Banding in Spherulites of Polymers Having Uncompensated Main-Chain Chirality

I. Saracovan,[†] H. D. Keith,[‡] R. St. J. Manley,[†] and G. R. Brown*[,§]

Department of Chemistry, McGill University, Montreal, QC, Canada H3A 2K6; Institute of Material Science, University of Connecticut, Storrs, Connecticut 06269-3136; and Faculty of Mathematics and Science, Brock University, St. Catharines, ON, Canada L2S 3A1

Received July 16, 1999; Revised Manuscript Received October 20, 1999

ABSTRACT: The study of twisting crystalline orientation in banded polymer spherulites has recently been revitalized by availability of optically active macromolecules that crystallize exclusively in isochiral (uncompensated) helical conformations. In such cases, handedness of twisting appears to be rigidly controlled by chirality of molecular conformation, and the twisting itself appears to derive from causes other than those believed to apply in optically inactive polymers. We discuss and evaluate methods for determining handedness of twisting, particularly in tightly banded spherulites, and illustrate them by application to poly(3-hydroxybutyrate), poly(3-hydroxyvalerate), and to enantiomeric polymer pairs in the cases of poly(epichlorohydrin) and poly(propylene oxide). Although rigidly controlled twisting in such polymers commonly shares the handedness of the underlying molecular conformation we have clear evidence in poly(3-hydroxyvalerate) that such a correlation is not universal.

Banding in spherulites, i.e., the presence of radially periodic structure attributable to a twisting of crystallographic orientation about radii that usually give rise to concentric rings or bands of extinction in polarized light microscopy, is a common occurrence and has been studied for more than a century. In early work upon minerals such as chalcedony and upon many organic and some inorganic compounds, correlation was found in almost all cases between such banding and chirality of molecular structure. This chirality was evidenced by optical activity, either of a nominally pure compound or of an active additive alloyed with an otherwise optically inactive host. However, correlation between handedness of twisting and the character of optical activity (*R* or *S*) was not straightforward in that a given optically active additive could on occasion produce twisting of opposite handedness when incorporated in different polymorphs of the same host. Details of this work (ca. 1890−1930), which failed to clarify mechanisms, can be found in sources we cite later[15−17] or in Bernauer's classic monograph on twisted crystals.[1]

Stimulated by the work of Keller[2] and Point,[3] the subject was revitalized in 1955 with a focus now upon synthetic polymers. Banding has been found, for example, in spherulites of many polyolefins, polyesters, and nylons but, surprisingly, without the agency of chiral influence detectable by optical activity. (In these polymers, whose molecules are devoid of asymmetric carbon atoms but may adopt chiral molecular conformations in crystal or melt, there is compensation (racemization) since right- and left-handed helices in like concentration are intimately associated.) In such banded spherulites, radially oriented lamellae twist cooperatively with one or other hand throughout given sectors; however, there is no overall preponderance of either hand within specimens containing several spherulites. A key factor in such banding in optically inactive polymers is "chain tilt", i.e. a situation in which molecular stems in chain-folded crystals are oblique to fold surfaces.[4−6] The manner in which chain tilt is believed, under various conditions, to induce unbalanced surface stresses and thus cause crystals to twist is discussed elsewhere (together with experimental support for that interpretation).[6]

Until recently, study of banded spherulites in those polymers that do exhibit optical activity has been confined to biological material of bacterial origin, notably poly(3-hydroxybutyrate) (PHB). In this case, evocative of early studies, molecular helices in crystals are isochiral and twisting of orientation is likewise of one hand only, both being left-handed.[6,7] An important new advance has been the development of means for preparing some polymers, poly(epichlorohydrin) (PECH) and poly(propylene oxide) (PPrO) in particular, in pure *R* and *S* enantiomeric forms.[8] Together with poly(3-hydroxyvalerate) (PHV), also of bacterial origin and like PHB exclusively in the *R* configuration, these polymers have afforded a long-awaited opportunity to develop phenomenology from which might emerge a clearer understanding of how banding arises in spherulites of enantiomeric materials (in such polymers chain tilt appears to be irrelevant[11]). Some results have already been reported,[9−11] and it is likely that as more enantiomeric polymer pairs are synthesized this will for a time remain an active field of research. Our purpose here is twofold: (a) to comment upon various methods applicable to the not-so-simple task with closely banded spherulites of reliably assessing twisting orientation as regards direction and its consistency and (b), by way of illustration, to report our investigations on PHB, PECH, PPrO, and PHV polymers which confirm and, to a degree, extend conclusions of other workers.

