

Asymmetries of Habit in Polyethylene Crystals Grown from the Melt

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ABSTRACT: Growth habits have been studied in polyethylene crystallized at relatively high temperatures in thin films of melt supported on substrates (including the case of one crystal growing on top of another). Two notable asymmetries have been found to be general in these highly elongated lamellae when, as is usual, they lie in the plane of the substrate. First, lateral growth is slower on faces which, because of chain tilt, overhang the substrate and form reentrant angles with it. Second, decoration by condensation of polymer vapor reveals that the structure of fold surfaces is different depending upon whether folding occurred at edges of crystals where these fold surfaces made acute or obtuse angles with tilted growth faces (this applies both to exposed fold surfaces and to fold surfaces in contact with substrates). Another asymmetry, also related to chain tilt, is found in some lamellae which grow edge-on to substrates and exhibit pronounced regular curvatures (radii $\sim 5 \mu\text{m}$). These various observations are discussed in relation to twisting orientation in banded spherulites of polyethylene; it is shown that they support a recently proposed interpretation of how axial torques may arise in radially oriented lamellae within these spherulites.

Introduction

Single crystals of linear polyethylene, when grown from dilute solution in poor solvents at fairly high crystallization temperatures corresponding to those at which spherulitic crystallization usually occurs in polyethylene melts, are lenticular in shape.¹⁻³ Unlike the pyramidal or ridged crystals of rhombic or slightly truncated rhombic habit produced by crystallization in xylene at lower temperatures, they are relatively flat. They are highly elongated along crystallographic b axes and in plan view usually appear symmetrical;⁴ their apices terminate at intersecting $\{110\}$ growth faces and lateral growth faces (close to $\{200\}$) are smoothly curved. There is an inherent structural asymmetry, however, in that stems of folded chains throughout a given crystal are similarly inclined with respect to the lamellar normal so that fold surfaces are parallel to $(h01)$ planes; they are usually parallel to (201) , this corresponding to a chain tilt of $\sim 35^\circ$ within (020) planes transverse to the long axis.² Thus, in two important respects—their elongation along b axes and their relatively uniform chain tilts within (020) planes—these solution-grown crystals resemble lamellae commonly found in polyethylene spherulites crystallized from the melt.^{5,6} However, crystals grown in intimate association one with another within such spherulites often exhibit additional features either absent from or much less pronounced in crystals grown from dilute solution. Among these are the occurrence of markedly nonplanar habits (bent cross sections and axial twists)^{6,7} and differences of crystallization rate at opposite $\{200\}$ growth faces (see later). Our purpose in this paper is to report some striking new observations of structural asymmetry in melt-grown lamellae that bear upon likely origins of these features.

Our approach follows closely that employed by Labaig⁸ who provided the first demonstration of lenticular habits in individual polyethylene crystals grown strictly from the melt (as distinct from moderately concentrated solution in paraffinic or other poor solvents). Using phase contrast optical microscopy to observe crystals formed in thin films of polymer, he studied dependence of aspect ratio, i.e., ratio

of dimensions along b and a axes (the latter as projected in planes of lamellae), upon crystallization temperature and molecular weight; he also followed growth until regular habits gave way at later stages of solidification to more complex morphologies partly dependent upon mutual impingements and depletion of melt. By means of electron diffraction he established that fold surfaces of crystals grown at high temperatures (~ 125 – 131°C) on supporting substrates correspond roughly to (301) planes, this implying larger than usual chain tilts of $\sim 45^\circ$. Labaig also observed that some lamellae, which he termed "couronnes" and which branch from lamellae of lenticular shape, exhibit pronounced curvature within their own planes and in a direction related to that of the corresponding chain tilt. In a closer study of polyethylene crystals grown under the conditions of his experiments we have now introduced decoration by polymer vapor to delineate fold domains and to detect variability of structure within fold surfaces.⁹ Several new features have been noted which appear to have direct bearing upon lamellar habits and lamellar organization in spherulites grown from the melt.

Experimental Section

The polymer used throughout was a fraction (NBS SRM 1483, $M_w = 32\,100$, $M_n = 28\,900$) which was deposited from 0.05–0.1% solution on freshly cleaved mica and, after evaporation of solvent, crystallized isothermally under nitrogen at temperatures in the range 125–130 $^\circ\text{C}$. Sufficient time was allowed for crystallization to proceed essentially to its fullest extent before quenching to room temperature. Nevertheless, some lower molecular weight components remained unsolidified until quenching (see, for example, the background in Figures 1 and 2); these did not interfere significantly with recognition of isothermal growth habits. Where applicable, specimens were decorated before shadowing by condensation of short polyethylene molecules produced by chain scission during evaporation of the polymer under vacuum from a hot tungsten filament, as in the technique developed by Wittmann and Lotz.⁹ They were shadowed in all cases at $\tan^{-1}(1/2)$ using Pt/C, then coated with C, and subsequently stripped and mounted on electron microscope grids.

Observations

General Overview. When isothermal crystallization is carried essentially to completion within the range of crystallization temperatures studied, lamellar aggregates show considerable variation in individual detail but little

