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

Band formation in HPC solutions by consecutive shears along orthogonal directions

P. L. Maffettone[a]; N. Grizzuti[a]; G. Marrucci[a]
[a] Dipartimento di Ingegneria Chimica, Università di Napoli, Napoli, Italy

To cite this Article Maffettone, P. L. , Grizzuti, N. and Marrucci, G.(1989) 'Band formation in HPC solutions by consecutive shears along orthogonal directions', Liquid Crystals, 4: 4, 385 — 391
To link to this Article: DOI: 10.1080/02678298908035484
URL: http://dx.doi.org/10.1080/02678298908035484

LIQUID CRYSTALS, 1989, VOL. 4, No. 4, 385-391

Band formation in HPC solutions by consecutive shears along orthogonal directions

by P. L. MAFFETTONE, N. GRIZZUTI and G. MARRUCCI
Dipartimento di Ingegneria Chimica, Università di Napoli, Piazzale V. Tecchio, 80125, Napoli, Italy

(*Received 14 June 1988; accepted 23 September 1988*)

Experiments of banded texture formation in lyotropic HPC aqueous solutions are reported. A parallel plate apparatus is used, which allows for consecutive shears along mutually orthogonal directions. In the double shear experiment, the effects of the following variables have been explored: first and second deformation shear units, shear rate of the second movement, delay time between the two deformations. The results show that the formation of a banded texture oriented orthogonally to the first shear is strongly enhanced by introducing the second shear motion. The mechanisms of formation of the texture are discussed.

1. Introduction

The general phenomenon of band formation due to shearing of a nematic, or cholesteric, polymeric liquid crystal has been studied in two respects. It was first shown that the bands correspond to a serpentine arrangement of the director field along the shear direction [1, 2]. Secondly, insofar as the appearance of a banded texture depends on shearing conditions, some quantitative information on threshold values and characteristic times has been collected [3, 4].

More in detail, it was shown that, for any given value of the shear rate, there exists a threshold value of the shear deformation below which bands do not form. Such a value is a decreasing function of the shear rate [3, 4]. It was also shown that the banded texture does not form immediately after the deformation. The induction time was found to decrease with increasing either the shear rate or the shear deformation or both [3]. Working with a parallel plate apparatus, Marrucci *et al.* [4] found a strong dependence of the threshold values upon the thickness of the sample, the banded texture forming more easily in thicker samples.

A quantitative estimate of band spacing and of its dependence on parameters has also been made recently [5]. It was found that the spacing is rather insensitive to shear conditions and appears to be mostly an intrinsic property of the material.

In this work, the parallel plate apparatus previously used [4] has been suitably modified to allow for consecutive shears of the sample along two mutually orthogonal directions. The effect of the second shear on the formation kinetics of the bands and on their evolution in time has been investigated. Aim of the work was that of gaining some insight into the so far unknown mechanism of band formation.

2. Materials and methods

A description of the basic parallel plate apparatus can be found in [4]. Whereas in the previous work one of the plates was held fixed, in the present modification that plate can be displaced along the direction orthogonal to the motion of the other plate. It should be mentioned, however, that, in order not to rebuild the whole apparatus, the additional movement could only be made at a fixed velocity (40 mm/s). Also, the displacement is limited to the range *c.* 1–10 mm. The parallel plates sit in a transmitted light microscope with the beam direction orthogonal to the plates. All observations are made with crossed polars oriented along the directions of the two shears.

The liquid crystalline polymer used is a 50 per cent wt aqueous solution of Hydroxypropylcellulose (HPC) supplied by Aldrich. The molecular weight used in this work is 100 000. With respect to the molecular weight of 300 000 used in the previous work [4], the 100 000 sample has the advantage of faster equilibration times, of the order of 1 hour at most. In fact, loading of the sample is inevitably accompanied by a squeezing flow, the effect of which must be relaxed before the experiment is started. A few runs were made with the 300 000 sample as well. They have shown a qualitatively similar behaviour, and their results will not be discussed. While waiting for the equilibration process, some loss of solvent may take place at the sample border. This is of no consequence, however, because the observation is always made far away (order of centimetres) from the sample border.

