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ABSTRACT

Samples of polypropylene crystallized under various sets of thermal conditions and various pressures have been fractured at liquid nitrogen temperatures. Both the free surface and the fractured surface have been examined by means of the light microscope and, through replication, by the electron microscope.

Upon slow cooling of bulk or thin film specimens, large spherulites are found and the fracture crack tends for the most part to run around the spherulite boundaries. Several examples are given. For rapidly cooled specimens the spherulites are considerably smaller and the tendency toward boundary fracture is reduced.

The fracture surface of samples crystallized under various pressures up to 16,900 psi have been observed both before and after annealing at elevated temperatures. Annealing tends to accentuate the surface features. The most pronounced surface features are striated bands, planar lamellae, and a crosshatched morphology. Electron micrographs of the various features are shown and a comparison is given of these results and those found for bulk specimens of polyethylene and teflon. Fracture has also been induced in aggregates of single crystals prepared from dilute solution and the nature of fracture implies a unique type of chain folding occurs in these single crystal lamellae. Both planar lamellae and a crosshatched fibrillar structure are also observed in solution grown crystals.

I. Introduction

In recent years, studies of the nature of fracture surfaces have provided information concerning the fine structure and internal morphology of polymeric materials. For example, in 1958 Bunn and co-workers<sup>(1)</sup> used the electron microscope to study the fracture surfaces of highly crystallized polytetrafluoroethylene. Instead of a spherulitic structure, they observed a series of more or less randomly oriented bands, of width ranging from about 0.2  $\mu$  to 1  $\mu$ , and with closely spaced striations running at right angles to the band. Further studies were made on teflon samples by Speerschneider and Li<sup>(2)</sup>, who found that slow cooling tended to give longer bands and wider striations. They also noted that under deformation the band structure became distorted and

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examples were shown of relative sliding, bowing, rotation and kinking of striations.

Fracture and deformation studies have also been carried out on polyethylene samples by various investigators. Anderson<sup>(3)</sup>, for example, noted the presence in bulk-crystallized Marlex 50 of 3 distinct types of lamellae. One of these types was similar to that observed in simple crystal studies, a second type appeared to have an unusually narrow width which varied with crystallization temperature and a third type appeared to be extended-chain lamellae. This latter type appeared in the form of striated bands similar to those observed by Bunn et al<sup>(1)</sup> for teflon. Geil and coworkers<sup>(4)</sup> have studied the fracture surfaces of polyethylene crystallized under high pressure. Under these conditions, most of the polymer appears to crystallize as extended-chain lamellae.

The purpose of the present study is to obtain information on the nature of fracture surfaces and on internal morphology in samples of isotactic polypropylene crystallized under various thermal conditions and under varying pressures. Bulk crystallized samples, thin film samples, and single crystal samples have all been studied. In the first two cases, the samples were fractured at liquid nitrogen temperature after first cutting a fine thin notch into the surface with a razor blade. The single crystal samples were prepared by the techniques recently described by Morrow et al<sup>(5)</sup> and Sauer et al<sup>(6)</sup> and were fractured by exposure of the polymer solution to ultrasonic vibrations. For the bulk and thin film samples prepared from the melt both the molded and fracture surfaces were examined by light microscopy and by electron microscopy using standard replicating techniques. The nature of fracture and deformation in the specimens prepared from dilute solution was studied by means of direct electron transmission pictures.

The polypropylene samples used throughout this study were taken from commercially available whole polymer which was found to be 95% to 98% insoluble in boiling n-heptane. The soluble material was removed through use of a standard Soxhlet extractor and the remaining insoluble material was then utilized for all of the tests described herein.

