Feature Article

A critical assessment of unbalanced surface stresses as the mechanical origin of twisting and scrolling of polymer crystals

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Abstract

Twisting of polymer lamellae manifested by e.g. appearance of concentric bands in polymer spherulites examined in a polarized optical microscope remains a topic of research and controversy. It has been interpreted variously as resulting from phenomena that take place during growth or from structural features of individual lamellae, or multilamellar aggregates. Phenomena that take place during growth are of general, or even generic character. They include non-linear diffusion processes leading to rhythmic crystallization, or self-induced compositional or mechanical fields generated near the advancing crystal front. Structural features include cumulative reorientation of lamellae at successive isochiral screw dislocations (possibly linked with surface pressure exerted by cilia) or different surface stresses on opposite fold surfaces of individual lamellae, as a result of different levels of congestion of folds.

This contribution reviews evidence that has accumulated in favor of lamellar twist induced by surface stresses that result from differential congestion of fold surfaces, as suggested initially (in 1984) and advocated for many years by Keith and Padden. Such differences in fold surface structure are occasionally amenable to experimental (even if only qualitative) verification, as illustrated by polymer decoration of polyethylene single crystals. Twist is expected when a two-fold symmetry parallel to the growth direction exists in the lamellar structure (crystalline core and fold surface). This symmetry often stems from chirality: most frequently atomic (configurational) or stem (conformational) chirality but chirality (or at least asymmetry) may also be introduced by chain tilt.

Possible origins of twisting in *chiral* polymers are also reviewed. In β sheets of fibrous proteins, the origin of twist stems from the atomic chiral centers in the crystalline core of the lamellae and its transfer to higher structural levels via the strong structural identity of the hydrogen-bonded β sheets. However, in a series of synthetic liquid-crystalline main-chain nonracemic chiral polyesters, the lamellar twist sense depends on the odd or even numbers of atoms in the aliphatic segment. For these and other more flexible chiral polymers, often with helical chain conformation, twisting appears to result from surface stresses associated with different fold structure or conformations at opposite fold surfaces, as suggested by a preliminary analysis of the Form III of isotactic poly(1-butene). Such differences in fold conformations result from, but are not directly related to, the specific helical hand of the polymer since they rest on the details of the chain conformation as it reaches the fold surface. This analysis accounts for the lack of one-to-one correspondence between configurational or conformational chirality of the polymer and lamellar twist sense (the one-to-one correspondence applies however for stereoenantiomers of a given polymer).

Twist is not the only known non-planar geometry of polymer lamellae. In a few cases, the lamellae are scrolled. Scrolling of polymer lamellae is also easily accounted for by the existence of surface stresses when the two-fold symmetry parallel to the growth direction is absent. Such surface stresses are again linked to disparities in fold volume, as first suggested for poly(vinylidenefluoride) in its γ Form and later for two long paraffins substituted near their middle carbon atom and that crystallize in hairpin fashion, and for scrolled crystals of polyamide 66.

The different nature and structure of polymer crystal fold surfaces, therefore, offer an unusual opportunity to decouple surface and bulk contributions and to analyze the origin of non-planar lamellar geometries at a sub-molecular level. Fold structure disparities and resulting unbalanced surface stresses provide a unified explanation for the formation of non-planar (both twisted and scrolled) lamellar crystals. They

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account for both the diversity of lamellar morphologies produced under the same crystallization conditions and for the similarity of lamellar morphologies produced under very different crystallization conditions.

1. Introduction

Lamellar twisting in polymer spherulites manifests itself in spectacular ways, such as the periodic banding in spherulites examined in polarized optical microscope (Fig. 1(a)), or the development of a pattern of concentric rings
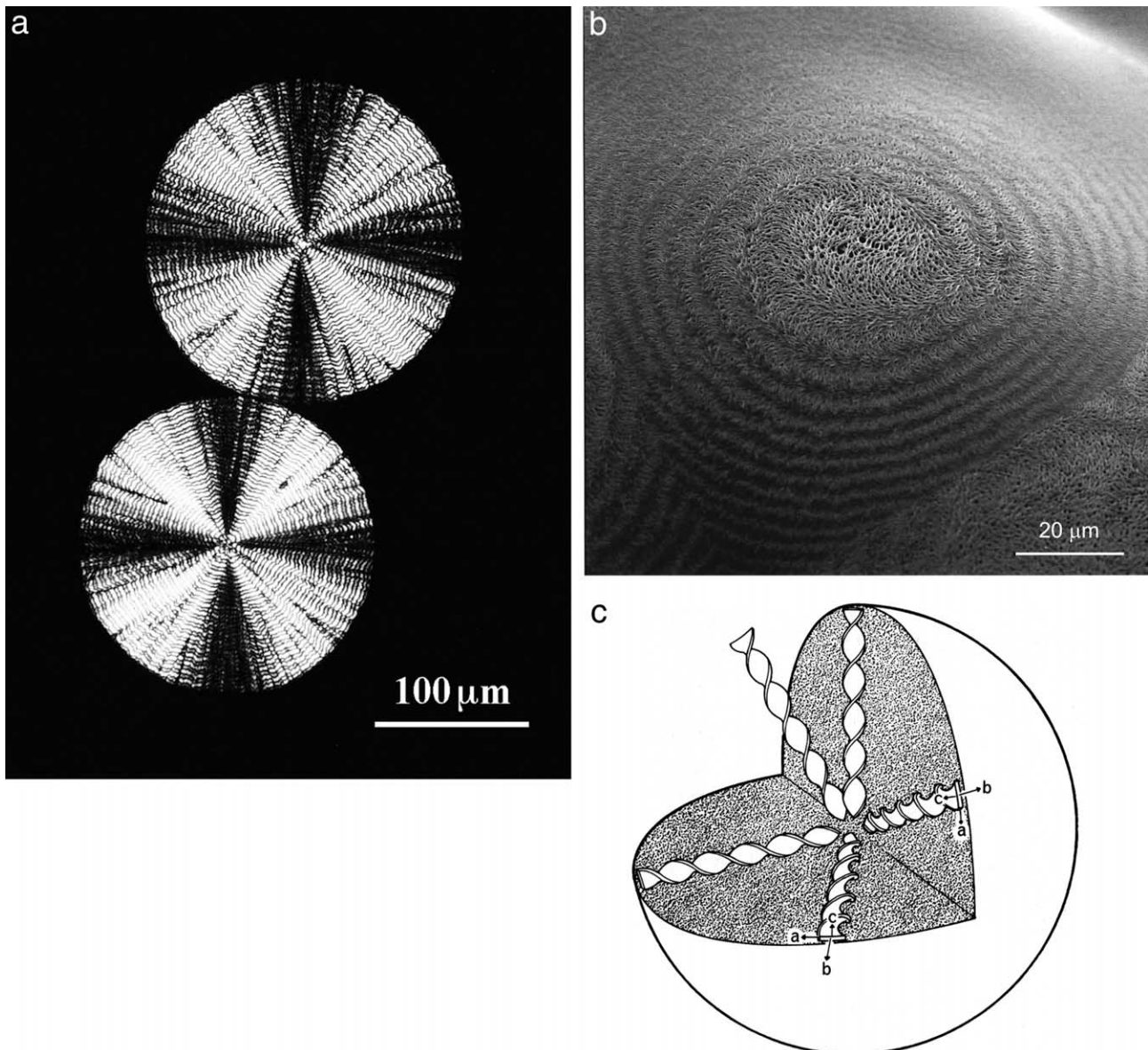

Fig. 1. Lamellar twist in polymer spherulites: lamellae twisting cooperatively and in phase. (a) Optical banding developing in growing spherulites of poly(ethylene adipate) as seen in polarized light microscopy. The band periodicity corresponds to a half twist periodicity. Note that the period comprises two bands of zero birefringence, indicating that the optical indicatrix is biaxial, and the radial growth direction is parallel to the unique axis. This optical pattern is analyzed in full detail in Refs. [2–4]. (b) Pattern generated on the surface of a polyethylene spherulite, as the twisting lamellae reach that surface (the spherulite center is beneath the surface). The concentric rings indicate that the twist is cooperative and in phase and correspond to regions where the lamellae are seen nearly flat-on. The lamellar profiles between these rings are C-shaped or (in the present case) inverted Cs when seen from the spherulite center outwards. These profiles correspond to the intersection of the twisting lamellae and the spherulite surface [5]. The polyethylene sample used (S-Clair) is reputed for its low nucleation density, which makes it very suited to illustrate the present effect. (c) Schematic representation of the lamellar twist in polyethylene spherulites, as illustrated by Barham and Keller [114]. Part (b) published courtesy Aldo Media, Paris. Part (c) reproduced with permission from Barham and Keller [114]. Copyright Kluwer Academic/Plenum Publishers.

made of C shaped lamellar edges on the spherulite surface (Fig. 1(b)). Optical banding observed in polymer spherulites was analyzed by Point [1] and, in 1959, by Keith and Padden [2], Keller [3] and Price [4]. The C-shaped lamellar profiles have been accounted for by Lustiger et al. [5]. The manifestations of lamellar twisting are by now well understood. Understanding of the origin(s) of lamellar twisting remains one of the major challenges in the research field of polymer morphology. It is apparently not yet settled, as attested by the fact that new theories and/or explanations are continuously proposed. Among the latter are contributions of Toda et al. [6] who elaborated on an earlier proposal of Bassett et al. [7,8] that links lamellar twist with repetition of isochiral screw dislocations in growing lamellae. Kyu et al. [9] considered a rhythmic crystallization process resulting from non-linear diffusion during growth, and Schultz [10] assumed self-induced compositional or mechanical fields generated near the advancing crystal front. These are only but the last of numerous explanations that have been provided over the years to account for lamellar twist. The situation is indeed quite complex, since lamellar twist is not limited to polymeric materials but is rather widespread in materials science. It is, understandably, tempting to propose 'unifying' theories that would encompass the whole spectrum of non-planar lamellar morphologies observed in polymeric as well as in non-polymeric materials. This 'universal' and unifying explanation, if it exists, has not yet been reached.

It may be worth, therefore, to adopt a more modest approach, and analyze what has been and what can still be learned about the origin of lamellar twist, and more general illustrations of non-planar lamellar geometries of crystalline polymers. In doing so, it is also possible to evaluate the relevance and possible weaknesses of recent and older explanations of lamellar twist. This approach has been used recently in a short but important contribution by Keith [11] ('Banding in Spherulites: Two recurring Topics'), which furthermore, puts the whole topic in historic perspective. The present review not only follows a very similar line, but also develops the case advocated by Keith—namely the decisive influence of uneven fold volume or encumbrance (different encumbrance may result from differences in conformations of otherwise identical folds) on opposite fold surfaces of lamellae, and resulting unbalanced surface stresses in generating non-planar geometries. Justification of the present paper may, therefore, be questioned. Presentation of different viewpoints or even advocacy of the same case but from different sources is however warranted by the state of confusion that still exists in the field.

The present contribution, therefore, develops, sometimes only with other words but, on purpose, always with simple words, the case in favor of unbalanced surface stresses as the origin of lamellar twisting. The same applies for lamellar scrolling, since unbalanced surface stresses can also induce lamellar scrolling. This contribution is structured as follows:

The experimental manifestations of lamellar twist are reviewed in Section 2.

Section 3 deals with twisting of achiral polymers. The experimental manifestations of lamellar twist are presented, and their analysis in terms of surface stresses supported by experimental evidences gained mostly on polyethylene (PE).

Sections 4 and 5 deal specifically with chiral polymers. Lamellar twisting has frequently been associated with the existence of chiral centers in the molecule, and the temptation to associate configurational chirality and lamellar twisting has often led to contradictory statements. Experimental evidences are reviewed in Section 4. In Section 5, building on these examples, possible ways are suggested to analyze the observed correlation – or lack of correlation-between lamellar twist and polymer and/or helical stem chirality. In this more speculative part, it is suggested that in many, but not all cases, lamellar twist of chiral polymers is only another manifestation of unbalanced surface stresses generated by folds, the difference in fold geometry/constitution being simply a consequence of the polymer and/or helix chirality.

Section 6 analyses the possible molecular origin of lamellar scrolling observed for two polymers and two model compounds. Here again, differences in fold encumbrance are likely, which links both twisting and scrolling of polymer lamellae with unbalanced surface stresses.

Section 7 deals with some general comments on lamellar twisting and the relevance of investigations on polymers in the context of lamellar twist in non-polymeric materials.

The conclusion is written as a short summary of the review, as a help to the reader less interested in or less aware of the details of the structural argumentation. It presents in a condensed form the main issues addressed in this contribution.

2. Experimental manifestations of lamellar twisting and its observation in bulk materials

Twisted individual lamellae are seldom observed in polymer science (a few examples will be provided later). Most frequently, lamellar twisting is revealed on the next 'organizational length scale', namely in spherulites grown from the bulk. Since these spherulites are multilamellar objects, analysis of their internal structure has long been and in many ways still remains a challenge. A global view of the structure of the spherulites, and of lamellar twisting, is provided by the analysis of their optical properties when observed with a polarized optical microscope. Point [1], Keith and Padden, [2] Keller [3] and Price [4] have shown that the concentric rings indicate rotation of the optical indicatrix (i.e. of the chain axis) along a radial direction, and furthermore, this rotation is in phase for the different lamellae.
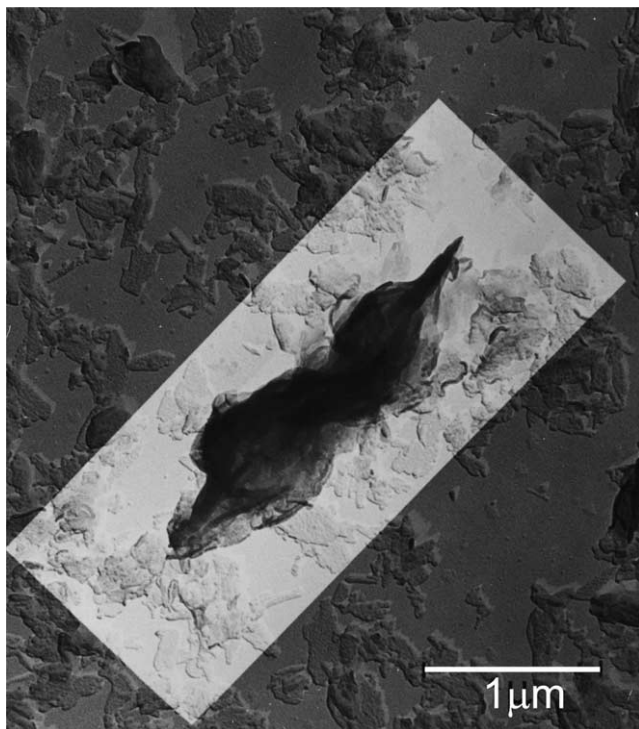
Fig. 2. One of the very early pictures illustrating the presence of twisting lamellae ('airscrew like units') in polymer spherulites, due to Keller and Sawada [13]. The PE spherulite was degraded with fumic nitric acid, revealing this fragment. Reproduced from Keller and Sawada [13] with permission from John Wiley.

The optical properties can only give an overall indication about lamellar orientation, or more precisely, about chain axis orientation in the spherulites. The internal structure is best investigated by degradation or etching techniques of the bulk material. An early picture of twisted polymer lamellae in PE spherulites subjected to a 'severe' degradation (using the fumic nitric acid method developed by Palmer and Cobbold [12]) was published by Keller and Sawada (Fig. 2) [13]. It clearly shows a twisting stack of lamellae that make a full turn (360° twist). However, major contributions to the observation of the internal structure of bulk polymers (and not only spherulites) had to await the development by Olley et al. [14] of a permanganic acid etching technique. Mild etching has provided the necessary insights into the lamellar shape and organization within the spherulites, including many essential details: recognition of zig–zag shaped (i.e. corrugated), S-shaped or C-shaped lamellar profiles, dominant and subsidiary lamellae, distinction between primary and secondary growth (the latter acting as an in-filling process), etc. Fine-tuning of the etching conditions and etchant nature has extended the range of polymers that are amenable to these analyses. In short, chemical etching has become (rightly) a standard technique when investigating the lamellar organization and morphology of the spherulite interior-and of virtually all bulk polymer morphologies, either spontaneous or induced (shish-kebabs, etc). A detailed analysis of these contributions is beyond the scope of this

review. It must also be stressed however that the chemical etching techniques enable merely a morphological analysis of the spherulite interior. The same actually holds true for atomic force microscopy (AFM) that by design provides only surface morphological information, which is often insufficient—but in situ, real time AFM observations provide invaluable information on the growth process itself. As will be seen later nonetheless, correlation of morphology and structural information (unit-cell orientation, etc.) is the key to the analysis of lamellar twisting. Significant insights into the origin of this twist, therefore, stem from investigation (mainly by electron diffraction) of thin films (in spite of the geometrical limitations on lamellar morphology) or even of single crystals, since the latter offer unmatched ease of examination.

When dealing with lamellar twist, both twist periodicity and twist sense must be determined. The twist periodicity is easily determined by the distance between equivalent rings in the optical microscope that measures a half-periodicity. (However, more complex patterns of rings exist for polymers with a biaxial optical indicatrix, as analyzed in the papers by Keith and Padden [2] and shown in Fig. 1(a)).

Determination of the lamellar twist sense in polymer spherulites is difficult but necessary since it must be correlated with various structural features (chain tilt, chirality of the polymer, etc). It is usually determined with the help of a 'universal stage' (Fedorow stage, that can be tilted) mounted on a polarized optical microscope. The working principles of this determination have been recalled recently [15]. When a spherulite is tilted in the polarized microscope about one arm of the Maltese cross, a zig-zag banding appears in the other arm of that cross. The zig-zag pattern is either that of a Z or a inverted Z, i.e. the orientation of the zig and the zags helps determine the lamellar twist sense. Also, there is a movement of the bands in the first arm. However, this method is not straightforward since the movements of the extinction rings are limited, and take place at a very small scale. Extinction rings are usually only a few micrometers apart. Since the tilt of the universal stage is limited (working angle: $\pm 30°$), the possible displacement of the extinction rings is only a corresponding fraction of the ring periodicity, i.e. is in the micrometer or sub-micrometer range. Also, since universal stages have become rare in 'modern' laboratories, this method may well become out-of-fashion in the future.

An easier and more 'modern' method to determine lamellar twist sense in polymer spherulites has been introduced by Lustiger et al. [5]. It relies on the observation of the spherulite surface by scanning electron microscopy (SEM). In essence, spherulites located near the surface of a sample are nucleated beneath (or at most in) that surface (this does not hold true for, and therefore rules out, sections of bulk polymers, since nucleation may have occurred above the plane of the section). As growth proceeds radially, the twisting lamellae, most of them tilted to the sample surface, impinge on that surface. Lustiger et al. have modelled the trace of such twisting lamella as they reach the sample

surface. For appropriate tilts, the trace generated is a simple C-shaped curve (Fig. 3(a)). This, therefore, provides an easy morphological criterion to determine the lamellar twist sense. When looking outwards from the center of the spherulite, left-handed twisted lamellae create C-shaped traces, whereas right-handed lamellae generate inverted C-shaped traces. An easy mnemotechnic method refers to the Greek letter φ: the left part of the letter indicates left handed twist, the right part right-handed twist. In one case at least, Saracovan et al. [15] have actually used both the optical method (with a Fedorow stage) and this morphological determination of lamellar twist, and confirmed their consistency. As an illustration also, in the PE spherulite shown in Fig. 1(b) only right-handed lamellae impinge on the surface. Fig. 3(b) shows the power of this morphological determination and discrimination of helical hand: the spherulite displays two different radial growth sectors that are made of left- and of right-handed twisted lamellae (the boundaries are indicated). Anticipating later analyses, this image indicates that the sense of twist remains identical in any individual radial sector—which implies that the feature inducing twist and even twist sense is 'memorized' during growth.

