

## Morphology of Polyethylene Crystallized from the Melt Under Pressure

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### Synopsis

The morphology of linear polyethylene crystallized under pressures up to 5300 atm. has been investigated. Electron micrographs of fracture surfaces obtained from these samples show that the majority of the polymer, at the highest pressures, crystallizes in the form of extended chain lamellae which can be as thick as  $3 \mu$ . Electron diffraction patterns show that the molecules are normal to the lamellae. At lower pressures part of the polymer crystallizes in the form of folded chain lamellae, the proportion increasing with decreasing pressure. Well defined kink bands can be observed in the thicker extended chain lamellae. It is suggested that either molecular weight fractionation or an end-to-end alignment of the molecules and subsequent folding takes place during the growth of the extended chain lamellae.

### INTRODUCTION

Linear polyethylene crystallized under pressure may have a density approaching the theoretical perfect crystal density and a melting point close to the limiting value for large, perfect crystals.<sup>1,2</sup> The morphology of such a sample is thus of considerable interest. In this paper we present a report of the investigation of the internal morphology of linear polyethylene crystallized under pressures up to 5300 atm. and with densities as high as 0.994 g./cc. Further details concerning the properties of these and other similar samples are described in a paper in preparation.<sup>2</sup>

Wunderlich<sup>1,3</sup> has previously discussed the growth of polyethylene single crystals from dilute solution under elevated pressure. The crystals in general resemble those obtained at atmospheric pressure at similar supercoolings (the melting point and therefore the crystallization temperature increases with pressure). At constant supercooling the thickness or fold period increases only slightly with pressure.

Anderson has pointed out<sup>4,5</sup> that at least three morphologically distinct lamellar structures can be observed in linear polyethylene crystallized from the melt at atmospheric pressure. These he has labeled types I, II, and

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III lamellae. Type I consists of broad, folded chain lamellae resembling those found in single crystals grown from solution. The smaller of the two small-angle x-ray diffraction long periods from melt crystallized polyethylene is essentially equal to their thickness.<sup>5-7</sup> Type I lamellae are found in both whole polymers and in fractionated samples. Whereas in fractionated polymer they can be observed on both exterior and fracture surfaces, in whole polymer they are usually visible only on exterior surfaces. When whole polymer is fractured, microdrawing apparently takes place in regions occupied by type I lamellae. The resulting "fracture" surfaces are covered with broken fibrils. This microdrawing is believed to be due to the presence of tie molecules connecting neighboring lamellae.<sup>5,7</sup> Type II lamellae consist of narrow or ribbon-like layers whose thickness is essentially equal to that of type I. They have been found only in higher molecular weight, fractionated samples and were not found in the samples discussed in this paper. Therefore, type II lamellae will be of no further concern to us here.

As observed on fracture surfaces, type III lamellae have an appearance similar to the bands observed to essentially occupy the entire volume of highly crystalline polytetrafluoroethylene.<sup>7,8</sup> Anderson has suggested<sup>5</sup> that they are probably similar to paraffin crystals, consisting of fully extended chains. Type III lamellae are found in whole polymer and in the lower molecular weight fractions. Each individual crystal is of about the same thickness over its lateral extent, but the crystals in a given sample may vary considerably in thickness. By varying the temperature of crystallization the relative proportion and thickness of types I and III lamellae can be varied for a given sample. With increasing temperature the fold period of type I, the maximum thickness of type III and the relative proportion of material crystallizing in type III increases. Although, with fractionated polymer, type III lamellae were found only in fractions with molecular weights below 12,000, Anderson suggested<sup>5</sup> that by waiting for longer periods of time at still higher temperatures it should be possible to obtain type III lamellae from polymer of much higher molecular weight.

## EXPERIMENTAL

Table I lists many of the properties of the samples used for this investigation. Samples of a linear polyethylene (Marlex 50) were enclosed in brass bellows and heated to the crystallization temperature at atmospheric pressure. The chosen pressure was then applied in 1-2 min. by using a pressurestat previously described.<sup>9</sup> The pressure and temperature were kept constant for the time listed, after which the temperature was reduced at a rate of 4°C./hr. to about 50°C., at which time the pressure was released and the sample removed. (For a full description of the sample preparation techniques, see Wunderlich.<sup>2,3</sup>) The atmospheric pressure samples (A and B, Table I) were prepared by quenching the sample quickly from the molten state to the crystallization temperature.

