Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Larson, R. G. and Mead, D. W.(1992) 'Development of orientation and texture during shearing of liquid-crystalline polymers', Liquid Crystals, 12: 5, 751 — 768
To link to this Article: DOI: 10.1080/02678299208029120
URL: http://dx.doi.org/10.1080/02678299208029120

LIQUID CRYSTALS, 1992, VOL. 12, NO. 5, 751–768

Development of orientation and texture during shearing of liquid-crystalline polymers

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(*Received 28 April 1992; accepted 28 May 1992*)

Using polarizing microscopy, we study the development of orientation and texture during slow shearing of liquid-crystalline solutions of poly(γ-benzyl-L-glutamate). Shearing of high molecular weight samples that are initially coarsely textured, or are uniformly oriented over regions of 1 mm^2, produces a steady state striped texture, for each of three different initial average orientations. The director field in the striped texture is on average aligned parallel to the flow direction, but with misalignment that varies periodically as we move in a direction orthogonal to flow, thus giving the sample a striped appearance under crossed polarizers, with stripes parallel to flow. After the stripes form, they become finer with increased shearing, or with increased shear rate. Along with the birefringent stripes, there are defect lines, parallel to the flow direction with a spacing similar to that of the stripes, i.e. 10 μm or less at steady state. The existence of separate time scales for the development of steady state orientation, and for the shrinkage of the texture length scale to a steady state, is consistent with a phenomenological scaling theory that had been postulated to explain the rheological behaviour of these fluids. Although the steady state striped texture is independent of initial orientation, transient textures during start-up of shearing are highly dependent on initial orientation; for some initial orientations, bands perpendicular to flow occur temporarily during shearing.

1. Introduction

When subjected to shearing fields of suitable strength, the director in a small molecule nematic typically orients at an angle only a few degrees away from the flow direction, except at thin boundary layers near walls [1–4]. Polymeric nematics, on the other hand, usually do not become uniformly oriented when sheared, but instead develop fine scale texture, involving inhomogeneities in the director field. It now seems likely that shear induces these inhomogeneities in polymeric liquid-crystalline polymers at least in part because of director tumbling, which occurs in nematics when the ratio of Leslie viscosities α_2/α_3 is negative [1]. For small molecule nematics, this ratio α_2/α_3 is usually positive except at temperatures close to a transition to a smectic A phase [5, 6]. For nematic solutions of rigid macromolecules, however, molecular theory predicts that $\alpha_3/\alpha_2 < 0$ [7], and experiments have recently confirmed this prediction for solutions of poly(γ-benzyl-glutamate) (PBG) and of poly(1,4-phenylene-2,6-benzobisthiazole) (PBT) [8, 9]. Thus while small molecule nematics are usually non-tumbling, the reverse may be true of polymeric nematics.

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For tumbling nematics, either small molecule or polymeric, the director can find no preferred angle of orientation, and therefore viscous torques tend to rotate it continuously in the shearing flow. If the director is initially oriented uniformly in the shearing plane (the plane parallel to both the flow and the shear gradient directions), and is pinned by anchoring conditions at the boundaries of the shearing apparatus, then for strong shearing, tumbling inevitably leads to a 'winding up' of the director in the plane of shear and consequently to spatial inhomogeneities of the director orientation in that plane [10]. A stability analysis of the wound up director field predicts that for typical values of the elastic and viscosity constants, the director will tip out of the shearing plane when the director field is wound up sufficiently [11]. This prediction has been confirmed in experiments on small molecule nematics for which $\alpha_3/\alpha_2 < 0$ [5, 6, 12]. If, on the other hand, the director starts out not in the shearing plane, but uniformly oriented normal to it, or if the director is driven out of the shearing plane by the instability mentioned above, then a strong shearing flow with $\alpha_3/\alpha_2 < 0$ again produces an instability; in this case the unstable mode involves director rotations that are spatially periodic in the direction orthogonal to the shearing plane, the visual evidence of which is the appearance of stripes oriented parallel to the flow direction [6, 13, 14]. This pattern is called a 'phase grating', and it has been observed in both small molecule and polymeric nematics when $\alpha_2/\alpha_3 < 0$ [9, 14]. Hence, when a tumbling nematic is strongly sheared, a three dimensional inhomogeneous director field seems to be the inevitable outcome, no matter what the initial orientation of the director is.

As previously mentioned, we have alluded to 'strong shear' as a condition for development of the three dimensional inhomogeneous director field from a homogeneous starting condition. By 'strong shear', we mean that the Ericksen number $E = V\eta d/K$ is large, where V is the velocity of the moving surface (the other surface being stationary), d is the gap between the surfaces, K is a characteristic Frank elastic constant, and η is a characteristic viscosity. Typical values of d and K are 0·01 cm and 10^{-11} N, respectively. Thus, for small molecule nematics, in which $\eta \approx 10^{-3}$ Pa s, E remains less than 100 for V as high as $1\,\mathrm{cm\,s^{-1}}$. For polymeric nematics, however, $\eta \approx 10$ Pa s, and therefore $E > 100$ unless V is extremely small, $10^{-4}\,\mathrm{cm\,s^{-1}}$ ($1\,\mu\mathrm{m\,s^{-1}}$) or less. Thus unless the shear rate is extremely small, polymeric nematics with $\alpha_3/\alpha_2 < 0$ are expected to become textured during shearing flow, even if they are initially homogeneous, an expectation that has been confirmed experimentally [9].

In fact, typically $V \gtrsim 10^{-2}\,\mathrm{cm\,s^{-1}}$, so that for polymeric liquid crystals, $E \geqslant 10^4$. At such high Ericksen numbers, there is plenty of viscous energy available to produce textures on length scales much smaller than the gap d. Marrucci [15] has proposed that after start-up of a steady shearing flow at a shear rate $\dot{\gamma} = V/d$, the length scale 'a' that characterizes the texture shrinks until the Frank elastic stress K/a^2 becomes large enough to resist further flow-driven refinement. Thus the value of 'a' at steady state reflects a balance between the viscous flow energy $\eta\dot{\gamma}$ and the Frank energy K/a^2. Under these conditions, it is useful to define a texture-based Ericksen number $E_{\mathrm{tex}} \equiv \eta\dot{\gamma}a^2/K$, which, if the above argument is corrent, should at steady state reach a value that is independent of $\dot{\gamma}$ [16]. Rheological measurements on textured liquid-crystalline polymers suggest that $E_{\mathrm{tex}} \approx 100$ in steady state shearing [16]. Thus, using estimates of K and η given earlier, we find $a \sim 10/\sqrt{\dot{\gamma}}$ microns. For typical shear rates in the range $1\text{–}100\,\mathrm{s^{-1}}$, the texture length scale should then be roughly $1\text{–}10\,\mu\mathrm{m}$, which agrees with experimental observations, including the observation that the texture becomes finer as the shear rate $\dot{\gamma}$ increases [17–19]. If the fineness of the texture approaches molecular dimensions, however, Frank theory breaks down [20].

