

LONG-CHAIN POLYMER CRYSTALS

Recently discovered aspects of polymer structure, particularly chain folding, have helped both experimentalists and theoreticians to study these substances.

Andrew Keller

CHAIN FOLDING is one of several unexpected features of long-chain polymer crystals that have come to light during the last decade or so. The polymers that exhibit these features are among our most important synthetic products—nylon and polyethylene, for example—and also abound in nature. The organization of their long-chain molecules therefore has practical as well as fundamental significance. Along with the new discoveries we find simplifications that make certain phenomena more reproducible experimentally, as well as more amenable to theoretical treatment, in polymers than in simpler substances.

Broad coverage of these topics is available in references 1-3. Those

three sources include further references to specific research.

Perhaps the most typical properties of long-chain polymers are associated with the amorphous state. These properties include low elastic modulus but high extensibility; the polymers display long-range elasticity and the whole range of viscoelastic behavior. The molecular basis for this behavior is related to the randomly coiled configuration of long chains in the amorphous state. Superimposed stress will readily extend the chains, but the system tends to return to the random state when stress is removed. Crystallinity, if present, stiffens the material somewhat, but does not alter those properties that distinguish polymers from simple polycrystalline substances.

Crystallinity can be present in all long-chain compounds if the chains have sufficient chemical regularity. It can arise as the chain grows (during polymerization)—a feature probably important for biological materials. It can be produced (reversibly) by stress as well. Here, however, we will be concerned only with crystallization from supercooled solutions and melts; this mode is the usual one for crystallization of simpler substances.

The traditional model

The usual polymer sample, as obtained by cooling from the melt, is polycrystalline. The individual crystals are too small to be seen by straightforward microscopy. Such a material, however, is only partially crystalline when assessed by a crystallinity-sensitive property (for example,

density or heat of fusion). It also displays some properties that are generally attributed to random chains in amorphous materials. The traditional way of accounting for this situation is shown in figure 1. The lattice revealed by x-ray diffraction is here confined to the regions, called "micelles," of parallel chains. X-ray crystallography can be used to determine the arrangement of atoms and define what is usually termed the crystal structure. With this model the questions of size, of shape and arrangement of the crystalline units, and of what happens to individual chains along their full length seem to be intractable problems, amenable at very best to some unpromising statistical treatment. Discovery of chain folding changed the prospects for our understanding.

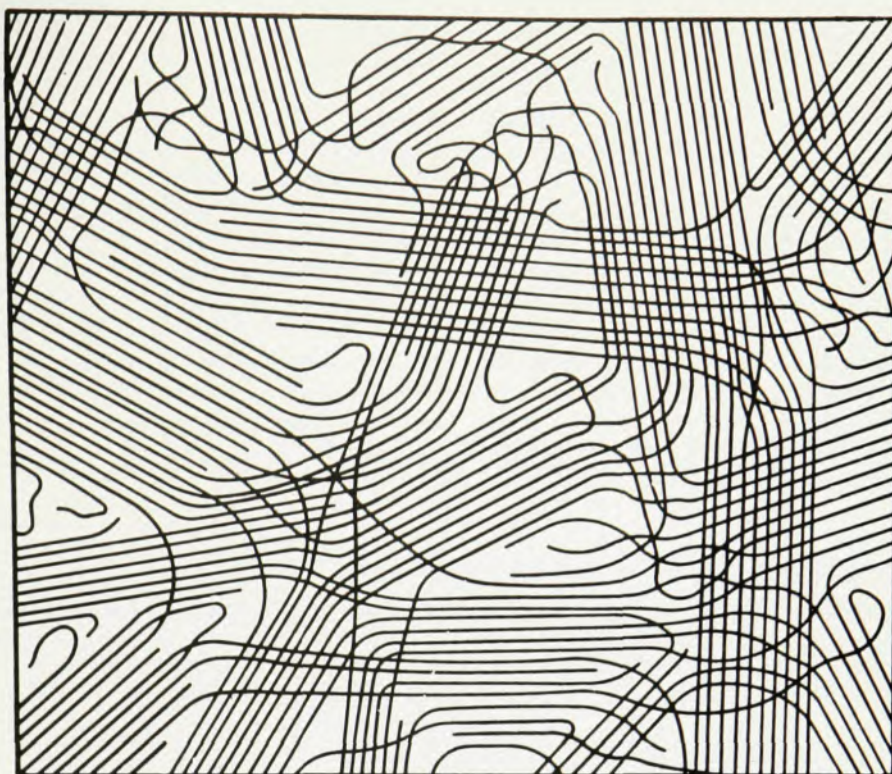
CHAIN-FOLDING PHENOMENON

We consider first the basic textural units, the microscopically definable single crystals, although this order is not the historical one. These single crystals can be studied most readily as obtained from solution. Whether or not such studies are relevant to the technologically more important problem of crystallization from the melt is often debated. The general belief, however, is that there is no difference in basic principle. Undoubtedly crystals from solution are simpler and better defined than crystals from the melt. Most important for the work in question is that these solution-grown crystals can be obtained in isolation; dispersion of polycrystalline products



