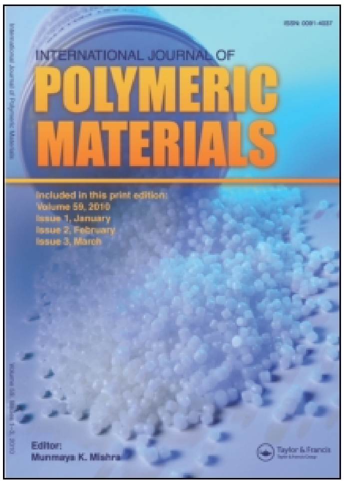

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Effect of Industrial Processing on the Morphology of Crystalline Polymers

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Effect of Industrial Processing on the Morphology of Crystalline Polymers

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Our understanding of crystallinity in polymers was greatly advanced by the discovery of the folded-chain lamella as the unit of structure in crystallization both from solution and the melt. Subsequently, it was found that the organization of lamellae into larger units is dependent on the nature of the nuclei initiating crystallization. Under quiescent conditions, nuclei are randomly distributed throughout the crystallizing volume and growth proceeds independent of neighboring structures. In the presence of shearing stress, either in a melt or in solution, nuclei are not randomly distributed but appear along "rows". However, what seems to be a row of nuclei actually is a special kind of nucleus, a fibril of oriented molecular chains, about 300 Å in diameter. The presence of these fibril nuclei determines whether the polymer will crystallize spherulitically or in a "row structure" morphology. The type of morphology, in turn, influences many of the physical properties, particularly the stress-strain relationship. Industrial processes in which "row structures" play a major role by virtue of crystallization under melt shear stress include blown film, injection molding and fiber spinning.

INTRODUCTION

With the advent of industrial production of synthetic polymers in the 1930's and 1940's based on the development of nylon and polyethylene resins, it was recognized that crystallinity was an important factor in determining the physical properties of the final product. In this period, numerous efforts were made, primarily using x-ray diffraction and optical microscopy, to understand the nature of this crystallinity. From these early efforts came the concept of the "fringed" micelle,[1] in which a single molecule would be included in a series of ordered crystallites and disordered amorphous regions. This simple two-phase concept provided a useful model for expressing quantitatively the relationships between crystallinity and bulk properties such as modulus, tensile strength, transitions, etc. This model was particularly useful in the development of mathematical expressions for characterizing physical properties. It proved so useful that it was widely accepted as fact even though direct evidence of its validity was lacking. The deficiency of this model became evident when more detailed studies of structure were made. The development of a more accurate knowledge of the crystalline texture of polymers, that is, polymer morphology, is discussed in detail in numerous articles. As an introduction to the application of morphology to industrial processing, some of the work on morphology of polyethylene spherulites by Bryant[2] will be reviewed since it is pertinent to later discussions. On the basis of observations in the optical microscope and measurements of the refractive index, Bryant was able to determine that the chain molecules were oriented with their long axes normal to the spherulite radii. This finding was difficult to understand in terms of growth behavior expected from the fringed micelle concept. Figure 1 shows Bryant's interpretation of the spherulite structure in terms of the arrangement of molecule units and crystal units. This interpretation was very difficult to rationalize in terms of the fringed micelle concept and clearly showed its inadequacy.

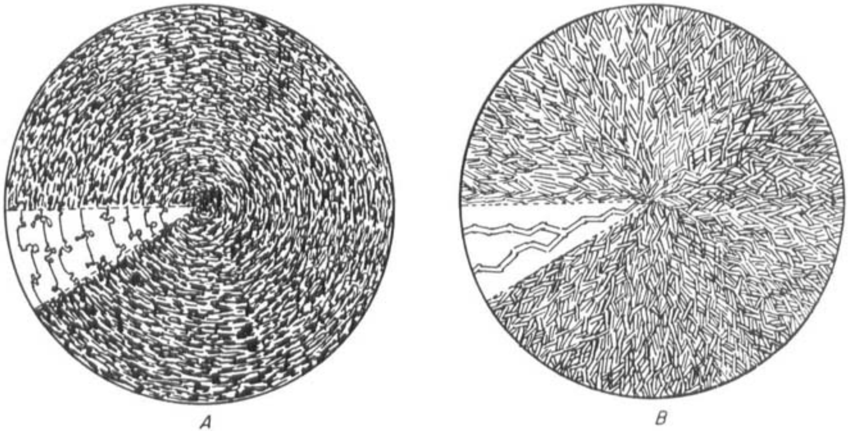

FIGURE 1 Idealized structure of polyethylene spherulite cross section (A) with molecule as structural unit; (B) with crystallite as structure unit [W. M. D. Bryant, Ref. 2].

