

FORMATION AND PROPERTIES OF LARGE CRYSTALLINE STRUCTURES IN POLYMERS

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The first ideas about the structure of polymers were conceived soon after the discovery that these substances are composed of long flexible chain-like molecules. It seemed natural to assume that, in such systems with entangled molecules of different shapes and sizes, there can exist no strict order in regions of greater size than the molecules. This general viewpoint on the structure of polymers was elaborated and quoted in almost every textbook on polymer chemistry: polymers were considered as systems of entangled flexible molecules, and an increase of local order was identified as crystallization. Although these ideas have been suspect for some time, it is only during the last few years that the wide use of electron microscopy has permitted the direct observation of the structures in polymers. The reality has been shown to be very far from the scheme proposed earlier.

Two years ago in Wiesbaden, I gave a report on the ordering processes in amorphous polymers¹. Electron microscopic investigations have shown that the simplest structural elements in polymers are globulae and packets of the chain molecules. In the case of globular structures, the elements consist of single coiled chains, and, in the case of packets, each element is composed of many parallel chains of molecules held together in such a way that the length of this packet is much greater than that of an individual molecule. These packets are the structural elements of the single polymer crystals which were first observed in the case of polyethylene².

Now we can follow in detail the gradual development of complicated structures in polymers through the various intermediate stages. The chain molecules form the long packets of chains which fold according to Keller's mechanism³ to form ribbons and lamellar structures. The latter can form spherulites and single crystals. Even for any one particular type of polymer, *e.g.*, polyethylene, the process of structure formation can proceed in various ways depending on external conditions. Helicoidal structures can be observed for polyethylene (*Figure 1*). On stretching such helices, they are converted into single-chain packets (*Figure 2*). Sometimes the whole polyethylene band consists entirely of such helices (*Figure 3*). Under special conditions, the polyethylene bands are not developed in plane, and higher structures are wholly built up of narrow ribbons (*Figure 4*).

Sometimes one can observe in the same photograph the existence of different polyethylene structures. At the centre of *Figure 5*, one can see the simplest structural elements—the packets of chains which are not yet ordered and folded. In addition, the first nuclei of folded structures can be observed as spots which have developed in strips that are arranged in a direction

perpendicular to that of the original packets. These strips are nothing more than a planar projection of lamellae which grow perpendicularly to the surface of the supporting film. If lamellar structures have not developed, ribbon-like structures arise which can also be observed in the central part of *Figure 5*. When the lamellae grow, the spherulites appear, and these turn into single crystals as is shown at the edges, and especially on the upper left-hand part, of *Figure 5*. Peculiar structures are found in polyethylene which is obtained by radiation polymerization (*Figure 6*). Here one can observe very large globulae, consisting of faintly-ordered strips. Thus, by changing the temperature, molecular weight, degree of branching, and sometimes by adding surface-active agents, one can influence structure formation and provide evidence for the existence of polymorphism in polymer systems. Polyethylene structures are discussed here only to demonstrate the numerous ways in which polymer structures are formed. The various successive stages in structure formation are now known rather well for polyethylene, but other mechanisms can doubtless operate for other polymers. This is consistent with the observation by some authors of single polyethylene crystals with different morphological forms.

There is now no doubt that any polymer with regular chains can be crystallized in the form of single crystals, provided that this process is carried out at a suitable temperature between the glass-point and melting-point of the given polymer.

In addition to the monocrystals of polyethylene, single crystals have been described of gutta-percha⁴, poly-4-methylpentene⁵, polyamides⁶, polyesters⁷, polypropylene, polystyrene⁸, polychlorotrifluoroethylene⁹ and poly(acrylic acid)¹⁰.

The isotactic polypropylene, when crystalline, gives single crystals of different forms depending on the crystallization conditions. The lamellar crystals (*Figure 7*) and hexagonal crystals (*Figure 8*) are formed by slow crystallization from xylene solution. Using a higher temperature and either trichloroethylene or (especially) tetralin as solvent, the fibrillar form appears (*Figure 9*). One can also observe the intermediate fibrillar structures of polypropylene which lead to elongated crystals (*Figure 10*).

If polychlorotrifluoroethylene is crystallized slowly from mesitylene, lamellar structures are produced (*Figure 11*) which are aggregates of small planar crystals. Such structures are intermediate between rather large crystals and spherulites. At higher temperatures (about 180°), well-formed crystals of two types are produced (*Figure 12*). Isotactic crystalline poly(acrylic acid) also exists in two forms: it gives well-formed rectangular crystals (*Figure 13*) under some conditions, and long fibrillar crystals (*Figure 14*) under others.

The original forms of crystalline isotactic polystyrene were examined. Its most typical form of crystalline structure is a star-like crystal obtained on slow crystallization from xylene (*Figure 15*). The structure of this type of crystal differs from the structure of lamellar crystals. Under high magnification (*Figure 16*), one can see the flaky structural elements which are perpendicular to the main axis of the crystal and under the big angle to the plane of supported film. By increasing the concentration of the solution up to 2 per cent, crystals larger than 100 μ can be obtained. A

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photograph of such a crystal, obtained with the aid of an optical microscope, is shown in *Figure 17*.

Thus it seems quite clear that every crystallizable polymer can form, under suitable conditions, all structures up to single crystals *via* the intermediate formation of ribbon-like, lamellar, fibrillar, and spherulitic structures. The multi-stage process of structure formation, and the widespread manifestation of polymorphism, are typical of polymer systems.

