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Polymer Crystallization Processes as Seen from the Growth Front's Perspective

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A critical analysis is presented regarding the possible processes that determine polymer crystal growth, based mostly on the analysis of the structure and morphology of polymer single crystals. This "forensic" analysis suggests that the interaction of the depositing stem with the growth front is the determining factor in the whole crystallization process, irrespective of any previous (pre)organization process, be it spinodal decomposition, formation of "smectic pearls" or precursor phases followed by local reorganization. This conclusion stems from the analysis of the structure and morphology of polymer single crystals, from the recognition that bulk crystallization leads to similar structures of the lamellae that build up the spherulites, and from the distinctly different structures and morphologies of polymers for which a precursor phase (with either smectic or nematic order) has been recognized. The latter situation, with an intermediate loose pre-order, prevails for polymers with inherent chain rigidity.

KEY WORDS: Polymer Crystallization / Growth Front / Deposition Processes /

We celebrate the fiftieth anniversary of the discovery, or more precisely of the correct analysis of chain-folded polymer single crystals.[1] Whereas the first mention, and therefore the concept of chain folding undoubtedly dates back to Storks in 1938 while investigating thin films of gutta-percha,[2] the later (1957) contributions of Keller, Fisher[3] and Till[4] have triggered countless investigations on the crystallization process of polymers. If the contribution of Storks sets the birth date of chain folding, the latter authors, and in particular Keller had the major merit to popularize and, more importantly, to transfer the concept of chain folding to bulk materials, thus opening the way to the "modern" analysis of the crystalline state of polymers.

This celebration provides an opportunity to reflect on how much single crystals have contributed to our understanding of polymer structure and polymer crystallization processes. The present contribution is concerned with the mechanisms of crystal growth. Indeed, polymer crystallization processes have seen a significant revival of interest (and controversy!) in recent years, mostly triggered by new experimental and theoretical contributions by various groups (Kaji,[5] Olmsted and Ryan,[6] Strobl[7]), as well as molecular simulations by, *e.g.*, Muthukumar,[8] Hu,[9] or Meyer.[10] These "modern" views on polymer crystallization postulate or involve frequently the existence of precursor processes or even of precursor "phases." They challenge in many ways the more classical views that, following Frank[11] and Lauritzen and Hoffman,[12] transpose to the polymer field the classical "nucleation and growth" scheme valid for small molecules. In this "nucleation and growth" scheme, an incoming stem attaches to the growth front (the so-called secondary nucleation, or primary surface nucleation step). This initial nucleation is followed by development of a growth strip on the growth front *via* lateral spread, *i.e.*, by attachment of further stems next to the initial nucleation site. Repetition of this process results in the so-called growth Regime II. In this regime, multiple nucleation events take place on any one single growth face layer, and lateral spread is limited by encounter of any single growth strip with strips nucleated and developing next to it. Of course, numerous more detailed analyses have been provided over time. Indeed, the long chain nature of polymers implies that the structural unit (the stem) considered in this process is not independent from the other stems. Also, attachment of a stem implies that the nearby parts of the chain become located close to the growth front. Many more detailed processes have been proposed, that either develop on the concept of precursors, or provide more details about the crystallization process. For example, Allegra and Meille[13] consider the possible existence of "bundles" in the form of pre-crystalline, high entropy aggregates under different crystallization conditions (solution or melt, from the glass, from a thermotropic mesophase). Other models attempt to describe in more detail the transition from the melt to the crystal state. They consider mostly adsorption of different portions of the chain or even of portions of the initial stem[14] followed by different mechanisms of reorganization, etc. All these models adopt (or more precisely adapt) the viewpoint of the nucleation and growth scheme. They will not be detailed any further in the present contribution.

The recent crystallization schemes mentioned earlier depart significantly from the simple nucleation and growth scheme. Indeed, since they involve processes (*e.g.*, spinodal decomposition) that generate some initial order (independently from the order generated by crystal growth itself), these schemes frequently consider crystal formation as the aggrega-

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tion of "precursor" states. As a rule, they deemphasize the role of the growth front. The growth "front" (if it can still be described as such) becomes merely a transition zone in which reorganization of the initial, supposedly disordered phase (frequently viewed as a smectic phase, or a precrystalline order or even, in an extreme scenario, as "lamellar clusters... made of several stacked lamellae"[15]) rearranges itself and reaches the state of a "mature" crystal. Again, these scenarii are developed to various degrees in the different crystallization schemes, with the contribution of Strobl being the most explicit. These views on polymer crystallization have been published in many papers. An excellent grouping can be found in a set of three volumes (180, 190 and 191 of Advances in Polymer Science), Guiseppe Allegra being the editor.[16]

These recent views have had a significant impact on the field. Many colleagues consider that their data provide supporting evidence for these schemes. However, these schemes have not reached universal consensus yet. Other colleagues consider them with reservation, or at least do not include them explicitly in their analyses. One of the present authors (BL) has expressed his concerns quite loudly in two contributions.[17,18] The first was triggered by, and published back to back with, one of Strobl's contributions: Gert Strobl accepted very elegantly this unusual confrontation of viewpoints in the printed literature. Together with two comments[19,20] this set of four papers provided an unusual "forum" on the topic. A more recent contribution by both of us analyzes our views on "the nucleation control in polymer crystallization," and details the "structural and morphological probes in different length- and time-scales for selection processes."[21]

