# Intrinsic Values of the Linear Expansion Coefficient for Nematic Poly(ethylene terephthalate)/*p*-Oxybenzoate Copolyester

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ABSTRACT: Intrinsic values of the linear expansion coefficient for a nematic copolyester are estimated with an aggregate structure model. Thermotropic nematic copolyester rods consisting of 40 mol % poly(ethylene terephthalate) (PET) and 60 mol % *p*-oxybenzoate (POB) were extruded at 220 °C, with widely differing molecular orientation induced by both shear and elongational stresses. Young's modulus of the extruded rod increased from 3.3 to 35 GPa, and the thermal expansion coefficient in the extruded direction decreased drastically during the early stage from $2.2 \times 10^{-5}$ deg$^{-1}$ to negative values and then leveled off at ca. $-6 \times 10^{-6}$ deg$^{-1}$. The physical and mechanical properties of the oriented PET/POB copolyester were analyzed with an aggregate model. The analysis reveals that the linear expansion coefficient changed linearly with the reciprocal of Young's modulus. The intrinsic values of the expansion coefficient for PET/POB copolyester parallel and perpendicular to the molecular axis are estimated to be $-1.0 \times 10^{-5}$ deg$^{-1}$ and $7.7 \times 10^{-5}$ deg$^{-1}$, respectively.

## Introduction

Thermotropic liquid crystal polyesters (LCP) have been investigated as high-strength, high Young's modulus materials.[1,2] Their superior mechanical and thermal properties are due to the molecular orientations induced by shear stresses and elongational stresses applied when they are extruded or molded.[3] These property changes, which are due to LCP molecular orientations, are similar to those for crystalline and amorphous polymers. However, in spite of detailed studies concerning the molecular orientation of the crystalline and amorphous polymers,[4,5] there are few reports concerning the degree of molecular orientation for LCP,[6-8] and there is no report analyzing physical property changes due to molecular orientation with an appropriate structure model.

This paper is concerned with the relationship between Young's modulus and the linear expansion coefficient over a wide range of molecular orientations for a nematic copolyester consisting of 40 mol % poly(ethylene terephthalate) (PET) and 60 mol % *p*-oxybenzoate (POB). It is analyzed by the aggregate model, and the linear expansion coefficients for the intrinsic unit are estimated.

## Experimental Section

**Material.** The material used was a copolyester consisting of 40 mol % PET and 60 mol % POB with an inherent viscosity of 0.67 dL g$^{-1}$.

**Rod Preparation.** PET/POB copolyester rods were extruded at 220 °C with a capillary 1.0 mm in diameter and 5.0 mm in length by using a Toyo Seiki Capillograph. Two series of rods were extruded under these conditions. One series was extruded with shear rates of 6.5–$6.5 \times 10^3$ s$^{-1}$ without elongational deformation. The other series was extruded at a constant shear rate of 122 s$^{-1}$ with elongational deformation ratios of 2.2, 3.3, 11, and 44. All the extruded rods were quenched immediately in water.

**Properties.** The dynamic moduli of the extruded rods were measured with a Toyo Baldwin Rheovibron DDV-3-EA at 3.5 Hz with sample lengths of 5 cm. Thermal linear expansions in the extruded direction were measured in the temperature range from −100 to +100 °C with a heating rate of 2 °C/min while applying appropriate tensions. A silica glass sample holder was used. The sample lengths were 2 cm. Linear expansion coefficients were determined by averaging the values in the temperature range from −20 to +20 °C, which is well below the glass transition temperature of the rod samples.[9]

## Results

**Shear-Induced Orientation.** The dynamic modulus of the extruded rods at various shear rates without elongational deformation increased linearly with the logarithm of the increasing shear rate from 3.3 to 11.1 GPa in the shear rate range from 6.5 to $6.5 \times 10^3$ s$^{-1}$ (Figure 1). The value of 3.3 GPa is very close to that of isotropic PET/POB copolyester (2.0 GPa)[1]. The highest values of 11.1 GPa is still smaller than those of extruded PET/POB fibers under ordinary conditions,[3] even though the shear rate was increased 3 orders in magnitude.

