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Viscosity measurements of nematic–polymer liquid crystal mixtures by light scattering

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It is shown that the fluctuations in the intensity of light transmitted by planar aligned nematic liquids between polarizers is determined by the rotational viscosity alone at sufficiently high frequency. The technique is applied to the determination of the viscosity of polymer liquid crystal mixtures. The most viscous mixture which was successfully aligned (60 per cent polymer) has a viscosity 230 times larger than the cyanobiphenyl monomers.

1. Introduction

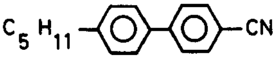
Liquid crystal polymers have considerable potential for future device applications. One of their most dramatically changed properties compared to conventional (monomer) liquid crystals is their greatly increased viscosity. In this paper we describe and use a novel light scattering technique to determine the viscosity of polymer–monomer mixtures. Measurements were made under conditions which did not require an independent measurement of the elastic constants.

Conventional light scattering measurements on liquid crystals detect the fluctuations in the light scattered out of the beam. In our technique, we use the magnitude of the fluctuations in the light intensity transmitted by an analyser to obtain the liquid crystal viscosity. These fluctuations in intensity are the result of heterodyne mixing between the strong unscattered transmitted field and the field due to fluctuations in the polarisation of the transmitted light. Although there is a characteristic time constant which depends on the elastic constants, in all cases examined there is a clearly defined regime at higher frequencies in which the scattered intensity is independent of the elastic constants.

These measurements are part of a study of a novel scheme for thermal imaging, in which the birefringence of a liquid crystal is used as a measure of its temperature, so that the liquid crystal forms a sensitive thermal infrared detector [1]. It is the first study aimed at understanding noise in a liquid crystal device of which we are aware.

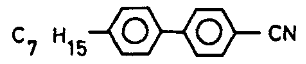
2. Liquid crystal materials

The monomeric nematic host used was the BDH Chemicals Limited eutectic mixture E1 [2] which contains



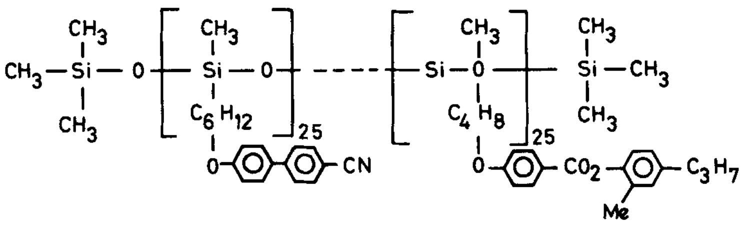
59 mol %

and



41 mol %

and has a nematic range from -1°C to 38°C. To this was added up to 60 per cent of the liquid crystal copolymer PG296 [3]



which has a glass transition temperature of 4°C and is smectic A up to 86°C. Although there were no immiscibility problems the mixtures containing large amounts of the polymer required shaking for long periods of time (weeks) before homogeneity was achieved. All the mixtures studied were nematic.

3. Theory

The analysis depends largely on the work of the Orsay group [4] who showed that director fluctuations behave as overdamped simple harmonic oscillators. Two sorts of normal modes were found, which can be described approximately as fluctuations of the director orientation and angular velocity. Only the former are of importance in the experiments we discuss. We expand the fluctuations in terms of sinusoidal modes

$$n_{x,y} = n_{0x,y}\sin\frac{q\pi x}{L}\sin\frac{m\pi y}{t}\sin\frac{r\pi z}{L}, \qquad (1)$$

where the coordinate system has the director parallel to z (in the absence of fluctuations), y normal to the plane of the cell, and x perpendicular to the other two directions. We consider only cells with planar alignment and zero tilt. L is the cell dimension in the x, y directions and t is the cell thickness. The two sorts of mode correspond to rotation of the director about the y axis (n_x) and about the x axis (n_y); the origin of the coordinates is at the corner of the cell. We shall take L to be large, so that the boundary conditions at the cell edge are immaterial, and consider illuminating a small square area of side a at the middle of the cell.

