

Structure Formation in Stretched Sheets of Poly(butylene Terephthalate)

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SYNOPSIS

Crystalline and amorphous sheets of poly(butylene terephthalate) (PBT) were drawn in the temperature range of 20–150°C. The molecular orientation and the relative amount of α - and β -form crystals in the stretched sheets were studied by wide-angle X-ray diffraction (WAXD) and density measurements. When crystalline PBT sheets are drawn at lower temperatures, α -form crystals are partially transformed into β -form crystals. Both α - and β -form crystals are formed by drawing amorphous PBT sheets. The relative amount of α - and β -form crystals is much more sensitive to drawing temperature than to draw ratio. The α -form crystallinity is higher at higher drawing temperature and increases slightly with increasing draw ratio. The second moments of orientation functions of α - and β -form crystals increase with increasing draw ratio, and the increase of the orientation function is suppressed at higher draw ratio. The orientation function of α -form crystals is higher than that of β -form crystals in a same sample.

INTRODUCTION

It is well known that poly(butylene terephthalate) (PBT) exhibits a reversible crystal transformation between α and β forms under mechanical deformation. The crystal structures of the two crystal forms have been extensively studied by X-ray crystallographic analysis.^{1–5} Although both crystal modifications belong to a triclinic system, the crystal unit cell repeating length of β -form crystal (stressed form) is longer than that of α -form crystal (unstressed form). This is because the conformation of the tetra-methylene group is more extended in β -form crystal than in α -form crystal. The mechanism of the stress-induced crystal transformation has been studied in detail by tensile and recovery measurements,^{6–8} wide-angle X-ray diffraction (WAXD),^{1–5,7,9} and infrared and Raman spectroscopy.^{7–12}

In spite of the extensive studies of the crystal transformation process of PBT, only a few works

have been reported on the structure development in hot-drawn PBT. Spruiell and his co-workers studied the structure and the mechanical properties of melt spun filaments of PBT and discussed the effects of spinning, drawing, and annealing conditions on the resulting structure and the physical properties of PBT.^{13,14}

In this work we prepared quenched PBT (Q-PBT) sheet as well as slowly crystallized PBT (SC-PBT) sheet and studied the structure of drawn SC-PBT and Q-PBT sheets by WAXD and density measurements. The aim of this work is to clarify the effects of thermal and drawing conditions on the structure formation of the drawn PBT sheets.

EXPERIMENTAL

Sample Preparation

The PBT sample studied in this work is a Duranex 2002 obtained from Polyplastics Co., Ltd. PBT sheets were extruded from a coat-hanger die using a twin-screw extruder, after the pellets were dried at 105°C. The die temperature was set at 255°C. Slowly crystallized PBT (SC-PBT) sheets were

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winded by a take-up roller whose temperature was controlled at 120°C. Quenched PBT (Q-PBT) sheets were obtained by quench-rolling the polymer melt between a pair of cooled rollers.

The samples with gauge dimension of 80 × 40 mm were cut from the sheets and were uniaxially drawn at 20–150°C using a tensile testing machine, UTM-III-10T (Orientec Co., Ltd.).

Characterization

The WAXD profile was obtained using a Ni-filtered Cu K α radiation (40 kV, 30 mA) produced by a Geigerflex XGC-20 (Rigaku Denki Co., Ltd.). The WAXD intensity was measured using a scintillation counter and a pulse-height analyzer. The second moment of crystal orientation function was evaluated from the azimuthal intensity distribution of meridional reflections.

WAXD pole figures were obtained by employing both transmission and reflection techniques. The WAXD intensity was corrected for background and absorption.

Density was measured with a carbon tetrachloride-*n*-heptane density gradient column at 25°C. The density of α -form crystal is calculated to be 1.404 g/cm³ by Yokouchi et al.³ and 1.396 g/cm³ by Boye and Overton.¹⁵ The density of β -phase crystal evaluated from the crystal structure³ was 1.283 g/cm³ and is close to the value of the density of amorphous phase, 1.281 g/cm³. The weight fraction crystallinity of α -form crystal was obtained by assuming that the density of α -form crystal was 1.396

g/cm³ and those of β -form crystal and of amorphous phase were 1.281 g/cm³.

RESULTS AND DISCUSSION

Characterization of Original Sheets

The WAXD profiles of as-extruded SC-PBT and Q-PBT sheets are shown in Figure 1. The SC-PBT sheet exhibits a lot of sharp reflections originating from α -form crystal. The crystallinity of the original SC-PBT sheet is evaluated to be 23% from the experimental value of density. Unlike the SC-PBT sample, only a broad reflection is observed in the WAXD profile of the Q-PBT sheet, and thereby the Q-PBT sheet is considered to have an amorphous structure.

A distinct difference was found in the deformation behavior between SC-PBT sheets and Q-PBT sheets. In the drawing process of SC-PBT sheets, the neck was formed at the initial stage and propagated along the specimen up to draw ratio, $\lambda = 3$, whereas Q-PBT sheets homogeneously deformed in the drawing process. The maximum draw ratio for SC-PBT and Q-PBT sheets reached 4–4.5 at each drawing temperature.

