

Structure and Properties of Crystalline Polymers

Supramolecular structure is complex, can be controlled, and influences mechanical properties.

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Since the first rational synthesis of linear macromolecules by Carothers (*1*) polymer chemists have been intrigued with the idea of tailor-making polymers for applications requiring particular physical and chemical properties not present in other materials. It seemed reasonable that an understanding of the relations between the chemical structure and properties of molecules would lead naturally to the synthesis of more useful polymers.

The polymer chemist has learned much about the kind of structure that leads to a rubber, a glass, or a tough plastic; to a high-melting crystalline polymer; to a polymer resistant to heat, oxidation, and solvents. The simple use of chemical structure to predict properties, and particularly mechanical behavior, has severe limitations. The reason is that normally the structure of the individual molecules contributes only indirectly to mechanical properties. Of more direct influence is the supramolecular structure, that is, the physical arrangement of the molecules with respect to one another. The supramolecular structure of crystalline polymers is so important that by rearranging the polymer molecules within the same polymer sample the mechanical

properties can change drastically, for example, from a state of brittleness to one of toughness or ductility.

Most of the extensive literature on the supramolecular structure of crystalline polymers has appeared within the last 10 years. As in many other fields, this period has been one of such rapid advancement that the interested non-specialist has been overwhelmed with new concepts, such as folded- and extended-chain crystals, crystal defects, and tie molecules. Lagging well behind the study of supramolecular structure is the study of its relationship to mechanical properties. This is, in part, the result of compartmentalization. Workers who study structure are not always interested in mechanical properties, and vice versa. Structure varies not only from one polymer to another, but also within the same polymer. Consequently, generalization is difficult, whether it concerns structure itself or the relationship of structure to mechanical properties.

A broad picture of the supramolecular structure of crystalline polymers is emerging, however. In trying to describe this picture, I will attempt to show how variation in structure is controlled by crystallization conditions and how these variations can affect mechanical properties.

The supramolecular structure of

polymers shown by x-ray diffraction patterns to be semicrystalline was first described by means of the fringed micelle model (2) shown in Fig. 1 (left). A two-phase system, the fringed micelle consists of relatively perfect crystals, several hundred angstrom units long, embedded in an amorphous matrix. Because the molecules are much longer than the crystals, a single molecule can pass alternately through several crystalline and amorphous regions.

The fringed micelle model, generally accepted until about 10 years ago, seemed to account successfully for a number of properties of semicrystalline polymers. Toughness and strength could be explained by the ability of crystallites to act as cross-links or tie points for the amorphous regions. The fringed micelle provided a simple mechanism for the orientation of the crystals during drawing or stretching. The resulting increase in strength and modulus in the stretch direction was consistent with an oriented system of polymer chains held together by crystalline tie points, as shown in Fig. 1 (right). As the knowledge of crystalline polymers increased, however, the fringed micelle model appeared to be grossly oversimplified, if not fundamentally incorrect. It did not conform with structural observations that were being made nor did it account for the broad range of mechanical properties that a single polymer could display.

Spherulites and Folded-Chain Crystals

The fringed micelle was not seriously questioned until the recognition in the mid-1950's that most crystalline polymers can be crystallized into an array of closely packed polyhedra (Fig. 2a) which are large enough to be seen with the optical microscope. During crystallization, these spherulites grow in the melt from many point sources (Fig. 2b). Increasing in size, they finally impinge on one another. Spherulites are not single crystals but aggregates of many crystals. Viewed under the polarizing microscope, the birefringent

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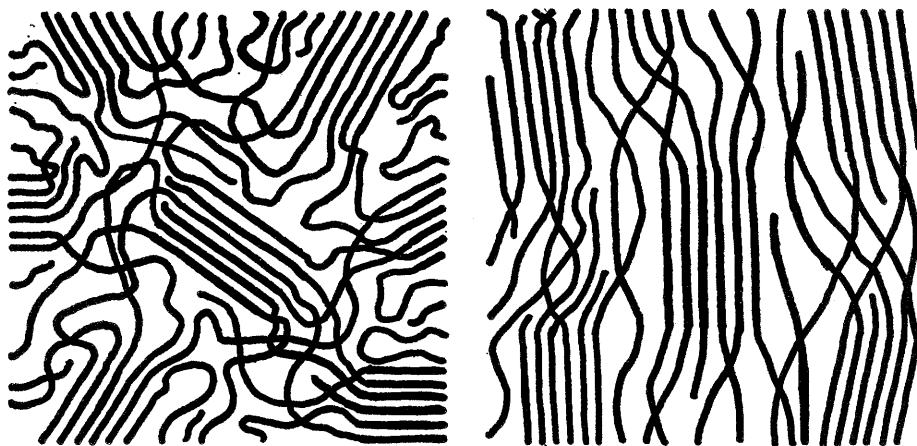


Fig. 1. Fringed micelle model. (Left) Unoriented; (right) oriented. A two-phase system, the fringed micelle consists of relatively perfect crystals embedded in an amorphous matrix of disordered chain segments. Because the molecules are much longer than the crystals, a single molecule can pass alternately through several crystalline and amorphous regions.

pattern of the spherulites indicates that the crystals are ordered, relative to one another. At the very least, supracrystalline order within spherulites adds a degree of organization to polymer structure not taken into account by the simple fringed micelle model.

A more severe shock to the concept of the fringed micelle was the discovery in 1957 of the folded-chain polymer crystal. At that time, several investigators (3) independently isolated single crystals of polyethylene by slow crystallization from dilute solution. These crystals were in the form of thin platelets or lamellae with a thickness of about 100 angstroms. Electron diffraction showed that the polymer chain in these lamellae was perpendicular to the plane of the lamellae. Because the lamellar thickness was only a fraction of the molecular length, the polymer chain must fold back and forth on itself within the crystal as shown in Fig. 3a.

