Liquid Crystals

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Liquid crystals: first active organics in electronics

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Liquid crystals: first active organics in electronics

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A Commentary on the paper "Anisotropic gels and plasticized networks formed by liquid crystal molecules", by R. A. M. Hikmet. First published in *Liquid Crystals*, **9**, 405–416 (1991).

Research on liquid crystals has always been an interdisciplinary and international pursuit. Biologists made the first observation of liquid crystals in the 1850s. The Austrian botanist Friedrich Reinitzer [1] recognized the phenomenon in 1888 during an experiment while heating cholesteryl benzoate. However, it was Otto Lehmann [2], who used an optical microscope equipped with a heating stage to detect the optical anisotropy of this new liquid state. In 1889 Lehmann used the term "liquid crystal" to describe this new state of matter. While the basics of the physics and chemistry of mesogens and mesogenic molecules became understood during the 1930s, it was not until the 1960s that investigations began towards practical uses for liquid crystals. The first liquid crystal displays were developed in 1968 based on the dynamic scattering mode [3]. Due to various short-comings of the dynamic scattering mode such as relatively high power consumption, limited lifetime, and poor contrast ratio it did not become a commercial success. The situation changed in 1969 [4, 5] with the discovery of the twisted nematic configuration which lead to improved displays. The industry received the much needed momentum after the invention of the cyanobiphenyls [6] in 1972 which enabled the production of commercial displays and they started appearing in digital watches and hand held calculators. Today, knowledge of such materials is widespread, and we make use of liquid crystal devices in our everyday lives. LCDs are used in hand held phones, lap-top computers, and they are replacing the cathode ray tubes as television screens at a fast rate.

In addition to their optical uses liquid crystals also play an important role in high strength fibres and they are also used as optical films such as compensators. Thermotropic chiral nematics whose pitch varies strongly with temperature can be used as crude thermometers, since the colour of the material will change as the pitch is varied.

The first time I became involved with liquid crystals was in 1987 when I joined Philips Research, a year before the centennial anniversary of the discovery of liquid crystals. Within Philips the potential of these materials was well appreciated. Chemists developed many new materials while physicists determined material properties, and applied scientists and engineers researched their use in displays. Basic research and applied display research complemented each other and worked in harmony in furthering our understanding of liquid-crystalline systems. Parallel to the developments in the area of displays, inspired by low molecular weight nematics, chemists started looking for new types of self-organizing linear polymers [7]. Along this line of research in the area of liquid-crystalline polymers, within Philips and initiated in 1985 by D.J. Broer, new types of mesogenic molecules with reactive end groups such as acrylates [8] were being investigated, mainly for their applications as optical fibre coatings because of their low expansion coefficients. My background being in polymer physics and in gels, I became fascinated by these reactive mesogens. It did not take me long to conduct my first experiment. I made a mixture of liquid crystals used in conventional display applications and a reactive mesogen (the pre-gel mixture). The mixture was liquid-crystalline and the macroscopic alignment of the director could very easily be induced in display cells. Subsequently, the polymerization of the mixture could be initiated using UV light. After the polymerization the cell remained highly transparent and anisotropic. The material could be taken out of the cell as a freestanding film, which was soft and very flexible. We discovered that these systems could be mixed with a wide range of compositions and still remain oriented after polymerization, depending on the type of reactive monomer used. These systems consisted of an anisotropic network containing mesogenic

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molecules, which are not chemically attached to the network, were named anisotropic gels and plasticized networks [9]. In these systems it was discovered that the thermal and electrical properties of the liquid crystal became influenced, to a large extent, by the polymer network. In these systems the network maintained its anisotropy at elevated temperatures and, for example, in the case of plasticized networks the director also remained aligned well above the clearing point. In the case of gels, the presence of a small amount of polymer network had a profound effect on the behaviour of the director including its switching behaviour under an applied voltage. One of the first applications of these materials was as "pre-tilt angle amplification layers" for supertwisted nematic (STN) displays [10]. Placing a layer of pre-gel mixture on top of a rubbed polyimide film could create such a pre-tilt amplification layer. The small tilt induced by the polyimide layer would increase within the nematic layer to reach much larger angles at the air interface where the director tended to adopt a homeotropic alignment. Thus by adjusting the thickness, forces acting on the liquid crystal could be balanced to obtain any desired tilt angle at the air interface. In this way the initial tilt angle induced at the polyimide interface became amplified. This tilted orientation could be frozen-in by polymerization and when such a layer was brought into contact with a bulk nematic the amplified pre-tilt angle became induced in the director to be used in the supertwisted nematic configuration. This was the first proof that, in addition to a uniaxial configuration it was also possible to obtain gels with other configurations. Soon after we could produce gels and plasticised networks in TN and chiral nematic configurations [11]. In chiral nematic gels and plasticised networks the presence of the polymer network had a temperature-stabilizing role. Systems showing temperature dependent reflection colours in the monomeric state stopped showing this property and after polymerization the position of the reflection band became temperature independent. The mesogenic molecules were free and when they were subjected to high enough temperatures they evaporated from the system leading to the collapse of the chiral nematic helix and the appearance of reflection colours at shorter wavelengths. This method was used to remove locally mesogenic molecules from a layer and in this way recordings could be produced.

