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Crystallization and Molecular Folding

The properties of high polymers are very sensitive to the way molecules fold during crystallization.

P. H. Lindenmeyer

The physical and in some instances even the chemical properties of crystalline high polymers can be varied over a rather wide range by thermal and mechanical treatments during their transformation into the solid state. For example, polyethylene can be converted from its usual tough, ductile, easily deformable form into a brittle, easily crushed, powdery material by controlling the conditions under which it is crystallized. These changes are reversible and therefore represent changes in the physical state rather than chemical decomposition.

Early attempts to explain the properties of crystalline high polymers evolved the "fringed-micelle" concept (*1*), in which small crystalline "micelles" were assumed to be completely embedded in an amorphous matrix of uncrystallized polymer. Since the polymer molecule was known to be many times longer than the crystalline micelle (or crystallite), a given polymer molecule was assumed to pass from one crystallite to another through the diffuse boundary or "fringed" ends of the crystalline "micelle." The crystallites were believed to act in many ways like cross-links in a rubber-like network of amorphous polymer. The plastic properties of crystalline polymers were assumed to be largely due to the matrix of amorphous polymer surrounding the crystallite, and the variation in these properties was attributed to the size and shape of these crystalline regions and to the fraction of polymer in the crystalline state (that is, the so-called degree of crystallinity). The "fringed-micelle" concept has proved to be extremely useful in qualitatively explaining many phenomena involved in the variation of the properties of crystalline polymers.

In 1949 Flory (*2*) introduced a theory of polymer crystallization which showed that a true thermodynamic equilibrium can exist between a crystalline and an amorphous phase at or near the melting temperature. This theory predicted the extent by which the melting point would be lowered by the presence of impurities, diluents, and noncrystallizable polymer segments. Although most of the predictions of Flory's theory have been subsequently verified, this has had very little effect on the "fringed-micelle" concept, and many workers in the polymer field still visualize a crystalline polymer as consisting of small crystalline regions completely surrounded by an amorphous material.

It was not until the discovery in 1957 (*3–5*) that single crystals of polyethylene of high molecular weight could be grown from dilute solution by a process of molecular chain-folding that people seriously began to question the "fringed-micelle" or crystalline-amorphous concept. The idea that long polymer molecules might crystallize by folding up into thin platelets (or lamellae), as proposed by Keller (*4*), had never been taken seriously, although evidence of lamellar structure and even of single crystals had appeared in the literature (*6*) much earlier. A considerable amount of activity has been devoted in recent years to an attempt to determine why, how, and under what conditions polymer molecules fold when they crystallize. Much to the surprise of almost everyone, it now appears that crystallization of polymers by some sort of molecular chain-folding mechanism is indeed the usual mode of crystallization, not only from dilute solution but also from the melt. In fact, it now seems very likely that crystalline polymers owe their desirable plastic properties to the fact that their molecules are folded in the crystal and can subsequently unfold to produce the large plastic deformations so characteristic of these materials. Thus a more quantitative understanding of the physical properties of crystalline high polymers lies in understanding why, how, and to what extent

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polymer molecules fold when they crystallize. Of almost equal importance is an understanding of how these molecules unfold during plastic deformation and how they refold during annealing and recrystallization. This article attempts to summarize some of the important developments in this very active and rapidly changing field of scientific investigation.

Crystallization from Dilute Solution

Single-crystal platelets of polyethylene of high molecular weight were discovered independently by Till (*3*), Keller (*4*), and Fischer (*5*). These platelets were of the order of 100 angstroms in thickness, and electron diffraction showed that the polymer chains were oriented essentially normal to the platelet, thus forcing the conclusion that the molecules, which were many times longer than 100 angstroms, must fold in some manner in order to fit into the crystal. The nature of this molecular chain-folding has been the subject of considerable debate in the past few years (*7*). Although there still exists opinion to the contrary (*8*), it now seems rather clear that these crystals are formed by the packing together of molecules which have a very regularly shaped fold. In the actual growth of the crystal, it is possible that the molecule first crystallizes in irregular-sized loops which subsequently adjust to form the regularly packed, uniformly shaped folds.

Evidence for this regularity of the molecular fold comes from careful studies of the external shape of these platelets (*7, 9*). Such studies have shown that they grow as hollow pyramidal structures rather than as flat platelets. Figure 1 shows the appearance of two such crystals under the electron microscope, and Fig. 2 is a line drawing illustrating the way the molecular folds are believed to control the external structure of the crystal. In this model the molecules are represented by thick ribbons. When these ribbons fold with a twist, as they must do in order to fit into the unit cell, the resulting fold has a distinct asymmetry which leads to the most efficient packing when the folds all lie in the (312) crystallographic plane. At the bottom of the platelet the twist is in the opposite sense, resulting in a false twist in the ribbon and giving a fold which has a symmetry inverse to that of the upper fold. Thus the (312) plane is repeated, this being the most efficient packing of the folds in both the upper and lower layers (*9a*).