Figure 2 shows the change in the linear expansion coefficient with increasing shear rate for the same PET/POB copolyester rods. The linear expansion coefficient decreased drastically from $2.2 \times 10^{-5}$ to "0" deg$^{-1}$ in the shear rate range from 6.5 to $6.5 \times 10^3$ s$^{-1}$ in spite of only a small change in the dynamic modulus.

**Deformation-Induced Orientation.** The dynamic modulus of the rods extruded with elongational deformation also increased almost linearly with the logarithm of the increasing elongational deformation ratio and reached 34.5 GPa at an elongational deformation ratio of 44 (Figure 3). This is greater than for the rods extruded without elongational deformation. It shows that elongational stress is more effective for molecular orientation of LCP than shear stress because the elongational stress is applied uniformly in the rod's radial direction, while the shear stress is applied only in the surface region of the rods.[10]

Figure 4 shows the change in the linear expansion coefficient with increasing elongational deformation ratio for this series of rods. They were negative and reached $-6 \times 10^{-6}$ deg$^{-1}$ at an elongational deformation ratio of 44. Their change was small compared with that of the rods extruded without deformation in spite of the large increase in dynamic modulus. These changes are similar to those in oriented crystalline and amorphous polymers.[5,11,12]

## Discussion

**Aggregate Model for Nematic LCP.** The morphology of an oriented nematic LCP is similar to that of oriented amorphous polymers but not similar to that of oriented crystalline polymers. That is, PET/POB copolyesters exhibit no crystalline reflection on wide-angle X-ray diffraction measurements and exhibit only broad reflections similar to amorphous polymers even in highly oriented states. In amorphous polymers, it is said that molecular bundles exist. This concept makes it possible to apply an aggregate model to the mechanical and structural studies in oriented amorphous polymers. On the other hand, in a nematic LCP also there exist domains with aligned molecules,[13] similar to the molecular bundles in amorphous polymers. Therefore, we adapted the aggregate model

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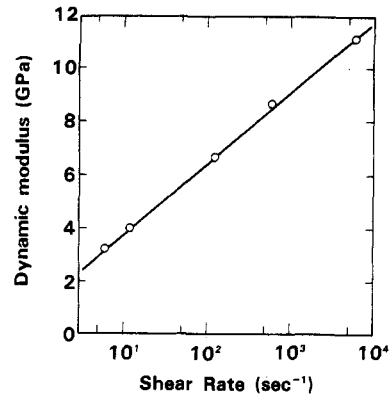


**Figure 1.** Dynamic modulus change with shear rate for extruded rods without elongational deformation.

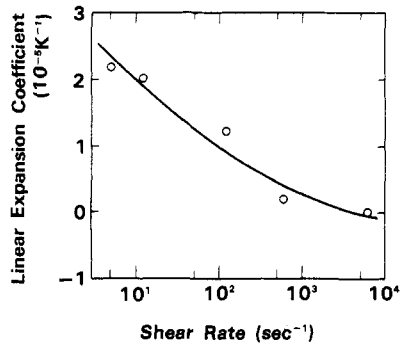


**Figure 2.** Linear expansion coefficient change with shear rate for extruded rods without elongational deformation.

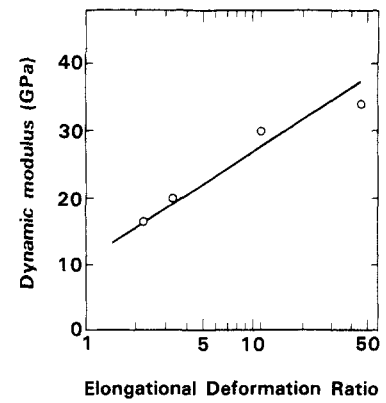


**Figure 3.** Dynamic modulus change with elongational deformation ratio. Shear rate for the extrusion was 122 $s^{-1}$.

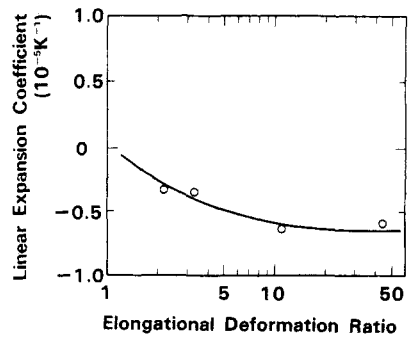


**Figure 4.** Linear expansion coefficient change with elongational deformation ratio. Shear rate for the extrusion was 122 $s^{-1}$.