As judged from the emphasis put during the recent ACS meeting in Boston celebrating the 50th anniversary of single crystals on the "modern" crystallization schemes,[22] we thought it necessary to recall or restate some of the merits of the nucleation and growth mechanism. In doing so, we do not wish to dismiss the analyses and processes introduced more recently. They may apply under specific circumstances and/or for specific polymers. Pre-order certainly exists for macromolecules that have sufficient inherent stiffness, or may well exist under certain crystallization conditions (probably unusual: deep quench, mechanical orientation, fiber spinning, etc). However, we tend to believe that extending the concept of "diffuse" interphase between the melt and the crystal to such "simple" polymers as polyethylene or polyolefins crystallized under quiescent conditions is excessive. For most "usual," flexible polymers and most "usual" crystallization conditions, the nucleation and growth scheme seems to bear more potential in explaining the end result—namely the single or more complex crystals that are formed.

In the present contribution therefore, we wish to recall some simple experimental facts relating to the structure and growth features of polymer crystals, with an emphasis on single crystals, but not excluding, and actually making the link with, bulk crystallization. In our view, these observations clearly suggest an intimate interaction between the depositing chain and the growth front. In many cases, it is difficult to conceive

or accept that these interactions are compatible with some form of late or delayed ordering, i.e., subsequent to the formation of a lesser defined precursor state or phase—, i.e., they call for a "nucleation and growth" type of mechanism (Note that hereafter, we adopt this terminology, i.e., we deemphasize the details of this scheme, as illustrated by the different growth regimes, etc. We will consider a "standard" polynucleation scheme as the most representative crystal growth process[23]). In our view, in many cases, nucleation and growth can explain (only, or at least, best) the observed features. We draw much of the material used in this context from our own contributions, or from contributions with which we are most familiar. Although such a bias eases our task, it does not render justice to other, equally important contributions from many colleagues. Again, staying in the spirit of a forum, the number of arguments is not a determining factor. The present analysis should be considered merely as a note of warning aimed at keeping a critical view on the recent crystallization mechanisms, and at the same time as a reminder of the merits of "older," more classical (or more conservative) crystallization schemes. Of course, and again keeping in the spirit of a forum, any equally argumented, opposing view that would explain these features using the various "modern" crystallization schemes will be more than welcome.

In the analysis, we consider various selection processes taking place in polymer crystallization at the growth front, and from that growth front's perspective. These selection processes translate in structures, morphologies and growth rates that are, at times, quite specific and that can be used to infer the growth mechanisms. Connections can be made between crystallization under mild conditions (single crystals, obtained at low undercooling or in solution) and bulk crystallization that lead to the formation of spherulites.

DISCUSSION

Crystal Morphology and Structure as Controlled by the Crystallization Process

Crystals have many features that can be traced to their mode of formation. Geometrically well defined, facetted single crystals such as, e.g., the lozenge shape of polyethylene crystals, limited by {110} growth faces, or the hexagonal crystals of poly(oxymethylene) frequently correspond to an homothethy of the unit-cell geometry and dimensions. Such facetted single crystals indicate that crystal growth is controlled by a surface nucleation process.

The crystal geometry can however differ from the mere homothethy of the unit-cell, which helps recognize different features of the growth process. For example, existence of (110) twin planes in polyethylene induces characteristic elongated crystal shapes (Figure 1). They tell that at the tip of the twin plane, two abutting (110) growth faces form an acute angle at which deposition of a new stem is easier. This preferred secondary (or primary surface) nucleation site exists only at the acute angle, and not at the opposite end of the twin plane, where this angle is obtuse. Similarly, it does not exist for (310)
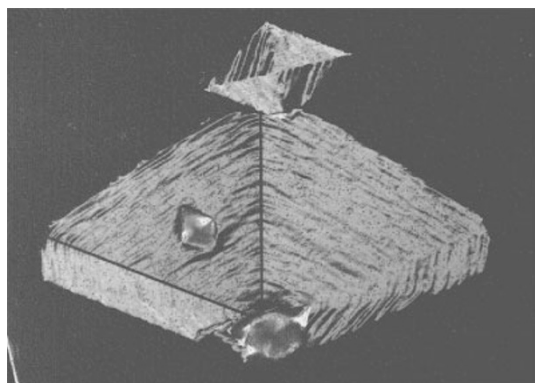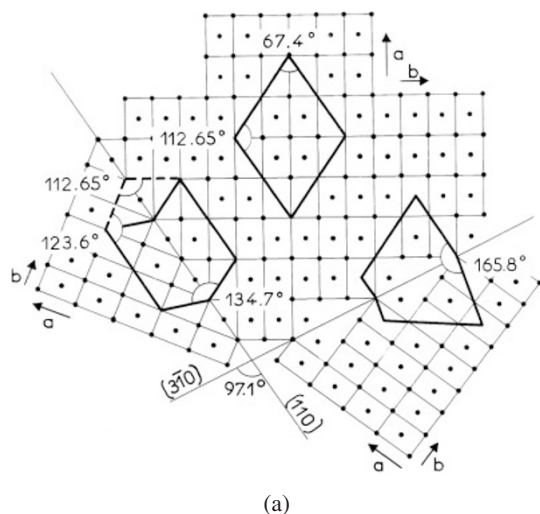
(a)

