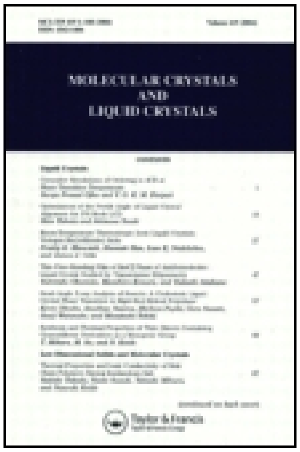

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Disclinations Observed During the Shear of MBBA

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We describe observations made with an optical microscope of the formation of two distinct types of disclinations during the shear of a small molecule nematic, MBBA. Once formed, these disclinations grow and deform in the shear field. We also report observations of the relaxation of these defects after the cessation of shear. The optical contrasts and associated distortions are shown to be more localised during shear than in the absence of flow. The two types of disclinations are believed to be singular structures of strengths $\pm\frac{1}{2}$ and non-singular structures of strengths ± 1.

INTRODUCTION

The characteristic threadlike textures which gave rise to the name "nematic" have been known to exist in small molecule nematic phases since the beginning of this century, and their presence has been employed to recognise the nematic phase following the example of Friedel.[1] The threads, now usually termed disclinations, correspond to singularities in the molecular alignment or director field of the nematic and are categorised by their strengths, s, whose definition can be found in general texts about liquid crystals (for example, see Refs. 2 and 3). In small molecule nematics, nuclei and line disclinations of strengths ± 1 and $\pm\frac{1}{2}$ have been observed with the optical microscope and examined theoretically. Detailed descriptions of the structures and properties of these defects can be found in Refs. 2 and 5.

Nuclei disclinations occur most readily in thin samples ($< 50\ \mu m$) of nematics and are generally believed to be line disclinations whose ends are pinned to the opposing surfaces bounding the sample. Optically, they appear under crossed polars as dark points from which two or four black brushes radiate (with $s = \frac{1}{4}$ no. brushes). Molecular configurations around these defects are assumed to have cylindrical symmetry. Frank[6] theoretically predicted these configurations by employing his modified version of the continuum theory for static nematics originally developed by Oseen.[7] His solutions are generally accepted and correlate well with optical observations. Mappings of his proposed molecular arrangements around point disclinations of strengths ± 1 and $\pm \frac{1}{2}$ are reproduced in Figure 1.

Line disclinations (commonly called nematic threads) appear in thick samples of nematics. They can be seen both in bright field and with crossed polars. Some float freely through the samples while others adhere to the surfaces and are motionless. Nehring[8] characterised two types of line disclinations created in a static (i.e. unsheared) sample of a nematic subjected to an electric field. These he called 'thick' and 'thin' threads—from their optical appearances. The thick threads he associated with non-singular, coreless disclinations of strength ± 1, in agreement with Meyer's[9] proposal of a continuous

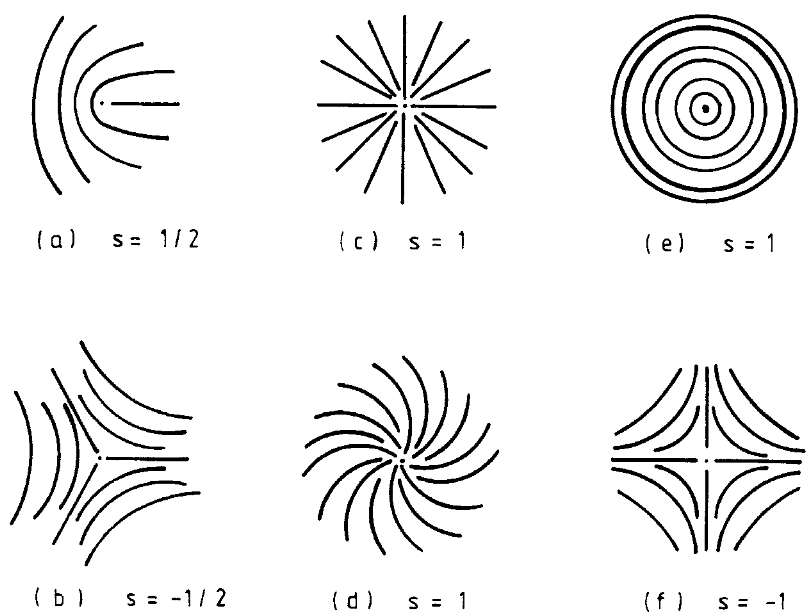

FIGURE 1 Schematic representation of molecular configurations around nuclei disclinations theoretically predicted by Frank.[6] Strengths of disclinations are indicated in the diagram.

structure for disclinations of integral strengths. Nehring believes the thin threads to be coreless singular disclinations of strength $\pm \frac{1}{2}$.

Line disclinations have been reported by several researchers[10-13] as forming during the shear of nematics. No one, however, appears to have studied in detail the behaviour of these defects in the shear field. In this paper, we describe our observations of the formation of defects and their subsequent behaviours in the nematic phase of 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA).

EXPERIMENTAL TECHNIQUE

The experiments were conducted with an apparatus which was specially designed to shear thin samples of material continuously under microscopic observation.[14] The sample is sandwiched between two glass discs (effective diameters of 9 mm), where the bottom disc can be rotated steadily relative to the top disc, creating a shear flow in the sample. The angular velocity of the bottom disc ranged from 0.005 to 0.1 revolutions/sec. in these experiments. The point of observation was maintained at a radial distance of 4 mm from the central axis of rotation. Therefore, at the point of observation, the linear velocity of the bottom disc ranged from 1.2×10^{-4} to 2.5×10^{-3} m/sec.

The MBBA was used as obtained from the manufacturer (Aldrich Chemical Co. Ltd.) without further purification. Samples of MBBA were homeotropically aligned (i.e. molecules oriented perpendicular to the surfaces) by treating the surfaces with a 0.5% solution of hexadecyltrimethyl ammonium bromide in ethanol. All experiments to be described were performed on samples with thickness 150 μm and at room temperature.

