

The Fine Structure of Fibers and Crystalline Polymers. II. The Growth of Crystalline Regions in Fibers

J. W. S. HEARLE, *Department of Textile Technology, Manchester College of
Science & Technology, University of Manchester, Manchester, England*

A considerable impetus has been given to studies of polymer crystallization following the growth of single crystals of polyethylene and other polymers. Many papers have been published dealing with the observation of single crystals, with mechanisms of crystal growth, with the folding of polymer chains within the crystal, with crystallization kinetics, and with detailed observations and explanations of special features of the structure of spherulites. As several review articles have been written¹⁻⁵ it is unnecessary to give here a long list of references.

The present paper is concerned with the application of some of these fundamental advances to systems of great practical importance. While the spherulitic growth in bulk polymers has been extensively studied and broadly explained (as discussed below) the application of similar ideas to other widely occurring forms of structure has been neglected. In particular, the mode of crystal growth in a system in which material is moving through a temperature gradient—for example, a fiber after extrusion—is discussed here. This paper is essentially concerned with the broad pattern of crystal growth in polymers. The relevance of these views to a discussion of the fine structure of fibers and crystalline polymers has been taken up in the previous paper in this series.⁶

Spherulitic Growth in Bulk Polymers

The characteristic radiating appearance of spherulites in bulk polymers and polymer films can be explained by the view that the spherulites are caused by the growth of branched fibrillar crystals from a central nucleus.

This is not the only possible view. An alternative, though less favored, explanation is that the spherulites consist of a radiating array of fringed micelles arising from a sequence of separate nucleation acts, induced by neighboring crystalline micelles and consequently spreading out from the center. Another view, which in practice would give an appearance very similar to that of branched fibrillar crystals, is that the crystallization proceeds by the growth of comparatively short bar-shaped crystals which nucleate in dendritic form on the faces of crystals previously formed.

Keller and Waring⁷ have illustrated this schematically, and Figures 1 and 2 are based on their diagrams and show, respectively, the pattern of growth of a single large spherulite and of several spherulites growing together. In

drawing these particular diagrams, it has been assumed that the crystalline fibril divides at regular intervals into three branches, one going straight on and the others diverging at 30° on either side. If followed indefinitely this would, of course, give rise to an overlapping which cannot occur in practice.

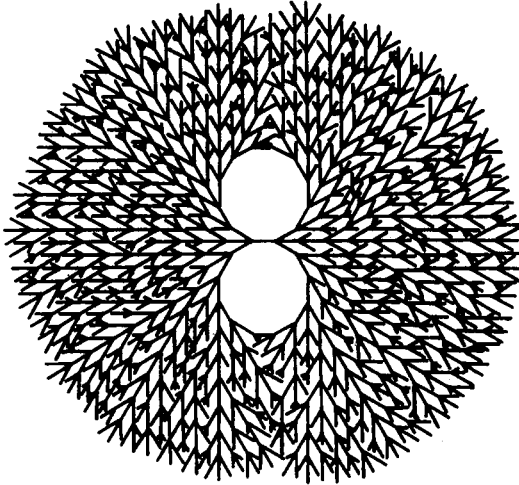


Fig. 1. Growth of spherulite.

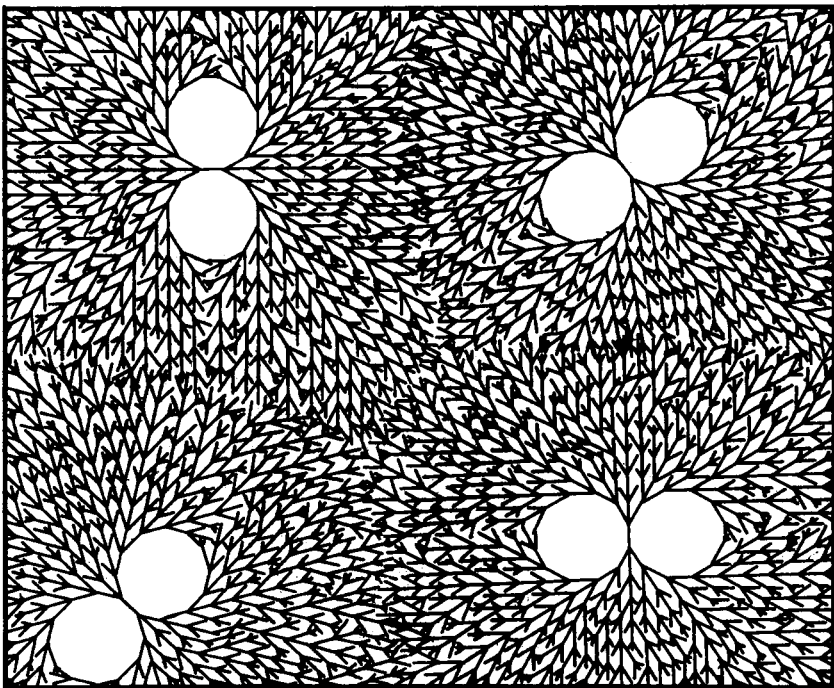


Fig. 2. Spherulites growing together.