(b)

Figure 1. Growth twins of polyethylene.[52] **(a)** Drawing of the untwinned single crystal, the (110) twin (left) and (310) twin (right). Note that enhanced secondary nucleation takes place only at the reentrant corner of the (110) twin, thus the extension of the twin in this direction. **(b)** A multiple (110) twin together with an untwinned crystal, both imaged here in dark field electron microscopy. Note the different size of the (110) twin and the untwinned crystal. The (310) twin (not shown) has the same size as the untwinned crystal. These crystals were produced by a self-seeding procedure, which implies that their growth started at the same time. Two of the (110) twin planes (on the left side) are highlighted by an optical trick made possible by electron microscopy dark field imaging. In short, the present image is defocused. The electrons scattered by the different components of the twin do not follow the same path in the microscope. Defocusing of the image separates (optically, that is, artificially) these components in the recorded image. When the focus is adjusted, the crystal is (correctly) imaged as a single entity.

twins, for which the angle between the twin components is too large and therefore does not create a suitable deposition site: no enhancement of the growth rate associated with the (310) twin plane is observed. In (110) twins, a given site of the growth front is preferred over all others, and this site can be located and characterized by a mere microscopic analysis of the growth front topography. Furthermore, this specific nucleation site induces an increased growth rate that extends over the whole length of the two nearby growth fronts. This feature illustrates the fact that a local perturbation is felt micrometers away on the growth face—a very long range indeed in molecular terms.
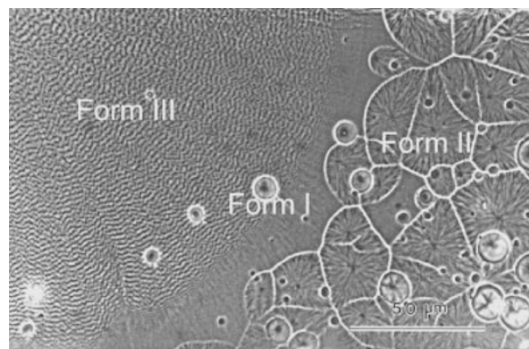

Figure 2. Simultaneous crystallization of isotactic poly(1-butene) in three different crystalline forms. Growth is performed in the presence of a trace of amyl acetate. The three different forms can be recognized by the characteristics of the spherulites. For example, spherulites of Form III have twisted lamellae and therefore display banding.[53] Optical micrograph, phase contrast.

Such a long-range impact indicates in turn the existence, and can only take place through the agency, of lateral spread.

Whereas polyethylene single crystals do indeed provide some information on nucleation and growth processes, analysis of more complex systems is frequently more telling. The most illustrative examples rest on the interplay and the mutual impact of crystal structure (at the unit-cell level) and the resultant morphology. Let us consider or recall some of these examples, some of which have already featured in previous contributions. They all illustrate the selection processes that take place at the growth front, or at least in the buildup of the crystals.

The selection processes at play for helical polymers have already been underlined on various occasions. We simply recall that, sometimes under the same crystallization conditions, a given polymer can grow in two (or even several) different crystal phases. In terms of crystal growth processes, this crystal polymorphism is particularly striking when the polymer is a polyolefin with helical molecular conformation. Indeed, the polyolefins are conformationally racemic, *i.e.*, can exist as right-handed and as left-handed helices. Selection of the helical hand takes place not only within any given crystal phase, but may also be different for coexisting, nearby growth fronts. Indeed, the α phase of isotactic polypropylene combines two different helical hands, as it is made of alternating *ac* layers made of right and of left-handed helices, whereas the β phase is chiral, with (at least locally) all helices of the same, given hand. For isotactic poly(1-butene), three crystal phases can be produced simultaneously, one of which is chiral (Form III), whereas the two others combine helices of opposite hands (Forms I and II), keeping also in mind that the three forms rest on different helix geometries.[24] Note that the growth rates of the three forms are significantly different—actually orders of magnitude different (Figure 2).[25]

Keeping again in mind that the crystallization conditions are identical, these differences (selection processes, growth rates) indicate that the crystallization process, even if it implies a "precursor" phase or molecular conformation, is mainly controlled by the growth front. Only the growth front can

convey the structural (mainly topographic) information to the depositing stem (or bundle, or smectic pearl, or precursor phase) that will determine its ultimate fate and kinetic pathway (*i.e.*, ultimately, growth rate) in one or the other form out of the three possible forms.