THE FOLDED CHAIN LAMELLA

As the need for more accurate, direct observations of the crystalline texture became increasingly evident, an observation of major significance was made with the electron microscope. In independent experiments by Till,[3] Keller,[4] and Fischer,[5] published in 1957, single crystals of polyethylene were grown from solution and the folded-chain mechanism of crystallization was proposed by Keller. This mode of crystallization, illustrated in Figure 2, was of great interest scientifically but its relevance to bulk crystallized material was not immediately evident. Therefore, a large number of experiments were performed to show that the folded-chain lamella is the basic structural unit of bulk material crystallized from both solution and the melt. For example, the lamella model and electron microscope data gave a more detailed insight into the structure of spherulites. Figure 3 shows an electron micrograph from a spherulite of polyethylene. This spherulite consists of folded chain lamellae, originating from the central nucleus and twisting along the direction of radial growth. If the twisting of the lamella is regular as in this

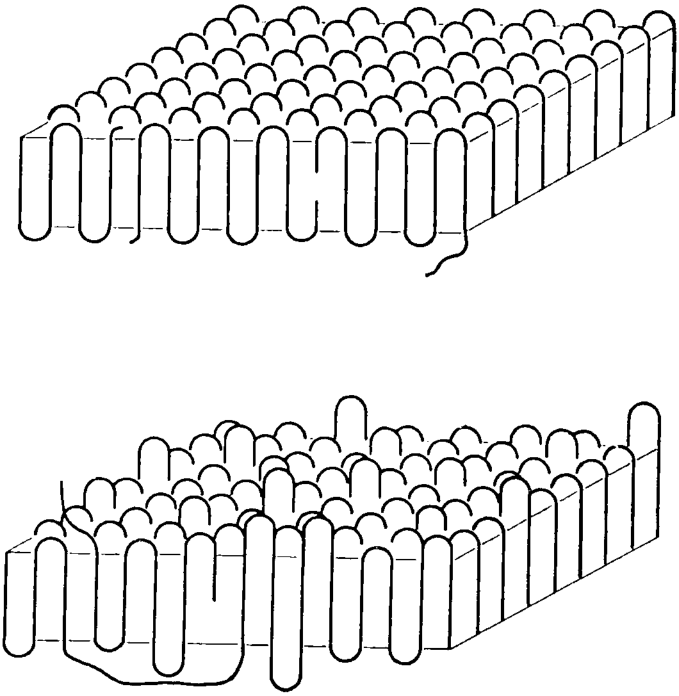

FIGURE 2 Folded-chain concept in crystal lamella. Top: Regular, adjacent re-entry. Bottom: Irregular, adjacent re-entry [Geil, Ref. 22].

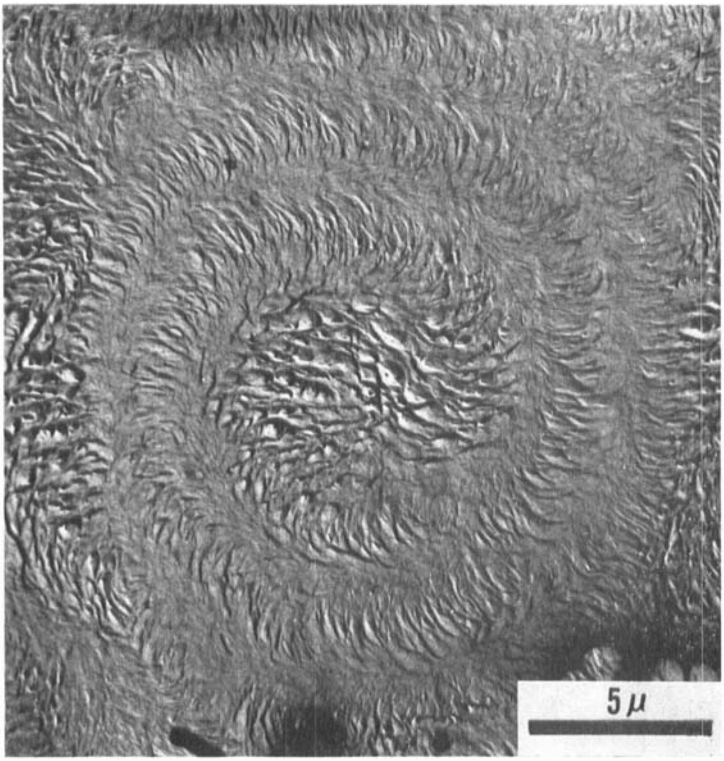

FIGURE 3 Ringed spherulite of linear polyethylene. Electron micrograph.

example, rings develop. It is interesting to note that this interpretation is entirely consistent with the conclusions of Bryant in Figure 1.