Extending the scaling argument of Marrucci, Larson and Doi [21] have proposed that for start-up of steady shearing in flow regimes for which Frank theory holds, the director field should become oriented, on average, parallel to the flow direction, while the texture length scale should shrink according to

$$\frac{dL}{dt} = \alpha\dot{\gamma}L - \beta\frac{K}{\eta}L^2, \tag{1}$$

where $L \equiv 1/a^2$ and α and β are constants. L can be considered to be the total length of defect lines per unit sample volume. At steady state, the above equation gives $E_{tex} = \dot{\gamma}\eta a^2/K = \beta/\alpha$, a constant, which is consistent with the conclusions discussed earlier. In the absence of shear, or when shear ceases, we obtain from equation (1) a prediction for the coarsening of the texture

$$a^2 - a_0^2 = \beta\frac{K}{\eta}t, \tag{2}$$

where a_0 is the texture length scale at time $t = 0$. Equation (2) is supported by scaling arguments and by recent experimental studies of the relaxation of disclination tangles in small molecule nematics [22]. It also correlates with rheological data for several textured lyotropic and thermotropic liquid-crystalline polymers [23–25]. After the onset of steady shearing of a sample with an initial texture size a_0, equation (1) predicts that the strain γ_{tex} required for the texture size to reach a value within a fraction F of its steady state value a_{ss} should be roughly

$$\gamma_{tex} \approx \frac{1}{\alpha}\ln\left(\frac{1}{F}(a_0/a_{ss})^2\right). \tag{3}$$

This formula holds when $a_0^2/a_{ss}^2 \gg 1$.

While the experimental work on textures in shearing flow has thus far concentrated on the length scales of the texture, little has been learnt about how these textures correlate with the director field or the orientational states of the material during shear. The theory referred to previously [21] predicts that shearing should induce orientation in the flow direction, and that the number of strain units γ_{orient} required to induce this orientation should be roughly

$$\gamma_{orient} \approx \frac{P}{2} = \frac{2\pi}{\sqrt{(1-\lambda^2)}}, \tag{4}$$

where $P/2$ is one half the period, in units of strain, required for a freely tumbling director to complete a rotation of π radians, and $\lambda \equiv (\alpha_5 - \alpha_6)/(\alpha_3 - \alpha_2)$, where the αs are Leslie–Ericksen viscosities. Molecular theory suggests a value of around 12 for $P/2$, while the period of stress oscillations in rheological studies is instead consistent with $P/2 \approx 25$ [21]. Thus the strain required to orient the director field is in general predicted to be different from that required to attain a steady state texture size a_{ss}.

To test this prediction qualitatively, we need to determine both the orientational state and the texture size scale during shearing of a liquid-crystalline polymer. For a static sample, well-established procedures of polarizing microscopy allow us to determine orientational patterns [26]. Here, we wish to apply these techniques to the transient textures that occur during shearing flow of a liquid-crystalline polymer.

2. Experimental

2.1. *Materials*

Here we study a sample of PBLG, the L enantiomorph of poly(γ-benzyl-glutamate), as well as two racemic mixtures of PBLG with PBDG, the D enantiomorph, all in the solvent metacresol. The concentrations and average molecular weights of the samples are reported in the table. Two of these samples, PBLG 186 and PBG118, were studied in an earlier publication [18]. PBLG186 is cholesteric, and the other solutions are nematic. The cholesteric texture is extremely fragile, however, so that under shear PBLG186 behaves like a nematic.

2.2. *Shearing cells*

To explore the development of texture during shearing of an originally quiescent sample, we have modified a polarizing optical microscope to allow attachment of two different shearing cells. The design of the first of these was described earlier [18]. It is a rotational device, and although it is capable of continuous unidirectional shearing motion for an arbitrary duration of time, the accuracy of the gap setting and the

Properties of PBG and PBLG samples.

Sample	wt% Polymer	Molecular weight M
PBG118	21	118 000
PBLG186	14	186 000
PBG198	15	198 000

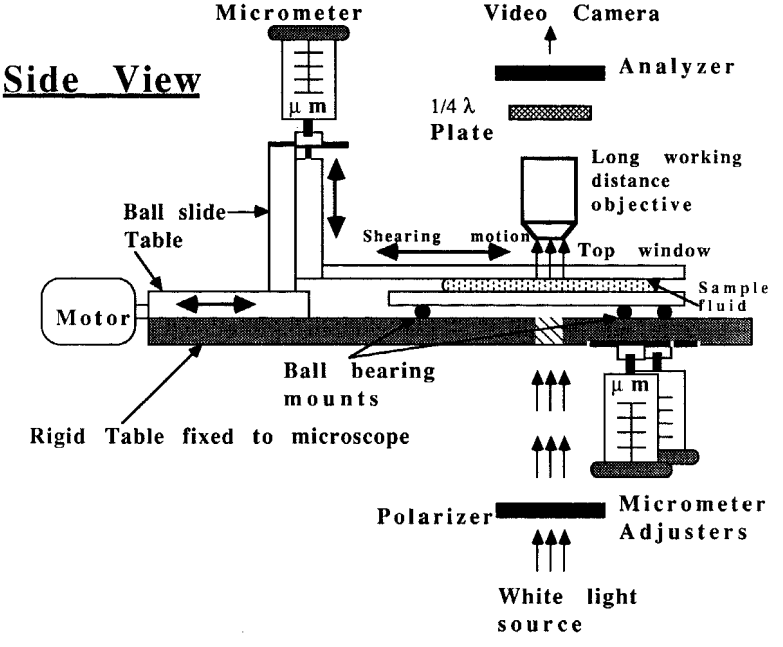

Figure 1. Sketch of translational flow cell.

parallelism of the shearing surfaces are no better than about 50 μm. Therefore, a second, translational, instrument was also constructed (see figure 1). In this second device, the sample is confined between two parallel plates made of borosilicate BK7 glass; the plates are flat to within 1 μm. The plate dimensions are 3 in. by 1 in.; the long dimension is parallel to the direction of translation. These glass plates were mounted on a linear translator constructed by the Daedal corporation; it consists of lower base to which one plate was mounted, and an upper mount for the other plate; the upper mount can be translated parallel to itself with a lead screw. The upper mount is stiff enough that deflections from perfectly parallel translation are less than 1 μm per inch of translation.

The lower plate was bonded with epoxy to the lower plate mount. The position of this lower mount was fixed to the base at three well spaced points, with the ability to move independently of two of these points; the window orientation could thus be varied continuously until the desired degree of parallelism between the lower glass plate and the upper mount was attained. Specifically, this lower mount was supported on the base by three 3/16 in. ball bearings seated in small conical dimples. The bearings were firmly seated in these dimples with stiff springs. One ball bearing was a rigidly fixed reference point, while the other two were attached to sensitive micrometers that could resolve 1 μm. To achieve a uniform parallel orientation, a sensitive dial gauge that could resolve 0·2 μm was mounted to the upper window mount of the linear translator, the probe arm of which was placed in contact with the surface of the lower window. By repeatedly traversing the window and adjusting the orientation of the window using the two micrometers, the bottom plate and the upper mount were made parallel to within a couple of microns. After thoroughly cleaning both plates, the top plate was laid on top of the bottom plate. While in intimate contact, the mount for the top plate was slowly lowered on to the top plate with the digital micrometer that controls and monitors the gap width. A layer of epoxy on the appropriate area of the upper surface of the top window was thereby brought into contact with the top plate mount, thus rigidly bonding the top plate to its mount. Since the top plate was fixed to its mount while lying on top of the lower plate, and both plates are flat to within 1 μm, parallel alignment of the two plates is assured.

The table velocity is controlled by a stepping motor connected to the leadscrew. The leadscrew was preloaded and has a negligible backlash. The minimum velocity of the translator is 5 μm s^{-1}.

