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SPECIAL LECTURES

SECTION B: PROPERTIES OF POLYMERS

SECTION C: FREE RADICAL INITIATED POLYMERIZATION

SECTION D: IONICALLY INITIATED POLYMERIZATION

SECTION E: CHEMISTRY OF HIGH POLYMERS

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 polymers[1]. 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 polyethylene[2].

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 mechanism[3] 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-percha[4], poly-4-methylpentene[5], polyamides[6], polyesters[7], polypropylene, polystyrene[8], polychlorotrifluoroethylene[9] 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 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-workers[11] by crystallization of poly(ethylene sebacate) from solutions in furfurol 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

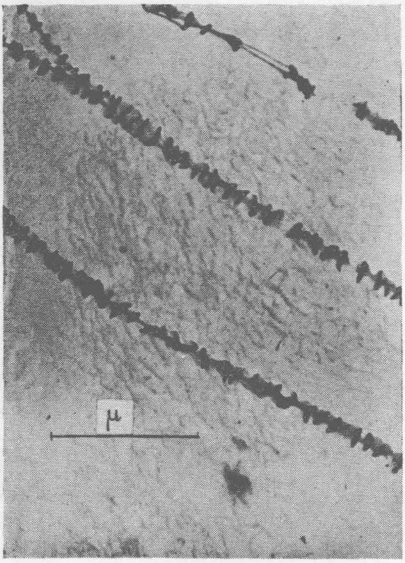

Figure 1. Helicoidal structures of polyethylene

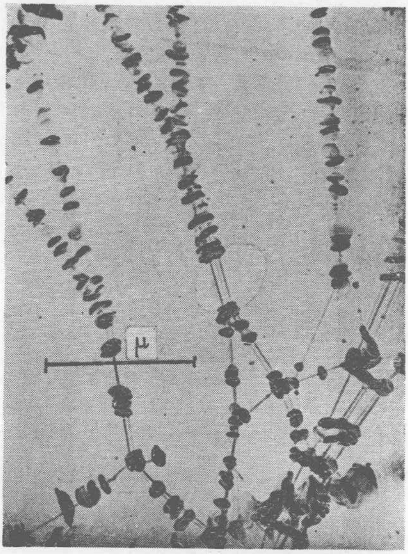

Figure 2. Single-chain packets formed by stretching helicoidal structures of polyethylene

