

# Crystallization of Polymers from Solution under Shearing Stress III Polybutene-1

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It was shown that the fibrous crystals of isotactic polybutene-1 crystallized from solution under shearing stress are also composed of the central threads with an extended chain character and the epitaxially deposited lamellae with a folded chain character. The characteristic behaviors in this polymer exist in; (1) that the resulting crystals possess the hexagonal modification of form I'; (2) that at low polymer concentrations the lamellar crystals with an orthorhombic modification of form III are precipitated in similar fashion to the case in the absence of stirring; (3) that the morphology in surface replica of thick deposited film is very similar to that of melt extruded polyethylene film crystallized in a highly stressed state.

## § 1. Introduction

In our previous papers<sup>1,2)</sup> of this series, we tried to clarify the crystallization mechanism of long chain polymers in solution under shearing stress using polyethylene and polypropylene. The effort in the previous papers has been directed toward the elucidation of the morphology of crystallized materials, with the purpose that such information would contribute to an understanding of the crystallization mechanism. In this paper, we have chosen isotactic polybutene-1, partly to enable us to extend the generality of our previous results, and also because it is interesting which modification of the crystals is provided from solution under shearing stress in view of peculiar polymorphism shown by this polymer.

The peculiar polymorphic behavior of isotactic polybutene-1 has recently been the subject of numerous investigations.<sup>3-14)</sup> According to the results of previous workers,<sup>3-14)</sup> the four polymorphic forms of isotactic polybutene-1 have been prepared as follows: (1) Form I: This hexagonal form is apparently the thermodynamically most stable form and can be prepared by the crystal-crystal phase transition of the form II on standing or under the influence of stress. (2) Form I': This form has the same crystallinity as form I but melts considerably lower than materials obtained from form II.

The direct formation of form I' occurs in the course of a Ziegler-type polymerization at relatively low temperatures, e. g., at  $-20^{\circ}\text{C}$ . (3) Form II: This is an unstable form having a tetragonal crystal structure and is the form that is first obtained when the polymer is crystallized from melt. (4) Form III: This is also a stable form and is prepared by precipitating the polymer from solution.

## § 2. Experimental

### Materials

The sample of isotactic polybutene-1 prepared in the Laboratory of Mitsubishi Yuka Company was used in this study. This sample had an intrinsic viscosity  $[\eta] = 2.28$  (dl/g) at  $60^{\circ}\text{C}$ , in heptane; this value corresponds to a viscosity-average molecular weight of 1,300,000 as calculated by the relationship reported by Stivala et al.<sup>15)</sup>

### Crystallization Procedures

Solution of the polymer was prepared in a tube (diameter 30 mm) from the sample with iso-amyl acetate as the solvent at the concentrations of 0.1% to 5% (by weight) by heating the polymer-solvent mixtures at  $120^{\circ}$  to  $130^{\circ}\text{C}$  for 30 min. and it was transferred to a water bath which has been held to the desired temperature. It was then stirred at the desired conditions of stirring (2500 rpm) with a stirrer (diameter 6 mm). Crystallization occurred at

solution in the form of ring fiber and the fiber clustered on the stirrer. When a few percent of the polymer was recovered, the stirrer was transferred to pure solvent of the same temperature and the materials deposited by subsequently crystallization were washed out for about 30 min. We obtained the film-like products on the stirrer.

### Preparation of Specimens for Electron Microscopy

The pseudoreplica method used in this study was identical to that previously described.<sup>1)</sup>

When the thick film products were obtained, they were shadowed by Pt-Pd and covered with a carbon film. The polymer was dissolved by hot heptane. Pieces of the replicating carbon were picked up on microscope grids for study.

### Electron microscopy

A Hitachi HU-11B was used for all of the microscopy described in this paper. Diffraction patterns were calibrated with the Debye-Scherrer rings from the Platinum.