2.3. *Polarimetry*

In the earlier publication, we described textures videotaped using the rotational shear cell. We noted the appearance of a striped texture during the flow, with stripes parallel to the flow direction. To determine the orientational pattern associated with these stripes, we need to examine the material under a variety of polarization conditions, not just the simple crossed polaroid conditions used earlier. For example, suppose one crossed polarizer is oriented at 0° with respect to x, the flow direction, and the other is parallel to the vorticity direction y, which is in the plane of the sample at 90° with respect to the flow direction. (Hereafter all orientations of optical elements are given relative to the flow direction, and in the plane of the sample.) Under such conditions, extinction of light can be achieved in some region of the sample if the director in that region is parallel to either of the polarizers. That is, light is extinguished both when the director is parallel to the flow direction and when it is parallel to the vorticity direction. Likewise, director orientations of either 45° or 135° will both

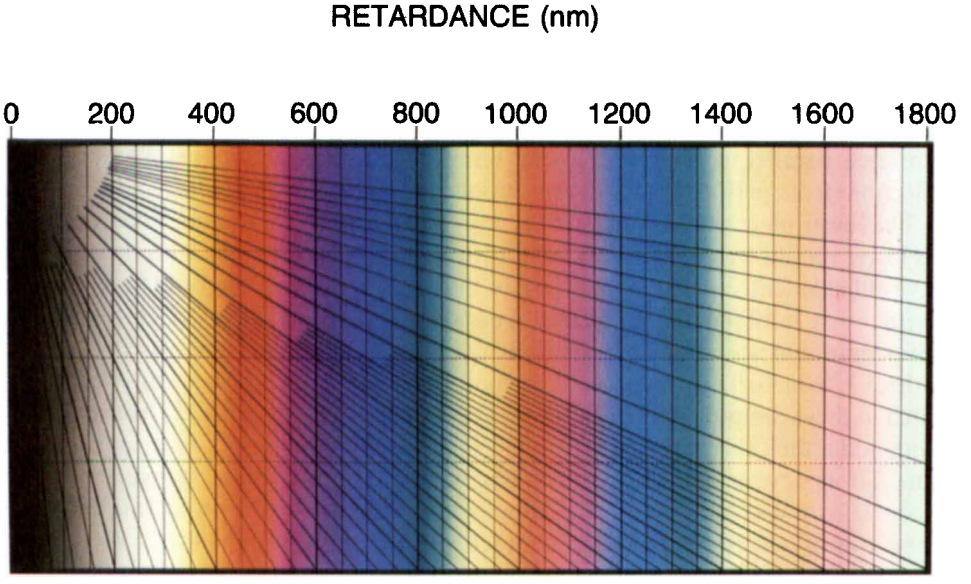

Figure 2. Newton's colour sequence showing colours produced by a birefringent sample illuminated by white light, as its retardance is increased.

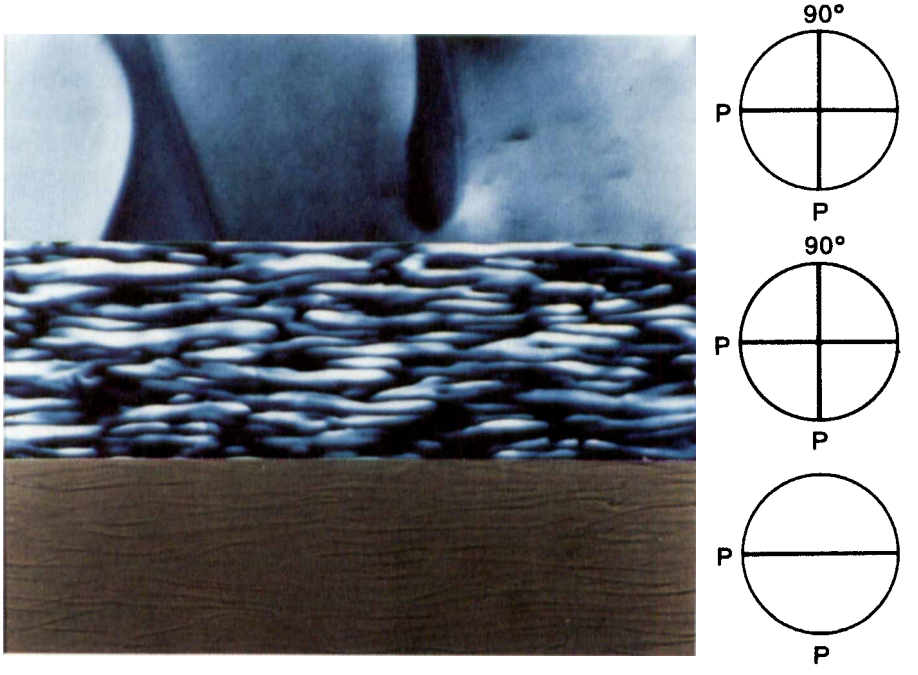

Figure 3. Sample of PBG198 in translational flow cell at a gap of 75 μm. In these and the following figures, except where noted, the magnification is $\times$ 10 and the width of the field of view is about 1 mm. The polarization conditions are depicted next to the photos. (*a*) The sample before shearing, (*b*) the sample after being sheared for 930 s at 0·05 s^{-1}, (*c*) the same as (*b*) except without the analyser so that the defect lines alone are imaged.

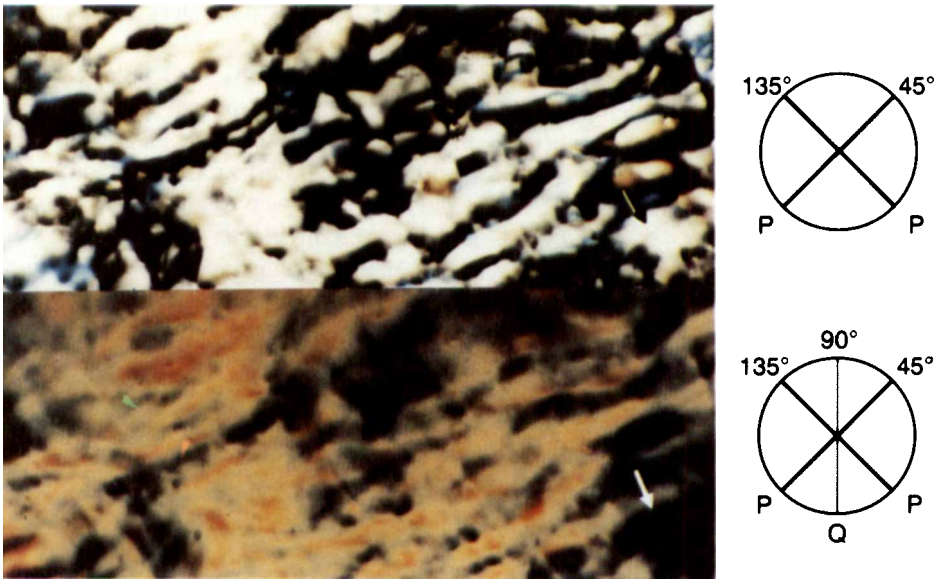

Figure 4. Sample of PBLG186 that has been subjected to about 8 strain units of shearing in the rotational device, viewed under crossed 45°–135° polarizers, with and without a quarter-wave plate. The shear rate is $\approx 0{\cdot}35\,s^{-1}$, and the gap is $\approx 125\,\mu m$. The arrows show one white area that turns dark when the quarter-wave plate is inserted. Most of the other areas turn yellow.