A number of theories have been advanced to account for chain-folding. Recently, Lindenmeyer (4) has helped to integrate these theories by showing that the folded-chain crystal represents the best energy compromise for which a mechanism of crystal formation is normally available. For instance, the fringed crystal is less stable than the folded-chain crystal because the free energy contribution of the crystal fringe is greater than that of the crystallographic folds. The folded-chain crystal is metastable, however. The most stable crystal is one of large lateral size in which all chains are extended and of the same molecular weight, with the end groups all lying in two surface planes. Lower surface energy—the re-

sult of greater thickness and smaller surface area—makes the extended-chain crystal more stable than the thinner, folded-chain crystal. However, except where the molecular weight is very low, no mechanism exists under normal circumstances for the growth of an extended-chain crystal. Therefore, according to this view, the normal mode of the polymer crystal is the folded chain.

Although the folded-chain crystal, in which the chain segments reenter in adjacent positions rather than in the random manner of a switchboard (Fig. 3b) is still questioned by some (5), the evidence for regular chain-folding in specific instances does seem to be conclusive.

Screw dislocations observed between crystals (6) and the hollow pyramidal shape of some single crystals (7) are difficult to understand except in terms of the crystallographic packing of folds and adjacent reentry. The question, therefore, seems to be not whether regular chain-folding can occur, but the extent to which it occurs with a specific polymer under a specific set of crystallization conditions.

The discovery that single-crystal lamellae can be grown from dilute solution led naturally to speculation about the structure of bulk- or melt-crystallized polymers. After all, the commercial fabrication of polymers is normally carried out by melting the polymer, injection-molding or extruding it into shape, then cooling it until crystallization occurs. Bulk-crystallized polymers are, however, more complicated structurally and more difficult to study than solution-grown crystals. Nevertheless,

by 1960, the lamellar structure of melt-grown spherulites had been established with reasonable certainty (8).

Figure 4 represents in simplified form what is now generally believed to be the structure of a spherulite. The lamellae, with a thickness and lateral extension of the same order as solution-grown crystals, radiate from the center. They branch and rebranch at small angles to the radius so as to fill the volume of the spherulite. In order for these lamellae to be comparable to solution-grown crystals the chain axis must be more or less normal to the radius of the spherulite. This has, in fact, been demonstrated by the use of the microbeam x-ray diffraction technique for polyamides, poly(ethylene terephthalate), and the polyolefins (9, 10). The lamellae may or may not twist in a regular manner, depending on the polymer and the crystallization conditions.

The disordered amorphous matrix of the fringed micelle model accounted very well for the diffuse halo in the x-ray diffraction patterns of melt-crystallized polymers and the low densities relative to the unit cell densities. The question arises of how to account for these x-ray and density observations in terms of the lamellar structure of spherulites in bulk-crystallized polymers. On this point, there is by no means universal agreement. One view, developed primarily by Lindenmeyer (11) which has gained in favor in the past few years, is that the structure of crystalline polymers is not unlike that of metals. Instead of a two-phase arrangement of amorphous regions containing long, molecular segments and crystalline regions, crystalline polymers are better described as crystals containing defects. In this defect model deviations from the unit cell density are attributed to dislocations within the lamellae, lamellar folds, and even voids.

In its purest form, this model does not allow for long sequences of randomly ordered polymer chains comparable to those within the amorphous regions of the fringed micelle model (12). The crystal lamellae consist primarily of folded chains with adjacent reentry. The folds may or may not form smooth planes on the surfaces of the lamella. Although a chain can pass occasionally from one lamellae to another instead of folding back on itself, these lamellar bridges are short and under tension.

Interlamellar Amorphous Model

A more conservative view of the lamellar structure of bulk-crystallized polymers, proposed by Flory and by Mandelkern (5), does not require regular folding with adjacent reentry. Chain segments frequently return to a lamella, but in the random manner of a switchboard (Fig. 3b). Having left a crystal, some molecules wander about before returning or entering another lamella. Thus, the considerable amount of disordered or amorphous material which normally exists between lamellae accounts in large part for the density deficiency of bulk-crystallized polymers.

Peterlin (13) takes a position somewhat intermediate to the crystal defect and conservative views. Accepting the important contributions of amorphous regions between lamellae, he retains chain-folding and adjacent reentry as essential features of the lamellae themselves. Regardless of the makeup of the lamellae, whether chain-folded or random, I shall call any model consisting of stacks of lamellae separated and connected by amorphous regions the interlamellar amorphous model (Fig. 5). The presence of amorphous regions makes the interlamellar amorphous model much closer to the fringed micelle model than to the crystal defect model.

My view, which is neither unique nor new, is that neither the interlamellar amorphous nor the crystal defect model is universally applicable to crystalline polymers. The closest approximation to the true state of polymer structure views these models as consisting of overlapping regions of a continuous spectrum of structural possibilities. At one end of the spectrum, the molecules are in a state of complete order. At the other, they are completely disordered. There is some question whether these extreme states are ever achieved in reality. A single crystal must contain end groups which spoil perfection, and amorphous polymers are recognized as having some degree of supramolecular order (14).

By varying the crystallization conditions, most crystallizable polymers can be made to cover a broad portion of this order-disorder spectrum. Slow crystallization from dilute solution at small degrees of supercooling produces relatively perfect crystal lamellae, because the molecular mobility is high and the chains are given time to fold