In the present contribution, we consider only the reasons for which lamellae (and, as seen next, even a single lamella) do twist, i.e., we tackle the feature(s) inducing twist just mentioned. If growing from the melt, we suppose that the lamella is, in Bassett's terminology [7], a 'dominant' one, i.e. that it grows in an undisturbed melt and sets the stage for later growth within more confined environments generated by these dominant lamellae.

3. Theories accounting for lamellar twisting in achiral polymers, their limitations and experimental support

Explanations provided to account for lamellar twisting have been reviewed and discussed in some detail by Keith and Padden [16,17], and more recently by Schultz [10], who gives a precious historical account of early proposals. The purpose of the present short sketch is not to repeat the various arguments that can be found in the initial proposals and these recent papers, but rather to point out in what respect they often fail to account for solid experimental observations.

Broadly speaking, explanations provided to account for lamellar twisting may be divided into two groups. The first group associates lamellar twisting with features that exist during growth or are generated by the growth process itself. These are rhythmic supply of material as assumed by Kyu et al. [9], or self-induced concentration or mechanical fields in the vicinity of the growth front as assumed by Schultz [10]. The second group of explanations accounts for lamellar twist by features of the morphology or structure of the lamellae themselves. These may be screw dislocations [6–8], or surface stresses induced by congestion at the fold surface [16].

These two groups of explanations differ markedly when it comes to analyze the causes of lamellar twist. The former cannot be checked a posteriori, since they do not leave any physical trace in the structure of the lamella, except for the twist assumed to arise from them. To the contrary, the latter can be (or could be) submitted to experimental check when (or if) proper experimental techniques are available. Indeed, the features that induce lamellar twist are part of, and remain as a permanent memory in, the structure. We now proceed to critically analyze their respective merits and weaknesses. Only rather general arguments will be given, since the details of the reasoning can be found in the original papers. In doing so, full justice may not be rendered to the elegance of the experimental demonstrations or mathematical analyses, or more generally to the valuable insights these investigations have brought. This simplified approach may lead at times to abrupt evaluations or oversimplifications, but will hopefully generate further debates and contributions.

3.1. Lamellar twisting determined by supply of material to the growth front: concentration fields and rhythmic supply of crystallizable material

Two recent theories invoke phenomena taking place at or near the growth front, i.e. suppose transient, temporary features taking place during the growth process itself. They assume concentration or mechanical fields, or rhythmic supply of 'nutrient' to the growth front. The major argument against these theories can be summarized in a few words: they are too general. The concentration or mechanical fields assumed by Schultz [10] are generic, and do not refer specifically to polymers. In essence, the model rests on the fact that during growth of a flat lamella, the crystallizable material is more depleted ahead of the growth front in the plane of the lamella than above or below it. As a result the lamellar growth front is tempted to reach to these more favorable domains, i.e. to twist. If this mechanism were to apply, twist would be a universal feature of lamellar growth, which is far from being the case.

Such theories cannot, and actually are not designed to account for the structural diversity observed in polymer spherulites. The crystal polymorphism of many polymers provides a very clear illustration of this diversity. Indeed, for several polymers, different polymorphs are formed under the same crystallization conditions, and yield very different lamellar morphologies. To list only a few of these examples:

Isotactic poly(1-butene) (iPBu-1) exists in three crystal modifications. As shown recently, lamellae that build up spherulites of Form III (4_1 helix conformation, orthorhombic unit-cell) are twisted. Lamellae of spherulites of Form II (11_3 helix conformation, tetragonal unit-cell) formed under the same crystallization conditions are essentially not twisted [18]. This example will be further developed later on (cf. Fig. 10(a)).
Poly(vinylidene fluoride) (PVDF) can crystallize in the α and γ modifications from the melt under the same
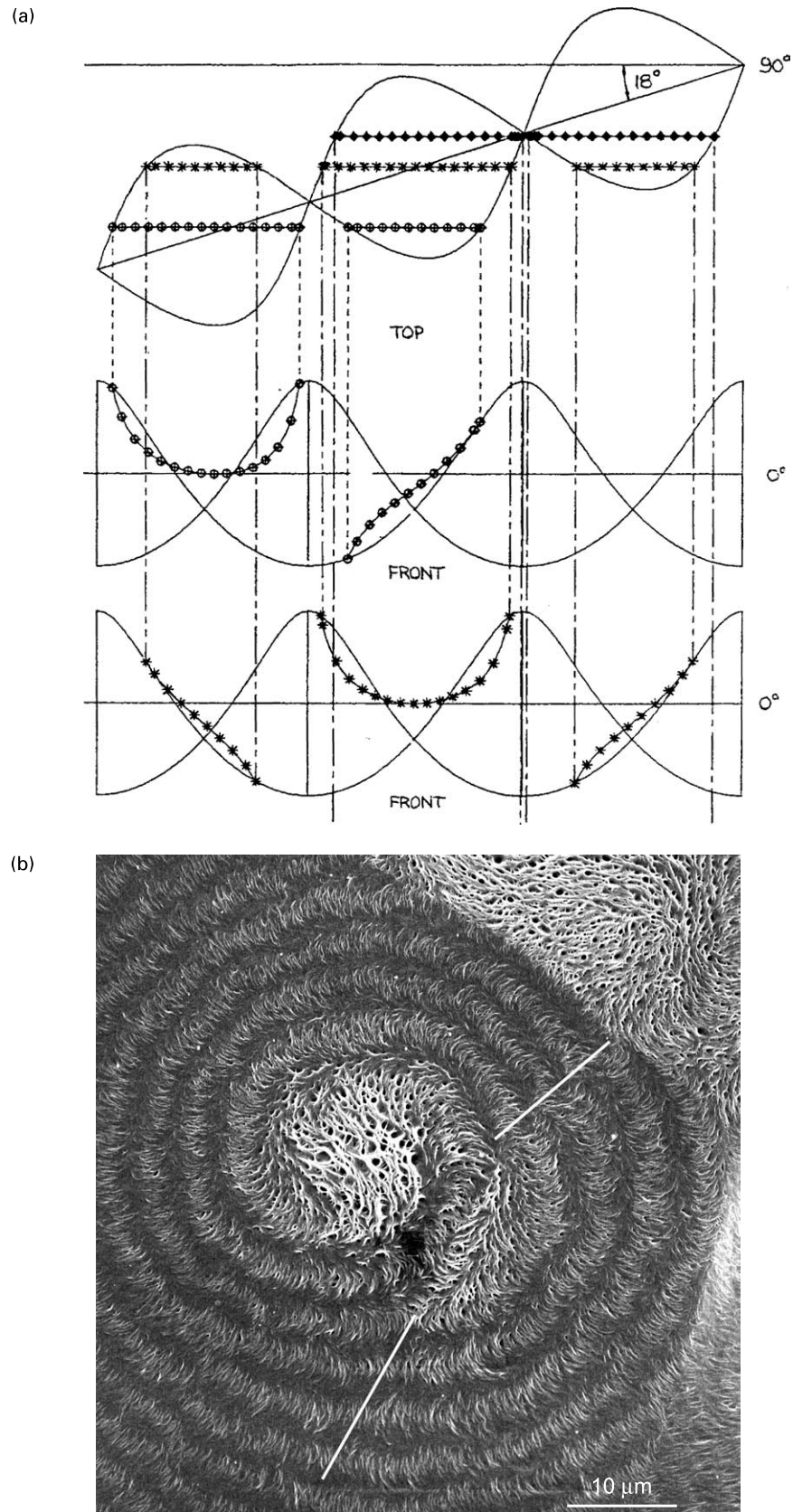
(a)

(b)

Fig. 3. Surface topography of polymer spherulites with twisted lamellae. (a) The lamellar profile of twisted lamellae impinging on the spherulite surface [5]. The lamella with a tilt angle of 18° is seen edgewise (parallel to the spherulite surface) on the top (indicated as 90°, parallel to the spherulite normal). Representative lamellar profiles generated on the surface are shown in the two lower drawings, as seen along the spherulite surface normal (indicated as 0°).

conditions. Spherulites of α phase display a tight lamellar twist [19], whereas the γ phase counterparts are made of scrolled lamellae [20]. This difference will also be further developed in later sections.

Polypivalolactone exists in two crystalline forms (α and γ) that crystallize at the same temperature. Only the γ form spherulites are ringed, suggesting lamellar twisting [21]. Some spherulites of polyamides and polyesters display clear optical banding, with however abrupt changes to non-banded spherulites when crystallized at slightly different temperatures [22–24].

Along the same line, poly(ethylene adipate) produces three types of spherulites at different crystallization temperatures, or even two different spherulite types at the same temperature [25–27], that differ by the crystallographic direction that is radial. Only one of these spherulites displays clear optical banding, suggestive of lamellar twisting.

All these examples illustrate the fact that lamellar twisting may, or may not, depend on crystallographic features of the lamella itself—in the latter case on the radial growth direction for an otherwise identical crystal structure. Those previously described explanations of lamellar twisting that do not take into account such diverse spherulite structures, or conversely, that do not account for such diversity (as e.g. the composition fields advocated by Schultz) are bound to be incomplete.

The above examples demonstrate that twisting is not a permanent or universal feature of lamellar growth, and its analysis must take into account the details of the crystal structure or polymorph. In addition, for each of these polymers and/or polymorphs, the details of the spherulite organization need to be considered: axis of the unit-cell that is parallel to the radial growth direction, chain tilt in the lamellae, etc. This different, structural approach is developed in the present contribution. Obviously, the explanations and structural interpretations are not available for each and every polymer or polymorph. However, a few cases that can or have been interpreted yield a very different picture of the origin of lamellar twisting.

Before moving on to these analyses, it may be worth pointing out the following features regarding the interpretation in terms of rhythmic growth proposed by Kyu [9]:

Keith [11] has already pointed out that rhythmic growth may be encountered occasionally, for example in thin film growth. A few experimental results support this inference. Kawashima et al. [28] have reported recently on a 'rhythmic' growth of this type for yet another polyester.

The rhythmic growth is observed during growth of a lozenge shaped single crystal that develops in relatively thin film. It is manifested by a succession of thinner and thicker growth crowns. They are generated by the fact that molten polymer diffuses to the growth front, which develops a rather thick part. This feeding generates a thin depletion layer in front of the growth front, in which growth proceeds as a flat-on, non-birefringent lamella. When the tip of this lamella reaches again a thicker, molten part, growth more akin bulk crystallization starts again. Repetition of this fluctuation in the growth process (or more exactly growth geometry) generates an alternation of birefringent and non-birefringent growth rings that reminds, but is different from, banded spherulites. This is typically a situation where diffusion controls growth, but the very specificity of the system indicates that it cannot be of general applicability in bulk crystallization.

Another possible manifestation of rhythmic crystallization or more exactly rhythmic features in polymer crystallization has been observed by Lovinger [29], Briber and Khoury [30], and later, by Okabe et al. [31]. It takes us back to twisted lamellar crystals. Lamellae of PVDF in the α modification tend to twist. When crystallized in thin films, however, the lamellae are observed to remain flat for some time, before an abrupt half turn sets in: Lovinger [29] interprets this behavior as resulting from the accumulation of stresses in the lamella, that are released by 'explosive' twist when reaching a 'saturation' point. Briber and Khoury [30] further note that the twist is accompanied by significant 'fanning out' of the lamellae, which results in a rhythmic multiplication of lamellar tips and overall lateral extension of the growth front. Such complex growth features will be considered only briefly later, which also illustrates the limitations that we set to the structural approach of lamellar twisting developed in this review.

3.2. Theories that associate lamellar twisting with structural features

Over the past 20 years or so, lamellar twisting in polymers, and most prominently in PE, has been accounted for by two major features of polymer morphology: screw dislocations and surface stresses associated with existence of chain folding.

3.2.1. Lamellar twisting as a result of screw dislocations
Following initial observations by Bassett and Hodge [7], the group in Reading has emphasized for many years that, at

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Note that the middle of the C shaped profile corresponds to the intersection of the twisted lamella when it is perpendicular to the spherulite surface, and becomes, therefore, the more prominent topographical feature of that surface. Reprinted from Ref. [5] with permission from John Wiley. (b) Scanning electron micrograph of a spherulite displaying growth sectors with different lamellar twist senses, observed in the same sample as Fig. 1. The boundaries between the radial growth sectors made of right- and left-handed twisted lamellae have been underlined. Cs and inverted Cs correspond to left-handed and right-handed twist of lamellae, respectively.

least in PE, lamellar twisting in spherulites is the global result of a succession of isochiral screw dislocations and each screw dislocation contributes to the overall twist by a quantum increment of lamellar splay. Lamellar splay at the screw dislocation center would result from the pressure exerted by cilia protruding from the fold surface. Isochirality of the screw dislocations would result from the chain tilt in the lamellae (for a recent review, see Ref. [7]). It must be pointed out that Bassett's more recent analyses acknowledge the role of surface stresses as a source of lamellar twisting. We quote: 'A link between banding and molecular inclination is to be expected because the underlying cause of banding is most probably relief of stress in basal or fold surfaces' [8]. However, the iteration of lamellar splay at successive screw dislocations or other branch points is considered to be the major cause for the overall fanning out of lamellae, and ultimately the development of banded spherulites. Since many papers emphasizing screw dislocations have been published by these and other authors, this issue needs to be analyzed briefly.

An approach based also on the impact of isochiral screw dislocations to account for lamellar twist has been used recently by Toda et al. [6]. These authors also establish the correlation between the non-planar lamellar morphology and the so-called 'chair' shaped single crystals observed and described a long time ago by Bassett et al. [32] (Chair-like crystals are a variant of the tent-like, four sectored single crystals in which the tilt of the chains is similar in all sectors and thus, generating a chair-type morphology). The argument may become quite involved, as assessed by a recent debate between Keith [11] and Toda et al. [6,33] about the exact correlation between the chain tilt in the lamellae and the sense (the right or left handed) of the screw dislocations. Keith, advocating surface stresses rather than the impact of screw dislocations, has presented a diplomatic, and at the same time, very realistic evaluation of the impact of screw dislocations [11]. We quote here that: 'Regardless of how they are formed, there is no question that isochiral screw dislocations and accompanying divergences in lattice orientation contribute in some measure to banding as Bassett and his group suggest, possibly with the help from some local cilia pressure. However, (…) Padden and I have been convinced that torsions, produced directly by unbalanced surface stresses in lamellae with favorable chain tilt, must be overwhelmingly the principal agency'. Keith points out in particular that 'band spacing in spherulites can become very small (about 1 µm) during rapid growth of densely packed lamellae that show minimal splaying', which makes the screw dislocation approach impractical.

Other arguments have been put forward—again by Keith [11]—regarding in particular the location of the screw dislocations in the growing lamellae. These would have to be located very near the growth tips—and indeed, Toda assumes that they take place on the 'front' of the (110) growth faces (in this case of PVDF), or even at the very tip of the growing lamella, at the seam between the two half lamellae bounded

by the (110) and the ($\bar{1}$10) growth faces [6,34]. Two elegant papers on the development of screw dislocations at the boundary of two growth sectors have appeared recently [35,36], which leave the debate open. Whether this view corresponds to a very realistic evaluation of the actual situation is doubtful. Growth under different crystallization conditions (many of which approach or mimic bulk crystallization) indicates that generation of screw dislocations very near the growth tips (as assumed by Toda et al.) is quite rare: most screw dislocations develop on the lateral edges of the lamellae (and frequently at reentrant angles—cf. Fig. 4). This argument holds true in particular for crystallization in the presence of paraffin (that mimics the molten environment of the spherulite during growth), i.e. under conditions that prevail when at least the first, 'leading' lamellae set the overall spherulitic pattern.

As can be seen later, another argument against the impact of screw dislocations has been put forth recently. Spherulites of some chiral polymers have a unique sense of lamellar twist, yet crystals (admittedly grown from solution) display screw dislocations of the two possible hands: the hand of screws and sense of lamellar twist, at least in chiral polymers, may not be univocally related.

Beyond these arguments, which are not conclusive in favoring either side, some very clear morphological evidence can be presented against screw dislocations as the sole (or even the major) cause of overall lamellar twist. The argument is very simple indeed: if screw dislocations are involved, twist can only be displayed by multilamellar entities produced by the different screw dislocations. If to the contrary the origin of twist is intralamellar and is, for example, a manifestation of stresses in the fold surfaces, single lamellae may or should be twisted.

An illuminating observation reported several years ago by Kunz et al. [37] in an apparently unrelated work must be presented at this stage. These authors investigated the crystalline morphology in physical gels of ultra-high
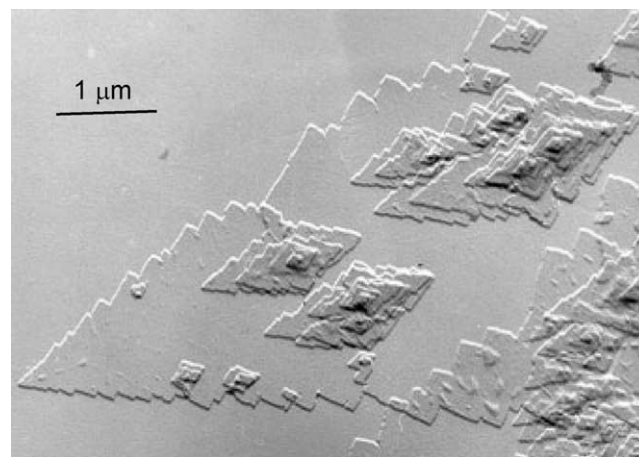

Fig. 4. Screw dislocation developing on the edges of a PE lamella. These ultimately 'giant' screw dislocations are an essential ingredient in filling up the space during spherulite growth [36]. Reproduced with permission from Keith and Chen [36].
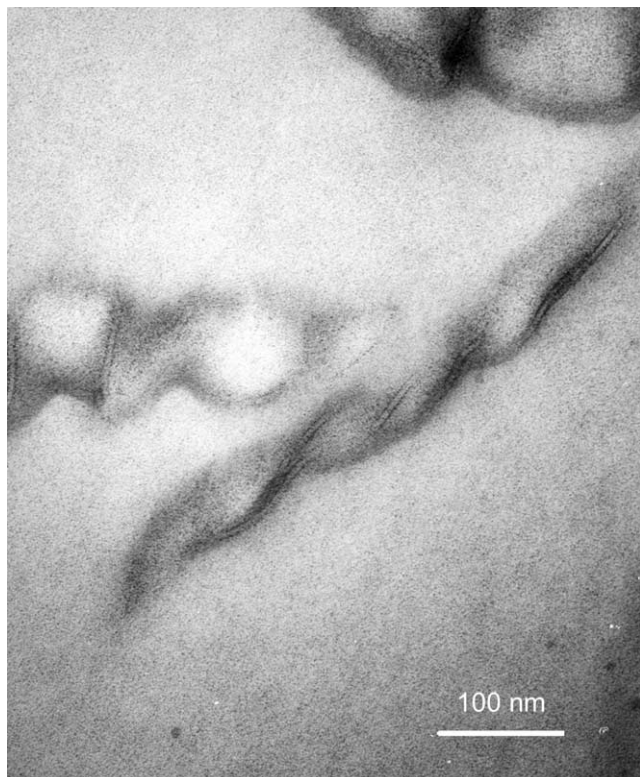
Fig. 5. Twisted lamellar morphologies obtained by Kunz et al. [37] when UHMWPE is crystallized in a decalin solution. Decalin is replaced by methacrylate that is polymerized to yield crystals of UHMWPE embedded in a hard PMMA matrix while keeping their original geometry (they have not collapsed on a support surface). The sample was microtomed and stained with RuO$_4$. Corrugated single lamellae (a feature well known in crystallization from dilute solution) are also formed. Transmission electron micrograph. Reproduced from Ref. [37].

molecular weight PE (UHMWPE). The gels were produced at concentrations of a few percent in decalin. In order to observe the pristine crystal morphology, the gel was never dried or freeze-dried. Decalin was replaced by methacrylate, which was later polymerized by UV. The UHMWPE physical gel, embedded in solid PMMA was microtomed and stained. The staining agent decorated preferentially the fold surfaces of PE, and underlined the three-dimensional lamellar morphology.