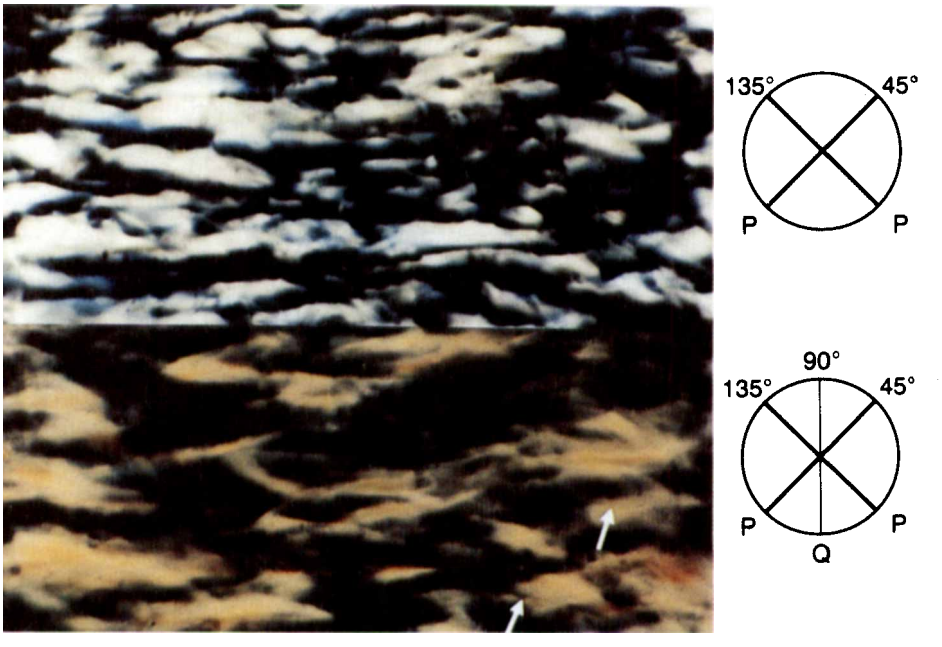

Figure 5. Same as figure 4, except about 16 strain units have been imposed. The arrows mark the locations of fine defect lines.

produce similarly coloured regions under crossed (0°–90°) polarizers. Thus under crossed polarizers alone, the direction of orientation is ambiguous.

The reason for this ambiguity is the symmetry of the observed coloured and brightness with respect to a change in sign in the retardance of light as it passes through the sample. This symmetry can be broken, however, if a quarter-wave plate is inserted between the sample and the analyser. If, for example, the polarizer and analyser are at 0° and 90° with respect to the flow direction, and if a quarter-wave plate is inserted with its slow axis oriented at 45°, then in regions where the director is oriented at 45° the sample will appear to be optically thicker, i.e. the observed retardance will be increased relative to what is observed with no quarter-wave plate. On the other hand, in regions where the director is oriented at 135°, the sample will appear to be optically thinner; the observed retardance will be decreased relative to what is seen with no quarter-wave plate. When the sample is illuminated by white light, the decrease or increase in the retardance is manifested by a shift up or down in wavelength along Newton's colour scale (see figure 2). The amount of the shift Δr is simply one quarter of a standard wavelength of 630 nm; i.e. $\Delta r = 630/4 = 158$ nm. We note that on Newton's colour scale, the darkest, or most nearly extinguished colours, are those that correspond to integral multiples of the average wavelength of white light, while the half-integral colours are the brightest. Thus both the colour and the brightness of the sample are shifted by insertion of a quarter-wave plate.

Of course, the director could be oriented parallel to the propagation direction of the light, that is perpendicular to both the flow and the vorticity directions. Regions of the sample where this is the case will be dark under crossed polarizers no matter what the orientation of those polarizers. After long periods of relaxation, we find that some large regions of the sample are oriented in this way, presumably because of the influence of the boundaries. But shearing flow strongly suppresses such perpendicular orientations, and during shear, regions where such orientations are dominant seem to be rare, or of small size. Of course, the orientation of the director varies across the gap (and therefore along the light path) and we expect some degree of net orientation normal to the surfaces, even during shearing flow. The amount of such orientation is not readily determined, without methods more quantitative than those employed here.

Although the shift in colour and brightness produced by the quarter-wave plate can, in principle, be observed for any overall sample retardance, the optimal retardance is somewhere around 250 nm. In this range, only a few colours, namely black, grey, grey-blue, and white, can be seen in the sample. Thicker samples show many more colours, which makes interpretation more difficult, while thinner samples are dark and have less contrast. For our samples, retardances in the optimal range are achieved for sample thickness around 75–150 μm. From the translational instrument, for which the gap can be determined to within 5 μm, the progression of colours with gap setting could be determined. From this correlation of gap setting with sample coloration, estimates of the true gap in rotational instrument could be obtained that are more accurate than the nominal gap setting, which is only accurate to within 50 μm or so.

Using crossed polarizers and a quarter wave plate, we can, as previously discussed, distinguish among various possible orientational states of a sheared sample, if the same texture can be observed under various polarization conditions. For a sample undergoing shear, this is difficult in general, since the sample is changing continuously in time. Here, however, we shall limit ourselves to low shear rates for which the texture evolves slowly, and changes slowly when shear is interrupted. Previous experiments have shown that the characteristic time λ_{tex} for the texture to change after cessation or

interruption of shear is inversely proportional to the interrupted shear rate [18]. The constant of proportionality is fortunately small, i.e. $\lambda_{tex} \approx 0{\cdot}01/\dot{\gamma}$. Thus if $\dot{\gamma}$ is low, say $\dot{\gamma} \sim 0{\cdot}5\,s^{-1}$, or less, we find that we can interrupt shearing for as long as 20 s or so without seeing a significant change in texture during the interruption period. This 20 s period allows us time to capture as many as four photographs of the sheared sample. Thus, in a typical experiment, we shear the sample for about 10 s, interrupt shearing for about 20 s to obtain a few photographs, and then continue shearing for another 10 s, and so on. In this way, we trace the development of orientation in the sheared sample. The lack of change in the sample during the interruption period was confirmed by taking, at the beginning and end of the interruption period, photographs under identical polarization conditions; when this was done at shear rates of 0·35 or less, the first and last photographs differed only slightly. We have also videotaped the evolution of texture during uninterrupted shearing, and find the same progression in the texture evolution that we see during interrupted shearing.

2.4. *Initial director orientations*

Since the initial director orientation in the sample is influenced by the sample loading, we followed a regular procedure for each shearing cell. In the rotational instrument, the sample is squeezed out between the two shearing surfaces until the desired gap is attained [18]. The squeezing drives radial fluid flow, and produces an average director orientation in the vorticity direction, which is perpendicular both to the shearing surfaces and to what will become the direction of shearing flow. After the sample is loaded, it is allowed to relax for at least 10 h before shearing begins. During this relaxation period, the texture coarsens considerably, but a significant degree of orientation in the radial direction remains. For the translational instrument, the sample is loaded, presheared, and then allowed to relax for at least 10 h. This produces an average director orientation parallel to the shearing flow. If the gap in the translational instrument is less than about 30 μm, then after about two days the racemic sample PBG198 spontaneously aligns almost entirely perpendicular to the glass surfaces, evidently because of anchoring conditions at the glass. This is a homeotropic alignment condition. The less viscous racemate, PBG118 requires only several hours to achieve a predominantly perpendicular orientation, and if the glass is clean enough, it becomes a uniformly oriented monodomain over an area of at least 1 mm^2.

3. Results

We find that, under all the above initial average director orientations, for the high molecular weight samples, PBLG186 and PBG198, shearing produces a steady state striped texture, with stripes oriented parallel to flow. Figure 3 (*a*) shows a sample of PBG198 in the translational instrument at a gap of 75 μm, that had relaxed for more than 10 h, thereby achieving a coarse texture. Figure 3 (*b*) shows the same sample, after it has been sheared at a rate of 0·067 s^{-1} for 930 s, i.e. 62 strain units. A striped texture is clearly evident. Figures 3 (*a*) and 3 (*b*) were taken under crossed 0°–90° polarizers. In figure 3 (*c*), the analyser was removed, leaving only the polarizer oriented at 0°. With only the single polarizer, the birefringence disappears and only the disclination lines themselves are visible. These lines are fine, so that they become less visible when sharply focused; in figure 3 (*c*) they have been defocused somewhat to make them easily visible. Note that the spacing between these lines is the same as the spacing between neighbouring dark and light areas in figure 3 (*b*); this spacing is around 10 μm, much smaller than the spacing of around 200 μm in the quiescent material (see figure 3 (*a*)).

