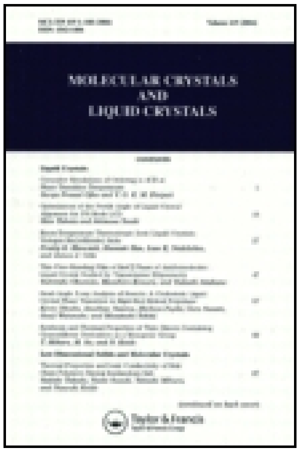


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Shear Induced Optical Textures and Their Relaxation Behaviour in Thermotropic Liquid Crystalline Polymers

D. J. Graziano [a] & M. R. Mackley [a]

[a] Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, England

Version of record first published: 20 Apr 2011.

To cite this article: D. J. Graziano & M. R. Mackley (1984): Shear Induced Optical Textures and Their Relaxation Behaviour in Thermotropic Liquid Crystalline Polymers, Molecular Crystals and Liquid Crystals, 106:1-2, 73-93

To link to this article: http://dx.doi.org/10.1080/00268948408080180

Mol. Cryst. Liq. Cryst., 1984, Vol. 106, pp. 73–93
0026-8941/84/1062-0073/$18.50/0

Shear Induced Optical Textures and Their Relaxation Behaviour in Thermotropic Liquid Crystalline Polymers

D. J. GRAZIANO and M. R. MACKLEY

Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, England

(*Received April 18, 1983; in final form September 21, 1983*)

We describe and classify optical textures observed in thermotropic liquid crystal polymers at elevated temperatures. The evolution from the static state to different textures observed as a consequence of controlled shearing experiments is reported together with the subsequent relaxation behaviour at the cessation of flow. Some of the observations show similarities with the behaviour of the phases of small molecule liquid crystals whilst others appear unique to liquid crystal polymers.

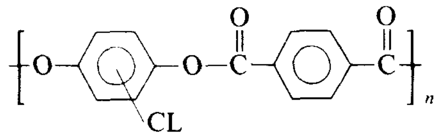
INTRODUCTION

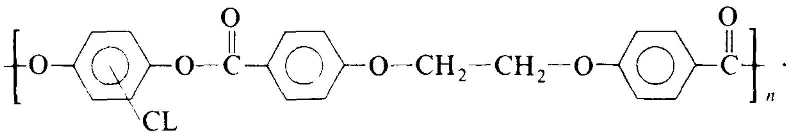
The ability of liquid crystalline polymers (LCP's) to form extended chain fibres with high strengths and elastic moduli has generated both industrial and academic interest in these materials. The attractive features of LCP's were first recognised in lyotropic systems (see, for example ref. 1), and fibres spun from mesomorphic solutions of LCP's are now being commercially manufactured and successfully marketed (for example, Dupont's 'Kevlar'). The recent discovery reported by Jackson and Kuhfuss[2] of thermotropic LCP's has aroused interest in these systems as well.

The thermotropic LCP's studied in this work are those composed of mesogenic units in the main chain as opposed to the so-called 'side-chain' LCP's. Quiescent samples of this type of polymer have been shown by Mackley, Pinaud and Siekmann[3] and Viney and Windle[4] to be rich in optical textures and microstructure. The object of this work was to determine the effects of shear on the microstructure of the materials. In this paper, we describe our microscopic observations of thin samples of LCP melts subjected to controlled shear programmes.

MATERIALS

The experimental work described in this paper was performed on a series of polymers kindly supplied to us by I.C.I. Petrochemicals and Plastics Division, Welwyn Garden City. The polymers, which we call the 'A Series Polymers', are 50:50 chlorophenyleneterephthalate: bis-phenoxyethane carboxylate copolymers made *via* methods described in a DuPont patent.[5] The macromolecule which results from the polymerisation is believed to be a random arrangement of the following repeat units:





Five polymers of this structure with varying molecular weights were available. The polymers and their inherent viscosities are listed below:

Polymer	Inherent Viscosity (10^{-3} m^3/kg)
A1	.056
A2	.074
A3	.107
A4	.098
A5	> .12

The inherent viscosities were determined from 0.5 wt % solutions of polymer in a 70/30 mixture of methylene dichloride and trifluoro-

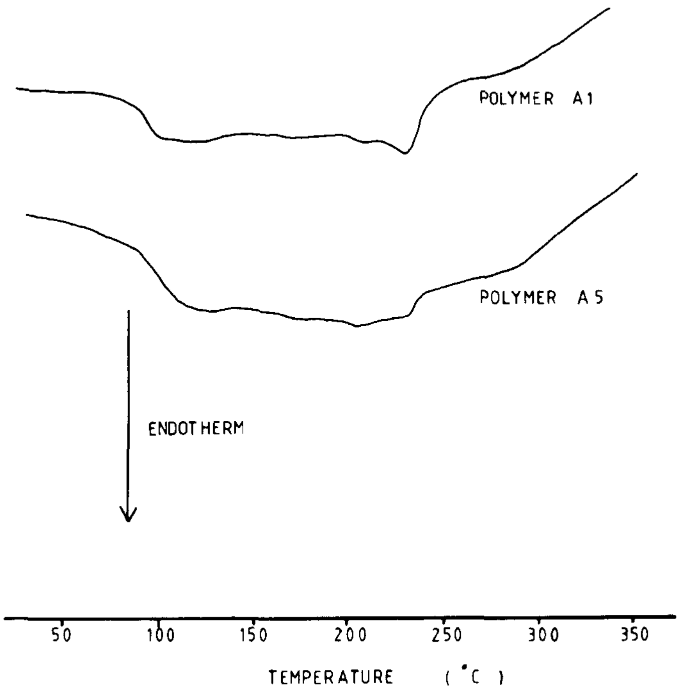


FIGURE 1 DSC thermographs of Polymer A1 and A5.

acetic acid by workers at I.C.I. (Griffin[6]). Molecular weights of these polymers are not known conclusively, but that of Polymer A1 is thought to be of the order of 20,000, and the inherent viscosities are related to the molecular weights *via* a Mark-Houwink exponent which may be as high as 1.8.

These polymers melt into mesomorphic phases which are believed to be of nematic order and which degrade before melting into an isotropic phase. DSC thermographs of the two polymers in the series, A1 and A5, which were studied most extensively appear in Figure 1 for reference. The traces were recorded at heating rates of 20 °C/min after the samples had been heated once to 360 °C and quench cooled with nitrogen. From the traces it is seen that both Polymers A1 and A5 experience a glass transition near 80 °C, and soften or melt near 230–240 °C. No crystalline melting peaks are evident in the traces.

Although the results described here involve only the A series polymers, similar investigations of different thermotropic LCP's have been performed and are reported elsewhere.[7] The polymers A1 and A5 were shown to be 'good' model systems in the sense that they displayed most of the phenomena observed in the other polymers.