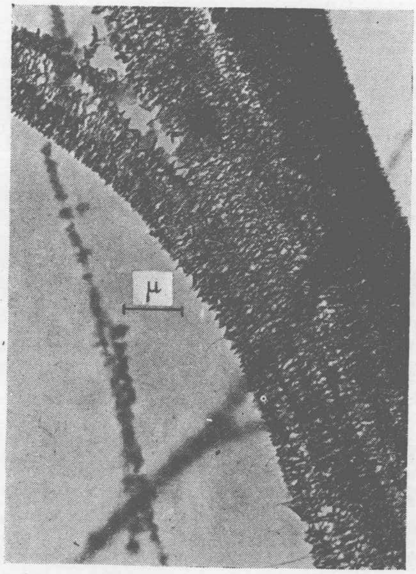

Figure 3. Polyethylene band consisting entirely of helicoidal structures

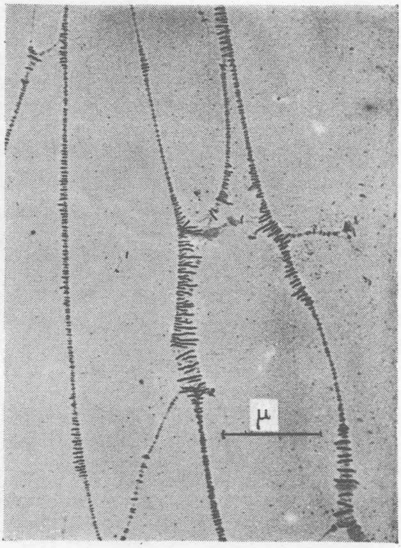

Figure 4. Polyethylene bands built up of narrow ribbons

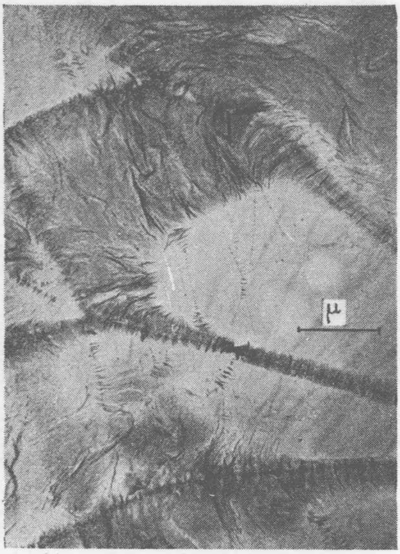

Figure 5. Various different structures of polyethylene

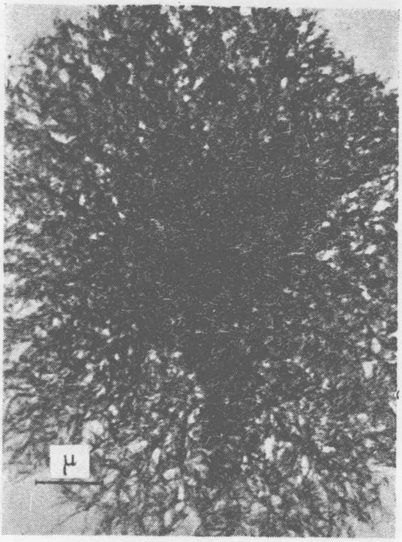

Figure 6. Large globulae (consisting of faintly-ordered strips) of polyethylene obtained by radiation polymerization

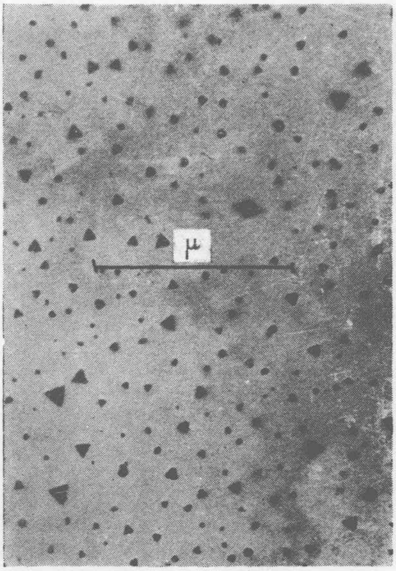

Figure 7. Lamellar crystals of polypropylene, formed by slow crystallization from xylene

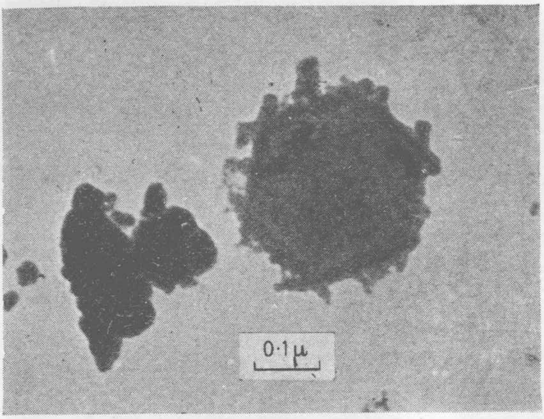

Figure 8. Hexagonal crystals of polypropylene, formed by slow crystallization from xylene

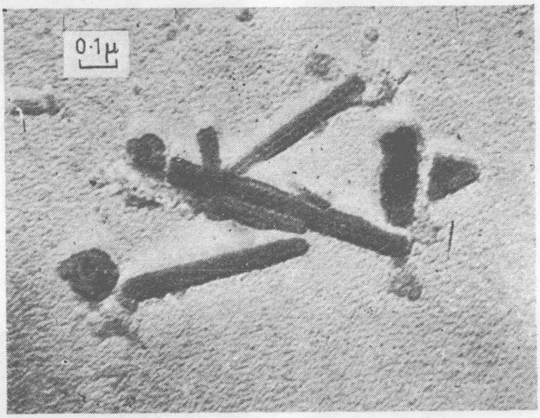

Figure 9. Fibrillar crystals of polypropylene, formed by crystallization from tetralin (or trichloroethylene)

