The Fine Structure of Fibers and Crystalline Polymers. I. Fringed Fibril Structure

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INTRODUCTION

In the light of many recent observations it is now widely accepted that in its simplest form the fringed micelle concept of the structure of crystalline polymers including most fibers is inadequate, despite its earlier success in explaining many features of polymer behavior. In the simple fringed micelle theory, it is supposed that the crystalline portions of the polymer are small crystallites, of the order of 50 A. in width and thickness and 500 A. in length; each long-chain molecule passes alternately through a number of these crystalline regions and through the noncrystalline regions lying in between them. Apart from any preferred orientation, the micelles are regarded as distributed more or less at random through the structure. Difficulties in accepting this view came first from the observation in the electron microscope of the presence in both natural and man-made fibers of fine fibrils with thicknesses of the order of 100 A. or less and apparently of effectively infinite length.[1,2] It is also now known that the characteristic form of crystallization of unoriented polymers in bulk is spherulitic, and it is generally believed that this spherulitic arrangement is due to a radiating growth from a central nucleus of branched fibrils, or of crystallites growing successively on top of preceding crystallites to give a continuous dendritic network. Long crystalline fibrils thus appear to be a commoner form as units of fine structure in fibers and crystalline polymers than the comparatively short crystalline regions of the fringed micelle theory.

In order to combine proved features of the fringed micelle theory with the experimental observations of fibrils, a *fringed fibril* structure has been proposed in a previous paper.[3] In this structure the fibrils are assumed to be long, imperfect, possibly branched, crystals made up of comparatively short segments of the long-chain molecules packed together. Any one long-chain molecule will pass alternately through a number of crystalline fibrils and through the noncrystalline regions between them. This idea has since been supported[4] and criticized[5] in its application to cotton and rayon, respectively.

A far better and more detailed understanding of the structure of crystalline polymers will undoubtedly follow from the recent and continuing work

on such aspects of polymer crystallization as the growth and morphology of single crystals from solution and of spherulitic structures in bulk polymers. These studies are outstanding academic advances in the subject, and have formed the subject of several reviews.[6–10] In the meantime, the scientist or technologist concerned with the properties and behavior of these materials needs a working model of structure which is an improvement on the old fringed micelle theory which served well in the past. For example, theories of the mechanical properties of fibers depend on the model used.

In another paper in this series,[11] it has been shown that recent advances in our knowledge of polymer crystallization can be applied to systems of technological importance, such as commercial fibers, and can give a broad picture of the expected pattern of crystallization. The present paper is concerned with finer detail and discusses the validity of the fringed fibril idea, and extends its application. It should be emphasised that, although the fringed fibril theory represented a marked change from the views of structure almost universally accepted a few years ago, it is close to some of the views of the fringed micelle theory originally put forward in the 1930's. The historical development of ideas of fine structure and alternative explanations of fibrillar fine structure have been commented on elsewhere,[12] and will not be mentioned further here.

It must also be emphasized that, despite the tendency to generalize about crystalline polymers, it is not reasonable to expect different types of polymer molecules to behave in the same way, although recent reports suggest that the similarities are more important than the differences. Furthermore, the fine structure of a particular polymer specimen will be very dependent on its previous history. In the final section of the paper, various types of polymer materials are discussed specifically.

FRINGED FIBRIL STRUCTURES: THEIR OCCURRENCE AND IMPLICATIONS

Single Polymer Crystals

In appropriate conditions, crystallization of polymers from dilute solution can yield single crystals. In these crystals the molecules have been shown to be folded back and forth along layers formed by a growing face, and it must be presumed that each long-chain molecule is completely fitted into the crystal in a long folded sequence as indicated schematically in Figure 1(a). No fringing will occur. This is possible because the molecules are well separated in the dilute solution, and can extract themselves completely so as to fit into the crystal.

Spherulitic Crystallization of Bulk Polymer

In crystallization from the melt or from concentrated solution, the entanglement of the molecules will prevent their complete separation from
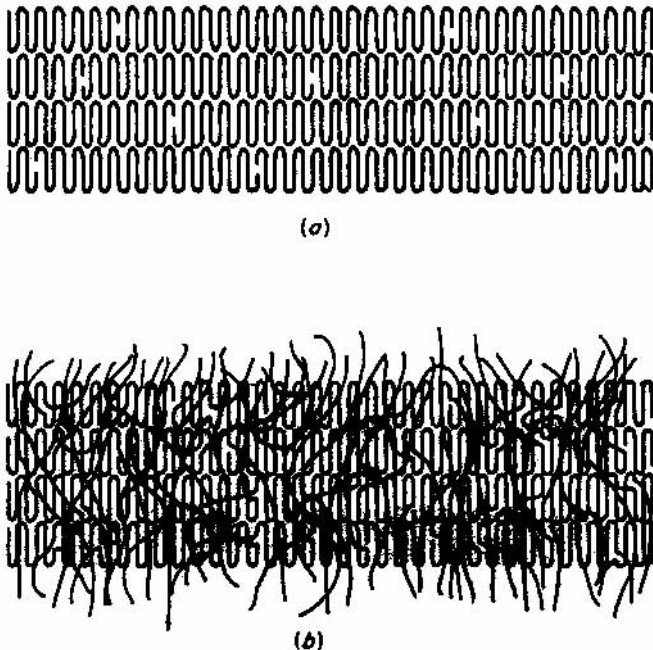
Fig. 1. Schematic views of complete packing of molecules in a portion of a polymer single crystal (a), fringed packing of short lengths of molecules in a fringed fibrillar crystal (b).

