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Rheology of a pyramidal liquid crystal

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We have measured the shear elastic modulus and the viscosity values of a pyramidal liquid crystal both normal and parallel to the columnar axis. It was observed that above frequencies of 50 Hz, the sample behaves as a Maxwell solid characterized by constant G and η values. The shear modulus is in the range of 10^6–10^7 N m^{-2}, typical for rubbers and polystyrene foams. The viscosity values are in the range of 10^3–10^4 Pas, comparable to polymer melts. The observations can be qualitatively explained by temporary entanglements between the side chains of the bowl-shaped molecules, as observed by previous X-ray studies.

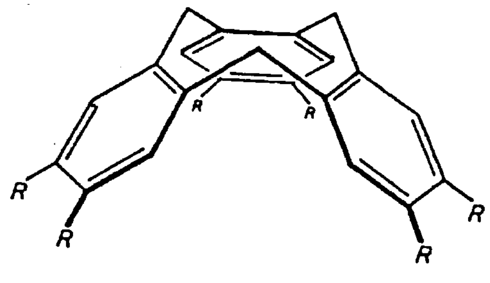
1. Introduction

Disc- or bowl-shaped molecules may stack in columns forming so called discotic columnar (Col) or columnar pyramidic (P) phases, respectively. A simplified picture of columnar liquid crystals [1] is that they are liquid-like along the columns and solid-like in the two-dimensional array of columns. This picture is mainly based on X-ray studies of discotic columnar phases which showed that the inter-columnar translational correlation order is greater than 200 columns [2], whereas the intra-columnar positional correlation length is in the range of 3–30 molecules [3, 4]. Due to the tendency for efficient molecular packing, bowl-shaped molecules yielding pyramidic phases must have a quasi-long-range positional correlation, which may render an elastic nature to the shear stress. Otherwise, columnar mesophases of pyramidal and discotic molecules are supposed to be similar regarding their mechanical properties. They all exhibit undulations of the columnar axes, molecular reorientation, and probably also molecular translation between columns [5]. Although the molecular structures of the columnar mesophases are well established, their defects and visco-elastic properties are still controversial. There are numerous studies on the visco-elastic properties of discotic columnar phases [6, 7–12], but to our knowledge, there has been no direct rheological study of pyramidal columnar phases.

In this paper we present the first rheological studies of a pyramidal columnar phase. We have measured the temperature and frequency dependences of the apparent shear viscosity and shear modulus of a tribenzocyclononene derivative in the pyramidic phase in both homeotropic and planar alignments.

2. Material studied

For our studies we chose hexanonyloxytribenzocyclononene [13], because its phase sequence is very convenient for study. The material was synthesized in the I.N. Stranski Institute (TU Berlin) by Dr. Detlef Loetzsch.



R=$C_9H_{19}O$-

This compound exhibits a single uniaxial mesophase, P_A between 18.7 and 61°C. Below 18.7°C it is crystalline, and above 61°C it is an isotropic liquid. X-ray studies have revealed [5] that the lattice parameter is 22.5 Å, i.e. much smaller than if assuming fully extended

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alkyl chains (34 Å). Even assuming that the chains are stretched along the edge of the pyramidic core, the molecular diameter would be 28 Å. Accordingly, the side chains must be highly folded with interpenetrations between neighbouring columns. This suggests that the correlation length is relatively high along the columns, i.e. the material is rather stiff. X-ray and optical microscopy have indeed revealed their high order and low mobility, classifying such materials as 'soft solids'.

3. Experimental set-up

For our measurements, a home-made sample holder (figure 1) was used; it was fabricated in the Max Planck Research Group at the Martin Luther University in Halle, Germany. The liquid crystal material (l.c.) is sandwiched between two 1 mm thick float glasses (2 and 2′). The glasses are firmly fixed to the upper (1) and lower (1′) heating plates, which enable the sample temperature to be varied between room temperature and 150°C with an accuracy better than 0.1°C. A pair of 1 mm thick piezoelectric plates (3 and 4), sensitive to a force appearing in the y and z directions, is attached to the bottom part of the lower heating plate. They are glued together through a spacer plate (5). The piezoelectric shear elements are attached via the spacer (6) to a piezoelectric ring (7), which is sensitive to forces in the x direction. The other end of the piezo-ring is fixed to an aluminium frame (8). The frame also holds a piezoelectric actuator (PSt 500/10/5 from Piezomechanik GmbH), which can shift the top plate of an empty cell with an amplitude maximum of 5 μm. The actuator was driven by a high voltage amplifier (LE 430/015 from Piezomechanik GmbH). The motion of the top plate was monitored by a piezoelectric accelerometer (BK 4375 from Bruel & Kjaer, sensitivity 0.1 mm s^{-2}). The sample holder was placed in a polarizing microscope (10), which enabled us to observe the texture of the liquid crystal during the measurements. A lock-in amplifier (SR 850 from Stanford Research) measured the vibration of the top plate and the forces on the lower plate in the frequency range 10–500 Hz.

