Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Computer Simulation of Liquid Crystalline Anisotropic structures

T. M. Nicholson [a]

[a] Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, U.K.

Version of record first published: 04 Oct 2006.

To cite this article: T. M. Nicholson (1989): Computer Simulation of Liquid Crystalline Anisotropic structures, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 177:1, 163-175

To link to this article: http://dx.doi.org/10.1080/00268948908047780

Mol. Cryst. Liq. Cryst., 1989, Vol. 177, pp. 163–175
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Computer Simulation of Liquid Crystalline Anisotropic structures

T. M. NICHOLSON

Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge CB2 3RA. U.K.

(*Received, April 21, 1989; in final form June 27, 1989*)

This paper describes the development of a computer simulation, based on the aggregate model, which enables the optical birefringent contrast generated by an arbitary, but known, variation in optic axis direction to be predicted. The simulator is applied to the structures surrounding disclinations in small molecule liquid crystals and to the banded textures observed in liquid crystalline polymers (LCPs) after high shear deformations. Extensions to the simulator may provide a model for the optical and rheological behaviour of LCPs under shear deformations.

1. INTRODUCTION

Optical microscopy is a popular tool for investigating anisotropic structures in materials. In particular the birefringent contrast observed when a sample of a crystal or liquid crystal is placed between crossed polarisers may be used to provide information about the orientation of the optic axis in the sample. In a liquid crystal, the optic axis orientation will vary throughout the sample, leading to a variation in the optical contrast observed. This paper describes the development and application of a computer simulation technique which can predict the optical contrast developed by an arbitrary, but known, variation in optic axis throughout the sample. If the molecular director, the preferred orientation of a symmetry axis in the molecules, is related to the optic axis, then a predicted micrograph may be generated from theoretical structures for the material, and compared with experimental micrographs to test the validity of the suggested structures.

2. THE OPTICAL SIMULATOR

The optical behaviour of a sample of liquid crystal placed between crossed polarisers is modelled by dividing the material into an array of cells (Fig. 1). Each cell is assumed to be uniaxially birefringent, with a uniform optic axis direction. This optic axis direction can vary from cell to cell. The method is therefore similar to the aggregate model[1] used to calculate elastic properties of such materials.

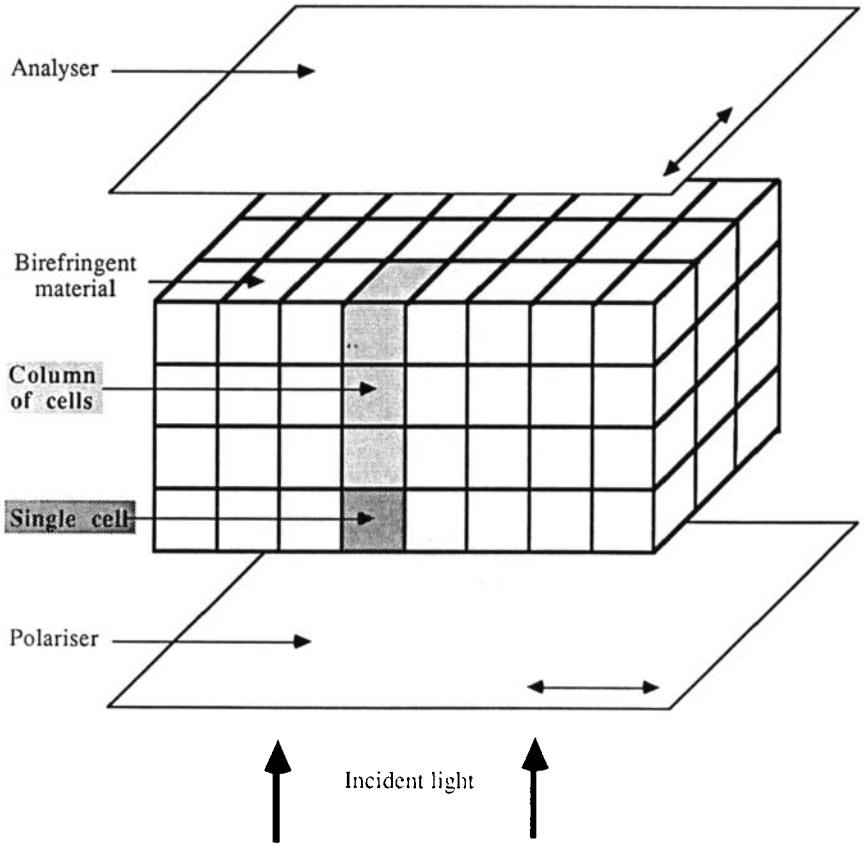

FIGURE 1 Schematic diagram of array of cells placed between crossed polarisers used in the optical simulator. The passage of light through each column of cells is considered in turn.

