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Crystallization of Polymers from Solution under Shearing Stress II Polypropylene

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Isotactic polypropylene was crystallized in the form of fibrous crystals from solution under shearing stress. The fibrous crystals consist of the oriented cluster of micro fibrils. From the electron microscopy and the electron diffraction study, it was found that the fine texture of this fibrous crystals is also the two component systems which are composed of the central threads with an extended chain character and the lamellae with a folded chain character deposited on the threads, as in polyethylene. Relatively larger lamellar structure than that of polyethylene was observed. The effect of crystallization conditions to the formation of the fibrous crystals from solution of isotactic polypropylene was described briefly. A characteristic melting behavior due to the melting of the central threads with an extended chain character was observed from the thermogram of differential scanning calorimeter.

§ 1. Introduction

In our previous paper[1], we reported the formation and the structure of the fibrous crystals of polyethylene on crystallization from solution under shearing stress. It was shown from the morphological observation and the electron diffraction study that the fibrous crystals were composed of the central threads with an extended chain character and the epitaxally deposited lamellae with a folded chain character. The thermal and mechanical properties of the fibrous crystals seemed to reflect the above structual model.

If such fiber formation in the crystallization from polymer solution under shearing stress is intrinsic properties of polymer chains, isotactic polypropylene may be thought to be crystal lized with the same fashion as in polyethylene.

Isotactic polypropylene is the homologue of polyolefin polymers and has helical chain conformation different from the *trans* zigzag chain comformation of polyethylene in the crystalline state. In this paper, we wish to show also the formation of fibrous crystals and to study the effect of crystallization conditions to the morphology in order to clarify the crystallization mechanism from solution under the stress.

§ 2. Experimental

Materials and Solvents

The polymer used in this study was isotactic polypropylene (Noblen E. B. $[\eta] = 3.2$ (dl/g) in decaline; Mitsui Chemical Co., Ltd.). Lower molecular weight samples ($[\eta] = 2.0$ and 1.5 (dl/g) in decaline; Mitsubishi Rayon Co., Ltd.) were also used. The solvents used were xylene and α-chloronaphthalene.

Crystallization Procedures

Solution of the polymer was prepared in a tube (diameter 15 mm) from the sample with xylene or α-chloronaphthalene as the solvent at the concentrations of 0.01% to 5% (by weight) by heating the polymer-solvent mixtures and it was transferred to an oil bath which had been kept to the desired temperature. It was then stirred at the desired conditions of stirring (900 to 5200 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 1 hr. Thus, 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[1].

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.

§ 3. Results and Discussion

Experimental results shown below are confined to the fibrous crystals deposited on the stirrer.

Apparent Maximum Crystallization Temperatures

The apparent maximum temperatures at which isotactic polypropylene can be crystallized from solution under stirring are significantly higher than those observed normally. This increased crystallizing temperatures depend upon the polymer concentrations as shown in Figure 1. The difference of the maximum crystallization temperature is considerably large; about 40°C at polymer concentrations of 1% to 5%.

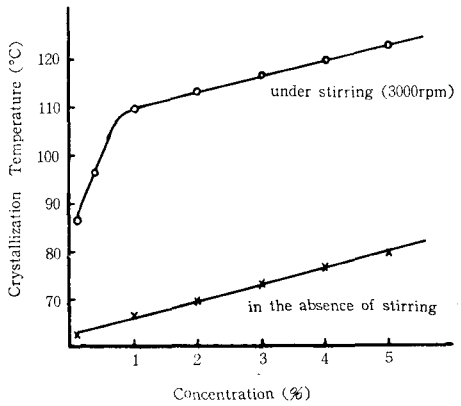

Fig. 1 Apparent maximum crystallization temperatures of isotactic polypropylene in xylene solutions as a function of the polymer concentrations under stirring rate of 3000 rpm and the absence of it, the determinations of the temperatures having been carried out at cooling rate of 0.3°C/min.

The deformation of polymer chains in solution due to the shearing stress induces the orientation of polymer molecules along the stress direction and makes the configurational entropy of chains decrease. Hence, crystallization under stress occurs at a higher temperature than that observed in the absence of stress.