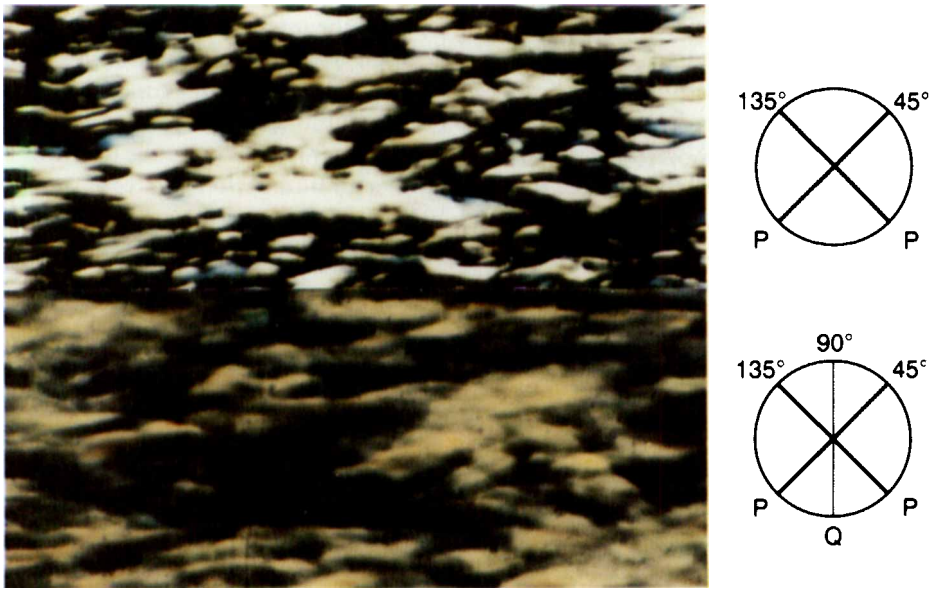

Figure 6. Same as figure 4, except about 24 strain units have been imposed.

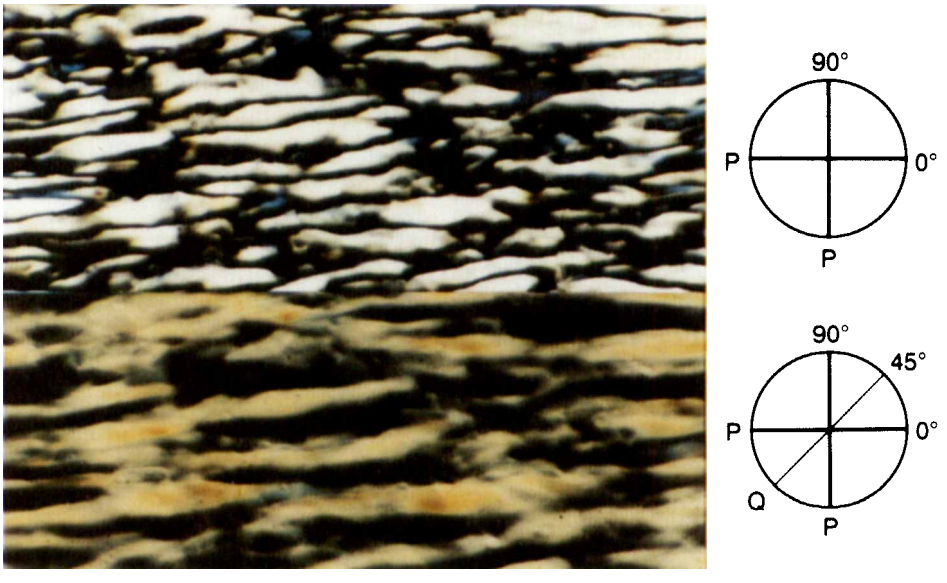

Figure 7. Same as figure 6, except here the polarizers are crossed at 0°–90°.

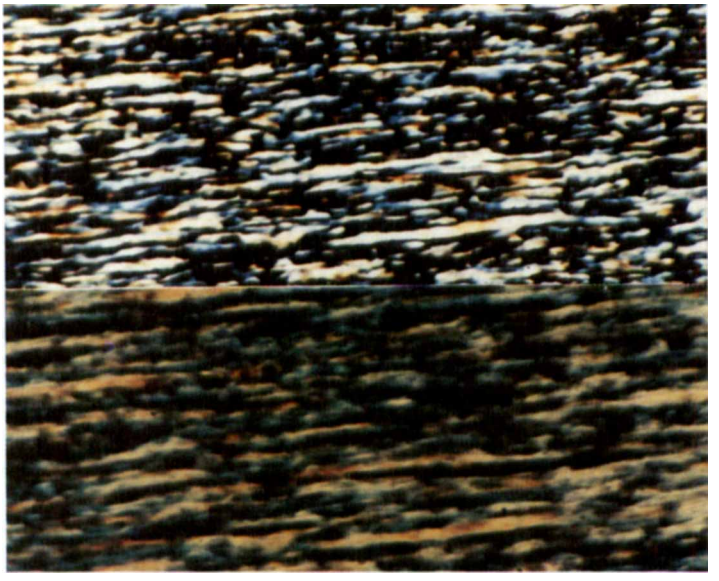

Figure 8. Same as figure 7, except about 110 strain units have been imposed.

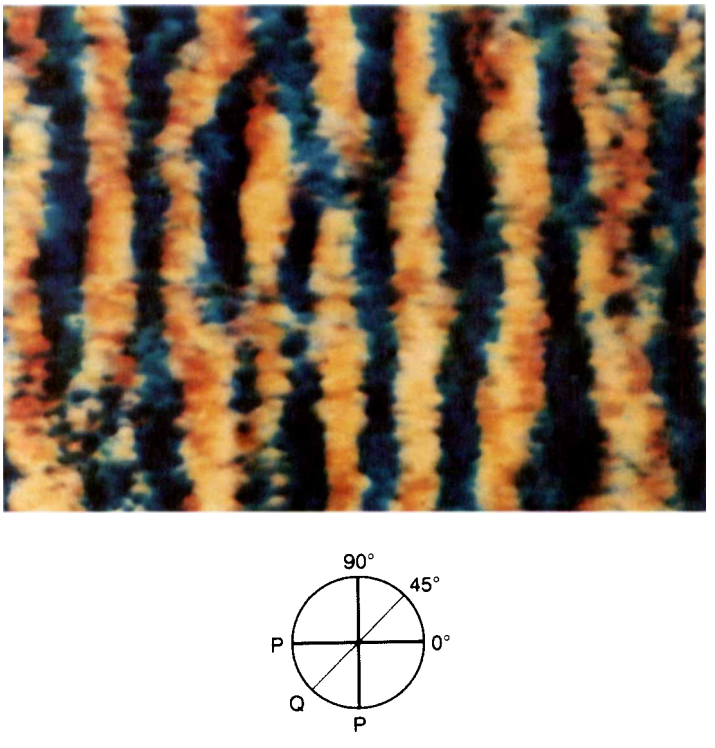

Figure 9. A sample of PBLG186 under crossed 0°–90° polarizers with a quarter-wave plate; the gap is about 150 μm. The sample had been sheared for about 120 strain units at a shear rate of $\approx 3{\cdot}0\,s^{-1}$ and then allowed to relax for about 100 s.

