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Morphology of Polyoxymethylene

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Synopsis

This paper reviews published data on the morphology of polyoxymethylene crystallized from the solution and melt. Recent work in these areas as well as the mechanism of deformation, effect of annealing, and structure of solid-state polymerized polymer are also described.

In comparison with the number of papers describing polyethylene only a limited number on the morphology of polyoxymethylene have been published. Nevertheless, it is nearly as well defined. The purpose of this paper is to review the published results as well as to describe briefly several new results that are presently being published in greater detail elsewhere.

SOLUTION CRYSTALLIZATION

Polyoxymethylene crystallizes from dilute solution, for a wide range of conditions of temperature and solvents, in the form of well-defined, basically hexagonal, lamellae about 100 A thick (*1*–*5*). In some cases, the range of conditions for which have not yet been determined, the crystals can be star-shaped (*2*) or can develop further re-entrant faces and become dendritic. The star shape has been suggested to result from the nucleation of new fold planes, primarily at the apices of the hexagon, which takes place faster than the fold planes complete their growth. As a result "impurities" and imperfect folds accumulate along the radii normal to the fold planes, that is, at the center of the plane faces of the hexagon. The

FIG. 1. Polyoxymethylene crystals grown from a 0.05% solution in bromobenzene at 115°C. (Micrograph of C. A. Garber.)

growth faces of the larger crystals in Fig. 1 are slightly curved, suggesting a tendency to the development of re-entrant faces.

In one of the early papers (*2*) it was suggested that polyoxymethylene crystals have a hollow pyramidal structure, similar to that reported of polyethylene in the same paper. No further evidence has been presented. The central pleats in Fig. 1 may arise from a pyramidal structure or the curved shape of the crystals, as described by Bassett (*4*) (see below). One notes in Fig. 1 that a small bump, presumably the nucleus, is visible at the center of each crystal.

An indication of the influence of the folds on the structure of the crystal is found in Bassett's report (*4*) interpreting some excellent moiré patterns he obtained from bilayer crystals. These patterns show that the crystals have, in addition to any pyramidal structure due to a staggering of adjacent folds, a slight curvature or dish shape. This curvature may result from a difference in spacing between adjacent $\{10\bar{1}0\}$ planes that are fold planes and those that are not. Bassett was able to show that in his crystals the $\{10\bar{1}0\}$ fold planes are 0.012 A farther apart than the $\{10\bar{1}0\}$ nonfold planes. This results in an expansion of the lattice in each fold domain along a radius normal to the growth face and the resulting curvature. Not only is this observation (which Bassett has also reported for poly-4-methylpentene-1) of importance to the understanding of the morphology of polymer single crystals, but it is also of significance with respect to x-ray crystal-size determinations of bulk polymers. If, as would be expected, a similar effect occurs, a portion of the x-ray line-broadening from which crystal size is determined would be due to this difference in spacing.

As in most polymers (*5*), the thickness of polyoxymethylene crystals for a given solvent is a function of crystallization temperature, increasing with increasing temperature (*6*). The influence of solvent is considerably greater than has been found for polyethylene (*5*). After growth a thickening of the crystals can occur during annealing (*5,6*). A temperature of at least 125 or 130°C is required, that is, one above the α transition. As in the case of polyethylene, thickening of single lamellae is accompanied by the formation of holes (Fig. 2). The holes, however, are much smaller and more closely spaced. Other than, perhaps, its effect on solution temperature and, therefore, supercooling, small amounts of comonomer in the polymer, as in Celcon (Celanese Corporation of America), do not appear to affect the morphology of the crystals. (It should be pointed out that occasionally diamond-shaped crystals are found in polyoxymethylene preparations. Some, but not all, of these crystals yield polyethylene diffraction patterns. Polyethylene crystals have also been observed in preparations of a number of other commercial polymers, the contamination apparently coming during production or shipping or from the solvent.)

