polymer papers

On isolated lamellae of melt-crystallized polyethylene*

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The growth, isolation and examination of individual melt-grown crystals of linear polyethylene is reported. Monolayers grown at 130°C have continuously curved elliptic prism faces (despite being grown under 'regime I' conditions) and fold surfaces close to {2 0 1}. Such monolayers, showing a sector boundary along their length, and distinct sectors differing very slightly in orientation across this boundary, have been revealed in dark-field electron microscopy. This is evidence for regularity in chain folding. A more frequent form is when a central screw dislocation is present near the centre of a lamella. The spiral terrace developing from this shows a remarkable habit in which adjacent layers splay apart, but growth soon stops, leaving the upper and lowermost layers plano-convex in outline. In every case, the planar outline is of a prism face making an acute angle with the previous layer. This is a consequence of growth having only occurred around screw dislocations of the appropriate hand: right-handed for a (2 0 1) surface. It is suggested that this habit, illustrating how spiral development selects screw dislocations of a consistent hand, may be the missing element in understanding the growth of banded spherulites in polyethylenes via systematic arrays of similar screw dislocations.

(Keywords: polyethylene; melt-grown crystals; banded spherulites)

We report here on the successful isolation and initial examination, by electron microscopy, of lamellae of melt-crystallized polyethylene. Three principal points arise. First, the observed curved growth faces are not obviously compatible with the current model of kinetic theories of growth. Secondly, the existence of distinct sectors establishes a degree of regularity in chain folding and strengthens the links with phenomena of solution growth. Thirdly, the asymmetric development around screw dislocations suggests a solution to the long-standing problem of the formation of banded spherulites.

Most, if not all, of the concepts salient to polymer crystallization have been derived from studies of the habits and structure of polymer lamellae (principally polyethylene) grown from dilute solution[1]. In these, the existence of distinct sectors[2], corresponding to different growth surfaces[3] and with systematically distorted lattices[4], confirmed the reality of regular chain folding. Non-planar habits indicated fold shapes and evidence for their interaction[5]. Most important was the demonstration that changing the crystallization temperature altered the thickness of a monolayer at its growing edge[6,7]. The fold length is, therefore, established unequivocally by a secondary process at the growth face, rather than by the primary act of nucleation. Practically all subsequent theories of the fold length and growth rate have been kinetic theories of secondary nucleation at growth faces[1,8].

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Such theories have been carried over to the problems of crystallization from the melt, mainly because of the paucity of direct information on the nature of melt-grown lamellae. It is obvious *a priori* that lamellae grown from the melt would be expected to be less regular, in view of the competition among molecules at growth faces, than when molecules crystallize more or less independently from dilute solution. But it has also been pointed out that the inference of a dichotomy between regularly folded solution-grown lamellae and irregularly folded melt-grown lamellae is not justified when the comparison concerns slowly crystallized solution-grown lamellae on the one hand and lamellae crystallized very rapidly from the melt on the other[9]. In particular, evidence for regularity in folding from solution has come primarily from electron microscopy, as cited above, and in principle one should examine melt-crystallized lamellae in the same way.

It has not previously been possible to achieve this, but many attempts have been made to extrapolate to the melt condition. One may cite studies on growth from concentrated solutions[10] and from solution in n-paraffins (regarded as low-molecular-mass polyethylene)[11]. Notable has been a very careful study of the internal structure of lamellae precipitated at high temperatures from poor solvents[12]. An alternative approach has been to fragment melt-crystallized polyethylene following digestion in nitric acid[13]. Labaig[14] has reported on polyethylene grown in very thin films, including replicas of the free surface. Meanwhile the internal lamellar organization of polyethylene and other polymers has become accessible following the introduction of the