A second type of fold, which results in a different packing, is shown for the sectors of the crystal which are bounded by (100) and (302) crystal planes. This fold is somewhat less interlocking in nature, and these sectors frequently are observed to dis-

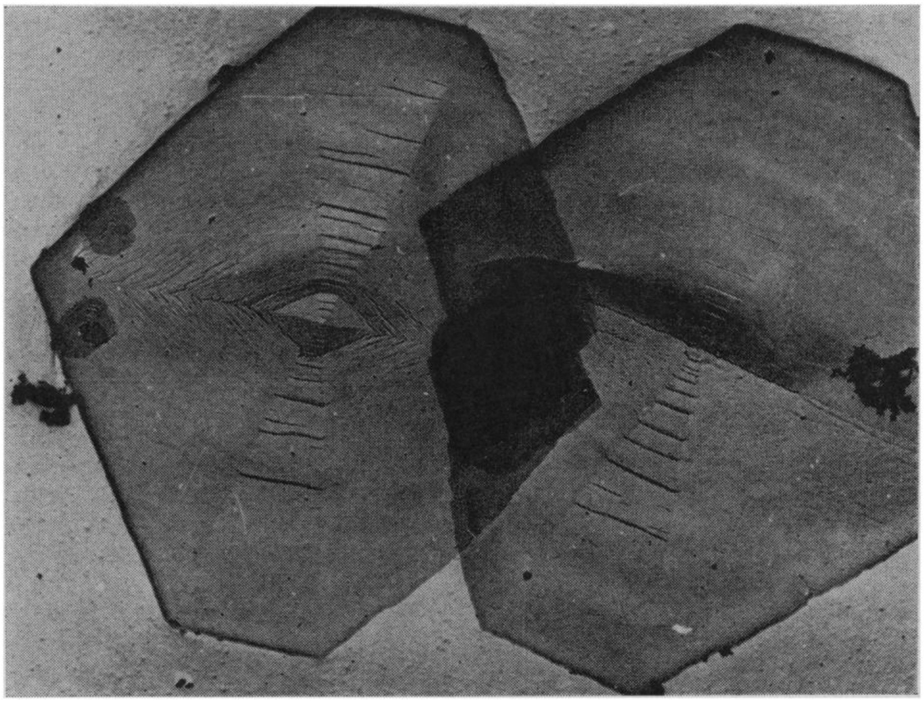

Fig. 1. Shadowed electron micrograph of two truncated crystals of polyethylene sedimented on glycerine. [Bassett, Frank, and Keller (*9*)]

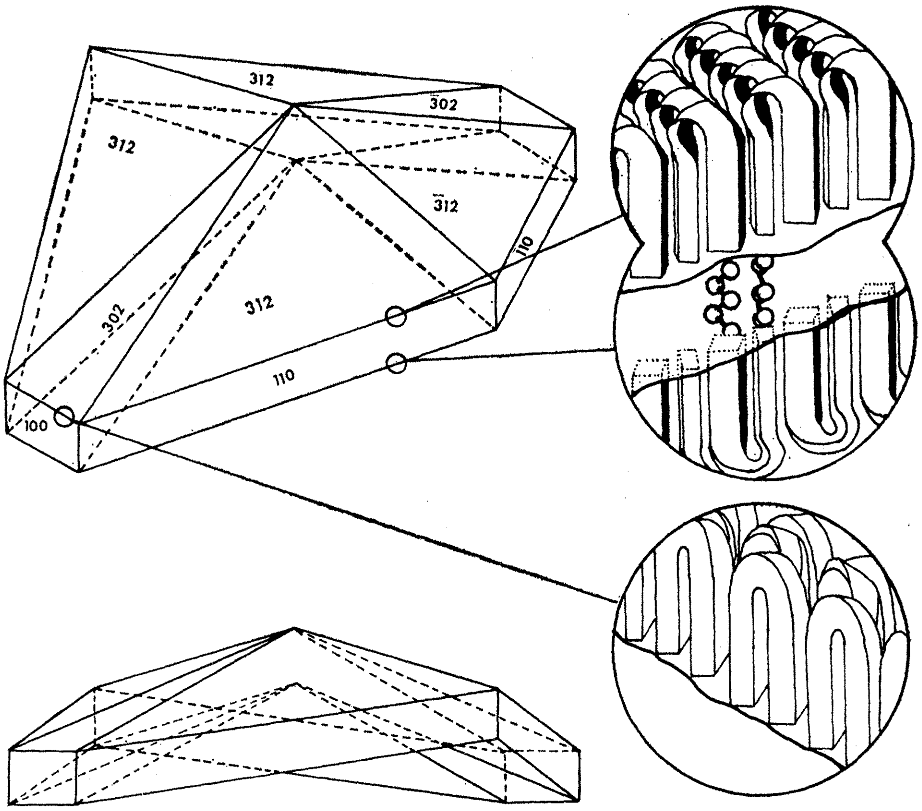

Fig. 2. Schematic representation of molecular folding in truncated polyethylene crystals. The vertical dimension has been greatly exaggerated, and the molecules are depicted as ribbons in order to illustrate the asymmetry of the molecular fold. The hollow pyramidal form of this crystal results from the packing of asymmetric molecular folds.