Usually the structures observed are not large, having a size of several μ . Only in the case of polystyrene could we observe the single crystals with dimensions up to 0.2 mm. Two questions arise: what are the maximal dimensions of structural forms in polymers, and what types of structure are produced during the processing of plastic materials? These problems are very important, because it can be supposed that all the above types of structure exist only under the specially-created artificial conditions, and that they cannot arise if these conditions are absent.

The largest single structural forms for spherulites were obtained by Professor Kozlow and his co-workers¹¹ by crystallization of poly(ethylene sebacate) from solutions in furfural at room temperature. The spherulites were formed on the internal surface of the flask as true hemispheres up to 10 mm in diameter (*Figure 18*). By cutting and splitting these spherulites, their structure could be investigated in detail.

Thus, for single crystals, as well as for spherulites, microscopic and even visible samples can be obtained. In the latter case there is no longer any need to use an electron microscope, and the usual microscopic technique can be employed.

Next, I want to describe some results on the structures of bulk polymers which were obtained using a technique similar to that in metallography with the aid of a metallographical microscope. Bulk specimens of polymer were broken at low temperature, or were cut and polished or etched as in the case of metals. As a rule, the structures observed were large enough for investigation under an ordinary microscope. Structural investigations on the low-temperature breaks of bulk polymer were first carried out by Bunn *et al.*¹², who were followed by several investigators who normally used the replica method with an electron microscope. The structures thus revealed were identical with those observed for thin films. For this reason, our own investigations were aimed at the study of rather large structures in polymers, similar to the metal structures.

The first data are concerned with polyethylene. The sections of bulk polyethylene were made with a microtome, and the quality of a slice was controlled under a microscope. The samples were then etched in benzene vapour, and examined under a metallographical microscope. *Figures 19* and *20* show low-density polyethylene that has been subjected to slow and rapid cooling respectively from the melt. It can be seen that etching a flat surface of bulk polymer results in the appearance of a microscopic relief picture of ordered regions with sharp boundaries. The spherulite structures are usually several μ in size in samples obtained by slow cooling. The very small spherulites, which are not visible under an optical microscope, are formed on rapid cooling of the melt. On slow cooling of a sample of high-density polyethylene, more nearly perfect structures are formed.

Much more nearly perfect structures can be observed in the case of polypropylene. Specimens of isotactic polypropylene with a molecular weight about 100,000 was prepared by very slow cooling (over many hours) of the 180° melt. Observations were made on breaks obtained at liquid nitrogen temperature, and sometimes on surfaces obtained as the result of cuts in the samples. Under these conditions large and well-formed spherulites of polypropylene were produced. Depending on the cooling procedure, the sizes of these spherulites vary from a few dozen to several hundred μ . If the sample is annealed for a long time at 130–140°, spherulites 20–30 μ in diameter are formed (*Figure 21*). By annealing the sample at a temperature of about 100°, one can obtain spherulites 200–220 μ in diameter (*Figure 22*), and this does not seem to be the limit. Thus we can see that the crystallization process in bulk polymer leads to the formation of large spherulites. The change in the type of spherulites as the temperature decreases is also very interesting. At high temperatures, the spherulites formed have a clear lamellar structure. On lowering the temperature, however, the lamellar structural elements turn into fibrillar ones; this change proceeds as far as the complete degeneration of spherulites, and the formation of a system of entangled fibrillae. It is typical that the breaks of samples with well-formed spherulitic structures occur at the boundaries of spherulites, and indeed this type of structural transformation is accompanied by an increase in the brittleness of the material.

It is also possible to observe that, simultaneously with spherulite formation in bulk polymer, very large (up to several hundred μ) perfect structures are formed which are very like single crystals of polypropylene (*Figures 23 and 24*). Thus, in bulk solid polypropylene, at temperatures which are several dozen degrees below the melting-point, ordering processes can proceed which lead to the formation of large spherulites and visible single crystals.

A similar process can be observed in the case of polyamides, although the spherulites and crystals are smaller than in the case of polypropylene. In moulded samples of the poly(hexamethylene sebacamide) (nylon 6–8), the spherulites are usually very small (*Figure 25*). The samples studied were sections from bulk polyamide, ground, polished, and etched with either a mixture of *o*, *m*, and *p*- cresols or sulphuric acid. After a short time, the spherulites increase in size to several μ , and, after 6 months' storage at the room temperature, attain a size of several dozen μ (*Figure 26*). These crystallization processes are sharply accelerated at elevated temperatures, and heating for some hours at 150–160° is sufficient to produce spherulites with a size of several μ . The structure of this polymer is highly dependent on the mechanical treatment. Thus, during a single bend of a plate, the sizes of the spherulites in the bending zone increase at once up to many dozen μ (*Figure 27*).