TABLE I

Sample	Crystallization conditions			Density measurements		X-ray measurements		Extr. melting point (DTA) °C.
	Temp., °C.	Pressure, atm.	Time, hr.	Density (25°C.),	Crystal-	Crystal-	Long period, A.	
				g./cm. <sup>3</sup>	linity, %	linity, %		
A	130	1	8	0.9799	89	89	400	—
B	130	1	8	0.9785	88	—	—	134.8
C	170.1	2000	8.5	0.9826	90	91	600	136.6
D	186	2760	8	0.9860	92	91	400	133.9
E	226	4800	8	0.9938	97	97	No discrete	140.1
F	236	5300	49	0.9921	96	93	or diffuse scatter	139.9

The density was measured by using 1 mm.<sup>3</sup> pieces, microscopically checked for voids, in a density gradient column at 25°C. The density crystallinity was determined by use of the average of Nielson's<sup>10</sup> and Gubler and Kovacs'<sup>11</sup> value for  $\bar{V}_a$  (1.173 cm.<sup>3</sup>/g.) and Swan's<sup>12</sup> value for  $\bar{V}_c$  (1.001 cm.<sup>3</sup>/g.). The x-ray crystallinity was measured on a General Electric XRD-5 diffractometer, the calculation being made by the method described by Hendus and Schnell.<sup>13</sup> The small-angle patterns were obtained by using a Jarrell-Ash-Frank optically focussing small-angle x-ray camera with a resolution of about 500 Å.

The melting points are extrapolated maximum melting points obtained by a DTA method previously described.<sup>2,14,15</sup> In some of the samples more than one DTA peak was found. As suggested by Anderson,<sup>5</sup> this is probably related to the presence of more than one morphological structure as observed in the electron microscope. In Table I the upper tail of the highest temperature peak is listed. (Further details are given elsewhere.<sup>2</sup>)

The samples were prepared for electron microscopy by immersing them in liquid nitrogen for a sufficient period of time to cool them, then fracturing them while still immersed. The two most highly crystalline samples (E and F) fractured readily at room temperature during handling. In these samples no difference was observed between the surfaces obtained at room temperature and those obtained following cooling. The micrographs of these samples in this paper are from surfaces obtained at room temperature. Following fracture the surfaces were shadowed with platinum, stripped with poly(acrylic acid), and backed with carbon (as described in detail in Chapter 1, of reference 7).

## RESULTS

### Electron Microscopy Observations

The fracture surfaces of the sample crystallized at atmospheric pressure resemble those described previously.<sup>5,7</sup> Over much of the surface, presumably in the areas corresponding to the occurrence of type I or folded chain lamellae, only an irregular, fibrillar structure was present. In a few

regions areas were observed of the order of  $100 \mu$  in size in which there were primarily the type III or extended chain lamellae. Within these areas fracture had occurred both between and within the lamellae. Those which were measurable varied between 300 and 600 A. in thickness, the 87 measured averaging 380 A. thick.

Considerably larger proportions of the samples crystallized at the intermediate pressures (C and D) are found to consist of the extended chain lamellae. In both samples, however, there is evidence of the presence of folded chain lamellae, i.e., there are regions which have a drawn, fibrillar appearance. The extended chain lamellae in sample C (Fig. 1) varied in thickness between 200 and 1000 A., averaging about 480 A. In sample D they varied between 300 and almost 3000 A., averaging about 800 A. in thickness (Fig. 2). The thicknesses of 68 and 115 lamellae were measured for the two samples, respectively.

No correction was made for the possible tilt of the lamellae with respect to the surface. In addition, a meaningful distribution of step heights would require a more random selection of areas (in general only areas displaying groups of larger lamellae were photographed) and some correction should be made for the presence of thin lamellae beneath the resolving power of the replicas.

