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WAXS studies of global molecular orientation induced in nematic liquid crystals by simple shear flow

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Global molecular orientation function coefficients for the nematic liquid crystal 4-cyano-4′-*n*-pentylbiphenyl (5CB) in shear flow are presented, being extracted from 2-dimensional Wide-Angle X-ray Scattering data. A linear increase in orientation parameter $\langle P_2 \rangle$ is observed with a logarithmic increase in shear rate. It is proposed that this arises from an increased number of LC directors aligning to the shear axis. Upon cessation of shear flow, the anisotropy is seen to relax away completely, over a time scale which is inversely proportional to the previously applied shear rate.

1. Introduction

Macroscopic alignment of nematic liquid crystals occurs under the influence of both a substrate and an external magnetic field [1, 2]. Pieranski and Guyon established that shear flow is able to create instabilities within the director field [3, 4]. Two types of instability are identified: a homogenous form which produces a uniform distortion in the shearing plane, and the formation of roll cells, where a director initially in the shearing plane becomes unstable to rotations out of that plane. This latter defines the regime of director tumbling, which occurs when the ratio of the second and third Leslie coefficients, α_2/α_3, is negative [5].

Molecular theory indicates that this ratio will be negative for nematics consisting of rigid rod molecules [6, 7]; nevertheless for 4-cyano-4′-*n*-pentylbiphenyl, referred to here as 5CB, $\alpha_2 = -83 \times 10^{-}3\,\mathrm{Pa\,s}^{-1}$ and $\alpha_3 = -2 \times 10^{-3}\,\mathrm{Pa\,s}^{-1}$, indicating that this is a flow aligning material [8]. It is further notable that this characteristic is a material property, and is not influenced by the introduction of a flow field. The flow aligning nature of 5CB has been confirmed experimentally by Müller *et al.* who monitored the aspect of director orientation in shear flow using polarized light, and observed that the director adopted a stable angle of tilt in the plane of the shear gradient [9]. In addition, Mather *et al.* have reported measurements of disclination densities in the shear flow of 5CB, which led them to hypothesize that disclinations are nucleated during shearing from boundary layers between domains [10].

This work presents an original description, via global molecular orientation parameters extracted from 2-dimensional WAXS data, of the degree of molecular orientation which is adopted in a low molecular mass liquid crystal (LMMLC) system in shear flow, as a function of the rate of applied shear. Time resolving measurements performed at a synchrotron X-ray source also provide a characterization of the relaxation of the induced orientation. This study of shear-induced global orientation in a low molecular mass liquid crystal system is performed as part of a larger programme: by comparison of these data with the effects observed in linear polymer systems [11, 12] it is hoped to gain a greater understanding of the often complicated responses of liquid crystal polymer (LCP) systems to shear deformation [13, 14].

2. Materials

5CB is a commercially available biphenyl liquid crystal, commonly used in watch and calculator displays, and is supplied by Merck Ltd, U.K. (formerly BDH Ltd). Its systematic name is 4-cyano-4′-*n*-pentylbiphenyl and it exhibits a nematic LC phase over a small temperature range between 24 and 35·3°C [15]. It exhibits a low dynamic viscosity at room temperature, comparable to that of water, and was studied in a specially designed low viscosity shearing rheometer, which is described in the following section.

3. Rheometer

The shearing rheometer in which all measurements were made comprises two circular, parallel aluminium plates mounted in a T plate frame. The two plates are bolted to the upright face of the rheometer support, and

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good concentricity is maintained by two supporting brackets mounted on the opposing side. The driveshaft is constructed as a separate unit which connects to the rotating plate by means of locating pins on the spindle of the plate. Entrance and exit apertures for the X-rays and their respective windows consist of 25 μm thick Kapton windows fitted in recesses over milled slots and apertures in the rheometer plates. Figure 1 presents scaled drawings of the rheometer driveshaft and rheometer plates. The driveshaft is shown in half scale relative to that of the plates; the fixed plate is shown as a cross-sectioned plan, with some hidden detail omitted for clarity.

