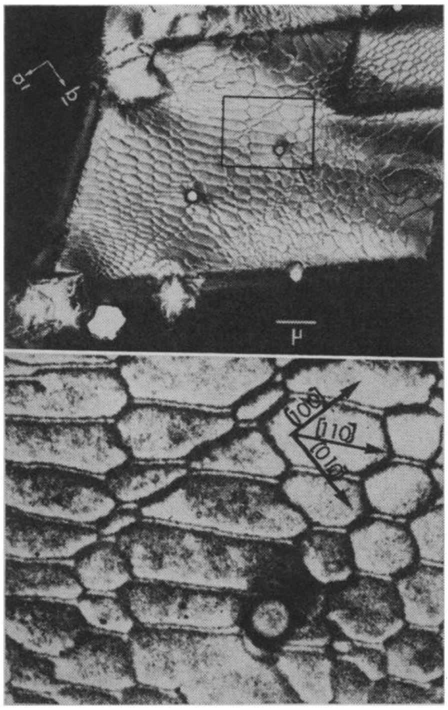
Dislocation Networks in Folded-Chain Polyethylene Crystals

Abstract. *Interaction between the fold surfaces of polymer crystals can be strong enough to concentrate any mismatch in orientation into a network of dislocations. Direct observation of these networks by diffraction contrast electron microscopy yields strong evidence in favor of polymer crystallization by a regular chain-folding mechanism.*

In the crystal-defect concept of polymer structure (*1*) it is assumed that a crystalline polymer is composed of small crystalline domains separated by arrays of various kinds of dislocations. Dislocations in polymer crystals have been detected by the moiré technique (*2*), which has also been used (*3*) to detect arrays of edge dislocations characteristic of tilt boundaries at the intersection of two regions of the same crystal grown at different temperatures.

In this report we show the direct observation of pseudo-hexagonal networks between superimposed folded-chain polyethylene crystals (see Fig. 1). These networks differ from the moiré patterns observed by Bassett and by Holland (*4*) in the extent of contact or interaction between the folds of the two crystals. This interaction has caused the mismatch in orientation between the two crystals to be concentrated into a network of dislocations. When the interaction across the fold surfaces is strong enough to form a network of dislocations we can equally well consider the system as a single crystal with two domains separated by an array of dislocations. Analysis of the Burgers vectors shows that these networks are frequently distorted arrays of screw dislocations which are characteristic of twist boundaries.

The material used was a fraction (molecular weight, 10,000) of a Marlex-50 type linear polyethylene. The crystals are approximately 100 Å in thickness and require about ten folds per molecule. Crystallization from 0.01 percent xylene solution was accomplished both isothermally and by slowly cooling the hot solution to room temperature. The suspension of crystallized material was sampled by depositing it in drops onto carbon-coated grids, and the grid-preparation was examined by direct transmission in an EM-200 Philips Electron Microscope. With this particular fraction and crystallization technique a predominance of bilayered crystals was produced (*4*). While most of these bilayered crystals produced moiré patterns of the type already re-



