Mechanical Properties of Drawn Smectic Mesophases. Poly(tetramethylenoxypropylene *p*,*p*′-bibenzoate)

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ABSTRACT: A smectic main chain polymer, poly(tetramethyleneoxypropylene *p*,*p*′-bibenzoate), PPO4B, with thermal transitions $T_g = 26$ °C and $T_i = 88.5$ °C was studied in and after a drawing experiment. Variation of both strain rate and temperature resulted in materials with normal and anomalous orientations of smectic layers. Mechanical properties vary correspondingly. Samples from PPO4B were drawn at different strain rates and temperatures. The stress−strain curves were recorded. The resulting oriented materials were studied by wide-angle X-ray scattering. Normal orientation (i.e., smectic layer perpendicular to draw direction) is established at high strain rate and low temperature. Anomalous orientation is achieved at low strain rate and high temperature. At intermediate values of the processing parameters a bimodal structure of both normal and anomalous orientation is observed. Dynamic mechanical analysis measurements in tensile mode were carried out on strips cut from oriented sheets in three directions, 0°, 45°, and 90° in relation to the draw direction. The value of the storage modulus in the drawing direction is highest in the case of normal orientation (smectic layer perpendicular to the straining direction). The highest value of the storage modulus coincides with the direction perpendicular to most of the smectic layers. Thus, for anomalous orientation the worst mechanical properties are in the fiber direction.

Introduction

Liquid crystalline polymers are a subject of increasing interest due to the favorable combination of some factors such as low density and exceptional mechanical properties. Their mechanical characteristics are the direct result of the high degree of molecular alignment that can be obtained in these materials. To improve the processing conditions, a more complete understanding of the influence of the experimental conditions on the alignment phenomena is necessary.

Drawing processes develop orientation in polymer chains, which produces changes in the elastic modulus of the material, and these changes are dependent on the drawing temperature and the strain rate. The elastic modulus is usually calculated from stress−strain measurements carried out by means of dynamometers. However, when only a small quantity of sample is available, the preparation of specimens for stress−strain tests is difficult, and it is more convenient to use another technique, which needs thinner and shorter specimens, as dynamic mechanical analysis (DMTA). The tensile mode of DMTA instrumentation allows to measure elastic moduli in a wide range of temperatures, which values are comparable and obviously higher than the ones obtained by stress−strain tests due to the different working frequencies.

Moreover, the mechanical anisotropy of a polymeric material can be evaluated from the values of the elastic modulus of specimens stretched at various temperatures and strain rates when those are cut at different chosen directions with respect to the drawing axis. It is sufficient to measure specimens cut at 0°, 45°, and 90°, i.e., along, diagonal, and perpendicular to the drawing direction, respectively. The mechanical anisotropy was also reported as a function of the values of moduli and loss tangent of stretched polymers,[1−5] and it was used to elucidate either the type (primary or secondary) of the dynamic mechanical relaxations[1] or, in semicrystalline polymers, the angle that forms the lamellae with respect to the draw direction.[3,5]

The most usual drawing behavior of semicrystalline polymers is the alignment of the macromolecular chains in a direction parallel to the deformation process. Nevertheless, some liquid crystalline polymers display, besides the normal orientation, an anomalous orientation[6−10] where the normal to the smectic plane orientates perpendicular to the draw direction, this anomalous behavior taking place in a particular range of experimental conditions.

In previous works it has been established the great influence of the strain rate in the development of one or other type of orientation.[9,10] To gain information about this interesting phenomenon, the influence of the temperature of the draw process is studied in this work, and special emphasis has been given to the study of the mechanical properties of a smectic polymer stretched under different strain rates and consequently with different types of orientation. As a tool for measuring the mechanical properties, a dynamic mechanical apparatus is used, and the sample probe is poly(tetramethylenoxypropylene *p*,*p*′-bibenzoate), PPO4B. This polybibenzoate only gives one type of mesophase, specifically a smectic S_{CA},[11] under different quenching or annealing conditions. The problems associated with the presence of several phases are therefore avoided.

