Plastic deformation of oriented lamellae: 3. Drawing behaviour of β-phase isotactic polypropylene

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Specimens consisting of oriented β-phase lamellae of isotactic polypropylene, obtained by crystallization in a temperature gradient, were drawn at various temperatures. The deformation behaviour was investigated by means of stress–strain measurement, X-ray scattering and scanning electron microscopy. Drawings were carried out in two directions, parallel to the lamellar axis (parallel drawing) and perpendicular to it (perpendicular drawing). The maximum apparent stress and Young's modulus on parallel drawing were always larger than those on perpendicular drawing. Wide-angle X-ray scattering patterns from the specimens drawn at various temperatures showed different deformation behaviours between parallel and perpendicular drawings, which may be explained by the difference of deformation mechanism at the initial stage. As a conclusion, the deformation mechanism is classified into two steps. In the initial stage of deformation, the β-phase material is deformed mainly by interlamellar slippage (the first step). Then, the β-phase crystals are destroyed by Petermann-type unfolding or local melting (the second step). The final c-axis-oriented texture is recrystallized through destruction of the β-phase material.

Keywords Drawing; polypropylene; X-ray; oriented lamellae; stress–strain; $\beta \rightarrow \alpha$ phase transition

INTRODUCTION

Many investigations have been made on drawing polymer materials and discussions on the deformation mechanism have been reported[1-9]. Peterlin *et al.*[3,4] explained that the original crystals are partly destroyed to blocks, the directions of molecular chains are gradually aligned to the draw direction by rotation and slip of the blocks, and they are incorporated into the final c-axis-oriented materials. On the other hand, Kobayashi[8] explained that the chains are completely unfolded from the original crystals, and are subsequently recrystallized to the c-axis-oriented crystals. Recently, Petermann *et al.*[9] investigated the molecular mechanism of plastic deformation by transmission electron microscopy, and found that plastic deformation occurs in a narrow region a few nanometres wide by simultaneous unfolding and bending of chain segments of all molecules within the deformation region, which is a deformation process that lies somewhere between those advanced by Peterlin and Kobayashi.

In previous papers[11,12], rolling deformation of oriented β-phase isotactic polypropylene (it-PP) prepared by the thermal gradient method was studied and it was concluded that (1) deformation proceeds mainly by rotation of lamellae, interlamellar slip and chain slip, and (2) c-axis orientation is attained not by incorporation of the original lamellar blocks but through the melting or unfolding of the original β-phase lamellae and subsequent recrystallization to the c-axis-oriented α-phase.

As mentioned in these papers, once the oriented β-phase crystals are destroyed, they do not recrystallize into the same crystalline form but are transformed to the more thermally stable α-phase crystals. Accordingly, our specimens have the advantage of being detected by X-ray diffraction at which stage of drawing the crystals are destroyed. Furthermore, since the original specimens are a-axis-oriented, the process of change of crystal orientation to the final c-axis-oriented material can be traced. In this paper, the results of drawing experiments of oriented β-phase it-PP are reported.

EXPERIMENTAL RESULTS

The original specimens of it-PP were made of a commercial it-PP sheet ($M_w = 2.55 \times 10^5$, 97% tacticity) supplied by Chisso Co. Ltd. The oriented β-phase lamellae of it-PP were prepared by crystallization in a temperature gradient as mentioned in the previous papers[10,11]. They consist of lamellae which have small-angle X-ray scattering (SAXS) period of about 230 Å. Screw-like twisted lamellae grown along the growth direction are shown in *Figure 1*. The a-axis of the hexagonal lattice is parallel and the c-axis (molecular chain axis) is perpendicular to the growth direction. Cartesian coordinates are defined in the specimen plate as shown in *Figure 1*, namely, x-axis is perpendicular to the plate surface, z-axis parallel to the lamellar axis (the growth direction), and y-axis perpendicular to these two axes. Plate specimens 0.20–0.25 mm thick were used. They were cut out with the same shape and size by a dumbbell-shaped cutter of 3 mm width.