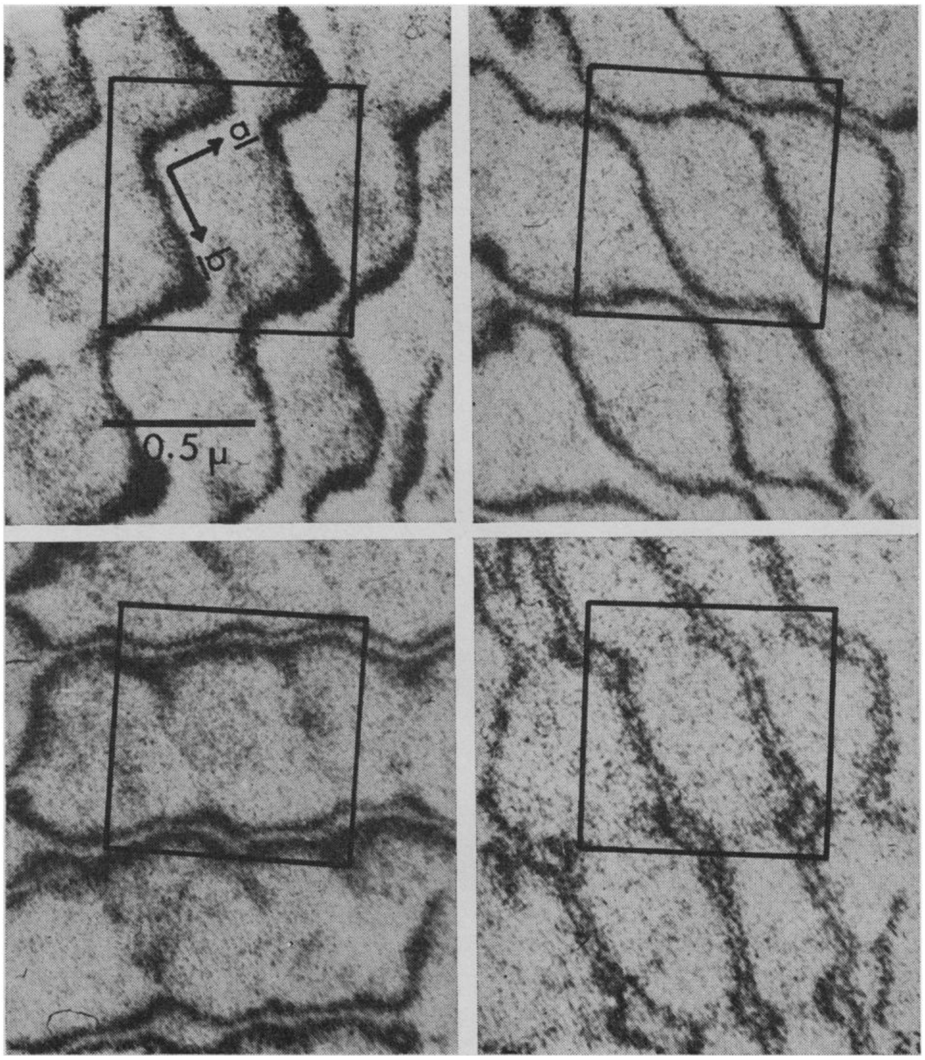


Fig. 1. (above). Dislocation network between two folded-chain polyethylene crystals. All strongly diffracting planes are contributing to the observed contrast. Bright-field technique. Contrast has been reversed in printing so that dark areas correspond to regions of high transmission. Lower photograph is an enlargement of insert above. Fig. 2 (right). Enlarged view of a network similar to that of Fig. 1 photographed with contrast restricted to a single diffracting plane. Upper left (110); upper right (1$\bar{1}$0); lower left (200); lower right (020).

ported, occasional crystals yielded patterns characteristic of networks (Figs. 1 and 2). If the network lies between the two crystals, the absence of contrast when the imaging plane contains the Burgers vector indicates that the network is composed of three sets of dislocations having Burgers vectors [100], [010], and [110]. The double image parallel to the [110] direction in Fig. 1 indicates a dissociation into partials as follows:

$$[110] \rightarrow [\tfrac{1}{2}\,\tfrac{1}{2}\,0] + [\tfrac{1}{2}\,\tfrac{1}{2}\,0]$$

The narrow ribbon of stacking fault between these two partials corresponds to a region in which the plane of the polyethylene chain in one crystal is twisted approximately 90° with respect to the other crystal. The absence of stacking-fault contrast is to be expected since $b \cdot g$ is integral for all strongly diffracting planes. Possibly the other two dislocations also dissociate into partials, and a complete analysis of the diffraction contrast exhibited by these dislocations should settle this question (*5*).