The complicated pictures of the destruction of the initial structures, and the formation of new structures, appear on stretching the sample. The main type of structure in this case is spherulitic, but quite often single crystals can be observed. Usually they arise simultaneously with an increase in the sizes of the spherulites, and are either conglomerates of rather small single crystals (*Figure 28*) or large single crystals over 100 μ in length (*Figure 29*). Thus we can follow in polymer systems the formation and

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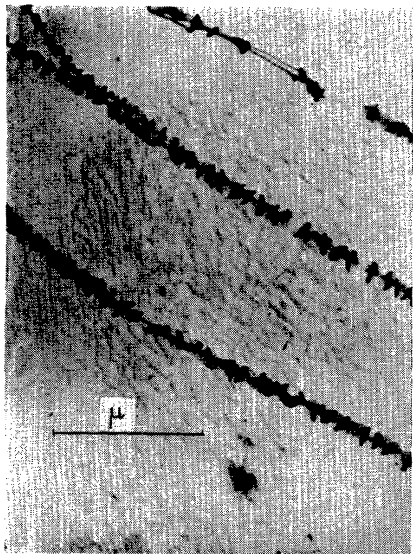


Figure 1. Helicoidal structures of polyethylene

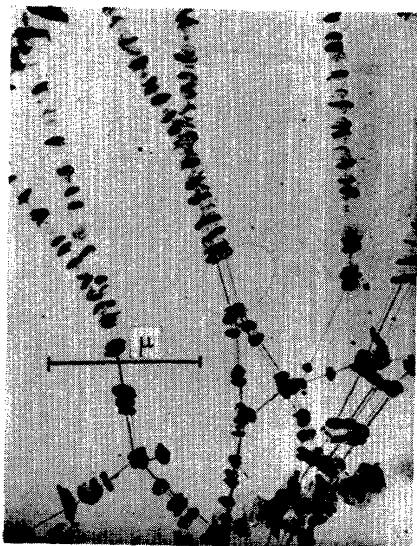


Figure 2. Single-chain packets formed by stretching helicoidal structures of polyethylene

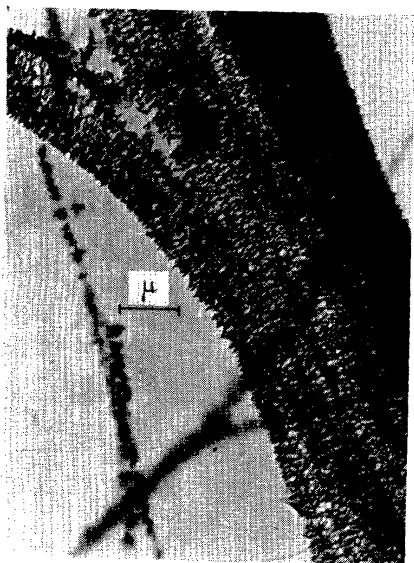


Figure 3. Polyethylene band consisting entirely of helicoidal structures

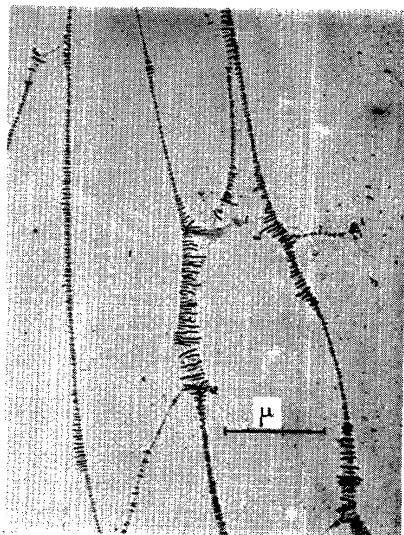


Figure 4. Polyethylene bands built up of narrow ribbons

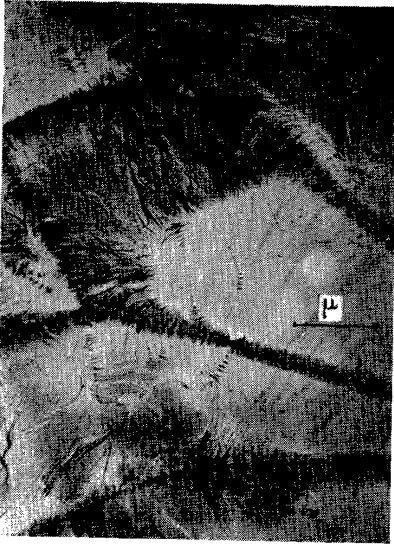


Figure 5. Various different structures of polyethylene

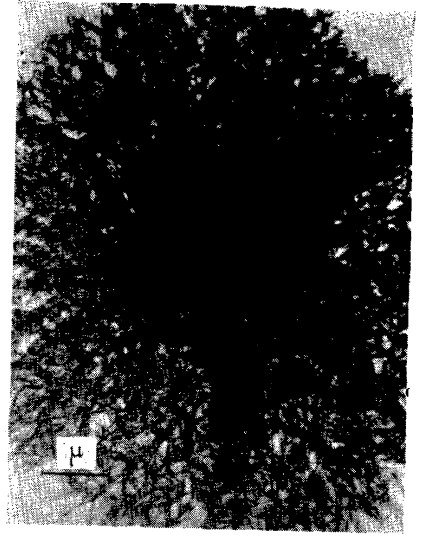


Figure 6. Large globulae (consisting of faintly-ordered strips) of polyethylene obtained by radiation polymerization

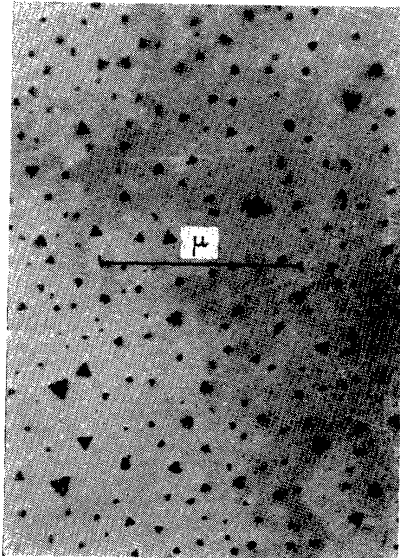


Figure 7. Lamellar crystals of polypropylene, formed by slow crystallization from xylene

