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Comments on: 'A critical assessment of unbalanced surface stresses: Some complementary considerations', by DC Bassett

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Abstract

The complementary considerations developed by Bassett are welcome additions to our paper that surveyed the origin of twist in polymer lamellae. They point to alternate mechanisms than those suggested by Keith and Padden. Polyethylene is not, however, an archetypical system, and the mechanisms uncovered may not have general value. Development of non-planar lamellar geometries associated with unbalanced surface stresses can have different origins. They all rest on structural asymmetries (with chains normal or not to the fold surface), either produced directly on crystallization, or after reorganization. This is best illustrated by the analysis of the structural origin of scrolled lamellae, for which different origins of unbalanced surface stresses have been uncovered for the three systems analyzed so far. In ultimate analysis, the unbalanced stresses are linked with the unbalanced fold structure and its orientation relative to the growth direction of the lamella.

Keywords: Unbalanced surface stresses; Lamellar twisting and scrolling

1. Introduction

The considerations developed by DC Bassett [1] regarding the critical assessment of unbalanced stresses in generating lamellar twisting complement significantly our contribution [2]. The experimental support for this contribution rests for the main part on very elegant experimental designs and investigation methods that help evaluate the details and the chronology of molecular processes taking place in polymer lamellae. In this respect, the use of highly oriented, high-melting polyethylene fibers as nucleating substrates of individual lamellae (or more precisely, of stacks of lamellae) provides major insights into the growth processes and the sequence of lamellar rearrangements taking place over time [3]. When combined with the etching technique that helps 'peel off' successive layers of growth, a precise analysis of the successive stages of the lamellar development becomes possible. In particular, it helps 'read' the sequence of molecular rearrangements and their time scale that Bassett emphasizes as essential ingredients in the development (or absence) of lamellar twisting.

In the spirit of the 'forum' initiated by David Bassett's contribution, we wish to add a few remarks on our own, which for the most part deal with minor points that in our opinion may deserve further investigation.

2. Development of surface stresses in polyethylene lamellae as result of deposition of inclined lamellae versus lamellar reorganization

The experimental results developed by Bassett deal with the development of surface stresses (associated with reorganization) in polyethylene lamellae as a function of crystallization temperature, molecular characteristics and growth regime. This detailed analysis had not been developed in our initial paper, since it was more specifically intended to deal with the general issue of the unbalanced surface stresses hypothesis rather than to analyze the details of their origin. For the sake of completeness, it must be stated that the mechanism proposed by Keith and Padden (K and P) [4,5] was actually formulated as a hypothesis rather than as an explanation. It is necessary to recall the drawing that introduced the unbalanced surface stresses associated with deposition of chains on inclined lamellae (Fig. 1, presented in Appendix I of the K and P paper) and the very words of the authors relating to it: 'It is recognized that these arguments are based upon largely unsupported, though commonly voiced, views about the conformations of chains near a growth front and

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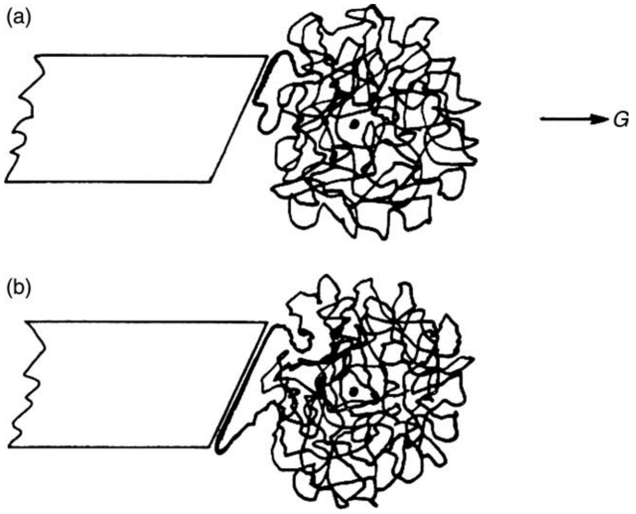

Fig. 1. The model of chain deposition on an inclined growth face presented by Keith and Padden in Appendix I of their 1984 paper and illustrating the 'formation at the lower fold surface of relatively tight folding' ('representation of an oblique growth face encountering a coiled molecule in the melt') [4].