The thicker lamellae, in sample D, as indicated by Anderson,<sup>5</sup> are similar in appearance to the bands observed in highly crystalline polytetrafluoroethylene.<sup>7,8</sup> Although generally the type III lamellae of various thicknesses

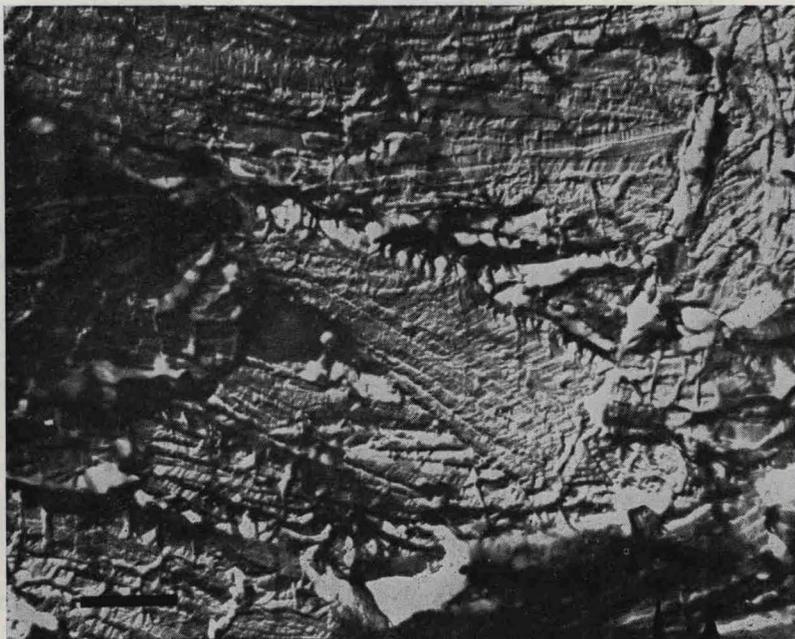


Fig. 1. Fracture surface of sample C (Table I). The scale bar on this and subsequent micrographs represents  $0.5 \mu$ .



Fig. 2. Fracture surface of sample D. The dark areas in this and the other micrographs are a result of polyethylene adhering to the replica.

were intermixed, as in Figure 2 a significant number of regions were observed in which all the lamellae were of the same thickness, this being on the order of 300–400 Å. The relative length of the striations, with respect to their separation, in the type III lamellae causes the thicker lamellae to have a different appearance than the thinner ones. However, there appears to be no basic difference in their structure. Structures similar in appearance to the thinner lamellae have been observed in moderately crystalline polytetrafluoroethylene ( $\sim 50$ – $70\%$ ).<sup>7,16,17</sup> In that case, however, all of the bands present were of about the same thickness and considerably smaller in lateral extent than in the case of the more highly crystalline polymer. In sample D the thick and thin lamellae appear to have equivalent lateral dimensions.

The general appearance of the fractured type III lamellae in sample C (Fig. 1) differs from that of the lamellae of corresponding thickness in sample D (Fig. 2); the fracture surface of each lamella and the whole surface appears smoother. Whether this is characteristic of the thermal treatment of the two samples during crystallization or a result of possible differences in the fracturing and replicating process is not known. One notes that the striations in Figure 1 (sample C) in many cases make an angle of other than  $90^\circ$  with the lamellae (this occurred only infrequently in sample D) and also appear more closely spaced than those in Figure 2.

The entire fracture surface of samples E and F and thus probably the whole sample is occupied by extended chain lamellae of various thicknesses

(Fig. 3). Samples E and F appear nearly identical, E perhaps having a few lamellae somewhat thicker than F. In both samples optical microscope observations of the replicas and also of the fracture surfaces themselves, indicates that the lamellae are organized in incipient spherulites, i.e., sheaf-like clusters are found. The center of such a sheaf is located at the lower left of Figure 3.



Fig. 3. Fracture surface of sample F. An entire lamella is attached to the replica on the left of the micrograph. This figure is printed as a negative.

The fracture process occurred both through the type III lamellae (right side of Figure 3) and between them (left side). In the latter case, entire lamellae often remained attached to the replica permitting the obtaining of single crystal electron diffraction patterns described in the next section. Although the striations could be observed on the fractured edges of the attached lamellae, the interlamellar surface was obscure. Apparently the large amount of attached polymer caused the replica to break up under the action of the beam. By limiting the beam current, as for the electron diffraction studies, somewhat better micrographs were obtained (Fig. 8), although at low magnification. These suggest that the thickness of a given lamella may vary somewhat, regions on the order of  $1 \mu^2$  being of nearly uniform thickness. Although no obvious structure was present within these regions, further investigation at higher magnification would be useful.