Although band spacings in polymer spherulites (increments in radius corresponding to rotation of orientation by π) may vary from less than 1 μm to almost 200 μm, most are about 10 μm or less. Within limits, higher crystallization temperature and moderate rather than high molecular weight tend to yield larger spacings in

[†] McGill University.
[‡] University of Connecticut.
[§] Brock University.
* To whom correspondence should be addressed.

10.1021/ma9911602 CCC: $18.00
Published on Web 12/07/1999

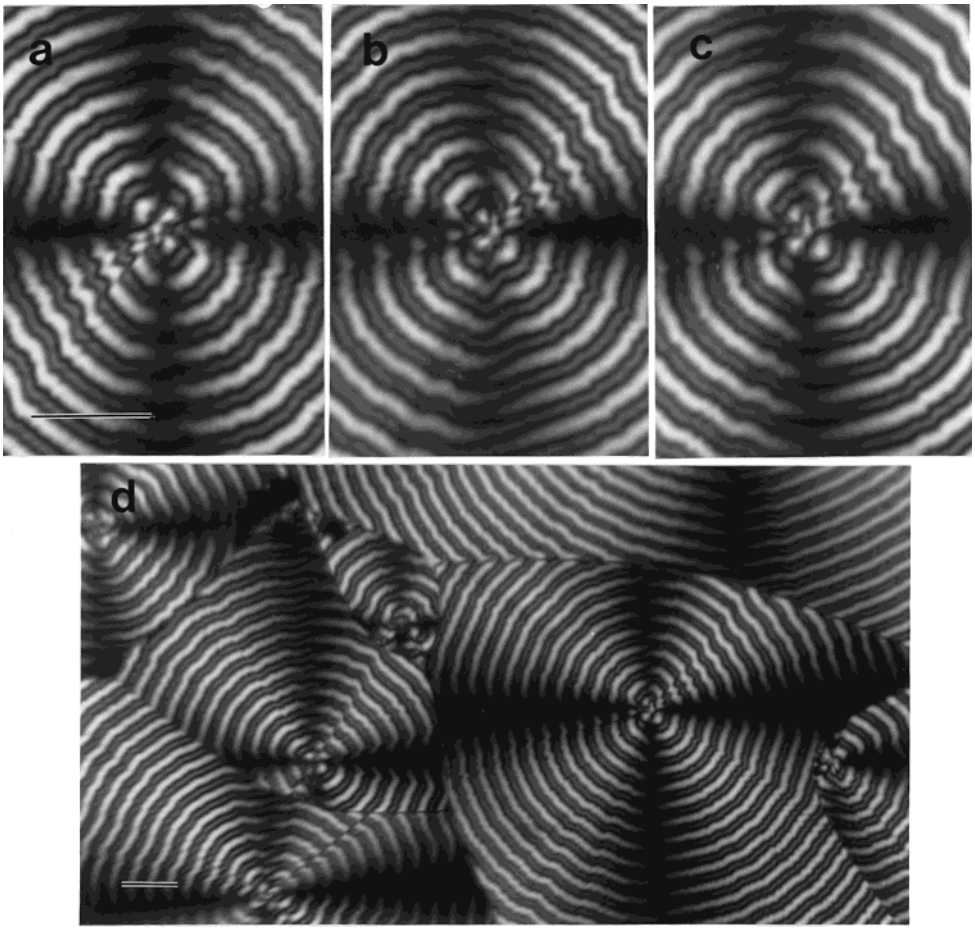

Figure 1. **(**a, b, c**)** A spherulite of PHB tilted at $\psi = 0°$, $\psi = +7°$, and $\psi = -7°$, respectively. **(**d**)** A field showing several such spherulites and consistency of left-handed twisting ($\psi = -7°$). The scale bars represent 25 μm.