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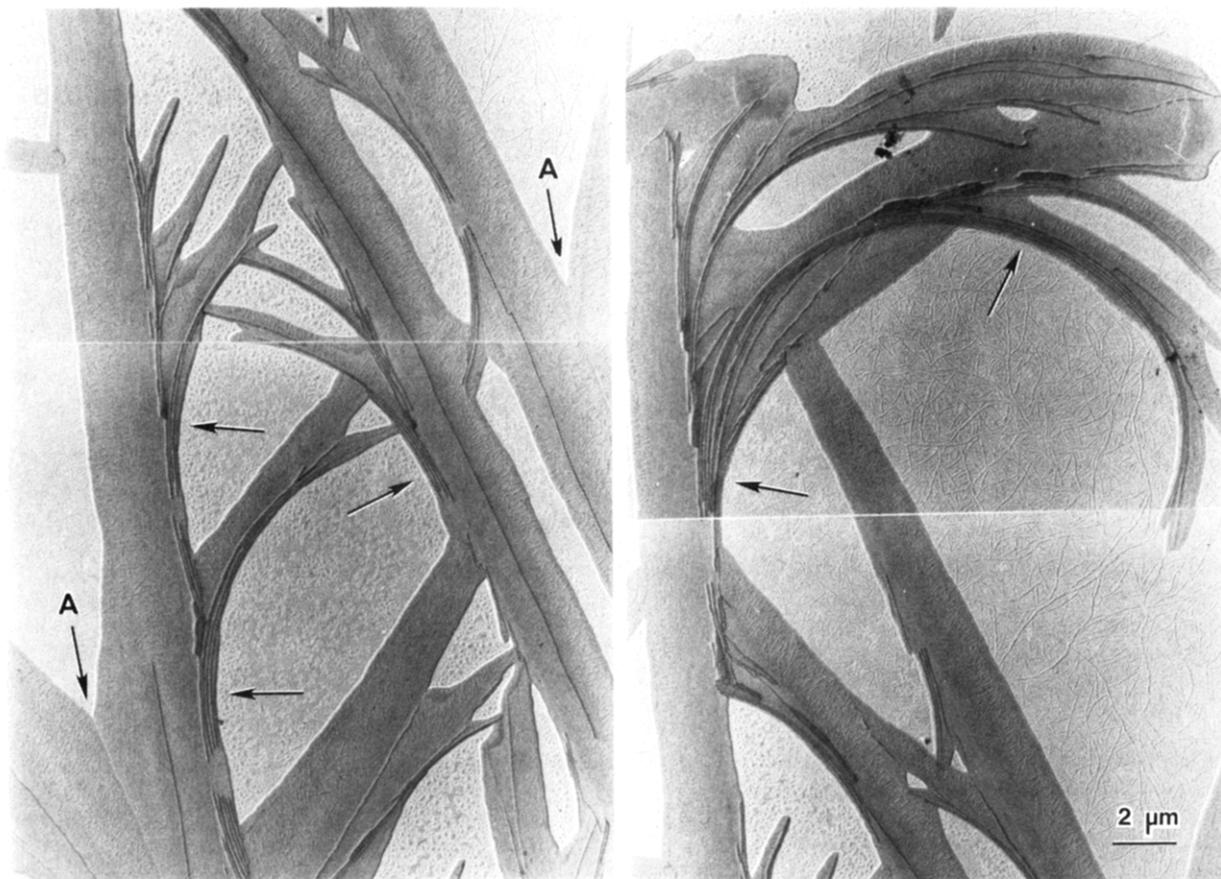


Figure 1. Montage showing a typical cluster of highly elongated crystals after decoration by deposition of polyethylene from the vapor phase. The region at the right is an upward continuation of the field shown at the left. Note the ridges (edge-on lamellae) formed predominantly at one side of each long crystal; many of these are curved and lead the growth of curved flat-on lamellar branches (arrows). Note also the troughs (A) formed between abutting lamellae whose chain tilts diverge (see later in text).

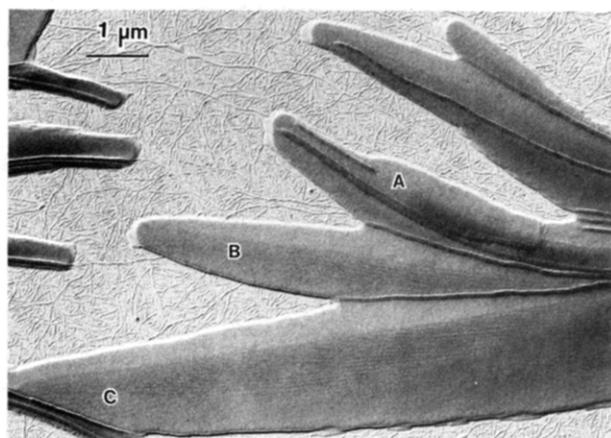


Figure 2. Undecorated crystals showing asymmetry of tip profile, asymmetry of curvature at lateral edges, and striae in the wakes of (110) facets at growth tips.

indication of a systematic trend with crystallization temperature. Their more striking characteristics are evident from Figure 1. Where free to grow without impingement upon neighbors, long bladelike lamellae commonly attain lengths of order $100\ \mu\text{m}$ but are usually limited in width to less than about $5\ \mu\text{m}$. Generally, they are relatively featureless on one slightly curved lateral face but often branch, sometimes profusely, from the other, branches commonly being markedly curved within their own planes as described by Labaig (see later, Figure 4). A prominent feature of the aggregates is occurrence along lamellae of narrow ridges rising to various heights up to about $150\ \text{\AA}$ above their surfaces and mostly concentrated along those

sides at which branching occurs. Many of these have a uniform width of about $650\ \text{\AA}$ throughout their lengths and, as will be seen later, are traces of lamellae in orientations more or less edge-on (though not necessarily orthogonal) to the substrate, these "edge-on" lamellae having intergrown with crystals that lie in the plane of the substrate.¹⁰ In the vicinity of branch sites, edge-on lamellae often curve uniformly away from parent lamellae, sometimes singly but frequently as parallel clusters. Curved "flat-on" branch lamellae are formed in intimate association with curved edge-on lamellae and their growth appears to follow along paths whose curvatures are prescribed by them. Thicknesses of lamellae lying on the substrate, as judged from shadowing, lie in the range $200\text{--}250\ \text{\AA}$ and are considerably closer to thicknesses estimated (with allowance for chain tilt) from initial Raman fold lengths ($l_g - 200\ \text{\AA}$)¹¹ than to values ($\sim 550\ \text{\AA}$) expected of crystals thickened isothermally during long residence at high crystallization temperature.¹² Thickening has apparently been restricted considerably by the presence of a supporting substrate although, as might be expected, this is not the case with edge-on lamellae. Having given this preliminary overview of what is an unusual and fairly involved morphology, we now proceed to an examination of its component elements.

Individual Lamellae. Figure 2 shows several lamellae near their growth tips in an undecorated specimen. Attention is drawn first to the finely textured background between the lamellae and particularly to the small but considerably thinner extensions to their tips, both produced during quenching by rapid crystallization of low molecular weight species which still remained molten after

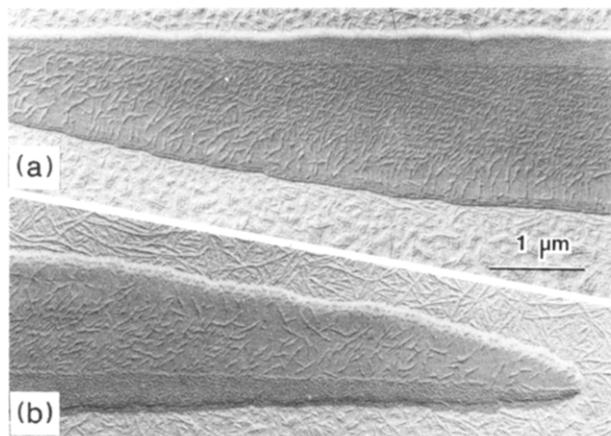


Figure 3. Detail of decoration on two lamellae with growth direction to the left in (a) and to the right in (b) (both at the same magnification). Note the fine scaled decoration on narrow sides bounded by less curved lateral edges and the coarser, rodlike decoration on broad sides bounded by faster-growing, more highly curved lateral edges.

