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## Liquid Crystals

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### Viscoelastic coefficients of glass-forming nematics

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## Viscoelastic coefficients of glass-forming nematics

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In this paper, we report measurements of the viscoelastic properties of nematic liquid crystals which exhibit a glass transition in the nematic phase. We have studied the Freedericksz transition in planar cells with a magneto-optical method.  $K_1$  was determined from the critical field, and the rotational viscosity,  $\gamma_1$ , from the response time for the director orientation by the external field. We found a temperature dependence of  $\gamma_1$  of the Vogel type, with absolute values ranging over several orders of magnitude, and  $K_1$  values similar to those of conventional thermotropic low molar mass nematics.

### 1. Introduction

We report here an experimental study of the viscoelastic properties of low molar mass thermotropic nematics which can be supercooled into a glassy state. Their elastic properties are comparable to those of ordinary low molar mass nematic liquid crystals, but dynamics show some interesting features. Although the measurements were performed well above the glass transition, viscosities become significantly higher than those of conventional nematics such as 4,4-dimethoxyazoxybenzene. The reorientation time of the director in external fields increases by several orders of magnitude.

For further investigation of the Freedericksz transition in planar sandwich cells we used the methods of Deuling [1] and Pieransky [2]. The ratio  $K_1/\Delta\chi$  was determined from the Freedericksz magnetic field and  $K_3/K_1$  came from the optical transmission versus field curve.  $\gamma_1/\Delta\chi$  was determined from the director relaxation after switching the field on or off. The anisotropic magnetic susceptibility was calculated using a group additivity scheme [3]. We have also measured the order parameter  $S(T)$  by  $^1\text{H}$  NMR spectroscopy. This allows an estimate of the  $\Delta\chi(T)$  curve to be made and of absolute  $K_1$  and  $\gamma_1$ ; these can be fitted to theoretical models.

### 2. Experimental

Figure 1 shows the experimental set-up. The cell is located between crossed polarizers with the director orientation at the glass surface among the  $45^\circ$  direction to the polarizer axes. The planar surface orientation of the director was obtained by SiO oblique evaporation on to the glass plates. For positive electric ( $\Delta\epsilon$ ) or magnetic ( $\Delta\chi$ ) anisotropy of the nematic, the director field  $\mathbf{n}=\mathbf{n}(z,t)$  in the cell, with  $z$  being the coordinate normal to the glass plates, can be changed by external fields perpendicular to the cell surface using field strengths above the Freedericksz threshold. Monochromatic light transmitted through the sample was recorded as a function of the

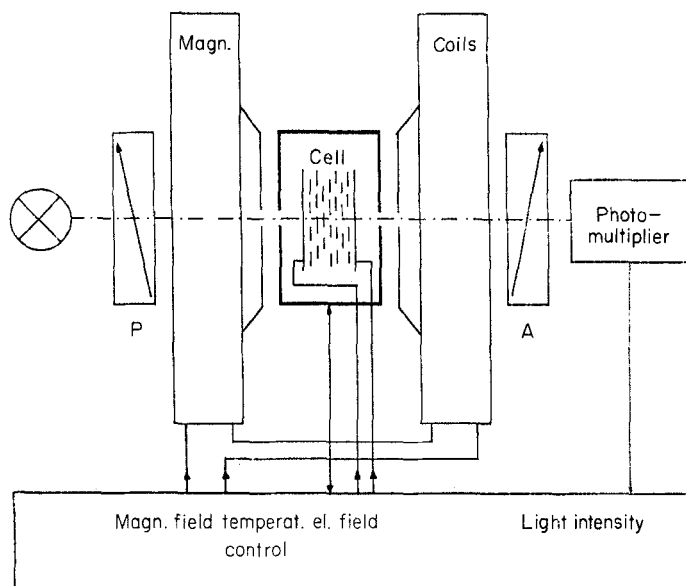


Figure 1. The experimental set up.

applied field strength for the determination of  $K_1$ , and as function of time after switching the field on/off for the  $\gamma_1$  measurements. The transmitted light intensity is sensitive to the phase difference between ordinary and extraordinary waves in the cell and can be used to determine  $\mathbf{n}(z, t)$  [1, 2]. Both samples investigated have a negative dielectric anisotropy [4], and so we could not use electric fields to switch the planar cells. All measurements were performed in an external magnetic field. The rise/decay time of the magnetic field (iron core magnet) was about 1 s and could be neglected in the calculation of the director relaxation times when these are of the order of minutes or more.

Figure 2 shows the chemical composition of the samples E2 and E2C1; both samples are four component eutectic mixtures. Substance 1 was synthesized by Weissflog *et al.* [5, 6], substances 2–5 were prepared by Schäfer *et al.* [7]. Their nematic–isotropic transition extends over a temperature interval of several Kelvin for each sample, as given in figure 2. The nematic phase could be easily supercooled below room temperature because the crystallization is strongly hindered.