solve before the rest of the crystal—evidence of their lower stability. The exact atomic arrangement in these molecular folds is not yet established, but it is clear that these folds must have at least the anisotropy of the ribbons in the model in order to produce the observed crystal faces.

The thickness of the platelet (which determines the length between molecular folds) increases with the crystallization temperature (*10*) and is generally considered to be a reciprocal function of the degree of supercooling. It is this variation of molecular fold-length which provides both a clue to the variation in properties with conditions of crystallization and the principal experimental data for the verification of theories which attempt to explain molecular chain-folding.

While much of the published research in this field has been concentrated on polyethylene, because of the ease of crystal growth and the lack of complicating factors, sufficient work has been done with other materials to demonstrate that the same general phenomena apply to nearly all crystallizable linear high polymers (*11*) and, in some instances, even to polymers whose crystallizability has been in doubt [for example, polyacrylonitrile (*12*)].

Molecular folding of polymers offers the possibility of explaining an observation that has long puzzled workers concerned with determining the crystal structure of high polymers. Those polymers (for example, cellulose, nylon-6) in which the molecule does not have a center of symmetry (that is, in which the molecule has a "head" and "tail" as well as a directionality along the chain) frequently crystallize into a unit cell in which adjacent chains are packed with alternate directionalities. The x-ray evidence which led to such conclusions has not always been conclusive, and many discussions have ensued concerning the probability that one polymer molecule will always find another molecule pointing in the opposite direction when it crystallizes. If crystallization occurs by a chain-folding mechanism it is obvious that adjacent chains will have antiparallel directionalities. As is frequently the case in science, the resolution of one problem only presents another more puzzling problem. Those polymers which are capable of forming interchain hydrogen-bonds (for example, polyamides, polyurethane, and cellulose) can conceivably fold in such a way that these bonds form either between folded chains of the same molecule (intramolecular hydrogen bonds) or between chains belonging to different molecules (intermolecular hydrogen bonds). This point is illustrated in Fig. 3, which shows a drawing of the α crystal structure of polycaprolactam (nylon-6) and indicates the way chains with different directionalities are packed. The simplest explanation of this arrangement is to suggest that chains *A*, *D*, and *H* fold into chains *B*, *E*, and *I* at the top of the crystal and that these in turn fold into *C*, *F*, and *J* at the bottom. This would result in the hydrogen-bonded sheets formed by chains *ABC*, *DEF*, and *HIJ*, each being composed of a single molecule. Of course, this is not the only possibility; for example, chain *A* could fold into *E*, chain *D* into *I*, and so on. It would seem reasonable to expect quite different behavior for crystals in which chain-folding occurred in these two different ways, and this problem is currently receiving considerable attention in various laboratories throughout the world.

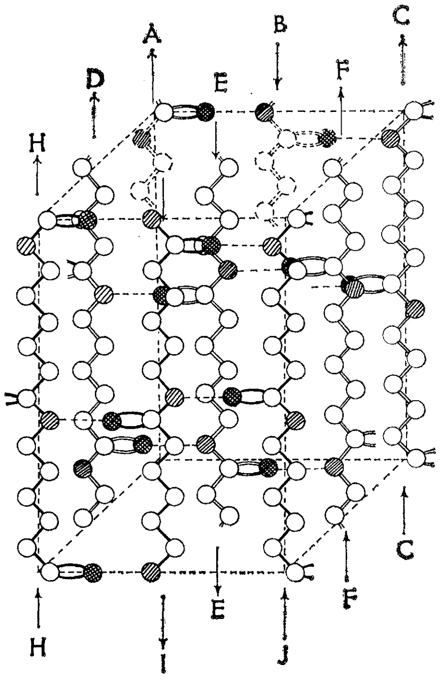

Fig. 3. Representation of the unit cell in the α crystal structure of polycaprolactam (nylon-6), showing the hydrogen-bonded sheets consisting of chains *ABC*, *DEF*, and *HIJ*. Molecular folding of chains *A*, *D*, and *H* into *B*, *E*, and *I* at the top of the crystal, followed by the folding of *B*, *E*, and *I* into *C*, *F*, and *J* at the bottom, results in hydrogen-bonded sheets containing whole molecules (that is, in intramolecular hydrogen bonding). Other possible folding—for example, of *A* into *E*, *B* into *F*, and so on—would result in intermolecular bonding.