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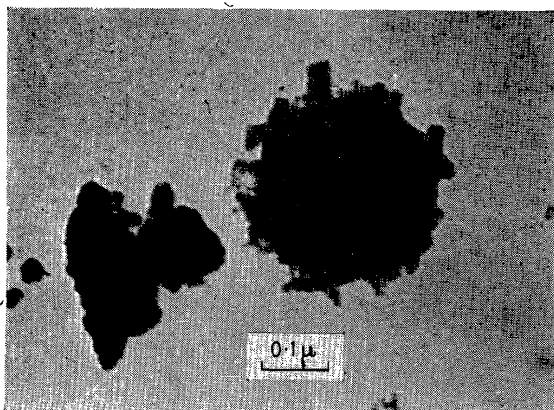


Figure 8. Hexagonal crystals of polypropylene, formed by slow crystallization from xylene

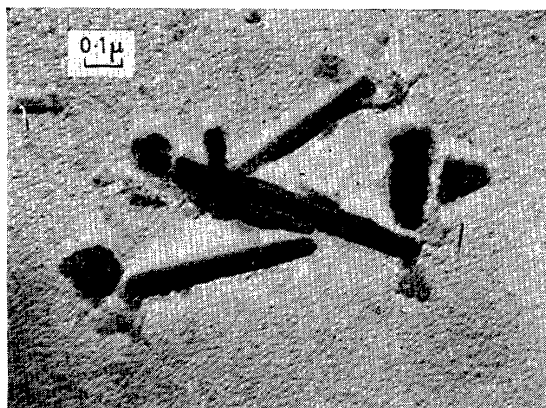


Figure 9. Fibrillar crystals of polypropylene, formed by crystallization from tetralin (or trichloroethylene)

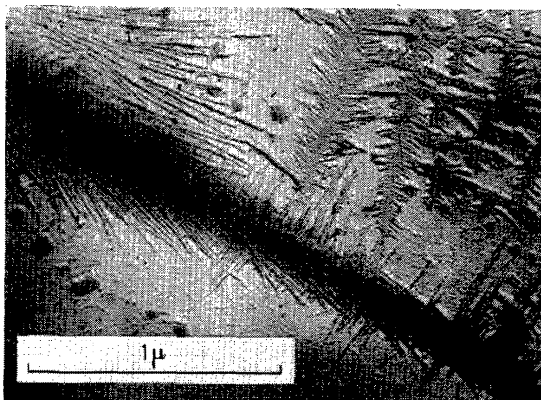


Figure 10. Fibrillar structures of polypropylene which develop into the elongated crystals shown in Figure 9

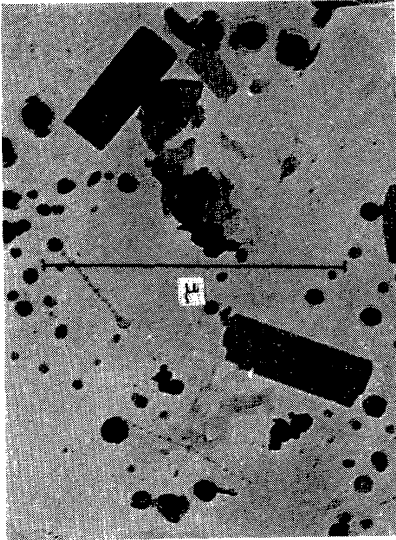


Figure 11. Lamellar structures (consisting of aggregates of small planar crystals) of polychlorotrifluoroethylene, formed by slow crystallization from mesitylene

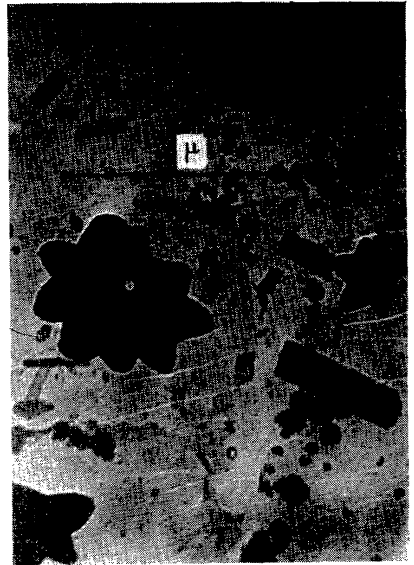


Figure 12. Well-formed crystals of polychlorotrifluoroethylene, formed by crystallization from mesitylene at 180°

