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Higher-order structural analysis of bacterial poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanote] highly oriented films

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Abstract

Bacterial poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] (PHBH) highly oriented films were prepared by the combination of roll and uniaxial drawing processes. The change in the higher-order structure of PHBH films was investigated by wide-angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). Extended films, which show superior mechanical properties and high ductility, have complicated structures. By roll extension, both deformed and undeformed spherulites co-exist, the former inclined to the direction perpendicular to the film surface. The latter were destroyed by further uniaxial extension. The tie-molecules between uniaxially oriented lamellae were extended and transformed to the β-form with a planar zig-zag conformation. Three kinds of structures, *c*-axis parallel to the uniaxial drawing direction, *c*-axis inclining to the normal vector of the film surface, and the β-form between lamellae, are intermingled in the film.

Keywords: Bacterial copolyester; Roll drawing; Higher-order structure

1. Introduction

Bacterial poly(3-hydroxybutyrate) (PHB) and its copolymers attract a great deal of attention for its biodegradable and biocompatible thermoplastics recently. Since this polymer has a glass transition point below room temperature, and the crystallization rate is quite low, the processing of PHB and its copolymers into fibers, films, and other products is very difficult [1]. For example, when these polymers are cooled from the melts, the spherulitic crystallization occurs and the products filled with the large spherulites are hard and brittle [2,3]. Cold drawing of such products is quite difficult even at an elevated temperature.

We have reported that PHBH films with superior mechanical properties and high ductility can be obtained by a uniaxial drawing after applying a roll drawing process [4]. The tensile strength and modulus of 178 MPa and 1.4 GPa, respectively, were achieved. The ductility to make high draw ratio possible was attributed to the result of roll drawing. The spherulites were deformed and oriented to some extent by the roll drawing. WAXD experiments revealed that the highly oriented α- and β-form crystals exist in a highly drawn PHBH films. However, these crystals are not oriented simply uniaxially.

The objective of this study is to analyze the higher-order structure of uniaxially stretched PHBH films after roll drawing.

2. Experimental

2.1. Materials and film preparation

The bacterial poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] (PHBH) with a weight-average molecular weight (M_w) = 480,000 and 3-hydroxyhexanoate content = 7.6 mol% was supplied by Kaneka Co. Ltd. The PHBH was dried in vacuo at 70 °C for 10 h before film forming process.

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PHBH was compression molded at 150 °C into films about 1 mm thick using a vacuum mold and quenched immediately to 2 °C. The films were crystallized in an oven at 40 °C for 12 h.

2.2. Roll and uniaxial drawing

The rectangular specimens 5 mm × 25 mm were cut from crystallized PHBH film. Roll drawing was carried out by a roll drawing apparatus (Imoto Machinery Co. Ltd.). The films were roll drawn at 40 °C between two-temperature controlled rolls of 40 mm in diameter at a rotation speed of 30 rpm.

Film rolls drawn up to × 2.0 were uniaxially drawn in a water bath at 80 °C at 500 mm/min by using a motor controlled uniaxial drawing apparatus. After drawing, the films were quenched in cold water.

2.3. X-ray analysis

Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature using a nickel-filtered Cu Kα radiation of wavelength 0.1542 nm, from a Rigaku RINT 2100 FSL system sealed beam X-ray generator operating at 40 kV and 20 mA. WAXD patterns were recorded on a flat camera using a point-collimated beam.

Small angle X-ray scattering (SAXS) patterns were obtained at the BL-9C (SAXS beamline) in the Photon Factory of the Research Organization for High Energy Accelerator, Tsukuba, Japan. No subtraction of the air scattering was conducted. The wavelength of X-rays, λ, was tuned at $\lambda = 0.1504$ nm.