Crystallization from the Bulk

The evidence for bulk crystallization by a chain-folding mechanism was first established by the observation of single-crystal electron diffraction from polymers crystallized from the melt in the form of very thin films (*13*). Electron micrographs of the surface of bulk-crystallized polymers also have shown lamellae very similar to those grown in thin films. The development of techniques for fracturing bulk-crystallized polyethylene and the investigation of molecular-weight fractions by Anderson (*14*) not only established the chain-folding mechanism as the predominant one in the interior of bulk-crystallized polyethylene but also showed that chain-folded lamellae are of two types; the two are of approximately the same thickness but the second type has a nearly uniform width of about two to three times its thickness. Figure 4 shows an example of these two types of folded-chain lamellae.

In addition to these two types of folded-chain lamellae, Anderson also found a third type of lamella which he showed to be composed of extended chains in which the thickness of the lamella corresponds to the length of the polymer chain (see Fig. 5). In order for the polymer to crystallize in this form, which resembles very much the crystal habit of the normal paraffins, it is necessary for the polymer molecules to fractionate (that is, to separate according to molecular length) so that each molecule can crystallize beside another molecule of approximately the same length. By crystallizing a series of polyethylene fractions of varying molecular lengths, Anderson was able to show that molecules longer than about 1000 Å crystallize into folded-chain lamellae while shorter molecules crystallize into the extended-chain form.

Since crystallization of a so-called whole polymer, with a wide distribution of molecular lengths, produces all three types of lamellae, he concluded that not only does polyethylene crystallize into folded-chain lamellae but that there is also a tendency for at least the shorter molecular chains to separate during crystallization and to form fractionated extended-chain crystals in which each molecule crystallizes next to another molecule of nearly the same length. He also showed that the greatest molecular length which could separate and form extended-chain crystals was dependent upon the conditions of crystallization. By carrying out crystallization at lower temperatures he was able to reduce the maximum molecular length which could separate.

This tendency of polymers to fractionate during crystallization plays an important role in the growth of spherulites—a mode of crystallization which is characteristic of most crystalline polymers. The phenomenological description of spherulite growth, as given most recently by Keith and Padden (*15*), is based upon the diffusion of impurities, noncrystallizable segments, and low-molecular-weight molecules away from the growing crystal face.

Crystallization under Pressure

Anderson's prediction that the length of molecule which could crystallize in the extended-chain form depended upon crystallization conditions was made at the St. Louis Meeting of the American Physical Society in 1963. At that same meeting Bernhard Wunderlich offered to send him samples of polyethylene which he had crystallized under pressures of up to 5000 atmospheres. When these samples were examined under the electron microscope (*16*) they proved to consist entirely of what were apparently extended-chain lamellae. Polyethylene crystals up to 3 microns long were observed.

Figure 6 shows examples of extended-chain crystals of polyethylene crystallized at 236°C under pressure of 5000 atmospheres. The molecules are parallel to the striations, and the distribution of crystal thicknesses is in good agreement with the known distribution of molecular lengths. This seems to indicate that molecular fractionation is nearly complete when crystallization occurs under pressure of 5000 atmospheres at 236°C. (The only alternative explanation would be that the primary nucleation step somehow controls crystal thickness and that the thickness of a given crystal is somehow determined by the longest molecule in the nucleus.) In any event, it is apparent that crystallization under pressure has produced a much greater tendency for the molecules to crystallize without folding, and that the resulting crystals have a melting point very close to the value estimated by extrapolation for a normal paraffin of infinite length (*17*).

Thermodynamics of Crystallization

The most thermodynamically stable polymer crystal is undoubtedly a crystal in which the molecules are not folded but are extended in whatever helical conformation provides the lowest free energy. (Throughout this article the term "extended-chain" means a molecule in its lowest energy conformation with no molecular folds. For the polyethylene molecule this conformation is the true, completely extended, planar zigzag chain; in other molecules it may be some other helical form.)

The end of a molecule must of necessity contain a group that is not identical with the repeating unit along the chain. For the greatest efficiency of packing (that is, the lowest energy) the chain ends must pack in a single crystallographic plane. If the molecules are all of the same length (as in a true normal paraffin) this kind of packing is possible. On the other hand, if there is a distribution of molecular lengths, then it is necessary for the molecules to separate according to molecular length (that is, to fractionate) in order to form the most stable crystal.