Assuming first that the optic axis for each cell lies in the plane of the sample, the overall contrast produced by a single column of cells may be calculated. Light incident on the bottom edge of the lowest cell will be plane polarised and may be represented by a complex amplitude

$$A = A_0 e^{i\omega t} \tag{1}$$

Within this first cell, light will be propagated along two mutually orthogonal vibration directions, parallel and perpendicular to the optic axis. The light amplitude along each of these directions will be

$$\begin{aligned} B_1 &= A_0 \cos\theta_1 e^{iwt} \\ C_1 &= A_0 \sin\theta_1 e^{i\omega t} \end{aligned} \tag{2}$$

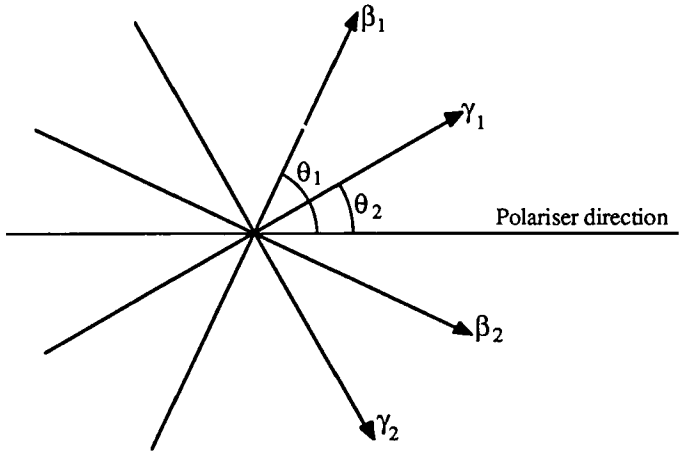

FIGURE 2 Definition of angles required for derivation of equations 2 and 4. β_1 and γ_1 are the vibration directions in the first cell; β_2 and γ_2 are the corresponding directions in the second cell.

where θ_1 is the angle between the polariser and the optic axis in this cell (Fig. 2). Because of the birefringence of the cell, light will propagate with a different refractive index along each vibration direction, and so at the top of this first cell, a phase difference δ will have been introduced, and the complex amplitudes will be

$$\begin{aligned} B_1' &= A_1 \cos\theta_1 e^{i(wt-\delta)} \\ C_1' &= A_0 \sin\theta_1 e^{i\omega t} \end{aligned} \tag{3}$$

In the second cell, the optic axis is at an angle θ_2 to the polariser, so the allowed vibration directions will be different. The complex amplitudes of light along these directions may be found by resolving along the new directions

$$\begin{aligned} B_2 &= B_1' \cos(\theta_2 - \theta_1) - C_1' \sin(\theta_2 - \theta_1) \\ C_2 &= B_1' \sin(\theta_2 - \theta_1) + C_1' \cos(\theta_2 - \theta_1) \end{aligned} \tag{4}$$

Again, during passage through the cell, a phase change will be introduced, and so the emerging complex amplitudes will be

$$\begin{aligned} B_2' &= B_2 e^{-i\delta} \\ C_2' &= C_2 \end{aligned} \tag{5}$$

This process is repeated for all the cells in a column. At the analyser, the final intensity is calculated by resolving along the direction of the analyser (which is perpendicular to the polariser) and is given by $\langle A_r A_r^* \rangle$ where

$$A_r = B_n' \sin\theta_n - C_n' \cos\theta_n \tag{6}$$

B'_n and C'_n are the final emerging complex amplitudes and θ_n the angle between the optic axis in the final layer and the polariser.

The phase change δ is related to the wavelength of the light λ, the birefringence $(n_e - n_o)$ and the thickness of a cell t by the expression

$$\delta = \frac{2\pi}{\lambda}(n_e - n_o)t \tag{7}$$

In the current simulation, monochromatic light is assumed and δ chosen so that the total phase change over all cells in a column is fixed at an arbitrary value $(\pi/2)$.

This can be repeated for each column of cells and hence a simulated optical micrograph generated.

For a general case, where the optic axis is not parallel to the plane of the sample, two effects have to be considered. Firstly light no longer propagates through the cells perpendicular to the sample plane for one of the vibration directions (the extraordinary wave). This leads to differences in the path length and hence the phase for this light wave. However, for typical values of the birefringence, this effect may be neglected.