3. Results and discussion

3.1. Higher-order structure of the PHBH films analyzed by WAXD

It has been reported that the PHB generally crystallizes in a left-handed 2_1 helix conformation (α-form) [5,6]. The orthorhombic unit cell dimensions of α-form are $a = 0.576$ nm, $b = 1.320$ nm, and c (fiber axis) = 0.596 nm [7]. In addition, another crystal form with a planar zig-zag conformation (β-form) can be observed in the highly drawn PHB fibers [8] (Fig. 1). Orts et al. suggested that the β-form chains emanate upon stretching from the amorphous domains between 2_1 helix α-form lamellae [9]. However, Furuhashi et al. [8] demonstrated that the β-form crystal generates when PHB is stretched at a low temperature close to its T_g.

WAXD patterns of PHBH films are shown in Fig. 2(a)–(f). WAXD through view patterns of the roll drawn PHBH films show ring patterns at $2\theta = 13.4°$ and 16.9°, identified as the reflections from (020) and (110), respectively, and an arc around $2\theta = 22°$, overlap of the reflections from (021), (101), and (111). These WAXD patterns indicate that the crystal orientation becomes higher with the roll draw ratio as shown in Fig. 2(b)–(d), although its degree is still low.

Fig. 2(e) and (f) shows the WAXD patterns of uniaxially drawn PHBH film to high draw ratio after roll drawing × 2.0. Although most WAXD reflections of the roll drawn films are from α-form, a broad spot from β-form at $2\theta = 19.1°$ on the equator as well as highly oriented α-form can be observed in the WAXD pattern of the uniaxially drawn films. It has been reported that the mechanical properties of the fibers and films of the bacterial polyesters are more improved with increasing β-form contents [4,8,10,11]. Iwata et al. reported that the first layer of β-form was clearly observed in the WAXD pattern as well as a broad reflection on the equator by using a synchrotron radiation [11]. However, our X-ray diffraction equipment only gave a broad reflection on the equator, so that the discussion on the detailed structure and the origin of the β-form were not possible unfortunately. It should be noted that the WAXD pattern shows a overlapping of arcs and rings from (020) and (110), respectively. Similar WAXD pattern was reported by Furuhashi et al. [8] and two different orientation types, c-axes parallel and perpendicular to the fiber axis, were proposed. However, this sort of overlapping cannot be observed in the edge view pattern. End view patterns do not show any particular orientation regardless of the draw ratio.

Most reasonable explanation to these WAXD patterns may be the existence of two different c-axes orientations, c-axis parallel to the uniaxial drawing direction and that perpendicular to the film surface. The degree of orientation of the former is fairly strong and that of the latter is low.

3.2. Higher-order structure of the PHBH films analyzed by SAXS

The spherulite deformation in the film due to the cold drawing process has been studied by using a small angle light scattering technique (SALS) [12]. Samuels et al. demonstrated that the Hv (the plane of the analyzer and that of the incident polarized light are perpendicular) and Vv (the plane of the incident polarized light and that of the analyzer are parallel) SALS patterns are strongly affected by the spherulite deformation. One can obtain the change in the spherulite shape, hence the degree of deformation, from the SALS patterns. Unfortunately this technique was not applicable to the PHBH films prepared in this study, since they are thick and highly opaque

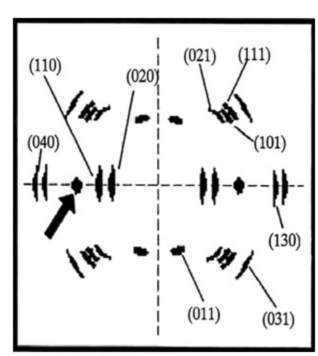


Fig. 1. Schematic explanation of typical WAXD pattern of PHB highly oriented fiber. Arrow indicates the reflection of β-form.

