



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 suggested⁵ 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.⁸ and Anderson,⁵ 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 polymer⁵ 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.^{7,19} Keith and Padden²⁰ 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