The molar anisotropic diamagnetic susceptibilities of both samples were estimated using a group additivity scheme [3]

$$\chi_a^M = 1.34 \times 10^{-8} \text{ m}^3/\text{mol} \quad (\text{E2})$$

and

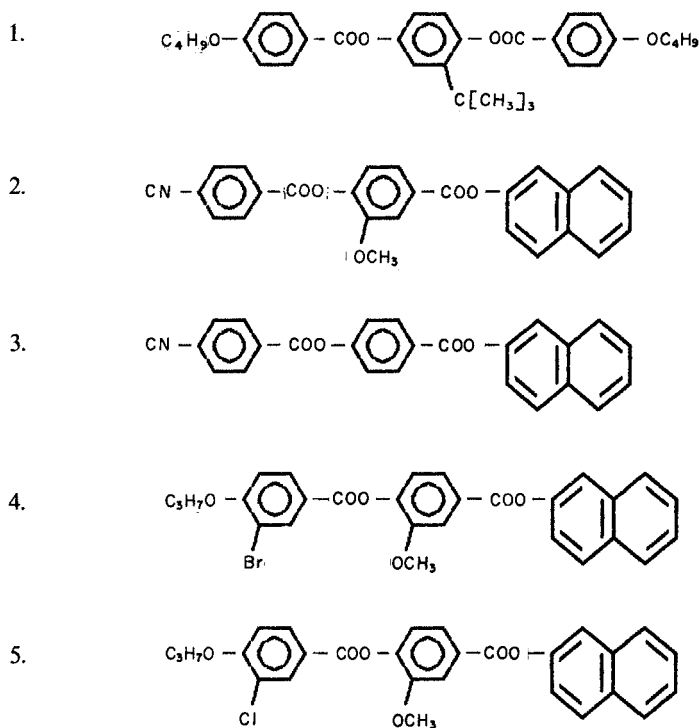
$$\chi_a^M = 1.28 \times 10^{-8} \text{ m}^3/\text{mol} \quad (\text{EC21})$$

The relevant quantity  $\Delta\chi$ , the volume susceptibility anisotropy, can be calculated from

$$\Delta\chi = S\chi_a^M\rho/M, \quad (1)$$

where  $M$  is the molar mass,  $\rho$  is the mass density and  $S$  the second rank orientational order parameter. The mass density assumed to be  $1 \text{ g/cm}^3$ , and so thermal expansion

## Components



## Mixtures

Mixture	Component/mol %					$T_{NI}/K$	$T_g/K$
	1	2	3	4	5		
E2	70	9	12	9	—	392–398.5	285
E2Cl	69.1	8.9	12.1	—	9.9	390–404	284

Figure 2. Chemical composition and transition temperatures for the mixtures investigated.

was neglected. For simplicity, we have assumed a single order parameter, and  $\Delta\chi$  is, in this approximation, proportional to  $S$ . The temperature dependence of the order parameter was determined by proton NMR spectroscopy. The lineshape of the proton spectra is governed by dipole-dipole coupling of the proton spins. As long as the intramolecular motions and geometry are constant, the lineshape,  $F(\omega)$ , scales with the order parameter

$$F(\omega) = [1/S(T)]F_0(\omega/S(T)), \quad (2)$$

where  $F_0(\omega)$  represents the general shape of the  $^1\text{H}$  NMR spectrum.  $S(T)$  can be determined from the experimental spectra at different temperatures apart from a temperature independent factor. The absolute value of the order parameter is found from the splitting of the two peaks in the spectrum which are assigned to the pair of ortho protons. The spectral shape does not change over a wide temperature range (from the isotropic-nematic transition above 380 K down to about 315 K), thus the

temperature dependence of the frequency splitting is equivalent to that of the scaling factor determined from equation (2), although less accurate. Figure 3 shows the proton NMR spectra of E2 at different temperatures, and figure 4 gives the order parameter as a function of temperature for both mixtures. On the right hand scale of figure 4, the corresponding values of  $\Delta\chi$  are indicated.