The selection process becomes all the more drastic in the case of stereocomplexes formed by racemic blends of the two enantiomeric forms of a given polymer. This is the case for poly(lactic acid) (PLA). The crystal structure of the stereocomplex rests on an intimate association of stems made of the two polyenantiomers poly(L-lacide) (PLLA) and poly(D-lactide) (PDLA). The stereocomplex crystal structure has the same *R3c* symmetry as Form I of isotactic poly(1-butene): every stem of PLLA (left-handed helix) is surrounded by three stems of PDLA (right-handed helix) and reciprocally.[26] In iPBu1 however, all these stems are parts of the same molecule, whereas in PLA they correspond to different molecules. In other words, generation of the stereocomplex crystal structure implies a molecular selection process, and not only a conformational selection (or rearrangement) process, as in the case of iPBu1 Form I (or, for that matter, Form II also). Again, this selection process must take place by necessity at the growth front. Let us simply recall (this argument has been developed on different occasions) that any imbalance of the racemic blend (concentration, molecular weight) results in a spectacular morphological imbalance.[27] In essence, the deposition processes of PLLA and PDLA stems are (of course) similar, but they take place on opposite sides of the same growth plane. If PLLA and PDLA are imbalanced, the front- and the back sides of this growth plane have different (rather than equal) growth rates, and the final single crystal morphology becomes triangular rather than hexagonal (Figure 3).

Here again, the conditions near to or at the growth front are similar—the precursors are the same, irrespective of their location near the front or the back of the growth plane. The difference in growth rates can only result from the selection, the sorting out process that takes place at the growth front. This sorting out process depends critically on the growth front topography, as determined by the helical hand and the location of the stems that compose it. Note that similar stereocomplexes are obtained with other similar systems, among which poly-(propylene-carbon monoxide).[28] More importantly perhaps, the growth process of these stereocomplexes (temperature variation of the growth rate, etc) does not differ in its major features from those of the homopolymers PLLA or PDLA crystallizing in a "conventional" crystal structure. In other words, these features are compatible with (or indicate?) a crystallization process that implies a selection process at the individual stem level.

Unconventional crystal morphologies reveal even more subtle interactions between the depositing stems and the growth front, *i.e.*, reveal finer details of the stem deposition and attachment processes involved in crystal growth. The crystal morphology of interest in the present context is that of isotactic poly(2-vinyl pyridine) (iP2VP) grown in thin films.[29] The crystal structure of iP2VP is a frustrated one, with three three-fold helices per cell.[30] A characteristic of frustrated structures is that the three helices are not related by any crystallographic element of symmetry: their angular setting in the unit-cell is "free" (from a crystallographic point of view).[31] The setting of the helices in iP2VP is such that, even in single crystals, the topography of the growth front is asymmetric: deposition towards the right and deposition towards the left on the growth front is not equivalent. Furthermore, this asymmetry is more pronounced on one side of the growth plane than on the other (here, we distinguish front/back rather than right/left). These two asymmetries lead to curious crystal morphologies of iP2VP single crystals (Figure 4). The crystal has indeed six growth sectors. However, the growth faces of three of these sectors (non-contiguous) are not normal to the radial growth direction: after initial deposition of stems (secondary nucleation step) further lateral spread is biased, *i.e.*, is preferentially oriented towards one side of the growth front. As a conse-
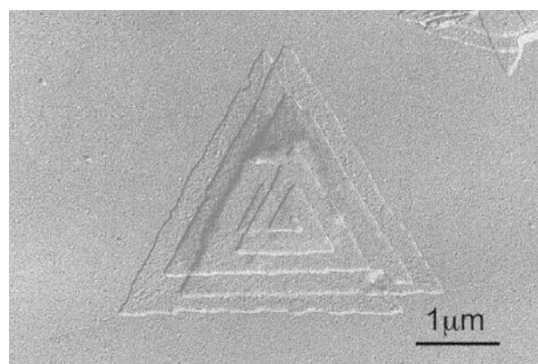

Figure 3. Triangular single crystals of the stereocomplex of Poly(L-lactic acid) and Poly(D-Lactic acid). The symmetry of the stereocomplex implies that every stem of PLLA is surrounded by three stems of PDLA. The symmetry is maintained, but the growth rates differ on opposite growth faces, when there is an imbalance in the PLLA and PDLA supply. A balanced supply (similar molecular weight and concentration of the polyenantiomers) yields the expected hexagonal symmetry of the crystal.[27]
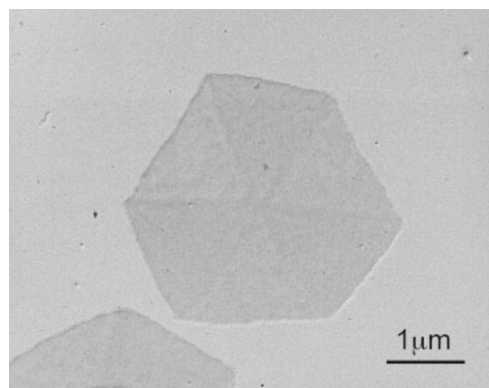

Figure 4. "Skewed" single crystals of isotactic poly(2-vinyl-pyridine). This unusual single crystal morphology stems from an asymmetry of the iP2VP frustrated structure. The growth face has niches that are tilted to the growth front normal. Completion of the growth front by lateral spread is asymmetrical, which results in faster growth of one side of the growth front relative to the other. Note further that the lower left corner is less asymmetrical due to exhaustion of the crystallizable material by the nearby crystal.[29]

quence, one side (right or left) of the growth face grows faster than the other, which results in the overall tilted growth front. On the opposite growth sectors however, the growth front is flat, reflecting an equal probability of lateral spread extension on both sides of the nucleation sites (Figure 4).