the bulk of the material and it will only be possible for comparatively short sequences to be fitted into the crystal. It can therefore, be expected that the resulting structure will have the form illustrated schematically in Figure 1(b) which shows molecules fringing off from the crystalline region.

Bulk polymers have a spherulitic crystalline structure, and this has been explained by the growth outwards from a central sheath of branched fibrillar crystals, with the molecules packed in such a way that their axes are perpendicular to the fibrillar axis. Following the view put forward in the previous paragraph, the pattern of organization would thus be one of fringed fibrils, in which the molecules are incorporated for short lengths in the crystalline parts—folding or spiralling so as to give the correct orientation—and then fringe off into the intervening noncrystalline regions, due to the interference with their continued packing in the crystal. Any one molecule will pass alternately through many crystalline and noncrystalline regions. This type of structure is illustrated schematically in Figure 2(a), and would combine the essential features of the fringed micelle theory as applied to crystallization of unoriented polymers (see for example, Bunn[14]) with the observed spherulitic, fibrillar, laterally oriented structure. In particular, the ideas of continuity between the crystalline and noncrystalline regions would be maintained, while the lack of sharpness in the x-ray diffraction pattern would be explained by the imperfections in the crystals.

In a somewhat different point of view put forward, for example, by Price,[13a] it is envisaged that because of entanglement in the melt, only comparatively short crystallites can grow from any one nucleation.   However, further nucleation proceeds from the faces of each crystallite, as in dendritic crystallization.   The spherulites thus grow by the successive growth of bar-shaped crystallites on top of one another.   Branching will occur to fill up the necessary expanding surface area of the spherulite, while noncrystalline material will fill in the spaces between the crystallites. This type of structure is illustrated schematically in Figure 2(b), which differs little, except in its finest detail, from Figure 2(a).   Both contain a continuous branched crystalline network, with molecules fringing off to fill the intervening space.   In Figure 2(b) there are distinct boundaries between successive crystallites, and it is possible that the fringing will be concentrated at these positions, and at the ends of the crystallites.

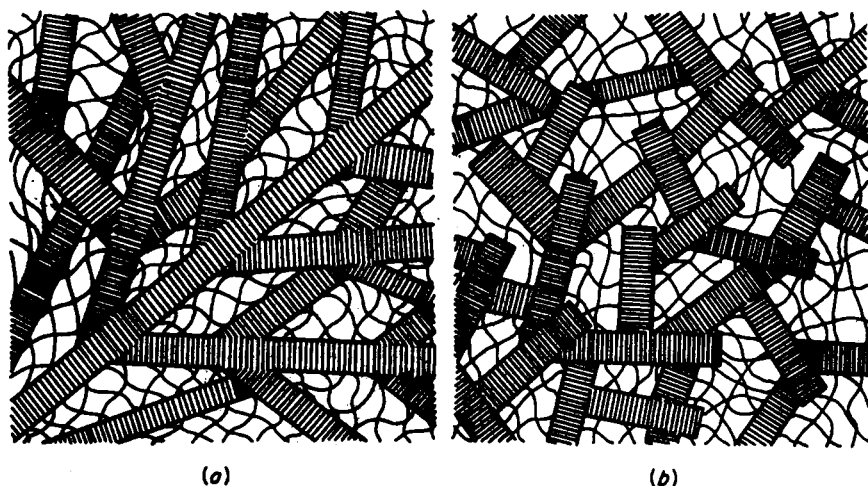(a)   (b)

Fig. 2. Fringed fibril structure in spherulitic crystallization (a); modification showing growth of successive crystallites on top of one another (b).

A more extreme point of view, suggested by Statton[13b] supposes that individual crystallites are separate from one another; but that the spherulites grow since the formation of a crystallite in one place will cause further crystallization in the near neighborhood.   This is a complete departure from the fibrillar structure proposed in the present paper, but it must be mentioned as a possible, though improbable, alternative.

In the next paper in this series[11] it has been shown that fibrillar crystallization in an unoriented fiber can be regarded as a special case of spherulitic crystallization, virtually as one long radial sector of a single giant spherulite, so that a fringed fibrillar structure similar to that discussed above would be expected.