Crystal Transformation in Drawn SC-PBT Sheet

Figure 2 shows the effects of drawing temperature (T_d) on the meridional WAXD profile of highly drawn SC-PBT sheets. The reflections observed at $2\theta = 31.5^\circ$, 39.6° , and 47.5° are assigned to the $\bar{1}04$,

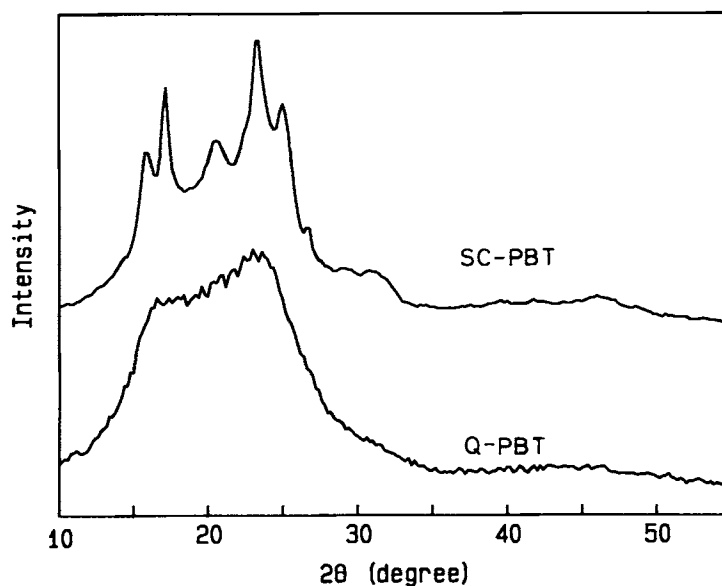


Figure 1 WAXD intensity distributions of isotropic SC-PBT (upper) and Q-PBT (lower) sheets.

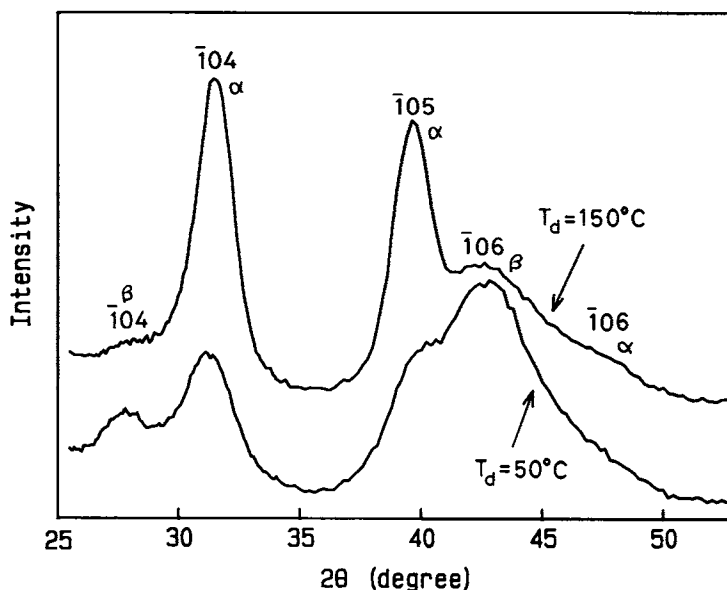


Figure 2 WAXD meridional profiles of highly drawn SC-PBT sheets: (upper) $T_d = 150^\circ\text{C}$, $\lambda = 4.21$; (lower) $T_d = 50^\circ\text{C}$, $\lambda = 4.6$.

$\bar{1}05$, and $\bar{1}06$ reflections, respectively, of α -form crystal, and those at $2\theta = 28.2^\circ$ and 42.6° are ascribed to the $\bar{1}04$ and $\bar{1}06$ reflections, respectively, of β -form crystal. The intense reflections of α -form crystal are observed in the sample drawn at $T_d = 150^\circ\text{C}$. As drawing temperature is lowered, the intensities of the reflections of α -form crystal decrease and the reflections of β -form crystal are intensified. α -Form crystals are shown to be transformed into β -form crystals by drawing SC-PBT

sheets at lower temperatures. The meridional reflections of β -form crystal are much broader than those of α -form crystal, suggesting that β -form crystals are small in crystalline dimension and have poor crystalline order.

Figure 3 shows the effect of drawing temperature on the equatorial WAXD profile of highly drawn SC-PBT sheets. The reflections observed at $2\theta = 17.2^\circ$ and 23.6° are attributed to the 010 and 100 reflections, respectively. The 110 reflection is weaker

