SHORT COMMUNICATIONS

Shear-Induced Orientation of a Liquid Crystal Copolyester

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It is well known that thermotropic liquid crystal copolyesters exhibit high Young's modulus and low linear expansion coefficients.[1,2] These superior properties result from shear- and/or deformation-induced molecular orientations.[2-4] Injection-molding[1] of the polymer is the main cause of shear-induced molecular orientation in the direction of the polymer melt flow, since the modulus in the direction of the flow increases with decreasing sample thickness. Melt-spinning[2] of the polymer is primarily responsible for deformation-induced molecular orientation, in that the axial modulus increases with increasing spinning rate. The relationship between molecular orientation and material properties, however, has been clarified only qualitatively.

This paper discusses the shear-induced orientation of a liquid crystal copolyester during extrusion through a capillary viscometer. The molecular orientation of extrudates as determined by X-ray diffraction is quantitatively related to both Young's modulus and the thermal linear expansion coefficient.

The material used was a well-known nematic copolyester[1] consisting of 60 mol% *p*-oxybenzoate (POB) and 40 mol% poly-(ethylene telephthalate) (PET) segment. The inherent viscosity was 0.39 dl g^{-1}. Rod samples were extruded with a capillary viscom-eter at various shear rates and 240°C where there was no draw down of the extruded rods. That is, molecular orientation resulted from shear induced by the capillary wall. The capillary diameter was 0.5 mm.

Figure 1 shows X-ray diffraction patterns taken with the beam perpendicular to the rod axes at room temperature for a series of extruded rods. The very strong reflection splits into two crescents on the equator with increasing shear rate. Reflection patterns of high shear rates are typical of an oriented nematic mesophase and the equatorial peak is mainly due to intermolecular scattering.[5] The reflection pattern observed by the equatorial scan was broad with an acute top, although it differs from the crystalline reflection[4,6] with a clearly separated amorphous background. The Bragg reflection angle ($2\theta = ca.$ 20.0°) of the equatorial peak is very close to the (220) reflection angle ($2\theta = 19.9°$) of pure POB crystal.[7]

Figure 2 shows the shear rate dependence of the orientation function $\langle P_2 \rangle = (3\langle \cos^2 \alpha \rangle - 1)/2$, determined by the azimuthal distribution of the equatorial peak, where α is the angle between the molecular axis and direction of the extrusion. The value of $\langle P_2 \rangle$ gradually increases from *ca.* 0.6 to *ca.* 0.8 with increasing shear rate, indicating that the strong orientation of the POB chain segment is in-
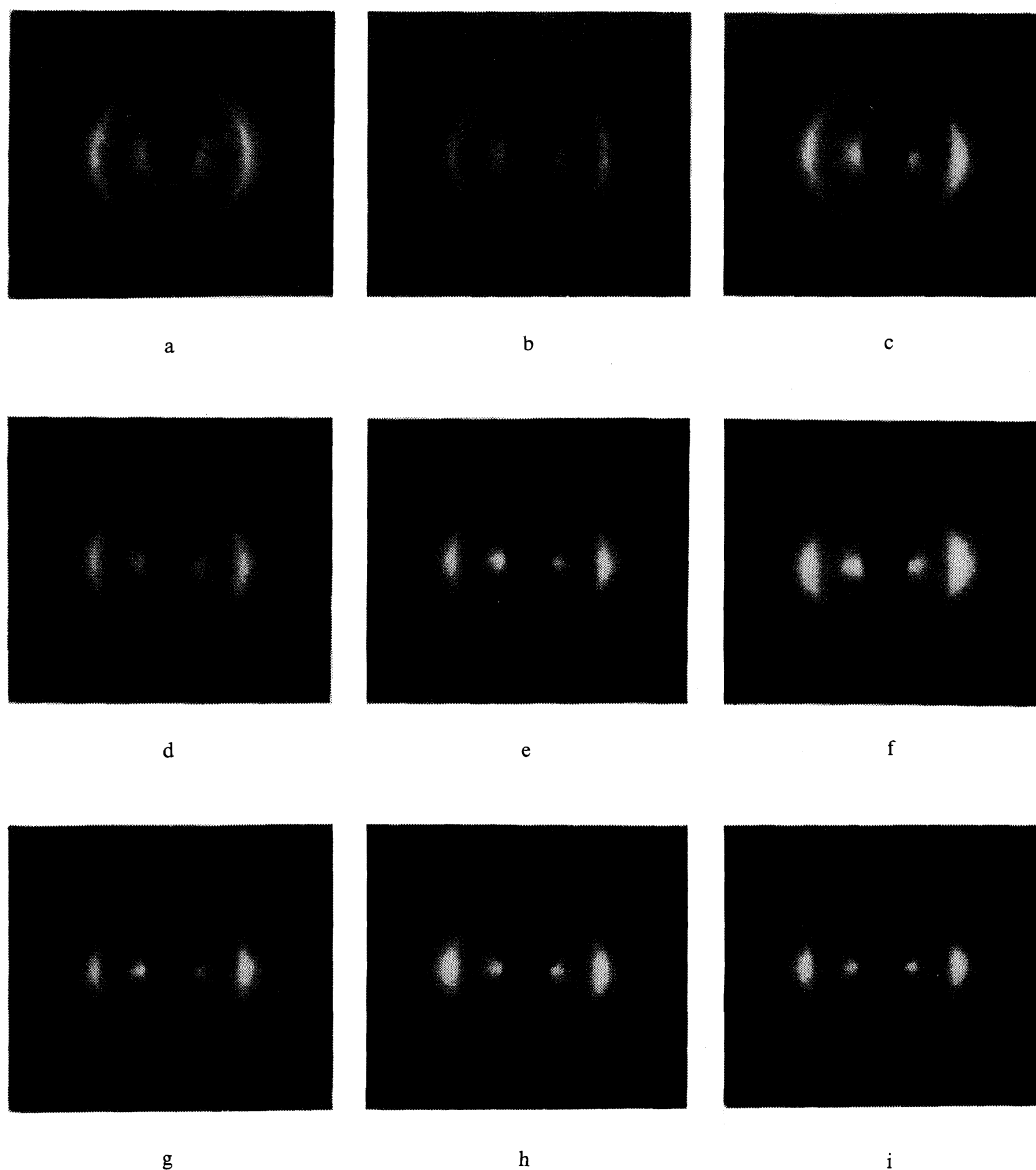
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Figure 1. X-Ray diffraction patterns for a series of oriented materials. Shear rates (s^{-1}): (a) 1×10^2; (b) 2×10^2; (c) 3×10^2; (d) 5×10^2; (e) 1×10^3; (f) 2×10^3; (g) 3×10^3; (h) 5×10^3; (i) 1×10^4. Ni-filtered Cu-K_α radiation; specimen-to-film distance 5 cm; extrusion direction vertical.