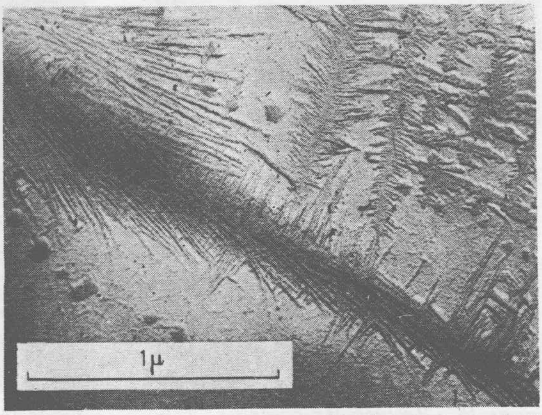

Figure 10. Fibrillar structures of polypropylene which develop into the elongated crystals shown in *Figure 9*

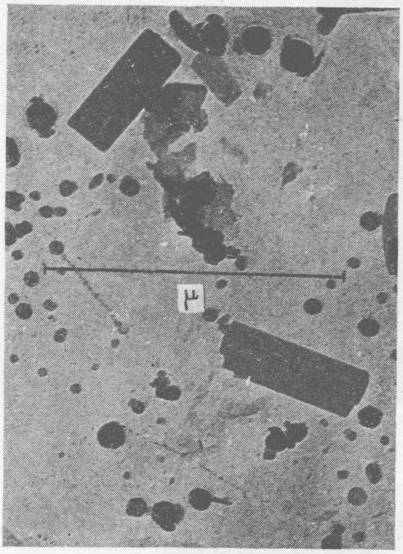

Figure 11. Lamellar structures (consisting of aggregates of small planar crystals) of polychlorotrifluoroethylene, formed by slow crystallization from mesitylene

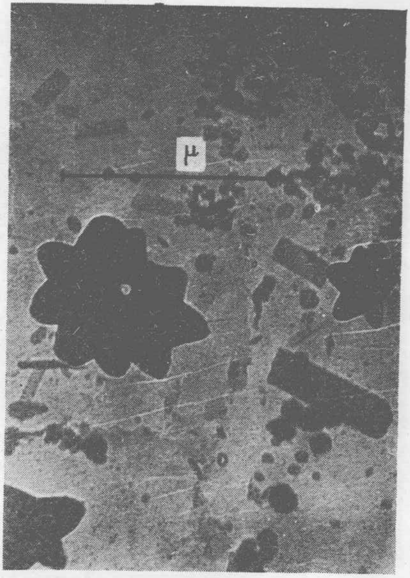

Figure 12. Well-formed crystals of polychlorotrifluoroethylene, formed by crystallization from mesitylene at 180°

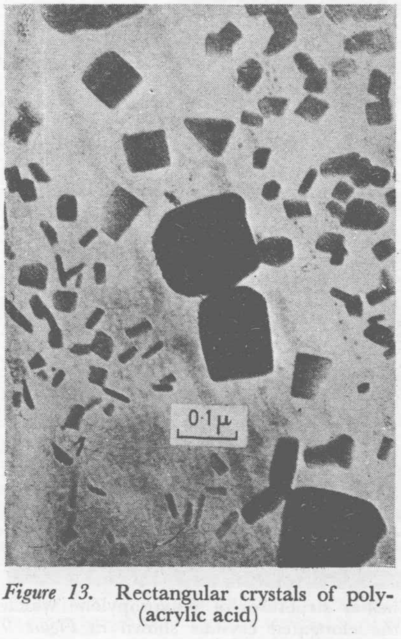

Figure 13. Rectangular crystals of poly-(acrylic acid)

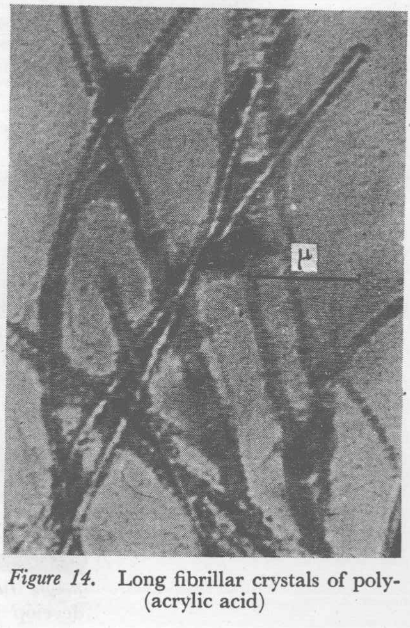

Figure 14. Long fibrillar crystals of poly-(acrylic acid)