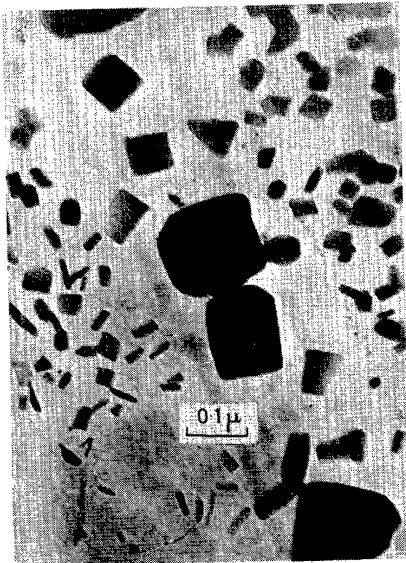


Figure 13. Rectangular crystals of polyacrylic acid

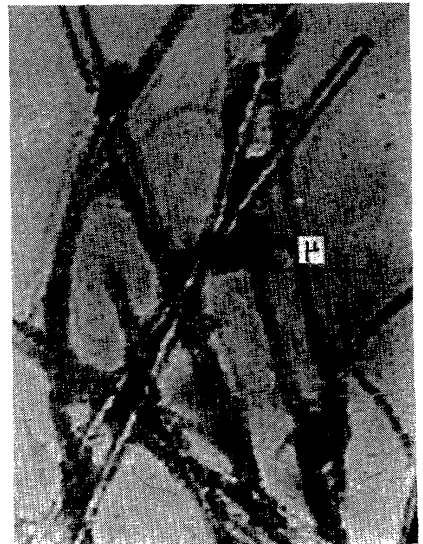


Figure 14. Long fibrillar crystals of polyacrylic acid

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Figure 15. Star-like crystals of polystyrene, formed by slow crystallization from xylene



Figure 16. Star-like crystal of polystyrene, showing flaky structural elements

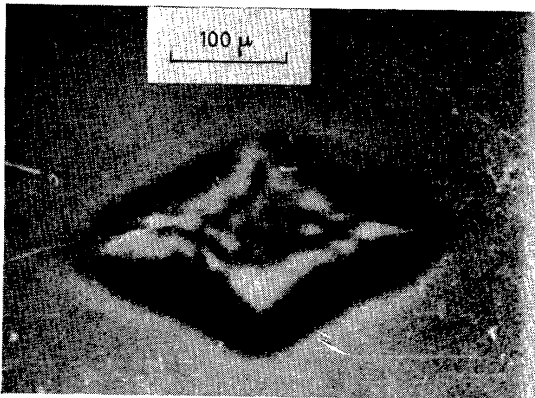


Figure 17. Large star-like crystal of polystyrene, formed by slow crystallization from a relatively concentrated (2 per cent) solution in xylene

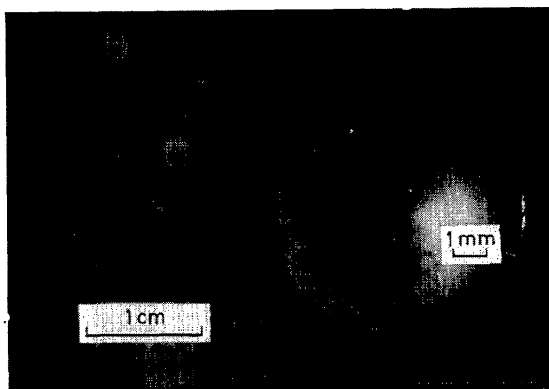


Figure 18. Large spherulites of poly(ethylene sebacate) obtained by crystallization from furfural at room temperature



Figure 19. Low-density polyethylene subjected to slow cooling from the melt

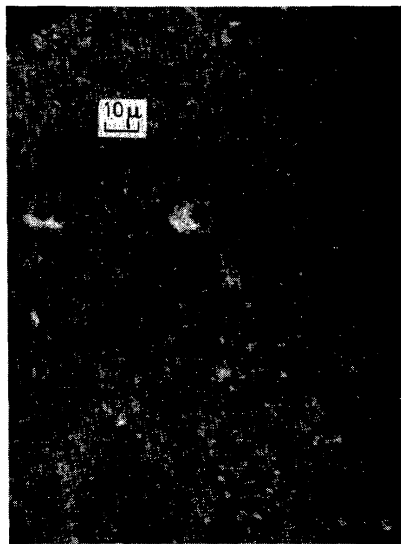


Figure 20. Low-density polyethylene subjected to rapid cooling from the melt

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Figure 21. Spherulites of polypropylene, obtained by annealing at 130–140°