The low viscosity material is maintained between the plates by a series of three seals. The first seal is a PTFE spacer seal set in a groove in the fixed plate. The fixed

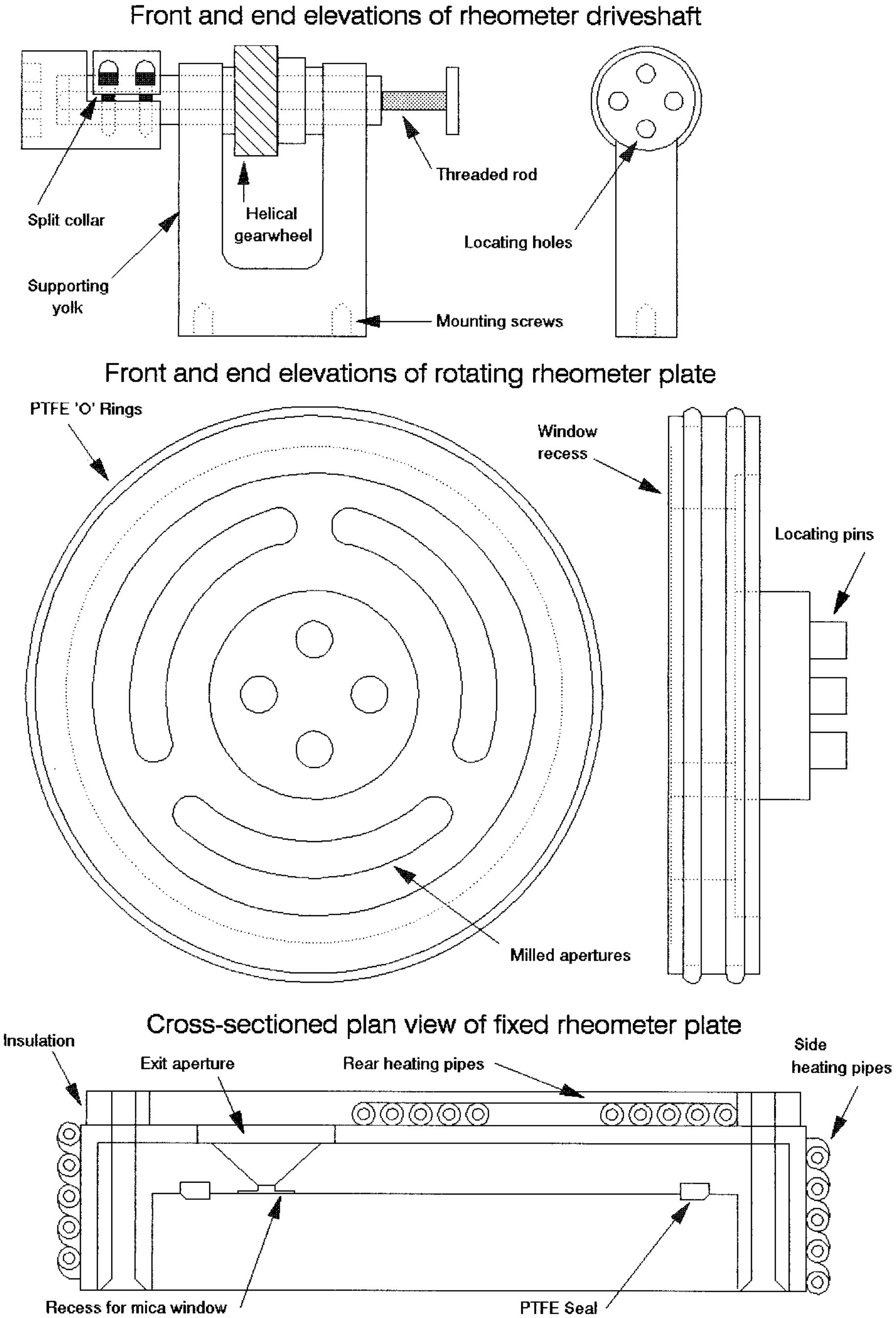
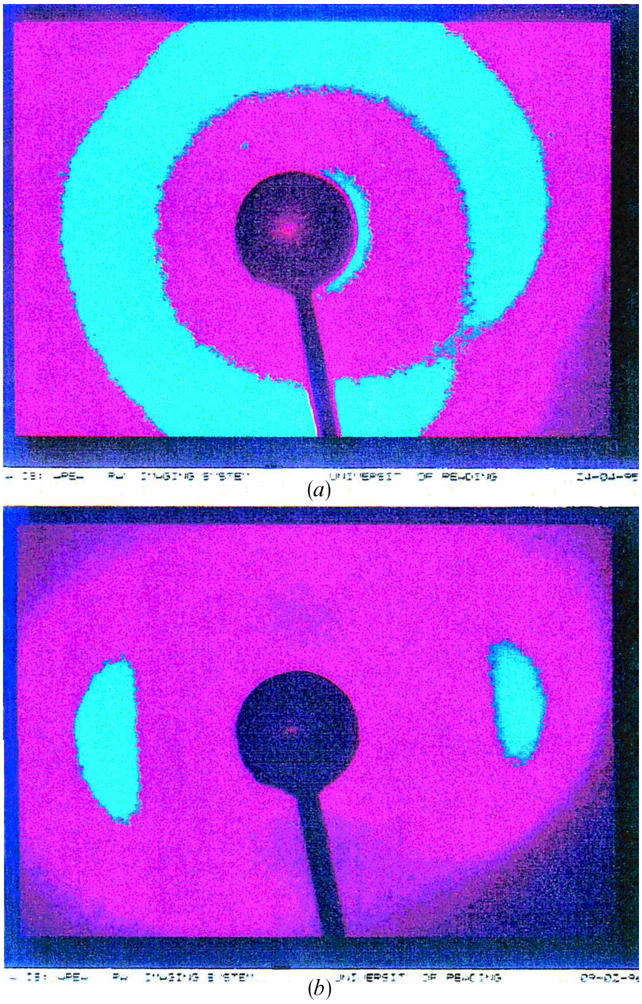