The drawing equipment used was Tensilon UTM-4 of Toyo Baldwin Co. Ltd, with a pair of handmade brass microclamps. The distance between the two clamps was 6 mm, and ink lines were marked on the specimen at intervals of 1 mm before drawing. Every drawing was carried out in a temperature-controlled silicone oil bath.

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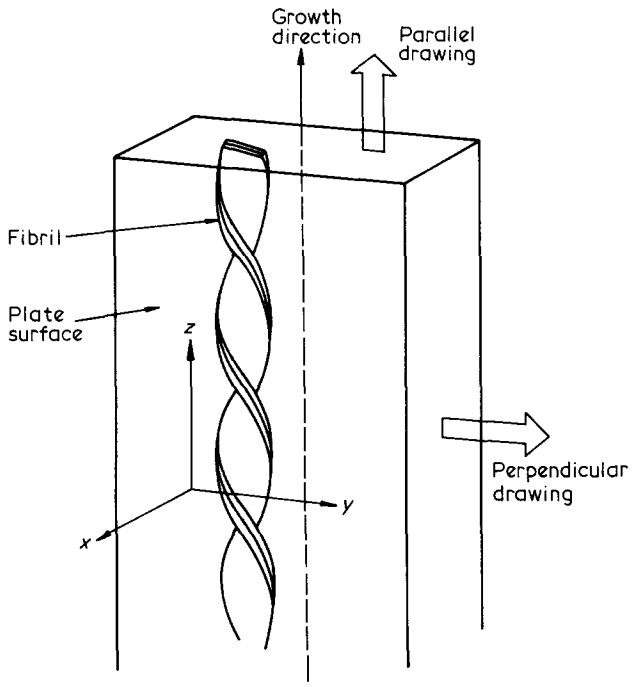

Figure 1 Definition of Cartesian coordinates relative to a specimen plate and definition of drawing directions. A fibril is shown schematically, consisting of stacked ribbon-like lamellae

The drawing rate was 0.4 mm min^{-1}. At each temperature, two kinds of drawing were carried out; drawing parallel to z-axis (parallel drawing), and drawing parallel to y-axis (perpendicular drawing). Some typical stress–strain curves on parallel and perpendicular drawings at several temperatures are shown in *Figure 2*. The ordinate axis shows the apparent stress σ which is the load divided by the sectional area of the specimen before drawing. The abscissa shows the average strain ε which is defined as follows:

$$\varepsilon = \Delta l / l_0$$

where Δl is the elongation and l_0, which is 6 mm, is the distance between the clamps before drawing. In the Figure, it is seen that the maximum apparent stress on parallel drawing is always larger than that on perpendicular drawing. The specimen is whitened as drawing proceeds beyond the yield stress. During parallel drawing, the specimen is whitened in a narrow region, while it is whitened over a wider region during perpendicular drawing. The overall stress throughout the curves decreases with increasing temperature on both drawings. On parallel drawing at room temperature, the specimens break at low values of strain, while on perpendicular drawing the specimen can be drawn even up to the strain $\varepsilon \simeq 1$. The specimens can be elongated more easily at higher temperatures on both perpendicular and parallel drawings, the former being more ductile than the latter. For example, at 55°C it could be elongated to $\varepsilon \simeq 11$ on perpendicular drawing, and to $\varepsilon \simeq 4$ on parallel drawing.

The values of Young's modulus, obtained from the gradient of initial rise of stress–strain curves, spread widely at low temperature on parallel drawing and the specimens are not ductile. The maximum gradient in the negative gradient region of stress–strain curve shows pronounced difference between parallel and perpendicular drawings.

