Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dielectric relaxation of liquid crystal molecules in anisotropic confinements

R. A. M. Hikmet[a]; B. H. Zwerver[a]
[a] Philips Research Laboratories, Eindhoven, The Netherlands

To cite this Article Hikmet, R. A. M. and Zwerver, B. H.(1991) 'Dielectric relaxation of liquid crystal molecules in anisotropic confinements', Liquid Crystals, 10: 6, 835 — 847
To link to this Article: DOI: 10.1080/02678299108036458
URL: http://dx.doi.org/10.1080/02678299108036458

LIQUID CRYSTALS, 1991, VOL. 10, NO. 6, 835–847

Dielectric relaxation of liquid crystal molecules in anisotropic confinements

by R. A. M. HIKMET* and B. H. ZWERVER
Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands

(*Received 15 May 1991; accepted 20 July 1991*)

The dielectric relaxation of the liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (K15) in the presence of an anisotropic network has been studied. Anisotropic networks containing K15 molecules were prepared by *in situ* polymerisation of liquid-crystalline diacrylate molecules in a mixture containing K15. By changing the network concentration, the effect of the network molecules on the behaviour of the K15 molecules, which were not chemically attached to the network, was investigated. With increasing network concentration it was found that the mean relaxation times of K15 molecules shifted to lower temperatures and that their distribution became broader. The activation energy associated with the relaxation, however, remained almost constant before showing some increase at high network concentrations.

1. Introduction

The behaviour of liquid crystal molecules at interfaces is of great academic as well as technological interest. The industrial interest originates from the fact that orientation-inducing layers are used in most liquid crystal electro-optic devices and these ensure their optimum performance. At the same time the orientation and the phase behaviour of liquid crystal molecules under restrictions which differs from that in the bulk are also of fundamental interest. In numerous theoretical [1–3] and experimental [4–7] studies the interaction of the molecules with solid interfaces has been described. Some of these studies deal with the director orientation at the interface in electric and magnetic fields [2–6] whereas others deal with phase transitions in small confinements [1, 7]. At an orienting surface the interaction between the nematic phase is frequently described in the framework of continuum theory [8] by the polar anchoring energy which is the energy required to turn the director at the interface away from its preferred orientation. Experimental as well as theoretical evidence indicates that the contributions to the anchoring energy come from the bulk elasticity as well as a specific surface term. In their studies of the temperature dependence of the anchoring strength, Yokoyama *et al.* [6] found that on a planar orienting SiO_x surface the orientational order of the liquid crystal molecules was different to that in the bulk. In his studies Sheng [4] investigated a semi-infinite sample of a nematic in contact with a wall where he found that a second, first order phase transition occurs at a temperature slightly above the bulk nematic–isotropic transition temperature. He also observed that the orientation of the molecules persists above the second transition temperature.

In their theoretical study Poniewierski *et al.* [1] discussed the nematic–isotropic transition for a system placed between plates. They predicted that the transition temperature may increase or decrease depending on the nature of the boundary

---

* Author for correspondence.

conditions. They also found that in all cases for sufficiently small thicknesses the transition terminates at a point above which the nematic and the isotropic phases are no longer distinct. In our recent study [9] the behaviour of a liquid crystal in anisotropic environments was examined. Liquid-crystalline diacrylates were polymerized in the nematic state in the presence of liquid crystal molecules without reactive groups. In this way anisotropic gels and plasticized networks were produced. The size of the anisotropic confinements of the liquid crysal could be adjusted by varying the amount of cross-linked molecules within the system. In accordance with the study of Poniewierski *et al.* [1] it was shown that with increasing network concentration a decreasing percentage of the liquid crystal molecules showed a first order nematic–isotropic transition and above a certain concentration the transition was totally absent. Here the dielectric relaxation behaviour of liquid crystal molecules and their response to electric fields in the presence of an anisotropic network is described.

2. Experimental

The molecular structure of the liquid crystal diacrylate C6M is shown in figure 1 together with that of K15 (BDH, Poole) without reactive end groups. The mixtures of the molecules were provided with 2 per cent w/w photoinitiator Irgacure 651 (Ciba Geigy). Dielectric measurements were carried out using a Hewlett-Packard 4194A Impedance/Gain-Phase analyser and a Micromet Eumetric system III dielectric spectrometer in the parallel plate mode. Alignment of the nematic was achieved in electric fields and was permanently fixed by photopolymerization of the diacrylates initiated using a high pressure mercury lamp ($10\,\mathrm{mW\,cm^{-2}}$). Dynamic mechanical thermo analysis (DMTA) was performed by Polymer Laboratories DMTA equipment in the bending mode. Threshold voltages were measured using a microscope equipped with a photomultiplier.

3. Results and discussion

Here it is appropriate to deal with anisotropic networks containing liquid crystal molecules in two categories: (i) networks where some of the liquid crystal undergoes a first order nematic–isotropic transition (anisotropic gels) and (ii) networks where no first order transitions are observed (plasticized networks). These categories will be dealt with separately.

