

A light scattering study on films of a nematic main chain thermotropic liquid crystalline polymer

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The morphology of a cast thin film of a thermotropic main chain polyester was studied using optical microscopy and small angle light scattering (SALS). It was found that the SALS pattern arising from the nematic texture is a four-leaf clover pattern where the lobes are oriented at 0° and 90°. The characteristic dimension associated with this pattern follows the coarsening of the texture upon annealing, thus providing a means of monitoring morphology changes in the film. Using this means it was possible to investigate the kinetics of texture evolution from the isotropic state to the final equilibrium nematic texture. It was found to be very fast. It was also found that the characteristic dimension associated with the pattern depends strongly on film thickness.

(Keywords: liquid crystalline polymer; thin film; nematic state; small angle light scattering)

INTRODUCTION

The morphology of liquid crystalline polymer (LCP) films in the thermotropic state has recently been the subject of many studies. The techniques used in these studies were mainly optical microscopy¹⁻⁶, TEM^{7,8} and small angle light scattering (SALS)⁹⁻¹³. The polymers were investigated both at rest^{1-5,7-11} and under flow^{6,12-14}.

The morphology of a film in the nematic state at rest is very different depending upon whether the film was previously subjected to orientation or not: in the case of an oriented film the most evident feature is a system of bands perpendicular to the shear direction¹⁵, while in a film not previously oriented the texture is usually the schlieren texture already described for low molar mass liquid crystals¹⁶. The banded pattern has been explained in terms of a sinusoidal arrangement of the chains about the shear direction¹⁷, while the schlieren texture characteristic of the nematic phase was interpreted in terms of a continuous director field with abrupt discontinuities at the disclinations¹⁸.

Disclinations are defects which affect the rheological behaviour of the liquid crystalline polymer^{19,20}. During cooling the disclinations can be frozen-in and retained in the solid state probably affecting the mechanical properties of, for example, moulded samples. Considering these facts, the study of disclinations has practical as well as fundamental ramifications. In this paper optical microscopy and the SALS technique were used to study the morphology of a thin film of thermotropic rigid main chain polyester.

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EXPERIMENTAL

The polymer was an experimental copolyester²¹ (provided by Granmont Inc.) consisting of phenylethyl hydroquinone, phenyl hydroquinone and terephthalic acid in the molar proportions 25:25:50. The d.s.c. trace of this polymer is shown in *Figure 1*: the transition solid-nematic is rather broad, starting at 260°C and being completed at 340°C; it degrades at ~400°C without reaching the isotropic state and there is no evidence of a glass transition temperature²². The inherent viscosity of this polymer was found to be 0.66 in phenol/trichlorobenzene 50/50 (v/v) at a concentration of 0.2% (w/v) at 85°C.

Films of different thickness were cast onto glass microscope slides from solutions of concentrations 3, 2, 1, 0.5, 0.25 and 0.12% of the polymer in a 60/40 (v/v) mixture of phenol/1,1,2,2-tetrachloroethane (Ph/TCE). Films were also cast from a solution of concentration 1% (w/v) of the polymer in a 50/50 (v/v) mixture of phenol/1,2,4-trichlorobenzene (Ph/TCB). The solvent was allowed to evaporate slowly at atmospheric pressure after which the films were dried at 180°C for 15 h, also at atmospheric pressure. All films so prepared were transparent and macroscopically amorphous. The samples were heated to reach the nematic state and then rapidly quenched to undergo microscopic and SALS characterization.

The micrographs, all taken between crossed polarizers, were taken using an Olympus Vanox microscope.

The photographs of the SALS patterns were obtained with the usual light scattering experimental set-up²³. Only the H_v patterns obtained with the sample between crossed polarizers²⁴ were recorded.