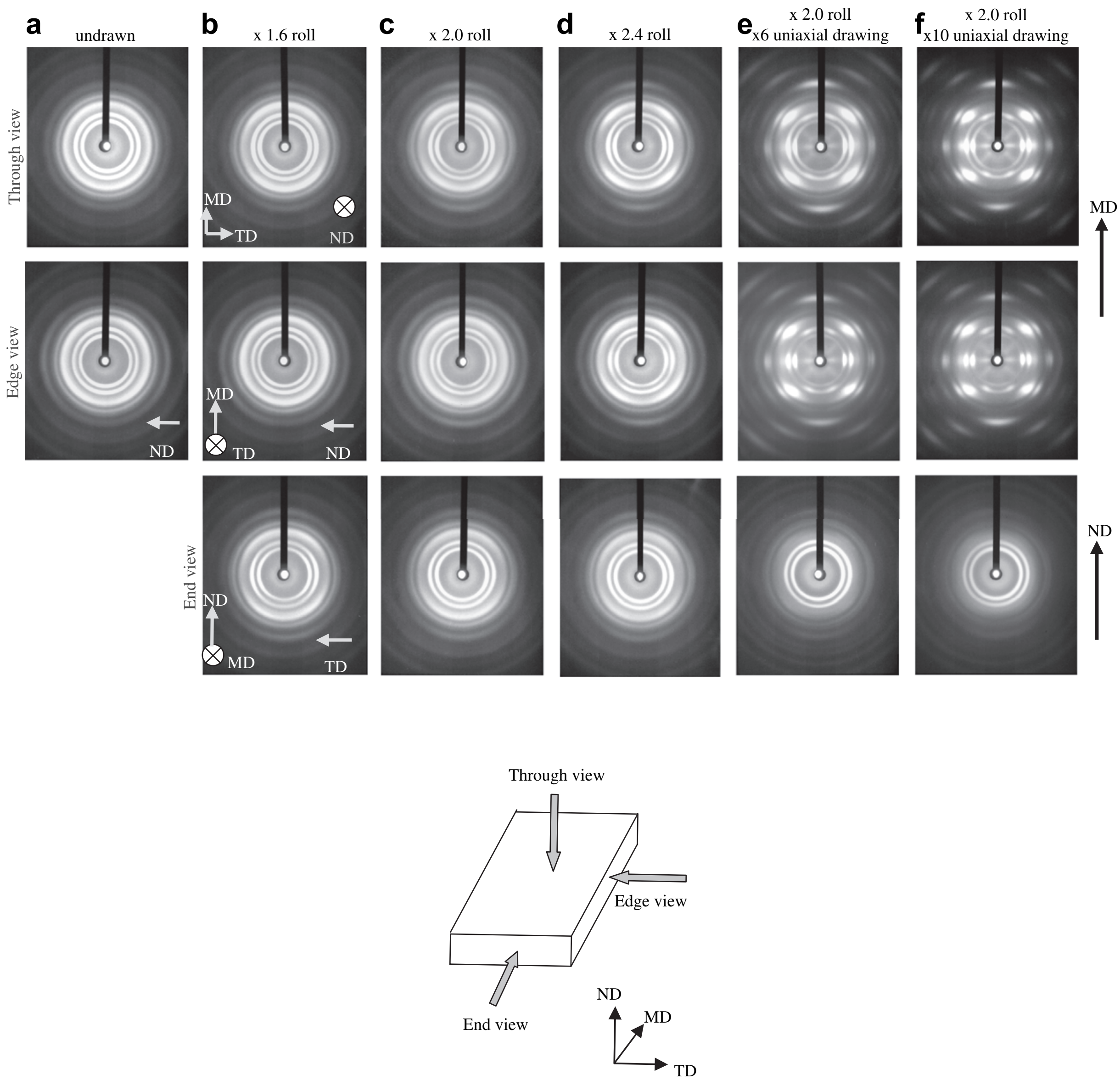


Fig. 2. WAXD patterns of undrawn, roll drawn and uniaxially drawn PHBH film.

to the visible light. So the detailed analysis was carried out using a small angle X-ray scattering technique.

Fig. 3(a)–(f) shows the SAXS patterns of PHBH films. Through view pattern of undrawn film shows a broad ring pattern indicating that the spherulites do not have any preferred orientation in the plane parallel to the film surface. The edge view pattern shows a stronger arc on the equator. This may be attributable to the difference in the cooling rates which causes some crystalline orientations through the film thickness.