5 days at the nominal crystallization temperature (129 °C). These extensions at growth tips emphasize an asymmetry of tip profile which in some instances, as with lamella A in the figure, can be seen to involve a short "facet" (judged from the angle ($\sim 60^\circ$) made with the b axis to be roughly (110)) on *one* side of the crystal only. Such asymmetries of tip profile, whether or not they involve discernible facets, correlate with differences of curvature at opposite lateral faces, the apices of tips lying on the less curved sides of the lamellae. (As is evident from Figures 1 and 2, branching also occurs on less curved sides and such behavior is found to be general.) Extending back from these apices are longitudinal boundaries (most readily seen when, as in lamellae B and C, they are not partly obscured by ridges) that separate regions where lamellae are either of slightly different thickness or have received different densities of shadowing (or both). Within broader regions faint striae can be seen in the wakes of faceted or generally oblique growth front at tips. Disparity in width between the two regions in each lamella and different curvatures of corresponding lateral faces clearly indicate that lateral growth has been faster on the more curved face bordering the broader region. Inspection of later micrographs will show that, despite local variations in habit often resulting from mutual impingement and/or depletion of melt, similar asymmetry in lateral growth is a common feature of all such lamellae grown in parallel contact with a substrate.

Many of the features just noted are highlighted by decoration, as shown in Figure 3 for lamellae whose lateral growth has been pronouncedly asymmetrical. It will be noted that patterns of decoration are quite different in regions on opposite sides of these lamellae, being fine-grained in narrower regions bordering less curved edges and considerably coarser in broader regions having more highly curved edges. (Although they are analogous to (200) domains in polyethylene crystals of truncated rhombic habit, we shall continue to refer to these as regions or sides of lamellae (sides not to be confused with growth faces); to describe them as fold domains would be inaccurate, particularly in the case of broader sides which appear to involve substantial chain folding of (110) as well as of (200) character.) In broader regions of the crystals there is some alignment of the decoration in rows (slightly convergent upon the b axis) corresponding to striae as in Figure 2 while, near their curved outer faces, rodlike decorating crystals have a character approaching more closely that observed in decoration of (200) fold domains in poly-

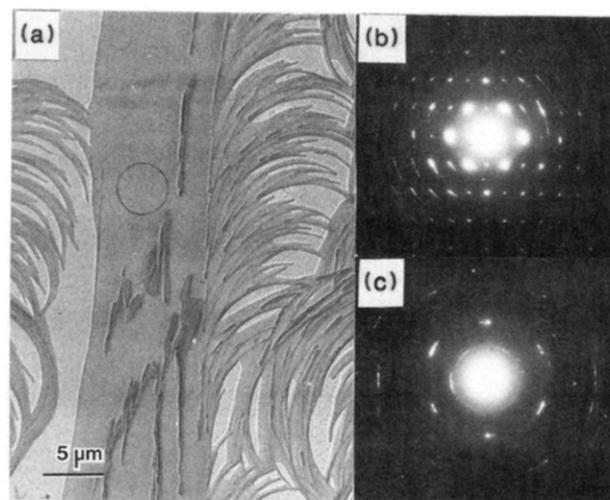


Figure 4. Selected area diffraction patterns from the area shown circled in (a). The pattern in (b), showing a c^* projection of reciprocal space, was taken with the crystal rotated by 45° counterclockwise about its upward facing long axis and (c), showing a corresponding a^* projection, with the crystal rotated 45° clockwise about the same axis. (See Figure 6 for a schematic drawing showing the direction of chain tilt in the crystal.)

ethylene crystals grown from dilute solution.^{9,13} The observed difference in texture of decoration on opposite sides of the crystals indicates a significant difference of structure at corresponding fold surfaces; similar indications are also to be seen in all decorated flat-on lamellae in our later micrographs, as is particularly apparent in regions that are relatively free of ridges.

Asymmetry of lateral growth rate and of structure at exposed upper fold surfaces undoubtedly has its origin in chain tilt. Figure 4 exemplifies a general finding that molecular stems tilt by approximately 45° toward the less curved (200) faces at which branching occurs; this is consistent with Labaig's observation (which we confirm) of similar tilting toward the centers of curved flat-on lamellae. Thus, slower lateral growth occurs on faces (predominantly (200)) that make acute (reentrant) angles with the substrate, and it is on these faces that chain folds on upper fold surfaces are formed in such a way as later to produce dense nucleation of fine decorating crystals.

As a point of obvious interest, lower fold surfaces were also decorated, as follows. Films of polyacrylic acid were cast from aqueous solution on crystallized specimens and, when dry, were detached so as to carry polyethylene crystals with them; the films were then inverted, decorated, shadowed, coated with carbon, and mounted on grids and the polyacrylic acid was removed by dissolution. Representative examples of electron micrographs obtained from such preparations are shown in Figure 5a-c. Broader and narrower regions of crystals are again distinguished by different qualities of decoration. Not unexpectedly, however, decoration patterns are now less regular and boundaries between regions of finer and coarser texture are appreciably less well defined. Nevertheless, it is clear from Figure 5a that broader regions are now decorated very finely and narrower regions much more coarsely, *the reverse of what was seen in decoration of corresponding regions at upper fold surfaces*. Figure 5b shows similar behavior at decorated lower fold surfaces in an area where curved branches begin to diverge from a parent lamella, whereas Figure 5c,d shows essentially similar regions near branch sites as they would have been seen from below (from the substrate) and from above. Thus, even within fold surfaces formed in contact with a substrate there are

