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Optically Active Polyethers. 3. On the Relationship between Main-Chain Chirality and the Lamellar Morphology of Solution-Grown Single Crystals

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ABSTRACT: The morphology of chiral (*R*)- and (*S*)-poly(epichlorohydrin) (PECH) single crystals grown from solution was studied to obtain insight into the mechanism by which the chiral character of the main chain can be transmitted to higher organizational levels, such as the lamellar twisting orientation in banded spherulites. Poor solvents were selected so that the crystallization from solution occurred at high temperatures, where the resulting lamellar habits simulate most closely those obtained in crystallization from the melt. Interestingly, the TEM examination of folded-chain single-crystal lamellae showed no morphological evidence that could be related to the chiral character, *R* or *S*, of the polyenantiomer. In addition, it was established that the handedness (or sense) of screw dislocations in these lamellae is not controlled by the main-chain chirality. This result supports previous evidence which shows that, although the screw dislocations may contribute to the banding through lamellar branching, they appear not to be primary determinants of either the handedness or magnitude of the twist of lamellae in banded spherulites. Similar morphology patterns were obtained for lamellar single crystals of chiral (*R*)- and (*S*)-poly(propylene oxide) and of the optically active biopolyester, (*R*)-poly(3-hydroxyvalerate), supporting the generality of these features. In searching further for chiral effects, the examination of lamellar morphology in large PECH aggregates, e.g., highly dendritic crystals and hedrites, grown from solution indicated that some of the lamellae are nonplanar while in solution. Some considerations pertaining to the factors that may contribute to the nonplanar habits observed in the morphology of these large aggregates are discussed as well.

Introduction

When observed by polarized light microscopy, melt-crystallized spherulites of certain semicrystalline polymers exhibit regularly spaced, circular birefringence extinction patterns. These “bands” are generated by an in-phase twisting orientation of lamellae in the radial growth direction.[1] Two approaches that share common elements have been proposed to describe the mechanism that leads to this banding, namely the models of Bassett[2−4] and of Keith and Padden.[5−7] In a recent elaboration of their viewpoint, Keith and Padden[7] identified two factors that contribute substantially to such twisting: (1) Chain tilting appears to be the major factor in vigorous twisting of achiral polymers. (2) For polymers with main-chain optical asymmetry, the chiral nature of the molecular chain may then determine the handedness of lamellar twist. The latter conclusion was prompted by the studies on melt-crystallized enantiomeric polymers such as poly(3-hydroxybutyrate),[7] PHB, and poly(epichlorohydrin),[8] PECH.

Although a chirality−morphology relationship in crystalline structures was earlier documented by Lotz et al.[9] for a globular protein, a potential correlation between the main-chain chirality and certain elements of lamellar morphology in banded spherulites of synthetic polymers was proposed by Singfield et al.[8] While not discounting other contributing factors, Singfield et al. suggested that the chiral identity of the molecular chain may determine the handedness of lamellar twisting and possibly the organization of lamellae in the banded spherulites of optically active polymers. More recently, the correlation between the sense of rotation of the index ellipsoid along the spherulite radii and that of main-chain molecular chirality was reported in a study of banded spherulites of the (*R*) and (*S*) enantiomers of poly(propylene oxide), PPrO, and of optically active (*R*)-PHB.[10]

Whereas previous studies[5,7,8,10] propose a correlation between the handedness of the helical chain and that of the twisting lamellae in banded spherulites, they do not provide insight into the mechanism by which the asymmetric character of the main chain is transmitted to the higher structural levels in the crystalline organization of optically active polymers. Therefore, new investigations were initiated in search of morphological habits that could be ascribed to main-chain chirality at the lamellar crystal level, i.e., (i) the individual lamella and (ii) the lamellar multiplication mechanism. Accordingly, this paper communicates the results of an investigation of the morphology of solution-grown single-crystal lamellae of PECH enantiomers, as well as two other polymers with main-chain optical activity, PPrO and poly(3-hydroxyvalerate) (PHV), which also form banded spherulites when crystallized from the melt. In addition, the morphology of complex crystal aggregates of PECH grown from solution is presented, and some considerations related to the origin of nonplanar habits of the lamellae in large crystals are discussed.

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Table 1. Melting Temperature (T_m), Average Molecular Weight ($\bar{M}_w$) and Unit Cell of PECH, PPrO, and PHV Used in Crystal Growth

	M_w ($\times 10^{-3}$ g/mol)	T_m (°C)	unit cell[c] (Å)
PECH			orthorhombic
(*R*)	1600	109	$a = 12.16$
(*S*)	1200	109	$b = 4.90$
			$c = 7.03$
			$Pna2_1$
PPrO[a]			orthorhombic
(*R*)	53	67	$a = 10.46$
(*S*)	52	66	$b = 4.66$
			$c = 7.03$
			$P2_12_12_1$
PHV	60−145[b]	109	orthorhombic
			$a = 9.32$
			$b = 10.02$
			$c = 5.56$
			$P2_12_12_1$

[a] Polydispersity index for the PPrO series varied from 1.47 to 2.00. [b] Viscosity-average molecular weight, $\bar{M}_v$, estimated using the Mark−Houwink−Sakurada constants for PHB.[14] [c] Crystallographic data were determined by X-ray analysis on racemic polymers, i.e., (*R*,*S*)-PECH,[15] (*R*,*S*)-PPrO,[16] and synthetic (*R*,*S*)-PHV.[17]

Experimental Section

Materials. The specialty chemicals, i.e., monomers and catalysts, were of the highest purity supplied by the Aldrich Chemical Co. and were used without further purification. All solvents were glass-distilled.