3.1. *Anisotropic gels*

Dielectric relaxation of low mass nematics including K15 has been described in various articles [10–12]. The highly elongated cyanobiphenyl molecules move around their long and short axes at totally different rates. The loss maximum for the movement

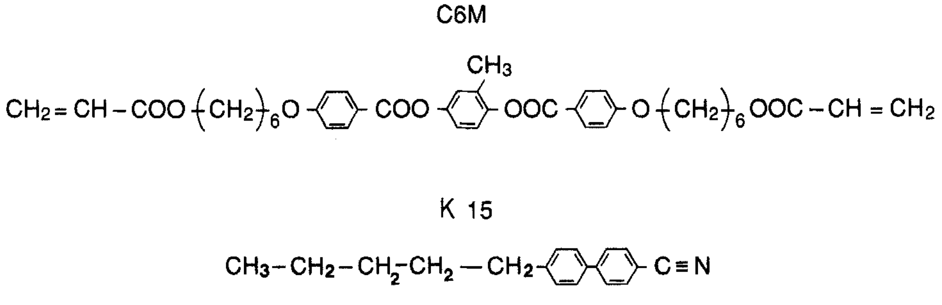


Figure 1. The liquid-crystalline diacrylate and K15.

around the long axis appears in the GHz range, whereas the movement around the short axis gives a loss maximum in the MHz range. In our studies we have investigated the low frequency relaxation of K15 molecules, which is related to their motion around the short axis. In figure 2 the real part of the dielectric constant (ε') is plotted at 25°C as a function of frequency for a gel containing 90 per cent w/w K15 (10 per cent network) for two different orientations of the molecules with respect to parallel plates. It can be seen that in the case where the preferred orientation of the molecules is perpendicular to the substrate, ($\varepsilon'_{\parallel}$), the decrease is much larger than in the case where the molecular orientation is uniaxially planar ($\varepsilon'_{\perp}$). The relaxation associated with the drop in $\varepsilon'_{\parallel}$ is expected to be due largely to the motion about the short axis of K15 molecules with a large dipole along their long axis. C6M molecules with a negative dielectric anisotropy were not expected to make a sizeable contribution at these high frequencies especially in the cross-linked state. In the rest of the experiments in order to study the effect of the network molecules on the motion of the K15 molecules about the short axis we used samples where the average orientation of the molecules was along the applied electric field. Figure 3 shows $\varepsilon'_{\parallel}$ measured at room temperature as a function of frequency for gels containing various amounts of network molecules together with K15 containing the photoinitiator. Here it can be seen that the maximum in the loss curve becomes less defined and shifts to lower frequencies as it decreases in magnitude with an increasing amount of the network. We shall deal with these effects separately.

First we wish to discuss the shapes of the loss curves. A broadening of the loss curves is usually associated with the broadening of the spectrum of relaxation times associated with the dispersion. We shall deal with this point in terms of the Cole–Cole function [13] which uses an empirical factor in the dispersion function and takes the form

$$\varepsilon^* = \varepsilon' + i\varepsilon'' = \varepsilon_u + \frac{\varepsilon_r - \varepsilon_u}{1 + (i\omega\tau)^{(1-h)}}, \tag{1}$$

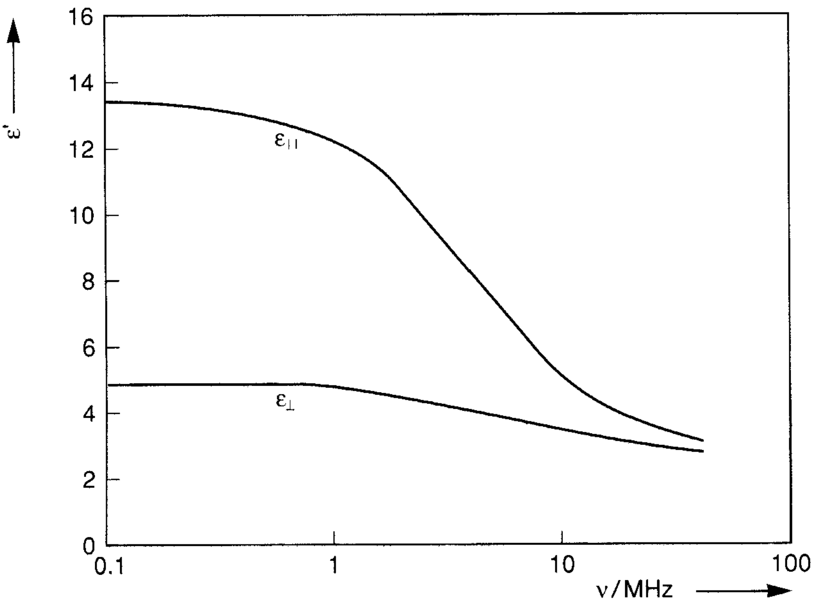


Figure 2. Dielectric permittivity as a function of frequency for a gel containing 10 per cent w/w of the network where the electric field was perpendicular = ⊥, parallel = // to the average molecular orientation.

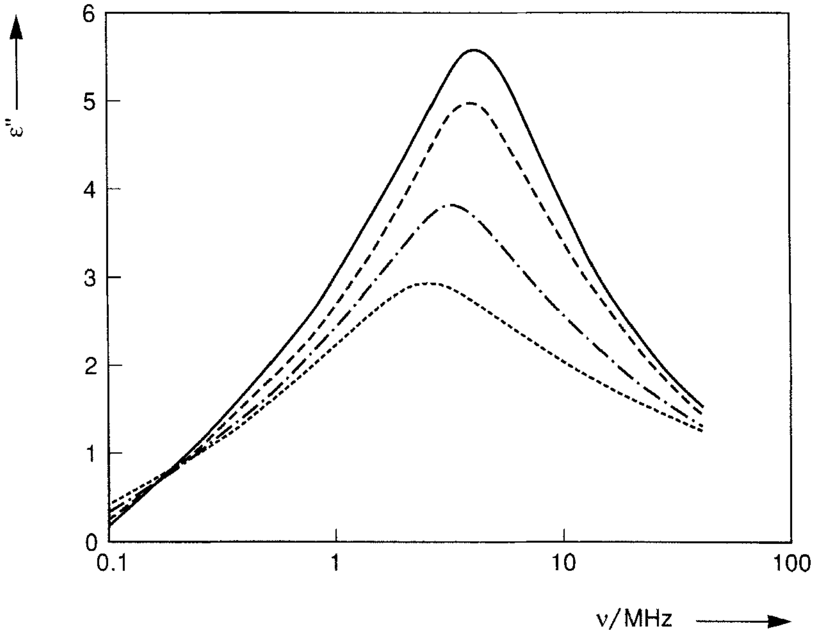


Figure 3. Dielectric loss as a function of frequency for gels containing various amounts of K15 —— = 100 per cent, - - - = 90 per cent, —·— = 80 per cent, ------ = 70 per cent w/w K15.