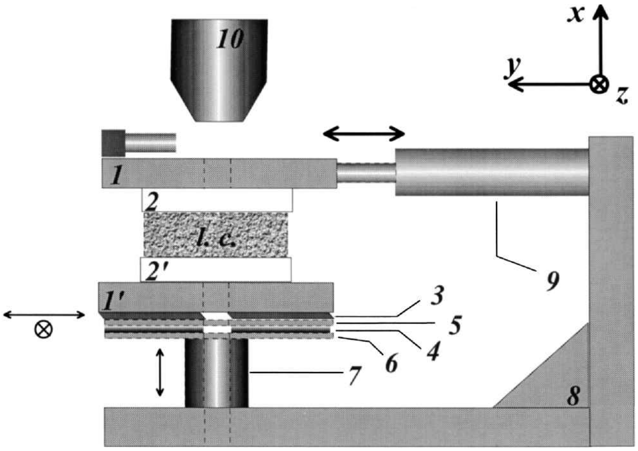
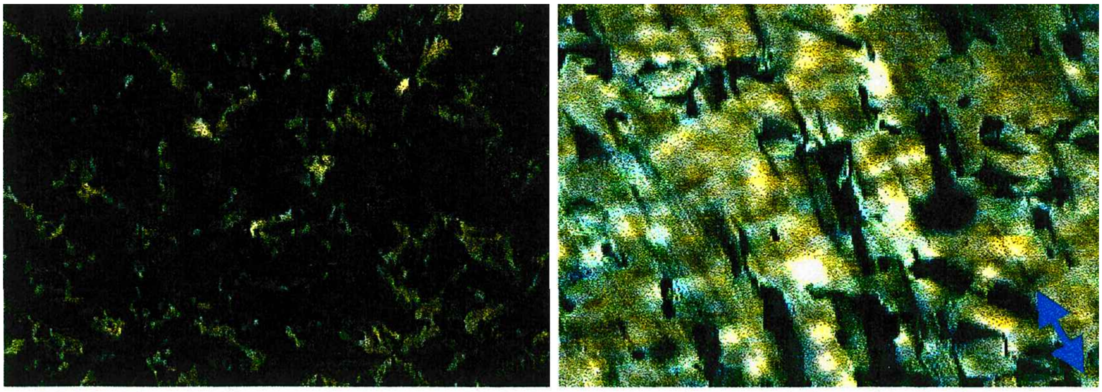


Figure 1. Schematic representation of the sample holder.

First we made an empty cell using 13 μm thick polyimide spacer strips. During the assembly of the empty cell, a d.c. voltage was applied on the piezo-ring (7), which shifted up the bottom plate by 0.2 μm, thus decreasing the sample spacing. The top plate was fixed to the actuator (9); meanwhile the sample thickness was set by a polyimide spacer. The parallelism (resolution better than 10^{-4} rad) of the plates was checked by observing the Newton fringes. After setting the spacing and the parallelism the voltage was removed from the piezo-ring. In this way the final sample thickness was about 0.2 μm wider than the spacers.



a b

Figure 2. Typical textures observed during the measurements (areas: 0.3 mm × 0.2 mm, $d = 13\,\mu m$, $T = 55°C$) using crossed polarizers (vertical and horizontal directions). The two-headed arrow (bottom right) indicates the shear direction. (*a*) A quasi-homeotropic texture formed spontaneously on slow cooling from the isotropic phase. (*b*) A relatively uniform planar texture formed on slow cooling from the isotropic phase whilst the top plate was vibrated with modulation by an amplitude of 3 μm (3 Hz superimposed upon 320 Hz).

First we tested the vibration of the top plate of the empty cell under various sinusoidal excitations from room temperature up to 100°C. The vibration amplitude and phase were found to be temperature independent. Due to the non-perfect electronic and mechanical isolation of the detectors from the piezo-actuator, there were weak signals on the detectors attached to the lower plate, but they were independent of the temperature. In the measurements on cells filled with material this background was deducted. At frequencies above 300 Hz, a few resonances were seen in the vibration spectra of both the accelerator and the detectors fixed to the lower plate. The resonances are characteristic of the mechanical eigen-modes of the whole sample holder. The lowest frequency mode (~320 Hz) seems to be connected to the first bending mode of the glass plates. Below 10 Hz the signals are too small to obtain reliable results. Between 10 and 200 Hz the signals are monotonous, indicating the frequency range where measurements can give useful results.