The gel is formed of corrugated lamellae that are known to result from alternation of the chain tilt sense in small sectors of solution grown single crystals. However, twisted individual lamellae are also observed, as shown in Fig. 5. This piece of evidence is sufficient to demonstrate that the lamellar twist has an intralamellar origin and does not necessarily imply screw dislocations. This also illustrates the fact that twist periodicity can be very small when the lamellae are narrow. In other words, the impracticability argument against screw dislocations for small periods of twist does not hold when the twist has an intra-lamellar origin.

This observation of Kunz et al. [37] which, again, was made in a different context, is of course an essential ingredient in the discussion on the possible origins of

lamellar twist developed next. It suggests a probable mechanical origin to lamellar twist and helps locate this origin within the individual lamella itself: if individual lamellae are twisted, the cause of lamellar twist must be intralamellar. Moreover, since crystallization takes place in a dilute or semi-dilute solution, growth rates are probably relatively low and impact of diffusion processes is most probably limited. In the same experiment indeed, corrugated lamellae are also produced, which are reminiscent of single crystals, and typical of slow growth rates, or crystallization of lower molecular weight material at low supercooling. This observation, therefore, also casts doubt on the impact of diffusion-controlled or diffusion-dependent processes such as rhythmic crystallization [9] or development of concentration fields [10].

3.2.2. Lamellar twist as a result of surface stresses

The suggestion that lamellar twist results from surface stresses is by no means new. In his book, Geil [38] and more recently, Schultz [10] provide an excellent summary of the case, some aspects of which only are recalled or cited here. We quote Schultz: 'Lehmann [39] suggested already in 1888 that the twisting of ribbon-like crystals is associated with surface stresses'. And also: 'Noting that lattice parameters at the surface of a crystal are generally dilated with respect to the core, Yoffe [40] in 1944 suggested that the stresses associated with such a gradient in lattice parameter could be reduced by twisting of thin, lath-like crystals'. Hoffman and Lauritzen [41] suggested that an equivalent effect may result from the spatial constraints created when imposing the existence of a fold near a crystalline core in chain folded crystals.

Geil in his book on 'Polymer Single Crystals' discusses in quite detail the impact of surface structure on lamellar geometry: 'the twisting of the lamellae may be due to a surface strain related to their nearly two-dimensional character' with 'an additional surface strain… introduced by the folds' (in Ref. [38], p. 259, also p. 401). In a recent private discussion, Geil pointed out the analogy of polymer lamellae with trimetallic strips, i.e. strips that have a heart made of one metal sandwiched between two identical layers made of another metal. On cooling (or heating), due to the different thermal expansion coefficients of the metals, these trimetallic strips twist. The analogy is almost perfect with polymer lamellae, and twist would result from balanced surface stresses (the two outer parts are symmetric). However, this analogy is not entirely satisfactory. Indeed, all polymer lamellae (made of a crystalline core sandwiched by two amorphous layers) are structural analogs of the trimetallic strip, which implies that all polymer lamellae should twist. Also, the very symmetry of the model implies that the twist sense cannot be predicted from the model, or preserved during growth, through e.g. screw dislocations, etc. This preservation exists in polymers (cf. Figs. 1(b) and 3). It implies that some other, and even some specific structural
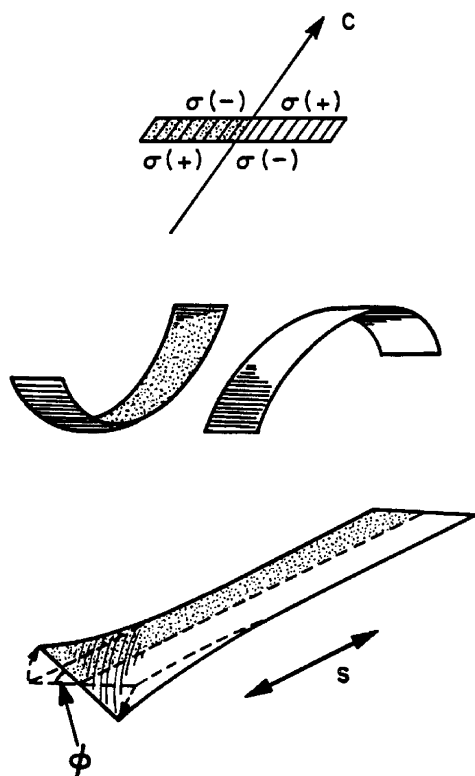
Fig. 6. The origin of lamellar twist, as suggested by Keith and Padden [16]. In the top view, the lamella is seen from its growth direction. Due to the asymmetry generated by chain tilt, differences in fold encumbrance (due to conformation differences, etc) are supposed to exist on opposite fold surfaces of the lamella. The resulting unbalanced surface stresses, if exerted on half-lamellae split along their growth direction (middle view), would induce a lamellar curvature, opposite for different half-lamellae (observed as the symmetrical growth of edge-on lamellae in Fig. 7(a) and (d)). In bulk crystallization however, the half lamellae are seamed together, and the whole lamella twists to relieve the surface stresses (bottom view). Adapted from Ref. [16].

element must be involved, that differentiates polymer lamellae from trimetallic strips.

In a seminal paper in 1984, Keith and Padden [16], who had investigated in much detail the structure and optical properties of PE [2], and who were triggered by the observation of Bassett that in spherulites, dominant lamellae adopt S-shaped profiles [7], elaborated on these premises. They developed a very simple model of unbalanced surface stresses that rests on a few postulates. The model was first developed for PE, but the principles are general, and valid for other polymers and systems as well. These postulates, and more importantly their genesis, experimental basis and underlying hypotheses must be recalled, especially since they will be the basis of most of the ensuing discussions and developments in this contribution.

Structural investigations indicate that in PE spherulites, the radial growth direction is the b axis. The chains are tilted in the ac plane, to the lamellar surface normal; tilt angles may range from 18 to 35° (usually) and even to 45° at high

temperature: fold surfaces are the (101), the (201) or, in rare cases (45° tilt), the (301) planes, respectively. When seen from the growing tip of the lamella, the cross section of the lamella is, therefore, a parallelepiped, and not a rectangle (Fig. 6).

Polyethylene spherulites are composed of radial sectors in which lamellae adopt a right-handed or a left handed twist. 'The sense of twist remains identical in entire growth sectors, with some spherulites being made of sectors of one or the other twist sense, the sectors being separated by sharp boundaries' [2]. Fig. 3 shows such radial sectors, as evidenced by the surface topography that reveals a characteristic change from a C shaped lamellar profile (indicating the left-handed lamellar twist) to an inverted C profile (right-handed twist). As already indicated, this constancy suggests that some form of simple structural information is memorized and preserved during growth of radial lamellae, including during development of screw dislocations and (although less probably) during lamellar branching.

Among simple structural features, chain tilt is the most likely candidate. Apparently, this correlation was first suggested in one of the authors' laboratory and presented in Labaig's thesis, in 1978 [42]. We quote that: 'The link between lamellar twist and lamellar molecular structure might be established experimentally by demonstrating the relationship, which appears likely, between the twist sense (the right or the left) of the lamellae and the tilt sense of the chains in these lamellae.... Transposed to spherulites, this hypothesis amounts to consider that the equal frequency of growth sectors with right or left lamellar twist simply reflects the probability, obviously equal, to find right and left tilts of the chains in the lamellae of the nucleus'. As pointed out by Keith [11] however, this reasoning was not pursued, although it had stated the correct premises.

Keith and Padden in their 1984 paper [16] elaborated independently on a 'mechanical' model that links chain tilt and lamellar twist (Fig. 6). They suggested that chain tilt induces surface stresses probably arising from differences in fold conformations on opposite sides of the lamella. When seen from the growth direction, the chains form an obtuse angle and an acute angle with the fold surface. If, due to the local environment (growth conditions, mechanisms by which the stems deposit or rearrange on the growth front) the fold conformation or encumbrance differs at these obtuse and acute angles, differential compression or dilation stresses are exerted on the lamella. If the lamella were split along its long axis in two crystal halves, these stresses would result in bending of each crystal half, in opposite directions, for simple reasons of symmetry. However, the two crystal halves are seamed together along this central line. Therefore, the opposite bending moments create a torque that results in the overall twisting of the entire lamella. These effects were re-created by Keith and Padden in a set of very enlightening experiments. A rubber strip was partly covered with an impermeable surface layer on opposite surface halves, to

recreate the asymmetry just considered, and soaked in a solvent. Swelling of the unprotected surface sides of the rubber generates a twist of the rubber strip along the length, as observed in polymer crystals [16]. Since swelling is isotropic, the strip is also bent in the transverse direction, and takes up an S-shaped profile already observed by Bassett et al. [7,8] for PE crystals. It is clear that surface stresses may exist in different directions, and lead to longitudinal lamellar twisting as well as transverse bending.

The 'mechanical' analysis of lamellar twisting introduced by Keith and Padden [16] therefore, rests on the existence of surface stresses in the fold surface, i.e. in the plane of the lamella rather than normal to it, as assumed by Bassett [7] for the pressure exerted by cilia. In any case, the latter would be effective only for multilamellar entities, and account for splaying of successive lamellae in screw dislocations, whereas we are dealing here with twisting of individual lamellae.

The analysis takes for granted that the chains are tilted to the lamellar normal or surface in a plane perpendicular to the growth direction, but the model is essentially based on two assumptions. First, the folds are different on opposite fold surfaces of the lamella (as a consequence of chain tilt, although the origin of these differences is not established); and second, half-lamellae would bend as a result of unbalanced surface stresses associated with different fold conformations

These two assumptions have been supported by experimental evidence gathered in a later work, performed during one of the authors' summer stays at Bell Labs, with Keith and Padden [43]. The evidence rests on the use of single crystals grown in thin films. The title of the paper: 'Asymmetries of habit in polyethylene crystals grown from the melt' may not have emphasized enough the relevance of this work to the more general issue of surface stresses and twisting of polymer lamellae, and thus of banded spherulites. It is, therefore, worth recalling some of the major experimental evidences collected and conclusions reached, especially in the context of a paper dealing with lamellar twisting.

Polyethylene (a NBS fraction, MW $\approx$ 32,000) when crystallized in thin film at relatively high T_c produces large, flat, lath-like crystals which are 'adorned' with what appears to be 'hooks' on one of their sides. A most spectacular optical micrograph of these crystals, not previously presented, is shown in Fig. 7(a). Similar crystals and hooks had been produced by Labaig in his thesis work and were at the origin of the suggested link between chain tilt and lamellar twist [42].

Electron diffraction analysis of these crystals [42,43] indicates that the chain axis is tilted by 45° to the lamellar surface. Indeed, tilting by + and −45° in the ac plane (around the long axis of the crystal) yields diffraction patterns normal and parallel to the chain axis direction (the b^*c^* and a^*c^* sections of the reciprocal lattice). This 45° tilt (the (301) fold plane) is the largest tilt recorded in PE lamellae, also observed only in mechanically deformed PE (double

orientation induced by rolling) [44]. In reality, the chain tilting in lamellar single crystals may be more complex than a single tilt angle in different sectors. However, these differences do not significantly affect the outcome of this analysis.

The crystals can be decorated with PE vapors. This so-called 'polymer decoration technique' [45] rests on the evaporation and subsequent condensation/crystallization of PE chain fragments ($\sim$ 10 nm long). Polyethylene decoration is a very sensitive technique since nucleation and crystallization of the PE rods is induced by the surface on which the PE vapors are condensed. It 'probes' the outermost surface of the underlying material, since only van der Waals forces are at play. Polymer decoration can reveal the orientation of folds in e.g. single crystals. However, the pattern of decoration may be significantly altered for different underlying surface structures [46,47]. This is precisely the result observed for the present crystals: the decoration pattern is different on opposite sides of the lamellar tip, with a clear boundary along the growth axis of the crystal (parallel to the b axis) (Fig. 7(b)). This difference is not linked with the fact that crystallization took place in a thin molten film and that an exposed (top) surface is decorated. Indeed, decoration of the opposite side of the lamella (that was in contact with the mica surface) yields a similar, but symmetrical decoration pattern. Although purely qualitative, this decoration experiment demonstrates that the first hypothesis in Keith and Padden's reasoning is valid. The fold surface created at the acute angle of the growing lamellae differs from that at the obtuse angles. The structural or conformational differences remain as yet undefined: conformation, density of loose loops versus sharp folds, etc. The same holds true for the processes that generate these differences: during the chain deposition as a result of the different substrate environment created by the presence of an obtuse or an acute lamellar edge, or as a result of structural rearrangements after the initial crystallization. Compared to the main contribution, namely an experimentally demonstrated difference in fold surface structure, these considerations are however of secondary importance, at least at this stage of the analysis.

The second feature of interest was totally unexpected. Probably because the crystals tend to bend in the transverse direction (the S-shape cross section observed by Bassett [7]), the crystals topple over on one of their edges, namely the lateral growth front for which the chain axis overhangs the mica surface at a 45° angle. Even a slight transverse bending moment may be sufficient to induce this local, but abrupt (after possible reorganization) reorientation of the lamella. As a result, chains now lie *flat on* the mica surface, and growth now produces *lamellae standing edge-on* on the mica surface, with the b axis of the parent and daughter lamellae remaining-initially at least-parallel (Fig. 7(c)). As a result of this edge-on orientation, half lamellae, i.e. lamellae 'split' along their growth axis (b axis) are produced, as assumed in the model of Keith and Padden (cf. Fig. 6 in the middle). These half-lamellae are bent, with the growth direction
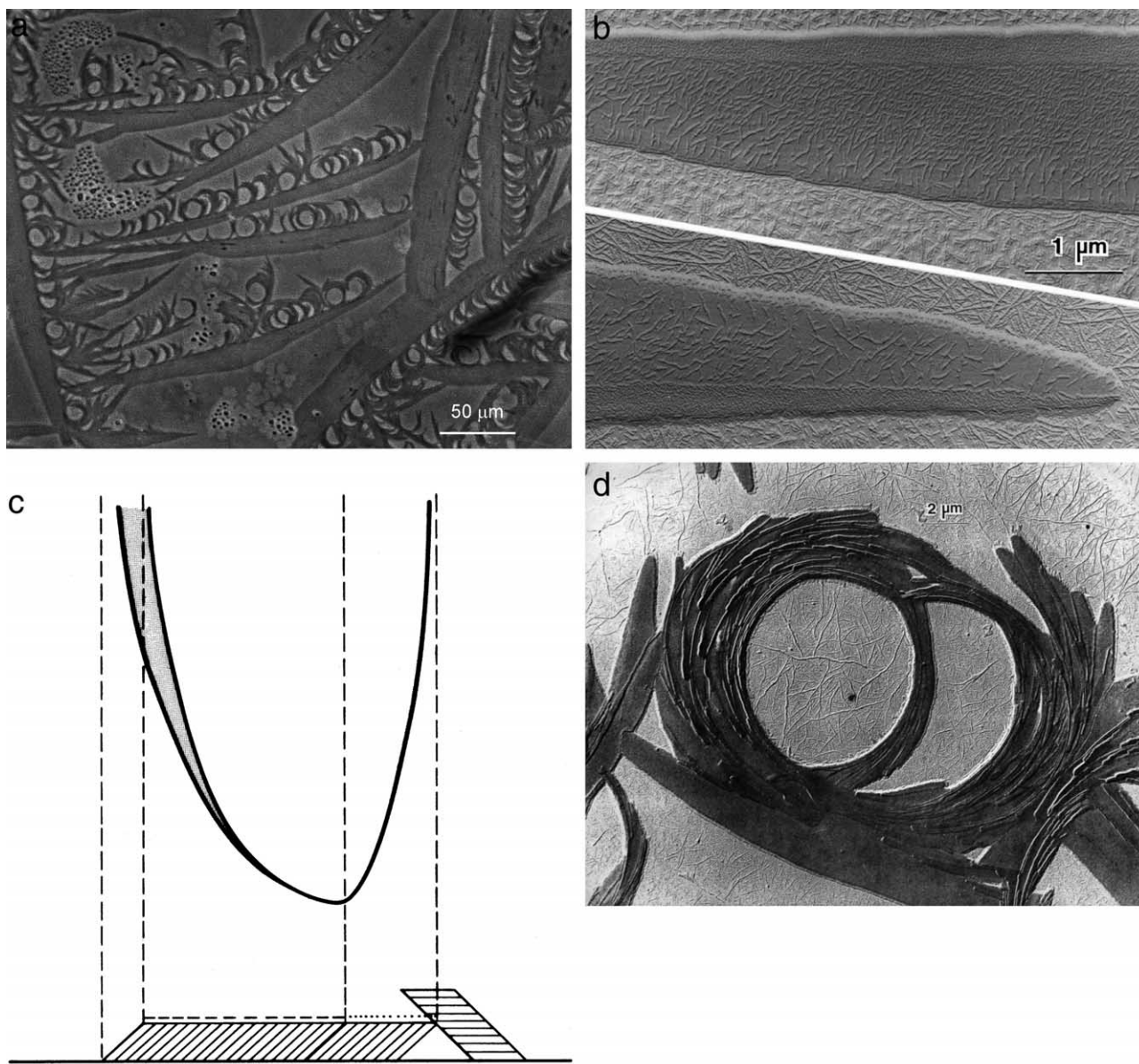
Fig. 7. (a) Single crystals of PE (MW 30,000, NBS fraction) produced by crystallization of a thin film at 135 °C under N_2 atmosphere. Note the development of 'hooks' on one side of the crystals. They correspond to edge-on growth of (half) lamellae. Optical micrograph, phase contrast. (b) Tips of flat-on single crystals as shown in part (a), decorated with PE vapors. Note the difference in decoration density and pattern, indicative of a different fold structure on opposite sides of the growth tip. Electron micrograph, Pt/C shadowing at $\text{tg}^{-1} = 1/3$. (c) Schematic representation of the structure and chain axis orientations in flat-on lamellae and edge-on ones shown in parts (a) and (b). (d) Close-up view of flat-on and curved crystals as seen in part (a). Note the radius of curvature of the edge-on crystals (≈ 5 μm) as well as the symmetrical curvature for lamellae growing in opposite directions. Electron micrograph, Pt/C shadowing at $\text{tg}^{-1} = 1/3$. Parts b–d in this figure reproduced from Ref. [43] with permission. Copyright 2004 American Chemical Society.

(parallel to the b axis) oriented progressively away from the initial one, while still remaining parallel to the mica substrate. The bending can result in quite spectacular complete turns of the growth front (Fig. 7(d)). The observed bending of half-lamellae split along their long axis supports the second assumption (existence, and imbalance of surface stresses) in the model of Keith and Padden. Moreover, bent crystals with two symmetrically related curvatures are generated. It is easily understood that when a lamella becomes oriented edge-on, growth in opposite directions should lead to mirror symmetry-in this case, of the bending moment. Note also that

for these relatively high T_cs and large lamellar thicknesses, the radius of curvature is several micrometers. This is difficult to translate in any definitive twist periodicity, except for noting that band periodicity in spherulites produced in this crystallization range are indeed larger than at low T_cs.

Finally, it should be noted that similar curvature of half lamellae growing edge-on has been observed during actual growth in real time by Hobbs et al. [48] using high temperature in situ AFM. Characteristically, the curvature is more pronounced or even exists only for the fastest growing lamellae, i.e. presumably when the b axis is parallel

to the substrate. These investigations of growth in real time confirm that for individual half lamellae growing edge-on the bending (curvature) 'sets in' immediately at or near the growth tip, which indicates that the underlying surface stresses exist and manifest themselves virtually at the deposition site.

The above experimental results are multiple:

Observation of twist in lamellar (as opposed to multi-lamellar) PE crystals grown from solution [37],
Evidence for differences in fold surface structure (revealed by polymer decoration) linked with chain tilt in the lamellae (revealed by electron diffraction) [43],
Observation of lamellar bending in crystals split along their long axis (crystal halves growing on edge) [43,48].