Lamellae have been observed with thicknesses of up to  $3 \mu$  in samples E and F. The average thickness, from low magnification micrographs covering areas representative of the whole sample, is about 2500 Å. The

most prominent feature of the lamellae are the striations (Fig. 3 and subsequent figures). It appears that in nondeformed lamellae the striations are perpendicular to the broad faces of the lamellae. In the case of polytetrafluoroethylene, drawing<sup>17</sup> or rolling<sup>7</sup> causes the striations to tilt within the lamellae. Deformation is probably also related to the presence of a few lamellae in these samples in which the striations are uniformly tilted and most certainly is the cause of the kinks to be described later.

The striations in samples E and F have a spacing of about 200 to 300 Å and are continuous across an entire lamella. The contrast between the striations is due in part to individual ribbons of material, one or more striations wide, adhering to the replica and in part due to the surface roughness of the fractured lamella. Each striation appears to correspond to a distinct structural entity. In a few regions it was possible to observe type III lamellae which had a smooth fracture surface (Fig. 4). Where the fracture plane changes levels, near the center of the micrograph, the appearance suggests that the striations correspond to the fracture edges of sheet-like structures. The structure of the lamellae would thus resemble that suggested by Speerschneider and Li<sup>17</sup> for polytetrafluoroethylene, except that the high crystallinity of these samples precludes an "amorphous" layer between the sheets.

It appears that the sheets can readily be broken up into nearly cylindrical structures, several hundred Angstroms in diameter and with a length corresponding to the lamella thickness (Fig. 5) or even larger (Fig. 6). In

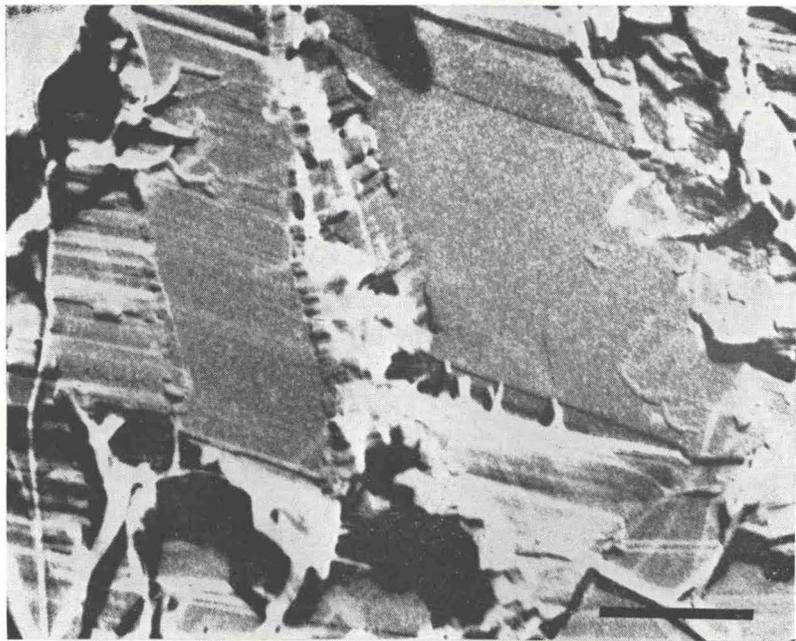


Fig. 4. Fracture surface of sample E, showing smooth fracture surface.

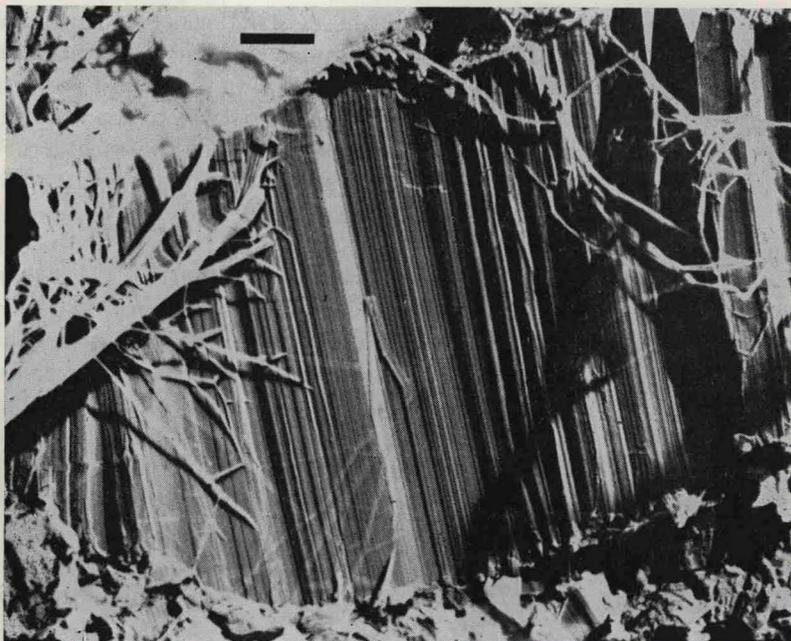


Fig. 5. Portion of the fracture surface of a large lamella in sample E. Several small kinks are present near the top center of the micrograph. This micrograph is printed as a negative.