To study the relation between drawing behaviour and the structure, a wide-angle X-ray scattering (WAXS) experiment was carried out at room temperature on drawn specimens. The direction of incident beams was limited to three directions x, y and z as defined in *Figure 1*, and they were named x, y and z patterns, respectively. The local draw ratio λ is defined as follows:

$$\lambda = d/d_0$$

where d_0 and d are the intervals between ink lines before and after drawing, respectively. Especially on parallel drawing, it is possible that the local strain $\lambda - 1$ is large even when ε is small in the necking region. WAXS patterns of the specimen drawn at 55°C at various draw ratios are shown in *Figure 3*. The patterns of the undrawn specimen show almost only the β-phase reflections (*Figures 3a* and *d*). The α-phase reflections appear (*Figures 3b* and *e*), and their intensity increases with increasing draw ratio (*Figures 3c* and *f*). From these WAXS patterns it can also be seen that: (1) at small draw ratio ($\lambda \simeq 2$) on perpendicular drawing, the {300} reflections from β-phase crystals are concentrated in the draw direction, which shows that the molecular chains are rotated towards the perpendicular orientation (*Figure 3b*), (2) on parallel drawing the azimuth of six arcs of {300} reflections from a-axis-oriented β-phase crystals does not change except for the spreading out of arc length (*Figures 3d* and *e*), and (3) the c-axis orientation of β-phase crystals is not found on both drawings. It is the α-phase and not the β-phase crystals that appear with c-axis orientation during drawing. SAXS pattern was not clear since it was covered with a strong streak resulting from voids in the specimen. However, on perpendicular drawing at the initial stage ($\lambda \leqslant 1.3$), the streak is not so strong and it can be recognized that the intensity of SAXS z pattern ring become weak in the draw direction.

Micrographs of the surfaces of drawn specimens obtained by scanning electron microscope (SEM) are shown in *Figure 4*. It is recognized by careful observation that wave-like uneven texture appears on the surface of perpendicularly drawn specimen (*Figure 4a*), while there are sharp cracks on flat surfaces on parallel drawing (*Figure 4b*).

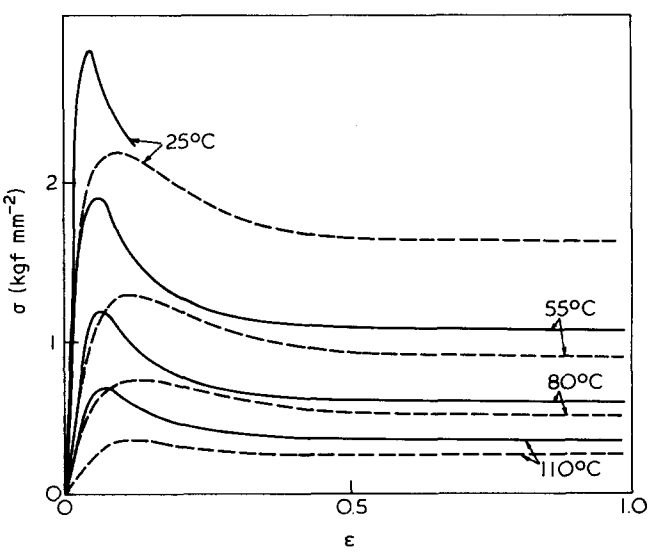

Figure 2 Typical stress–strain curves at various temperatures; σ is the stress and ε the strain. Solid lines show the curves on parallel drawing and broken lines on perpendicular drawing