duced by shear stress at 240°C. A relatively intense orientation (*ca.* 0.6) was achieved at low shear rates.

Figure 3 shows Young's modulus of the extrudates plotted against the shear rate. The modulus increases monotonically from *ca.* 6 GPa to *ca.* 18 GPa with shear rate. This increase in modulus corresponds to the orientation of POB chain segments, as shown in Figure 2.

The linear expansion coefficient also decreased with increasing shear rate, leveling off
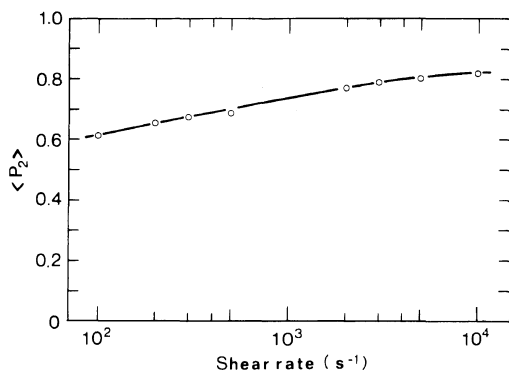
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Figure 2. The orientation function $\langle P_2 \rangle$ *vs.* shear rate. Azimuthal scan was made at $2\theta = 20.0°$.
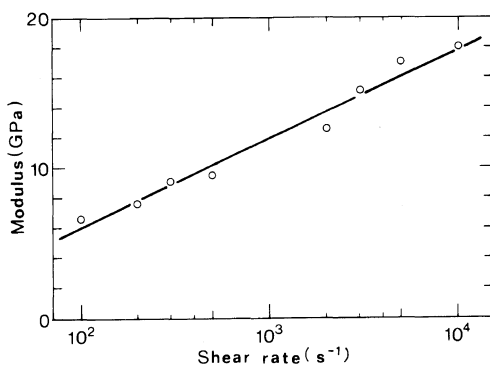

Figure 4. Thermal linear expansion coefficient *vs.* shear rate.

Figure 3. Young's modulus *vs.* shear rate.

increasing molecular orientation, Young's modulus increased, whereas thermal linear expansion coefficient decreased and leveled off at a value nearly equal to zero. The thermotropic liquid crystal copolyester with a low thermal linear expansion coefficient value has been investigated as a coating material[9] for optical fibers. By using low thermal linear expansion polymers for coating materials, fiber micro-bending loss due to contraction of the coating material at low temperatures can be greatly diminished.

$(\leq 1 \times 10^{-6}°C^{-1})$ at a shear rate of *ca.* $10^3\,s^{-1}$ (Figure 4). From Figures 2—4, the linear expansion coefficient is shown to be remaining unchanged in the shear rate range of 10^3—$10^4\,s^{-1}$, despite the increase in $\langle P_2 \rangle$ and the modulus. The changes in Young's modulus and linear expansion coefficient for shear rate are now not explicable, while similar changes have been observed for a highly drawn crystalline polymer,[8] these changes can be explained in terms of differences in crystalline and amorphous orientation behavior for the draw ratio.

The order of molecular orientation of the thermotropic liquid crystal copolyester was found to increase with increasing shear rate. X-ray analysis showed that the increase in molecular orientation to be due probably to the *p*-oxybenzoate segment alignment. With
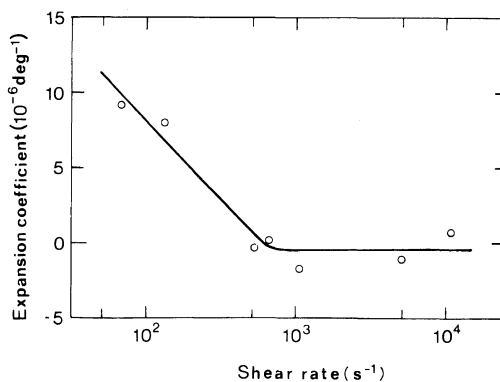
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