tion of 20 mg/liter for the triple-peaked band between 270 and 290 mμ or 5 mg/liter for the peak at 219 mμ. The same changes are observed in eluates of IAA spotted on filter paper, standing for a variable length of time in the diffuse light of the laboratory (*2*). The great lability of IAA under those conditions has been used for an investigation of smog which showed that auto-oxidation of IAA is delayed in an air-conditioned laboratory as compared with one not air-conditioned. Hourly, daily, and seasonal variations have been observed (*3*).

Oxidation of solutions of IAA converts it to deuterauxin, which in turn polymerizes and gathers on the surface as a very thin film (*4*). This film, examined under the microscope, is seen to be made up of coalesced, slightly refringent disks, about 10 μ in diameter. The disks produced on the surfaces of dilute solutions are not visible under the optical microscope but can be collected on copper grids and observed in the electron microscope. They exhibit circular electron diffraction bands corresponding to spacings of reticular planes of 1.2, 2.0, and 3.7 Å (*5*).

Conversion of IAA to deuterauxin, which polymerizes and thus becomes unavailable to the coleoptile sections, explains the early, reversible stages of inactivation. The film disappears by boiling, and restoration of activity by heat may be due to simple depolymerization of deuterauxin.

Inactivation also occurs in nonbuffered solutions, although it is less pronounced than in acidic solutions. It may, at least in part, account for the so-called "occasional" variations observed in the coleoptile elongation test which has usually a duration of 24 hours (*1*).

Hull *et al.* (*6*) have attributed to air pollutants the daily and seasonal fluctuations in sensitivity of the *Avena* curvature test. These authors suggest that decreased sensitivity is an effect on the growth response of the coleoptile and does not lie in the destruction of applied IAA by the pollutants. In the light of the present work, it seems likely that decreased sensitivity is an indirect effect of inactivation of endogenous auxin by air pollutants.

It would seem that reversible inactivation of IAA through the in vivo effect of oxidizing agents may play an important role in plant growth regulation.

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Surface Recrystallization of Polyethylene Extended-Chain Crystals

Abstract. *Rough fracture surfaces of extended-chain polyethylene crystals become unstable at temperatures below the bulk melting point. There is no way for the extended chains, which are up to 20,000 methylene units long, to change position without collapse. As a result, the rough surfaces smooth out on heating by covering themselves with oriented folded-chain lamellae.*

Flexible, linear high-polymer molecules like polyethylene are difficult to transform from the random melt to an equilibrium crystal in which all chains are parallel and fully extended. The long chains, typically 10 to 100,000 Å, cannot be added to a growing crystal in one step. The crystallization path leads first to thin folded-chain crystal lamellae which subsequently tend to rearrange to a thermodynamically more stable crystal with extended chains. The folded-chain lamellae are often only of the order of 100 Å thick. On their path to the fully extended-chain crystal they normally freeze into a metastable state with only little larger fold length (*1*). Recently, using high-pressure techniques (*2*), we have grown almost fully extended-chain crystals of polyethylene. The character of the resulting material is completely changed. Instead of a tough plastic, a brittle polycrystalline aggregate results. A fracture surface of such extended-chain material which was crystallized at 4350 atm and 227°C for 20 hours followed by 1.6°C per hour cooling is shown in an electron micrograph (Fig. 1). Of interest is the rough appearance of the fracture surface of the crystals. The many striations are at right angles to the lamellar surface, parallel to direction of the molecular chain (*3*). We carried out a statistical analysis of the surface roughness and were able to show that a similar surface structure would be formed by a crack propagating through a crystal, the crack taking randomly a left or right path around any molecular chain it encounters (*4*). Many surface chains are thus in elevated ridges with a large specific surface area and have been rendered less stable than the bulk by the process of fracturing.