OBSERVATIONS

At shear rates below about 1 sec^{-1} (for a specimen thickness of 150 μm), the MBBA molecules flow align (as shown by the flow birefringence of the samples), without forming defects. This shear regime has been investigated previously by Wahl and Fischer[12] and Wahl[15] in homeotropically aligned samples of MBBA using a similar but larger-scale apparatus to that employed in the present work. They showed that the molecular orientation was determined by two competing forces: surface-dictated alignment (perpendicular to the surfaces) and flow-dictated alignment (parallel to the surfaces).

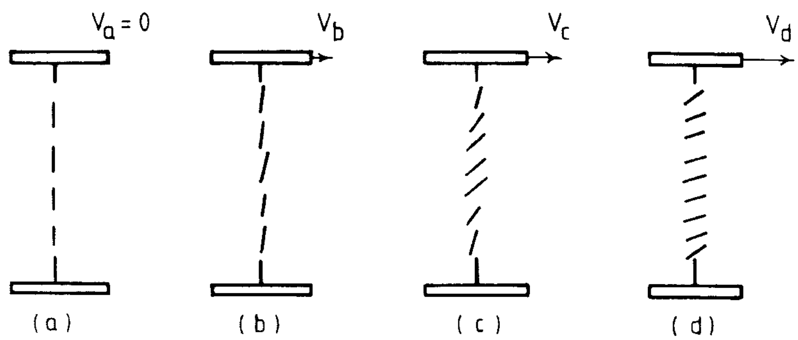

FIGURE 2 Schematic representation of shear-induced molecular orientation in samples of MBBA with homeotropic boundary conditions as proposed by Wahl and Fischer.[12] Shear created in sample by moving top plate at relative velocities as indicated in diagram, where $0 = V_a < V_b < V_c < V_d$.

A schematic representation of the effect of shear on the molecular orientation of a homeotropically aligned nematic as proposed by Wahl and Fischer appears in Figure 2. At rest (Figure 2a) and at low shears (Figure 2b) the surface-dictated alignment dominates, and the bulk of the molecules remain aligned perpendicular to the surfaces. As the shear is increased (Figure 2c), an increasing number of molecules align in the flow direction until at high shears (Figure 2d), a saturation in the flow alignment is reached. The degree of flow alignment was found experimentally to be a unique function of the product of the sample thickness and the velocity of the moving plate. This relationship was also shown to be in agreement with predictions of the Ericksen-Leslie continuum model as described by Leslie.[16]

Wahl and Fischer observed the formation of disclinations in their samples once the saturation in flow alignment had been reached, but they did not study these textures in detail. In our experiments we recognised two types of disclinations as shown in Figure 3. The optical appearances of these two types are similar to those described by Nehring,[8] and in accord with his terminology, they have been named 'thicks' and 'thins'.

Thicks are distinguished from thins both by their optical appearance and by their behaviour during and after shear. Both thicks and thins can be seen in bright field as well as with crossed polars. The optical contrast of these structures differ when they are flowing from when they are static (and consequently relaxing). Descriptions of the latter case will be deferred until the relaxation process is discussed.

Viewed with polarised incident light, with no analyser, the thins during shear, appear as narrow black threads. The observed optical