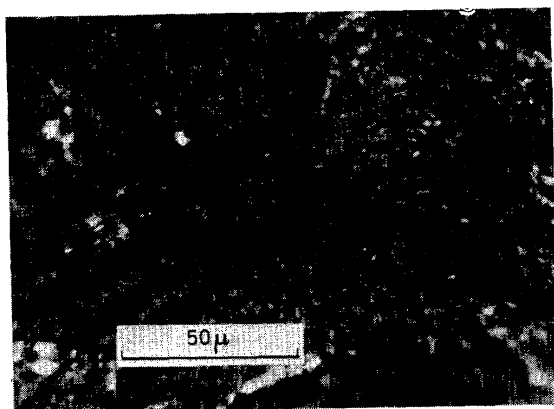


Figure 22. Large spherulite of polypropylene, obtained by annealing at 100°

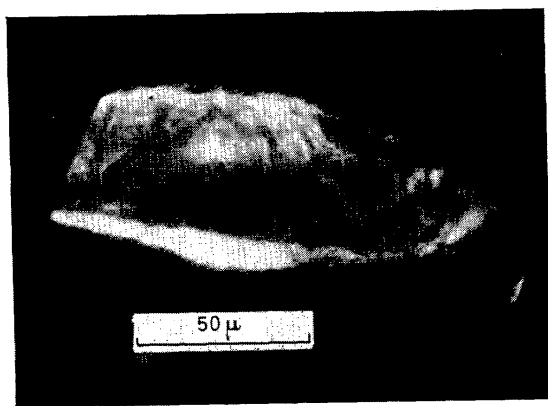


Figure 23. Large single crystal of polypropylene

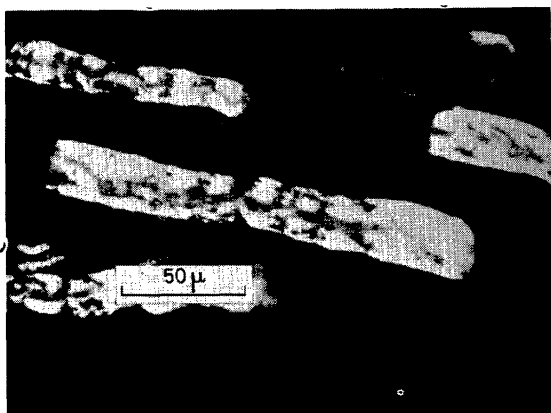


Figure 24. Large single crystals of polypropylene

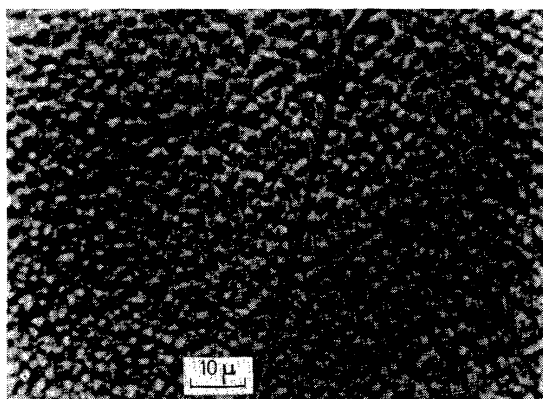


Figure 25. Small spherulites of moulded poly(hexamethylene sebacamide) (nylon 6-8)

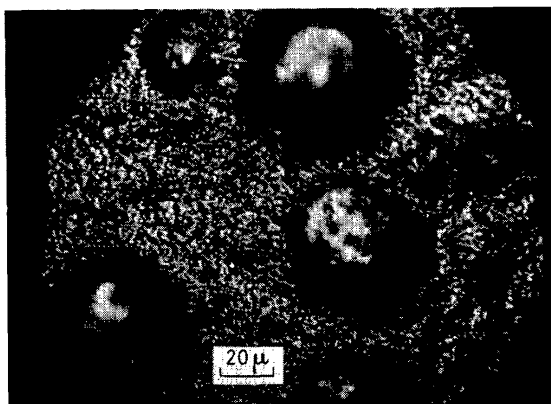


Figure 26. Large spherulites of moulded poly(hexamethylene sebacamide) (nylon 6-8) after 6 months' storage at room temperature

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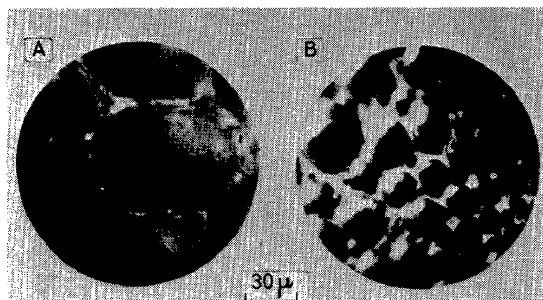


Figure 27. Effect of mechanical treatment on the size of spherulites of poly(hexamethylene sebacamide) (nylon 6-8). A shows spherulites in a plate of poly(hexamethylene sebacamide) after a single bend; for comparison, B shows spherulites in the same plate before bending

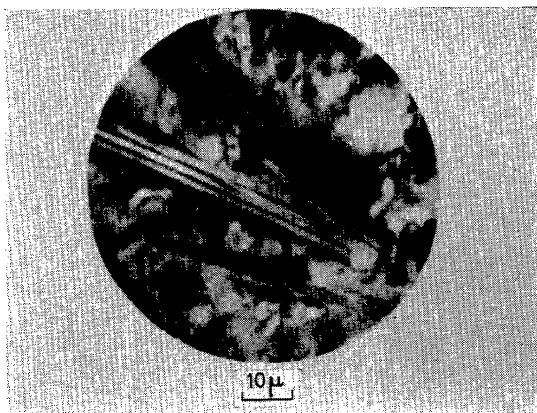


Figure 28. Small single crystals of poly(hexamethylene sebacamide) (nylon 6-8) obtained by stretching

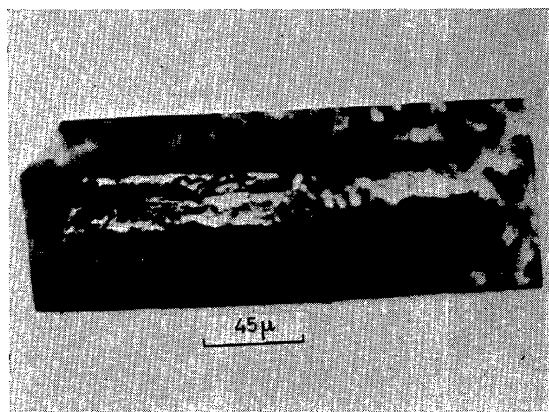


Figure 29. Large single crystal of poly(hexamethylene sebacamide) (nylon 6-8) obtained by stretching