The free energy of a nematic liquid crystal due to fluctuations is given by (see equation (III.1) of [4])

$$F = \frac{1}{2}\left[K_{11}\left(\left(\frac{\partial n_x}{\partial x}\right)^2 + \left(\frac{\partial n_y}{\partial y}\right)^2\right) + K_{22}\left(\left(\frac{\partial n_x}{\partial y}\right)^2 + \left(\frac{\partial n_y}{\partial x}\right)^2\right) + K_{33}\left(\left(\frac{\partial n_x}{\partial z}\right)^2 + \left(\frac{\partial n_y}{\partial z}\right)^2\right)\right], \qquad (2)$$

where the K_{ii} are liquid crystal elastic constants. We have examined the contribution of the tilt modes n_y of equation (1) to the measured signal and find that for a zero tilt alignment it vanishes to first order. We shall not consider these modes further.

The free energy of the twist modes n_x of equation (1) is found, by integrating equation (2) over the cell volume, to be

$$F = \frac{\pi^2 n_{x0}^2}{16}\left(K_{11} q^2 \pi^2 t + K_{22}\frac{m^2\pi^2 L^2}{t} + K_{33} r^2 \pi^2 t\right), \tag{3}$$

and the mean square fluctuation amplitude is deduced by setting this equal to $kT/2$ by the equipartition principle. It is convenient to simplify the notation at this point by introducing an approximation which is justified later (see equation (8)). The modes which dominate the light intensity fluctuations are found to be those with wavelength $\lambda/\Delta n$ normal to the cell. The fluctuations are averaged over the size of the illuminated area of the cell, which has the effect of suppressing modes with high spatial frequency in the plane of the cell (see equation (11)), so that only modes with small q and r are important. Since the size of the illuminated spot (a) is much larger than $\lambda/\Delta n$ the term in brackets in equation (3) can be approximated by putting q, $r = 0$. Thus

$$\langle n_{x0}^2 \rangle = \frac{8kTt}{L^2 m^2 \pi^2 K_{22}}. \tag{4}$$

The fluctuations can be temporally resolved using the fluctuation-dissipation theorem, giving, in a bandwidth of 1 Hz at an angular frequency ω,

$$\begin{aligned} \langle n_{ox}^2(m, \omega)\rangle &= \langle n_{ox}^2\rangle \frac{4\Delta\omega_m}{\omega^2 + \Delta\omega_m}, \\ &= \frac{32kTt}{L^2 m^2 \pi^2 K_{22}} \frac{\Delta\omega_m}{\omega^2 + \Delta\omega_m^2}, \end{aligned} \tag{5}$$

and the characteristic frequency ($\Delta\omega$) is given by

$$\Delta\omega_m = \frac{K_{22} m^2 \pi^2}{\gamma_1 t^2}, \tag{6}$$

where γ_1 is the rotational viscosity. The extra term $(C_2 Q_2/P_2)$ in the denominator given in equation (IV.17) of [4] depends on the angle between the mode wavevector and the director, and vanishes for finite m with q, $r \sim 0$.

The light transmitted by the cell in the presence of a (static) twist fluctuation with q, $r = 0$ can be characterised to first order in mode amplitude by a Jones matrix of the form

$$\begin{pmatrix} \exp(i\theta) & -\varphi\exp(-i\delta) \\ \varphi\exp(i\delta) & \exp(-i\theta) \end{pmatrix}, \tag{7}$$

where $\theta = \pi\Delta n t/\lambda$, with Δn the birefringence and λ the wavelength of light. We know of no analytic means of determining φ and δ which determine the polarization state of emerging light but it is straightforward to calculate them numerically by dividing the cell into many thin layers. We find that the result can be represented accurately by

$$\varphi = \frac{\pi m n_m \theta \sin(\theta - m\pi/2)}{\theta^2 - m^2\pi^2/4},$$

and

$$\delta = \frac{m\pi}{2}. \tag{8}$$

Explicit calculations show that only modes with $\theta \sim m\pi/2$ need be considered in this expression, and that the finite cell thickness gives rise only to relatively small structure in φ as the parameters are varied. It is then reasonable to treat m as a continuous variable, with

$$\varphi = n_m \theta. \tag{9}$$

When the light is incident polarized parallel (or perpendicular) to the director, and analysed at some angle ψ from extinction, the amplitude transmitted by the analyser is

$$\sin\psi \exp(i\theta) + \varphi \cos\psi \exp(i\delta), \tag{10}$$

where the first term is the fluctuation independent transmission and the second is the forward scattered amplitude.