Thickening of the crystals parallel to the chain axes during growth occurs, as in all polymer crystals, by a screw-dislocation mechanism. Barnes and Price (*3*) have related the radial size of

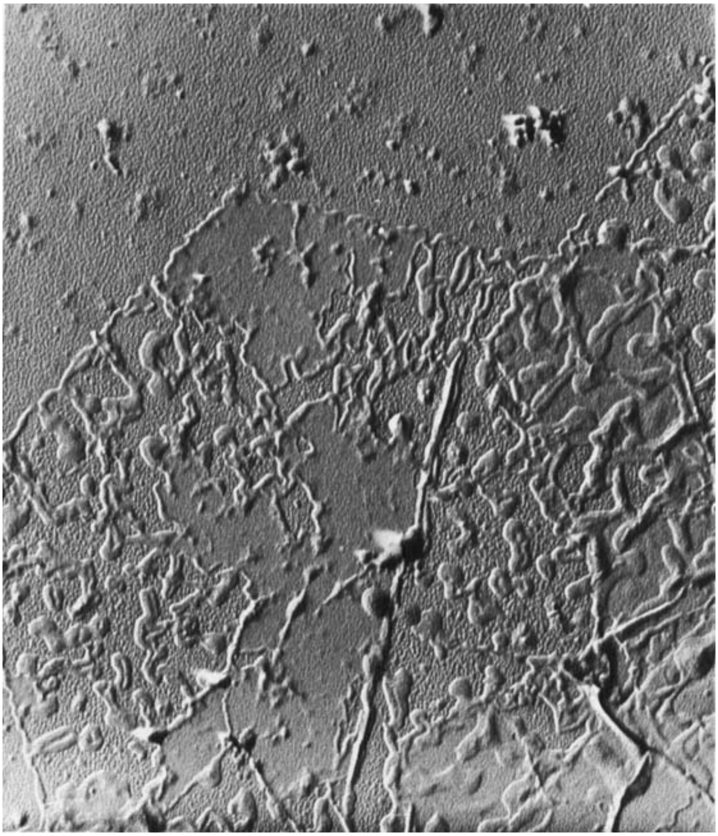

FIG. 2. Crystal of polyoxymethylene annealed at 165°C for 10 min. (Micrograph of D. R. Carter.)

the successive lamellae to screw-dislocation growth theory and shown that it is only partially applicable. The spacing increases with distance from the center of the spiral. In addition, the successive lamellae are found to be slightly rotated, often in a regular, alternating manner (2). This rotation may result from the difference in fold plane–nonfold plane spacing reported by Bassett.

Van der Heijde (7) has described "hedgerow" or "shish-ke-bob" crystals grown from dilute solutions of polyoxymethylene prepared by solid-state polymerization of trioxane. They consist of long fibrils with an apparent helical structure, on which a number of lamellae have grown more or less normal to the fibril axis. The mechanism of growth of these structures is not yet known. Similar structures, except that the helical structure of the fibril has not been observed, have been grown from polyethylene solutions that are maintained above normal crystallization temperatures and stirred (*8,9*).

Hedrites or axialites of polyoxymethylene have been grown from 1% solutions in phenol (*1*). They formed a skin on top of the solution, as it was slowly cooled over a period of several days, and thus may correspond to crystallization from an even more concentrated solution. Although electron micrographs are not available, the axialites are believed to consist of a stack of uniformly oriented lamellae, probably arising from a screw dislocation.

MELT CRYSTALLIZATION

Polyoxymethylene crystallized from the melt in thin films yields samples that give easily obtained, clear replicas. As the film thickness increases, the surface tends to become obscured. In other polymers this has been attributed to low-molecular-weight polymer or additives, exuding to the surface. In addition, well-defined small-angle x-ray diffraction maxima are observed. Although both of these features suggest that polyoxymethylene would be an excellent polymer for a morphological study of polymers crystallized from the melt, only a few reports have been published (*10–12*).

A connecting link between solution-grown single crystals and melt-grown spherulites is provided by the melt-grown axialites. When thin films of polyoxymethylene are crystallized slowly from the melt, hexagonal and oval axialites are formed (*10*) (Fig. 3). These structures, as for the solution-grown axialites, have an axis of symmetry normal to the lamellae of which they are composed. The hexagonal axialites yield single-crystal-like x-ray diffraction patterns (the spots are slightly arced) when the beam is parallel to their axis. In the hexagonal axialites this axis, which appears also to be a screw-dislocation axis, is normal to the substrate, whereas in the ovals it is parallel to the substrate. The ovals consist of a sheaf of lamellae that diverge only slightly as they grow out from the center. Cracks can be observed between the lamellae. The regions at the end of the short central axis (the axis of the sheaf of lamellae) are formed by lamellae more or less parallel to the substrate. Their origin and relation to the sheaf is not known.