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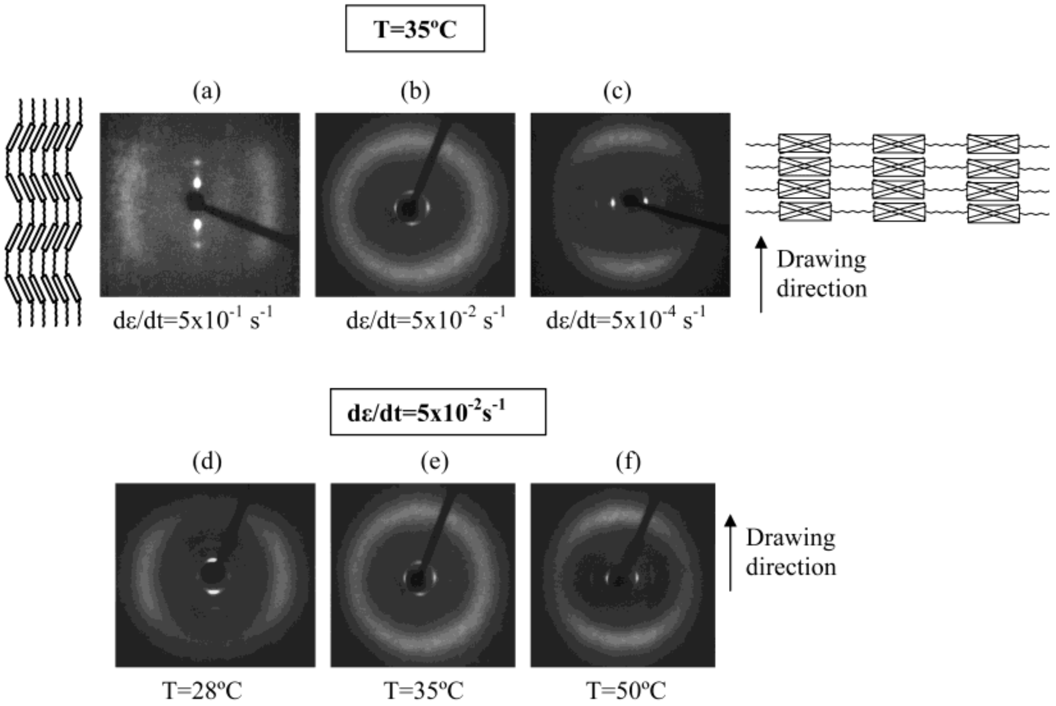
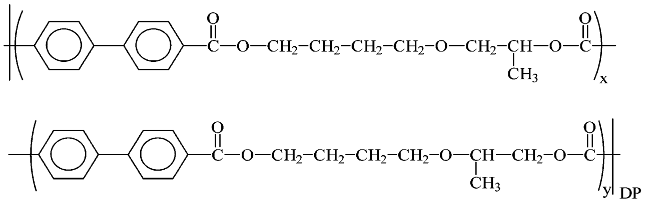


Figure 1. X-ray diffractograms of PPO4B samples that were drawn with different strain rates, dϵ/dt, at various temperatures, T.

Experimental Part

The ether−diol used as spacer in the polymer synthesis was prepared by ring-opening reaction of propylene oxide with 1,4-butanediol (200% excess) in the presence of sulfuric acid as catalyst.[11] This reaction was performed under vacuum at room temperature. The diol was purified by consecutive distillations at reduced pressure. Since the opening of the propylene oxide ring can occur in two different positions, a mixture of ether−diols is really obtained.[11] The polymer was synthesized by melt transesterification of the diethyl ester of *p,p′*-bibenzoic acid and the mixture of ether−diols, using isopropyl titanate as catalyst. The molecular structure of PPO4B, as deduced from the corresponding ^{1}H NMR spectrum, is the following:



$$\left[\left(-C_6H_4-C_6H_4-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-CH_2-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-O-\overset{O}{\overset{\|}{C}}-\right)_x\left(-C_6H_4-C_6H_4-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-CH_2-O-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-\overset{O}{\overset{\|}{C}}-\right)_y\right]_{DP}$$

where x and y take the values of 0.54 and 0.46, respectively; i.e., PPO4B is really a copolymer.