Figure 1. Driveshaft, rotating plate and fixed plate components of the AXIS low viscosity shearing rheometer. The driveshaft is shown in half scale relative to the plates.



(*a*)

(*b*)

Figure 2. WAXS diffraction patterns of a 0·5 mm thick nematic LC 5CB sample at rest (above), and subjected to a simple shear rate of $\gamma = 510\,\mathrm{s}^{-1}$ (below).

plate has edges which enclose the rotating plate, and between these two surfaces are located two standard size (BS241) PTFE 'O' rings, mounted in circumferential grooves in the rotating plate. Together these three seals provide a suitably complex overall seal to maintain water in the rheometer for over four hours before significant leakage begins. Temperature control for the rheometer is effected with a circulating heater bath, allowing temperatures between 20 and 65°C to be reached, controlled to within ±2°C at the X-ray port.

The sample was transferred onto the surface of the fixed plate of the shearing cell using a syringe. When the sample area (which is defined by the limiting PTFE spacer seal) was filled, the rotating plate was lowered into place above it. Vacuum grease was spread around the junction of the two plates to improve the overall seal, and then the two plates were loaded together into the main rheometer framework.

4. X-ray measurements

All measurements presented here were performed on beam-line 16.1 at the Synchrotron Radiation Source at Daresbury, U.K., using a beam of wavelength $\lambda = 1{\cdot}41$ Å, and diameter $\varnothing \sim 0{\cdot}4$ mm. X-ray scattering data were collected using the Area X-ray Imaging System (AXIS) developed at the University of Reading [16]. AXIS collects a 2-dimensional X-ray diffraction pattern in 40 ms using a 50 mm diameter area X-ray camera based on an intensified CCD architecture, designed and manufactured by Photonic Science. AXIS co-adds a number of incoming frames to provide a more intense image with reduced statistical fluctuations, using an integrated image processor manufactured by Data Translation. Integration times for the diffraction patterns were 10 s, (250 frames). The high degree of co-ordination within the AXIS system permits the user to ascribe accurately a given diffraction pattern with the point in time at which shearing commences or ceases.

Degrees of orientation are quantified from the WAXS data using global molecular orientation function coefficients extracted from the relative changes in the scattering intensity throughout a range of azimuthal angles for a fixed scattering vector; the procedure uses methods described previously [17]. These measures of orientation are coupled with the employment of a global director, which describes the dominant direction of ordering of a large number of smaller domains. Within each domain the orientation is described by a local order parameter, whose magnitude is dependent on temperature, as described by the theory of Maier and Saupe [18]. The global orientation parameters presented here, $\langle P_2(\cos\alpha)\rangle_{\mathrm{G}}$, are therefore given by the product of the local order parameter, $\langle P_2(\cos\alpha)\rangle_{\mathrm{L}}$ and the distribution of the directors, $\langle P_2(\cos\alpha)\rangle_{\mathrm{D}}$ [19]:

$$\langle P_2(\cos\alpha)\rangle_{\mathrm{G}} = \langle P_2(\cos\alpha)\rangle_{\mathrm{L}} \times \langle P_2(\cos\alpha)\rangle_{\mathrm{D}}. \quad (1)$$

Thus the macroscopic average of many domains within a nematic LMMLC may realize any orientation value between zero and the value of the nematic order parameter.