## II. Results and Discussion

### 1. Samples Molded at Atmospheric Pressure

A light micrograph of the free surface of a bulk polypropylene sample which was crystallized by first melting the powder and then holding the sample at 123°C for 68.5 hours is shown in Fig. 1. The spherulites are large, of the order of several hundred microns, and well formed. The slide shows the material on both sides of a fracture which was induced by giving the sample a sudden blow after ex-

posure to liquid nitrogen temperatures. Under these conditions, as Fig. 1 shows, the crack tends to run along the spherulite boundaries. These boundaries, according to Keith and Padden<sup>(7)</sup>, contain a high percentage of impure material and may act as a source of weakness.

Both banded and non-banded spherulites can be observed and voids can sometimes be seen between adjacent spherulites. The fracture crack may well start at one of these voids and then propagate through the weakened boundary layer material around the spherulite edges. The actual final fracture also indicate that crack propagation can occur directly through the spherulites. Fig. 2, for example, shows a light micrograph of a portion of the actual fracture surface of the same sample whose free molded surface is shown in Fig. 1. The radiating fibrillar nature of the spherulites is now visible.

Fracture tests have also been run on some thin film samples grown from the melt between glass slides. Growth is now inhibited in a direction perpendicular to the plane of the glass slides and a 2-dimensional spherulite, or cylindrulite<sup>(8)</sup> is now obtained. With this method of crystallization it is easier to see the influence on the polypropylene structure of changes in cooling rate. Fig. 3, for example, shows the structure that is obtained upon slow cooling of the molten film. The spherulites shown in this light micrograph are of the order of a hundred microns or so. Each spherulite develops from an individual nucleus and continues to grow until interference occurs with neighboring spherulites. Occasionally as Fig. 3 shows, small voids or boundary cracks appear along adjacent spherulite edges. Fig. 4 gives a light micrograph of the free surface on both sides of a fracture again induced at liquid nitrogen temperatures in order to curtail plastic deformation. Here too the crack has passed mostly around the spherulite boundaries.

If the molten film is rapidly quenched, crystallization is much more rapid, many nuclei form, and the resulting spherulites are now quite small, of the order of microns rather than hundreds of microns. A light micrograph is shown in Fig. 5. There is now no pronounced tendency for a fracture crack to propagate along spherulite boundaries.

Although the light microscope is useful for observing spherulite formation and the means of propagation of large scale fracture, it does not give any indication of the fine structure of the material that is being fractured. For this purpose, it is necessary to use the electron microscope. Most of the subsequent figures have been obtained by making a replica of the actual fracture surface, shadowing this replica with platinum to enhance the contrast, and then observing the structure by transmission electron microscopy using an Hitachi 11-A electron microscope.

## 2. Samples Molded at a Pressure of 1000 psi

Fig. 6 shows an electron micrograph of a portion of the replica of the fracture surface of a bulk polypropylene sample. This particular sample was subject to a pressure of about 1000 psi and then crystallized by cooling rapidly from about 180°C.

The fracture surface displays a number of interesting features. These include flat lamellae, striated bands and, near the center of the slide, an apparent crosshatched morphology. The bands are of the order of 0.2  $\mu$  in width and are rather similar to, though not as regular as, those observed in teflon by Bunn and coworkers.<sup>(1)</sup> The striations are essentially at right angles to the band and are spaced several hundred angstroms apart. Some of the bands show evidence of slip between adjacent striations while other bands have chevron-type markings indicative of kinking of striations. Speersneider and Li<sup>(2)</sup> observed similar signs of deformation on fracture surfaces of teflon.

The three separate structural features are not seen on each micrograph. Sometimes the band feature, or the lamellae are more evident while on other micrographs, the crosshatched structure is more pronounced.

It should be mentioned that before the replica of the fracture surface shown in Fig. 6 was made, the polypropylene sample was annealed. In this particular specimen, the annealing given was 55 minutes at 158°C. The purpose of the elevated temperature annealing was to more clearly bring out the structural features present on the fracture surface. It is recognized that this treatment will necessarily mean that the replica is not truly representative of the original fracture surface. Hence in most instances electron micrographs were made of surfaces replicated both before annealing and after annealing.

