Polymer Bulletin 13, 253-258 (1985)

Polymer Bulletin

Orientation

II-I Phase Transformation of Melt-Crystallized Oriented Lamellae of Polybutene-1 by Shear Deformation

Yasuna Fujiwara

Shizuoka University, Faculty of Science, Shizuoka 420, Japan

Summary

Modification II-I transformation of polybutene-1 was investigated on oriented lamellae, which were melt-crystallized in the temperature gradient. WAXS photograph of as-grown specimen showed prefered orientation of [110] to the lamellar axis, and after transformation it showed "twelve point pattern" due to dual orientation of hexagonal lattice. By shear deformation parallel or perpendicular to lamellar axis, WAXS photograph showed the appearance of "six point pattern" due to single orientation of hexagonal lattice, and also the enhancement of transformation rate. These were explained by the growth of hexagonal nuclei formed by the slip in the tetragonal crystal.

Introduction

It has been found by Petermann et al. that modification II (tetragonal) to modification I (hexagonal) transformation of isotactic polybutene-1 (PB) is a nucleation-controlled process. (GOHIL et al. 1982) There are many papers concerning the promotion of this transformation by deformation such as drawing, but there are few that refer to the crystallographic orientational relation in the lateral packing of molecular segments of modification II and transformed modification I. A paper noteworthy in this connection is TEM observation and electron diffraction study of PB single crystals from solution by Holland and Miller. (HOLLAND et al. 1964) The observed "twelve point pattern" from twinned hexagonal crystals after the transformation of a tetragonal single crystal, which demonstrates the existence of orientational relation in the case of single crystal.
In the present paper we are going to elucidate the existence of orientational relation also in the case of specimens grown from the melt. We also intend to discuss the nucleation mechanism from the observation on the growth of hexagonal crystals in the tetragonal matrix by applying shear deformation to the specimen.

Experimental

The sample used is low molecular weight isotactic polybutene-1

(PB) from Scientific Polymer Products Inc. (Melt index 20, Density 0.91). By use of the temperature gradient crystallization method melt-crystallized specimens of modification II were grown in the form of 0.4 mm thick plates. The transporting speeds of specimen in the temperature gradient used were 50 μm/h for the specimen of Figure 2, and 100 μm/h for that of Figure 3. WAXS photographs were taken by Rigaku 4012 x-ray generator equipped with Toshiba fine focus tube. Ni-filtered Cu radiation was used. The diameter of x-ray collimator was 0.23 mm, and flat film was used. All the x-ray experiments were carried out at the room temperature, ca.23°C.

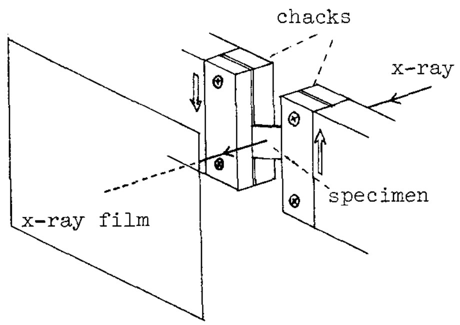

Fig. 1 Illustration of the sample holder

For the shear experiment a specimen was clamped by chacks in the sample holder, sheared and submitted to x-ray diffraction. (Fig. 1) Two types of shear deformation were performed: (i) shear stress perpendicular to the growth direction, namely perpendicular to lamellar axis ("⊥ Shear"), and (ii) shear stress parallel to the growth direction, namely parallel to lamelar axis ("|| Shear"). The value of shear deformation used was ca. 0.5 for both cases. The exposure time of x-ray was 20 min. for each photographs.