### 3. Theory

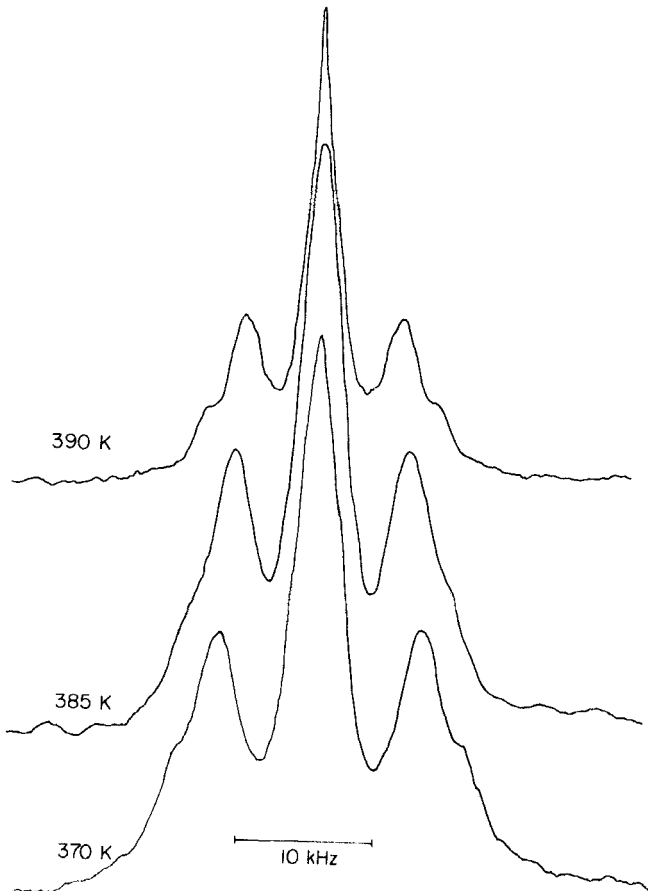
In samples with strong planar anchoring of the director at the glass surface, stable director deformations in the cell exist only above the critical fields

$$B_c = \pi/d(K_1\mu_0/\Delta\chi)^{1/2} \quad \text{or} \quad U_c = \pi(K_1/\epsilon_0\Delta\epsilon)^{1/2}. \quad (3)$$

The dynamics of these deformations is determined from the equilibrium of viscous, elastic and electromagnetic torques on the director. We give the solutions for magnetic fields here. In the limits of small deformations (near  $B_c$ ) flow coupling can be neglected in planar cells, and the small angle approximation

$$\gamma_1 \partial\theta/\partial t = K_1 \partial^2\theta/\partial z^2 + \Delta\chi/\mu_0 \cdot B^2(\theta - 2/3\theta^3) \quad (4)$$

can be used, where  $\theta(z, t)$  is the angle between the surface orientation of the nematic and the director at location  $z$ . Strong surface anchoring requires  $\theta(0, t) = \theta(d, t) = 0$ , where  $d$