Morphology

It was shown with a polarizing microscope that the film like materials obtained from solution under shearing stress have a macroscopic oriented texture to the stress direction as in the case of polyethylene. A more detailed observation of the crystals was carried out by electron microscope. Figure 2 shows a representative morphology of isotactic polypropylene crystallized at 119°C from a 1% solution in xylene under stirring rate of 4000 rpm. The fibrous crystals with about 500 A in width were observed and they grow to the stress direction. On closer examination, the transversal banded structure due to the lamellar crystallization was observed periodically along the fibers. Electron diffraction pattern of the fibrous crystals is shown in Figure 3. This pattern shows definitely a c axis orientation along the fiber axis. Even though the crystals are composed of many structual units, polymer chains are oriented parallel to the fiber axis. We shall also conclude that the fibrous crystals of isotactic polypropylene obtained from solution under stirring are composed of the central threads with an extended chain character and the lamellae with a folded chain character nucleated on the threads. The fibrous crystals in Figure 4 show a different type of appearance. They were crystallized from a 1% solution of isotactic polypropylene in α-chloronaphthalene at 132°C under stirring rate of 4000 rpm. The transversal lamellae are relatively large and the fibrous crystals grow as if they would consist of the lamellae piled along the fiber axis. However, we can observe the existence of the central threads even in this case. When xylene was used as a solvent, we could observe not so large lamellae as in the case of α-chloronaphthalene. This fact means that the conformation of polymer chains in xylene is different from that in α-chloronaphthalene.

Furthermore, to examine the effect of molecular weight we tried the crystallization of lower molecular weight samples. The sample of isotactic polypropylene whose intrinsic viscosity in decaline at 130°C is $[\eta]=1.5$ (dl/g) could not be deposited on the stirrer in the form of fiber. The sufficient length of polymer chains is required in order to obtain the fibrous

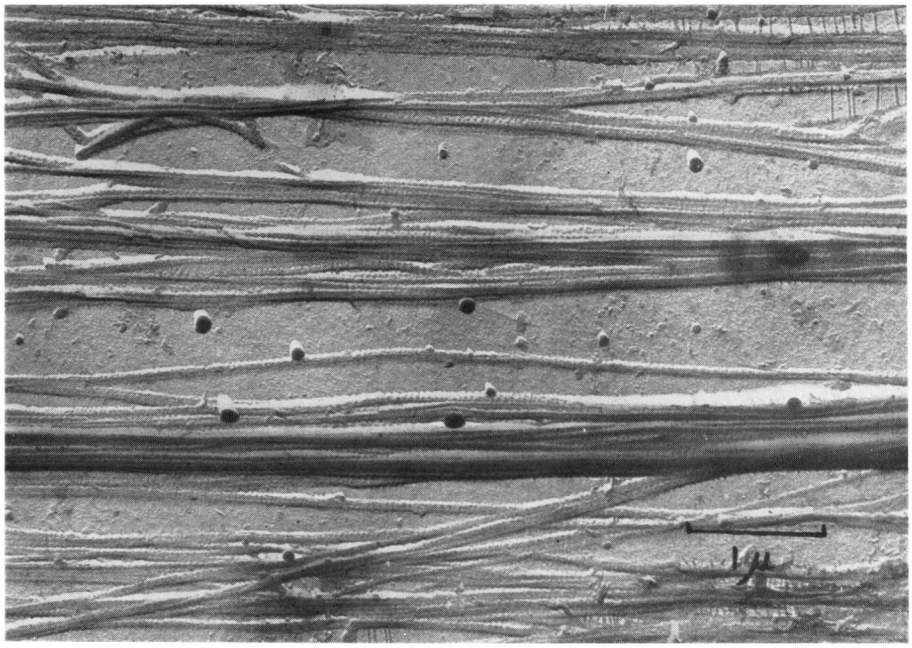

Fig. 2 Electron micrograph of isotactic polypropylene crystallized at 119°C from a 1% solution in xylene under stirring rate of 4000 rpm. It shows that the crystals are fibrous about 500 A in width and in closer examination they have the transversal banded structure due to the lamellar crystallization which is observed periodically along the fibers.

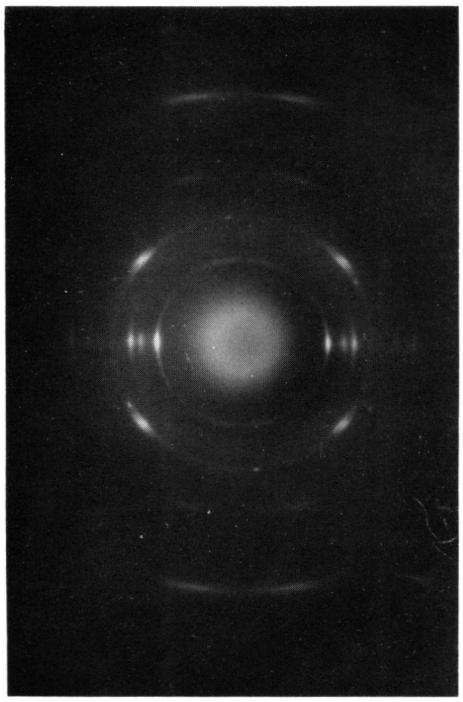

Fig. 3 Electron diffraction pattern from the fibrous crystals of isotactic polypropylene. Sample was prepared with the same crystallization condition as that in Fig. 2.

crystals from solution under stirring.