a given polymer. Ideally, specimens for optical examination should show birefringence still in the gray-white range of interference color, implying a thickness no more than about 10 μm and, in the case of very small band spacings, less if possible. However, one must often make do with best efforts. Consideration of spatial resolution shows that, for identification of twist direction, neither conoscopic methods (as used by early workers on monomeric compounds with band spacings varying from 0.05 to 1.0 mm) nor microbeam X-ray diffraction holds promise of utility. In choosing between the alternatives of light microscopic methods based upon optical properties averaged over volumes of order 1 μm^3, on one hand, and direct observation of individual twisted crystals (easily resolvable in principle by electron microscopy), on the other, the latter may at first seem distinctly preferable. In terms of versatility, speed of execution, and reliability and ease of interpretation, however, this has generally proved not to be the case in the present context (see below). In most circumstances, polarizing microscopy using a Fedorow universal stage to achieve controlled tilting of specimens has with comparative ease provided clearly unambiguous indications of twisting direction along given radii, and often in a manner that permits very rapid survey for consistency over large areas of specimen. In this regard there are two related approaches which, following some preliminary details about the materials studied, are described below.

Although the four polymers of immediate interest all crystallize in orthorhombic structures [PECH ($a = 12.16$ Å, $b = 4.90$ Å, $c = 7.03$ Å); PPrO ($a = 10.46$ Å, $b = 4.66$ Å, $c = 7.03$ Å); PHB ($a = 5.76$ Å, $b = 13.20$ Å, $c = 5.96$ Å); and PHV ($a = 9.32$ Å, $b = 10.02$ Å, $c = 5.56$ Å)] and are accordingly optically biaxial, each with dissimilar principal refractive indices $N_3 > N_2 > N_1$, they present quite different optical situations in their spherulites. In PHB spherulites the intermediate axis of the indicatrix (optic normal), N_2, is radial and, as viewed between crossed polars, there are double rings of extinction with alternating broad and narrow bands of positive and negative birefringence, respectively (see Figure 1). Inspecting the unit cell[12] with its obvious disparities in polarizability along *a*, *b*, and *c* axes, we can at once identify *a* (known to be radial[7]) with N_2, *b* with N_1, and *c* (chain axis) with N_3. In PPrO (see Figure 2), what appear to be single (but may well be unresolved double) extinction rings superimposed upon uniformly negative birefringence suggest pseudouniaxial character with closely similar polarizabilities ($N_1 \approx N_2$) normal to the chain axis *c* and thus to N_3. However, even knowing from microbeam X-ray diffraction that *b* is radial (see legend to Figure 3), we cannot without other information correlate it with N_1 or N_2. In PECH spherulites, there is no extinction other than a Maltese cross along the axes of polarizer and analyzer, but there are concentric bands weakly delineated by smooth alternation of greater and lesser negative birefringence (reminiscent of cos^2 interference fringes). Microbeam X-ray diffraction shows *b* to be radial (Figure 3a) and therefore to be identical with N_1. N_3 is doubtless along *c* and N_2 along *a*. In PHV, there are similarly weakly delineated bands but here superimposed upon positive birefringence, indicating an unusual situation in which N_3 must be radial; however, because of chain-folding,[11] N_3 *cannot*