As the optic axis moves out of the plane of the sample, the birefringence will change, and hence the phase change introduced between the two components of light being propagated through a cell will vary. The phase change in one cell will be given by

$$\delta = \delta_0 \cos^2 \phi \tag{8}$$

where δ_0 is the phase change for an in-plane optic axis and ϕ is the angle that the optic axis makes with the plane normal to the direction of light propagation ($\phi = 0$ in the 2-D case).

Thus the optical contrast for any arbitrary variation in optic axis may be calculated, given an expression relating the variation in optic axis orientation with position. In most of the simulations shown in this paper a grid size of $70 \times 50 \times 25$ was used.

3. DISCLINATIONS IN SMALL MOLECULE LIQUID CRYSTALS

A simple structure to which to apply the optical simulator is the molecular director around disclinations in small molecule liquid crystals (SMLCs). Assuming that the optic axis follows the director for these materials, and that the elastic constants (k_{11}, k_{22}, k_{33}) are equal, then the optic axis variation in the sample plane is as described by Frank[2] and given by the expression

$$\theta = s\alpha + c \tag{9}$$

where θ is the optic axis orientation at all points along a line from the centre of

the disclination at an angle α from a reference direction, s is the strength of the disclination, which is restricted to integer and half-integer values, and c is a constant.

Examples of simulator output for these structures are illustrated in Fig. 3 where the expected dark brushes are seen around the disclinations. The optic axis variations generated by equation 9 are shown together with the simulator results. A comparison of Fig. 3b ($s = 1$, $c = 0$) and 3c ($s = 1$, $c = \pi/2$) shows that there is a 90° uncertainty in the optic axis direction for a given resultant contrast level; these two differing structures lead to the same optical intensity variation.

In the case where $s = \pm 1$, Meyer[3] argued that a lower energy structure exists if the director is allowed to 'escape' into the third dimension, and derived an

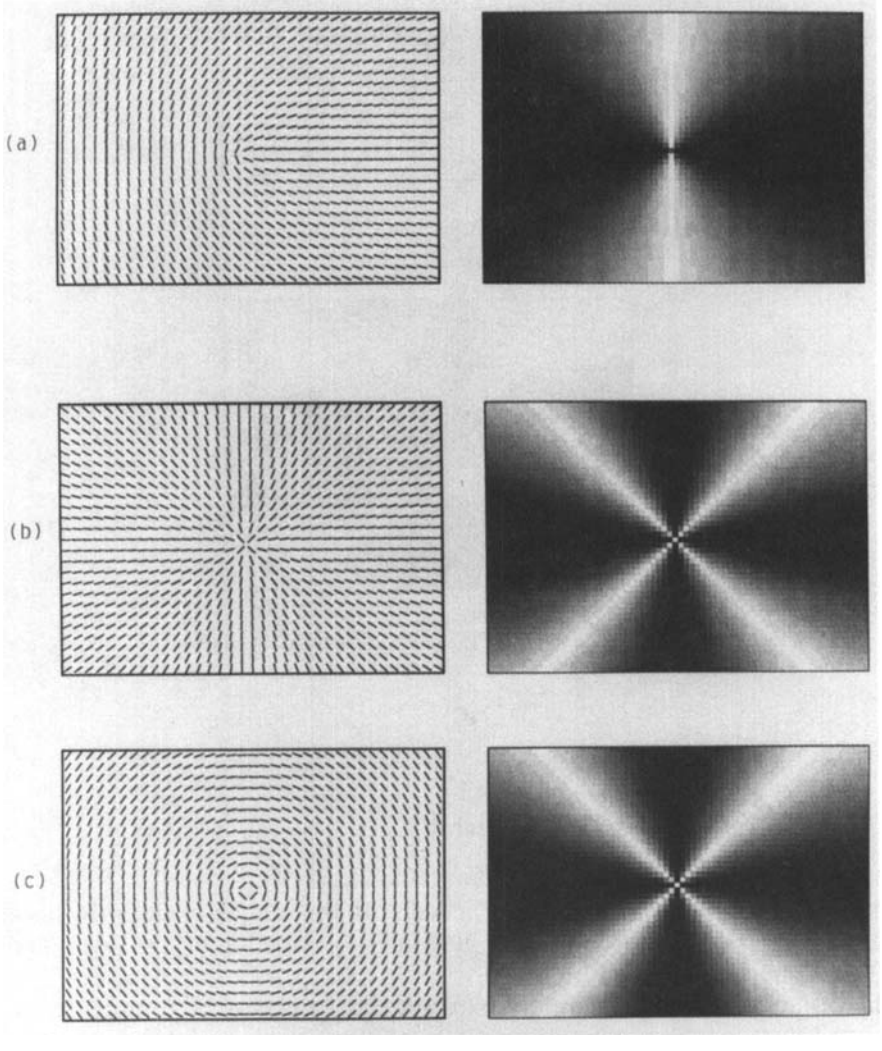

FIGURE 3 Optic axis direction maps and optical simulator output for simple disclinations: (*a*) $s = \frac{1}{2}$, $c = 0$; (*b*) $s = 1$, $c = 0$; (*c*) $s = 1$, $c = \pi/2$.