Results and Discussion

WAXS photographs taken on fresh specimen show sharp prefered orientation of tetragonal crystals of modification II such that [110] direction is almost parallel to the growth direction. Other aspect appearing in them is that it is not a perfectly uniaxially oriented fiber pattern where c-axis is distributed uniformly around the fiber axis, but c-axis often shows some degree of orientation, sometimes resulting in asymmetrical WAXS pattern in the right and left side. It indicates that the domains of lamellar stack, which can be regarded as single-crystal-like, is fairly wide and in cases comparative to the size of x-ray collimator. Figure 2 is an example of WAXS pattern of as-grown specimen in the course of spontaneous transformation. In this photograph "twelve point pattern" from hexagonal crystals of transformed modification I is also seen. This is quite similar to the case of Holland et al. who have observed a pattern of this type in

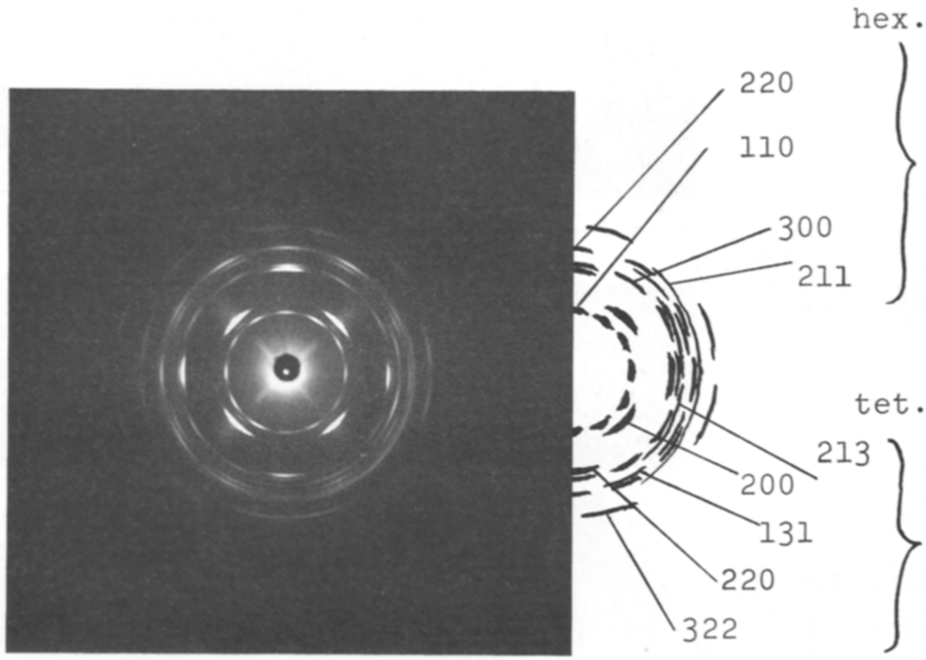

Fig. 2 WAXS photograph of oriented lamellae of PB.
In the course of spontaneous phase transformation from tetragonal to hexagonal. Lamellar axis almost vertical. Camera distance 45 mm.

their electron diffraction photograph on a solution-crystallized single crystal of PB after transformation. (HOLLAND et al. 1964) This indicates that there is a crystallographic orientational relation between original and transformed crystals. To form a hexagonal nucleus molecular segments must change their conformation from 11_3 to 3_1 helices on the one hand, and their lateral arrangement from tetragonal to hexagonal packing on the other hand. The latter change necessitates a local displacement between molecular segments. Then if shear stress is applied to the specimen externally to cause internal slip, it may be expected that nucleus formation of modification I is enhanced. From this expectation specimen plates were subjected to shear deformation and accompanying changes in the WAXS pattern were investigated.
In Figure 3 are shown changes of WAXS photographs with time for specimens before and after ⊥ shear (a,b,c,d), || shear (e,f,g,h) and also without shear (i,j,k) deformation as the control.
From these photographs it is found:

1) II-I transformation is enhanced by either shear deformation.
2) The transformed hexagonal pattern of sheared specimens does not show twelve point pattern as in the case of spontaneous transformation, but shows "six point pattern".
3) The orientation of hexagonal six point pattern after ⊥ and || shear is 90° rotated each other, relative to the direction of the original lamellar axis.
4) The tetragonal pattern showed inclination of ca. 13-15° which is about half the given shear angle, whereas the transformed hexagonal pattern did not show such an obvious inclination.