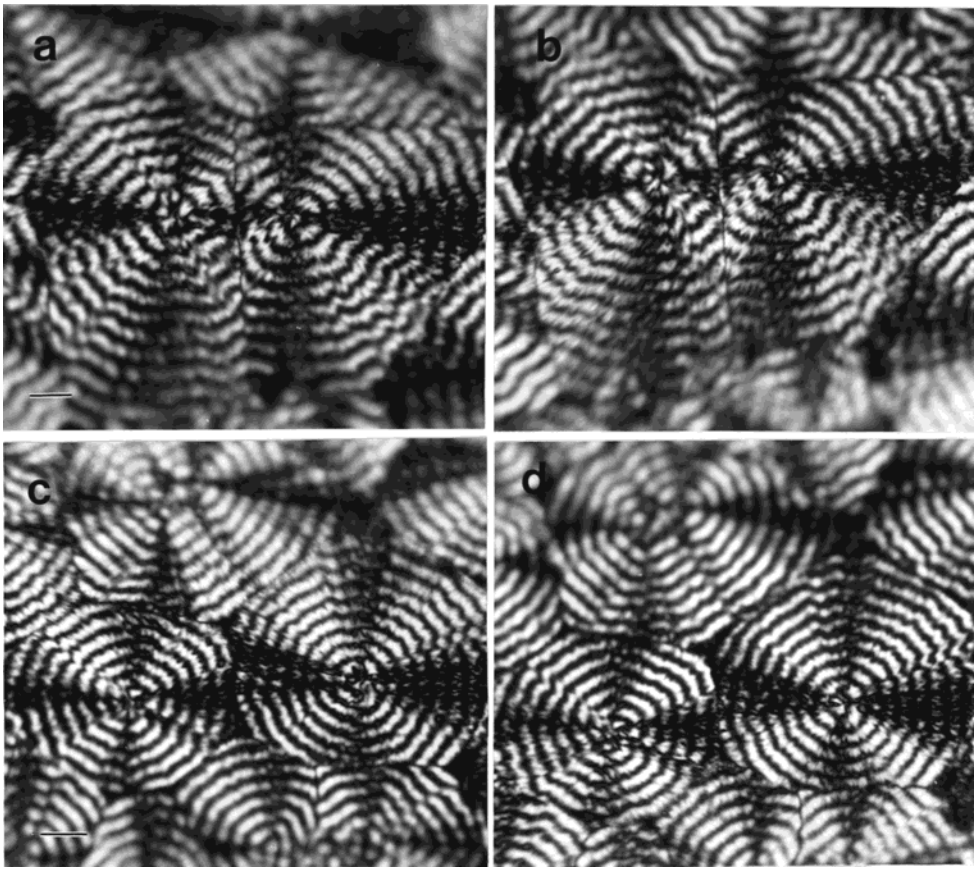

Figure 2. **(**a, b**)** Spherulites in *(R)*-PPrO tilted at $\psi = +20°$ and at $\psi = -20°$, respectively. (c, d**)** Spherulites in *(S)*-PPrO tilted at $\psi = +20°$ and at $\psi = -20°$, respectively. The scale bars represent 25 μm.

in this case be associated with chain axis *c*. It is evident from the crystal structure[13] that, in comparison with PHB, molecular helices are compressed along *c* and transverse polarizabilities are considerably enhanced by larger side groups. Microbeam X-ray diffraction in this case has shown that *b* is radial (Figure 3b), but whether *c* is to be associated with N_1 or N_2 is difficult to judge from likely polarizabilities.

There are two principal consequences of tilting banded spherulites under the polarizing microscope. There will always be movement of bands,[14] but in each case this is limited to at most one-third of a band spacing since practicable tilts from the plane of focus are restricted to the range $-30°$ to $+30°$. A more useful approach when there are rings of extinction, as is common, is tilting about an axis parallel to one arm of an extinction cross; this then provides a sensitive indication of twisting along the perpendicular arm in the form of its developing a zigzag character. In Figures 1 and 2 we show, in a conventional manner, the results of tilting about a horizontal *OX* axis (parallel to polarizer) and note behavior along $\pm OY$ axis for various tilts ψ which are reckoned to be positive if right-handed about *OX*, i.e., a positive ψ corresponds to raising $+OY$ and lowering $-OY$. In both uniaxial and biaxial spherulites the inclinations of zigzags reverse on changing the sign of ψ, and would also reverse (without changing sign of ψ) upon reversal of the hand of twisting. Analyses of this behavior may be consulted,[15-17] but the essential results may be stated simply.[18] For right-handed twisting and positive ψ the zig along $+OY$ is inclined from lower left to upper right and the zag along $-OY$ from lower right to upper left. Note in Figure 2a,b how this arrangement for positive ψ and its mirror image for negative ψ indicate right-handed twisting in *(R)*-PPrO and how its opposite (Figure 2c,d) denotes left-handed twisting in *(S)*-PPrO. Such departure from simple extinction arms along the $\pm Y$ axes is so sensitive to tilting that slight nonplanar orientation attributable to nucleation at one confining surface is often apparent without tilting.[15] It is then vital to judge behavior by tilting away from a condition without zigzag (a locally effective zero of ψ). There are several important advantages to this technique. It is applicable even to very small ($\approx$2 μm) ring spacings, in both uniaxial and biaxial spherulites, merely by qualitative observation without further specimen preparation, and it is especially convenient for assessing consistency over large areas of specimen (see Figure 1d).

