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Molecular weight effect on the obtainment of parallel and perpendicular orientation in thermotropic poly(diethylene glycol *p,p′*-bibenzoate)

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Summary

The effect of molecular weight on the uniaxial orientation process has been analyzed in two samples of thermotropic poly(diethylene glycol *p,p′*-bibenzoate), evaluating the influence of that parameter on the type of orientation obtained. Several strain rates and deformation temperatures have been tested in order to map out the conditions for obtaining the two different kinds of orientation. The results show that in the lower molecular weight PDEB sample (M_w = 31200) it is rather easy to get exclusively perpendicular "anomalous" orientation, with the molecular axes aligned transversely to the stretching direction. However, it is extremely difficult to obtain 100 % parallel "normal" orientation. On the contrary, either type of orientation or a mixture of them can be easily developed for the higher molecular weight PDEB sample (M_w = 102900).

Introduction

The technological and academic significance of liquid crystalline materials derives not only from their applications in displays but also is due to the production of high modulus fibers in liquid crystalline polymers (LCPs), taking advantage of the inherent anisotropy of the constituent molecular chains [1,2]. Thus, stretching processes develop orientation in polymer chains, which produces changes in the elastic modulus of the material, and these changes are dependent on draw ratio, drawing temperature and strain rate. Evidently, as in any kind of fiber, the ultimate properties depend upon the degree of orientation achieved and considerably high moduli can be obtained along the polymer chains, provided that the most usual stretching behavior of polymers is the alignment of the macromolecular chains in a direction parallel to the deformation process. However, the enhancement of properties in the direction of the chain does inevitably involve the deterioration of those properties in the perpendicular direction [1,3].

On the other hand, it has been reported that some LCPs with smectic or nematic mesophases may exhibit, under particular circumstances of uniaxial stretching or shear deformation, a kind of anomalous orientation [4-11], where the chain axes are

perpendicular to the stretching direction. As a consequence, the best mechanical properties in such systems are found in the direction normal to the fiber [6]. New prospects are, therefore, envisaged from this particular behavior.

In those previous works, the great influence of the strain rate in the development of one or other type of orientation has been established. To gain more information about this interesting phenomenon, a preliminary investigation of the effect of molecular weight on the orientation process has been performed in two samples of thermotropic poly(diethylene glycol *p,p'*-bibenzoate), PDEB, evaluating the influence of that molecular parameter on the range of temperatures and strain rates at which either parallel, perpendicular or a combination of both orientations are observed.

Experimental Part

A first PDEB sample was synthesized by melt transesterification at 240°C of the diethyl ester of *p,p'*-bibenzoic acid and diethylene glycol, using tetraisopropyl titanate as catalyst. The polymer was purified by precipitating a chloroform solution into methanol. This sample will be named as PDEB-LW.

Part of this polymer was heated up to 270°C, maintaining the temperature for several hours under vacuum before ending the reaction, in order to obtain a higher molecular weight polymer, labeled as PDEB-HW.

The chemical structure of these PDEB samples, ascertained by solution NMR, is the following:
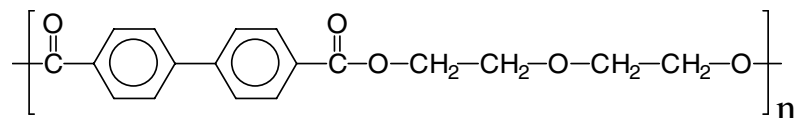
Size-exclusion chromatography data were obtained using an Alliance GPCV 2000 gel permeation chromatograph, equipped with two detectors: the conventional refractive index concentration detector and a viscometer. The dual detection and universal calibration (obtained from measurements in different polystyrene standards using chloroform as eluent at 35°C) allow the determination of absolute molecular weight values. The results for the two PDEB samples are presented in Table 1, showing a considerable difference in molecular weight.

Table 1. Molecular parameters obtained by SEC.