Overall through view patterns of roll and uniaxially drawn films show a typical two-point pattern, suggesting that the crystalline lamellae and amorphous regions are stacked alternately along drawing direction. Two-point pattern on the meridian indicates a periodic two-phase structure in this draw ratio range. A weak and broad reflection of the film roll drawn to a low ratio suggests that the distribution of the layer thickness is rather defective and disordered. Further the meridional wide reflection is originated from the periodic structure with a smaller lateral dimension. The intensity of the two-point pattern increased much and the width tended to be narrower with increasing uniaxial draw ratio.

Edge view patterns of roll and uniaxially drawn films show much more complications. A definite four-point reflection and a vague two-point reflection on the meridian can be observed at a draw ratio $\times$ 1.6. This vague reflection becomes more apparent with increasing roll draw ratio. This suggests an existence of the two kinds of lamellar structures; one in which lamellar normals are inclined from drawing direction to the film normal giving a four-point pattern and the other in which lamellar normals are almost parallel to the drawing direction giving a two-point pattern, respectively. The four-point pattern tends to incline more to the equator with increasing roll draw ratio. This is in agreement with the report of Stachurski and Ward who analyzed the spherulite deformation of the films

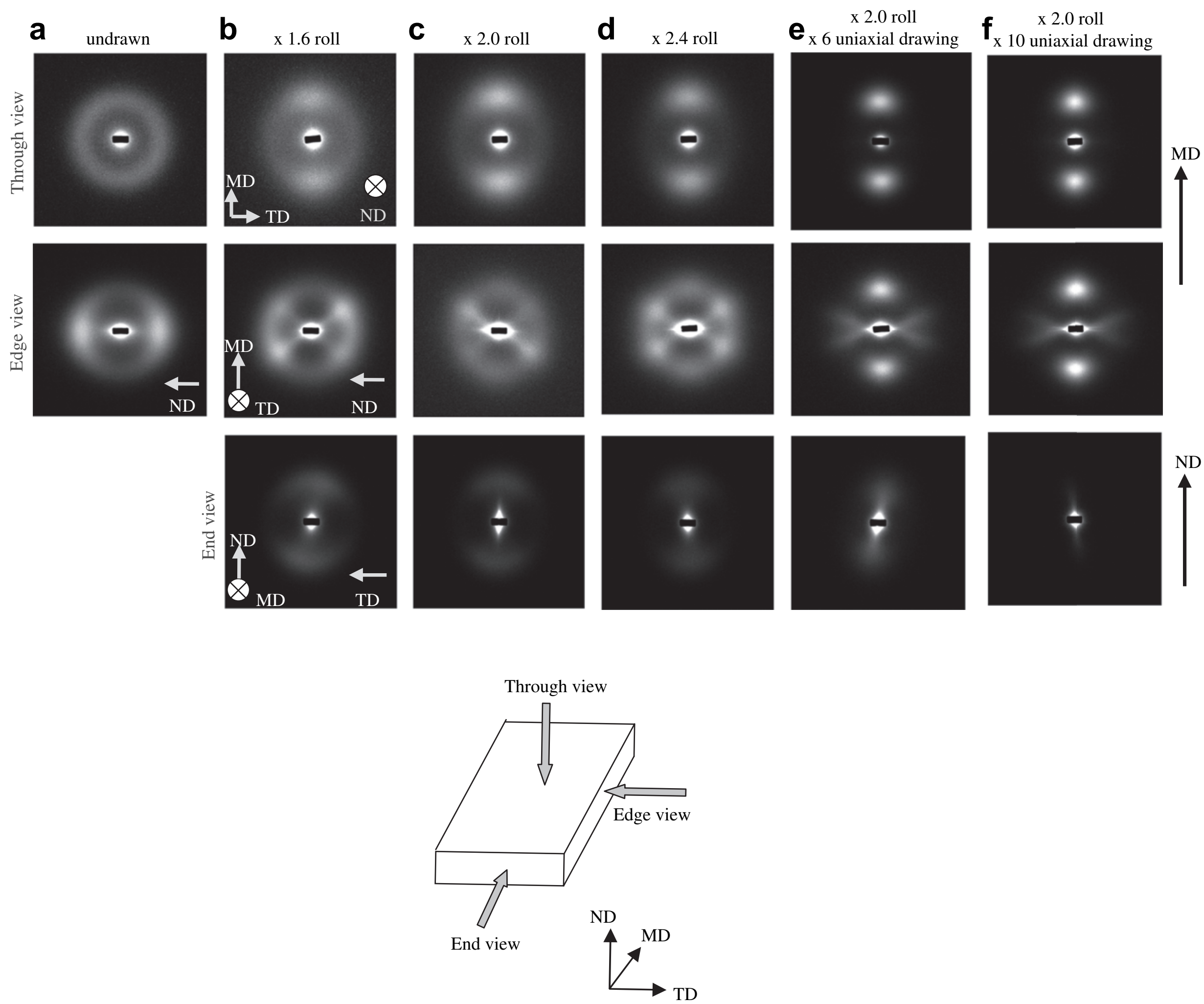