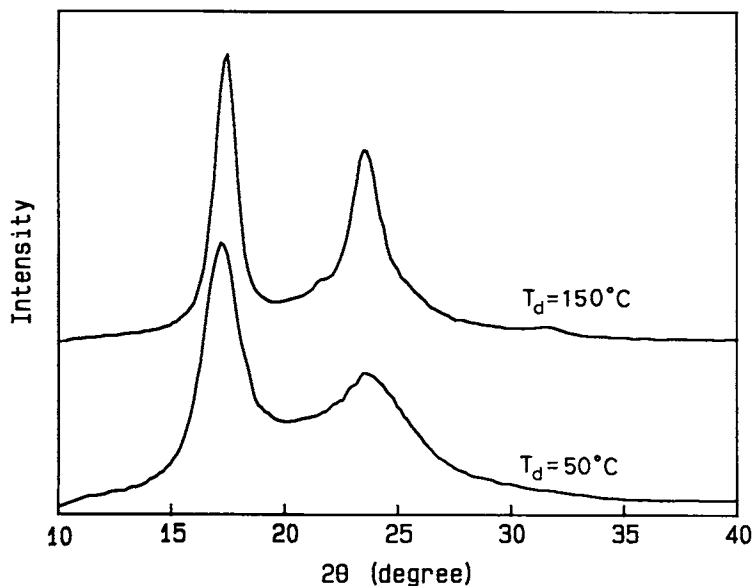


Figure 3 WAXD equatorial profiles of highly drawn SC-PBT sheets: (upper) $T_d = 150^\circ\text{C}$, $\lambda = 4.21$; (lower) $T_d = 50^\circ\text{C}$, $\lambda = 4.6$.

than those reflections and may be hidden behind the 100 reflection. Although the content of α -form crystal increases with the rise in drawing temperature, the peak positions of the equatorial reflections are not affected significantly by drawing temperature. This is because the crystal lattice constants a and b of β -form crystals are similar to those of α -form crystals. The equatorial reflections are broadened at lower drawing temperatures, suggesting that the interchain correlation in β -form crystals is disordered.

Figure 4 shows the effect of draw ratio λ on the meridional profile of SC-PBT sheets drawn at 90°C . The relative intensity of the reflection of α -form crystal to that of β -form crystal increases slightly with increasing draw ratio.

The degree of α -form crystallinity in drawn SC-PBT sheets is shown in Figure 5. The degree of crystallinity is much more sensitive to drawing temperature than to draw ratio. The degree of α -form crystallinity increases with the rise in drawing temperature. At a given drawing temperature, the degree of α -form crystallinity increases only slightly with increasing draw ratio.

If a SC-PBT sheet is stretched at lower temperatures, α -form crystals are partially transformed into β -form crystals. In the range of small strain, defor-

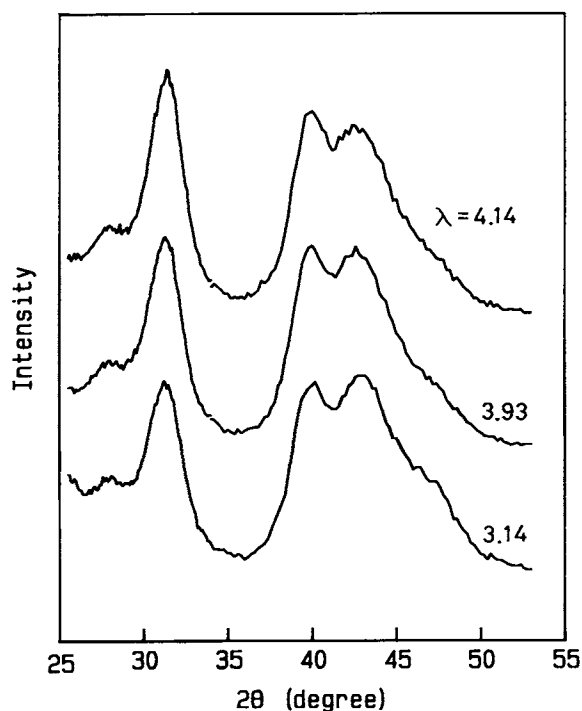


Figure 4 Change of WAXD meridional profiles of SC-PBT sheets ($T_d = 90^\circ\text{C}$) with draw ratio, λ .

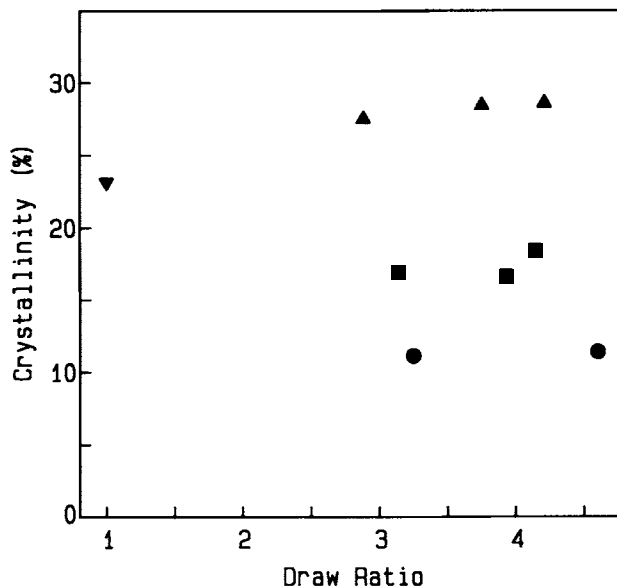


Figure 5 Degree of crystallinity of α -form crystals in the drawn SC-PBT sheets as a function of draw ratio: (▲) $T_d = 150^\circ\text{C}$; (■) $T_d = 90^\circ\text{C}$; (●) $T_d = 50^\circ\text{C}$; (▼) original SC-PBT sheet.