where ε_r and ε_u are the static and the high frequency permittivities, respectively. In this expression τ represents the mean effective relaxation time of overlapping dispersion processes. The parameter h represents the distribution of the relaxation times and diminishes when a single relaxation time is effective. Cole–Cole arcs for the gels containing various amounts of the network are shown in figure 4. Here it can be seen that for K15 in the absence of the network a semicircle is obtained. This conforms well with earlier observations [12, 14] and shows that the relaxation can be described with a well-defined single relaxation time. As the network concentration increases, the Cole–Cole arcs deviate from being semi-circular and tend to become depressed semicircular arcs indicative of broadening of the distribution of relaxation times associated with the rotation of K15 molecules about their short axes. The plot of the distribution parameter h estimated at room temperature as a function of network concentration is shown in figure 5. Here it can be seen that with increasing network (decreasing K15) concentration the distribution parameter also increases, indicating an increased influence of the network molecules on the relaxation behaviour of the K15 molecules.

The effect of a decrease in the mean relaxation time with increasing network concentration was studied as a function of temperature. The variation of relaxation time with temperature for cylindrical molecules with a dipole moment along the length of the cylinder is best described by the Bauer [15] equation

$$\tau=\frac{2\pi I}{RT^{1/2}}\exp\left(\frac{-\Delta S_B}{T}\right)\exp\left(\frac{\Delta H_B}{RT}\right), \tag{2}$$

where I is the molecular moment of inertia, ΔH_B and ΔS_B are the activation enthalpy and the entropy, respectively. Bauer plots for various gels are shown in figure 6. It can be seen that for K15 molecules in the absence of the network there is a jump in the

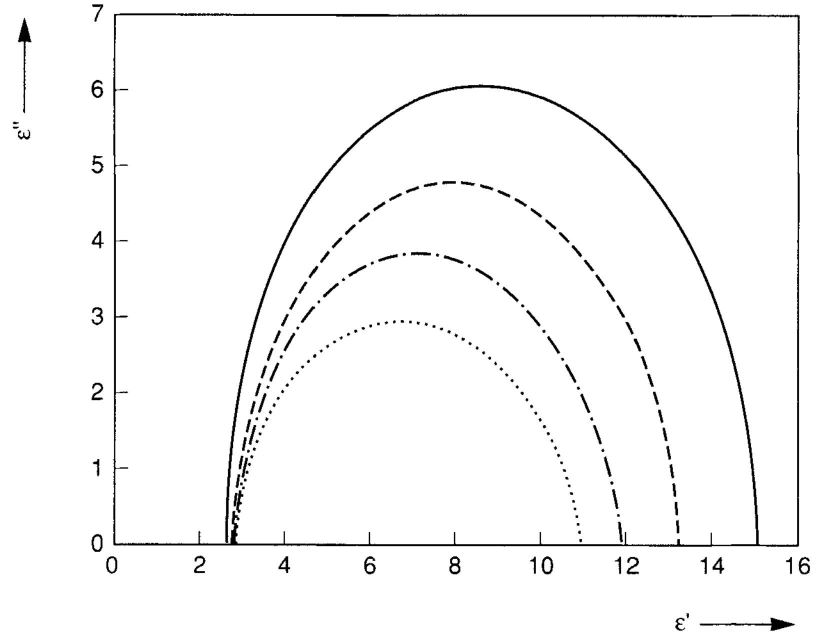


Figure 4. Cole–Cole plots for the dielectric relaxation of K15 molecules in gels containing various amounts of the network. —— = 100 per cent, – – – = 90 per cent, —·— = 80 per cent, ------ = 70 per cent w/w K15.

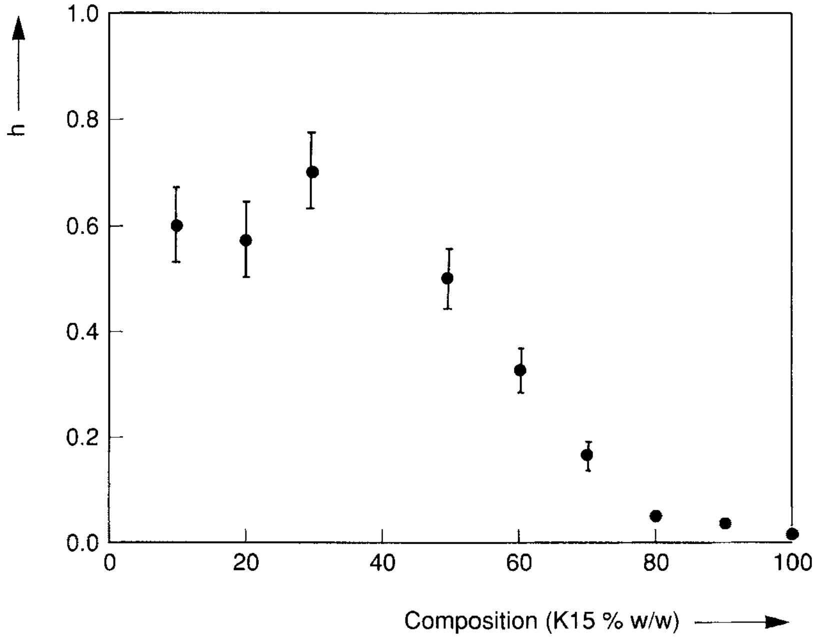


Figure 5. Cole–Cole distribution parameter for the dielectric relaxation of K15 molecules as a function of network concentration.