Consequently, two further rules are introduced: (1) the growth is assumed to proceed at a uniform rate out from the center, and the branch which reaches any region first necessarily has priority, so that any branches which would subsequently cross the prior branch are stopped short; (2) where two branches reach the same point at the same time, a random choice is made between them.

The limitations of this diagrammatic approach are obvious. In reality, the growth will be in three dimensions, not only in two; the branching may occur at irregular intervals and angles, though simple crystal structures do commonly show regular branching; and secondary crystallization may fill in some of the spaces. Nevertheless, the diagrams are generally similar in form to observed spherulites, and serve very well for the purposes of the present paper, which is not concerned with the finer details of structure. Thus, no consideration will be given here to such important topics as (a) the exact nature of the central nucleus, (b) the mechanism of branching, (c) the exact form of the crystalline fibrils, which may be fringed^{6,8} and which may be of any shape—e.g., circular strands, flat ribbons, curled-up crystals, etc.—and (d) the periodicities and interference effects which can be observed in spherulites and which may be due to a twisting of the fibrils.

The nature of the arrangement of the molecules in the radiating fibrillar structure is of great importance. It has been shown that the orientation of the molecules is perpendicular to the lengths of the fibrils, and this is probably associated with a folding of the molecules similar to the folding found in single crystals. Studies of spherulitic growth as a problem in crystalline form will in time elucidate the detailed structure of the crystalline regions. The other problem of the relation between crystalline and noncrystalline regions has been discussed.⁶

Crystal Growth in a Moving Medium Such as an Unoriented Extruded Fiber

In contrast to the amount of work on the spherulitic crystallization of polymers in bulk, there have been few studies of other practical systems, despite the suggestions in Keller's earlier papers.⁹⁻¹¹ In these he describes the special forms which can occur when nucleation is limited to a plane (e.g., a surface) or a line (e.g., a flaw or a flow line). He also refers to crystallization in undrawn extruded nylon filaments, which show orientation of the molecules perpendicular to the extrusion axis, and in which the filament can be regarded as part of a giant spherulite with the fiber axis as a radius. The development of this idea would be fruitful.

Figure 3 shows an extruded filament moving with velocity v_f away from the point of extrusion,* together with the temperature gradient resulting from its cooling and the corresponding typical curve for rate of growth of

* In practice, the filament accelerates and becomes attenuated as it flows down, and therefore v_f is not constant. An appropriate curve should be drawn in Figure 3 for the line $V_c = v_f$. However, this will not affect the qualitative argument given in this paper.

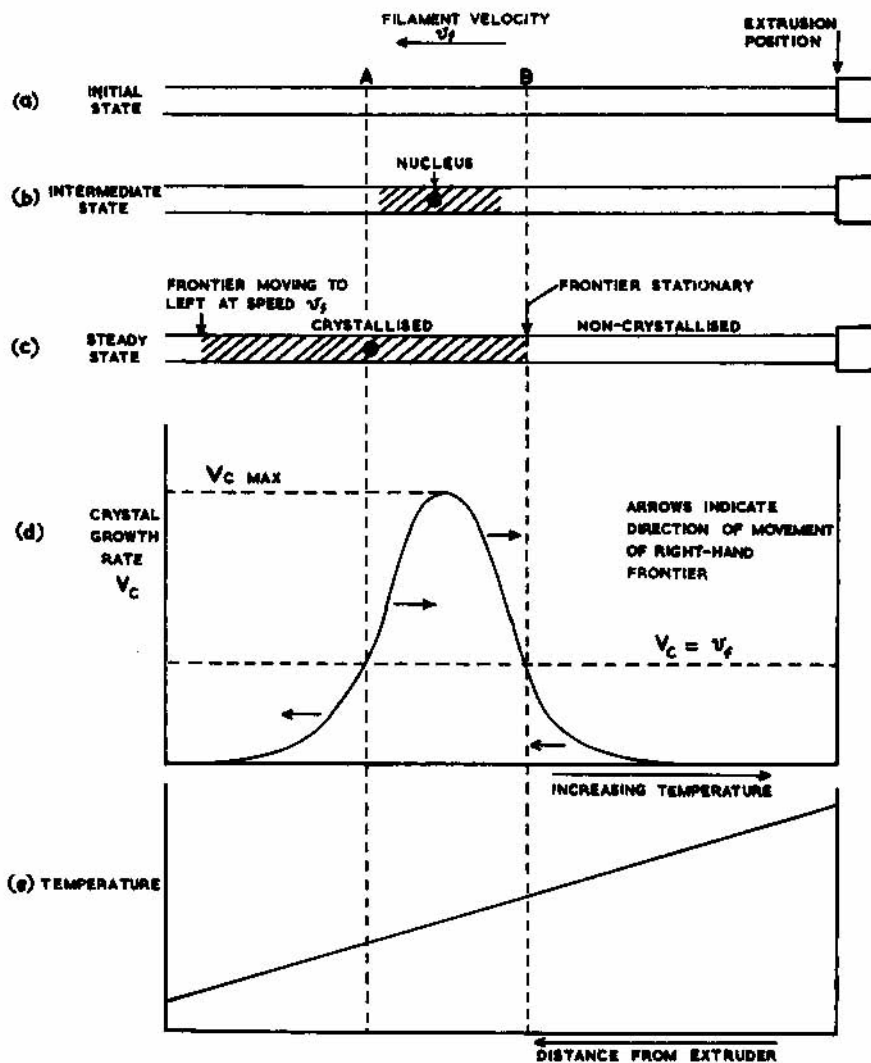


Fig. 3. Crystallization in extruded filament.