### Thermal Analysis

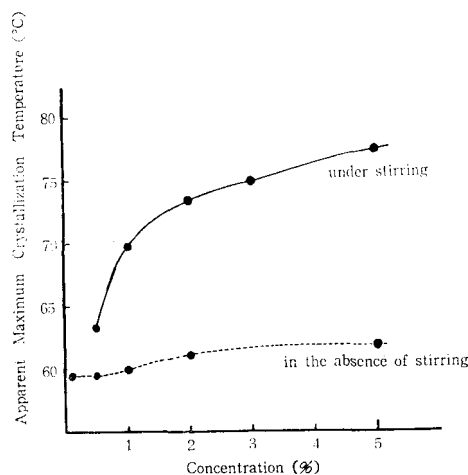
A Perkin-Elmer Differential Scanning Calorimeter was used. The temperature scale was calibrated by the onset of the melting of indium at 429°K., heated at the same rate as the sample.

## § 3. Results and Discussion

### Apparent Maximum Crystallization Temperatures

The ability for molecules to sustain deformation by stress is a characteristic property of polymer molecules. Since the deformation of polymer molecules allows the configurational entropy to decrease, less entropy remains to be sacrificed in going over to crystalline state. Hence, crystallization under stress occurs at a higher temperature than would normally be observed in the absence of stress.

Figure 1 shows the apparent maximum crystallization temperatures (the cloud points) of isotactic polybutene-1 with *iso*-amyl acetate as the solvent as a function of the polymer concentrations under stirring (2500 rpm) and the absence of it, the determinations of the temperatures having been carried out at the cooling rate of 1°C/hr. Values of the apparent maximum crystallization temperatures under stirring (solid line) become markedly higher than those in the absence of it (dotted line)



**Fig. 1** Apparent maximum crystallization temperatures of isotactic polybutene-1 with *iso*-amyl acetate as the solvent as a function of the polymer concentrations under stirring and the absence of it, the determinations of the temperatures having been carried out at cooling rate of 1°C/hr.

and the difference between the crystallization temperatures increases with the polymer concentrations. From these results we may conclude that the tendency toward crystallization of isotactic polybutene-1 in solution is greatly enhanced by shearing stress produced by stirring.

This increased tendency toward crystallization are similar to that of polyethylene and isotactic polypropylene described in previous papers.<sup>1-2)</sup> However, the different phenomena were observed in this polymer that at polymer concentrations less than about 0.5%, the fibrous crystals are not deposited on the stirrer but the crystals are precipitated in similar fashion as the case in the absence of stirring. This phenomena seem to be concerned with the decrease of stress effect to polymer molecules due to the decreases in the viscosity of solution.

And we found from x-ray diffraction study further interesting facts that the fibrous crystals have a hexagonal modification but the precipitated crystals in both cases of the presence and absence of stirring have an orthorhombic modification. It is interesting to note that the crystallization mode under high shearing stress differs from that under low shearing stress or in the absence of stress. This will be discussed later.