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'FRINGED-MICELLE' representation of a crystalline polymer. The traditional model is shown here in a version by Charles W. Bunn. —FIG. 1

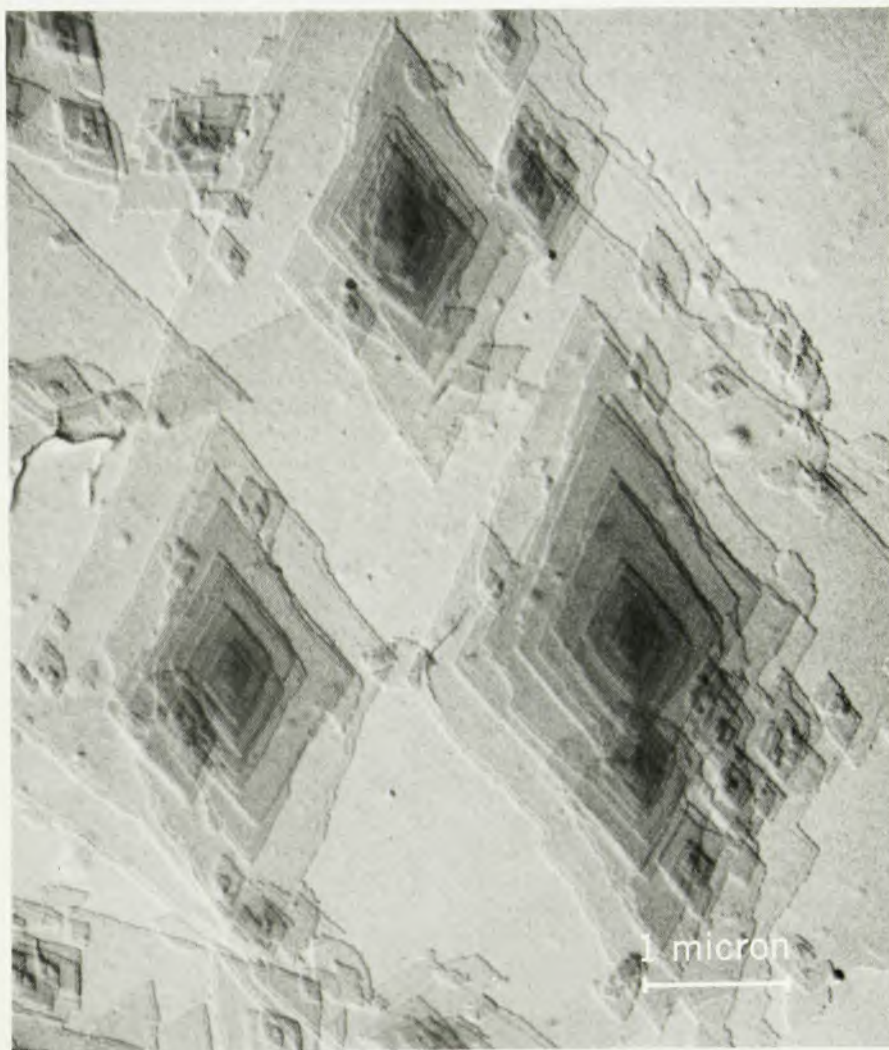


from the melt remains a problem to the present day.

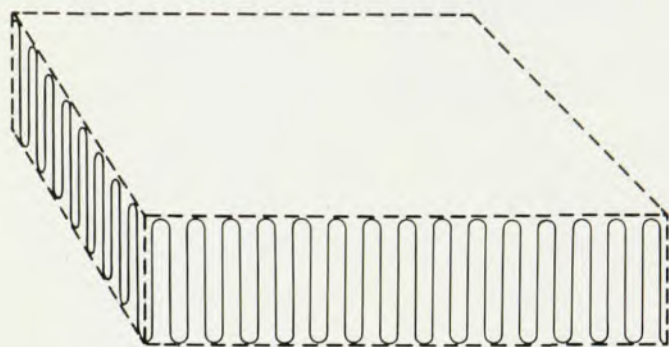
A solution-grown crystal consists of uniformly thick lamellae, or plates, bounded by prism faces (see figure 2). Such crystallographically defined entities were unexpected, and even more unexpected was their lamellar habit. Long chains were traditionally expected to give rise to crystals that are elongated in the chain direction and thus fibrous. Electron-diffraction patterns of individual crystals confirmed the single-crystal nature of these units, and revealed that the chains are perpendicular (or inclined at a specific, large angle) to the basal plane of the lamellae. The lamellar thickness is of the order of 10^{-2} microns and is independent of chain length, which can be more than, say, 10 microns and in any case is not uniform in a given material. The chain-folding model reconciles these apparently conflicting features (see figure 3). The chain-folding concept was a new departure in the study of macromolecular ordering, and proved to be a general feature of long chains with a variety of chemical structures.