## 3. Samples Molded at a Pressure of 10,000 psi

Fracture surfaces, as well as free surfaces, have been examined for several samples of polypropylene, which have been taken to 180°C, subject to a pressure of 10,000 psi and then held for two hours at a lower temperature of 145°C. An electron micrograph of a portion of the replica of the free surface of this sample is shown in Fig. 7. There is evidence of hexagonal crystal growth of the polymer itself as well as of hexagonal impurity crystals (dark areas on the slide). Electron diffraction patterns of these impurity crystals, see Fig. 8, show them to be crystals of titanium sesquioxide (Ti<sub>2</sub>O<sub>3</sub>) or  $\alpha$ -aluminum oxide (Al<sub>2</sub>O<sub>3</sub>).

These impurity crystals result from the catalysts used in the polymerization process. It appears that during fracture the bond bet-

ween these impurity crystals and the polymer is weakened or broken. Hence when a replica is made of the fracture surface, the catalyst crystals will frequently adhere, as Fig. 7 shows, to the replica. We consider it quite likely that these catalyst crystals serve as nuclei for the growth of the hexagonal modification of polypropylene and this possibility is now being further explored.

An electron micrograph of a portion of the replica of an unannealed fracture surface is shown in Fig. 9. There is here no evidence of bands per se, but rather of an oriented or crosshatched overgrowth possibly superimposed upon broad lamellae.

Two electron micrographs of a portion of the replica of the fracture surface of samples annealed for 40 minutes at 159°C before replicating are seen in Fig. 10 and 11. The oriented or woven feature is now much more pronounced. In Fig. 10, the fibrillar like elements are more oriented in one direction as though one were looking at a section of a radial arm of a spherulite. In Fig. 11, the woven or crosshatched feature is more pronounced. A texture, somewhat similar to this, is obtained also from dilute-solution crystallized polypropylene<sup>(5,6)</sup>

## 4. Samples Molded at a Pressure of 16,900 psi

To investigate more fully the morphology of samples molded at higher pressures a special pressure mold was constructed. This apparatus, somewhat similar in design to that described by Kardos<sup>(9)</sup>, permits one to crystallize samples 1/4" in diameter and up to 3" in length at various hydrostatic pressures and varying temperatures. The melting temperature was found to increase considerably with increase of hydrostatic pressure. For example, at a pressure of 16,900 psi, the estimated melting point from measurements of specific volume is about 220°C.

Fracture studies were carried out on several samples exposed to a pressure of 16,900 psi, taken to a temperature above 220°C and then crystallized by holding the pressurized specimen for 17.5 hours at a temperature of 194°C. After fracturing at liquid nitrogen temperature, replicas of the fractured surface were made both before and after annealing. An example of the type of structure obtained on the unannealed fracture surface is shown in Fig. 12. The morphology is not well defined but there is evidence of planar lamellae and of some more or less hexagonal shaped craters or extensions.

The fracture surface of a similar specimen but one which was annealed for 15 minutes at 162°C prior to replicating is shown in Fig. 13. The surface features are now accentuated and for the most part present a mosaic-like appearance. There are two prominent sets of cross-markings and the individual blocks or units between these mark-

ings are mostly diamond-shaped. Some, however, also have a hexagonal appearance with indications of spiral growth steps.

##### 5. Samples Crystallized from Dilute Solution

To supplement the fracture studies of the bulk samples, it was felt that studies of the morphology of both unfractured and fractured samples of solution-grown crystals would be helpful. These crystals were prepared according to the procedures recently outlined<sup>(5,6)</sup> and the resulting samples obtained both from quick cooling and from constant temperature growth were examined with the electron microscope.