They all support the analysis of Keith and Padden [16] stating that lamellar twist in PE derives from unbalanced surface stresses associated with different fold encumbrance at opposite fold surfaces of the lamellae. The structural feature that is at the root of unevenness of fold encumbrance is the chain tilt in the lamella. The sense of chain tilt is actually also the structural element that introduces 'chirality' in the process, since it imparts either the right- or the left-handed lamellar twist (in agreement with the early inference of Labaig). Since the origin of twist lies in the structure of the individual lamella, the contribution of reorientations associated with multilamellar entities (splaying of lamellae at screw dislocations, etc) may not be an essential ingredient in setting the overall banding of spherulites. The role of screw dislocations remains however essential in the space filling process associated with spherulite growth. Moreover, the sense of the chain tilt must be maintained through the screw dislocation, as illustrated by the constancy of lamellar twist sense in the radial growth sectors (cf. Figs. 1(b) and 3). This preservation of tilt sense is indeed demonstrated in very enlightening results obtained by Bassett, who could visualize these individual screw dislocations by etching away, or otherwise dissolving the bulk of the material that surrounded these screw dislocations during growth. However, it is clear that the above analysis is not in accord with a recent analysis of Bassett's [8,49]. He emphasizes the role of screw dislocations as the major cause of lamellar twist, and of resulting banding in spherulites. Moreover, Bassett also develops a scheme in which the torque of the lamellae '…would also be expected to produce different patterns of folding on opposite surfaces (of the lamellae)'. 'This feature has been observed but…according to this interpretation would be a consequence rather than the cause of twisting and banding'. The experimental evidence provided by Fig. 7(b) contradicts this assertion: indeed, the difference in fold structure is established in lamellae that are flat (constrained by the glass surface) and moreover are present at the very tip of the growing lamellae. The simple chronology of events demonstrates that differences in fold structure predate lamellar twist (and even exist in the absence of twist),

which reverses the conclusions of Bassett: differences in fold structure induce (and are not induced by) twisting.

To conclude this section, it may be worth emphasizing the fact that determining the existence of surface stresses in the fold surfaces of PE lamellae has been a very challenging issue, mostly because PE is a featureless, achiral polymer that is not expected to display chiral features. In retrospect, it appears as a fortunate exception, since similar experimental checks are not available for most other systems investigated.

It is also clear that the impact of surface stresses on the overall morphology should, and can, be manifested in many different ways depending on the disparity of stress fields on opposite fold surfaces, on orientation of stress, or relative size of stressed domains. Exploring the latter issue, Keith and Padden [17] could shape the initially flat rubber strip into helicoïds wrapped around a cylinder. They simply created an imbalance in the size of swollen areas by shifting the limit of the two swollen domains away from the middle of the rubber strip. The impact of surface stresses also depends on lamellar thickness or lamellar width, as illustrated by the sharp variation of the periodicity of extinction rings in PE spherulites with the crystallization temperature.

Imbalance of fold geometry or conformation can thus be validly considered as a generic origin of lamellar twist in polymer spherulites. This imbalance may arise from chain tilt in the lamellae. Chain tilt is a frequent feature of polymer crystals, and is probably a significant ingredient in the widespread observation of lamellar twist. This would hold true for many polymers with monoclinic (*ab* plane tilted to *c*) or triclinic unit-cells when the fold surfaces of the lamellae are parallel to that *ab* plane. This inference has already been pointed out by many authors, and has been discussed recently in detail by Keith [11]. Representative examples of this class of polymers appear to be aliphatic polyesters. They frequently have monoclinic unit-cells with (001) fold surfaces. In spherulites of monoclinic polyesters that display spectacular optical banding, the radial growth direction is parallel to the unique axis of the cell i.e. the chains are tilted in the lamellae as for the PE case just considered. When, however, the growth direction differs from that unique axis, optical banding is not observed [26,26,50]

4. Lamellar twist in chiral polymers

The above analyses suggest that lamellar twist is due to unbalanced surface stresses associated with the existence of folds with different bulkiness on opposite fold surfaces of the lamella. However, it is known that spherulites of chiral polymers are frequently banded, implying that their lamellae twist. The phenomenon is rather common, and is sometimes described as the 'chirality effect'. An obvious question then comes to mind: does the origin of the twist lie in the crystalline core, or in the fold surface? If the origin is in the crystalline core of the lamella, is it a result of the packing or of the chain conformation? Would lamellae be twisted if they
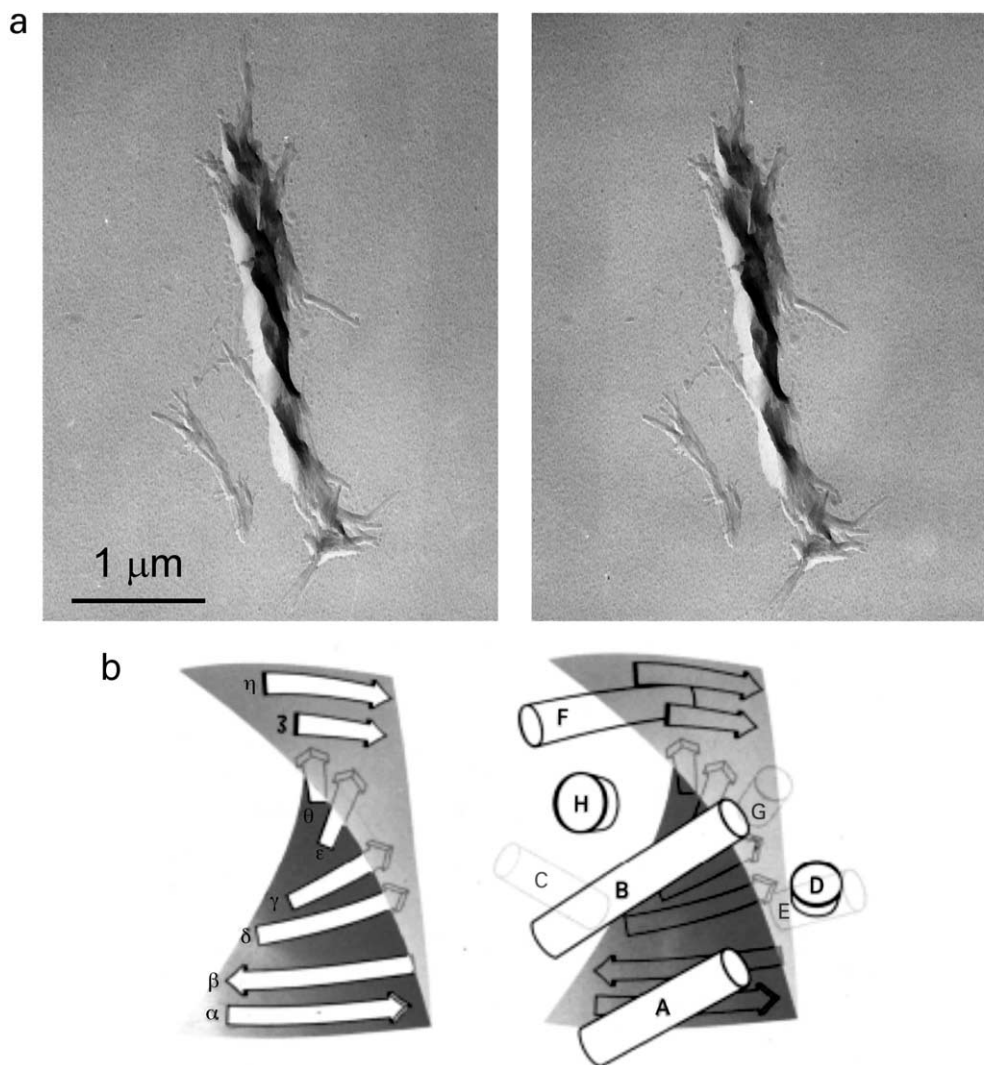
Fig. 8. (a) Single crystal of Bombyx mori L. silk fibroin crystallized from an aqueous solution of LiBr by slow dialysis against water. Stereopair, electron micrographs, shadowed with Pt/Carbon at $tg^{-1}=1/3$. Reproduced from Ref. [51]. Copyright 2004 Kluwer Academic/Plenum Publishers. (b) Schematic drawing of the chain conformation of a globular protein (Carboxypeptidase A) illustrating the coexistence of twisted β sheets and of α helices, the latter shown as cylinders in the right hand side drawing (random parts are omitted). Note that the twist of the sheets is left-handed when seen along the hydrogen bond direction, as it is in the crystals of B. Mori silk (part (a)). Note also that (as indicated by the arrows) strands α, β and δ are antiparallel, whereas most of the rest of the sheet is made of parallel strands. Illustration, Irving Geis from "The Structure and Action of Proteins" by R.E. Dickerson and Irving Geis, published by Harper and Row, 1969. Rights owned by Howard Hughes Medical Institute. Not to be reproduced without permission.

were made of short chiral chains that are in extended form, with no folds (provided of course that the chain ends are not too bulky)? Conversely, does the chiral chain conformation induce different folds at opposite fold surfaces? In other words, is lamellar twisting of chiral polymers amenable to the above analysis that involves imbalance of surface stresses?

As developed now, the origin of lamellar twist of chiral polymers depends on the specific polymer and may either lie in the crystalline core or, more frequently, in the fold surfaces. As an example of the first situation, we recall first an analysis of twisting in silk fibroin. However, the β sheets of silk fibroin have a strong structural identity, and silk fibroin appears to be rather specific as regards the origin of twist.

Analysis of lamellar twist in more conventional chiral polymers examined next suggests that the configurational and conformational stem chirality generates different fold conformations and/or structures on opposite fold surfaces, which in turn induce lamellar twisting.

4.1. Lamellar twist of silk fibroin: twist originating in the crystalline core

A spectacular twist is observed for single crystals of silk fibroin, produced by the common silkworm, Bombyx mori L. As illustrated by the stereopair shown in Fig. 8, crystallization from a dilute solution generates single crystals-actually stacks of single lamellae ≈ 6 nm thick. The crystals

are in the β sheet modification and display a left-handed twist (twist periodicity: 1 μm). The origin of the twist can be traced down to the chirality of the peptide residues of the chain, thanks in great part to a comparison with the structure of globular proteins, a possibility that does not exist for any other synthetic polymer. It is necessary to summarize this analysis in the context of the present paper since this work was published in Journal of Molecular Biology [51], and was until recently little known to the 'synthetic' polymer community.

Silk fibroin is a fibrous protein made mainly of achiral glycine residues (NH–CH$_2$–CO) alternating with L-alanine (NH–C*H(CH$_3$)–CO) and L-serine (NH–C*H(CH$_2$OH)–CO) in a 2/1 ratio, thus the sequence: (Gly-L-Ala-Gly-L-Ala-Gly-L-Ser)$_n$.

To a good approximation, by replacing the OH group of Serine by a hydrogen atom, the sequence can be further simplified to (Gly-L-Ala)$_n$. The latter synthetic polypeptide displays the same structural characteristics and lamellar twist as silk fibroin [52]. Analysis of the crystal twist includes several steps [51]:

On 'the β plateau' of the conformational energy map of poly(L-peptides) [53], the minimum energy conformation is slightly away from conformations that would yield strict two fold screw symmetry of the chain. As a result, the near extended chain conformation of silk fibroin in the β modification is slightly twisted, with a *right-handed* twist when seen along the chain direction.

Inter-chain hydrogen bonding generates a β sheet that has a left-handed twist when seen along the hydrogen bond direction (and the growth direction of the crystal). (The apparent change of twist sense simply results from the fact that the direction of observation is at right angles to the initial one. This change of twist sense can be checked easily by observation of a metallic screw).

Packing of the sheets side by side preserves the sheet twist and results in the observed left-handed crystal twist.

The origin of both chain and β sheet twists as described above is easy to trace down by examining the structure of some globular proteins or enzymes [53]. Some of these globular proteins are made of one or a few small β sheets (made of only several stretches of the chain), together with stretches of α helices and/or more disordered parts of the chain. The β sheets are not submitted locally to the constraints of a three-dimensional crystal lattice since their environment is typically made of stretches of the protein chain that are 'disordered'. These β sheets display, therefore, their 'spontaneous' geometry. Both the chains within the sheets and the β sheets themselves are indeed twisted. Being made of shorter stems (typically five to eight residues) and being also less constrained by their environment, the twists of these β sheets are however more pronounced (Fig. 8(b)).

The lamellar twist of silk fibroin, therefore, has its origin in the crystalline core. Is this a general feature of chiral polymers, or is it a specificity of silk fibroin and β sheets of polypeptides in general? Several features of β sheets of proteins suggest that we are dealing with a rather specific (but probably not unique) situation. Indeed, (i) the polypeptides are made of flat, trans-planar peptide residues, with only a single 'joint' in terms of main chain rotational freedom (around (H)N–C$_\alpha$ and C$_\alpha$–C(O) bonds, ϕ and ψ angles of the conformational energy map); and (ii) any departure from crystallographic symmetry is 'locked-in' by the dense array of hydrogen bonds between chains in the β sheet (H bonding to each of the two neighbors chains for every 0.35 nm repeat distance along the chain). As a consequence, the β sheet has a strong structural identity and 'rigidity'. In essence, crystal twisting in silk fibroin stems from the fact that the configurational asymmetry arising from the residue chirality is conveyed, via the chain conformation and the β sheet rigidity, to the whole crystal.

The conformation of the folds has apparently no significant influence in determining the twist of silk fibroin crystals, as suggested—again—by a comparison of the β sheets in fibrous and in globular proteins. In fibrous proteins, they are probably tight, as demonstrated for synthetic analogs of silk fibroin produced by genetic engineering. The folds are so-called β turns that include only one peptide residue in the chain reversal, or even tighter γ turns. In globular proteins to the contrary, the disordered sections of the chain connecting stretches involved in the β sheet(s) cover the whole range from tight (the β and the γ turns) to very loose. So loose indeed that, occasionally, the 'fold' or more precisely the 'loop' connects the top and bottom parts of the (individual) sheet to generate neighbor parallel stems, a situation that cannot exist in chain folded crystals (cf. Fig. 8(b)). In spite of these disparities in fold conformation, the chains and sheets maintain the same twist in globular proteins and fibrous protein crystals. The twist of silk fibroin crystals is, therefore, a genuine characteristic of, and has its source in, the crystal lattice rather than the fold surface.

The above analysis of the origin of twist in silk fibroin is made possible by the availability of detailed crystal structures of globular proteins, which gives access to local conformations of the chains (both ordered and disordered) with atomic resolution. This situation has barely any other parallel in synthetic polymers. This may explain why a similar detailed correlation cannot be established with certainty for other chiral polymers. In the next sections, correlation between configurational and conformational chirality and lamellar twist is considered.

4.2. Lamellar twist dependent on configurational chirality for enantiomers of chiral polymers

The lamellar twist of silk fibroin provides a clear example of straightforward link between configurational chirality (residue chirality) and crystal twist. It indicates that chirality sweeps through the various levels of structural organization. Indeed, for silk fibroin, the unique, left-handed lamellar twist

observed for the crystals is in itself a direct proof of the direct link between residue chirality (the L-peptides) and crystal twist. This hypothesis was further substantiated with the synthesis of Poly(Gly-D-Ala), the synthetic enantiomer of both silk fibroin and its model polypeptide Poly(Gly-L-Ala). The crystals produced from solution have the expected right-handed (i.e. opposite) twist [51].

In a series of studies, Brown and colleagues have investigated the impact of chirality on lamellar morphologies of several other polymers and biopolymers. Singfield et al. [54–56] investigated the (R) and (S) enantiomers of Poly(epichlorohydrin) and of polypropylene oxide. They observed, in line with the earlier results on silk fibroin, that enantiomers of a given chiral polymer produce lamellae that have opposite twists.

4.2.1. Lamellar twist independent of configurational and conformational chirality for homologous series of chiral polymers

A univoqual correlation between lamellar twist and (chemical) chirality of the polymer as just discussed suggests that the configuration of the asymmetric carbon plays a major role in inducing the chirality. This, however, turns out not to hold true when considering series of polymers that have the same chiral center, but different chain constitutions (e.g. residue length). In this context, results obtained on a series of main-chain chiral polyesters, and later on two natural polymers provide essential pieces of information about possible (or unlikely) origins of lamellar twisting of 'soft' polymer crystals. They need to be presented in some detail.

A series of non-racemic chiral polyesters [PET(R^*-n)] all have a right-handed chiral center (R^*) and are synthesized from (R)-(−)-4′-{o-[2-(p-hydroxy-o-nitrophenyloxy)-1-pro-pyloxy]-1-nonyloxy}-4-biphenylcarboxylic acid [57–64]. They bear, therefore, a chiral center, attached to an aliphatic dialcohol with different lengths of the paraffinic sequence: C_7 to C_{11}. The first member of the series to be synthesized [PET(R^*-9)] can exist as flat single crystals when crystallized on a substrate, but also as the most spectacular twisted lamellar crystals observed so far in crystalline polymers (Fig. 9). The crystals are single lamellae, and twist periodicities are in the μm range. Electron diffraction data indicate that the chains are close to normal to the lamellar surface, at least in flat crystals. Polymer decoration indicates that the path of the chain in the folds is parallel to the long axis of the crystal. Furthermore, all the crystals have the same twist, and changing the handedness of the chiral center from right to left [PET(S^*-9)] reverses the lamellar twist-which is in line with the above observations on enantiomeric pairs of the same polymer.

Strikingly however, crystals of polyesters with the same configuration of the chiral moiety but attached to paraffinic moieties with different lengths may display either right or left-handed twist, depending on the paraffin segment length of the particular polyester considered. Specifically, samples PET(R^*-9) and PET(R^*-11) produce crystals with right-

handed twist, whereas PET(R^*-10) produces crystals with left-handed twist. This unexpected feature has been summarized in a paper with a provocative title: 'Left or right, it is a matter of one methylene unit' [62].

The above results indicate that, even for these polyesters in which the chiral center is relatively small compared to the whole repeat unit, the chemical (configurational) chirality is not the sole decisive factor in fixing the lamellar twist sense. Since the link between configurational chirality of the repeat unit and chirality of lamellar twist suffers exceptions (if only one exception-which is demonstrated through this example) configurational chirality is not the (only) decisive factor in defining the lamellar twist sense.

With the same problem in mind, Brown and his collaborators have made a very thorough analysis of various chiral polymers, and notably of bacterial and synthetic polyesters. These authors arrive to the same conclusion regarding the absence of correlation between lamellar twist sense and chiral features of the molecule and helices. These studies need to be described in some detail.

No correlation between main chain chirality and lamellar morphology was observed for two poly(β-hydroxyalkano-ates), Poly(3-hydroxybutyrate) (PHB) [–C(=O)–CH$_2$–C*H(CH$_3$)–O–] and Poly(3-hydroxyvalerate) (PHV), [–C(=O)–CH$_2$–C*H(CH$_2$CH$_3$)–O] [15,49–52,65]. The two polymers differ only by the size of the substituant (methyl or ethyl) attached to the chiral carbon atom. PHV crystallizes from the melt as big, banded spherulites that display a right-handed twist (Note that, using the morphological criterion of C and inverted C lamellar profile on the spherulite surface, the authors underline that lamellae are predominantly right-handed, but do not further dwell on what appears to be a mental restriction) [65]. On the contrary, PHB spherulites display invariably a left-handed lamellar twist. These two polymers however, share the same chirality of the asymmetric carbon and as indicated, differ only by the fact that the side chain of PHV has one more carbon atom than PHB.

These two polyesters further provide an essential insight into the correlation of lamellar twist and conformational chirality. Many chiral polymers adopt helical conformations that are also chiral, i.e. the helices are left-handed or right-handed. The 'chirality information transfer' from configur-ation of the chiral atom to the helix is well established and quasi-universal. It rests on the minimization of short-range inter-atomic interactions. Helix chirality can differ, or not, from the residue chirality: for an (S) enantiomeric polymer it can be right-handed or left-handed, but the helix handedness is fixed.