The experiment was typically carried out in the following way. First, the sample was sheared with a fixed shear rate in the z direction up to a chosen value of the deformation, possibly insufficient for the spontaneous appearance of the banded texture. Then, after a fixed delay time, the second shear deformation, along the orthogonal direction x, was started, with a chosen value of the shear rate. The value of the displacement along x at which the banded texture first appeared was recorded.

In some instances, by continuing the second deformation, the subsequent evolution of the structure was also observed. In particular, the sequence of interference colour changes was recorded up to the disappearance of the banded texture.

In order to compare the double shear results with the single shear ones, 'calibration' runs have been made in which the times of first appearance of the banded texture resulting from a single shear were determined as a function of the shear units.

Throughout this work, a constant sample thickness of 300 μm has been used. All experiments have been run at room temperature (*c.* 20°C).

3. Results and discussion

3.1. *Single shear experiment*

Figure 1 shows the 'calibration' results for the single shear experiment. The value of the shear rate is 130 s^{-1}, which is the same value as that constantly used in the first deformation step of the double shear experiments to be presented in the following. (As mentioned previously, one of the two motions has a fixed velocity of 40 mm/s. We have chosen that motion to be the first in the sequence.) Figure 1 reports the induction time t_i (from the end of the applied deformation to the first appearance of the banded texture) as a function of the shear deformation units, γ. Consistently with the results reported in [3], t_i decreases with increasing γ. Notice further that, in the range explored, t_i is of the order of several hundred seconds. Over a total time of about one hour, the banded texture vanishes, being replaced by the typical grainy structure of a relaxed sample.

As regards the threshold value of the applied shear deformation, it should be mentioned that a value of $\gamma = 4{\cdot}4$ did not give rise to a banded texture over a time

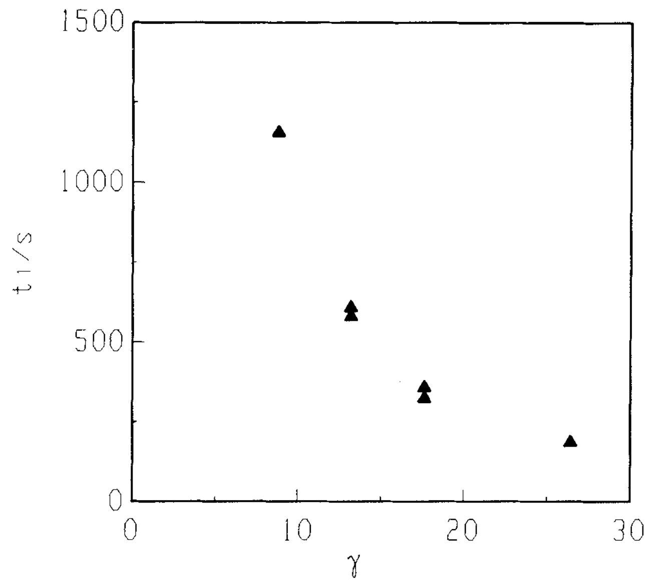

Figure 1. Induction time for band appearance in the single shear experiment as a function of the deformation. The shear rate is $130\,s^{-1}$.

of about one hour. After this time, the grainy structure was again observed. Thus, the threshold value is somewhere between 4·4 and 8·8 shear units.

Needless to say, the stripes formed in the single shear experiment run perpendicular to the shear direction.

3.2. *Double shear experiment*

It is important to note immediately that, in the double shear experiments, the stripes always formed perpendicularly to the direction of the *first* shear deformation.