Polymer Syntheses. Chiral (*R*)- and (*S*)-PECH were synthesized from the corresponding monomers (enantiomeric enrichment, ee, in excess of 97%) via ring-opening polymerization using the Vandenberg coordination catalyst, $AlEt_3/H_2O$ (1:0.6).[11] Subsequently, the chiral PECH materials were fractionated by extraction with acetone (Soxhlet extractor, 24 h);[12] only the high molecular weight fractions were used for single-crystal preparations.

Chiral (*R*)- and (*S*)-PPrO samples were obtained from the corresponding high molecular weight fractions of PECH by side-chain modification reactions using $LiAlH_4$.[13] The recovered polymers were dissolved and subsequently crystallized from acetone solution at low temperatures; only the acetone-crystallizable fraction at −6 °C was used for single-crystal preparations. The NMR spectra verified complete replacement of Cl by H.

All of the samples were dried in a vacuum oven at an appropriate temperature and then stored under vacuum (no antioxidants were added). Table 1 lists relevant physical characteristics of the PECH and PPrO materials and of the (*R*) form of the optically active PHV biopolyester. The PHV used for the growth of single crystals is one of the bacterial samples described by Steinbüchel et al.[14] Its melting temperature was determined in this study while the other characteristics are taken from the literature, as indicated. All of the melting endotherms were obtained at a heating rate of 10 °C/min using a Perkin-Elmer DSC-7C thermal analysis system. The viscosity-average molecular weights, $\bar{M}_v$, of the PECH materials were determined by measurements using 1-chloronaphthalene solutions at 100 °C following the procedures described in ref 11. In the case of the PPrO samples, the $\bar{M}_w$ and the polydispersity were determined by GPC using tetrahydrofuran solutions at 22 °C, relative to polystyrene standards.

Single-Crystal Growth Conditions. Single crystals were grown under quiescent conditions in poor solvents. The growth of the PECH crystals was performed from high-purity mesitylene and 1-octanol solutions at concentrations ranging from 0.005% to 0.05% w/v. The isothermal crystallization was conducted at high temperatures, particularly when 1-octanol was used, so that single-crystal lamellae were obtained at moderate to rather low undercoolings, i.e., crystallization temperatures varying from 69 to 107 °C. The PPrO single crystals were grown in 1-octanol only, at 0.005% concentration and temperatures of 52 and 61 °C.

The undercooling, ΔT, is defined as the difference between the observed dissolution temperature, T_d, and the crystallization temperature, T_c. The T_d was determined by observing the temperature at which the crystals disappeared while heating 0.5 mg of material in 10 mL of solvent at a rate of ca. 20 °C/min. For the PECH materials in mesitylene the T_d was 97 ± 1 °C. When 1-octanol was used, the T_d coincided with the DSC melting endotherm, which was 109 °C.

For any given crystal growth, samples of the chiral pair, (*R*) and (*S*), were prepared simultaneously. They were initially heated until complete dissolution was achieved, ca. 15−20 °C above T_d. Then the flasks were immersed in a thermostatic bath preset at the T_c. At the end of crystallization period, the samples were slowly cooled (ca. 0.25 °C/min). The crystals were recovered by gentle centrifugation followed by the removal of mother liquor to concentrate the sample to ca. 20% of the initial volume. The crystals were preserved in these suspensions at room temperature until the TEM examination.

Transmission Electron Microscopy. For TEM imaging, droplets of the concentrated crystal suspension were deposited onto carbon-coated copper grids placed on filter paper. To remove the residual solvent, the grids were kept at room temperature for at least 30 min under vacuum (5−10 Torr). Subsequently, the grids were shadowed with Pt/C at a 30° angle. The images were taken on Philips EM 400 and Philips EM 400T transmission electron microscopes in the bright field mode at an accelerating voltage of 80 kV.

Electron diffraction was performed at an acceleration voltage of 120 kV on a Philips EM 400T microscope equipped with a low-dose unit. The diffraction images were obtained on unshadowed single-crystal specimens using only the previously unirradiated regions of the lamellae. Gold was used to calibrate for the measurements of *d* spacings.

PHV Spherulites. Spherulites were grown with an unrestrained top surface by isothermal crystallization of thin films at temperatures varying from 70 to 90 °C, following the procedures described in ref 8. The atomic force microscope (AFM) imaging of the PHV spherulites was performed using an AutoProbe CP scanning probe microscope (Park Scientific Instruments) with pyramidal silicon nitride tips (Microlever, 0.6 μm). The images were obtained by scanning the sample in the constant-force mode (force between 0.6 and 1.0 mN/m) at a frequency of 1.0 Hz. With the exception of flattening, no further processing of the original images was applied.

Results and Discussion

Chain Tilting. As mentioned in the Introduction, chain tilting (an oblique orientation of molecular chain axis with respect to the surface normal in folded-chain lamellae) is considered a root cause of lamellar twisting. Tilting of the molecular chain axis can be an inherent characteristic of the crystalline structure conferred by low symmetry of the unit cell, e.g., monoclinic or triclinic. Typical examples are the single-crystal lamellae of polyamide-6,6 (46°)[18a] and poly(ethylene terephthalate) (25°−35°),[18b] where the numbers in parentheses are the measured tilt angle. On the other hand, an orthogonal orientation of the chain *c* axis to an *a*−*b* basal plane in crystals of higher symmetry (e.g., orthorhombic or hexagonal) does not eliminate the possibility of chain tilting in lamellar structures. In some cases, tilting of the chains seems to be forcibly induced at growth fronts during fast crystallization, by a need to accommodate bulky folds at disordered fold surfaces. The best studied polymers in this category are polyethylene (ca. 35°),[19] α-poly(vinylidene fluoride) (ca. 25° about the *b* axis),[20] and γ-poly(vinylidene fluoride) in which a slight tilt required by a monoclinic unit cell (β = 93°) is enhanced to 28.5° about the *b* axis.[18c]