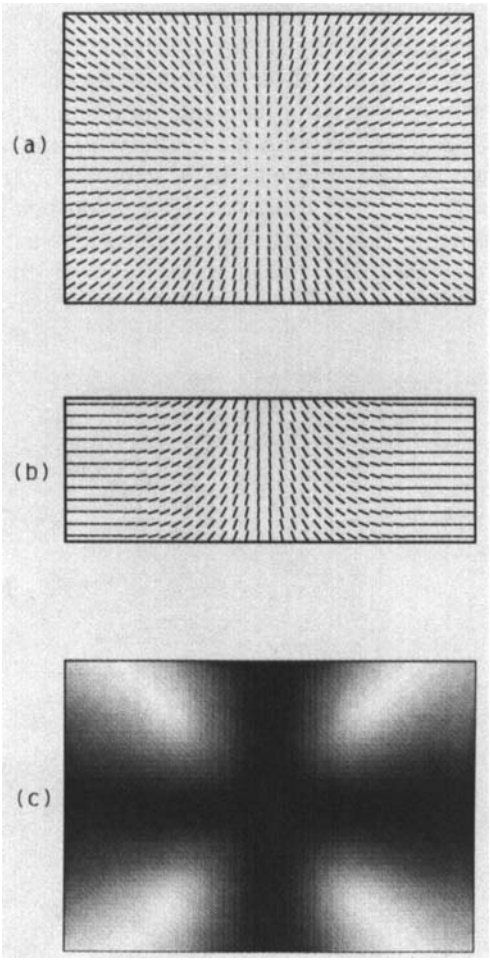

FIGURE 4 'Escaped' $s = 1$ disclination. (*a*) Plan view of optic axis variations; (*b*) side elevation of optic axis variations; (*c*) simulator output.

expression for this

$$\phi = 2 \tan\left(\frac{r_0}{r}\right) - \frac{\pi}{2} \tag{10}$$

where ϕ is the angle that the director makes with the sample plane, r the distance from the core and r_0 a constant. Fig. 4 illustrates this case for an $s = 1$ disclination, and should be compared with Fig. 3b.

The case when the elastic constants are not equal may also be considered. When $s \neq 1$ these structures may be described by the equations of Nehring and Saupe[4]. For a SMLC, a typical value of this non-uniformity is $k_{33}/k_{11} = 2.3$ (*p*-azoxyanisole[5]). This has a large effect on the behaviour of the dark bands surrounding an $s = \frac{1}{2}$

disclination, as may be seen in Fig. 5 where simulated micrographs are presented for four different polariser angles for the cases $k_{33}/k_{11} = 1$ and $k_{33}/k_{11} = 2.3$. A similar, but smaller effect is observed for $s = -\frac{1}{2}$ and $s = -1$ disclinations.

By way of a comparison between experimental and theoretical optical contrast variations, Fig. 6 shows both actual micrographs and simulator output for a group