We now assume that the forward scattered light intensity when integrated over the illuminated area is independent of q and r. This assumption is valid when $a \gg \lambda/\Delta n$, as was the case in our measurements. After performing this integration we find

$$I = I_0 \left(\sin^2\psi + n_m \theta \sin 2\psi \frac{4L^2}{qr\pi^2 a^2} \sin\frac{q\pi a}{2L} \sin\frac{r\pi a}{2L} \right), \tag{11}$$

where I_0 is the incident light intensity and q and r are both odd. If L is large, we can integrate over q and r in quadrature to give

$$\frac{\langle \Delta I^2 \rangle^{1/2}}{I_0} = \langle n_m^2 \rangle^{1/2} \theta \sin 2\psi \frac{L}{2a}, \tag{12}$$

as the root mean square fluctuation in the light intensity in a bandwidth of 1 Hz. Substituting for $\langle n_m^2 \rangle$ from equation (5), and with $\Delta\omega_m$ from equation (6), we finally obtain the light intensity fluctuations in a bandwidth of Δf to be

$$\frac{\langle \Delta I^2 \rangle^{1/2}}{I_0} = \frac{\pi \Delta n \sin 2\psi}{\lambda a} \left(\frac{8kTt}{\gamma_1(\omega^2 + \Delta\omega_m^2)} \right)^{1/2} \Delta f^2, \tag{13}$$

where

$$\Delta\omega_m = \frac{4\pi^2 K_{22} \Delta n^2}{\gamma_1 \lambda^2}.$$

The only liquid crystal properties involved when $\omega \gg \Delta\omega_m$ are Δn and γ_1. The magnitude of these fluctuations thus gives directly the value of γ_1.

4. Experiment

The noise spectrum of the light transmitted by a system comprising source, polarizer, liquid crystal cell and analyser is superficially easy to measure. However, in the liquid crystal polymer mixtures discussed here the measurement frequencies involved are low and measurements must be carried out with considerable care. The experiments were carried out in thin liquid crystal films held in the conventional sandwich cell, consisting of two parallel glass plates (flat to better than 1 μm in 1 cm) separated by polyester spacers, approximately 10 μm thick. The polymer/E_1 mixtures were drawn into the cell by capillary action but filling a 1 cm^2 cell could take over 20 min when the most viscous mixtures were used, even at 100°C. The required

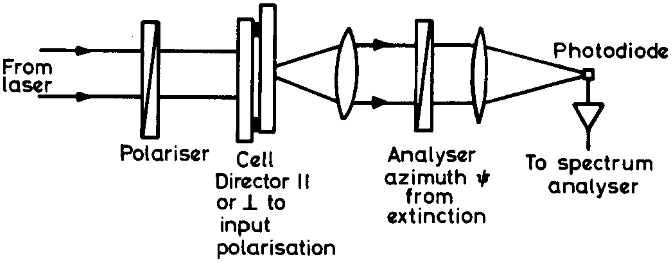


Figure 1. Simplified experimental layout.

parallel alignment with zero tilt was given by coating the inside surfaces of the glass with SiO evaporated at 60° incidence [5]. For a homogeneous alignment it was necessary to heat the cell above T_{NI} during filling; on cooling to room temperature all the disclination loops eventually collapsed, taking several hours for the 60 per cent mixture and leaving the majority of the cell free of all defects detectable with a polarizing microscope. Only near the filling end of the cell was the alignment defective indicating possible contamination of the SiO surfaces by some component of the polymer.