For dilute samples of isotactic polypropylene prepared from a 0.4% solution in  $\alpha$ -chloronaphalene and crystallized at a temperature of 115°C, it was observed that crosshatched polyhedral aggregates, or quadrites, several microns in length and width tended to form. Some of these are shown in Fig. 14. They appear to consist of thin lamellae standing on edge and aligned along the principal diagonals of the quadrite. Near the edges, however, the lamellae tend to collapse upon the carbon substrate. They are seen as individual lath-shaped crystals in the higher magnification picture of Fig. 15. In this case, the precipitate was prepared from a 0.01% solution at 115°C. From shadow length measurements, the thickness of the crystalline units can be inferred as 125-150 Å. It is now known that these individual lath-shaped elements are well-formed, highly-ordered, single crystals of isotactic polypropylene. They give a sharp electron diffraction picture of the type shown in Fig. 16. All the reflections shown are (hko) reflections and hence the molecular or chain axis is at right angles to the surface of the planar lamellae. The lamellae are thus folded chain crystals and the crystal structure is the usual (Natta) monoclinic form.

One interesting aspect of Fig. 15 is that it shows that one lamellae has accidentally split parallel to its long axis. A second lamellae has passed through the split in the first lamellae apparently unimpeded. This is but one piece of evidence indicating that there is a unique type of uniaxial chain folding<sup>(6)</sup> occurring in polypropylene crystals viz. the fold planes appear to be parallel to the long axis of the lamellae (the a crystallographic axis).

It was found possible to fracture some of these thin crystal elements by subjecting the dilute polymer solution to ultrasonic vibration. In other instances, fracture occurred during transfer to the carbon grids. One example of a fractured crystal lamella is shown in Fig. 17. The fracture, in this instance, occurred nearly parallel to the short dimension of the lath-shaped crystal (b crystallographic axis). In other instances fracture occurred parallel to the long axis of the crystal. In this latter instance, no fibrils were seen. However,

when fracture occurred along a perpendicular plane to the long direction then, as Fig. 17 shows, many fibrils are present. This is what one would expect if the fold planes were parallel to the long axis of the lath-shaped crystals. Various other fractured crystal surfaces have also been studied. In all cases where fracture occurs at right angles to the long axis fibrils are seen while no fibrils have ever been observed when the fracture is parallel to the long axis of the platlet.

Fig. 18 gives an electron micrograph of an interesting structure that is obtained when a dilute solution is allowed to cool rapidly. In this case a multiple-twinned lamella grows from a single nucleus. Electron diffraction pictures of similar lamellae show they are poorly formed single crystals in the monoclinic modification.<sup>(5)</sup> As the crystal grows, the arms branch and considerable dendritic growth takes place. These multiple-armed lamellae, as well as the quadrite structures obtained from isothermal crystallization, appear to be an early stage in the development of spherulites.

Another interesting aspect of Fig. 18 is that one of the branches, unlike all the others, appears to have crystallized in a definite crosshatched arrangement rather than in the form of a flat elongated lamella. This fact indicates that a crosshatched fibrillar like structure is a possible crystal form of isotactic polypropylene even when grown by dilute solution techniques.

References

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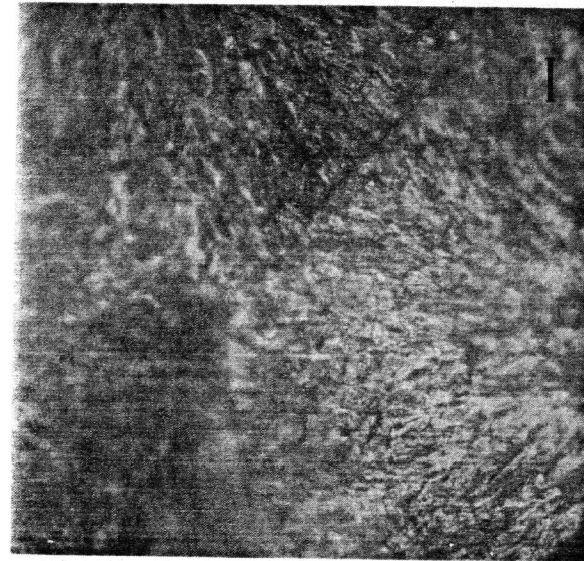


Fig.2. Light micrograph of a portion of the fracture surface of a bulk polypropylene sample (indicating mark corresponds to 40  $\mu$ ).