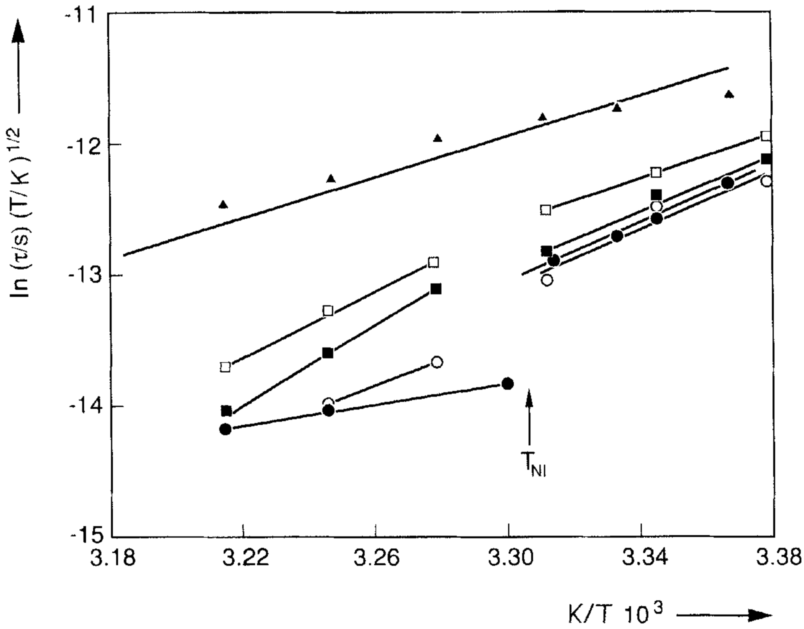


Figure 6. Bauer plots for the relaxation of K15 molecules in gels containing various amounts of K15. ● = 100 per cent, ○ = 90 per cent, ■ = 80 per cent, □ = 70 per cent, ▲ = 60 per cent w/w K15.

relaxation time corresponding to the nematic–isotropic transition temperature (T_{NI}). This discontinuous change is associated with the introduction of the nematic ordering potential. According to the treatment of Martin *et al.* [16], the nematic potential imposes a retardation factor $G_{\parallel}$ on the relaxation time around the short axis $\tau_{\parallel}$

$$\tau_{\parallel} = G_{\parallel}\tau_0, \tag{3}$$

where τ_0 is the relaxation time in the absence of the nematic potential and it is found by extrapolation from the isotropic state.

In figure 6 it can be seen that the discontinuity at T_{NI} decreases rapidly with increasing network concentration. This effect can be related to the existence of two K15 populations of (i) molecules which can undergo first order phase transition, and (ii) molecules which remain oriented above T_{NI} in a gel. In the previous publication [9] it was shown that in a gel containing 90 per cent K15 almost 40 per cent of these molecules do not undergo a first order phase transition at T_{NI} whereas the rest became isotropic. Therefore the relaxation time observed above T_{NI} for this composition is a mean, corresponding to the dispersions for the two populations. For the gel containing 30 per cent network (where 75 per cent of the K15 is bound [9]), the absence of a discontinuity at T_{NI} is probably due to the domination of the dispersion by the bound molecules.

The values of ΔH_B and ΔS_B were calculated from figure 6 with $I = 17{\cdot}5 \times 10^{-44}\,\mathrm{kg\,m^2}$ [10] and are given in table 1. It can be seen that in the absence of the network both ΔH_B and ΔS_B for K15 are higher in the nematic phase than in the isotropic phase. This effect is considered to be due to the nematic potential ΔH_N which imposes a barrier on the motion of the molecules about their short axes. Furthermore, such a motion produces a large disruption on the local order, giving rise to a higher ΔS_B in the nematic phase than in the isotropic phase. Moreover when gels containing

Table 1. Activation energies and entropies for the relaxation of K15 molecules in gels containing various amounts of K15.

K15 conc. (% w/w)	ΔH_B/kJ mol^{-1}	ΔS_B/kJ K^{-1} mol^{-1}
100 (N)	90·8	0·23
100 (I)	34·9	0·05
90 (N)	89·5	0·22
80 (N)	87·1	0·21
70 (N)	90·0	0·22
60 (N)*	92·9	0·24

N = measured below T_{NI}; I = measured above T_{NI}; * = from loss tangent measurements.

various amounts of the network are compared, it can be seen that ΔH_B and ΔS_B remain almost constant with increasing network concentration. In the nematic phase the dispersion is best described by the Debye diffusive equation relating the relaxation time to the bulk viscosity (η) and the nematic potential as follows [14]:

$$\tau \propto \eta G_{\|} \propto \exp\left(\frac{\Delta H_N + \Delta H_{\text{visc}}}{RT}\right). \tag{4}$$

Since ΔH_B remains almost unchanged with increasing network concentration, this indicates that ΔH_N and ΔH_{visc} remain the same as in the bulk. This effect will be discussed further in the section on plasticized networks.