how these chains move as they attach themselves to that front. While these views seem persuasive in the case of crystallization from solution, they may be of questionable value in the context of solidification from the melt. There is as yet little or no reliable knowledge of just how in these circumstances molecules approach growth fronts and adjust their conformations during crystallization. The argument proposed here probably has validity but this cannot be claimed with confidence. There may be other molecular mechanisms that would lead to similar consequences and seem no less plausible. It is for this reason that in the main text the suggested differences in degrees of overcrowding at opposite fold surfaces is advanced as a postulate rather than a demonstrable premise' [4]. All along their paper also, K and P raise the importance of structural rearrangements during and after deposition of the chains on the growth front. This concern features even in the title of their paper: '… and the role of transient states…'

Similarly, we did not analyze the origin of the unbalanced surface stresses, especially in the case of polyethylene. Commenting on the decoration experiments results, we pointed out that: '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' [2].

Based on very careful observations with PE [3,6], Bassett indicates two scenarii [1], that indeed differ from Keith and Padden's hypothesis: for HDPE, twisting, only observed in regime II growth, results from the reorganization, after the initial deposition of stems that are initially normal to the lamellae and become tilted to remove surface stresses. For LDPE, chains do deposit on tilted lateral growth faces under Regime I growth conditions (as assumed by K and P), but it is the thickening and reorganization of lamellae that induces chemical defects to migrate to the surface of the lamellae and generates the twist.

Bassett's contribution has, therefore, established two 'other molecular mechanisms that would lead to similar consequences and seem no less plausible'. This is indeed a very major contribution, since these molecular mechanisms are quite elusive and cannot, as a rule, be apprehended by investigating the bulk of the spherulite.

3. Generalization of the mechanisms to other polymers and other growth conditions

Again in line with the 'forum' spirit, we would take issue with David Bassett when he suggests: 'The proposal (of deposition of molecules on an inclined lamella being relevant to twisting) has no basis for polyethylene, the archetypical flexible polymer and is, therefore, unlikely to apply elsewhere'. In our contribution, we have attempted to illustrate that there are many possible ways to generate surface stresses, and it would appear excessive to rule out any specific mechanism. The need to consider specific analyses is best illustrated when considering the origin of lamellar scrolling. In the three examples covered in our contribution (polyvinylidene fluoride, γ form, polyamide 66 and the parafins with a substituant attached near the middle of the chain—the latter a contribution from David Bassett), the molecular origin is indeed different, but in all three cases it results in differences in fold volume or encumbrance, and therefore in unbalanced surface stresses (irrespective of the perpendicular or inclined stem orientation in the lamellae). We also pointed out that single crystals of isotactic poly(1-butene) in Form III formed in solution can be scrolled—which probably is linked with yet another molecular origin (Fig. 2). These crystals coexist with 'conventional', flat or pyramid shaped Form II single crystals, which indicates that surface stresses may be produced even under very 'mild' crystallization conditions.

In a more general context, one may wonder what is the safest indicator of unbalanced surface stresses in polymer crystals—especially when they are weak, and therefore difficult to point out. Absence of the ringed pattern in spherulites is not a sufficient criterion to rule out twisting. The ringed pattern is associated with cooperative and in phase twisting. Ryshenkow [7] has established that a sharp transition from ringed to non-ringed spherulitic growth in selenium is associated with loss of cooperativity (in the case of selenium, of branching, and not of twist). In polymers, absence of cooperativity becomes likely for long twist periods and reduced density of 'leading' lamellae at the growth front,

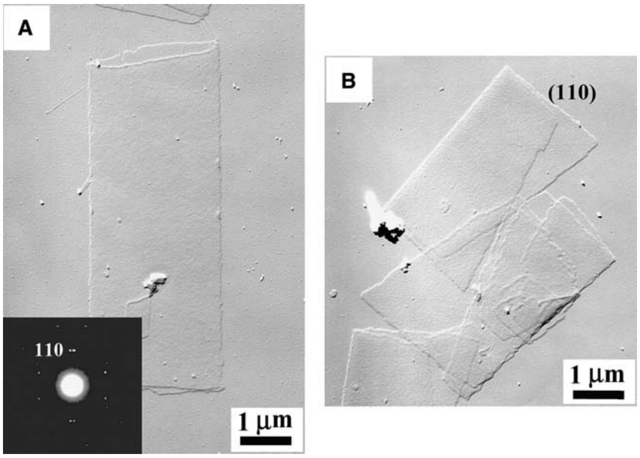

Fig. 2. (a) TEM bright image of a scrolled iPBu-1 Form-III single crystal collapsed after deposition onto carbon film. The insert is a selected area electron diffraction pattern of the crystal. (b) TEM bright field image of iPBu-1 Form-III single crystals showing the initial stage of scrolling.

which is associated with high temperature growth. Similarly, topological constraints may hide an inherent tendency to twist. In this respect, growth of highly packed lamellae with different (opposite) stem inclinations (and thus opposite twist sense) may result in growth of ‘flat’ lamellae, in which the tendency to twist is counterbalanced by neighbors.