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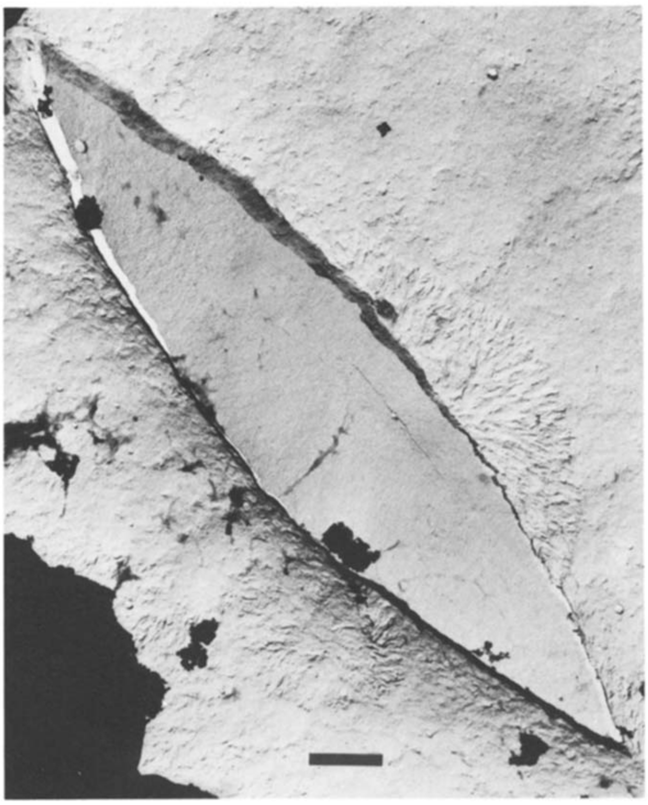

Figure 1 A polyethylene monolayer crystallized at 130°C and revealed by permanganic etching. Bar = 1 μm

technique of permanganic etching prior to electron microscopy[15,16]. The work described here has used permanganic etching coupled with differential dissolution to provide evidence that not only integrates and places previous work in perspective but also provides important new evidence in three main areas.

In this paper we report principally on the crystallization of one polyethylene (Rigidex 140–60, BP Chemicals) whose average molecular mass was measured as $\bar{M}_m = 9.2 \times 10^4$, $\bar{M}_n = 1.4 \times 10^4$, by the PSCC at RAPRA, Shawbury, Shropshire. When a 30 μm thick film was crystallized at 130°C for 23 h and then quenched into freezing isopentane, a variety of isothermally grown lamellar crystals was produced within a matrix of banded spherulites. The largest population (some 70%) was of elliptic monolayers (*Figure 1*) or of similar lamellae associated with a giant screw dislocation (*Figure 2*). The remaining populations consisted of twinned and multilayer habits.

The lamellae of *Figures 1* and *2* have been revealed by permanganic etching, using an agitated solution of 0.7% w/v potassium permanganate in a 2:1 mixture of concentrated sulphuric:orthophosphoric acids at room temperature for 1 h, followed by two-stage replication[15,16]. The photographs are of shadowed carbon replicas of the etched crystals, which tend to stand proud of the surrounding matrix. As lamellae are ablated laterally they have most often, though not always, lost their original growth surfaces. When these are identifiable unambiguously they show, as do the extracted crystals of *Figure 3*, outlines that are continuously curved to the growth tips. We describe this as an elliptic habit.

Elliptic habits of polyethylene lamellae were first reported by Keith[11], who grew them from solution in n-paraffins. The long axis is along *b*, and continuous curvature is the limit of habits possessing two {1 1 0} facets at each tip. Similar shapes were obtained by Labaig[14] in 5 and 0.5 μm thick films. He considered these equivalent to those of Keith although our results suggest that there would have been differences in internal structure. The monolayer of *Figure 1* is planar, as are those of Labaig grown at high temperature. Keith's monolayers, however, showed a linear microstructure

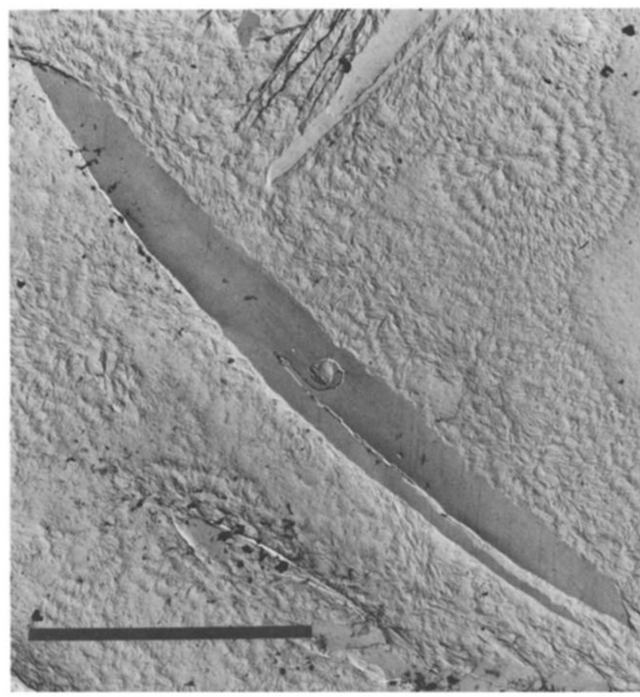

Figure 2 Spiral development around a screw dislocation in polyethylene crystallized at 130°C; replica of a permanganically etched surface. Bar = 10 μm