EXPERIMENTAL TECHNIQUE

The experiments were performed in a specially designed apparatus which allowed us to subject thin samples of LCP's to controlled shears at elevated temperature while observing them with an optical microscope. The equipment is described in detail elsewhere.[7] The polymers are opaque to light for sample thicknesses larger than 50 μm, and we were, therefore, forced to use smaller thicknesses, typically 10 to 30 μm. This thickness constraint led to experimental difficulties which could only be resolved by adopting an oscillatory shear mode. Ranges of experimental conditions investigated are listed below:

Parameter	Range	
Temperature	200–280 °C	(±2 °C)
Sample Thickness	10–30 μm	(±10 μm)
Frequency of Strain Oscillations	.05 to 40 rad/sec	(±10%)
Displacement Amplitude of Strain Oscillations	50 to 300 μm	(±10 μm)

OBSERVATIONS

We have recognised three distinct shear-induced optical textures which occur in a wide range of main chain thermotropic LCP's. These textures will be introduced by describing their occurrence as the shear rate of a sample of Polymer A1 is increased. Shear rate values at which the textural transitions occur cannot be explicitly declared for two reasons. Firstly, in the oscillatory shear mode, the shear rate is a function both of frequency and amplitude and is continually changing with time. It is, therefore, not easily characterised by a single value. Secondly, the accuracy of our thickness measurements (±10 μm) was not high enough to determine meaningful shear rates in samples with thicknesses ranging from 10 to 30 microns. Experimental conditions under which the various textures have been observed are, however, detailed in figure captions or the text where appropriate.

The relaxation of the shear-induced optical textures after the cessation of shear has also been investigated and will be described. The optical behaviour of the highest molecular weight polymer (A5) will also be described as it behaves somewhat differently from Polymer A1. Finally, the effect of increasing the molecular weight in the A series polymers will be detailed.

Polymer A1

A static sample of molten Polymer A1 with thickness less than 50 microns, constrained between two glass surfaces, adopts an optical texture (when viewed under crossed polars) of dark threads lacing through a background of varying colour. Figure 2 presents photomi-

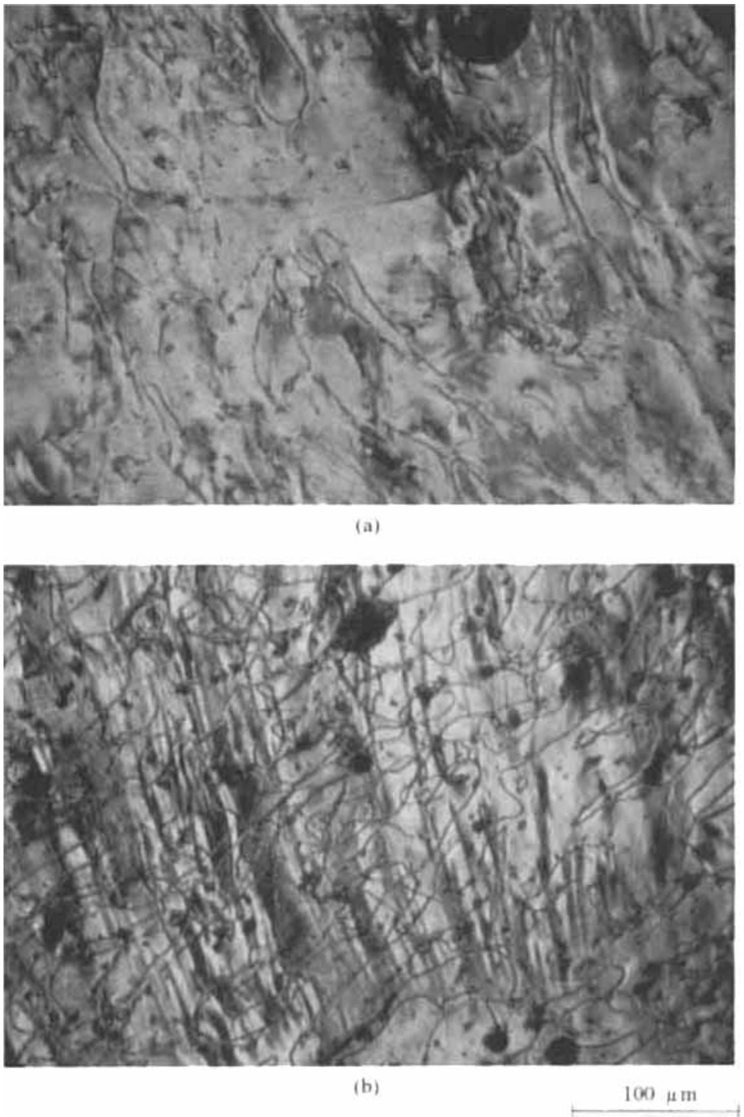


FIGURE 2 Quiescent samples of molten Polymer A1 at 240 ° C, viewed with crossed polars. Sample thickness of (a) is 30 μm and of (b) is 10 μm. (*See* color plate I, Volume 111.)

crographs of quiescent samples of the polymer at 240 °C with two different sample thicknesses (30 and 10 μm) for comparison.

Two types of threads were observed in the quiescent samples of Polymer A1. These have similar appearance to the 'thicks' and 'thins' recognised by Nehring[8] in a small molecule nematic subjected to an electric field and by us[9] in a small molecule nematic subjected to shear flow. The 'thin' threads (appearing optically as narrow dark lines of width about 1 micron) are the most common.

'Thick' threads are seen only in samples of thickness greater than 20 microns and are generally shorter in contour length than the thins. Both types of threads are mostly in the form of closed loops and no free floating ends have been observed. Ends are sometimes pinned, however, to the glass surfaces. The threads can be seen in bright field as well as with crossed polars.

Threads which are not attached to the surface are mobile. If a very slow shear is invoked in the material, these threads deform, and those not pinned at their ends to the surfaces flow with the bulk. If the shear is continued, the threads pinned to opposite surfaces break up into dark lines which elongate in the flow direction. Similar lines develop around pieces of debris, presumably because of localised high stresses or velocity gradients surrounding these obstacles. With time, the entire field is dominated by the presence of dark lines, and their abundance makes tracing their origins impossible. We have named this texture the 'line texture'. Figure 3 presents photomicrographs which illustrate several stages in the development of a dense line texture.

The lines of this texture are different to the thin threads of the quiescent melt. They do not appear to be loops, but instead appear to be short lines (10 to 50 μm) with free floating ends. As the lines flow, they deform and change shape, but remain extended in the flow direction. The line texture is not optically uniform. The density of lines varies from point to point in the field of view and is generally greatest in the vicinity of debris.