Fig. 3. SAXS patterns of undrawn, roll drawn and uniaxially drawn PHBH film.

upon roll drawing [13]. They demonstrated that the overlapping reflection which consists of the two-point pattern of the meridian and the four-point pattern of the diagonal direction becomes apparent with roll draw ratio.

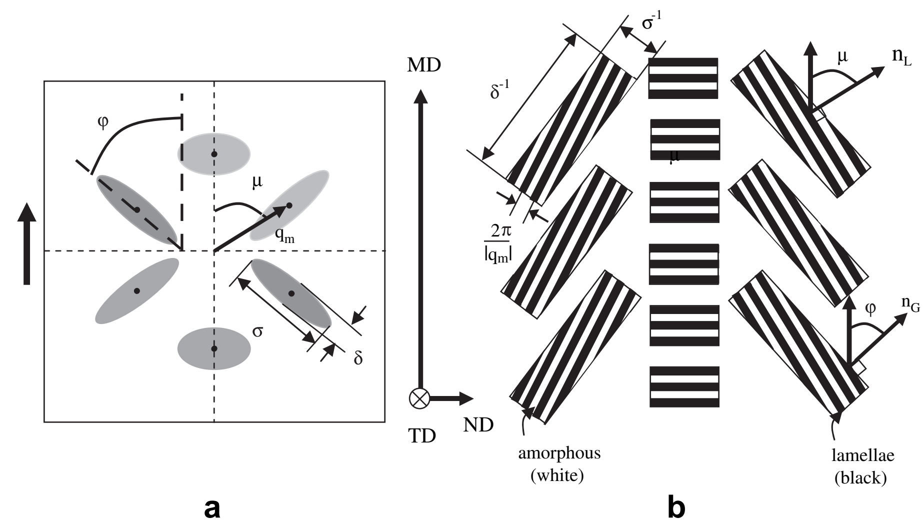
End view shows only a featureless pattern with streaks. This may be an indication of the slight spherulite deformation to the transverse direction.

Fig. 3(e) and (f) shows the SAXS patterns of uniaxially drawn PHBH films after roll drawn to $\times$ 2.0. Through view patterns show a two-point pattern more definite than the pattern of roll drawn films. This suggests the existence of the lamellar block which highly oriented to the uniaxial drawing direction.

Edge view patterns still keep their mixed pattern, the two-point reflection on the meridian and the four-point reflection which faces across the equator. It was observed that the four-point reflection inclines near to the equator with increasing uniaxial draw ratio in the similar way to the roll drawn films. This means that the *c*-axes in some lamellar blocks orient more to the film normal direction with increasing uniaxial draw ratio.

Overall through and edge view patterns of roll and uniaxially drawn films, two-point reflections on the meridian indicate the existence of a layer structure, that is so-called shish–kebab structure [14]. Kebabs are oriented parallel to the roll and uniaxial drawing direction.