The above asymmetry in initial deposition and oriented lateral spread depends critically on the unusual crystal structure of iP2VP. However, it seems to have a more widespread applicability. It is indeed a key feature in the analysis of crystal morphologies performed by Shcherbina and Ungar.[32] These authors analyze the lenticular shape of polyethylene single crystals grown in poor solvents (parafins or, e.g., higher alkohols) or of polyvinylidene fluoride (PVDF),[33] or also that of rounded crystals of polyethylene oxide grown in bulk, at low undercooling. They point out that the (110) growth face of PE or PVDF is jagged. Due to the setting of the chains in the unit-cell, attachment of stems is easier on one side of the growth face than on the other. In other words, straightforward crystallography suggests that there may be a right versus left asymmetry in the lateral spread rate. This analysis leads to a very general description of the rounded (as opposed to flat) shapes of crystal growth faces that had eluded earlier analyses. In a recent and as yet unpublished work presented at this meeting, Goran Ungar has extended this analysis to describe the shape of the iP2VP crystals described above (Figure 4).[34] It should be underlined that in an earlier experimental and theoretical investigation of the lateral habits of polyethylene single crystals, Toda[35] pointed out that the rounded faces of the crystals are not consistent with a roughened surface but rather are explained by a nucleation-controlled growth. An additional moving boundary condition is implied that is different from but has the same structural consequences as the anisotropic growth considered by Ungar.

Whereas analysis of the link between crystal structure and crystal morphology could be extended to a number of other systems, the above morphological/structural indicators suggest in a quite straightforward manner that the depositing stems "read" the topography of the growth front. Similar conclusions can be drawn from more local probes that rest on the orientation of stems in the unit-cell. They deal with growth processes and growth rates of multiply twinned crystals.

Growth of Twinned Crystals

Twin planes are local perturbations of the crystallographic lattice. As such, they can be used as a structural probe at a length scale that is commensurate with the structural entities that build up the crystal, namely the stems. Indeed, understanding (or better, visualizing) the structural and molecular organization across the twin plane helps reach very local organization mechanisms involved in growth processes.

Twinned crystals of polyethylene have already been considered earlier. They result from the development of a twinned seed crystal. Further growth merely memorizes and transfers on a "macroscopic" scale (that is, that of the crystal as a whole) the initial crystal axes orientations of the twinned seed. However, some other polymers allow analysis at a more local scale. For the most part, these are polymers in which the twinning does not change the orientation of the unit-cell axes, but merely affects the orientation or azimuthal setting of the structural elements within the cell. Two examples are worth mentioning in this respect: the β phase of syndiotactic polystyrene (βsPS) and isotactic polycyclohexane (PVCH).

In a set of very enlightening works, Tsuji and his collaborators have been able to image the crystal lattice of βsPS grown under a variety of experimental conditions.[36] They have shown that, as the crystallization conditions become more drastic, the crystal structure displays repeated (or polysynthetic) twinning, which is indicated by streaked diffraction patterns. Analysis of the streaking as well as direct molecular imaging of the stems and of their setting in the crystal lattice (a technical prowess) indicates that the twinned domains can be quite narrow, sometimes with a breadth of only two or three molecular layers.[37] The additional element is that the twin planes are normal to the growth front. In other words, the depositing stem reads the orientation in the lattice of the underlying stem (i.e., of the growth front), and perpetuates this orientation during further growth. Note again that this pattern is reproduced at a very local scale—in growth domains of the growth front with widths down to a few stems.

As illustrated in a similar set of experiments (but in which imaging at molecular resolution could not be achieved), single crystals of isotactic polyvinylcyclohexane (PVCH) displayed very similar features.[38] PVCH has a tetragonal unit-cell with $I4_1/a$ symmetry.[39] The four-fold helices are tilted relative to the unit-cell edges, which creates a possibility of twinning by merohedry. At very high crystallization temperatures, growth in thin films of PVCH produces essentially untwinned single crystals only. At lower Tc's, the crystals are polysynthetic twins. More precisely, and as shown by dark field electron microscope imaging, each of the four growth sectors of the square crystals is composed of elongated, twinned domains with their major boundaries normal to the growth front (Figure 5). Again, the growth process (i.e., deposition of new stems on the growth front) preserves the azimuthal orientation of the helix in the growth front, and crystal growth merely perpetuates this orientation.