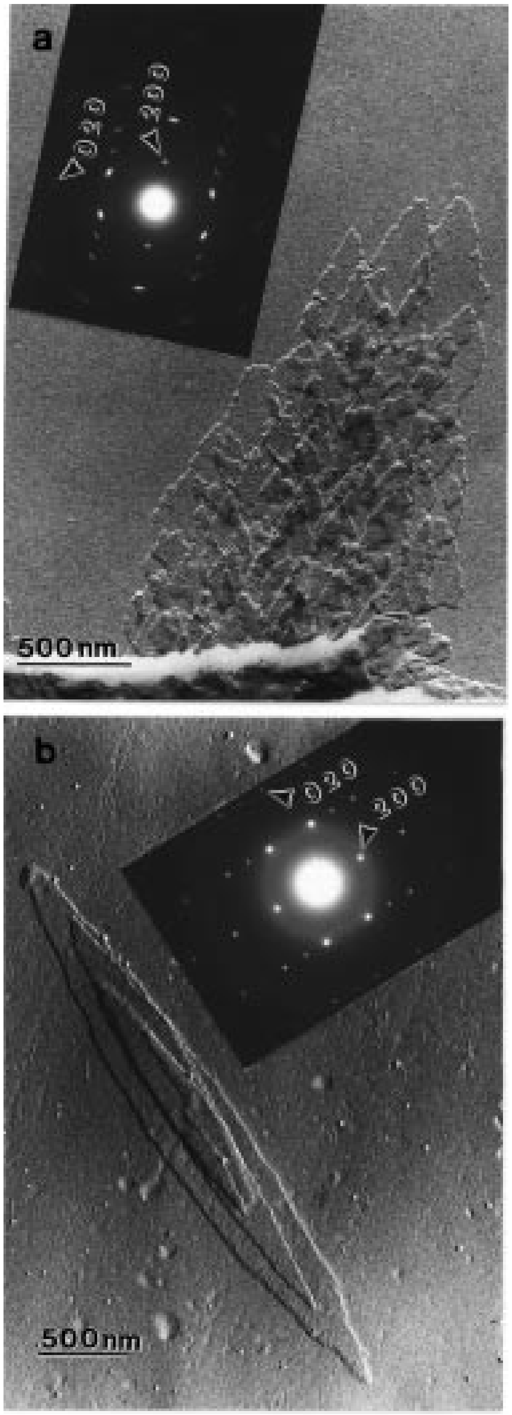

Figure 1. Single-crystal lamellae and the corresponding electron diffraction pattern of **(**a**)** (*R*)-PECH grown in mesitylene at 0.015% w/v and a temperature of 90 °C for 24 h and **(**b**)** (*R*)-PPrO grown in 1-octanol at 0.005% and a temperature of 52 °C for 24 h.

To date there are no reports concerning the alignment of stems in chain-folded crystal lamellae of optically active PECH and PPrO. Evidence for chain tilting was sought with several crystal specimens grown from both 1-octanol and mesitylene solutions. Electron diffraction patterns were taken normal to the surface of flat lamellae, using areas with least interference (overlapping) of the neighboring lamellae. Characteristic selected-area diffraction patterns are shown in Figure 1, where the crystallographic axes *a* and *b* are correctly oriented to correspond to the crystal axes. Both are composed exclusively of (*hk*0) reflections, their spacing agreeing consistently within experimental error with corresponding values obtained previously in X-ray diffraction studies of racemic PECH[15] and PPrO.[16] This result is in accord with an orthogonal orientation of the chain *c* axes as is reasonable in terms of the orthorhombic symmetry of unit cells (see Table 1). Further, this is expected since it is common experience that the crystallization of polymers from dilute solutions at low growth rates occurs without perceptible chain tilting.

Having eliminated chain tilting in single-crystal lamellae of PECH and PPrO as a factor contributing to lamellar morphology, at least in the case of crystals grown from solution, our study was then directed to (i) the characteristic habits of the individual lamellae and (ii) their multiplication by the screw dislocation mechanism.

Lamellar Morphology. The study focused on an examination of the morphology of single crystals grown from dilute solutions. Poor solvents were selected so that the crystallization occurred at low ΔT, where the resulting lamellar habits simulate most closely those obtained in crystallization from the melt.

In view of the previous report by Singfield et al.[8] of the appearance of chirality-induced topography effects in the lamellar organization of banded PECH spherulites, the initial studies were directed toward these enantiomers. For the chiral (*R*)- and (*S*)-PECH single crystals, regularly facetted lamellae were never observed, even when the crystal growth was carefully conducted at relatively low undercoolings. Instead, complex lamellar structures showing ill-defined lateral habits were the dominant crystal morphology. According to the revised kinetic crystallization theory of Hoffman and Miller, such featureless lateral growth habits are expected for crystallization of ultrahigh molecular weight polymers (range E−E′), even at low undercoolings.[21]

The micrographs in Figure 2 show the morphology of the lamellar terraces found in PECH crystals obtained from 1-octanol at low undercoolings. Inspection of the lateral habits of the individual lamellae of both (*R*) and (*S*) enantiomers reveals no morphological features that can be ascribed directly to molecular chirality. The basic growth habit of the lamellar crystals is the rhombic (or lozenge-shaped) type which develops further into lateral profiles with a pronounced roundness on both the {020} and {110} growth faces so that the {110}/{020} boundaries become practically undistinguishable. The investigation of numerous lamellar single-crystal specimens demonstrated that for a given polyenantiomer specimen screw dislocation patterns of *both* right- and left-handedness occur randomly. This pattern was found consistently for both the (*R*)- and (*S*)-PECH lamellae.