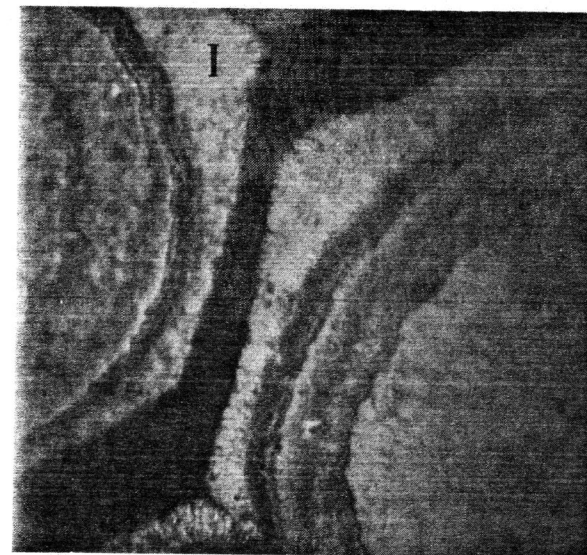


Fig.1. Light micrograph of the free surface of a bulk polypropylene sample in the vicinity of a fracture crack (indicating mark corresponds to 30  $\mu$ ).

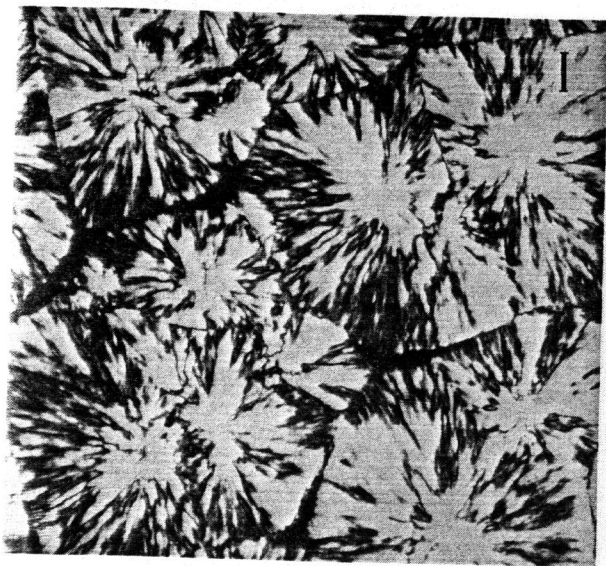


Fig.3. Light micrograph of free surface of a slowly-cooled, thin-film sample of polypropylene (indicating mark corresponds to  $10\mu$ ).

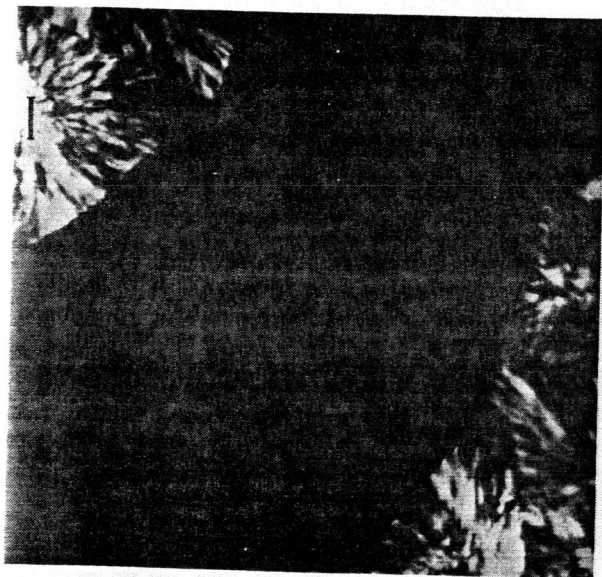


Fig.4. Light micrograph of free surface of a slowly-cooled, thin-film sample of polypropylene in the vicinity of a fracture crack (indicating mark corresponds to  $10\mu$ ).