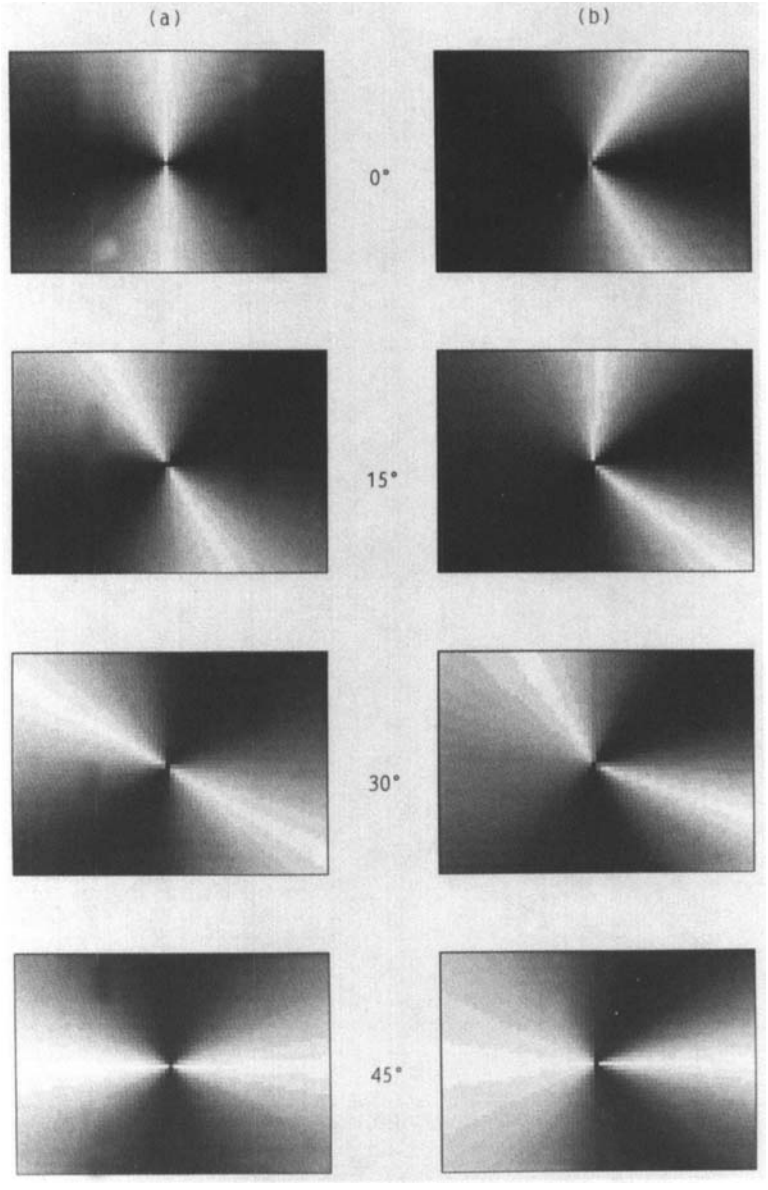

FIGURE 5 Simulator output for $s = \frac{1}{2}$ disclinations. (*a*) Equal elastic coefficients ($k_{33}/k_{11} = 1$). (*b*) Unequal elastic coefficients ($k_{33}/k_{11} = 2.3$).