Sample	M_n	M_w	$[\eta]$ (dL/g)
PDEB-HW	39700	102900	0.70
PDEB-LW	15800	31200	0.34

Films of the two samples were obtained by compression molding in a Collin press between hot plates (215°C) at a pressure of 1.5 MPa, and a subsequent quench to room temperature between water-cooled plates in the press.

Differential scanning calorimetry (DSC) experiments were recorded using a Perkin-Elmer DSC7 calorimeter connected to a cooling system and calibrated with different standards. The sample weights ranged from 6 to 8 mg, and the scanning rate was 20°C/min in both heating and cooling experiments.

The uniaxial stretching measurements under tension were performed using a Minimat 2000 dynamometer, calibrated according to standard procedures. Dumb-bell shaped specimens with gauge dimensions around 20 mm in length and 2 mm in width were punched out from the polymer sheets with a standardized die. Thickness of specimens ranged from 0.3 to 0.5 mm. Tensile testing was carried out at different temperatures, from 60°C to 140°C, and at several crosshead speeds.

The X-ray diffraction photographs corresponding to the different oriented fibers were taken, at room temperature, with a flat plate camera attached to a Phillips 2 kW tube X-ray generator using nickel-filtered Cu Kα radiation. The distance from sample to film (around 7.1 cm) was determined by using aluminum foil as standard.

Results and Discussion

The DSC curves corresponding to the two PDEB samples are represented in figure 1. The curves on cooling from the isotropic melt (lower part of the figure) are rather similar, showing a sharp exotherm at around 190°C and the glass transition at around 50°C. More differences are observed in the subsequent melting curves (upper part of figure 1), which show again the glass transition and a final endotherm at a significantly higher temperature in the case of sample PDEB-HW. It has been reported that PDEB develops a smectic mesophase [12-15] with consecutive mesogens arranged in an alternating antiparallel fashion, SmC_{alt} mesophase, typical for polybibenzoates with odd spacers [16-18]. This mesophase can be easily quenched down to room temperature, although, as reported before [14,15], it can develop a phase of higher order by annealing for a long time at temperatures above the glass transition (and below the isotropization).

The transition temperatures and enthalpies corresponding to the two analyzed PDEB samples are presented in Table 2. The effect of molecular weight is clearly reflected on the glass transition and isotropization temperatures, since the values obtained for
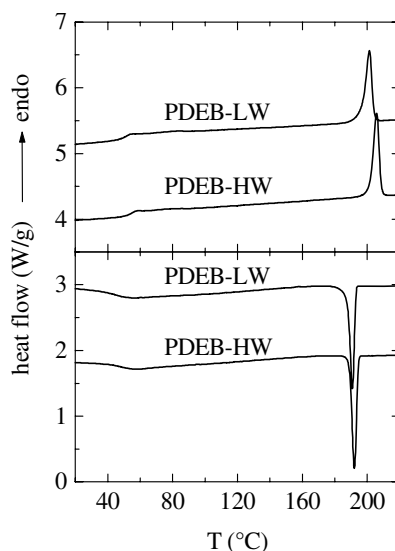

Figure 1. DSC curves corresponding to the cooling from the isotropic melt (lower frame) and subsequent heating (upper frame) for the two PDEB samples. Scanning rate: 20°C/min.

sample PDEB-HW are 4 - 5 degrees higher than those exhibited by the lower molecular weight sample. On the contrary, the differences are practically inside the experimental error for the temperature of liquid crystallization and for the enthalpy of isotropization, although this last magnitude seems to be slightly higher for PDEB-LW.

Table 2. Glass transition, isotropization, and liquid-crystallization temperatures, enthalpy of isotropization, Young modulus and stress at yield for the two PDEB samples in figure 2.