ROLE OF NUCLEATION

From experiments of the type described above, it was concluded that crystallization begins from a nucleus and proceeds with the growth of folded-chain lamellae until molecules available for crystallization are depleted as would occur with the intersection of two growth fronts of a spherulite. The same basic mechanism of growth via the folded-chain lamella operates for crystallization from both solution and the melt. Many types of secondary phenomena may occur such as splitting of lamellae into branches, spiral growths, rejection of noncrystallizable molecules into interlamella regions, etc. However, the model which has proved most useful in describing the crystallization process is the lamella. While the example discussed above is polyethylene, the lamella type of growth is characteristic of nearly all crystallizable polymers, including polyoxymethylene which is used in subsequent examples. The spherulite is the type of morphology found in crystallization of polymer which during crystallization is *quiescent*. Nuclei are situated in the solution or melt, more or less at random. That is, there is no direct correlation between the location of one nucleus and that of another. However, the type of nucleation found under quiescent conditions is not the same as that which generally occurs in industrial processing of crystalline polymers. Processes such as extrusion, spinning and molding involve crystallization while the polymer is under *stress* from shearing of the crystallizing volume. It is the understanding of the role that stress plays in controlling nucleation which provides the key for relating the spherulitic structure to the different types of structures found in industrial products.

The initial understanding of the effect of stress on nucleation came from the work of Keller[6] who stretched a piece of polyethylene while it crystallized. He found that crystallization was initiated from a continuous series of nuclei along the flow lines and produced a row of oriented lamellae which he termed the "row structure". An electron micrograph of a row structure of polyethylene is shown in Figure 4.

Subsequently, in a study by Keller and Machin,[7] the relationship between the "row structure" and an odd morphological growth called the "shish

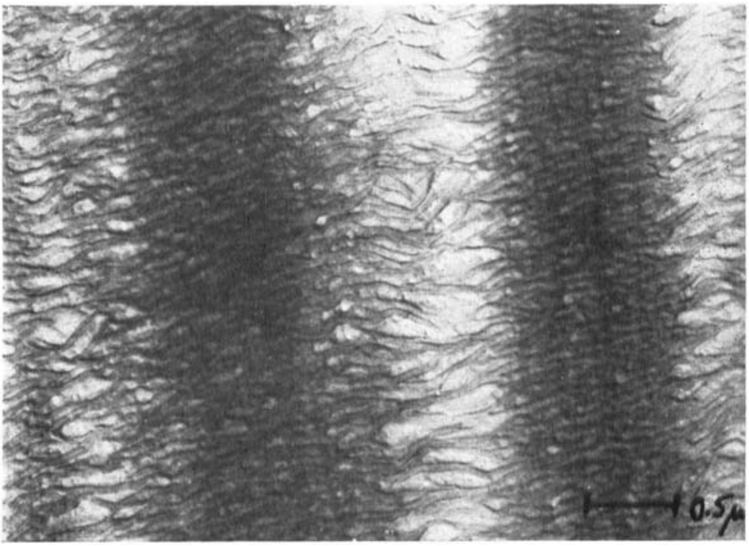

FIGURE 4 "Row Structure" in film of polyethylene. Electron micrograph [Keller and Machin, Ref. 7].

kebab" was established. The "shish kebab" structure was found in polyethylene crystallized from stressed (stirred) solution by Pennings *et al.*[8] A schematic representation of this structure is shown in Figure 5. Under stress, a small amount of material is drawn into a very small fiber, or fibril, perhaps only a dozen molecules in diameter. These fibrils act as nuclei for subsequent overgrowth of folded chain lamellae. The plane of a lamella is perpendicular to the fibril nucleus. Keller and Machin[7] proposed that this type of mechanism of nucleation was responsible for the "row structures" in polyethylene. Thus, the key to understanding the difference between the spherulitic structure formed from crystallization of a quiescent melt and the "row structure" formed from a stressed melt is the distribution of the nuclei. Spherulities are produced from a random distribution of nuclei which very likely are foreign particles in the melt. "Row structures" are produced from a central fibril which is, in effect, a row of contiguous nuclei. A second conclusion by Keller and Machin of significance is the effect of the degree of stress on the nature of the "row structure". As shown in Figure 6(A), under high melt stress the lamellae grow without twisting; under low stress (or no stress) the lamellae twist as growth proceeds from a nucleus. Thus, there is a direct correlation between a segment of a "row structure" crystallized under low stress and the radial section of a ringed spherulite as shown in Figure 3.

