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Real-time WAXS study of induced orientation in a liquid crystalline polyester under the influence of a magnetic field

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Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

Abstract

The in situ variation of induced orientation within a liquid crystalline polyester under the influence of a magnetic field was investigated during heat treatment, by means of wide-angle X-ray scattering (WAXS) using synchrotron radiation. The kinetics of molecular orientation, both from the melt and from the solid state, is analyzed in a wide temperature range ($T = 190-260$ °C) in terms of the variation of the Hermann's orientation function, as derived from the analysis of the WAXS patterns. The temperature range examined corresponds to the coexistence of, both, the nematic and the isotropic phases. The orientation function data are discussed in the light of Kohlrausch-Williams-Watts equation. Results reveal that the final degree of orientation reached shows a maximum around 200–230 °C that depends on whether the molecular orientation is developed during cooling down from the molten state or whether it arises upon heating up from the solid state. In the latter case, the orientation rate is found to be higher owing to the initial director orientation field at right angles from the magnetic field.

Keywords: Magnetically induced orientation; Polymer liquid crystal; WAXS

1. Introduction

Thermotropic liquid crystalline (LC) polymers are well known to easily orient under the influence of external fields. The physical properties of these materials are strongly dependent on the final molecular orientation achieved. While structural changes produced by mechanical deformation have been widely investigated [1], presently there is an increasing interest in the development of orientation by means of magnetic fields [2,3]. The ability of a polymer to align under a magnetic field relies on the diamagnetic anisotropy of the molecular segments which constitute the backbone structure. Magnetic orientation could be envisaged as an alternative processing route to produce materials with enhanced optical and mechanical properties. The theory describing the orientation of low molecular weight nematic liquid crystals inside a magnetic field is well established [4]. It is emphasized the competition between the effects due to the sample walls and the magnetic field, the former effect decreasing exponentially with the distance. The use of strong magnetic fields (6 T) has been recently shown to be capable of inducing orientation even in polymers (PET [5], PEN [6], iPS [7], iPP [8]…) which do not present typical mesophases. It has been suggested that during the induction period of crystallization of these systems transient liquid-crystalline structures are formed that could be responsible for the magnetic orientation. The role of such mesophases appearing during the first stages of polymer crystallization is still a matter of controversy [9,10]. As far as we know, a detailed real-time study of the development of orientation in LC polymers under the influence of conventional magnetic fields by X-ray diffraction methods is still missing. In a former study, magnetic orientation kinetics of thermotropic main-chain LC polymers has been reported as a function of time and temperature of orientation [11]. However, measurements were performed after quenching to room temperature from the mesophase. Preliminary experiments [12] have shown the possibility of magnetically orienting a thermotropic main chain liquid crystalline polyester at temperatures corresponding to the nematic phase. The aim of the present

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study is to present new X-ray scattering data on the variation of in situ induced orientation within a LC copolyester under the influence of a magnetic field of 0.8 T during heat treatment at temperatures, where a nematic phase is present.

2. Experimental

2.1. Materials

The studied thermotropic main chain liquid crystalline polyester has the following schematic chemical formula: $-[CO-(CH_2)_8-CO-O-\Phi-CO-O-\Phi-O]_n-$, where Φ represents the benzene ring. The synthesis and properties of a series of polyesters, including the present one, has been recently reported by one of us [13]. These materials have been shown to be formed by alternating sequences of repeating units. Similar polyesters, but including more statistical sequences, have been previously synthesized and characterized by Strzelecki and Liébert [14] and later by Krigbaum [15]. These authors report that the nematic phase of this material extends over a broad temperature range (155–320 °C in one case and 205–300 °C in the other). In addition the nematic–isotropic (N → I) transition appears as an almost imperceptible endotherm indicating the presence of a wide biphasic region. In our case, due to the controlled structure, the phase transitions occur at higher temperature and are better defined by somewhat smaller temperature ranges.

Samples were sealed inside glass capillaries of 1 mm in diameter to prevent material loss from the surrounding vacuum and placed in an oven. This confined environment minimizes any possible degradation of the samples when heated up to 300 °C. During the filling process in the melt, molecules tend to align themselves along the capillary main axis due to the orientational flow.