Another effect to be observed in figure 4 is the decrease of ε_r with increasing network concentration. According to Bordewijk [17], dielectic constants are related to the molecular parameters by

$$(\varepsilon_{r\|} - \varepsilon_{u\|}) \frac{\varepsilon_{r\|} + (\varepsilon_{u\|} - \varepsilon_{r\|})\Omega_{\|}}{\varepsilon_{r\|}(\bar{\varepsilon}_{u\|} + 2)^2} = \frac{N\langle \mu_{\|}^2 \rangle g_{\|}}{9\varepsilon_0 kT}, \tag{5}$$

where $\Omega_{\|}$ is the depolarization factor, N the particle density, $\bar{\varepsilon}_u = (2\varepsilon_{u\perp} + \varepsilon_{u\|})/3$ and $\langle \mu_{\|}^2 \rangle$ is related to the dipole moment μ by

$$\langle \mu_{\|}^2 \rangle = \tfrac{1}{3}\mu^2[1 - (1 - 3\cos^2\beta)S], \tag{6}$$

where S is the order parameter and β is the angle between the molecular long axis and the dipole moment and $g_{\|}$ defines the molecular correlations; in the absence of correlations $g_{\|} = 1$. Keeping the limitations of this treatment in mind, $g_{\|}$ for K15 in the absence of network molecules was estimated to be 0·43 which is of the same order as the values obtained for other cyanobiphenyl molecules [18]. In figure 7 $\varepsilon_{u\|}$ and $\varepsilon_{r\|}$ are plotted as a function of K15 concentration, it can be seen that $\varepsilon_{u\|}$ remains almost constant, while $\varepsilon_{r\|}$ decreases with decreasing K15 concentration. Extrapolated lines for $\varepsilon_{u\|}$ and $\varepsilon_{r\|}$ merge at zero K15 concentration. This linear relationship between the oscillator strength $(\varepsilon_{r\|} - \varepsilon_{u\|})$ and the volume fraction of K15 indicates that the association between the K15 molecules remains almost unperturbed even in the presence of a large number of network molecules.

4. Plasticised network

Having demonstrated the influence of the network on the behaviour of K15 at one end of the concentration range where K15 dominates, here we have investigated the behaviour of K15 in a rigid matrix. Figure 8(a) shows ε'' as a function of frequency measured at various temperatures for a plasticised network containing 20 per cent K15.

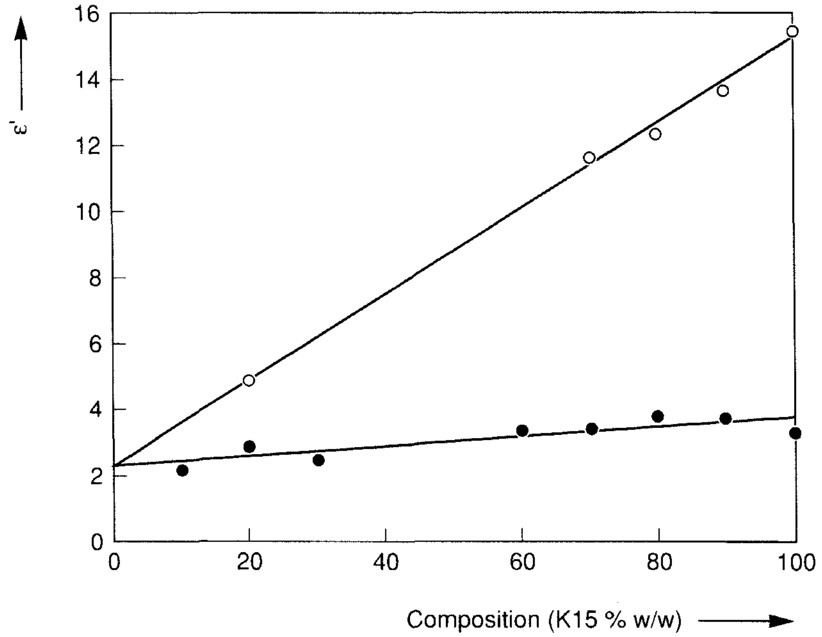
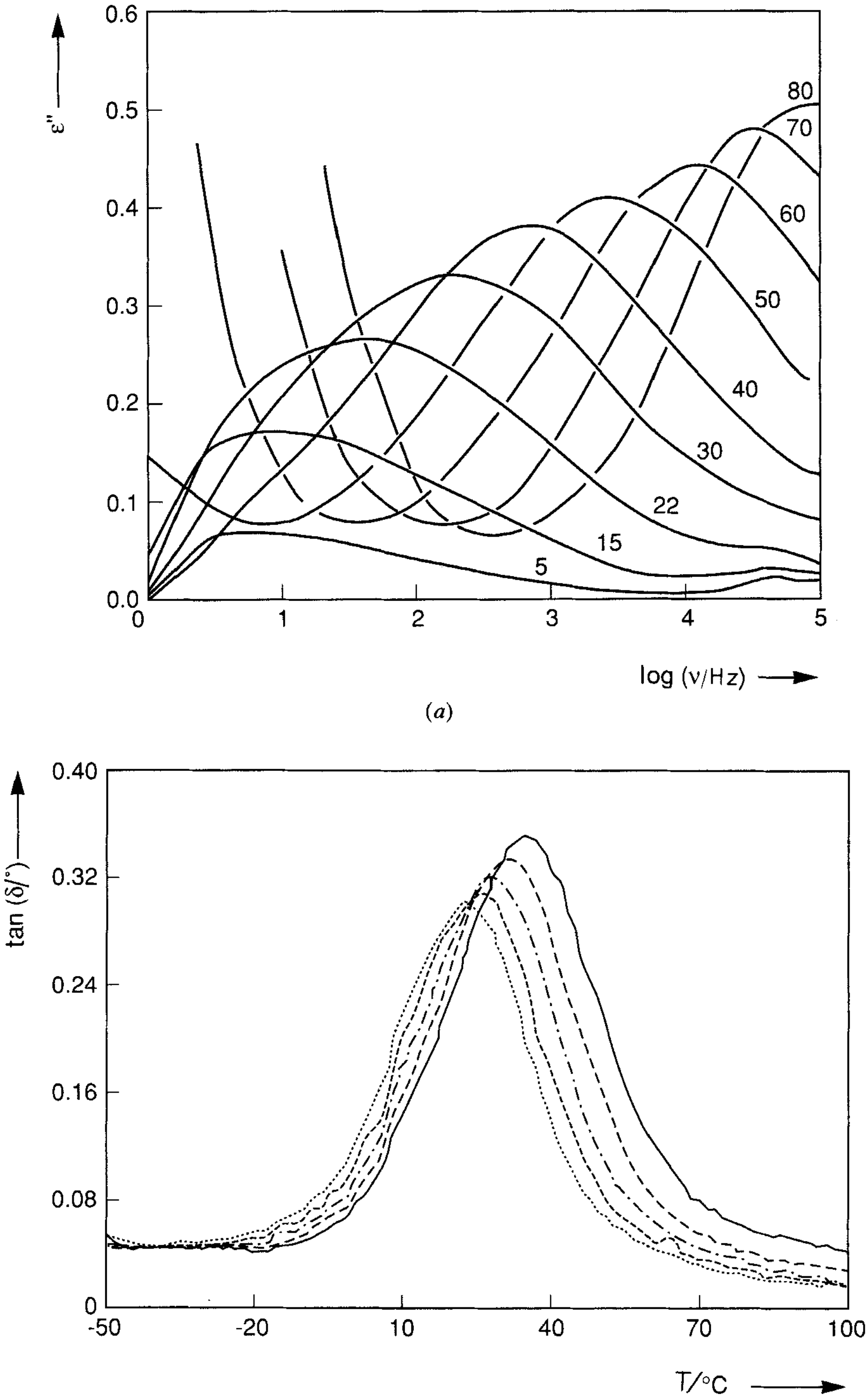