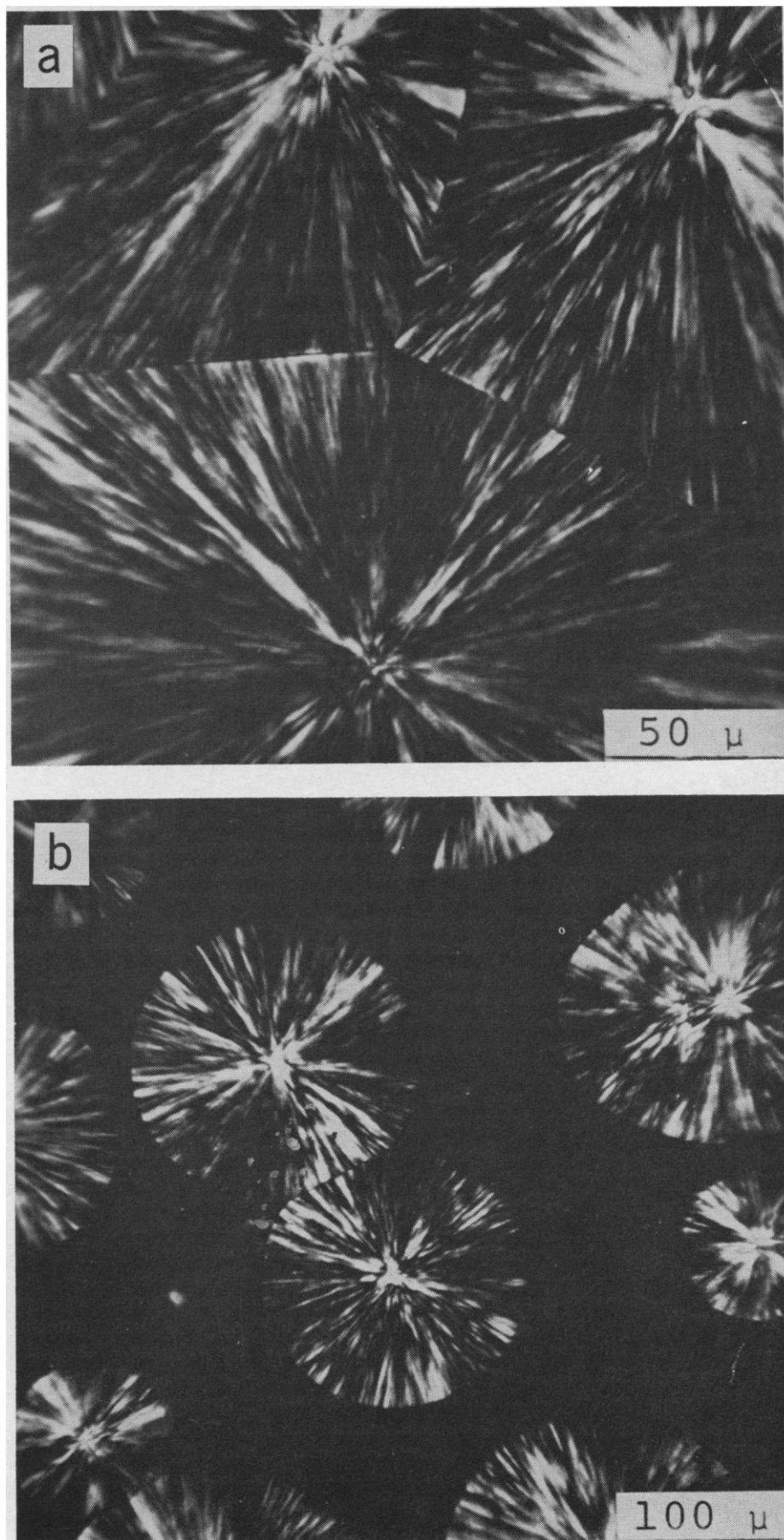


Fig. 2. Spherulites. (a) In melt-crystallized polypropylene; (b) polypropylene spherulites growing in a melt. Beginning from point sources, they increase in size until they impinge on one another.

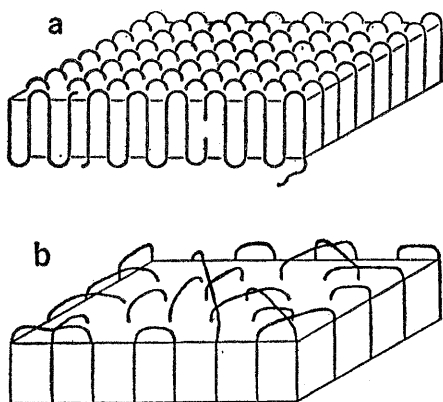


Fig. 3. Models for the structure of crystal lamellae. (a) Folded-chain model; (b) switchboard model. In both models, the molecular segments within the crystal lattice lie perpendicular to the lamellar surface.

evenly on themselves. The dilution effect lowers the probability of a second molecule participating in the lamellae until the first chain is consumed. As the temperature is lowered and the concentration increased, molecular mobility is lowered and the nucleation and growth rates of lamellae increase. The result is a decrease in crystal perfection, as tie molecules and entrapped chain segments between lamellae play an increasingly important role. At very high degrees of supercooling, mobility becomes so restricted that, with many polymers, crystallization can be prevented altogether. Thus, crystallization from dilute solution with little supercooling leads toward a high state of order, and bulk crystallization at low temperatures favors disorder.

The crystal defect model has been shown to function very well on the

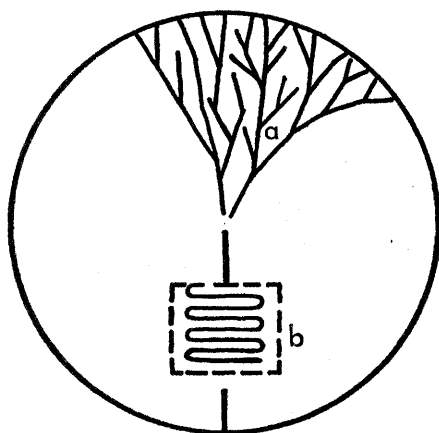


Fig. 4. Structure of a spherulite. (a) Branching of the lamellae, and (b) enlargement of a portion of a folded-chain lamella showing the chain axis perpendicular to the radius of the spherulite.

ordered end of the spectrum. But, as disorder increases, the interlamellar amorphous model describes more accurately the state of the polymer. Finally, with so-called amorphous polymers, the lamellar structure seems to disappear altogether. The important distinction is that, whereas crystals grown from dilute solution are better described in terms of crystal defect theory, polymers crystallized under commercial conditions, for example, from the melt or from concentrated solutions at high degrees of supercooling, are more accurately characterized with the interlamellar amorphous model. Whether the lamellae are switchboard-like or involve adjacent reentry or both is, however, still open to question.

