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A critical assessment of unbalanced surface stresses: Some complementary considerations

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Abstract

The wide-ranging survey of twisted growth in polymers by Lotz and Cheng cites extensive evidence consistent with the relief of surface stress being the underlying cause. This complementary note contributes to the discussion by making three main points. First, it is necessary to go further and explain the key issue of how a consistent twist is maintained when, as commonly, this habit has a lower symmetry than the crystallographic lattice. Detailed study has shown that, in polyethylene, this occurs by reorganization of the initial fold surfaces. Second, the suggested explanation by Keith and Padden that, in polyethylene, the asymmetric habit derives from molecules adding to lamellae with inclined fold surfaces is invalid being doubly inconsistent with observation. Third, twisting has now been linked to faster growth by study of row structures in polyethylene. This produces inherently rough fold surfaces in Régime II whose internal stresses drive reorganization and twisting. For slower (Régime I) growth, fold surfaces form with and maintain ordered packing so providing no basis for twisting. These new insights radically alter the context of twisted growth and provide a firm factual basis for further work.

Keywords: Lamellar twisting; Fold-surface re-organization; Isothermal thickening

1. Introduction

Lotz and Cheng [1] have recently published a valuable survey of twisting growth in polymers pointing out that a wealth of evidence is consistent with an origin in the relief of surface stress. The purpose of this note is to widen the context in which this intriguing topic is presented by drawing attention to some additional, complementary, considerations. It points out, first, that the key issue, which has long delayed understanding of twisted growth is how a consistent twist is created, in e.g. polyethylene, with a lower symmetry than the crystal lattice. While the relief of surface stress has always been a strong candidate for the prime cause, its attribution still leaves this key problem unsolved.

The second point is that for polyethylene it has now been shown how the twist develops as a monolayer reorganizes its fold surfaces to increase the separation of folds, with isothermal lamellar thickening, developing an S-profile [2]. It is then propagated with consistent hand into daughter lamellae via isochiral screw dislocations. The earlier suggestion of Keith and Padden [3] that twisting in polyethylene is related to differential stresses in opposite fold surfaces assuming molecules add to lamellae with {201} surfaces has been shown to be invalid in part because in reality the fold surface is {001} at the growth front. This proposal also had difficulty in explaining why, in polyethylene, twisted growth is restricted to Régime II.

Research monitoring the inclination of molecules to the fold surface throughout the growth of polyethylene row structures has now clarified this matter [4]. The reason is that growth is so rapid in Régime II that fold surfaces have perforce to form rough {001} surfaces with poorly-packed folds creating stresses which twisting helps relieve. In Régime I, on the other hand, the slower growth rate allows fold surface to organize their packing before the next molecular layer adds to the growth front. Accordingly fold surfaces form as, and remain, {201} thereby providing no basis for twisting. This is the third point and a new scenario for twisted growth. The basic cause is the inherently rough, stressed, fold surfaces created when fold stems crystallize rapidly. Slow growth, on the other hand, allows fold surfaces to order as they form giving no surface stress for twisting to alleviate. This is a powerful new insight on which to base future work.

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2. Discussion

2.1. Banded growth in linear polyethylene

Polyethylene is arguably the most important system on which to study the origin of co-operative twisting or banding partly because this is the archetypal flexible linear macromolecule, displaying basic patterns of behaviour, and partly because the relevant morphological information is particularly complete thereby reducing speculative interpretation. Banding does not occur for all crystallization temperatures but is characteristic of Régime II and its faster growth; the slower growth of Régime I is untwisted [5].

When it became possible to examine lamellar morphologies systematically this distinction was found to correspond to a difference of fold surface, and accompanying profile, of dominant lamellae, i.e. those which establish the skeletal geometry of a spherulite [6]. In Régime I fold surfaces are {201} with chains inclined to lamellar normals at $\sim 35°$. Such lamellae and fold surfaces we term inclined. For Régime II and banded growth, the profile of dominant lamellae viewed down the growth direction, *b*, is S-shaped (or C-shaped of half the width) in which fold surfaces change their inclination to the chain axis, *c*, continuously in the range $\pm\sim 35°$. Moreover, the sense of the S is uniquely correlated with the hand of the twist [6]. Evidently the origin of the S-profile is central to that of twisting or banded growth.

The explanation offered by Keith and Padden [3] for the generation of the S-profile and repeated by Lotz and Cheng [1] is that if, in Régime II as in Régime I, molecules add to lamellae with inclined, {201}, fold surfaces, there will be an inherent asymmetry between opposed fold surfaces, one making an acute, the other an obtuse angle with the chain axis. Keith and Padden supposed that this led, via differences in fold congestion, to a twisting stress and thence to banding and the S-profile. As discussed below, in Régime II molecules do not add to lamellae with {201} surfaces and the supposed asymmetry does not exist [4]. It does exist in Régime I and then leads to the development of an arrow-shaped lamellar habit, of lower symmetry than the lattice, but no twisting [7].