The kinetic measurements of the texture coarsening process were obtained by monitoring the time evolution of the characteristic dimension of the SALS pattern of

samples heated on a home-built heating stage with a temperature control of $\pm 1^\circ\text{C}$, as schematically shown in Figure 2. The heating stage was brought to the set temperature and the sample was placed upon it. It took ~ 30 s for the film to reach the nematic state and to display the SALS pattern. From this instant, the temperature of the film was presumed to be uniform and

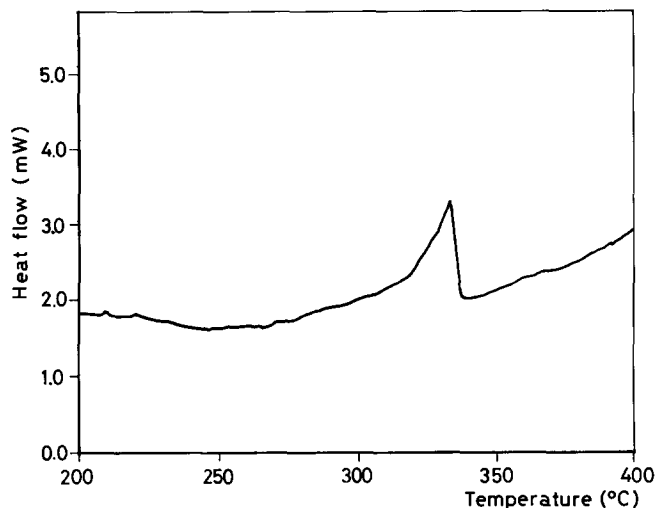


Figure 1 D.s.c. thermogram (heating rate $10^\circ\text{C min}^{-1}$)

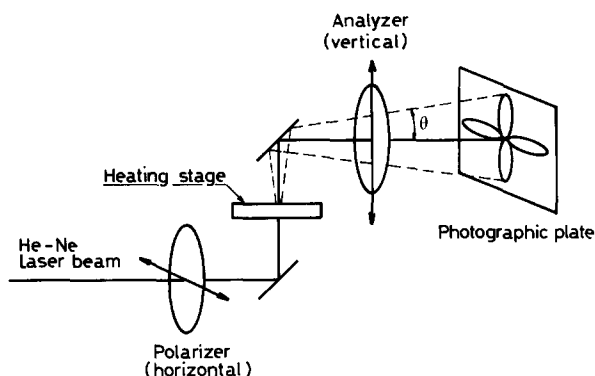


Figure 2 Experimental SALS set-up used to perform the kinetics measurements at elevated temperatures

equal to the set temperature due to the low thickness of the film, i.e. $\sim 1-6 \mu\text{m}$, and to the large heat capacity of the heating stage. In evaluating the kinetics of the process this instant was defined as $t = 0$ and the photographs were taken every 10 s for up to 20 min.

Casting from solutions of different concentrations led to films of different thickness as determined using a micrometer ($\pm 0.5 \mu\text{m}$).

RESULTS

When heating the film to a temperature in the thermotropic temperature range a nematic texture starts to develop. The initial stage of this texture as it appears in the polarizing microscope is shown in Figure 3. It is a very fine texture whose features are not resolvable and thus cannot be analysed in detail. The SALS pattern corresponding to this texture is also shown in Figure 3. It is a four-leaf clover pattern with lobes oriented along the directions of the polarizer and analyser, i.e. azimuthal angles, μ , of 0° and 90° , having a maximum intensity at a scattering angle θ_{max} . The value of θ_{max} was visually estimated directly from the photographs. Upon continued heating of the film, the texture coarsens until reaching equilibrium. An example of such a coarsened texture at equilibrium is shown in the photomicrograph in Figure 4. This texture mainly is made up by closed loops which open up and move randomly to join other loops as the crossed polarizers are rotated. Coarsening centres²⁵ are also present in these samples as shown in the photomicrograph in Figure 5. The coarsening centres are larger and especially numerous in samples cast from the Ph/TCB solution.

Disclination points are the traces of the disclination lines emerging to the film surface¹⁶. As such, they are points which do not move when rotating the crossed polarizers. In this sense it was not possible at the magnification employed to describe the morphology shown in Figure 4 in terms of disclination points, aside from a few disclinations of strength +1 which are probably the precursors of the coarsening centres.