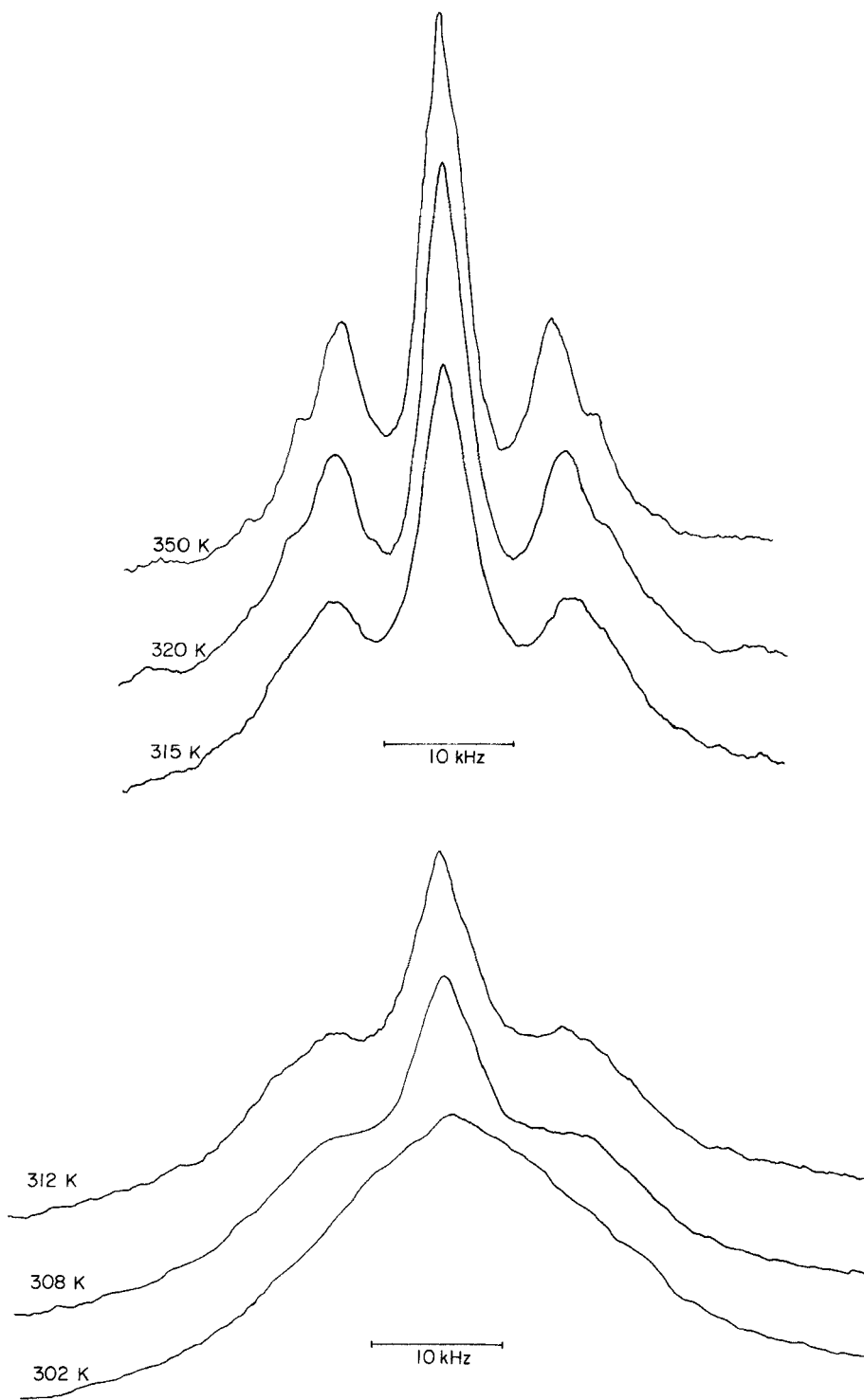


Figure 3. The proton NMR spectra of E2 at different temperatures.

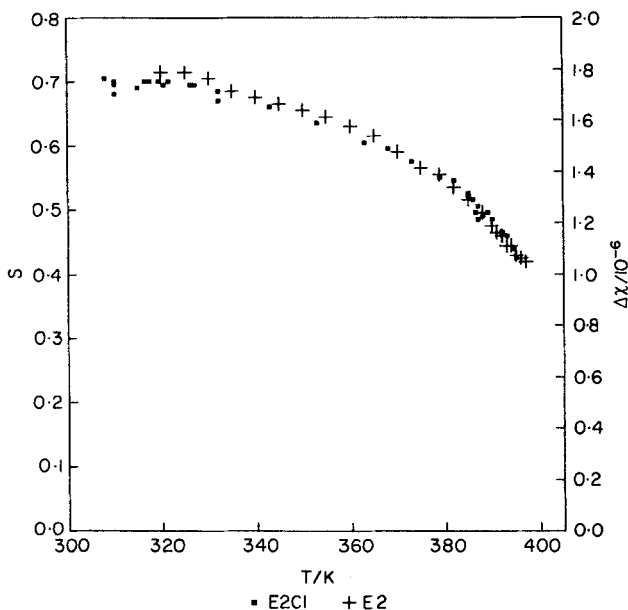


Figure 4. The temperature dependence of the second rank order parameter,  $S$ , measured by proton NMR. The diamagnetic susceptibility anisotropy scale on the right hand is based on the calculations with  $\Delta\chi_0 = 2.5 \times 10^{-6}$ .

is the cell thickness. Restriction to the lowest mode  $\theta(z, t) = \theta_M(t) \sin(\pi z/d)$  yields analytic solutions for the time dependence of the maximum deformation angle  $\theta_M$  of the director at  $z = d/2$  [2].

### 3.1. Switching the field on from zero to $B$ at time $t = 0$

$$\theta_M^2(t) = \theta_M^2(\infty) / [1 + (\theta_M^2(\infty) / \theta_M^2(0) - 1) \exp(-2t/\tau)]. \quad (5a)$$

This corresponds to an exponential increase of the deformation and subsequent exponential saturation with the time constant

$$\tau = \gamma_1 d^2 / (K_1 \pi^2 B_c^2 / (B^2 - B_c^2)) = \tau_0 B_c^2 / (B^2 - B_c^2). \quad (5b)$$

### 3.2. Switching the field off from $B$ to zero at time $t = 0$

$$\theta_M^2(t) = \theta_M^2(0) \exp(-2t/\tau_0) \quad (6a)$$

corresponding to an exponential decay of the director deformation with the characteristic time constant

$$\tau_0 = \gamma_1 d^2 / (K_1 \pi^2). \quad (6b)$$

The intensity of transmitted light through the cell as function of time

$$I = I_0 \sin^2(\pi l(t)/\lambda), \quad (7)$$

where  $\lambda$  is the wavelength, is determined by the optical path difference  $l$  between the ordinary and extraordinary waves in the cell. It depends upon the cell thickness, the

