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Anomalous orientation of poly(trimethylene oxy-2 methyl trimethylene p–p' bibenzoate) as revealed by means of tensile tests

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Abstract

Poly(trimethylene oxy-2 methyl trimethylene p–p' bibenzoate) is a linear thermotropic liquid crystal polymer that may or may not develop anomalous orientation depending on the applied strain rate. X-ray diffraction patterns show that macromolecular chains tend to align perpendicularly to the deformation direction for the slowest analysed strain rates and in parallel to the deformation direction for the highest rates. The study of the strain–stress curves reveals that plastic deformation of this polymer can be controlled by two different microscopic mechanisms whose relative contributions to the overall strain are rate dependent. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermotropic polybibenzoates; Anomalous orientation

1. Introduction

Among the many reasons for the great technological interest in liquid crystal polymers, LCPs, their exceptional mechanical properties and their relative ease of processing must be emphasised. These two characteristics are intimately connected because the excellent mechanical behaviour of LCPs can only be achieved by means of the adequate molecular orientation that results from a correct processing. This is one of the motivations for researching the relationships between strain and anisotropy for this kind of material.

It has been reported that molecular chains of both liquid crystalline and non-liquid crystalline linear polymers tend to align parallel to the flow direction during the processing of the melt or parallel to the deformation direction when they are strained in the solid state. Chain orientation is a phenomenon unique to polymers that arises as a consequence of the strong direction dependency of the properties of the polymer chains. The nature of this feature and its relationship to mechanical properties of both kinds of polymer (liquid crystal and non-liquid crystal polymers) have been extensively analysed [1–5]. However, some exceptions to this general behaviour, which are identified by the term "anomalous orientation", have been found among linear thermotropic LCPs. It has been proved that chains can be aligned in a direction that is not parallel to the deformation direction when some polymers are processed under favourable conditions either by melt flow or by liquid crystalline state or solid-state straining [6–8]. The aim of this paper is to present some previous results about the development of anomalous orientation during the tensile deformation of a liquid crystalline poly-bibenzoate.

2. Experimental part

Poly(trimethylene oxy-2 methyl trimethylene p–p' bibenzoate), PTMTB, is an LCP that was synthesised by melt transesterification of diethyl p–p' bibenzoate with the corresponding ether diol whose formula is displayed in Fig. 1. It has been reported that PTMTB is able to develop a smectic phase of type S_{CA} [9].

Diffraction patterns were obtained at room temperature by using a flat-plate camera attached to a Philips 2-kW tube X-ray generator. Two different tensile testers were used for registering stress–strain curves and for orienting the samples, an Instron dynamometer for the highest strain rates and an MT2.05 Deben Microtest testing module for the lowest ones.

3. Results and discussion

Fig. 2 shows the stress–strain curves for PTMTB samples

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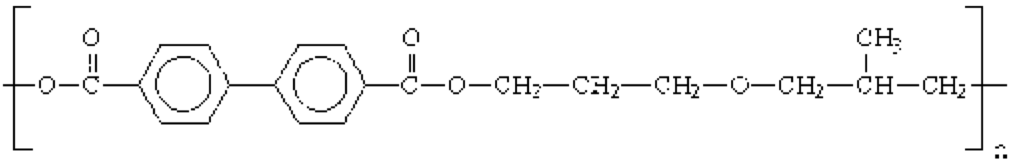

Fig. 1. Formula of poly(trimethylene oxy-2 methyl trimethylene p–p' bibenzoate), PTMTB.

that have been drawn with different rates and the corresponding X-ray diffraction patterns. The observation of these photographs clearly reveals that the increase of the deformation rate induces a drastic change in the geometry of the reflections. Depending on the draw conditions, layer reflections can appear on the equator, on the meridian or at both positions. For the highest studied deformation rate, the smectic layer reflection is concentrated on the meridian and the intermesogen reflection on the equator. This is the usual diffraction pattern for an oriented smectic polymer: the smectic layer normal, i.e. the chain axis, tends to align in a direction that is parallel to the fibre axis. The X-ray diffractogram that corresponds to the lower deformation rate exhibits a pattern in which the layer reflections appear on the equator and the intermesogen reflection on the meridian. This pattern shows an anomalous orientation: the smectic layer normal seems to lie perpendicular to the fibre axis and, consequently, the molecules appear to align at an angle of 90° to the draw direction. Finally, it is interesting to consider the intermediate deformation rate pattern that is present both on the equatorial and on the meridian layer reflections. It seems that both types of orientation coexist in this sample.