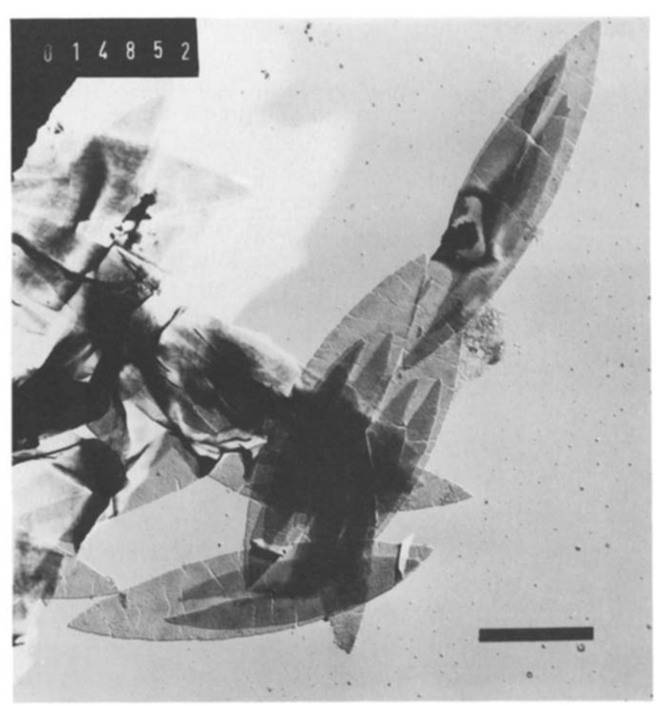

Figure 3 Polyethylene crystals grown at 130°C, extracted from their matrix then redispersed on a carbon film. Note the asymmetric spiral development. Bar = 10 μm

parallel to *b* which he interpreted as due to collapse of a hollow pyramidal structure during specimen preparation[11]. We have not found such fine structure in our lamellae but we do observe two sets of fine lines corresponding to the traces of {1 1 0} planes (barely visible in *Figure 1*) and a fine line dividing the crystal into two along the long axis.

The planarity of monolayers agrees with the observations of Bassett, Hodge and Olley for this molecular mass and crystallization temperature[17]. (We have also reproduced the formation of internally ridged lamellae[18], now seen to be within an elliptic outline, for lower molecular masses and crystallization temperatures[17].) The molecular inclination is also the same. We have determined this, in the first instance, by measuring the projected thickness of a lamella lying in the plane of the specimen. One of the two narrow 'edges' can be seen to have a finite width perpendicular to the long axis (e.g. *Figure 2*). Measurement of this width as a function of the angle of rotation about the long axis gives, with a little trigonometry, a value of θ, the chain inclination *c* to the lamellar normal, of some 35°. Previously a broad distribution for this parameter had been found with an average value[18,19] of $31 \pm 1°$. The fold surfaces are thus, approximately, the familiar {2 0 1}, for which $\theta = 34.4°$*. This is also confirmed by electron diffraction as described below.

Fuller examination of these melt-crystallized lamellae has become possible following the introduction of a method for dissolving the surrounding matrix. This has a lower dissolution temperature because of its lower crystallization temperature and reduced lamellar thickness. In initial experiments (involving also Dr A. S. Vaughan) it proved possible to dissolve the matrix in xylene at 105°C, filter off the residual (isothermally grown) lamellae, then redisperse and transfer them, with a supporting carbon film, to electron microscope grids. Although the external habit was as expected, unfortunately the single-crystal texture had been lost and electron diffraction patterns were rings. A complex surface texture had also been introduced reminiscent of those reported for annealed solution-grown lamellae[6]. Subsequent repetition of this procedure, but using decalin as solvent at 102°C, has, however, proved successful in retaining not only shape but single-crystalline texture. The diffraction pattern for lamellae (as in *Figure 1*) normal to the electron beam is two 0 2 0 spots along the direction of the long axis. Rotation around this axis by 35° in one direction produced the quasi-hexagonal pattern of the *h k* 0 reflections. This confirms that the fold surfaces are near {2 0 1} and *b* is parallel to the long axis. (A slight broadening of the 0 2 0 into narrow arcs is consistent with the curvature of the long axis observed in sedimented lamellae.)