One of the early effects observed for the gels is electrically-induced light scattering. As opposed to the polymer dispersed liquid crystals (PDLC) [12] studied during the same period the gels were transparent after polymerization. Upon applying an electric field across the film, the gels became increasingly turbid and started to scatter light [13]. The light scattering was very much related to the configuration and the alignment of the director. In the uniaxially planar alignment state the gels selectively scattered only one linear polarized component of light in the direction of the alignment of the director. Thus such gels performed as switchable scattering polarizers. In the case of the chiral configuration, the polarization dependence could be made to disappear completely. In the same way gels with a homeotropic orientation and negative dielectric anisotropy showed polarization independent electrically-induced light scattering [14].

These anisotropic gels obtained using diacrylates showed scattering when they were subjected to electric fields. In order to avoid scattering new types of gels were developed. Here we used a pre-gel mixture consisting of a monoacrylate, a small fraction of diacrylate (typically less than 1%) and a conventional mesogen [15]. In these new types of gels as for the case of the gels based on diacrylates the behaviour of the director was dominated by the anisotropic polymer network. However, due to the low cross-link density the polymer network was much more flexible and just like a nematic it became isotropic when heated above the clearing temperature of the system. Furthermore, these gels would switch just like conventional nematics without showing excess scattering. The presence of the network in such gels created a memory function so that the director reverted to its initial configuration with ease. It was demonstrated that such gels could be switched back and forth between a very complicated configuration such as a specularly reflecting chiral nematic in a Grandjean texture and a transparent homeotropically aligned state. In this way we could create fast switching mirrors [16]. In addition to coloured mirrors as often observed for chiral nematics, broad-banded switchable chiral nematic mirrors were also produced. In these mirrors, in addition to facilitating reversible switching, the polymer network also stabilized a pitch gradient within the cells, which was necessary to obtain a broad reflection band with a silver colour.

In gels the switching voltage threshold is determined by the amount of the polymer network within the system. This effect was used as an opportunity to create patterns in the gels by intensity modulation of UV light used for polymerization. The polymerization rate of the monomers in areas illuminated with higher intensities proceeds at higher rates than in areas illuminated with lower intensities. As a result reactive monomers diffuse to those areas with lower reactive monomer concentration. Thus higher polymer concentrations are formed in areas illuminated with higher intensity than in areas with lower UV intensity. Subsequently when an electric field is applied across the whole sample, areas with lower polymer network concentration start switching at lower voltages than areas with a higher polymer concentration [15]. In this way recordings made using modulated intensity is made visible upon application of a voltage. This method was subsequently used to produce various switchable optical components such as lenses [17].

Gels were also used in network stabilization of ferroelectric liquid crystals [18]. In this concept a small amount of network was used and any preferred director alignment could be stabilized. This was also an easy method for obtaining reproducible gray levels using ferroelectric liquid crystals with ease.

Except for some niche applications, such as fast shutters for CCD cameras, liquid crystal gels are currently not in mass production. One of the interesting directions of research regarding these gels, as mentioned previously, involves their use as optical components. An application that is currently being investigated in this area involves active manipulation of a beam of light from a light source. Using such optical elements one can electrically adjust the shape, direction, collimation and the colour temperature of a light source. Such elements can easily be integrated with a solid-state lighting module incorporating light emitting diodes, thus increasing its functionality.

I was lucky to be able to participate in this exciting field and follow developments in various other areas. Looking back I can see a more general process of scientific discovery where various disciplines worked together and learned from each other. Liquid crystal displays have entered our everyday lives while revolutionizing the display world. The results of those who helped this revolution provide great inspiration both for us and future generations of scientists to continue investigating this and other fields of science.

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Anisotropic gels and plasticized networks formed by liquid crystal molecules

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Two component mixtures containing liquid crystalline diacrylates and liquid crystal molecules with no reactive groups have been made. Upon photopolymerization of the mixtures anisotropic networks containing liquid crystal molecules which were not chemically attached to the networks were created. In these systems the behaviour of the liquid crystal molecules was found to be dominated by the network molecules. Even when the liquid crystal molecules in these networks were heated above their isotropic transition temperature they remained partly oriented, thus contributing to the anisotropy of the system.

1. Introduction

Recently the use of low molar mass-liquid crystalline acrylates in the production of anisotropic networks has been demonstrated [1–5]. These molecules possess low viscosities and they can be macroscopically oriented by simple surface treatment, by flow and in electric and magnetic fields [6]. The induced orientation can subsequently be frozen in by isothermal photopolymerization of the system. Networks obtained in this way are highly cross-linked and they possess anisotropic thermal, mechanical, electrical and optical properties. Here a new kind of anisotropic network which contains molecules which are not chemically attached to the network is described. These systems are produced by *in situ* photopolymerization of diacrylates in the presence of low molar mass liquid crystal molecules containing no reactive groups. Materials ranging from anisotropic gels (networks containing a large amount of cross-linked molecules) can be made and in this way the mobility of the molecules within the system is controlled. These new kinds of materials can be used in a wide range of applications including optical components and new display principles [7]. In this study the polymerization behaviour of diacrylates in the presence of non-reactive liquid crystal molecules, anisotropic optical properties of the systems and the behaviour of these molecules in small confinements in the presence of an anisotropic environment is described.