It appears that the safest test to establish the existence of surface stresses is observation of individual lamellae, if possible in their ‘pristine’ environment. This approach was pioneered by David Bassett in his investigation of the internal structure of polymers using the etching technique—in combination with deep quench after partial crystallization, to ‘freeze in’ original lamellar morphologies. It was indeed this technique that revealed the S and C shaped lamellae that demonstrate unbalanced surface stresses under ‘normal’ growth conditions.

Several examples of individual twisted crystals (examined after growth is completed) have been described in our contribution [2]: silk fibroin, the achiral polyester, high M_w polyethylene produced from a gel.

A more recent evolution of this approach relies on hot stage atomic force microscopy, and makes it possible to investigate the lamellar morphology while it is growing. Lamellae of poly(ε-caprolactone)—a polymer that, unlike many other polyesters, was not known to form ringed spherulites—have been shown to grow in a twisted way.

Growth of lamellae on edge that become bent (as recalled in our Fig. 6) [2] is also a very telling indicator. Although growth of polymer lamellae in thin films is artificial in many ways, it is ideally suited to reveal the existence of surface stresses (or at least the longitudinal component of surface stresses, not the transverse one)—and even of weak stresses, since the lamellae develop over micrometers or tens of micrometers. When such half-lamellae are bent, this is a direct (and in our view, an undisputable) indicator of the existence of unbalanced longitudinal surface stresses, i.e. of an essential ingredient at the origin of lamellar twist.

Observations by a growing number of laboratories confirm the formation of bent half lamellae under a variety of circumstances, and therefore of the widespread existence of longitudinal stresses. This applies for a range of temperatures: we note that the bent half crystals of polyethylene shown in our Fig. 6 were obtained at very high temperature—135 °C—which would be well in Regime I for the linear polyethylene used (SClair) [2]. This observation suggests that surface stresses are still present and active at such high temperatures, although they may be too weak to manifest themselves in the form of banded spherulites.

The in situ growth of edge-on polyethylene crystals followed with high temperature AFM by Hobbs et al. is equally informative [8]. These authors show in real time that some (but not all) crystals are bent and that bent crystals grow faster than the ‘straight’ ones. The origin of this difference is not yet established, but the very fact that some crystals are bent indicates unbalanced surface stresses—and therefore, possibly, inclined chains after reorganization. By implication, in the straight crystals, the surface stresses must be balanced, which would be compatible with ‘perpendicular’ orientation (prior to reorganization) as observed by Bassett.

Bent crystals have also been reported in thin films of poly(L-lactic acid) (PLLA) [9], a chiral polymer. More recently, they were observed in thin films of poly(ε-caprolactone) (PCL) [10]. The latter crystals are remarkable in the sense that they display very long bent crystals that occasionally (but only occasionally) switch from one sense of bending to the opposite (Fig. 3)—which would be compatible with reversal of the sense of inclination, and, therefore, fully compatible with a reorganization starting from an initial perpendicular stem orientation.

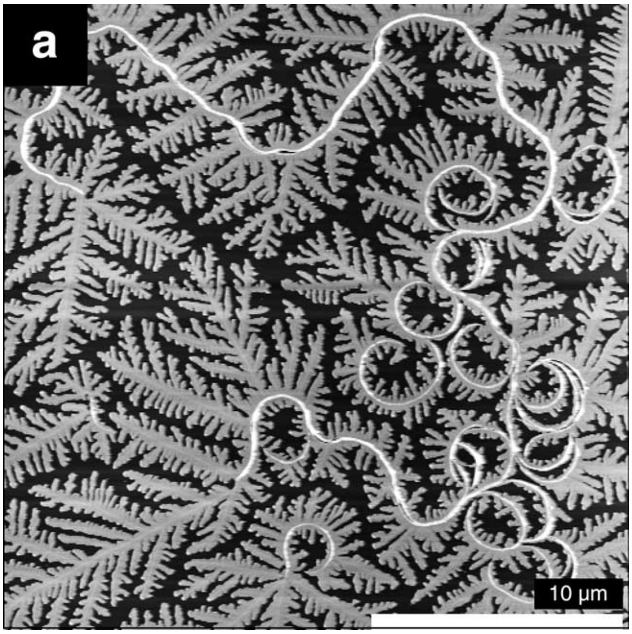

Fig. 3. Bent crystals of PCL produced upon crystallization of a 6 nm thick film of poly(ε-caprolactone). Bent crystals are lighter, dendritic growth of flat-on crystals has a darker shade of grey. Courtesy V. Mareau and R.H. Prud’homme [10].