An area of the cell 5 mm in diameter was checked for uniformity of alignment and was illuminated with light from a HeNe laser (633 nm) of power approximately equal to 2 mW. The illuminated region was imaged by a lens system (approximately $f/5$) via the analyser on to a photodiode (see figure 1). The area of the cell contributing to the scattered light was thus defined by the photodiode area and was typically 70 μm in diameter. Changes to the f number of the system had no effect on the results provided the sampled area was not broadened by diffraction; illuminating only the sampled area to define it gave the same results.

The AC signal from the photodiode was measured with a Fourier transform spectrum analyser (Panasonic VS 3310) having an effective bandwidth of 0·25 Hz and the small fluctuations observed from the more viscous mixtures required integration of the spectrum for up to 10 min. The DC signal gave $I_0 \sin^2 \psi$. The temperature of the cell was maintained only to 20°C ± 2°C since it was found that at these temperatures (well away from T_{NI}) a change of 10°C changed the measured noise by less than 10 per cent.

Other experiments using different configurations of apparatus verified that a less coherent source (a mercury lamp filtered to 10 nm linewidth) gave the same results, and the wavelength dependence of equation (13) was verified using a 1·5 μm laser and germanium detector. The measured root mean square noise was shown to be inversely proportional to a and for cell thicknesses between 5 μm and 30 μm it was proportional to $t^{0.5 \pm 0.02}$. The variation with analyser angle for $\psi > 3°$ was as predicted in equation (13), but at smaller angles the noise tended to a small constant value associated with incomplete extinction due to its time-averaged value. It was most convenient to use ψ of 10° for the viscosity measurements where equation (13) applied accurately.

Because these measurements were the first step in investigating much lower noise levels [1], considerable care was taken in selecting and setting up the optical components. All the optics including the cell were antireflection coated to prevent multiple passes through birefringent components and the apparatus was set up on a pneumatic optical table. Despite much work, laser noise and vibration were never adequately eliminated at frequencies less than 1 Hz and so the low frequency regime of equation (13) ($\omega < \Delta\omega_m$) was not studied for the viscous mixtures. Where noise was low the system noise power (electronic noise and photon noise) measured using an isotropic cell was subtracted from the measured noise power; the reduction was only significant for the 60 per cent mixtures.

E1 is a well-studied mixture. Its birefringence is 0·192 at 20° and 633 nm. Its elastic constant K_{22} is taken to be that given by Schadt and Gerber [6] for a closely related mixture ($4{\cdot}6 \times 10^{-12}$N) (60:40 7CB:5CB). Their values for K_{11} and K_{33} ($8{\cdot}7 \times 10^{-12}$ and $12{\cdot}3 \times 10^{-12}$N respectively) agree well with those determined by Bradshaw and Raynes [7]. Similarly, its rotational viscosity γ_1 is taken to be 0·13 kg/ms [8]. We have therefore a check on the theory for the scattering measured on pure E1, being able to calculate the noise spectrum from equation (13) without fitting. The result is shown in figure 2, and the agreement is seen to be excellent, thus verifying the theory in a known case. We take this as strong evidence that the approximations introduced in the theory are justified, and that the mechanism for the fluctuations is correctly identified.