### Morphology and structure of the Fibrous Crystals

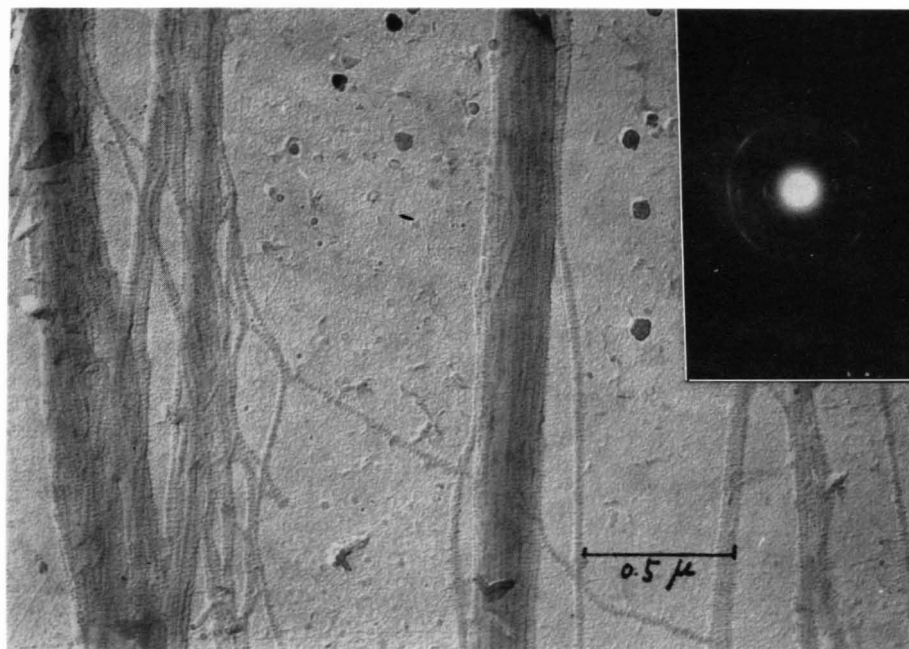
It was shown with optical microscope that the texture of film like materials deposited on the stirrer consists of aggregates of a number of fibrous crystals which are oriented in the direction of shearing stress as in the cases of polyethylene<sup>1)</sup> and polypropylene.<sup>2)</sup> A more detailed observation of the crystals by electron microscope also revealed the morphology similar to that of polyethylene observed in our previous papers.<sup>1)2)</sup> Figure 2 shows a representative morphology of isotactic polybutene-1 crystallized at 67°C from a 2% solution in *iso*-amyl acetate and its corresponding electron diffraction pattern. This electron micrograph has shown that the crystals are fibrous about 300 Å in width and in closer examination they have the regular repeating lamellar structure of 150~200 Å on the central threads. This observation supports that the crystals are composed of the two component systems of extended chain fibers and folded chain lamellae as originally suggested by Pennings and Kiel<sup>6)</sup> and confirmed by us in previous papers. Electron diffraction study showed that the polymer chains in crystals are aligned in the

stress direction giving a *c* orientation fiber pattern and their crystal structure is a hexagonal form which is different from that of the normally crystallized materials from solution.

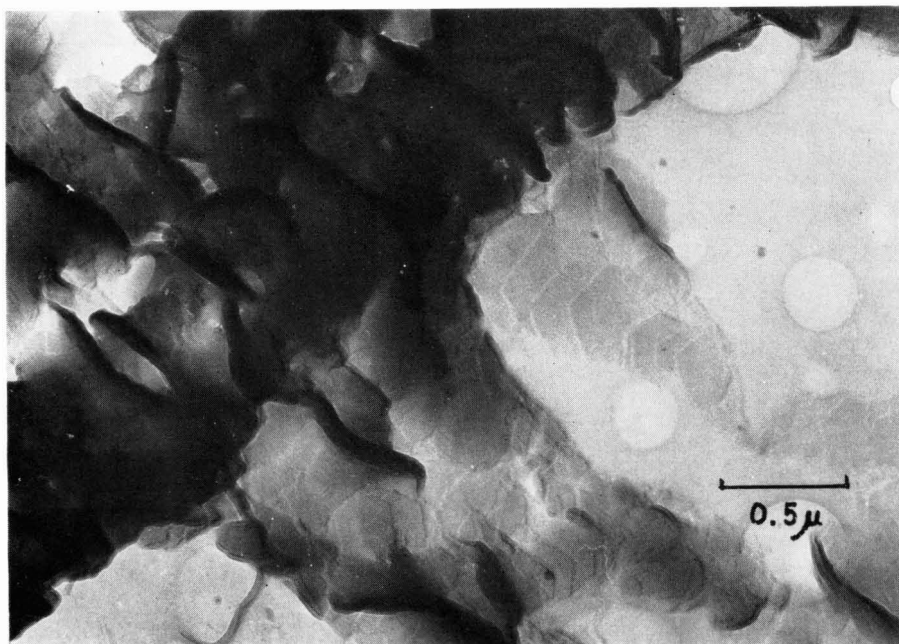
When the crystals were prepared at 62°C from a 2% solution in *iso*-amyl acetate, the lamellar platelets grew to large sizes and they were shaped like hexagons consistent with their hexagonal crystal structure as shown in Figure 3.