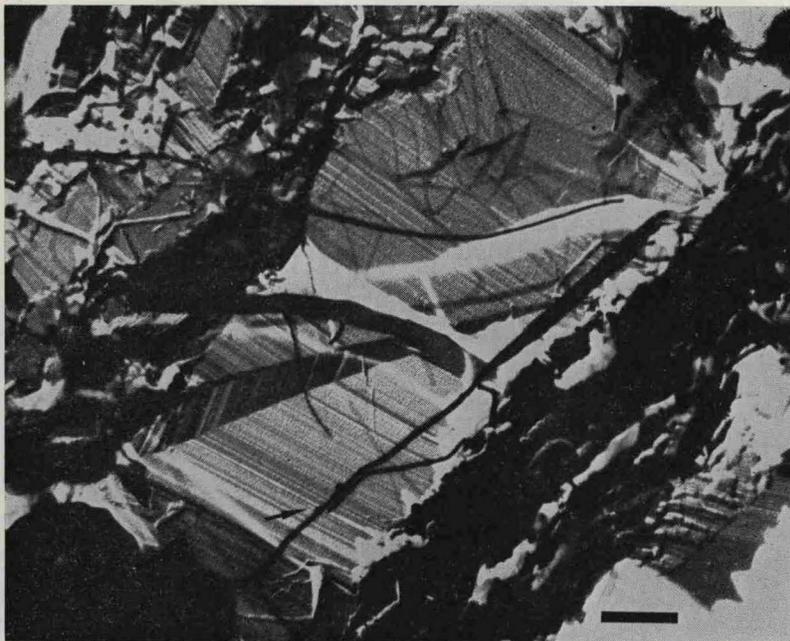


Fig. 6. Long "fiber" (arrow) and large kink on the fracture surface of a lamella in sample E. The surface structure of the lamella is also visible to an extent.

Figure 5 a piece of the lamella two striations wide has been partially removed from the surface and folded back on itself. The overall length is just equal to the lamella thickness. In Figure 6, however, the "fiber" lying parallel to the lamella is more than twice as long as the corresponding lamella thickness. It remained attached to the lamella on the right side, the thicker portion corresponding to the width of the lamella at that point. At the end of the thick region it has split into "fibers." It is believed that these fibers are portions of the sheets, as is the piece in Figure 5. The fact that it is wider than the striations is probably due to its being cylindrically coated with platinum and carbon. The implications of the fact that it is longer than the lamella thickness is discussed in the last section of this paper. Similar fibers have also been observed on other micrographs of these samples to be several times as long as the thickness of the lamella to which they are attached; the most prevalent type of fiber or ribbon, however, is that whose length is equal to the corresponding lamella thickness. The fibers of low contrast on these two, and other figures, were formed when the Pt replica was stripped from the sample.

Many of the thicker type III lamellae have one or more kinks visible on their fracture surface. Usually, as in Figure 6, they extend from one side of the lamella to the other, the striations clearly changing direction at the kink. There is often a related change in the fracture plane. The change in level and slope of the fracture plane at the kinks makes it difficult to determine the angle through which the striations kink. It can be as large as  $90^\circ$  and often appears to be about that angle. Occasionally, instead of extending directly from one surface of the lamella to the other, the kink results in the formation of an isolated patch of displaced material, as to the right and above the partially removed piece of material in Figure 5, or it may reverse directions several times within the lamella. The latter structure may also be due to the presence of several intersecting kinks.

### Electron Diffraction Observations

Geil has shown<sup>7</sup> that it is often possible to remove portions of the polymer from the surface along with the replica by using the technique utilized for these preparations. Electron diffraction patterns from this material have been related to the single-crystal nature of the lamellae in polyethylene<sup>7</sup> and annealed polyoxymethylene.<sup>18</sup> It was also found, as mentioned previously, that considerable quantities of the polymer in samples E and F remained attached to the replicas. Some of the contrast of the striations and the fibers observed on the fracture surfaces are due to this polymer.