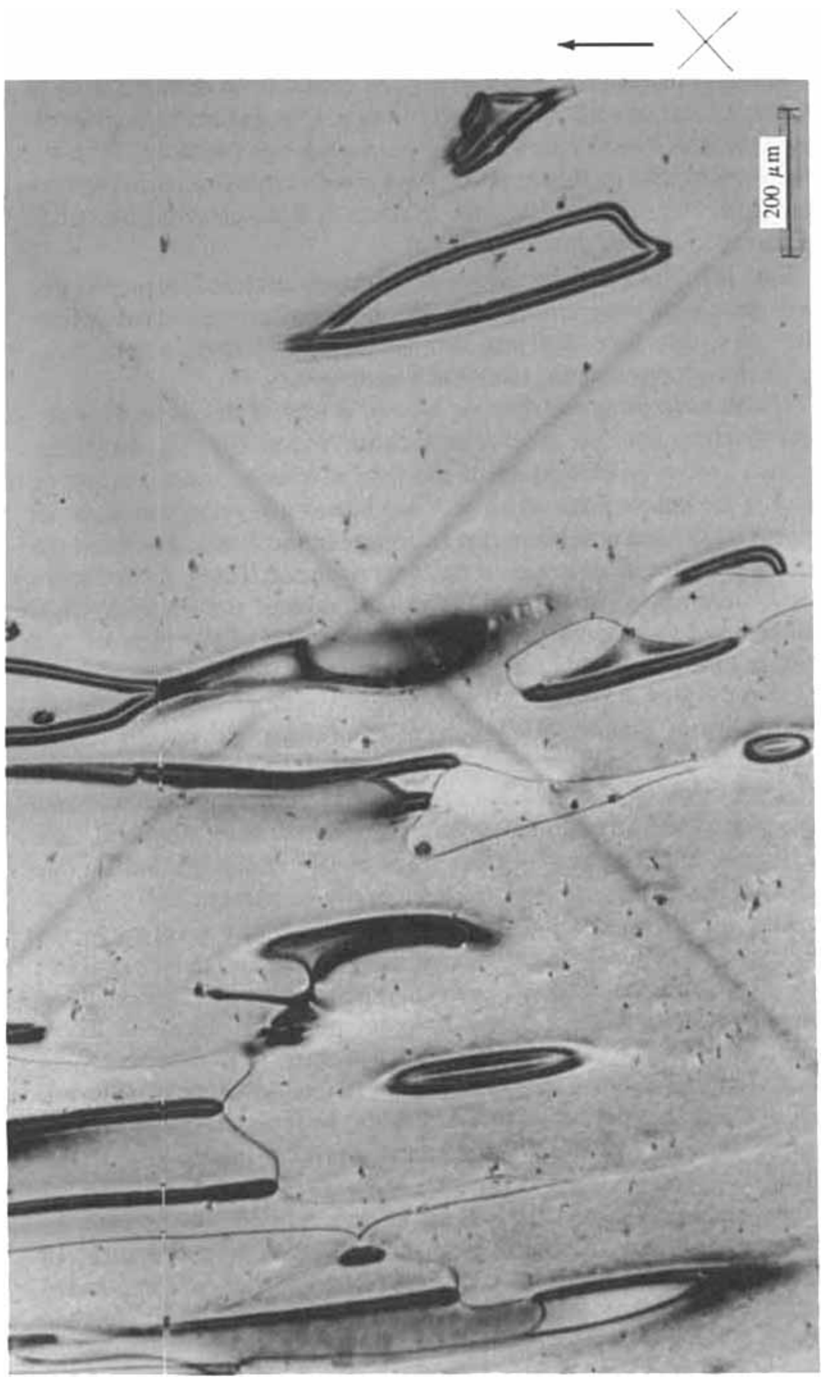

FIGURE 3 Thick and thin threads in a sheared sample of MBBA. Crossed polars, 45 degrees to shear direction. Shear rate = 4 sec^{-1}; direction of flow is vertically upward in print. Sample thickness = 150 μm, room temperature.

contrast of the thins are independent of the direction of polarisation of the incoming light. The optical contrast generated by the thicks are, however, dependent on the polarisation direction as demonstrated in the photomicrographs appearing in Figure 4. In Figure 4a the incoming light is polarised parallel to the flow direction (vertically upwards in the print), and in Figure 4b, it is polarised perpendicular to the flow direction. Nehring found a similar effect of light polarisation on the appearance of thick threads.

Both the thicks and the thins exist primarily as closed loops. No free ends have been observed. A thick can, however, exist attached at both ends to a thin loop, forming two thin-thick-thin node points. Also, some thick loops contain thick-thick node points.

Thicks were observed forming around pieces of debris in the samples which are thought to serve as nucleation sites. The thick loop once formed grows by elongating in the flow direction, either trailing or leading the debris. Eventually, the loop breaks away and travels on its own. Thicks have also been seen to appear in the material without the visible presence of debris or a nucleation source. Thins, on the other hand, were not observed forming in the midst of the material. They are believed to originate at the outer boundaries of the samples and then to migrate towards the centre.

Once formed, the thicks and thins interact with their environment in a complicated manner. They behave as unbreakable threads which, because of their small diameters, have little effect on the velocity and director fields of the bulk material. Figure 5 presents a time-series sequence of an isolated thick loop from infancy, elongating and then deforming in the flow field. The loops elongate, deform and tumble because of the presence of a shear gradient perpendicular to the surfaces and spanning the depth of the sample (the gradient in the radial direction across the circular sample is assumed to be negligible in the experiments). If the plane containing the loop lies at an angle to the plane of the disc surfaces, different positions along the loop's length will be subjected to different velocities. The distribution of these varying velocities along the loop's contour will determine how it will deform. If a loop lies parallel with the surfaces, its entire contour will be travelling at the same velocity, and it is free to shrink and relax.

The number density of both thicks and thins increases with increasing shear rate. At the highest shears studied (approximately 10 sec^{-1}), the entire field of view was covered with a complicated mesh-like network of interacting thick and thin loops.

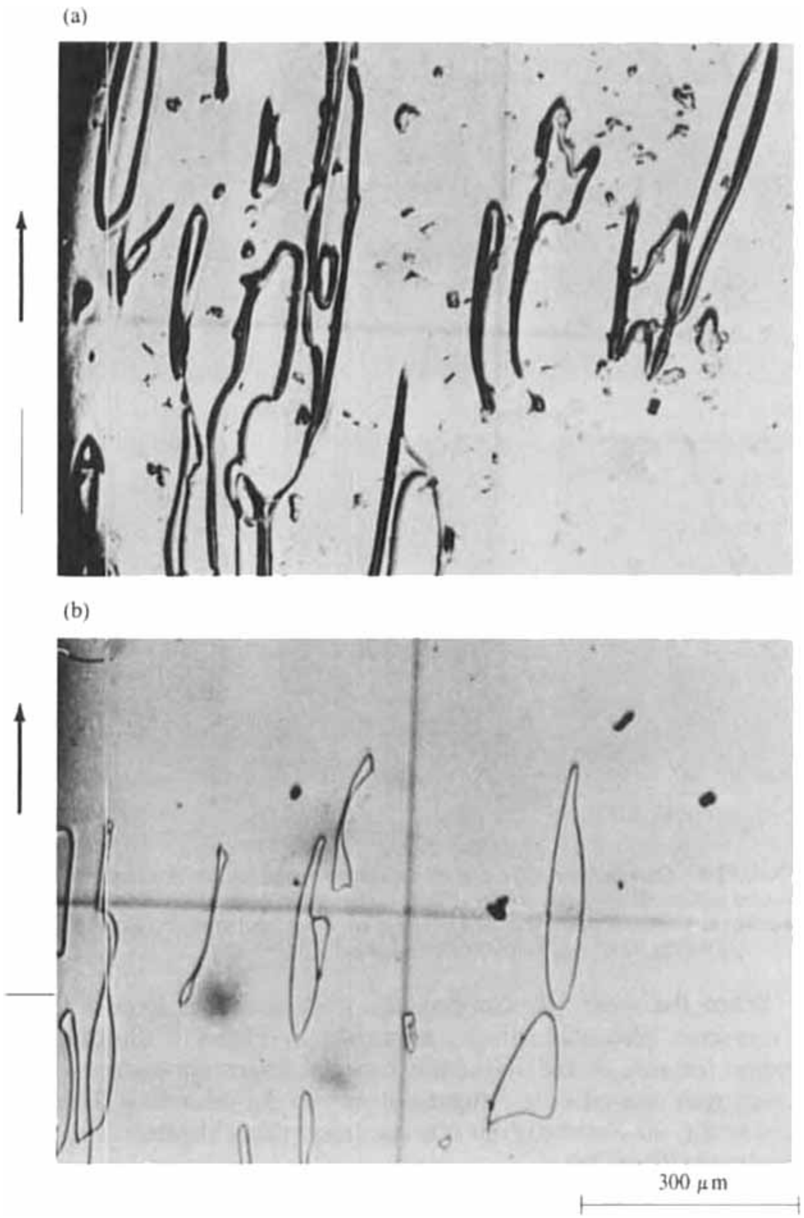

FIGURE 4 Effect of polarisation of incident light on optical contrast of thick threads. Shear rate = 4 sec^{-1}; direction of flow is vertically upward in prints. Sample thickness = 150 μm; room temperature. (a) Incident light polarised parallel to flow direction, no analyser. (b) Incident light polarised perpendicular to flow direction, no analyser.