A number of earlier studies had suggested 'a correlation between the handedness of the helical chains and the twisting lamellae' and even 'the (lamellar) twisting… commonly shares the handedness of the underlying molecular confor-mation' [65]. However, according to earlier structural investigations, PHV and PHB both form left-handed helices, whereas the lamellae are, as stated before, right- and left-handed, respectively. Saracovan et al., therefore, point out
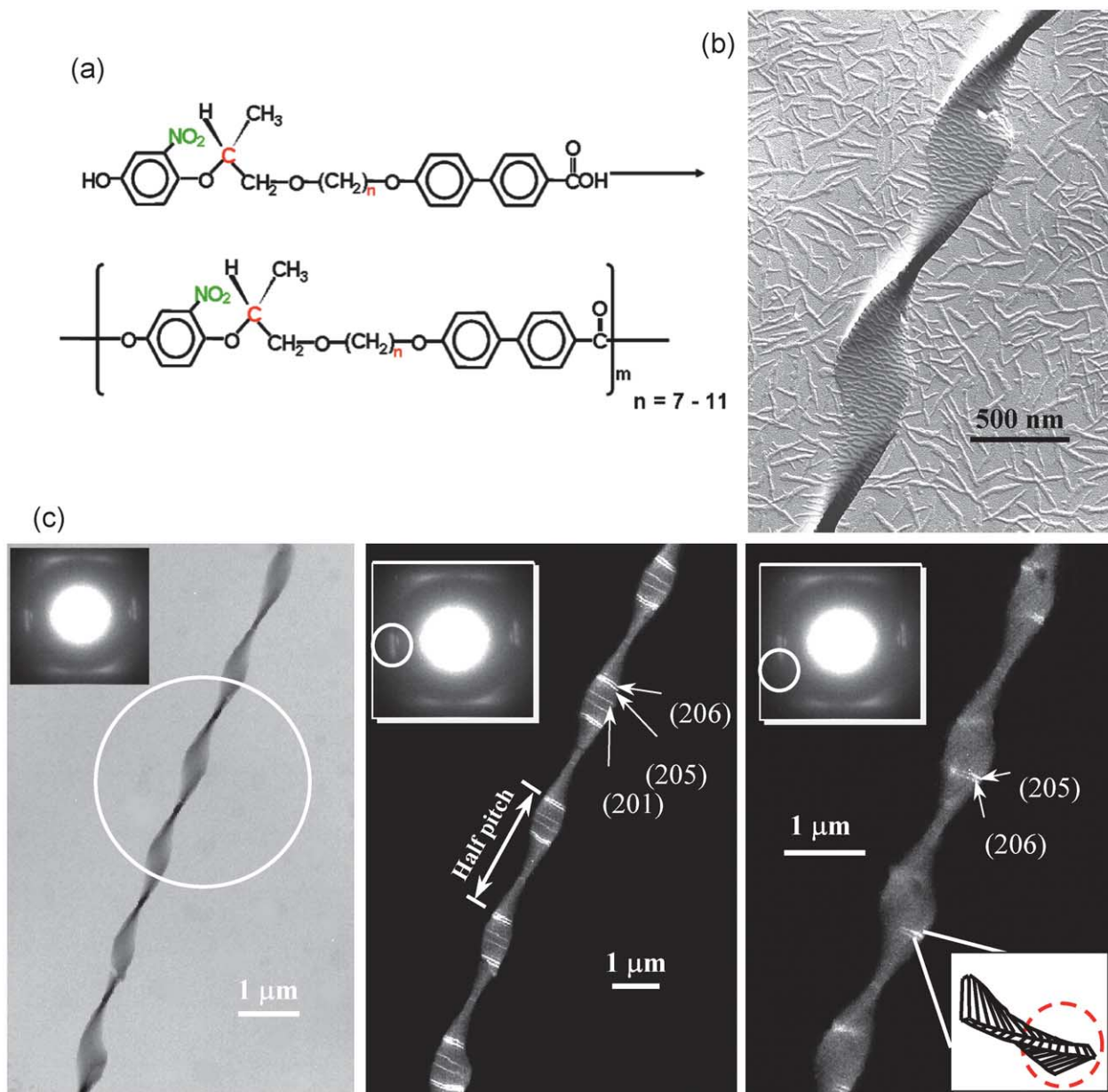
Fig. 9. (a) Chemical structure of the main-chain non-racemic chiral polyester PET(S^*(or R^*)-9). (b) Part of a single crystal of PET(R^*-9) observed by transmission electron microscopy, after decoration with PE vapors. The orientation of the PE rods on the crystal indicates that the chain folds are essentially parallel to the long axis of the crystal. Lamellar twist half-periodicity: 1.5 μm. Reprinted from Ref. [57] with permission. (c) Dark field imaging of a crystal as in part (b). The reflections circled in the inset have been used to generate the dark field image. Note that these reflections correspond to the bright planes arrowed in the DF image. The separation of these planes is fully in agreement with a regular twist of the lamella, and may be explained on the basis of a double twisted lamellar geometry. Reprinted from Ref. [61] with permission. Copyright 2004 American Chemical Society.

that, whereas a single helix hand determines a single lamellar twist, a simple correlation between helix hand and lamellar twist (e.g. right gives right) does not exist. Along a similar line, they point out that, for a given chiral polymer, lamellar crystals grown from solution display both right and left-handed screw dislocations. To quote: '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 the primary determinants of either the handedness or magnitude of the twist of lamellae in

banded spheruilites'. They thus conclude that 'the ultimate origin of lamellar bending and twisting is still an open question in the crystallization of enantiomers with helical chains… and the factors suspected to provoke lamellar bending and twisting must be the focus of further investigations'.

To conclude this lengthy, but much needed review of earlier structural investigations on lamellar twisting, it is necessary to point out that for chiral polymers, the 'final' chirality apparent in the lamellar crystals is the ultimate

outcome of a cascade of chiralities that exist at different length scales. These are, to use a nomenclature introduced by Li et al.: [63] the chiral center (bonds attached to the chiral atom), conformational chirality (helical hand), helical mono-domains (lamellae) or single crystals, and object (clustering of monodomains or crystals) chirality. Summarizing the experimental findings, the chirality information may, or may not be transferred to higher organizational levels:

Chiral center (atom) and helix hand are strongly, but not univoqually correlated (e.g. *R* to right-handed helix sense). Conformation and packing energy analysis of molecules in the unit-cell can usually handle this issue,
Helix hand and screw dislocation sense are not correlated,
Helix hand and lamellar twist are strongly, but not univoqually (right to right) correlated. This is the 'critical' link that is 'evocative of continuing investigation',
Lamellar twist and chirality of the object are strongly and univoqually correlated, since both are morphological levels of organization. (This correlation is valid in case of geometrically unconstrained growth: the PE lamellae in Fig. 7 are constrained to remain parallel to the support mica sheet and are therefore flat, although all the structural ingredients of twisting are present).

We proceed now to examine the factors that induce lamellar twist, taking into account the above at times rather contradictory experimental findings, and suggest possible means to approach molecular insights on the origin of this lamellar twist.

5. Is lamellar twist in chiral polymers a consequence of chain fold organization?

The above examples illustrate that (except when the chains are rigid and the structural elements have a strong 'identity' (e.g. the β sheets)), lamellar twist and even more so lamellar twist sense is not 'written' in the crystalline core chirality, either configurational or conformational (helical hand). For several 'soft crystals' made of flexible polymers, this correlation does not hold, or at least suffers exceptions—and one exception is sufficient to establish the case [62,65]. Furthermore, the crystalline core chirality does not impose a definite hand for the screw dislocations, which rules out these screw dislocations as a possible vector that mediates or defines lamellar twist. Why then, for most polymers, including 'flexible' polymers, is lamellar twist frequently (usually) associated with molecular chirality?

It is unlikely that the twist stems from the crystalline core structure, as for silk fibroin. Of course, many of these chiral polymers adopt a helical conformation, and slight departures from strict crystallographic symmetry (even for irrational helices) could possibly induce a 'crystalline core' lamellar twist. However, most of the helices are relatively 'flexible' (which we describe as 'soft crystals'). Isotactic poly(1-

butene) (iPBu-1) (considered later) can exist in three closely yet different helical modifications: 3_1, 11_3 and 4_1 [66]. The helices probably depart locally from strict helix symmetry since, except for the 3_1 helix, the crystal symmetry differs from the helix symmetry. Such a conformational 'flexibility' (even if confined within narrow limits) appears inconsistent with the development of large-scale features such as lamellar twist. To generate lamellar twists, the local small confor-mational departures must be persistent and be repeated over and over again, and there must be no possibility of nearby compensating feature. For the β sheet, the conformational departures are indeed repetitive and the twist is 'locked in' in the structure at a relatively early stage of crystal growth.

In the present, more speculative part of this contribution, we suggest that lamellar twist of chiral polymers (and some achiral polymers as well) results, as for PE, from differences in fold conformations on opposite fold surfaces of the lamellae. The differences in fold conformations would be a direct consequence of the helix chirality rather than chain tilt as in PE lamellae. In other words, helix chirality would not modify directly the crystal lattice (as in silk fibroin), but rather would generate unbalanced fold conformations that result, in a logical way, from the helical chain conformations. Lamellar twisting of chiral polymers would thus be yet another, but only another, manifestation of unbalanced surface stresses in (single) polymer lamellae. This line of reasoning, still very qualitative at this stage, is now briefly outlined for the Form III of iPBu-1. In essence, it follows a line of reasoning introduced earlier by one of the authors to analyze the lamellar scrolling of γPVDF examined later (in Section 6.1 of this contribution). It rests on the hypothesis that surface stresses are generated with only very small differences in constitution-and, presumably, conformation-of the folds.

5.1. On possible sources of differences in fold conformations in polymer crystals.

It is likely that any repeated feature that is susceptible to induce a small difference in fold volume (or more exactly encumbrance) is potentially a source of surface stresses and may induce lamellar twist (or, as seen later, scroll). For most polymer fold surfaces, differences in fold volume (or encumbrance) are most probably due to differences in fold conformations. If the chemical constitution, chain confor-mation, chirality, crystal structure etc. are favorable, it may well be that some particular fold conformation(s) is (are) preferred. Furthermore, if these preferred fold conformations are segregated on one side of the lamella (as also suggested by the scrolling of the substituted parafins and polyamide 66, cf. later), we have a clear source of differential surface stresses, and potential lamellar twisting (or scrolling).

In order to tackle this issue, our approach is the following. We consider polymers, or specific crystal polymorphs of polymers that display clear cooperative lamellar twisting (banded spherulites). We attempt to get insights on some possible fold conformation(s), if possible of low or lowest

energy, thus most probable and frequent one(s). We check if similar folds can be made, or if different folds must exist on the opposite side of the lamella. If different folds must exist or are possible, the lamellae are likely to twist or scroll.

Low energy fold conformations have been computed for e.g. PE [67–69], or can be determined by structural analysis of e.g. single crystals of cyclic paraffins. Possible fold conformations have been investigated for chemically and structurally more complex polymers by Napolitano and Pirrozzi [70–74].

The present approach is similar in its spirit to the early investigations performed by Reneker and Geil [75] on the tent-like habits of PE single crystals. These authors considered several packing schemes (idealized, but nevertheless realistic) of PE folds that account for the observed slopes of the fold surfaces in PE single crystals. In a similar way, we consider potential variations in fold conformations and locations of the different folds relative to the crystalline core and lamellar basal surface. No assumption is made about the complete fold conformation. Rather, using the crystal structure as a starting point, features of the beginning and/or the end of the fold, as it leaves from and returns to the crystal lattice are identified.

It is probable (but the reasoning does not depend on this assumption) that low energy folds are short folds provided of course that they are not overly strained. This hypothesis is supported by experimental evidence. In PE single crystals for example, the (110) and (020) sectors have different thickness and melting temperatures, presumably associated with the different fold energies and lengths in the (110) and (020) growth sectors (corresponding interchain distances: 0.445 and 0.494 nm, respectively) [76].

Most polymers, and for that matter, chiral polymers with a helical conformation in particular, have conformations that deviate from the trans-planar conformation of PE. As a consequence, the path of the main chain atoms may be (is usually) away from the helix axis. As the main chain path winds around the helix axis, it approaches the path of neighbor helices. Several different folds can link these different 'nearest neighbor' points of emergence of the crystalline stems on the fold surface, which may be significantly smaller than the standard inter-chain (more precisely inter-helix axis) distance usually considered. Given the variability in inter-helical paths distances, helical polymers certainly offer a much wider range of potential low energy (short) folds.

The discrepancy between a fold length and an inter-helix distance turns out to be a possible source of imbalance in the fold surfaces. It needs however, several additional features to be 'expressed' (in the sense used by molecular biologists about genes) in lamellar twisting. These may include chain tilt, preferred 'end points' of the fold depending on the main chain conformation, and/or specific growth faces that are of say {110} type in orthorhombic unit-cells. The reasoning is now illustrated for spherulites of iPBu-1 in Form III (the 4_1 helix conformation in the orthorhombic unit-cell), the lamellae of which are highly twisted.

5.2. Lamellar twist of isotactic poly(1-butene), Form III: impact of different fold conformations?

Spherulites of Form III have been obtained and identified recently [18]. Their lamellae are twisted, in sharp contrast with essentially non-twisted lamellae that build up spherulites of Form II produced under the same conditions (Fig. 10(a)) [18].
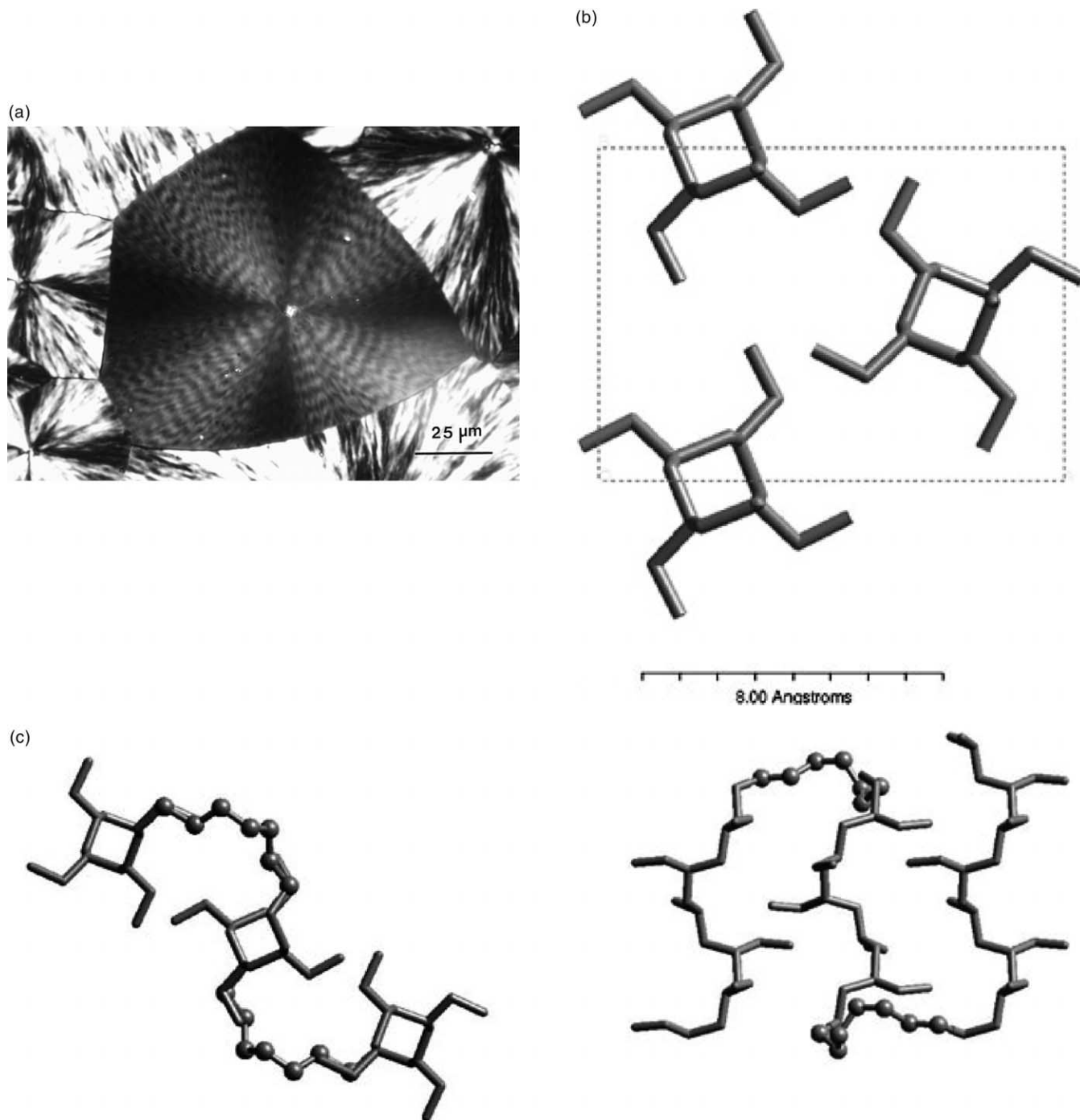
Form III of isotactic PBu-1 is most adequate for the present analysis because it possesses many ingredients that allow analysis of potential sources of surface stresses. The crystal structure rests on a 4_1 helical conformation, the structure is chiral, and the orthorhombic unit-cell symmetry differs from the chain symmetry (this will become an important ingredient in the analysis). The lamellae display spectacular twist in spherulites (and scrolling when crystallization takes place in solution). Finally, two other different crystal forms exist (with the 3_1 and the 11_3 helices) that are 'racemic' i.e. blending the right- and the left-handed helices [66].

Following the reasoning developed above, different surface stresses probably exist in the Form III twisted lamellae. This analysis leads us to examine its possible folds and fold conformations, as they are 'induced' by the crystal structure. The crystal structure of iPBu-1 Form III is known in quite detail. An initial crystal structure determination based on powder X-ray diffraction data established the essential features of the structure: cell geometry and symmetry, helix conformation and packing [77]. Later, a very detailed electron crystallography analysis was performed, based on over 120 independent reflections [78]. The structure thus determined is shown in Fig. 10(b). The orthorhombic unit-cell contains two isochiral and anticline 4_1 helices. The unit-cell uses symmetry elements of the orthorhombic unit-cell (2_1 screw axes of the $P2_12_12_1$ space group), i.e. does not take advantage of the four-fold symmetry of the helix. Some statistical packing of up- and down-pointing chains must of course exist, as is common in polyolefin structures [79–81].

The radial growth direction in spherulites is known to be along the *a* axis [18]. Solution crystallization indicates existence of well-developed (110) growth faces. We will make the reasonable assumption that similar (110) growth faces exist in bulk crystallization, at least near the tips of the growing lamellae. The situation is actually very reminiscent of PE: it is indeed also in (110) faces that the inter-chain distance is shortest.

We further consider that the (110) growth front, made of antiparallel nearest neighbor helices linked by chain folds is a significant, or at least representative, structural feature. This assumption appears reasonable on several grounds. It corresponds to the actual crystal structure of Form III made of antiparallel chains. It fulfills the conformational restrictions set on the chain folding of polyolefins, as described by Petraccone et al. [82] which allow antiparallelism of isochiral chains, or parallelism of antichiral chains.

We assume that a given proportion of chain folds must be

Fig. 10. (a) Morphology of iPBu-1 spherulites in the Forms II and III obtained by crystallization in thin film in the presence of amylacetate (needed to generate Form III spherulites) [18]. Note the very weak birefringence and banding of the Form III spherulite. The weak birefringence is linked with the near-isotropy of this crystal modification ($n_a \approx n_b \approx n_c$), the banding with lamellar twist. Optical micrograph, polarized light. Reproduced with permission from Lotz and Thierry [18]. Copyright 2004 American Chemical Society. (b) Crystal structure of isotactic poly(1-butene) in its Form III, in c axis projection. Note the four-fold helical symmetry of the chain and the orthorhombic unit-cell geometry. (c), (d) A strip of three stems of iPBu-1 Form III in the (110) plane, as seen in c axis projection (c) and parallel to the b axis direction (d). For illustrative purposes only, a possible 'preferred' path of the fold is shown in balls and sticks. It 'starts' and 'ends' by following the 'crystallographic' path of the side-chains in neighbor stems, and comprises three additional carbon atoms. For clarity, the side-chains in the fold are not considered. Note that the path of the folds interacts differently with the lamellar core and lamellar surface on the 'top' and 'bottom' ends of the stems, i.e. on opposite fold surfaces of the lamella.