Consistent with what is known about supramolecular structure, the interlamellar amorphous model is the most useful approach to understanding the mechanical properties of bulk-crystallized polymers. Many of the variations in mechanical behavior that a crystalline polymer can be made to display can be explained most reasonably by differences in the character of the interlamellar regions.

First of all, without interlamellar ties, crystalline polymers would not be very useful as plastics. Analogous to a brick wall without mortar, stacks of solution- or melt-grown crystals, where tie molecules are largely absent, are extremely friable. Large, relatively perfect, solution-grown spherulites are brittle for the same reason. As more tie molecules are added, a point is reached where an applied stress can be sustained, sufficient to cause the crystal lamellae to deform by the slipping and unfolding of chains within the lamellae without fracture. Thus, tie molecules reduce brittleness by conferring ductility.

But ductility in a laminar structure proves nothing about the nature of the tie molecules; that is, ductility does not distinguish between short segments under tension and long, randomly coiled, or looped segments sandwiched between lamellae. The excellent elasticity of most crystalline, commercial plastics from moderate extensions probably does afford such a distinction. Very short tie molecules would transfer a stress directly to the crystals causing intralamellar slip and chain-unfolding with the result that the sample would deform irreversibly. Amorphous regions containing long segments connecting lamellae can, however, extend and re-

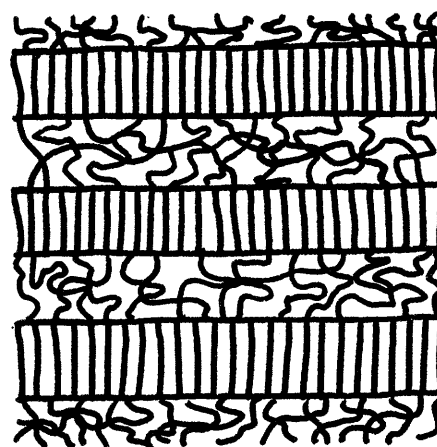


Fig. 5. Interlamellar amorphous model for bulk-crystallized polymers. The crystal lamellae are tied together by amorphous regions similar to those in the fringed micelle model. A molecule having passed through a lamella may either pass on to another lamella through an amorphous region or reenter the same lamella. Whether reentry is adjacent (Fig. 3a), or the switchboard-type (Fig. 3b), or both, has not been firmly established.

cover much in the manner of a rubber. Thus, the contribution of tie molecules under tension cannot be very great in polymers with good recovery properties (15).

The fact that crystalline polymers with a moderate degree of crystallinity show glass-transition behavior is difficult to understand without postulating the presence of flexible amorphous regions. When a polymer is cooled through the glass-transition temperature, this behavior appears as a change from ductile to brittle failure. This is particularly apparent when the sample is strained at impact rates. Whatever theoretical disagreement may exist over glassy performance, it is generally recognized as the property of disordered molecular segments. Crystal defects and tie molecules under tension would not contribute significantly to property changes below the glass-transition temperature. Because crystalline commercial plastics invariably show glass-transition behavior, a sizable number of disordered molecular sequences seems assured.

Use of the interlamellar amorphous model can be demonstrated by the data on impact behavior for two samples of polypropylene, one crystallized by rapid quenching and the other by slow cooling (Table 1). Tested above the glass-transition temperature, the quenched sample with the greater amorphous contribution shows higher elongation and energy absorption during the impacting

process. Below the glass-transition temperature, both samples become very brittle and can hardly be distinguished from each other. This is exactly the kind of behavior expected from differences in the interlamellar amorphous regions. Above the glass-transition temperature, the greater amount of amorphous material manifests itself in better impact properties. At low temperatures, however, the amorphous regions become stiff and lose the ability to deform and absorb energy. Hence, brittleness not only increases but is nearly the same for both samples.

Bulk-crystallized polymers are not simply a series of stacked lamellae separated by amorphous regions. These lamellar units are arranged radially within spherulites. Any consideration of the fracture behavior of spherulitic polymers must also take into account the nature of interspherulitic boundaries. There is little reason to believe that interspherulitic and interlamellar regions differ in composition. Fracture studies have, in general, shown that cracks form about as readily between as within spherulites; Fig. 6 shows both kinds of cracks within the same sample of deformed polypropylene. If crystallization is carried out very slowly, voids can form between spherulites. Acting as fracture sites, these voids cause fracture to occur preferentially in the interspherulitic regions. The result is a brittle material of little commercial value.

Control of Supramolecular

Temperature variation and the use of solvents during crystallization are two ways of controlling and modifying supramolecular structure. Other means which also have profound effects on mechanical properties are: (i) the addition of 1 percent or less of substances which can alter the course of crystallization by their nucleating or surface activity, (ii) aging and annealing subsequent to primary crystallization, and (iii) orientation.

The crystallization process through which spherulites are formed involves sequential steps of nucleation and spherulite growth. Nucleation can be either homogeneous or heterogeneous. The former occurs spontaneously from the polymer molecules; the latter, from the surface of a foreign substance which, when added intentionally, is called a nucleating agent. The homo-

Table 1. Effect of crystallization conditions on impact properties of compression-molded polypropylene.

Crystallization conditions	Crystallinity, from density (%)	Impact data			
		23°C	Above T_g^*	-10°C	Below T_g^*
		Elongation (%)	Energy (kg cm cm ⁻²)	Elongation (%)	Energy (kg cm cm ⁻²)
Water quenched	52	11-34	940-2600	2.2	257
Cooled slowly	67	4.2	54	1.7	208

* Glass-transition temperature.

Table 2. Effect of nucleation, spherulite size, and crystallinity on impact properties of compression-molded polypropylene.

