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Intrinsic Birefringence of Poly(butylene terephthalate)

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Abstract: Theoretical refractive indices were calculated by summarizing bond polarizabilities for α and β form crystal of poly(butylene terephthalate). The principal direction at which the polarizability indicates minimum was almost parallel to the normal direction of phenylene ring. The principal refractive indices revealed 1.411, 1.713, 1.760 for α form crystal, and 1.398, 1.708, 1.768 for β form crystal. The resulting intrinsic birefringences for c-axis orientation of α and β form crystals were 0.153 and 0.215, respectively.

1. Introduction

Double refraction is the phenomenon that a ray forks off in two directions caused by the anisotropy of refractive index represented as index ellipsoid whose principal values (principal refractive indices) are nonidentical in general. In the case of usual fiber, one of principal axes is put parallel to the fiber axis and the others are indistinguishable because of a rotational symmetry. Birefringence (Δn) is defined as the difference between the refractive index parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the fiber axis.

Δn is the summation of 1) orientational birefringence (Δn_{orr}) based on the preferred orientation caused by the stress in a spinning or drawing, 2) form birefringence based on the shape of crystallites and voids, and 3) induced birefringence temporary originated by outer forces. Molecular orientation factor (f) is defined by Eq.1

$$f = \Delta n_{\text{orr}} / \Delta n^0 \quad (1)$$

where Δn^0 is the birefringence owing to fully extended chains along the orientation axis and is called intrinsic birefringence. For usual fibers, the birefringence almost equals to Δn_{orr} in the equation (1), therefore it is used for a simple, easy and precisional measuring method of molecular orientation f , which can be calculated using Eq.2

$$f = \Delta n / \Delta n^0 \quad (2)$$

According to Bunn[1], Δn^0 can be estimated theoretically using bond polarizabilities and results of crystal structure analyses. Δn^0 also can be estimated by the ex-

trapolation of experimental data. Δn^0 of typical polymers are collected in some literatures [2,3]. However, there are no reports for the Δn^0 of poly(butylene terephthalate) (PBT).

Two crystal forms have been reported for PBT [4]; α form crystal formed by annealing under relaxed state, and β form crystal rearranged reversibly from the α form with stretching along the chain axis. Mencik [5] analysed the α form crystal structure, and Yokouchi et al. [6] and Hall & Pass [7] analyzed for both the α and β form crystals. Stambaugh et al. [8] discussed about a tilt angle, an inclination of the chain axis from orientation axis for the α form crystal. Grasso et al. [9] independently analysed the β form crystal with consideration of the tilt angle and obtained the crystal structure which close to that of Hall & Pass. Desborough & Hall [10] and Hall [11] compared the crystal structures reported, and noted that results for the β form crystal are not identical each other, whereas every structure data for the α form crystal is almost identical, and Hall & Pass's structure fits with the experimental results very much.

In this study, Δn^0 was estimated using Bunn's method for the crystal structure of PBT analysed by Hall & Pass, and was compared with experimental results and results obtains by the other structures.

2. Theory

There is the well-known Lorentz-Lorenz formula 3 for the refractive index (n) of isotropic materials,

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2} \quad (3)$$

where α , and N mean polarizability, and a number of atoms per unit volume, respectively. If α is defined as a summation of polarizabilities in the unit cell, N will equal to the reciprocal of the unit cell volume, and will be proportional to the crystal density. Eq. 3 induced originally for isotropic material can be extend to anisotropic material using diagonal components of second order tensor α_{ij} which can be calculated by Eq. 4

$$\alpha_{ij} = \sum_k (P_{Lk} - P_{Tk}) \cos \phi_{ik} \cos \phi_{jk} + P_{Tk} I_{ij} \tag{4}$$

where P_L and P_T are bond polarizabilities parallel and perpendicular to each covalent bond (k) axis, i and j indicate components of orthogonal coordinate (X, Y, Z), ϕ is an angle between coordinate axis and bond axis, and I_{ij} is unit tensor. The values P_L and P_T are listed in Table 1, and the angle ϕ is calculated from atomic coordinate. Polarizabilities are summed up for all covalent bonds in the unit cell. It is convenient to use orthogonal coordinate to replace the original crystal coordinate, because both the α and β form crystal systems of PBT crystal are triclinic. We define that Y and Z axes coincide with crystallographic b^* and c axis (chain axis). Therefore X axis is put in the ac plane and is perpendicular to the c axis.

Table 1 Bond Polarizabilities[1]

	$P_L \times 10^{31}/m^3$	$P_T \times 10^{31}/m^3$
$C_a - C_a^{*1}$	22.5	4.8
$C_a - C$	14.0	3.0
$C - H$	8.2	6.0
$C = O$	20.0	10.0
$C - O$	14.6	1.7
$C - C$	9.7	2.6

*1 C_a : Aromatic Carbon

Principal refractive indices are obtained by substituting eigenvalues of polarizability tensor in Eq. 3, and are expressed n_1, n_2 , and n_3 in ascending order. The corresponding eigenvectors are expressed V_1, V_2 , and V_3 . Average refractive indices can be determined by average polarizabilities obtained by Eq. 5 led from Eq. 4.

$$\sum_k (P_{Lk} + P_{Tk}) / 3 \tag{5}$$

Intrinsic birefringence for c axis orientation (Δn_c) and for V_3 axis orientation (Δn_p), which means the maximum value of intrinsic birefringence, are also determined by Eqs. 6 and 7

$$\Delta n_c = n_z - (n_x + n_y) / 2 \tag{6}$$

$$\Delta n_p = n_3 - (n_1 + n_2) / 2 \tag{7}$$

Table 2 Structural Parameters[7]