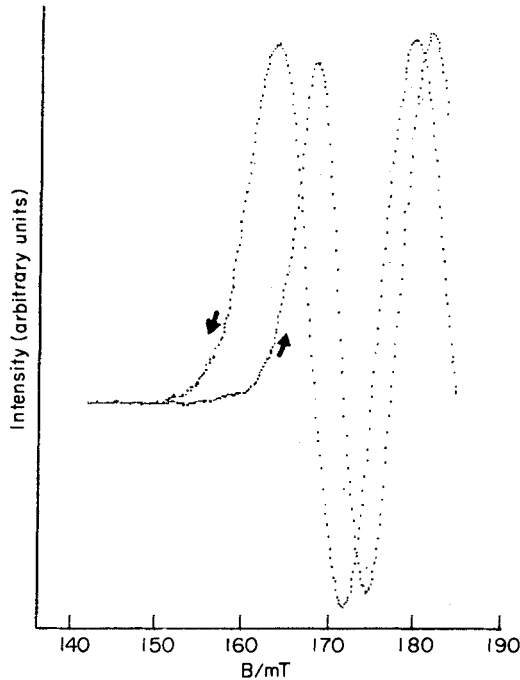


Figure 5. The hysteresis of the intensity versus time at low temperatures for a slow field scan (0.015 mT/s).

refractive indices  $n_e$  and  $n_o$ , and upon  $\mathbf{n}(z, t)$ . For small deformations,  $\theta_M^2(t)$  is proportional to  $l_{\max} - l(t)$ , ( $l_{\max} = l(\theta_M \equiv 0)$ ). The ratio  $\gamma_1/K_1$  is found from  $\tau_0$  by fitting experimental transmission curves to equation (7) using equations (5) and (6), after the field is switched on or off.

The elastic constant  $K_1$  was calculated from the critical field  $B_c$  according to equation (3), while the field was quasistatically swept in the experiment. At low temperatures, the sample is very viscous and the transmission curves show a hysteresis, if the field is swept through  $B_c$  in different directions. The response times of the director are very large then, and it is impossible to keep the field sweep quasi-static; figure 5 shows a corresponding experimental curve. Nevertheless,  $B_c$  can be determined from both up and down sweep curves. We have solved the equation of motion for the director numerically, and the hysteresis was fitted with properly chosen  $K_1$  and  $\gamma_1$  and known sweep rate.

#### 4. Results and discussion

The temperature dependence of the elastic constant  $K_1$  of the samples is shown in figure 6. Both the order of magnitude as well as the temperature and order parameter dependence are comparable to ordinary low molar mass nematics.

Using the  $n_e$  and  $n_o$  data measured by Schulze [18] (see figure 7), the ratio  $K_3/K_1$  was also determined from the static deformations using the Deuling procedure [1]. The  $K_3$  data are of lower accuracy than  $K_1$  in particular at low temperatures because of the hysteresis in the transition curves which influences the position of the extrema in the quasi-static transmission curve. However,  $K_3$  is found to be greater but of the same order of magnitude as  $K_1$  (see figure 8).



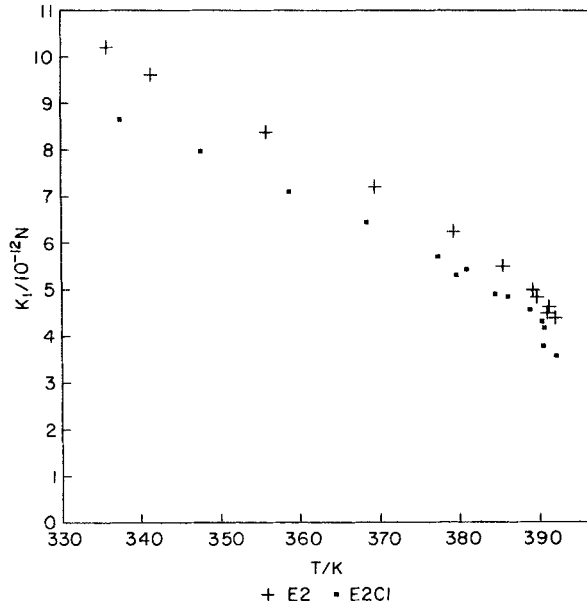


Figure 6. The temperature dependence of the splay elastic constant  $K_1$  of mixtures E2 and E2Cl.

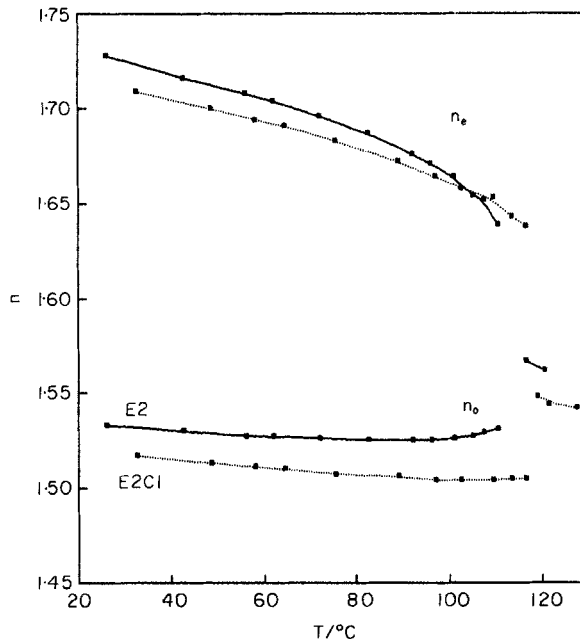


Figure 7. The refractive indices  $n_e$  and  $n_o$  of E2 and E2Cl.