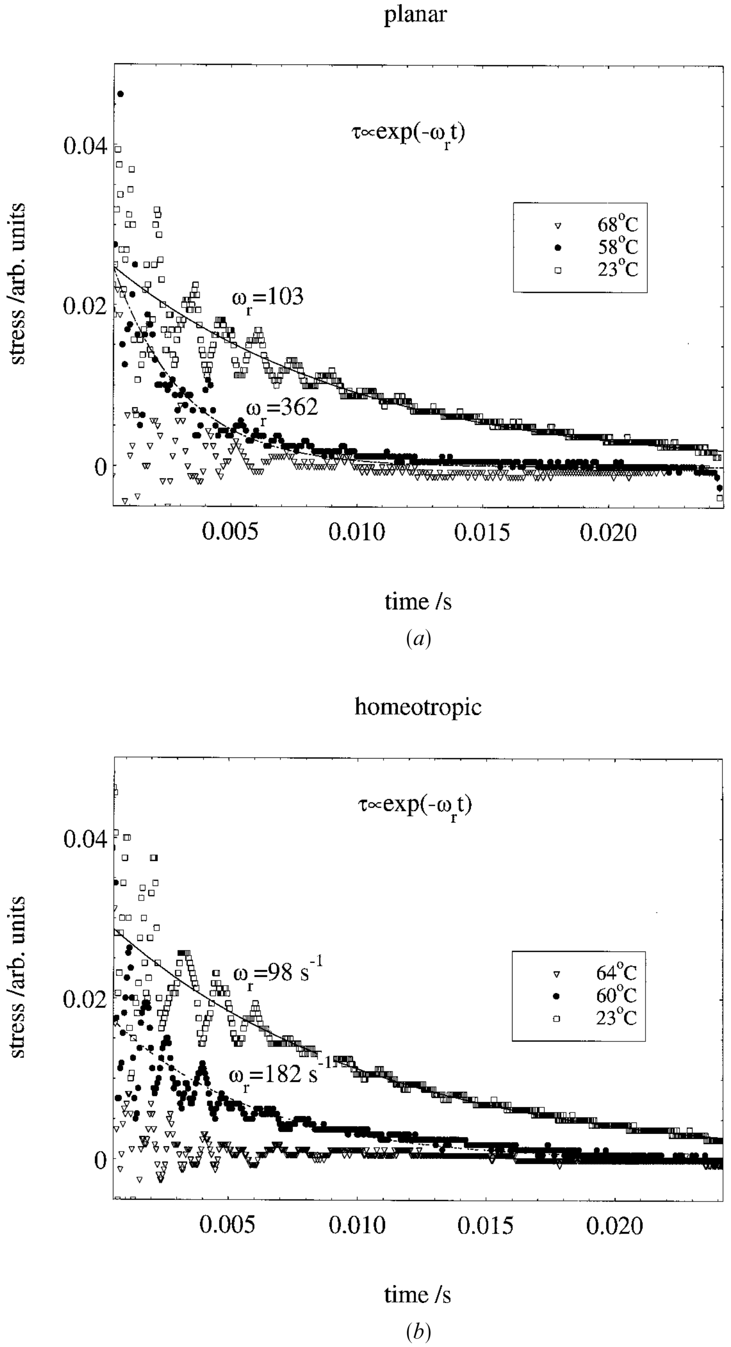


Figure 3. Time dependence of the shear stress transmitted to the lower plate due to rectangular shear excitation of the upper plate with a frequency of 30 Hz. (*a*) Planar alignment, (*b*) homeotropic alignment.

4. Theoretical background

A visco-elastic material is characterized by a viscosity modulus η, and an elastic shear modulus G (as a review see, for example [14]). They can be modelled by combination of springs for elastic terms and dashpots for viscous terms. In the best known, so-called Maxwell-type material, a spring and a dashpot are connected in series. In this case the shear stress τ and the strain γ are related as:

$$\tau = G\gamma + \eta\frac{\partial\gamma}{\partial t}. \tag{1}$$

For constant deformations ($\delta\gamma = 0$) the time dependence of the stress reads:

$$\tau = \gamma_0 G \exp(-tG/\eta). \tag{2}$$

Filling the cell of figure 1 with a viscoelastic material, the movement of the upper plate (1) can be described as follows:

$$F(t) = Ey(t) + GA\frac{\partial y(t)}{\partial x}\bigg|_{x=d} + \eta A\frac{\partial \dot{y}(t)}{\partial x}\bigg|_{x=d} + m\ddot{y}(t). \tag{3}$$

