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The relaxation of a magnetically orientated liquid crystalline polymer

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The relaxation of the orientation induced by the action of a magnetic field on a thermotropic liquid crystalline polymer is examined. The polymer is a main-chain random copolyester available as a molecular weight series covering the range 4600–14400. The rate of loss of orientation is modelled using a similar function to that used to describe the orientation process, all induced orientation being lost over a period of 30 min. Microstructural studies show the complete loss of the domain structure developed on magnetic orientation, and also indicate that the orientation and relaxation cycle gives a microstructure which is coarser than that in the untreated samples. The influence of the crystallization process on the induced orientation is also examined.

(Keywords: liquid crystalline polymer; relaxation; magnetic fields)

Introduction

Magnetic fields have an orientating influence on liquid crystalline materials resulting from the diamagnetic anisotropy of the molecules. The magnetic orientation of liquid crystalline polymers has been studied by several workers[1–9]. An advantage of working with thermotropic random copolymers is that on quenching from the nematic state, the induced orientation may be frozen in, and the resulting crystallization does not overtly affect the orientated structure. Previous work from this laboratory on main chain random copolyesters has extensively examined both the kinetics of the magnetic orientation process over a range of molecular weights[8], and the change in the microstructure observed in these materials on orientation[10]. This communication considers the relaxation of induced orientation once the field has been removed. If the magnetic field is removed while the sample is held in the nematic state, the polymer 'relaxes', and the induced orientation is found to decay away rapidly[9,11–13].

Experimental

Materials. This study was made using series of random copolyesters based on repeat units of 1,4-oxybenzoic acid (HBA) and 2,6-oxynaphthoic acid (HNA) (*Figure 1*). The polymers, synthesized by Hoechst Celanese Corporation, had a mole ratio of 75/25 (HBA/HNA). Three molecular weights were examined, and the weight average molecular weights, M_w, as determined by inherent viscosity measurements in pentafluorophenol/hexafluoroisopropanol, are listed in *Table 1*, along with the melting temperatures as determined by d.s.c.

Orientation and relaxation. The polymer sample was finely ground (to approximately 50 μm particle size), held between the poles of a water-cooled electromagnet and taken to about 30°C above its melting point under a gentle flow of nitrogen gas. After melting, a field of 1.12 T was applied for 30 min to achieve the maximum level of orientation for this field strength[8]. The sample was then rapidly removed from between the poles of the magnet and held for a set period of time before removing the heat source and quenching the sample with a jet of nitrogen gas.

Measurement of orientation. The degree of preferred orientation, expressed as the second harmonic coefficient of the orientation distribution function $\langle P_2 \rangle$ was measured by analysis of the wide angle X-ray diffraction patterns of the quenched samples. The main equatorial diffraction maximum ($2\theta = 19.9°$) was scanned azimuthally and corrected for background and intrinsic width, and the intensity distribution was analysed to give $\langle P_2 \rangle$ as outlined in refs 14 and 15.

The background intensity for the azimuthal scan was calculated using the background from the smallest half-width profile (the best orientated sample), averaging the intensity over the final 25° in ϕ. This was subtracted from all intensities, the background being weighted to the total area under each of the measured azimuthal curves.

A correction was also made for the intrinsic azimuthal width of the reflection being used. The assumption is made that in a perfectly orientated sample, the equatorial peak of the two-dimensional pattern would be equiaxial in profile, the intrinsic azimuthal width being taken as equal to the radial width of the reflection. The value of $\langle P_2 \rangle$ corresponding to this intrinsic azimuthal width was found to be 0.97 and the $\langle P_2 \rangle$ values were corrected by dividing by this value.

Microstructural observations. The scanning electron microscope was used to examine fracture surfaces of samples prepared by cooling in liquid nitrogen and scoring prior to fracture. Samples were prepared for

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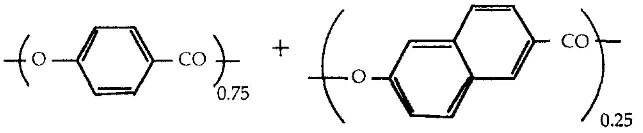

Figure 1 The chemical structure of the random copolymer of HBA/HNA

Table 1 The copolyesters of 3 : 1 HBA/HNA with different molecular weights

M_w	Melting temperature (°C)
4600	271
5000	272
8600	274
14400	288

viewing optically in transmission by wet grinding to a thin (20 μm) section. The grinding was done with successively 1200 and 4000 grit silicon carbide papers, and finishing with 1 μm and 0.25 μm diamond-impregnated medium-nap cloths. The samples were attached with wax to a grinding support with a boron nitride collar which set the exact thickness of the sample and ensured that the two surfaces were parallel.