Fold length

Chain folding introduces a new structural parameter, the fold length, that corresponds to the lamellar thickness. In these systems then, study of a macroscopic feature, the crystal thickness, gives information on a molecular parameter. We have a situation where study of morphology becomes part of determining the crystal structure in the more general sense of the

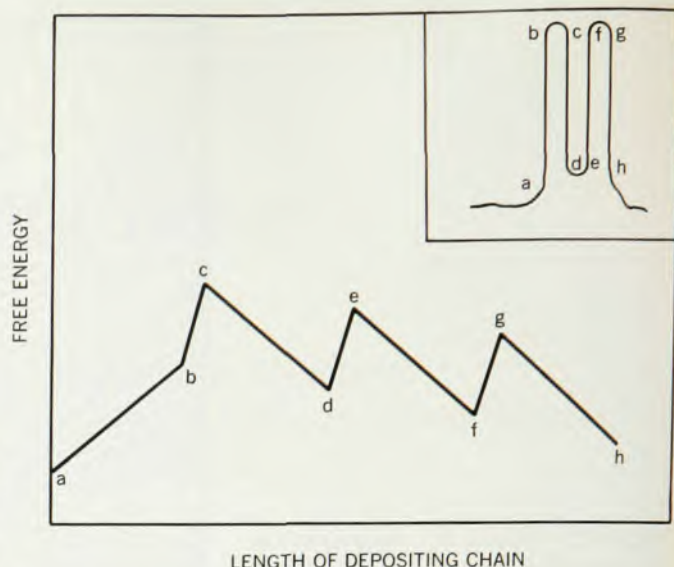


SOLUTION-GROWN crystal of polyethylene. Electron micrograph shows uniformly thick lamellae bounded by crystallographic prism faces. From ref. 4. —FIG. 2



CHAIN FOLDING. Vertical scale is contracted in this diagram; in real polymer crystals the fold stem length would be equal to 20–40 times the separation distance between adjacent stems. From ref. 2.

—FIG. 3



FREE ENERGY AS A FUNCTION OF CHAIN LENGTH during chain-folded deposition of a molecule. Insert correlates free-energy levels a, b . . . with the chain-folded structure. Adapted from refs. 5 and 6.

—FIG. 4

word. Crystal thickness can, of course, be directly determined from electron micrographs. A more representative measure, however, is provided by x-ray diffraction. The stacks of uniform lamellae in a sedimented mat of crystals give rise to discrete reflections at small angles. Such reflections have been observed previously in the bulk system and have remained essentially unaccounted for. By analogy with these single-crystal mats, they can now be identified with lamellae and consequently with the fold length.

Fold length is, as I have implied, a variable quantity. For a given system it depends primarily on the degree of supercooling and therefore on crystallization temperature. The higher the crystallization temperature, the greater the fold length. In the well explored polyethylene-xylene system, for example, the fold length can assume values between 9×10^{-3} and 1.7×10^{-2} microns, depending on the crystallization temperature. These values are surprisingly reproducible in the hands of a large number of investigators. The crystal once formed can then increase its fold length when subsequently heated to higher temperatures. An initial fold length of, say, 1×10^{-2} microns can be readily increased to 5×10^{-2} microns. It is increasingly apparent that this refolding is also the principal recrystallization feature when polymers are annealed under more general circumstances.

Theoretical considerations

The newly emerging facts naturally require explanation. Principal features are the occurrence of chain folding itself, the uniformity of the fold length and its dependence on both crystallization and annealing temperatures. One approach tries to account for all of these features by thermodynamic considerations. There is, according to this approach, a particular fold length that corresponds to the state of minimal free energy for the system. Although the problem is not yet fully resolved, however, theories based on kinetic considerations appear to be more strongly supported by experiment and, in any case, are worked out in more detail.

The state of lowest free energy consists of crystals built of completely extended chains. Kinetic considerations predict that folding then occurs because in this way crystallization can proceed faster. Experiments show that fold length varies with crystallization temperature and is determined entirely by the degree of supercooling at which a given molecule deposits onto the existing crystal face. The existing fold length in that face has no influence; this distinction becomes important if, for example, crystallization temperature is altered during growth, or if a seed crystal of different history is introduced.

Consider the deposition of a new chain onto a smooth crystal substrate,

taken to be of infinite thickness for the sake of simplicity. The increase in free energy when new surface forms will be larger than the decrease due to creation of more crystal; total free energy will therefore be an increasing function of the length of the depositing straight-chain portion (see figure 4, part ab). There is a finite probability that the chain will, at some stage, fold back on itself. Part of the new surface created by the first segment will then be covered. At first the fold (bc in figure 4) causes a sharp increase in free energy, but beyond this point the resultant free energy will decrease as the folded-over chain continues to deposit (cd).

After all the side surface of the first deposited segment is covered (d), further deposition would again create new surface and increase the total free energy. New folds, however, would repeat the process: first a sudden increase in free energy (e, g) because of the fold, followed by a progressive decrease as the next straight segment is laid down adjacent to the preceding one (ef, gh). If the crystal is to grow at all stages, d, f and h must be of progressively lower free energies.

This last condition sets a lowest limit for the thermodynamically permissible fold length. Attachment of each straight segment must compensate for the increase in free energy caused by the fold and if growth is to occur there must also be a net gain in stability. If this condition is satisfied,

continued folding will then lead the system to a state of free energy lower than it had when the chain started its deposition. That is, points equivalent to d, f, h . . . will sink below a in energy as the folded deposition continues. At this stage, the folded ribbon becomes stable against detachment and the polymer crystal is able to continue its growth.