Figures 9 and 10 show the experimental ratios  $\gamma_1/\Delta\chi$  versus temperature. Taking into account the  $\Delta\chi$  data in equation (1), the absolute values of the rotational viscosity range from 0.17 Pa s near the clearing point to more than 2400 Pa s at the lowest temperatures which were accessible to the experiment. Below 315 K it was not possible to determine  $\gamma_1$  because of increasingly large relaxation times.

The temperature dependence of  $\gamma_1$  was fitted to several models. In particular, we used an equation of the Vogel–Fulcher–Tamman type [8–11], with an additional order parameter dependent pre-exponential factor which accounts for the nematic order [12–15]

$$\gamma_1 = AS^\alpha \exp [B/(T - T_0)], \quad \alpha = 1, 2 \quad (8)$$

and an order parameter independent term  $B$ . The best agreement was found with  $\alpha = 2$ , although it is difficult to discriminate between  $\alpha = 1$  and 2 within the experimental accuracy. The pre-experimental factor  $S^\alpha$  influences the curve mainly in the vicinity of the clearing interval. The choice of  $T_0$  in equation (8) determines the form of the temperature dependence at low temperatures. We should be aware that the temperature dependence of  $\gamma_1$  may be more complex, in particular, an order dependence of  $B$  is discussed by Diogo and Martins [12], and the exponential might be split into two terms containing the thermal activation and free volume contributions. As we have not measured the thermal expansion and mass density of the samples, we were not able to relate the experimental data to these physical quantities and so we have preferred equation (8) which gives a very satisfactory fit of the experimental data with few parameters.

As  $\Delta\chi (= S\Delta\chi_0)$  is linearly related to the order parameter according to equation (1), with the temperature independent factor  $\Delta\chi_0 \approx 2.5 \times 10^{-6}$ , the Vogel–Fulcher–Tamman equation with  $\alpha = 1$  gives a straight line in the  $\ln(\gamma_1/\Delta\chi)$  versus  $1/(T - T_0)$  plot,

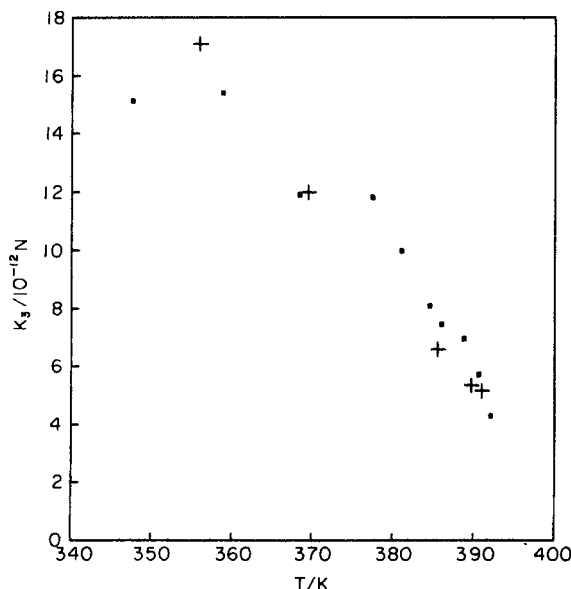


Figure 8. The temperature dependence of the bend elastic constant  $K_3$  for mixtures E2 (+) and E2Cl (●).

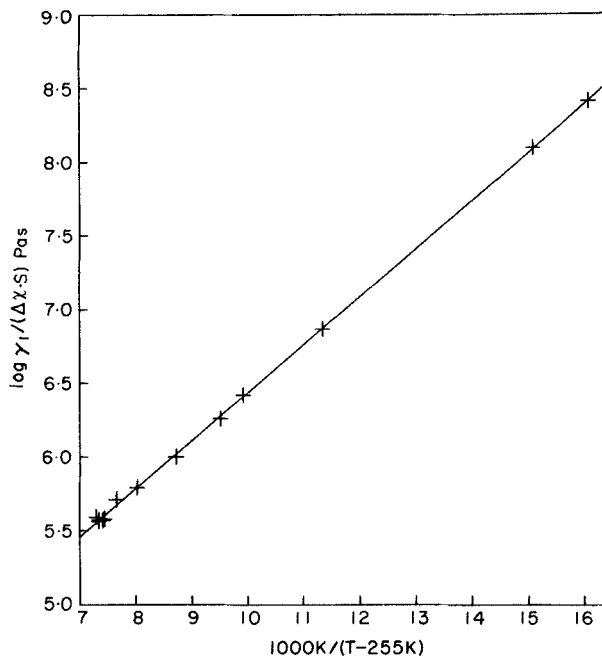


Figure 9. The temperature dependence of the rotational viscosity of E2.  $\gamma_1/\Delta\chi$  is the measured quantity that was divided by the order parameter  $S$  determined by NMR in this figure to yield a straight line in the  $\gamma_1/S^2$  versus  $1/(T-T_0)$  plot.

