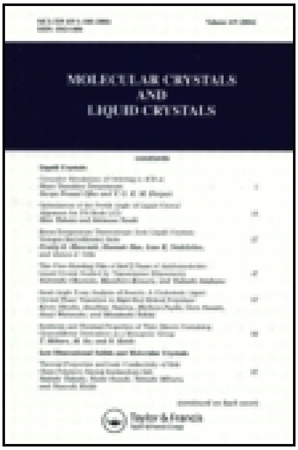

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From Liquid Crystalline Molecules to Anisotropic Gels

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From Liquid Crystalline Molecules to Anisotropic Gels

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Two component mixtures containing liquid crystalline (LC) diacrylates and LC molecules with no reactive groups were made. Upon photopolymerization of the mixtures anisotropic networks containing LC molecules which were not chemically attached to the networks were created. In these systems the behavior of the LC molecules was found to be dominated to a large extent by the network molecules. Even when the systems were heated above the isotropic transition temperature of the LC molecules they remained partly oriented, thus contributing to the anisotropy of the system. Networks containing LC molecules were clear and did not give rise to excess scattering of light. Upon application of an electric field across the system, it turned translucent making the system suitable for display applications.

Keywords: networks, gels, anisotropic gels

INTRODUCTION

Recently the use of low mass liquid crystalline (LC) acrylates in the production of anisotropic networks was demonstrated.[1-4] These molecules possess low viscosities and they can be macroscopically oriented by a simple surface treatment, by flow and in electric magnetic fields. 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 networks which contain molecules which are not chemically attached to the networks will be described. These systems are produced by in situ photopolymerization of liquid crystalline (LC) diacrylates in the presence of low mass LC molecules containing no reactive groups.[5] Materials ranging from anisotropic gels (networks containing a large amount of free molecules) to plasticized networks (networks containing a large amount of cross-linked molecules) can be made and in this way the mobility of the molecules within the systems is controlled. These new kinds of materials can be used in a wide range of applications including optical components and new displays which work on the principle of light scattering.[6]

Here the production a new system composed of LC molecules and an anisotropic network, the behavior of LC molecules in small confinements in the presence of an anisotropic environment, electrically induced light scattering from these systems and their use in scattering displays is described.

EXPERIMENTAL

The structures of the LC diacrylates (C6M, C6) and the molecule containing no reactive groups (K15) used in this study are given in Figure 1. Diacrylates C6M and C6 were synthesized previously.[2] Molecules without reactive groups (K15 and E7) are commercial products purchased from BDH in England. The mixtures were provided with a 2% w/w photoinitiator α,α-dimethoxydeoxybenzoin (Irgacure 651 from Ciba Geigy). Polymerization kinetics were followed by a Perkin Elmer DSC-2C modified for UV radiation.[7] An Abbe refractometer which could be heated up to 140°C was used for the refractive index measurements. 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, were obtained between two substrates provided with uniaxially rubbed polyimide layers on their inner surfaces and spaced with 2 and 7 μm fibers. The polymerization of the uniaxially oriented samples was initiated by UV radiation on a 100 W high pressure mercury lamp (366 nm 10 mW cm^{-2}). X-Ray diffraction patterns were recorded by a Statton camera using a Ni filtered Cu K_α radiation.

Electro-optic responses of the gels were measured using a polarizing light microscope provided with a photomultiplier and a rotary compensator. The electric pulse applied was a sinusoidal wave modulated with a square wave. Electrical pulses from the signal generator and the response of the photomultiplier were fed into a storage oscilloscope. Results could then be plotted on an X-Y recorder.