The lines are visible in bright field and are thus believed to result from localised light scattering. The lines move freely within a bright background which does not extinguish light at any position of crossed polars relative to the direction of flow.

As the shear rate is increased, the lines break up into short, dark, curled entities with apparent diameters of about two microns. These entities flow along the streamlines whilst continually changing their shapes, and the overall view of them during shear resembles a 'vat of teeming worms'. A texture dominated by these entities has been named, therefore, a 'worm texture'.

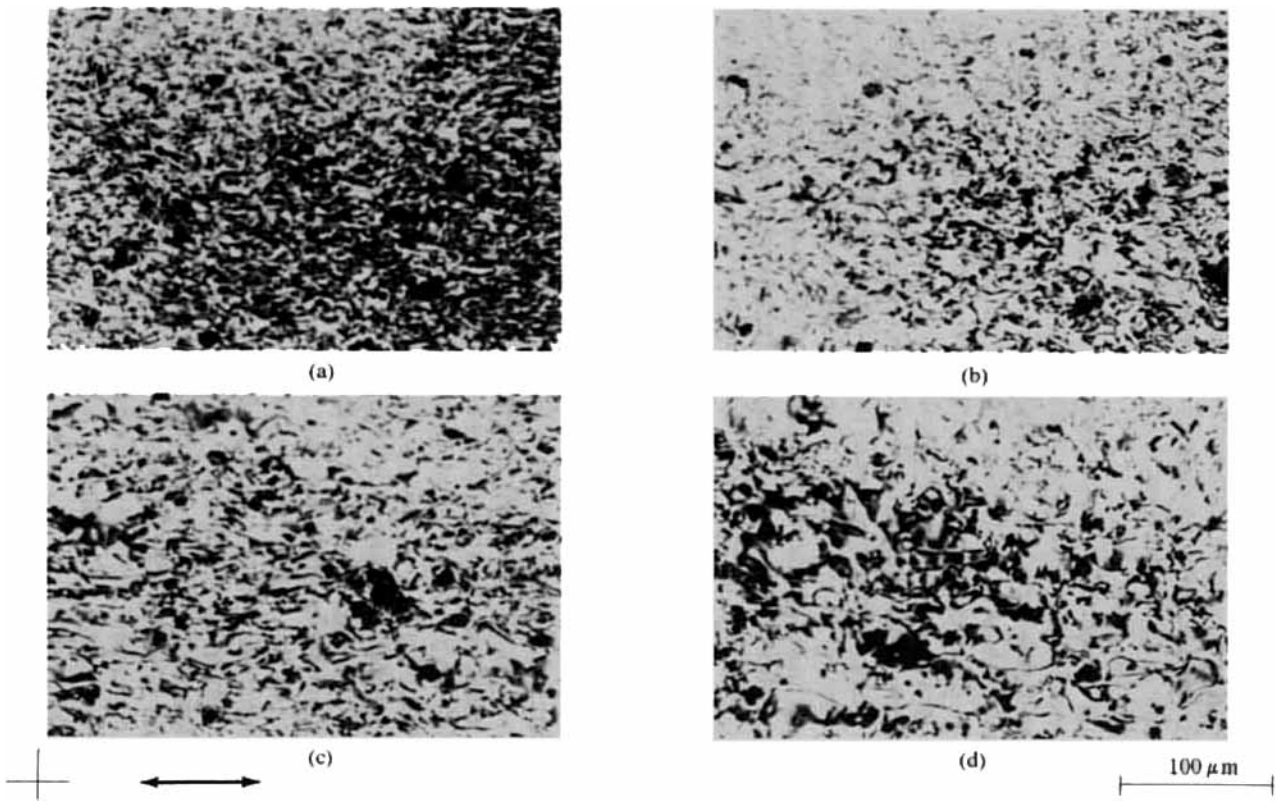


FIGURE 3 Photomicrographs depicting the development of a dense line texture in Polymer A1 at 260 °C. Sample thickness = 15 μm amplitude of strain oscillations = 100 μm. Crossed polars aligned at 0 and 90 ° to flow direction which is horizontal, right and left across prints. Angular frequencies are (a) 0.09, (b) 0.09, (c) 0.16 and (d) 0.24 rad/sec.

The worms can be seen in bright field although they are more distinct when viewed with crossed polars. As with the line texture, the background of the worm texture is bright and does not extinguish light of any crossed polarisation direction. Worms are evenly distributed in the sample as shown in Figure 4. The density of worms increases with increasing shear rate.

At still higher shear rates, a sharp transformation can be induced into a texture whose optical appearance is dependent on the direction of crossed polarised light. In this texture, the sample extinguishes maximum light when the crossed polars are aligned at 0 and 90° to the flow direction. The sample transmits maximum light with the crossed polars at 45° to the flow direction, and a retardation of the sample can be measured. This retardation is independent of the shear conditions, and a birefringence of 0.03 ± 0.02 for the flowing polymer is suggested by an averaging of all results. This texture, whose optical behaviour indicates that flow alignment of some species is occurring, has been labelled the 'ordered texture'. Photomicrographs presented in Figure 5 illustrate the effect of the direction of the crossed polars on the appearance of the ordered texture.

Thus, as the shear rate is increased in the Polymer A1, transitions from the quiescent thread texture to the line texture to the worm texture to the ordered texture progressively occur. The shear rates at which these transitions occur decrease as the temperature is decreased. In general, the ordered texture is favoured at low temperatures, high shears and small thicknesses, whereas the worm and line textures exist under less severe shear conditions and higher temperatures.

Relaxation after shear cessation from any of the three shear-induced optical textures to a completely quiescent texture occurs over several tens of seconds. The relaxation process can be divided into two stages. In the first stage, the texture changes to one of thin threads in a background of varying birefringent colours. The nature of this change depends on the original texture. In the second stage, the density of thin threads decreases as the closed loops shrink and vanish. This stage is similar for all starting textures. The first stage of the relaxation process generally occurs over a faster time scale than the second stage.