Sample	T_g (°C)	T_i (°C)	T_{lc} (°C)	ΔH_i (J/g)	E (MPa)	σ_y (MPa)
PDEB-HW	53	206	192	17.9	8.4	0.98
PDEB-LW	49	201	191	18.4	2.7	0.15

Much higher differences between the two PDEB samples are found when analyzing the stress-strain and the orientational behaviors. Thus, figure 2 shows the stress-strain curves for specimens of the two PDEB samples with different molecular weight when stretching at 110°C with a strain rate of 4.95 min^{-1} (crosshead speed of 99 mm min^{-1}). A greater initial slope, and consequently higher elastic modulus, is observed in PDEB-HW sample compared to its homologous with lower molecular weight, PDEB-LW. Moreover, a significant larger yield stress value is found for the specimen with the higher molecular weight. The corresponding values of the Young modulus and yield stress for those two samples are presented in Table 2.
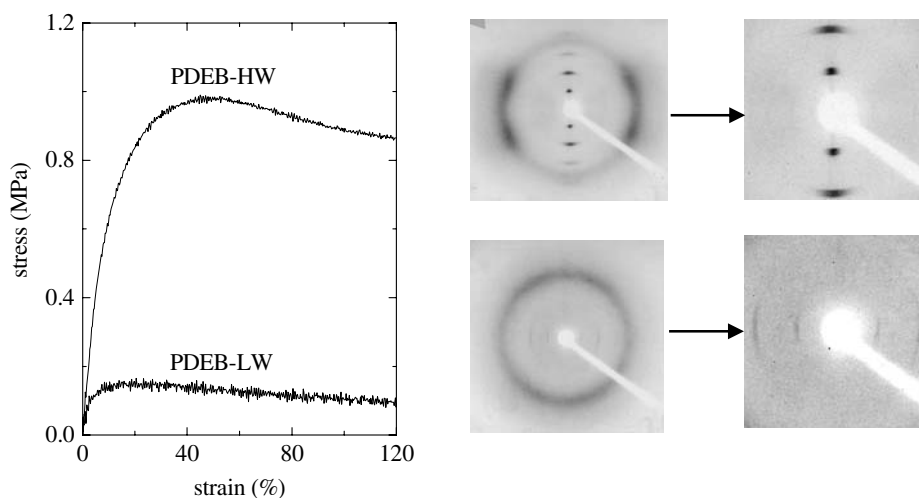
Figure 2. Stress-strain diagrams for specimens of the two PDEB samples, stretched at 110°C and a strain rate of 4.95 min^{-1}, and corresponding X-ray photographs of the stretched fibers (stretching direction: vertical), showing the amplification of the low-angle region.

The X-ray photographs of the fibers obtained at the end of these stress-strain experiments are also shown in figure 2. The photograph at the top, corresponding to the stretched fiber of PDEB-HW, exhibits four narrow diffractions located in the

meridian, arising from four orders of the smectic layer spacing, determined to be around 1.56 nm. Moreover, a broad wide-angle diffraction halo is also observed, presenting split maxima above and below the equator. These features are characteristic of the SmC_{alt} mesophase [16]. Since at least four orders of the smectic layer diffraction are visible, it follows that the mesophase of PDEB implies smectic layers very well positioned on the lattice and with molecules rather well arranged inside the layers [1] (of course lacking of three-dimensional order).

On the other hand, since the smectic layer diffractions appear on the meridian, it means that the molecular axes are aligned with the stretching direction, as corresponds to a "normal" parallel orientation.

On the contrary, the diffractogram corresponding to the stretched fiber of PDEB-LW (lower photograph in figure 2) exhibits the layer diffractions on the equator, as observed in the amplification of the low-angle region, indicating that now the molecular axes are aligned perpendicularly to the stretching direction ("anomalous" orientation). Moreover, although the overall intensity of this photograph is not as high as the one for the specimen of PDEB-HW, yet 3 or 4 orders of the layer diffraction are observed, indicating again a considerable degree of smectic layer order and positioning.