5. Steady state shearing of nematic 5CB

The WAXS diffraction pattern of the cyanobiphenyl evidences a single broad halo of intensity, with a maximum value at a reciprocal space vector of $1{\cdot}3\,\text{Å}^{-1}$ (figure 2). This peak arises from intermolecular scattering, and is hereafter referred to as the intermolecular peak. During shearing, the pattern evidences two symmetrical lobes of intensity with maxima on the equatorial. The figure indicates that the LC directors are becoming aligned in the (approximately) vertical direction, parallel to the shear direction.

Figure 3 indicates the degrees of shear-induced

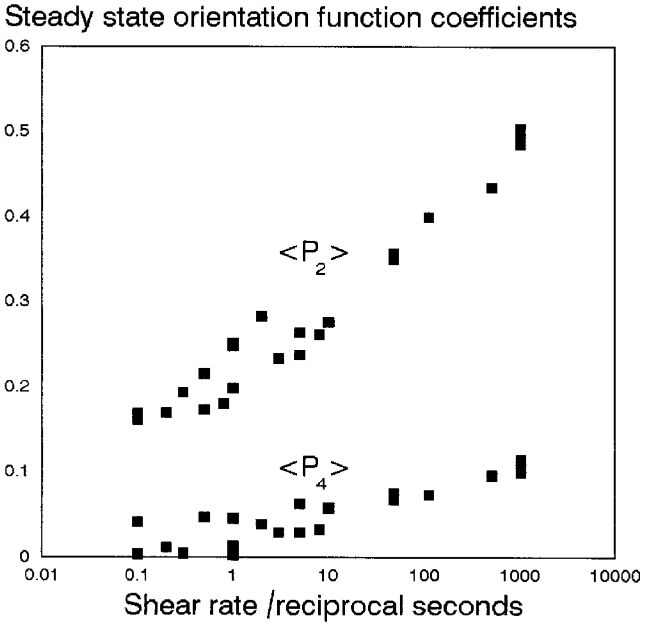


Figure 3. Orientation function coefficients $\langle P_2 \rangle$ and $\langle P_4 \rangle$ adopted in a nematic LC 5CB sample at 25°C subjected to simple shear flow, as a function of the rate of applied shear. The degree of uncertainty associated with each measurement is $\pm 0{\cdot}002$.

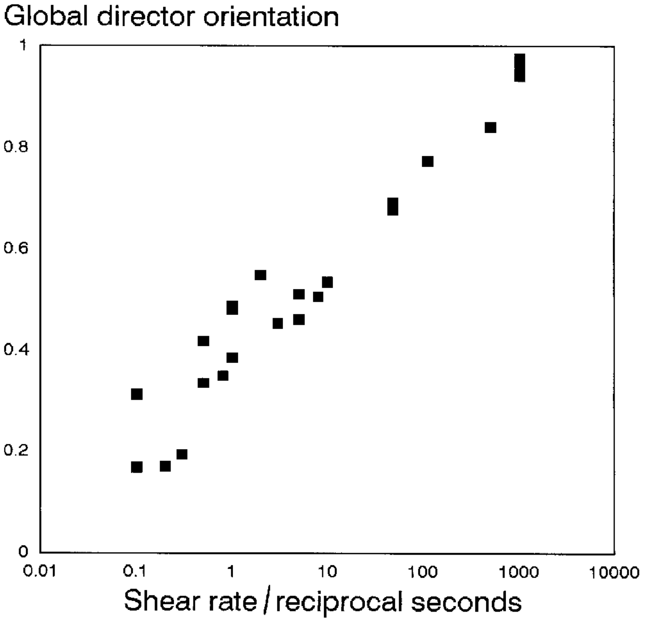


Figure 4. Global director orientation $\langle P_2 \rangle_D$ adopted in nematic 5CB subjected to simple shear at a reduced temperature of $T = 0{\cdot}97T_{NI}$. The degree of uncertainty associated with each measurement in $\pm 0{\cdot}05$, arising from the calculation of the associated nematic order parameter: $S = 0{\cdot}52 \pm 0{\cdot}05$.

orientation in steady state shearing of 0·5 mm samples of 5CB at 25°C ($0{\cdot}97T_{NI}$). Each of the data points is a mean value obtained from averaging many measurements made in steady state shear. For all shear rates investigated, $0{\cdot}1\ \mathrm{s}^{-1} < \gamma < 1020\ \mathrm{s}^{-1}$, the sample achieves its steady state orientation value rapidly: within a single integration period of 10 s. The position of the intermolecular peak did not change during shear, indicating that there was no shear-induced alteration of the packing density of the LC molecules. The development of global orientation within the nematic increases linearly with a logarithmic increase in shear rate, and no limiting plateau level of orientation is reached within the shear rate range investigated.