More interesting morphology was observed in surface replica of thick deposited film at the same crystallization condition as that in Figure 3, as shown in Figure 4. This electron micrograph shows that the plane of larger lamellar crystals is roughly perpendicular to the stress direction and this morphology is very similar to that of melt extruded polyethylene film crystallized in a highly stressed state as described by Keller and Machin.<sup>17)</sup>

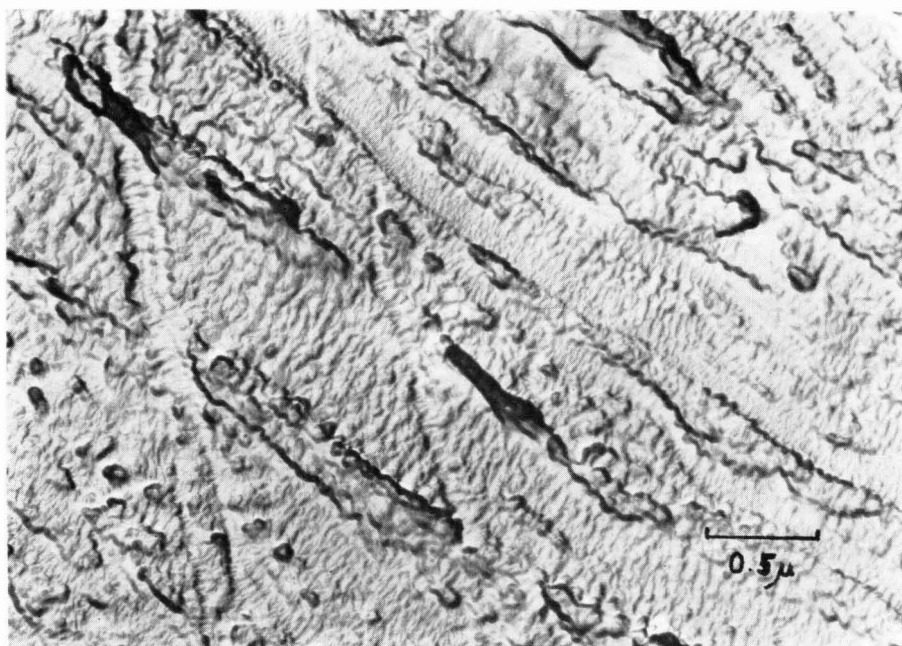
The common feature of the crystals shown in Figure 2 to Figure 4 is the development of a lamellar texture perpendicular to the stress direction. And the lamellar size depends upon the crystallization condition. It may be thought that the perpendicular growth of lamellae is caused by the central threads



**Fig. 2** Electron micrograph and electron diffraction pattern of isotactic polybutene-1 crystallized at 67°C from a 2% solution in *iso*-amyl acetate under shearing stress (2500 rpm). It shows that the crystals are fibrous about 300 Å in width and in closer examination they have the regular repeating lamellar structure of 150~200 Å on the central threads.



**Fig. 3** Electron micrograph of isotactic polybutene-1 crystallized at 62°C from a 2% solution in *iso*-amyl acetate under shearing stress (2500rpm). It shows that the lamellar platelets grow to large sizes and they are shaped like hexagons consistent with their hexagonal crystal structure.