Results

The role of crystallinity. The WAXS method used here relies on quenching the sample to the solid state prior to orientation measurement and is consequently reliant on the solid state structure faithfully reproducing that of the nematic phase. On quenching, small crystallites are formed from localized matching of the random sequences along the polymer chains[16]. These are embedded in a glassy matrix which, necessarily, reflects the structure in the nematic phase unless the crystallization process unduly disrupts the director field. The nematic phase consists of local alignment of the polymer chains and so the crystallization process requires only the longitudinal shifting of the laterally aligned chains for sequence matching, and indeed there is evidence of ordering along the chain axis in the nematic state[17]. Transmission electron microscopy studies made on the crystallites formed on quenching the samples from the nematic phase indicate that the glassy matrix orientation is not affected by the presence of small, discrete crystallites[18].

The contributions to the WAXS scattering from the crystalline component (which results in a relatively sharp equatorial peak) and the glassy component (which produces a broad equatorial halo reflecting the greater distribution of intermolecular distances) may be separated in order to determine whether the crystals that form are less well orientated to the field because the local orientation has been sacrificed in order for the favoured crystallization to occur.

The orientation of the crystalline and glassy regions may be measured separately by analysis of an azimuthal scan in intensity, as described above, and the contributions to the intensities from each of the phases may be found by taking a radial scan in 2θ and estimating the trace of the broad halo (from the glass) under the relatively sharp peak (from the crystals) centred on $2\theta = 19.9°$. A well orientated sample was scanned in 2θ at various azimuthal angles and the areas under the peak and the halo were calculated. From each of these areas, determined as a function of ϕ, the corresponding $\langle P_2 \rangle$ was determined, the background intensity and the intrinsic width of the reflection being taken into account separately for each of the two phases.

Table 2 The order parameters $\langle P_2 \rangle$ of the crystalline and amorphous phases and that calculated using the total measured intensity from a single, well orientated sample

	$\langle P_2 \rangle$
Total intensity	0.890
Crystalline phase	0.902
Amorphous phase	0.844

Table 2 gives the orientations calculated using the total intensity and the intensity from each of the two contributions. These data indicate that both the crystals and the amorphous regions are highly orientated to the field. The fact that the orientation of the crystalline phase is greater (by 7%) than that of the glass suggests strongly that the crystallization on quenching does not disrupt the orientation, for one would then expect the crystals to be less well orientated to the field than the molecules in the glass. The reason why the orientation of the crystals is observed to be slightly greater than that of the surrounding glass may be attributed to the fact that the areas of slightly better mutual orientation would be more likely to crystallize.

The indications are, therefore, that the crystallization process does not change the nematic structure on the scale used in the orientation measurements or in microscopy. Consequently the solid phase structure as observed here will reproduce the structure observed in the nematic. The quench method thus provides an added advantage, that of observing the microstructures produced in the liquid crystalline phase from bulk samples in which orientation measurements may also be taken.

The orientation data given in *Figure 2* and the orientation measurements described in ref. 8 are calculated from the whole main equatorial intensity, thus incorporating both the crystalline and glassy elements.

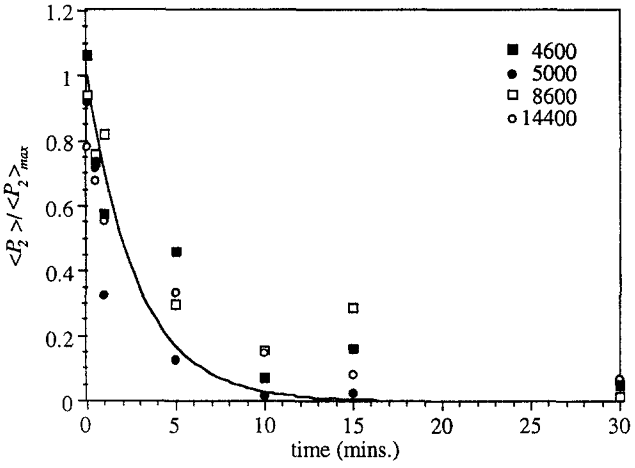

Figure 2 Experimental measurements of $\langle P_2 \rangle / \langle P_2 \rangle_{\max}$ against time for all molecular weights, where $\langle P_2 \rangle_{\max}$ is the minimum orientation achievable as predicted from the curve-fit to orientation data[8]