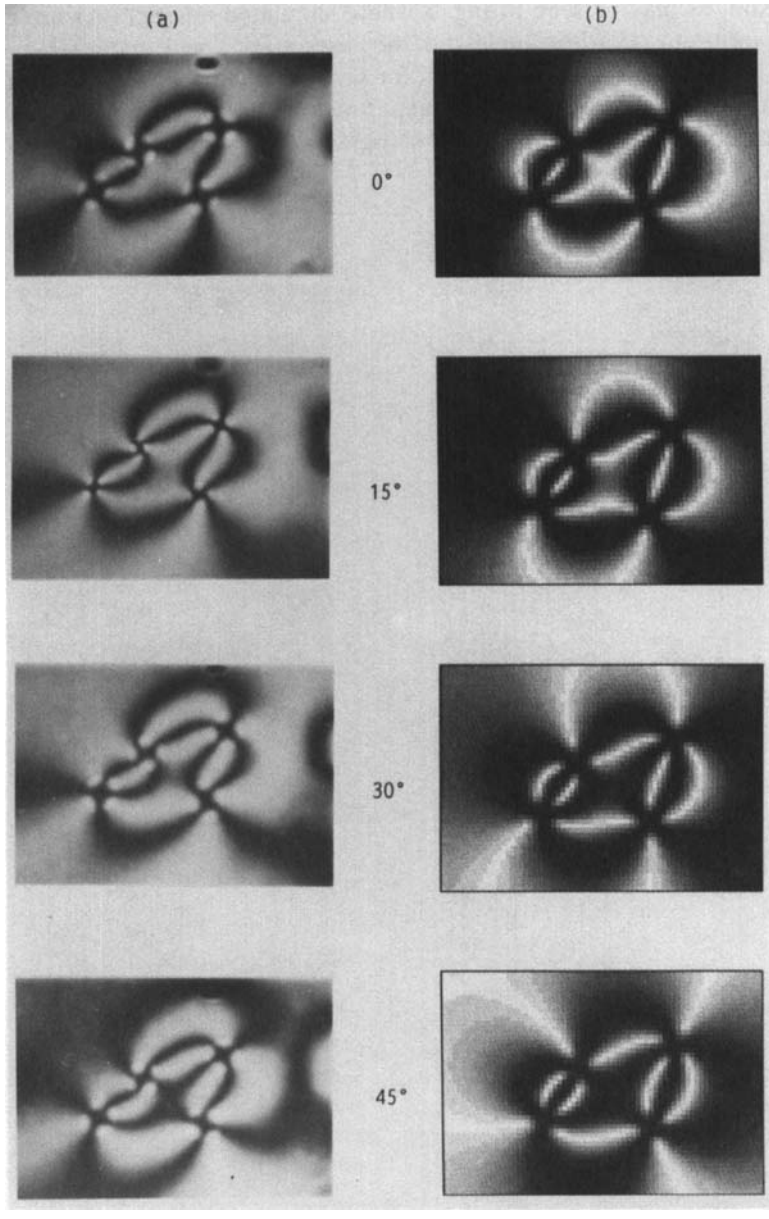

FIGURE 6 (*a*) Optical micrographs of a group of four disclinations in MBBA. (*b*) Corresponding simulator output. The angles indicate the polariser orientation measured in an anticlockwise direction from horizontal.

of four disclinations observed for MBBA. It can be seen that there is good agreement between the two patterns within the area bounded by the disclinations. Outside this area the theoretical micrographs differ from the experimental ones. This may be explained by the presence of more distant disclinations and global orientation variations in the real structure which are not considered in the simulation.

Two other striking differences can be observed between the actual and simulated micrographs. In the simulator output, distinct white bands are observed which are not so obvious in the experimental micrographs. These are an artefact caused by the limited number of grey levels used by the laserprinter in generating the simulator output. The experimental micrographs show light circular regions surrounding each disclination; these are not reproduced on the simulator output. These could possibly be caused by out of plane components of the optic axis allowing lower order birefringent colours to be seen. The simulator allows only a single order of birefringence and only considers monochromatic light.

Given the general agreement between the experimental and simulated micrographs, it appears that the assumption made above of a correlation between the optic axis and the director holds well in this case.

4. BANDED STRUCTURES IN LIQUID CRYSTAL POLYMERS

Banded textures have been observed in many LCP systems which have undergone high shear deformations.[6,7,8] These bands appear, when the sheared polymer is observed between crossed polarisers, perpendicular to the prior shear direction. Many structures have been suggested for such banded textures. For Kevlar, a pleated structure has been proposed[6] where molecules align alternatively at $\pm$ 5° to the draw direction. For a thermotropic LCP, known as BN[8], a sinusoidal structure has been suggested from optical evidence.

The optical simulator provides a tool by which such suggested structures may be investigated. An example is shown in Fig. 7 where micrographs of banded structures in polymer BN are compared with two proposed structures. In the first, the optic axis remains in the plane of the sample and varies such that the angle between the shear direction and the optic axis (the deviation angle) follows a sinusoidal variation.

$$\theta = b \sin x \tag{11}$$

where x is the position along the shear direction and b the maximum deviation angle. This maximum devation angle may be found by plotting the positions of the extinction bands (which indicate where the optic axis is parallel to either the polariser or the analyser) as a function of polariser angle; in the micrographs shown this was found to be 23°.

In the second proposed structure the optic axis is no longer confined to the plane of the sample, but varies in the third dimension with the same sinusoidal behaviour, thus giving a helical structure.

In the micrographs (Fig. 7a), a regular pattern of light and dark bands is observed at 0°. By 15°, as a consequence of pairs of dark bands moving towards each other[8],