Figure 2 shows typical results of the double shear experiment performed with a delay time of 15 s between the two deformations. The abscissa in figure 2 gives the shear units of the first displacement, γ_I, which plays a similar role as γ in figure 1. The ordinate is the band appearance time, t_a, measured from the start of the second deformation (made at a shear rate of $0.086\,s^{-1}$). By comparing figures 1 and 2, it is apparent that the second deformation strongly favors band formation. Indeed, even summing to the time values reported in figure 2 the delay time of 15 s, the resulting time is much less than t_i (at equal γ). It so appears that the banded texture forms much sooner as a consequence of the second, orthogonal deformation. It should also be noted that, differently from the single shear case, bands form at $\gamma_I = 4{\cdot}4$ as well. Thus, the second shear also lowers the threshold value of the first deformation.

The appearance time decreases even further if the shear rate of the second deformation, $\dot{\gamma}_{II}$, is increased. In fact, it is found that what really determines the band appearance in the course of the second deformation is the product of $\dot{\gamma}_{II}$ times t_a, i.e. the units of the second shear deformation, called γ_{II}. Figure 3 shows this result. All data in this figure were obtained with a delay time of 15 s. Although the spread of the data in figure 3 is considerable, no systematic dependence of γ_{II} on $\dot{\gamma}_{II}$ is apparent. In fact, the spread appears to be intrinsic to the band appearance phenomenon, as shown by the fact that all data points are repeated twice under supposedly identical conditions,

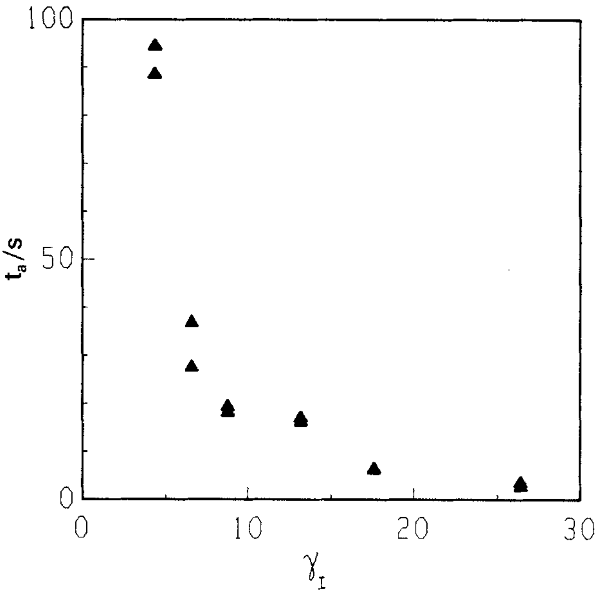

Figure 2. Appearance time for the banded texture after starting the second deformation as a function of the shear units of the first deformation. (Delay time = 15 s, $\dot{\gamma}_I$ = 130 s^{-1}, $\dot{\gamma}_{II}$ = 0·086 s^{-1}).

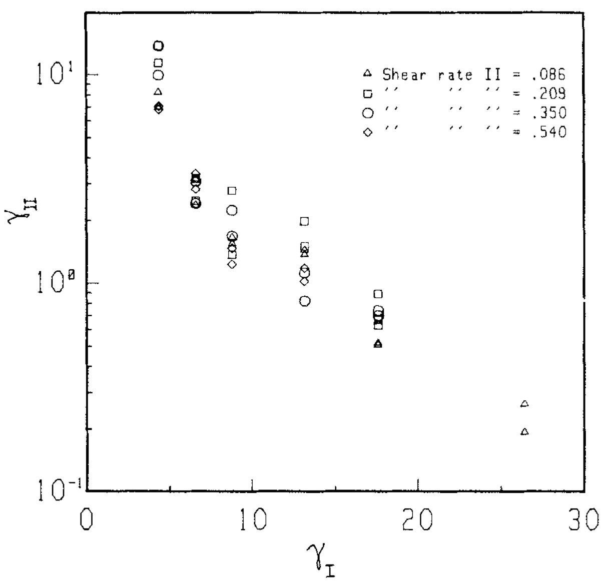

Figure 3. The shear units of the second deformation at band appearance as a function of the shear units of the first deformation for different values of $\dot{\gamma}_{II}$. (Delay time = 15 s, $\dot{\gamma}_I$ = 130 s^{-1}).

and yet they show a considerable difference in t_a, by as much as a factor of 2. In this regard, it should be remembered that we are dealing with visual observations through a microscope. Now, since the bands appear gradually, to become progressively more distinct and clear, a subjective decision is inevitably involved about the 'instant' when the bands have 'appeared'. This is, in our opinion, the main source of scatter in the data. Additionally, but only for values of t_a of the order of a few seconds, it should be remembered that t_a is measured manually. The latter remarks explains why the rightmost data point in figure 3 was obtained only with the lowest value of the second shear rate. For all larger values, the appearance time was too short to be measured.