Kinetic data. *Figure 2* shows the loss of orientation in samples of four different molecular weights. In each case the temperature was 30°C above the melting temperature listed in *Table 1*. The $\langle P_2\rangle$ vs. time curves indicate a rapid decay in orientation initially, which slows as the orientation decreases, until eventually all orientation is lost. The kinetics of magnetic orientation were modelled on the rate of orientation decreasing in proportion to the difference between the actual orientation at any time and the maximum equilibrium value. Hence for orientation:

$$\frac{\langle P_2\rangle}{\langle P_2\rangle_{\max}} = 1 - \exp\left(-\frac{t}{\tau_o}\right) \qquad (1)$$

$\langle P_2\rangle_{\max}$ is the maximum level of orientation achievable, which was found to be dependent on the applied field strength. τ_o is a constant defining the rate of orientation.

In a similar way to the orientation, the data for the relaxation kinetics may be modelled by an exponential decay:

$$\langle P_2\rangle = \langle P_2\rangle_0 \exp\left(-\frac{t}{\tau_r}\right) \qquad (2)$$

where τ_r is the relaxation constant analogous to τ_o, and $\langle P_2\rangle_0$ is the starting orientation, which in this case is expected to be $\langle P_2\rangle_{\max}$ at this field strength for all samples. The best-fit curve for this expression from all the data is shown in *Figure 2*. The data are normalized with respect to $\langle P_2\rangle_{\max}$ as calculated from orientation measurements[8].

In many cases, the data give a poor fit to this expression on account of their scatter. The range of error is considerably greater than that from the method of $\langle P_2\rangle$ determination[8]. The fit to the exponential was found to be better for the orientation measurements[8]. The relaxation data from all four molecular weights overlap within the extent of the scatter shown in the data for the samples of molecular weight 4600 and 5000. There is no trend in the rate of relaxation with molecular weight that may be determined from these data, an observation in marked contrast to that made on orientation. *Figure 3* shows how both the orientation time constant, τ_o, and the maximum level of orientation achievable, $\langle P_2\rangle_{\max}$, for a field strength 1.12 T vary with molecular weight, from the data published in ref. 8. The characteristic time for orientation is shown to increase with molecular weight in the range 1.14–7.49, and the maximum level of orientation to decrease in the range 0.87–0.74. The relaxation constant determined using equation (2) for the data from all the molecular weight samples together is 2.8 ± 0.5, and thus, even with the large scatter in these data, it is possible to see that there is no increase in the relaxation time constant with molecular weight to the same extent as for orientation.

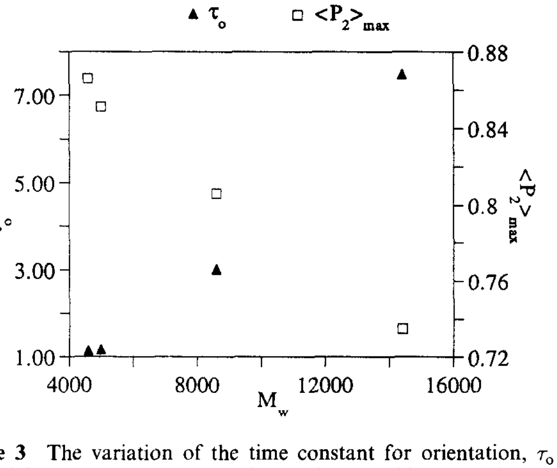

Figure 3 The variation of the time constant for orientation, τ_o as defined from equation (1), and the maximum achievable orientation, $\langle P_2\rangle_{\max}$, with molecular weight from data in ref. 8. For all data the field strength was 1.12 T, and the temperature was 30°C above the melting point

These data do show that on removal of the field there is a rapid and complete loss in the induced orientation, and in agreement with Platé *et al.*[11], who studied polymers with flexible spacers, the relaxation time constant is of the same magnitude as those of orientation. *In situ* methods for determination of the degree of orientation would be of considerable advantage in the measurement of the kinetics of the orientation and, in particular, the relaxation processes in these materials as only a single sample is required for a complete orientation and relaxation process.