	α	β
$a/\text{\AA}$	4.89	4.69
$b/\text{\AA}$	5.95	5.80
$c/\text{\AA}$	11.67	13.00
α/deg	98.0	101.9
β/deg	116.6	120.5
γ/deg	110.0	105.0
$\rho \cdot \text{cm}^3/\text{g}$	1.367	1.359
α_8/deg	119.0	126.1
α_9/deg	105.1	111.1
α_{10}/deg	112.9	112.6
τ_1/deg	179.3	171.3
τ_2/deg	-177.8	-175.3
τ_3/deg	-94.5	-157.1
τ_4/deg	-79.3	144.4
θ/deg	4.4	17.8

3. Results and Discussion

Hall and Pass reported four variations of the chain conformation for the α form crystal and two variations for the β form crystal by slightly arranging initial model. Table 2 lists the conformations having the least R factor values in obtained conformations. Figure 1 illustrates the notation of each symbols, and bond lengths and bond angles common to two crystal forms. θ is the rotation angle of the chain around the chain axis, and is defined zero when phenylene normal is put in the ac plane. If the rotation from the ac plane to the phenylene normal is anticlockwise looking in the negative c direction, θ will be positive. Figure 2 illustrates the chain conformations of the α and β form crystals used in this study. Terephthalate residue is almost planar for both crystal forms. Therefore conformation mainly depends on rotation angles of butylene residue. There is a turn of chain direction between the butylene and terephthanoyl residue for the α form crystal having gauche like conformations (Fig. 2-B), whereas the chain in the β form crystal is almost linear because of every trans conformations. As mentioned above, however, the conformation in β form crystals change widely, perhaps causing by crystal form

unstability. Especially the chain conformation analysed by Yokouchi et al. is somewhat nonlinear, because the value -113° for τ_4 is comparatively small.

Refractive indices and (X, Y, Z) components of eigenvectors, which are calculated using the conformation in Table 2, are listed in Tables 3 and 4, respectively. The eigenvectors are also illustrated in Fig. 2. The direction of each V_1 is almost parallel to phenylene normal. The Δn_p equal to the Δn_c for the β form crystal whose V_3 direction is almost parallel to the c axis.

Table 5 lists intrinsic birefringences calculated for each the reported structures. Variation of the results for the α form crystal is comparatively small as variation of the structure data. The results for Mencik's data is relatively large. This is probably caused by larger crystal density (1.41 g/cm^3) than the value of Table 2. Whereas the results for the β form conformation analysed by Yokouchi is relatively small. This is caused by smaller crystal density (1.28 g/cm^3) and nonlinearity of chain described above.

There are many researches reported on Δn_c of PET (poly(ethylene terephthalate)). The most of them ranges from 0.22 to 0.23 [2,3]. The conformation of the ethylene residue is almost trans form as well as the butylene residue of the β form PBT crystal. Therefore the slight difference of Δn_c between β form PBT and PET is explained by smaller polarizability anisotropy of methylene fraction than phenylene residue.

The maximum value 0.155 has been reported for Δn of high-speed spun PBT fiber [12] having the α form crystal, whereas Δn for the fibrous sample analysed by

Table 3 Calculated Refractive Indices

	α	β
n_x	1.435	1.432
n_y	1.714	1.668
$n_z (n_c)$	1.728	1.765
n_a	1.558	1.533
n_b	1.658	1.707
n_1	1.411	1.398
n_2	1.713	1.708
n_3	1.760	1.768
$\bar{n}$	1.619	1.614
Δn_c	0.153	0.215
Δn_p	0.198	0.215

Table 4 Calculated Components of Eigenvectors

	α			β		
	V_1	V_2	V_3	V_1	V_2	V_3
X	0.960	0.127	-0.250	0.937	0.343	-0.062
Y	-0.064	0.967	0.245	-0.340	0.938	0.063
Z	0.273	-0.220	0.937	0.080	0.038	0.996

Table 5 Calculated Intrinsic Birefringences

		Mencik [5]	Yokouchi [6]	Hall & Pass [7]
α	Δn_c	0.168	0.153	0.152-0.153
	Δn_p	0.208	0.209	0.197-0.198
β	Δn_c		0.171	0.209-0.215
	Δn_p		0.182	0.210-0.215

Fig. 2 Projection of chain in α form (A, B) and β form (C, D) poly(butylene terephthalate) crystals onto b^*c (A, C) and ac (B, D) planes. Principal directions of refractive index ellipsoids are also illustrated.

Hall & Pass is 0.183 ± 0.007 , which is larger than Δn_c calculated for the α form crystal, and is unreasonable. This larger value seems to be due to the form birefringence added to the high orientational birefringence caused by highly drawing and long time annealing under tension, and also a possibility that the ratio of trans conformation in the amorphous phase exceeds that of the crystalline phase. Furthermore, the effect of tilting c axis from orientation axis to V_3 direction should be small, because the reported tilt angle ranging from 1.5 to 3.5° [7-9] is smaller than the angle between c axis and V_3 about 24° , and some errors originate probably from assumption in this work, such as separating polarizabilities to each covalent bonds without surrounding effects and extending Eq. 2 to anisotropic materials. Experimental approach with attention to the form birefringence and the contribution of amorphous phase should be needed for more precise intrinsic birefringence values.

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