mation process is elastic and the crystal transformation is reversible. When the polymer sheet is stretched beyond the yield point, the spherulitic structure is transformed into the microfibrillar structure. The β -form crystals formed under stress are incorporated into the microfibrillar structure and are stabilized by residual stress after the drawing tension is removed. Lu and Spruiell reported that the β -form content was proportional to the drawing stress.¹³ The β -form content greatly increases as drawing temperature is lowered, suggesting that the higher residual stress is generated in the sample drawn at lower drawing temperature. On the other hand, the stretching process above necking draw ratio is characterized by the deformation of the microfibrillar structure. With further increasing draw ratio, the microfibrillar structure is deformed accompanied by the unfolding of lamellae crystals and the reorganization of crystalline texture. The content of the α -form crystal, which has higher degree of crystalline perfection than the β -form crystal, slightly increases in the deformation process of the microfibrillar structure.

Structure Formation in Drawn Q-PBT Sheets

Figure 6 shows the effects of drawing temperature on the meridional WAXD profile of highly drawn Q-PBT sheets. The WAXD profile of the Q-PBT

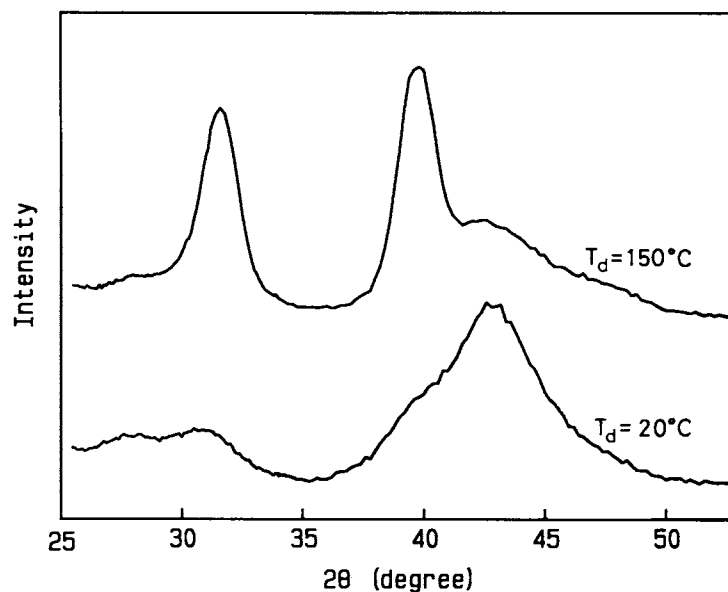


Figure 6 WAXD meridional profiles of highly drawn Q-PBT sheets: (upper) $T_d = 150^\circ\text{C}$, $\lambda = 4.08$; (lower) $T_d = 20^\circ\text{C}$, $\lambda = 3.84$.

sheet drawn at room temperature is dominated by broad reflections of β -form crystal, while intense reflections of α -form crystal are observed on the WAXD profile of the Q-PBT sheet drawn at 150°C . β -Form crystals with poor crystalline order are

formed by drawing Q-PBT sheets at lower temperature. At higher drawing temperature, however, the growth of α -form crystals exceeds that of β -form crystals.

Figure 7 shows the effect of draw ratio on the meridional WAXD profile of the Q-PBT sheets drawn at 90°C . The intensities of the $\bar{1}04$ and $\bar{1}05$

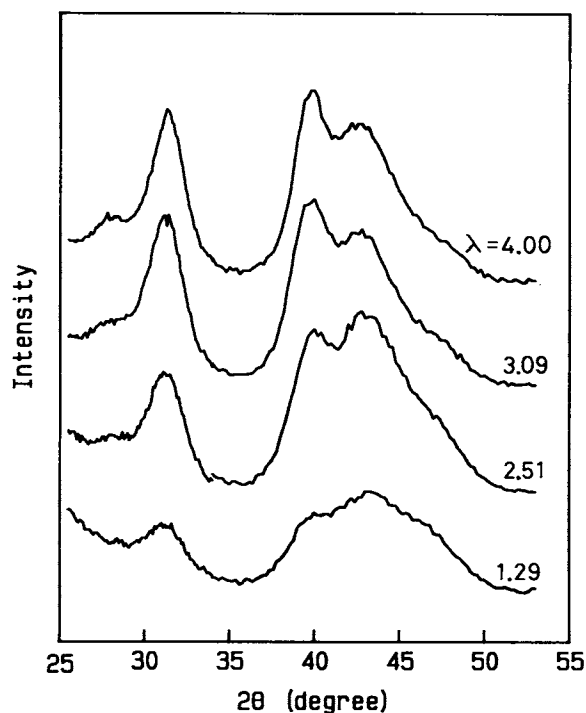


Figure 7 Change of WAXD meridional profiles of Q-PBT sheets ($T_d = 90^\circ\text{C}$) with draw ratio, λ .