In this equation $F(t) = F_0 \exp(i\omega t)$ is the force of the piezoelectric actuator (at a constant frequency, proportional to the voltage applied on the actuator). $E = 1.6 \times 10^8\ \mathrm{N\,m^{-1}}$ is the stiffness of the piezo-actuator (data given by the producer), $A = 2.2\ \mathrm{cm}^2$ is the sample area, and $m \sim 0.2$ kg is the mass of the moving part of the sample holder. Below 1 kHz the last term is negligible. The flow is laminar (the relevant Reynolds number $Re = vd\rho/\eta \approx 10^{-5}\ \mathrm{Pa\,s}/\eta \ll 1$, where $\rho \sim 10^3\ \mathrm{kg\,m^{-3}}$ is the density and $d = 13\ \mu\mathrm{m}$ is the sample thickness), and accordingly $\partial y/\partial x \cong y/d$. Measuring only the steady term of the vibration with the frequency of the exciting force, i.e. $y(t) = y_0 \exp(i\omega t)$, we get

$$|y_0| \equiv s = \frac{F_0}{(a^2 + \omega^2 b^2)^{1/2}} \quad \text{and } \tan\phi = \frac{\omega b}{a}. \tag{4}$$

In this expression $a = E + GA/d$ and $b = \eta A/d$. Within the resolution of the experimental set-up in the isotropic phase far from the phase transition: $\eta(\mathrm{iso}) \sim \eta(\mathrm{air}) \sim 0$ and $G(\mathrm{iso}) \sim G(\mathrm{air}) \sim 0$. This enables us to define $|y_0(\mathrm{iso})| \equiv s_0 = F_0/E$ and $\tan\phi(\mathrm{iso}) \equiv \tan\phi_0 \approx 0$. With these we get

$$G = \frac{Ed}{A}\left\{\frac{s_0}{s}\frac{1}{[1 + \tan^2(\phi - \phi_0)]^{1/2}} - 1\right\} \tag{5}$$

$$\eta = \frac{Ed}{A}\frac{s_0}{s}\frac{\tan(\phi - \phi_0)}{\omega[1 + \tan^2(\phi - \phi_0)]^{1/2}}. \tag{6}$$

The force, f transmitted by the liquid crystal sample onto the lower plate is expressed as

$$GA\frac{\partial y}{\partial x}\bigg|_{x=0} + \eta A\frac{\partial \dot{y}}{\partial x}\bigg|_{x=0} = f \exp(i\omega t). \tag{7}$$

Assuming that the gradient along the film is constant, y can be taken from equation (4). Accordingly the measured amplitude D and phase of ξ of f can be expressed as

$$D = F_0 \frac{\left[\left(aG\frac{A}{d} + \omega^2 b^2\right)^2 + \omega^2 b^2 E^2\right]^{1/2}}{a^2 + \omega^2 b^2} \tag{8}$$