The depth of focus of the $\times 10$ ($NA = 0{\cdot}22$) objective used to obtain these photographs is enough to image structures throughout most of the 75 μm gap. Thus, in figure 3(*c*), defect lines throughout much of the gap are projected on to a plane, yielding an apparent spacing a_{app}, of 10 μm. If we can assume that structures throughout the entire gap are in fact imaged on to this plane, the true defect line spacing is $a_{true} = (ha_{app})^{1/2} = 30\,\mu$m, where h is the gap. Despite this correction, it is obvious that as a result of shear, the defect lines are much more closely spaced and, though wavy, are generally parallel to the flow direction. We have videotaped these defect lines during continuous shearing, and have verified that their appearance is not altered by the brief interruptions in shear required to obtain photographs.

We now examine the development of the striped texture more carefully. Figures 4–8 show a sample of PBLG186 in the rotational shear device with a gap of 125 μm at three different strains; the sample was sheared at a rate of about $0{\cdot}35\,s^{-1}$. At low shear rates such as this, for the first 3 or 4 strain units of shearing, the defect structure typically translates in the flow with only a slight distortion. The director field reorients somewhat during this period, however, as evidenced by changes in the colour and intensity of light in the regions between defect lines. After about 5 strain units, a new, finer texture appears. Figure 4 shows the sample after it has been sheared for about 8 strain units. In both figures 4(*a*) and (*b*), the sample is between crossed 45°–135° polarizers; in figure 4(*a*) there is no quarter-wave plate, while in figure 4(*b*), the quarter-wave plate is oriented with its slow axis in the vorticity direction, 90° with respect to the flow direction. Most of the white areas of figure 4(*a*) become yellow when the quarter-wave plate is inserted; although a few areas, such as that marked by an arrow, turn dark when the quarter-wave plate is inserted. The areas that turn yellow have been shifted up Newton's colour scale, while the areas that turn dark have been shifted down that scale (see figure 2). Since PBLG has a positive intrinsic birefringence, the yellow areas have average director orientations roughly parallel to the slow axis of the quarter-wave plate, which is parallel to the vorticity axis, while the areas that turn dark are more nearly parallel to the flow direction. Most of the white areas of the sample are therefore oriented more nearly parallel to the vorticity direction than the flow direction; this is a residual effect of the loading procedure for the rotational instrument, described above. Figure 5 shows the same sample after application of about 16 strain units, with the same polarization conditions as in figure 4. About half of the white areas of figure 5(*a*) now turn dark when the quarter-wave plate is inserted. (Note the many fine defect lines in figure 5; arrows mark the location of a couple of these in figure 5(*b*). As seen already in figure 3(*c*), the defect lines are generally parallel to the flow direction.) Figure 6 shows the same sample after application of about 24 strain units; most of the white areas of figure 6(*a*) turn dark when the quarter-wave plate is inserted. Thus, the orientation is now predominantly in the flow direction. Hence, starting from a deliberately misaligned state, roughly 24 strain units are required to achieve alignment in the flow direction.

Figure 7 again shows the sample after application of 24 strain units; this time, however, the polarizers are crossed at 0°–90°. When the polarizers are crossed this way with no quarter-wave plate (see figure 7(*a*)) dark lines parallel to the flow are clearly evident with white stripes between the dark lines, similar to figure 3(*b*). On insertion of a quarter-wave plate with the slow axis oriented at 45°, the white stripes turn alternately yellow and dark. Thus, there is a periodic clockwise and counterclockwise misalignment from the flow direction. The degree of this misalignment was estimated by rotating the quarter-wave plate until the contrast between yellow and dark areas

was maximized. This occurred at an angle in the range 35°–45°. The width of the yellow and black stripes here is roughly 25 μm. These yellow and black stripes are clearly evident also at a strain of 16 units, but are wider, namely around 50 μm. As the shear continues, the stripes get finer and finer; at 56 strain units they are perhaps 15 μm wide. Figure 8 shows them at 110 strain units, where their width is down to about 10 μm, which is about as narrow as they become at this low shear rate. (Figure 8 (*a*) shows some orange coloration not present in the other photos when the quarter-wave plate is absent; this is apparently caused by the imperfection of gap control in the rotational instrument.) At a higher shear rate, $\dot{\gamma} \approx 3\,s^{-1}$, the stripes become even finer, as fine as a few microns or even less.

Thus, the texture length scale and the orientation seem to develop over separate time scales. Starting from an orientation predominantly in the vorticity direction, it takes about 24 strain units for the director field to become oriented predominantly in the flow direction, but with periodic misalignment from that direction. The misalignment is most easily visualized as 'stripes' parallel to flow when the polarizers are at 0°–90°. Then, with continued shearing, this striped texture becomes finer until a steady state stripe width is reached; achieving this steady state length scale can take up to 100 strain units. When the shear rate is increased, the stripes at steady state become finer, and the number of strain units required to reach this steady state becomes greater (although the time required becomes less). Also, we observed that the coarser the initial texture is, the longer it takes to reach the steady state texture. Finally, if during shearing the shearing direction is suddenly reversed, the process of texture refinement does not seem to be reversed, interrupted, or significantly affected. All of these observations are qualitatively consistent with equation (1).

When flow stops after prolonged shearing at a sufficiently high shear rate, the striped texture relaxes, and a peculiar banded texture emerges with bands aligned perpendicular to the flow direction. These bands were first observed by Kiss and Porter [27] and have been much studied and discussed in the literature [28]. At a low shear rate for PBLG186, $\dot{\gamma} \approx 0{\cdot}35\,s^{-1}$ or less, the bands take minutes to form and are very weak. At $\dot{\gamma} \approx 3{\cdot}0\,s^{-1}$ they form more quickly and are much more distinct. At this higher shear rate, they form about 20 s after shear ceases, are initially about 15 μm wide, and grow to 50 μm after 100 s. Under crossed 0°–90° polarizers, the bands consist of dark lines separating white bands. Kiss and Porter observed that if a quarter-wave plate is inserted with its thick axis oriented at 45°, the white bands become alternately blue and yellow. Figure 9 shows a photograph of the texture of PBLG186 at a gap of around 150 μm under crossed 0°–90° polarizers with a quarter-wave plate at 45° after it has been sheared for 60 s at $3{\cdot}0\,s^{-1}$, and then allowed to relax for 100 s. The alternate yellow and blue stripes originally observed by Kiss and Porter are clearly evident. This colour variation implies that the director orientation is misaligned alternately clockwise and counterclockwise from the flow direction. This variation is similar to that which exists in the 'striped' texture induced by flow, except that the 'stripes' during flow are parallel to the flow direction, while the 'bands' that form after flow ceases are oriented in the vorticity direction. Note in figure 9 that a residual image of the thin stripes parallel to flow can still be seen superimposed on the bands.

For samples that are initially aligned roughly parallel to the flow direction in the translational flow cell, the progression is similar to that shown in figures 4–8, except for the absence of the global reorientation away from the vorticity direction that occurred in figures 4–6. With alignment initially in the flow direction, the stripes appear after about 5–10 strain units, sooner than with samples initially aligned in the vorticity

direction. As shear continues, these stripes become finer, just as they did with samples aligned in the vorticity direction. Steady state refinement is reached after about 30 strain units at this low shear rate of $0{\cdot}05\,s^{-1}$; 50 or more strain units are required at higher shear rates. Typically, during shearing that starts from the initially parallel average orientation, before the stripes form, bands oriented perpendicular to the flow direction appear, and then give way to the stripes. Like the bands that form after cessation of shearing, these bands consist of a periodic misalignment from the flow direction. The spacing between neighbouring bright bands is typically $40\,\mu m$, and seems to be independent of gap, at least over a limited range of gaps.