2.2. Techniques

Orientation experiments on the above mentioned material were performed using a permanent magnet of 0.8 T. The initial orientation direction was perpendicular to the magnetic field aiming to induce an orientation at right angles from the existing molecular alignment. The selected orientation temperature was rapidly reached from both the solid and the molten state (302 °C). The experimental setup was built in the soft condensed matter X-ray diffraction beamline A2 at HASYLAB, DESY (Hamburg, Germany). Synchrotron radiation with a wavelength of 0.15 nm was used. Two-dimensional wide-angle X-ray scattering (WAXS) patterns were recorded using a multi-wire Gabriel detector of 180×180 mm^2. X-ray accumulation time for each pattern was set to 60 s. Corrections due to background and detector response were accomplished.

3. Results and discussion

3.1. Dependence of orientation upon temperature

Fig. 1 shows DSC heating and cooling scans of the material as received and during a second temperature cycle. All scans, after the first one, show on heating two broad endotherms with maxima near 150 and 230 °C, respectively. The corresponding cooling exotherms occur at slightly lower temperatures. As reported before [15], the N → I transition covers a wide range of temperatures, suggesting the presence of a biphasic region with non-well defined limits, where both nematic and isotropic phases coexist. From the calorimetric data, we have selected orientation temperatures between 165 and 260 °C, although some of these temperatures could only be partially studied.

The changes in orientation, as revealed from X-ray diffraction patterns, are shown in Fig. 2 as a function of increasing temperature. In the solid state, at 85 °C, the initial flow orientation along the meridian is still clearly visible. Once in the nematic region, the initial orientation is preserved for a certain time, before the appearance of a transient isotropic state (249 °C) which is immediately followed by the magnetic field induced orientation (253 °C). The new oriented state, in the direction of the equator, further improves at higher temperatures. At 294 °C, the thermal fluctuations of the system are no longer compatible with any ordered structure and a final permanent isotropic state develops. The latter temperature is somewhat higher than the N → I transition shown in Fig. 1. However, it must be considered that we are not dealing with the as-received material, but with one which has been previously melted. In such a case, the N → I transition becomes very broad with an upper temperature limit in the range 270–290 °C. Furthermore, it is known that the presence of a magnetic or electric field may shift the N → I transition to higher temperatures [16]. In summary, for the semiflexible copolyester studied, with increasing temperature, the initial

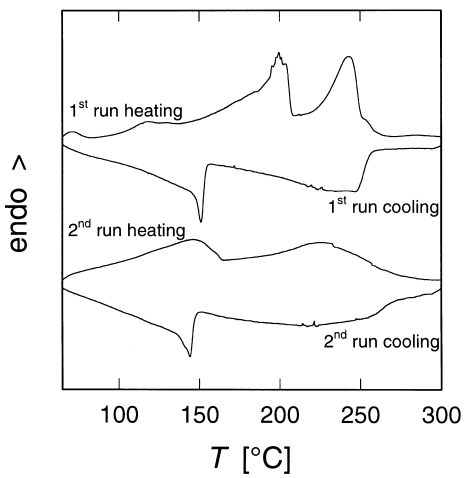

Fig. 1. Heating and cooling scans of the LC polyester as received and during a second temperature cycle.

