solution in very poor solvent (tetradecanol) at limiting high temperature (118 °C). However, the polymer involved was exceptionally polydisperse ($M_w = 100\,000$,

M_n = 10 000), and what crystallized may have been a small content of very long chains while others remained in solution.

As of this writing, Bassett[4,6,9] and Vaughan[7] have consistently repudiated our original proposal that chain tilt and consequent bending moments play a key role in banding, specifically citing apparent incongruity as regards chain tilt in the case of PVF_2 (see later) and making no acknowledgement of our later supportive experiments.[5] Nevertheless, in developing an interpretation involving quasidiscontinuous twisting, now based primarily upon isochiral dislocations, Bassett attributes selectivity in chirality, with no indication of detail, to structure in fold surfaces that, by implication, in some manner reflects chain tilt.[6,9] Toda and Keller,[8] as we have seen, are more explicit in recognizing a convergence of views on this topic, but consider that correlation between chirality and chain tilt "ensures the validity of the original Bassett model". Inherent in this conclusion, however, are several major difficulties.

Contributions of Isochiral Dislocations to Twisting

We have noted that isochiral dislocations are spaced at least 0.25 μm apart in isolated lamellae, and all indications from etched sections are that this holds true within spherulites. The population of dislocations giving rise to viable branches within these spherulites is further limited by available space; indeed, in steady-state isothermal growth the frequency of such branching must vary inversely with radius (although band spacing remains constant). A very important aspect of the Bassett model, therefore, is enhancement of rotation at dislocations through splaying. Even if formed entirely in consequence of lamellar curvature, a giant dislocation would, based on topological grounds alone, produce a maximum rotation less than 10° (calculated for a lamella 220 Å thick with a dislocation whose strain field is assumed confined within a region 0.25 μm in diameter). Accordingly, the maximum torsion that isochiral dislocations 0.25 μm apart, if unaided by splaying, could produce is 40°/μm along a radius. Even if such a dense population of dislocations were realized, banding with spacing 1 μm would then call for average rotation *per dislocation* to be enhanced by splaying to 45°. For anything of this kind to result from repulsion between parent and daughter lamellae, and have significant effect, would require (i) extreme curvature in the splaying daughter over a small area of contact with its parent and (ii) availability of considerable space between leading lamellae for oblique branches to develop. With regard to (i) we ask: if compression of cilia exerts such potent force, why would marked splaying not be a universal accompaniment to dislocations in polymer lamellae?; why would strain energy become so concentrated at a costly sharp bend? Further, we believe that (ii) is at odds with observation that lamellae at growth fronts in spherulites having smaller band spacings are fairly closely stacked.

With larger band spacings these arguments lose some of their considerable force; nevertheless, the strongly negative impact of another problem remains unchanged. Enhanced splaying of a daughter lamella away from its parent in response to *mutual* repulsion implies coexistence of both with, at best, the parent lamella *retaining its original azimuthal orientation*. Of these two the parent, already a leading or dominant lamella, is the one unlikely to have its continuing growth stifled by possible overcrowding, either at this or at later branching events. How, then, does observed twisting with band spacings measuring a few microns come about? How is cooperativeness in phasing achieved? In our view, the quasidiscontinuous model of banding, when its implications are measured against phenomena for which it is required to account, does not stand up to critical examination. We conclude that isochiral dislocations may play a part in banding but, being neither the primary determiners of hand of twisting nor the major contributors to torsion, their role is a minor one.

Additional Remarks on Polyethylene

The following points are worthy of mention. (a) Banding in PE tends to be more regular in polymer of moderate molecular weight, particularly when there is an appreciable content of relatively short chains. Cooperativeness in lamellar orientation seems to be achieved only with difficulty in polymer of higher molecular weight, and banding may then be apparent in some regions of a spherulite but not in others. (b) In a coarser-textured spherulite at whose center the axis of a "starting sheaf" can be identified, it should be possible to test an expectation from chain tilt that, along radii leading away in opposite directions along that axis, twisting should be of opposite hands. This we have confirmed using a Fedorow universal stage; thereby illuminating previous observation that sectors with right- and left-handed twisting commonly occur together in the same spherulite.[12] (c) In a context quite different from banding, isolated lamellae in the form of uniformly twisted helicoids have recently been found in crystallization of high molecular weight PE from gels.[31] Dislocations were not involved but the circumstances were certainly conducive to development of surface stresses. (These helicoids are reminiscent of an earlier observation by Keller and Sawada.[32])