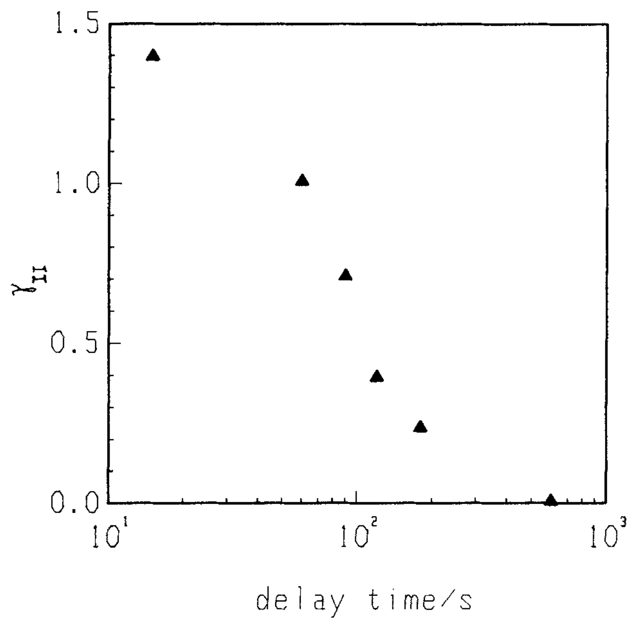

Figure 4. The shear units of the second deformation at band appearance as a function of the delay time. (γ_I = 13·2, $\dot{\gamma}_I$ = 130 s^{-1}, $\dot{\gamma}_{II}$ = 0·086 s^{-1}).

Finally, the effect of the delay time at a fixed value of γ_I is shown in figure 4. The value of γ_{II} steadily decreases with increasing the delay time, approaching zero when the latter approaches the value of the 'spontaneous' appearance time of 600 s, as obtained in the single shear experiment (see figure 1).

All the evidence shown in figures 1–4 indicates unequivocally that the second, orthogonal deformation greatly enhances the process of formation of the banded texture. This result is perhaps more easily interpreted than the phenomenon of spontaneous formation. In this regard, we recall the theory developed by Meyer and co-workers [6] for the case of a nematic aligned along the z direction, when subjected to a magnetic field along the orthogonal direction x. Meyer shows that in this experiment a periodic alignment of the director field around the z-direction, resulting in a striped texture parallel to x, can be dynamically favored over a uniform reorientation. The striped structure is particularly preferred in polymeric systems, due to the large anisotropy of the viscosity.

By analogy with the case considered by Meyer, we might assume that, in the double shear experiment here considered, the first shear deformation generates a degree of orientation of the nematic axis in the z-direction, whereas the second deformation plays an analogous role to that of the magnetic field along x.

Also, by extending the above analogy, it becomes possible to formulate an assumption on the origin of the phenomenon of band formation under 'spontaneous' conditions, i.e. in the absence of any apparent driving force orthogonal to the initial alignment. Indeed, we are tempted to assume that the band formation *always* requires some form of driving force orthogonal to the initial alignment. The question then arises on what kind of driving force can possibly be present in the spontaneous process.