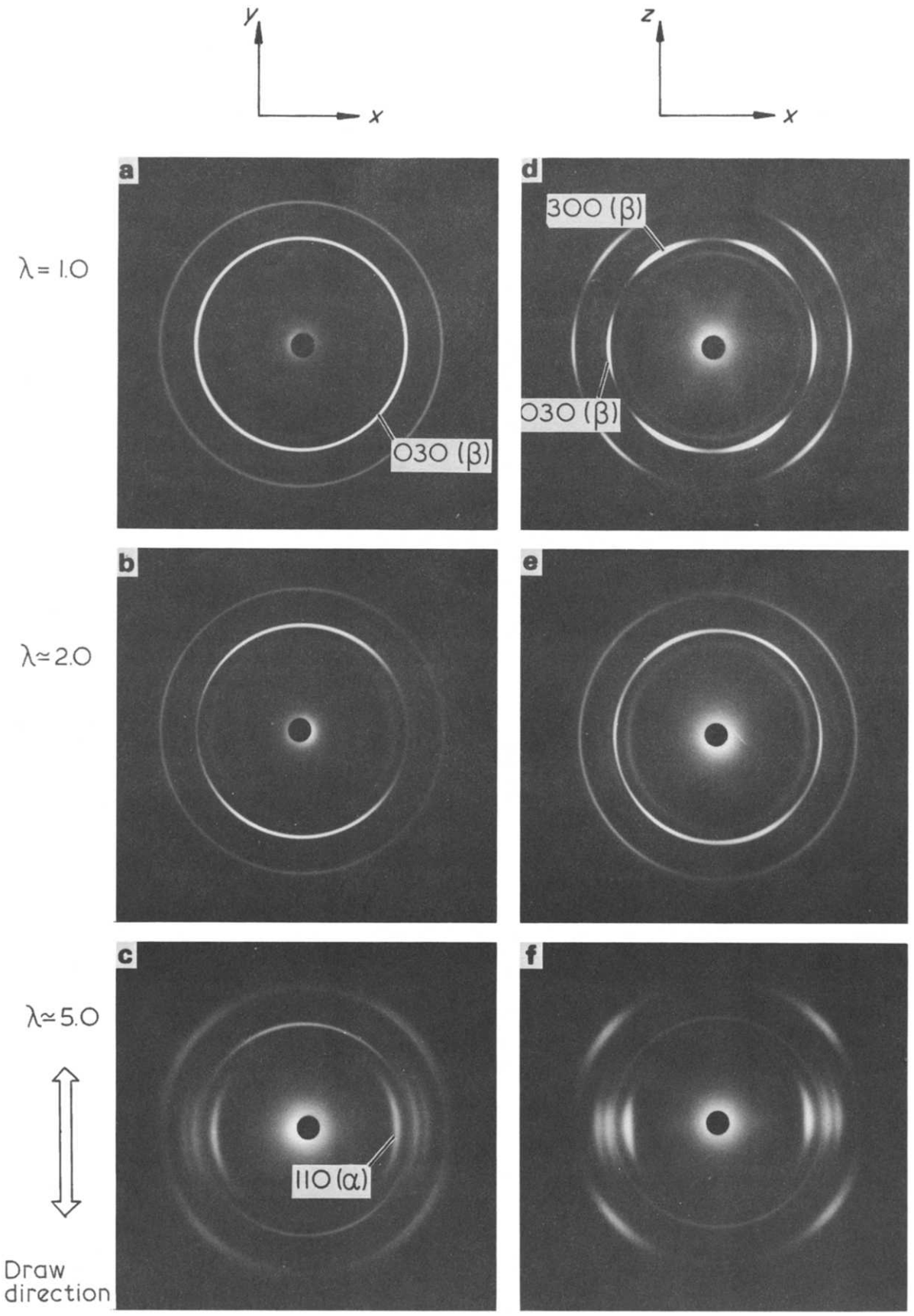

Figure 3 WAXS *z* patterns of the specimen on perpendicular drawing (*a–c*) and *y* patterns on parallel drawing (*d–f*), all drawn at 55°C

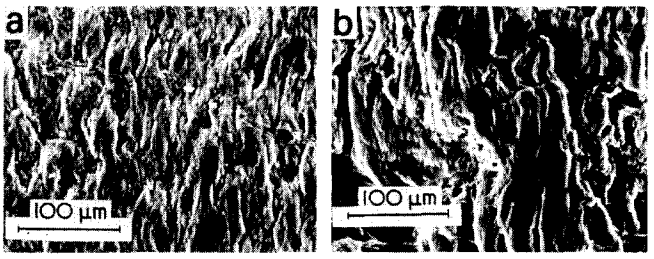

Figure 4 SEM photographs of the surfaces of specimens drawn at 70°C. (a) Perpendicular drawing; lamellar axis is vertical and draw direction horizontal; $\lambda \simeq 2$. (b) Parallel drawing; lamellar axis and draw direction are horizontal; $\lambda \simeq 2$

DISCUSSION

Hay and Keller[1] have formerly mentioned from the experiments of drawing two-dimensional spherulites that the deformation of spherulites occurs in a structurally complex process and it cannot be explained by a single mechanism, and that an individual microscopic process cannot be introduced from macroscopic properties since they give only an average value. However, it seems that deformation of oriented lamellae should reflect the microstructural process to some degree. That is, our parallel drawing corresponds to the drawing of a narrow radial portion of a spherulite along the radius, and our perpendicular drawing corresponds to the drawing of this portion perpendicularly to the radius. Accordingly, two deformation behaviours can be distinguished and the difference in the deformation process in relation to lamellar structure may be studied by the comparison of both cases.