Crystallization conditions	Nucleation	Spherulite diameter (μm)	Crystallinity, from density	Impact data, 23°C	
				Elongation (%)	Energy (kg cm cm ⁻²)
Water quenched	No	~ 2	52	11-34	940-2600
Cooled slowly	No	~ 20	67	4.2	540
Quenched	Yes	< 2	62	4.4	510
Cooled slowly	Yes	< 2	73	3.6	470

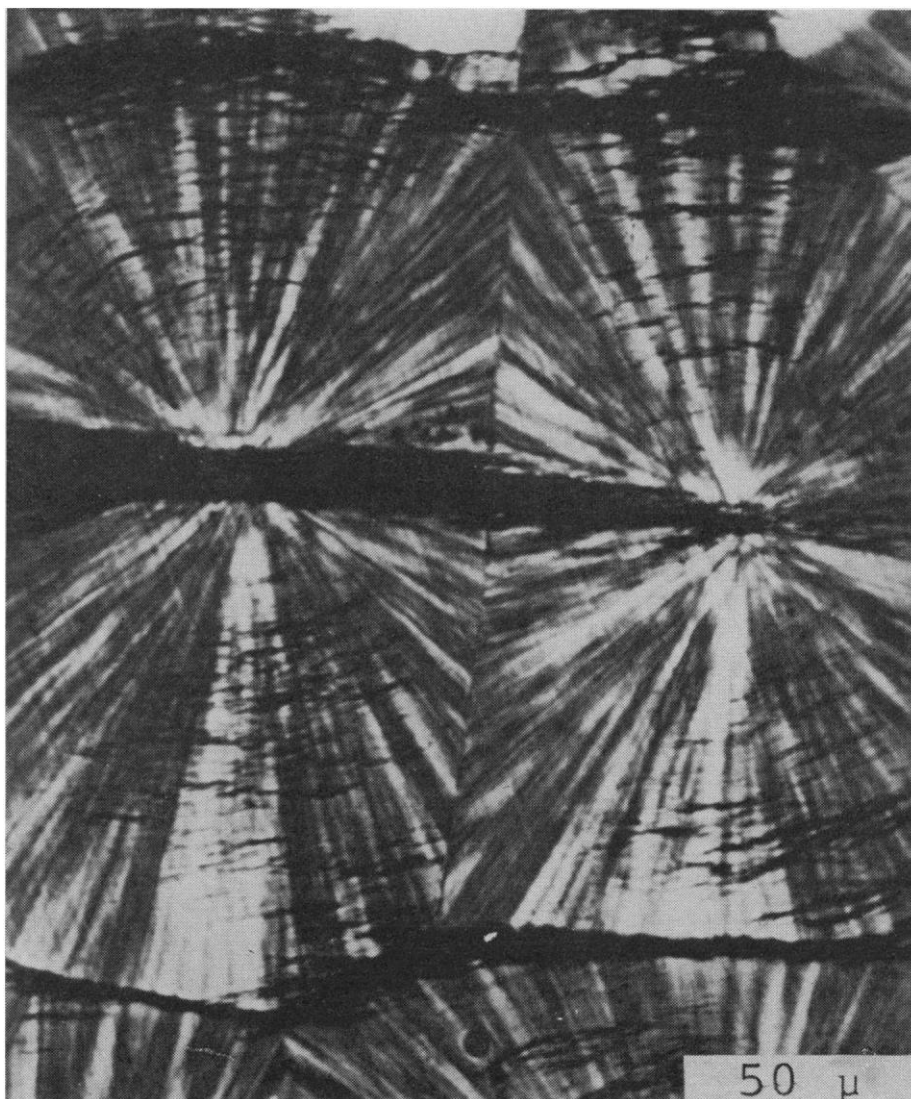


Fig. 6. Strained sample of polypropylene. There are cracks within and between the spherulites. Stretch direction vertical.

geneous nucleation and growth rates, which are negligible close to the melting point, increase with supercooling to a maximum, and decrease, again becoming negligible at the glass-transition temperature (16). The spherulite size depends on the ratio of the nucleation to the growth rate, decreasing as this ratio increases. Because the temperature at which the rate peaks is usually higher for growth than for nucleation, high crystallization temperatures favor large spherulites, while low temperatures favor small ones. The temperature effect is so great that, with many polymers, the spherulite size can be varied several thousandfold.

Nucleating agents reduce the size of spherulites by increasing the number of nuclei. The effect is pronounced at high temperatures where the rate of homogeneous nucleation is slow. Because spherulites scatter light, nucleating agents have the practical effect of improving clarity through size reduction. By increasing the number of nuclei, nucleating agents also increase the crystallization rate. Some polymers, such as isotactic polystyrene, cannot be crystallized to an appreciable extent within a practical time period without a nucleating agent. The temperature for a reasonable rate of spherulite growth is too high for a significant amount of homogeneous nucleation to occur. Kargin and co-workers (17) found that, whereas isotactic polystyrene will not crystallize to any significant extent in 3 hours without nucleation, 2 percent indigo causes appreciable crystallization within 15 minutes.

Because large spherulites contribute to brittleness, it has been suggested that nucleation should decrease brittleness. The effect of spherulite size on impact properties is, however, by no means certain. Normally, conditions which lead to large spherulites, such as crystallization at high temperatures, also lead to higher crystallinity. The latter, rather than the size of the spherulites, may cause the brittleness. The impact data in Table 2 for polypropylene films crystallized at two cooling rates, with and without a nucleating agent, argue against spherulite size as the controlling factor. In this case, good impact properties seem to correlate with low crystallinity. That impact properties should depend more on spherulitic character than size would not appear to be unreasonable.

The crystallization of some polymers

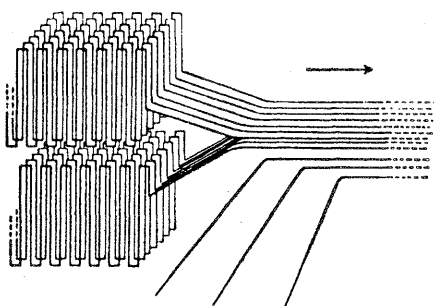


Fig. 7. Kobayashi's mechanism for orientation. Upon drawing, rows of folded chains unfold and combine with other rows of unfolded chains into extended chain crystals.

is strongly influenced by surface-active agents, which increase the homogeneous nucleation rate and lower the growth rate by reducing the surface energy. As with nucleating agents, the result is smaller spherulites. At higher concentrations, some surface-active agents have the opposite effect. For example, 0.1 percent of a certain dye-stuff in nylon 66 reduces the spherulite size while 1 percent actually increases the size (18). Apparently, at the higher concentration, the surface-active agent acts as an antinucleating agent.