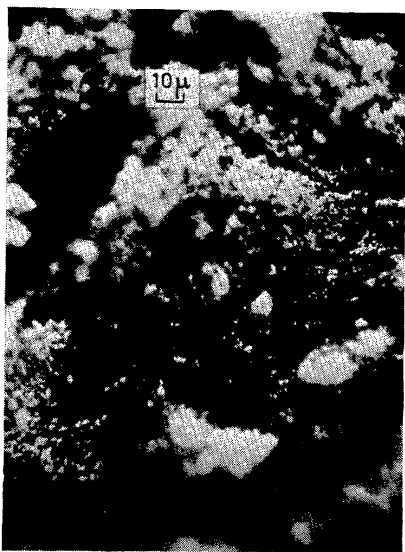


Figure 30. Small single crystals of polycaprolactam obtained by mechanical stress (physical blows on the sample)

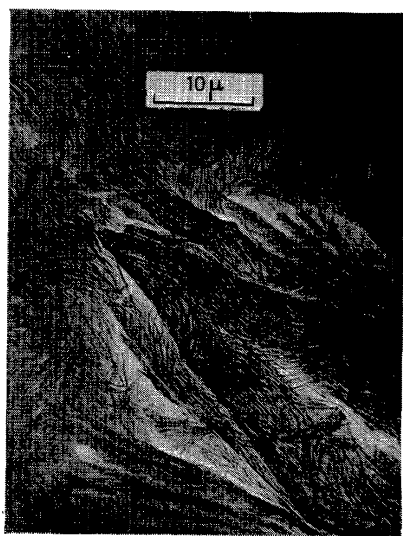


Figure 32. Spherulites of polyethylene heated to just below the melting-point for 2-3 min, and then maintained at 70° for 2.5 h; during this treatment, some of the spherulites have acquired the geometrical forms of polyethylene crystals although retaining a spherulitic micro-structure

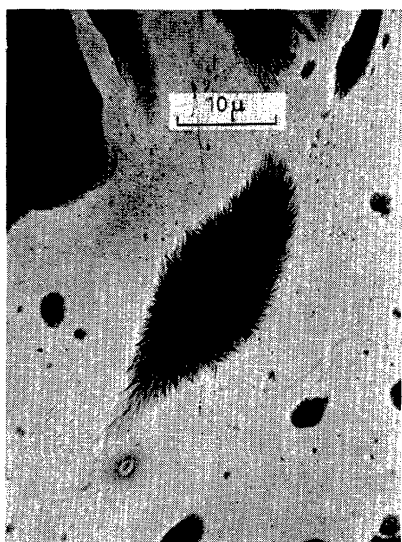


Figure 31. Spherulite of polyethylene obtained by heating the crystalline polymer to 110-115°; in this instance, the spherulite has retained the shape of the original crystal during conversion by the heat treatment

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Figure 33. Micro-diffraction picture of structures shown in Figure 32; the picture is identical with that obtained with single crystals

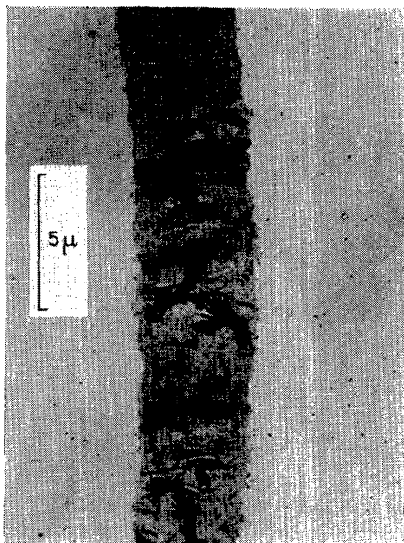


Figure 34. Highly asymmetric fibrillar crystals of polycaprolactam fibre

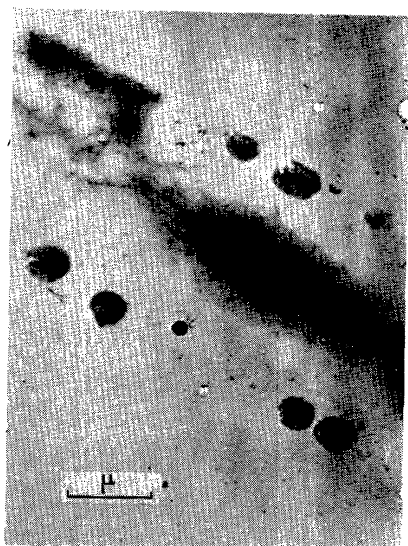


Figure 35. Structure of poly(ethylene terephthalate); even in the highly-orientated fibre, there is sufficient mobility of the structural elements for transformation processes to take place, and, in this example, there are quite large structures whose growth is not directly linked with the orientation of the fibre

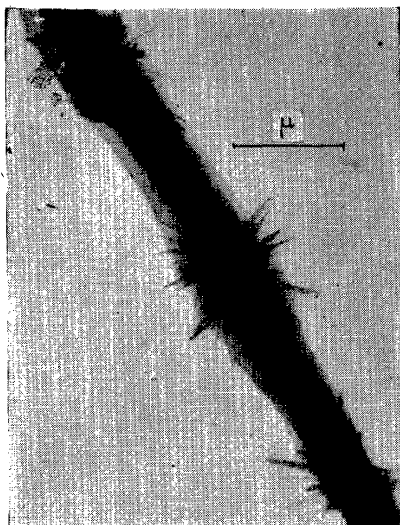


Figure 36. Large secondary fibrillar structures in the orientated regions of polycaprolactam fibre