Microstructures. The microstructures of magnetically untreated and magnetically orientated samples have previously been examined using scanning electron microscopy (SEM) and transmission optical microscopy[10]. It seems reasonable to relate the fibril direction as observed by SEM in the fractured specimens to the local director, but further confirmation has been found by examination of the fracture surface etched in 2% potassium permanganate in mixed sulfuric and phosphoric acids[19,20] to reveal the platelet crystallites, which are known to lie normal to the chain axes[21]. The crystallites are found at all times to lie normal to the local axis of the fibrils[10]. The untreated samples (powder melted and quenched with no field applied) contained 'swirls' of material, well aligned locally, but with no preferred orientation direction for the sample as a whole, as shown in ref. 10. The magnetically treated samples with high levels of orientation had a distinctive domain structure consisting of well aligned regions, bounded by discrete boundaries which are inversion walls[22], the director rotating through 180° as the wall is traversed[10].

On complete relaxation to zero global orientation, the microstructure, as observed optically in transmission between crossed polars (*Figure 4a*), resembles that of the magnetically untreated specimen, but with a larger size scale. The extent of the well aligned regions in the magnetically untreated specimen reflects the particle size of the powder from which the sample was formed and are of the order of 50 μm. In the relaxed sample, the aligned regions are of the order of 200 μm across, indicating that the orientation process and the formation of the domain structure has eliminated at least some of the defects from the structure. Scanning electron micrographs of the fracture surfaces of relaxed specimens (e.g. *Figure 4b*) show no 'swirl' pattern as observed in samples never magnetically orientated, as these were a consequence of the original powder. Similarly, they show no evidence of the domain structure, as observed on magnetic orientation. The relaxed structures do, however, show no overall global orientation to the axis along which the field had been applied, and reveal regions of the sample in which the fibres appear to change direction abruptly and in a zig-zag fashion reminiscent of the banded