To characterize the structure of PHBH roll and uniaxially drawn films in detail, some structural parameters were evaluated from the SAXS edge pattern exhibiting the six-point pattern [15]. A set of five parameters were chosen as shown schematically in Fig. 4(a) to characterize the shape and orientation of the streak-like spots. Parameters δ and σ denote the width and the length of the four-point streak, respectively, while μ and φ designate the oblique angle of the **q** vector pointing toward the peak top from the origin and the angle between the meridional direction and the long axis of the four-point streak, respectively. Note that the q_m is the magnitude of the **q** vector at the peak top. These five parameters characterize the structure of PHBH roll and uniaxially drawn films, as schematically illustrated in Fig. 4(b). Here the black bar corresponds to the lamellae and the white region between lamellae corresponds to the amorphous region, and the



Edge view

Fig. 4. Schematic representation of PHBH SAXS pattern.

black-and-white stripe stands for alternating lamellar microdomains. The PHBH roll and uniaxially drawn films are therefore composed of polygrains.

Fig. 5 shows the changes in μ and φ estimated from SAXS edge view pattern of PHBH roll and uniaxially drawn films. The oblique angle of μ increased slightly with increasing roll draw ratio. This indicates that the lamellae normal tends to incline to the direction perpendicular to the film surface with increasing roll and uniaxial draw ratio. On the contrary, another oblique angle φ decreased. It means that the grain becomes inclined to the counter direction to the direction of the lamellae movement. Further drawing by the uniaxial extension in turn increased both μ and φ, resulting in more inclined lamellae and the grain parallel to the film surface.

The change in the long period of the lamellar crystals oriented to the drawing direction in the roll and uniaxially drawn films was determined from the SAXS through view pattern. Further that of the lamellar crystal inclined to the film surface in the roll drawn film was also determined from the edge view pattern. These are plotted in Fig. 6.

The long periods of the roll drawn film determined from the four-point edge view pattern are slightly larger than that determined from the two-point through view pattern. This would indicate the difference in the deformation mechanisms in the roll drawing. The spherulite originally existed in the film was compressed and deformed by the roll drawing. Some of the lamellar block rotated and their c-axes oriented to the drawing direction. The other lamellar blocks were subjected to the shear deformation as Stachurski and Ward [13]

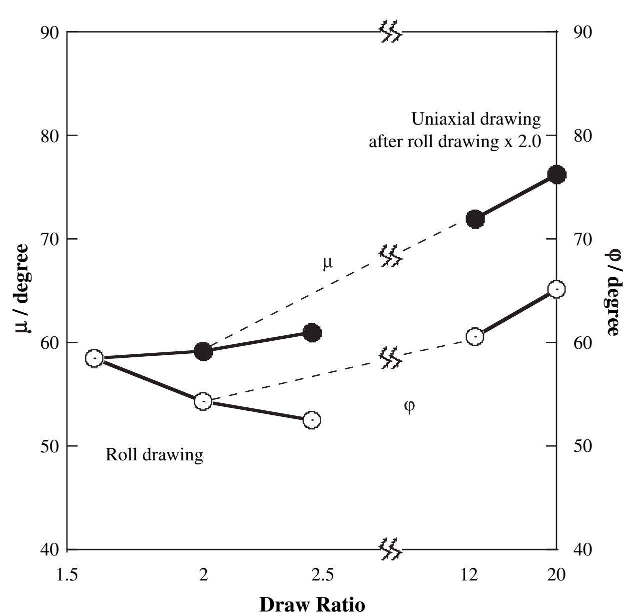


Fig. 5. Oblique angles μ and φ.

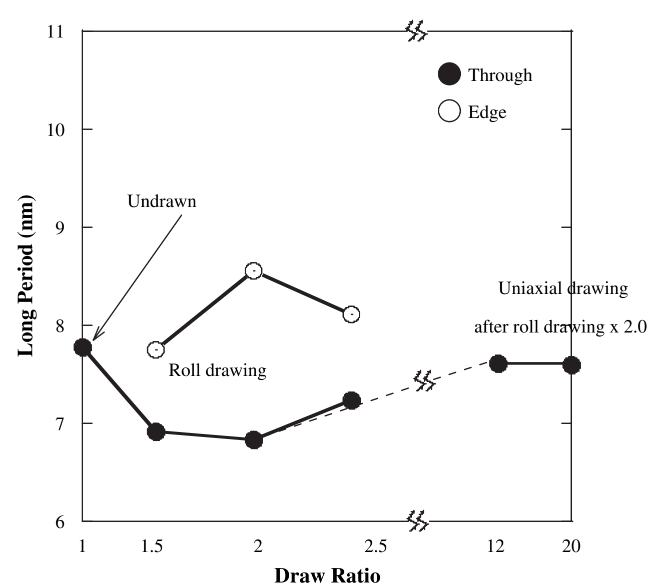


Fig. 6. Long period of PHBH films.