2. Experimental

The structures of the diacrylate (C6M) and the molecule not containing reactive groups (K15) used in this study are given in figure 1. The diacrylate C6M was synthesized in Philips Research Laboratories and the details regarding the syntheses can be found in [2]. K15 is a commercial product purchased from BDH (Poole, England). The monomers were provided with a 2 per cent w/w photoinitiator α,α-dimethoxydeoxybenzoin (Irgacure 651 Ciba Geigy). Differential thermal calorimetry was carried out using a Perkin–Elmer DSC-7. The heating rate chosen was 10°C min^{-1} and sample quantities of the order of 5 mg were used. Polymerization

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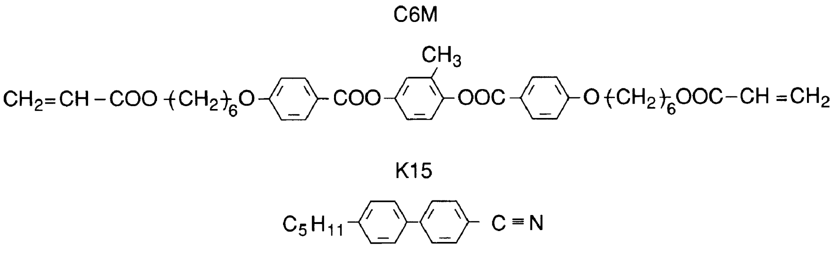

Figure 1. The molecular structure of the monomers.

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kinetics were followed by a Perkin–Elmer DSC-2C modified for UV irradiation [8]. Optical measurements were carried out using a polarizing microscope provided with a rotary compensator. Sample temperatures were regulated using a Mettler FP 5 hot stage. An Abbe refractometer which could be heated up to 140°C was used for the refractive index measurements. Dynamic thermal mechanical analysis was performed using a Polymer Laboratories DMTA apparatus. Infrared measurements were carried out using a Nicolet 7199 Fourier transform infrared instrument provided with a wire grid polarizer and a heating cell. Uniaxially oriented samples, for birefringence measurements, were obtained in glass cells which were provided with uniaxially rubbed polymide layers on their inner surfaces and spaced with 7 μm fibres. Uniaxially oriented samples used in the infrared measurements were obtained between two potassium bromide plates provided with uniaxially rubbed polyethylene layers. The cell thicknesses were controlled with 2 and 7 μm fibres. The polymerization of the uniaxially oriented samples was initiated by UV radiation from a 100 W high pressure mercury lamp (366 nm 10 mW cm^{-2}).

3. Results and discussion

3.1. *Monomeric mixtures*

The phase diagram for the mixture of C6M and K15 is shown in figure 2, this behaviour is typical of that observed for mixtures of two nematics [9]. The mixtures show a prononounced eutectic and as a function of the mole fraction of K15, the nematic to isotropic transition temperature, T_{NI}, falls on a curve not obeying the theoretically predicted straight line. This deviation from linearity which is often observed for mixtures of two nematics, is usually associated with the difficulties with the packing of dissimilar molecules [9].

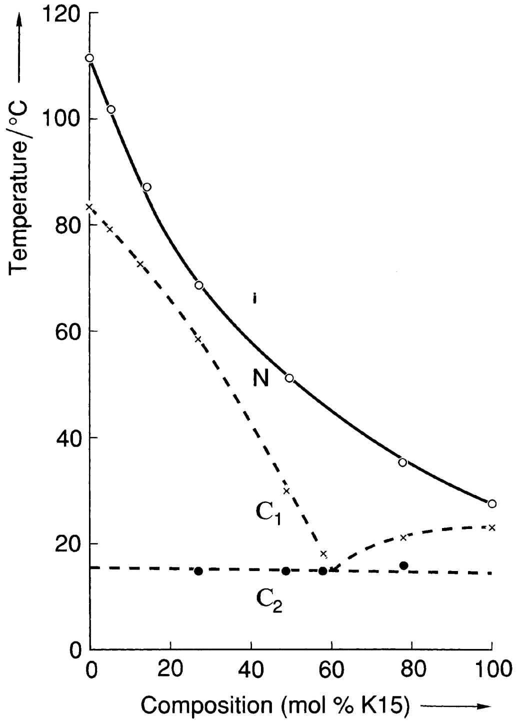

Figure 2. The phase diagram of the binary mixture of C6M and K15.

In figure 3 the refractive indices of the single components and their mixtures are shown as a function of temperature. Ordinary refractive indices (n_o) of the materials were measured using the refractometer and the extraordinary refractive indices (n_e) were calculated from the birefringence of the uniaxially oriented samples. Here it can be seen that for a given material n_o remains almost unchanged as a function of temperature while n_e decreases rapidly with increasing temperature as commonly observed for liquid crystals [9]. Refractive indices also depend on the composition of the mixtures and increase with increasing K15 content of the mixture at a given reduced temperature. The order parameter, *S*, for the mixtures was estimated from the refractive indices using [10]

$$S=\left\{\frac{\bar{\alpha}}{\alpha_{\parallel}-\alpha_{\perp}}\right\}\frac{n_e^2-n_o^2}{\bar{n}^2-1}, \qquad (1)$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular polarizabilities in the direction parallel and perpendicular to the optic axis of the molecules respectively and $\bar{\alpha}$ is the mean polarizability. The mean refractive index $\bar{n}$, is given by $\sqrt{\left[\left(2n_o^2+n_e^2\right)/3\right]}$. The polarizability term was estimated from Haller plots [11] which predict a linear relationship between $S(\alpha_{\parallel}-\alpha_{\perp})/\bar{\alpha}$ and $(1-T/T_{NI})$. These values were then used to produce figure 4 where the order parameter for various mixtures is plotted as a function of the reduced temperature. This plot again shows a typical behaviour observed for liquid crystals where the order parameter decreases with increasing temperature before falling to zero at the T_{NI}.