Figure 4 shows complementary dark-field micrographs of a lamella, taken through 2 0 0 and $\bar{2}$ 0 0 spots, respectively. Bright contrast appears in alternate halves of the lamella and, where the sector boundary ridge can be resolved (near the tip), lying on either side of it. Although sector boundary ridges to crystal corners have been seen previously (e.g. in isotactic polystyrene grown at 220°C[21]) this is, so far as we are aware, the first time that distinct sectors have been identified by diffraction contrast in the lamellae of a melt-crystallized polymer.

* At least three papers[13,14,20] report higher values, namely $\theta \simeq 45°$, but in all cases not in the original specimens but in those given prolonged immersion in fuming nitric acid. It may well be, therefore, that there is a systematic difference in chain inclination between these direct and indirect measures. It is known that nitric acid treatment introduces bulky carboxyl groups into fold surfaces which would tend to increase the tilt

At this stage it is convenient to discuss first the elliptic habit and then the implications of sectorization. Curved growth faces imply roughness on the atomic scale, i.e. notches in the language of kinetic theories of polymer crystallization. The crystals we have examined are, however, grown well within regime I whose basic assumption is that growth occurs at well separated notches on otherwise smooth surfaces[1,8]. This would appear to be incompatible with our observations, although recently Hoffman (private communication) has pointed out that curved surfaces, forming part of an ellipse, can develop under regime I growth.

Whilst it has long been known that the enhancement of growth produced by notches can be sufficiently small for them not to grow out (e.g. the maintenance of microsectors in curved solution-grown lamellae[7]), Sadler has recently claimed[22] that the modest effects of enhancement constitute a large quantitative discrepancy with the predictions of mainstream kinetic theories and has proposed an alternative approach, the so-called 'roughness-pinning' model supported by computer simulation[23]. Nevertheless, the complexities of polymer crystallization and especially growth from the melt are such that all models so far proposed are more or less severely approximated. No model, for example, is yet able to give a qualitatively adequate theory of isothermal lamellar thickening, which occurs for melt but not for solution growth[1]. Secondary nucleation theories have had many successes, not least a quantitative description of the changes in kinetics referred to as regime theory[1,8]. Although curved growth faces point to a need for revision, it is not necessarily the case that such theories must be abandoned.

Further experiments with different molecular lengths show that the length/width ratio increases for elliptic lamellae formed from shorter molecules. Conversely for

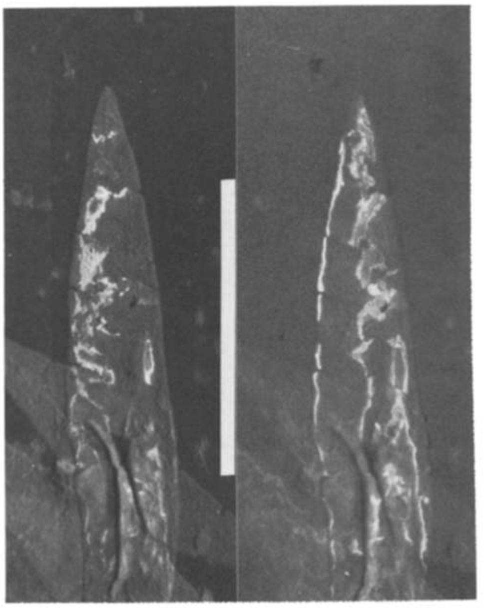

Figure 4 A pair of dark-field micrographs of an extracted polyethylene monolayer taken through the 2 0 0 and $\bar{2}$ 0 0 reflections, respectively, in the same rotated setting. Bar = 10 μm

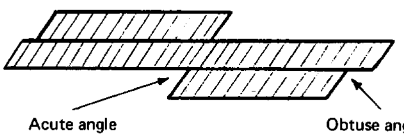

Figure 5 Sketch of the meaning given to acute and obtuse angles in interpreting *Figure 3*. Note that, in practice, because of splaying, successive layers will not always be exactly in contact

molecular mass $\gtrsim 2 \times 10^5$ the elliptic shape gives way to more or less regular facets including four close to $\{1\,1\,0\}$ meeting at the tips. Indeed very small $\{1\,1\,0\}$ facets are visible on the upper layer in *Figure 3*. These reinforce the point that there is no large effect on growth rate whether there are notches or not.