RESULTS AND DISCUSSION

Monomeric Mixtures

In Figure 2 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

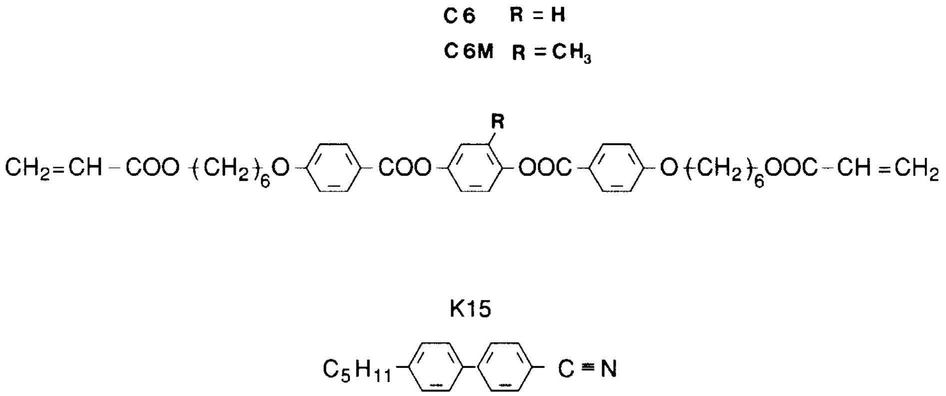

FIGURE 1 Molecular structure of the monomers.

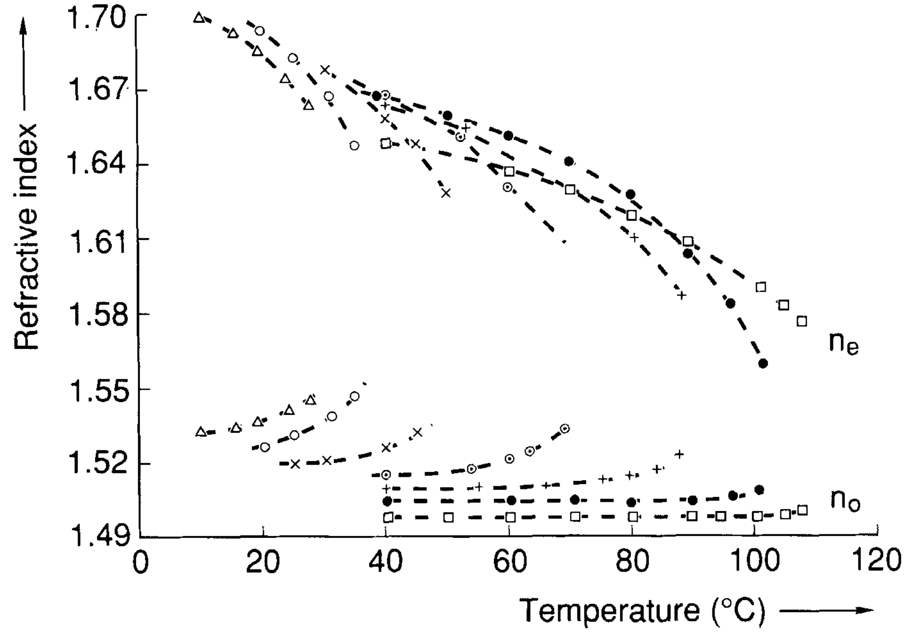

FIGURE 2 Refractive indices of various mixtures of C6M and K15 containing 2% photoinitiator as a function of temperature. □ = C6M, ● = 90% w/w C6M, + = 70% C6M, ⊙ = 50% C6M, × = 30% C6M, ○ = 10% C6M, △ = K15.

measured using the refractometer and the extraordinary refractive indices (n_e) were calculated from the birefringence of the uniaxially oriented samples in cells. 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 also commonly observed for LC systems.[8] Refractive indices also depend on the composition of the mixtures and increase with increasing K15 content of the system at a given reduced temperature. The order parameter for the mixtures was estimated from the refractive indices using the equation below.[9]

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

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular polarizabilities in the direction parallel and perpendicular to the optical axis of the molecules respectively and $\bar{\alpha}$ is the mean polarizability. The mean refractive index $\bar{n}$, is given by $\sqrt{(2n_o^2 + n_e^2)/3}$.

The polarizability term was estimated from the Haller plots[10] which predict a linear relationship between $S(\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}$ and $(1 - T/T_c)$. These values were then used to plot Figure 3 where the order parameter for various mixtures is plotted as a function of reduced temperature. This plot shows a behavior typical of that