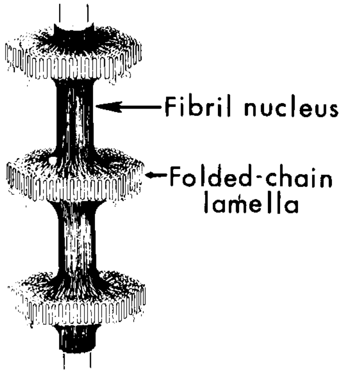

FIGURE 5 Schematic representation of "shish kebab" structure [Pennings *et al.*, Ref. 8].

In addition to effects of stress, Pennings, van der Mark and Keil[9] discuss effects of temperature. High solution temperature favors formation of the extended chain backbone; low temperature favors folded chain lamellae. They also propose a mechanism for the uncoiling of chains under stress to

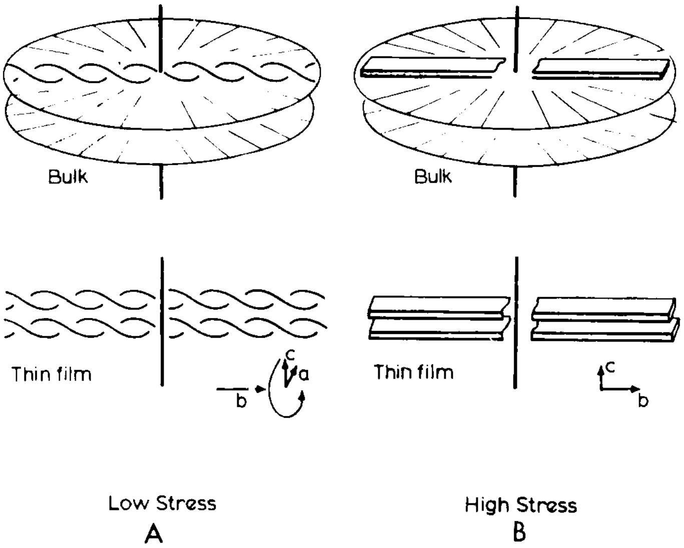

FIGURE 6 Effect of stress on development of row structure [Keller and Machin, Ref. 8].

create fibrils. Additional evidence for the extended chain nature of the central fibril has been derived from differential scanning calorimetry and infrared data by Pennings and van der Mark.[10] Pennings, Pijpers and Kovacs[11] report that the concentration of nucleating fibrils increases with increasing shear rate.

The effects of variations of temperature and stress on "row structures" in polymer crystallized from the melt has been reported by Hill, Keller, and Walton.[12] From investigations of lightly crosslinked polyethylene, they came to conclusions similar to those for stirred solutions described above. At temperatures too high for spontaneous nucleation, crystallization of fibrils could be induced by shearing the melt. Increasing the stress increased the number of fibrils and also caused the lamella overgrowths to maintain a planar conformation as in Figure 6(B). Their study also suggested that reduction of stress promotes growth of lamellae.

EXTRUDED FILM

Examples of "row structures", crystallized under conditions of low melt stress, have been found in extruded films of polyethylene and polyoxymethylene and in blown film in which the lateral expansion is not great. Garber and Clark[13] investigated the "row structure" in blown film of polyoxymethylene. They reported, for the first time, direct experimental verification of the fibril nuclei proposed by Keller and Machin. These fibril nuclei, while too few in number to have any measurable effect on the physical properties, are critical to the structure in that they produce a highly oriented assemblage of lamellae. As shown in Figure 7, lamellae grow from fibril nuclei, twisting in a fairly regular manner similar to the illustration in Figure 6(A) for crystallization under low stress. This type of film has a much higher elongation than a spherulitic form of the material. On the basis of electron micrographs and x-ray data from blown film of polyoxymethylene, Garber and Clark proposed a mechanism of deformation based on (1) the formation of a net-like structure in which the elements are bundles of twisted lamellae, and (2) a cooperative shearing and rotation of lamellae