Maier–Saupe theory predicts an order parameter $S = 0{\cdot}52$ at this reduced temperature [18], a prediction which has been experimentally corroborated for 5CB to an accuracy of $S = 0{\cdot}52 \pm 0{\cdot}05$ [8, 18]. This allows the director orientation to be calculated from equation (1) (figure 4), and reveals that the LC molecules are close to fully aligned under the shear flow of $\gamma = 1020\ \mathrm{s}^{-1}$: $\langle P_2 \rangle_D = 0{\cdot}96 \pm 0{\cdot}05$. Thus the gradual development of the orientation with increasing shear rate is understood in terms of the increasing stress aligning more of the LC directors towards the direction of shear.

The aspect of the global director during shear is noted to be tilted from the shear direction. The magnitudes of the tilt as a function of the rate of applied shear are given in figure 5. It should be noted that the degree of uncertainty in this global director aspect measurement is itself a function of the degree of orientation. For global

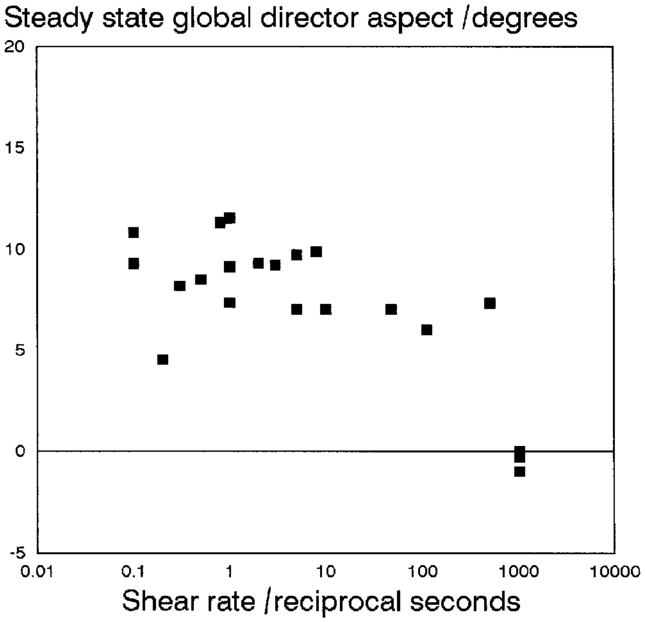


Figure 5. Angle between the global director and the shear direction in 5CB in shear flow, as a function of the applied shear rate. The associated degree of uncertainty is discussed in the text.

orientation parameters $\langle P_2 \rangle > 0{\cdot}2$ the uncertainty in the axis measurement is small: ±2°; but as the global orientation decreases, it becomes more difficult to assert the aspect of the global director. Clearly in the limiting case, for an isotropic distribution of scattering units, the uncertainty in establishing the axis of orientation becomes ±90°, as the global director is equally well defined at all angles.

The magnitude of this deviation angle, typically ~8°, is of similar order to the anticipated magnitude of the Leslie tilt angle, which occurs in the plane of the shear gradient. Heynderickx *et al.* simulate a maximum tilt of 9° in the shear flow of nematic MBBA at 32·5°C [20], although it is noted that this study was simulated for a reduced temperature of $0{\cdot}75T_{\mathrm{NI}}$, whereas these studies are conducted at reduced temperatures of $T > 0{\cdot}9T_{\mathrm{NI}}$.

A fluid mixture of cyanobiphenyls which exhibits a nematic phase between 6 and 100°C was employed to investigate the temperature dependence of the shear-induced orientation effects outlined above. It was found that the effect of increased temperature resulted in lower global orientation parameters for a given shear rate, throughout the entire shear rate range investigated here. This reduced orientation was not fully accounted for by the reduction in the nematic order parameter which is anticipated at elevated temperature [18].