The lamellar morphology of solution grown single crystals of PPrO is less complex because both the (*R*)- and (*S*)-PPrO enantiomers had a significantly lower molecular weight (see Table 1) as a result of chain cleavage that accompanies the reductive dechlorination reaction used to convert the corresponding PECH enantiomers. In addition, although the derivatization reaction does not alter the absolute configuration of the asymmetric carbons, it decreases the side chain polarity; i.e., the conversion of the CH_2Cl groups of PECH to the CH_3 groups of PPrO makes the pendants less polar, and the resulting change in dipole moments may affect the chain packing characteristics. By extension, some changes in the characteristics of the lateral profiles could be expected for the PPrO lamellae.

Figure 2. Screw dislocations of opposite handedness (designated by arrows) in the lamellar morphology of (*R*)-PECH isothermally crystallized from 1-octanol at a concentration of 0.005% w/v and a temperature of 107 °C for 153 h. The screw dislocations in single-crystal lamellae of (*S*)-PECH showed a similar pattern.

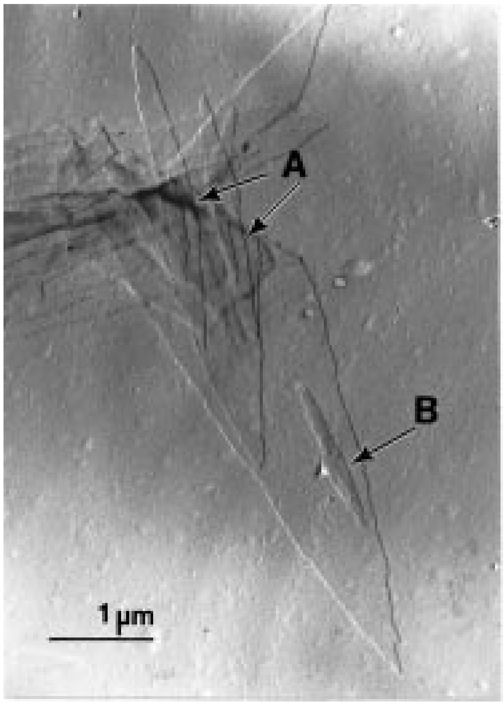

Figure 3. Lamellar structures in crystals of chiral (*R*)-PPrO displaying screw dislocations of opposite handedness: **(**A**)** two right-handed and **(**B**)** an incipient left-handed. Similar patterns were found in (*S*)-PPrO crystals isothermally crystallized under the same conditions, i.e., 0.005% w/v and a temperature of 52 °C for 24 h.

Indeed, crystals of chiral (*R*)- and (*S*)-PPrO grown from 1-octanol exhibit an elliptical (or lenticular) shape with high axial ratios (length along *b* axis/length along *a* axis); typically, axial ratios of 7.0−10.4 were seen for crystals grown for 24 h. It is interesting to note that the lamellae showing small (0.70−3.25) to relatively large axial ratios (5.5−6.0) have been reported for polyethylene (PE) crystallized from the melt[22] or crystallized from dilute solution in poor solvents at high temperatures.[23] Lenticular profiles with high axial ratios are expected when the rate of the step propagation on the lateral {200} growth faces is considerably smaller than the rate of advance of growth faces bordering the tips along ⟨020⟩ axes. Similar to the PE lenticular crystals, the main characteristic of the PPrO crystals is the curved lateral habits on the {200} growth faces. In the absence of distinct boundaries between {200} and {110} growth facets, the curved {200} faces extend toward the apexes of the lamellae.

The crystal illustrated in Figure 1b is representative of the lamellar overgrowth by screw dislocation in the (*R*)- and (*S*)-PPrO enantiomers. Again, the individual lamellae show no morphological characteristics that can be attributed to the main-chain chirality. As illustrated in Figure 3, coexistence of screw dislocations of opposite handedness was observed consistently in the lamellar structures of a given enantiomer sample.

It is of interest that the lateral profiles of the individual PECH lamellae display dissimilarities from the PPrO crystals, which certainly reflect the effects of the side-chain polarity on the crystalline microstructure. Several characteristics in the overgrowths of PECH, such as the highly curved {020} growth faces and a tendency of lamellae to roll (see the Nonplanar Habits section), are held in common with elements of the crystalline morphology of other polar polymers, e.g., the α-form crystals of poly(vinylidene fluoride) (PVF_2)[24−26] and nylon-6,6.[27]

Poly(3-hydroxyvalerate). In both optically active PPrO and PECH, the TEM observations show no indication of the manifestation of chirality in the lamellar morphology of solution-grown single crystals. Although the results are certainly convincing, some concerns remain because the PECH enantiomers were synthesized from monomers with a small amount of enantiomeric “impurity” (quoted ee > 97%). Since the Vandenberg-type catalyst, $Et_3Al/0.6H_2O$, is known to be stereospecific but not stereoselective, “chiral defects” could be incorporated randomly. Hence, the absence of a morphological manifestation of chirality at the lamellar level might be attributed to these “chiral defects”.

To pursue this matter further, the microstructure of (*R*)- and (*S*)-PECH was verified by high-resolution 500 MHz ^{13}C solution NMR, using the Cheng and Smith method.[28] Expansion of the methylene region gave no detectable split of the resonance signal at 68.77 ppm, indicating that the polyenantiomers may be considered to be 100% isotactic, i.e., with all the asymmetric carbons in either the *R* or *S* configuration. This agrees with the conclusion reached previously in a similar study of PECH enantiomers.[12] In addition, PECH synthesized via Vandenberg’s method is documented for the lack of inverted sequences, i.e., head-to-head or tail-to-tail.[13,28,29]

To conclusively eliminate uncertainties associated with the “chiral purity” of the synthetic polyethers, the study was extended to include an investigation of the lamellar morphology of another optically active polymer, poly(3-hydroxyvalerate). A biopolyester from the poly(3-hydroxyalkanoate) series, PHV, is 100% isotactic, with all of the asymmetric carbons in the *R* configuration.[14,17] It was preferred over the better studied PHB[30]