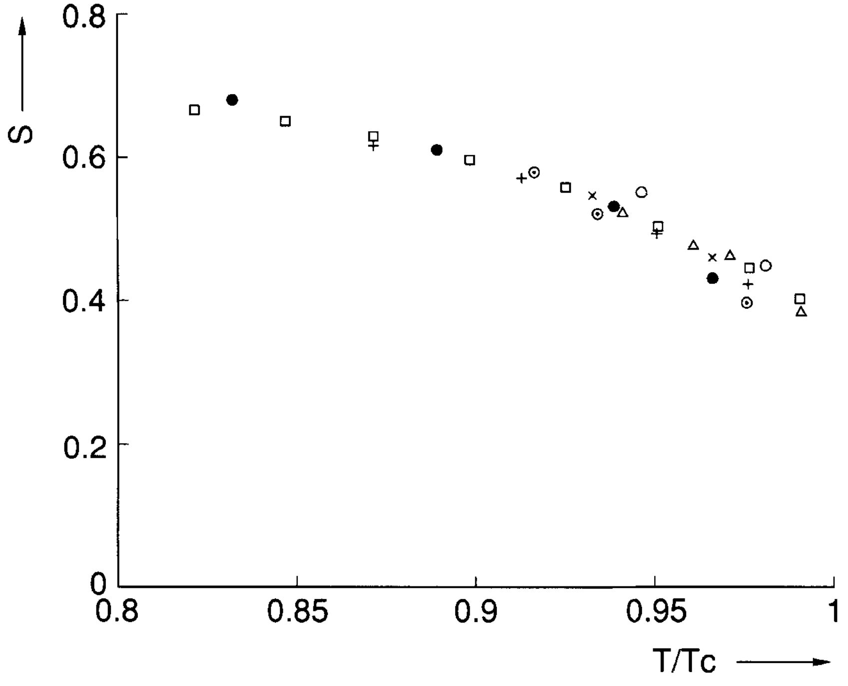

FIGURE 3 Order parameter as a function of reduced temperature for various systems. □ = C6M, ● = 90% w/w C6M, + = 70% C6M, ⊙ = 50% C6M, × = 30% C6M, ○ = 10% C6M, △ = K15.

observed for LC molecules where the order parameter decreases with increasing temperature before discontinuously becoming zero at the clearing temperature T_c.

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%) will be referred to as gels where as the other 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 4 shows a typical curve obtained for a mixture containing 50% w/w K15 molecules where the development of the reaction enthalphy 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. Upon initiation of polymerization the rate of polymerization starts increasing, indicating that termination of the radicals is already reduced at low conversions due to the formation of a network. The maximum rate is reached at an early stage of the reaction after which the rate decreases and falls below the detection limit after about two minutes. The conversion of the acrylate groups at the end of the reaction was calculated to be more than 70%.

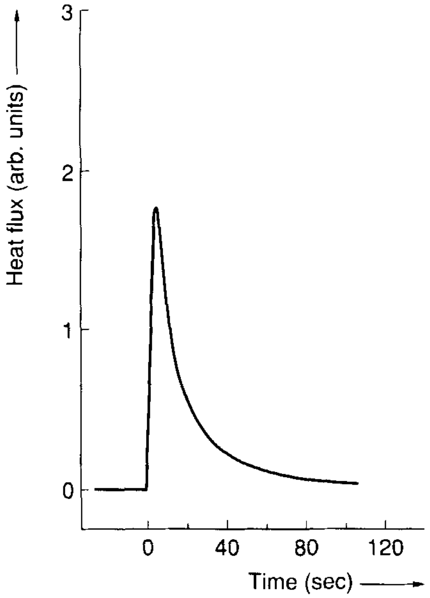

FIGURE 4 Heat flux of a polymerization reaction as a function of time.

Optical Properties of the Anisotropic Gels and the Plasticized Networks

Birefringence of various mixtures as a function of temperature is shown in Figure 5. Here it can be seen that at all temperatures the systems remain birefringent as opposed to the behavior shown by the mixtures prior to polymerization. Gels show a large decrease in their birefringence at about 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 birefringence around 30°, which also corresponds to the clearing temperature of bulk K15, are probably caused by the disorientation of the K15 molecules. The birefringence observed at high temperatures (residual birefringence) increases with increasing concentration of the crosslinked acrylate networks. In the first instance the residual birefringence is expected to be caused by the network molecules which remain oriented even at high temperatures. On closer inspection it was found that the residual birefringence was always higher than what would be expected from the oriented network fractions only. This indicated that some of the K15 molecules remained oriented above their isotropic transition temperatures contributing to the birefringence of the system. In order to investigate this point further order parameters of the two compounds making up the systems were determined by infrared (IR) dichroism.[11] For a uniaxially symmetric system the dichroitic ratio, R is given by