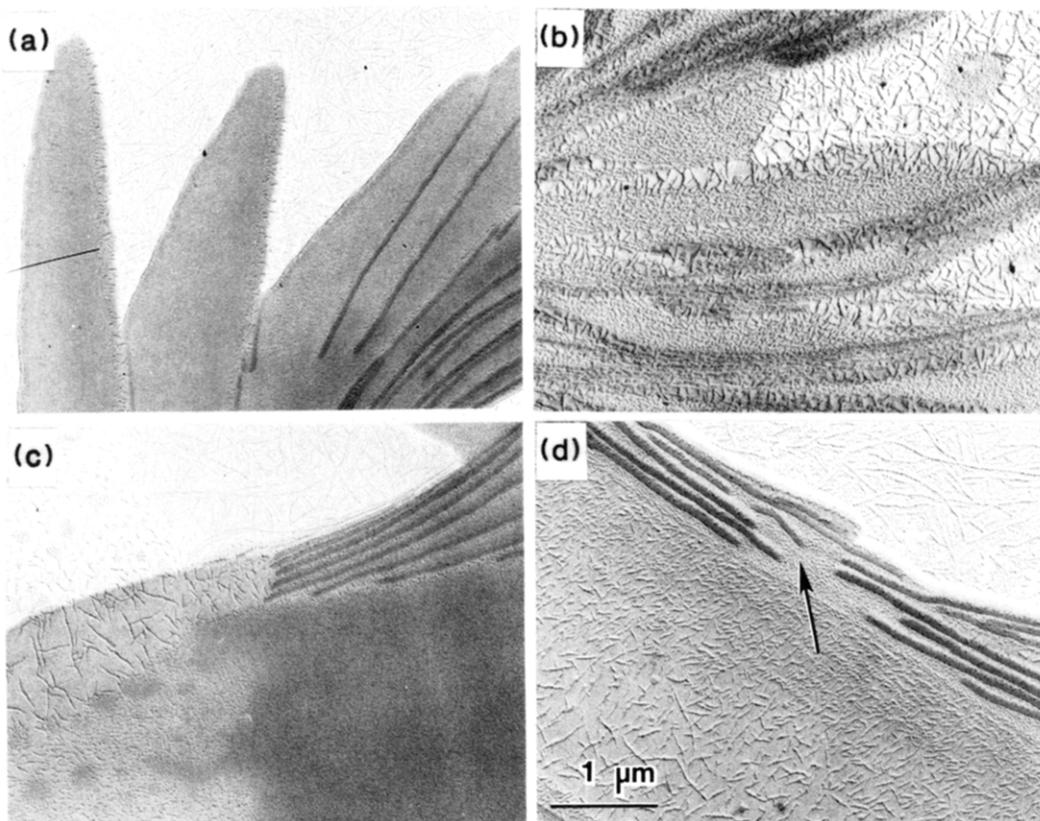


Figure 5. (a)–(c) Decoration of lamellar surfaces originally grown in contact with a substrate; broad sides now show fine scaled decoration and narrow sides show coarse, rodlike decoration. (d) Region on the upper surface of a crystal where curved edge-on lamellae have formed which should be compared with (c), showing a similar region on a lower surface grown in contact with a substrate; note the reversal of coarse and fine decoration. (All at the same magnification.) The arrow in (d) indicates a short edge-on lamella curved toward the parent crystal.

qualitative differences in structure, showing dependence upon chain tilt in respective growth faces similar to that found in the case of upper fold surfaces. While proximity of the substrate may have some influence upon fold structure in our crystals, it is to be emphasized that the dominant influence underlying differences in fold structure as we have observed them is distinction between how folds are formed at acute- and at obtuse-angled edges of tilted growth faces. As will be seen later in our discussion, this is a result of considerable significance. (We have perhaps been fortunate in that our flat-on crystals did not undergo significant isothermal thickening which might otherwise have obscured important differences in fold structure as initially produced during crystal growth.)

Edge-on Lamellae and Curved Growth on Substrates. Reference has already been made to narrow ridges within crystals and to the likely role of some of them in leading the growth of curved flat-on lamellar branches. These ridges appear to be traces of edge-on lamellae (their identification as such will become clear presently) formed at advancing fronts of flat-on crystals (or possibly in some instances where growing crystals abut¹⁴), often to be later engulfed partly or wholly within them. It has been established from dark field images produced by beams diffracted from (020) planes that fast-growing *b* axes in these edge-on lamellae are parallel to long directions lying in the plane of the substrate; as will be seen below, chain axes almost certainly also lie in or close to this plane. The heights to which such lamellae rise above the substrate are therefore limited both by inherently slow upward growth along vertical *a* axes and by depletion of melt within very thin films. Despite its unusually large aspect ratio, however, each edge-on lamella may be regarded as a “half-

crystal” in the sense that it corresponds closely to what would be arrived at by cleaving an extremely elongated lenticular lamella in the (200) plane along its axis, then taking one of the resulting sides (“halves”), and standing it upright with the cleavage face in parallel contact with the substrate. The mode of formation of such edge-on lamellae is not clear. A seemingly simple and direct mechanism would be for a change in the fold plane from (301) to (30 $\bar{1}$) to occur at a growing lateral face of a flat-on crystal; with a chain tilt of $\sim 45^\circ$ this could produce a new lamella standing more or less perpendicularly to the substrate. However, upward growth of such a new lamellae could occur only at more highly curved lateral faces bordering the broad side of a lamella and, curiously enough, this is clearly not where edge-on lamellae are initiated in preponderance. On the contrary, most are formed at lateral edges on narrow sides where growth faces *overhang* the substrate at $\sim 45^\circ$, yet seldom are their planes parallel to these overhanging faces. Surprising as it may seem, those edge-on crystals that curve away from a parent lamella appear to be tilted in the opposite direction, as indicated by a schematic drawing in Figure 6. A clear demonstration of this unusual circumstance is provided by the stereopair shown as Figure 7. These micrographs were taken by using exceptionally large tilts of $\pm 20^\circ$ to accentuate depth perception and, apart from what stands out under a stereoscope, coarse decoration on the exposed face of the outer edge-on lamella (more easily seen without stereoscopy in the enlargement of the left-hand micrograph) is also consistent with this crystal being inclined toward rather than away from the parent lamella and having chain axes more or less in the plane of the substrate. On the other hand, edge-on lamellae that are not markedly curved, or occa-

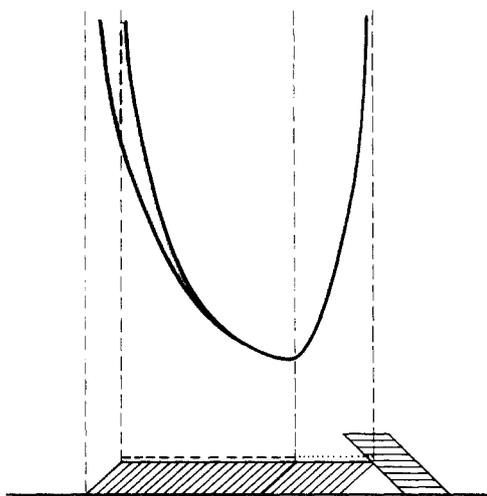


Figure 6. Schematic plan and elevation drawing of a typical lamella illustrating direction of chain tilt and associated asymmetries of lateral growth and of fold surface structure as revealed by coarse decoration (indicated by dashes) and fine decoration (indicated by dots). Also shown in the elevation is the disposition and chain orientation typically found in a curved edge-on lamella formed at the overhanging lateral edge of a flat-on crystal (also see Figure 7).

sional short ones that curve toward the parent (as marked by an arrow in Figure 5d), are probably inclined differently with respect to their parent lamellae. However, the latter is largely inference (see later discussion).