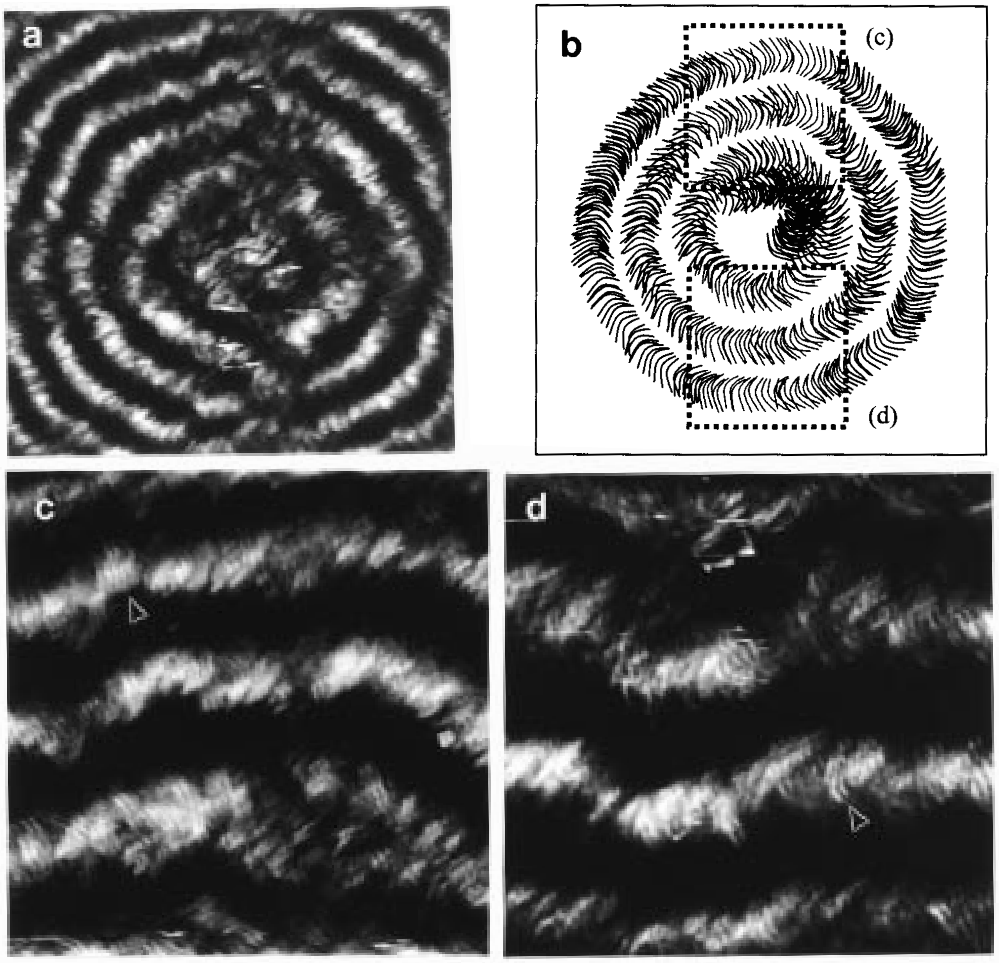

Figure 4. (a) AFM image (80 × 80 × 0.3 μm) of the center of a bacterial PHV spherulite crystallized from the melt at 75 °C with an unrestrained surface. **(b)** Schematic diagram showing the backward "C"-shape of lamellar edge profiles in the spherulite ridges. The labeled squares indicate the scanned areas on the spherulitic surface (a), which correspond to the images shown in (c) and (d). **(c)** and **(d)** Two examples of high magnification images (25 × 25 × 0.2 μm) collected on the C-shaped ringed sectors closest to the spherulite center. The edge profile (designated by an arrowhead) of the twisting helicoids suggests the right-handed twisting of lamellae in the radial direction.

because crystallization of PHV from dilute solution results in less aggregated single crystals. In addition, the electron diffraction patterns of PHV single-crystal lamellae show no evidence of chain tilting.[31,32] Nonetheless, the most important argument for examining the PHV crystals was its ability to crystallize from the melt as banded spherulites (Figure 4a).

In terms of optical behavior, these spherulites are unusual in that they are entirely positively birefringent and, as seen in films under the polarizing microscope, exhibit rings not by extinction but as contrast between alternating bands of larger and smaller birefringence. Dr. H. D. Keith[33] has examined several such specimens provided by us and, during tilting on a Fedorov universal stage (with crossed polars at ±45° to the tilt axis), has observed and recorded ring movements unambiguously and consistently indicative of right-handed twisting.[34] Our preliminary investigations of the spherulitic topography using the AFM technique appear to confirm the right-handed twisting of lamellae in the PHV spherulites grown from the melt with an unrestrained top surface.

Despite the complex organization of the lamellae at the spherulitic surface, the handedness of lamellar twisting in the radial direction was determined by using the helicoid projection criterion devised by Lustiger et al.,[35] which requires the inspection of the C-shaped lamellar edge profiles in the spherulite ridges. Thus, from the perspective of an observer located at the spherulite center and looking in the radial direction, the appearance of the backward "C"-shape in the lamellar ridges is indicative of the right-handed twisting of the helicoids (see the schematic diagram in Figure 4b). Indeed, the topological images of the surface, presented as examples in Figure 4c,d, suggest that the twist of lamellae is *predominantly* right-handed.