crystallization V_c in the polymer. Initially [Figure 3(a)] the material will be wholly noncrystalline. If a nucleus forms between A and B, the crystallization will then proceed in all directions in an attempt to form a spherulite. Toward the left, crystallization will continue at a speed V_c relative to the filament, until the temperature has fallen to a value at which V_c is negligible. The crystalline frontier on this side will thus move to the left in space at a speed $(V_c + v_f)$ and, when V_c has fallen to a negligible value, will merely travel along with the fibril at a speed v_f . However, what happens on the other side is more interesting. Since V_c is greater than v_f in the region between A and B, the frontier of the crystalline region will move to the

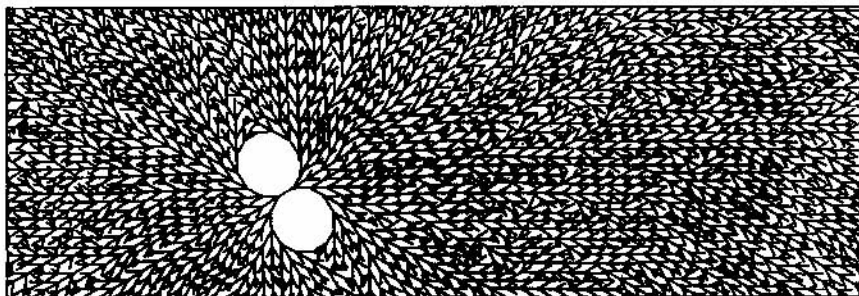


Fig. 4. Form of crystallization in filament.

right with a speed $V_0 - v_f$. When the frontier reaches B , V_0 equals v_f , and thus a steady state will be achieved; the rate of growth of the crystalline fibrils through the material will be just balanced by the mass transfer of material in the opposite direction. If the initial nucleus forms to the right of B , where V_0 is less than v_f , then crystallization will proceed but the crystalline material will be carried back faster than it forms until the right-hand crystalline frontier reaches B , when a steady state will again be achieved. On the other hand, if an initial nucleus forms to the left of A , where again V_0 is less than v_f and the crystalline material is carried back, no position of stability can be reached, and the only result will be the formation of a small spherulite whose size depends on the time available before the temperature falls to a value at which the rate of crystallization is negligible. At the point A itself, the condition for stability $V_0 = v_f$ is also satisfied, but this is a metastable state which would not survive.

The type of structure which would result from this form of growth, suggested above, assuming no further nucleation occurs, is shown in Figure 4. It may be noted that, because of the priority rule, the growth is predominantly forward, so that the structure is to a considerable extent oriented parallel to the fiber axis. An extreme version of this structure, shown in Figure 5(a), is one in which branching has been completely suppressed: this is a form similar to the growth out from a surface, described by Keller.⁹ Figure 5(a) shows perfect orientation of the crystals parallel to the axis of the undrawn filament and, if the molecules are folded or coiled in the crystal, they will be oriented perpendicular, or nearly perpendicular, to the filament axis. Keller¹⁰ has reported the occurrence of this type of orientation.

However, in practice one probably should not trust the highly schematic arrangements in Figures 1, 2, and 4 too much. Owing to local irregularities in the arrangement of the molecules, in temperature distribution, in strain, in the chances of crystal growth, and in the imperfections of the crystal, a more disordered structure may well result. An example of this extreme, having no preferred orientation, is shown in Figure 5(b). Some disorientation will also occur on the release of tension in the filament.

So far it has been assumed that the whole crystallization proceeds as a small sector of a single giant spherulite originating from one nucleus.

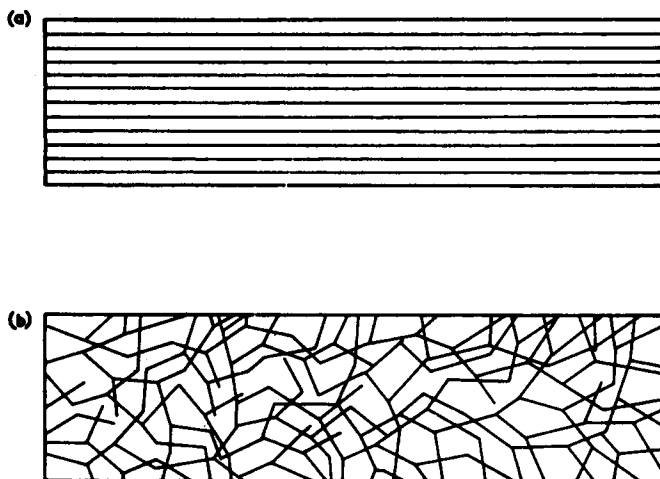


Fig. 5. (a) Extreme form of crystallization with branching suppressed completely; (b) extreme form of crystallization with considerable disorder in the fibrillar growth. The lines represent fibrillar crystals.