Fig. 2 shows the strain–stress curves measured for two PTMTB samples that were drawn with different strain rates, $d\varepsilon/dt$. It can be seen that the geometry of these curves is strain rate dependent: the higher $d\varepsilon/dt$, the sharper the stress maximum. The sharpness of these maxima can be quantitatively described by means of the equation

$$\sigma = E\varepsilon\frac{1 - D_1\varepsilon}{1 + D_2\varepsilon} \tag{1}$$

where E is the Young modulus and D_1 and D_2 are adjustable parameters. The D_1/D_2 ratio plays an important role in this model because it controls the shape of the curve [10,11]. The experimental results on the variation of this ratio with the strain rate are summarised in Fig. 3. This figure shows that the room-temperature stress–strain curves of the studied polymer are similar to those of elastomers ($D_1/D_2 \ll 1$) for $d\varepsilon/dt$ values that are lower than $10^{-1}\ \mathrm{s}^{-1}$ whereas they resemble those of a rigid polymer ($D_1/D_2 > 1$) for the highest strain rates.

The yield stress, σ_y, dependence on strain rate experimental results is displayed in Fig. 4. It can be seen that σ_y is a monotonically increasing function of strain rate and that the slope of the σ_y vs. $\log(d\varepsilon/dt)$ curve changes for a strain rate value close to $10^{-1}\ \mathrm{s}^{-1}$. These results can be analysed in terms of the Eyring model [12] by considering yielding as a thermally activated process. According to this phenomenological model, the increase of the yield stress of many

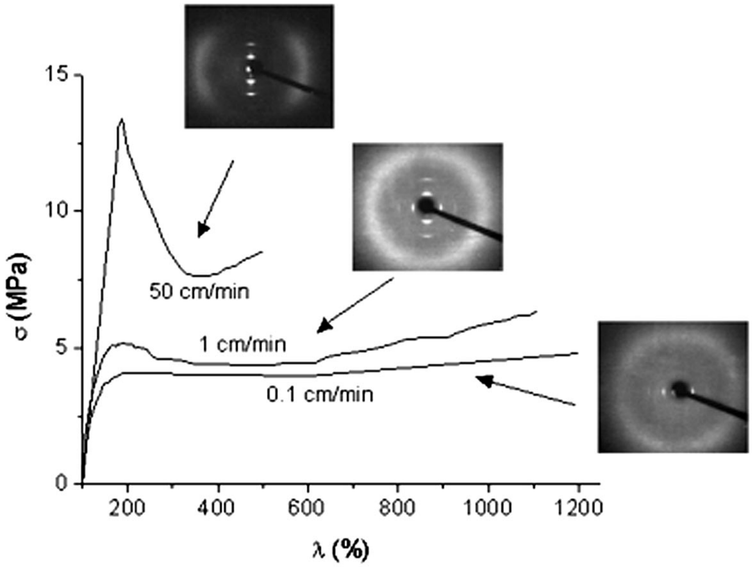

Fig. 2. X-ray diffractograms and stress–strain curves for three PTMTB samples that were oriented with different strain rates (fibre axis is in the vertical direction). Photograph (a) shows anomalous orientation whereas (c) corresponds to the usual molecular alignment and (b) can be related to an intermediate structure.