An electron diffraction pattern and corresponding bright field micrograph of the material adhering to a fracture surface of the lamella is shown in Figure 7. The diffraction patterns here and from other similar samples are fiber-like (on the original of Figure 7 both  $\{110\}$  and  $\{200\}$  reflections are visible) and of relatively low intensity. The length of the crystals is such that one would expect the  $\{002\}$  reflection to be visible. Even with longer

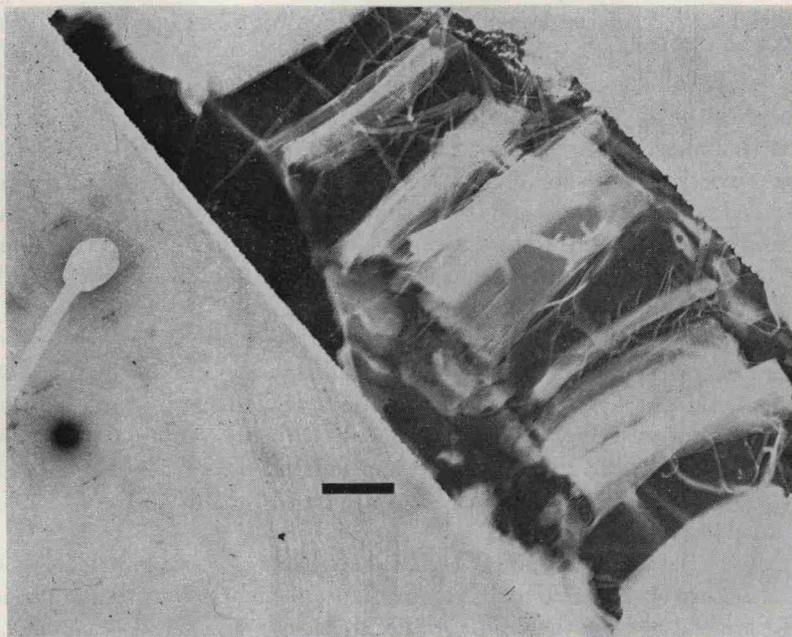


Fig. 7. Selected area electron diffraction patterns from the material adhering to the fracture surface of a type III lamella in sample E. The area giving rise to the patterns was recorded on the same plate as the pattern; the patterns should be rotated counter-clockwise about  $10^\circ$  to compensate for the rotation of the image in the microscope. This figure is printed as a negative.

exposure times and larger areas it was not possible to observe it. This may be due to a tilting of the lamella surface, however, and not to its absence. Likewise, the low intensity of the  $\{110\}$  and  $\{200\}$  reflections is probably due to the fact that only a few of the crystal's planes may be properly oriented to reflect. The alignment of the molecules parallel to the striations has been confirmed by observation of the optical birefringence of lamellae attached to the replica.\*

Good single-crystal diffraction patterns, sometimes with several orders of reflections and resembling those obtained from solution grown polyethylene single crystals, were obtained from regions in which an entire lamella remained attached to the replica (Fig. 8). Tilting of these lamellae with respect to the beam resulted in the type of pattern shown, the center of intensity of the pattern being displaced from the center of the pattern. Comparison of the selected area image that was taken at low intensity in conjunction with Figure 8 and which was unfortunately out of focus, and the subsequent micrograph shown in Figure 8, which was focused using an intensity sufficient to give a visible image on the microscope screen, indicates that some beam damage had occurred. However, the appearance of various regions of nearly uniform thickness is believed to be real.

\* The optical birefringence measurements were made by E. W. Fischer.