Occasionally however, it does not. Since twinning by merohedry introduces a relatively mild local perturbation, PVCH single crystals provide also the possibility to investigate the formation of growth twins, that is, the deposition of stems in twinned orientation relative to the substrate growth front. This possibility stems from the tetragonal symmetry of the unit-cell, which allows twin planes in two orthogonal directions, normal and parallel to the growth front. Some major insights can be gained from the analysis of such growth twins.[40] First, the edge of the newly formed twinned domain is parallel to the growth front, which suggests that its width corresponds to the extent of lateral spread of the domain initiated by a twinned secondary nucleation process. Indeed, this lateral spread is limited by its encounter with the two nearby, untwinned lateral spreads on the growth front (in the so-called polynucleation regime). Second, the average width of
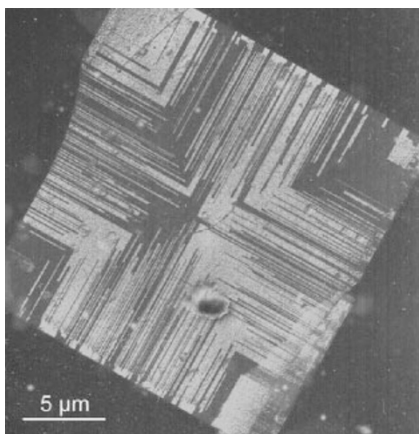
Figure 5. Single crystals of isotactic poly(vinylcyclohexane). The growth sectors are made of multiple smaller domains, all oriented normal to the growth front. These correspond to twinned domains, imaged here by dark field electron microscopy.[38] New domains are generated as a result of growth twinning. The width of these domains can be considered as a measure of the so-called lateral spread associated with each secondary nucleation event on the growth front, and can be measured as a function of the crystallization temperature.[40]

the newly formed twinned domain provides a measure of the secondary nucleation (or primary surface nucleation) density. The lateral size of the domains decreases with crystallization temperature, which indicates that (as expected) the density of secondary nucleation increases on decreasing the crystallization temperature. The number of stems deposited per strip (*i.e.*, by lateral spread) ranges from about 60 at 220 °C to 15–20 at 120 °C, under the experimental conditions used (dilute solutions of PVCH in squalane). Admittedly, these experiments do not correspond, strictly speaking, to "conventional" crystal growth since twinned domains are observed. They provide however the first experimental values of a critical parameter in polymer science, namely the extent of lateral spread.[40]

These experiments should be complemented with measurements of the actual growth rate. Combined with the extent of lateral spread, they would provide the first measure of the rate of secondary nucleation, assuming that the concept of nucleation and growth is valid. One further characteristic of the growth process of twinned PVCH crystals may however limit the validity of this measurement. In a manner very similar to the (110) twins of polyethylene, but to a much lesser extent, the twin plane in PVCH single crystals introduces a jag in the growth front: one side of the twin plane is "ahead" of the other side by half a stem width. This introduces a preferred nucleation site where more interaction with the substrate takes place—a situation described as "fractional" secondary nucleation.[38] Because of this "fractional" nucleation, the measured growth rate would be larger than the "true" growth rate of an untwinned crystal, much like, but probably to a lesser extent than, the (110) twin in polyethylene.

The above observations and analyses indicate that the growth rate determined for crystalline polymers may depend on a number of factors. Only factors relating to the crystallog-

raphy have been considered here. Equally important is the lamellar thickness, an issue that has been developed in a number of elegant contributions. To some extent however, it is more difficult to use or to rely on lamellar thickness as a defining criterion. More exactly, it is hardly a discriminating criterion when discussing the validity of crystallization schemes. Indeed, adjustment of lamellar thickness through thickening or thinning in the vicinity of the growth front (as observed for example in low molecular weight polyethylene oxide or long parafins, with ample longitudinal mobility along the chain axis[41]) corresponds to a (admittedly early) post-crystallization mechanism. It does not reflect the details of the deposition process itself—except to point out that this deposition process is not an equilibrium one, at least as far as the lamellar thickness (or stem length) is concerned. In other words, lateral interactions (of the stem with its neighbors), that is, crystallographic criteria, are in the present context, probably more telling and critical because their role seems more prominent in the early stages of the deposition process. Longitudinal ordering on the other hand (adjustment of lamellar thickness) comes only as a later process, probably when some of the major crystallographic features (*e.g.*, helical hand) are already fixed.

Alteration of Crystallization Conditions

Modification of crystallization conditions can alter the crystallization process in many ways. Abrupt changes in crystallization temperature, pressure, etc can induce for example different crystalline phases. Most telling in this context are indeed transitions from one crystal phase to some other phase that differs by the chain conformation or crystal symmetry. Situations in which the transformation or transition involves a liquid-crystalline phase and a crystal phase are the most illustrative. Indeed, liquid-crystalline phases are, presumably, very similar to the postulated precursor phases (of whatever type they may be), since the latter assume relatively loose intermolecular interactions. Note that liquid-crystalline phases have frequently hexagonal symmetry. The transition therefore either starts from or ends up as a hexagonal phase.

The fact that the transitions involve two different cell symmetries therefore provides a means to investigate molecular rearrangements at a very local scale. Two examples are worth mentioning in this context. First, the transition from the hexagonal phase of polyethylene formed at high pressure to the conventional orthorhombic phase when pressure is released. Second, transitions in polymers that are known to form liquid-crystalline phases at high temperatures.