Oriented Fibers

In oriented polymers, the molecular axis is parallel to the fibrillar axis (and to a lesser extent, depending on the degree of orientation, to the axis of the fiber as a whole) so that the original view of the fringed fibril structure, Figure 3, would hold. This structure consists of long, imperfect, fibrillar crystals with the chain molecules entering or leaving the fibril at intervals and passing continuously through crystalline and noncrystalline
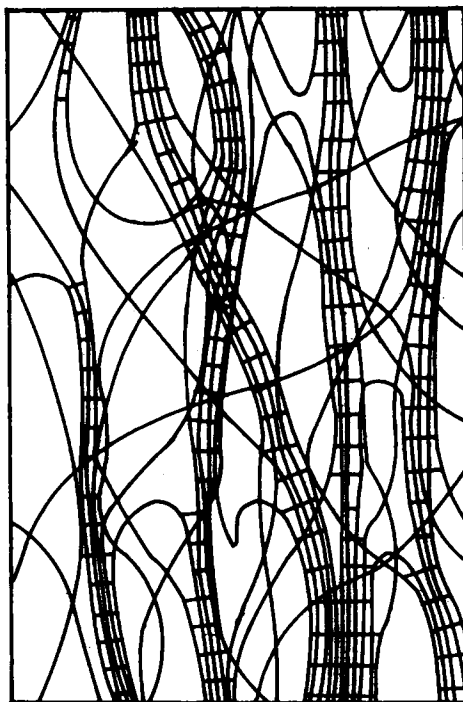

Fig. 3. Fringed fibril structure in oriented polymer, after Hearle.[3]

regions.   The formation of such a structure would be a natural consequence of crystallization continuing along existing lines, as indicated in Figure 4, rather than continually deriving from fresh nuclei, as would be necessary to give a fringed micelle structure.   As described in the next paper,[11] occasional nucleation would give rise to fresh fibrils, and other fibrils would occasionally terminate; some branching of fibrils might also occur.   The entanglement of the chains would prevent the continuous incorporation of the whole length of one molecule in a particular fibrillar crystal.

Long Periodicities. Modified Fringed Fibril Structure

One feature of fiber structure which is not explained by the above fibrillar model is the occurrence in the x-ray diffraction photographs of evidence of

long periodicities (of the order of 100 A. or more).   Hess[14] has explained this
by a structure in which crystalline and noncrystalline regions alternate
along the length of a bundle of molecules.   However, the structure indi-
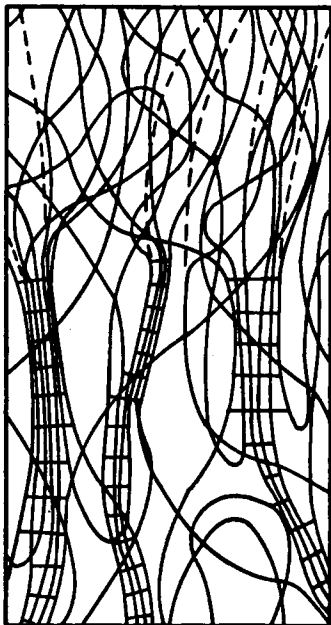cated by his diagrams seems a very artificial arrangement.   An alternative

Fig. 4. Lines of development of fibrillar crystals indicated by dotted lines.
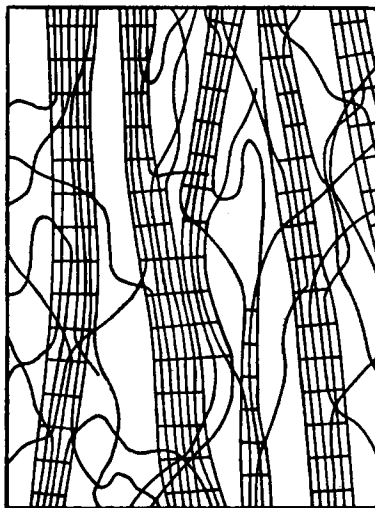

Fig. 5. Fringed fibril structure with molecules branching at regular intervals.   N.B.:
When taken in three dimensions the planes containing imperfections will be more clearly
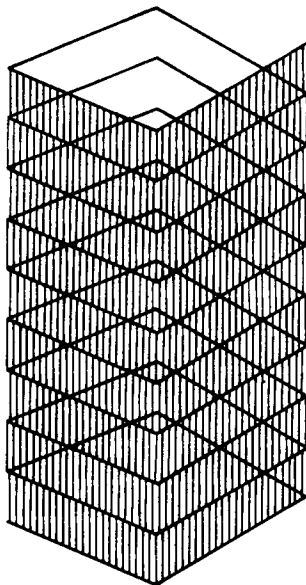defined.

Fig. 6. Growth of fibrillar crystal by screw dislocation showing the surface at which fringing off of molecules occurs.

explanation, which introduces some features of Hess's view, is that the molecules branching off from the fringed fibril do not do so in random positions as in Figure 3, but do so only at positions occurring at regular intervals. This would give the type of structure shown in Figure 5. It is only in some specific experiments that such a structure would be expected to behave differently from that of Figure 3.