Thermal Properties

We investigated the melting behavior of the fibrous crystals of isotactic polypropylene from solution under shearing stress, with a Perkin-Elmer differential scanning calorimeter. The heating rate of 10°C/min. was used. Main peak at 167°C and second peak at 176°C were observed in the melting curve of the fibrous crystals prepared from a 1% solution in α-chloronaphthalene at 139°C. The secod peak disappeared when the sample was reheated after melting and recrystallization. The whole fusion curve which begins to occur at 150°C and finishes at 180°C is shown in Figure 5. The melting behavior at higher temperature containing the second peak is characteristic to the fibrous crystals compared with the results of the bulk crystallized sample[2] and the solution grown sample[3] in isotactic polypropylene. It is contributed to the central threads with an extended chain character.

§ 4. Conclusion

It was found that isotactic polypropylene are crystallized in the fibrous form from solution under shearing stress. Electron micro-

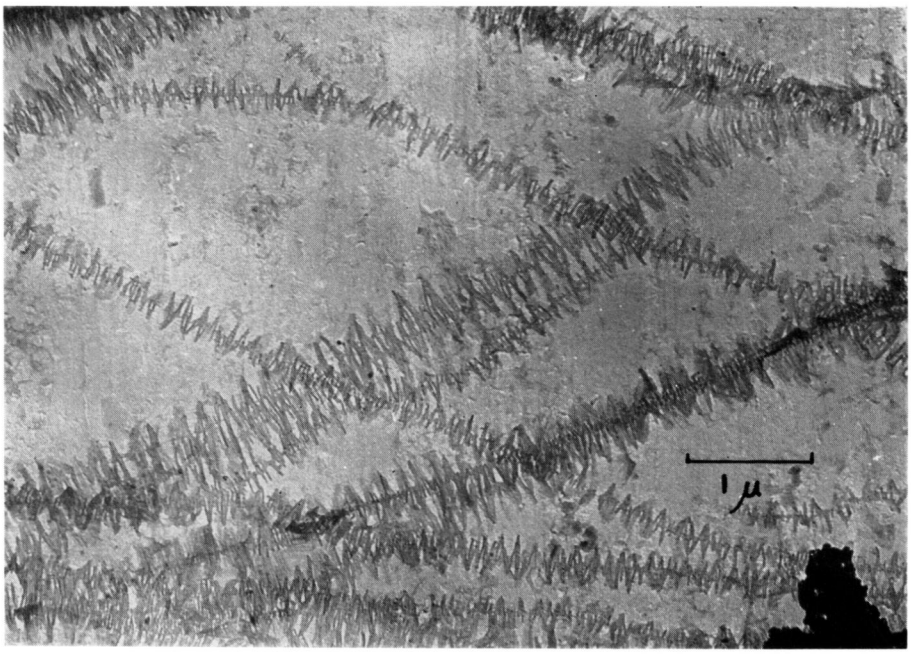

Fig. 4 Electron micrograph of isotactic polypropylene crystallized from a 1% solution in α-chloronaphthalene at 132°C under stirring rate of 4000 rpm. The fibrous crystals grow as if they would consist of the lamellae piled along the fiber axis.

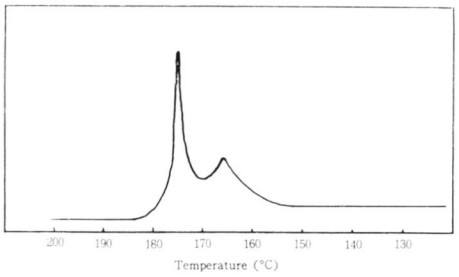

Fig. 5 Representative DSC thermogram for the isotactic polypropylene fibrous crystals which is obtained at 130°C from a 1% solution in α-chloronaphthalene. Heating rate is 10°C/min.

graphs and electron diffraction patterns indicate that the fibrous crystals are composed of the two component systems which are central threads and lamellar crystals nucleated on the threads. The melting behavior at higher temperature due to the melting of the central threads with an extended chain character was observed from DSC thermogram. The experiment on lower molecular weight samples showed that the sufficient length of chains is required for fibrous nucleation.

References

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2) K. KAMIDE and M. SANADA: *Chem. of High Polymers* (in Japan) **24**, (1967) 662
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