3.2. *Photopolymerization of the mixtures*

Anisotropic networks containing free molecules were formed by photopolymerization of the mixtures. In the following sections networks containing a high amount of free molecules (>70 per cent) will be referred to as gels whereas the others will be called plasticized networks. The photopolymerization reaction of the mixtures was followed using DSC. A small quantity of a material (about 1 mg) was placed in the sample compartment which was flushed with nitrogen. The polymerization was initiated using a 4 W fluorescent lamp (intensity of 0.2 mW cm^{-2} at 350 nm). Figure 5 shows a

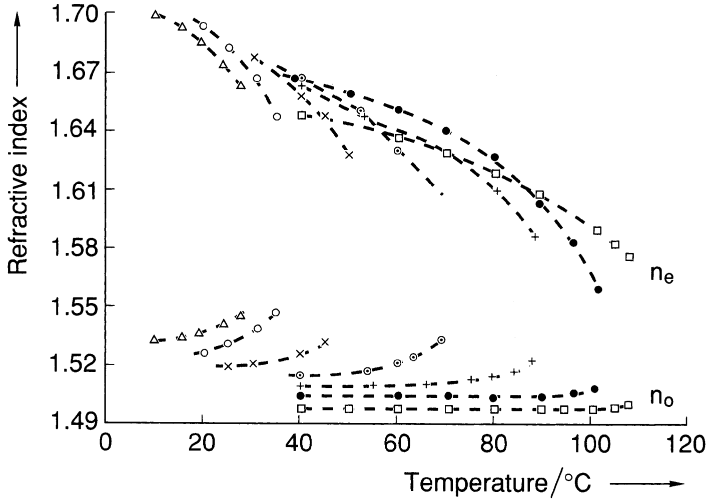

Figure 3. The refractive indices of various materials. □ = C6M, ● = 90 per cent w/w C6M, + = 70 per cent C6M, ⊙ = 50 per cent C6M, × = 30 per cent C6M, ○ = 10 per cent C6M, Δ = K15.

typical DSC curve obtained for a mixture containing 50 per cent w/w K15 where the development of the reaction enthalpy as a function of time is shown. The shapes of the curves obtained for the mixtures are very similar to those obtained for conventional diacrylates [8]. Upon the initiation of the polymerization the rate of polymerization starts increasing instantly indicating that termination of the radicals is already reduced at low conversions due to the formation of a network [8]. The maximum rate is reached after about 6 s, after which the rate decreases and falls below the detection limit after about 2 min. By partial integration of such DSC curves the rate of polymerization was estimated at various conversions using the value of 78 kJ mol^{-1} for the heat of polymerization of the acrylate groups. In figure 6 the polymerization rate at 30°C is plotted as a function of conversion for various mixtures. Here it can be seen that the maximum reaction rate and the conversion at the maximum rate increases with increasing acrylate concentration within the mixture. Since the mobility in the mixtures containing a high amount of non-reactive molecules is quite high the decrease of the rate at low

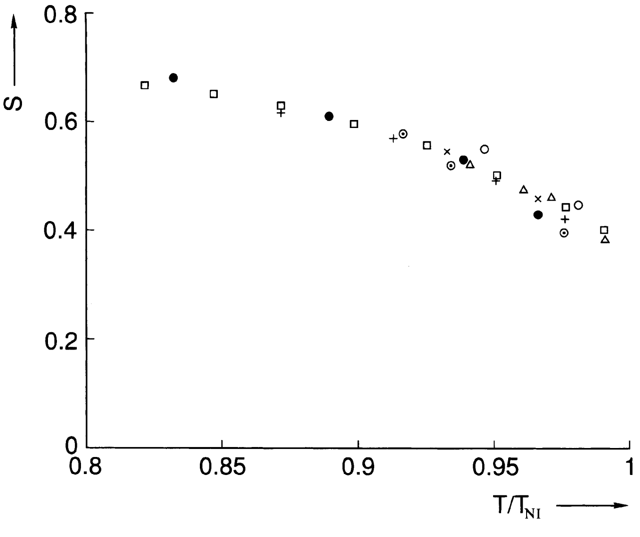

Figure 4. The order parameter as a function of reduced temperature for various mixtures. □ = C6M, ● = 90 per cent w/w C6M, + = 70 per cent C6M, ⊙ = 50 per cent C6M, × = 30 per cent C6M, ○ = 10 per cent C6M, Δ = K15.

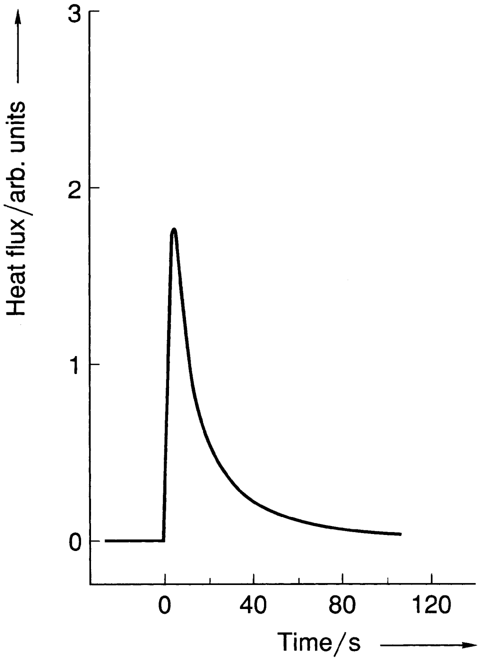

Figure 5. The heat flux of the polymerization reaction as a function of time.