In the meantime it has been shown how the S-profile actually develops by the re-organization of initially rough {001} fold surfaces towards the preferred {201} condition. Individual lamellae, growing in Régime II, start to develop their S-profile when inclined fold surfaces form in the central, older, part [2]. In so doing, the axis normal to the S cross-section forms not along *b* but inclined, by $\sim 20°$, to this, i.e. the S-profiled habit, unlike the crystal structure, does not have twofold symmetry around the *b* axis. This, phenomenologically, is how the asymmetric habit is introduced into the orthorhombic structure; it is then propagated by new lamellae, of the same hand, generated at a sequence of isochiral screw dislocations. The asymmetry itself is consistent with, and presumably relates to, the disordered placement of folds. This will largely survive a change to inclined packing but does not require the reorganized fold surface to adopt the crystallographic symmetry of stem packing.

Direct confirmation of the role of fold surface re-organization has come from observing the inclination of fold surfaces to the chain axis from the start of growth through to the interface with the melt. This is possible using linear nucleation in which polyethylene lamellae grow epitaxially on a high-melting polyethylene fibre to form a row structure and monitoring the inclination at different distances from the fibre surface. There is a clear distinction between growth in Régimes I and II [4]. For the former, lamella nucleate at $\pm\sim 35°$ to the fibre axis and retain {201} fold surfaces throughout. Banded growth, on the other hand, starts with thin lamellae nucleating perpendicular to the fibre, i.e. with {001} fold surfaces. These, which we term perpendicular lamellae, then separate, with some failing to propagate, and thicken isothermally with dominant lamellae developing S-profiles. At the growth front, however, molecules continue to add to lamellae with {001} surfaces. It follows that re-organization of initial {001} fold surfaces, which will be rough to increase fold separations, is the origin of banded growth in polyethylene.

2.2. Re-organization and surface stress

The central role of fold surface re-organization underlines a basic principle of polymeric crystallization namely that, for rapid crystallization, surface organization is secondary to the deposition of stems. It is always possible to offset the free-energy penalty of a poorly-packed surface by crystallizing longer stems in a thicker lamella. But such a surface is metastable with respect to improved packing, which will be explored by the mobile molecules over time. For polyethylene improvement means adjustment towards the preferred {201} fold surfaces in which folds are further apart. The same explanation fits the observation of banded spherulites in quenched, integrally-folded, monodisperse *n*-alkanes [8] which presumably then form with rough basal surfaces which, over time, will convert to {201} but will have contributed to the formation of spherulites as opposed to the parallel lamellar stacks of slower, extended-chain growth.

In thermodynamic terms a twist by itself will increase the free energy of the system and will only occur if it is more than offset by a reduction from lowered surface stress, i.e. improved surface packing: the higher the initial surface stress the greater the possible twist. Two considerations follow: the difference between systems, which do and do not have inclined lamellae and the variations in surface stress within a system in relation to its growth rate. On the first point, if a system increases fold separation by adopting inclined lamellae as in polyethylene surface stress due to fold congestion is evidently more of a factor than when lamellae are always perpendicular as in isotactic polypropylene. Nevertheless, twisting is not ruled out in such cases but will depend upon the initial level of surface stress, which will depend, in turn, upon the openness of the crystal structure, specifically the cross-sectional area per fold stem, and the growth rate.

The growth rate is a major factor in all cases in that surface packing will improve for slower growth rates as molecules have more time to explore alternative conformations, in conjunction with isothermal lamellar thickening, before the next layer is added to the interface. This accords with experience in that the twist period is less for faster growth.

For polyethylene, crystallization in Régime II gives fold surfaces, which, initially, are {001}. They will be rough, to increase the local separation of folds, and correspondingly stressed. As has been documented for individual lamellae [2] and lamellar assemblies in row structures [4], the molecular mobility associated with isothermal lamellar thickening produces inclined surfaces in central regions, which, with the constraint of lamellar continuity, gives a region with an S-profile. Regions to front and rear will experience a twisting stress to extend the S-profile along its perpendicular axis which, being inclined to *b*, will generate a sequence of isochiral screw dislocations [2]. At each of these, new lamellae, with the same sense of twist, are inserted. The local compliance will be greatly increased when the lamella dislocates and the azimuth of the new lamella inserted much rotated accordingly, as in Figs. 3b, 4 and 5a of Ref. [2], to give what Lotz and Cheng [1] have termed a 'quantum of twist'. The twist is thus inserted mainly at screw dislocations but these are not, pace Lotz and Cheng [1] (p. 589), the major cause of twist and banding.