6. Relaxation effects

Time resolving relaxation spectra were obtained for the 5CB LMMLC system by continuing to monitor the X-ray diffraction data *in situ* after shearing had ceased. The synchrotron X-ray source provides suitably high fluxes to achieve a temporal resolution of 10 s. Two examples of the orientation function coefficients measured for 5CB during relaxation from prior shear rates of $\gamma = 1\ \mathrm{s}^{-1}$ and $1020\ \mathrm{s}^{-1}$ are given in figure 6. The axes of the directors in the shear plane are not observed to change during relaxation of the 5CB sample, but remain at the last shear-induced value. The relaxation is such that the degree of orientation always recovers the initial measure before shearing began. Fluctuations are noted to exist in the relaxation curves, and they tend to be more prominent in the relaxations subsequent to prior shear rates of lower magnitudes, such as the example given (figure 6).

By measuring the time taken for the orientation parameter to fall from the steady state shear value $\langle P_2 \rangle$s to $\langle P_2 \rangle$s/e, a relaxation constant can be quantified for each relaxation experiment. The results of these calculated relaxation constants as a function of prior shear rate are shown in figure 7. It can be seen that there is a linear decrease in the relaxation constant associated with a logarithmic increase in the shear rate from which the sample relaxes.

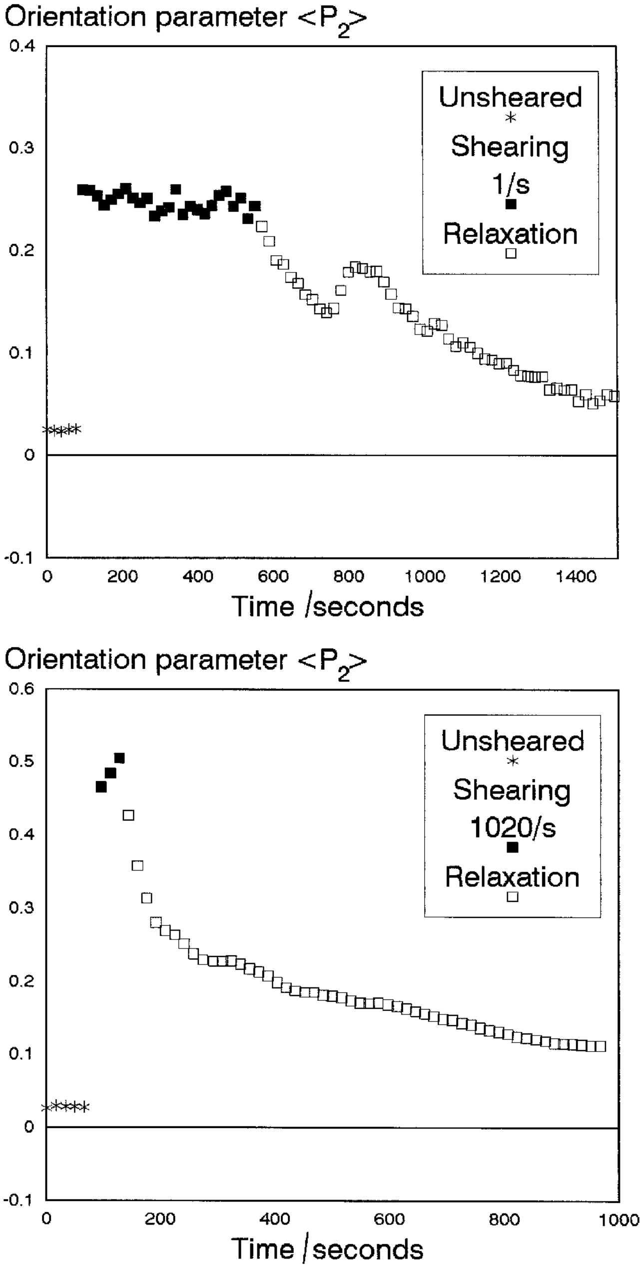


Figure 6. Evolution of the global orientation parameter $\langle P_2 \rangle$ as a function of time, in an unsheared state (*), during the application of simple shear (■), and during relaxation upon cessation of flow (□); for shear rates $\gamma = 1\ \mathrm{s}^{-1}$ (left) and $\gamma = 1020\ \mathrm{s}^{-1}$ (right). The degree of uncertainty associated with each measurement is ±0·002.