PPO4B forms a smectic mesophase S_{CA} that presents the isotropization temperature, T_i, at 88.5 °C and the glass transition, T_g, at 26 °C. Under different conditions of annealing the mesophase remains stable, and transformations to other mesophases are not observed.[11]

The stress−strain curves were determined using Instron and Minimat 2000 dynamometers. The specimens for these experiments were punched out from a polymer film in the liquid crystalline state. The film was prepared by molding the material in a Collin press at 100 °C and then cooling it at room temperature. The thickness of specimens was in the range from 0.4 to 0.6 mm. The strain rates were measured from the displacement of marks in the homogeneous drawn portion of the final specimen.

Dynamic mechanical measurements were carried out with a Polymer Laboratories MkII dynamic mechanical thermal analyzer working in the tensile mode at frequencies of 1, 3, 10, and 30 Hz. The temperature was varied from −140 to 70 °C at a rate of 1.5 °C/min. The apparent activation energy (ΔH) of the different relaxations was calculated by using the Arrhenius law for the frequency−temperature shift: $f = f_0$ exp($\Delta H/RT$). Four different samples of PPO4B were used: unoriented, stretched at a high strain rate (2.1×10^{-1} s^{-1}), at an intermediate one (5.5×10^{-2} s^{-1}), and at a low strain rate (2.1×10^{-4} s^{-1}). The oriented samples were obtained by drawing at 35 °C (up to a elongation around 500%) dumbbell-shaped specimens with dimensions 40 mm in length and 40 mm in width. The specimens for dynamic mechanical experiments were cut out into a rectangular strip 2.2 mm wide. In the case of oriented samples, three different cutting directions were measured: along (0°), diagonal (45°), and perpendicular (90°) to the drawing direction.

Wide-angle X-ray diffraction photographs of oriented fiber were taken at room temperate using 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 the film was determined by using aluminum foil as standard.

Results and Discussion

Figure 1 shows the X-ray diffractograms of fibers of PPO4B that were obtained at different conditions of strain rate and temperature. It is clear that there are differences in the direction of orientation as a function of both parameters. Figure 1a shows the picture of the fiber stretched at the higher strain rates (5.5×10^{-1} s^{-1}), presenting the usual diffraction for smectic polybibenzoates with an odd number of groups in the spacer, in which the axes of the mesogens and of the spacer do not coincide. The outer diffraction splits into two, above and below the equator, with a minimum of intensity in this axis. The diffraction due to the smectic layers appears like spots in the meridional at 1.82 nm. These features correspond to a mesophase of type S_{CA}.[12,13] The fiber oriented at the lower strain rate (5.5×10^{-4} s^{-1}) (Figure 1c) presents a similar diffraction pattern, with two main differences: one, the most important, its orientation is rotated 90°. This implies that the normal to the smectic layer is perpendicular to the drawing direction of the fiber. The other difference is related to the external halo of the diffraction pattern: the diffraction is more diffuse, as if a part of the lateral order had been lost. A close inspection also reveals that now the maximum of intensity is in its middle position; thus, it looks like the diffraction is due to a smectic S_A, but is not true, because there is not any change in the smectic layer spacing with the type of orientation. The absence of splitting of the external halo must be due to a poor aligning of the mesogenic groups. The diffraction pattern of the fiber stretched at the intermediate strain rate (5.5×10^{-2} s^{-1}) (Figure 1b) indicates the coexistence of the orientations corresponding to fibers stretched to the highest and lowest strain rates. The pattern looks as if the fibers had been simultaneously stretched in two perpendicular directions; it is seen that there are good orientations in both directions, and residual rings of unoriented polymer are not observed.

However, the strain rate is not the only one variable that controls the preferential orientation of the macromolecules during the drawing process of this smectic polybibenzoate. The photographs of parts d, e, and f of Figure 1, which correspond to the X-ray diffraction patterns of three samples oriented with the same strain rate (5.2×10^{-2} s^{-1}) at three different temperatures, 28, 35, and 50 °C, respectively, demonstrate that orientation is also temperature dependent. Although those temperatures are very close, it must be kept in mind the closeness of T_g and T_i. It is seen clearly in the pictures that an increase of the temperature in the draw process corresponds with a decrease of the orientation in the direction of the fiber. This behavior can be interpreted as that the factors that tend to reduce the intermolecular forces favor the anomalous orientation appearance, corroborating the qualitative observations in our laboratory that soft liquid crystal polymers present anomalous orientation easily while very high rates of deformation are needed to obtain normal orientation.