commonly used for oriented amorphous polymers[14] as the macroscopic structure model for nematic LCP. This model is a one-phase model similar to a paracrystalline model adopted to aramid fibers.[15]

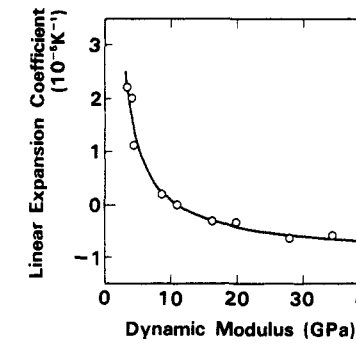


**Figure 5.** Relationship between the linear expansion coefficient and the dynamic modulus.

The orientation function, $f_L$, which denotes the averaged value for the degree of molecular orientation over the aggregate, is defined by

$$f_L = (3\overline{\cos^2\theta} - 1)/2 \quad (1)$$

where $\theta$ is the angle between the extruded direction and the symmetry of the intrinsic unit and the bar denotes the average over the aggregate.

The linear expansion coefficients of oriented nematic LCP can be calculated by using either the series model or the parallel model. In the series model, uniform stress is assumed throughout the aggregate as a first approximation, while uniform strain can be assumed in the parallel model. In the series model, Young's modulus, $E$, and the linear expansion coefficient, $\alpha$, in the extruded direction are given by

$$1/E = (1 - f_L)/E_0 + f_L/E_\parallel \quad (2)$$

$$\alpha = (1 - f_L)\alpha_0 + f_L\alpha_\parallel \quad (3)$$

where $E_0$ and $\alpha_0$ are Young's modulus and the linear expansion coefficient for the isotropic material, respectively. $E_\parallel$ and $\alpha_\parallel$ are the same values for the intrinsic unit parallel to the molecular axis. The linear expansion coefficient, $\alpha_\perp$, of the intrinsic unit perpendicular to the molecular axis is given by

$$\alpha_\perp = (3\alpha_0 - \alpha_\parallel)/2 \quad (4)$$

From eq 2, $f_L$ is denoted as

$$f_L = (E_\parallel/E)(E - E_0)/(E_\parallel - E_0)$$

With $E_\parallel \gg E_0$, $E_\parallel - E_0$ can be reduced to $E_\parallel$, and this expression can be simplified to

$$f_L = 1 - E_0/E \quad (5)$$

Equation 5 shows that dynamic moduli can be used as parameters of the degree of molecular orientation. From eq 3 and 5, the relation between the linear expansion coefficient and Young's modulus is given by

$$\alpha = \alpha_\parallel + (\alpha_0 - \alpha_\parallel)E_0/E \quad (6)$$

In a similar way, the relationship between the linear expansion coefficient and Young's modulus for the parallel model can be given by assuming $E_\parallel \gg E_0$ and $|\alpha_\parallel E_\parallel| \gg |\alpha_0 E_0|$. The same equation with eq 6 is given in the parallel model, too. Here the relation between $f_L$ and $E$ is given by

$$f_L = (E - E_0)/E \quad (7)$$

Therefore, it can be said that eq 6 holds generally in the aggregate model both when assuming the series connection and when assuming the parallel connection of the aggregate.