The transformation of the hexagonal to the orthorhombic modification of polyethylene is associated with the investigation of polyethylene crystallization under high pressure. Under these conditions, a hexagonal phase is formed, that displays high longitudinal mobility. The crystals formed under these conditions have a rounded shape, indicating that there is no preferred growth face for this liquid-crystalline form.[42] When the sample is quenched during crystallization, the remainder of the material crystallizes in the conventional orthorhombic

form. Moreover, the liquid-crystalline single crystals experience a transition to the orthorhombic form as well. In a very elegant work, DiCorleto and Bassett[42] used a selective dissolution technique that removes the last formed crystals, and leaves only the thicker and transformed single crystals initially produced under high pressure. Strikingly, these single crystals display sets of corrugations oriented 120° apart. These corrugations are well known in PE crystallization, and indicate the orientation of the *b* axis of the orthorhombic unit-cell. Existence of these three orientations of the *b* axis indicates that the transformed crystals keep in their structure the memory of their initial hexagonal unit-cell symmetry, *i.e.*, of their "precursor" liquid-crystalline state.[17,43]

Similar situations are encountered with many other systems. To stay with "flexible" macromolecules, let us simply mention the case of "chiral polyolefins." This is a short hand means to name polyolefins that bear a chiral side chain—for example isotactic poly(4-methyl-hexene-1) (P4MH1). These polymers had been investigated in the late 1960-early 70s.[44] Their structure and crystallization characteristics are reinvestigated in the frame of the debate on polymer crystallization processes.[45] The main chain of these polymers is a priori flexible. However, the chiral atom in the side chain introduces a slight preference for a given main chain conformation. Repetition of this slight preference along the polymer backbone generates a definite preference for one helical conformation, *via* a "macromolecular amplification of chirality."[46] As a result, the polymer adopts a helical structure in solution as well as in the melt. On cooling from the melt, the polymer forms first a chiral liquid-crystalline phase at about 180 °C. The liquid-crystal phase transforms to the crystalline phase only at 120 °C. This transformation implies reversal of helical hand of one stem out of two, since the crystal structure is made of helices of both hands. This "delayed" crystallization, after an initial liquid-crystalline state, is very reminiscent of the process considered in the recent crystallization schemes. The feature of interest is again the fact that the transformation from the hexagonal liquid-crystalline phase to the tetragonal crystalline phase generates three orientations of the latter phase, thus reflecting the symmetry of the liquid-crystalline phase it evolved from.[45] This polymer provides the opportunity to test the crystallization behavior of more elaborate systems. In particular, it is possible to mix the two polyenantiomers of P4MH1. In the liquid-crystalline phase, both helical hands are therefore present. Under these conditions, a crystalline tetragonal lattice is formed at higher temperatures (at 180 °C). Not unexpectedly, the crystals have a square shape, and only one orientation of the lattice is generated, indicating that no intermediate liquid-crystalline phase was formed in the process.[18,47]

Slight modifications of the crystallization conditions can also lead to significant differences in the growth process and/or its outcome. Let us simply recall that, within a small temperature interval, transitions may take place from one crystal form to another or from one spherulite radial growth direction to another. Such transitions are frequently associated with significant jumps in the growth rate. Such transitions are known to take place in, *e.g.*, poly(ethylene adipate).[48] Again, such small modifications of the crystallization conditions are unlikely to affect possible precursor states to any significant extent. They are most probably associated with differences in the deposition process, as triggered by modifications of crystal structure stability, or growth front topography, etc.

Growth of Single Crystals Versus Bulk Crystallization

Polymer single crystals provide easy systems to analyze growth processes at a local scale. However, single crystals are produced under special conditions—dilute solution, limited growth rates, etc. Growth conditions in bulk differ from those of single crystals, if only due to the higher viscosity. Does this imply that the crystallization processes are significantly different? They are certainly different for very high molecular weights, for which chain entanglements become a serious hindrance to the local reorganization of chains when they enter a crystal. The consequences are the lower crystallinity of these very high molecular weight materials (even for the "featureless" polyethylene), and the absence of well defined spherulitic structure, implying a loss of structural/morphological correlation at long distances. It should be pointed out that a similar, more drastic limitation applies to the stereo-complexes of polyenantiomers discussed earlier. Indeed, the stringent alternation of different molecules (*e.g.*, PLLA and PDLA) that make up neighbor stems implies a more drastic selection process. It has been shown that, in bulk crystallization, at least one of the component must have sufficient mobility, which translates in a molecular weight lower than 30,000.[49]

Is the crystallization process different in nature for more "standard" bulk crystallization and solution crystallization? It does not seem to be so. One of the major indicator stems from the fact that, at high crystallization temperature, single crystals can be produced in the bulk. They do not differ from similar crystals produced from solution: polyethylene forms lenticular crystals both from the bulk and when crystallized at high temperature from poor solvents (parafin, higher alcohols).[50,51] Also, many single crystals can be produced from thin films, for which growth conditions are similar to the bulk, except for the geometrical constraints introduced by the substrate. The latter however do not fundamentally affect the crystallization process, or even highlight some of its features. For example, when chains are tilted in the lamellae, growth may be asymmetric. In polyethylene crystallized in thin films on glass or mica, the growth rate in the $+a$ direction differs from that in the $-a$ direction due to chain tilt (the growth front makes an acute or an obtuse angle relative to the substrate). This effect does also exist in screw dislocations grown in the bulk, when the growing layer "feels" the underlying layer in the screw dislocation.