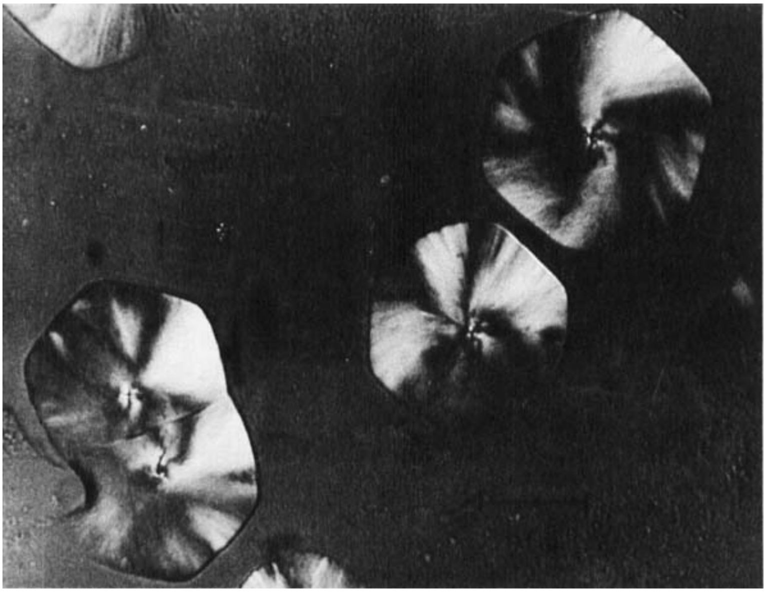

FIG. 3. Axialites of polyoxymethylene crystallizing in a thin molten film of polyoxymethylene at 161°C. They have a diameter of 100 μ. [Crossed polaroids, gypsum filter (*10*).]

Under less regular crystallization conditions (thicker films, faster rates) spherulites are formed that display a typical Maltese cross in the optical microscope (*13*). In general, they are nonbanded, although spherulites with a band or ring structure have been grown under thermal conditions that would yield axialites in sufficiently thin films (*5*) and have also been grown (by O'Leary in our laboratory) by means of the evaporation of hexafluoroacetone sesquihydrate solutions (Fig. 4).

In the electron microscope the spherulites are seen to be composed of radially oriented lamellae (Fig. 5) (in the banded spherulites they appear to twist about the radii as in polyethylene (*5*)). The nucleus is seen to consist of a sheaf of lamellae which has been suggested to arise, as in the axialites, from a central screw dislocation but with various orientations with respect to the surface. Electron diffraction patterns from individual lamellae stripped from the surface show (*14*) that the molecules are folded within the lamellae. Interleaving of the lamellae from neighboring spherulites occurs at their boundaries. Replicas of fracture surfaces show that the lamellae are present throughout the sample (*11*).

The origin of the discrete small-angle x-ray diffraction from polyoxymethylene is not yet clear. In general, one, sometimes two (*15*) or even three (*16*), maxima can be observed. The largest and most intense maximum does not appear to be directly related to the lamella thickness observed in the electron microscope when more than one maxima are presented (*16*); when only one is present, the two values appear equal in some cases but not in others (*17*).

Carter and Baer (*15*) have suggested there may be two types of lamellae, differing in their fold surfaces, present in a sample. In DTA measurements two melting peaks are observed for isothermally crystallized samples. They find that in plots of lamella thickness (using Bragg's equation) versus melting point the largest period versus the highest melting point extrapolates to an expected equilibrium melting point of about 205°C, whereas the second period versus the lower melting point is in agreement with similar solution-grown single-crystal data and extrapolates to a melting point of 181°C. The latter temperature is below that at which solid-

FIG. 4. Banded spherulite of polyoxymethylene prepared by evaporation at room temperature of a hexafluoroacetone sesquihydrate solution. [O'Leary, (*19*).]