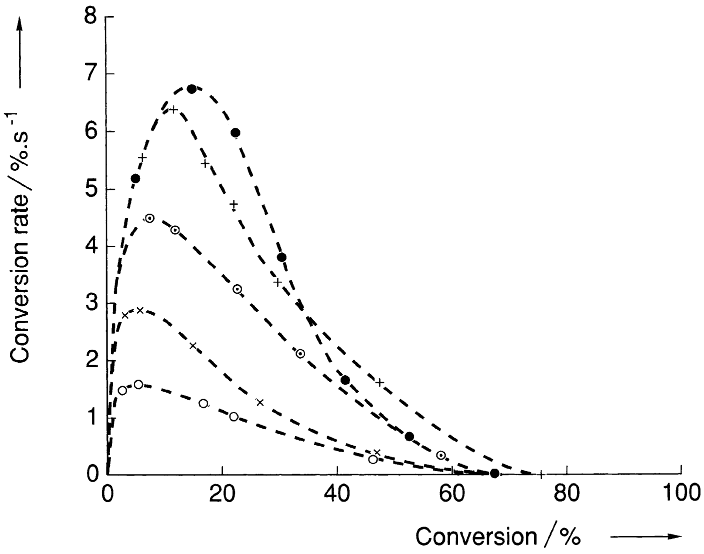

Figure 6. The polymerization rate as a function of temperature for various samples. ● = 90 per cent w/w C6M, + = 70 per cent C6M, ⊙ = 50 per cent C6M, × = 30 per cent C6M, ○ = 10 per cent C6M.

conversions (around 10 per cent) is probably caused by the depletion of the acrylate groups and the increase in the viscosity of the system. Furthermore, in figure 6 the conversion of the acrylate groups as detected by DSC is of the order of 70 per cent. However infrared measurements using the vinyl absorbtion band at 840 cm^{-1} showed that the degree of conversion was much higher than 70% indicating that the polymerisation reaction continued further below the detection limit of the DSC.

3.3. *Optical properties of the anisotropic gels and the plasticized networks*

Following the photopolymerization of the monomeric mixtures the materials remained clear and did not give rise to excess scattering of light as observed using a light microscope provided with a photodetector. Refractive indices of the anisotropic gel and the plasticized networks were measured using the Abbe refractometer and the results for various compositions are shown in figure 7. Here it can be seen that both n_e and n_o of the mixtures decrease with increasing temperature. For networks containing more than 30 per cent w/w K15 this effect is largely due to the decrease in density with increasing temperature. For the sample containing 50 per cent w/w K15 it can be seen that n_e decreases faster than n_o indicating that there is also a considerable decrease in the orientational order within the system. In figure 8 the birefringence of various mixtures are shown as a function of temperature. Here it can be seen that at all temperatures the systems remain birefringent as opposed to the behaviour shown by the mixtures prior to polymerization (cf. figure 2). Gels show a large decrease in their birefringence at around 30°C which is then followed by a more gentle decrease. Plasticized networks, however, in general do not show any rapid decrease in birefringence. The large decreases in the birefringence around 30°C which also corresponds to the clearing temperature of bulk K15, is probably caused by the disorientation of the K15 molecules. The birefringence observed at high temperatures (residual birefringence) increases with increasing concentration of the cross-linked acrylate networks. In the first instance the residual birefringence is expected to be a linear

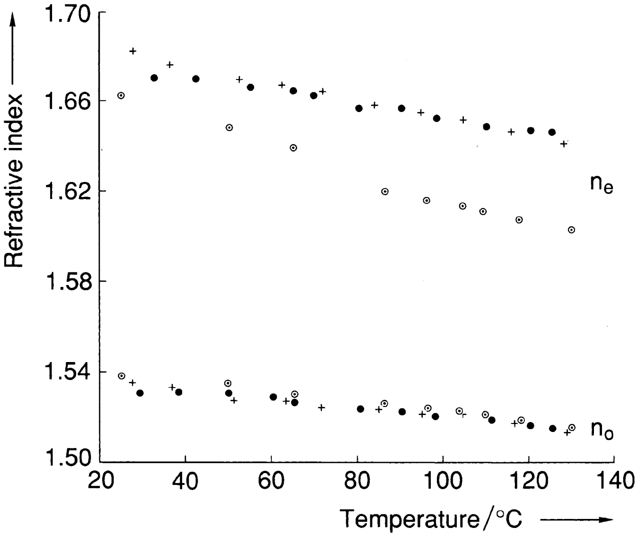

Figure 7. The refractive indices of various polymerized materials. ● = 90 per cent w/w C6M, + = 70 per cent C6M, ⊙ = 50 per cent C6M.