and

$$\tan\xi = \omega\frac{bE}{aG\frac{A}{d} + \omega^2 b^2}. \tag{9}$$

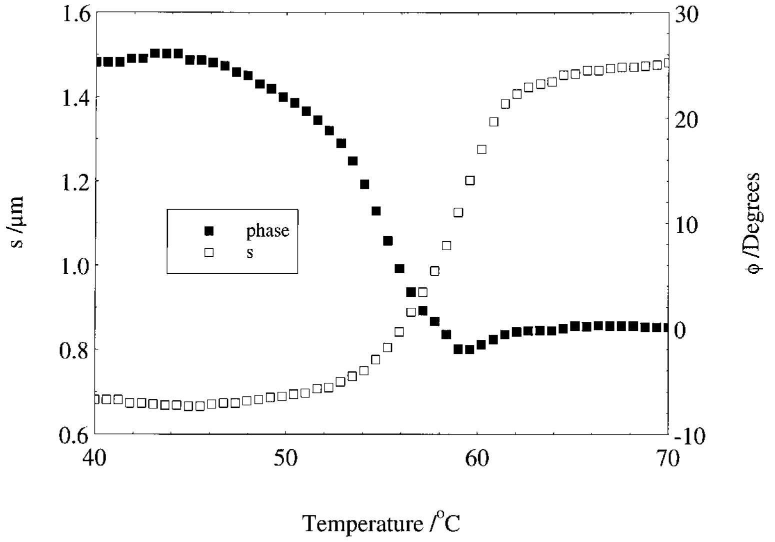


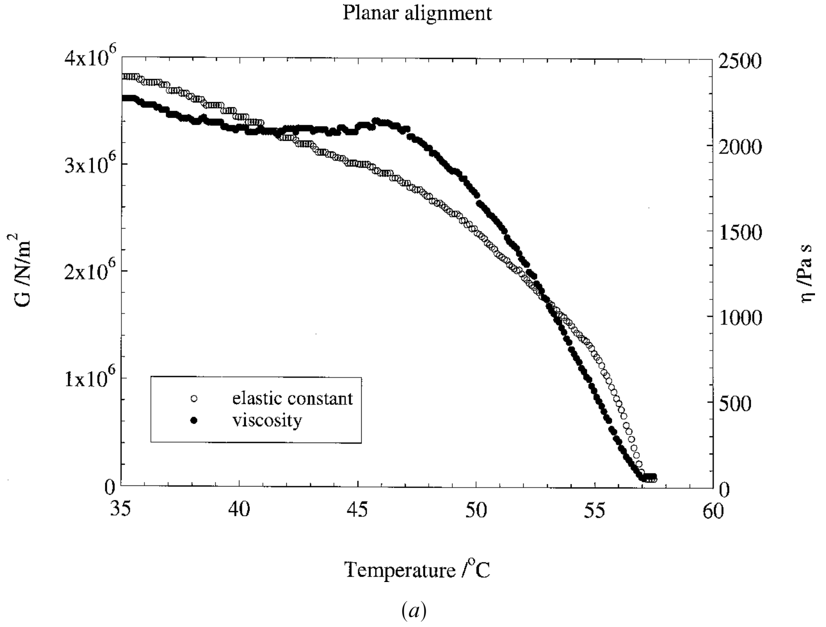
Figure 4. Temperature dependences of the amplitude (s) and phase of the vibration (ϕ) of the top plate under a periodic force ($f = 175$ Hz).

Provided that the viscous term is dominating ($G \ll \eta\omega$), $D = F_0\ \omega b/(\omega^2 b^2 + E^2)^{1/2}$ whereas for an elastic-like material $D = F_0\ AG/da$, i.e. it is constant.

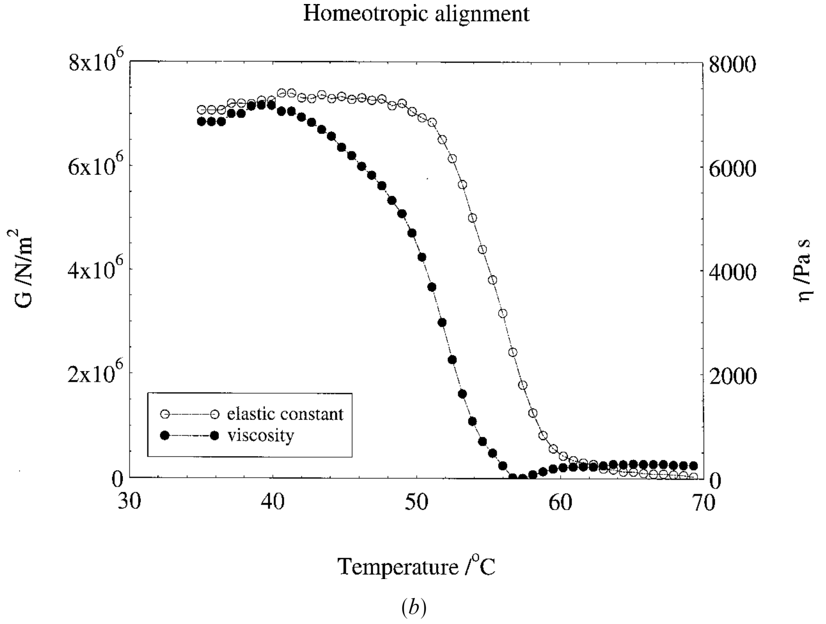
5. Alignment of the sample

For precise quantitative experimental studies, aligned samples are required. This is an especially difficult task in the case of columnar phases [15]. In contrast to calamitic phases, the application of a magnetic field usually does not result in oriented samples, because they have negative diamagnetic anisotropy. Goldfarb *et al.* [16], however demonstrated that by cooling the sample slowly in a magnetic field, while spinning it about an axis perpendicular to the field direction, a single domain forms with the director parallel to the spinning axis. It is also possible to obtain highly oriented free-standing strands by growing and annealing them in a special oven [3, 4]. In thin films, surface effects usually promote homeotropic alignment [17] (columns are normal to the film surface), whereas shearing the glass plates promotes planar alignment [8, 18, 19] (columns are parallel to the surfaces).

In our studies we obtained both homeotropic and planar alignments in the same sample holder. We had



(*a*)



(*b*)

Figure 5. Temperature dependence of the viscosity (η) and shear modulus (G) at different frequencies for (*a*) planar and (*b*) homeotropic alignments.

cleaned the ITO coated substrates, which under conditions of slow cooling resulted in relatively good homeotropic alignment. Typical textures observed between crossed polarizers are shown in figure 2(*a*). The quality of the homeotropic alignment could be further enhanced by vibrating the bottom plate vertically (x direction) with an amplitude of about 0.2 μm.

To achieve a planar alignment, we vibrated the top plate parallel to the fixed lower plate during slow cooling from the isotropic phase. Since the maximum amplitude of the vibration could not be larger than 3 μm, a shear at a constant frequency had only minor effects on the alignment. We observed, however, that at around 320 Hz the vibration amplitude had a maximum (resonance) effect and an irregular flow appeared. This resulted in a random planar texture. Modulating this vibration with a low frequency square wave, the texture appearing become fairly uniform with the columns parallel to the shear direction. Such a texture is shown in figure 2(*b*).