In the first stage of relaxation from the line texture, the lines disappear either by shrinking from both ends and vanishing, or by coalescing to form the threads which further diminish during the second stage of the relaxation. The 'worms' also relax by vanishing or coalescing to form threads. The worm texture does not relax through the line texture, however. The relaxation process (and accompanying photomicrographs) described by Millaud, Thierry and Skoulious[10] for

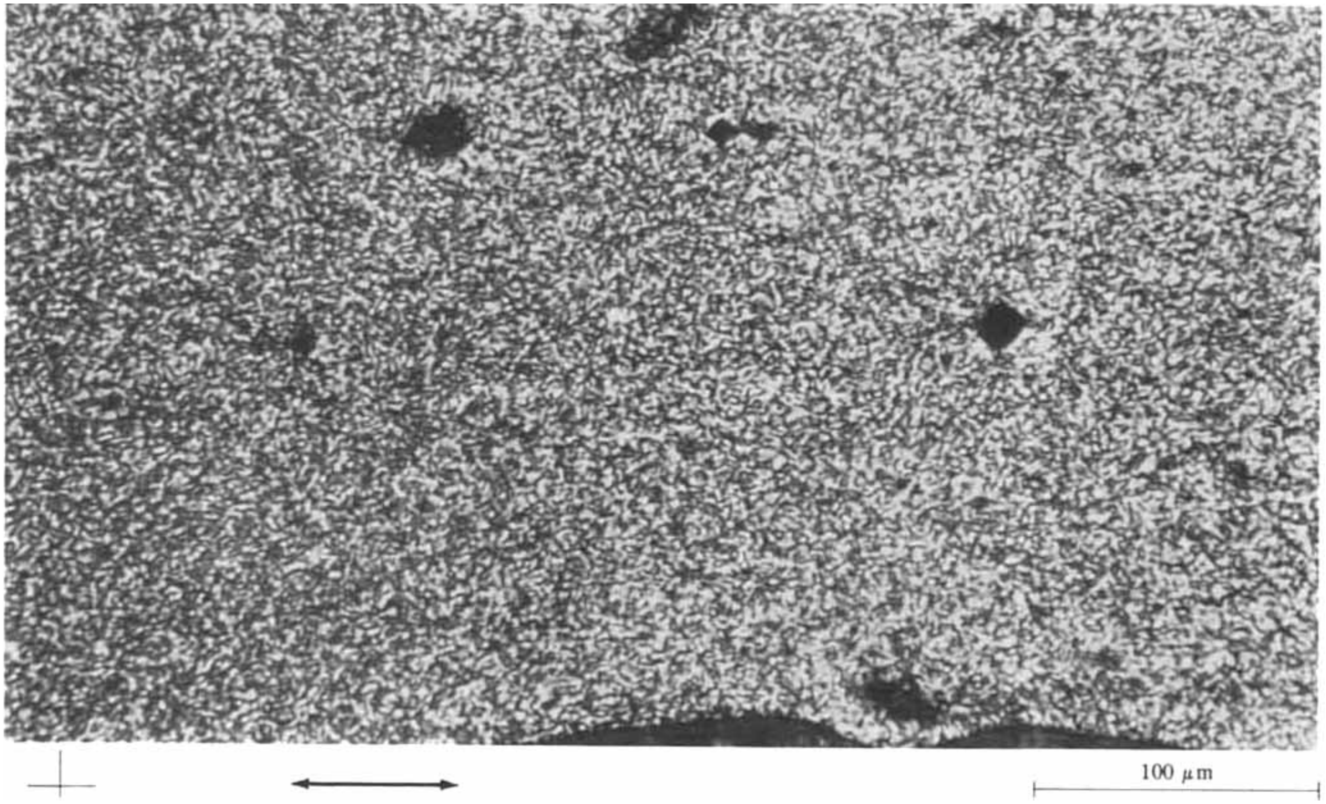


FIGURE 4 Worm texture in Polymer A1 at 240 °C. Sample thickness = 15 μm. Amplitude = 100 μm. Angular frequencies = 1.3 rad/sec. Crossed polars aligned at 0 and 90 ° to flow direction which is horizontal, right and left across prints.

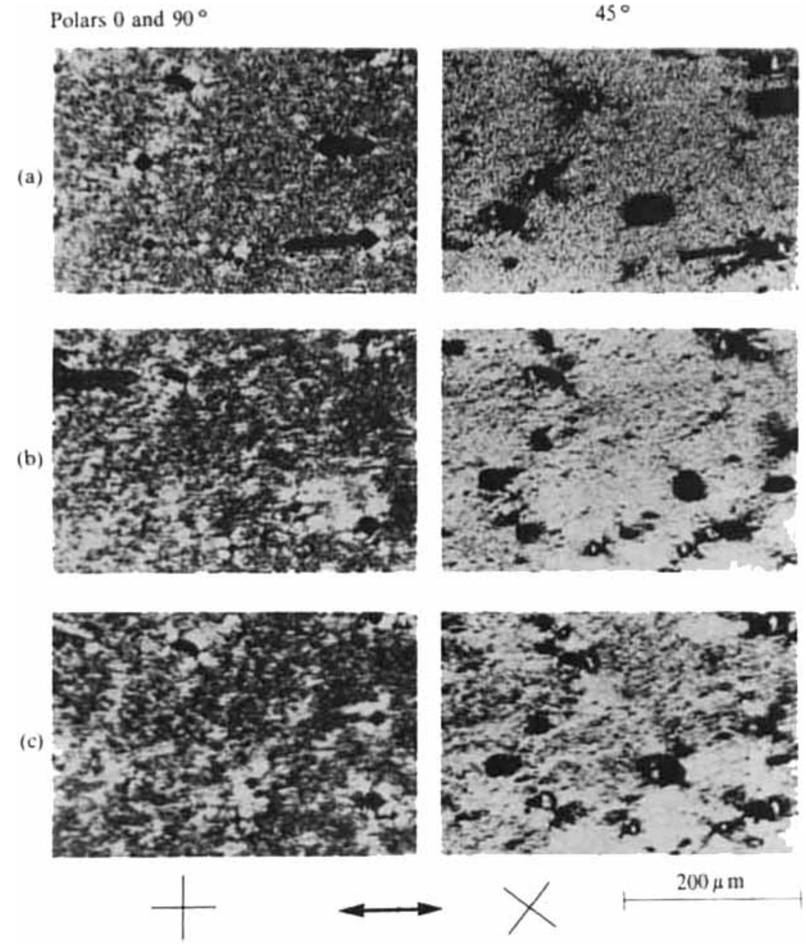


FIGURE 5 Effect of crossed polars direction on optical appearance of ordered texture in Polymer A1, 220 °C. Sample thickness = 10 μm, amplitude = 100 μm, angular frequency = 2.1 rad/sec. Crossed polars aligned as indicated relative to flow direction which is horizontally right and left across prints. Photographs taken at different positions in strain cycle: (a) $\pi/2$, (maximum amplitude), (b) $3\pi/4$ and (c) π radians (zero amplitude).

solutions of polyphenylene-terephthalamide is qualitatively similar to the observed relaxation from worms to threads in this study.