Poly(vinylidene fluoride)

Detection and measurement of chain tilt in polymer crystals under the electron microscope requires careful application of selected-area diffraction and/or dark-field techniques in combination with a goniometer stage. That the situation in α-PVF_2 may deserve closer scrutiny first drew our attention when Bassett, Olley, and Raheil[4] cited banding in α-PVF_2 along with supposed absence of chain tilt as a case against our proposals. However, neither their claim that lamellae in the banded spherulites are flat nor an early study of solution-grown crystals of α-PVF_2 by Okuda et al.[33] appeared to us adequate to support definitive assignment of chain tilt. Our colleague, Dr. A. J. Lovinger, then examined crystals (multilayered aggregates) he had earlier grown from melt [see Figure 14 of ref 24] in the particular polymer (M_w = 541 000, M_n = 337 000) to which Figure 2b refers, and found a chain tilt of 25° about the **b** axis (radial in spherulites). One of us has recently joined with him in confirming the result directly for lamellae in spherulites.[17] Existence of such a tilt might have been anticipated, given that a chain tilt of 28.5° had been known for some time in γ-PVF_2[34] and the fact that in chain axis projection the unit cells of α- and γ-forms differ in area by no more than 0.2%. Whatever the congestion in fold surfaces of one, it cannot be much different in the other. The close analogy between banding in PE and in α-PVF_2, illustrated in Figure 2b, apparently reflects a close analogy in morphological circumstance.

Bassett, Olley, and Raheil made a point also of having observed chain tilt in S-bent lamellae of γ-PVF$_2$, whose spherulites exhibit an unusual morphology devoid of banding. More recently, Vaughan[7] has shown that lamellae in this polymorph are strongly curved around radii, being virtually scrolled. He too remarked that the model of Keith and Padden does not account for observed behavior, specifically absence of banding. We point out in return that there are *two* truly exceptional features of γ-PVF$_2$ spherulites, surely not unrelated. Apart from the unusual lamellar packing, it is very rare for a polymer to crystallize directly into a strongly polar structure within relatively wide lamellae. Dipoles distributed along the chains in γ-PVF$_2$ line up in directions roughly across the widths of lamellae, and fringing fields would not only be relatively strong but of considerably longer range than in the case of an isolated dipole. A scrolled interleaving of lamellae that are oppositely poled might well be a favorable arrangement. Be that as it may, we suggest that bending moments associated with chain tilt are present and partly relieved by curvature; in this instance, however, the influence controlling how curvature and lamellar organization develop would appear to be electrostatics. In overgrowths on γ-PVF$_2$ lamellae grown in thin films of melt the prominence of (020) facets *normal* to the radial growth direction (**b**) in spherulites[34] is another unusual feature that doubtless reflects a strong influence of electrostatics. Facets in such overgrowths are interfaces between crystal and air rather than between crystal and melt of considerable dielectric constant; there is then good reason for development of (020) facets over which the normal component of dielectric displacement (**D**) is essentially zero.

Polymers Other Than Polyethylene and α-Poly(vinylidene fluoride)

In effect, banding represents a chirality at the level of lamellar organization that, in turn, reflects some chiral influence at molecular level. In addition to chain tilt around radial axes, as already discussed in the cases of PE and α-PVF$_2$, there are several other chiral factors that might arise with chain molecules, and these various influences, singly or in combination, all appear to contribute to banding in various polymers. Although it is rare, some polymers exhibit chirality at the most basic level by existing in chemically enantiomeric forms; poly(D-(−)-3-hydroxybutyrate), for example, is an optically active polyester produced by microorganisms, and optically active poly(epichlorhydrin) has recently been synthesized in both *R* and *S* forms.[35] Otherwise, none of the chain molecules of immediate interest is optically active, although many adopt helical conformations. In such cases, however, there is usually compensation in that helices of right and left hands are equally populous, and in crystals they either pair off or else pack each surrounded by nearest neighbors of opposite hand. Banding, accordingly, is rare in these polymers, not only for this reason apparently but also because chain (axis) tilt is usually absent (molecular packing fractions are commonly smaller with helical conformations). On the other hand, there are numerous polymers whose extended conformations are not helical, including PE, PVF$_2$ and many polyesters and polyamides, which do exhibit banding with small ($<10\ \mu$m) spacings. Chain tilt appears to be the vital common factor in these polymers although, in terms of regulating chirality, not necessarily so directly or decisively as in PE or α-PVF$_2$.