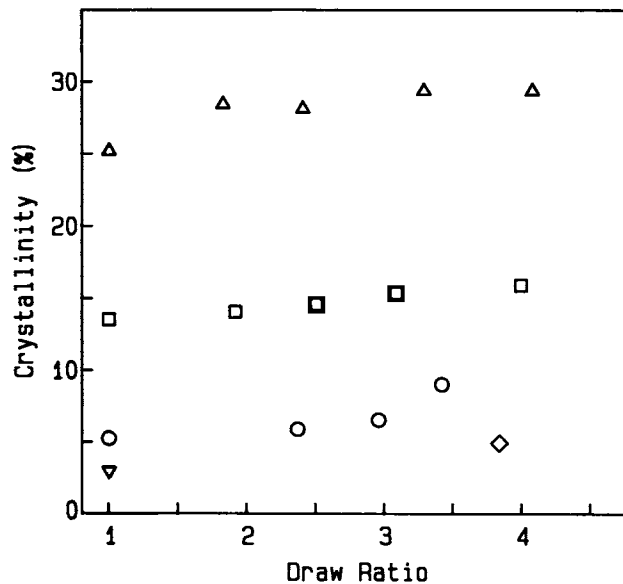


Figure 8 Degree of crystallinity of α -form crystals in the drawn Q-PBT sheets as a function of draw ratio: (Δ) $T_d = 150^\circ\text{C}$; (\square) $T_d = 90^\circ\text{C}$; (\circ) $T_d = 50^\circ\text{C}$; (\diamond) $T_d = 20^\circ\text{C}$; (∇) original Q-PBT sheet.

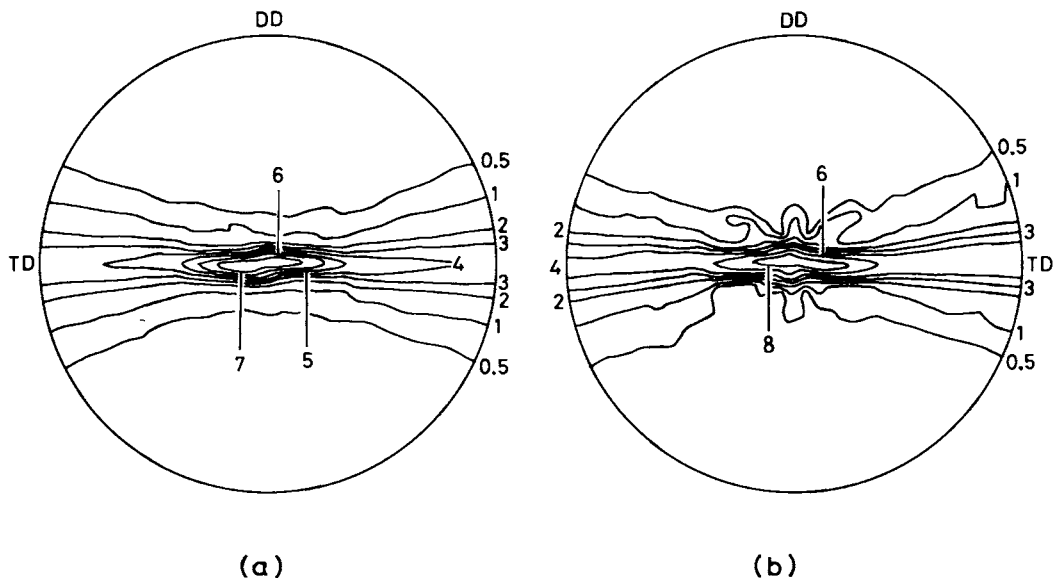


Figure 9 100 pole figure of α -form crystal: (a) SC-PBT sheet, $T_d = 150^\circ\text{C}$, $\lambda = 4.21$; (b) Q-PBT sheet, $T_d = 150^\circ\text{C}$, $\lambda = 3.75$.

reflections of α -form crystals increase significantly with increasing draw ratio compared with the reflections of β -form crystals.

Figure 8 shows the degree of α -form crystallinity in drawn Q-PBT sheets as a function of draw ratio. The degree of crystallinity of isotropic samples annealed at each drawing temperature is also shown in Figure 8. The degree of α -form crystallinity increases markedly with the rise in drawing temper-

ature. The α -form crystallinity in drawn Q-PBT sheets is higher than the crystallinity of isotropic Q-PBT sheets annealed at the drawing temperature. α -Form crystallinity in Q-PBT sheets tends to increase with increasing draw ratio. The growth of α -form crystals in the drawing process is mainly caused by the thermal effects at the drawing temperature and is facilitated by the orientation of molecular chains.