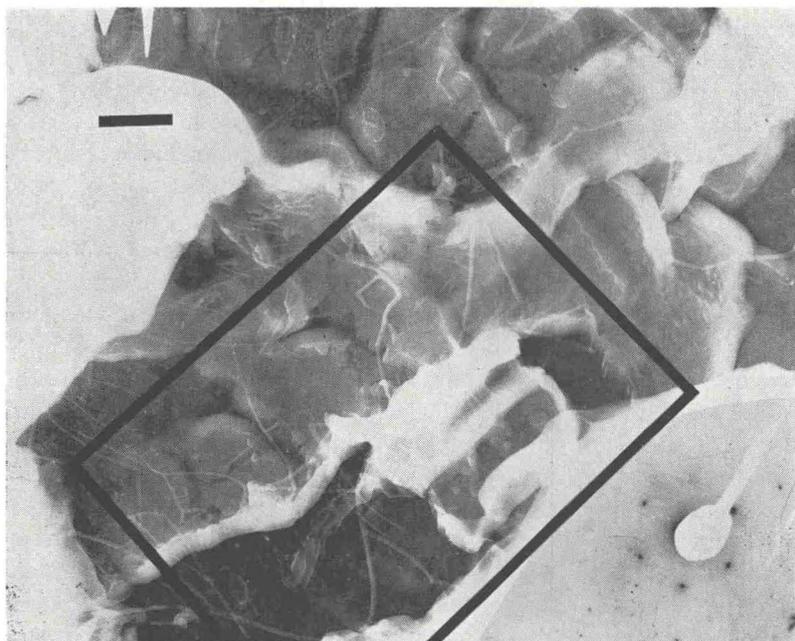


Fig. 8. Selected area diffraction pattern and corresponding bright field image of a Type III lamella in sample E. The area giving rise to the pattern is indicated on the micrograph, which is printed as a negative.

### DISCUSSION

Anderson suggested<sup>5</sup> that the molecules in the type III lamellae lie parallel to the striations. The electron diffraction patterns demonstrate this conclusively. The cause of the striations and the arrangement of the chains within the lamellae is somewhat more difficult to interpret. As indicated previously, it appears as if the type III lamellae are made up of sheet-like structures on the order of 300 Å thick, of indeterminate, but large, length and of a width equal to the thickness of the lamella. In an undeformed lamella these sheets are oriented normal to the lamellae. However, they can easily be broken up into rod-like units of nearly square or circular cross section. It has not yet been possible to determine the orientation of the unit cell within the sheets or the rods, except for the parallel alignment of the molecules with the rod's axis. The rods may be nearly perfect crystals, the boundaries between the rods being similar to subgrain boundaries in metals. The individual lamellae would correspond to the grains.

One can visualize at least two possible ways of incorporating the molecules in the rods and thus the lamella: (1) the length of the rods (and thus the thickness of the lamella) corresponds to the length of the molecules incorporated in that rod; (2) the molecules within a given rod may be of any length, being arranged end to end; folding may take place at the end of the rod similar to that which occurs in solution-grown single crystals, or may be such as to connect adjacent rods.

The first possibility, as suggested by Bunn et al.<sup>8</sup> and Anderson,<sup>5</sup> requires that a fractionation in terms of molecular weight takes place during crystallization. In the case of the samples crystallized at the lower pressures (C and D) and that crystallized at atmospheric pressure it also suggests that the low molecular weight material is segregated into regions which may be microns in dimension, and that it crystallizes independently of the high molecular weight material which is crystallizing in the form of type I lamellae. Anderson's work with the fractionated polymer<sup>5</sup> would be in agreement with this suggestion. The observed thicknesses of the type III lamellae in the E and F samples is also reasonable in terms of this suggestion; the average thickness corresponds to a sort of number-average molecular weight of 28,000. Corrections need to be made for the lack of counting many of the thinner type III lamellae (because of low replica resolution and sample distortion during replica stripping), tilt of the lamellae with respect to the surface, and the volume occupied by the lamellae of various thicknesses.

If this possibility of fractionation during crystallization is correct, it indicates that molecules can move over large distances during crystallization. In addition, it indicates that even in the case of the largest molecules the effect of size on the thermodynamic properties remains significant. At first glance this possibility appears unlikely. However, evidence for molecular motion over distances of up to 1 mm. during crystallization at atmospheric pressure has been published.<sup>7,19</sup> Keith and Padden<sup>20</sup> also postulate (and have some evidence for) a not too different type of motion to occur during spherulite growth. Proposed experiments using fractionated polyethylene should prove or disprove this possibility. The implications of this fractionation, segregation process for the mechanical properties of polymers, as for instance mechanical relaxations, stress-strain relations and stress crack, are rather obvious and will not be discussed here.