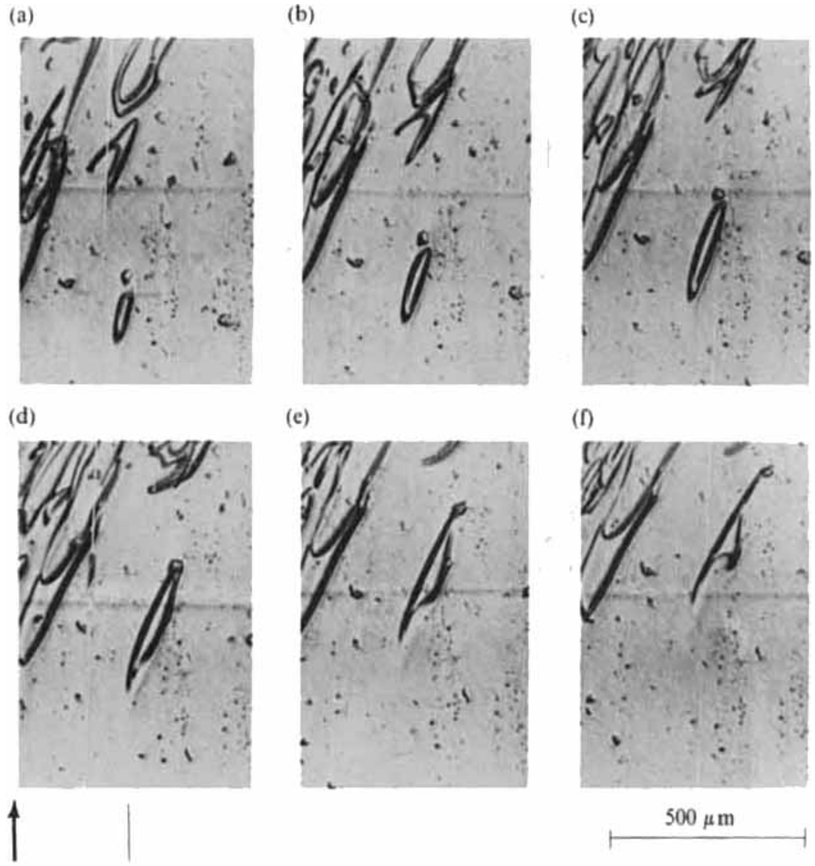

FIGURE 5 Growth and deformation of an isolated thick loop. Incident light polarised parallel to flow direction, no analyser. Shear rate = 4 sec^{-1}; direction of flow vertically upward in prints. Sample thickness = 150 μm; room temperature. (a) to (f) time sequence during shear, exposures two seconds apart.

When the shear was stopped, the thick and thin loops relaxed. Time-series photomicrographs appearing in Figure 6 illustrate the major features of the relaxation process. These photographs were taken with crossed polars aligned at 45° to the prior flow direction, and hence, the observed field is bright (due to flow alignment) at shear cessation (Figure 6a).

The first observation to note is that the thin loops and nodeless thick loops remain intact during relaxation and shrink by collapsing to a point. A thick loop with nodes, however, separates at its node points during relaxation. One of the segments vanishes while the other segment shrinks along its contour. This behaviour is seen more clearly in the time-series photographs of Figure 7.

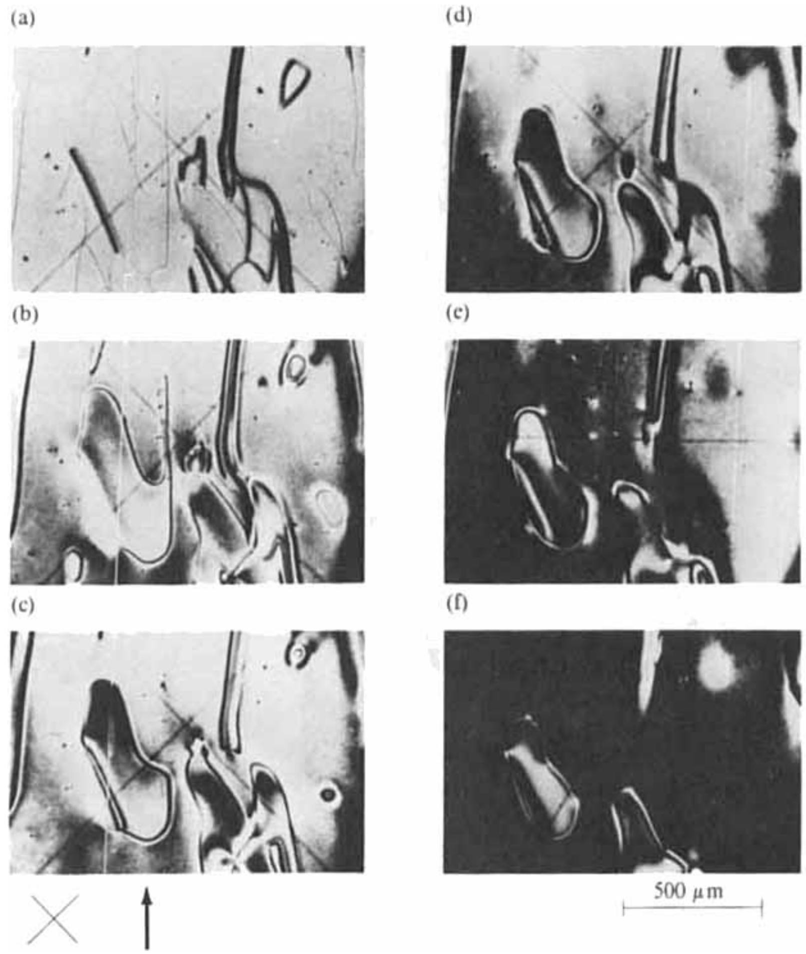

FIGURE 6 Relaxation of thick and thin loops observed with crossed polarised light. Prior shear rate = 4 sec^{-1}; direction of prior flow is vertically upward in prints. Sample thickness = 150 μm; room temperature. (a) 0 sec., (b) 10 sec., (c) 20 sec., (d) 30 sec., (e) 40 sec., and (f) 1.0 min. after shear cessation. Note that whereas the crossed polars are inclined at 45° for all but one of the micrographs, for (e) they are 0 and 90°

Secondly, the defects are seen to relax over a different time scale from the surrounding material. In the last frame of the sequence presented in Figure 6, the bulk of the sample has returned to its surface-dictated homeotropic alignment (indicated by the extinction of crossed polarised light) while the defects remain in view.