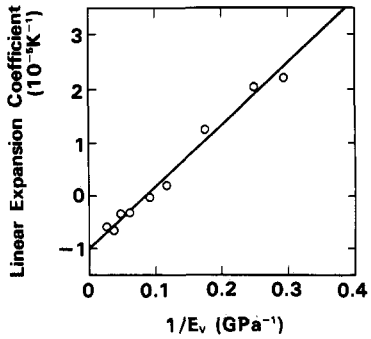


**Figure 6.** Linear expansion coefficient vs. the reciprocal of dynamic modulus.

**Relationship between the Linear Expansion Coefficient and the Dynamic Modulus.** The orientation properties of the PET/POB copolyester were analyzed by using extruded rods exhibiting a wide range of dynamic modulus from 3.3 to 34.5 GPa. Figure 5 shows the relationship between the linear expansion coefficient and the dynamic modulus for the two series of extruded rods (Figures 1–4). The linear expansion coefficient decreased drastically during the early stage and then leveled off to a negative value on the order of $-10^{-6}$ deg$^{-1}$. This change is similar to that for such oriented crystalline and amorphous polymers as polyethylene, poly(oxymethylene), polypropylene, and poly(ethylene terephthalate),[5] in spite of their structural differences.

For oriented crystalline and amorphous polymers, the limiting negative value of the linear expansion coefficient is explained by thermal vibration of molecular chains using chain models.[5] The linear expansion coefficient for an aramid fiber (Kevlar)—a lyotropic liquid crystal polymer—is also negative and similar in order.[16] From these results, the limiting value of the linear expansion coefficient for all these polymers is thought to be determined by the thermal property of the chain segment[17,18] and to not depend on their morphological structure. Accordingly, the limiting values of the linear expansion coefficients for the PET/POB copolyester can be estimated.

Figure 6 shows the relationship between linear expansion coefficient, $\alpha$, and the reciprocal of the dynamic modulus, $E_v$, for extruded PET/POB rods. The value of $\alpha$ changes linearly with $1/E_v$, as predicted theoretically by eq 6. This result supports the adaptation of the aggregate model for oriented PET/POB copolyester. Figure 6 can be expressed as

$$\alpha = -1.0 \times 10^{-5} + (11.6/E_v) \times 10^{-5} \quad (\text{deg}^{-1}, \text{GPa}) \quad (8)$$

When the value of the dynamic modulus, is input for the isotropic PET/POB copolyester ($E_0$ = 2.0 GPa) in eq 8, the value of $\alpha_0$ can be determined

$$\alpha_0 = 4.8 \times 10^{-5} \text{ deg}^{-1} \quad (9)$$

The value of $\alpha_\parallel$, therefore, is determined

$$\alpha_\parallel = -1.0 \times 10^{-5} \text{ deg}^{-1} \quad (10)$$

With eq 9 and 10, eq 4 can be rewritten

$$\alpha_\perp = 7.7 \times 10^{-5} \text{ deg}^{-1} \quad (11)$$

These values are on the same order as those for crystalline polymers.[5,17] Therefore, it seems that the ultimate value of the linear expansion coefficient for the PET/POB copolyester's intrinsic unit parallel to the molecular axis is also determined by the thermal vibration of the chain segment.

## Conclusions

PET/POB copolyester rods exhibiting Young's moduli from 3.3 to 34.5 GPa were made by shear- and elongation-induced molecular orientations. The linear expansion coefficient decreased drastically from $2.2 \times 10^{-5}$ deg$^{-1}$ and leveled off at ca. $-6 \times 10^{-6}$ deg$^{-1}$. The expansion coefficient changed linearly with the reciprocal of Young's modulus. This result is explained with the aggregate model by assuming both series connection and parallel connection of the aggregate. The intrinsic values of the expansion coefficient for the PET/POB copolyester parallel and perpendicular to the molecular axis are estimated to be $-1.0 \times 10^{-5}$ and $7.7 \times 10^{-5}$ deg$^{-1}$, respectively.

**Acknowledgment.** We thank Sinzo Yamakawa for his encouragement throughout the work. Thanks are also due to Takashi Uetake for his help with the extrusion experiment.

**Registry No.** (Ethylene glycol)·(4-hydroxybenzoic acid)·(terephthalic acid) (copolymer), 25822-54-2.

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