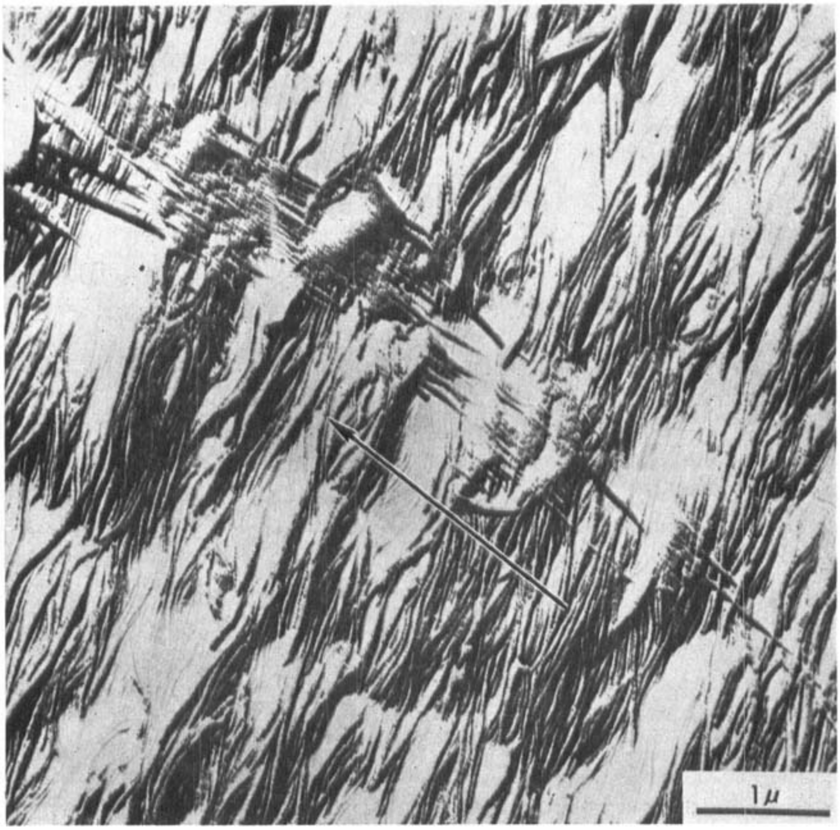

FIGURE 7 Surface of blown film of polyoxymethylene showing the nucleating fibrils aligned in the extrusion direction with twisted bundles of lamellae oriented normal to the fibrils. Electron micrograph [Garber and Clark, Ref. 13].

relative to each other similar to shearing of a deck of cards. This is the interpretation of the electron micrograph in Figure 8. By virtue of the initial orientation of the twisted lamellae bundles, the opening of the net-like structure with the concurrent shearing of the lamellae can proceed cooperatively such that a large total elongation results from comparatively small localized changes in the "row structure". The orientation of the lamellae,