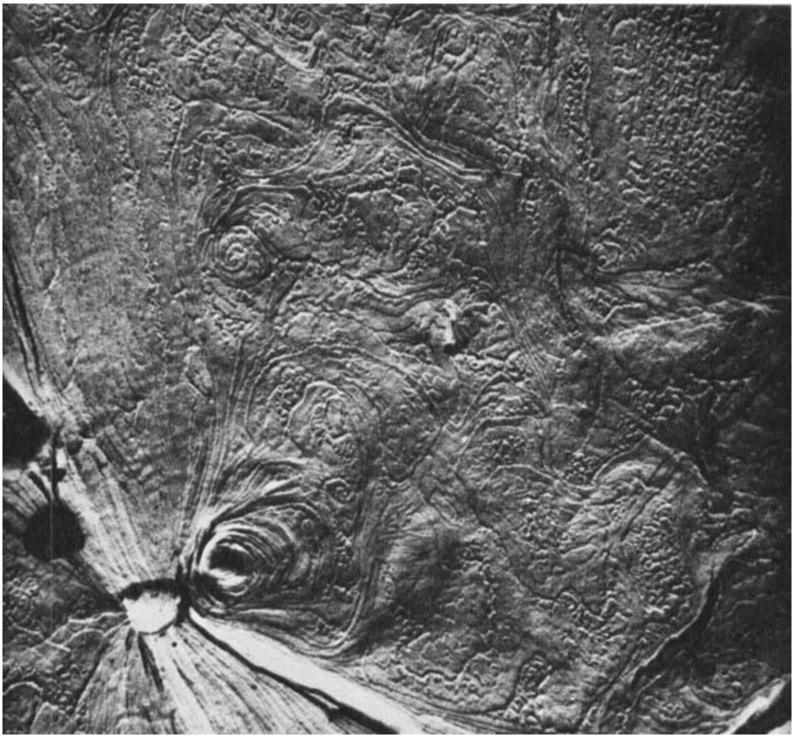

FIG. 5. Electron micrograph of a replica of the center of a polyoxymethylene spherulite. The spacing between the micron markers represents 1 μ.

state polymerized polymer melts. The present relationship between small-angle x-ray diffraction and polyoxymethylene morphology is clearly not satisfactory, and more work is in progress.

Annealing of bulk-crystallized polyoxymethylene at temperatures above about 130° (the required temperature increases with increasing lamella thickness) results in a small increase in long-period spacing. The relative increase for equivalent annealing times and temperatures, when measured at room temperature, is considerably less than for polyethylene. O'Leary and Geil have recently shown that both the intensity and the long period change reversibly with temperature, when measured at the annealing temperature (*18*). This reversible change is in addition to the above-mentioned, more usual, but small irreversible increase associated with an increase in lamella thickness during annealing. This effect is also not adequately explained at the present time.

Sulfuric acid (*12*) and iodine (*19*) appear to selectively etch polyoxymethylene, revealing spherulitic structure on molded surfaces. So far, however, the etching has not permitted detailed observations of the internal structures of samples. Various debris, including repolymerized single crystals of polyoxymethylene similar to those obtained from formaldehyde in sulfuric acid (see last section), obscure the surface. In some samples fibers resembling the interlamellar links observed in polyethylene (*20*) have been observed (*19*).

ORIENTATION AND DEFORMATION

Highly oriented transcrystalline layers are formed on commercially molded polyoxymethylene. In these layers the lamellae are oriented normal to the surface and, in injection moldings,