In the next paper,[11] it has been suggested that the growth of the oriented fibrillar structure might proceed by a screw dislocation mechanism. This would give rise to the crystal growing at a step giving a spiral structure of the type illustrated in Figure 6. In filling up a step one would expect complete segments of molecules to be incorporated, but fringing off of molecules might occur before the next layer of the crystal is formed as the step comes round again. Thus, all the imperfections would be concentrated on the surface generated by the top and bottom of the step. This would give rise to the long periodicity.

Fringed Micelle Theory as Limiting Case of Fringed Fibrillar Theory

It has been suggested above that subsequent nucleation acts may cause fresh fibrils to form, and indirectly cause others to terminate. If this happens the fibrils will be of finite and not of infinite length. The fibrillar lengths will depend on the frequency of nucleation. In an extreme situation, nucleation may occur so frequently that the fibrils are short: this gives a structure which is equivalent to the usually accepted fringed micelle structure, Figure 7. As discussed in Part II, this type of structure would
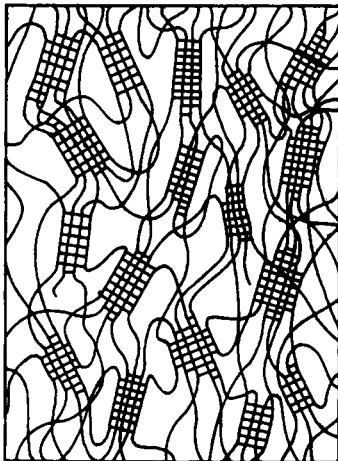
Fig. 7. Fringed micelle structure, regarded as fringed fibril structure with very short fibrillar length.

develop when the nucleation rate is very high compared with the crystalline growth rate, or when a large number of prenuclei are already present in the solution or melt. It seems probable that this type of structure does occur in some materials.

Evidence for and against the Fringed Fibril Structure

The fringed fibril theory and the older fringed micelle theory differ principally in the length of the crystalline regions. In the fringed micelle theory, these regions are comparatively short (of the order of 500 A.) whereas in the fringed fibril theory they are very long. In other respects, the two models are very similar and so the many arguments used in support of the fringed micelle theory can be used to support the fringed fibril theory in preference to that of any other structure such as the embedding of crystalline regions in a quite separate matrix of noncrystalline material. The physical and chemical characterictics of crystalline polymers are well explained by a structure in which both crystalline and noncrystalline regions are present and are joined together in a continuous molecular network: the presence of both sorts of regions accounts for the occurrence of both crystalline and amorphous diffraction in the x-ray photograph as well as for the limited accessibility to water and other chemicals, while the continuity of structure is necessary to explain the mechanical coherence and toughness of the materials.

The chief argument in favor of very long crystalline regions is the observation of fibrillar structure in electron microscope studies. Fibrils (with diameters of the order of 100 A., i.e., the appropriate diameter for crystalline regions) have been found in almost all crystalline polymers, although there are some doubts about the situation in regenerated cellulose and this is discussed in detail later. It has also been mentioned in this paper, and is

discussed in more detail in Part II, that a fibrillar pattern of crystalline growth is inherently likely to occur: in contrast to this the universal sharp termination of crystalline micelles is unlikely (however, it may be noted that in Figure 7 the sharp termination has been avoided). Owing to the impossibility of the chains disentangling themselves from the melt or from concentrated solution, fringing off from the fibrils must occur, giving the continuous network of the fringed fibril structure.

There are several arguments in favor of short crystalline regions, put forward by Michie et al.,[5] which must be considered.

The periodicities with a spacing of about 200 A. indicated by the low-angle x-ray studies of Statton[15] and others, suggest that this may be the length of crystalline units occurring in sequence in alternation with non-crystalline regions. However, an alternative explanation of this effect, based on the characteristic mode of crystallization, has been suggested in the previous section of this paper.

When regenerated cellulose is attacked by acid hydrolysis and then disintegrated by ultrasonic vibration, short particles with a length of the order of 200 A. are found.[16] However, this treatment is so severe that it cannot be taken as evidence that these particles are present as separate units in the original material. After both chemical and mechanical attack it would not be surprising if the fibrils broke up into short particles. And, if the imperfections do occur at regular intervals as suggested in the previous section these would be built-in positions of weakness. (Although accepting the observation of short particles as evidence of the micellar structure, Michie et al. later discount the evidence from observation of microfibrils in regenerated cellulose because these appear only after a rigorous swelling treatment).

Values for the crystallite length have also been estimated from the limiting degree of polymerization found after acid hydrolysis. It is assumed that the molecules in the noncrystalline regions are attacked, but not those in the crystalline regions, so that when the hydrolysis slows
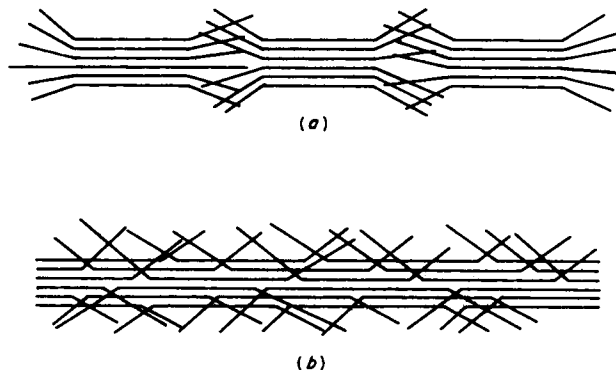