The relaxation of the worms, or their disappearance, is accompanied by an increase in the total light intensity transmitted by the sample as can be seen in the time-series photomicrographs in Figure 6. Therefore, the relaxation process could be followed by recording the change

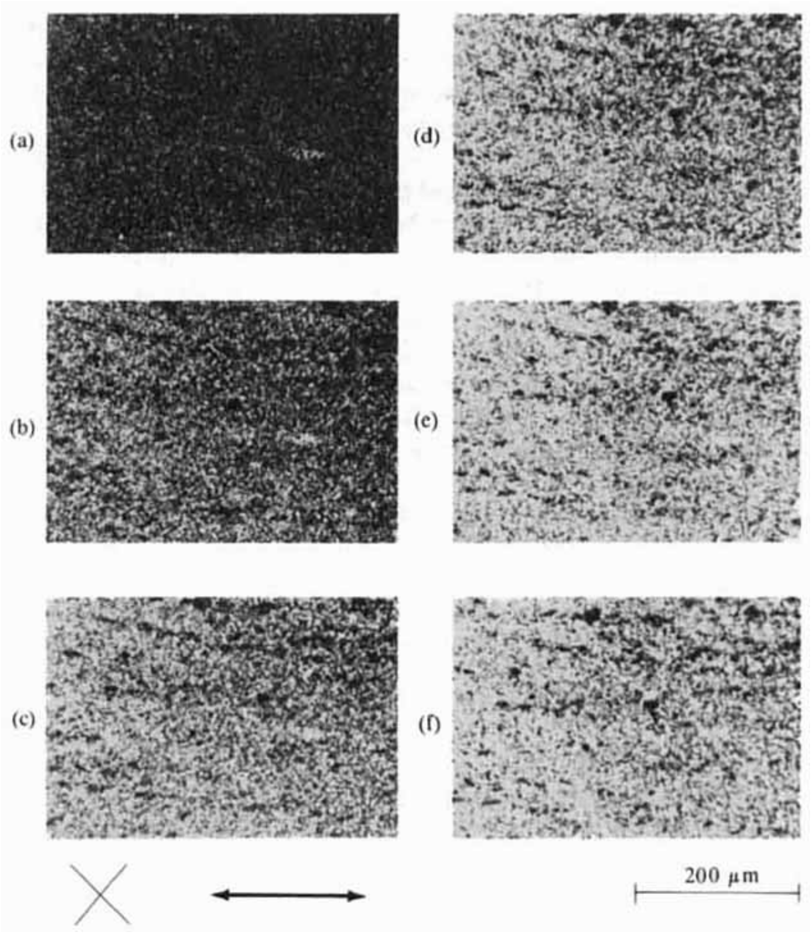


FIGURE 6 Relaxation from worm texture in Polymer A1 at 240 ° C. Sample thickness = 15 μm, prior amplitude = 270 μm, prior frequency = 2.1 rad/sec. Crossed polars aligned at 45 ° to prior flow direction which was horizontally right and left across prints. Time-series sequence: (a) 0 sec., (b) 1 sec., (c) 2 sec., (d) 3 sec., (e) 4 sec. and (f) 5 sec. after shear cessation.

with time of the transmitted light intensity as measured by a photomultiplier. Such measurements were taken for relaxations after shears at different frequencies and amplitudes and at different temperatures. The light intensities were found to increase exponentially with time in the first few seconds after shear cessation, so an 'initial time constant', τ_i, for the process could be defined. This time constant decreased with increasing frequency, amplitude and temperature. Time constants were of the order 2 to 20 seconds.

Upon cessation of shear in the ordered texture, the worm texture develops within 0.3 seconds and subsequently relaxes as described above. The formation of the worms occurs simultaneously with the disappearance of the measurable birefringence of the sample.

In oscillatory shear, the test samples are subjected to a shear rate which is continually changing and periodically stopping and reversing direction. Therefore, a balance between texture development and texture relaxation must be reached. We found in our experiments that upon initiation of the oscillatory shear and after a start-up period of two to three strain cycles, an optical texture response develops which oscillates in a steady, repeatable fashion. We believe that the time independence of the optical texture response oscillations is a very important result which suggests that under a given set of shear and thermal conditions, a specific uniform texture with a specific density will always occur.

The periodic response of the optical textures is most clearly seen in traces of the total transmitted light intensity of a sample during shear. As an example, such traces with varying light conditions for a sample in the worm texture are presented in Figure 7. The oscillations in light intensity of Figure 7 result from the partial relaxation of the worms at

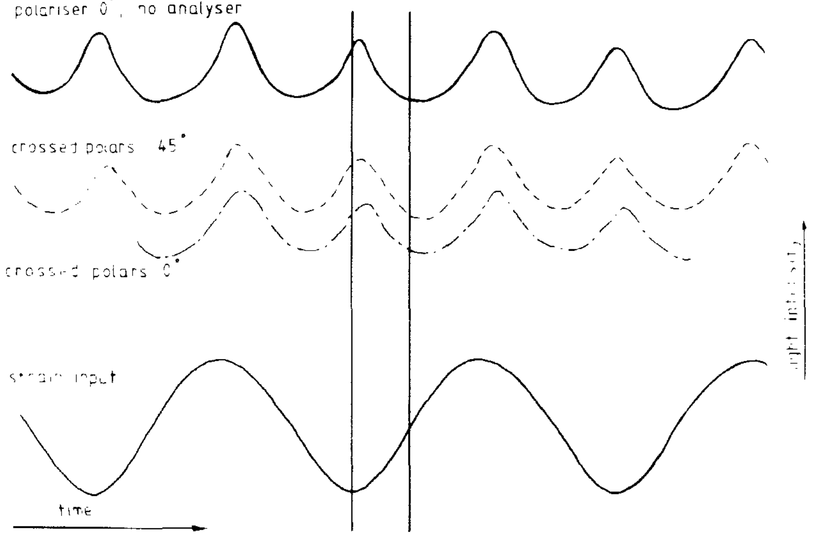


FIGURE 7 Total transmitted light intensity traces during shear in worm texture of Polymer A1 with varying light conditions. 260 °C, angular frequency = 0.9 rad/sec.

and around the positions in the cycle where shear stoppage occurs, and hence from a periodic change in worm density.

Polymer A5

A completely relaxed, quiescent sample of Polymer A5 adopts a worm texture. A texture of threads like that of quiescent samples of Polymer A1 does not occur in the Polymer A5. Nor does the Polymer A5 ever adopt the line texture.

It is only for very low shears (typically: thickness > 20 μm, frequency > 0.1 rad/sec, amplitude $\simeq 200$ μm, temperature $>$ 240 °C), that the worm texture in the Polymer A5 remains stable. At relatively low shears, the samples adopt the ordered texture which is the dominant texture during shear of this polymer. The sample retardations measured in the ordered texture are independent of the shear conditions (i.e. frequency and amplitude of strain oscillations), and a birefringence value of 0.11 ± 0.03 for the flowing polymer is calculated from an average of all experiments.

In the Polymer A5, optical textures generated during the relaxation process following shear cessation are more varied than those which occur during shear. Three models of relaxation from the ordered texture have been recognised:

(1) Relaxation to worms which remain intact after long times or which relax slowly.