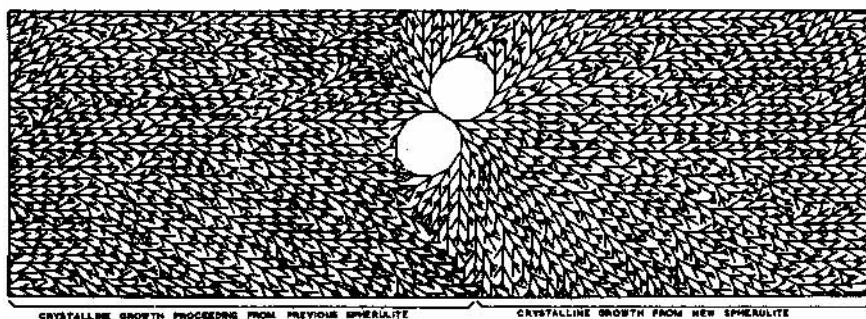


Fig. 6. Effect of subsequent nucleation.

However, even though crystallization is already proceeding in this way, a nucleus may subsequently form in the uncrystallized region to the right of *B*. This will give rise to structures of the type shown in Figure 6, which might show occasional flaws or sources of weakness if the nucleation is infrequent. If the nucleation occurs very frequently, then there will be no opportunity for the crystallization to proceed to the steady state shown in Figure 4, and the resulting structure will consist of a large number of spherulites, somewhat like the structure shown in Figure 2 but asymmetrical to a greater or lesser degree. With an extremely high nucleation rate, at which spherulites were unable to develop fully, a fringed micellar structure (as shown in Figure 7 of the previous paper⁶) would result. Ranges of intermediate states between the fibrillar, the spherulitic, and the micellar are, of course, possible. In passing, it should be noted that other specialized structures, such as the row structure described by Keller,¹⁰ in which

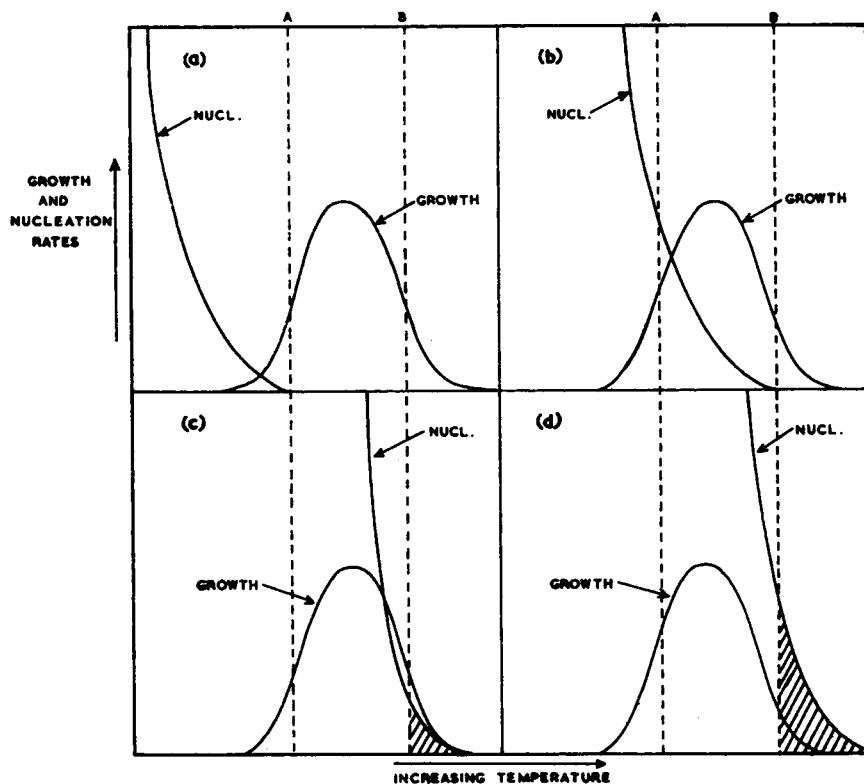


Fig. 7. Comparison of nucleation and growth rates.

the nucleation or growth are limited in some particular way, may develop. Apart from such special effects, we may consider the influence of various factors on the resulting structure.

Effect of Filament Velocity

It is clear from Figure 3 that lowering of the filament velocity will cause the point *B*, at which crystallization occurs in the steady state, to move to the right, and will thus cause the crystallization to occur at a higher temperature. Conversely, an increase in filament velocity will cause *B* to move to the left, and the crystallization temperature will fall. The maximum filament velocity at which crystallization will occur is given by $v_f = V_{c,max}$. Above this velocity, the filament will be quenched without continuous crystallization, though there may be some growth of spherulites from individual nuclei, depending on the length of time available at a temperature with an appreciable crystallization rate. In the region of $v_f = V_{c,max}$ irregular results may be expected in practice.