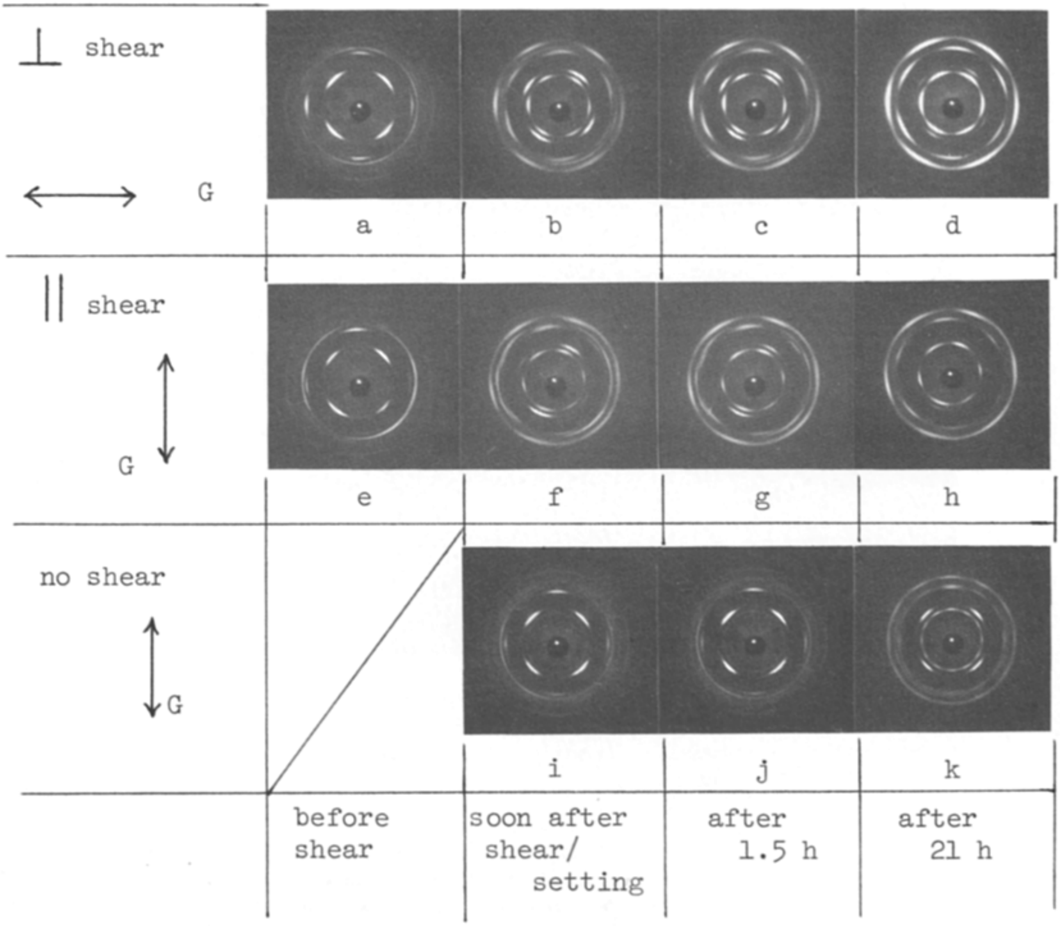

Fig. 3 WAXS photographs showing the progress of transformation with time for sheared and non-sheared specimens. The original lamellar axis is indicated by G. Camera distance 23 mm.

By examining the change of (hk0) reflections in either modification, one can follow the structural change in those lamellae which are parallel to the x-ray film, which will be named as F-lamellae for convenience.