6. Experimental results

The relaxation of the shear stress was measured under a low frequency (< 30 Hz) using rectangular shear excitation forms. The time dependences at different temperatures for the planar and homeotropic alignments are shown in figure 3. It can be seen that two processes go on simultaneously: (i) the shear stress decays exponentially; (ii) a damped vibration appears with a ground frequency of about 320 Hz. As both processes decay within the period of the rectangular excitation, this measurement practically gives information about the process at constant strain, γ_0. The damped vibration is due to the excitation of the eigen-modes of the sample holder (mainly the bending of the glass plates). The exponential decay corresponds to the Maxwell model as expressed in equation (2). Parameter ω_r of the fits corresponds to the ratio G/η, and gives the relaxation frequency in s^{-1}. It was found that ω_r are independent of the strain up to $\varepsilon = s/d < 0.2$. In both alignments the relaxation frequencies increase with temperature. At room temperature they are practically equal, whereas at higher temperatures ω_r (planar) $\sim 2\ \omega_r$ (homeotropic).

We also measured the temperature dependence of the phase and the displacement of the vibration of the top plate for both homeotropic and planar alignments. An example for homeotropic alignment at 175 Hz is seen in figure 4.

In the isotropic phase, far away from the phase transition, the displacement and the phase of the top plate are practically the same as for an empty cell. Accordingly, equations (5) and (6) can be used to calculate G and η. In figures 5(*a*) and 5(*b*) we show the temperature dependences of the viscosity and shear modulus at 175 Hz for the planar and homeotropic alignments, respectively. The main difference between the rheological properties of the planar and homeotropic alignments is that in the columnar phase the G/η ratio is more than twice that for the homeotropic alignment. This indicates that the elastic part is more dominant in this alignment. Interestingly, however, both G and η are smaller in the homeotropically aligned samples. The temperature dependence of G/η as calculated from G and η measured at 32 Hz, is plotted in figure 6. Far from the phase transition ($\Delta T > 5$°C), the viscosity and shear modulus are independent of the strain up to $\varepsilon < 0.25$. Near to the transition, however, the apparent shear moduli decrease monotonously with increasing strain, but the apparent viscosity remains constant up to $\varepsilon = 0.15$ (see figure 7).

The frequency dependences of the amplitudes of the forces transmitted to the bottom plate are shown in figure 8. From the measured forces one can deduce the apparent viscosity and elastic constant by using equation (8). In the range of 50–200 Hz the curves could be fitted with constant η and G values. They have the same order of magnitude as those obtained from the movement of the upper plate. Below 50 Hz the fitted viscosity increases with decreasing frequency, whereas the apparent shear modulus has only a minor frequency dependence. The measurement on the bottom plate is more sensitive to the electrical isolation. For this reason the results obtained from the measurements on the top plate (see figure 5) are more reliable.

7. Discussion

In discotic columnar liquid crystals, assuming no intercolumnar molecular positional correlation, we would measure pure viscous behaviour in both geometries [6]. In the homeotropic alignment, however, Durand *et al.* [7, 8] observed that the apparent columnar curvature constant, $K_{app} \sim 10^{-6}$ N, i.e. 6 orders of magnitude larger than that observed by X-ray diffraction [9], or by

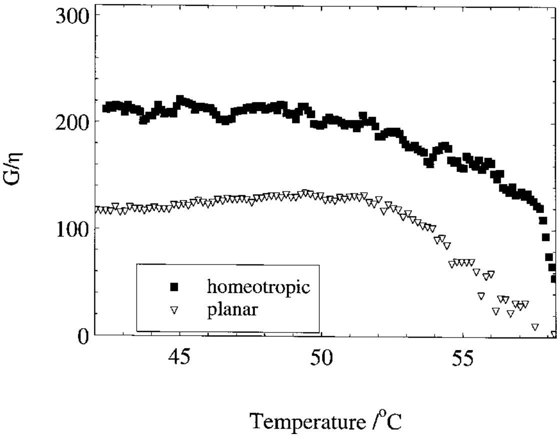


Figure 6. Temperature dependence of G/η at 32 Hz.