Flory shows that the alignment of LC directors is energetically favourable, and thus by this argument alone no relaxation of global orientation is anticipated [21]. This argument is valid for monodomain systems, and thus the observation of the relaxation phenomena suggests that the LMMLC system may well exhibit an increasingly polydomain texture under shear, with the

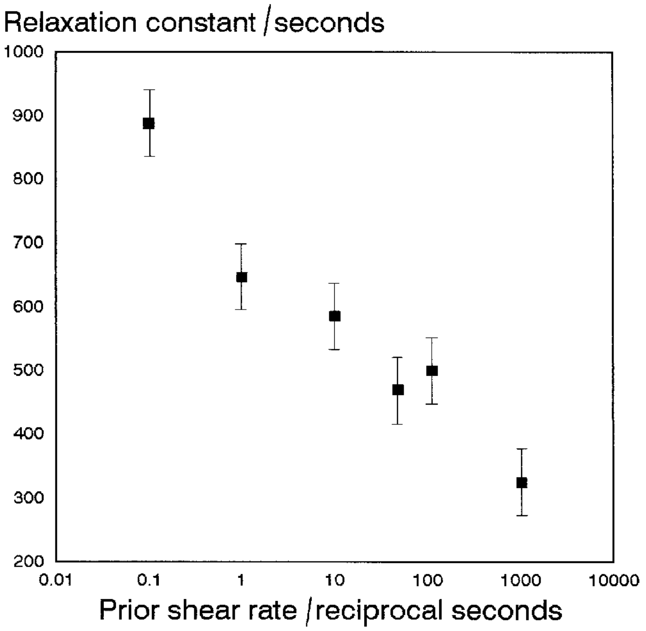


Figure 7. Relaxation constants shown as a function of the previously applied shear rate for the nematic low molecular mass liquid crystal 5CB.

defect structures acting as the source of the relaxation phenomena.

Contributions to the relaxation trend from the elasticity of the anchoring of directors to the surface are hoped to be small, by reason of the choice of Kapton for the window material. Minimization of this effect also facilitates comparison of these systems with their polymeric LC counterparts, whose relaxations are not affected by such a phenomenon. Thus consideration of the relaxation of these LMMLCs can be centred around the mechanics of the shear imposed deformations upon the director field.

Larson and Mead explain the mechanics of relaxation in LCP systems in terms of the stored elastic energy within the Frank stresses of the distorted director field acting as the driving mechanism for the reorientation of the material [22]. The elastic torque associated with this energy is balanced during the shear by the hydrodynamic torque contributed by the shear field. Thus for higher shear rates, the disclination density increases and the domain size reduces, giving rise to a greater stored elastic energy and a proportionally faster relaxation process. Experimental corroboration of this reasoning, that shorter relaxation times are realized from higher prior shear rates, has been found in LCP systems by Keates *et al.* in their study of the lyotropic LCP hydroxypropylcellulose [14] and by Zachariades *et al.* in their study of a blend of poly(ethylene terephthalate) and poly(hydroxybenzoic acid) [23].

It is noted that the data presented here, which are collected from LMMLC systems, indicate this same generic trend: that the faster relaxations of orientation occur subsequent to the higher shear rate treatments. This suggests a possible commonality of behaviour, that the relaxations within the LMMLC system (figures 6 and 7), may be driven by shear-induced disclinations resulting in reorganizations of directors upon cessation of shear. That the disclination density is reduced upon relaxation has been reasoned theoretically and observed experimentally using optical techniques and the LMMLC system MBBA [24, 25].

The inflections which occur in the curve of $\langle P_2 \rangle$ during relaxation have been observed in a previous shear and relaxation study of the lyotropic LCP hydroxypropylcellulose and were noted, as here (figure 6), to occur most prominently in relaxations from low shear rates [14]. In the LCP materials, the annealing of unfavourable defects by the relaxation process causes a greater number of directors to enter the shearing plane. The result is a serpentine arrangement of the directors within the shear plane, which has been associated with the phenomenon of the banded texture [26, 27]. It is known that the orientation parameters determined from WAXS patterns concern only projections of the directors in the plane of shear and that interactions in other planes are unable to be probed in this way [19]. This presents a possible means by which the orientation could rise during the relaxation process as directors return to the shearing plane although the precise explanation for the presence and nature of these inflections remains unknown.