'tight' (link nearest neighbor stems), if only to compensate the density difference between crystalline core and amorphous fold surface [83]. Although this density difference is more marked in PE than in iPBu-1 (and in particular in its Form III), the argument still holds.

Analysis of a 'growth strip' in the (110) plane (Fig. 10(c)), made for simplicity of three stems linked by two folds reveals some interesting structural features. In particular, the backbone bonds of the two chains are rotated relative to the *a* and *b* axes, but in a symmetrical way, as a result of the 2_1 axes of the unit-cell (hereafter the chain orientation in the *ab* plane is described as the azimuthal setting). Since however, the (110) plane is rotated relative to these axes, the azimuthal setting relative to the (110) plane (which from now on will become the plane of reference) is different for the 'corner' and the 'middle' chain of the unit-cell, i.e. for the up and down helices. On this basis, the corner and middle chains play different roles regarding for example chain folding. This difference holds true even in case of up–down disorder. Indeed, the up-down disorder affects only little the positions of the outer atoms (rule of isostericity), i.e. in a first approximation it nearly maintains the azimuthal orientation of the helices.

The chains are not tilted in the lamellae. The 'transition points' between the crystalline stems and the folds that link them in a growth strip are most probably in the same, or in nearby planes parallel to the (001) plane. We take the last atoms of the two stems that are still in their crystallographic position as indicating the 'beginning' and the 'end' of the fold, i.e. the sites of emergence (both ends) of a fold.

The analysis of the preferred (lowest energy) fold should be performed using a methodology similar to that used by Pirrozzi and Napolitano [70–74]. Since the reasoning does not depend on the exact fold conformation(s), Fig. 10(c) and (d) show a fold path that has been built in a very simple way. It starts and ends by following the paths of the C_2H_5 side chains of neighbor helices. The conformation of these side chains is indeed compatible with the underlying crystal structure, yet represents a clear departure from the initial stem direction (helical path). (Note that this transition cannot be made by a simple exchange of the main and side-chains at the C(H) atom, since this would correspond to a defect in tacticity: a change in conformation from trans to gauche is implied, as suggested for the folds determined by Petraccone et al. [82] for polypropylene).

Two folds, located on opposite ends of the stem, are made for each stem. These two folds start from positions along the chain axis that are apart by an integer number of helix turns plus one half. These two folds are 'equivalent' in a crystallographic sense (the conformational angles, etc. are the same) since they are linked by the screw axis symmetry of the middle chain of the strip (four-fold symmetry, which includes the two-fold symmetry at play here). However, although the two fold conformations as shown here are identical, the interactions of the folds with the crystalline core of the lamella are significantly different, with respect to both the (110) growth face and the end (001) surface. For the (110) growth face, as seen in Fig. 10(c), the azimuthal setting of the chains is such that one of the folds is closer to the neighbor (110) substrate layer than the other. For the (001) end surface, the two folds 'leave' differently the crystalline core of the lamella. Indeed, the first bond of the side chain (CH–CH$_2$ bond) is not normal to the helix axis, which generates a kind of herringbone arrangement. On the opposite ends of the stem, this bond is oriented either away from, or towards the lamellar surface. The folds, even when geometrically identical, must therefore, adapt to different local environments, which is most probably done by conformational changes, and results in different fold 'encumbrance'.

The asymmetry in fold environment just analyzed cannot be removed by assuming statistical up–down substitution of chains at any given site. Indeed, statistical substitution does not modify the azimuthal setting of the chains and thus, maintains the asymmetry in environment of the resulting folds. Applying a 2π rotation of the layer shown in Fig. 10(c) around an axis normal to it (normal to the (110) plane) in order to exchange the location of the folds (down become up, up become down) and generate a possible statistical symmetry is not acceptable either. This operation changes the azimuthal setting of each chain in the parent crystal lattice and modifies the orientation of both the *a* and the *b* axes. This operation would create a rotation twin, with a (110) composition plane. In chain axis projection, it would be perceived as a conventional (110) twin. However, lamellar twisting is a feature of untwinned crystals.

Considering now the pattern of folding that exists on the other side of the growing lamellar tip, i.e. on the ($\bar{1}$10) growth plane, we note that it is related to the present one by a mere two-fold screw axis parallel to the radial growth direction-the *a* axis. This two-fold screw symmetry implies that any one type of fold present on the upper lamellar surface on one side of the lamella growth tip exists on the lower surface on the other side of the tip. In short, different environments exist for folds made on the surface of crystals of chiral helices, even when chains are normal to the lamellar surface. This intrinsic asymmetry is likely to generate different fold conformations or different fold patterns (since a wider range of possible folds is probable for helical polymers) and ultimately an asymmetry in lamellar structure similar to that induced in PE lamellae by chain tilt. In other words, the twisting of chiral polymers is amenable to an analysis in terms of unbalanced surface stresses similar to that developed for PE by Keith and Padden [16].

5.3. Extension to other polymer phases.

The possibility that surface stresses are generated by asymmetries in fold encumbrances on opposite sides of a lamella appears quite general and should be amenable to a 'structural' analysis that blends knowledge of the crystal structure and inferences on the possible or probable fold
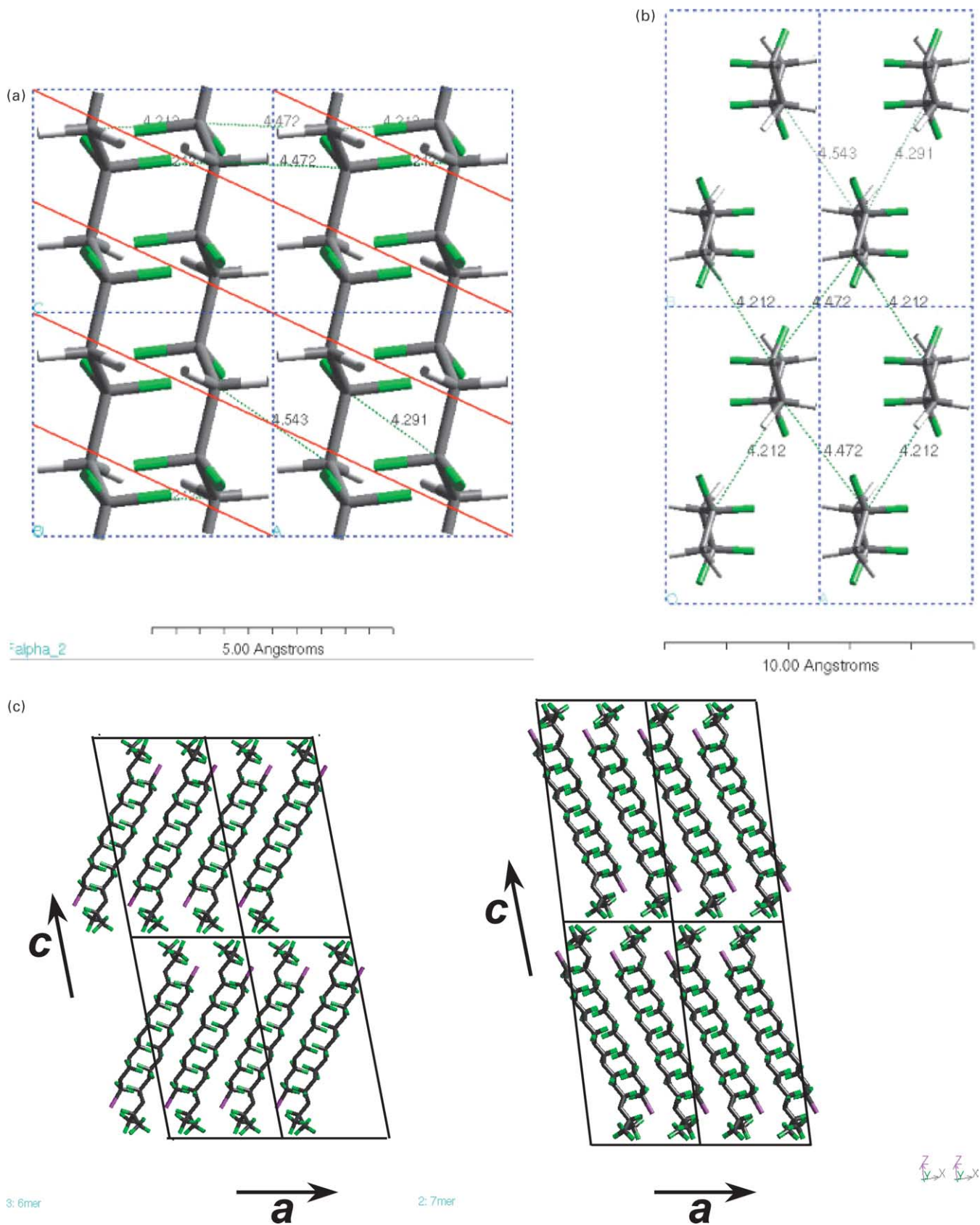
Fig. 11. (a) Crystal structure of αPVDF as seen along the *b* axis. The crankshaft conformation of the chain would be more apparent in an *a* axis projection of the structure. This *b* axis projection underlines the fact that the bonds most parallel to the chain axis are all tilted away from the chain axis, but in one direction only, which differentiates this structure from that of PE (in which tilts of successive C–C bonds are symmetrical relative to the *c* axis). The oblique (102) planes

conformations. At this stage, it may be worth underlining possible guidelines for further investigations and analyses.

Some ingredients appear favorable in inducing different fold conformations on opposite sides of a lamella. These are any one or all of the following: (i) chain tilt (ii) main chain path away from the crystallographic axis of the chain (enabling the existence of different fold length, thus conformations) (iii) isochirality of the helical stems, as a result of configurational chirality (chiral polymers) or crystal structure (chiral polymorphs). Searching for such features in polymers that display lamellar twist may well provide a consistent picture about the origin of twist in polymer lamellae. In this search, and as an illustration of the method used, it may be worth giving some guidelines to evaluate the lamellar twist in spherulites of the α form in PVDF [19,30]. This polymer and crystal phase are of particular relevance in the present context, since it has been much investigated by Toda et al. [6].

The crystal structure of the α form in PVDF is well known [84–86]. The chains adopt a TGTG$^-$ conformation. The unit-cell is rectangular (α, β and γ=90°), with parameters $a=0.496$, $b=0.964$, $c=0.462$ nm but with a monoclinic symmetry ($P2_1/c$). It contains two chains that are packed in antiparallel mode with respect to the chain direction as well as the direction of the dipoles.

In single crystals of the α form of PVDF grown from the melt (Lovinger and Keith [87], Toda et al. [35,88]) the stems are frequently tilted in the *ac* plane at some 25° to the lamellar surface normal (stems parallel to it have also been reported in solution crystallization). Toda et al. make the important observation that the single crystals are always or more frequently of the so-called chair type, as opposed to the boat or tent-like type: on opposite growth sides of the crystal center, the slope of the fold surface is not modified in chair type crystals whereas it is opposite in boat or tent-like crystals. This specificity suffers exceptions under certain growth conditions for PVDF, but in PE both populations are found in equal proportions.

It is tempting to relate the prevalence of the chair-like habit of αPVDF single crystals with the lower symmetry of the unit-cell, and the resulting differences in fold conformations that are associated with this lower symmetry. When seen along the *b* axis, the chain conformation of αPVDF is not symmetrical: the bonds that are most nearly parallel to the chain axis are tilted on one side only relative to the chain axis (Fig. 11(a)). This implies that folds made in the (102) plane must be geometrically different from those made in ($\bar{1}$02) planes since they start from and reenter in the crystal at different angles. Lovinger and Keith have shown that the fold surface is (102), as deduced from the sense of rotation (of the specimen stage) needed to align the chain axis in single crystals with the electron beam. This result suggests that the folds made in this (102) plane are energetically preferred (because of more favorable conformation, less crowding, etc) over folds in the ($\bar{1}$02) plane. If the (102) fold surface is preferred, only chair-like single crystals habits are possible; tent-like αPVDF single crystals would be twins with a (100) twin plane crossing the crystal center. This situation does not of course exist for PE, in which successive carbon–carbon bonds have symmetric tilts relative to the chain axis: tent-like crystals can exist for untwined single crystals.

The fact that specific, oblique planes are more adequate to house bulky folds or features is also supported by the recent elucidation of the crystal structures of oligomers of PVDF of formula $CF(CF_3)_2$–$(CH_2$–$CF_2)_n$–I with $n=6$, 7 and 8 [89]. In the present case, the bulky substituents at one of the chain ends are again segregated and located at *iso*-conformational sites along the chain and generate what would be—in that case—($\bar{1}$02) end surface (Fig. 11(c)). For a helix or a crankshaft chain geometry, the extra volume associated with the folds (or here the substituant) is more easily accomodated when the folds start and end at preferred conformational sites along the chain. In αPVDF, one notes that in the {110} growth planes, the shortest distances between stem paths are significantly shorter than the interchain distance (0.542 nm): 0.421 and 0.447 nm across *bc* sheets with facing fluorines and hydrogens, respectively (Fig. 11(a) and (b)). A combination of short folds with preferred 'starts' and 'ends' leads again to a situation in which different fold conformations may exist, although the details of their organization are not yet accessible. In short, for the α form of PVDF the two causes of lamellar twist considered above for linear and helical chains may be combined: as in PE lamellae, the chains are tilted to the lamellar surface normal; in addition, the crankshaft chain conformation may introduce more pronounced disparities in fold conformation than in PE.

The above provisional analysis of αPVDF single crystals structure underlines potential asymmetries in the lamellar structure that may well account for a number of manifestations of lamellar twisting, bending etc that would require a development on their own. Briber and Khoury [30], Lovinger [29], Okabe et al. [31] Toda et al. [6] have investigated the crystallization of PVDF under various conditions: thin film growth, bulk crystallization, as well as growth from compatible blends of PVDF with various acrylic polymers. The observed asymmetries suggest however that unbalance

(corresponding to the fold surface) are indicated. Short inter-stem distances in the (001) plane (top) and a plane nearer to the (102) plane (bottom) are indicated. Note that the former distances link $C(H_2)$ and $C(F_2)$ and the latter either $C(H_2)$ and $C(H_2)$ or $C(F_2)$ and $C(F_2)$ groups. (b) Crystal structure of αPVDF as in part (a) seen along the *c* axis. Note that the inter-stem distances are larger across *bc* planes with facing hydrogens than with facing fluorine atoms. (c) The crystal structure of oligomers of PVDF (in its α form) as determined by Tashiro and Hanesaka [89]. The unit cells differ for the odd- and even-mers (the structure of the 8-mer, not shown, is similar to the 6-mer). However, the substituted chain end is located at the same 'level' of the crank-shaft conformation of the chain, that here sticks most out of the crystal end surface, which would correspond to a ($\bar{1}$02) plane in αPVDF. Part (c) reproduced from Tashiro and Hanesaka [89] with permission. Copyright 2004 American Chemical Society.
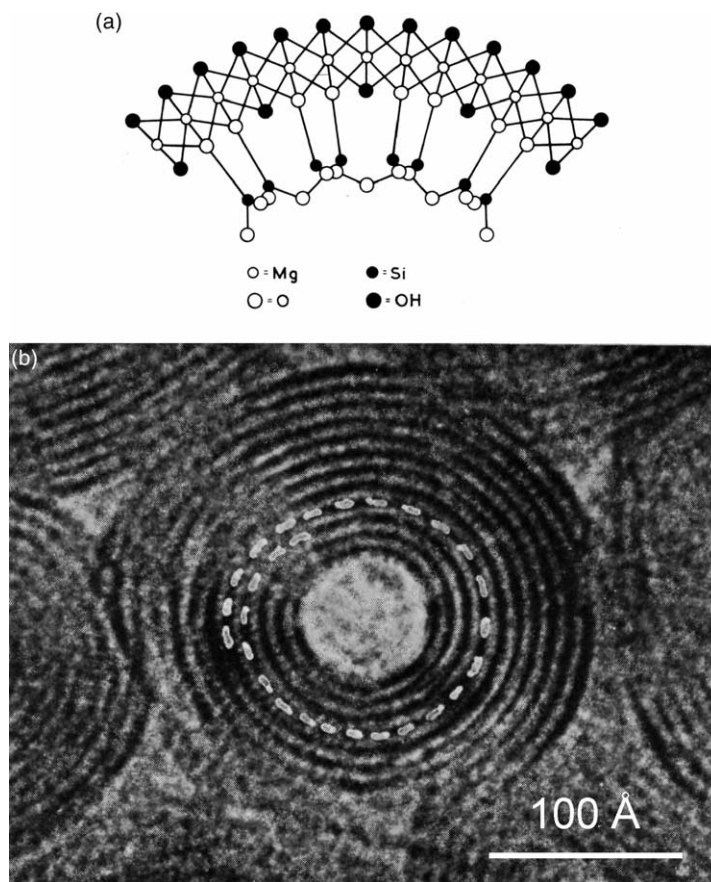
Fig. 12. (a) Model of the crystal structure of asbestos chrysotile, as seen along the needle axis. (b) Cross section of an asbestos needle as examined in transmission electron microscopy, and displaying its scrolled layers. Note the existence of a central hole, and the limited overall diameter, imposed by the limited bending elasticity of the layers. In the spiral, the number of layers may vary, or the needle may be made of concentric layers. Part (a): reproduced from Monkman [94]. Part (b) due to Yaka K, Acta Cryst 1971;26:659 as reproduced in Ref. [94]. Copyright International Union of Crystallography (http://www.journals.iucr.org/).

of surface stresses may sometimes result in a component that is not in a plane perpendicular to the growth direction, but rather oblique to it. This would account for the tendency of αPVDF single crystals to wind on the surface of a cylinder (much like the poles that signal barbers shops in the US) [90]. The abrupt changes in growth direction of crystals growing flat-on on a substrate suggests a similar trend: the fast growth direction changes seem to be linked with what appears to be a flipping over of the polymer lamella.

To summarize, the analyses developed above illustrate that the helices or crankshafts of the stems in the crystalline core exert conformational constraints on the folds as they leave or reenter the lamella, and that these constraints may induce different fold encumbrance. Of course, the conformation of the entire fold is not accessible through this analysis. Further insights may be gained via a detailed molecular/conformational analysis of the possible folds. However, their results will be difficult to confront with hard evidence: the resolution experimentally achievable has not yet reached such molecular details—except in very favorable cases (cyclic paraffins, oligopeptides). It remains that differences in fold encumbrance (conformation, constitution)

provide a logical molecular basis for the existence of unbalanced surface stresses in the lamellae of very different polymers (chiral, achiral, with or without chain tilt)—and thus for the origin of lamellar twisting.

6. Lamellar scrolling as a result of surface stresses

Twisting is not the only regularly curved lamellar morphology observed in polymers. Quite strikingly, some polymer lamellae are scrolled. Scrolling has been observed in single crystals grown from solution for iPBu-1 in its Form III [91]. It has also been observed in some polyamides [92,93], and other polymers. Whereas not of general occurrence, scrolling represents yet another lamellar morphology that must be accounted for.