(2) Relaxation to worms which then relax rapidly leaving a background with optic axis oriented in the prior flow direction and a low density of bright-field entities.

(3) Relaxation to a texture characterised by bands aligned perpendicular to the prior flow direction.

Above temperature of 240 °C, the ordered texture of Polymer A5 generally relaxes through the worm texture. The development of worms and simultaneous loss of measurable birefringence occurs within a few seconds, the time decreasing with increasing temperature and shear rate. At low shears (typically: thickness > 20 μm, frequency < 0.5 rad/sec, amplitude $\simeq 200$ μm), the worms once formed are stable for long times. At higher shears, however, they relax after formation by vanishing or coalescing to form thin, short threads. These threads are typically much shorter and more numerous than those found in quiescent samples of Polymer A1. Often they lie perpendicular to the prior flow direction.

The background of the relaxed worm texture is unidirectionally birefringent with a slightly higher retardation value than the ordered texture during shear, but with the same extinction angle. The retardation value of this texture is constant for any one sample and independent of the prior shear history. The measurable birefringence in the static sample vanishes within five minutes leaving a texture of short, dark lines and worms in a bright background which does not extinguish crossed polarised light at any direction.

At 220 °C, the worm texture generally does not develop during the initial stages of relaxation. Instead, a series of equidistant bands or striations form perpendicular to the prior flow direction after the cessation of shear. The bands can be seen in bright field, but they are more distinct when viewed with crossed polars. Colour photomicrographs of the bands with crossed polars aligned at 0 and 90 ° and at 45 ° to the prior flow direction which appear in Figure 8 illustrate the nature of the birefringence of the texture. In between striations, the material extinguishes light with crossed polars aligned parallel and perpendicular to their lengths. With the crossed polars at 45 ° to their lengths, these areas become bright, and a retardation can be measured. The value of the retardation is a constant for any particular sample and is, in fact, identical to that measured in the relaxed worm texture of the same sample.

Photographs appearing in Figure 9 depict the long time behaviour of the banded texture. With time, after formation, the bands fade out of view leaving a homogeneous texture aligned in the flow direction (Figure 9d). After 2 to 3 minutes, the striations reform but with less regularity than the earlier ones (Figure 9c). Gradually, these striations transform to a texture of worms and short, dark lines in a bright background which does not extinguish light at any crossed polar direction (Figure 9f).

The banded texture is not generated solely at 220 °C. In general, it is a low temperature, high shear relaxation phenomenon in Polymer A5. Striations of bands perpendicular to the shear direction have been observed in other LCP systems by other researchers. Kiss and Porter[11] observed striations both during and after flow in solutions of poly-(γ-benzyl-L-glutamate) in *m*-cresol. They suggest that the texture is caused by the molecules aligned in alternating directions of ±45 ° to the flow. Such alignment, however, is inconsistent with the optical properties of the striated texture we observed.

Banding perpendicular to the draw directions has been observed in fibres of DuPont's Kevlar.[12,13] This banding is thought to be due to a 'pleated sheet structure' as described by Dobb, Johnson and Saville,[12] in which the molecules are aligned at alternating angles of ±5 ° to the draw direction. Descriptions by Simmens and Hearle[13] of the stria-

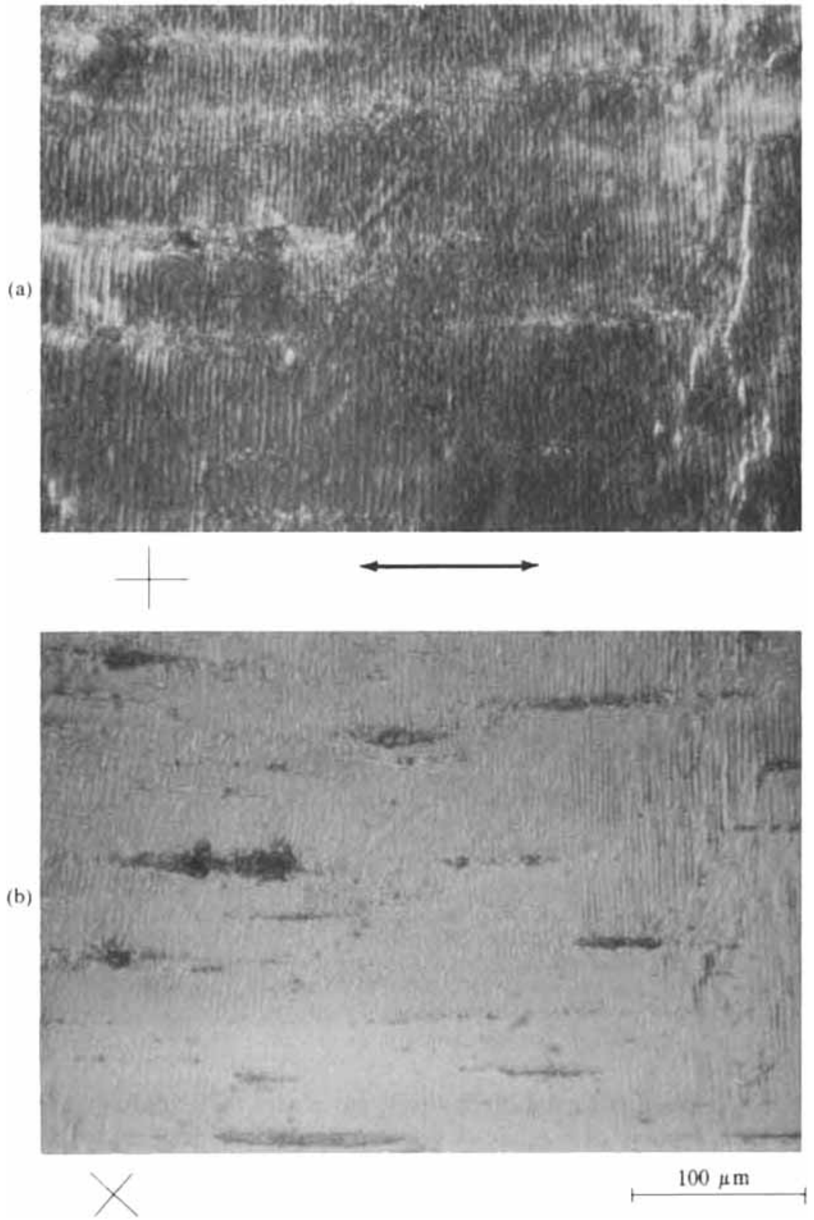


FIGURE 8 Effect of crossed polarisation direction on optical appearance of banded texture in Polymer A5 at 220 °C. Sample thickness = 15 μm. Crossed polars aligned at (a) 0 ° and 90 °, (b) 45 ° to prior flow direction which is horizontally right and left across prints. (*See* color plate II, Volume 111.)