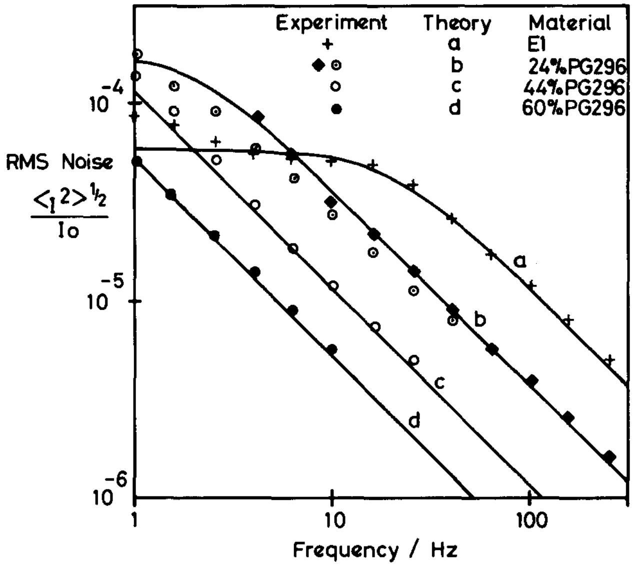


Figure 2. Experimental noise spectra for the series of E1/PG296 mixtures given in the table. For clarity our continuous spectra have been represented by series of points. Continuous lines are theoretical spectra calculated from equation (13) using the viscosity values given in the table. Light wavelength, λ = 633 nm; analyser angle, ψ = 10°; cell thickness, t = 10 μm; sample diameter, a = 70 μm.

Viscosity measurements on a liquid crystal polymer have been reported by Taratuta *et al.* [9] using conventional light scattering. The material was poly-γ-benzylglutamate in a nematic phase. The measurements were made simpler than usual by the very low birefringence of this material which makes multiple scattering very improbable. This is not a problem in our measurements, which are dominated by heterodyne rather than homodyne terms. They found that only some of the anisotropic viscosities were enhanced in the polymer, and that one of these was γ_1 (the component we measure).

The viscosity and elastic constants of monomer–polymer mixtures similar to those in the present work have been reported by Coles and Sefton [10]. The technique used was angle dependent light scattering in a homeotropic alignment, and the separation of viscosity and elastic constants was achieved using an electric field. They avoided the problem of multiple scattering by the use of a heterodyne technique. The quantitative accuracy of their measurements (1·5 per cent) was superior to our technique, but the range of concentrations studied extended only to 20 per cent polymer.

The birefringence of the 44 per cent mixture was measured as 0·1531 with an Abbe refractometer with a sodium light source ($\lambda = 589{\cdot}6\,\mathrm{nm}$) and corrected to 633 nm assuming the same dispersion as E1. To enable both components of the refractive index to be measured, the liquid was aligned homeotropically by a lecithin surface coating. Since the dependence of the birefringence Δn (and therefore the predicted noise (see equation (13)) on the polymer concentration is not strong, we have used a linear interpolation to deduce the birefringence of the other mixtures. The error introduced in this way is expected to be about 1 per cent. Coles and Sefton [10] found that K_{22} varies only slightly with polymer concentration. A factor of two reduction might be expected in our polymer range. Since the forward scattering spectra are nearly independent of the elastic constants, we have, however, fitted the data assuming a constant K_{22}, since above 20 per cent polymer only frequencies less than 1 Hz are affected by K_{22}. The results are shown in figure 2 where, for clarity, the continuous FT spectra have been represented by series of points. The $1/f$ character of the noise spectra is consistent with a value of $\Delta\omega_m$ which is greatly reduced; the reduced magnitude of the scattering shows that the cause is an increase in the viscosity. The scattering intensity is reduced by a factor of about 20 between E1 and the 60 per cent polymer mixture, associated with a viscosity increased by a factor of approximately 230. Clearly the results are not highly accurate: the dependence on the viscosity is only as a square root, and there are significant experimental errors. We have deliberately included two curves for the 24 per cent mixture which do not match very well to indicate the size of the experimental error. Each spectrum can be fitted with an accuracy better than this and the fits have been verified by careful measurements at single frequencies, but there remain unidentified systematic errors in repeating the complete experiment, causing an error in determining the magnitude of the fluctuations at the ~ 10 per cent level, and therefore causing an estimated inaccuracy in γ_1 of ± 5 per cent.

Table 1. Viscosity of polymer liquid crystal mixtures.