Thus the most stable crystal of a polymer with a distribution of molecular lengths is a crystal in which the chains are not only completely extended in their lowest-energy conformation (that is, without molecular folds) but also fractionated (or separated into chains of equal length) so that each molecule can crystallize next to another molecule of the same or nearly the same length. Naturally, formation of such a crystal requires both time and a high degree of molecular mobility, and it is unlikely to occur except under very unusual conditions (pressure of 5000 atmospheres and temperature of 236°C may come close to providing such conditions for polyethylene).

Under the usual conditions of crystallization only a very few of the more mobile molecules (those of lower mo-

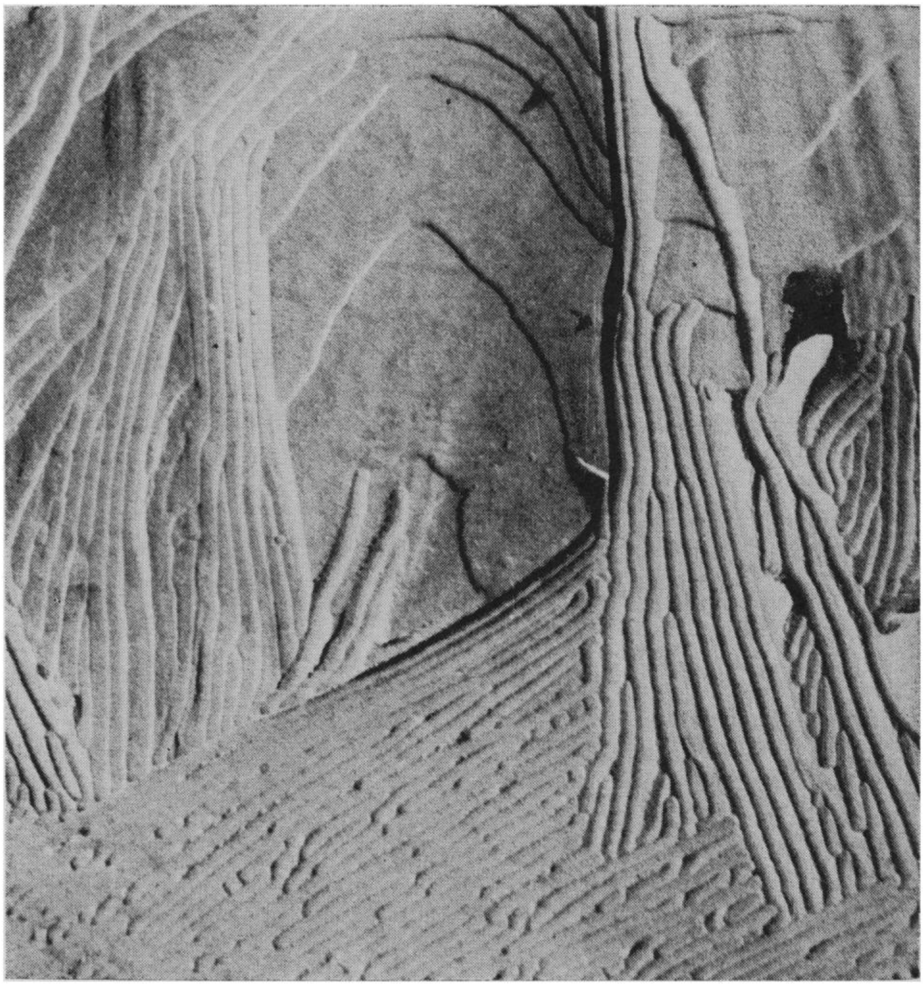

Fig. 4. Electron micrograph of a replica of an internal fracture surface of isothermally bulk-crystallized polyethylene. The wide lamellae are unfractionated folded-chain crystals. The narrow lamellae are also folded-chain crystals composed of at least partially fractionated molecular chains. [Anderson (*14*)]

lecular weight) can crystallize in this most stable form. With sufficient supercooling the remaining molecules may crystallize into other, less stable, crystalline forms (those involving molecular folding). However, there still remains a potential thermodynamic driving force which tends to cause these less stable crystals to transform either into fractionated extended-chain crystals or into a relatively more stable folded-chain crystal (that is, one with a longer molecular fold-length). This is the driving force responsible for the changes which occur during annealing.

In an early attempt to explain the existence of crystals with molecular chain-folding, Peterlin and Fischer (*18*) observed that the most important difference between polymer crystals and ordinary crystals lies in the large anisotropy of forces which hold the crystal together. In the direction of the polymer chain the crystal is held by covalent bonds comparable in strength to those of a diamond; perpendicular to this direction the bonding forces are less by several orders of magnitude. Peterlin and Fischer argued that the relative ease with which such a crystal can undergo translational vibration along the chain axis, or torsional vibration about this direction, yields a term in the expression for the free energy which increases with the length of the chain in the crystal. As a result of this contribution, the total free energy of the crystal per unit length of chain reaches a minimum as the length of chain in the crystal increases. This minimum in free energy represents a metastable equilibrium state. At still greater chain lengths other factors predominate and the free energy again decreases. Attempts to account for the variations in the molecular fold-length of polyethylene crystals from dilute solution with variation in temperature of crystallization have been reasonably successful (*19*). The behavior of crystals grown from solution at temperatures less than 110°C is consistent with the assumption that they represent a metastable thermodynamic equilibrium state. On the other hand, the thermodynamic explanation cannot account for the molecular folding which occurs in crystallization from the melt.