Most polymers continue to increase in density long after spherulite growth is complete. This post-densification in

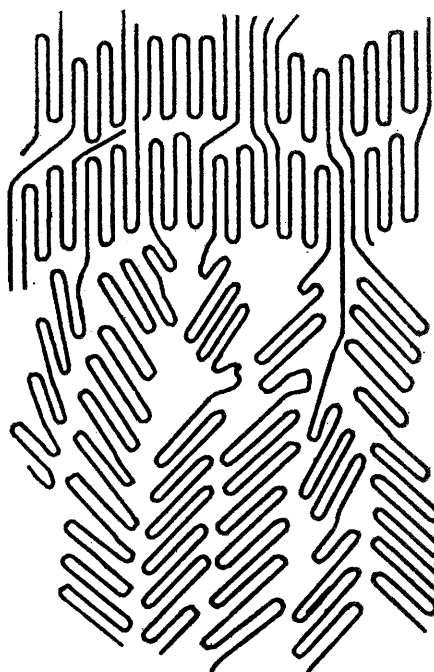


Fig. 8. Peterlin's mechanism for orientation. Lamellae are tilted and broken into clumps (bottom) which then rearranged in the fully oriented structure (top) as stacks of lamellae.

the intra- and interspherulitic regions is called secondary crystallization to distinguish it from the primary process of spherulite growth. Secondary crystallization is thought to occur by at least two mechanisms: (i) a thickening of the lamellae, during which chain segments are pulled in from the amorphous regions; the driving forces for this process are the reduction of the surface energy of the lamellae and the amount of the amorphous material; (ii) crystallization between the lamellae of molecules of low molecular weight and imperfect stereoregularity that were rejected during spherulite growth (19).

The rate of lamellar thickening increases with temperature. If a crystallized sample is annealed, the density decreases at first as the lamellar surfaces and crystals containing low molecular weight and nonstereoregular molecules melt. With time, the density increases to well above the initial value as the lamellae increase in thickness.

As might be expected, secondary crystallization can increase brittleness. Yang and Stein (20) found that aging causes the spherulites of polybutene-1 to crack during deformation. Cox (21) made some observations on the effects that aging at room temperature and annealing have on the brittle behavior of linearly drawn polypropylene film. Tested perpendicularly to the stretch direction, freshly prepared films were ductile but became brittle with age. This brittleness was lost immediately after annealing at 100°C, but reappeared with time at a faster rate than originally. The density of the film increased at each stage of the process. The problem is to reconcile the loss of brittleness with the increase in density following annealing. Possibly a large portion of the brittleness, which developed originally was caused by the crystallization between lamellae of tie molecules having imperfect stereoregularity. Annealing could have melted these imperfect crystals which caused a return to ductile behavior; brittleness returned as recrystallization occurred. An increase in the lamellar thickness during annealing would account for the density increase. The contribution of lamellar thickening to brittleness during annealing is indicated by the faster rate of embrittlement in the annealed than in the fresh film. At the very least, these experiments illustrate the complexity of secondary crystallization and its effects on mechanical properties.

Orientation

Orientation is the best known, most dramatic, and probably most important means for modifying the structure and properties of linear polymers. Alignment of the polymer chains parallel to one another during the drawing process can increase the strength and stiffness in the stretch direction by more than 25 times. Perpendicular to the stretch direction, oriented polymers are weak and tend to split. This tendency is normally of little consequence for fibers where stress is usually applied only in the stretch direction. In packaging film, however, splitting is undesirable. Films are, therefore, frequently drawn in two directions at right angles to each other so as to orient the molecules randomly within the plane of the film.

While the fringed micelle model was still generally thought to be applicable to unoriented polymers, the structure of oriented crystalline polymers was naturally thought of in terms of an oriented fringed micelle (Fig. 1, right). Even with the recognition of the lamellar structure of spherulites and the acceptance of folded-chain crystals in unoriented polymers, until quite recently the extended chain aspect of the fringed micelle model was generally retained as the structural basis of oriented polymers. The mechanism of orientation did, however, require modification. Kobayashi (22) proposed that, upon drawing, rows of folded chains unfold and combine with other rows of unfolded chains into extended chain crystals as shown in Fig. 7.

Evidence for lamellar structure in oriented polymers has been accumulating over the past several years. From theoretical x-ray studies, Bonart and Hosemann (23) suggested that drawn polyethylene consists of folded and unfolded chains passing through lamella-like crystals. Not until 1964 was the lamellar structure in drawn polyethylene definitely established by Hay and Keller (24). After etching samples with nitric acid, they observed lamellae 100 to 500 angstrom thick lying transverse to the stretch direction. Commenting on their similarity to single polymer crystals, these authors speculated that the lamellae in these drawn samples consist of folded-chain lamellae and are connected by tie molecules to provide cohesion.

Peterlin (13) postulated that, in the orientation of spherulitic polyethylene,

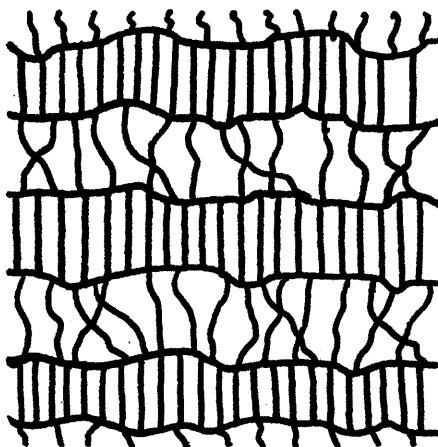


Fig. 9. Interlamellar amorphous model for an oriented polymer showing a considerable amount of lateral cohesiveness to the lamellae and the oriented amorphous regions. Stretch direction vertical.

lamellae are broken into clumps which are then arranged in the fully oriented structure as stacks of lamellae (Fig. 8). With the exception of a small amount of chain unfolding during the breaking up of lamellae, the folded-chain structure remains largely intact. This mechanism was suggested by the structure of fibrils that are formed when very thin spherulites of polyethylene are drawn.

