Thermal Expansion of a 60 mol% *para*-Hydroxybenzoic Acid/40 mol% Ethylene Terephthalate Liquid Crystalline Copolyester Oriented in a Magnetic Field

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ABSTRACT: The thermal expansion is investigated for a 60 mol% *para*-hydroxybenzoic acid/40 mol% ethylene terephthalate liquid crystalline copolyester oriented in a magnetic field (6T). The high-temperature expansion coefficient of the oriented samples shows an anisotropy; it is negative (shrink) to the orientation direction, while it is positive (expand) to the direction perpendicular to the orientation. The X-ray diffraction measurement indicates that the positive expansion coefficient is attributed to the increase in the mean spacing of the oriented chains.

KEY WORDS Thermal Expansion / Magnetic Orientation / Liquid Crystals / Poly(ethylene terephthalate-*co*-*p*-oxybenzoate) / Thermotropic Copolyester /

Thermotropic liquid crystalline copolyesters¹ provide high-strength materials when they are oriented. The molecular orientation of these polymers is usually attained by the external forces such as shear and elongation stresses applied through the extrusion or molding processes. These forces, however, do not apply homogeneously throughout a sample, resulting in imperfect orientations, even in a skin-core structure in the case of shear.² A magnetic field is an alternative for attaining molecular orientations.^{3–5} This is due to the diamagnetic anisotropy of the backbone structure of the polymers and to the propensity of these polymers to form mesophase. A number of studies have been reported on the kinetics of orientation,^{6–8} and the structures⁹ and properties^{10,11} of the oriented samples. Though the induction speed of magnetic orientation is crucial in an actual application, a magnetic field may provide an additional means of orientation in the processing of thermotropic liquid crystalline copolyesters.

Several studies have been reported on the thermal properties of thermotropic liquid crystalline copolyesters^{1,12–14} and other liquid crystalline polymers.^{15–17} In this study we report the thermal expansion, at higher temperatures, of a 60 mol% *para*-hydroxybenzoic acid/40 mol% ethylene terephthalate liquid crystalline copolyester (PHB/PET) oriented in a magnetic field (6T). The result is discussed in terms of the aggregate model in comparison to the study¹³ with a different orientation method and with lower temperatures. In addition, the microscopic thermal expansion is measured by the X-ray technique and compared with the macroscopic one.

EXPERIMENTAL

Material

PHB/PET used in this study was a Unitika copolyester, Rodrun LC-3000; the nominal molecular weight is several thousands.¹⁸ Unoriented films were prepared as follows:

pellets as received were dried under a vacuum at 80°C for 5 h, hot-pressed at 220°C for 5 min, and quenched immediately in ice water followed by a vacuum dry for more than 24 h.

Oriented Samples

An unoriented film (15 mm × 60 mm × 50 μm) was placed between polyimide sheets (50 μm), with a polyimide frame of the same thickness inserted as a spacer, and then was put between two copper plates and screwed tightly. The pair of copper plates were hung in a glass cylinder (diameter of *ca.* 80 mm) equipped with a heater and a thermocouple under the atmosphere of nitrogen gas. The whole glass cylinder was inserted in a superconducting magnet (6T). Since the orientation speed is dependent on the temperature and the time of heat treatment,⁸ samples with various orientations were prepared by varying these factors: heat-treatment temperatures between 235 and 245°C and the heat-treatment time of 30 or 60 min. The samples were slowly cooled in the magnet. The oriented samples were subjected to the X-ray measurements for the determination of the degree of orientation prior to the thermal mechanical analysis.

Thermal Mechanical Analysis

Thermal expansion was measured by a Seiko TMA/SS 100 system. Measurements with applied loads of 0.1 g and 1 g were carried out for unoriented and highly oriented samples to check the effect of elongation due to the load. Since no significant effects were observed, a 0.1 g load was chosen for all the measurements. A specimen was heated up to 160°C with a heating rate of 5°C min⁻¹ followed by a cooling down to 50°C with the same rate, then it was heated again up to 160°C (second heating). Thermal expansion was determined using the slope between 60 and 160°C of the second heating data.

X-ray Measurements

A MAC Science MXP was used for X-ray

measurements. A broad equatorial peak about $2\theta \cong 20^\circ$ was used to monitor the change in chain spacing over the temperature range between 20 and 170°C. The degree of orientation was estimated by the equation $f = (180^\circ - H)/180^\circ$ where H is the half width of the azimuthal distribution.