Growth rate depends on the length of the straight stem. A longer stem requires a larger free-energy rise as the first attachment therefore has a lower probability. States d, f . . . however, will be correspondingly lower; after folding, the system becomes more stable and the detachment rate slower. The reverse is true for shorter stems. The different theories, in their varying degree of sophistication, calculate the resultant of this attachment and detachment rate and obtain the net growth rate as a function of fold length.

Even such qualitative considerations indicate that the growth rate must be a maximum at some particular fold length. Quantitative treatment shows that the fold-length distribution established by these considerations has an adequately sharp maximum to account for experimental observations. For numerical evaluation, we need the change in free energies involved when the crystal lattice and the crystal surface are formed. Evaluation of the lattice energy, to a good approximation, requires only knowledge of the heat of fusion and of the degree of supercooling; supercooling is, in any case, one of our variables. We can divide the surface free energy into terms appropriate to the side and basal surfaces. The basal term includes formation of the folds, and is therefore particularly significant.

The theories do account for the observed fold length, as well as its variation with crystallization temperature, with a very plausible choice of parameters. The maximal uncertainty, expressed in terms of the somewhat problematical fold-surface energy, is well within a factor of three.

Results are predictable

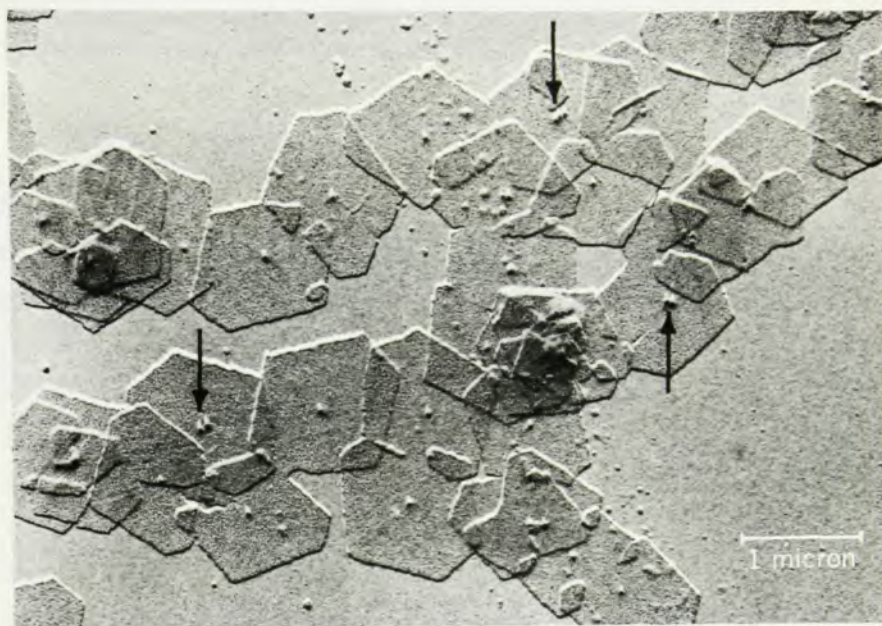
The situation here deserves some reflection. Our system is unique for nucleation studies. Once nucleated it does not continue to grow along the chain direction, so that a dimension closely related to the critical nucleus, the lamellar thickness, remains con-

stant throughout the continued growth of the crystal. In quantitative nucleation and crystal-growth studies of even *simple* substances, achieving both experimental reproducibility and agreement between experiment and theory is notoriously difficult.

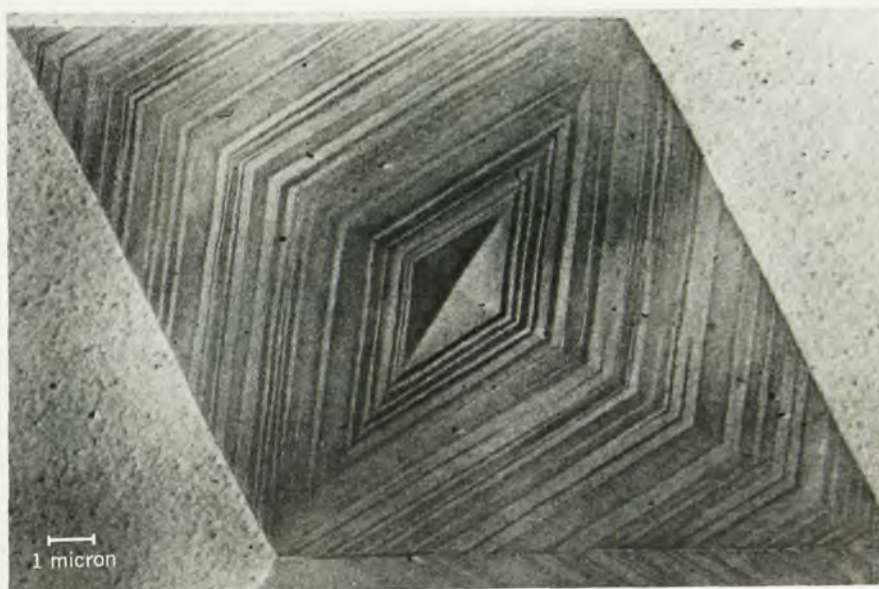
Such highly reproducible experimental results, and the satisfactory agreement between these results and even the most highly idealized theory on a system as complicated and impure as a polymer, are quite noteworthy. The long-chain nature of the molecules is probably responsible for this agreement. Thus the chains will

tend to fold with the appropriate fold length; a length that can not be affected by anything other than the principal and controllable variables of the theoretical treatments.