The relation between branching and occurrence of curved edge-on lamellae is well exemplified by Figure 8 showing early stages of such branching. It will be noted that here, as in Figure 1, some branches split away and grow more or less straight; nevertheless, where there is curved growth of lamellae in flat-on orientation it is always along exposed convex faces of edge-on crystals. Corresponding growth does not occur on exposed concave faces unless it derives initially from lateral spreading of narrow sides of parent lamellae through gaps between edge-on lamellae. Such spreading is seen in the middle of the crystal in Figure 8 (arrows), but as is evident both from this example and from Figure 1, the extent to which there is subsequent development along concave lamellar faces is variable.

Figure 9 which shows part of a crystal in a specimen quenched after isothermal crystallization for 2 days at 128 °C, reveals interesting features that may illuminate the manner in which growth of edge-on crystals that tilt oppositely to faces of parent lamellae (again see Figure 6) is initiated. On the more curved broad side, accelerated growth during quenching has resulted in continuing lateral spreading notable only for development of a highly irregular boundary. All along the edge of the narrow side, however, small stacks of lamellae have formed which appear to lean against the parent lamella, and certainly encroach upon its upper fold surface. This behavior, enforced by rapid increase in driving force, seemingly represents pronounced manifestation of whatever process underlies a more sporadic and orderly nucleation of curved edge-on crystals during prolonged slow crystallization at high temperatures.

Behavior in Thicker Films and Relevance to Spherulitic Texture. In common with other morphologists we have from time to time noted indications of asymmetry of profile at tips of lamellae at boundaries between polyethylene spherulites. However, since observation of detail is often uncertain with overlapping lamellae in relatively thick specimens, and because segregation

during crystallization might cause uneven distribution of readily crystallizable polymer at boundaries between impinging spherulites, there has been ambiguity and no conclusion drawn. To our knowledge, there is in the literature no explicit suggestion that asymmetrical lateral growth may be common among lamellae in polyethylene spherulites.²¹ Results of the present study have prompted us to examine this possibility further.

In order to improve conditions for viewing we have examined spherulites of coarse texture in films of polyethylene that are on average no more than several lamellae thick. These were crystallized on mica at 105 °C from 10% solution in dotriacontane, and Figure 10 shows stacked lamellae near the boundary of such a spherulite after removal of the paraffin. There has been some branching at screw dislocations within the field although this is not immediately apparent because development of surface layers around the dislocations is quite irregular; the inset may aid the reader by showing an example of more regular growth at such dislocations (arrows). Several features are noteworthy. First, almost all the lamellae are clearly asymmetrical with respect to the average direction of radial growth, with more curved lateral edges facing to the right. From the disposition of these lamellae it would appear that the principal cause of the observed asymmetry is not depletion of melt but, rather, the circumstance that within a compact stack each crystal perceives the immediately underlying crystal as a substrate, its growth then being influenced in the same way as in the case of individual lamellae grown on mica. Second, it will be noted that right-hand edges of lamellae are everywhere sharply and well defined, whereas left-hand edges become more poorly defined toward the bottom of the micrograph, indicating that they have become increasingly buried under overlapping layers. Thus, lamellae within the stack are packed in echelon with broad sides raised slightly out of the plane of the substrate and dislocations are of such a hand as to produce new layers also conforming to this pattern.

Spherulites grown under similar conditions to that in Figure 10 but in somewhat thicker films exhibit lamellar twisting of a kind well-known in banded polyethylene spherulites and, in our view, the situation depicted in Figure 10 represents a tendency toward left-handed twisting that is frustrated in such a thin film by adhesion of basal layers to the substrate. Indeed, we believe that results of the present study provide strong support for an earlier interpretation of twisting orientation and, in order to clarify the intent of some further experiments, it is necessary to anticipate later discussion by indicating the essential substance of that proposal and the circumstances which prompted it. Bassett and Hodge⁶ had observed that, as seen in cross section, lamellae in polyethylene spherulites are often bent into S shapes and, moreover, that the sense of these shapes (which lack reflection symmetry) could be correlated with handedness of twisting and was apparently related to chain tilt. Keith and Padden⁷ then suggested that bending and twisting moments may be built into polymer lamellae as a consequence of differences in regularity of folding and associated compressive stress within congested fold surfaces, depending upon whether they are formed at acute- or at obtuse-angled edges of tilted growth faces; larger stresses were considered to accompany less regular structure in fold surfaces formed at acute-angled edges. [On this view, bending moments would be of opposite sign in opposite sides ("halves") of an elongated lamella in polyethylene, their transverse components then causing S-bending in cross section and opposing longitudinal components causing axial twisting