By ⊥ shearing, internal slip is supposed to take place along tetragonal (110) plane at many cites in F-lamellae and at these cites hexagonal nuclei can be generated. (Figure 4) Transformation starts from these nuclei, proceeds thereafter predominantly on them and brings about the single orientation of hexagonal [110], as seen in Figure 3d.

By || shearing, similar slip may take place along tetragonal (1$\bar{1}$0) plane in F-lamellae which brings about the generation and growth of hexagonal crystals in a similar manner, but with the orientation 90° rotated to the above case, as seen in Figure 3h. Interlamellar slip may be favoured because the lamellar surfaces are parallel to the stress. This may also act to relax the applied stress.

In any case nucleation of modification I nuclei is enhanced by the shear deformation. From the above mechanism the orientation

of the resultant hexagonal crystals becomes not dual.
On the contrary, when modification II lamellae are left to transform spontaneously, dual orientation of hexagonal crystals is resulted owing to the dual nucleation from the symmetry of tetragonal lattice, which leads to the twelve point pattern.
As for the behavior of those lamellae which are edge-on to the x-ray film, which will be named as E-lamellae for convenience, it is considered that by interlamellar slip tye-chains may exert tensile stress to some of molecular segments in the lamella, which is activated to become hexagonal nucleus. (GOHIL et al. 1982, WEYNANT et al. 1982) The occurence of such nucleation in E-lamella cannot be denied, but as our aim in this investigation is to know the behavior of F-lamellae it will not be discussed further.

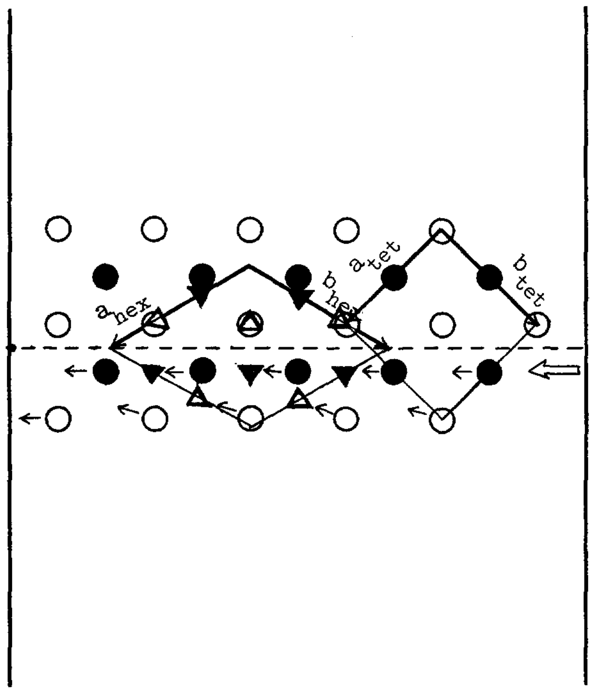

Fig. 4 The initial stage of formation of a modification I nucleus by shear deformation. Lamellar axis vertical. (110) slip plane is indicated by a broken line. White and black circles show molecules of right- and left-handed 11_3 helices, respectively. White and black triangles show molecules of right- and left-handed 3_1 helices, respectively.

Acknowledgement

The author is grateful to Dr. T. Asano, research assistant of Shizuoka University, for his valuable advice and discussion in the consideration of the transformation mechanism.

References

GOHIL,R.M., MILES,M.J. and PETERMANN,J.: J. Macromol. Sci. Phys., B21, 189 (1982)
HASSE,J., KÖHLER,S. and HOSEMANN,R.: Z. Naturforsch. 33a, 1472 (1978)
HOLLAND,V.F. and MILLER,R.L.: J. Appl. Phys. 35, 3241 (1964)
WEYNANT,E. and HAUDIN,J.M.: J. Materials Sci. 17, 1017 (1982)

Accepted March 14, 1985

C