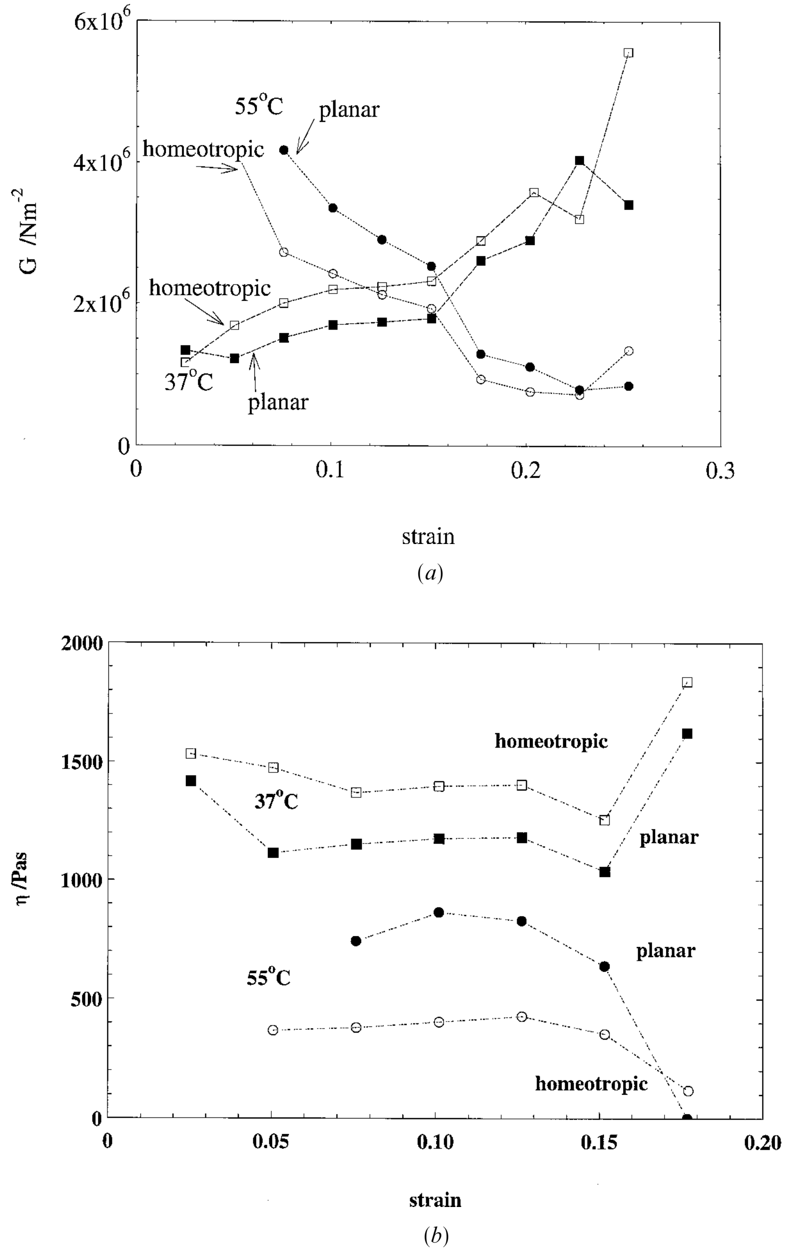


Figure 7. Shear modulus (*a*) and viscosity (*b*) as a function of shear strain at 55°C and 37°C.

surface tension and compressibility measurements [10]. Rayleigh scattering measurements [11] indicated later that the columnar mesophase behaves as a 3D crystal leading to the large K_{app} when the columns are bent over distances larger than 0.3 μm. A possible mechanism to explain these observations was proposed by Prost [6, 12] who showed that a large density of column ends (lock-in fault lines) or grain boundaries could make the material stiff. The shear stress G can be approximated as K_{app}/d^2. This corresponds to $G \sim 10^5\ \mathrm{N\,m^{-2}}$, and an average size of the order of microns for the grains [6]. So far, however there is no experimental evidence of these defects.

In the pyramidal columnar phase, we have found that the apparent shear elastic constants $G \sim 10^6\ \mathrm{N\,m^{-2}}$, which would correspond to less than a tenth of a micron grain sizes. Under constant strains, however, we observed that the stresses relax in a few hundredths of a second without any permanent stress (see figure 3). This indicates that there are no permanent bonds or grain boundaries between the columns (or at least they are relatively weak). For this reason we think that the measured viscoelastic behaviours under periodical shear strains are due to entanglements between the side chains of neighbouring columns as observed by X-ray studies [5]. Just as in polymer melts, the entanglements generate

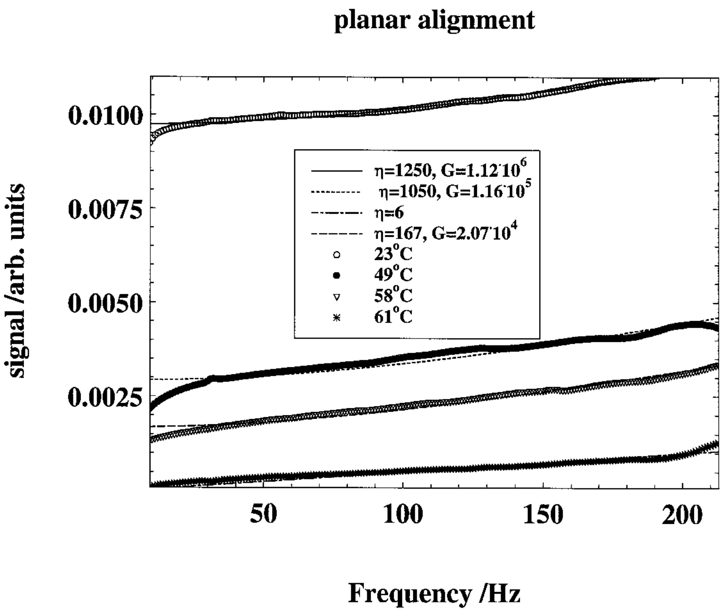


Figure 8. Frequency dependences of the forces transmitted to the lower plate at different temperatures: lines are fits using equation (8).