The {001} fold surfaces of perpendicular lamellae, unlike the fold surfaces of as-grown inclined lamellae, will not have inherently different fold congestion as considered by Keith and Padden [3]. While they will have different fold positions, they will be statistically equivalent. No doubt the initial differences in the arrangement of folds in opposed {001} surfaces will have some influence on the nucleation of regions of inclined packing within them but whether it will be a controlling one is difficult to judge a priori. Once such inclined regions have nucleated they determine the sense of twist and, via screw dislocations, its propagation.

2.3. Isothermal thickening and time-dependent changes

The influence of isothermal lamellar thickening, characteristic of melt crystallization, will be to tend to reduce surface free energies and stresses. Changes of fold configuration and inter-fold separation over time are probable with, possibly, some change of fold position and/or removal with the necessary incorporation of new material to maintain lateral dimensions. Even for Régime I, surface conditions may not remain as first laid down in the linear polymer. For linear-low-density polyethylene there is the additional factor of excluded comonomer units which, with isothermal thickening, leads to twisting in Régime I [9].

Here crystallization begins with {201} fold surfaces and no twisting. There will be a degree of fractional crystallization in which only those molecular sequences with a sufficient distance between adjacent comonomer units will be able to crystallize. However, isothermal thickening will bring these into, and so stress, fold surfaces. Twisting is observed to develop when lamellae have thickened but more weakly than in Régime II causing a greater band period and a discontinuous increase of gradient in a plot of band period against crystallization temperature [9]. The surface stresses leading to twisting are not those due to adding molecules to an inclined lamella [3] but will be spread across the fold surfaces according to how and where the excluded comonomer units have been brought into the surface.

2.4. The Keith–Padden proposal

The mechanism for twisting and banded growth proposed by Keith and Padden [3] is specific to polyethylene and assumes that in Régime II molecules add to lamellae with inclined fold surfaces. Experiment shows that this proposal is invalid for two reasons. First, it is not the case that, in Régime II, molecules add to inclined lamellae; on the contrary, the fold surfaces are {001} where molecules add to lamellae. The proposal, therefore, has no basis for polyethylene, the archetypal flexible linear polymer and is, therefore, unlikely to apply elsewhere.

Second, in linear-low-density polyethylene, twisting does occur in Régime I when molecules add to inclined lamellae as was assumed. Nevertheless, this does not occur for the reason suggested. This follows because it does not occur initially but only when lamellae have thickened (making them more resistant to deformation). An additional surface stress is then present, due to excluded branches being brought into fold surface regions [9]. The stresses produced simply by adding molecules to inclined lamellae are insufficient by themselves, otherwise they would have caused twisting at the original, more compliant, lamellar thickness. Note also that the thickness of lamellae which twist in the linear-low-density polymer will be less than those which do not twist in Régime I for linear polyethylene; thickness is not, therefore, a controlling factor in whether twisting occurs.

The many examples where the relief of surface stress is implicated in twisted growth [1] require explanations other than the invalid Keith–Padden hypothesis. A principal candidate, given its established role in polyethylene, is the re-organization of initially rough fold surfaces created by faster growth.

3. Conclusions

1. The prime cause of twisted growth in polyethylene is the re-organization of the initial {001} fold surfaces to a less-congested state.
2. An additional cause, for the linear-low-density polymer, is bringing excluded branches into, and thereby stressing, fold surface regions.
3. The Keith–Padden proposal that addition of molecules to inclined lamellae causes twisting in polyethylene is invalid, being doubly inconsistent with experiment.
4. Twisting is linked to the faster growth of Régime II because this produces inherently rough fold surfaces whose internal stresses drive reorganization and twisting. For slower (Régime I) growth, fold surfaces form with and maintain ordered packing so providing no basis for twisting.

References

[1] Lotz B, Cheng SZD. Polymer 2005;46:577.

[2] Patel D, Bassett DC. Polymer 2002;43:3795.

[3] (a) Keith HD, Padden FJ. Polymer 1984;25:8.
(b) Keith HD, Padden FJ. Macromolecules 1996;29:7776.

[4] Abo el Maaty MI, Bassett DC. Polymer 2001;42:4957.

[5] Hoffman JD, Frolen LJ, Ross GS, Lauritzen JI. J Res Nat Bur Stand 1975;79:671.

[6] Bassett DC, Hodge AM. Proc R Soc London, Ser A 1981;377:25.

[7] Bassett DC, Olley RH, Al Raheil IAM. Polymer 1988;29:1539.

[8] Bassett DC, Olley RH, Sutton SJ, Vaughan AS. Macromolecules 1996;29:1852.

[9] Abo el Maaty MI, Bassett DC. Polymer 2002;43:6541.