Scrolling of layers or lamellae is not infrequent in materials science. A layered silicate, Asbestos chrysotile, provides a clear example that can be explained by the specificity of the crystal structure (Fig. 12(a)) [94]. The layer of chrysotile is made of two different sheets. One sheet is a network of linked SiO_4 tetrahedra (Si_2O_5) and the other sheet
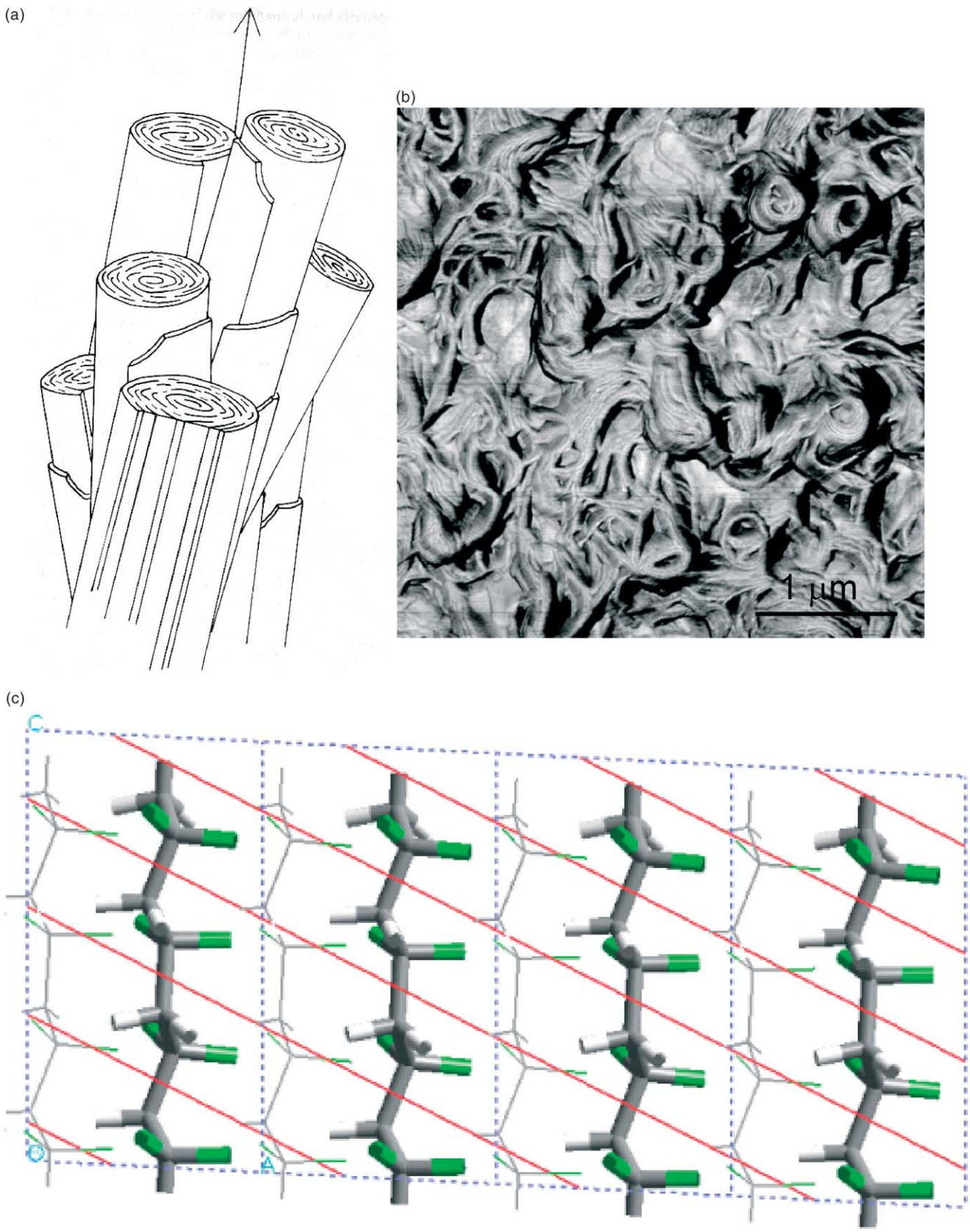
(a)

(b)
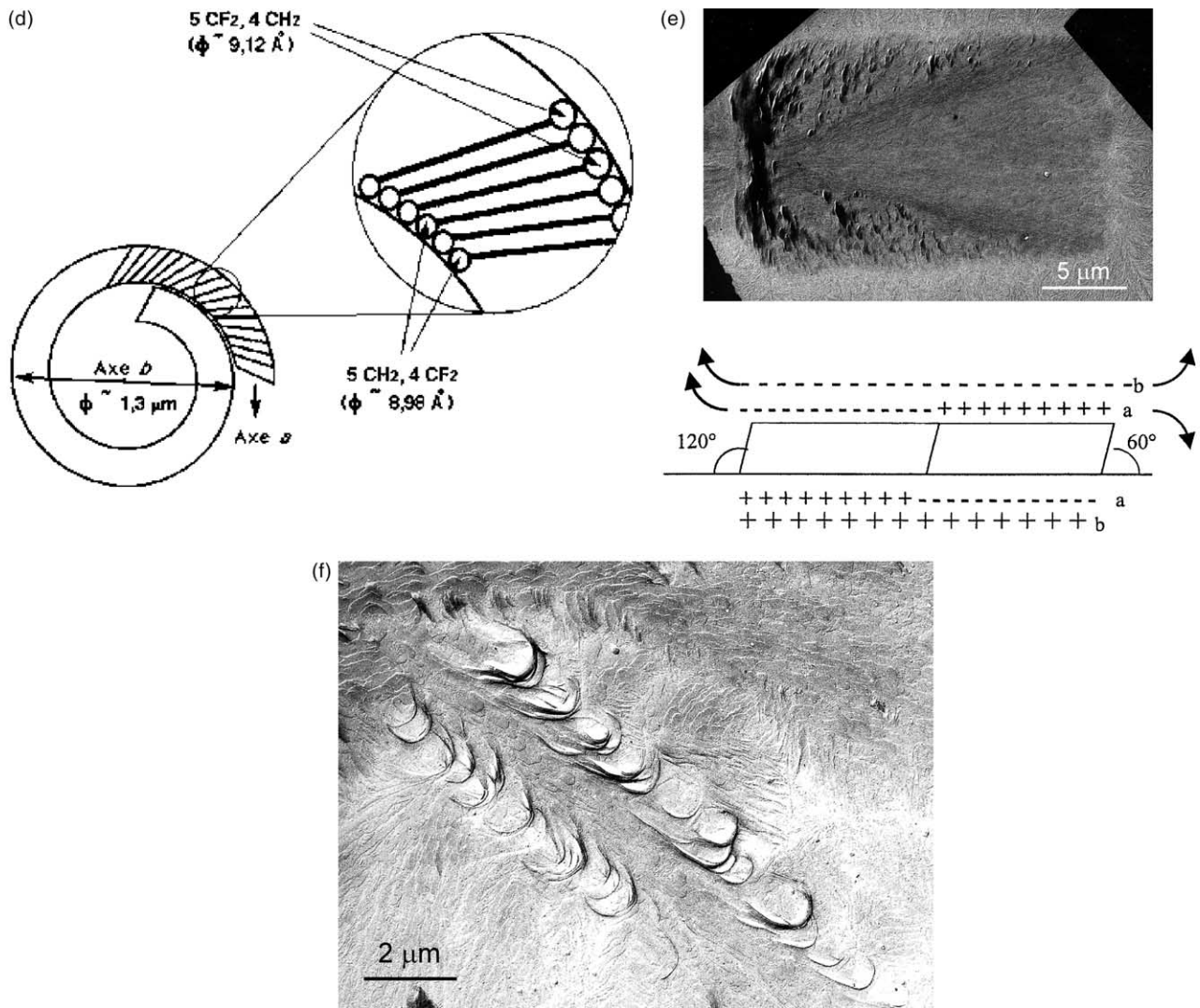
1 μm

(c)

Fig 13. Continued on next page

Fig. 13. (a) Schematic illustration of the scrolled geometry of radiating lamellae in spherulites of γ phase poly(vinylidene fluoride), as drawn by Vaughn [20]. (b) Surface of a spherulite of γPVDF as seen along a radius of the spherulite and imaged by AFM. (c) Structural implications of the observed 28.5° tilt in γPVDF lamellae. The chains have a clear crank-shaft conformation that would again (cf. legend to Fig. 11(a)) be better apparent in a *b* axis projection than in this *a* axis projection. The fold surface (underlined) bisects the chain path at nearly isoconformational locations, suggesting that the folds have also isoconformational starting and finishing points along the chain. This fact combined with the polarity of the structure generates folds with an odd number of carbon atoms. The compositional imbalance of folds arises from the 'extra' carbon being a CH_2 or a CF_2 on opposite fold surfaces. (d) Schematic representation of the splay of chains in a lamellar crystal of γPVDF arising from the 10 $Å^3$ difference in fold volume on opposite fold surfaces. The volume difference is supposed distributed over the whole fold length, and results in different fold 'cross sections' (represented by the different diameter of the circles at the ends of the stems), thus inducing a 0.04° splay of the chains in the lamella. About 10^4 chains are needed to complete one 360° turn, thus a scroll diameter of ≈1–2 μm. (e) Single crystals of γPVDF grown in thin film [101]. Note that the crystal origin is not at the center, as evidenced by the growth sectors. Scolled overgrowths develop only in three growth sectors, profusely on the left-hand side one, and less so in the top and bottom ones (*a* axis horizontal, *b* axis vertical). The radial growth direction in spherulites is parallel to *b*, i.e. is not the fastest growth direction of the single crystal. The drawing represents the respective contributions to scrolling along the *a* axis of fold constitution (opposite on the whole surface of the crystal) and chain tilt (that depends on the growth direction). Addition of these effects leads to small scroll diameters on the left side growth sector and larger diameters on the right side growth sector (cf. part f). (f) Part of a crystal as in part (e) but grown in a thicker film. On the other lateral edges of the crystal, the lamellae rotate sideways and start growth on edge, generating a pattern very similar to that of PE (cf. Fig. 7(a) and (d)). These lamellae tend to curve, and ultimately to scroll. For these edge-on lamellae, the scroll axis (and spherulite radial growth direction) would be normal to the plane of the sheet. Part (a) reproduced with permission from Vaughan [20]. Copyright 2004 Kluwer Academic/Plenum Publishers. Part (b) courtesy of Dimitri Ivanov. Part (d) reproduced from Lotz et al. [95]. Copyright 2004 Elsevier.

a brucite type octahedral layer. The two sheets are linked by covalent bonds. Two thirds of the hydroxyl ions at the base of the brucite layers are substituted by the Oxygens at the apices of the Si–O tetrahedra. The brucite and SiO_4 tetrahedra have

however different 'unit-cell' dimensions in the plane of the sheet. As a result, the layer curves and ultimately scrolls, with the 'tighter' sheet inside to release or reduce the surface stresses. The sheets have limited bending elasticity, which

sets both a minimum diameter of the scroll of about 8 nm (thus generating a cylindrical central cavity) and a maximum diameter, usually 30 to 38 nm (mean value, maximum reported value: 85 nm) (Fig. 12(b)).

We consider here scrolled polymer lamellae for which a molecular analysis of the fold structure has been made: for melt crystallization, the γ form of poly(vinylidene fluoride) (γPVDF) [95], and two model systems, namely alkanes centrally branched with a methyl or a butyl group and that fold in a hairpin fashion [96] and for solution crystallization, the α form of polyamide 66 (PA66) [93]. Other scrolled morphologies have also been reported but the molecular origin of the observed morphologies is not yet established (possible role of disclinations, as suggested by Geil? [97]).

6.1. Lamellar scrolling of the γ form of poly(vinylidene fluoride)

At relatively high T_c, the melt crystallization of PVDF yields spherulites [98] of two of its numerous crystal modifications: the α and the γ phases (these forms are also known as Forms II and III, respectively, a nomenclature used in Japan). The α phase spherulites are made of tightly twisted lamellae, as evidenced by their optical banding. The γ phase spherulites have more ill defined optical properties. By chemical etching, Vaughan [20] could establish that they are made of lamellae that are scrolled around a radial axis (Fig. 13(a)). Scrolling is best seen down the radius of the spherulites (Fig. 13(b)). Their diameters are in a relatively wide range: from sub-micron to 1–2 μm.

An explanation to account for the scrolled lamellae of γPVDF that also rests on surface stresses has been suggested by Lotz et al. [95] Contrary to asbestos however, the stresses are created in the outside, amorphous fold surface, and impart a deformation on the crystalline core of the lamella. The reasoning takes into account several original features of the γPVDF crystal structure, which turns out to be 'polar' in several respects. In essence, the chain conformation of γPVDF is based on $T_3GT_3G^-$ sequence [99]. Its geometry is almost a regular crankshaft. This crankshaft is polar, i.e. 'has a sense': conformationally similar carbon atoms of the main chain bear hydrogens on one end of the stem, and fluorine on the other end. The unit-cell itself is polar with respect to chain sense: all chains are 'parallel' (or, to use the proper word, since we are dealing with conformation only: are 'syncline' (or ' isocline')). The chain tilt in the lamella (28.5°) indicates that the fold surface is the (104), or the (1̄04) (Fig. 13(c)) [100]. 'Conformationally similar' (but in the present case, not identical, cf. Fig. 13(c)) carbon–carbon bonds of the main chain are regrouped in this plane, which implies that the ends of the folds, as they enter the crystal, are fixed [95] (a similar situation exists for the α phase of PVDF, cf. *supra*. The α phase has however conformationally 'antiparallel' chains).

It follows that on one fold surface of the lamella, every fold 'starts' and 'ends' at CH_2 groups, and on the other fold surface every fold starts and ends at CF_2 groups. As a result,

the folds have an odd number of carbon atoms. However, the chemical constitution of the fold is different on opposite fold surfaces, even when assuming folds with an equal number of carbons, since they are made of a given number (supposed identical) of CH_2–CF_2 units plus, depending on the fold surface, either a CH_2 or a CF_2. This difference in chemical constitution translates in a difference in fold volume. This difference in fold volume must translate in differences in fold diameters since the fold ends locations are fixed. This in turn suggests that the fold volume differences are distributed along preferred crystallographic planes, namely fold planes. Segregation of the different folds on opposite fold surfaces induces a small splaying of the stems in the crystalline core that, when repeated many times, results in the observed scrolling of the lamella (Fig. 13(d)).

A reasonable estimate of the impact of the difference in chemical constitution of the folds on lamellar geometry can be made. At $T_c \approx 150$ °C, the volume difference between CH_2 and CF_2 groups is only 10 Å^3 (33.5 versus 44.3 Å^3) or roughly 3% of the total fold volume (about 350 Å^3, assuming nine carbon atoms in the fold). For a lamellar thickness of 10 nm, the splay between successive chains is only 0.04°. It needs be repeated nearly 10^4 times to complete one turn (360°), which in turn implies a scroll radius of ≈ 1–2 μm, as is indeed observed [20,95].

Recent experiments indicate that PVDF scrolling may be more complex than analyzed initially [101]. Indeed, the chains are tilted in PVDF lamellae, as they are in PE lamellae. Differences in fold conformation as a result of chain tilt, as documented in the case of PE (cf. Fig. 6, top), may also exist in the γ phase of PVDF. Their contribution may add to, or counterbalance the tendency to scroll: these antagonistic or additive effects are sketched in Fig. 13(e). Supporting evidence for such contributions can be found, as for the PE case considered earlier, in the morphology of single crystals grown in thin films. These single crystals display indeed conspicuous growth sectors that make it possible to evaluate the tendency to scroll in each specific growth sector. The differences are vividly shown in Fig. 13(e). In this crystal, the growth center is way off the geometric center, indicating significant differences in growth rates, as also observed for the PE crystals (Fig. 7). In addition, very tightly scrolled overgrowths develop on the top surface of three growth sectors: (1̄00) at the left, and (010) at the top and bottom of the figure. In all cases, the scroll axis is parallel to the *b* axis of the crystal and the scroll diameter is only fractions of μm. Lamellar thickness is very small, possibly to accomodate the tight scroll. In the right hand side, (100) growth sector, no such tightly scrolled overgrowths are observed. The lamella would actually like to bend towards the supporting glass slide. This is illustrated, somewhat indirectly, in Fig. 13(f) that shows a similar, more mature single crystal. During further growth indeed, the edges of the lamellae may twist by 90°, and these edges give rise to lamellae oriented edge-on. As seen in Fig. 13(f), these edge-on lamellae bend during further growth (the *b* axis, which is also the scroll axis is now

normal to the substrate surface) and the radius of curvature (or scroll diameter) is in the µm range. (Note that micrographs similar to Fig. 13(e) and (f) were first presented in Ref. [29]). These observations strongly suggest that two contributions are at play: the 'chain tilt' effect (as in PE) and the 'chemical composition of the fold' effect (the latter only being specific to PVDF) (sketch in Fig. 13(e)). The tendency to scroll is very strong when these effects are additive, which results in tight scroll diameters (and also thinner lamellae). Lamellae in which the 'chain tilt' effect and the 'chemical composition of the fold' effect are opposite (as for the edge-on crystals in Fig. 13(f)) have larger scroll diameters.

6.2. Lamellar scrolling in centrally substituted alkanes

Recent results of White et al. [96] also link scrolling with a clear-cut difference in fold constitution and structure. These authors investigated alkanes with 191 main-chain atoms in which either a methyl or a butyl branch is attached near the middle carbon atom: $C_{96}H_{193}CHRC_{94}H_{189}$ with R either CH_3 or C_4H_9. These alkanes crystallize in a hairpin fashion, whereas the linear paraffins of similar length crystallize in the extended form. This hairpin conformation ensures that the substituents are attached to the fold. The lamellae are scrolled, with a thinner scroll diameter for the larger, more bulky butyl substituents (1 µm versus 2 µm, respectively). A representative picture of these scrolls can be seen on the cover of this journal.

Not surprisingly, the authors analyze this scrolling in terms similar to those developed earlier for the γ phase of PVDF. They suggest that the methyl or ethyl substituents are segregated on one side of the lamellae, whereas both 'straight' paraffin chain ends are located on the other side (while, again, assuming that the stresses are normal to a preferred (fold?) plane). In a 'model' polymer therefore, a direct link can be established between lamellar scrolling and the presence of a bulky group at the fold. Furthermore, the magnitude of these stresses (materialized by the scroll diameter) can be linked with the total volume (encumbrance) of the fold. However, the crystallization process seems to be more complex. In particular, White et al. [96] point out that the lamellae may be planar or cylindrical (scrolled), and that the two habits can even be parts of the same lamella. The planar habit suggests that the substituants are randomly

distributed on both sides of the lamella, i.e. that the hairpins may pack in opposite directions, with chain ends on both surfaces. This relieves to some extent the surface stresses. The cylindrical habit, usually formed at the higher temperatures, is however, the more stable one. Clearly, further insights are to be expected soon through investigation of these and/or related model systems.

6.3. Lamellar scrolling in polyamide 66 single crystals

The origin of scrolling in solution grown single crystals of polyamide 66 has been suggested to arise from yet another source of unbalance in fold structure. Polyamides are known to form densely hydrogen-bonded sheets and the folds are most likely located in the more flexible aliphatic segments of the repeat unit. For PA66, this leaves two possibilities. Folding may take place in the acidic or in the amide part of the repeat unit, and thus be made of four or six atoms of carbon, respectively. The existence of two potential folds introduces a clear possibility of difference in fold encumbrance.