We recall that all samples of polymeric liquid crystals have a polydomain structure, i.e. they contain a large number of disclinations. One may therefore expect that, upon deforming the material, along with a general alignment of the nematic axis, local regions of large curvature will also be created, due to the presence of disclinations. During the subsequent relaxation, the Frank elasticity stored in those regions will act as an internal driving force for a reorganization of the material. Since the reorganization process will generally involve motions with transversal components (i.e. orthogonal to the previous shear), the initial step of this rearrangement might well be the formation of a banded texture. In the course of time, the same driving force, i.e. Frank elasticity, will finally reestablish an essentially random overall structure. It is a general observation that the banded texture, once formed, becomes progressively less definite, and then disappears completely, the final texture being similar to that of the undeformed sample.

Returning to the results of the double shear experiment, it is worth noticing that, whatever the mechanism responsible for the spontaneous process may be, its effects superimpose on those due to the second shear deformation. This is particularly apparent from the data in figure 4. As the delay time between the two deformations is increased, since the process of spontaneous band formation (due to the first deformation) is already going on (although the bands are not yet visible), the amount of the second deformation necessary for band appearance decreases. Of course, when the delay time reaches the induction time of the spontaneous process, the additional driving force generated by the lateral deformation is no longer required.

It should finally be mentioned that, in the double shear experiment, once the banded texture has appeared, it is possible to follow its evolution due to the progress of the second deformation. Under crossed polars, a continuous colour change of the bands can be observed. The sequence of colours seems to follow the classical Newton scale. At very large values of the second deformation (of the order of several tens of shear units), the bands essentially disappear. They leave a very thin, dark trace over a uniformly coloured, though somewhat spotted, background. It seems sensible to infer that, under these conditions, the nematic axis has been substantially reoriented along the x direction. This is confirmed by the appearance of a new banded texture, oriented orthogonally to the previous one, readily induced by a small displacement (a third one!) along the z direction.

4. Conclusions

The main conclusion of this work is that the banded texture typical of a shear deformation forms very rapidly when a second shear, orthogonal to the former, is applied. Furthermore, even in cases where the first deformation by itself was insufficient to generate the texture, the second deformation equally produced the band structure.

A second conclusion concerns the cooperation between the mechanism of spontaneous formation and the one induced by the lateral motion. Indeed, since the spontaneous process has an induction period, if we allow more time to elapse before starting the lateral motion, a smaller deformation is required for the appearance of the banded texture.

A third conclusion is that the banded texture, oriented in the usual way, i.e. perpendicularly to the first shear, remains visible up to large values of the second deformation, in spite of the fact that, most probably, the nematic axis is being reoriented along the direction of the latter motion. The reorientational process is presumably responsible for the observed colour changes. In the end, an orthogonal reorientation seems essentially achieved, as proved by the appearance of a second banded texture, orthogonal to the original one.

Although the mechanisms responsible for these phenomena are not yet clearly formulated, it seems plausible to link the formation of a banded texture under shear to a similar effect observed under a magnetic field orthogonal to the nematic axis, and interpreted by Meyer [6]. The comparison requires that the first shear be effective in orienting the sample, whereas the second shear should play the role of the magnetic field, i.e. it attempts to reorient the nematic axis in the orthogonal direction. Although in the single shear case no external source of reorientation is imposed, there might exist an internal one due to the polydomain structure of the material, i.e. the Frank elasticity of the deformed structure.

This work has been supported by the Ministero della Pubblica Istruzione, Rome.

References

[1] VINEY, C., and WINDLE, A. H., 1986, *Polymer*, **27**, 1325.
[2] NAVARD, P., and ZACHARIADES, A. E., 1987, *J. Polym. Sci., Polym. Phys.*, **25**, 1089.
[3] MARSANO, E., CARPANETO, L., and CIFERRI, A., 1988, *Molec. Crystals liq. Crystals*, **158**, 267.
[4] MARRUCCI, G., GRIZZUTI, N., and BUONAURIO, A., 1988, *Molec. Crystals liq. Crystals*, **153**, 263.
[5] FINCHER, C. R., 1988, *Molec. Crystals liq. Crystals*, **155**, 559.
[6] LONBERG, F., FRADEN, S., HURD, A. J., and MEYER, R. E., 1984, *Phys. Rev. Lett.*, **52**, 1903.