temporary bonds between the columns. The relaxation time $\tau_r \sim \eta/G$ corresponds to the lifetime of molecular entanglements [20]. Strains acting longer than τ_r are able to suppress the entanglements between columns resulting in a completely viscous behaviour. At frequencies larger than the relaxation frequency ($\omega_r = 1/\tau_r$), entanglements lead to rubber-like elastic responses. The relatively broad linear viscoelastic range and the shear thinning at higher strains are also analogous to those of polymer melts with temporary entanglements.

To summarize, we have presented a new method to align columnar liquid crystals in both planar and homeotropic geometrical configurations. We have measured the shear elastic modulus and the viscosity values of a pyramidal columnar liquid crystal both normal and parallel to the columnar axis. It was observed that above frequencies of 50 Hz the sample behaves as a Maxwell solid characterized by constant G and η values. The shear modulus is in the range 10^6–10^7 N m^{-2}, typical for rubbers. The viscosity values are in the range of 10^3–10^4 Pa s. These are typical for systems (e.g. melts of low-density polymers) described by temporary network models [20]. Accordingly, the temporary entanglements between the side chains of the bowl-shaped molecules, as concluded from X-ray studies [5], can qualitatively explain the observations.

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References

[1] Chandrasekhar, S., Sadishiva, B. K., and Suresh, K. A., 1977, *Pramana*, **9**, 471.

[2] Fontes, E., Heiney, P. A., Ohba, M., Haseltine, J. N., and Smith, A. B., 1988, *Phys. Rev. A*, **37**, 1329.

[3] Safinya, C. R., Liang, K. S., Varady, W. A., Clark, N. A., and Anderson, G., 1984, *Phys. Rev. Lett.*, **53**, 1172.

[4] Fontes, E., Heiney, P. A., and de Jeu, W. H., 1988, *Phys. Rev. Lett.*, **61**, 202.

[5] Poupko, R., Luz, Z., Spielberg, N., and Zimmermann, H., 1989, *J. Am. chem. Soc.*, **111**, 6094.

[6] De Gennes, P. G., and Prost, J., 1992, *The Physics of liquid crystals*, 2nd Edn (Clarendon Press).

[7] Cagnon, M., Gharbia, M., and Durand, G., 1984, *Phys. Rev. Lett.*, **53**, 938.

[8] Gharbia, M., Cagnon, M., and Durand, G., 1985, *J. Phys. Lett.*, **46**, L-683.

[9] Levelut, A. M., 1983, *J. chim. Phys.*, **80**, 149.

[10] Sallen, L., Oswald, P., Geminard, J. C., and Malthete, J., 1995, *J. Phys. II Fr.*, **5**, 937.

[11] Gharbia, M., Othmann, T., Gharbi, A., Destrade, C., and Durand, G., 1992, *Phys. Rev. Lett.*, **68**, 2031.

[12] Prost, J., 1990, *Liq. Cryst.*, **8**, 123.

[13] Zimmermann, H., Poupko, R., Luz, Z., and Billard, J., 1985, *Z. Naturforsch*, **40a**, 149.

[14] *Elasticity, plasticity and structure of matter*, 1971, edited by R. Houwink and H. K. Decker (London: Cambridge University Press).

[15] Chandrasekhar, S., 1998, *Handbook of Liquid Crystals*, Vol. 2b, edited by D. Demus, J. Goodby, G. W. Gray, H. W. Spiess and V. Vill (New York: Wiley VCH), Chap. VIII.

[16] Goldfarb, D., Luz, Z., and Zimmermann, H., 1981, *J. Phys. (Fr.)*, **42**, 1303.

[17] Vauchier, C., Zann, A., Le Barny, P., Dubois, J. C., and Billard, J., 1981, *Mol. Cryst. liq. Cryst.*, **66**, 103.

[18] Itoh, I., Tanaka, A., Fukuda, F., and Miyamoto, T., 1991, *Liq. Cryst.*, **9**, 221.

[19] Bock, H., and Helfrich, W., 1992, *Liq. Cryst.*, **12**, 697.

[20] Larson, R., 1987, *Constitutive Equations for Polymer Melts and Solutions* (Boston: Butterworths).