Electron diffraction showed that the molecules lie in the fibril direction. In earlier studies, where fibrils were observed across cracks in single crystals, it was assumed that fibrils were extended chain crystals. This led Kobayashi to propose the orientation mechanism shown in Fig. 7. However, from electron micrographs of iodine-stained fibrils that were pulled out

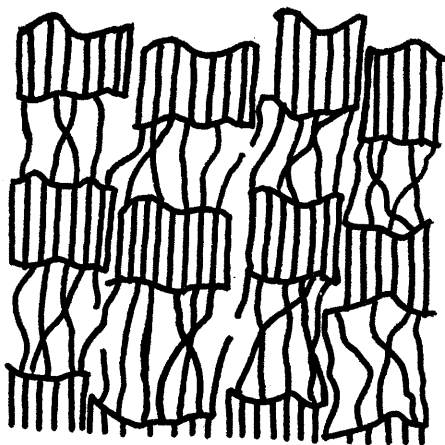


Fig. 10. Fibrils in drawn crystalline polymers formed during cold-drawing or hot-drawing to a very high draw ratio.

from very thin spherulites, Peterlin found an alternating sequence of regions along the fibrils which he ascribed to amorphous (accessible to iodine) and crystalline (impenetrable by iodine) portions. Because the periodicity of 135 angstroms agreed very well with the thickness of the unoriented lamellae, he concluded that the latter do not lose their original character during orientation; instead, they are broken into smaller clumps as is required by the width of the fibrils (approximately 200 angstroms).

Recently, Samuels (25) obtained evidence that lamellar orientation is also the mechanism by which molecules become oriented in spherulitic polypropylene. Both small- and wide-angle x-ray diffraction studies of a series of polypropylene films drawn various amounts indicated that the crystal lamellae orient at the same rate as the molecules within the lamellae. These observations can only mean that the crystalline regions within the undrawn material remain substantially intact during the drawing process. The conversion of chain-folded lamellae into extended-chain crystals, as proposed by Kobayashi (22), is a discontinuous process, inconsistent with Samuels' observations.

Lamellae which have been broken into small clumps approximately 200 angstroms wide (13), cannot really be considered lamellae. Their lateral dimensions are no longer large relative to the thickness. The model of an oriented polymer, which consists of broken lamellae tied together by amorphous regions, thereby differs from the oriented fringed micelle (Fig. 1, right) only to the extent that the crystals consist of folded chains or chains of the switch-board type.

X-ray diffraction studies by Hosemann (26) and Peterlin (27) of oriented, bulk-crystallized polyethylene indicate a much higher degree of lateral cohesiveness in the crystalline regions than a few hundred angstroms, though considerable surface waviness of the lamellae is probably present. The results of dynamic mechanical measurements on oriented polymers of ethylene, propylene, ethylene oxide, formaldehyde, and tetrahydrofuran led Takayanagi and co-workers (28) to conclude that the crystalline and amorphous regions in these polymers are continuous in the lateral direction. These regions alternate, for the most part, in the stretch direction. The latter conclusion was also

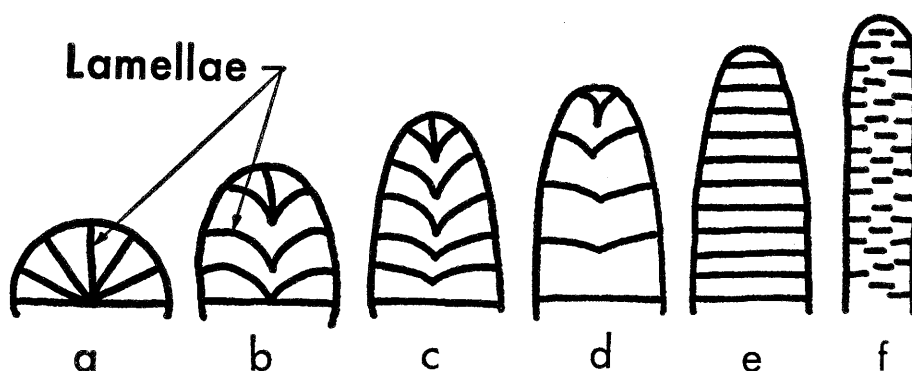


Fig. 11. Samuels' mechanism for lamellar orientation within spherulites. (a) Undeformed spherulites; (b-e) spherulite deformation and lamellar orientation; (f) fibril formation through breakup of the lamellae. Detailed structure of the lamellae and amorphous regions, before and after fibril formation, are shown in Figs. 9 and 10.

reached by Samuels (29) from sonic modulus measurements on polypropylene. Thus, the oriented interlamellar amorphous model, shown in Fig. 9, is a reasonable model for the structure of these oriented polymers.

The work of Hosemann (26) and Takayanagi (28) seems to indicate, however, that true lamellar structure is present only when these polymers are heated during drawing (hot-drawn) or annealed after drawing at room temperature (cold-drawing). Cold-drawing, by itself, causes a breakup of the original lamellae into blocks which are not in crystallographic register with one another. This breakup of the lamellae is accompanied by the formation of long fibrils, 100 to 400 angstroms wide, as shown in Fig. 10. (Presumably, these fibrils are of the same character as those pulled out from Peterlin's thin spherulites, which were also cold-drawn.) Upon annealing, the fibrils disappear as the crystal blocks move back into crystallographic register to reform the lamellae. The lateral coherency of the lamellae is, therefore, highly dependent upon drawing and annealing conditions.