To get a more detailed information about the differences among all these diffraction photographs, the intensity profiles along the meridian (to avoid the loss of intensity in this peak due to the tangent plane approximation the appropriate tilting angle was used[14]) and equatorial directions were obtained by means of an image-analysis program. A sector integration was used covering angles of 45° above and below the equator and at both sides of the meridian. The intensity profiles were transformed to logarithmic scales in order to consider the optical transfer function.[15] The profiles of a sample that was stretched with a strain rate of 0.05 s^{-1} at 35 °C are shown in Figure 2a. The second order of the layer spacing can also be observed, although with a very low intensity, in this specimen where the intensities of the meridian and the equatorial are approximately the same.

The amount of anomalous orientation can be described by means of the percentage of anomalous intensity, %AI, which can be evaluated by using the expression

$$\%\mathrm{AI} = \frac{\mathrm{Ae}}{\mathrm{Ae} + \mathrm{Am}} \times 100$$

where Ae and Am are the integrated scattering intensity of the whole inner diffraction in the equatorial and meridian directions. Parts b and c of Figure 2 show the variation of %AI with draw ratio and stretching temperature, respectively, for some PPO4B samples. It can be observed that the tendency to the development of the anomalous orientation increases as the temperature raises (when the rest of the variables controlling the process remain unchanged) and that the lower the strain rate is, the higher the %AI results.

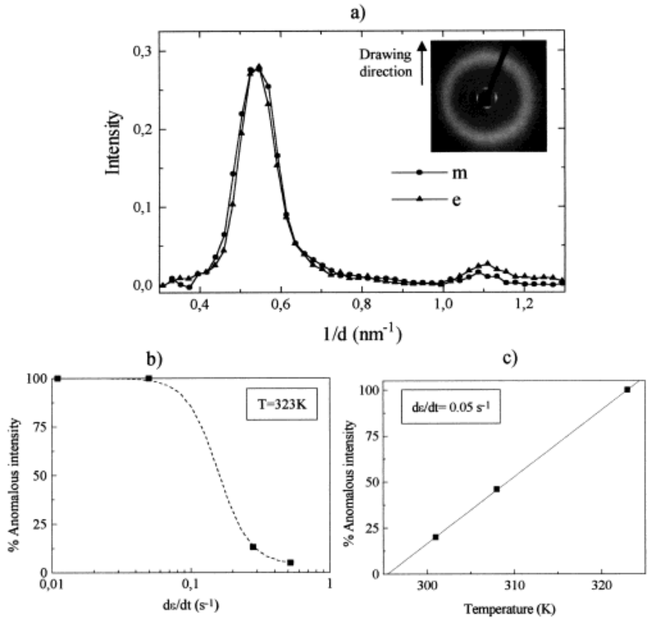


Figure 2. (a) Total scattering intensity of the diffractions on the meridian (m) and equator (e) as a function of the reciprocal-lattice vector for a PPO4B sample that was drawn at 35 °C with a 0.05 s^{-1} strain rate. (b) Dependence of the percent of anomalous intensity on the strain rate. (c) Influence of the stretching temperature on the development of the anomalous orientation.

Most of the mechanical properties of polymers are structure-dependent, and consequently, it can be expected that the development of anomalous orientation in these materials can be also monitored by means of the stress−strain curves that describe the macromolecular chains alignment process or by means of DMTA measurements undertaken on the stretched samples. The next paragraphs show the results of the application of these techniques to the analysis of the orientation mechanism of the polybibenzoate studied.

Stress−Strain Behavior. The stress−strain curves that were obtained by drawing different PPO4B samples at 35 °C, with strain rates that cover approximately 3 decades ranging from 5.5×10^{-4} to 5.5×10^{-1} s^{-1}, have been depicted in Figure 3. The curve that corresponds to the highest strain rate shows a clearly marked maximum that is related to the development of the neck. A region where the slope of the curve is an increasing function of the strain, a phenomenon that is known as strain hardening, follows this maximum. The other curves also display the first of these features, but the yield stress becomes less pronounced and the sharpness of the peaks decreases as the strain rate does. The stiffness of the polymer, measured by the initial slope of the stress−strain curves, is a decreasing function of the strain rate. Strain hardening can also be found in the curve that was obtained with a 5.5×10^{-2} s^{-1} strain rate, but its magnitude is lower than that of the 5.5×10^{-1} s^{-1} strain rate curve. This behavior is not observed for the slower deformation processes, for which the stress remains practically unchanged after the fall that follows the maximum, and the material does not harden.