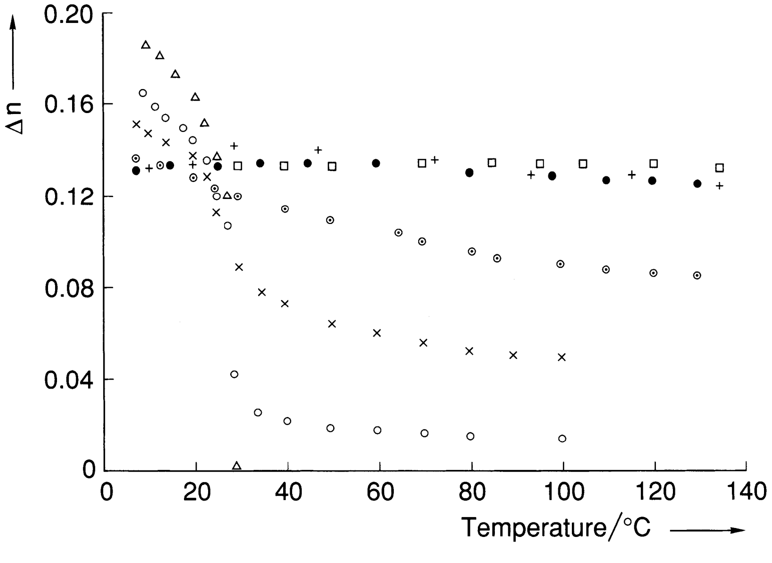

Figure 8. The birefringence of various polymerized materials as a function of temperature. □=C6M, ●=90 per cent w/w C6M, +=70 per cent C6M, ⊙=50 per cent C6M, ×=30 per cent C6M, ○=10 per cent C6M, Δ=K15.

function of the volume fraction of the network molecules which remain oriented even at high temperatures. However the residual birefringence was always found to be higher than the theoretically expected values. This indicates that some of the K15 molecules remain oriented above their nematic–isotropic transition temperatures, thus contributing to the birefringence of the system. In order to investigate this point further infrared dichroism [12] was used. For a uniaxial system the dichroitic ratio, R, is given by

$$R=\frac{\varepsilon_{\|}}{\varepsilon_{\perp}}=\frac{(4\cos^2\alpha)\langle\cos^2\theta\rangle+(2\sin^2\alpha)\langle\sin^2\theta\rangle}{(2\cos^2\alpha)\langle\sin^2\theta\rangle+(\sin^2\alpha)\langle 1+\cos^2\theta\rangle}, \tag{2}$$

where $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are absorption coefficients measured with the IR beam polarized parallel and perpendicular to the optic axis of the uniaxially oriented liquid crystal, respectively, θ is the angle between the direction of the molecular long axis and the optic axis and α is the angle between the direction of this long axis and the direction of the vibrational transition moment. Assuming molecular cylindrical symmetry, the quantity S_o which is related to the order parameter S is given by

$$S_o=\frac{R-1}{R+2}=S(1-3/2\sin^2\alpha). \tag{3}$$

Figures 9 and 10 show S_o as a function of temperature obtained for K15 molecules from the dichroism of the C≡N stretching vibration at 2230 cm^{-1} and for the network molecules from the collective C–H out of plane vibrations of the benzene rings at 763 cm^{-1}, the benzene ring *C*=*C* skeleton vibrations at 1580 cm^{-1} and benzene ring–oxygen stretching vibrations at 1245 cm^{-1} [13]. For the network molecules (see figure 9) except for the gel containing 90 per cent w/w K15 molecules the order parameter shows only a slight change with increasing temperature. For the case where a large change is observed it is probably as a result of the disorientation of pendant groups present in the system. For K15 molecules (see figure 10) it can be seen that except for the system containing 10 per cent w/w network molecules in all cases the order parameter decreases gradually with increasing temperature. For the gel containing 10 per cent w/w network molecules a sudden change in the order parameter at about 30°C is observed. Here it is important to point out that even though the order parameter of the K15 molecules at temperatures well above their T_{NI} decreases it never becomes zero even in the case of the gel containing 90 per cent w/w K15 molecules. These results, which are in good agreement with the birefringence measurements, show that even at temperatures well above their T_{NI} some K15 molecules remain oriented. Together with this, the fact that the gels show a sudden drop in their birefringence accompanied with a drop in the order parameter of the K15 molecules at about 30°C indicates that the systems possibly contain two populations of K15 molecules. One population is strongly bound to the network and does not undergo a first order nematic–isotropic transition whereas the other population behaves like bulk K15. In order to check this possibility further, DSC measurements were performed. Small quantities of samples were polymerized in DSC pans and the transition enthalpy involved in N–I transition (ΔH_{NI}) was recorded for various gels containing various amounts of network molecules. In figure 11 DSC curves

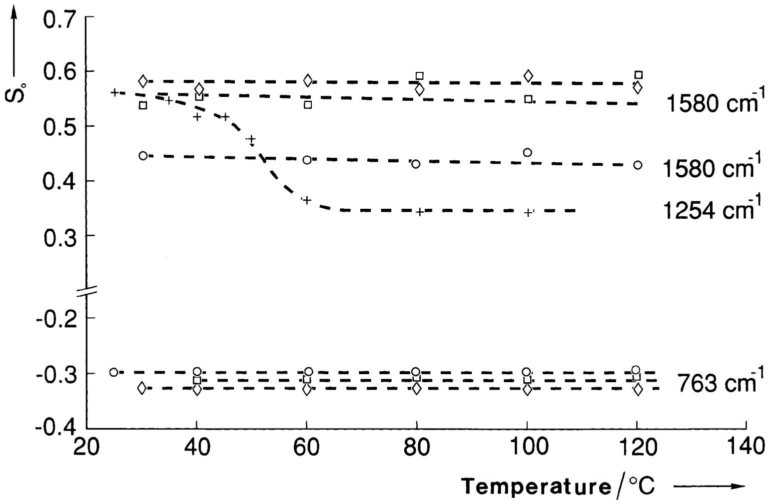

Figure 9. The order parameter S_o of the network molecules estimated from IR dichroism. □=90 per cent w/w C6M, ○=70 per cent C6M, ◇=30 per cent C6M, +=10 per cent C6M.