For continuous crystallization, when v_f is less than $V_{c,max}$ the length of the path over which the temperature falls will not alter the process described

in this simple model. Thus it should be possible to make the cooling more rapid by reducing the length over which cooling occurs—but not by speeding up the filament—without causing other changes to occur. Nonlinearity in the temperature gradient will also be without effect. At first sight these effects may appear surprising, but the process is quite analogous to a conveyor belt system in which operations have to be performed on each object by a series of operatives: the speed of the conveyor belt is important but the distances between operatives can be varied without altering the effectiveness of the operations.

The above view of the crystallization behavior would have to be modified if the rate of crystallization depends not only on the temperature but also to some extent on the temperature gradient in the neighborhood. An alternative way of stating this is to say that the action of crystallization of a polymer may be regarded as occurring in a finite volume near the growing face, owing to the necessity for long polymer chains to become straightened and disentangled. (In the previous analogy of a conveyor belt, one can add the conditions that the operatives need space to work in or that time for development must be allowed between each operation.) These factors would be expected to have an influence in crystallization if the rate of cooling were rapid.

Comparison of Nucleation and Growth Rates

Figure 7 shows four comparisons of growth rates and nucleation rates at various temperatures, though it should be noted that these two quantities are not dimensionally the same, so that absolute numerical comparison is not possible. In Figure 7(a) the nucleation rate is very low between *A* and *B*, so that it will be difficult to get the crystallization to start. In Figure 7(b) there is a fairly high probability of nucleation between *A* and *B*, but a very low rate of nucleation to the right of *B*: this is possibly an ideal state of affairs, since the initial nucleation will occur as required but subsequent nucleation, giving flaws, will be unlikely. The conditions in Figure 7(c) are less favorable, since there is a substantial nucleation rate to the right of *B*, which could only be avoided by reducing the filament velocity to a very low value. Finally, in Figure 7(d) the nucleation rate is so great that the resulting structure would be dominated by nucleation and thus be spherulitic or micellar—again this might be a suitable condition as it will give a fairly uniform structure.

If n is the number of nuclei forming per unit volume per unit time at a given temperature, then the number of nuclei forming per unit length of filament in the region to the right of *B* is given by the integral $\int (nA/v_t)d$, where *A* is the area of cross section and d is an increment of length between the point of extrusion and *B*. The dependence of this integral on the values of n in the temperature range corresponding to *O*-*B* is clear, and is illustrated by the shaded areas in Figure 7. For a given temperature drop occurring linearly (or with any other constant form) over the whole range, this integral will clearly be proportional to the length between *B* and *O*, so that the number of nuclei formed would be reduced on speeding up the rate

of cooling and keeping the length $O-B$ to the minimum possible value. In practice, since n falls off rapidly with increasing temperature, it is only necessary that the rate of cooling should be rapid in the region near to B .

The dependence of the integral on the filament velocity v is more complex: the direct effect of increasing v_t is to reduce the integral, but increasing v_t also has the effect of displacing B to the left, thus increasing the length $O-B$ and, moreover, extending it into a region where n is rapidly increasing. In addition, changing the speed v_t may alter the temperature distribution and thus shift the growth curve and change the length $O-B$: this also will usually tend to increase the value of the integral.

One special case which may occur is when there is some constant level of prenucleation present, in addition to the nuclei developing randomly and spontaneously as the temperature falls. If a large number of "prenuclei" are present, they will dominate the crystallization and a spherulitic structure may be expected; or, if the density of nuclei in this situation, or in the situation typified by Figure 7(d), is great enough, then the full development of the spherulitic structure may be prevented because of the interference in growth from neighboring nuclei and, in the extreme, a structure like the fringed micelle structure would result.

It is clearly important to establish which of the situations shown in Figure 7 occur in practice in various systems.

Other Systems

Growth in Oriented Man-Made Fibers

It has been suggested in the previous section of this paper that crystalline growth in an unoriented extruded fiber can be regarded as a special case of spherulitic growth in a bulk polymer. However, if the molecules are oriented more or less parallel to the fiber axis before crystallization, the usual form of crystal growth will not be possible. In particular, it will not be possible for crystalline fibrils to grow approximately parallel to the fiber axis, having the molecules laid down with their lengths perpendicular to the fiber axis. It is known that in oriented crystalline fibers the molecules lie parallel (to an extent depending on the degree of orientation) to the fiber axis. It thus appears inevitable that the crystal growth proceeds by longitudinal accretion, as in Figure 8(a), rather than by the lateral accretion, as in Figure 8(b), which occurs in spherulitic growth. Molecular folding in the crystal, if it occurs at all (and this seems unlikely in an oriented structure), must be back and forth along the length of the crystalline fibril.