Finally, the optical appearances of the thick and thin loops differ during relaxation from when they are flowing. The optical contrasts of the loops broaden during relaxation. The differences in optical con-

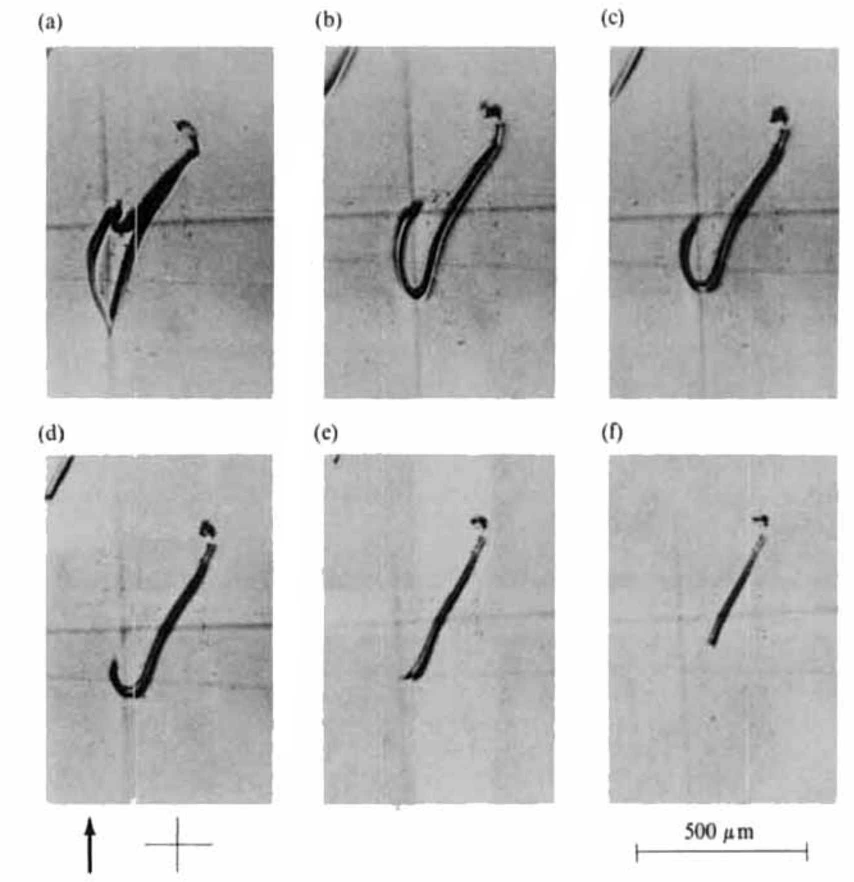

FIGURE 7 Relaxation of thick loop with nodes. Incident light polarised parallel to prior flow direction; no analyser. Prior shear rate = 4 sec^{-1}; direction of prior flow is vertically upward in prints. Sample thickness = 150 μm; room temperature. (a) 0 sec., (b) 10 sec., (c) 20 sec., (d) 30 sec., (e) 40 sec., and (f) 50 sec. after shear cessation.

trast of a thick loop during shear and in the absence of shear are shown most clearly in microdensitometer traces of the optical contrast as presented in Figure 8. The traces appearing in this figure are representative of the optical contrasts scanning across a thick loop (perpendicular to its length) during shear and approximately 5 seconds after the cessation of shear. A thin loop, in addition to having its optical contrast broaden during relaxation, is also seen to trap the material within it into an orientation different from that outside (as seen in Figure 6f). Therefore, although the thin loops appear to have

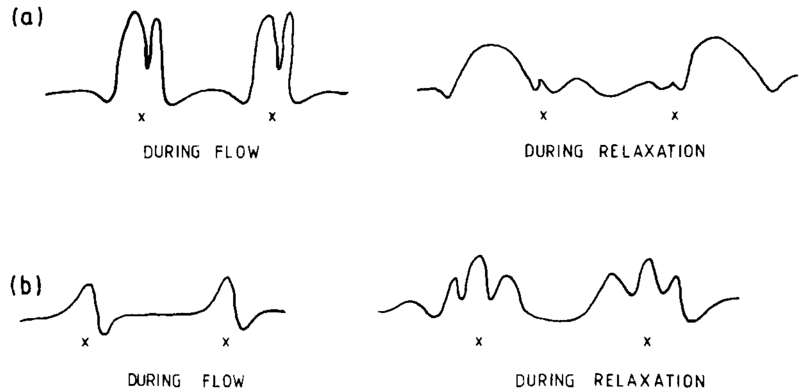

FIGURE 8 Representative microdensitometer traces showing the optical contrast "across" thick loops during flow and relaxation (> 5 sec. after shear cessation). (a) Polariser parallel to flow direction, no analyser. (b) Polariser perpendicular to flow direction, no analyser.

little effect on the overall orientation of the material during shear, in the absence of shear, their presence determines the orientation of the material within and around them.

DISCUSSION

Our observations are consistent with Nehring's[8] belief that thick threads are coreless disclinations of strength ± 1 and thin threads are singular disclinations of strength $\pm \frac{1}{2}$. According to topographical arguments forwarded by Saupe,[4] disclination lines of strengths $\pm \frac{1}{2}$ should either form closed loops or end at the surfaces. All the thin loops we observed were closed, and we observed no free ends. By the same arguments, Saupe suggests that disclination lines of strengths ± 1 can either form closed loops, end at the surfaces, or end on $\pm \frac{1}{2}$ lines. We observed both closed loop thicks and thicks attached at both ends to thins. Further support for Nehring's proposals comes from observations of the relaxation of the loops.