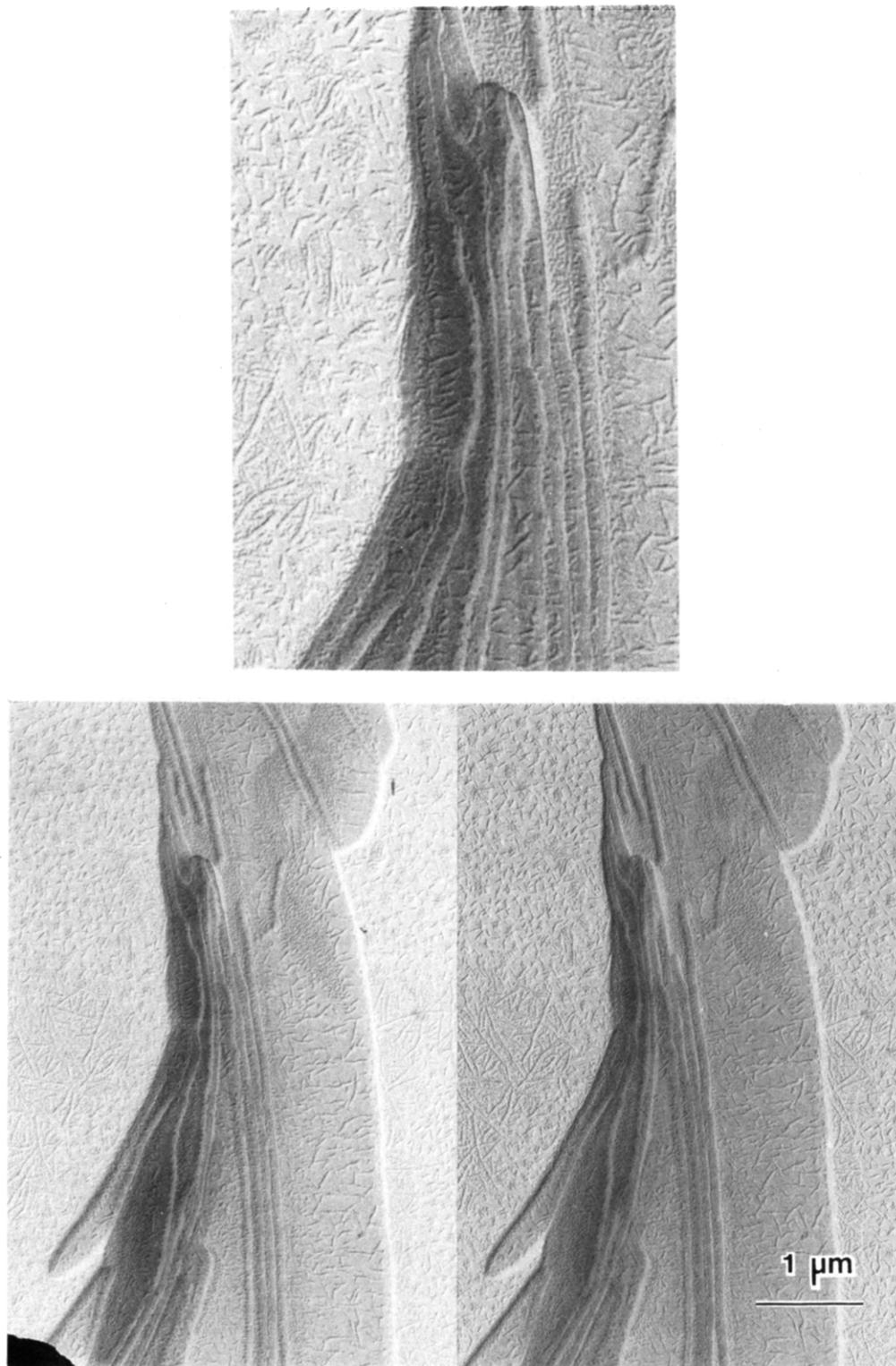


Figure 7. Stereopair illustrating the orientation of curved edge-on lamellae with respect to parent flat-on crystals. Above is an enlargement of the left-hand micrograph to highlight decoration of the exposed fold surface of the outer edge-on lamella.

(see Appendix 2 and Figure 8 of ref 7).] This interpretation is, of course, crucially dependent upon a specific causal relationship between direction of chain tilt and handedness of twisting.¹⁵ Bassett and Hodge judged chain tilts from striae seen at side faces of lamellae exposed by permanganic etching of cut surfaces of bulk specimens; the striae, however, were too fine to show clearly in their published micrographs. We have here attempted an independent verification of correlation between chain tilt and handedness of twisting by examining spherulites of polyethylene crystallized from the melt (without paraffinic

solvent present) in films just thick enough to show banding under the electron microscope; crystallization temperatures were chosen to provide convenient band spacings of several micrometers.

Chain tilts in given regions could easily be assessed by using either surface decoration or combinations of electron diffraction and dark-field observation in tilted specimens. On the other hand, corresponding assessment of handedness of twisting within films thin enough for good electron transmission proved unexpectedly difficult either by stereoscopy using large tilts ($\pm 20^\circ$) or by replication of

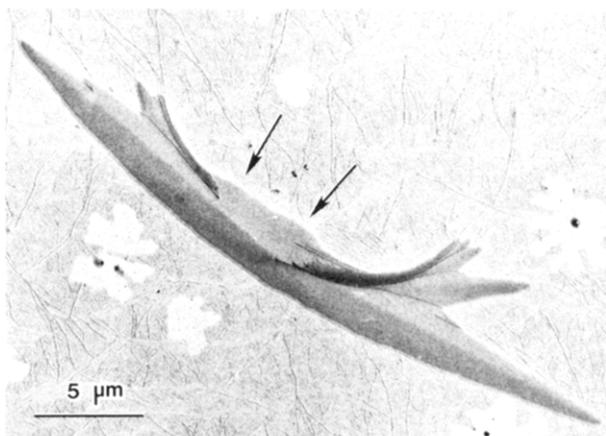


Figure 8. Early stage in the development of curved branches following convex faces of curved edge-on lamellae. Arrows indicate spreading of the parent crystal between the edge-on lamellae.

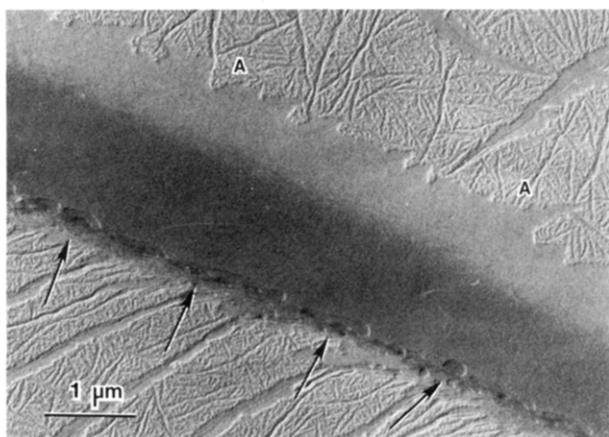


Figure 9. Part of a crystal quenched before isothermal crystallization was complete. Note the continuation of growth, with a reduction in lamellar thickness, on the more curved side (AA) and the formation of clusters of lamellae (arrows) which lean against or mount the parent crystal at its less curved overhanging edge (see text).

exposed free surfaces. Seemingly favorable areas were examined independently by each of us in a number of specimens but only in about one-third of these cases was there agreement that chain tilt and handedness of twisting could *both* be identified with confidence. In each such case, it was further agreed that twisting was consistent with larger compressive stresses occurring at fold surfaces formed at acute-angled edges of growth faces. This result is consistent with identification of chain tilts by Bassett and Hodge; it is also consonant both with indications from Figure 10 and with the previous interpretation of S-bending and its correlation with twisting orientation already alluded to. We note that asymmetry of lateral growth would tend to increase twisting moments;⁷ however, this might be expected only in spherulites of fairly compact texture and not in those of open texture (as formed at high crystallization temperatures) in which dominant lamellae are well separated at growth fronts.¹⁶