The observation of dislocation network formation between two folded-chain polyethylene crystals has important significance with regard to the nature of the molecular folds. Although some workers (*6*) suggested a regular molecular folding of the chains, and although the subsequent description of the hollow pyramidal nature (*7*) and the cleavage properties (*8*) support this conclusion, others (*9*) have concluded that a layer of amorphous material occurs on the fold surface of these crystals. We feel that it is very difficult to interpret the careful determination of the crystallographic nature of the fold surface with any model other than that of regular molecular folding. From our observations we conclude that the molecular folds must be sufficiently regular so that the molecular forces across the folds are strong enough to align the two crystals perfectly in some regions and to concentrate any misalignment into a network of dislocations. In other words, the molecular fold surface should be considered as a crystallographic plane which can pack with another similar fold plane and continue the crystal along the direction of the chain axis. Thus not only can a polyethylene molecule crystallize by a regular molecular folding mechanism but also such a chain-folded crystal is not restricted in size along the chain axis by the fold length.

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Dolomitization of the Mid-Pacific Atolls

Abstract. *The origin of the dolomite which occurs beneath the atolls of Funafuti, Kita-daitō-jima, and Eniwetok in the Pacific Ocean can be explained by the reaction of hypersaline brines with transported or buried reef skeletal material. Dolomitization could have taken place at the sediment surface in shallow restricted back-reef lagoons and tidal flats or below the surface by reflux action. Measurements of oxygen isotopes in samples of dolomite can be interpreted as indicating an origin from evaporated, isotopically-heavy sea water.*

Many hypotheses have been offered to explain the origin and distribution of dolomite $CaMg(CO_3)_2$ which occurs beneath the atolls of Funafuti, Kita-daitō-jima, and Eniwetok in the western and southern Pacific Ocean. These hypotheses were summarized and discussed recently by Schlanger (*1*). Interest in the dolomites stems from their uncomplicated geological history and their isolated location far from any source of magnesium-bearing solutions other than sea water. Paleontological studies have shown that the ancient calcareous organisms which have been dolomitized are similar to forms now living on the atolls, so that fossil materials which now consist of dolomite must originally have been made up of calcite and aragonite.

In summarizing the available information and hypotheses of origin, Schlanger (*1*) states:

> Any attempt to explain the formation of dolomite in these atolls must take the following into account:
>
> 1) The vertical distribution of dolomite in all drilled atolls . . . . [It is not a simple function of depth and, therefore, pressure.]
>
> 2) The presence of dolomite as a distinct mineral phase in limestones that contain as little as 2- to 3-percent $MgCO_3$. Leaching of originally magnesium-rich rocks could not account for these traces of dolomite . . . .
>
> 3) The differing susceptibility [from drill hole to drill hole] of any single fossil group to dolomitization . . . .
>
> 4) The apparent lack of effect of primary porosity on dolomitization . . . .
>
> 5) The lack of co-existent dolomite and aragonite . . . . [Only calcite occurs with dolomite.]
>
> 6) The lack of correlation between length of immersion in sea water and intensity of dolomitization suggests that mere prolonged soaking in magnesium-rich water does not by itself cause dolomitization.
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> 7) The wide variety of secondary textures seen in limestone from these atolls suggest that emplacement of dolomite takes place in several ways with different paragenetic sequence [including massive replacement, layered void filling with interlayers of calcite, and volume-for-volume replacement with preservation of organic structures].
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> 8) The fact that the dolomite from these atolls is structurally calcium rich [protodolomite of Goldsmith and Graf (*2*)].
>
> 9) The fact that most of the limestone from both atolls and higher islands in the Pacific is not dolomitized. Therefore, one must look at dolomitization as an 'abnormal' rather than as a 'normal' diagenetic effect.
>
> 10) That the three-dimensional distribution of dolomite in the subsurface of any atoll is unknown . . . .

In this report a new hypothesis is outlined which successfully meets all the above requirements.

The formation of dolomite in present day sediments has only recently been demonstrated unequivocally. Radiocarbon dating has shown that dolomite is forming in the coastal region of South Australia (*3*), on the west coast of the Persian Gulf (*4*), on the island of Bonaire in the Netherlands West Indies (*5*), in the Bahama Islands