In the previous paper[11], it was shown that the oriented β-phase specimen consists of fibrils which are several 10 μm or less in width, extending along the growth direction and twisting helically with a pitch of about 200 μm. If a fibril is a twisting aggregation of stacked lamellae, it must be a bundle of definite width. As the specimen begins to be whitened over a wide area at the initial stage of perpendicular drawing, the deformation seems to occur simultaneously widespread over the specimen.

On perpendicular drawing, the change of WAXS pattern (*Figure 3b*) as mentioned above, together with the change of SAXS *z* pattern, seems to show that the deformation is attained by interlamellar slip (the first step of deformation). At a higher draw ratio (*Figure 3c*), β-phase crystals are destroyed and *c*-axis-oriented α-phase crystals are recrystallized (the second step of deformation). In the β-phase crystals (hexagonal lattice) all helices are of the same sign, whereas in the α-phase crystals (monoclinic lattice) helical molecules are incorporated as right- and left-handed helices alternately. Accordingly, $\beta \rightarrow \alpha$ phase transformation needs rewinding of helices and cannot take place without local unfolding or melting and subsequent recrystallization.

On parallel drawing, WAXS patterns show (*Figures 3d* and *e*) that the *a*-axis orientation is maintained although the degree of orientation becomes lower through the drawing. These facts show that the deformation scarcely proceeds by interlamellar slip. At a higher draw ratio (*Figure 3f*), the specimen recrystallizes to *c*-axis-oriented α-phase crystals, similarly to the case of perpendicular drawing. It seems that parallel drawing should be attained mainly by the second step of deformation.

The difference in the drawing behaviours between perpendicular and parallel drawings may be explained by this difference in the initial stage of deformation. That is, in the initial stage of perpendicular drawing, the deformation proceeds mainly by the first step, and the further deformation is attained by the second step. However, the first step hardly appears in parallel drawing, and the deformation proceeds mainly by the second step. The fact that perpendicular drawing gives smaller stress than parallel drawing corresponds to the result of Hay and Keller[1], who mentioned that the deformation begins from perpendicular sectors in two-dimensional spherulites.

SEM photographs show that wave-like uneven texture spreads homogeneously all over the specimen in the initial stage of perpendicular drawing (*Figure 4a*). This texture is likely to show slightly deformed fibrils of the original β-phase specimen. The homogeneity of waves on the photograph is consistent with the results obtained from X-ray diffraction studies, that is, the first step of deformation proceeds mainly by the interlamellar slip which occurs homogeneously in the fibrils. On parallel drawing, at a low draw ratio ($\lambda \simeq 2$), 'cracks' yield and the specimen is severely deformed in the cracks, while it seems that it remains undeformed between the cracks (*Figure 4b*). The deformation should be attained by the crystal destruction at the crack by neck formation. These facts indicate that the deformation on parallel drawing proceeds mainly by crack formation, and the residual undeformed β-phase crystals hardly change until they are destroyed. The specimen is more ductile on perpendicular drawing than on parallel drawing, and the Young's modulus and yield stress are smaller on perpendicular drawing than on parallel drawing at each temperature. These may be due to the difference of deformation mechanism between both drawings. Fibrils seem to be anisotropic in the mechanical properties, namely, they are stiff in the direction parallel to the axis, and soft in the direction perpendicular to it.