The previous results show that the shape of the stress−strain curves is a function of the strain rate and, consequently, is related to the nature of the orientation,

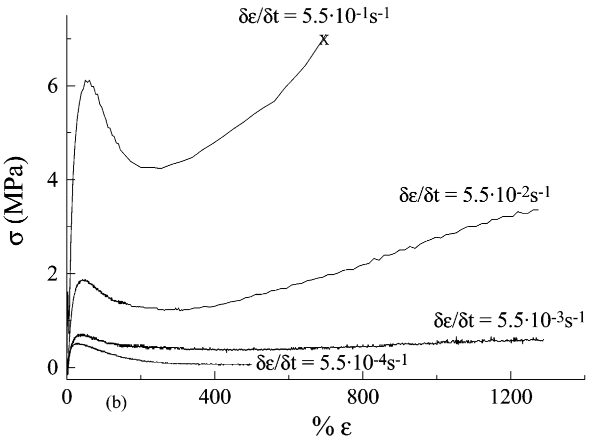


Figure 3. Stress−strain curves for four different PPO4B samples that were oriented with different strain rates, $d\epsilon/dt$, at 35 °C.

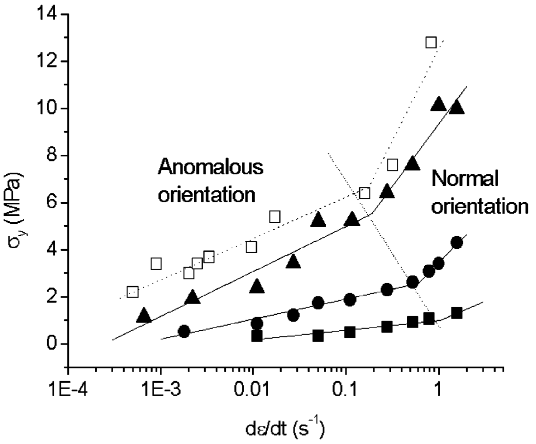


Figure 4. Dependence of the yield stress, σ_y, on the strain rate, $d\epsilon/dt$, for two polybibenzoates that were drawn at different temperatures (■, PPO4B at 50 °C; ●, PPO4B at 35 °C; ▲, PPO4B at 28 °C; □, PTMTB at 20 °C[9]).

either normal or anomalous, that is being developed during the stretching process. It has been found that the curves that correspond to the greatest deformation speeds, i.e., those that describe the development of normal orientation, resemble those of rigid polymers whereas the curves that are related to the appearance of anomalous orientation are similar to those of elastomers. This kind of behavior parallels the previously reported one for other liquid crystalline polybibenzoates forming low order smectic mesophases that were stretched at temperatures above that of the glass transition and below the isotropization temperature.[9]

This parallelism is enhanced if the dependence of yield stress on strain rate is considered. Figure 4 shows the present results for PPO4B and those that were reported earlier for poly(trimethylene oxy-2-methyl trimethylene *p,p′*-bibenzoate),[9] PTMTB. These results, which seem to point out to the fact that the development of anomalous orientation is a phenomenon common to certain families of liquid crystal polymers, can be analyzed in terms of the Eyring model that describes yielding as a thermally activated process.[16] It has been found that the variation of the yield stress, σ_y, of many amorphous and semicrystalline polymers, with strain rate, $d\epsilon/dt$, can be explained in terms of the equation

$$\sigma_y = \sigma_y^0 + \left(\frac{RT}{v}\right)\log(d\epsilon/dt) \qquad (1)$$

where R is the gas constant, T the absolute temperature, and v the activation volume. According to this model, the tensile yield stress is (for many decades) a linear function of the logarithm of the strain rate, the slope of which is inversely proportional to the activation volume. It has been suggested that this activation parameter is an increasing function of the number of chain segments that are involved in each of the conformational changes that controls the yielding,[17] i.e., is related to the cooperativity of the segmental motions.