The high degree of control over crystallization in polymers can be continued to the microscopic observations on crystal growth. Thus polymer crystal growth can be seeded in a convenient and well controlled manner. The seeding process itself is too large a subject for us here; we need only note that, as a result of it, all crystals will start to grow simultaneously and will have the same size (see figure 5).



UNIFORM MONOLAYER CRYSTALS of polyethylene obtained from the self-seeding technique; arrows point to multiple seeds. From ref. 7. —FIG. 5



RIDGED MONOLAYER crystal of polyethylene is illustration of sectorization phenomenon. Electron micrograph is from ref. 8. —FIG. 6

With enough seeds, multilayer formation is suppressed and all layers are single.

Details of the lateral habit, for example, the degree of lozenge truncation, are reproducible functions of the crystallization temperature and concentration. Thus we can grow crystals consisting of single layers of equal, preselected thickness (fold length), lateral dimensions and habit, and we can readily measure and study lateral growth rates. Even the growth rate turns out to be a readily reproducible quantity. Such a high degree of control over size, including all crystal dimensions, shape and growth rate, is not easily exercised over the crystallization of most simple substances. Again, in one way and another, the long-chain nature of the units has a specific, dominant influence on the crystallization.

STRUCTURAL CONSEQUENCES

The folded arrangement of the chains has some characteristic and unique consequences for the structure. In the foregoing discussion, we envisaged crystallization as a laying down of chain-folded ribbons along the prism faces. These ribbons will always be parallel to the appropriate prism face; hence the ribbon planes will take up different orientations in different portions of the crystal, and they will retain these orientations as they become incorporated in the crystal interior on continued growth (see figure 3). The result will be a division of the crystals into sectors or fold domains—as many as there are prism faces.

Division into sectors

Accordingly, subdivision of a single crystal into sectors of different fold-plane orientation should follow from chain folding. This prediction was soon verified in a variety of ways. For example, different sectors melted or transformed at different temperatures, indicating that differences in fold-plane orientation with respect to the underlying crystal structure can lead to differences in the thermal stability of the corresponding crystal sectors. The fold-plane direction proved to be the direction of both clean and easy cleavage, in agreement with expectations.

The distinctions between sectors may be apparent in the microscope, too, without any external interference with the sedimented crystal. This is

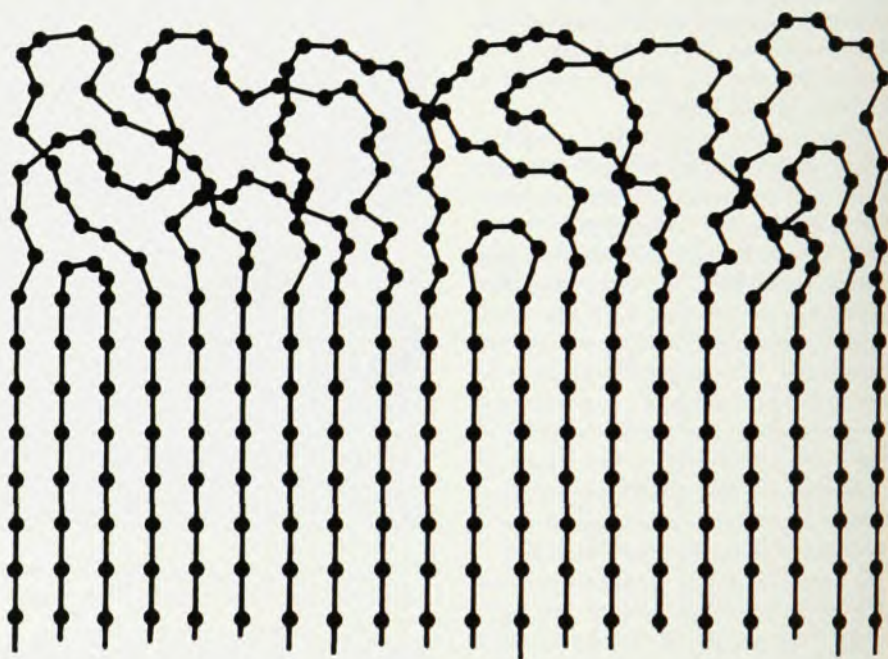
primarily because, in many cases, the crystals are not planar but possess a hollow pyramidal or more complex three-dimensional structure when floating in the liquid. In all these cases the sectors are distinct; in the pyramidal structure, for example, they correspond to the differently inclined facets—similar to the panels of a tent. Such structures may collapse on sedimentation and give characteristic wrinkles and striations. Under special circumstances such three-dimensional effects can be preserved (see figure 6).