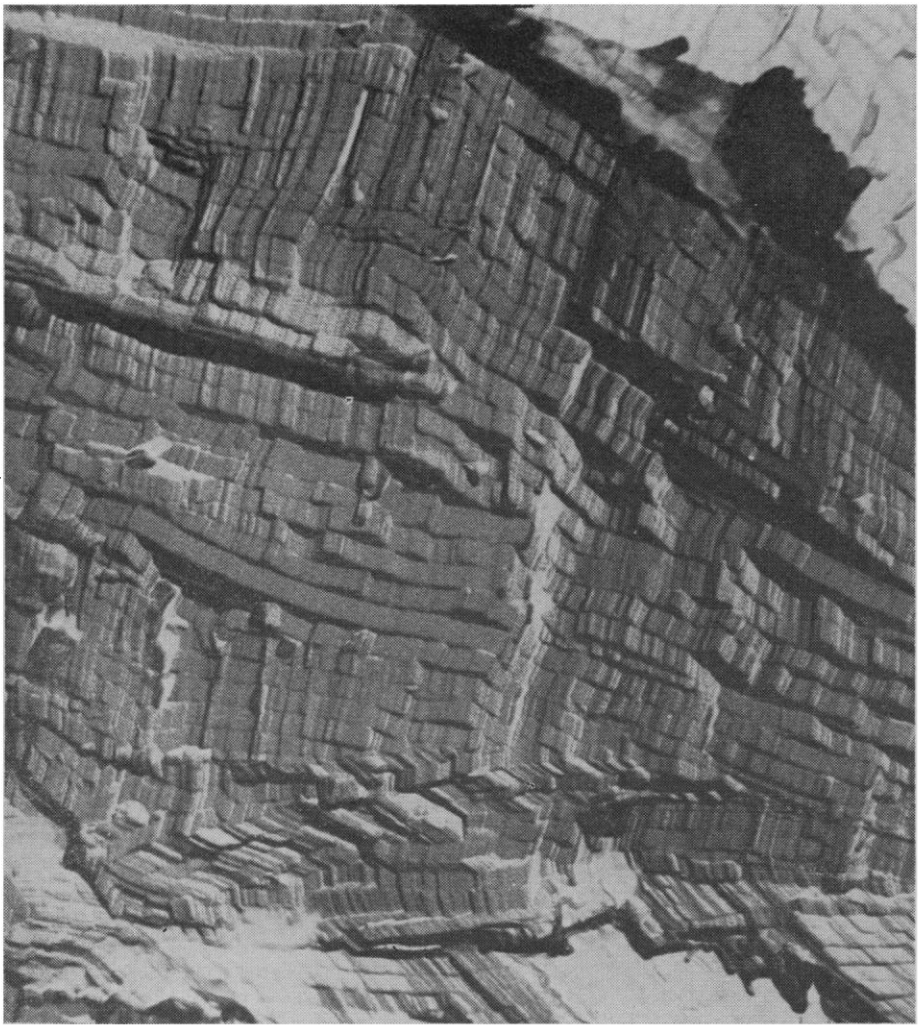
Fig. 5. Electron micrograph of a replica of an internal fracture surface of bulk-crystallized polyethylene. The lamellae are fractionated extended-chain crystals with the molecular chains running parallel to the striations and the ends of the molecule forming the surfaces of the lamellae. [Anderson (*14*)]

Kinetics of Crystallizations

In other attempts to explain the occurrence of molecular chain-folding in polymers use has been made of the kinetics of crystallization and, in particular, nucleation theory. The earliest kinetic theories, by Price (*20*) and by Lauritzen and Hoffman (*21*), attempted to account for the observed platelet thickness by assuming that it did not differ greatly from the fold-length in the critical-sized nucleus. Later theories, by Frank and Tosi (*22*) and by Price (*23*), have modified the original strictly kinetic approach.