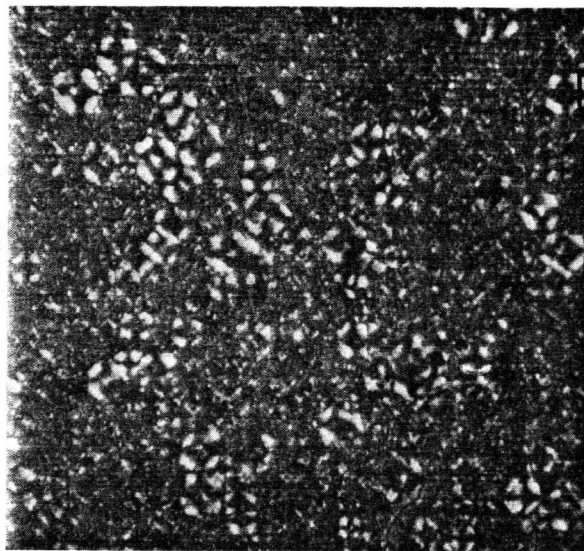


Fig.5. Light micrograph of a rapidly-quenched, thin-film sample of polypropylene (indicating mark corresponds to  $10\mu$ ).



Fig.6. Electron micrograph of replica of fracture surface of a bulk polypropylene sample molded at a pressure of 1000 psi (indicating mark corresponds to  $0.5\mu$ ).

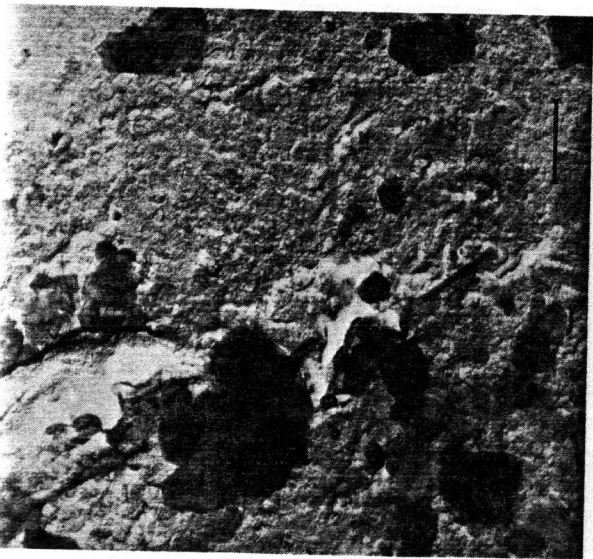


Fig.7. Electron micrograph of replica of free surface of a bulk polypropylene sample molded at a pressure of 10,000 psi (indicating mark corresponds to 0.25 $\mu$ ).

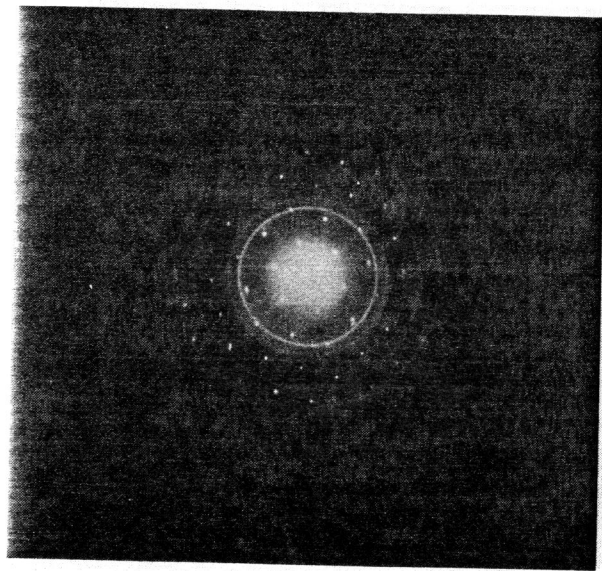


Fig.8. Electron diffraction pattern of impurity crystals.