Finally, direct observation of three-dimensional, twisted lamellae as they are growing has been reported recently [11], and incorporated in our contribution [2] as a note added in proof. As indicated in this paper, several phenomena could be followed, that add new elements to the scenario of lamellar development. The authors observed 'twisting, bending, backward growth, branching, … interaction between leading and trailing lamellae that contributes to cooperative stacking of the twisting lamellae' [11]. The distinctive feature of tapping mode AFM is that it 'feels' individual structural elements that develop within a liquid (here melt) environment. Combined with high-temperature hot stages and real time observation, this technique has become a privileged investigation tool when dealing with polymer crystal growth. Beyond the technical challenges raised by the collection of undisputable experimental evidence, analyzing the molecular origin of unbalanced surface stresses remains, however, the major challenge to reach a true understanding of complex polymer morphologies.

4. Conclusion

The comments of Bassett are welcome additions to our contribution on the role of unbalanced surface stresses in inducing twisted and scrolled lamellar morphologies. They have the merit to raise further issues that were barely covered in our initial presentation. They rightly emphasize the fact that 'surface stresses leading to twist can occur for different reasons'—and Bassett points out two of them in the case of polyethylene.

We have taken the opportunity of the forum initiated by David Bassett to point out further difficulties that must be overcome when analyzing surface stresses in polymer lamellae.

Establishing the existence of the unbalanced stresses cannot rely exclusively on the observation of ringed spherulites. Weaker imbalances that do not result in such ringed spherulites may be at play. They are, in our view, best revealed by the growth pattern of individual lamellae: C or S shaped individual lamellae, twisting (or scrolling) of whole lamellae, or bending of half lamellae growing on edge. Taking into account these more elusive manifestations may indicate that structural asymmetries of lamellae may be found over a wider range of molecular parameters (M_w, chemical structure, etc.) and crystal growth conditions (temperature, concentration, etc.) than suggested by the mere formation of banded spherulites.

Establishing the sequence of molecular processes that lead to the unbalanced surface stresses is an even more challenging undertaking. The experimental prowess and insightful contributions of David Bassett in this domain illustrate the practical challenges that need to be overcome in order to approach them.

Establishing the molecular origin of the unbalanced surface stresses remains the major intellectual challenge in this process. K and P suggested one possible means to generate such an imbalance that, if later found to be questionable in its detailed mechanism (the sequence of molecular events just mentioned) is nevertheless correct in its basic assumption: the formation of non-symmetrical fold surfaces. Later analyses, so far more successful for scrolled lamellae, also showed that many different processes and sources of fold surface imbalance are likely to exist. Since the essential ingredients of twisting and scrolling are now reasonably well established, the future challenges lie in the molecular analysis of these surface stresses.

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References

[1] Bassett DC. Polymer 2006;47. doi:10.1016/j.polymer.2005.11.089
[2] Lotz B, Cheng SZD. Polymer 2005;46:577.
[3] Abo el Maaty MI, Bassett DC. Polymer 2001;42:4957.
[4] Keith HD, Padden Jr FP. Polymer 1984;25:28.
[5] Keith HD, Padden Jr FP. Macromolecules 1996;29:7776.
[6] Abo el Maaty MI, Bassett DC. Polymer 2002;43:6541.
[7] Ryshenkow, Thesis, University of Paris 1985.
[8] Hobbs JK, Humphris ADL, Miles MJ. Macromolecules 2001;34:5508.
[9] Kikkawa Y, Abe H, Fujita M, Iwata T, Inoue Y, Doi Y. Macromol Chem Phys 2003;204:1822.
[10] Mareau VH, Prud'homme RE. Polymer 2005;46:7255.
[11] Xu J, Guo B-H, Zhang Z-M, Zhou J-J, Jiang Y, Yan S-K, et al. Bull Am Phys Soc 2004;49:954 [Paper 297]. Xu J, Guo B-H, Zhang Z-M, Zhou J-J, Jiang Y, Yan S-K, et al. Macromolecules 2004;37:4118.