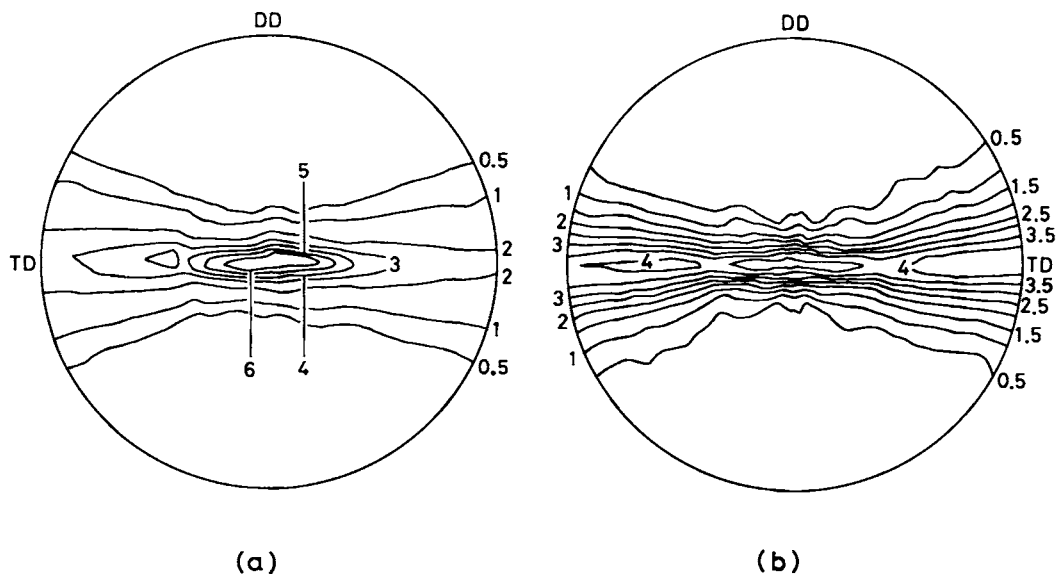


Figure 10 100 pole figure of β -form crystal: (a) SC-PBT sheet, $T_d = 50^\circ\text{C}$, $\lambda = 4.60$; (b) Q-PBT sheet, $T_d = 50^\circ\text{C}$, $\lambda = 3.15$.

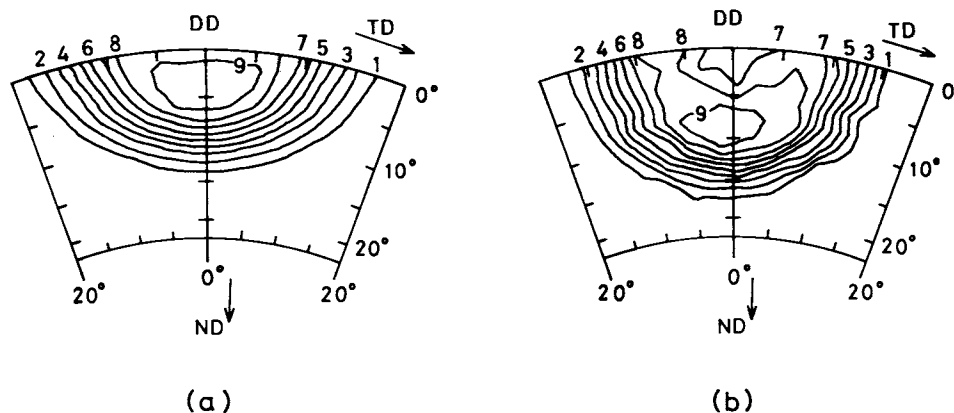


Figure 11 $\bar{1}04$ pole figure of α -form crystal: (a) SC-PBT sheet, $T_d = 150^\circ\text{C}$, $\lambda = 4.21$; (b) Q-PBT sheet, $T_d = 150^\circ\text{C}$, $\lambda = 3.75$.

WAXD Pole Figures

The 100 pole figures of the PBT sheets highly drawn at 150°C are shown in Figure 9. Although the 100 reflections of the two crystal modifications overlap each other, the pole figures are dominated by the 100 reflection of α -form crystal at higher drawing temperature. The principal axes of the sheets are labeled DD (draw direction), TD (transverse direction), and ND (normal direction). The contour lines for the 100 reflection are drawn in units of the intensity of random sample. The 100 pole is distributed in the TD-ND line and shows a maximum at ND. At $T_d = 150^\circ\text{C}$, the 100 pole figure of the highly drawn Q-PBT sheet is analogous to that of the highly drawn SC-PBT sheet. The 100 plane of α -form crystal is shown to be aligned in the sheet plane and might be a plane of slippage in the deformation process. In this work, PBT sheets were uniaxially drawn without fixing the width of sheets. The 100 plane orientation in the PBT sheet suggests that

the stress field is not necessarily uniaxial even in the uniaxial drawing of PBT sheets.

Figure 10 shows the 100 pole figures of the PBT sheets highly drawn at 50°C . At lower drawing temperature, the pole figures originate mainly from β -form crystals. In the highly drawn SC-PBT sheet, the 100 plane of β -form crystal also tends to align in the sheet plane. On the other hand, the 100 pole in the highly drawn Q-PBT sheet is uniaxially distributed in the TD-ND plane.

Figure 11 shows the $\bar{1}04$ pole figures of α -form crystals in the PBT sheets highly drawn at 150°C .