The sectors exist because the folds are essentially confined to planes that are parallel to the prism faces. The sloping of facets, as in figure 6, implies that the folds are staggered to

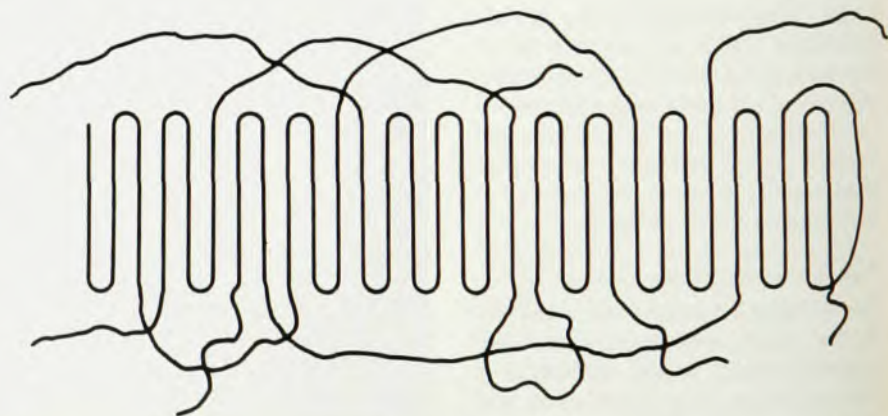
form a surface that is oblique with respect to the chain direction. In crystals such as the one in figure 6, the chains in the straight stems all have the same orientation, which is perpendicular to the overall plane of the crystal and so to the plane of the paper. Such oblique fold surfaces can be associated with specific space requirements or geometries of the folding portions of the chains themselves.

Structure of the fold

What then is the detailed structure of the fold? We can readily verify, through models, that carbon chains can be folded back on themselves by rotations around carbon-carbon bonds. This folding can be achieved in a variety of ways; the particular



INTRINSICALLY DISORDERED fold surface. The two-dimensional representation is that of E. W. Fischer. From ref. 3. —FIG. 7



COMPOSITE FOLD SURFACE. Schematic representation shows adjacently re-entrant folds and elements of surface looseness. From ref. 2. —FIG. 8

method is largely dependent on how many bonds are to be included in the folds. Sketches such as in figure 3 imply that the folds are sharp, and considerations such as arise from the pyramidal geometries suggest that they are geometrically well defined and can be considered as parts of the crystal structure. Indeed there are attempts to map out the energetically most favorable geometrically defined fold paths.

Another way of thinking, however, has raised some different and overriding problems. We can here profitably turn to the traditional models of crystallinity. A crystalline polymer, according to these models, always contains amorphous material that is responsible for its typical "polymeric" behavior. The relevant parameter for the system is, therefore, the "degree of crystallinity" or the "amorphous-crystalline ratio," normally assessed by measuring an appropriate macroscopic property such as density or heat of fusion. When we apply such a measure to an aggregate of otherwise clearly defined single crystals, we note a crystallinity deficiency, conventionally attributable to the presence of amorphous material. We then have the paradoxical situation of an amorphous component within the confines of a single crystal.

Disordered material

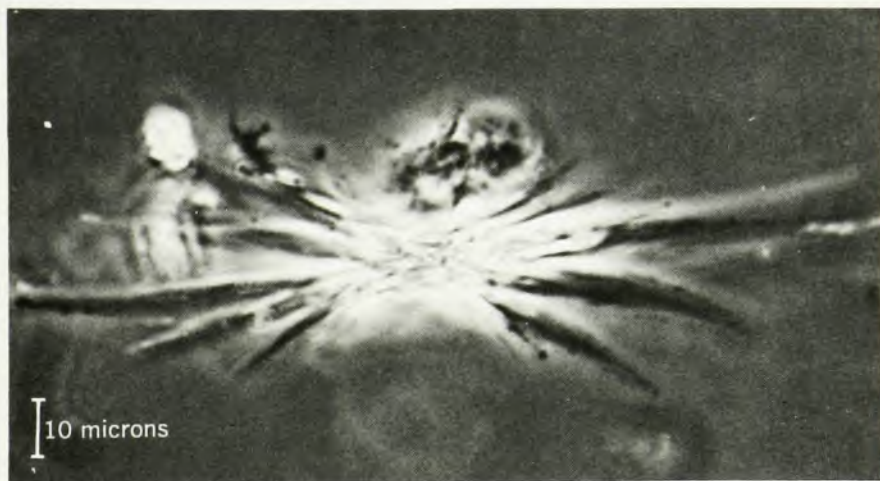
A question arises: How is this amorphous material to be envisaged in relation to the lamellar crystal? We can argue, on a variety of grounds, that the disordered material must be along the fold surface. One extreme view says that the fold surface should be completely disordered, the molecules folding with random re-entry like leads on a telephone switchboard (see figure 7). Such a picture is clearly at variance with the regularity implied by figure 6 as well as by many further crystallographic effects in other types of electron micrographs.