As for the movement of rings, it is obvious that with right-handed twisting rings will move to the left with increasingly positive tilt and conversely with left-handed twisting or oppositely directed tilt. However, such movement along *OX* tends to be obscured by extinction. It is then appropriate to rotate polarizer and analyzer into crossed positions at $\pm 45°$; even then, reliable fiduciary features are required for reference in photography. Singfield, Hobbs, and Keller[10] used boundaries in films for this purpose in establishing right-handed twisting in *(R)*-PPrO with a band spacing of 16.4 μm, left-handed twisting in *(S)*-PPrO with a spacing of 11 μm and similarly in PHB with a spacing of 11 μm. This method is also applicable to bands not associated with extinction. In *(R)*-PECH and *(S)*-PECH spherulites with 2.75 μm band spacings, we have just been able (using a 40$\times$ objective) to detect motion during tilting that indicates right-handed and left-handed twisting, respectively. In Figure 4 we show the use of adventitious

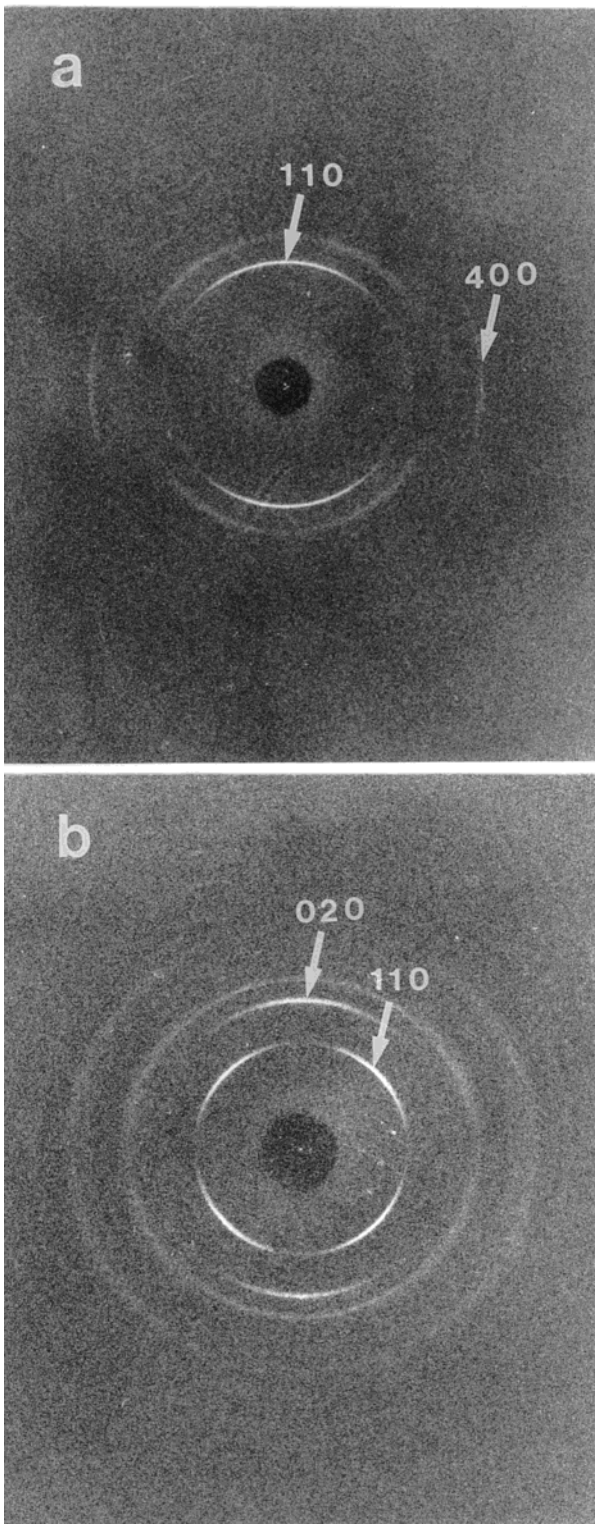

Figure 3. Microbeam (selected area ≈50 μm in diameter) X-ray diffractograms indicating orientation of unit cell relative to (vertical) radial direction in **(**a**)** PECH and **(**b**)** PHV. The *b* axis is radial in both cases and has similarly been found to be so in PPrO.