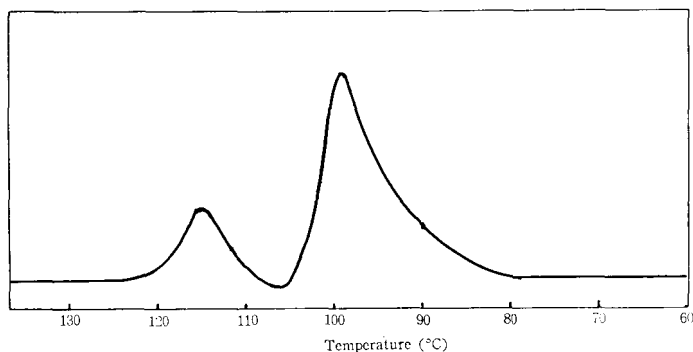


**Fig. 4** Electron micrograph of carbon replica of thick deposited film at the same crystallization conditions as that in Fig. 3. It shows that the plane of larger lamellar crystals is roughly perpendicular to the stress direction.

produced by the stress. These results strongly support a working hypothesis of Keller and Machin<sup>17)</sup> in which row nucleation is the basic process of crystallization under stress or during flow.

### The Modification of the Fibrous Crystals

As mentioned in previous section, it was determined that the crystal structure of fibrous crystals is a hexagonal form. However, two different modification of form I and form I' has been identified for the crystals having a hexagonal form in isotactic polybutene-1. We tried to clarify which modification is produced from solution under stress, from the results of thermal measurements.



**Fig. 5** A DSC curve of the fibrous crystal of isotactic polybutene-1 obtained at 65°C from a 2% solution in *iso*-amyl acetate under shearing stress. It represents the process; form I' → melt → form II → melt.

Figure 5 represents a typical DSC curve of the crystals obtained at 65°C from a 2% solution of isotactic polybutene-1 in *iso*-amyl acetate. Between 80°C and 123°C two peaked endotherms were observed. The low melting peak is at 99°C and the high melting peak is at 115°C. Based on the melting points of various modifications in isotactic polybutene-1 determined by previous workers, it seems to be reasonable that the present DSC curve represents the process; form I' → melt → form II → melt. Furthermore, the feature of this curve is in accord with the observation of Boor and Youngman<sup>14</sup> on form I' which was obtained by conducting Ziegler-Natta polymerization at relative low temperature.

From these results we shall conclude that the direct formation of form I' is possible in the crystallization under stress. The detailed nature of form I' obtained in such crystalliza-

tion will be published separately.

It is interesting to consider why this polymer is crystallized in the modification of form I'. It seems to be a reason that a tighter packing of the chains in the hexagonal crystal structure is greatly accelerated by the application of shearing stress. However, there is a remaining question for the reason why the formation of the lower melting form I' rather than form I is favorable under these crystallization conditions.

### § 4. Conclusions

It has been shown that the fibrous crystals of isotactic polybutene-1 crystallized from solution under shearing stress are also composed of the central threads with an extended chain character and the epitaxially deposited lamellae with a folded chain character. From these results, it was concluded that the concept of row nucleation mechanism suggested by Keller and Machin<sup>17)</sup> can be applied to crystallization of isotactic polybutene-1 under shearing stress as well as to that of polyethylene and polypropylene.

The characteristic behaviors in this polymer exist in; (1) that the resulting crystals possess the hexagonal modification of form I' different from that of the normally crystallized materials; (2) that at low polymer concentrations the fibrous crystals can not be deposited on the stirrer but the lamellar crystals with an orthorhombic modification of form III are precipitated in similar fashion to the case in the absence of stirring; (3) that the morphology in surface replica of thick deposited film is very similar to that of melt extruded polyethylene film crystallized in a highly stressed state.

It is evident from the above, that isotactic polybutene-1 has proved to be an extremely interesting subject of investigation of the crystallization of long chain polymers in solution under shearing stress and there is little doubt that some of the problems remaining for the crystallization mechanism at the present time will be solved in due course.

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