Our intention in the following is not to undertake a general review of specific polymers but rather to assess within classes of behavior the extent to which interpretations discussed in earlier sections might apply or need extension. We shall note points in need of clarification, particularly where there are immediately promising opportunities for continuing research.

(a) Polyesters and Polyamides. Behavior in these polymers of relatively low crystallographic symmetry strongly supports a view that, in the absence of enantiomorphism or helical conformations, chain tilt is a rigid requirement for banding to occur although, as we have seen with γ-PVF$_2$, it does not ensure it. In spherulites of triclinic polymers it would indeed be surprising for chain tilt not to have a component around radii that could influence chirality of twisting in some manner akin to what we encountered in PE. These are not easy materials for study, however, and little is yet known about morphology in the banded spherulites they tend to produce at small size under restricted experimental conditions. Familiar examples are poly(ethylene terephthalate) and the polyamides nylon 6,6 and nylon 6,10. An exceptional case that seems significant is that of nylon 6, which (to satisfy unusual requirements for hydrogen bonding) crystallizes in a monoclinic cell with chains normal to the basal plane; not only is absence of chain tilt in lamellae well established in this polymer[36] but its spherulites appear never to show any hint of banding. It would be interesting to know if higher homologues, nylon 8, nylon 10, etc., behave similarly.

Among aliphatic polyesters of ethylene glycol, those that crystallize in orthorhombic structures do not show banding in their spherulites. On the other hand, the adipate, suberate, and sebacate polyesters all crystallize in monoclinic structures, almost identical in chain-axis projection, and all form similarly banded spherulites.[37−39] In each case, the **a** axis of a unit cell is radial and chains (in **ac** planes of reflection symmetry) are tilted by about 25° *toward* the radius. Hence there is presumption of bending moments about *transverse* **b** axes, but seemingly to net chiral influence. Lamellae in such circumstances, particularly when also under radial tension during growth (see Figure 5), might well become helical in the manner we simulated in some early experiments (see Figure 3 of ref 3). They would, however, be free to adopt either hand of twisting in response to an initial chance stimulus. There is yet another puzzling aspect to banding in these spherulites. It is quite clear, from their double-ringed extinction patterns (which correspond to twisting of biaxial indicatrices precisely about optic normals that are *perpendicular* to symmetry axes (**b**)) and also from electron diffraction studies, that throughout the spherulites lamellae with chains tilted toward and away from the growth direction are equally populous and in some manner superimposed or interleaved.[39] How within densely packed lamellae these features relate to one another and to chirality is unclear, and appeal to possibility of isochiral dislocations seems no less beset by difficulties. This is notably an area calling for renewed morphological investigation aimed at illuminating specific questions. Marked contrast with banding in PE spherulites is further emphasized by very small dependences of spacing upon crystallization temperature; plots of log *S* vs log ($1/\Delta T$) yield modest slopes ∼ 1.25, indicative of significant differences in mechanism. Reemphasizing the pre-eminent role of chain tilt, we cite the behavior of poly(ethylene