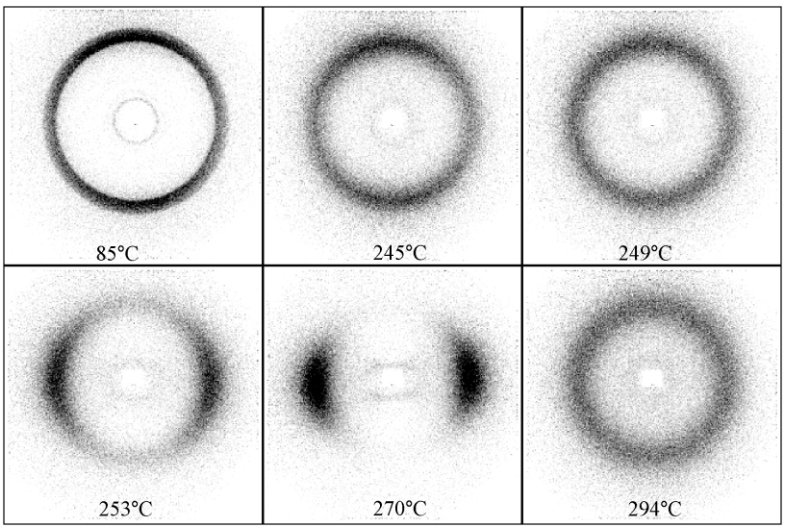

Fig. 2. WAXS patterns of the investigated LC polyester under the influence of a magnetic field of 0.8 T (in the vertical direction), as a function of temperature.

uniaxial orientation undergoes a transient isotropic state before the new magnetic induced orientation appears.

3.2. Kinetics of orientation

Let us next follow in detail the kinetics of orientation of director field, as described by the variation of the Hermann's orientation function, at different annealing temperatures in the nematic phase. Fig. 3 illustrates the Hermann's orientation function, f, calculated from the X-ray patterns, as a function of annealing time t. Results are taken at different temperatures from, both, the molten (a) and the solid state (b). In both cases a sigmoidal increase of the orientation function is found. In case that the orientation temperature is reached from the solid state (Fig. 3b), the initial negative values correspond to the flow induced oriented state inside the capillaries, which is perpendicular to the magnetic field. After approximately four minutes at the corresponding temperature, f becomes zero, which represents the above mentioned isotropic state. It is interesting to notice that the orientation process appears to be much faster when the orientation temperature is achieved on heating from the solid (Fig. 3b) than when cooling from the melt (Fig. 3a) (the maximum orientation rate from the molten state is included in the temperature interval studied). This result could be related to the different initial orientation of the system. When orientation is achieved from the solid state, it implies an initially existing director field perpendicular to the magnetic field direction, while on cooling from the melt it starts from an isotropic distribution of director orientations. According to NMR results on main-chain nematic polymers [17], one finds indeed a different director reorientation behaviour in case that the initial rotation is $\pi/2$. The different reorientation behaviour has been explained in terms of the influence of the magnetic field on the long-wavelength thermal fluctuations of the nematic director [17].

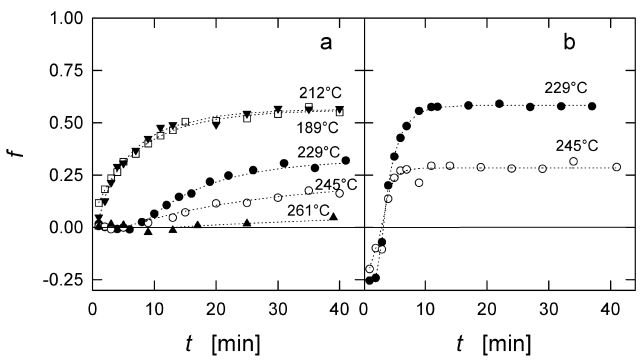

Fig. 3. Hermann's orientation function f derived from the WAXS patterns taken at different temperatures: (a) from the molten state, (b) from the solid state; as a function of heating time.

The orientation kinetics at each temperature can be adjusted according to a Kohlrausch-Williams-Watts (KWW) equation which has been previously used for the description of slow relaxing systems [18]

$$f = f_m + (f_M - f_m)[1 - e^{(\frac{t-t_0}{\tau})^\beta}] \quad (1)$$

The corresponding parameters are collected in Table 1: f_M denotes the maximum value of the Hermann's orientation

Table 1
Values for the maximum orientation function, f_M, the coefficient β, mean relaxation time, τ, and induction time t_0, taken at different temperatures from the melt and from the solid state