The contrast in *Figure 4* implies that there is a slight difference of orientation of $\{2\,0\,0\}$ planes across the sector boundary in a sedimented crystal. No such effect would be anticipated in the absence of preferred fold shapes. This is evidence that folds tend to have symmetrically opposed shapes across the sector boundary. The same type of symmetry relation between fold shapes would exist for adjacent facets in ridged lamellae with alternating $\{2\,0\,1\}$ facets formed at 130°C by polyethylene of $\simeq 3 \times 10^4$ mass[18,19]. Adjacent sectors in solution-grown lamellae have been shown to have symmetrically related lattice distortions in the plane transverse to the chain axis[4,24]. The measurements so far made would not reveal this, but there is indirect evidence in *Figure 3* that it probably exists. This is found in the cracks, generally along $\langle 1\,1\,0 \rangle$, at the edges of lamellae (bridged by fine threads) which suggest that the lamella was slightly dished, in the way familiar for solution-crystallized lamellae[1] and previously found for melt-grown isotactic polystyrene[21]. We thus have firm evidence for a degree of ordering of chain folds in polymeric crystallization from the melt.

Finally we consider the remarkable development of lamellae seen in *Figure 3*. It is evident that this is asymmetric and arrow-shaped, giving each crystal a directionality that is not present in the orthorhombic lattice or in a monolayer as in *Figure 1*. Further examination of the darker layers in *Figure 3*, which are the upper and lower layers of a spiral terrace, shows that they have stopped growing at one side, leaving a straight edge. In every case inspected at high magnification, it has been found that when growth has stopped the growth face makes an acute angle with the underlying lamella; see *Figure 5*. (This can be ascertained from which side of a lamella the projected growth surface can be resolved.) The reason for cessation is probably due to some kind of impingement on the underlying layer, i.e. a geometrical constraint due to proximity, bearing in mind that, as shown in *Figure 2*, adjacent layers are not in overall contact but are seen to be splaying slightly apart at their edges. Such elongated layers would, therefore, be expected to meet along a central line approximately parallel to their long axes as is observed. The evidence is that growth can continue beyond impingement, i.e. the spiral will develop, when the angle between the growth face and the underlying lamella is obtuse but not when it is acute (*Figure 5*). This implies that only one of the two possible spiral terraces can develop, i.e. that one which exposes growth faces making the obtuse rather than the acute angle to the layer over which growth must proceed.

Spiral terraces have only been observed around right-handed screw dislocations for (2 0 1) fold surfaces and left-handed for $(2\,0\,\bar{1})$ surfaces, a right-hand screw being one which advances the helix for a clockwise rotation. The consistently asymmetric development shown in *Figure 3* lends itself to an outline explanation for the long-standing problem of the formation of banded spherulites. There are essentially two issues, namely (i) what is the lamellar morphology in banded spherulites that requires explanation and (ii) how does it form? The old view, following from the knowledge of the continuously spiralling average molecular orientation about the radius, was that one had continuously twisted lamellae[1,25]. This is not the case, certainly for polyethylene, nor for α-poly(vinylidene fluoride). Indeed it is questionable whether lamellae can adequately be regarded as simply being laths extended along the radius. Bassett and Hodge[26,27] showed that banded spherulites of polyethylene were built on a framework of dominant lamellae whose profile viewed down the radius (*b*) was S- (or C-) shaped. There was a consistent sense of chain tilt in neighbouring lamellae with individual dominants being essentially untwisted for radial lengths $\approx 1/3$ of the band period[26]. Changes of orientation and progression of the average twist occurred sharply around what, topographically, were screw dislocations of consistent sign but apparently developing only two or three layers of a spiral terrace[27]. Moreover, the sign of these dislocations is the same as in *Figure 3*. Subsequently, Keith and Padden[28] proposed a common origin for S-profiles and continuously twisting lamellae. This lay in bending moments supposed to arise from different allowed shapes of folds adding to opposite edges of growth faces inclined to lamellar normals. No direct evidence exists as to whether or not any such bending moments are substantial. We note that they would be predicted to be maximized for the lamellae of this paper for which growth is slow and growth faces are indeed inclined to lamellae normals. Yet these lamellae are substantially flat (*Figures 1* and *2*) rather than S-shaped. In our view the explanation for banded spherulites lies elsewhere. For example. S-profiled lamellae are not necessarily associated with banded spherulites. Lamellae in banded spherulites of α-poly(vinylidene fluoride) are flat; cf. figure 5 of ref. 29. Conversely in unpublished work in this laboratory S-profiled lamellae have been found in γ-poly(vinylidene fluoride), in which chains are inclined to lamellar normals, but spherulites are unbanded.