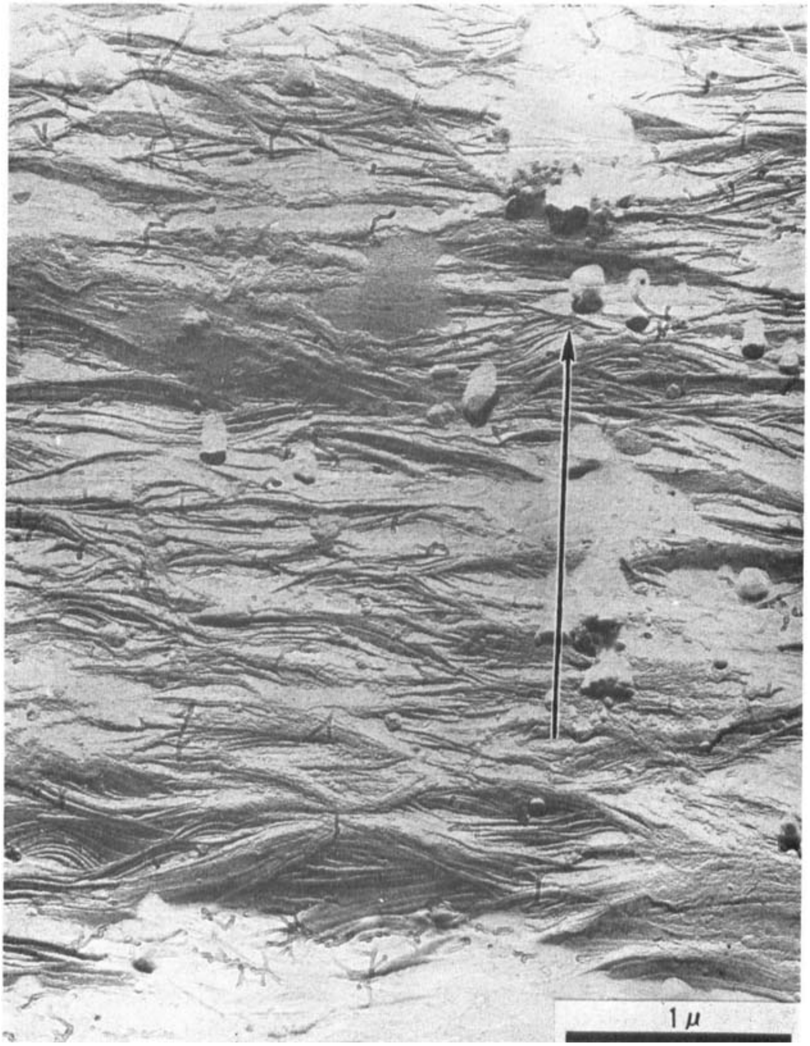

FIGURE 8 Surface of blown film of polyoxymethylene after 30% elongation showing shearing and rotation of lamellae. Electron micrograph [Garber and Clark, Ref. 13].

resulting from fibril nuclei, causes these small changes to have an additive effect on the macroscopic elongation. In contrast, spherulitic film of polyoxymethylene seldom shows an elongation greater than 10%. While higher elongation of spherulitic film can be obtained by drawing at elevated temperatures, massive destruction of lamellae occurs as reported by O'Leary and Geil.[14]

It has long been known that extruded film of polyethylene or blown film in which the degree of expansion is not great has an x-ray diffraction pattern which, on casual inspection, appears to have "*a*-axis orientation".[15] That is, the unit cell *a*-axis appears to be aligned preferentially in the direction of extrusion. A more accurate analysis of the x-ray data has been given by Lindenmeyer and Lustig[16] who interpret the data as a preferred orientation of the *b*-axis perpendicular to the extrusion direction with the *a*- and *c*-axes displaced about the *b*-axis. This interpretation is consistent with the "row structure" described by Keller and Machin[7] if we assume that fibrils initiate growth of lamellae, which under the relatively low stress of the process conditions, twist as they grow about the *b*-axis which is the direction of fastest growth. Varying the blow ratios may cause varying degrees of twist intermediate between the extremes of Figure 6.

INJECTION MOLDING

The crystallization processes occurring during injection molding have been studied by Clark[17] who determined the morphology of a molded bar of polyoxymethylene. As shown in Figure 9, the structure consists of a skin (to 0.005″), an inner layer called the "transcrystalline layer", and a core. The skin and the "transcrystalline layer" develop from a "row structure". Clark proposes that fibril nuclei are formed at the surface as the initial melt crystallizes on the mold wall. The initial polymer entering the mold crystallizes very rapidly, fixing itself to the wall while additional polymer spurts into the mold under high pressure. This portion of the melt crystallizes under high shear stress which creates fibril nuclei from which the lamellae grow without twisting. "Row structures" of the type illustrated in Figure 6(B) are formed. An electron micrograph of a replica from the surface is shown in Figure 10. The fibril nuclei are not resolved.

As the mold is filled, the shear stress becomes negligible and a fairly sharp boundary is formed between the lamellae which crystallize while the mold is filling (high melt stress) and those which crystallize after (low melt stress). This boundary is seen in Figure 9 at a depth of 0.005″. Under conditions of low stress, crystallization continuing from this boundary is similar to that illustrated in Figure 6(A) in which lamellae twist along the growth