We now report on the study of a property of the rough fracture surface. The extended-chain bulk polyethylene melts at 138.7°C (*5*). The surface stability was investigated by heating the identical fracture surface of Fig. 1 for 3 minutes to 120°C. On replication we searched for the same location (Fig. 2). All lamellae are covered with "ripples" aligned normal to the original striations. The smaller striations have disappeared, and the bigger ones are more rounded.

The most likely explanation we can offer at this point is that the molecular chains in large surface area ridges become unstable at these temperatures and tend to reorganize in order to reduce surface area. Since there is no way to roll stretched flexible polymer chains from a ridge into a valley, they collapse first by complete or partial melting. As a result, the chains have then the same restriction any polymer melt has in crystallization. Folded-chain crystals must be grown first even if an extended-chain crystal is present as a nucleus (*6*). These folded chain crystals are seen in Fig. 2 directly as ripples. The alignment of the crystallographic chain with the substrate is preserved so that in many cases the orientation of the substrate chain can be deduced from the ripple direction.

The observation of surface recrystallization of extended-chain crystals must be compared to three other observations. (i) Drawing folded-chain single crystals, Geil found that fibers are pulled out when cracks form which are not parallel to growth faces. When

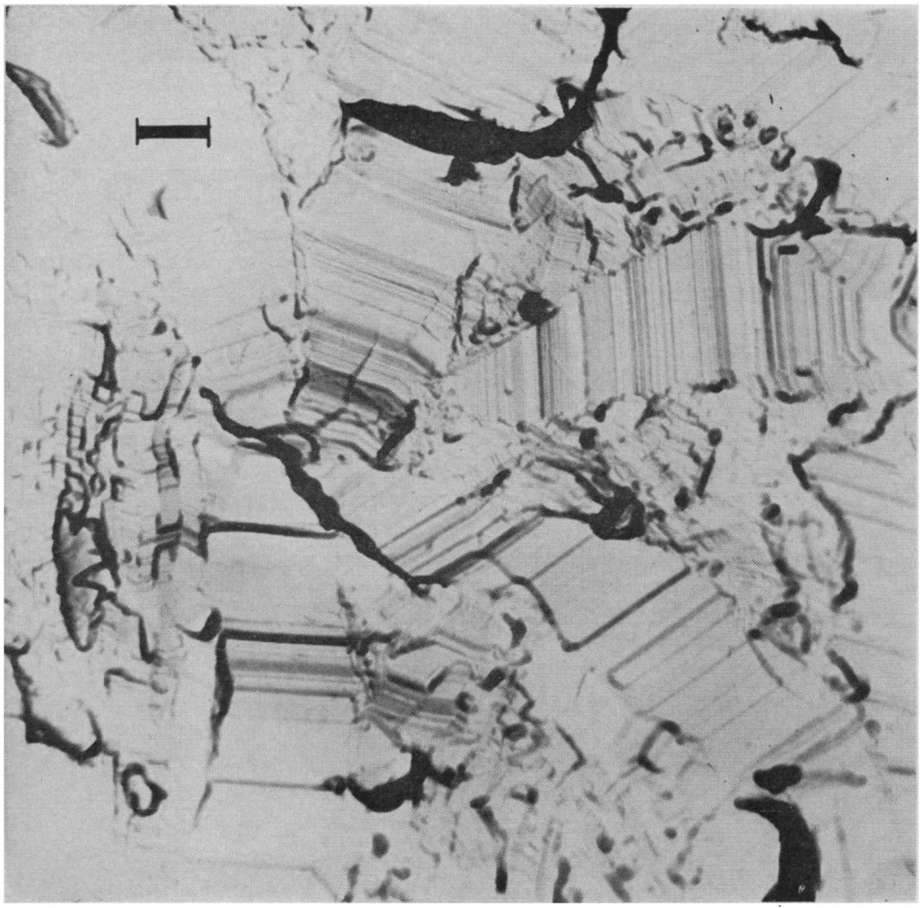

Fig. 1 (top left). Electron micrograph of a replica of the fracture surface of extended-chain polythylene. The scale bar represents 1 μ.