Compared to PHV, banding in PHB spherulites invariably involves left-handed twisting of lamellae,[7,10] yet in both PHV and PHB biopolyesters the molecular chains form left-handed helices.[17,36] This is a significant finding which strongly questions the proposed simple correlation between the handedness of twisting lamellae and that of the helical chain (see the Introduction) because it proves that the left-handed helices can be related with either the left-handed or right-handed twisting of lamellae in banding of polymers with main-chain chirality. This suggests that, although a unique handedness of helical chains may ensure an invariable (i.e., unmixed) handedness of the twist in banding of a given polyenantiomer, it may not be the only factor determining the handedness of lamellar twisting. Nev-

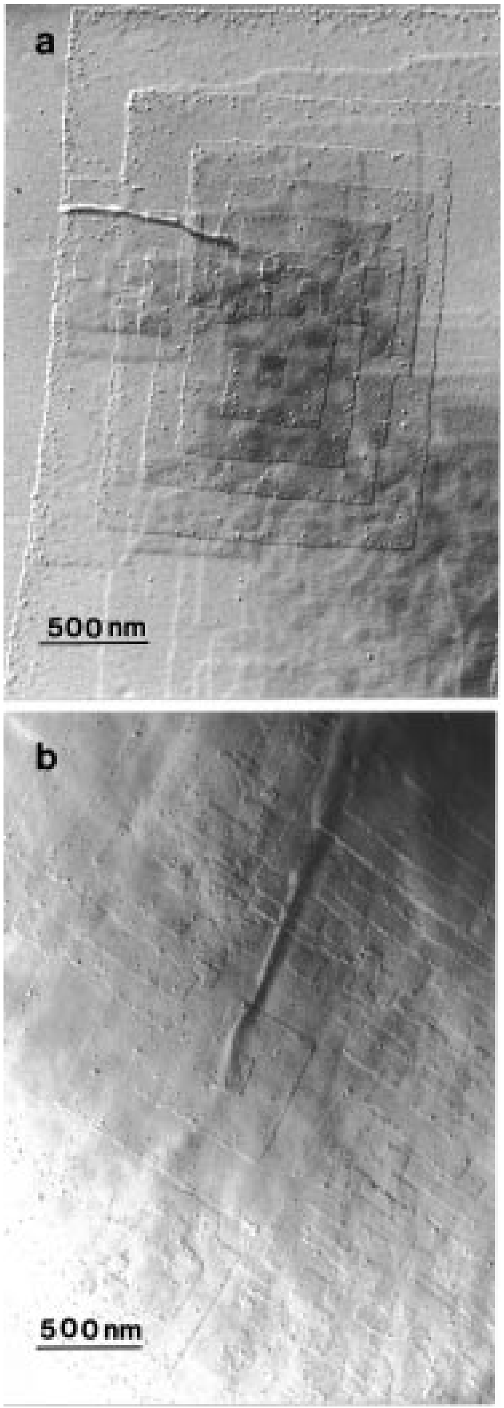

Figure 5. Lamellar morphology of bacterial PHV crystals grown from an ethanol solution at 0.1% w/v concentration and a temperature of 75 °C for 24 h. The square lamellae further multiply into spiral terraces by screw dislocations of either handedness: **(**a**)** left-handed and **(**b**)** right-handed.

ertheless, these observations are instantly evocative of topics for continuing investigation.

When isothermally crystallized from dilute ethanol solutions, PHV single crystals display planar, almost square-shaped lamellae that multiply by screw dislocations into multilayered terraces. Like PECH and PPrO, the morphology of individual PHV lamellae shows no characteristic habits that can be related to the chiral identity of the constitutive chains. As illustrated in Figure 5, the handedness of screw dislocations in PHV crystals is not unique; i.e., spirals of both right and left sense are evident. This provides further strong evidence that the lamellar morphology and the handedness of screw dislocations in the lamellar terraces of solution-grown single crystals are not controlled by main-chain chirality.

Nonplanar Habits. In searching further for chiral effects, we examined as well the morphology of PECH crystal lamellae found in a relatively advanced state of crystalline development that more closely approaches the complexity of the lamellar organization of melt-crystallized spherulites. Highly dendritic and hedrite-type crystalline morphologies can be obtained under fast crystallization kinetics when the growth is controlled by the diffusion of chains to the growth front, a condition which is experimentally created by higher undercoolings and/or an increased concentration (e.g., at least 0.1%).[37] In the present case, it appears that diffusion-controlled growth is achieved even at relatively low concentrations due to the high molecular weight of the PECH, in agreement with an early observation made by Bassett and Keller.[38]

As exemplified in Figure 6, highly dendritic crystals and hedrites with various degrees of morphological complexity were obtained from mesitylene solutions at high crystallization temperatures (90−100 °C) and relatively low concentrations (0.01−0.05% w/v). Although drying of the crystals on the TEM grid may distort some of the original habits, careful viewing of the morphology of the crystal aggregates suggests that the individual lamellae are nonplanar. Indeed, the shape of the lamellar edges indicates a tendency of the lamellae to bend more or less symmetrically along the longest axis (*a* axis of the crystal), which results in warped and buckled lamellae (Figure 7). Such behavior appears to be related to the twisting of lamellae observed in the melt-crystallized dendritic structures of PECH (see Figure 8c in ref 8).

It is interesting to note that the bending appears to be more pronounced in the lamellae located closer to the center of the aggregate and to diminish progressively toward the periphery. Consequently, warped and buckled lamellae are more frequently found in the central region of the crystal aggregate while the lamellae located at the periphery are essentially planar (see Figure 6b).

The observation of nonplanar habits in large lamellar aggregates of PECH again opens the possibility of chain tilting. However, attempts to examine chain tilting in the nonplanar lamellae were obviated by the multiple interference of the spots in the electron diffraction pattern that resulted from the overlapping of the lamellar layers. Not surprisingly, the electron diffraction patterns obtained on the lamellae located at the periphery of the crystal aggregate (where no apparent bending is observed) showed no evidence of chain tilting.