It is, of course, possible that what appears to be longitudinal growth may, when viewed in sufficient detail, turn out to be lateral growth. A possible mechanism is illustrated in Figure 9(a). However, further work on the mode of crystallization of polymers will be needed to establish this definitely. It may be that both forms of fibrillar crystallization—i.e., with transverse molecular orientation in the fibrils in spherulites, and with longitudinal orientation in the fibrils in oriented fibers—will turn out to be special cases

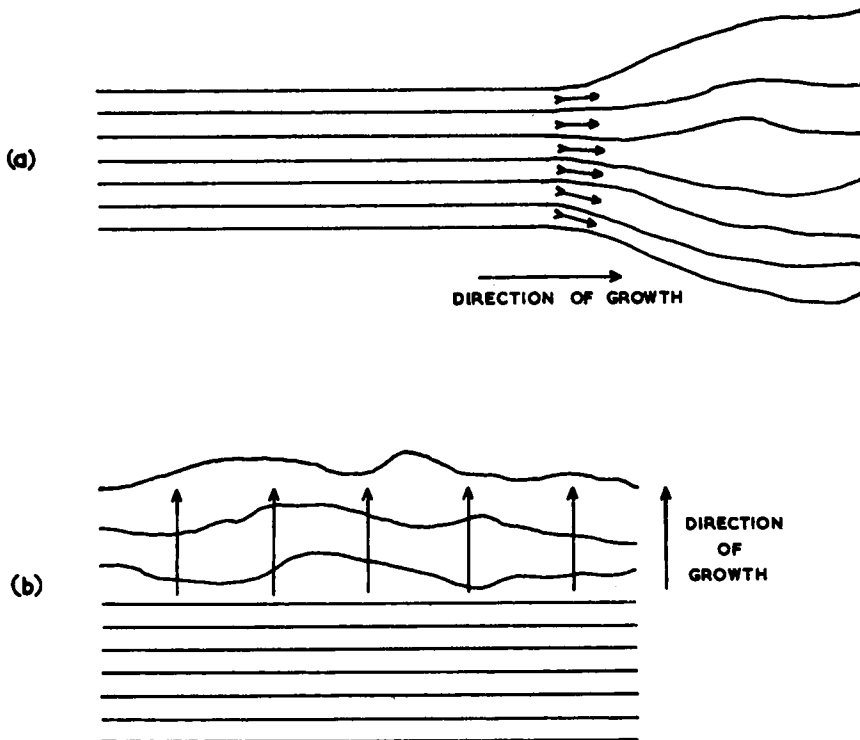


Fig. 8. Comparison of probable growth methods: (a) longitudinal accretion in an oriented structure; (b) lateral accretion typical of spherulitic growth.

of similar mechanisms of growth of single polymer crystals through screw dislocations, adapted to meet the particular circumstances. The relation between single crystals and spherulitic crystallization has been considered,¹ but it is still far from clear.

The growth of single fibrillar crystals could proceed in an oriented structure from a screw dislocation, as shown in Figure 9(a). This sort of growth, with the suppression of growth on the side faces, has been suggested¹² as a mechanism for the formation of metallic crystal whiskers, as illustrated in Figure 9(b). If the growth in the side faces is not suppressed, then single crystals form in the usual way, Figure 9(c). There would thus appear to be a close affinity between the well-established mode of growth of single polymer crystals and the mechanism suggested here for the formation of fibrillar crystals in oriented structures. The only difference is that, because of the previous arrangement of the structure, molecular folding is unlikely in the fibrillar crystal: it will be easier for the molecules to pack in without folding. The energy considerations which determine folding in the single crystal will not apply.

During the crystallization of an oriented structure, branching of fibrillar crystals is likely to be much less pronounced than in the crystallization of an