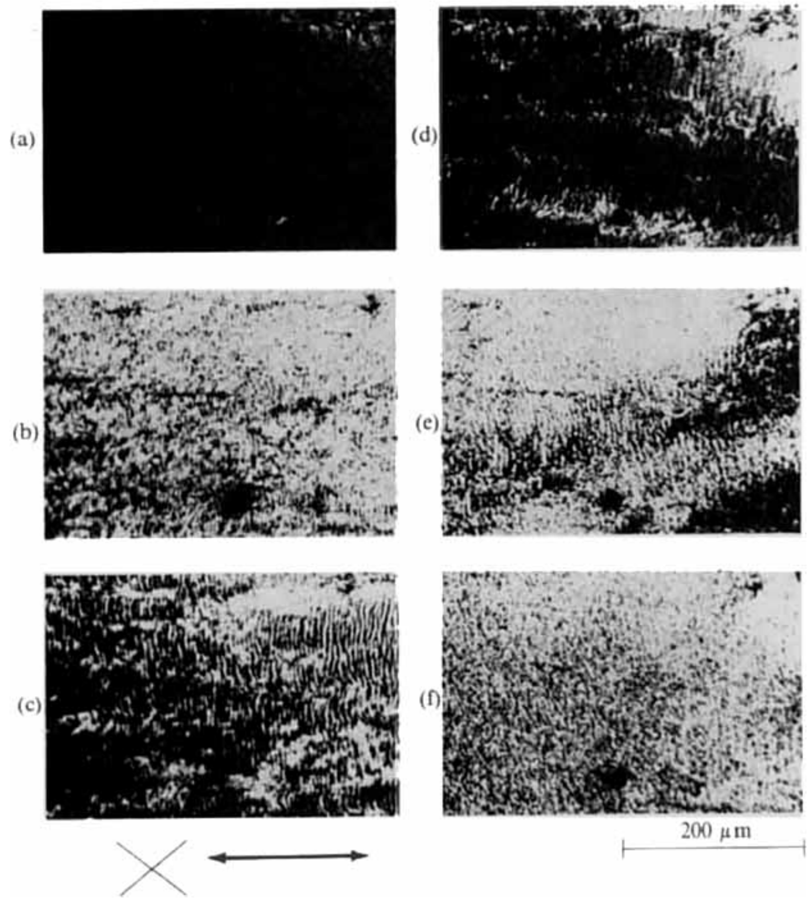


FIGURE 9 Long-time relaxation behaviour of striated texture in Polymer A5 at 220 ° C. Sample thickness = 15 μm, prior amplitude = 270 μm, prior angular frequency = 2.1 rad/sec. Crossed polars aligned at 45 ° to prior flow direction which is horizontally right and left across prints. (a) 0.0 min., (b) 0.5 min., (c) 1.0 min., (d) 2.5 min., (e) 5.0 min. and (f) 7.0 min. after shear cessation.

tions observed in Kevlar qualitatively agree with those of Polymer A5, but the spacing of 0.5 microns in Kevlar fibres is less than that of Polymer A5 striations (1 to 3 microns).

More relevantly, banded structures have been observed in quenched thin films of four thermotropic LCP's recently reported by Donald, Viney and Windle.[14] Their analysis of the texture by optical and election microscopy suggests that the molecules adopt a smoothly curved as opposed to a crimped structure.[15,16] The striations they observed, however, were in samples generally thinner than ours (i.e. $< 5\ \mu m$).

In the Polymer A5 at 200 °C, the ordered texture created during flow does not relax upon shear cessation. A temperature of 200 °C is well below the final melting temperature of the polymer as determined from the DSC trace of Figure 1, but the melt appeared mobile during shear and supercooling is, therefore, suspected.

In summary, the long time-relaxed texture of the Polymer A5 is that of worms and thin, short dark lines in a bright background which does not extinguish light at any crossed polars direction. This texture, though, occurs only after several minutes of relaxation. The initial relaxation behaviour of the polymer is dependent on its shear and thermal history.

Effect of molecular weight

The optical behaviour of the lowest (A1) and the highest (A5) molecular weight polymers in the A series have been shown to differ in some respects. The behaviours of Polymers A2 and A3 partially bridge the gap, and the Polymer A4 behaves identically to Polymer A5.

The quiescent textures of Polymers A2 and A3 are similar to those of Polymer A1. With the onset of shear, however, the threads of the static texture break up into the worm texture without first adopting the line texture. The relaxation of the worm texture of these two polymers is similar to that described for Polymer A1, and initial time constants for the process could be evaluated. Figure 10 presents curves of the time constant plotted against frequency of prior strain oscillations for the Polymers A1, A2 and A3. The relaxation time constants are seen to increase with increasing shear rate.

The transition from the worm texture to the ordered texture was observed at less severe conditions and higher temperatures in the Polymers A2 and A3 relative to Polymer A1. At high temperatures (240 °C and above), the ordered texture relaxes through the worm texture in these polymers. At low temperatures (220 °C and below) and at high shears, the ordered textures relax through the striated texture. The striations, however, are not as stable as those observed in Polymers A4 and A5, and relax within several seconds after formation.

DISCUSSION

The experiments performed on the A series Polymers have shown that shear has a significant and specific effect on the microscopic textures,

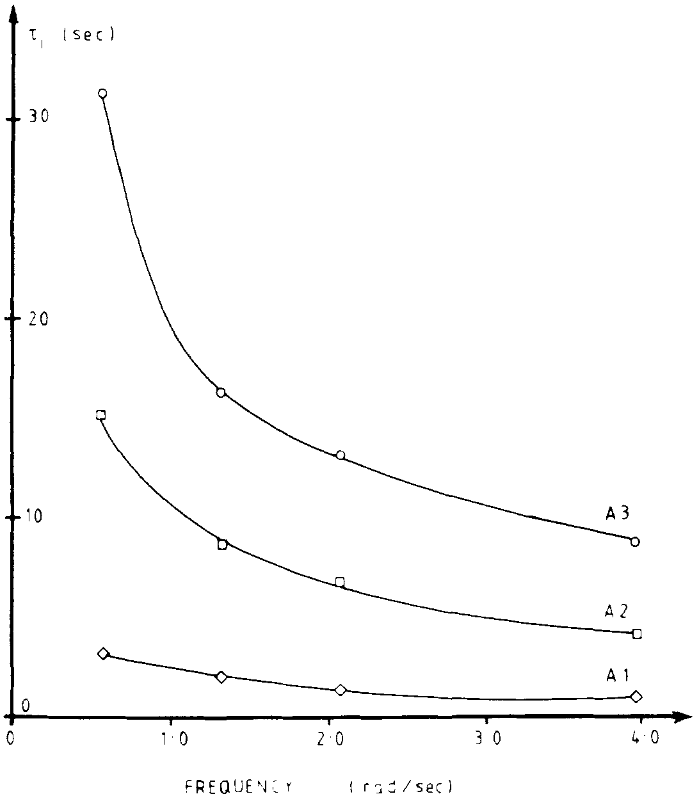


FIGURE 10 Initial time constant for worm texture relaxation *versus* frequency; effect of molecular weight at 260 °C. ◇ = Polymer A1, □ = Polymer A2 and ○ = Polymer A3.