for various gels are shown. Here it can be seen that the onset of the transition remains almost constant for all the samples. In figure 12, ΔH_{NI} calculated by only taking K15 molecules into account, is plotted as a function of composition. Here it is clear that with increasing network concentration ΔH_{NI} decreases and above 30 per cent w/w network content the transition falls below the detection limit for the DSC. This result supports the earlier observations and indicates that in these systems there are two populations of K15 molecules which are (i) strongly bound, (ii) not bound, to the network molecules. Assuming that the molecules which are not bound undergo a N–I transition with the enthalpy observed for bulk K15, the fraction of the molecules bound by the network was calculated, the results are plotted in figure 12. Here it can be seen that as expected with increasing network fraction more K15 molecules become bound. According to this figure, in the gel containing 70 per cent w/w K15 molecules almost 80 per cent w/w of these molecules are bound by the network which made up only 30 per cent w/w of the gel.

3.4. *Relaxation behaviour and the structure of the polymerized samples*

In order to investigate the relaxation behaviour of the plasticized networks DMTA measurements were carried out. Loss tangent plots for various networks are shown in figure 13. Here it can be seen that with increasing K15 concentration the high temperature transition peak

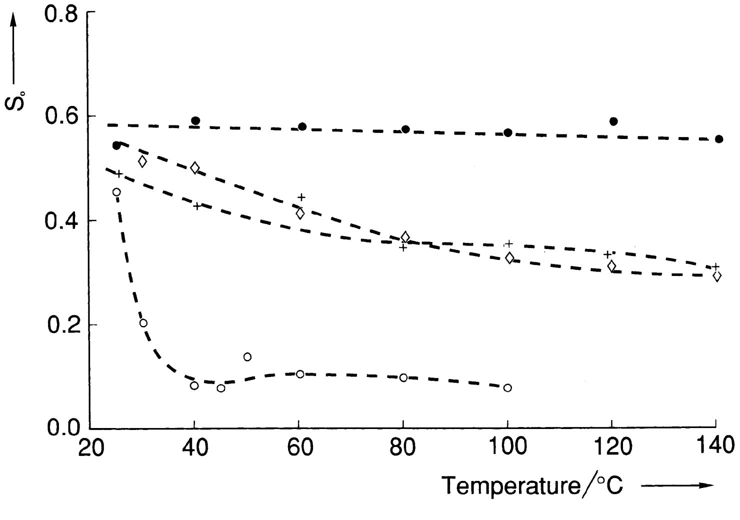

Figure 10. The order parameter S_o of K15 molecules in various networks estimated from IR dichroism, ● =90 per cent w/w C6M, +=70 per cent C6M, ◇=30 per cent C6M, ○=10 per cent C6M.

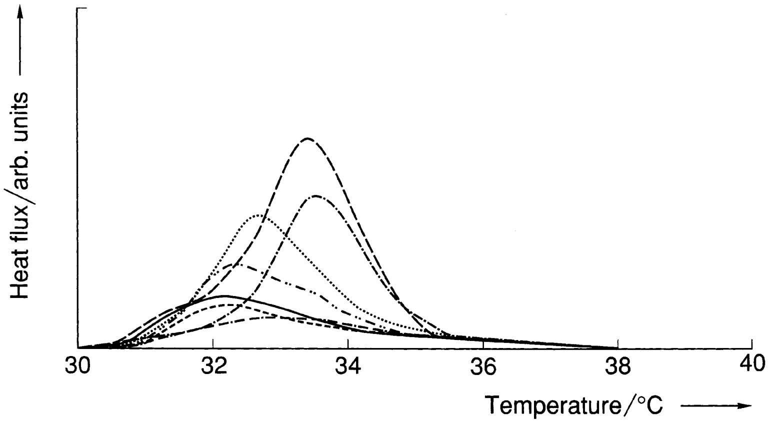

Figure 11. The DSC curves of various gels showing nematic to isotropic transitions. — — –=100 per cent K15, –·–·–=95 per cent K15,····=90 per cent K15, –··–··–=85 per cent K15, ——=80 per cent K15, ----=75 per cent K15,·—·—·=70 per cent K15.