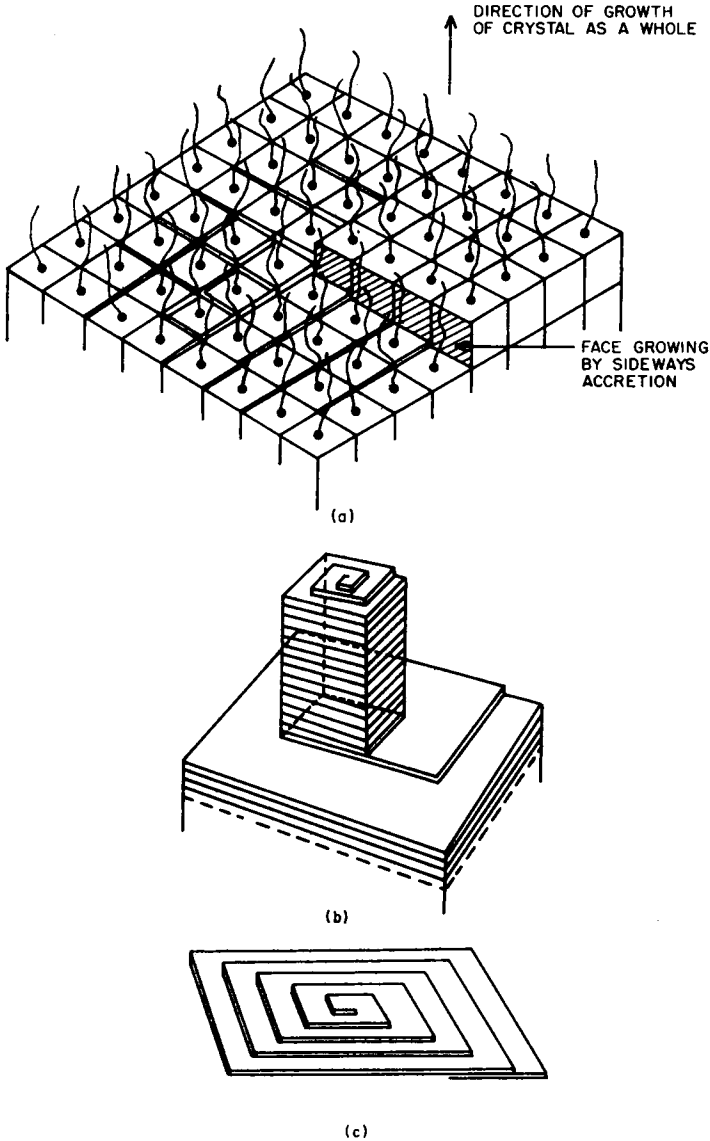


Fig. 9. (a) Possible mode of crystallization from a screw dislocation (after Frank¹²) in an oriented structure; (b) growth of dendritic branch (whiskers) from the face of a single crystal (after Amelinckx¹³); (c) growth of single crystal from screw dislocation.

unoriented structure, and growth will proceed preferentially along the direction of orientation. Therefore, the formation of spherulites is less likely. In other ways the arguments of the previous section will apply to the growth of crystals in an oriented fiber which is moving continuously into a region in which crystallization occurs. The only differences will be (1) at the onset of crystallization, when the initial stages of formation of a collec-

tion of growing fibrillar crystals may differ in form from the spherulitic growth, and (2) if nucleation occurs subsequently in the region to the right of *B*, in Figure 3, the form of the occlusion will be different from that shown in Figure 6.

As an example, we may take the extreme case in which no branching of the fibrils occurs. In this situation individual nucleation of each fibril would be needed, giving the initial form illustrated schematically in Figure 10(a). Subsequent nucleation would cause the formation of a fresh fibril, which would probably replace an existing fibril, as in Figure 10(b). Once

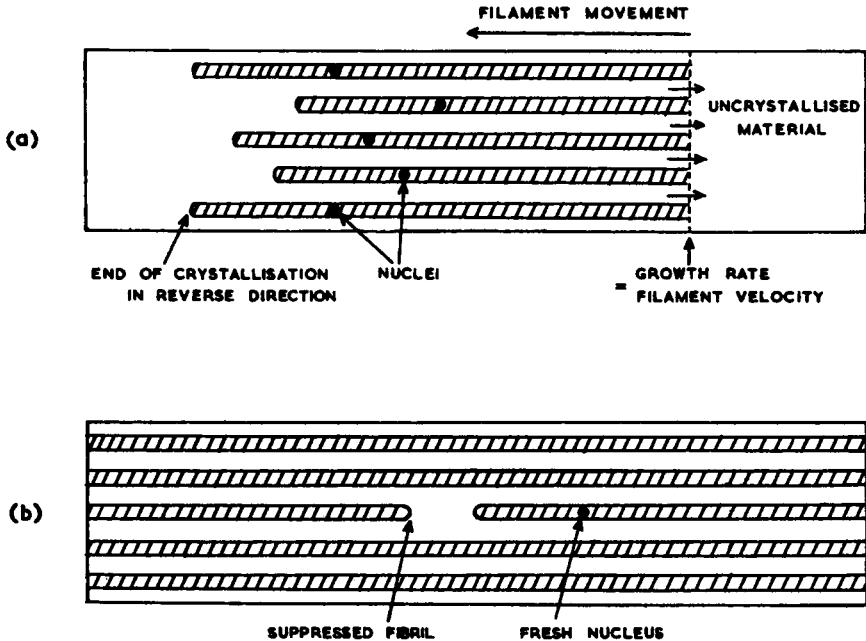


Fig. 10. Crystal growth in oriented structure with no branching of fibrils: (a) initial establishment of crystalline pattern; (b) subsequent nucleation, giving rise to a fresh fibril.

again, it is necessary to make the reservation that in reality the structures are likely to be much more irregular than is indicated in these schematic diagrams, and that some branching, giving rise to forms intermediate between those of Figure 10 and the spherulitic structures in Figures 4 and 6, is likely.

Crystallization during Drawing of Synthetic Fibers

Most synthetic fibers are drawn to several times their extruded length in order to give satisfactory properties. It is during this process that the final crystalline structure is established. In some materials, the undrawn

fiber is noncrystalline, and the drawing promotes orientation of the molecules, which is followed by crystallization: this is an example of the crystal growth in an oriented structure discussed in the previous section, although the necessity for orientation before crystallization may cause some unusual limitations in the pattern of crystal growth.

In other fibers the undrawn material is crystalline. In such a situation there are two alternative possibilities: (a) the crystalline structure of the undrawn fiber may be completely destroyed, giving rise to an intermediate stage of oriented noncrystalline material, or (b) the crystal structure of the undrawn fiber may be transformed into an oriented crystalline structure with only localized disruption of the crystalline fibrils, followed by recrystallization in a similar geometrical pattern. These two possibilities will clearly give rise to different final structures. The first will give forms similar to those discussed in the previous section, whereas the second will leave the pattern of spherulitic growth clearly present. In either case, the initial effect of stretching will be an increased alignment of the fibrils, thus improving the *transverse* orientation of the molecules, as confirmed by Keller,¹⁰ and then this will be followed by a change to longitudinal orientation of the molecules.