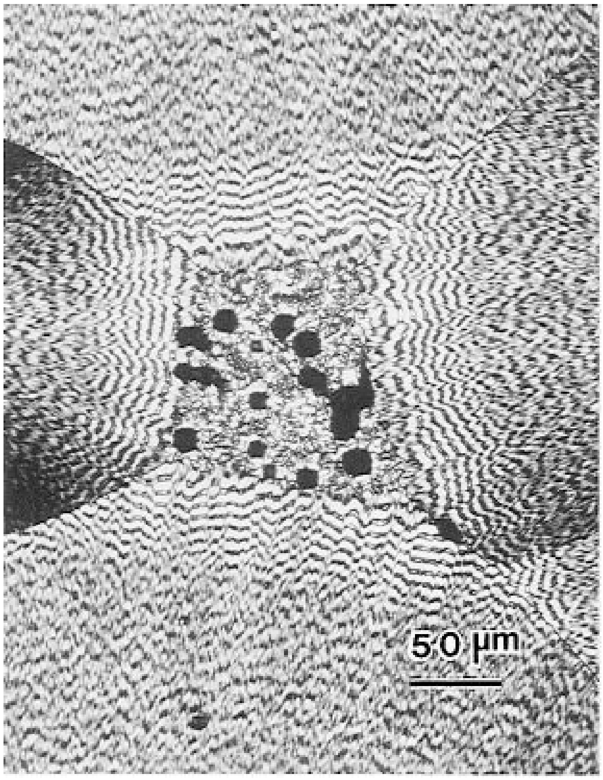

Figure 5. Illustration of radial tension in growing spherulites. When a pocket of melt becomes trapped between growing spherulites, radial tension is no longer relieved by viscous flow and cavitation soon results, with dense nucleation at newly created surfaces. Note the effect on incipient banding of increasing radial tension (which may not be entirely mechanical since supercooling will also change). The spherulites were grown isothermally at 58 °C in a blend of poly(ethylene sebacate) with 1 wt % poly(vinyl butyral)—see ref 40. (Crossed polarizers are at 45° to edges of the field.)

azelate), which is orthorhombic with spherulites generally not banded; when blended with 1−2% poly(vinyl butyral), however, it crystallizes as a monoclinic polymorph with a chain tilt ∼ 27° and its spherulites are then banded with a spacing of about 4 μm.[40]

The point has been made elsewhere[3] that absence of chain tilt in solution-grown crystals does not rule out the possibility that modest tilt may develop in corresponding crystals grown from melt, since these may have greater disorder in their fold surfaces. Such a possibility may underlie some instances in which fairly widely spaced banding appears in unusual circumstances as, for example, in poly(ϵ-caprolactone) where it occurs only at crystallization temperatures close to the highest attainable[41,42] (in this case $\log S$ vs $\log(1/\Delta T)$ has slope about 3.5, not inconsistent with such a view). Behavior in this polymer, however, can change drastically upon blending with uncrystallizable diluents.[40]

(b) Polymers in Helical Conformations. Banding is rare in helical polymers and where it does occur, invariably with large spacing, it is a response to an influence whose very weakness makes its identification all the more difficult. Moreover, there are few examples, apparently because chain tilt is rare in these materials. Poly(ethylene oxide), however, is monoclinic with a chain tilt but in our experience it forms banded spherulites (spacings 100−200 μm) only when the content of relatively short chains is fairly large.[43] Chain folding in the monoclinic α-form of isotactic polypropylene is complicated by multisectoring[44] and by a unique branching mechanism[45] but chain tilt, if any, is small so that absence of twisting in spherulites is not surprising. On the other hand, in lamellae of the trigonal β-form chain tilt appears to be absent yet within a limited range of crystallization temperature spherulites are banded, with spacings varying from 75 μm at 125 °C to 90 μm at 133 °C. Curiously, these spacings pass through a minimum of 60 μm at 128 °C (values for polymer of molecular weight 178 000).[46] The manner in which helices pack in this polymorph is still uncertain and compensation by right- and left-handed helices might not be well regulated.[47,48] There is no question that understanding of banding in polymers of this class is at present seriously lacking. However, in an early electron microscopic study comparing replicas of banded and unbanded spherulites, both in PEO and β-PP, we noted that lamellae seem appreciably wider in banded than in unbanded structures; this suggested that, in some cases at least, appearance of banding may not be an indiction of onset of twisting so much as of conditions such that interleaving of twisted lamellae begins to enforce cooperative phasing.