The second possibility above also raises a considerable number of problems which cannot be answered until more is known of the crystallization process. For instance, what determines the thickness of the lamellae; it is not believed likely that they form at different temperatures as the sample is cooled. In addition, one is still faced with the problem of unentangling the supposedly randomly coiled molecules in the melt, aligning them and then placing them end to end. The high density precludes the existence of large quantities of defects in the crystals. If this possibility is correct, it is believed most likely that the molecules are folded at the ends of the rods and re-enter the same rod. However, the presence of a few fibers considerably longer than the rods, as in Figure 6, suggests also the possibility that the molecules are grouped into fibers corresponding to the rods and that these fibers are folded to form the sheets. Further investigation of the structure and formation of these long fibers is needed.

With either possibility the cause of the formation of rod-like crystals and their association in the form of sheets within the lamellae is not clear. We suggest that the lateral size of the rods may be limited by the accumulated

strain at the ends of the crystal, whether this consists of reentrant folds or of endgroups. If the entire crystal is folded at the end the size might be limited because of this. If the molecules are folded at the ends and re-enter the same rod, one wonders why the lamellae have a different characteristic fracture than the type I lamellae in which they are presumably also folded.

It is not known just when during the sample preparation process the kinks formed in the lamellae. One suspects that they are due to some increase in pressure following growth; possibly they may have formed during the fracture process. Deliberate attempts to induce their formation may help explain the deformation process in polymers. As in the case of polytetrafluoroethylene,<sup>7,17</sup> the presence of these large morphological structures should simplify study of polymer deformation.

At the present time we cannot interpret the small-angle x-ray diffraction measurements listed in Table I. The values for samples C and D are in satisfactory agreement with the relative melting points but not with the lamella thicknesses observed in the electron microscope. Also, one wonders that the diameter of the rod-like crystals does not contribute to the diffraction pattern. The measured spacings were near the maximum resolution of the presently available camera; it is hoped to remeasure the samples in the near future. The relative melting points of C and D are also difficult to explain in view of the fact that the thicker type III lamellae, as observed in the microscope, are in the sample with the lower melting point.

It should be evident from this discussion that there remains a considerable area of research in this field of the structure of polymers crystallized under high pressure. It is believed likely that polymers other than polyethylene can also be crystallized in the form of these extended chain lamellae. The structure of the bands in polytetrafluoroethylene, which was first explained in terms of a structure like that discussed in possibility (1) above<sup>8</sup> and then in terms of folded chains,<sup>7,21</sup> is probably related to these type III lamellae.

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### Résumé

La morphologie du polyéthylène linéaire cristallisé sous des pressions allant jusqu'à 5300 atmosphères a été examinée. Des micrographies électroniques des surfaces de rupture obtenues à partir de ces échantillons montrent que la majorité du polymère, aux pressions les plus élevées, cristallise sous forme de lamelles de chaînes étirées, qui peuvent atteindre une épaisseur de 3 microns. Des spectres de diffraction électronique montrent que les molécules sont normales par rapport aux lamelles. A des pressions plus basses une partie du polymère cristallise sous forme de lamelles à chaînes repliées, dont la proportion augmente avec une diminution de la pression. Des bandes de superposition bien définies peuvent être observées dans des lamelles à chaînes étendues plus épaisses. On suppose que le fractionnement du poids moléculaire ou bien un alignement des molécules bout-à-bout, suivi par un repliement des chaînes, a lieu pendant la croissance des lamelles à chaîne étirée.

### Zusammenfassung

Die Morphologie von unter Drucken bis zu 5300 Atmosphären kristallisiertem linearen Polyäthylen wurde untersucht. Aus elektronenmikroskopischen Aufnahmen von an diesen Proben hergestellten Bruchflächen geht hervor, dass im Falle der höchsten Drucke der Grossteil des Polymeren in Form von bis zu 3 Mikron dicken, aus entfalteten Ketten bestehenden Lamellen kristallisiert. Elektronenbeugungsdiagramme zeigen, dass die Moleküle senkrecht zu den Lamellen stehen. Bei niedrigeren Drucken kristallisiert ein mit sinkendem Druck zunehmender Anteil des Polymeren in Form von aus gefalteten Ketten bestehenden Lamellen. In den dickeren, aus entfalteten Ketten bestehenden Lamellen konnten deutliche Knickbanden festgestellt werden. Es wird angenommen, dass während des Wachstums der aus entfalteten Ketten bestehenden Lamellen entweder eine Molekulargewichtsfractionierung oder eine End-zu-End-Ausrichtung der Moleküle und anschliessende Faltung auftritt.

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