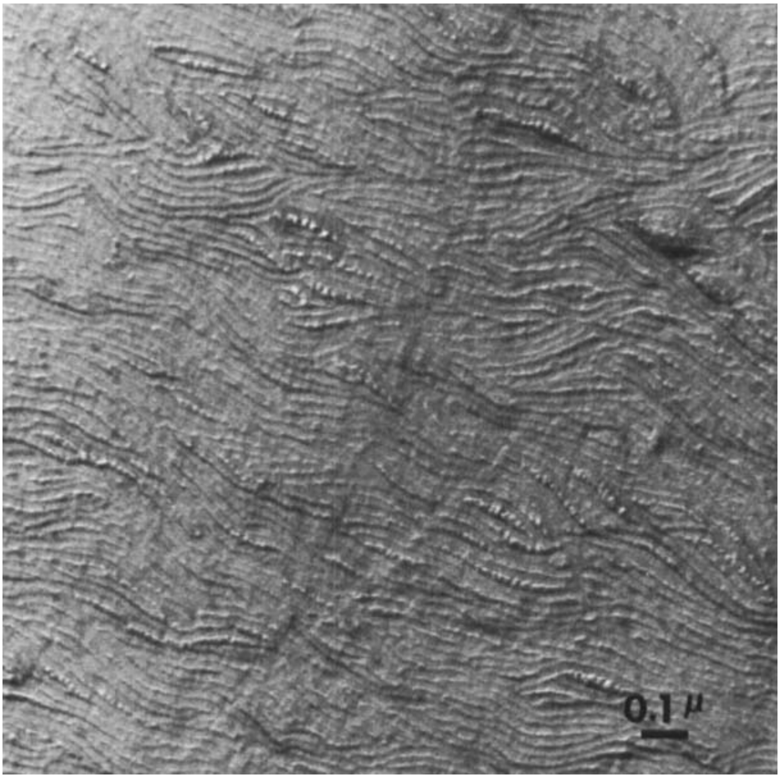

FIG. 6. Surface replica of an injection-molded annealed sample drawn approximately 15%. [Davis, (*21*).]

normal to the flow direction. Davis has shown that this orientation, which would be expected to affect the physical properties of moldings, is clearly revealed by annealing treatments (*21*). If the samples are slightly drawn numerous fibrils are found to stretch across cracks between the lamellae (Fig. 6). He interprets these fibrils as also being interlamellar links.

Polyoxymethylene samples, when drawn at room temperature or below, tend to break in a brittle fashion. Even slow-cooled samples, however, can be drawn at temperatures above about 100°C. Gross aspects of the type of draw depend on the crystallization conditions. In rapidly cooled samples macronecking takes place, the deformation zone extending over a distance corresponding to a number of spherulites (*19*). In slow cooled samples (Fig. 7) micronecking occurs, the deformation being highly localized with abrupt boundaries between drawn and undrawn material (5).

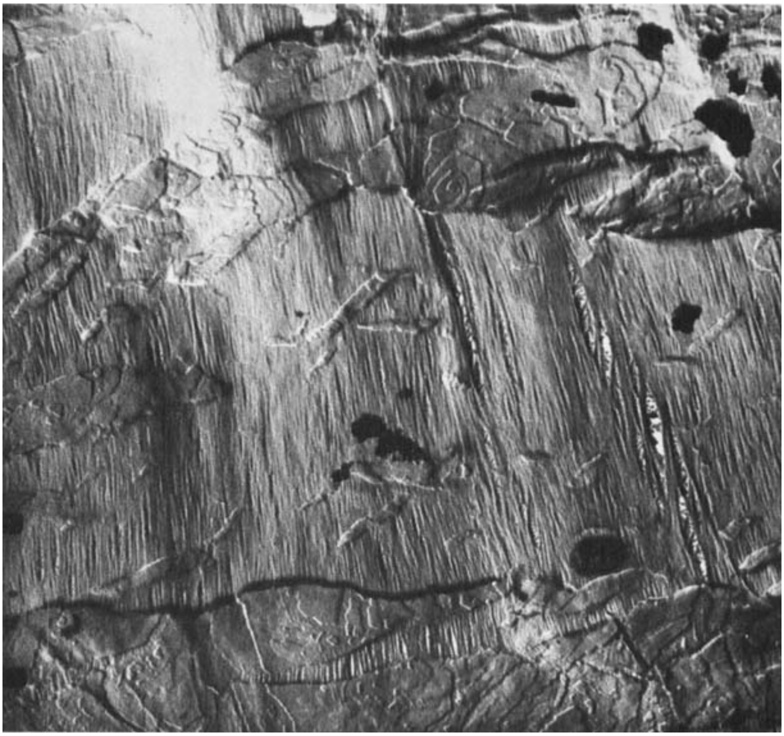

FIG. 7. Micronecking region of a partially drawn slow-cooled film of polyoxymethylene. The spacing between the micron markers represents 1 μ.

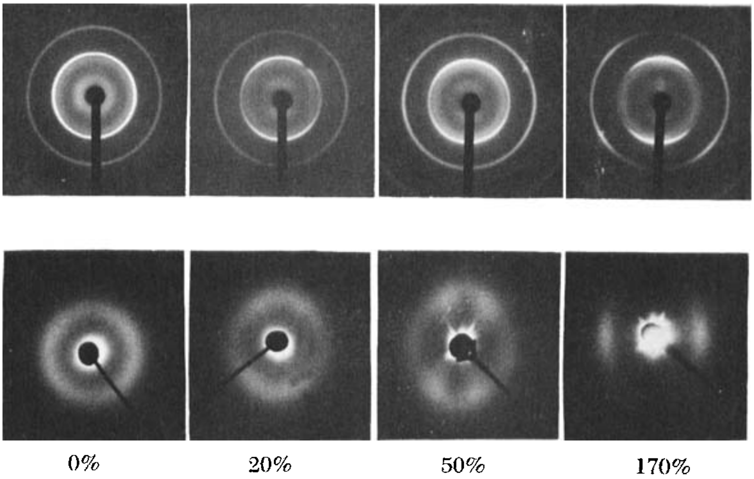

FIG. 8. Wide- and small-angle x-ray diffraction as a function of amount of draw. [O'Leary, (*19*).]