Numerous other examples could be given, that illustrate the fact that growth of single crystals does indeed reflect, or at least does not differ significantly from that of bulk systems. At this stage, it should be merely pointed out that the possibility to analyze growth and structural features of single crystals (which

897

have been the major material in this discussion) is quite welcome. The conclusions drawn from these investigations can be safely transferred, with relatively little adjustments to bulk crystallization. This is very fortunate given the structural complexity of spherulites, and the inherent difficulties that are to be faced when investigating them, especially at the molecular level implied by the analysis of growth processes.

CONCLUSION

Single crystals have changed our perspective and our approach of polymer crystallization processes. They provide easily accessible model materials that are further ideal for a wide range of structural investigation techniques. Moreover, many of their features are representative of less "ideal" crystallization conditions, in particular of bulk crystallization. Their analysis features therefore prominently in the theories of polymer crystallization.

In the debates over crystallization schemes in polymers, the major part of the available information has been gathered by investigating polyethylene crystallization. Admittedly, the structural and conformational simplicity of this polymer makes it an "archetype" in such an analysis. At the same time however, information provided by such simple systems is, by design, relatively limited. In essence, the chain (stem in the crystal) is virtually featureless. Indicators are the crystal axes orientations (e.g., twins), the crystal habit (faceted versus rounded crystals) and lamellar thickness, and of course growth rates. Similar probes are used in most analyses of other polymer crystals.

The wide variety of existing crystalline polymers offers a much broader range of experimental probes. All of these polymers should be used to evaluate the merits of any crystallization scheme—keeping in mind that different schemes may apply for specific polymers (e.g., liquid-crystalline ones) or specific crystallization conditions (e.g., possibly, solution versus bulk, or moderate versus deep quench). The fact that liquid-crystals and crystals have usually different crystal symmetries can help establish or dismiss the existence of a precursor liquid-crystalline phase. Moreover, the variety of unit-cell symmetries in polymer crystals offers a means to access very local processes. For example, the growth twins in PVCH provide a means to access experimentally the extent of lateral growth (the so-called lateral spread)—for which only estimates were available.[40] This possibility stems from a fortunate combination of unit-cell symmetry and stability of the twinned deposit. On a more local scale, the helical hand of achiral polyolefins is also a precious probe, as developed in earlier analyses.[17]

Many features of the crystal (stem organization, helix and unit-cell symmetry, orientation of axes, lamellar thickness) are either fully or in part (lamellar thickness) determined in the very early stages of the crystallization process. The crystallographic evidence accumulated so far suggests that selection processes needed to build up a crystal are very stringent indeed. Even if one considers a "usual" concentration of defects in the crystal (edge dislocations, etc) these represent, statistically, a very small proportion of the overall crystal, i.e., of the total number of stems involved. There is virtually no microtwinning in most crystals. When such microtwinning exists in the developing crystal, available evidence either by dark field imaging (cf. the PVCH crystals) or even at molecular resolution (cf. the βsPS crystals) suggests that it is "read" by the depositing stem and perpetuated along the growth direction. Similar conclusions can be drawn for most growth processes analyzed at a sufficiently small scale—in essence, when it is possible to infer the very local crystallographic organization of the system. This applies to the growth of polymers. It applies also for heterogeneous systems, for example in epitaxial crystallization of a polymer on a low molecular weight, or on a different polymer substrate.[18] In this case, no "molecular" transfer of information between the substrate and the deposit can take place that would determine the helical hand, etc. The only possible interaction left is some form of topographic adjustment at a local scale—in fact within van der Waals interactions range. These interactions are however stringent enough to dictate the crystal form that is produced, and within each of these forms the crystallographic contact plane, or even the helical hand of the polymers interacting with the substrate.

When considered from the growth front's perspective, growth of polymer crystals appears as a very local selection process, in which the only piece of information conveyed to the depositing molecule is the topography of the growth front. Matching of the correct stem (i.e., adjustment of, e.g., the setting of the chain, of the helical conformation and helical hand) with this local topography mainly implies interactions within van der Waals range. In this respect, the growth front is, literally, "short sighted." The growth front's limited perspective therefore defines the relevant range of interactions that dominate the crystallization process. Since these interactions define or determine major features of the crystallization process—the crystal modification that is formed, the associated growth rate, etc—the growth front's perspective, limited as it may be, dominates the crystallization process. Schemes that deemphasize the direct interaction between the depositing stems and the growth front and that leave the generation of the crystal to some undefined and delayed ordering of a precursor phase may not be able to account for the varied features of polymer crystallization processes and of the resultant crystals. To the contrary, crystallization schemes that give precedence to the local interactions between the growth front and the depositing stem and thus assume some type of "nucleation and growth" process appear as the most plausible.

Polymer Journal

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