7. Conclusions

Original measurements of the orientation function coefficients in steady state simple shear are presented for the low molecular mass liquid crystal (LMMLC) system 4-cyano-4′-*n*-pentylbiphenyl (5CB), from the WAXS data collected using the AXIS system. The aspects of the directors from which the orientation parameters are calculated are also presented. The orientation parameters increase linearly with a logarithmic increase in the applied shear rate. It is proposed that this arises from an increased alignment of LC directors to the direction of shear. Calculation of the global director orientation indicates that the sample is close to fully aligned, $\langle P_2 \rangle_D = 0{\cdot}96 \pm 0{\cdot}05$, at a shear rate of $\gamma = 1020\ \mathrm{s}^{-1}$.

The shear-induced orientation is observed to relax upon cessation of shear flow. Relaxation constants are observed to reduce linearly with a logarithmic increase in the previously applied shear rate, in a similar manner to that observed in polymeric LC systems [14, 23]. Inflections in the orientation curves are also observed during relaxation, and are noted to reduce in prominence as the previously applied shear rate increases.

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References

[1] Cladis, P. E., 1972, *Phys. Rev. Lett.*, **28,** 1629.

[2] Paul, R., Jha, B., and Dunmur, D. A., 1993, *Liq. Cryst.*, **13,** 629.

[3] Pieranski, P., and Guyon, E., 1974, *Phys. Rev. A*, **9,** 404.

[4] Dubois-Violette, E., Guyon, E., Janossy, I., Pieranski, P., and Manneville, P., 1977, *J. de Mécanique*, **16,** 733.

[5] Leslie, F. M., 1979, *Adv. Liq. Cryst.*, **4,** 1.

[6] Kuzuu, N., and Doi, M., 1983, *J. Phys. Soc. Jpn*, **52,** 3486.

[7] Kuzuu, N., and Doi, M., 1984, *J. Phys. Soc. Jpn*, **53,** 1031.

[8] Blinov, L. M., and Chigrinov, V. G., 1994, *Electrooptic Effects in Liquid Crystal Materials* (New York: Springer Verlag).

[9] Müller, J. A., Stein, R. S., and Winter, H. H., 1994, *Rheol. Acta*, **33,** 473.

[10] Mather, P. T., Pearson, D. S., and Larson, R. G., 1996, *Liq. Cryst.*, **20,** 527.

[11] Pople, J. A., Mitchell, G. R., and Chai, C. K., 1996, *Polymer*, **37,** 4187.

[12] Pople, J. A., Mitchell, G. R., Sutton, S. J., Vaughan, A. S., and Chai, C. K., 1997, to be submitted.

[13] Keates, P., Mitchell, G. R., Peuvrel-Disdier, E., Riti, J. B., and Navard, P., 1994, *J. Non-Newt. Fl. Mech.*, **52,** 197.

[14] Keates, P. A., Mitchell, G. R., Peuvrel-Disdier, E., and Navard, P., 1996, *Polymer*, **37,** 893.

[15] BDH Liquid Crystals Ltd, 1992, *Advanced Materials Division Datasheet 3*, Poole, U.K.

[16] Pople, J. A., Keates, P. A., and Mitchell, G. R., 1997, *J. Synchrotron Rad.*, in press.

[17] Mitchell, G. R., and Windle, A. H., 1988, in *Developments in Crystalline Polymers—2*, edited by D. C. Bassett (London: Elsevier Applied Science), Chap. 3.

[18] De Jeu, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (New York: Gordon & Breach Science).

[19] Mitchell, G. R., 1989, *Comprehensive Polymer Science*, Vol. I, edited by C. Booth and C. Price (New York: Pergamon Press), Chap. 31.

[20] Heynderickx, I., Potze, W., and Ter Maten, E. J. W., 1994, *J. Non-Newt. Fl. Mech.*, **55,** 137.

[21] Flory, P. J., 1956, *Proc. R. Soc. Lond. (A)*, **234,** 60.

[22] Larson, R. G., and Mead, D. W., 1989, *J. Rheol.*, **8,** 1251.

[23] Zachariades, A. E., Navard, P., and Logan, J. A., 1984, *Mol. Cryst. liq. Cryst.*, **110,** 93.

[24] Bedford, S. E., Nicholson, T. M., and Windle, A. A., 1991, *Liq. Cryst.*, **10,** 63.

[25] Bedford, S. E., and Windle, A. H., 1993, *Liq. Cryst.*, **15,** 31.

[26] Kiss, G., and Porter, R. S., 1980, *Mol. Cryst. liq. Cryst.*, **60,** 267.

[27] Picken, S. J., Moldenaers, P., Berghmans, S., and Mewis, J., 1992, *Macromolecules*, **25,** 4759.