(a)

(b)

Fig. 8. Explanation of limiting degree of polymerization: fringed micelle theory (a); fringed fibril theory (b).

down, the limiting degree of polymerization is assumed to approximate the crystallite length (the value would be slightly higher if some recrystallization occurs). This state of affairs is illustrated in Figure 8(a) and indicates crystallite lengths of the order of 150 A.[17] But on the fringed fibril theory, the attack in the noncrystalline regions would also take place, and the limiting degree of polymerization could represent the length of each segment of the chain molecules incorporated continuously in a crystalline fibril. This is illustrated in Figure 8(b). Alternatively it is possible, if the mechanism suggested in the previous section is correct, that the hydrolysis would attack right across the plane in which the imperfections occur, and so give a limiting degree of polymerization in good agreement with the length of particles observed after disintegration.

The other arguments against the fringed fibril concept used by Michie et al. are concerned with the mechanical properties of fibers. These appear to rest on the misconception that the mechanical behavior would be determined solely by the crystalline superstructure. This is not so: due to imperfections in the fibrillar arrangement, the noncrystalline regions lying between will play a large part in determining the mechanical behavior. In fact, the fringed fibril theory forms a sound basis for the re-examination of molecular theories of mechanical behavior of fibers, and this is discussed further in another paper in this series.[18]

Viewing the evidence as a whole, the fringed fibril theory is supported, and the objections to it cannot be sustained. It must be regarded as the most probable form of structure, though there is the possibility of a fringed micelle structure as a limiting case when nucleation is frequent.

SURVEY OF DIFFERENT TYPES OF POLYMER AND FIBERS

Synthetic Linear Polymers in Bulk

Synthetic linear polymers in bulk may be either amorphous—in the rubbery or the glassy state—or partly crystalline. If they do crystallize there is abundant evidence that the structure is usually spherulitic, Figure 9(a) with the spherulites developed to a size which depends on the relative incidence of nucleation and growth as determined by the conditions of crystallization. In some circumstances, particular morphological features may develop within the spherulite, and in others particular forms of nucleation, such as nucleation on a surface or a line, may prevent normal spherulitic development. These forms are illustrated in Figure 9(b) and 9(c).

The molecules in the crystalline fibril are folded or coiled so that they are oriented approximately perpendicular to the fibril axis but, since only comparatively short segments of the polymer molecules will be able to be extricated from the mass of chains, the fibrils will be fringed fibrils linked by molecules passing through intervening regions as illustrated schematically in the drawings in Figure 9. The molecular network will be continuous, and the appropriate model to use in working out the behavior of the normal spherulitic structure will be one of a radiating array of interlinked fibrils.
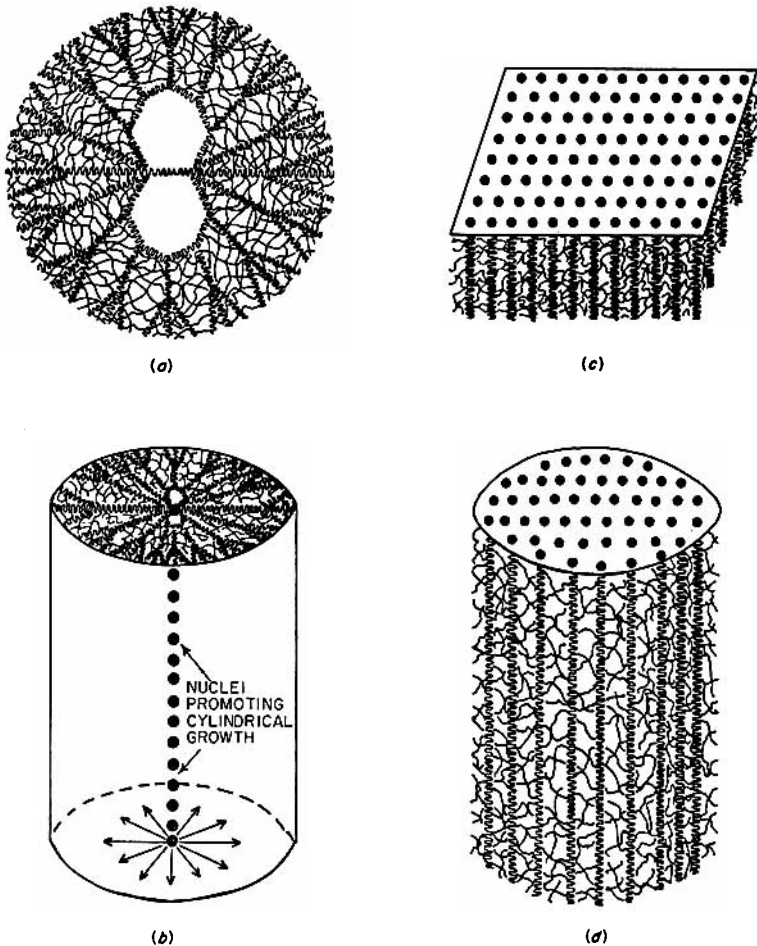
Fig. 9. Fringed fibrillar structure in spherulitic crystallization: normal spherulite growing in three dimensions (a); cylindrical structure from nucleation along a line (b); growth from nuclei on surface (c); growth in an undrawn fibre (d).