Figure 7. Static = ○ and high frequency = ● permittivities of various gels as a function of K15 concentration.

It can be seen that the loss peak which is associated with the rotation of K15 molecules becomes sharper and increases in intensity as it moves to higher frequencies with increasing temperature. Figure 8(*b*) shows the DMTA results obtained for the same sample where tan δ curves corresponding to the α process which can be associated with the glass transition are plotted. Figure 9 shows Arrhenius plots for the α peak ($T_{\tan}\delta_{\max}$) from DMTA measurements together with the data from the dielectric measurements. Here it can be seen that at a given temperature K15 relaxation occurs at frequencies higher than the network relaxation frequencies. This is rather different from the behaviour observed for the mixtures of side chain liquid crystal polymers and a low molar mass nematics where the rotation of both low mass and polymer molecules about the short axis is coupled and occurs at temperatures above the α transition [19]. In table 2 activation energies from Arrhenius ΔH_A and Bauer plots ΔH_B and ΔS_B from dielectric measurements for K15 together with ΔH_A for the α transition from DMTA measurements. It can be seen that ΔH_A for the α relaxation is always higher than the activation energies measured for K15 from dielectric measurements. In the first instance this result might lead us to think that the rotation of the K15 molecules about their short axes is not coupled to the α transition. However, when figure 8(*a*) is inspected closely, it can be seen that the dielectric loss peak disappears around 5°C. This indicates that below the glass transition rotation of K15 molecules about their long axis is frozen-in the same way as for side chain liquid crystal polymers. Here it is also interesting to note that ΔH_B for the network containing 30 per cent w/w K15 is amost the same as the value obtained for K15 alone in the nematic phase. At higher network concentrations there is an increase in ΔH_B. The fact that the relaxation frequencies decrease with increasing network concentration is probably due to the change in the free volume within the system. The effect of the free volume change manifests itself in the decrease of the glass transition with increasing network



(*a*)

(*b*)

Figure 8. (*a*) Dielectric loss as a function of frequency measured at various temperatures. (*b*) Mechanical loss tangent as a function of temperature measured at various frequencies —— 30, —— 10, —·— 3, - - - 1, ······ 0·3 Hz, for a plasticised network containing 20 per cent w/w K15.

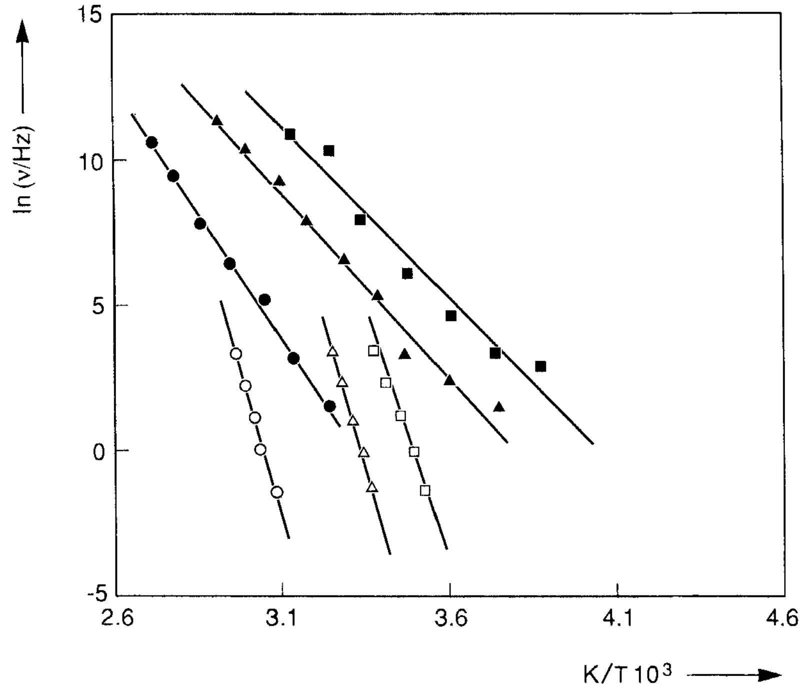


Figure 9. Arrhenius plots (open symbols) for the dielectric relaxation of K15 molecules and α transition (filled symbols) from mechanical loss tangent curves in networks containing various amounts of K15. ○ = 10 per cent, △ = 20 per cent, □ = 30 per cent w/w K15.

able 2. Activation energies and entropies for the dielectric relaxation of K15 molecules in varic plasticised networks together with the activation energy associated with the α transition..