Figure 9 presents a schematic representation (in two dimensions only) of a possible molecular configuration around a coreless disclination of strength ± 1 (a 'thick') derived from Meyer's[9] proposals. During shear, the distortions around such a defect are assumed to be localised and concentrated to such an extent that they scatter light, leading to the observed optical contrasts of the thicks. If such distortions are expanded to larger dimensions, they would appear between crossed polars, as alternating bright and dark bands which move sideways or separate or converge as the crossed polars are rotated.

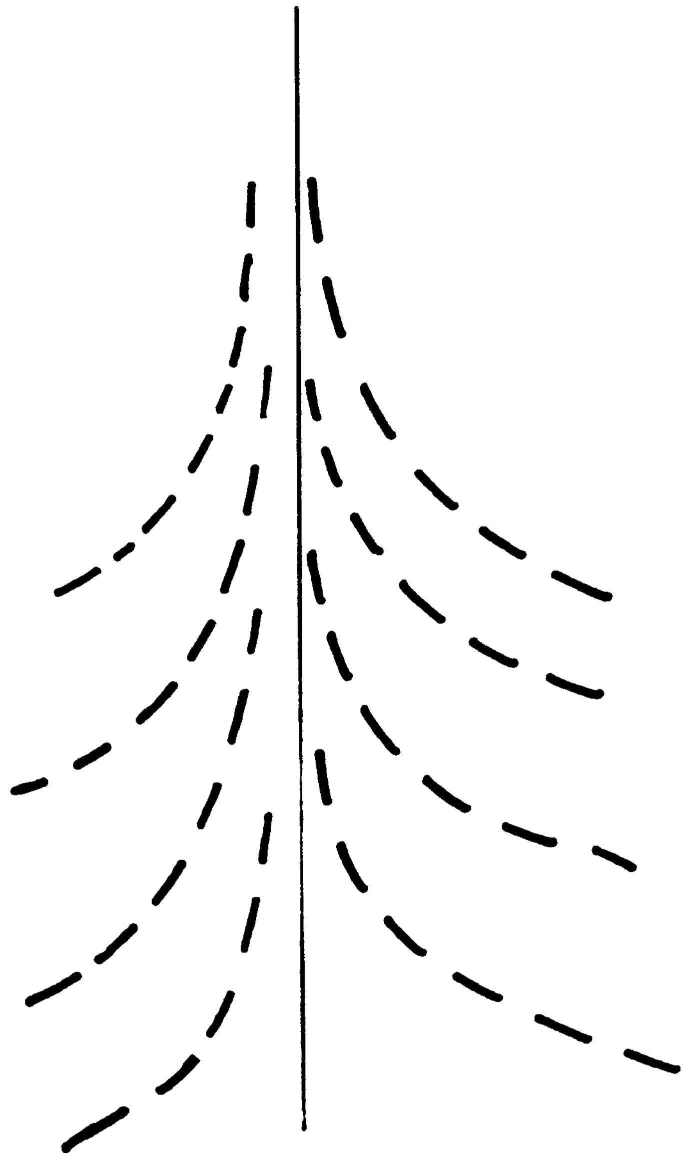

FIGURE 9 Schematic representation of possible molecular configuration around thick thread, drawn in two dimensions only. Structure adapted from Meyer.[9] Continuous line represents axis of non-singular disclination. Dashed line represents configuration of molecules.