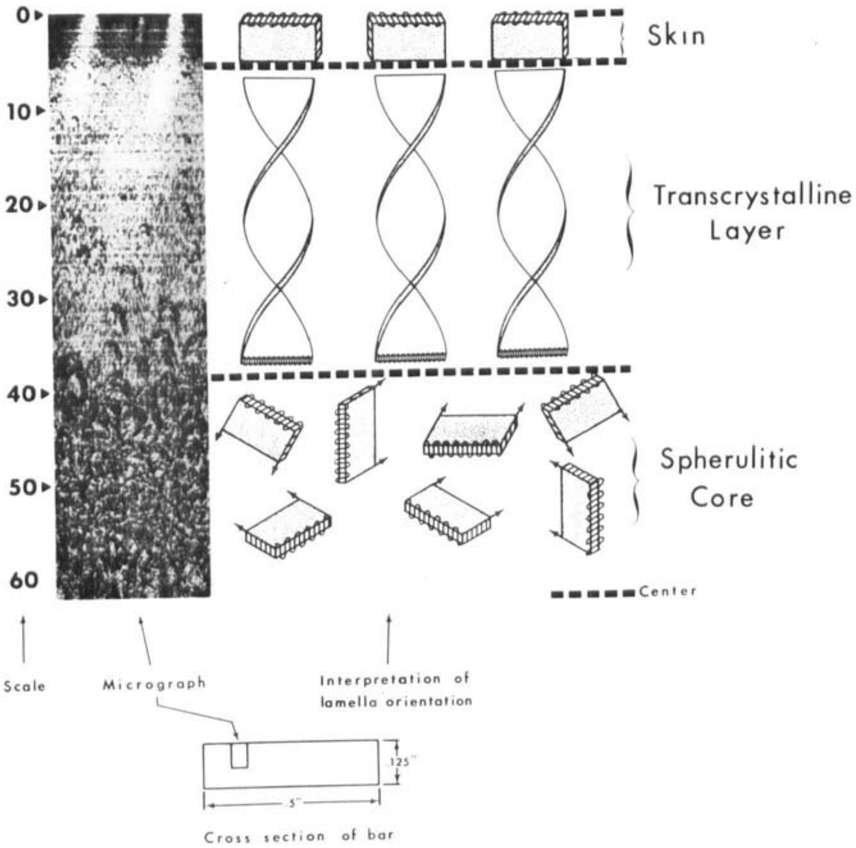

FIGURE 9 Portion of cross section of bar observed under crossed polaroids and interpretation of structure. Boxes and ribbons represent folded-chain lamellae. Perspective is distorted for emphasis; the scale on the left is in mils [Clark, Ref. 17].

direction. However, it is likely that growth in the "transcrystalline layer" is initiated by the lamellae formed in the skin rather than from new fibril nuclei since shear stress is low. The influence of the strong temperature differential between the mold wall and the melt will cause the growth direction to be perpendicular to the wall. Except for the lack of fibril nuclei, the morphology of the transcrystalline layer is similar to that of the blown film of polyoxymethylene described previously.

As crystallization proceeds into the interior, the temperature of the melt is lowered to a point at which new nuclei can form spontaneously. Nuclei are formed at random, with no correlation among them. The polymer

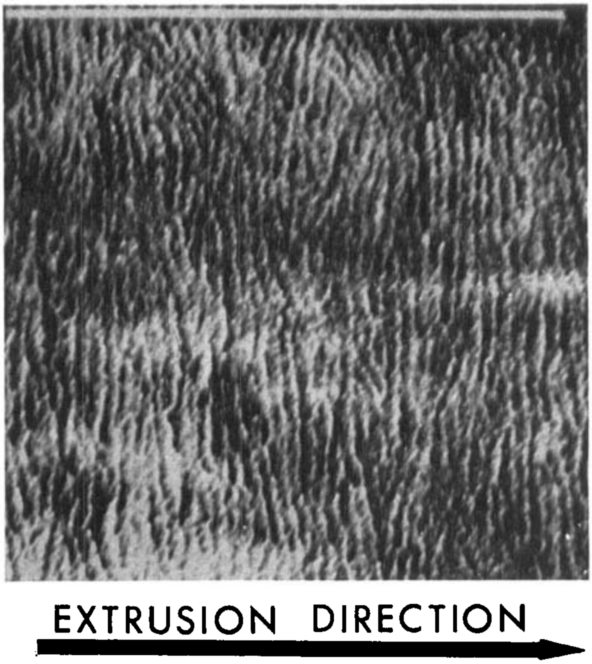

FIGURE 10 Surface of injection molded bar of polyoxymethylene showing lamella edges. Electron micrograph [Clark, Ref. 17].

crystallized in the skin and "transcrystalline layer" insulates the molten core and prevents strong temperature gradients from developing. The crystallization conditions at the core are similar to those of a quiescent environment; thus spherulites develop. In polyoxymethylene, spherulites tend to be poorly formed and have a somewhat granular appearance.

Thus, in an injection-molded bar of polyoxymethylene, we find three types of morphology: (1) a skin formed from fibril nuclei in an environment of high melt stress as the mold is being filled, (2) a transcrystalline layer continuing the lamellar growth from the skin but with a twisting of the lamellae in the absence of melt stress, and (3) a core in which new nuclei develop spontaneously in a quiescent environment and grow into spherulites.

As described previously, blown film of polyoxymethylene having a "row structure" can undergo a co-operative deformation of lamellae and chains within lamellae to achieve a degree of elongation not possible in a spherulitic structure. This would explain the direct relationship between the relative amount of row oriented structure (skin plus "transcrystalline layer") in injection molded bars of polyoxymethylene and the elongation-to-break.