(c) Enantiomorphic Polymers. Polymers in this category are common in biology, but of these, poly(D-(−)-3-hydroxybutyrate) (PHB) is the only one known to us that crystallizes from melt to form banded spherulites.[49] Our experience has been that banding in this polymer *invariably* involves twisting that is left-handed. (Such identification must be made carefully using a Fedorow universal stage; spherulites grown in a film between cover slips may nucleate at either surface, causing them to present different extinction patterns that to the unwary suggest twisting with opposite hands.[12]) In spherulites of the two enantiomeric forms of poly(epichlorhydrin) (PECH) Singfield, Klass, and Brown[50] have recently shown that banding is in each case exclusively of one hand dependent upon the chirality of the constituent enantiomer. In addition, they emphasize direct evidence from atomic force microscopy that lamellae twist smoothly. (Crystallization in an equimolar blend of polyenantiomers yields unbanded spherulites consisting of relatively flat lamellae.) These authors consider that isochiral helices attach to growth faces with slight rotation between successive layers and that the key factor determining hand of twist is chiral identity of the chains. We share their view and, indeed, had suspected something of the kind in PHB where, in addition to twisting with one hand only, banding (with strong dependence of spacing on crystallization temperature) occurs only at unusually large supercooling (>80 °C), behavior very different from that in Figure 2. We did not have means to experiment with reversed or mixed chiralities, but were struck by resemblance to a long known correlation between enantiomorphism and twisting in monomeric compounds, and by a tantalizing analogy with chirality in the packing of asymmetrical molecules in cholesteric liquid crystals. Heuristic value of such an analogy is very limited, however, since cholesteric phases and their rapid variation of pitch with temperature are themselves poorly understood. Whether or not chain tilt is involved in PHB or PECH is uncertain but, in any event, laying down successive sheets of inevitably ill-fitting isochiral helices on a crystal surface imposes its own repeating chiral influence. Such an influence could well be potent and it is no surprise that spacings reach down to values substantially less than 10 μm in both PHB and PECH. That behavior is very different from that in PE or α-PVF$_2$ is clearly signaled by slopes in log S vs log($1/\Delta T$), about 15 in PHB and about 1.5 in PECH.

Summary and Conclusions

From the foregoing it scarcely needs emphasis that a supposed "unique cause" for twisting orientation in banded polymer spherulites is a chimera. (In effect, Bernauer[1] reached a similar conclusion about banding in monomeric compounds and minerals in his classic text of 1929 on twisted crystals.) Situations vary considerably from polymer to polymer. Our information is most extensive in the case of polyethylene and, even then, it is still open to the reader to assess and build upon existing interpretations. It seems fair to say that in cases in which twisting can be vigorous (band spacings $\leq 10\,\mu$m) one or other of two factors is certainly involved. These are (i) chain tilt, which promotes a generation of surface stresses in lamellae that translate in various ways into torques about radii, and (ii) isochiral helicity as in the case of polyenantiomers. Insofar as isochiral dislocations are involved in such cases it appears to be in a secondary role. In other circumstances, involving twisting with large pitch, interpretation is more problematical; the above major factors could operate in less potent form and, in addition to the ever-present possibility of isochiral dislocations, there are other circumstances such as imperfect compensation of chirality in the packing of symmetrical molecules in helical conformation. It seems that careful appraisal of many well-directed (and, as far as possible, quantitative) morphological studies, in combination with more critical theoretical investigations than any yet formulated, will be needed to reach significantly better understanding in this extensive subject.

In concluding, we make the obvious point that (i) above played no part in materials studied by Bernauer and his contemporaries and observe that in their spherulites, being comprised of smoothly twisted acicular crystals rather than interleaving lamellae, bands generally became increasingly jagged and ill-coordinated with increasing radius. Enantiomorphism and chiralilty of structure, on the other hand, played a larger part than they realized; natural products used as supposedly inert thickners were not, in fact, without some chirality of structure, and some compounds with cubic space lattices (sodium bromate is an example) are now known to be enantiomorphic.[51] Even so, there still are puzzling cases such as hippuric acid, which has no evident chirality of structure and yet consistently produces beautifully banded spherulites when crystallized from melt.[52]

Lastly, we note that, although banding as we have used the term (to describe smooth twisting of orientation as averaged on the scale of light-optical resolution) is a common feature of polymer and other spherulites, the term is also applied legitimately to other phenomena encountered in inorganic, and especially in mineral, spherulites. In such cases material density or crystallinity vary periodically with radius (usually on a fairly coarse scale) with or without repeating discrete changes in orientation. An instance of such behavior in a dilute blend of α-PVF$_2$ with poly(ethyl acrylate) has recently been reported by Briber and Khoury.[53] We have omitted this in the above survey since, although there are bands of extinction, the morphology seems distinctly different.

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Appendix 1: Experimental Procedures

Rates of primary nucleation are usually large in polyethylene melts, particularly in polymer of higher molecular weight or polymer in which a preferred molecular orientation has been induced. The procedure seemingly best suited to preparing relatively large spherulites for optical microscopy, equally applicable to blends as to virgin samples, is to cast films of melt upon clean #1 microscope cover slips held at slightly above $T_m°$ (145 °C), cover them with similarly heated slips pressed gently to establish contact, and plunge the sandwiched specimens into a thermostatically controlled (±0.1 °C) silicone oil bath at desired crystallization temperature. Commonly, we cast polymer from 1% w/v solution in distilled xylene and allowed 2−3 min after visible signs of complete evaporation before covering; results so obtained were indistinguishable from those obtained with films dried thoroughly in a vacuum oven. As far as possible, heated specimens were maintained under nitrogen to minimize oxidation and, as a further precaution, traces ($\leq$0.1% of polymer content) of antioxidant were often added to casting solutions.