The analysis of Figure 4 proves that these liquid crystal polybibenzoates that form mesophases of low order can present two different yielding regimes that are characterized by different activation volumes. According to this, it can be concluded that the yielding of these polymers is controlled by two different microscopical deformation mechanisms, and their contribution to the macroscopic deformation is strain rate dependent. The experimental results show that the slope of the lines changes at a critical strain rate, $(d\epsilon/dt)_{cr}$, that ranges from 1 to 10^{-1} s^{-1} depending on the drawing temperature. The deformation mechanism that develops the normal orientation is predominant over that responsible of the anomalous orientation for strain rates higher than the critical value, and the opposite is true for the lowest values of the strain rate. Figure 4 shows that when the drawing temperature approximates the isotropization temperature, $(d\epsilon/dt)_{cr}$ increases and, consequently, the difficulty in obtaining normally oriented structures increases. This trend reflects the role that the lateral cohesion between chains in the mesophase plays on the development of anomalous orientation because increasing the drawing temperature decreases the order of the mesophase.

It can also be seen that the activation volume that is obtained for the normal orientation regime is smaller than that obtained for the anomalous orientation one. This result points to the fact that the structural units involved in the anomalous orientation are more voluminous than those responsible for normal orientation. Even though one must take into account that, in general terms, eq 1 considers that only one deformation mechanism participates in the yield, it is evident from these results that a single mechanism is present only in extreme conditions of deformation rate, either very high or very low. Therefore, the meaning of the value of the slope must take into account this fact and probably would be more exact to trace curves, through the points in Figure 4, whose slopes in both extremes of the plot would give more correct values of the activation volumes.

DMTA Measurements. Three dynamic mechanical relaxations are observed in PPO4B, named α, β, and γ in order of decreasing temperatures. The α relaxation is considered the glass transition of the polymer, and its temperature location (25.6 °C at 10 Hz for the unstretched polymer) parallels the DSC value (26 °C for a scanning rate of 10 °C/min). It can be seen as a profound decrease in the storage modulus plot, and its apparent activation energy (>400 kJ mol^{-1}) corresponds to motions occurring at the glass transition temperature.

The β relaxation takes place in the temperature interval around −70 °C (tan δ basis), and its activation energy is around 80 kJ mol^{-1}. It shows the complex nature typical of polyesters, including motions of the carboxyl and phenylene groups, does not display varia-

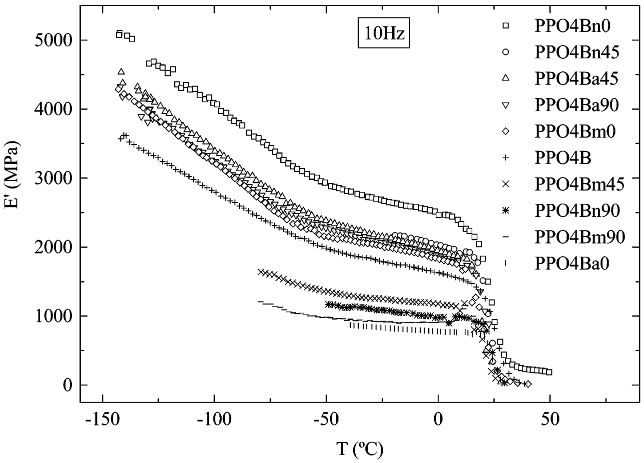


Figure 5. Storage modulus, *E*′, as a function of the temperature, *T*. Sample identification: *n* means normal orientation, *a* means anomalous orientation, and *m* means mixed orientation. The angle between the drawing direction and the cutting axis of the specimen measured in the tensile DMTA apparatus is indicated with 0, 45, or 90 at the end of the sample's code.