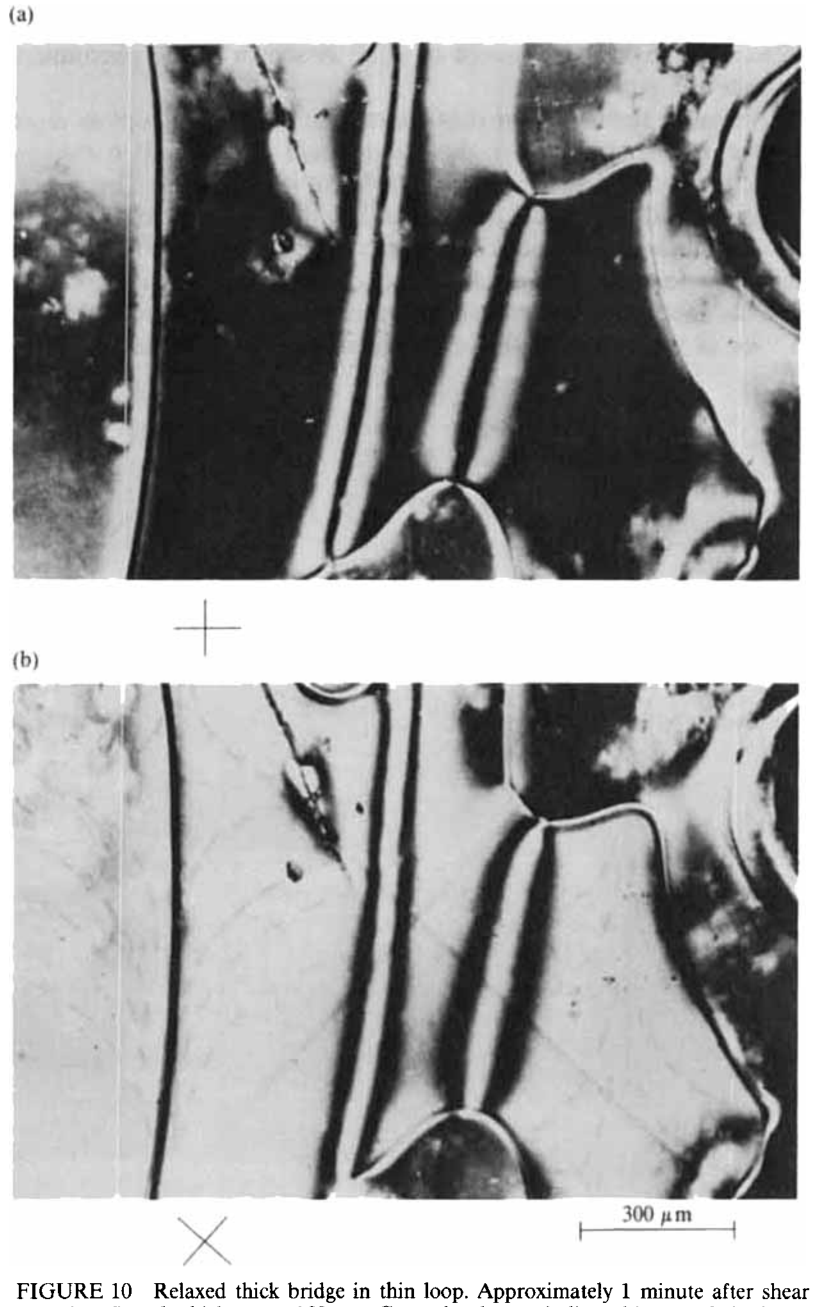

FIGURE 10 Relaxed thick bridge in thin loop. Approximately 1 minute after shear cessation. Sample thickness = 150 μm. Crossed polars as indicated by crosshairs in (a) and (b).

Such bands are exactly those which appear when a thick line bridged across a thin loop is allowed to relax as shown in the photomicrographs of Figure 10.

Assuming the molecular configuration around thick loops as represented in Figure 9, the node points could correspond to the two structures (in two dimensions only) shown in Figure 11. These structures around the node points are identical to the configurations around nuclei disclinations of strength ± 1 proposed by Frank (Figure 1). Therefore, an expanded version of them would, under crossed polars, appear as a point from which four black brushes radiate which rotate as the crossed polars are rotated. Figure 12 represents photo-

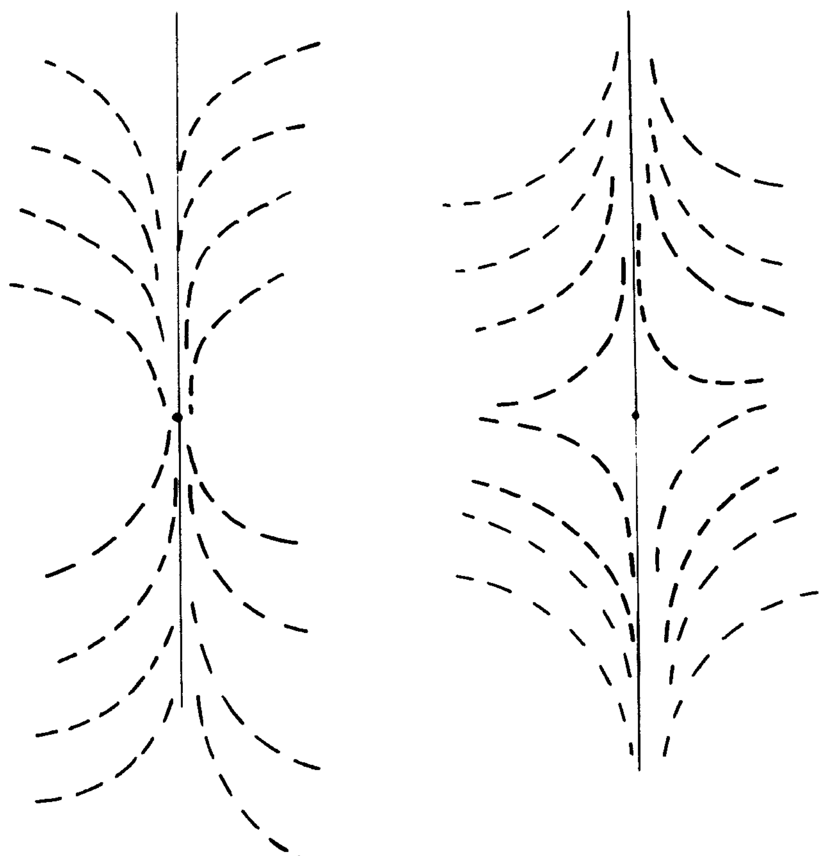

FIGURE 11 Schematic representation of molecular configurations around node points of thick threads, drawn in two-dimensions only. Continuous lines represent axes of non-singular disclinations. Dashed lines represent configuration of molecules. Dots represent node points.