Additional experiments stretching at different temperatures and strain rates have been performed on the two PDEB samples. Focusing the attention on PDEB-LW, the results show that above 100°C and at the tested strain rates, photographs rather similar to that at the bottom of figure 2 are obtained, meaning that in all cases an exclusively perpendicular orientation is developed. The stretching temperature has to be reduced to values close to the glass transition in order to develop a certain amount of parallel orientation. Thus, the photograph at the top of figure 3, obtained at a stretching temperature of 60°C and with a strain rate of 0.50 min^{-1} (crosshead speed of 10 mm min^{-1}), indicates a mixture of the two orientations, as seen in the amplification; the corresponding radial integration of the photograph leads to the values of 60 and 40 % of parallel and perpendicular orientations, respectively.

Considering these results and the fact that at these low stretching temperatures the specimens are getting very brittle, it follows that it is extremely difficult to obtain 100% parallel orientation in this PDEB-LW sample, while it is rather easy to get exclusively perpendicular orientation.

The behavior is completely different in the case of PDEB-HW, since, as commented above, 100% parallel orientation is deduced from the photograph at the top of figure 2, when stretching at 110°C. Moreover, the bottom right diffractogram in figure 3, corresponding to a fiber of PDEB-HW stretched at 140°C with a strain rate of 0.50 min^{-1}, indicates that under those conditions exclusively perpendicular orientation is developed.

Consequently, it is rather easy to obtain either type of orientation for this higher molecular weight PDEB sample. Furthermore, a mixture of the two orientations can be also easily developed, as it can be observed in the bottom left photograph of figure 3, stretching at 120°C and at 0.50 min^{-1}, where a 69% of parallel and a 31% of perpendicular orientation is deduced.

All the relevant results for the different tested stretching temperatures and strain rates are collected in figure 4, where each point represents the actual conditions of the experiment, and the number above them are the percentages of parallel orientation deduced from the corresponding integrations. From these values, the conditions for obtaining each type of orientation in sample PDEB-HW can be approximately

defined, with a region of exclusively parallel orientation at high strain rates and low temperatures, a zone of 100 % perpendicular orientation at low strain rates and high temperatures, and a region of mixed orientations at "intermediate" stretching temperatures and strain rates.

PDEB-LW

60°C, 0.50 min⁻¹

PDEB-HW



120°C, 0.50 min⁻¹   140°C, 0.50 min⁻¹
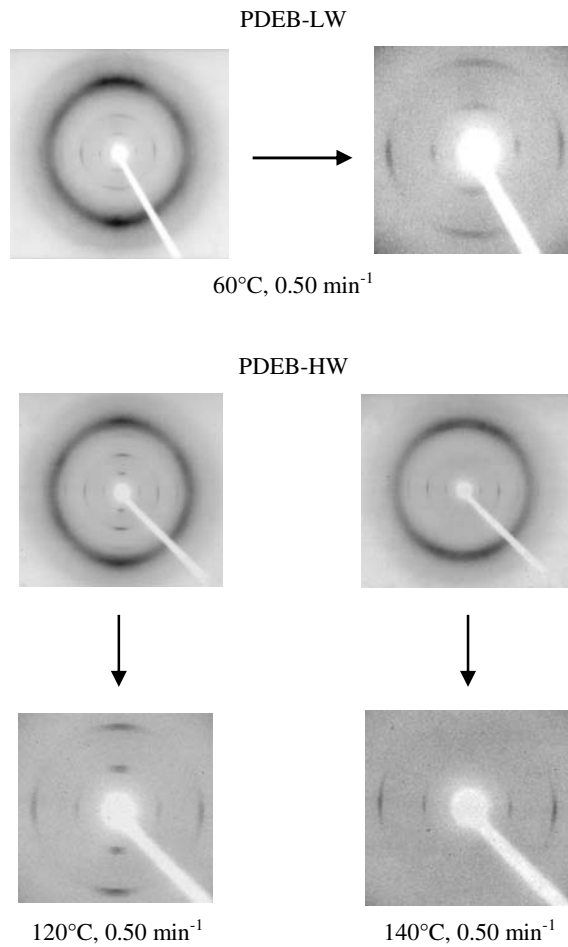
Figure 3. X-ray photographs corresponding to fibers of the two PDEB samples stretched under the indicated conditions (stretching direction: vertical), showing the amplification of the low-angle region.