The SALS pattern corresponding to the equilibrium

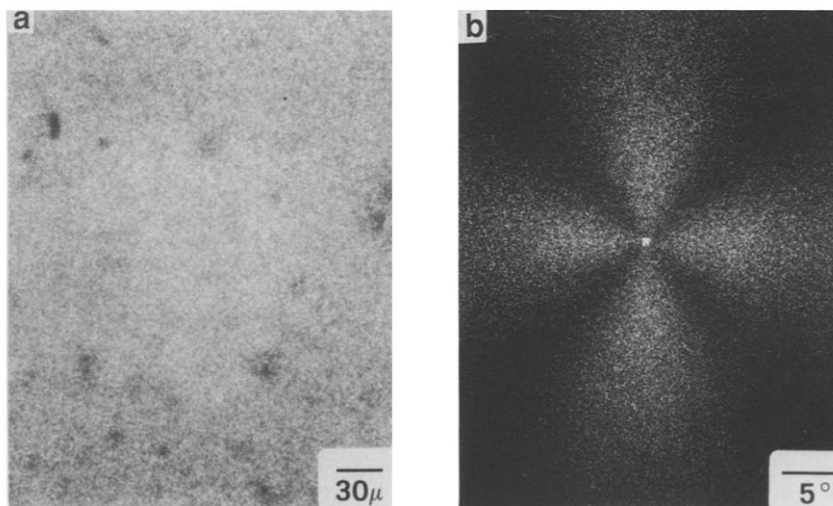


Figure 3 (a) Optical photomicrograph (crossed polarizers) of the nematic texture as it first appears and (b) the corresponding SALS pattern

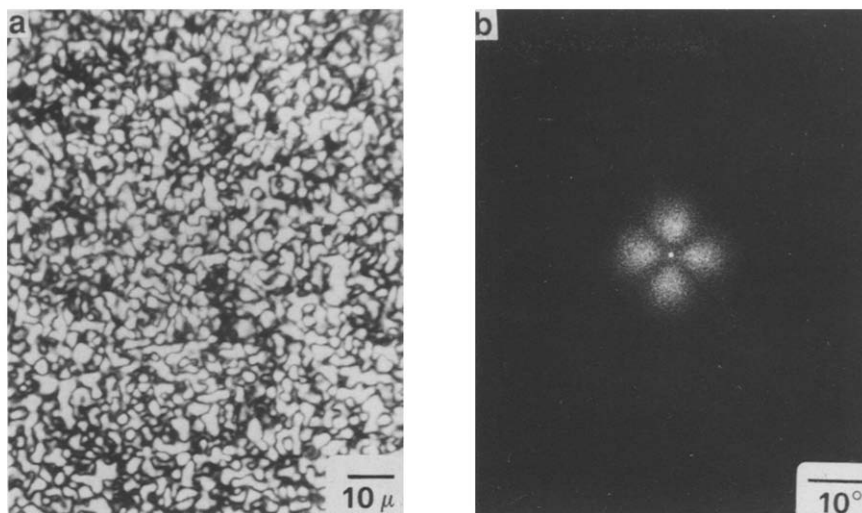


Figure 4 As for Figure 3, but at equilibrium

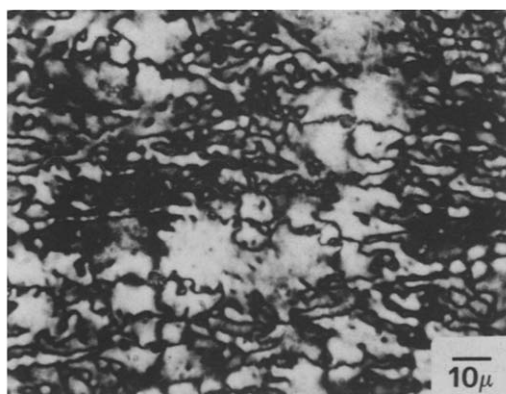


Figure 5 Optical micrograph (crossed polarizers) of the coarsening centres

texture is shown in Figure 4. In comparison with the pattern shown in Figure 3, the decrease of θ_{\max} is evident.

The SALS pattern arising from the coarsening centres themselves is shown in Figure 6. This pattern was obtained from a sample which showed coarsening centres in a partially oriented texture as shown in Figure 6. This sample was placed between the polarizers in the extinction position, i.e. the orientation direction of the film coincided with one polarizer direction with the result that the coarsening centres were the only birefringent sources. Note that the scattering lobes for the coarsening centres are located at $\pm 45^\circ$. In a nematic unoriented sample the scattering pattern arising from the coarsening centres can be superimposed on the pattern arising from the nematic state leading to a circularization of the pattern.