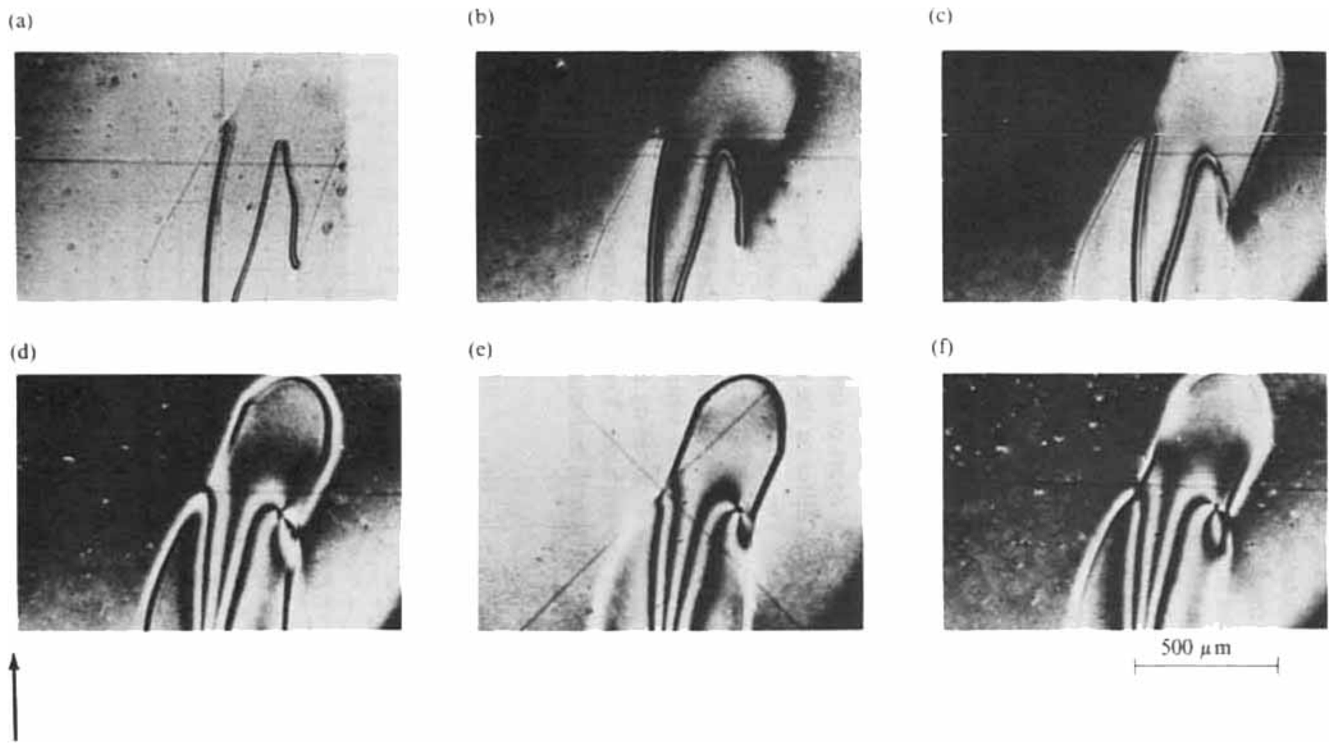

FIGURE 12 Relaxation of thick bridge (with node) in thin loop leading to *Schlieren* texture. Sample thickness = 150 μm. (a) 0 sec., (b) 10 sec., (c) 20 sec. after shear cessation; (a) to (f) *circa* 1 minute after shear cessation. Crossed polars parallel to cross hairs in pictures.

micrographs of a thick line with a node point bridged within a thin loop which relaxes to just such a birefringent pattern.

Any possible model for the molecular arrangement around a thin loop must account for the observation that during relaxation, the loop traps within its boundaries material with an orientation which differs from that outside and which has a component coplanar with the surfaces (which leads to a birefringent texture). Such a structure can be drawn which would be associated with a disclination of strength $\pm \frac{1}{2}$ as presented in Figure 13. Waltermann[17] and Hilltrop and Fischer[13] hint at similar configurations around disclinations formed during Poiseuille flow of homeotropically aligned MBBA. They also believe these disclinations to be of strengths $\pm \frac{1}{2}$.

The two most striking observations of the thick and thin loops concerns their tenacity during flow and their relaxation behaviours. The loops elongate, deform, and tumble in flow, but always remain intact. They do not break apart or split open.

The disclination loops differ in the dynamic, flowing situation from the static, relaxing one. The optical contrasts of the flowing loops are very 'tight' or narrow which suggests that the director distortions around them are severe, and very localised. The loops appear to affect the alignment only of molecules within a small region around them, with the flow alignment dominating elsewhere. A similar situation is believed to occur at the surfaces. The boundary layer, in which the surface alignment is retained, reduces as the shear rate is increased

FIGURE 13 Schematic representation of proposed molecular configuration around a thin loop lying parallel to surfaces with homeotropic surface alignment. (a) and (b) represent orthogonal cross-sections of the loop sliced perpendicular to the surfaces. In section (a) (which is parallel to the prior shear direction) the director lies within the plane of the paper and the disclination loop cores are shown as two heavy dots. In section (b) which is orthogonal to (a) the loop cores are again shown as heavy dots. The lighter dots within the loop correspond to homogeneous alignment within the loop.

until a saturation level is reached where the thickness is of the order 1 μm.[15]

During relaxation, the 'sphere of influence' of the loops increases, and their optical contrasts broaden. In the absence of flow, the distortions in the director field dictated by the defects compete solely with the surface-dictated alignment. Viscous torques are removed, and the system adopts a configuration which minimizes its curvature-elasticity free energy.

The experiments have revealed some interesting behaviour of disclination loops during and after shear in a small molecule nematic. They have not, however, explicitly shown why these loops form in the material during shear, and, therefore, some theoretical considerations of this question would be desirable.

Acknowledgments

We wish to acknowledge and thank Sir Charles Frank for his assistance in constructing the director map of the $\pm \frac{1}{2}$ disclination loop. We also wish to thank Mr. D. Pike for his help in carefully preparing our photographic material.

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References

1. G. Friedel, *Ann. Phys.*, **18**, 273 (1922).
2. S. Chandrasekhar, "*Liquid Crystals*", Cambridge University Press, 1977.
3. P. G. de Gennes, "*The Physics of Liquid Crystals*", Clarendon Press, Oxford, 1974.
4. A. Saupe, *Mol. Cryst. Liq. Cryst.*, **21**, 211 (1973).
5. M. Kléman in "*Advances in Liquid Crystals*", Vol. I (Ed. G. H. Brown) Academic Press, New York, 1975, pp. 267–311.
6. F. C. Frank, *Discuss. Faraday Soc.*, **25**, 19 (1958).
7. C. W. Oseen, *Trans. Faraday Soc.*, **29**, 883 (1933).
8. J. Nehring, *Phys. Rev.*, **A7**, 1737 (1973).
9. R. B. Meyer, *Phil. Mag.*, **27**, 405 (1973).
10. P. E. Cladis and S. Torza, *Phys. Rev. Lett.*, **35**, 1283 (1975).
11. P. E. Cladis and S. Torza, *Conf. Proc.: Colloid Interface Science*, **4**, 487 (1976).
12. J. Wahl and F. Fischer, *Mol. Cryst. Liq. Cryst.*, **22**, 359 (1973).
13. K. Hilltrop and F. Fischer, *Z. Naturf.*, **31a**, 800 (1976).
14. D. J. Graziano, Ph.D. Thesis University of Cambridge, (1983).
15. J. Wahl, *Z. Naturf.*, **34a**, 818 (1979).
16. F. M. Leslie, *Archs Ration. Mech. Analysis*, **28**, 265 (1968).
17. Th. Waltermann, *Phys. Lett.*, **69A**, 208 (1978).