Nor can we readily apply the successful kinetic theories for such a case; indeed the reason why chains should fold at regular intervals would remain unaccounted for. In addition, selective chemical degradation experiments were found to chop the chains into fragments that are integral multiples of the fold length. The sizes imply that representative portions of the folds are very short.

Entropy considerations applied to chains held between fixed ends, on



REGULARLY ROTATED TERRACES can be seen in this electron micrograph of a polyethylene crystal replica. From ref. 9. —FIG. 9



EDGEWISE VIEW of simple multilayer polyethylene crystal in suspension. Splaying layers are revealed in this phase-contrast photomicrograph. From ref. 10. —FIG. 10

the other hand, require the chains to have a certain amount of looseness in the folds. The amount of looseness should increase with temperature; this increase would cause the crystal to melt from the basal surface downward and would be the main cause of the broad melting range in crystalline polymers.

This whole problem is a very complex and controversial one that can not be adequately presented here. We may simplify it by raising the following alternatives. Can the folds be sharp and regular, or must they necessarily be loose, as required, for example, by the thermodynamic argument

we have just mentioned? Or could irregular elements cause the disorder that experiment apparently requires—elements that arise, more or less accidentally, in addition to the sharply folded structure that the whole system would assume, if it had the chance, during deposition (see figure 8)? An attractive aspect of this explanation is that it permits the regularity required by morphological evidence. Current studies show another possible way to produce crystallinity deficiency at the fold surface. These studies, based on earlier theoretical considerations, picture a slightly rough fold surface consisting of folds that are

adjacently re-entrant but fluctuate somewhat in length.

The fold-surface problem is currently a central one for those of us who study polymer crystals. It is not only intrinsically interesting, but is also the first real, structural enquiry into the nature of the disordered material in a partially crystalline polymer.

Multilayer development

We have been considering only individual crystal layers. Although folding does terminate crystal growth along the chain direction, the crystal can thicken by mechanisms other than the continued deposition of the same chain. Thus screw dislocations with displacement (Burgers) vectors equal to the lamellar thickness lead to spiral terrace development (figure 2). Alternatively, new layers can nucleate on top of existing ones; loose hairs (see figure 8) emanating from their surface presumably promote this mechanism. In either case we get a superposition of layer surfaces that introduces a variety of possibilities.

In the exceptional case, the fit of layers can be crystallographically exact. In other special instances the layers can be slightly rotated with respect to each other, but have sufficient interaction between them to bring them in register over extended areas. The unavoidable misfit is concentrated into a network of dislocations. Both of these effects are at variance with a fold surface as disordered as the surface in figure 7. More frequently the rotation is large enough to disrupt crystallographic continuity between layers, but exceptionally it can occur in surprisingly regular sequence over a number of terraces (see figure 9).

The most significant interruption of crystal continuity between consecutive layers is apparent from the edge-on view of the crystals in suspension. This view reveals that the layers can splay apart and thus become physically separated (see figure 10). As concentration increases, more complex sheaves of layers form in this way, but there is also a certain amount of apparently noncrystallographic coherence between layers. This coherence is most likely caused by an increasing number of "tie" molecules threading through two or more layers, and it leads continuously to the bulk, melt-crystallized system. Here we will merely remark that imperfect superposition of layers is the major obstacle



SPHERULITES of poly(trimethylene glutarate) grown between glass surfaces. Photomicrograph with crossed polarizers shows concentric banding associated with helicoidally twisted arrangement of crystals. From ref. 11. —FIG. 11

to growing the more massive polymer single crystals that are required for most experiments in conventional solid-state physics.

Melt-crystallized material

The texture of the bulk, melt-crystallized material had been studied with a polarizing microscope before the results on chain-folded crystallization were known. These studies established that the essential mode of crystallization is in spherulites, corresponding to radially symmetric growth of crystalline units (see figure 11). The spherulites themselves develop from sheaves that gradually fan out into spherical objects during their growth. A periodically varying orientation of birefringent units, associated with a helicoidally twisted arrangement of the crystals around radial directions of the spherulites, causes the concentric banding in figure 11. The origin of the regular twist is unknown. Crystal morphologies, however, could be tied up by studying crystallization from solution.

We can show that the basic units are lamellar. The lamellae, presumably in the form of ribbons, branch to form sheaves. Multilayer crystals

from solution indicate this branching (see figure 10). They will all tend to grow radially within the spherulites into which the sheaves eventually develop, twisting in an airscrew-like fashion with the lamellar planes parallel to the radius. We do not as yet know the mode of space filling and other details of the spherulitic architecture. The lamellae themselves are, to all indications, the result of chain folding, but with an increased proportion of molecular ties between the layers providing the observed mechanical cohesion. Assessment of the relative number of ties and folds is a major unsolved problem.

All observations of the bulk system are handicapped because crystalline units can not be obtained in isolation without seriously disturbing the sample. The most informative technique, selective chemical attack, disperses the sample into lamellae by removing the ties between the layers along with all other amorphous material. The folds, however, are also cut in the process. Thus, although this dispersion enables us to observe the morphology of the crystal proper, information on ties and folds has to be obtained indirectly. This information is being pursued



"SHISH-KEBABS" grown in an agitated xylene solution. Electron micrograph shows fibrillar crystals with lamellar overgrowth. From ref. 12. —FIG. 12

through study of the molecular-weight distribution in the disintegration products.