Interpretation and Discussion

Asymmetries of Lateral Growth and of Fold Structure. Retardation of growth at reentrant corners between substrates (including other crystals) and overhanging growth faces is attributable, we believe, to a circumstance recently analyzed by Mansfield and Hoffman in a different context.¹⁷ Because their conformational entropies would be reduced, coiled polymer molecules

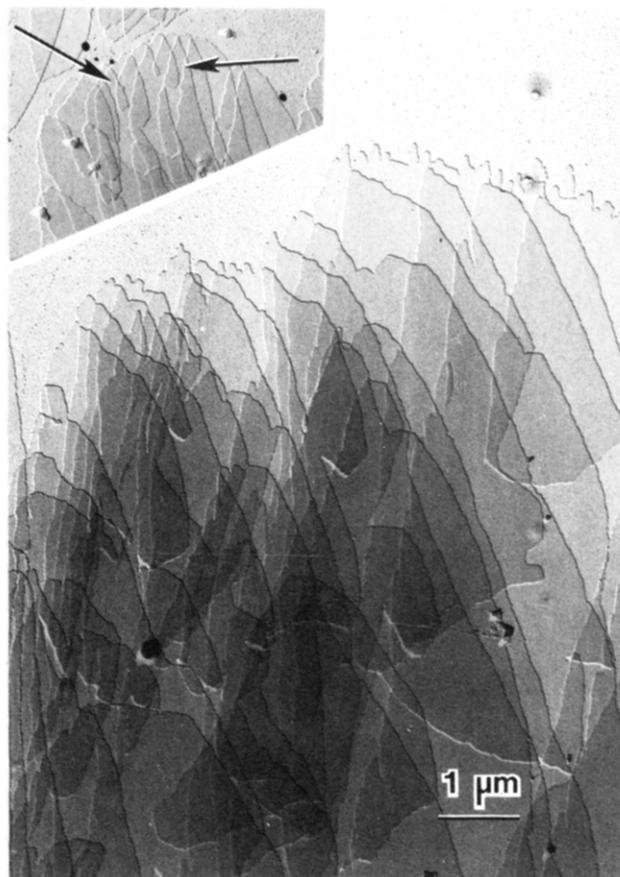


Figure 10. Cluster of lamellae at the boundary of a spherulite showing asymmetry of profiles and stacking in echelon (see text). The inset shows how marked anisotropy of growth rate in radial and tangential directions influences development of layers at screw dislocations (arrows); this may assist the reader in interpreting more irregular development of layers at dislocations in the larger micrograph.

resist being forced into tight corners; however, the present implication of this simple observation is not immediately obvious. On one hand, it is clear that molecular segments do penetrate reentrant corners at growth faces of our crystals and also that the driving force for crystallization is sufficient to drive loops of crystallizing molecules onto lower fold surfaces at these corners, though apparently not so readily as at growth faces that tilt toward the solid rather than toward the melt phase. On the other hand, surface nucleation, which initiates the addition of new layers on a growth face, is likely to be considerably retarded. According to the theory of Lauritzen and Hoffman,¹⁸ the crucial step involved is attachment of the first stem of a new molecule, an activated process opposed by a free energy barrier. The effective driving force at this stage is small, and since the coiled molecule in question will not in general already extend into the reentrant corner, the free energy barrier governing the nucleation rate may be enhanced significantly by an additional entropic contribution. On a different view of crystallization with chain folding expounded by Sadler,¹⁹ similar reasoning again leads to the conclusion that growth at a reentrant corner could be retarded considerably.

In relation to the structure at fold surfaces we cannot as yet interpret observed differences in patterns of decoration well enough to be sure of their significance in relation to different states of order at these surfaces. In terms of a simple rationale offered tentatively in an earlier paper,⁷ one might expect a higher degree of order (and a lower level of compressive stress) when folds are formed

at obtuse-angled edges of growth faces. If valid, this would suggest that coarse rodlike decoration is indicative of better ordering of folds, as seems reasonable both in terms of observations by Wittmann and Lotz on chain-folded crystals of very regular habit grown from dilute solution⁹ and of a recent result reported by Ungar, Organ, and Keller.²⁰ Final judgment on this question must await further experimental study.

Edge-on Lamellae and Curved Growth on Substrates. There are many puzzling aspects to formation of edge-on lamellae at overhanging growth faces of flat-on crystals on substrates. In the few cases where regularly curved edge-on lamellae grew to sufficient height for clear observation, we know that they cant *toward* parent crystals (again see Figures 6 and 7); otherwise consistent behavior suggests that this is probably a general property of the many edge-on lamellae which diverge from parent crystals with remarkably uniform curvatures of radii all close to 5 μm . We attribute such regular curvatures to bending moments introduced at tilted growth faces in the manner already discussed, curvature *away* from parent crystals then being consonant with this view. [We emphasize that these regularly curved lamellae (which, as previously noted, can be considered as edge-on "half-crystals") have identifiable chain tilts, have grown under conditions of crystallization such that differences of structure at opposite fold surfaces are demonstrable, and have radii of curvature about transverse axes comparable in magnitude to those observed ($\sim 2 \mu\text{m}$) in cross sections of S-bent lamellae in polyethylene spherulites;⁶ this combination of circumstances appears to include direct experimental support for each stage of the argument advanced in Appendix 2 of ref 7 to account for twisting moments in lamellae within banded polyethylene spherulites.] Short edge-on lamellae seen occasionally to curve irregularly toward parent crystals, and never to grow longer than about 0.5 μm (See Figure 5d), might then be canted in the same direction as the overhanging growth faces of flat-on crystals against which they are formed. Of those edge-on lamellae that are not appreciably curved none grew to sufficient height for it to be clear how their planes are oriented, whether they are canted with respect to the substrate or in which direction. Regardless of this uncertainty, consistency would nevertheless suggest that such crystals should also be subject to significant bending moments, yet there is little overt manifestation of a resulting curvature. However, it will be noted in Figures 1, 2, and 8 that relatively straight edge-on lamellae occur mostly at boundaries between straight flat-on branch lamellae or as ribs within parent flat-on lamellae. They may have grown only along paths traced out (during advance of flat-on lamellae along a substrate) by reentrant corners formed either where flat-on crystals with essentially parallel chain tilts abut or where indentations occur at growth tips within individual crystals. Unlike their counterparts initiated at *exposed* edges on flat-on lamellae and free to grow along curved paths, edge-on lamellae formed at reentrant corners may therefore grow within confined spaces already defined by essentially straight boundaries so that incipient tendencies toward bending are strongly suppressed.