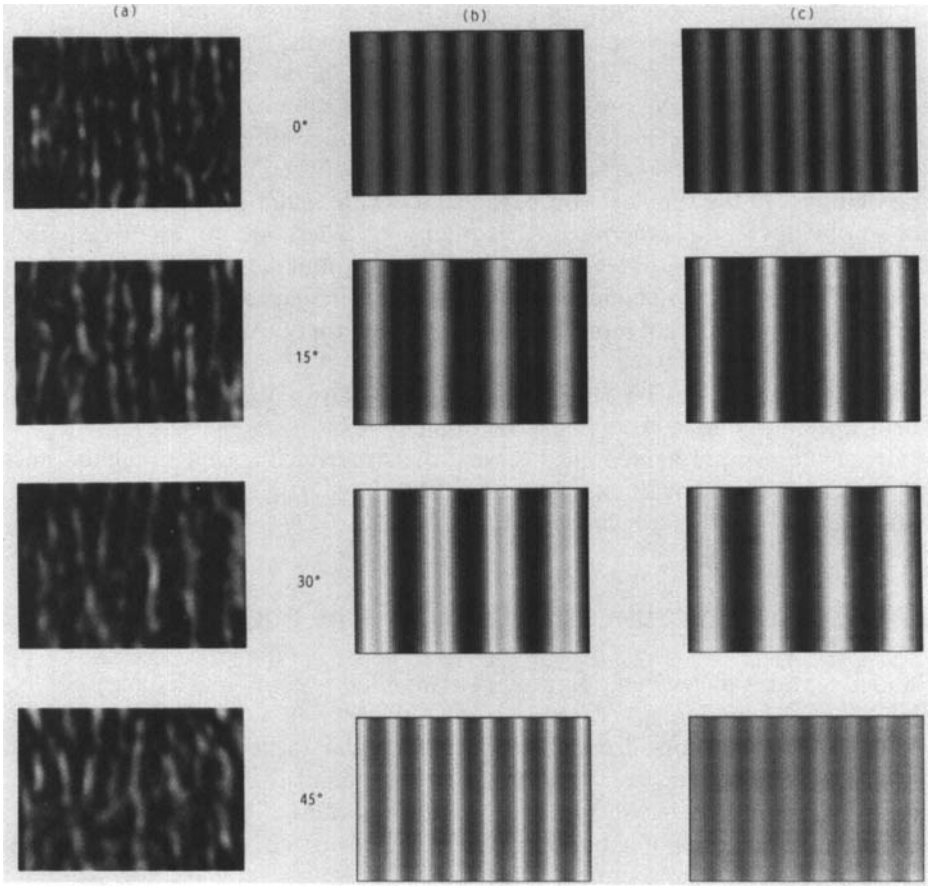

FIGURE 7 (*a*) Optical micrographs of the banded texture in liquid crystal polymer BN. (*b*) Simulator output for a sinusoidal optic axis variation. (*c*) Simulator output for a helical optic axis variation. The angles indicate the polariser orientation measured in an anticlockwise direction from horizontal.

every alternate light band has become much lighter, while at 30° pairs of dark bands have totally merged and bright and dark bands alternate with a period of twice that at 0°. At 45° the overall contrast range is much reduced and there is some sign of a recovery of the original periodicity.

The sinusoidal structure (Fig. 7b) correctly reproduces the intensity variations at 0° and 15°, but by 30° it shows the start of the development of new darker bands in the middle of the light bands, for which there is no evidence in the optical micrograph. In addition, at 45° the contrast range is similar to that at 0°.

The helical structure (Fig. 7c) models the optical micrographs more accurately, with no sign of new dark bands emerging at 30°, and a much reduced contrast range at 45°. Thus the use of the optical Simulator provides further evidence of out of plane components of the optic axis in the banded structure, as has been suggested by previous experiments[9].

Electron microscopy, which provides more direct information about variations in the orientation of the molecular director, suggests[9] that the behaviour of the molecular director and the optic axis differ. Thus in this case the assumption of a correlation between optic axis and molecular director does not hold, and the simulator only gives information about optic axis variations.

5. THE RELAXATION BEHAVIOUR OF LCPs

A similar computer simulation, based on the aggregate model, is being developed to model the change in orientation parameter and elastic modulus in LCP systems subjected to shear or draw deformations.[10,11] Each cell in the simulation is assumed to be uniformly oriented with elastic properties equal to that of fully aligned anisotropic polymer. Initially these cells are assigned random orientations which are then affected by the applied deformation process. At any stage in the simulation, the global orientation function or the elastic modulus may be calculated by an averaging process, or the optical contrast calculated by use of the optical simulator.

Good correlation between experiment and model have been obtained for the variation of orientation function during draw of polymer BN[11] and also ultra-high molecular weight polythene.[10]

In the case of shear deformation, optical observations[12] suggest that the presence of defects has an important effect on the structures observed. Disclinations present in unsheared samples appear to multiply under large shear deformations, with an apparently uniformly birefringent structure being formed at very high shears. Upon relaxation the banded structure is sometimes observed after the cessation of high shears. Rheological oscillatory experiments[11] show a difference in the behaviour of an LCP under low and high shear deformations. At low strains the material is linearly viscoelastic, while at higher strains (above about 10%) the storage and loss moduli (G' and G'') fall sharply with increasing strain.

In order to model this behaviour, defects have been introduced into the simulation in the form of cells in the array which are set to random invarient orientations. These 'nuclei' are allowed to migrate through the array of cells, affecting the orientation of cells through which they pass, thus providing a mechanism for the disruption of liquid crystalline order. Without such a process there would be no mechanism for the relaxation of a fully aligned liquid crystal order, since this is the lowest free energy configuration for such a material.

Fig. 8 illustrates the effect of these nuclei during the relaxation of a fully aligned array of cells in terms of director orientation maps an optical simulations. At present the model is unable to predict the development of banded structures and work is in progress to enable the calculation of the rheological behaviour of such systems.