What we now propose is an outline mechanism for banding of polyethylene spherulites in which screw dislocations play a central role. This starts from the observations cited above whereby increments of twist occurred successively about screw dislocations of the same sign displaced along a radius. What *Figure 3* supplies is a demonstration of a mechanism of self-selection of dislocations of consistent sign: right-handed for a (2 0 1) fold surface. This is the same sign as found previously in banded spherulites although not then stated in this way. Moreover, the relation of twist to growth direction, previously expressed as that in which the concave surfaces of an S would tend to rotate so as to scoop up the melt when travelling along a radius[27], links the growth direction to the sign of the dislocation. If we apply the same rule to the crystals of *Figure 3* and consider how similar crystals would be arranged along a spherulitic radius, we infer that the incomplete terraces would be towards the outside. This would also place three layers on the outside and two on the inside, in a manner appropriate to a branch point.

In practice dislocations occur repetitively along a radial lamella, thereby creating what has been previously described as a multiply connected morphology[27]. Our proposal can readily account for this in terms of a relaxation of the impingement constraints with increasing radial distance from the dislocation. Splaying of adjacent lamellae will eventually release any geometrical constraint to growth and allow a further spiral turn to develop, but displaced down the radius; and so on. We do not here make any specific comment on why lamellar normals diverge so rapidly around screw dislocations, but it has been clearly observed. However, we do note that there would have been a modest 'twist', i.e. a deviation of the normals of the upper and lower portions of crystals in *Figure 3* with respect to their basal layer. This would arise from splaying apart of lamellae linked at their centres and is directly visible in *Figure 2*.

Splaying of lamellae, especially dominant lamellae, is a familiar phenomenon of polymer morphology. The resulting divergence of orientation contributes very significantly to the development of three-dimensional, ultimately radial, growth in spherulites. It has been suggested that it is a consequence of pressure of uncryatallized cilia between lamellae[30,32]. With further evidence to hand, namely similar splaying angles for melt-crystallized polyethylene lamellae differing by one order of magnitude in thickness, there is possibly also an argument in the statistics of the geometry of approach of coiled molecules to the growth face. Be that as it may, what we are suggesting is that, from previous work[27], the morphology of banded spherulites is based on a succession of radially displaced screw dislocations of the same hand. Now *Figure 3* reveals an asymmetric development which could be the way in which the sign of screw dislocations is determined and, by simple extension, propagated along a radius.

The suggestion that arrays of similar screw dislocations could lead to banded spherulites was proposed previously by Schultz and Kinlock[31]. Our proposal differs from theirs. First, the involvement of lamellar splaying greatly accentuates the twist and thereby reduces the necessary dislocation density. Secondly, their explanation for the dislocation arrays lies, as is also the case with Keith and Padden[28], in the nature of folding at the surface of one lamella. The effect observed in *Figure 3* concerns instead the interaction between folds in adjacent layers.

In summary, the isolation and examination of isolated melt-grown polyethylene lamellae has led us to make the following conclusions:

(1) Wholly curved growth faces form on lamellae grown well within regime I, a fact not obviously compatible with current kinetic theories.

(2) The existence of distinct sectors implies a degree of regularity in chain folding from the melt.

(3) The asymmetric development around screw dislocations associated with the sense of chain tilt, coupled with the observed splaying apart of dominant lamellae, suggests a mechanism for the development of banded spherulites in polyethylene.

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