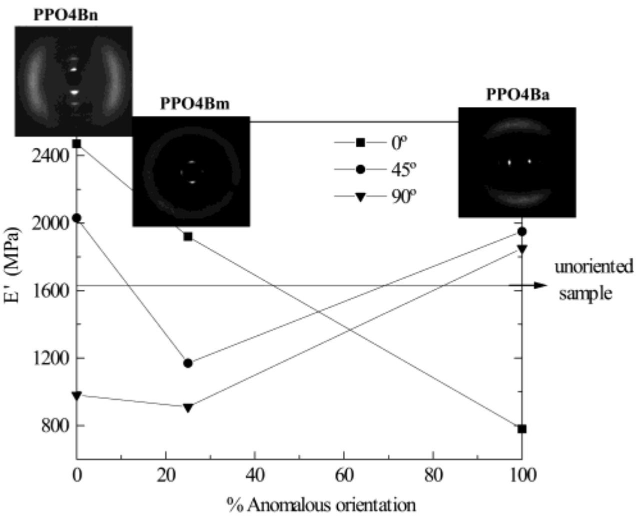


Figure 6. Storage modulus, *E*′, at 0 °C for the different samples studied, as a function of percentaje of anomalous orientation. Upper, the corresponding X-ray diffractograms.

tions in the temperature location for the different specimens studied and has been also found in all the other members of the polybibenzoate series.[18]

The γ relaxation occurs around −125 °C (tan δ basis). Its temperature location and apparent activation energy (45 kJ mol^{-1}) are similar to those of the γ relaxation displayed by polymers containing polymethylenic sequences as polyethylenes and polyethers. We have also found this relaxation in polybibenzoates containing oxyethylene spacers and have concluded that the oxygen atom plays an equivalent role to the methylenic group and that the motions responsible for the γ relaxation are kink formation, inversion, and migration in the mesophase.[19]

Figure 5 shows the storage moduli of the original specimen and of the ones stretched at 2.1×10^{-4}, 5.5×10^{-2}, and 2.1×10^{-1} s^{-1} and cut along three different directions reported in the Experimental Part. Some specimens were brittle at low temperatures, and they were measured in a temperature range more reduced than the general one (from −150 to 40 °C).

To better compare the results obtained for the moduli, the value at a temperature of 0 °C, below the onset of the glass transition, has been selected. In Figure 6, these results are collected for three samples stretched at three different strain rates and measured along three different directions. The values of storage moduli have been represented as a function of the percentage of anomalous orientation. As a reference, a line of points has been marked with the value of the storage modulus of the unoriented sample. Looking at the storage modulus value of the sample in the direction of the stretching (at 0°), it is seen that its value diminishes while the percentage of anomalous orientation grows. The highest value of the modulus corresponds, as expected, to the highest value of normal orientation and the minimum value of the modulus, with the highest orientation perpendicular to the stretching direction, while intermediate values are obtained for mixed orientation. This is the expected behavior, i.e., the maximum mechanical properties in the fiber direction.

The results that correspond to 0% of anomalous orientation (the fiber made with the highest strain rate) show also an expected behavior. Thus, decreasing values of the modulus are obtained for increasing angles between the cutting and the stretching directions: the maximum value is at 0° and the minimum at 90°. This behavior is similar to that of semicrystalline polymers at temperatures below the glass transition and corroborates the above-mentioned results obtained from stress−strain measurements.

A reverse situation is observed for the modulus that corresponds to the samples with 100% of anomalous orientation, where the minimum value of the modulus is obtained for the sample cut at 0°. Moreover, those cut at 45° or 90° in relation to the stretching direction both show a slightly higher modulus than the unoriented sample and certainly lower than the one measured along the fiber direction and 0% of anomalous orientation. It should be kept in mind that the angle of 90° coincides with the direction of the normal to the smectic planes (chain axis), as demonstrated by the corresponding X-ray picture.

Regarding the data of the three samples with 75/25 (normal/anomalous) orientation, they show a decreasing modulus in the order 0° > 45° > 90°. It is seen in Figure 6 that the presence of a 25% of anomalous orientation decreases the mechanical properties in the fiber direction about a 20%, without improving the corresponding ones in the transverse direction.

It is important to consider, however, that the sample with a 0% anomalous orientation and measured at 0° exhibits a modulus significantly higher than the one with 100% anomalous measured at 90°, meaning that for the anomalous orientation the packing efficiency is less effective than in the usual way of orientation in which chain axis and direction of stretching coincide.