Synthetic Linear Polymers as Undrawn Fibers

Undrawn synthetic fibers may be either noncrystalline as in Terylene (polyethylene terephthalate) of crystalline as in nylon (polyamide). If they are crystalline, the structure will usually be a fringed fibril structure (with molecular orientation perpendicular to the axis of the fibril) similar to a small segment of a giant spherulite, as shown in Figure 9(d). In another paper in this series,[11] the possible occurrence of modifications of this simple structure is discussed.

Synthetic Linear Polymers as Drawn Fibers

The drawing of synthetic fibers orients the molecules parallel to the fiber axis, and may be expected to produce a fringed fibrillar structure with

the molecules lying approximately parallel to the axis of the crystalline fiber, as shown in Figure 3 or 5. The appropriate model will thus be a more or less effectively oriented system of interlinked fibrils, in which each fibril is an imperfect crystal. There may be some differences in detail, depending on whether the fibers are crystalline or not before drawing. If nucleation is frequent a fringed micelle structure will result.

Almost all synthetic fibers are crystalline and can be expected to have the above structure. One probable exception is the acrylic fibers which do not appear to develop any perfect crystalline packing. There are strong crosslinks between neighboring $-C\equiv N$ groups, and it is likely that an oriented structure is maintained with only a roughly ordered packing of the chain molecules which may not be differentiated into fibrillar and inter-fibrillar regions.

Protein Fibers

Wool fibers have an extremely complex morphology at all levels of structure. The finest observable units are microfibrils with widths of the order of 100 A. This is entirely compatible with a fringed fibril structure. However, the detailed interpretation of the wool structure is still a matter of controversy. Feughelman[19] describes a model of the wool fiber in the following terms:

These mechanical properties of the set fibre can be understood in terms of a molecular model for wool, which has already been proposed to explain other mechanical properties. The structure of wool as displayed by its mechanical and allied properties was considered to consist of two phases in parallel (see Fig. 10), one phase being highly water-absorbing and also mechanically very much weakened by the water, and the other phase water-impenetrable and hence unaffected mechanically by water.[20] From the work on electron microscopy of Mercer, Rogers, Sikorski and others[21-25] together with the infrared and x-ray results of Fraser and MacRae[26, 27] the water-impenetrable phase was identified with the microfibrils in wool and the water-penetrable with the matrix. The microfibrils are considered to consist of well-organized keratin α-helices, whereas the matrix consists of opened-up or distorted coils of polypeptide chains held together by covalent links, inter- and intra-chain hydrogen bonds, salt links and Van der Waals forces. Except for the covalent links, all these forces are drastically affected by the presence of water.

In the microfibrils, it has been postulated[28,29] that two types of zone exist in series (X and Y). These zones are present alternately along the microfibril. Both zones, it was proposed, consist of α-helices in an organized packed state with the zones X capable of opening out prior to zones Y when the fibre is stressed. These latter zones are possibly cross-linked to themselves and their surrounding matrix, and may have more bulky side chains, which introduce steric hindrance. In this model the yield region of the load-extension curve of a wool fibre in water at room temperature ($\sim 20°C.$) corresponds to the opening out of the X zones, and the post-yield region to the opening up of the Y zones. If the temperature (T) of the water in which the fibre is being tested is raised above the transition temperature(Tc) of the fibre,[30] cross-linking and the effect of steric hindrance associated with zones of type Y, disappear progressively with increase in temperature above this critical temperature.

This model could be modified and interpreted on the fringed fibril theory in the following way. The microfibrils are the crystalline regions, with the

protein chain molecules fringing off to pass through the interfibrillar matrix. The zones X which open out first might represent regions in the fibril in which the branching of the molecules from the fibril occurs; this would give the structure illustrated in Figure 11. Alternatively, the alternation
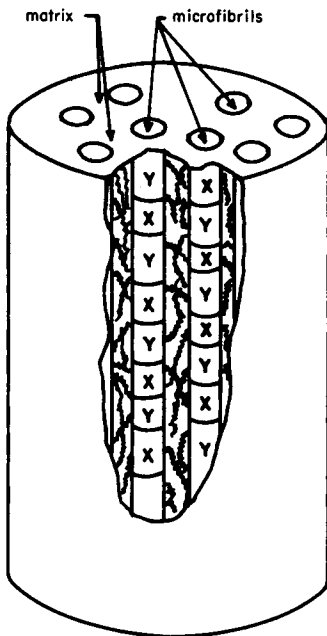