The fully drawn material, in both cases, consists of 100-A-diameter fibrils, the fibrils being most clearly revealed when some degree of biaxiallity is present to split the fibrils apart.

O'Leary has been studying the wide- and small-angle x-ray diffraction patterns from polyoxymethylene as a function of draw ratio (*19*). These results show (Fig. 8) that there is considerable change present in the small-angle pattern (it becomes 4-point-like) when little or no change is visible in the wide-angle pattern. With further draw a new small angle maximum appears on the meridian, while the original spacings disappear. These patterns are at present interpreted (*19*) as resulting from a breakup and loss of diffraction from lamellae oriented normal to the draw direction at low elongations, at the same time that tilting of the molecules is taking place in lamellae parallel to the draw direction. The fully drawn material is viewed as consisting of irregularly packed small blocks of folded molecules.

Upon annealing of the drawn material there is a major increase in intensity of the diffraction maxima as well as a shift to smaller angles (*18*). The change in both angle and intensity are partially reversible. The irreversible portion is believed to result from a regularizing of folds and development of lamellae oriented normal to the draw direction and an increase in the fold period similar to that seen in unoriented samples. The origin of the reversible portion, which can correspond to a change in periodicity of 100 A or more, is, as in unoriented samples, not yet known.

AS POLYMERIZED POLYMER

When formaldehyde is polymerized in concentrated sulfuric acid over a long period of time, hexagonal rod-shaped crystals develop (5). The length-to-width ratio is found to vary widely in different preparations. The chains are presumably fully elongated in these crystals, although Fischer has reported (22) the presence of striations with a 200-A spacing normal to the hexagonal axis. The morphological significance of the striations is not yet known.

Recently considerable interest has been shown in the preparation of polyoxymethylene by means of solid-state polymerization. Samples prepared by the irradiation of trioxane are found to consist of closely packed 250-A-diameter fibrils (Fig. 9). Electron diffraction shows that the majority of the molecules in each fibril are parallel to the axis of the fibril but that a significant number of

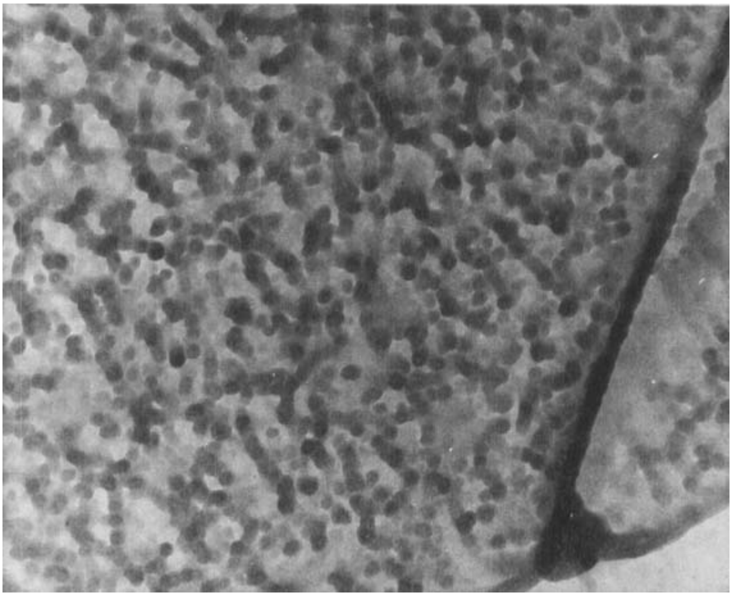

FIG. 9. Fracture surface of irradiation-polymerized trioxane. The surface is normal to the *c* axis of the polymer, the fibers being approximately 250 A in diameter.

molecules (and crystals) lie at an angle to the fibril. Their arrangement in the fibril cannot be explained at present.

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