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

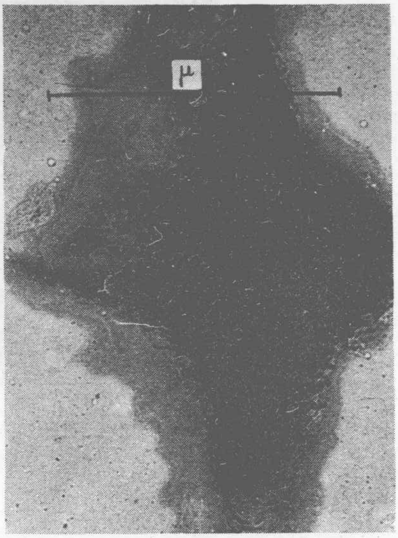

Figure 16. Star-like crystal of polystyrene, showing flaky structural elements

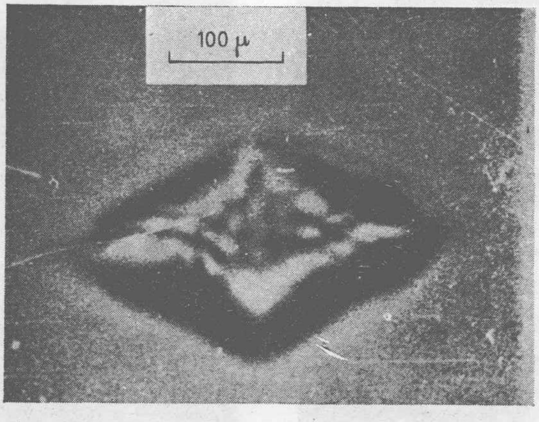

Figure 17. Large star-like crystal of polystyrene, formed by slow crystallization from a relatively concentrated (2 per cent) solution in xylene

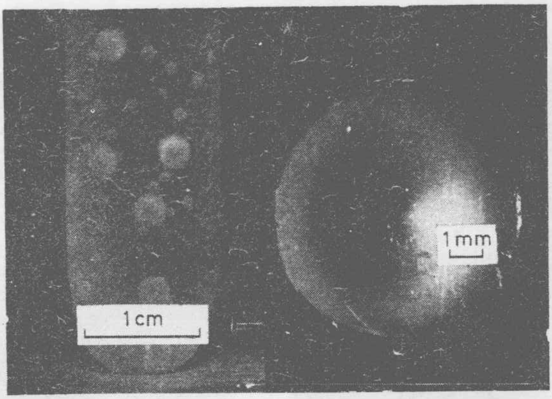

Figure 18. Large spherulites of poly(ethylene sebacate) obtained by crystallization from furfurol at room temperature