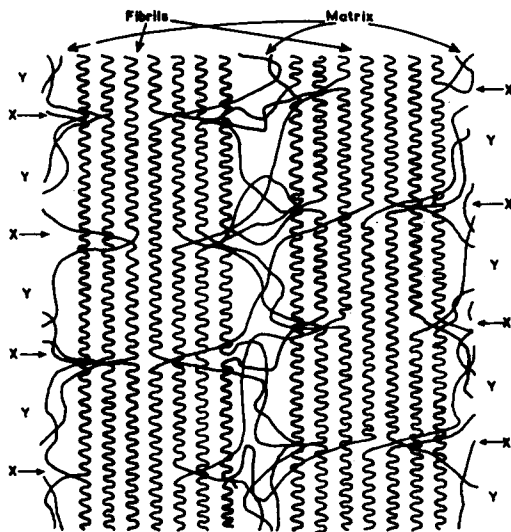Fig. 10. Diagrammatic representation of model of wool after Feughelman.[19]

Fig. 11. Interpretation of model of wool structure on fringed fibril theory.
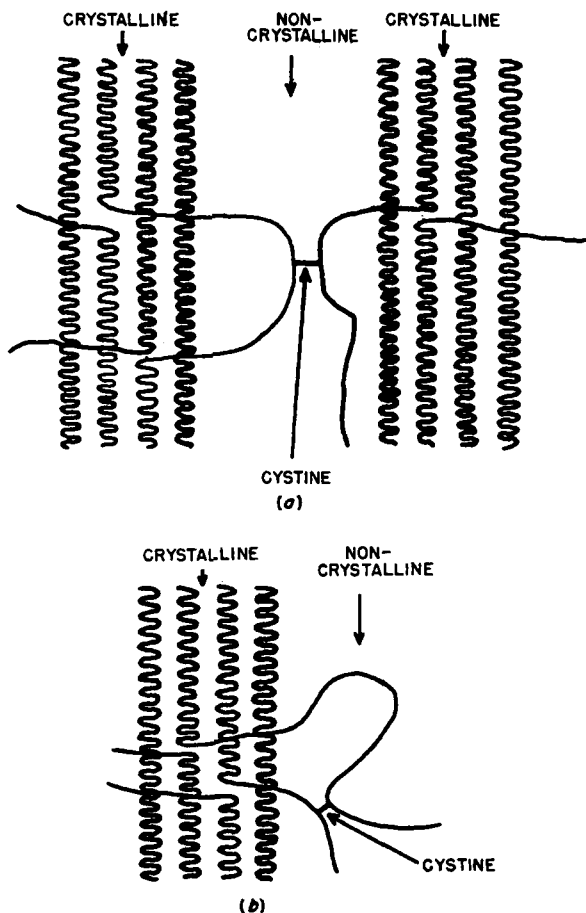
Fig. 12. Portions of chains containing cystine groups forced out into the matrix. When linked chains in different fibrils (a); when linked chains in same fibril (b).

in zones X and Y may be caused by differences in the chemical constitution of the keratin.

It may be noted that Woods[31] considers that Feughelman's model is too simple, and suggests (without any strong objection from Feughelman) that the interfibrillar matrix may be an active elastic component in parallel with the microfibrils. This would be the case if the portions of molecules in the matrix are normally coiled into an approximation to the α helix, but can be stretched out into the β chain. The same sort of mechanism (except that it is determined by entropy mechanisms of chain kinking) can be suggested for nylon fibers.[18]

Crewther and Dowling[32] have suggested that the fibrillar material and the matrix have different chemical constitutions, and Crewther[33] suggests that this is evidence that the fibrils are completely separate from the matrix, and that the two regions are not molecularly interlinked as they

would be in a fringed fibril structure. In taking this view, there is the tacit assumption that the two types of protein constitution occur in different groups of chain molecules. An alternative view is that they alternate along the length of each chain molecule as in a block copolymer. If this is so, the crystallizable parts would fit into the fibrils, while the noncrystallizable parts would come out into the matrix.

It is believed that the matrix is considerably richer in cystine groups linking neighboring chains together. But this may be cause rather than effect, since most portions of molecules containing cystine groups may be forced into the noncrystalline regions. Where two molecules are linked together by a cystine group, they could only fit into the crystalline structure if both chain molecules were in exactly the correct positions in the crystal and this is highly improbable. It is more likely that the two chains linked by the cystine group will be in different crystalline fibrils, so that the cystine group would be very likely to finish up in the matrix between the fibrils, as in Figure 12(a). Alternatively if both chains are in the same fibril they are likely to be displaced either laterally or longitudinally so that again the cystine group with other portions of the chain gets forced out of the fibril, Figure 12(b).

In silk, the protein chains are fully extended, and the structure is likely to be a more or less oriented fringed fibril structure as in the synthetic fibers. There is evidence that silk is a natural block copolymer in which only certain segments will fit into the crystalline regions, while others will always be in the noncrystalline regions.

Regenerated protein fibers are generally very poorly crystalline.