Table I Meridional Reflections of α - and β -Form Crystals

hkl	d_{hkl} (\AA)	2θ (degree)	γ (degree) ^a
α Form			
$\bar{1}04$	2.867	31.19	10.64
$\bar{1}05$	2.303	39.11	9.31
$\bar{1}06$	1.901	47.85	12.24
β Form			
$\bar{1}04$	3.152	28.32	14.13
$\bar{1}05$	2.542	35.30	12.11
$\bar{1}06$	2.095	43.19	14.80

^a Angle between reciprocal lattice vector and fiber axis.

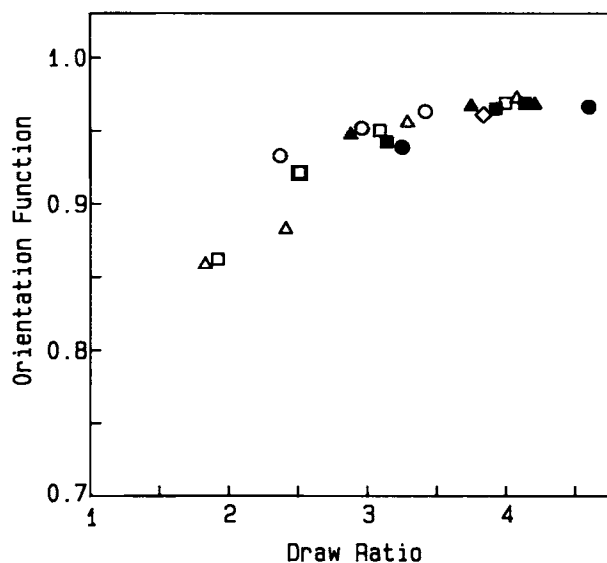


Figure 12 The second moment of orientation function of α -form crystals as a function of draw ratio: (\blacktriangle , \triangle) $T_d = 150^\circ\text{C}$; (\blacksquare , \square) $T_d = 90^\circ\text{C}$; (\bullet , \circ) $T_d = 50^\circ\text{C}$; (\diamond) $T_d = 20^\circ\text{C}$; (\blacktriangle , \blacksquare , \bullet) SC-PBT sheets; (\triangle , \square , \circ , \diamond) Q-PBT sheets.

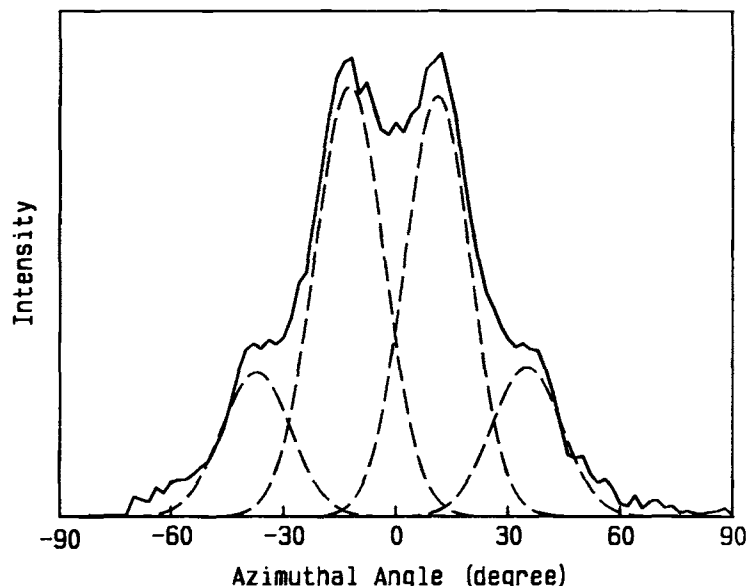


Figure 13 Azimuthal WAXD intensity distribution of the $\bar{1}06$ reflection of β -form crystals in the SC-PBT sheet ($T_d = 90^\circ\text{C}$, $\lambda = 4.14$).

The intensity contours labeled 1, 2, . . . , and 9 represent 10, 20, . . . , and 90% of the maximum intensity, respectively. The $\bar{1}04$ pole is uniaxially distributed around DD showing a maximum at 5° – 10° from DD. The $\bar{1}04$ pole maximum tilts from DD, because the reciprocal lattice vector of the $\bar{1}04$ reflection is inclined from the crystal c axis. Table I shows the inclination angles of the reciprocal lattice vector from the crystal c axis, which are calculated from the lattice constants.

Orientation Function

The second moment of orientation function of α -form crystals was obtained from the azimuthal intensity distribution of the $\bar{1}04$ reflection. The second moment of orientation distribution function was calculated from the observed intensity profile, $I(\phi')$, after the off-meridional character of the $\bar{1}04$ reflection was corrected, according to the procedure proposed by Gupta and Kumar:¹⁶

$$\langle \cos^2 \phi' \rangle = \frac{\int_0^\pi I(\phi') \cos^2 \phi' \sin \phi' d\phi'}{\int_0^\pi I(\phi') \sin \phi' d\phi'} \quad (1)$$

$$\langle \cos^2 \phi \rangle = \frac{\langle \cos^2 \phi' \rangle}{\cos^2 \gamma} \quad (2)$$

$$f = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \quad (3)$$

where ϕ is the angle between the fiber axis and draw

direction, ϕ' is that between the reciprocal lattice vector of the $\bar{1}04$ reflection and draw direction, and γ is the tilting angle of the reciprocal lattice vector of the $\bar{1}04$ reflection from the fiber axis.