Samuels (25) found that fibril formation can occur during the hot-drawing of polypropylene film, but only above a certain draw ratio which increases with temperature. His mechanism for the orientation and fibrillation processes on the spherulitic and subspherulitic levels in hot-drawn polypropylene is pictured in Fig. 11. The spherulites deform at the same rate as the film itself. The lamellae remain largely intact until almost completely oriented as in Fig. 9. Further drawing causes them to cleave into crystal blocks a few hundred angstroms wide (Fig. 10). Finally, lamellar cleavage with fibril

formation become the predominating deformation process.

The amorphous regions between the lamellae in an unoriented polymer play an important role in the orientation process. Without tie molecules, it is difficult to understand how orientation of the molecules within the lamellae would occur at all. During drawing, the amorphous regions also become oriented, though at a somewhat slower rate than the crystals (29, 30). Orientation of the noncrystalline material has important consequences for the properties of drawn polymers. As orientation increases, tie molecules become more closely packed and crystal-like, thereby reducing the absorption and diffusion rate of solvents. Relaxation of oriented amorphous regions is largely responsible for the shrinkage which occurs on annealing. Indeed, the effects which the orientation of the tie regions have on the properties of drawn polymers provide additional support for the view that tie molecules in unoriented polymers are in a state of relaxation, as pictured by the interlamellar amorphous model.

Summary

Through control of the crystallization process many polymers can be made to exhibit a broad spectrum of structural possibilities, ranging from a state of high disorder to one of high order. Emphasis has been placed on bulk-crystallized polymers which normally fall near the center of this spectrum. This was done in part because polymers are most commonly fabricated in this manner, and also because the amount of attention given in recent years to crystals grown from dilute

solution has tended to obscure important aspects of the structure of bulk-crystallized polymers. Differences in the structure of the interlamellar regions account most reasonably for many of the variations in mechanical properties that crystalline polymers can be made to display.

The interlamellar amorphous model, proposed here as a structural model for bulk-crystallized polymers, largely neglects the lamellae themselves, because so little is known about the structure of the lamellae of bulk-crystallized polymers and how variations in lamellar structure can affect properties. This model is intended, therefore, as both a working hypothesis to aid further investigation and as an outline to be filled in as more is learned about the supramolecular structure of crystalline polymers (31).

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32. I thank Dr. A. Peterlin for permission to use Fig. 8; Dr. P. H. Geil for Fig. 3; Wiley-Interscience Inc. and Dr. Geil for Fig. 7; and W. W. Cox for the photomicrographs and the data in Tables 1 and 2.

Mechanism of Rhythmic Synchronous Flashing of Fireflies

Fireflies of Southeast Asia may use anticipatory time-measuring in synchronizing their flashing.

John Buck and Elisabeth Buck

The Dutch physician Engelbert Kaempfer, after a voyage downriver from Bangkok to the sea in 1680, wrote, "The glowworms. . . represent another shew, which settle on some Trees, like a fiery cloud, with this surprising circumstance, that a whole swarm of these insects, having taken possession of one Tree, and spread themselves over its branches, sometimes hide their Light all at once, and a moment after make it appear again with the utmost regularity and exactness . . ." (1). Since then more than 30 similar reports of oriental firefly displays have appeared (2), and it has been claimed that the concerted flashing continues "hour after hour each night for months" (3).

Synchronous flashing has commanded attention as a spectacle and in relation to its function (4). However, the greatest interest in the flashing has centered on mechanisms by which synchrony might be attained and maintained. The complexity of this problem is shown by the fact that, even excluding the suggestion that the phenomenon is due to twitching eyelids of the observer (5), several quite different explanations have been proposed. The possibility that the synchrony is an illusion (6) needs also to be kept in mind because of certain human perceptual limitations that will be mentioned later, and because of ex-

perimental evidence that the mind tends to read order into a display of randomly flashed lights (7). In view of the variety of puzzles associated with concerted flashing we are glad to be able to describe some observations and measurements made recently in Thailand (8). In comparing these data with previous reports we exclude all single-episode or irregularly repeated synchrony, whether occurring mysteriously (9) or evoked by a clearly identified cause such as an explosion (10). We also exclude as trivial all rhythmically repeated mass flashing which is driven or cued from outside the participating congregation (11). However, because of the basic physiological interest of synchronization we include in our analysis related behavior in the only animals beside fireflies that seem able to perform endogenous mass acts of rhythmic synchronism—man and certain sound-producing insects (12).

Types of Synchronism

Mass rhythmic behavior implies alternation of times in which the individual acts are relatively frequent ("episodes") with times in which they are infrequent or absent. In the type of display seen in Thailand all the flashing may be concentrated within an interval

shorter than 20 percent of each cycle length (see below) and is readily recognizable as synchronism. However, even a display in which the individual acts had a sinusoidal frequency distribution would be strikingly different from randomness and might well be construed as "synchronous." It is clear, therefore, that biological synchrony can only be defined in arbitrary quantitative terms. Similarly, a given range or span of coincidence with the communal flash can be attained by a variety of basically different processes. Hence, to indicate the types of information needed to analyze synchronization we outline below some mechanisms that have been observed or proposed in various organisms.

Inertial synchrony. In this mechanism the individual rhythms, after being put into synchrony by a single nonrecurrent triggering stimulus, continue in step because their natural periods are approximately equal. Such synchrony can occur, for example, in a population of microorganisms after an inhibitor of cell division has been washed out (13). It also occurs between runners during the first few strides after the starting gun. In fireflies the rhythmic flashing of individual flying males is well known (14, 15), and it has been suggested by several observers that some rare or accidental event, such as the sudden darkness preceding a late afternoon thunderstorm or the ending of a shower of rain (16), might set off the whole population in step. Transient synchronous flashing seen after an inhibitory sweep of bright artificial light (17) suggests that lightning could have a similar effect. Such inertial cycling might conceivably apply to certain rare and brief displays reported in American fireflies (2), but it is completely inadequate to account for the sustained nightly synchrony in oriental concerts. Even if one assumes that the start of flashing is triggered by, say, an exquisite sensitivity

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