K15 conc. (% w/w)	ΔH_B/kJ mol^{-1}	ΔH_A/kJ mol^{-1}	ΔS_B/kJ K^{-1} mol^{-1}	$\Delta H_A(\alpha)$/kJ mol^{-1}
30	97·6	96·5	0·21	300
20	105·6	104·3	0·22	315
10	141·4	140·1	0·29	319

concentration and influences the viscosity η which can be represented by a Vogel–Fulcher law [20]

$$\eta=\eta_\infty \exp\left(\frac{A}{T-T_0}\right), \tag{7}$$

where T_0 is the Vogel temperature, located below T_g.

In figure 10 $T_{\tan}\delta_{\max}$ measured at 0·33 Hz is plotted as a function of K15 concentration. It can be seen that with increasing network concentration $T_{\tan}\delta_{\max}$ shifts to higher temperatures indicating a decrease in the free volume. The fact that K15 at concentrations as low as 30 per cent in an anisotropic network has activation energies as in the bulk indicates that to a large extent the molecules behave as in the bulk. The reduction in the relaxation frequency and in the increase in h with increasing network concentration must be associated with the inhomogeneity of the system. In figure 8 the

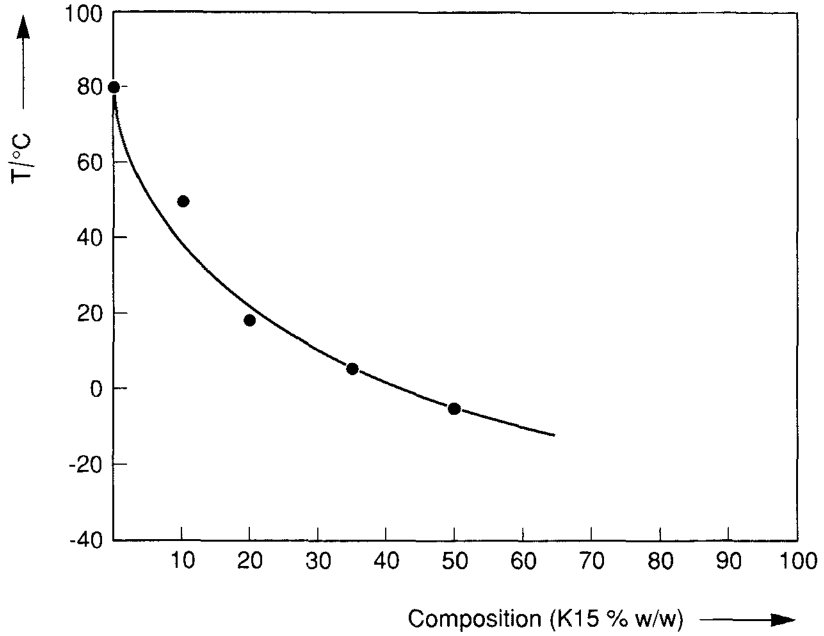


Figure 10. Peak α transition temperature measured at 0·33 Hz as a function of K15 concentration.

sharpening and the increase on the intensity of the loss peaks are indicative of this inhomogeneous distribution. Further the existence of the two populations [9] of K15 molecules can be associated with the distribution of domain sizes containing K15 and the existence of a domain size below which no first order transition for K15 is observed. With increasing network concentration the domains also decrease in size down to a level below which no first order transition is observed, as theoretically predicted [1]. However, this distribution of domain sizes also causes fluctuations in the free volume, hence the relaxation times. At the same time up to network concentrations as high as 70 per cent ΔH_B stays the same as in the bulk above which an increase can be seen. An increase in the activation energies close to the glass transition temperature was also observed for some polar liquids. Here the observed increase is also associated with the shift in the glass transition with increasing network concentration. For polar molecules, one of the suggestions for explaining the increase in the activation energy close to the glass transition invokes an increase in molecular associations [21], whereas other theories invoke a distribution of energy barriers caused by an inhomogeneous distribution of free volume within the glass forming liquid [22]. In figure 7 it can be seen that for 20 per cent w/w K15 $\varepsilon'_{r\parallel}$ and $\varepsilon'_{u\parallel}$ fall on extrapolated lines, indicating that the association between K15 remains the same as in the bulk. Therefore the increase in the activation energy of K15 in the presence of a large amount of network is due to coupling of the glass transition of K15 to the network which shows a temperature dependent activation energy.

4.3. *Electrical switching*

Having shown the effect of the network molecules on the dielectric relaxation behaviour of K15, here we wish to show the influence of these molecules on the

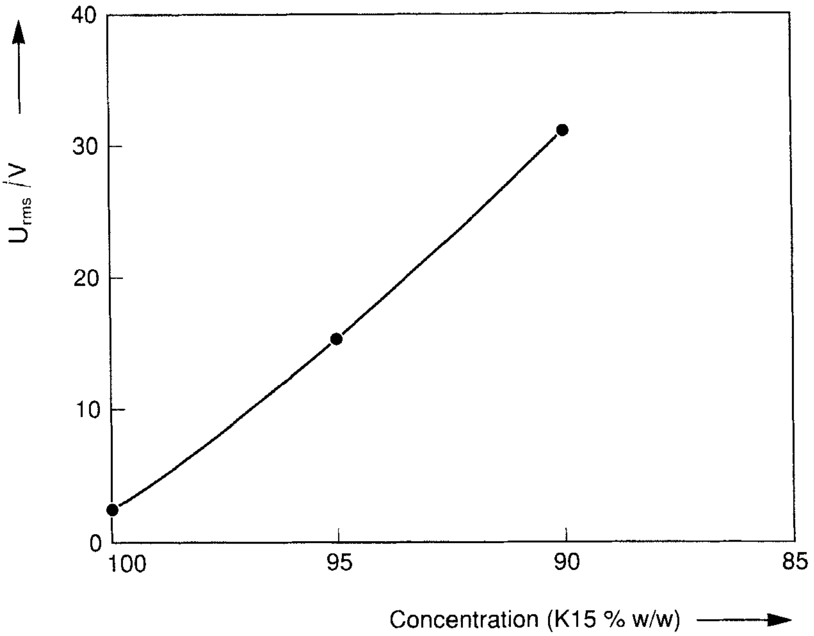


Figure 11. Threshold voltage for various gels measured as a function of K15 concentration.