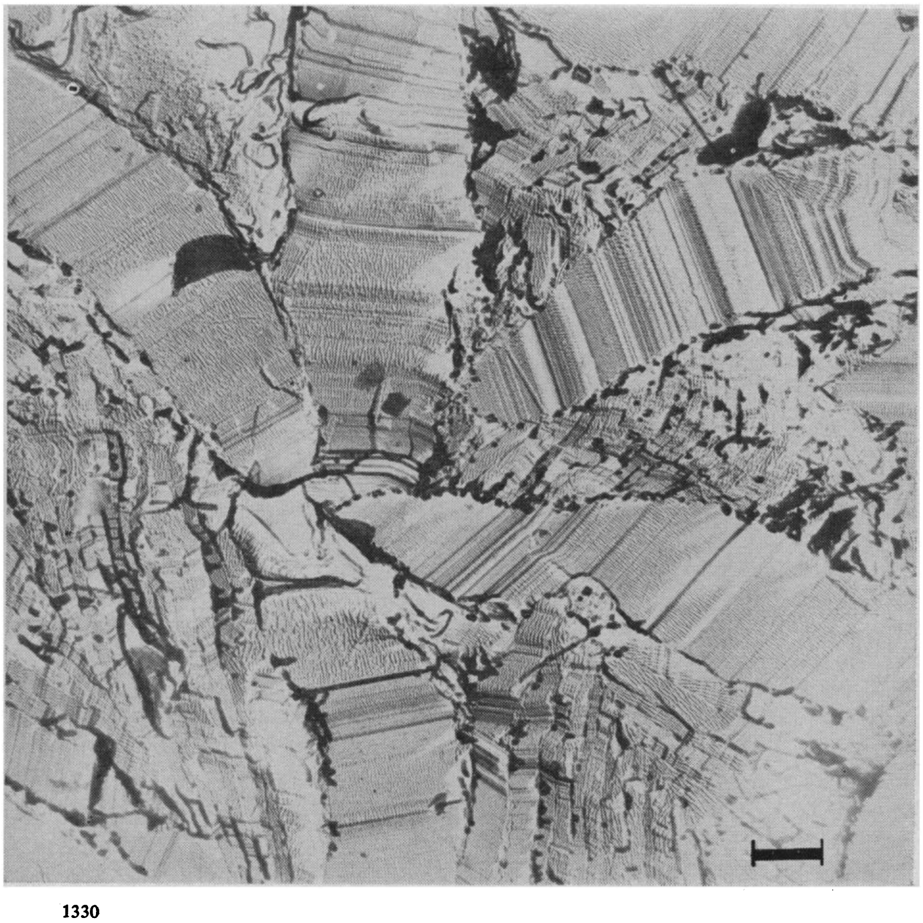

Fig. 2 (bottom left). Electron micrograph of a replica of the same fracture surface as in Fig. 1, but taken after the sample was heated for 3 minutes to 120°C. The scale bar represents 1 μ.

annealed at 120°C, ripples 200 to 300 Å thick cover the pulled out fibers (*7*). (ii) Pennings and Kiel found string-like fibrous polyethylene crystals from stirred solutions. On top of these crystals which are, for the most part, extended-chain crystals, folded-chain crystals deposit in later stages of crystallization and give the appearance of shish kebabs (*8*). (iii) Keith and coworkers on crystallizing polyethylene from a paraffin solution found that string-like bundles of tie molecules form between spherulite branches (*9*). With these bundles as substrates for further polymer crystallization, folded-chain lamellae, again with the shish kebab appearance, grow on the fibrous backbone (*10*).

In all cases an extended-chain crystal could serve as a nucleus for later folded-chain crystal growth. Large surface area extended-chain crystals, however, are unstable, collapse, and recrystallize into folded-chain crystals. As a result small extended-chain nuclei may not form spontaneously and then initiate extended-chain crystal growth. Fold period extension is a secondary process for the production of extended-chain crystals from polymer melts or solutions.

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