The conclusion is that the direction with enhanced mechanical properties of the oriented mesophase corresponds to the normal to the smectic plane, whatever would be the strain rate, even though the mesophase with anomalous orientation presents worse mechanical properties that the one with normal orientation.

The development of the anomalous orientation of PPO4B under uniaxial stretching, described in this paper and assessed by different experimental techniques, can be described in terms of the relative slip of the smectic layers as a whole, as it has been proposed previously by Krigbaum[20] for explaining the shear behavior of other liquid crystalline polymers. This kind

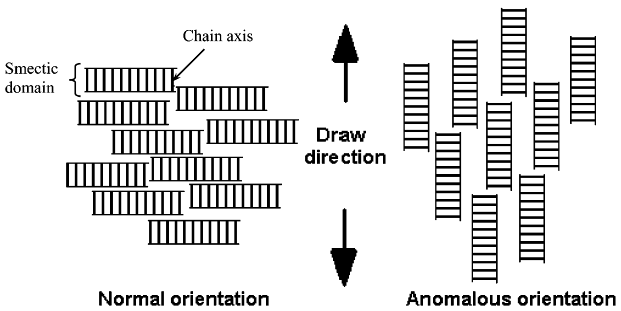


Figure 7. Bidimensional scheme of the structure of normally and anomalously orientated samples.

of explanation has also been used to describe the anomalous orientation of Vectra type polymers that can develop nematic mesophases under shear[21] and that of some fibers of smectic-forming polybibenzoates that were prepared by drawing the smectic melt.[7] In fact, the X-ray diffractograms corresponding to the anomalously oriented samples of uniaxially drawn PPO4B are coherent with the schematic representation in Figure 7. The increment of the activation volume that accompanies the development of the anomalous orientation can be related to the slipping of the smectic domains as a whole in opposition to the flow parallel to the chains that are involved in normal orientation.

To give a reasonable explanation of the phenomena of anomalous orientation that can be presented in some mesophases, it has to be considered that in semicrystalline polymers the organization of the solid state comprises interconnected crystalline and amorphous regions, but in the liquid crystal state only domains exist. The simplest model that permits to explain the experimental data of orientation by drawing of a mesophase of low order like a S_{CA} consists of assuming that the domains have a geometric shape in which an axis is much longer than the other two and that inside of these domains the macromolecules are oriented with their molecular axis perpendicular to the longer axis. Furthermore, the interactions between the different domains are weak. The tie molecules, if any, are very few between different domains, and the tighten forces between domains are mostly cohesive forces. When the sample is stretched at low rate of deformation, the domains, without being broken, are aligned with their longer axis in the stretched direction and, consequently, with the macromolecules in the transverse direction. At high rates of deformation the domains are broken and reorganized, and the macromolecular behavior governs the orientation process; consequently, the macromolecules are aligned in the stretched direction. According to this model, when the interactions between the domains are increased, i.e., the order in the mesophases grows (going from S_A, to S_B, or S_E, etc.), the phenomenon of the anomalous orientation will be produced with more difficulty because the domains will have more hindrance for moving independently.

In summary, it was clearly shown that two types of response, in this case orientation, can be induced by a external excitation, in this case a tensile test, in the smectic PPO4B as a function of two variables, strain rate and temperature. One orientation, as expected, places the chain axis in the direction of stretching and the other one in the transverse direction. Different amounts of material can be found in one or another direction depending of both variables, but in any case no polymer is oriented in intermediate directions. Low rates of deformation, quasi-equilibrium conditions, favor that the perpendicular to the smectic planes, and consequently the chain axis of the macromolecules accommodate transversely to the flow, showing that with this peculiar arrangement the domains minimize the free energy of the system. Increasing temperatures, keeping constant the rate of deformation, also favor this molecular disposition. These results show that intermolecular interactions play an important role in the way that chain axes are allowed to be placed.

The physical properties of polymers depend critically on their molecular orientation. However, as long as the direction of macromolecular alignment in liquid crystalline polymers is a function of the strain rate, the best mechanical properties are not always in the fiber direction. It is generally observed that high degrees of molecular orientation lead to increased strength and stiffness along the alignment direction, but from the data shown in Figure 6 this is not always the case: for anomalous orientation the worse mechanical properties coincide with the fiber direction, and the best are in the transverse direction.

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