The reason why the decrement of apparent stress in the negative gradient region is steeper on parallel drawing than on perpendicular drawing may be explained as follows. On parallel drawing, tension is applied to the stiff fibrils in the axial direction, and the stress rises steeply giving large Young's modulus. When a weak fibril can keep up no longer, it yields to the stress and it is deformed with unfolding. Then the other fibrils in this region should face a heavier load and they yield successively from the weaker ones. This leads to neck formation. Thus the stress falls steeply, and the deformation proceeds through neck formation. On the other hand, on perpendicular drawing, the decrement of the sectional area is gradual and the change of the apparent stress is not steep, since the deformation by interlamellar slip and chain slip may occur at every place in the specimen simultaneously or successively. The tendency that the decrement of apparent stress is steeper on parallel drawing than that on perpendicular drawing may be reinforced because the abscissa of the stress–strain curve shows the average strain over the specimen between clamps and not the local strain. On parallel drawing, the difference between the average strain ε and the local strain $\lambda-1$ should be large, since the deformation mainly takes place locally. The average strain ε including the undeformed region appears to be smaller than the local strain $\lambda-1$. Accordingly, the negative gradient in the stress–strain curve becomes apparently steeper. On the other hand, on perpendicular drawing, the difference between ε and $\lambda-1$ should be small,

since the deformation takes place widespread over the specimen. Therefore, the apparent strain ε is close to the true (local) strain and thus the gradient does not become so steep.

Peterlin[3] suggested that the drawn materials contain folded-chain blocks fractured from the original crystal. But the original β-phase hexagonal crystals are not observed in the final *c*-axis-oriented α-phase monoclinic materials in our experiments. As mentioned above, $\beta \rightarrow \alpha$ transformation of this sample needs the rewinding of helices in the crystals and cannot take place without local unfolding or melting and subsequent recrystallization.

It seems also to be difficult to apply the model proposed formerly by Kobayashi[8] assuming complete unfolding of chains from lamellae to our case, because the obtained draw ratio is too small.

Petermann *et al.*[9] showed from the transmission microscopic investigation of melt-drawn polymer film that plastic deformation occurs basically by the unfolding and bending of the molecules in a deformation region only a few nanometres wide. By dark-field micrographs they indicated that negligible chain tilt happened ahead of the neck, because the lamellae appeared dark to the very edge at which fibre formation occurred. Their results were consistent neither with the model proposed by Peterlin nor with the model of Kobayashi, and they have proposed a revised model, which contains simultaneous unfolding of chain segments of all molecules within the neck region. They also pointed out that the observations reported were relevant only to the plastic deformation process of single-layer or double-layer crystals or melt-drawn films, and that in multi-layer crystals of spherulitic structure intra- and intercrystalline shear might occur.

The samples used in our experiment were bulk and consisted of multi-layer lamellae, but they have uniaxial orientation. From our results, the second step of deformation proceeds through $\beta \rightarrow \alpha$ transformation both on parallel and perpendicular drawings. We cannot estimate from our experiment what happens in the necking region. However, $\beta \rightarrow \alpha$ transformation requires a region where the molecules are able to move freely for the rewinding of the helices. From these considerations, $\beta \rightarrow \alpha$ transformation may occur through Petermann-type unfolding or local melting.

CONCLUSIONS

(1) On parallel drawing, the deformation is attained mainly by the second step, namely, by crystal destruction. The drawing proceeds in narrow regions in the specimen, hardly changing the orientation of those β-phase crystals which are left undestroyed.

(2) On perpendicular drawing, the deformation is attained mainly by the first step up to relatively high draw ratio. The drawing proceeds in wide regions in the specimen changing the orientation of β-phase crystals around the lamellar axes.

(3) In both cases of parallel and perpendicular drawings, as the deformation proceeds further, crystal destruction subsequently follows. Similarly to the case of rolling deformation, when the original *a*-axis-oriented lamellae are drawn to the final *c*-axis-oriented materials, $\beta \rightarrow \alpha$ transformation must take place. This needs the rewinding of helices of chains in the crystals. Accordingly, crystal destruction through local unfolding by Petermann's model or local melting followed by subsequent recrystallization must take place during drawing.

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