Conclusion

Fibrillar structures occur very commonly—almost universally—in crystalline polymers, and a branched fibrillar structure gives a satisfactory explanation of spherulitic structure. The present paper shows how similar ideas can be applied to situations in which the crystallization is complicated by the movement of the material through a temperature gradient so that fresh material is continually supplied to the crystallizing zone. Similar results would be achieved by the movement of a temperature gradient through the material, and so may be applicable to the cooling of many plastic materials in commercial applications.

An analysis of this situation shows how the resulting structures will depend on the relations between the material velocity, the crystalline growth rate, and the nucleation rate. Where nucleation is rare and crystalline growth is rapid, a fringed fibrillar structure will result, but if nucleation is frequent, and becomes the dominant mechanism, a spherulitic or micellar structure will be found. Practical applications in determining the best conditions for extrusion should follow from this. In oriented polymer systems, somewhat different structures will result but a similar analysis applies.

This paper has been concerned with the broad picture of the growth of crystalline regions, with little reference to the packing of individual molecules. The first paper in this series⁶ includes a discussion of the relevance of these views to a description of the fine structure of crystalline polymers, and the patterns to be expected in particular materials.

References

1. Keller, A., in *Growth and Perfection of Crystals*, R. H. Doremus, B. W. Roberts, and D. Turnbull, Eds., Wiley, New York, 1959, pp. 499-528.
2. Mandelkern, A., in *Growth and Perfection of Crystals*, R. H. Doremus, B. W. Roberts, and D. Turnbull, Wiley, New York, 1959, pp. 467-495.
3. Keller, A., *Makromol. Chem.*, **34**, 1 (1959).
4. Morgan, L. B., *Progress in High Polymers*, **1**, Heywood, London, 1961, pp. 235-277.
5. Keller, A., in *Fibre Structure*, J. W. S. Hearle and R. H. Peters, Eds., Textile Institute and Butterworth's, in press.
6. Hearle, J. W. S., *J. Appl. Polymer Sci.*, **7**, 1175 (1963).
7. Keller, A., and J. R. S. Waring, *J. Polymer Sci.*, **17**, 447 (1955).
8. Hearle, J. W. S., *J. Polymer Sci.*, **28**, 432 (1958).
9. Keller, A., *J. Polymer Sci.*, **15**, 31 (1955).
10. Keller, A., *J. Polymer Sci.*, **21**, 363 (1956).
11. Keller, A., and A. O'Connor, *Nature*, **180**, 1289 (1957).
12. Frank, F. C., *Discussions Faraday Soc.*, **5**, 48 (1949).
13. Amelinckx, S., in *Growth and Perfection of Crystals*, R. H. Doremus, B. W. Roberts, and D. Turnbull, Eds., Wiley, New York, 1959, p. 144.

Synopsis

The ideas of spherulitic crystallization as found in bulk polymers are applied to crystal growth in a moving medium such as an extruded fiber. It is shown that the structure will depend on the velocity of motion and the crystalline growth and nucleation rates. If growth proceeds from a single nucleus a sector of a giant spherulite will form, growing at a front where the crystalline growth rate equals the velocity of motion but, if nucleation is predominant, then a structure of small spherulites or micelles will form. The effects of orientation and drawing are considered. A detailed mechanism of crystal formation in an oriented structure by means of a screw dislocation is discussed.

Résumé

On a appliqué les idées de cristallisation en sphérolites, telles qu'on les trouve dans les polymères en bloc, à la croissance des cristaux dans un milieu mobile comme celui d'une fibre extrudée. On a montré que la structure dépendra de la vitesse de mouvement, de la croissance cristalline et des vitesses de nucléation. Si la croissance procède à partir d'un seul nucleus, il se formera un secteur d'un sphérolite géant, qui croît à l'endroit où la croissance cristalline et la vitesse de mouvement sont égales. Par contre, si la nucléation prédomine, il se formera de petits sphérolites ou des micelles. L'influence de l'orientation et de l'étirement est considérable. On discute un mécanisme détaillé de formation du cristal dans une structure orientée à l'aide d'une dislocation hélicoïdale.

Zusammenfassung

Die Vorstellungen über sphärolithische Kristallisation, wie sie bei Polymeren in Masse auftritt, werden auf das Kristallwachstum in einem bewegten Medium, wie eine extrudierte Faser, angewendet. Es ist eine Abhängigkeit der Struktur von der Bewegungsgeschwindigkeit und der Geschwindigkeit von Kristallwachstum und Keimbildung zu erwarten. Bei Wachstum von einem einzigen Keim aus wird sich ein Sektor eines Riesensphärolithen bilden, der an einer Front gleicher Kristallwachstums- und Bewegungsgeschwindigkeit wächst; bei vorherrschender Keimbildung wird eine Struktur kleiner Sphärolithe oder Mizellen entstehen. Einflüsse von Orientierung und Reckung werden in Betracht gezogen. Ein Mechanismus der Kristallbildung in einer orientierten Struktur durch Schraubenversetzung wird im einzelnen diskutiert.

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