Cai et al. reported on an original observation of PA66 single crystals produced in solution at the same crystallization temperature T_c after self seeding at increasing temperatures T_s: with increasing T_s, the PA66 lamellae produced at T_c are first flat, then scrolled and then flat again [93]. This observation can be rationalized based on the above existence of two different fold types (Fig. 14). Increasing T_s yields seeds with increasing thickness. At the lower and upper T_s, both fold surfaces would be made of say acidic folds, the lamellar thickness differing by one full chemical repeat unit (diacid and diamine parts). However, for intermediate T_s, it is possible that the thickness is only half a repeat unit larger (acid part or amine part). In that case, two different types of folds must be involved, i.e. located in the acidic and amine parts of the chemical repeat unit, and made of four and of six carbon atoms, respectively. As a result of hydrogen bonding, these different folds are by necessity segregated in opposite surfaces of the lamella, thus inducing a difference in fold encumbrance. In the present case, it is the observed sequence of flat-scrolled-flat lamellae that lends strong support to the proposed mechanism and thus, to the unbalanced surface stresses. The full details have not yet been worked out for the single crystals. The orientation of the scroll axis, which differs from the hydrogen bond direction may be related to different geometries and orientations of the folds in
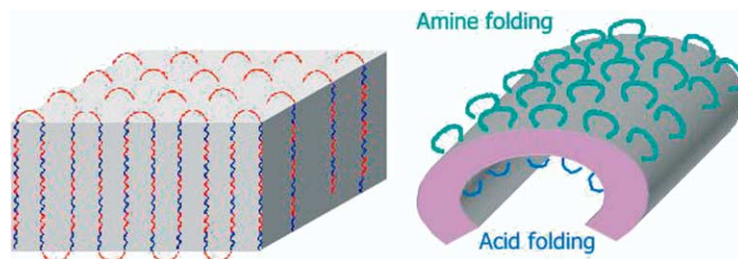

Fig. 14. Schematic illustration of two different folding patterns that may generate flat and scrolled crystals of Polyamide 66. Flat crystals are formed when folds on opposite sides of the lamella are made of similar parts of the chain (either amide or acidic part). Scrolled crystals are made when opposite fold surfaces are made of different parts (amide as opposed to acidic). Illustration courtesy of Dr Chris Li, Drexel University.

opposite fold surfaces [102] (a suggestion for which we are thankful to F. Khoury, private communication). Determination of the lamellar thickness (which appears difficult) should help correlate the changes in crystal morphology with increments in lamellar thickness, etc. As such however, this analysis appears to be applicable to the bulk crystallization of polyamides. Several polyamides display indeed a curious sequence of spherulite birefringence when the temperature of crystallization varies. In particular, one observes changes from a positive to a negative birefringence [22]. Since the hydrogen bonding direction is by far the fastest growth direction, such changes in birefringence would make sense if, under specific crystallization conditions, the lamellae become scrolled: the fastest growth direction is radial for the 'flat' lamellae and at a significant angle or even nearly normal to the spherulite radius for scrolled lamellae (scroll axis orientation presumably radial).

7. General comments and relevance to twist in non-polymeric materials

7.1. Crystal symmetry, chain tilt, twist and scroll in polymer lamellae

The chirality of (probably most of) flexible polymers, although present in the lamellar core (helix chirality-but 2_1 helices may be a special case) induces lamellar twist through asymmetric constraints that the (helix) chirality puts on the fold conformation and structure. Lamellar twist of chiral polymers is mediated via a secondary feature (the fold surface structure asymmetry), even when the chains are normal to the fold surface. The details of the connection between crystalline core and folds determine the surface stresses and associated sense of twist. As a result, the different twist sense observed by Li et al. [62] for chiral polyesters that differ by one carbon atom in the main chain may well be amenable to structural analysis. Indeed, the extra atom carbon 'reverses' the orientation of the last aliphatic bond in the crystal structure, at the crystalline core-fold surface interface and, therefore, influences the fold conformation, all other structural features remaining equal. The situation with PHB and PHV that have identical configuration and helix chiralities, but different side group lengths may be more complex to analyze.

Lamellar twist in chiral polymers results from conformational differences at the fold surface, induced by the 'polarity' of the underlying chiral crystal lattice. Due to the chiral nature of the lattice, the structure of the entire lamella (including fold surfaces) lacks a mirror symmetry. Absence of (or at least reduced) twist may also be observed for chiral but racemic polymer phases (or blends of enantiomers that do not co-crystallize) if the lamellar structure is a mosaic of small enantiomeric domains separated by antiphase boundaries. The β phase of isotactic polypropylene, a frustrated, chiral phase [103–105] may be representative of this

conjunction. It displays significant crystallographic disorder and little tendency to lamellar twist. Only the so-called type IV spherulites (in the terminology of Padden and Keith [106]) produced at high temperatures display optical banding, perhaps associated with isochiral screw dislocations.

Lamellar twist is not normally expected if the crystalline core and fold surfaces in any single growth sector of the lamellae can be mirror images, with the middle plane of the crystal as a mirror plane. This condition supposes that stems are normal to the fold surface, and that the crystal phases are structural or conformational racemates. This is precisely the situation encountered for the two other crystal phases of iPBu-1, Forms I′ and II, that display no, or little lamellar twist, contrary to the Form III analyzed above.

Lamellar twist is likely if the crystal lattice or fold surface structure on one side of the tip of growing lamellae is related by a two-fold axis or a two-fold screw axis parallel to the growth direction. Generation of two-fold axis symmetries may correspond to a structural characteristic of the lamella. Chain tilt relative to the lamellar surface (as in PE) is the most representative and probably frequent example of this situation. However, introduction of a plane of symmetry in the growing lamella, for example by a reversal of the chain tilt, cancels the tendency to twist: this is the situation observed in 'corrugated' lamellae that are also observed in the PE gels mentioned earlier.

Lamellar twist in bulk-crystallized materials and scrolling observed for single crystals grown in solution are most likely different manifestations or consequences of the same surface stresses. The two lamellar morphologies are observed for iPBu-1 in its Form III (chiral form of a chiral but racemic polyolefin), for polyepichlorhydrin (chiral polymer) and for some polyamides (Polyamide 66).

It is worth emphasizing that since overall lamellar twist is the result of very tiny local departures from crystallographic symmetry, the structural differences in fold conformation they imply may not be amenable to experimental check. The successful use of polymer decoration [45] to highlight the structural differences of fold surfaces in PE crystals [43] appears as a fortunate exception. Polyethylene decoration is most probably not discriminative in the specific example of iPBu-1: the size of the side chain and its conformational freedom blur the underlying helical path. Conformational energy analysis of model fold conformations as performed by Napolitano and Pirozzi may also be insufficient to model the conformational adjustments considered above, given the approximations that need be made in developing a structural model. Indeed, the local departures at the ends of the stems (near the folds) were estimated to be about 0.01 nm in twisted crystals of silk fibroin [51], or 0.005 nm in scrolled lamellae of the γ phase of PVDF [95]. They are representative of most or all twists or scrolls observed in polymers. They are below the 'limit of detection' or of reliability of presently available conformational and packing analysis methods. It is to be feared that whereas molecular understanding of unbalanced

surface stresses may be tracked at a local level, their experimental demonstration will remain difficult to achieve.

7.2. On other geometries of polymer lamellae

The present review addresses mainly or exclusively twist and scroll geometries of polymer lamellae. These are certainly not the only regularly curved lamellar geometries observed in polymer crystals. Most noteworthy are the so-called 'bowl-like' entities formed in solution and described in quite detail in the 1970s [107]. Several polymers were crystallized in solution and display these bowl-like geometries: isotactic poly(4-methyl-pentene-1) (P4MP1) [108], polyoxymethylene (POM) [109], and poly(chloro-trifluoro-ethylene) [110]. The P4MP1 case is particularly well documented since a wide range of crystallization temperatures was covered. The crystals are essentially flat and bounded by smooth growth faces when grown at high temperature (e.g. at 90 °C, in an equimolecular mixture of xylene and amyl acetate). The crystals become more curved when the crystals are formed at lower T_c values and become distinctly hollow bowl-shaped in a temperature range between 70 and 50 °C.

The details of the lamellar organization of these bowl-like crystals, which in spite of their unusual geometry remain 'single' crystalline-like have been investigated in quite details by Khoury and Barnes. The major feature is that the bowls are made of multiple, serrated layers. The curvature results from the multiplicity of these new lamellae that are formed, much like in dendritic growth, along the growth tips (that are also the growth sector limits) of the crystals. At each new multilamellar growth center, the crystal is pyramidal in shape (much like the tent-like habit of PE single crystals). Accumulation of successive conicalness at growth tips of a rather symmetric crystal (square for P4MP1, hexagonal for POM) results in the overall bowl shape. The latter is, therefore, the result of a combination of high crystal symmetry, dendritic-type growth and tent-like habit. It should be noted that the tent-like habit is related with an additional source of surface stresses, namely the slight disparity in interplanar distances existing between equivalent crystallographic planes in a single crystal that contain, or do not contain, folds (the former are the growth faces of the crystal).

Bowl-like crystals, or other rounded shapes have been observed for many other polymers, which suggests yet another origin for such geometries. They are frequently associated with specific crystallization conditions-in a poor solvent and/or at a low T_c. In polymer/poor solvent systems, a liquid–liquid phase separation can take place at high temperature, above the crystallization temperature, with formation of small droplets of a concentrated polymer phase dispersed in a more dilute phase. On cooling and crystallization, growth seems to be confined near the boundaries of the droplets, and the final crystal is a mere 'frozen in' template of the initial droplet shape. Such

observations have been reported on PE/poor solvents systems that display after crystallization round PE particles [111]. In addition, the growth mechanism depends on the presence or absence of heterogeneous nuclei in the droplets. It should be mentioned that similar PE particles have been obtained by Garber and Geil using a deep quench procedure [112].

These observations and analyses underline the importance of local chemical and physical conditions for polymer crystallization, sometimes hampered or enhanced by the local environments, on the ultimate lamellar morphology. Such confined growth is actually a significant part of the development of polymer spherulites. It corresponds to the filling-in process that takes place behind the primary growth front and accounts for the vast majority of the spherulite structure. Due to the limited space, it cannot unfortunately be included in the present contribution that is primarily concerned with the establishment of the initial 3-dimensional framework of the spherulites.

7.3. Relevance of the analysis to lamellar twist of non-polymeric materials

The above analysis has dealt only with polymers, but twisting in non-polymeric systems is well known. Keller [113] has summarized some of this knowledge in a Discussion during a meeting on Polymer Crystallization in Mons. We quote: 'Banding as seen under the polarizing microscope is a general feature in crystallizing matter. It was first reported in 1892 by Michel Levy and Munier Chalmas in Calcedony, and interpreted in empirical terms as we know it today (hence exact!) 100 years ago!… Clearly, explanation relying on specific polymeric features, while possibly relevant to the particular systems, cannot suffice to account for the phenomenon in general. In the literature, the best summary is the book: 'Gedrillte Kristalle' by F. Bernauer (From 'Forschungen zur Kristallkunde', Heft 2 (1929), Berntraeger, Berlin). He examines over 230 cases and sees no unique explanation. That was before polymers!…' [113].

The origin of twisting in minerals and small organic molecules (among others) is certainly a complex issue, and a rhythmic development of branches, very reminiscent of the screw dislocations observed in polymers, appears as a significant contribution. However, lamellar twisting in these systems has also been considered to arise from small increase in unit-cell dimensions near the lamellar surface, a place in which the full crystallographic symmetry no longer applies. While reasonable and attractive, this suggestion is virtually impossible to check experimentally, since the unit-cell changes are very small indeed. It would however account for the fact that twisting is more frequently observed when the underlying unit-cell symmetry is low (monoclinic, triclinic).

The above analysis in terms of surface stresses for crystalline polymers appears to be highly relevant to the more general issue of twisting of non-polymeric materials with lamellar geometry only (not for acicular crystals). Indeed, it

underlines also the role of surface stresses generated by lattice expansion. However, polymers offer the possibility to de-couple the 'mechanical' contributions arising from the different 'layers'. Indeed, the stresses arise from a physically distinct and clearly identifiable layer of chain folds attached to, but distinct from, the crystalline core, and can be analyzed almost independently from that crystalline core. The structural complexity of polymer lamellae thus turns out to be an unexpectedly advantageous feature that may contribute to the analysis of lamellar twist in the lower molecular weight and mineral crystals.

8. Conclusion and summary

Analyzing the origin of lamellar twist in spherulites remains a challenge because the mere observation of the building lamellae in such complex three-dimensional entities is a difficult task. The etching technique developed by Olley et al. [14] has been most useful in this endeavor, and significant insights have resulted over the years. However, consensus (when it is reached!) on the morphological manifestations and the structure of spherulites does not mean agreement on the intrinsic cause of lamellar twisting. Which of the growth factors (e.g. self induced fields or rhythmic supply of 'nutrient') or the structural factors (screw dislocations, chain tilt, configurational or conformational chirality) govern the process? Even the sequence of events is not clearly understood: does the lamellar twist precede or follow the development of screw dislocations?

One line of reasoning considers that there must be 'a… generic basis for twisting in the many, diverse systems in which it is observed' [10]. If so, lamellar twist can only be explained by invoking growth features, for example cyclic feeding of the growth front [9] or, considering that 'crystal morphologies develop more often in response to kinetic conditions' assume 'self-induced fields' (mechanical or concentration) that are generated by the growth process itself [10]. However, 'generic' theories of this kind cannot account for the structural diversity of polymer spherulites: under the same crystallization conditions, different crystal polymorphs yield twisted, or untwisted, or scrolled lamellae.

The structural approach of lamellar twisting has been far more productive in understanding the diversity of polymer spherulite morphologies. Different structural length scales have been considered that cover all the aspects of lamellar morphology and structure: configuration and conformation of the chain, unit-cell symmetry and chain tilt, screw dislocations. Fortunately the impact of the different length scales on the final morphology can be evaluated almost independently, thanks to the wide variety of polymers and crystal polymorphs that display lamellar twisting: non-chiral, chiral, with centro-symmetric or non-centrosymmetric unit-cells, etc… In this respect, polymers are ideal systems to analyze the origin(s) of lamellar twisting.

Although screw dislocations are a major feature in spherulite morphology, they do not seem to take precedence in establishing lamellar twist in polymer spherulites. Lamellar twist would be observed in multilamellar objects only, but twisted single lamellae of PE have been observed. Also, solution grown single crystals of a chiral polyester display screw dislocations of both hands, whereas the spherulites display only one sense of lamellar twist: the latter specificity excludes screw dislocations (non-specific) as a reliable intermediate between molecular and lamellar chirality.

The structural analyses suggest that lamellar twist is linked with some, often tenuous, features of the structure of the lamellae themselves that introduce unbalanced surface stresses on the lamellar surface. This hypothesis, first presented by Keith and Padden in 1984 [16], is able to explain twisted lamellar morphologies. It can also account for scrolled lamellae, a case that was not considered initially. In short, twist is associated with a two-fold axis parallel to the growth direction (which may exist in the unit-cell itself, or result from chain tilt in the lamella), whereas this symmetry does not exist for scroll.

The experimental and conceptual challenges then remain to determine or infer, and in favorable cases confirm experimentally, the existence of these unbalanced surface stresses, i.e. to differentiate presumably minute structural features in or near the fold surface. The initial hypothesis of Keith and Padden associating the twist in PE spherulites with differences in the fold surface resulting from chain tilt could be confirmed by polymer decoration of the fold surface, which indeed indicates, if only qualitatively, such differences. Further, half lamellae that grow edge-on are bent, which is a direct morphological consequence of unbalanced surface stresses. These results were obtained for PE, a polymer with a 'simple' structure (all trans, nearly cylindrical chain, orthorhombic cell symmetry). They strongly support the contention that lamellar twist has a structural origin. These results also underline the fact that molecular and conformational aspects are of utmost importance when analyzing lamellar twist.

Chiral polymers provide excellent investigation means in this endeavor. The configuration and helix conformation and handedness are usually known: correlation between configurational and/or conformational features and the final lamellar twist can be made. Configuration and conformation certainly play a role, since lamellae of enantiomers of a given polymer have opposite twist sense. However, the impact of the configuration on higher levels of organization is limited, to say the least. This has been shown in series of polyesters that bear a chiral carbon atom, but differ either in the repeat unit main chain or side chain length or constitution: lamellar twist may be reversed by addition of a single CH_2 unit in the main chain.

These results are puzzling and at times apparently contradictory: they demonstrate that the crystal structure by itself cannot account for the existence, and if so, for the sense of twist of the lamellae. To quote an earlier paper, they 'are

instantly evocative of continuing investigations' [65]. A possible consistent picture emerges however if, as for PE, the origin of twist arises from differences in the fold surface. As is most apparent for helical or crank-shaft chain conformations, the conformation of the chain differs on opposite sides of the lamella as it reaches the fold surface. As a consequence, the fold conformations and/or encumbrance are likely to be different, thus providing the unbalanced surface stresses at the root of lamellar twisting. In this scheme, lamellar twisting is indeed a consequence, but only an indirect consequence of molecular chirality. The direct relationship between chain and lamellar twist chirality observed for enantiomers does not hold, since lamellar twist is determined by finer details of the crystalline core/fold surface transition.

Scrolling of lamellar polymer crystals is merely a different manifestation of unbalanced surface stresses. Three examples of scrolled lamellae have been analyzed so far, all in terms of unbalanced fold volume, i.e. unbalanced surface stresses. The clearest example is provided by centrally substituted paraffins, in which the reduction in diameter of the scroll could be related with the bulkiness of the substituant (methyl or butyl), assumed to be segregated on one side of the lamella. For polyamide 66 crystals, the succession of flat/scrolled/flat crystals depending on annealing (self-seeding) temperature suggests that either similar or different fold types (made at the diamine segment or the diacid segment) are present in opposite fold surfaces of the lamella. Analysis of the scrolled lamellae of PVDF in its γ modification suggests a segregation of folds that differ in their composition by replacement of a CF_2 by a CH_2. The spectacular scrolls would thus result from a volume difference of 10 Å^3 per fold, a figure that provides the only 'quantitative' insight so far available about structural differences that may induce lamellar scroll or twist.

The latter examples illustrate the usefulness of investigating polymer crystals. Their composite nature, with a crystalline core and less ordered lamellar surfaces makes it possible to differentiate and to decouple the impact of core and surface structure—and makes it possible to underline the role of the latter. These examples also show how and why small, but repetitive differences in fold length and/or structure and/or conformation can induce spectacular lamellar scrolls (and presumably twists). It will be a major challenge to analyze these differences in sub-molecular detail by e.g. molecular modeling and conformational energy analysis. However, it must be noted that the analysis of lamellar twisting or scrolling in terms of unbalanced surface stresses supports the generally accepted assumption that, as a rule, surface stresses (linked with e.g. lattice expansion near the crystal interface) apply for non-polymeric materials.

A thorough structural analysis of other twisted and/or scrolled lamellae must be made to confirm the generality of these analyses. Technical improvements may well help in this endeavor. Indeed, the advent of atomic force microscopy and even better, of AFM at high temperature offers the possibility to investigate in a non-invasive way the development of growth of polymer spherulites, and of the outermost lamellar tips. Factors such as the delay (in time) and location of screw dislocations development, lamellar reorganization, lamellar bending, etc…can be evaluated, and compared with molecular processes that have been established via structural analyses: progressive tilting of the chains in PE lamellae [8], delayed scrolling in the substituted paraffin crystals [96], etc. These further studies should help establish the chronology and kinetics of a process that has been analyzed so far mainly from a more static, structural point of view. Of course, they set a diverse and demanding challenge to polymer morphologists.

Note added in proof: A recent work by Xu et al. (J Xu, B-H Guo, Z-M Zhang, J-J Zhou, Y Jiang, S-K Yan, X Gao, L Li, Q Wu, G-Q Chen, JM Schultz, Bull. Amer. Phys. Soc. 1004, 490, 954 (Paper 29 7) is very relevant to the issues considered here. They investigate in real time and at high temperature the crystallization of chiral poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), a chiral polyester. They are able to follow the development of individual lamellae and make a number of interesting observations. The following is an extensive quote of their summary (APS meeting, March 2004): "The crystals exhibit complicated growth behavior: twisting, bending, backward growth and branching. The lamellae twist continuously. The lamellae twist before screw dislocations appear, demonstrating that screw dislocations are not causal of twisting, although twisting is amplified near screw dislocations... All the observed twisting occurred in the right-handed sense, apparently resulting from the chirality of the chains. Increased crystallization temperature results in decreased magnitude of lamellar twisting and bending". The full report of this work has appeared recently (Macromolecules 2004;37:4118).

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