No appreciable change was observed either in texture or in scattering pattern for the temperature range 310–370°C for films of constant thickness, i.e. $\sim 3 \mu\text{m}$. At 380°C degradation is severe and the birefringence at equilibrium is weak.

The kinetics of the texture coarsening process was measured at 320°C. The process was very fast, taking < 10 s for the pattern to reach the equilibrium dimension. Similar results were obtained at 350°C.

The characteristic dimension associated with the scattering pattern at equilibrium is heavily dependent on

the film thickness. The dependence of the reciprocal of the scattering vector Q_{\max} [see equation (1)] at equilibrium at 320°C on the film thickness is reported in Figure 7. For thicknesses $\geq 6 \mu\text{m}$ the pattern has no azimuthal dependence as shown in Figure 8. The texture which builds up this pattern is more complex and the extinction lines are not continuous as in Figure 4 but are broken and enter the bulk as shown in Figure 8. This kind of pattern approaches the equilibrium dimension more slowly than the four-leaf clover pattern requiring > 3 min as opposed to 10 s.

DISCUSSION

The four-leaf clover scattering pattern described above seems to have a general spectrum of validity, being reported for the nematic phase of both rigid and semiflexible main chain LCPs¹⁰ and also for a cholesteric²⁶ and a lyotropic nematic polymer²⁷, disregarding the nature of the disclinations. Recently it was reported also for micelles²⁸. In LCPs this pattern is believed to arise from the spatial arrangement of the disclinations which mark the boundaries between areas of uniform orientation, often called domains¹⁰. The characteristic dimension associated with this pattern, i.e. the value of θ_{\max} , can be related to the disclination density, i.e. the size of the domains. A characteristic length L relating to domain size can be defined⁹ using the reciprocal of Q_{\max} , where Q_{\max} is the scattering vector corresponding to the angle θ_{\max} :

$$Q_{\max} = (4\pi/\lambda) \sin(\theta_{\max}/2) \quad (1)$$

and λ is the wavelength of light employed ($0.6328 \mu\text{m}$). The relationship between L and Q_{\max} suggested by SALS theory²⁹ is:

$$L = 2\hat{u}/Q_{\max} \quad (2)$$

where \hat{u} is an approximately constant scaling factor, as yet undetermined for a nematic LCP.

It is instructive to make a comparison of the value L/\hat{u} as determined from $2/Q_{\max}$ in the SALS experiment and the domain size as it is observed visually from independent measurements of the texture using polarized optical microscopy. Such a comparison is presented in Table 1. From these results \hat{u} has a value close to 1, i.e.

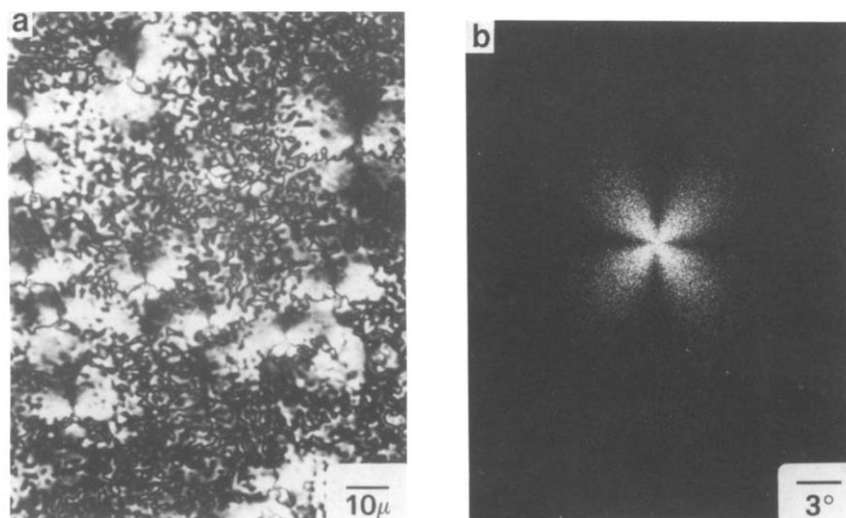


Figure 6 As for Figure 3, but of coarsening centres in a partially oriented texture