Composition polymer percentage	Rotational viscosity $\mathrm{kg\,m^{-1}\,s^{-1}}$
0	0·13 [6]
24	1
44	8
60	30

The viscosity values deduced from the fits given in the table show that it increases approximately exponentially with polymer content at a rate which is close to that found by Coles and Sefton [10] in the low polymer concentration range; see figure 3. At the highest viscosity measured, the reorientation time of the fundamental fluctuation ($m = 1$) would be of the order of 50 s.

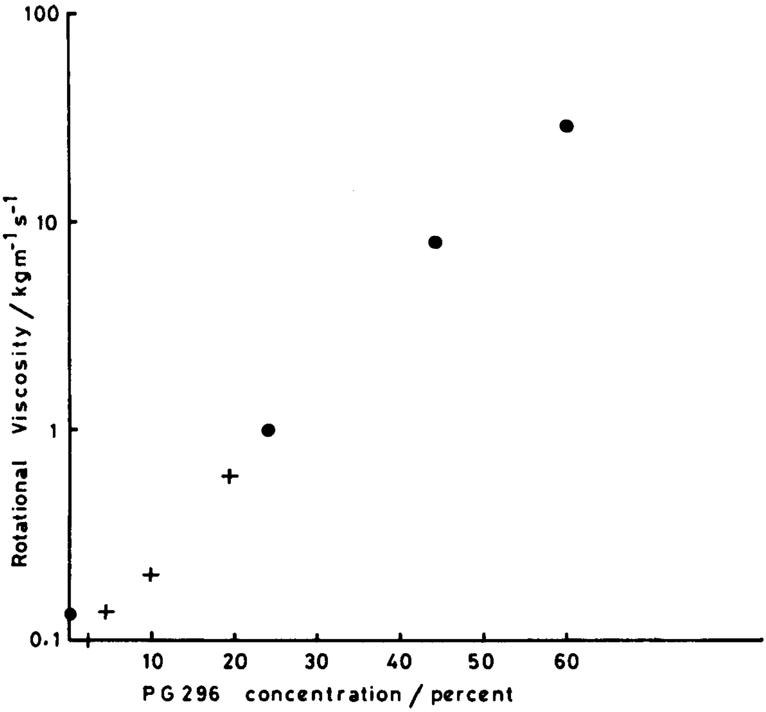


Figure 3. Variation of the measured rotational viscosity γ_1 with PG296 polymer concentration. ●, This work; +, Coles and Sefton [10].

5. Conclusion

We have shown that the viscosity of liquid crystals can be measured by light scattering up to the most highly viscous mixtures which can be aligned and we have used the technique to determine the viscosities of monomer–polymer mixtures. The reduction in the fluctuations in highly viscous mixtures shows that not only do they have a potential for long persistence displays, but also that the fundamental noise in such devices is much lower than in the conventional alternative.

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References

[1] HUMPHREYS, R. G., and TARRY, H. A., 1988, *Ifrared Phys.*, **28**, 113.
[2] HULME, D. S., RAYNES, E. P., and HARRISON, K. J., 1974, *J. chem. Soc. Chem. Commun.*, **3** 98.
[3] GEMMELL, P. A., GRAY, G. W., and LACEY, D., 1985, *Molec. Crystals liq. Crystals*, **122**, 205.
[4] Groupe d'Etude des Cristaux Liquides, 1969, *J. chem. Phys.*, **51**, 816.
[5] GUYON, E., PIERANSKI, P., and BOIX, M., 1973, *Lett. appl. Engng. Sci.*, **1**, 19.
[6] Schadt, M., and GERBER, P. R., 1982, *Z. Naturf.* (*a*), **37**, 165.
[7] Bradshaw, M. J., and RAYNES, E. P., 1983, *Molec. Crystals liq. Crystals*, **99**, 107.
[8] Schadt, M., and GERBER, P. R., 1982, *Z. Naturf.* (*a*), **37**, 179.
[9] Taratuta, V. G., Hurd, A. J., and MEYER, R. B., 1985, *Phys. Rev. Lett.*, **55**, 246.
[10] COLES, H. J., and SEFTON, M. S., 1985, *Molec. Crystals liq. Crystals Lett.*, **1**, 159.