Cellulose Fibers

The natural plant fibers are rather highly crystalline and fine fibrils are observed as the basic building units. All the evidence is compatible with a fringed fibril structure. This is, in fact, essentially the view proposed by Frey-Wyssling[34] when he states that the elementary microfibrils are separated (and joined) by paracrystalline cellulose. The only special feature is that the fibrils have axes lying on helices round the fiber axis. Thus in cotton the fibrils (and the chain molecules) lie at an angle of about 30° to the fiber axis.

The interpretation of regenerated cellulose fiber structure offers more difficulty. In ordinary rayon fibers, there is little evidence of a fibrillar structure, except that "examination of regenerated cellulose under the electron microscope, after a short swelling in hydrochloric or sulphuric acid, reveals elongated, thread-like particles, substantially longer than the crystallites but of approximately the same width."[35] This is interpreted by Michie et al.,[5] not as evidence of a fibrillar structure, but "in terms of the structure concluded by Statton[15] to exist in viscose rayon, that is a 'superlattice' of discontinuous crystallites of the type originally proposed by Hess and Kiessig[36] for synthetic polymers." In the absence of conclusive evidence of crystalline fibrils in viscose rayon fibers, the fringed

micelle structure with short crystalline regions remains a possible, perhaps a probable, form of structure.   On the whole, a fringed micelle structure gives the simplest explanation of the mechanical properties.[18]

It would not be surprising if ordinary viscose rayon fibers had a structure rather different from that of other fibers, since they are formed by the precipitation and crystallization of cellulose as the rayon solution enters the acid bath.   This could well lead to small crystallites, just as in low molecular weight materials precipitation gives small crystals.   A tendency to a fringed micelle structure would also occur if prenuclei or local associations of molecules were extensively present in the rayon solution.   After coagulation, the solvent has to be removed, leaving void spaces between the solidified cellulose (this might be the origin of the fibrillar appearance observed on acid swelling), and the fibers are then stretched to orient the structure.

In other forms of rayon, the sequence of operations is different.   In Fortisan, a cellulose acetate fiber is formed, stretched, and then regenerated into cellulose; in the Lilienfeld process, a solid fiber of another cellulose compound is formed with concentrated sulphuric acid as an intermediate stage in the coagulation process, and this is stretched and then regenerated; and in the polynosic fibers, precipitation of the cellulose xanthate is caused by use of a weak acid bath, and the solid xanthate fiber is stretched before regeneration.   In all these processes the crystallization (induced by regeneration) occurs in a solid oriented fiber, and this is thus much more like the production of a synthetic fiber.   The fibers produced in the above ways certainly have a fibrillar structure; microfibrils have frequently been observed in Fortisan, though as they are less easily separated than those in native fibers it is likely that they are interlinked by branching; and the polynosic fibers show under the microscope a coarse fibrillar structure, similar to that in cotton except for a somewhat irregular orientation, on squashing an acid-swollen fiber.   A microfibrillar fine structure for a polynosic fiber has recently been confirmed by electron microscope studies and contrasted with the absence of well-developed microfibrils in ordinary rayon.[37]   The mechanical properties of polynosic fibers are also compatible with a fringed fibril structure.[18]   It thus appears that the viscose rayon process is once more demonstrating its versatility by possibly providing both fibers with a fringed fibril structure and fibers with a fringed micelle structure.

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Synopsis

The inadequacy of the fringed micelle concept of the structure of crystalline polymers has led to the suggestion of a fringed fibril structure.   Single crystal, spherulitic forms of bulk polymer, and oriented fibres are considered, and a modified fringed fibril structure, which will account for long periodicities, is proposed.   The fringed micelle structure is viewed as a limiting case of fringed fibril structure.   The evidence for and against the fringed fibril structure is discussed.   The paper concludes with a survey of structures of different types of polymer and fibers.

Résumé

L'inaptitude du concept des micelles frangées pour la structure des polymères cristallins a conduit à l'hypothèse d'une structure de fibres frangées.   On a considéré un cristal simple, des formes sphérulitiques du polymère en bloc et de fibres orientées, et on propose une structure modifiée de fibres frangées pouvant expliquer de longues périodicités.   On

considère la structure de micelles frangées comme un cas limite de la structure de fibres frangées. On discute les arguments pour et contre la structure de fibres frangées. Cette communication se termine par un examen des structures de différents types de polymères et de fibres.

Zusammenfassung

Die Mängel des Konzepts der Fransenmizellen für die Struktur kristalliner Polymerer haben zur Aufstellung einer Fransenfibrillenstruktur geführt. Einkristalle, sphärolithische Formen bei Polymermassen und orientierte Fasern werden in den Kreis der Betrachtung gezogen und eine modifizierte Fransenfibrillenstruktur zur Erklärung der langen Periodizitäten angegeben. Die Fransenmizellenstruktur wird als Grenzfall der Fransenfibrillenstruktur betrachtet. Umstände die für und gegen die Fransenfibrillenstruktur sprechen werden diskutiert. Die Arbeit schliesst mit einem Überlick über die Struktur verschiedener Polymer- und Fasertypen.