T (°C)	From	f_M	β	τ (min)	t_0 (min)
189	Melt	0.564	0.86	7.1	−0.34
212	Melt	0.567	0.82	5.5	0.75
229	Melt	0.332	1	11.3	7.4
245	Melt	0.211	1	19.4	7.1
261	Melt	0.081	1	44.3	12.4
229	Solid	0.587	1	2.17	3.0
245	Solid	0.289	1	1.31	3.0

function, f_m represents the starting orientation which is usually negligible, β is a coefficient which takes the value of 1 when approaching a Debye behaviour, τ is the mean relaxation time depending on the nematic rotational viscosity and t_0 is the induction time prior to orientation. Although the KWW equation is purely phenomenological, it resembles the exponential behaviour derived by Pieranski et al. [19], for the orientation of an infinite liquid crystal in a weak magnetic field, using the Leslie-Ericksen continuum theory.

Fig. 4 shows the KWW linear representation corresponding to the experimental data of Fig. 3. Straight lines are defined by the fitted parameters of Table 1. Large deviations from the linear behaviour are observed when the system approaches an orientation equilibrium state (Fig. 4b). Such deviations could be explained by the existence of two different orientation regimes: the faster one corresponding to the bulk of the material and the second one could be due to liquid crystalline domains partially bound by surface interaction forces at the boundaries and possibly by impurities [20].

The maximum values of the Hermann's orientation function, f_M are plotted versus the orientation temperature in Fig. 5 (open symbols). Maximum values for the obtained orientation after quenching to room temperature are also included (solid symbols).It is observed that the latter values are larger for those samples oriented from the solid state, while the opposite behaviour is found for most of the samples oriented from the melt. A clear explanation, why in one case the final orientation improves on quenching, while it seems to decrease in the other case, is still missing. One may think that this behaviour could be related to the occurrence of a different nematic domain structure in both cases. Fig. 5 also indicates that the highest degree of overall orientation is obtained at a temperature of about 210 °C from the melt and at a slightly higher temperature, near 230 °C, when heating from the solid state (Hermann's orientation function around 0.6).

The variation of the mean relaxation time τ with orientation temperature (Fig. 6a) is closely related to the maximum degree of orientation. For those samples oriented from the melt, the minimum value of the relaxation time (at 212 °C), which denotes the fastest orientation kinetics, gives rise in parallel to the highest degree of orientation. At still lower temperatures (189 °C), the system starts to orient before reaching thermal equilibrium as revealed by the negative induction time shown in Table 1. Excluding, thus, the low temperature value, the mean relaxation time seems to follow, for those data obtained from the melt, an Arrhenius-type linear behaviour of dependence:

$$\tau = A e^{\frac{B}{T}} \tag{2}$$

where A and B are constants (Fig. 6b).

Finally it is shown how the high orientation obtained in the liquid crystalline phase after one hour at 229 °C coming from the solid state (Fig. 7a) can be transferred back into the solid (Fig. 7b) by quenching the material inside the magnetic field. Both X-ray patterns reveal important details on the molecular organization of the material. The first one at 229 °C (Fig. 7a) shows a splitting of the low-angle reflection into two maxima displaced on either side of the meridian by a certain angle. This observation suggests the presence of a cybotactic nematic phase, i.e. a nematic phase including smectic C-type cybotactic clusters [21]. On the other hand, at room temperature a well defined fiber diagram is obtained (Fig. 7b) which provides sufficient information to carry out the calculation of the unit cell parameters of the

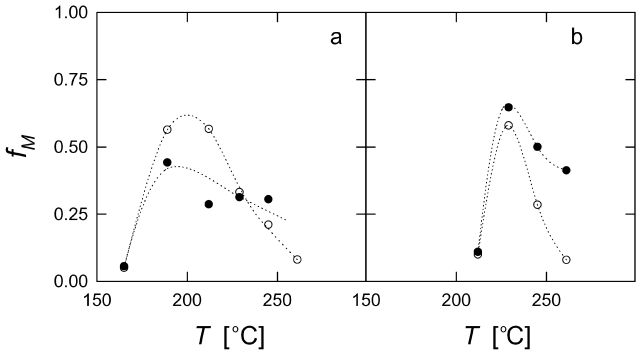

Fig. 5. Plot of f_M vs temperature: (a) from the molten state, (b) from the solid state. Open symbols: maximum orientation function values at given temperatures; Solid symbols: f-values after quenching at room temperature.