and presumably the microstructure, of LCP's. Graziano[7] has reported that the shear-induced textures observed in the A series polymers also occur in a variety of other thermotropic LCP's. A review of the literature suggests that similar textures have been observed in lyotropic LCP's as well. For example, photomicrographs appearing in papers by Panar and Beste[17] and Millaud, Shierry and Skoulious[10] indicate that a worm texture which is created in shear in polyamide systems relaxes to a texture of thin threads when the shear is removed. Millaud *et al.* found no effect of chain structure in the optical behaviour of their systems. Birefringence studies on the lyotropic poly(phenylene terephthalamide) systems performed by Onogi, White and Fellers[18] hint at the transition from worm texture (or what they call polydomain structure) to some ordered state whose birefringence is relatively insensitive to shear rate.

These shear-induced optical textures which occur in a wide range of LCP's do not occur in isotropic polymer melts or solutions, nor in small molecule liquid crystals (SMLC). The recurrence of similar textures in the different LCP systems suggests that they are more a consequence of the intermolecular order than of the chain structure and composition of individual molecules. The intermolecular order of these species is distinguished from that occurring in isotropic polymers because of the rigidity of their macromolecules. The free energy of concentrated solutions or melts of flexible polymers is minimised by the coiling up and intertwining or entangling of the molecules. Rigid macromolecules are not expected to coil. Instead, the energy level of a system of them is reduced by close packing arrangements of the rigid rods. Systems of closely packed rigid molecules are expected to behave differently in shear from systems of entangled, flexible molecules.

The optical textures observed in the LCP systems, however, are not known to occur in SMLC systems either. The differences in the polymeric liquid crystals from their small molecule counterparts could result from their increased length, their polydispersity, their compositional irregularities or from their flexible linkages (in some LCP's only). The studies of the A series polymers with varying molecular weights suggest that the molecular length may be the prime factor. Increasing the molecular length was shown to have a similar effect to increasing the shear rate, i.e. increasing either parameter increases the likelihood of transitions from thin threads to the worm texture to the ordered texture.

Increasing the molecular length of a rigid species would tend to decrease the mobility and independent motion of its molecules. The experimentally observed trend of increasing worm texture relaxation time constants with increasing molecular weight supports this hypothesis (assuming that relaxations in the polymers are linked to the mobility of their molecules). The mobility of the molecules in turn affects the configurations which they adopt during shear.

If a shear gradient exists in a sample, neighbouring molecules are forced to move at different velocities. In order to retain the undistorted structure of the quiescent melt, the molecules must be able to slip past one another freely. In a small molecule nematic, at low shears, the molecules align in the flow direction which reduces their viscous drag and allows them to flow past one another easily (see for example ref. 19). As the molecular length is increased, however, the independent motion of the molecules becomes hindered by their lengths. The molecules can no longer flow past one another easily and are, therefore, forced to restructure in the flow field. Structural changes created by shear should occur, therefore, more readily in systems with longer molecules. This trend is supported by the observations of the A series polymers.

Further support for the relationship between molecular mobility and structural changes in shear comes from the observed effect of temperature on the optical behaviour of the LCP's. Decreasing the temperature reduces the mobility of the molecules as shown by the decreased rate of relaxations which occur at lower temperatures. Decreasing the temperature was also shown experimentally to lower the shear rates at which optical texture transitions occurred.

The shear-induced optical textures which have been recognised are presumably associated with specific microstructures. The optical information, however, is not sufficient to determine the cause of the textures. Clearly, supplemental data from analytic techniques such as x-ray diffraction, electron microscopy and NMR which gives direct information on molecular order is required to determine the microstructures leading to the various optical textures. The optical observations, however, should be useful in ascertaining plausible mechanisms for the development of the microstructures in shear and during relaxation.

Acknowledgments

We wish to acknowledge I.C.I. Petrochemicals and Plastics Division, Welwyn Garden City, for their gift of materials and financial support of this research. We wish to thank Dr. B. P. Griffin, Mr. F. N. Cogswell, and Dr. A. M. Donald for helpful discussions on the work. D. J. G. is grateful to the Winston Churchill Foundation for financial support.

References

1. J. L. White and J. F. Fellers, *J. Appl. Polym. Sci. Polym. Symp.*, **33**, 137 (1978).
2. W. J. Jackson and H. Kuhfuss, *J. Polym. Sci.: Polym. Chem. Ed.*, **14**, 2043 (1976).
3. M. R. Mackley, F. Pinaud, and G. Siekmann, *Polymer*, **22**, 437 (1981).
4. C. Viney and A. H. Windle, *J. Mat. Sci.*, (1982).
5. T. C. Fletcher, *USA Patent* No. 3,911,013, filed by E. I. du Pont de Nemours and Co. (1976).
6. B. P. Griffin, private communication (1982).
7. D. J. Graziano, Ph.D. Thesis, University of Cambridge (1983).
8. J. Nehring, *Phys. Rev.*, **A7**, 1737 (1973).
9. D. J. Graziano and M. R. Mackley, submitted to *Mol. Cryst. Liq. Cryst.*
10. B. Millaud, A. Thierry, and A. Skoulious, *J. Phys. (Paris)*, **39**, 1109 (1978).
11. G. Kiss and R. S. Porter, *Mol. Cryst. Liq. Cryst.*, **60**, 267 (1980).

12. M. G. Dobb, D. J. Johnson, and B. P. Saville, *J. Polym. Sci.: Polym. Phys. Ed.*, **15**, 2201 (1977).
13. S. C. Simmens and J. W. S. Hearle, *J. Polym. Phys. Ed.*, **18**, 871 (1980).
14. A. M. Donald, C. Viney, and A. H. Windle, *Polymer*, in press.
15. C. Viney, A. M. Donald, and A. H. Windle, submitted to *J. Mat. Sci.*
16. A. M. Donald and A. H. Windle, submitted to *J. Mat. Sci.*
17. M. Panar and L. F. Beste, *Macromolecules*, **10**, 1401 (1977).
18. Y. Onogi, J. L. White, and J. F. Fellers, *J. Non-Newtonian Fluid Mechanics*, **7**, 121 (1980).
19. J. T. Jenkins, *A. Rev. Fluid Mechs.*, **10**, 197 (1978).