FIBER SPINNING

Fiber spinning might at first seem to be the simplest of examples for crystallization under stress, but it possibly is the most complex commercial process. The high degree of control which is attainable in temperature gradients and stress gradients, both during and after crystallization, makes it possible to create a very large and complex series of morphological structures. However, it is here that the concept of fibril nucleation of a "row structure" may ultimately have the greatest usefulness. Studies in Japan by Katayama *et al.*,[12] give insight into the morphology of the spinning process. By making a series of measurements along a spinning line using optical microscopy and x-ray diffraction, they studied a fiber of polyethylene in its various stages of crystallization. They learned that the chain molecules become oriented only on crystallization several centimeters from the spinning orifice. Their data show that the chains crystallize as folded chain lamellae perpendicular to the stress (spinning) direction. On the basis of the experimental data of Katayama, *et al.*, we propose that a melt spun fiber of polyethylene crystallizes first in a "row structure" which in a subsequent drawing operation is deformed. Using a mechanism proposed by Peterlin for deformation of polyethylene spherulites, we propose that in post drawing operations, molecules initially tilt within lamellae followed by their breaking up into small chunks of folded-chain material. This irregular structure of folded and unfolded chains can adjust during annealing to reform lamellae of a slightly different type having many more chains connecting adjacent layers. Thus, we propose that the "row structure" is an intermediate structural unit in the melt spinning of polymers which crystallize readily such as polyethylene. If the polymer shows a strong tendency to supercool, such as nylon-66, we can expect the drawing forces which produce fibrilar morphology to predominate over the crystallization forces of row nucleation which produce a lamellar morphology. The resulting fiber will consist primarily of extended chain units with chain folds incorporated as defects rather than being well organized into a lamella surface. Such a structure has been proposed for drawn fiber of nylon-66 by Dismore and Statton[19] and may characterize the morphology of high tenacity fibers.

In contrast to fibers of high tenacity prepared by drawing melt spun crystalline polymers, another type of fiber can be prepared from some of these polymers which can be classed as a "pure row structure". These fibers differ from high tenacity fibers in many ways but most remarkable is the high degree of elastic recovery from large extensions in length. Fibers of this type have been prepared from polypropylene, polyoxymethylene, and poly-3-methy-1-butene which typically show a recovery of over 90% from length extensions of 50%. Quynn and coworkers[20] have termed these unusual fibers "elastic 'hard' fibers". Clark[21] suggests the term "row oriented" fibers since they are characterized by ordered rows of folded-chain lamellae, that is, "row structures". Both Quynn and Clark conclude that the retractive forces from deformation are energy driven and *not* entropy driven as in rubber or drawn high tenacity fibers. Clark has proposed that the deformation mechanism involves bending or shearing of lamellae between the molecules to create voids as illustrated in Figure 11. Elongation results from the cumulative effects of small displacements of molecules within lamellae. These displacements are reversible in direction with the energy forces within the crystal providing the retractive force. Measurements of specific volume, small angle x-ray diffraction and high pressure mercury porosimetry show that the elongation and retraction of "row oriented" fibers involves creation and destruction of a large number of very small voids. The negative slope of the stress vs. temperature curve supports the conclusion that the retractive forces are energy rather than entropy driven. It is beyond the scope of this paper to discuss these elastic fibers in detail but their existence offers additional evidence for the importance of the concept of row nucleation in understanding the creation of fibers of widely different properties from the same original polymer.

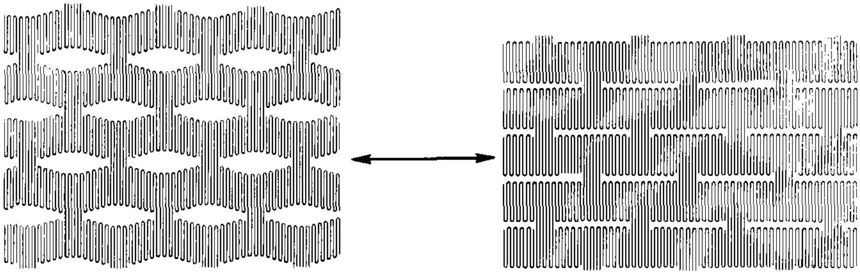

FIGURE 11 Proposed mechanism for elastic deformation of "row oriented" fibers. Lamella thickness has been decreased relative to interchain separation for clarity. Drawing is idealized.

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