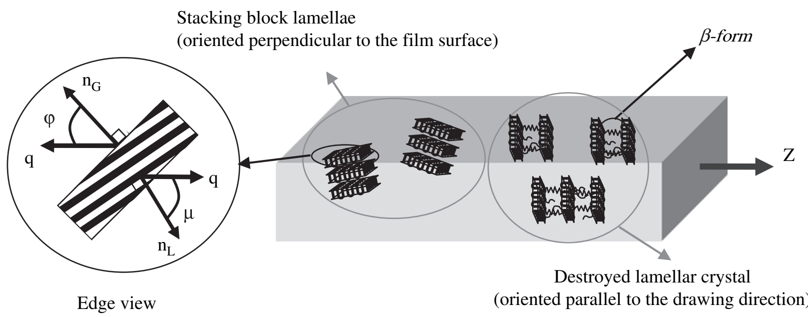


Fig. 7. Schematic illustration shows three kinds of crystal structures in uniaxially drawn films after roll drawing (*Z*: uniaxial drawing direction (// roll drawing direction) n_L: normal vector of the truncated lamellar microdomains, n_G: normal vector of the lamellar block (grain), μ: oblique angle of the *Z* and **q** vector, φ: oblique angle of *Z* and n_G).

suggested and the *c*-axis tended to incline to the film surface. Due to this shear deformation, lamellar crystals were stretched resulting in the large long period. The long period from four-point pattern of edge view patterns increased slightly up to the roll draw ratio of $\times$ 2.0 and then decreased when higher roll draw ratio (above $\times$ 2.0) was applied to the PHBH film. It was considered that the amorphous region was extended to the normal vector direction of the truncated lamellar micro-domains (n_L) up to roll draw ratio $\times$ 2.0. On the other hand, the compressive force was acted above roll draw ratio $\times$ 2.0, which resulted in decrease of the long period.

The long period of the lamellar crystal oriented to the drawing direction was increased significantly after applying uniaxial extension. This phenomenon may be a result of the extension of the tie-molecules between lamellae and the extended tie chains formed the β-crystal.

From these changes in the long periods, two kinds of structural reorganization are speculated. Firstly, the roll extension deformed some lamellar blocks. This was corresponded to the model of Stachurski and Ward; rotation of the micro crystallites of the circumference of *b*-axis (long axis of lamellae) was occurred by shear between lamellae [13]. Secondly, the rest of the lamellar block was destroyed by uniaxial extension and β-form was evoluted.

4. Conclusions

Films of the bacterial polyester with superior mechanical property and high ductility can be obtained by a uniaxial drawing after applying a roll drawing process [4].

From WAXD and SAXS patterns of the roll and uniaxially drawn PHBH film, the existence of (020) ring reflection of through and edge view WAXD patterns and four-point reflection of edge view SAXS patterns show that spherulites were deformed by roll drawing and their *c*-axes in some lamellar crystal inclined toward normal vector of the film surface. The others were destroyed and oriented to the uniaxial drawing direction by uniaxial extension; this can be concluded from the degree of orientation of WAXD patterns and the existence of two-point reflection on the meridian of through and edge view SAXS patterns. Besides, the tie-molecules between uniaxially oriented lamellae were extended and the β-form with a planar zig-zag conformation was generated.

Because of these results, it is concluded that three kinds of structures, *c*-axis parallel to the uniaxial drawing direction, β-form crystal between lamellae and *c*-axis inclined to the normal vector of the film surface are intermingled in this roll and uniaxially drawn PHBH film is schematically shown in Fig. 7.

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