motes as fiduciaries in establishing right-handed twisting in PHV with a relatively small band spacing of 7.1 μm and total ring movement <2.4 μm. This last result was reported previously without detail[11] and is significant in that *(R)*-PHV helices are believed to be left-handed.[13] As with monomeric analogues there appears, therefore, not to be a simple correlation between chirality (helicity) and direction of twisting. Together with

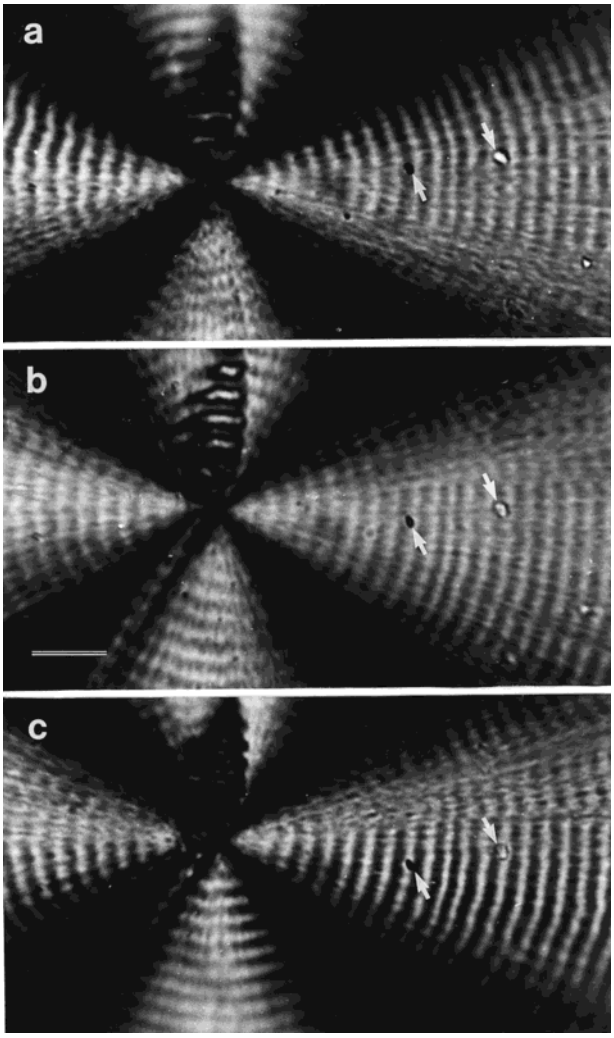

Figure 4. Movement of bands relative to two motes acting as fiduciaries in a spherulite of PHV. Tilts are $\psi = -30°$, 0°, and +30° in **(**a**)**, **(**b**)**, and **(**c**)**, respectively. Tilting is about a horizontal axis with polars at ±45°; note that smooth leftward movement in **(**a**)**−**(**c**)** indicates right-handed twisting and extends in all over one-third of a band spacing. The scale bar represents 25 μm.

very slight rotation (0.018° with band spacing 10 μm and interplanar spacing 10 Å) between successive planes of molecules transverse to radii, this suggests (in a manner analogous to the origin of thermal expansion in solids) a role of anharmonicity in thermal vibrations dominated by the most strongly repulsive intermolecular contacts in specific ill-fitting crystalline packings. Band spacings in Figures 1, 2a, and 2c were 8.0, 11.3, and 9.04 μm, respectively; in the hope that it may help later workers we again emphasize the superiority of the zigzag method (especially with small band spacings) when it is applicable.