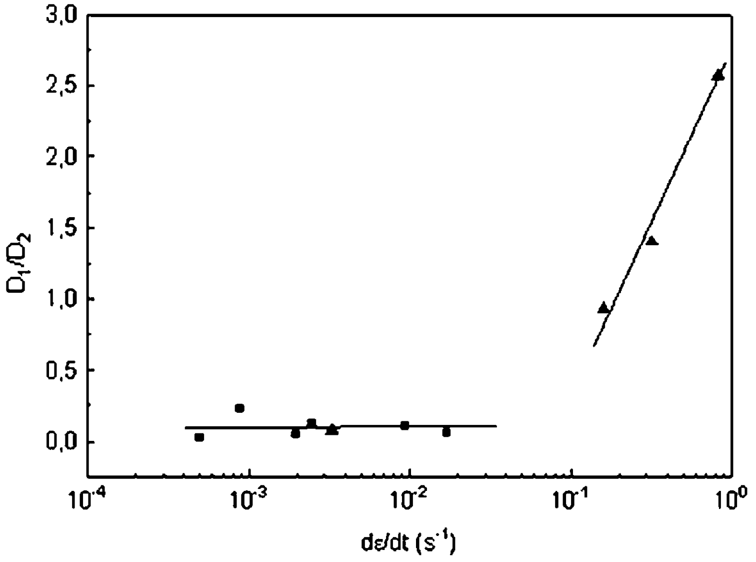

Fig. 3. Influence of the strain rate, $d\varepsilon/dt$, of the stress–strain curves of PTMTB as measured by the ratio of the parameters in Eq. (1) (■: Deben tester, ▲: Instron tester).

polymers and elastomers that is observed when $d\varepsilon/dt$ becomes greater can be described by using the expression

$$\sigma_y = \sigma_y^0 + \frac{RT}{v}\log(d\varepsilon/dt) \qquad (2)$$

where R is the gas constant, T, the absolute temperature and v, the activation volume. This parameter has been related to the number of chain segments that participate in an elementary successful deformation process, i.e. it is a measurement of the cooperativity of segmental movements in the plastic deformation [13,14]. The change in the slope of this line points to the existence of two microscopical deformation mechanisms with different activation volumes. As expected, an increase in the strain rate is related to a reduction in the cooperativity.

The simultaneous analysis of X-ray diffraction and tensile testing results allows one to conclude that the plastic deformation of PTMTB at room temperature can be controlled by two different microscopical deformation mechanisms. Both experimental techniques show that the contribution to the macroscopic deformation of each one of these mechanisms is strain rate dependent. In addition, it has been found that the relative weights of both mechanisms are approximately equal for strain rates in the order of $10^{-1}\ s^{-1}$.

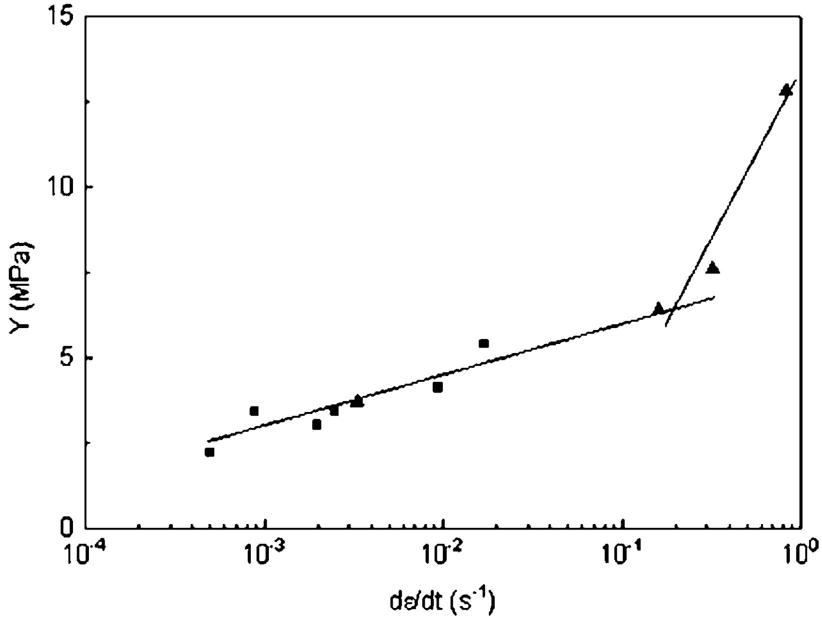

Fig. 4. Dependence of the room-temperature yield stress, σ_y, on the strain rate, $d\varepsilon/dt$, for PTMBT (■: Deben tester, ▲: Instron tester).

The deformation mechanism that prevails for the greatest strain rates leads to a normal orientation: the polymer chains tend to align parallel to the draw direction. The strain–stress curves that are obtained for these high clamp speeds are similar to those of relatively rigid polymers, they present a well-developed necking and elongation at break around 400%. On the contrary, the diffraction pattern for the most slowly drawn samples is anomalous and it could be assigned to an orientation of the molecular axis perpendicular to the fibre axis. The aspect of the load–extension curves that are registered for the lowest strain rates resembles that of ductile polymers with a not too well-developed stress maximum and with an elongation at break greater than 1200%.

Acknowledgements

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