Fig.9. Electron micrograph of replica of portion of fracture surface of an unannealed bulk sample of polypropylene molded at 10,000 psi (indicating mark corresponds to 0.5 $\mu$ ).

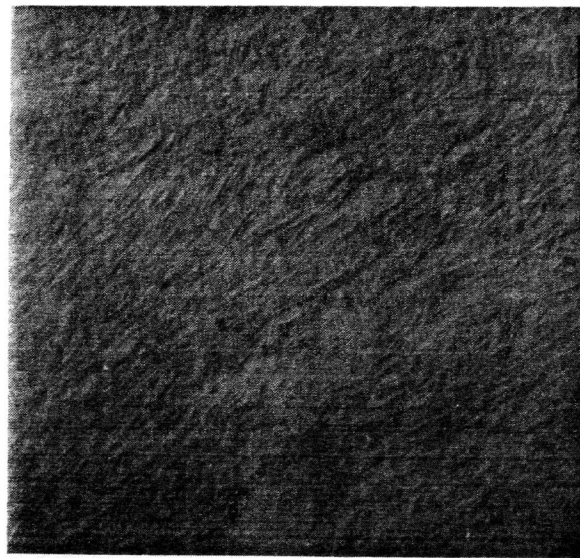


Fig.10. Electron micrograph of replica of portion of fracture surface of an annealed bulk sample of polypropylene molded at 10,000 psi (indicating mark corresponds to 0.5 $\mu$ ).



Fig. 11. Electron micrograph of replica of portion of fracture surface of an annealed bulk sample of polypropylene molded at 10,000 psi (indicating mark corresponds to  $0.5\mu$ ).



Fig. 12. Electron micrograph of replica of portion of fracture surface of an unannealed bulk sample of polypropylene molded at 16,900 psi (indicating mark corresponds to  $0.5\mu$ ).

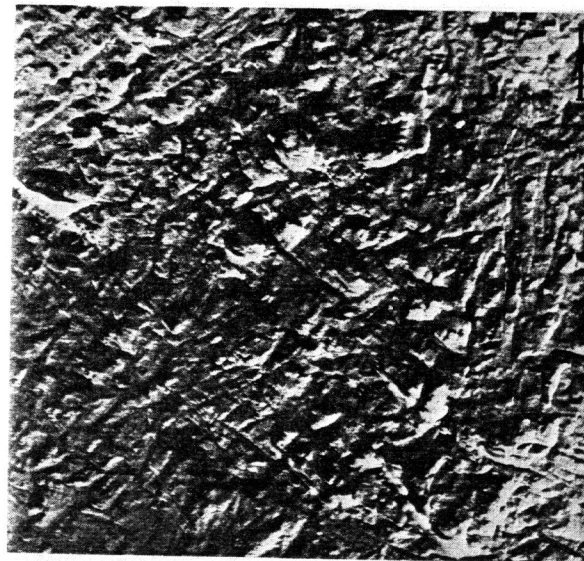


Fig. 13. Electron micrograph of replica of portion of fracture surface of an annealed bulk sample of polypropylene molded at 16,900 psi (indicating mark corresponds to  $0.5\mu$ ).



Fig. 14. Electron micrograph of polyhedral aggregates of polypropylene crystallized at  $115^{\circ}\text{C}$  in a 0.4% solution of  $\alpha$ -chlorophthalene (indicating mark corresponds to  $1\mu$ ).





Fig.15. Electron micrograph of lath-shaped polypropylene crystals at edge of quadrite. Material crystallized at 115°C from a 0.01% solution in  $\alpha$ -chloronaphthalene (indicating mark corresponds to 0.25  $\mu$ ).