RESULTS AND DISCUSSION

Negative thermal expansion in the direction of chain orientation is common in highly oriented polymers including polyethylene,^{19,20} polyoxymethylene,¹⁹ polypropylene,^{19,21} aromatic polyamides,^{15,16} and thermotropic liquid crystalline copolyesters.¹²⁻¹⁴ Below the transition temperature, the expansion is of the order of -10^{-5} K⁻¹ or less, irrespective of polymers. Intrinsic value of $\alpha_{\parallel}$ for PHB/PET obtained as the limit of high orientation by the mechanical process has been reported to be -10^{-5} K⁻¹ for the temperature range between -20 and 20°C.¹³ Negative thermal expansion of the direction of fiber axis in crystalline phase is also reported.^{22,23}

In Figure 1, the thermal expansions parallel and perpendicular to the orientation direction, $\alpha_{\parallel}$ and $\alpha_{\perp}$, respectively, are plotted against the degree of orientation. $\alpha_{\parallel}$ at high degree of orientation shows large negative value which is almost one order higher than the reported expansions.¹³ This is probably due to the temperature range employed in our study (60 to 160°C which falls between the glass transition temperature, *ca.* 58°C and the temperature, *ca.* 197°C, of the main DSC peak). Thermal analyses carried out on a series of *para*-hydroxybenzoic acid/ethylene terephthalate copolyesters indicate the glass transition temperature around 80°C,²⁴ which, according to the NMR,²⁵ dielectric,²⁶ and dynamic mechanical²⁷ studies, might be associated with the onset of rotational motions of the ethylene units. Above the transition temperature, the absolute values of thermal expansions increase rapidly because the expan-

sion is dominated by the rubbery nature of polymer.¹⁹ The level of -10^{-4} K^{-1} at the high degree of orientation in the present study seems still too high compared to the thermal expansion of a number of mechanically oriented thermotropic liquid crystalline copolyesters measured above their transition temperatures.¹⁴ The reason for the discrepancy is not yet clear at present, but possibly attributed to the uniform and high orientation attained by magnetic field.

The aggregate model²⁸ has been used for describing physical properties of amorphous polymers. According to this model, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are linear functions of the degree of orientation f :

$$\alpha_{\parallel} = \frac{1}{3}(a_{\parallel} + 2a_{\perp}) - \frac{2}{3}(a_{\perp} - a_{\parallel})f,$$

$$\alpha_{\perp} = \frac{1}{3}(a_{\parallel} + 2a_{\perp}) + \frac{1}{3}(a_{\perp} - a_{\parallel})f$$

with $a_{\parallel}$ and $a_{\perp}$ being the intrinsic thermal expansions parallel and perpendicular to the chain direction. f is related to the average of $\cos^2 \theta$:

$$f = (3\langle \cos^2 \theta \rangle - 1)/2,$$

where θ is the angle between the orientation direction and the chain direction. The degree of orientation determined in this study by using

Figure 1. Thermal expansions $\alpha_{\parallel}$ and $\alpha_{\perp}$ plotted against the degree of orientation. Two data points indicate that the measurement was done for two specimens.

the azimuthal distribution is an equivalence of f . Looking at Figure 1 from the view point of the aggregation model, we find that our results fit the model with respect to the linear dependence of $\alpha_{\parallel}$ and $\alpha_{\perp}$ on f , but do not with respect to the relation of slopes for $\alpha_{\parallel}$ and $\alpha_{\perp}$: here $2|\alpha_{\parallel}| = |\alpha_{\perp}|$, while $|\alpha_{\parallel}| = 2|\alpha_{\perp}|$ if the model holds.

Takeuchi *et al.*¹³ showed in their study on the thermal and mechanical properties of PHB/PET oriented mechanically by shear and elongation that the relation between the thermal expansion and the Young's modulus is reasonably explained by the aggregate model. The discrepancy between their results and ours is likely attributed again to the temperatures employed in the measurements: their measurement was done below the transition temperature while ours was above it. The orientation method may also be a reason for the discrepancy.

X-ray diffraction of mesophase gives a broad equatorial peak corresponding to the mean spacing of molecules.²⁹ Since the peak around $2\theta \cong 20^\circ$ of PHB/PET is close to the (220) reflection of the crystal of PHB homopolymer,³⁰ this peak might indicate the lateral spacing probably due to PHB-rich regions in the mesophase. In Figure 2, the molecular spacing is plotted against the temperature both for the oriented and unoriented samples. Two curves are almost identical. The thermal expansion estimated by

Figure 2. Temperature dependence of molecular spacing for the oriented and unoriented samples. Data for the unoriented sample are shifted downward by 0.2 for the clarity.

the slope is about $18 \times 10^{-5} \text{ K}^{-1}$, very close to the macroscopic expansion of $\alpha_{\perp}$ observed at high degree of orientation. The lateral macroscopic expansion is therefore attributed to the increase in molecular spacing between mesogen groups; in the intermediate degree of orientations, the lateral macroscopic expansion is partially canceled by the axial shrinkage.

Since the order of $\alpha_{\perp}$ is same as that for oriented flexible polymers above their glass transitions,^{19,20} the ethylene unit fluctuation appears primarily responsible for the lateral expansion. In contrast to the case of axial expansion, the fluctuation of phenylene groups about the chain axis might also contribute to the lateral expansion³¹; even rigid polymers such as polyamides have the $\alpha_{\perp}$ of 4.7 to $12.0 \times 10^{-5} \text{ K}^{-1}$.¹⁵ In addition, the motion of phenylene groups might be enhanced by more mobile ethylene units.

The analyses are in progress on detailed structures and physical properties of PHB/PET to elucidate the effect of the magnetic field and will be reported elsewhere.

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