For a thinner sample, $30\,\mu m$, nearly homeotropic alignment is obtained if a racemic sample is allowed to relax for an extended period, namely two days for PBG198 and half a day for PBG118. When such a sample is subjected to slow shearing flow at $\dot{\gamma}=0{\cdot}16\,s^{-1}$, the sample retains its uniformity for some 15 strain units while the director rotates toward the flow direction. During the first 15 strain units, substantial alignment toward the flow direction is achieved, while there is negligible alignment in the vorticity

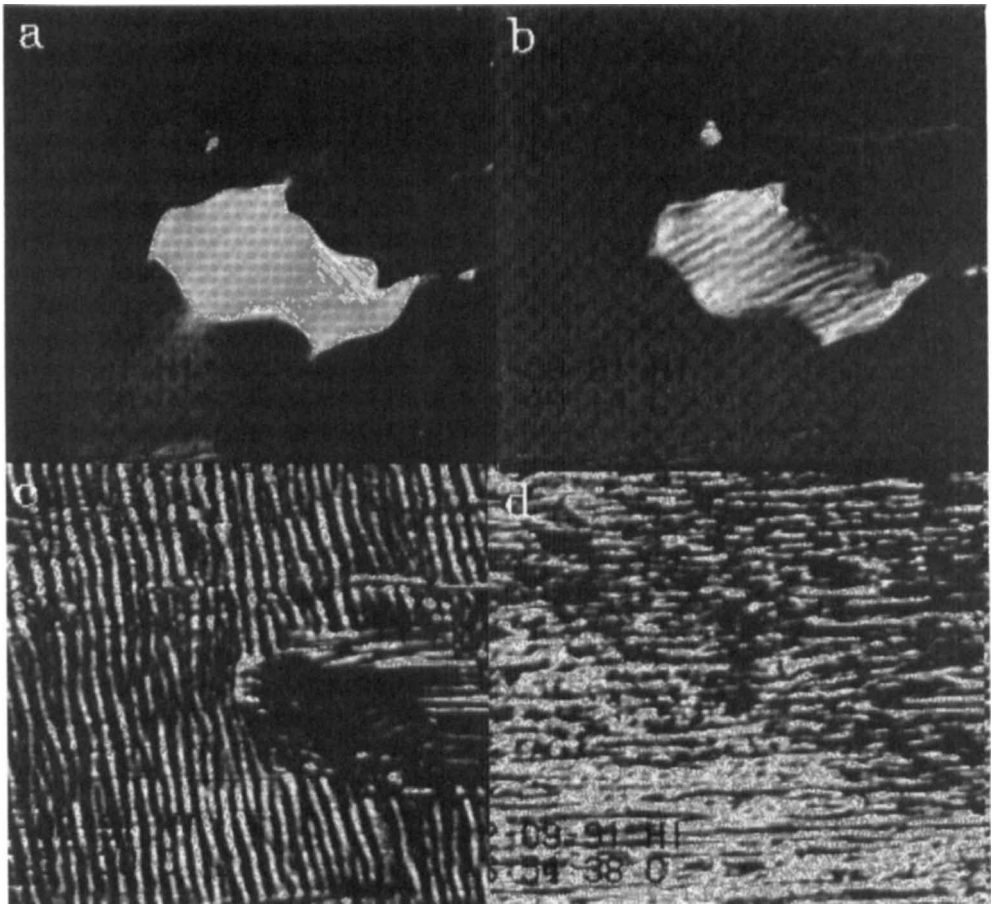

Figure 10. A sample of PBG198 at a gap of $30\,\mu m$ between crossed polaroids at a magnification of $\times 5$; (*a*) before shearing begins; (*b*) after 14 s of shearing at $\dot{\gamma}=0{\cdot}16\,s^{-1}$; (*c*) after 90 s of shearing; (*d*) after 338 s of shearing.

direction. This was determined by noting that when the sample is between crossed 45°–135° polarizers, it brightens soon after start-up of shearing, while when it is between crossed 0°–90° polarizers, it remains dark for the entire 15 strain units. After about 15 strain units, significant alignment toward the vorticity direction develops, and, at the same time, orientational inhomogeneities appear. For PBG198, a transient banded texture with bands perpendicular to the shearing direction appears after 15 strain units; later still, after about 40 strain units, these bands disappear and are replaced by stripes parallel to the flow direction. As usual, these stripes become finer with continued shearing.

The transient bands occur for initially parallel and for initially homeotropic alignment, but for some other alignment conditions, they do not occur. This is illustrated in figure 10, which shows videotaped images during shearing at $\dot{\gamma} = 0{\cdot}16\,s^{-1}$ of PBG198 at a gap, h, of 30 μm. The contrast of these images has been computer enhanced to make the structures more visible. The sample resides between crossed 0°–90° polarizers. The black area in figure 1 (*a*) is a region of homeotropic alignment, while the grey area is misaligned; by rotation of the crossed polaroids the grey area was found to have an average orientation of around 35° with respect to the flow direction.

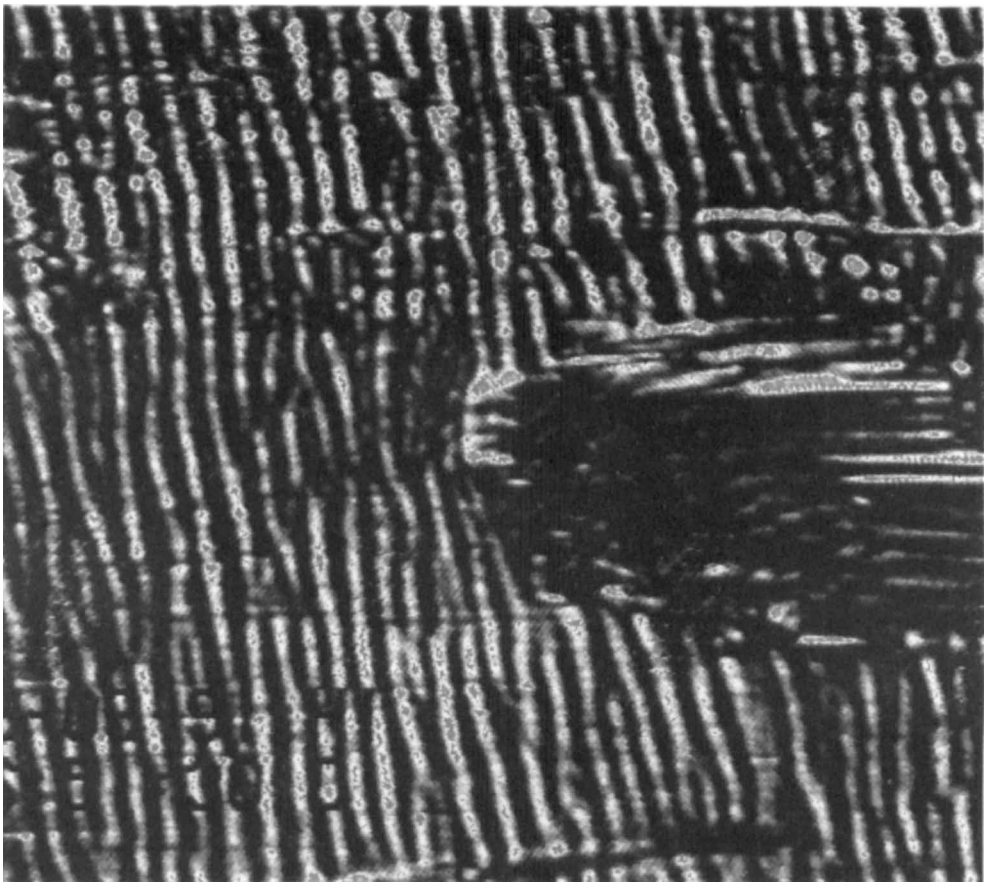

Figure 11. An enlarged view of figure 10(*c*), showing the banded texture during shear.