Band spacings were measured either directly under a microscope using a filar eyepiece micrometer or from photomicrographs taken at calibrated magnifications. Where possible, bands with large curvature near centers of spherulites were avoided, and measurements made over as many bands as possible in several spherulites in each of a number of similar specimens were averaged. A convenient feature of specimens prepared in the above manner was that most films were sandwiched between glass in continuous broad annuli around their peripheries but were thinner, at times considerably thinner, near their centers where they crystallized open-faced but protected from silicone oil. This permitted easy comparison of band spacings in films of different thickness or, in films of comparable thickness, between those that were open-faced and those enclosed between glass surfaces. Except for very thin weakly birefringent regions where spacings tended to be slightly smaller, we found no systematic variations of significance other than around outer fringes of specimens where coarser textures and larger spacings (attributable to plastication by oil and/or oxidative degradation) were easily recognized and avoided. Constancy of band spacings along radii, together with estimates of heat transfer in relation to crystallization kinetics, indicated that crystallizations were effectively isothermal at temperatures down to 110 °C or slightly lower.

Appendix 2: Formation of Isochiral Dislocations

Growth of facetted crystals at appreciable rate is invariably influenced by diffusive processes, and spreading of layers from protuberant corners where surface nucleation is favored is a prominent concern. Faster generation of new layers at these corners places greater demands upon diffusion for availability of crystallizable units, and from this alone it can be shown that spreading layers tend to bunch together and build into steps many layers high which move more and more slowly as they do so.[54,55] This is the origin of the steps (lacunae), like the teeth of a saw, that are familiar features of growth faces on dendritic polymer crystals,[10,26] and also to be expected at transient stages in growth of a lamella such as we have depicted in Figure 4. Here these multilayered steps separate facets close to (110) or $(\bar{1}10)$ in index (only close because of monomolecular layers still spreading on them) and act like slow-moving re-entrant corners.

Whereas re-entrant corners stimulate surface nucleation in monomeric compounds, they behave quite differently in polymers. Entropic barriers significantly impair penetration of crystallizing macromolecules into such corners and, indeed, this underlies the asymmetrical lateral growth of polyethylene lamellae on substrates.[5] When the movement of a step becomes sufficiently slow, the advance of surface layers in its immediate vicinity might be as indicated by arrows at the first step on the left shoulder of the lamella in Figure 4. In any event, if a reluctance of chains to penetrate into the corner should then give rise to a few adjacent rows of vacant stem sites extending in from the growth front, they would create a defect that, with small likelihood of healing itself, would grow into a slit or tear of increasing length while blocking layer spreading from either direction. Successive positions of growth fronts around such defects are indicated for both sides of the lamella as 1, 2, and 3 on the schematic. (Knowing what to look for one can often recognize very narrow slit defects of this kind at re-entrants in dendritic crystals). These fronts can only advance normal to themselves until out-of-plane displacements develop to a stage at which growth can resume on otherwise inaccessible sides of a slit. The overlapping character of this continuing growth then establishes what topologically are giant screw dislocations. For these to be isochiral requires a compelling reason for the displacements to be controlled accordingly.

Considering behavior around slit defects on either side of the lamella, we emphasize areas of likely faster and slower growth (the disparity would not be large) by symbols F and S. Moments responsible for S-bending would produce displacements from the mean plane of the lamellae indicated by U or u for "up" and D or d for "down", capital letters indicating regions where displacements would be larger. Disparities in this case are attributable both to relative distances off-axis and to the possibility that, where growth is faster, there has been less time for relaxation of bending moments. Once overlapping growth begins, it would be as indicated, thereby initiating dislocations that in this case are clearly right-handed at both sides of the lamella. Occasional generation of dislocations of opposite hand as a result of fluctuating circumstances is not ruled out, but there would be a strong preference for dislocations to be isochiral with one another and with lamellar twisting.

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