According to Keith and Padden,[5−7] bending and twisting of lamellae suggest the presence of relatively large unbalanced stresses at opposite fold surfaces that, in turn, imply the tilting of stems. Although not evident in the planar lamellae grown at low crystallization rates, primarily for reasons associated with the symmetry of the orthorhombic unit cell, tilting of stems could be induced, in some cases, during the rapid crystallization. This has been invoked previously to justify chain tilting in lamellar structures grown at high crystallization rates in other polymers with an orthorhombic unit cell.[5,7,19,39,40] It was suggested that at high growth rates, when the crystallization kinetics are controlled prima-

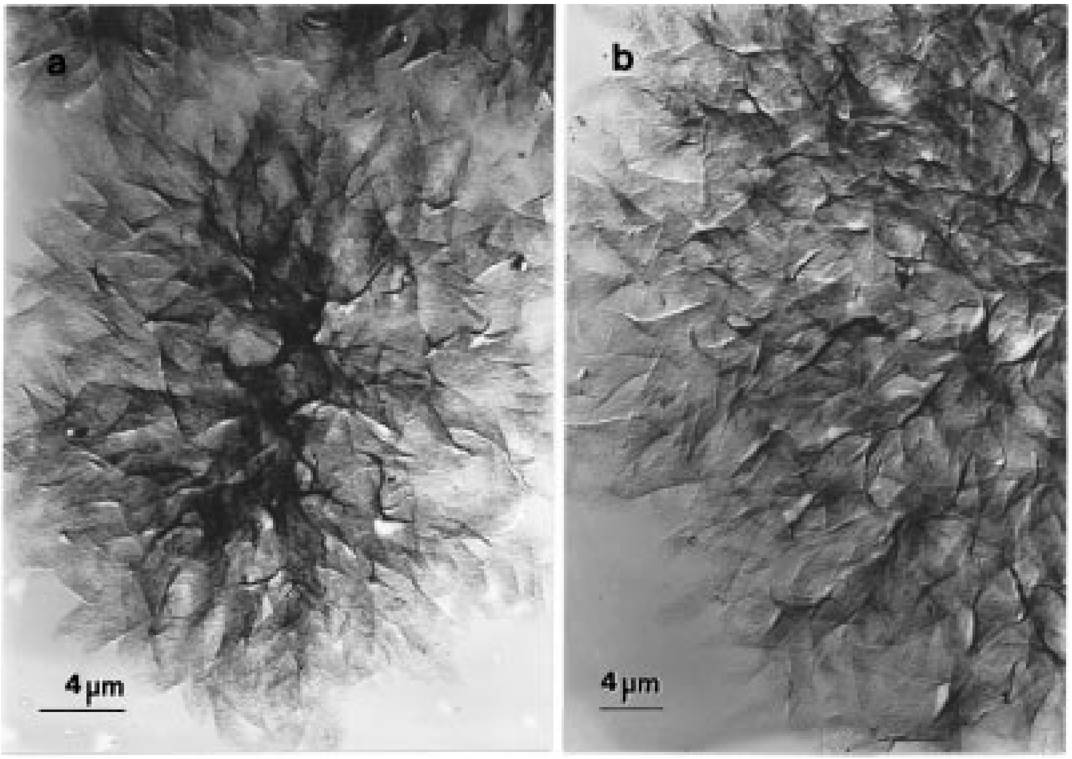

Figure 6. Large-scale crystalline aggregates (hedrite-like structures) obtained from mesitylene solutions at 0.04% w/v concentration of (*S*)-PECH and a temperature of 90 °C: **(**a**)** general overview and **(**b**)** close-up view showing an assembly of lamellae where the nonplanar effect diminishes gradually toward the periphery of the aggregate.

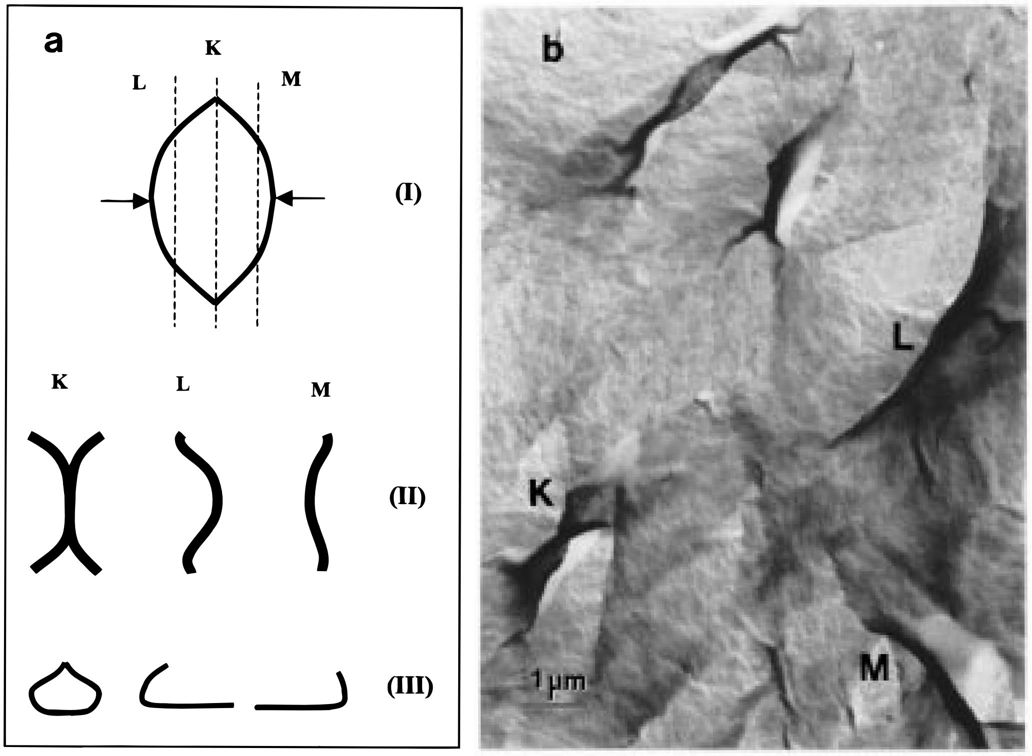

Figure 7. (a) Schematic diagram illustrating the bending along the longest lamellar axis (I). When viewed from the top (II), the characteristic shape of lamellar edges is indicative of buckled (K) and warped (L and M) lamellae. The corresponding lamellar cross sections (III) cannot be observed under bright-field operating mode in TEM. **(**b**)** Close-up view showing the bending effects in the lamellar morphology of large crystalline aggregates of PECH. Some of the lamellar edges, visible as the darkest features in the TEM micrograph, are labeled to exemplify the characteristic edge profiles (II) presented in the schematic diagram.