Acknowledgments

I would like to thank Drs. M. R. Mackley and A. M. Donald for all their advice throughout the progress of this work, and the S.E.R.C. for funding through a research studentship.

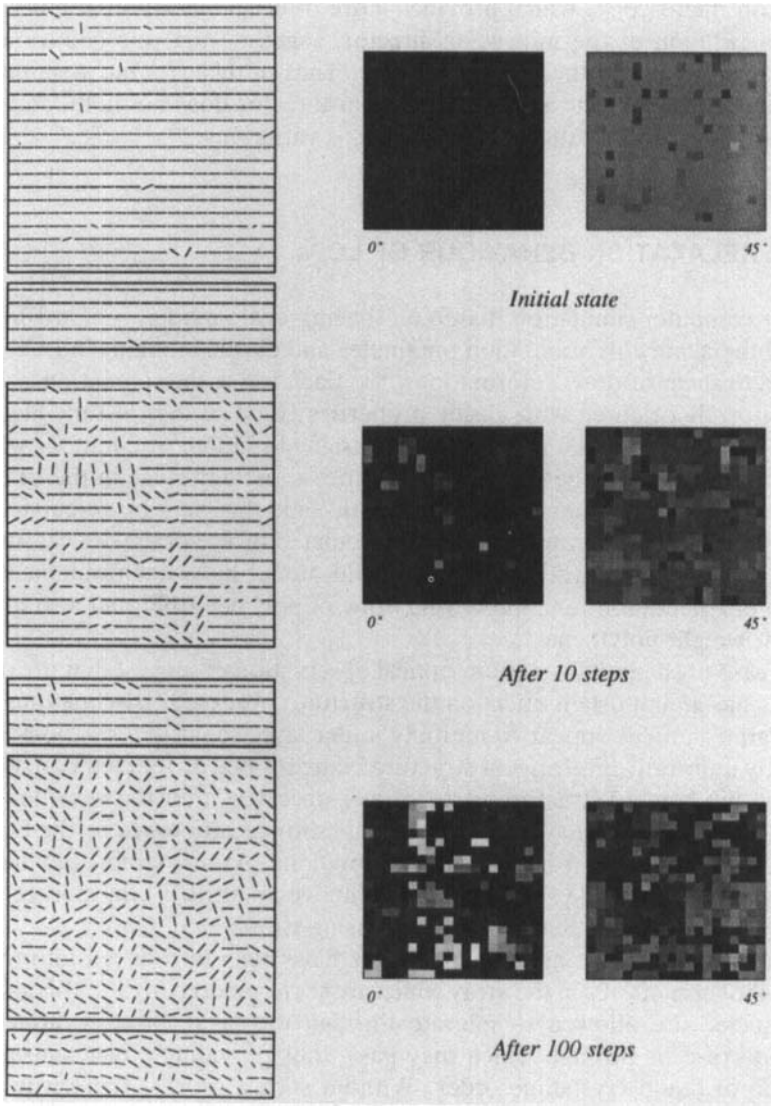

FIGURE 8 Optic axis direction maps (plan view and side elevation) and optical simulator output (for two polariser orientations) showing the relaxation of a fully oriented structure due to the introduction of 'nuclei'.

References

1. I. M. Ward "*Mechanical Properties of Solid Polymers*," (John Wiley and Sons, Chichester, 1971).
2. F. C. Frank, *Discuss. Faraday Soc.*, **25**, (1958).
3. R. B. Meyer, *Phil. Mag.*, **27**, 405 (1973).
4. J. Nehring and A. Saupe, *J. Chem. Soc. Faraday Trans. II*, **68**, 1 (1972).
5. A. Saupe, *Z. Naturforsch*, **15a**, 815 (1960).
6. S. C. Simmens and J. W. S. Hearle, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 871 (1980).

7. D. Graziano and M. R. Mackley, *Mol. Cryst. Liq. Cryst.*, **106**, 73(1984).
8. C. Viney, A. M. Donald and A. H. Windle, *J. Mat. Sci.*, **18**, 1136 (1983).
9. C. Viney, A. M. Donald and A. H. Windle, *Polymer*, **26**, 870 (1985).
10. P. Gao, M. R. Mackley and T. M. Nicholson, *Polymer* in press.
11. T. M. Nicholson, *Ph.D. Thesis*, University of Cambridge (1988).
12. N. J. Alderman and M. R. Mackley, *Faraday Discuss. Chem. Soc.*, **79**, Paper 12 (1985).