All of the above refers to what an observer with superhuman eyesight would see. It also corresponds to what would be seen at the focal plane of a photomicrographic camera vertically above the specimen because two inversions of image, one by the objective lens and one by the projection eyepiece, would then restore a true representation of the object. As seen in the microscope, however, there is generally a single image inversion which causes all of the above to be reversed. Observers should check their instruments carefully. Even experienced workers find it advisable at the outset to draw up for ready reference a chart of what is to be expected

in various circumstances! As a final note of caution to the unwary, we point out that, for various reasons, banding may display a tightly wound spiral character. This is not unrelated to twisting but of itself provides no indication of its handedness, as is obvious from noting that turning a specimen over changes the direction of spiralling but not that of twisting; spiralling is commonly another manifestation of nonplanar orientation in the specimen.

Whereas individual twisted lamellae grown from solution or gel have been seen clearly by electron microscopy,[19] their counterparts in banded spherulites are so intergrown and closely packed as mostly to render interpretation of direct transmission micrographs quite ambiguous. Although calling for considerable manipulative expertise, surface replication and scanning (SEM and AFM) methods are useful as confirmatory tools, but further development and experience may be needed to make them capable on their own of yielding definitive determinations of twisting.

Acknowledgment is made to the Petroleum Research Fund, administered by ACS, for partial support of this research. Additional financial support from the National Sciences and Engineering Research Council (NSERC), Canada, is also acknowledged with gratitude. Professor R. H. Marchessault (McGill University) kindly provided samples of bacterial PHB and PHV.

References and Notes

(1) Bernauer, F. *Gedrillte Kristalle*; Bornträger: Berlin, 1929.
(2) Keller, A. *J. Polym. Sci.* **1955**, *17*, 291, 351.
(3) Point, J. J. *Bull. Acad. R. Belg.* **1955**, *41*, 982.
(4) Keith, H. D.; Padden, F. J., Jr. *Polymer* **1984**, *25*, 28.
(5) Keith, H. D.; Padden, F. J., Jr.; Lotz, B.; Wittmann, J. C. *Macromolecules* **1989**, *22*, 2230.
(6) Keith, H. D.; Padden, F. J., Jr. *Macromolecules* **1996**, *29*, 7776.
(7) Barham, P. J.; Keller, A.; Otun, E. L.; Holmes, P. A. *J. Mater. Sci.* **1984**, *19*, 2781.
(8) Singfield, K. L.; Brown, G. R. *Macromolecules* **1995**, *28*, 1290.
(9) Singfield, K. L.; Klass, J. M.; Brown, G. R. *Macromolecules* **1995**, *28*, 8006.
(10) Singfield, K. L.; Hobbs, J. K.; Keller, A. *J. Cryst. Growth* **1998**, *183*, 683.
(11) Saracovan, I.; Cox, J. K.; Revol, J.-F.; Manley, R. St. J.; Brown, G. R. *Macromolecules* **1999**, *32*, 717.
(12) Cornibert, J.; Marchessault, R. H. *J. Mol. Biol.* **1972**, *71*, 735.
(13) Yokouchi, M.; Chatani, Y.; Tadokoro, H.; Tani, H. *Polym. J.* **1974**, *6*, 248.
(14) Bands caused by rhythmic crystallization excepted, but these would be irrelevant in the present context.
(15) Keith, H. D.; Padden, F. J., Jr. *J. Polym. Sci.* **1959**, *39*, 101, 123.
(16) Price, F. P. *J. Polym. Sci.* **1959**, *39*, 139.
(17) Keller, A. *J. Polym. Sci.* **1959**, *39*, 151.
(18) While preparing this article, it occurred to one of us that these results can be derived in essential detail by approximate methods much simpler than those described in refs 15−17; a note will be submitted for publication.
(19) Kunz, M.; Dreschler, M.; Möller, S. *Polymer* **1995**, *36*, 1331.

MA9911602