Without going into the mathematics involved, one can obtain a qualitative picture of the kinetic theories as follows. Experimental measurement of crystal growth rates (*10*) shows that growth is controlled by nucleation—that is, each molecular layer deposited onto the growing crystal must first form a two-dimensional nucleus of sufficient size to be stable. The early kinetic theories assumed that the molecular fold-length of this critical-sized nucleus does not increase significantly as the growth of that particular molecular layer proceeds. Hence, the crystal thickness (and consequently the molecular fold-length) can be equated with the fold-lengths of a molecule in the critical-sized nucleus. Expressions for the dimensions of the critical-sized nucleus can be derived in terms of the free energy of formation per unit volume and the surface energies of the nucleus. Although these expressions may fit some experimental data on measured molecular fold-length, they generally fail to give quantitative results over the entire range. In addition, the measured melting points of these thin crystal lamellae are invariably significantly higher than the crystallization temperature, indicating either that the crystals grow with a fold-length significantly greater than that of the critical-sized nucleus or that they subsequently increase their fold-length by some sort of creep-up or refolding mechanism.

The existence of a process which permits the crystal to increase in thickness has been clearly established as occurring during the annealing of folded-chain crystals (*24*). Recent evidence reported by Hoffman and Weeks (*25*) indicates that a similar thickening process may also operate during isothermal crystallization from the melt. Thus, the best available evidence at this time indicates that, while the molecular fold-length may be determined by the kinetics of crystallization, this fold-length is substantially greater than that of the critical-sized nucleus.

Annealing or Recrystallization

Since the folded-chain crystals are not the most stable crystalline form, there exists a thermodynamic driving force which tends to make them change to a more stable form. Annealing of single folded-chain crystals at temperatures above their crystallization temperature causes an increase in thickness or in molecular fold-length (*24*). Later work, by Fischer and Schmidt (*26*), showed that the increase in fold-length with annealing actually is logarithmic with time. They also showed that extrapolation from a plot of density versus the reciprocal of fold-length gives the crystallographic density, and that this is true, also, for polyethylene heated to a high temperature and then shock-cooled. However, annealing at temperatures below 110°C or the annealing of drawn polyethylene at all temperatures led to extrapolated densities which were quite different from the crystallographic density. Furthermore, it is necessary to anneal at temperatures above crystallization temperature before substantial changes in structure occur.

The mechanism by which the folded-chain crystal changes its thickness is not completely established, but the change is believed to occur without a complete melting and recrystallization. Reneker (*27*) has suggested that a point defect might move along a single chain with a resultant translation of one unit cell as the point defect moves through the crystal. Holland (*28*) has recently shown that the annealing of single crystals of polyethylene involves the formation of a large number of partial dislocations which could account for the increase in molecular fold-length by a motion known as the "climb" of these dislocations. Consideration of the kinetics of this thickening mechanism (*29*) seems to favor this latter proposal.

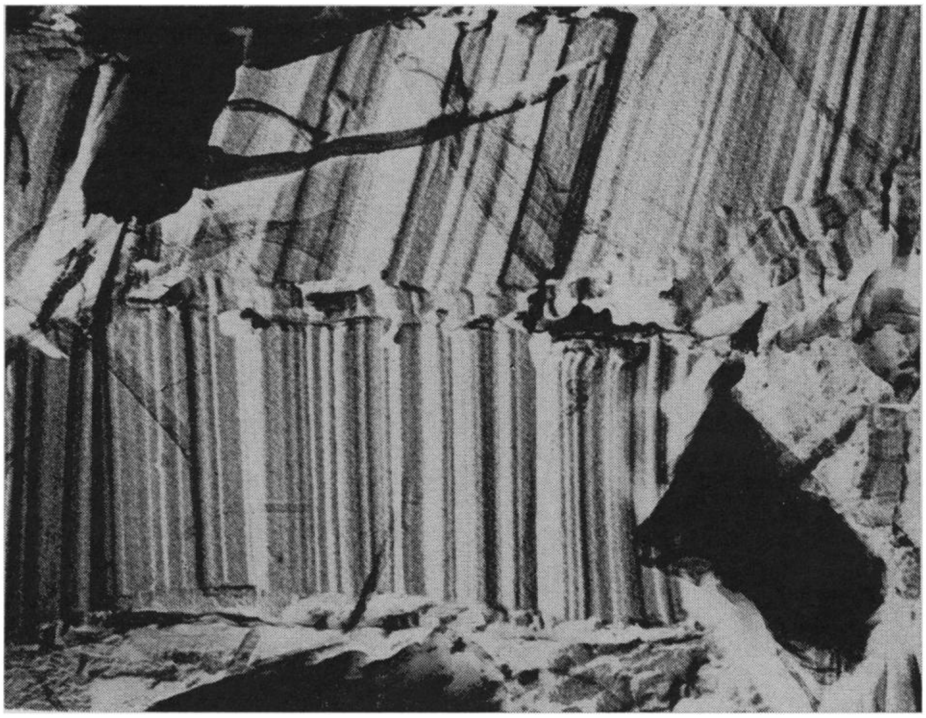

Fig. 6. Electron micrograph of a replica of an internal fracture surface of polyethylene crystallized at 236°C under pressure of 5000 atmospheres. The molecules in these extended-chain crystals must be longer than 2 microns (20,000 Å). [Anderson]

Although the exact mechanism is still uncertain, it is clear that, because of their inherent thermodynamic instability, folded-chain crystals tend to increase their stability by increasing their molecular fold-length whenever the temperature exceeds the crystallization temperature. It is also very likely that this annealing process also involves a further rejection of molecules of lower molecular weight, which subsequently crystallize into stable, fractionated, extended-chain crystals.