rily by a combination of diffusion and chain dynamics effects, irregular folding of molecular chains generates bulky folds and hence a rather disordered state.[7,39] Chain tilting is provoked by a need to relax an overcrowded surface to create adequate space for these bulky folds. This is also consistent with the observation that nonplanar effects, such as the warping and buckling observed in the PECH crystal aggregates, become

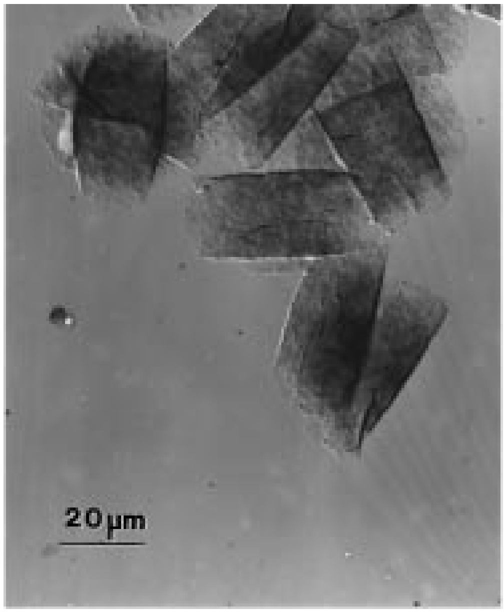

Figure 8. Rolled (scroll-like) lamellar morphology found in (*R*)- and (*S*)-PECH crystals grown in mesitylene at 0.005% w/v and a temperature of 95 °C for 24 h.

progressively less pronounced toward the periphery such that the lamellae located at the edges are essentially planar and without perceptible chain tilting. The lamellae at the periphery are generated during the late stages of crystallization when the diffusion and chain dynamics factors are less important either due to the more frequent incorporation of lower molecular weight fractions (fractional crystallization effect) or because the mother liquor is practically exhausted of polymer.

The curved {020} growth faces of PECH lamellae can be regarded as an alternative cause, which provokes nonplanar habits in the lamellae of large crystal aggregates. As shown in Figure 8, virtually scrolled (or rolled) crystals were routinely obtained from dilute mesitylene solution at low ΔT. It is perhaps not a coincidence that such peculiar characteristics also have been reported for other polar polymers. For example, a rolled lamellar morphology has been described previously by Geil for polyamide-6,6 crystals precipitated from glycerin[27] and more recently by Vaughan in the spherulitic textures of melt-crystallized γ-PVF$_2$ grown at high temperatures.[26] To date, there is no general consensus as to the cause of the scrolled interleaving of lamellae observed in these polymers.

Summary

The present study of the morphology of single-crystal lamellae grown from dilute solution indicates that the chiral character of a polyenantiomer, conferred by the asymmetric carbons of the main chain, is *not* transmitted to the lamellar morphology. This behavior was consistently observed for the lamellar morphology of the single crystals of both chiral PECH and PPrO and conclusively established by the similar results obtained for PHV crystals. Furthermore, there is no experimental evidence to indicate that the handedness of screw dislocations is controlled by factors related to the optical asymmetry of the main chain. This result suggests that, within the context of solution-grown crystals, the screw dislocation mechanism makes no contribution, apart from ensuring lamellar continuity, in transmitting the main-chain chirality to the lamellar twisting and furthermore to the organization of twisting lamellae reported for the PECH banded spherulites.[8] This seems to be consistent with the conclusion reached by Keith and Padden[7] concerning the contribution of screw dislocations to the helicoidal twisting of lamellae. On the basis of the available data for polyethylene, they demonstrated that while the screw dislocations may contribute to the banding through lamellar branching, they appear to play only a minor role in determining the handedness of the twisting.

Studies of solution-grown single crystals of *Bombix mori* silk fibroin by Lotz et al.[9] led them to conclude that the handedness of the helical twist of lamellar aggregates in silk fibroin and other polypeptides with a β-sheet structure is dictated by the chirality of the peptide residue sequence. However, they carefully pointed out that the lamellar twist observed in globular proteins and the twisting orientation of the lamellae in synthetic polymers have different origins. That is, the twist in globular proteins involves the *lamellar core* as opposed to the lamellar twisting orientation in banded spherulites of synthetic polymers which results from stresses in the *lamellar surfaces*. Thus, the conclusions of the present work are not in conflict with those reached previously by Lotz and co-workers.

The examination of lamellar morphology in large crystalline aggregates has not established any meaningful motif that can be unambiguously attributed to the influence of main-chain chirality. However, one interesting morphological characteristic observed in the large aggregates is nonplanarity of the lamellae. Two factors, chain tilting and the curved {020} growth faces, may contribute to bending of PECH lamellae. Nevertheless, the ultimate origin of lamellar bending and twisting is still an open question in the crystallization of enantiomers with helical chains, where the requirements of packing isochiral (same handedness) helices add extra constraints at the growth front. Within the frame of this rationale, the relation between main-chain chirality and the factors suspected to provoke lamellar bending and twisting must be the focus of further investigations.

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