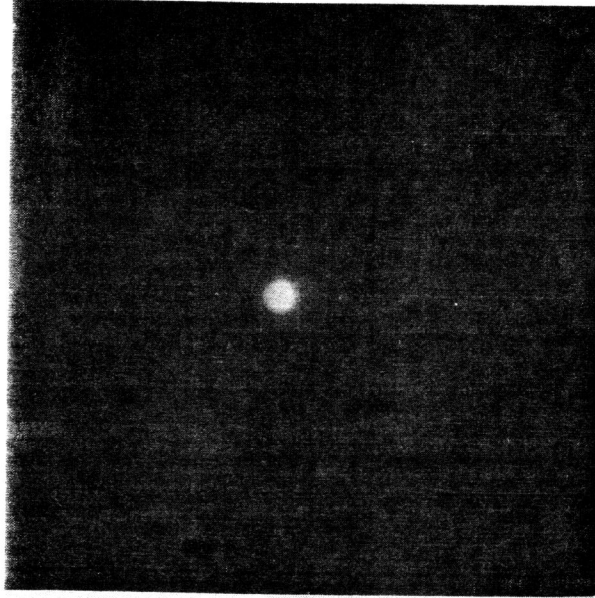


Fig.16. Electron diffraction picture of lath-shaped polypropylene crystals showing monoclinic structure.

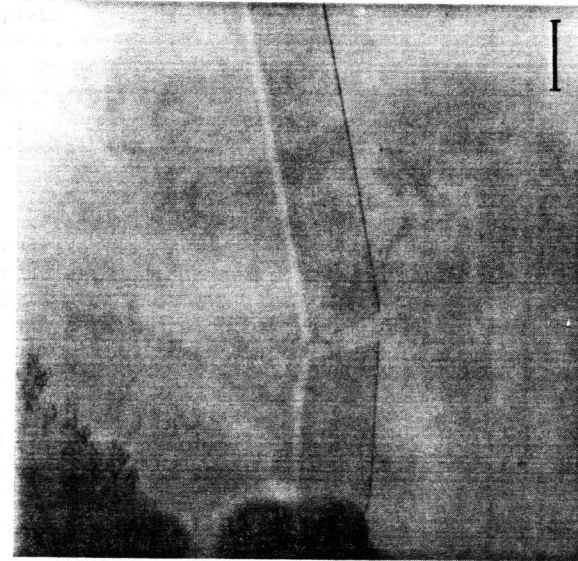


Fig.17. Electron micrograph of lath-shaped polypropylene crystal accidentally fractured nearly parallel to b crystallographic axis. Material crystallized at 112°C from a 0.04% solution in  $\alpha$ -chloronaphthalene (indicating mark corresponds to 0.5  $\mu$ ).

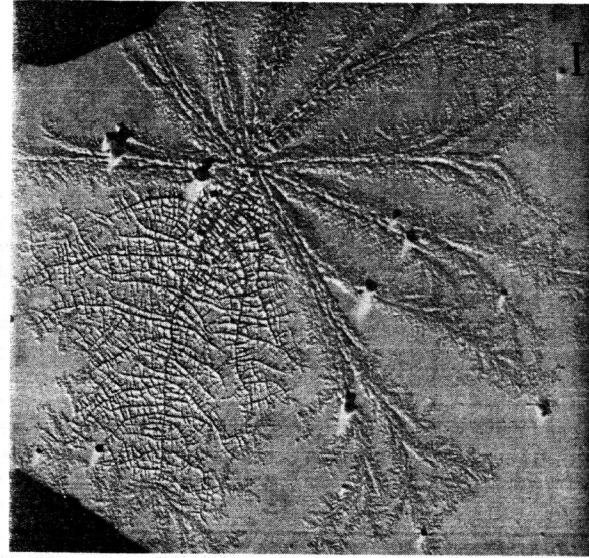


Fig.18. Electron micrograph of an incipient spherulite of polypropylene prepared by crystallization of a polymer fraction ( $M_w = 70 \times 10^3$ ) in a 0.004% solution in  $\alpha$ -chloronaphthalene and subsequent rapid cooling (indicating mark corresponds to 1  $\mu$ ).