Figure 10(*a*) shows the sample at rest before shearing begins; in figure 10(*b*) the sample has been sheared for 14 s. Note in figure 10(*b*) that the misaligned region forms stripes that are oriented at an angle of nearly 45° with respect to the flow direction. The initially homeotropic area remains dark under crossed 0°–90° polarizers; under crossed 45°–135° polarizers it is evident that the director in the initially homeotropic region has been rotated toward the flow direction. As shearing continues, the stripes in the misoriented region quickly rotate to become parallel to the flow direction. Figure 10(*c*) shows the sample after it has been sheared for 90 s, i.e. for 15 strain units. The initially misaligned region has been translated to the right in the flow field and it now contains stripes parallel to the flow direction. The initially homeotropic region is, however, filled with bands that are nearly perpendicular to the flow. Figure 11 shows an enlarged view of figure 10(*c*). Figure 10(*d*) shows that after the sample has been sheared for 338 s, or 56 strain units, the bands have disappeared and are replaced by stripes parallel to the flow direction, and both the initially homeotropic and the initially misaligned regions finally have similar textures.

4. Discussion

We have found that, for a variety of initial director orientations, including homeotropic alignment, a striped texture appears after prolonged shearing of PBG samples of high molecular weight. Using crossed polarizers and a quarter-wave plate, we have deduced that the striped texture consists of alternating misalignment relative to the flow direction, as illustrated in the 'herring-bone' patterns of figure 12. These depictions are idealizations; the stripes we actually observe have a finite length (see figures 7 and 8). The stripes have a range of aspect ratios ranging from about 1 to 6 or so.

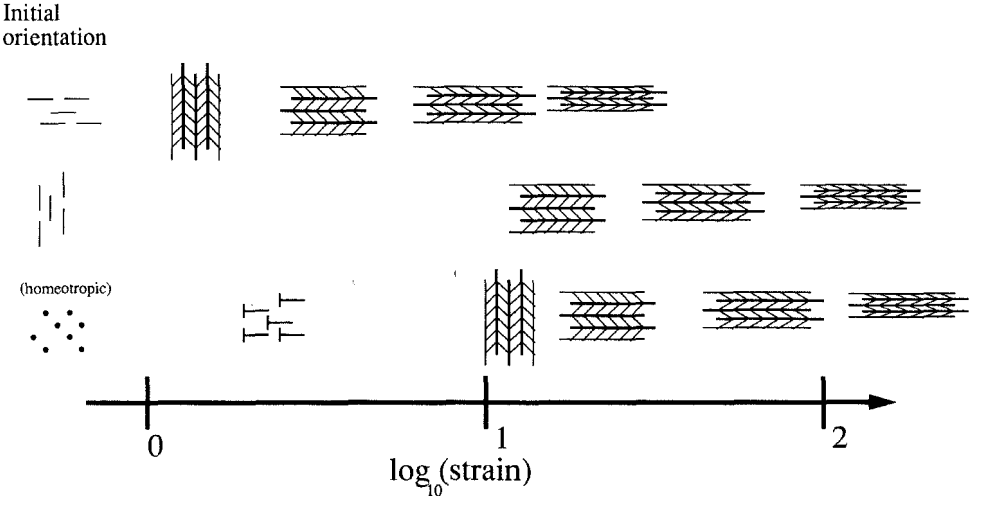

Figure 12. A schematic illustration of the development of birefringent textures as a function of shearing strain at low shear rates ($\dot{\gamma} \approx 0{\cdot}05$–$0{\cdot}5\,s^{-1}$) for high molecular weight samples PBLG186 and PBG198 as deduced using polarizers and quarter-wave plates. The flow direction is horizontal and the vorticity direction vertical. The top and middle sequences are for coarse initial textures with average alignments parallel to the flow and vorticity directions, respectively; and the gap is around 100 μm. The bottom sequence is for an initially homeotropic alignment and for a small gap of around 30 μm. The initial orientation affects the transient textures, but not the final texture.

From Fourier analysis of this pattern, we obtained an average aspect ratio of about 3 [18]. We estimate the misalignment angle associated with the stripes to be 35°–45°. This misalignment is consistent with recent birefringence measurements that show that during steady state shear, the sample-averaged molecular orientation (or order parameter) of PBLG samples is only half that of a static monodomain [29].

Figure 12 summarizes the texture evolution for shearing of three different initial textures. For samples initially aligned roughly parallel to the flow direction (see top of figure 12), the herring-bone striped orientational pattern is established by the time 5–10 strain units have been imposed on the sample, while 15 strain units are required for samples aligned in the vorticity direction (see middle of figure 12), and as many as 40 strain units for samples with small gaps and homeotropic initial alignment (see bottom of figure 12). The large number of strain units required in this latter case to obtain the stripes might be due, not to the homeotropic orientation *per se*, but to the thinness of the gap. For this small gap, 30 μm, the Ericksen number is of order 100 for PBG198. Various kinds of stripes parallel to flow, including a 'phase grating', were also observed by Srinivasarao and Berry for PBT solutions [9]. Although the relationship between their observations and ours is not yet clear, it does seem that formation of a striped texture may be a ubiquitous phenomenon in shearing flows of tumbling nematic polymers. In the case of a phase grating, the stripes are associated with a secondary flow consisting of roll cells [13].

A detailed analysis of the mechanism of formation of these stripes will probably require a three dimensional non-linear analysis of the equations of nemato-dynamics. However, as discussed in the Introduction, whether the direction of a tumbling nematic is initially in the shearing plane, or orthogonal to it, the director field is unstable at high Ericksen number, typically to the formation of roll cells oriented parallel to flow. These roll cells produce misalignment of the director and hence variations in birefringence such as those we have observed. Thus the formation of roll cells, and hence of stripes, might be inevitable for tumbling nematics at high enough Ericksen number.

Once the stripes form, further strain makes the stripes become finer, until a steady state stripe width is achieved after imposing 30–100 strain units, depending on the shear rate and the initial director orientation (see figure 12). The strain required to reorient the director is thus typically less than that required for the texture to achieve a steady state length scale. This finding is roughly consistent with the scaling theory discussed in the Introduction. The strain required to reorient the director, namely 15 strain units, is consistent with molecular theory and with the tumbling period deduced by rheological studies [21]. For samples with wide gaps, 75 μm or greater, the texture length scale seems to decrease gradually after start-up of shearing. Given an initially coarse texture length scale of 100 μm and a final length scale of 10 μm, the strain, $\gamma_{tex} = 50$–100, required to come to within about 5 per cent ($F \approx 0{\cdot}05$) of the final stripe spacing is consistent with equation (3) if the phenomenological parameter α has a value of about 0·1–0·2. A similar value of α can be deduced from rheological data gathered during interrupted shear experiments [30].

For samples with small gaps, 30 μm or less, large uniformly oriented regions can persist without becoming textured for some 15 strain units. Thereafter, in high molecular weight samples, a banded texture with band spacings of around 40 μm appears. Later, these are replaced by stripes with a similar spacing. Equation (1) does not seem to be relevant to these thin samples.

Although the final orientation and texture do not seem to depend much on the starting orientation or coarseness of the texture, the transient textures that occur on the

way to steady state are sensitive to the initial direction orientation, and hence to the sample loading and pre-shearing procedure. This is consistent with the observation that transient rheological data for liquid-crystalline polymers are sensitive to flow history [23]. The orthogonal banded texture that occurs temporarily during shearing flows seems, in particular, to occur only for some initial orientations, in particular for initially parallel and initially homeotropic conditions (see figure 12). Bands perpendicular to flow during shearing were first reported by Kiss and Porter [27], but later workers have failed to reproduce their findings [29]. In light of our observations, it is likely that these differing observations were caused by differences in starting orientations produced by the varying experimental procedures.

We wish to acknowledge a helpful discussion with Wesley Burghardt.

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