These regions are considerably shifted to lower temperatures (by around 60°C) in the case of PDEB-LW, in such a way that it was not possible to define the zone with exclusively parallel, normal orientation, since the glass transition is being approached, and the specimens get very brittle for the tests, as commented above.

The explanation for the existence of these two types of orientation derives from the premise that there are segregated independent domains in the low-ordered polymeric

mesophases [1,2,11,14,19]. As stretching takes place, two processes might occur: on the one hand, a mechanism that implies the rupture of these domains and the orientation of chains parallel to the stretching direction. On the other hand, another mechanism that keeps integrity of these domains can take place, leading solely to the alignment of the domain axes with the deformation direction, so that the macromolecular chains are aligned perpendicularly. The higher values of molecular weight and viscosity for the PDEB-HW sample (see Table 1) lead to a mobility reduction, hindering domain orientation and making its rupture easier than its preservation. Consequently, macromolecular PDEB-HW chains will have a higher probability of developing parallel orientation. It might be also possible that the higher chain lengths prevent, additionally, the development of segregated domains that afterwards can be individually oriented.
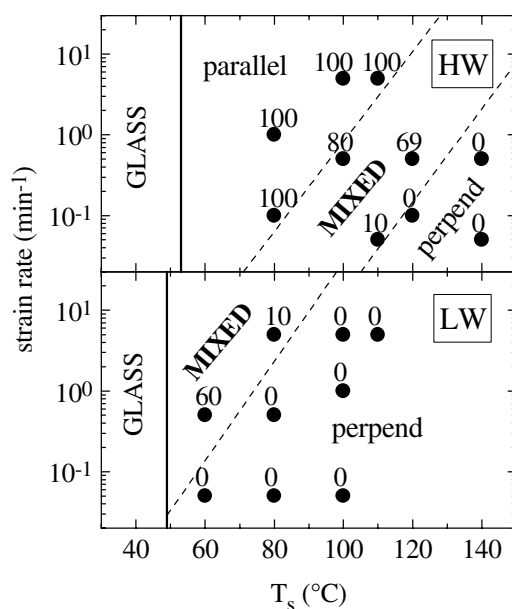
Figure 4. Mapping of the conditions to obtain the two different types of orientation in liquid crystalline specimens of PDEB-LW (lower) and PDEB-HW (upper), as a function of stretching temperature, T_s, and strain rate. The points represent the conditions of the different experiments, with the percentage of parallel orientation above them.

The effect of molecular weight on the obtainment of the two types of orientation has been already reported [10,11] in nematic HBA/HNA copolymers under shear flow. It was found there that for "high" molecular weights (M_w higher than around 14000) the possibility of perpendicular orientation is completely lost, attributed to the difficulty of relaxing the entanglements in those "high" molecular weight chains.

The results found in this work also indicate that the higher the molecular weight the more difficult is to obtain the perpendicular orientation for a certain temperature and strain rate (and draw ratio). However, and considering that the two PDEB samples analyzed here are both of high or relatively high molecular weights, the most

interesting conclusion from these results is that in the case of PDEB what is difficult, by stretching, is specifically the obtainment of normal parallel orientation in low molecular weights.

Additional experiments on these two PDEB samples, and in new ones to be synthesized with different molecular weights, are being planned in order to map out more precisely the stretching conditions and molecular characteristics for the obtainment of the two types of orientation, and to compare the results with those reported for other systems.

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