Whatever their configuration, edge-on lamellae present their fold surfaces to flat-on crystals that adjoin or impinge upon them. Not unexpectedly, they form barriers that abruptly halt further advance of flat-on crystals which impinge upon them obliquely from neighboring aggregates. What is particularly surprising is the way in which curved flat-on crystals appear to follow along, seemingly in intimate contact with overhanging convex fold surfaces of

curved edge-on lamellae; epitaxy seems most unlikely, not least because the overhanging surfaces in "contact" lean in opposite directions. There appears to be some interesting but as yet unexplained intermittent behavior associated with ongoing crystallization at overhanging crystal faces (whether they be growth faces or fold surfaces) as is also suggested by the observation illustrated in Figure 9. It might be that sufficient molecular orientation is induced in the melt confined within a sharply reentrant region bordering one growing crystal to cause nucleation of crystals with a different orientation, or perhaps nucleation is induced at menisci formed by local cavitation along the apex of the reentrant; such hypotheses, however, are highly speculative and by no means convincing.

Lamellar Twisting. We have already alluded to a previously suggested interpretation of twisting orientation in banded polymer spherulites and to the hypothesis upon which it was based.⁷ It has now been confirmed, at least in the case of polyethylene, (a) that there are differences of structure at opposing fold surfaces of lamellae whose growth faces are appreciably tilted, (b) that significant longitudinal bending moments are present in such crystals, (c) that when the crystals twist, fold surfaces which are convex outward are those formed at acute-angled edges of tilted growth faces, and (d) that screw dislocations formed at growth fronts of twisting lamellae are predominantly of the same hand (right or left) as the torque anticipated from bending moments associated with a particular direction of chain tilt and are presumably generated largely in response to such a torque.

Registry No. Polyethylene, 9002-88-4.

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- (15) Recognizing that the only structural asymmetry then apparent in polyethylene crystals was chain tilt, Labaig was first to suggest a connection with the asymmetry implied by locally cooperative twisting of given hand in banded spherulites, though he did not pursue it further. Two of us (H.D.K. and F.J.P.) regret that we had not yet become aware of this important insight at the time our earlier paper⁷ was written and did not acknowledge it.
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and his collaborators have also observed asymmetrical lateral growth of one lamella growing upon another as substrate (in their case at screw dislocations exposed by permanganic acid etching of bulk samples of polyethylene).

Melting and Crystallization of Gelation Crystallized Ultrahigh Molecular Weight Polyethylene

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ABSTRACT: Melting and crystallization phenomena of gelation crystallized ultrahigh molecular weight polyethylene (UHMWPE) were studied by means of small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), and small-angle light scattering (SALS). The initial morphology of the gelation crystallized UHMWPE is similar to stacked single crystal mats with preferential *c*-axis orientation normal to the film surface. Annealing below T_m has resulted in a drastic increase of SAXS long period which has been customarily attributed to lamellar thickening. However, WAXD studies show a remarkable reduction of crystallinity during annealing, indicative of melting and recrystallization rather than lamellar thickening. When the temperature increases beyond T_m , the WAXD crystalline peaks disappear, but a slight amorphous orientation persists in the melt state. SALS and SAXS scattering also occur in the melt, suggesting the presence of melt anisotropy of UHMWPE associated with the slow diffusion of extremely long chains. Upon cooling from the melt (200 °C), well-grown truncated spherulites developed with the appearance of concentric fringes characteristic of lamellar twisting. The average diameter of these spherulites is 100 μm with a twist period of 2-3 μm .

Introduction

Gel processing of ultrahigh molecular weight polyethylene (UHMWPE), such as gel extrusion, spinning, and drawing, has been the subject of recent interest for its potential in applications such as high strength and high modulus fibers.¹⁻⁵ It is therefore natural that most studies have been focused on the establishment of the relationship between structure and properties of gel processed UHMWPE.⁶⁻¹¹ Little attention has been paid to the melt behavior of the materials because conventional melt processing methods are not applicable due to the very high melt viscosity associated with extremely high molecular weight.

A number of studies report on the peculiar melt behavior of UHMWPE. Pennings and co-workers^{8,9} observed the presence of superheated crystals in the melt (190 °C) of the solution-grown shish-kebab structure, showing the change of orthorhombic to hexagonal structure as a result of the crystal *a*-axis expansion. The transformation of the orthorhombic to the hexagonal rotator phase was observed by Matsuo and Sawatari¹⁰ in a cross-linked UHMWPE melt, who showed that the hexagonal phase was stable up to 230 °C. The authors concluded that such ordered melt is associated with the strong superheating behavior of cross-linked UHMWPE.

We are intrigued by the observation of Zachariades and Logan,¹² who observed the birefringent UHMWPE melt above the crystal melting temperature. The authors noted that the melt anisotropy of UHMWPE cannot be accounted for solely by the superheating of the crystalline phase or orientation effects in the melt. Instead, they suggested that an ordered region, reminiscent of smectic liquid crystals having orthorhombic (type E) or hexagonal

(type B) structure, might exist in the melt.

Recently, the melt behavior of UHMWPE was studied by Wunder and Merajver¹³ using Raman spectroscopy in the temperature range of 135-208 °C, a region where the melt anisotropy was observed. The authors confirmed the presence of ordered regions in the UHMWPE melt in which part of the polyethylene chain is in an environment that is similar to that of the orthorhombic polyethylene crystal. They concluded that the melt anisotropy of UHMWPE arises primarily from slowly melting superheated oriented crystals but not from a smectic liquid crystalline phase.

It is felt that further investigation on the structure of ordered UHMWPE melt is needed to reconcile the different opinions. In this paper the melting and crystallization of gelation crystallized UHMWPE has been examined by using small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), small-angle light scattering (SALS), and optical microscopic methods. We address three issues: (1) the lamellar thickening or melting and recrystallization during annealing below T_m , (2) the melt structure above T_m , and (3) the formation of large spherulites during recrystallization from the UHMWPE melt.

Experimental Section

UHMWPE ($M_w \sim 6 \times 10^6$, Himont Co.) was dissolved in Decalin by rigorously stirring at 155 °C for 30 min in a nitrogen environment to prevent oxidation of the specimens. The polymer concentration was 0.4% (w/v) and Irgonox-1076 (Ciba-Geigy Co.) was added as antioxidant (0.1% w/w on polymer). The hot solution was quickly transferred to a stainless-steel tray and slowly cooled under quiescent conditions to form gels. Decalin solvent oozed out during gelation crystallization and was removed gradually by siphoning. During gelation crystallization, the gels were slightly pressed between glass plates to improve the uniformity and surface smoothness of the film. The residual Decalin

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