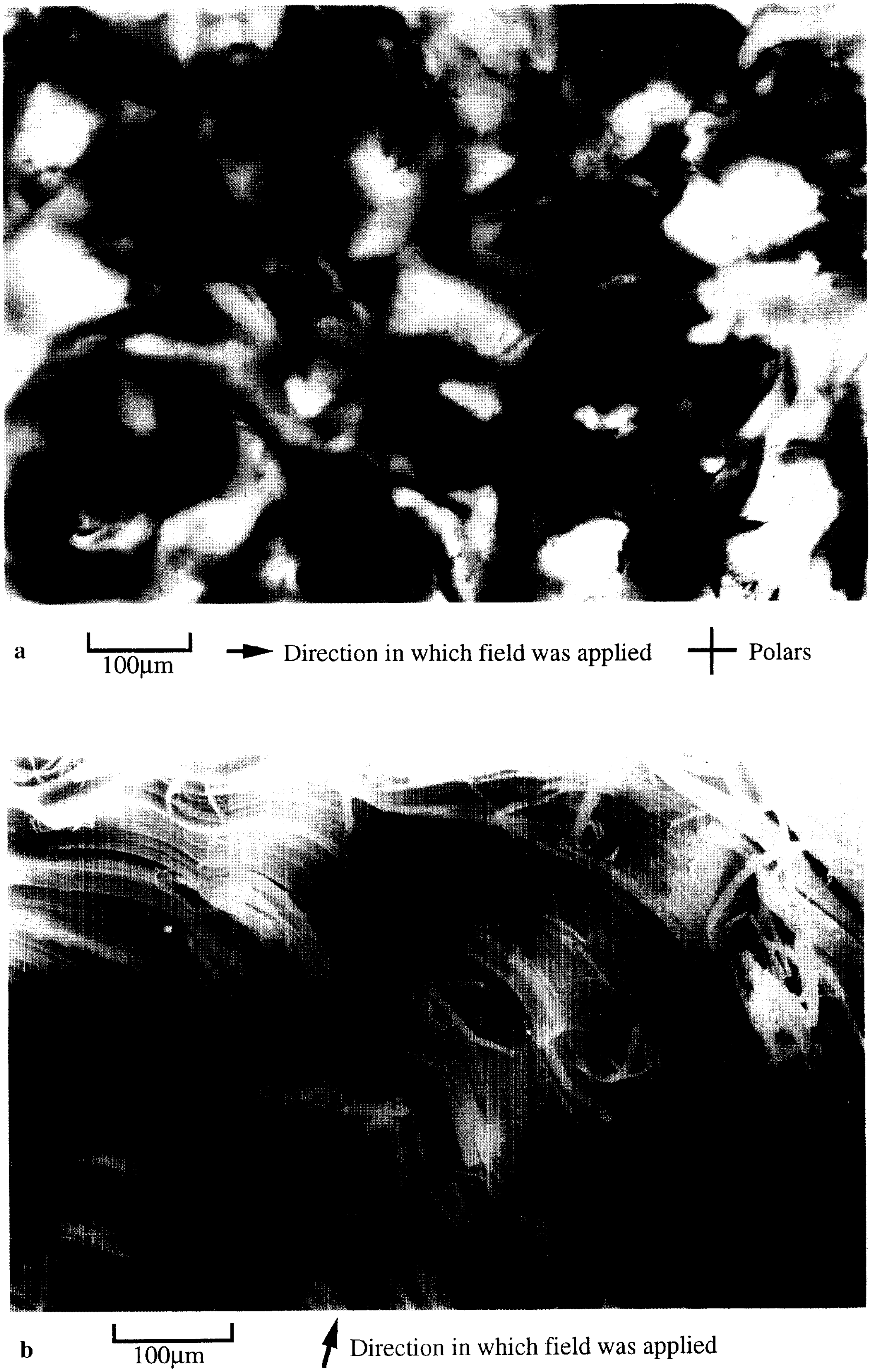

Figure 4 (a) Transmission optical micrograph taken with crossed polars and mercury lamp showing the microstructure of a fully relaxed sample ground to a thin film. (b) Scanning electron micrograph of a fracture surface of a fully relaxed specimen. In both cases, the sample ($M_w = 5000$) had been orientated at 300°C for 30 min in a field of 1.12 T and subsequently relaxed for 15 min out of the field before quenching

texture observed as a transient in samples relaxing after shear[23]. However, transmission polarizing microscopy (*Figure 4a*), while confirming the absence of domains, does not show any banded texture.

General discussion

The major question raised by these studies is why an orientated liquid crystalline polymer should relax at all on removal of the aligning field, for one would expect the equilibrium state of a nematic to be that of perfect global alignment. The issue is similar to that raised by the presence of banded textures[23] in mechanically orientated liquid crystalline polymers which have the opportunity to relax briefly prior to solidification. The view that there is an elastic network which entropically contracts, thus buckling the orientated nematic phase from within, may be tenable for banded textures where the orientation process is much more rapid[24]; however, the model for the relaxation of magnetic orientation is probably much more simple. The regions in which the orientation changes rapidly with position, those which form the domain boundaries, are effectively compressed by the field, and will expand in order to minimize their distortion energy once the field is removed. The boundaries will consume the domains they once delineated. This process of orientational loss will also tend to cause the polymer to contract along the previous field axis. Material that was towards the centre of the domains in the orientated specimen will thus also be subject to compressive stresses, and thus the observation of buckled regions in fully relaxed specimens (*Figure 4b*) is not untoward.

Finally, for these specimen sizes of around 10 mm × 10 mm × 1 mm, we cannot eliminate the possibility that specific boundary conditions, such as homeotropic boundaries at the walls of the sample container, are also responsible, in part, for the orientation loss.

A comparison of the timescale of decay in the orientation induced by magnetic orientation (about 5 min) with that for stress relaxation after shearing (about 5 s)[24] gives an insight into the different processes involved. In the case of magnetic orientation, the increased alignment to the field is induced, at least over long timescales, by the motion of topological defects within the sample and by the compression of those defects which cannot be eliminated. By contrast, the elastic stresses from shear over short timescales are induced in the material as a whole over and above the disclinations, and may very rapidly decay.

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