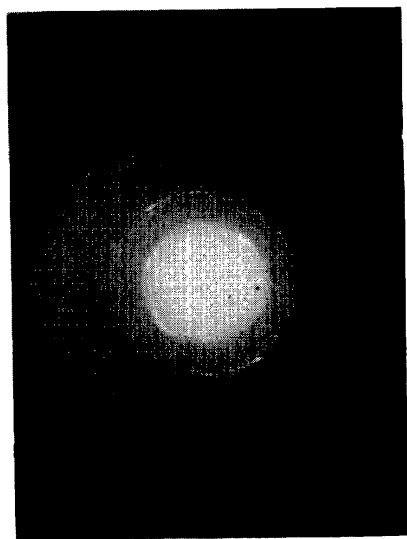


Figure 37. Micro-diffraction picture of highly-orientated secondary fibrillar structures of polycaprolactam shown in *Figure 36*

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destruction of all types of secondary structures under the influence of temperature and mechanical stress. This is all the more important since mechanical properties, especially brittleness (and, therefore, the impact strength and the resistance towards the action of abrasives), depend in a high degree on the structure of the material. If one follows the change in these properties with increasing size the spherulites, a maximum is observed in these properties at sizes of 1–2 μ . The further growth of spherulites results in a decline in the mechanical strength of the material.

Analogous phenomena are observed in polycaprolactam, but there is a greater tendency here for the formation of single crystals. It occurs particularly easily under mechanical stress. Thus, hitting the sample results in the destruction of the spherulites, and the production of large numbers of small single crystals (*Figure 30*).

Therefore, the production of large structures takes place not only on cooling melts or solutions, but also as the result of structural rearrangements in solid polymers. What is the mechanism of such rearrangements? Every process of this type needs molecular mobility, but the mobility of large molecules in solids is insignificant. It is impossible to imagine that structure formation results from diffusional displacement of polymer molecules, and it is still less likely that high structures are formed, not directly from chain molecules, but from packets of chains which play the rôle of initial structural elements. Probably the rearrangement of polymer structures is possible because they have rather small differences from one another.

We have studied the possibility of mutual transformations of single crystals into spherulites, and of spherulites into single crystals. On heating single crystals of polyethylene in the temperature range 110–115°, we have observed the conversion of these crystals into single fibrillae, and the formation of spherulites which often maintain the form of the initial crystals (*Figure 31*). At this temperature, sharp increases of parameters a and c were observed, with preservation of parameter b and an increase of molecular mobility as mentioned by Slichter¹³.

For carrying out the reverse process, the film containing the spherulites (supported on glycerol) was heated just below the melting-point for 2–3 min, and then kept at 70° for 2.5 h. During this treatment, some spherulites acquire the right geometrical forms (*Figure 32*), although retaining a typical spherulitic micro-structure. At the same time, micro-diffraction shows a single crystal picture for these regions (*Figure 33*). Therefore, the very small rearrangements of structural elements—ribbons or fibrillae—result in the mutual transformation of large structures. Such a mobility can always be realized on the surfaces of cracks and on any sites of defective structure. It seems to us that, in such systems consisting of slightly mobile structural elements, it is reasonable to speak about the migration of defects, about the peculiar mobility of "holes" if one utilizes the analogy with the mechanism of P -conductivity in semiconductors.

All these data have been concerned with the free growth of structures in isotropic media. It is very probable that, in oriented polymer systems, and particularly in fibres, other morphological forms of high structures can appear. Thus, electron-microscopic investigations on ultra-thin slices always reveal very asymmetric crystals of fibrillar type, as can be seen in the

case of polycaprolactam fibre (*Figure 34*). The most curious fact is that, even in highly-orientated fibres, sufficient mobility of structural elements can be realized for carrying out the transformation processes in the solid polymer. One example of structure produced in poly(ethylene terephthalate) fibre is shown in *Figure 35*. Here we can also see rather large structures, the growth of which is not directly linked with the orientation of the fibre. Sometimes it is possible to observe directly the rise of secondary structures in the orientated regions (*Figure 36*). On this figure one can see the large fibrillar structure in the polycaprolactam fibre; in some places bunches of secondary crystals are observed. On average, the fibre is highly-orientated, as can be seen from micro-diffraction data (*Figure 37*).

Thus we see that structureless polymers composed of random entangled chains are most probably the exception rather than the rule. We recognize now that a very great variety of structures exists, ranging in size from the microscopic to the visible. We can now assume with confidence that several important properties of polymers are closely connected with the development of structure. It seems that structural investigations will become as essential for polymers as metallography is for metals.

Summary

It was found that practically all crystallizable polymers could be obtained in large morphological structural forms up to single crystals with dimensions of several mm. The formation of such big crystals is a multi-stage process. It seems that polymorphism is a characteristic feature of polymer structures. It was shown that polyethylene, for example, could exist in the form of particular helices besides the well-known structures. The different morphological crystalline forms could be observed for polypropylene, polystyrene, polychlorotrifluoroethylene, poly(acrylic acid), *etc.* Especially large single crystals are formed in the case of gutta-percha. Very large spherulites are obtained from poly(ethylene sebacate). The dimensions of such forms are up to several mm, so that there is the possibility of investigating precisely the fine structure. Large structural forms also appear in solid polymer blocks, and can be found on the breaks and cuts with the aid of electron and optical microscopes after partial dissolution of the surface using bad solvents.

Preparation of large single polymer crystals provided the possibility of a direct microscopic study of its deformation and destruction, which are similar to those in single metal crystals. It can be affirmed now that many particularities of mechanical properties of crystalline polymers are connected especially with the existence of large structural forms.

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