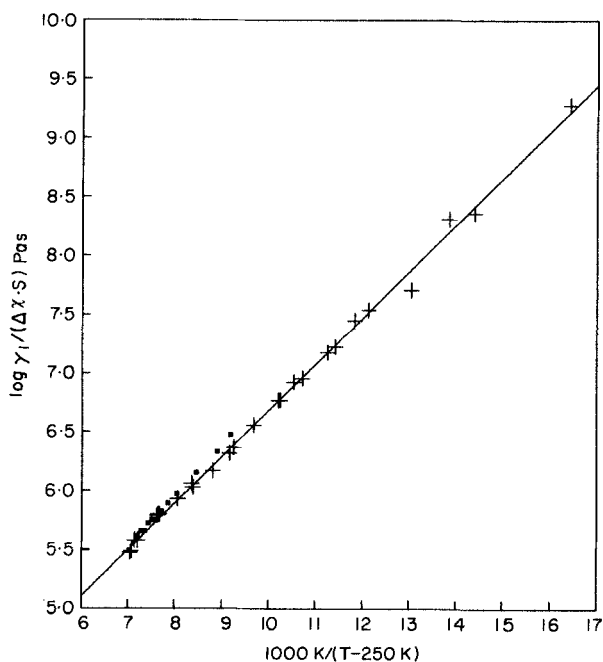


Figure 10. The temperature dependence of the rotational viscosity of E2Cl. (See comment to figure 9, dots and crosses refer to different samples.)

while  $\alpha=2$  gives a straight line for the plot of  $\ln(\gamma_1/(\Delta\chi S))$  versus  $1/(T-T_0)$  (see figures 9 and 10). The factors  $B$  in the exponent determined from these fits are

$$B=1025 \text{ K}, \quad T_0=255 \text{ K} \quad (\text{E2}, \alpha=1),$$

$$B=748 \text{ K}, \quad T_0=255 \text{ K} \quad (\text{E2}, \alpha=2)$$

$$B=1060 \text{ K}, \quad T_0=250 \text{ K} \quad (\text{E2Cl}, \alpha=1)$$

$$B=900 \text{ K}, \quad T_0=250 \text{ K} \quad (\text{E2Cl}, \alpha=2).$$

The onset glass temperature is 285 K (taken as the lower edge of the threshold in the DSC curve). Extrapolating the  $\gamma_1$  data to this temperature, we expect a rotational viscosity of the order of  $4 \times 10^8$  Pa s. This would correspond to relaxation times for the director configuration of about  $10^8$  s in a magnetic field of about 1 T.

Additional shear viscosity measurements for E2 were performed with a commercial viscosimeter, RHEOTEST 2 [16]. In this experiment, the friction of a cone rotating in the liquid crystal is determined. Although there are no definite boundary conditions for the director field, we can assume that the director is aligned tangentially by the rotational motion (in flow direction), and the measured quantity may be assigned approximately to the Miesowicz viscosity  $\eta_1$  [17]. The absolute values found for this quantity are lower than the  $\gamma_1$  data (see figure 11). If a fit similar to equation (4) is performed, the resulting  $T_0$  and  $B$  coincide within the experimental error limits ( $T_0=247$  K, see [4]).

Furthermore, some information on the internal molecular motions can be deduced from the NMR measurements. The spectra reveal a dramatic change below about 315 K. Typical proton spectra are given in figure 3. The lines are broadened during cooling in the critical temperature range. In principle, two effects could be responsible for this effect, a distribution of the director orientations in the sample or a slowing of the molecular motions. We exclude the first for the following reasons. The reorientation