Freederickz transition. In figure 11 the root mean square (1 kHz) voltage required for reorienting the nematic is plotted as a function of composition. The threshold voltage V_T for a nematic in the bulk is given by [23]

$$V_T = \pi \left(\frac{4\pi K_{11}}{\Delta\varepsilon} \right)^{1/2}, \tag{8}$$

where $\Delta\varepsilon$ is the dielectric anisotropy and K_{11} is the splay elastic constant. In figure 11 it is clear that this equation is not obeyed and the threshold voltage increases very rapidly with increasing network concentration. At only 10 per cent network (90 per cent K15) there is a large increase in the threshold voltage and it reaches a level so that for all practical purposes switching becomes almost impossible. In figure 2 it can be seen that the effect of the network on the mean relaxation time of the K15 molecules is minimal. However, the large increase in the threshold voltage indicates interaction with the network molecules. This indicates that threshold measurements are more sensitive to the interaction between the network and K15 than the dielectric relaxation of K15 molecules about their short axes.

5. Conclusions

Here it has been shown that anisotropic network molecules influence the dielectric relaxation of K15 molecules about their short axes to a large extent. It was found that with increasing network concentration mean relaxation times shift to lower temperatures and the single relaxation time effective in pure K15 is replaced by a distribution of relaxation times which becomes broader. The discontinuous increase in the mean relaxation time at T_{NI} observed for K15 in the absence of the network becomes less defined with increasing network concentration and in networks containing more than

20 per cent of the w/w network, there is almost no discontinuity to be observed. This behaviour conforms well with earlier observations and indicates that some of the molecules remain ordered above their T_{NI}. The activation energy associated with the relaxation of K15 molecules on the other hand remains almost unchanged with increasing network concentration and only in systems containing more than 70 per cent w/w network an increase is observed. This indicates that the interaction between K15 and the network results in an increase in the free volume, which also manifests itself in a decrease of the α transition temperature with respect to the pure polymer. Finally a large increase in the threshold voltage by the inclusion of a small number of network molecules indicates that threshold measurements are more sensitive in detecting interactions between network molecules and K15 molecules.

References

[1] PONIEWIERSKI, A., and SLUCKIN, T. J., 1987, *Liq. Crystals*, **2,** 281.
[2] BARBERO, G., and STRIGAZZI, A., 1989, *Liq. Crystals*, **5,** 693.
[3] GLEESON, J. T., and PLAFFY-MUHORAY, P., 1989, *Liq. Crystals*, **5,** 663.
[4] SHENG, P., 1982, *Phys. Rev.* A, **26,** 1610.
[5] LUCK'YANCHENKO, KOZUNOV, V. A., and GRIGOS, V. I., 1985, *Russ. Chem. Rev.*, **54,** 129 and the references therein.
[6] YOKOYOMA, H., KOBAYASHI, S., and KAMEI, H., 1987, *J. appl. Phys.*, **61,** 4501.
[7] KUZMA, M., and LEBLES, M. M., 1983, *Molec. Crystals liq. Crystals*, **100,** 103.
[8] FRANK, F. C., 1958, *Discuss. Faraday Soc.*, **25,** 19.
[9] HIKMET, R. A. M., 1991, *Liq. Crystals*, **9,** 405.
[10] PARNEIX, J. P., LEGRAND, C., and DECOSTER, D., 1983, *Molec. Crystals liq. Crystals*, **98,** 361.
[11] DAVIES, M., MOUTRAN, R., Price, A. H., BEEVERS, M. S., and WILLIAMS, G., 1976, *J. chem. Soc. Faraday II*, **72,** 1447.
[12] SCHELL, K. T., and PORTER, R. S., 1990, *Molec. Crystals liq. Crystals*, **188,** 97.
[13] COLE, K. S., and COLE, R. H., 1949, *J. chem. Phys.*, **9,** 341.
[14] DE JEU, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach).
[15] BAUER, E., 1944, *Cah. Phys.*, **20,** 1.
[16] MARTIN, A. J., MEIER, G., and SAUPE, A., 1971, *Symp. Faraday Soc.*, **5,** 119.
[17] BORDEWIJK, P., 1974, *Physica*, **75,** 146.
[18] KEDZIORA, P., and JADZYN, J., 1990, *Liq. Crystals*, **8,** 445.
[19] SEIBERLE, H., STILLE, W., and STOBL, G., 1989, *Proceedings of the 18th Freiburg Liquid Crystal Meeting*.
[20] BLENDER, J. T., and SHLESINGER, M. F., 1988, *J. statist. Phys.*, **53,** 531.
[21] HEDVIG, P., 1977, *Dielectric Spectroscopy of Polymers* (Adam Hilger).
[22] DAVIES, M., 1969, *Dielectric Properties and Molecular Behaviour*, edited by T. M. Sugden (Reinhold Co.).
[23] GOODMAN, L. A., 1974, *Introduction to Liquid Crystals*, edited by E. B. Priesly, P. J. Wojtowicz and P. Sheng (Plenum Press).