lower than the 2.7 found in a similar experiment using a lyotropic LCP²⁹. The advantage of deriving the domain size from the SALS scattering pattern is that the averaging over the complex morphology required in the photomicrograph is performed inherently via the physics of the light scattering experiment to give the result as $2\hat{u}/Q_{max}$. It is possible to equate the two measurements on the basis of Abbe's theory of image formation in the microscope³⁰ upon which the interconvertibility of the primary and secondary images, i.e. SALS patterns and micrographs, is based. In the absence of special cases of anomalous diffraction, the two manifestations of the data are interconvertible by a spatial Fourier transform which could be performed either numerically or optically³¹.

A few *ab initio* calculations have appeared which calculate the scattering pattern starting from one single disclination point of different strength or from a collection of disclination points. The resulting four-leaf clover pattern has been obtained starting either from an isolated disclination point of strength +1 or a system of three disclinations of strength $\pm 1/2$ (ref. 11) or from a dipole of two disclination points of strength $\pm 1/2$ (ref. 32).

The above calculations are restricted to two dimensions. The films used here to obtain the SALS pattern are relatively thick, i.e. $\geq 1 \mu\text{m}$. Below that thickness the scattering intensity drops and a pattern is no longer obtainable. At these thicknesses it is reasonable to think that the texture changes also in the third dimension. A short description of one possible arrangement of disclination lines along the z-axis has been given by Shiwaku *et al.*³³.

The morphology and texture of LCPs is by no means unique. Since the free energy differences between the various states are small, apparently insignificant perturbations such as wall boundary conditions or flow history can have a marked effect on producing a variety of metastable morphologies³⁴.

The two interfaces glass-polymer and polymer-air are different and consequently it is possible that the texture will be different at the two interfaces. Specific polymer-glass interactions² and competition effects between polymer anchoring on the glass plate and the free surface have been noted¹⁷. An unusual flow profile of a LCP solution was explained by the presence of

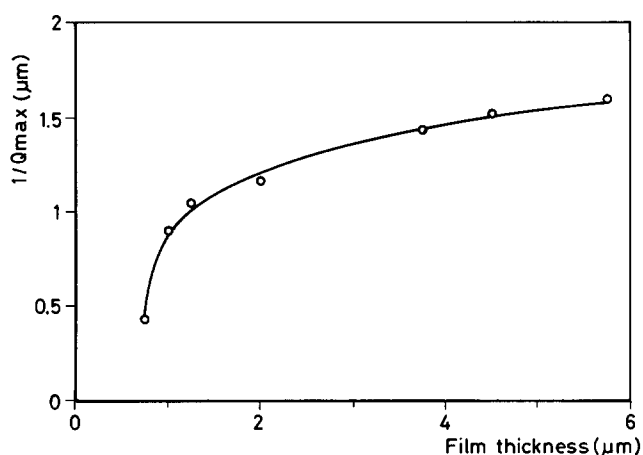


Figure 7 Reciprocal of the scattering vector, Q_{max} , as a function of film thickness

ordered layers near the glass walls³⁵. These effects would permit a continuous texture change in passing from one interface to the other in the samples employed here.

The dependence of the characteristic pattern dimension on the film thickness could be due to either multiple scattering effects³⁶ or a change in texture along the z-axis. The persistence length of wall ordering propagation could be expected to be of the order of the characteristic length describing the domain size. Note that in this work the domain size, especially at the equilibrium texture is of the order of the sample thickness, as shown in Table 1. Moreover the domain size at equilibrium, evaluated from SALS as $2/Q_{max}$, is approximately equal to the sample thickness, assuming $\hat{u} \sim 1$, as shown in Figure 7 for thickness $\leq 2 \mu\text{m}$. This result suggests the possibility that the domains, at this sample thickness, might be spherical. At greater thicknesses the domain size becomes approximately constant.