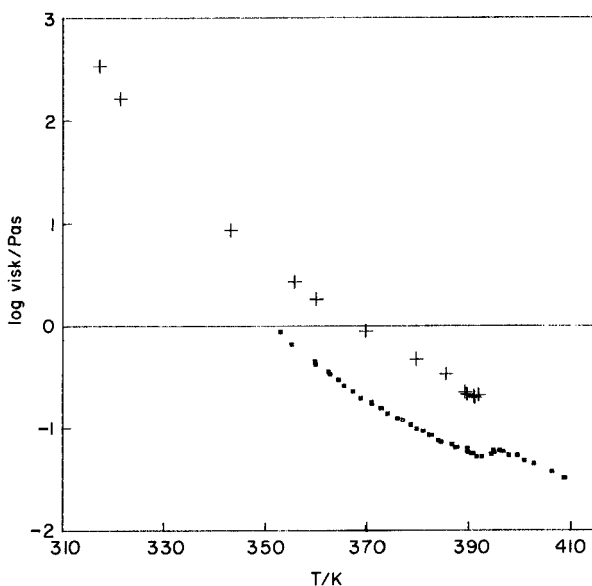


Figure 11. The temperature dependence of the rotational (+) and shear (■) viscosities of E2.

time of the director below 315 K is very large as seen from the viscosity data, while the spectra are broadened immediately. Moreover, the original lineshape is reestablished after heating the sample again. On the other hand, dielectric relaxation data for sample E2 measured by Kresse [4] support the proposition that the correlation time of molecular reorientations about the short axes crosses the time domain of the proton spectra. Above this temperature range, where these motions are fast on the NMR time scale, the proton spectra have a temperature independent shape (see figure 3). The critical slowing down of the reorientation process leads to the broadening of the spectra because some intramolecular dipolar couplings are no longer averaged.  $^{13}\text{C}$  NMR measurements confirm this conclusion. While the proton decoupled  $^{13}\text{C}$  spectra consist of separated sharp lines at high temperatures in the nematic phase, these lines vanish completely in roughly the same temperature range as found for  $^1\text{H}$  NMR. We can explain this by the same effect. First, the proton decoupling r.f. power becomes insufficient at low temperatures where the  $^{13}\text{C}$ - $^1\text{H}$  dipolar coupling is less motionally averaged. Secondly, several  $^{13}\text{C}$  positions become inequivalent if the averaging process is slow on the NMR time scale. The lines are smeared out and disappear, too.

We have shown the viscous behaviour of two low molar mass compounds with unusually high viscosities in the nematic state. At low (room) temperatures, the dynamic range typical of polymeric liquid crystals is reached. Molecular motions become very slow already in the nematic phase, with a dramatic influence on the NMR lineshapes. The latter effect could be studied in detail using a model of motional averaging of NMR spectra (e.g. [19]) to reveal the correlation time temperature dependence of the processes involved.

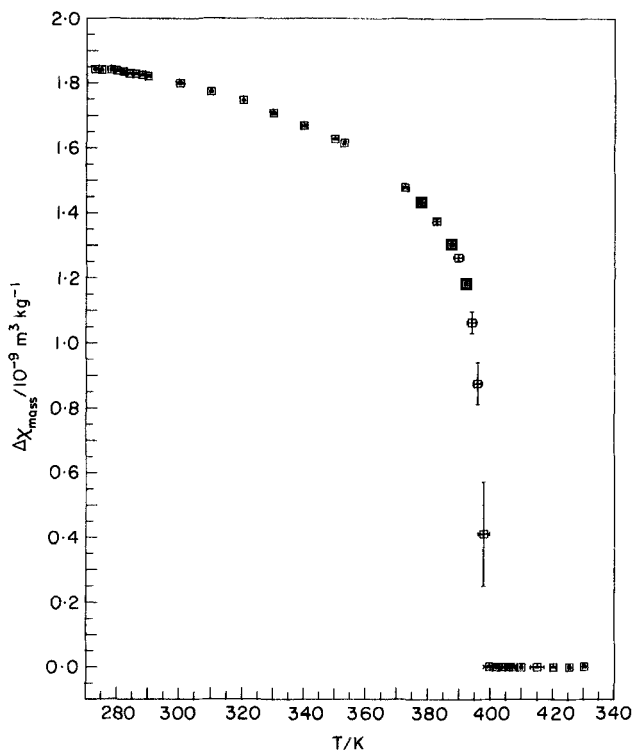


Figure 12. The temperature dependence of  $\Delta\chi$  for E2 measured by SQUID susceptometry.

The authors are much indebted to Dr. W. Weissflog and Dr. W. Schäfer for carrying out the synthesis of compounds 1–5, to Dr. H. Schulze who provided the refractive index data and to Professor H. Schmiedel for critical discussions.

#### Addendum

After preparation of the manuscript, we received experimental data for the diamagnetic susceptibility anisotropy of sample E2 measured by SQUID susceptometry. The temperature dependence of  $\Delta\chi$  is given in figure 12. Our estimated data (see figure 4) are in good agreement with these results. That means that the order parameter dependence of the form  $\Delta\chi = \Delta\chi_0 S$  is confirmed and the value of  $\Delta\chi_0$  calculated with the group additive system is quite realistic.

We are very indebted to Dipl.-Ing. Stephan Türk at the Max-Planck-Institut in Mainz for performing the SQUID measurements.

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