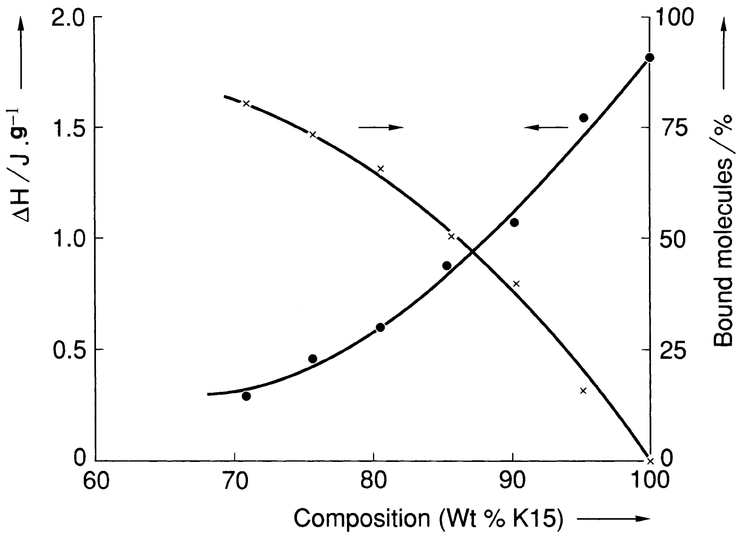

Figure 12. The heat of the nematic–isotropic transition for K15 and the fraction of bound K15 molecules in gels containing various amount of K15.

(T_α) corresponding to the relaxation of the whole system [5] becomes more intense and appears at lower temperatures. This is typical behaviour for plasticized systems [14], indicating an increased mobility within the system. For a two phase system as the composition of the system is changed T_α corresponding to pure compounds remain in their position and only change in intensity. Here the large shift in the position of the T_α also indicates that there is a strong interaction between the network and K15 molecules.

Finally, scanning electron microscopy was used to look at the morphology of the gels. For this purpose a gel which contained 70 per cent w/w K15 molecules was used. Micrographs were obtained after extracting the K15 molecules and covering the sample with gold. An electron micrograph of the sample is shown in figure 14 where the existence of parallel lamellar structures can clearly be seen. Within the sample molecular orientation is uniaxial indicating that the network molecules lie in the plane of these lamellae. For phase separated liquid crystal molecules in cured isotropic acrylate systems irregular bush-like structures and porous structures are obtained [15]. The fact that the structure of the anisotropic gels observed here is very different to those obtained for systems showing phase separation on a macroscopic scale also indicates the novelty of these systems where the phase separation is probably on a microscopic scale.

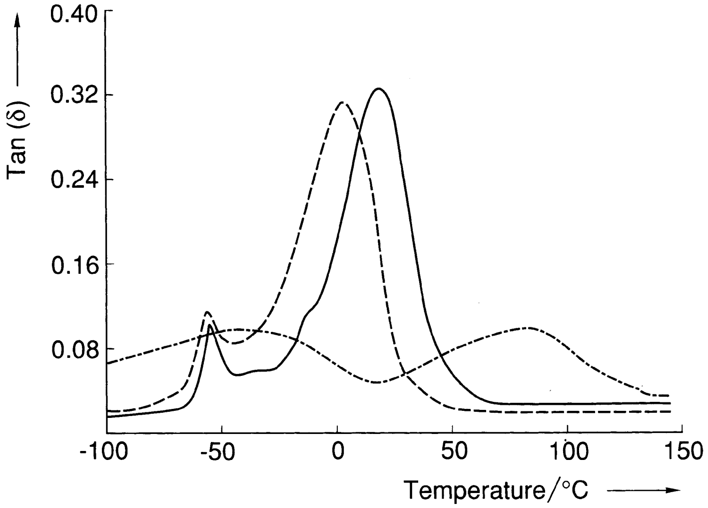

Figure 13. The loss tangent curves of networks containing various amounts of K15·–·–·=100 per cent C6M, ——=70 per cent C6M, - - - -=50 per cent C6M.

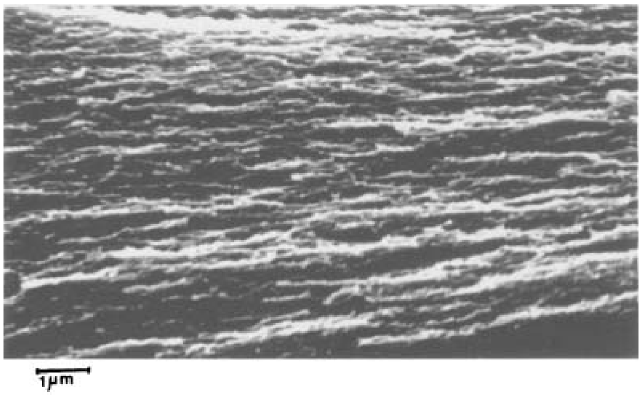

Figure 14. Scanning electron micrograph of a gel which contained 70 per cent w/w K15.

4. Conclusions

Here it was shown that anisotropic networks containing liquid crystal molecules which are not chemically attached to the network can be made. At all compositions the systems did not cause any appreciable light scattering and looked very clear. In the systems the behaviour of the liquid crystal molecules was found to be dominated by the network and even at temperatures much higher than the nematic–isotropic temperature of the liquid crystal they remained partly oriented. In this way it became possible to identify two populations of these molecules within the anisotropic networks: (i) molecules strongly bound by the network which do not undergo a first order nematic–isotropic phase transition, and (ii) molecules free to behave like those in the bulk. At network concentrations as low as 30 per cent w/w it was found that 80 per cent w/w of the liquid crystal molecules within the network were bound and did not show a nematic–isotropic transition. Anisotropic networks containing more than 50 per cent w/w LC molecules did not show any detectable nematic–isotropic transition peaks or melting peaks. These materials were glassy and showed a main mechanical relaxation peak which appeared at lower temperatures with increasing liquid crystal concentration.

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