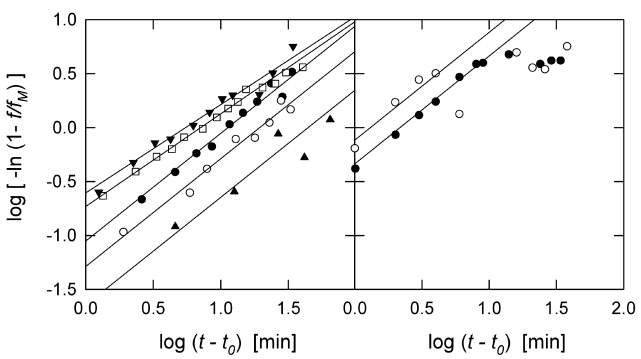

Fig. 4. KWW representation of the experimental data of Fig. 3; f_M : maximum value of the orientation function; t_0 : induction time before orientation.

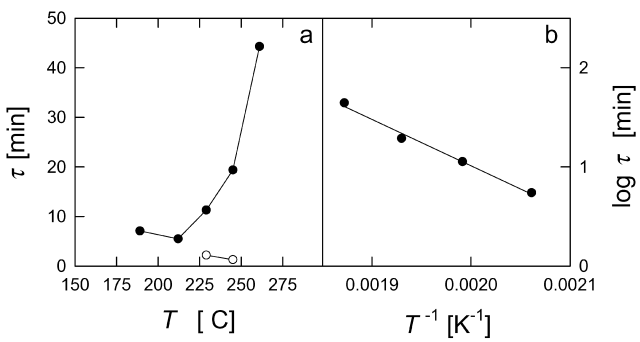

Fig. 6. (a) Variation of the mean relaxation time τ with temperature. (b) Arrhenius plot of τ. (solid symbols: orientation from the melt; open symbols: from the solid state).

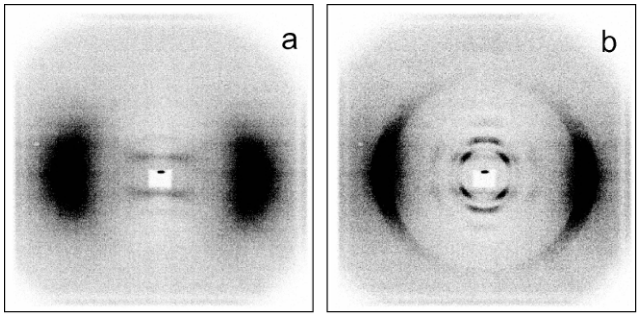

Fig. 7. WAXS pattern of the LC polyester obtained under the field of 0.8 T (in the vertical direction): (a) after 1 h at 229 °C from the solid state and (b) after quenching the material in the magnetic field at room temperature.

crystalline phase of the system. This analysis will be the object of a separate publication.

4. Conclusions

(1) The LC polyester samples, initially oriented along the flow axis (meridian), in the presence of a magnetic field (applied at right angles to the initial orientation) undergo, with increasing temperature, a transient isotropic state followed by a magnetic field-induced orientation along the equator direction.
(2) The orientation obtained in the LC phase at high temperature, can be transferred with certain variations into the solid state by quenching the material under the presence of the magnetic field at room temperature.
(3) For each temperature, the kinetics of molecular orientation of the LCP in the presence of the magnetic field is described, in the first stages of the process, by a Kohlrausch-Williams-Watts equation.
(4) The orientation process seems to occur faster when the orientation temperature is reached on heating from the solid than when cooling from the melt. This result is probably related to the different initial orientations, i.e. whether the director field is perpendicular to the magnetic field direction or there is an isotropic distribution of director orientations.
(5) The mean relaxation time, for those samples oriented from the melt, exhibits a minimum value for a temperature near $T = 210$ °C that corresponds to the maximum degree of overall molecular orientation reached. The temperature variation of τ follows an Arrhenius-type behaviour.

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