Figure 12 shows the orientation function of α -form crystals as a function of draw ratio. The orientation function increases with increasing draw ratio and tends to saturate at higher draw ratio. The orientation function is not affected significantly by drawing temperature and the crystallinity of the original sheet.

Figure 13 shows the azimuthal WAXD scan at $2\theta = 43^\circ$. The reflections expected in this Bragg angle range are summarized in Table II. Two central peaks in the azimuthal intensity profile originate from the $\bar{1}06$ reflection of the β -form crystal. The peak position of the $\bar{1}06$ reflection is displaced from the meridian because the reciprocal lattice vector of the $\bar{1}06$ reflection is inclined from the fiber axis. Besides

Table II Reflections of β -Form Crystals Expected in the Range of $2\theta = 42.5^\circ$ – 45°

hkl	d_{hkl} (Å)	2θ (degree)	γ (degree)*
$\bar{1}06$	2.095	43.19	14.80
$\bar{1}15$	2.113	42.80	35.65
$\bar{1}25$	2.020	44.85	39.00
005	2.047	44.23	38.04
$\bar{2}15$	2.022	44.82	38.94
$0\bar{2}5$	2.057	44.02	37.70

* Angle between reciprocal lattice vector and fiber axis.

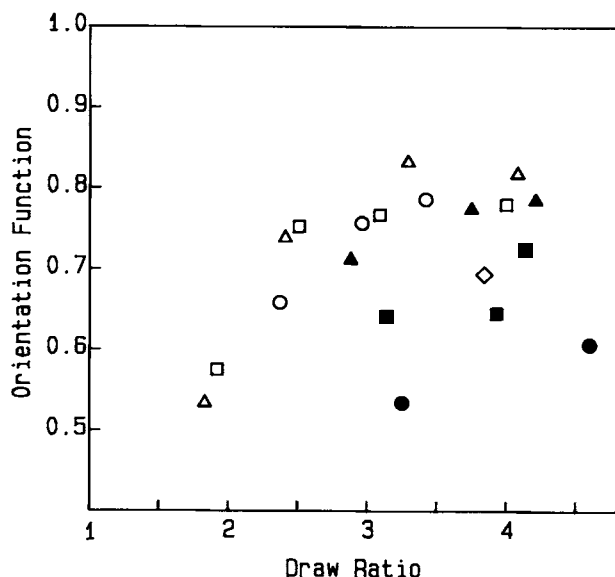


Figure 14 The second moment of orientation function of β -form crystal as a function of draw ratio: (\blacktriangle , \triangle) $T_d = 150^\circ\text{C}$; (\blacksquare , \square) $T_d = 90^\circ\text{C}$; (\bullet , \circ) $T_d = 50^\circ\text{C}$; (\diamond) $T_d = 20^\circ\text{C}$; (\blacktriangle , \blacksquare , \bullet) SC-PBT sheets; (\triangle , \square , \circ , \diamond) Q-PBT sheets.

the $\bar{1}06$ reflection, there comes the contribution to the azimuthal profile from the $\bar{1}15$, $\bar{1}25$, 005 , $\bar{2}15$, and $0\bar{2}5$ reflections whose reciprocal lattice vectors are inclined by 30° – 40° from the fiber axis (Table II). The second moment of the orientation function of β -form crystals was calculated from the azimuthal intensity distribution by using Eq. (1)–(3), after the contributions from the other reflections are subtracted from the observed intensity profile by the Gaussian curve-fitting procedure.

Figure 14 shows the second moment of orientation function of β -form crystals as a function of draw ratio. The orientation function increases with increasing draw ratio. At a same draw ratio, the orientation function in the drawn SC-PBT sheets increases with the rise in drawing temperature. In a same sample, the orientation function of α -form crystals is higher than that of β -form crystals.

CONCLUSIONS

The structure formation in the stretched PBT sheets was studied as a function of draw ratio, drawing temperature, and the crystallinity of the original sample. The α -form crystallinity is sensitive to drawing temperature and is higher at higher drawing temperature. The second moments of orientation functions of α - and β -form crystals increase with increasing draw ratio and the increase of the orientation function is suppressed at higher draw ratio.

α -Form crystals have higher crystalline order and more easily orient to the draw direction than β -form crystals.

When SC-PBT sheets are stretched beyond the yield point, α -form crystals are partially transformed into β -form crystals. β -Form crystals are developed by the extension of the molecular conformation under the external stress and are stabilized by the residual stress after the external stress is removed. With further increasing draw ratio, however, the content of α -form crystals increases slightly in spite of the increase of the external draw stress.

Both α -form and β -form crystals are developed by stretching amorphous Q-PBT sheets, and the relative amount of the two crystal forms is sensitive to drawing temperature. α -Form crystals are formed mainly by the thermal effect at the drawing temperature, and the growth of α -form crystals is facilitated by the orientation of molecular chains.

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