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

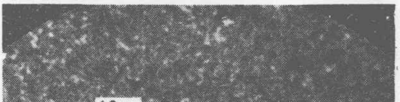

Figure 20. Low-density polyethylene subjected to rapid cooling from the melt

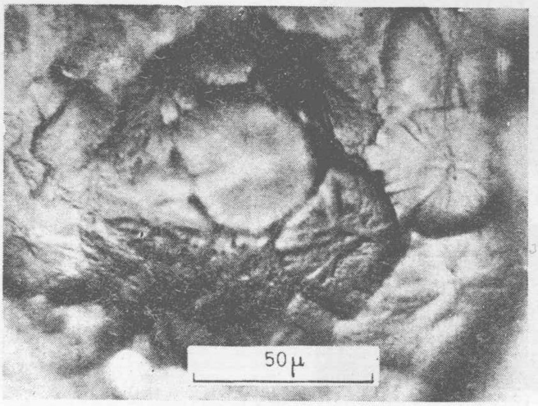

Figure 21. Spherulites of polypropylene, obtained by annealing at 130–140°

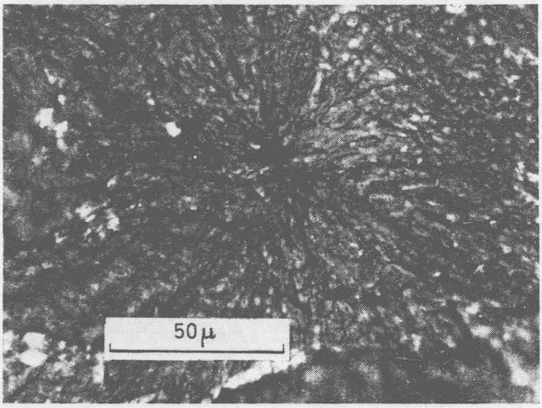

Figure 22. Large spherulite of polypropylene, obtained by annealing at 100°

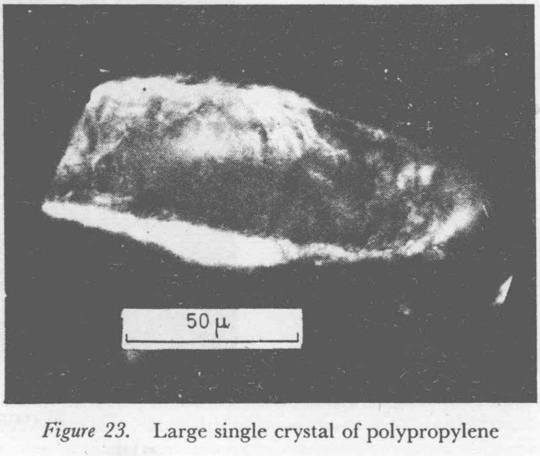

Figure 23. Large single crystal of polypropylene

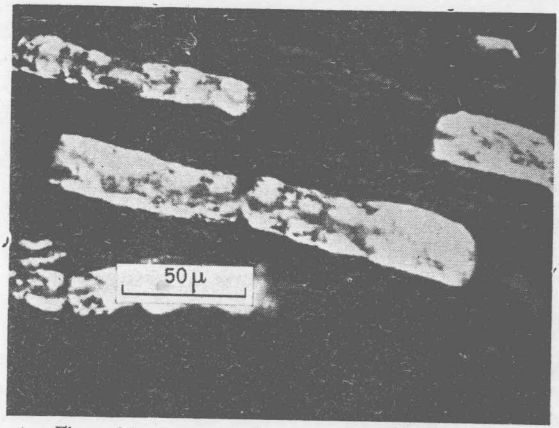

Figure 24. Large single crystals of polypropylene

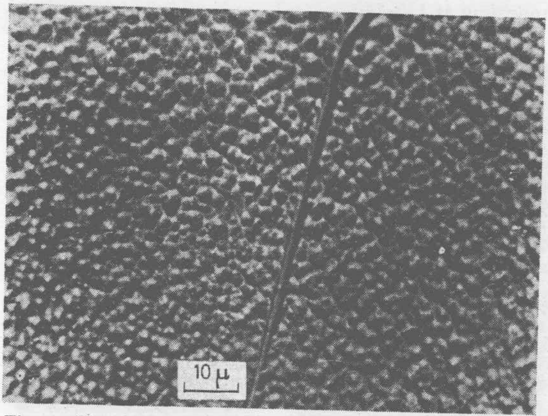

Figure 25. Small spherulites of moulded poly(hexamethylene sebacamide) (nylon 6–8)

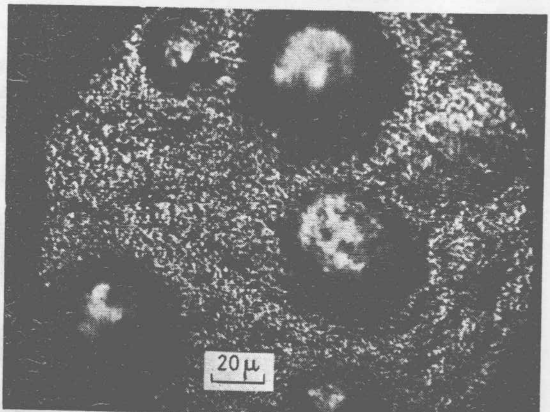

Figure 26. Large spherulites of moulded poly(hexamethylene sebacamide) (nylon 6–8) after 6 months' storage at room temperature