Deformation behavior

There is then a hierarchy of structures within a sample of a technological polymer. This hierarchy includes the chain itself, the crystal lattice, the lamellae, the fold, tie molecules and disordered material residing in one way or another within the fold surface. Beyond this are the superlamellar structures such as sheaves and spherulites. Each of these elements can contribute to a given property. Whereas it may be too optimistic to expect a complete picture, one can often select the structural unit that really matters for a particular property under a given circumstance.

Deformation behavior is a particularly important property, in the elastic as well as in the plastic range, and is being intensively studied. Thus we can pull out randomly coiled amorphous chains as in the traditional picture of rubber elasticity. At the other end of the ordering scale, we can have mechanically induced twinings, phase transformations and slips within the lattice proper, often in a reversible manner, just as in conventional crystalline solids. Between these extremes are the effects associated with the characteristic submicroscopic morphology of the polymers. We can have, for example, slip or shear that involves relative displacement of lamellae or lamellar packets as well as extension of the chain-folded structures. Whether one or the other factor is dominant depends on sample type, on the magnitude and time scale

of the stress and on the temperature.

In addition, different effects can be at play in different sample portions; when uniaxial stress is applied to a spherulitic sample, for example, the stress will be parallel to some of the radii and perpendicular to others. Even along a given radius, it will have a different relation to the winding units in the different phases of the twist. All of the processes we have mentioned are strongly anisotropic, and we can expect different ones within closely adjacent localities of the same sample.

SOME FURTHER CRYSTAL FORMS

Two manifestations of crystallinity other than chain-folded lamellar crystallization promise to be of great fundamental importance.

Extended-chain crystals

Crystallization of polyethylene melts under pressure of around 5000 atmospheres, for example, leads to a brittle product that resembles the usual polycrystalline solids rather than conventional polymers and has almost no amorphous content. Replicas of fracture surfaces reveal broad lamellae of thicknesses comparable with the length of the molecules. These observations suggest that the entities consist of extended chains.

The origin of this crystal form is not well understood. Most likely refolding to greater chain extension, following the usual chain-folded crystallization, is responsible for these crystals; this is an effect that would be promoted by the high temperatures occurring in crystallization under pres-

sure. Many problems arise, such as the segregation of molecules of differing lengths (fractionation) that would be necessary if extended chains were grouped in more or less uniform lamellae. Nevertheless, as they stand, these crystals represent the closest approach to the thermodynamically most stable crystal form to date, and so are of special significance.

Fibrous crystals

I have stated here that the concept of lamellar crystallization seemed to clash with the traditional expectation that long chains give rise to fibrous entities. A recent development, however, has brought the fibrous element back into the picture in an unexpected fashion. The effects in question all relate to crystallization under flow or stress.

The basic phenomenon was observed when a rotary stirrer was immersed in a supercooled solution. The result was a fibrous precipitate. The fibers, termed "shish-kebabs," had a composite structure; they were platelets strung on a fibrous backbone (see figure 12). Here the fibers formed first and the platelets grew onto them afterwards. The platelets are the usual chain-folded layers and convey nothing new besides demonstrating, in an extreme fashion, that the fold length is not influenced by the substrate on which the chain-folded deposition starts. The fibrous backbone, however, is a novel feature.

The fibers can also be obtained in isolation. The chains are found to be parallel to the fiber axis, and the fibers have higher thermal stability and mechanical strength than the polymer in its more usual form. All this information suggests again that the chains are extended but in this case induced by stress during crystallization. Even if more detailed studies also reveal a significant amount of chain folding within these fibers, their distinctive extended-chain characteristics remain undisputed. It is the longest molecule in the distribution that is particularly prone to precipitate in this form; hence the potential value of stirring-induced crystallization for fractionation.

Evidence of such fibrous, at least partially extended, chain crystallization is accumulating in stressed and flowing melts as well. The essential point is that only a minute amount of such fibrous crystal formation is required to act as nuclei for the usual la-

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mellar crystallization of the entire molten mass. Because these nucleating fibers are parallel to the flow and stress direction, the lamellar crystal growth they cause will proceed in a direction perpendicular to the stress, imparting an oriented texture to the sample as a whole.

The overall impression is a texture consisting of columns of lamellae in which the lamellae have grown transversely to the direction of the orienting influence. Accordingly the fibrous crystals can have three kinds of effects on the sample: they speed up solidification, produce a characteristic overall orientation because of their influence on the direction of the oriented overgrowth, and, finally, the nucleating fibers themselves have distinctive properties. All these effects could be of great importance to technology for melt extrusion, spinning and injection molding, and might well be relevant to the formation of naturally occurring fibers. They are certainly further, very specific, manifestations of the long-chain nature of the molecules. Their combined existence with the usual chain-folded crystallization represents an unexpected reconciliation of two aspects of polymer crystallization that previously appeared to be mutually exclusive: the formation of lamellar and fibrillar structural elements.

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