In spite of its importance, deformation of folded-chain polymer crystals is probably the least understood aspect of this subject at the present time. The direct experimental approach is formidable, since these crystals are only 100 to 200 Å thick and measure only a few microns in the other two directions. Even so, methods have been developed (*11*, chap. 7; *30*) by which one can deform such crystals by known amounts and in fixed directions. The results thus far indicate the importance of at least two mechanisms: (i) deformation twinning, and (ii) transformation into polymorphic crystalline phases.

Although the exact mechanisms are not yet understood, it is known that, under large deformations, these folded-chain crystals form fibrils in which the polymer molecules are essentially parallel to the fibril axis and are still in nearly complete crystallographic register. It is also reasonable to expect that some (although not necessarily all) of the molecules must have been unfolded in the deformation process. The problem of measuring and controlling the number of molecules that are unfolded and the number that remain folded is at present the most exciting area of research in this field, since it is apparent that physical properties might be grossly affected by changes in this ratio.

Summary

The long-chain nature of the polymer molecule, together with the usual broad distribution of molecular lengths, makes it kinetically very unlikely that the molecule will achieve, on crystallization, its thermodynamically most stable form. Under most crystallization conditions a large portion of the polymer molecules crystallize into folded-chain crystals. Only a small fraction of the molecules of lower molecular weight, initially rejected from the growing folded-chain crystals, succeed in

achieving the stable, fractionated, extended-chain crystalline form. The physical properties of the resulting polycrystalline structure are very strongly dependent upon the amount and kind of molecular folding which has occurred. In general, folded-chain crystals are tough and ductile and tend to produce low modulus and high elongation, whereas extended-chain crystals are brittle and tend to have higher modulus.

Calculations based upon the large anisotropy of bonding forces indicate that there may exist under some conditions (for example, in polyethylene at temperatures below 110°C) a true metastable equilibrium state which restricts the size of growing crystals. However, it is most likely that the folded-chain crystals result from strictly kinetic factors—that the observed fold-length is that fold-length which can grow fastest. Such folded-chain crystals are metastable in the sense that, below their growth temperature, their rate of change to a more stable form is negligibly slow. However, when heated to temperatures above the original crystallization temperature, they undergo annealing. This process consists of a refolding of the molecules into crystals with longer, and hence more stable, molecular fold-lengths. At the same time, the annealing process involves a rejection of somewhat longer low-molecular-weight molecules, which ultimately crystallize into stable, fractionated, extended-chain crystals. The increase in the ratio of extended-chain to folded-chain crystals, along with the greater fold-length, is consistent with the increase in density and modulus which accompanies annealing.

When a folded-chain crystal is deformed, at least some of the molecules are unfolded in some manner (as yet not understood) which results in retention of the molecules in a substantially crystalline array. The crystals of partially unfolded molecules which result from the deformation of folded-chain crystals are the major components of most oriented films and fibers. Our understanding of the physical properties of these materials rests upon our ability to determine the relative amounts and the distribution of extended-chain, folded-chain, and partially unfolded-chain crystals.

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Meteorites and the Moon

Cosmic-ray ages and contaminants provide evidence that meteorites may come from the moon.

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Some years ago I presented a paper before the National Academy of Sciences arguing that there was some evidence that stone meteorites came from the moon (*1*). I advanced two arguments, first, that the low cosmic-ray ages of stone meteorites were consistent with orbits moving in the earth's neighborhood, while the higher cosmic-ray ages of the irons were consistent with an asteroidal origin, and second, that the polymict character of many stones, both chondritic and achondritic, indicated that they had places of origin physically near each other, such as neighboring regions on the moon or other planetary bodies. During the years since then I have considered other features of the meteorites which might be consistent with a lunar origin. The differing composition of the chondritic meteorites and the nonvolatile fraction of the sun, particularly with respect to iron, indicates that these objects are mixtures of materials from various sources such as might have been produced by the great collisional processes on the moon. The origin of chondrules is a controversial subject, but collision processes may produce melted silicate objects of complicated structure, and it seems probable that chondrules will be found on the lunar surface or below the surface layer affected by micrometeorite bombardment. Finally, I argued (*2*) that if biological material is present in some of the carbonaceous chondrites, then this would be consistent with the approximate solar composition of the inorganic elements

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