While the four-leaf clover scattering pattern arising from the nematic texture has the lobes oriented congruently with the polarization directions (Figure 3), the four-leaf clover pattern arising from the coarsening centres has the lobes rotated 45° from the polarization directions (Figure 6). This pattern is very similar to that obtained from a spherulitic superstructure²³ and was

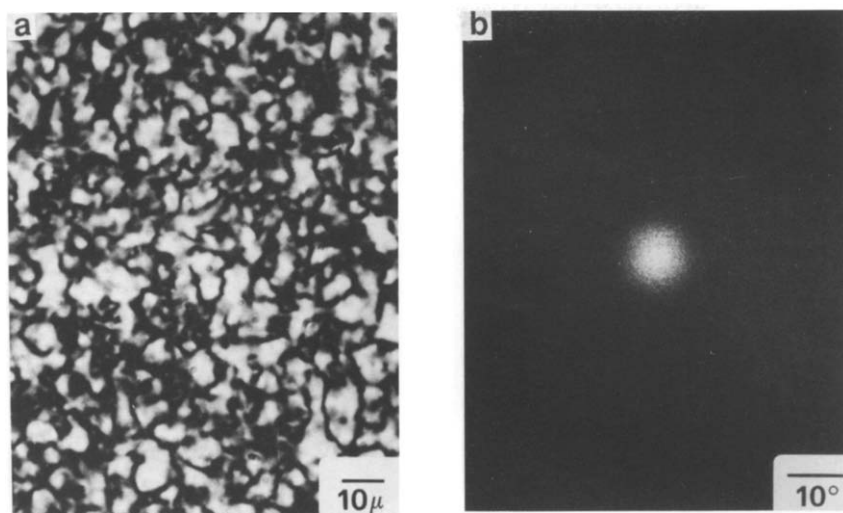


Figure 8 As for Figure 3, but of a film of thickness $\geq 6 \mu\text{m}$

Table 1 Comparison of the average domain size^a as evaluated by SALS and polarized optical microscopy

	SALS ^b (μm)	Polarized optical microscopy ^c (μm)
Initial morphology ^d	1.3 ($\theta_{\text{max}} = 9^\circ$)	<1.5
Equilibrium morphology ^e	2.3 ($\theta_{\text{max}} = 5^\circ$)	2–3

^aIn comparing the averages provided by these two techniques, the physics dictates that microscopy gives a number average while SALS gives a mass average. While this precludes a rigorous quantitative comparison, a qualitative similarity within the given level of measurement approximation is nonetheless found

^b $2/Q_{\text{max}}$

^cVisual estimate of domain size

^dFigure 3

^eFigure 4

reported for the thermotropic nematic mesophase in a very narrow temperature interval before the isotropization transition³⁷. The coarsening centres are, indeed, areas of material with a coarse radial texture which increase in number and size during the annealing. For polymers which can reach the isotropic state, the pretransitional region has a morphology made up mainly of coarsening centres²⁵.

The kinetic process of texture evolution was found to be too fast to allow a determination of the kinetic law. Using the correlation in equation (1), Rojstaczer *et al.*⁹ found that the size of the domains scales with time as:

$$1/Q_{\text{max}} \sim t^{0.37} \quad (3)$$

Shiwaku *et al.*⁵ studied the effects of thermal annealing on the texture using optical microscopy and found a value of 0.35 for the exponent, in good agreement with the above equation. Both experiments were performed using LCPs with flexible spacers. Rojstaczer *et al.*⁹ also reported that the process for attaining an equilibrium morphology in a rigid main chain LCP is very fast. They attributed this difference to different Frank's elastic constants, i.e. a stiff chain is expected to have larger values of the elastic constant leading to faster relaxation of the orientational fluctuation. Our results are in agreement with these findings.

CONCLUSIONS

SALS measurements were performed at high temperature on a main chain thermotropic LCP. Changes in nematic texture on thermal annealing were observable in the scattering pattern and were in good agreement with observations in the polarizing microscope.

The four-leaf clover scattering pattern arising from the coarsening centres is rotated by 45° from that of the nematic texture to lie at $\pm 45^\circ$ with respect to the cross polarizer axes.

The scattering vector, Q_{max} , as well as the shape of the scattering pattern shows thickness dependence and must be considered in more detail.

The value of the constant \hat{u} is lower than the corresponding value reported for lyotropic LCP and is close to one.

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