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

Where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are absorption coefficients measured with the IR beam polarized

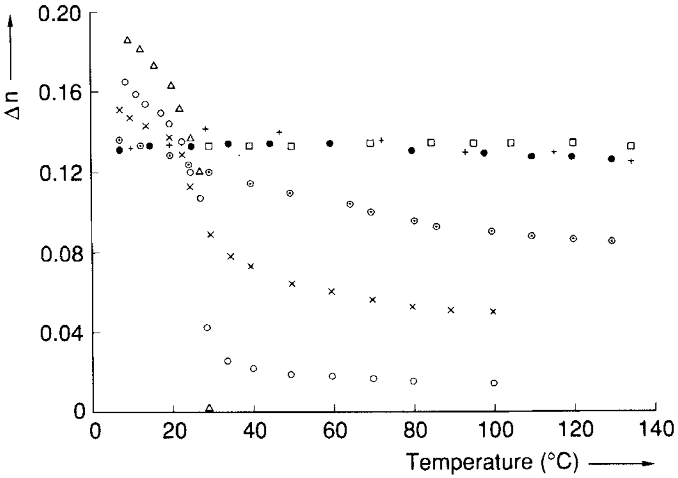

FIGURE 5 Birefringence of various polymerized mixtures of C6M and K15 as a function of temperature. □ = C6M, ● = 90% w/w C6M, + = 70% C6M, ⊙ = 50% C6M, × = 30% C6M, ○ = 10% C6M, △ = K15.

parallel and perpendicular to the optical axis of the molecule, respectively, θ is the angle between the direction of the long axis of the molecule and the optical axis of the uniformly oriented liquid crystal and α is the angle between the direction of the long axis of the molecule and the direction of the vibrational transition moment. Assuming cylindrical symmetry for the molecules, the quantity S_o which is related to the order parameter S is given as

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

Figures 6 and 7 show the order parameter, S_o, obtained for K15 molecules from the dichorism 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$\overset{..}{-}$C skeleton vibrations at 1580 cm^{-1} and benzene ring-oxygen stretching vibrations at 1245 cm^{-1}.[12] For the network molecules (Figure 6) except for the gel containing 10% w/w network molecules the order parameter shows only a slight change with increasing temperature. In the case where a large change is observed it can be as a result of the disorientation of many pendant groups present within the system. For K15 molecules (Figure 7) it can be seen that in all cases, the order parameter of the molecules decrease with increasing temperature. In the case of the system containing 90% w/w K15 molecules a sudden change in the order parameter at around 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_c transition temperature decreases, it never becomes zero even in the case of the gel containing 90% w/w K15 molecules. These results, which are in good agreement with the birefringence measurements, show that even at temperatures well above their T_c transition temperature some K15 molecules remain oriented. Together with this, the fact that the gels show a sudden drop in

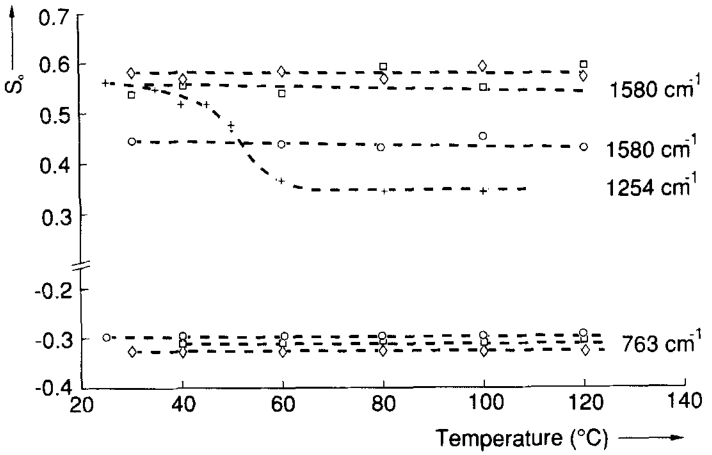

FIGURE 6 Order parameter S_o of the network molecules estimated from IR dichroism. □ = 90% w/w C6M, ○ = 70% C6M, ◇ = 30% C6M, + = 10% C6M.

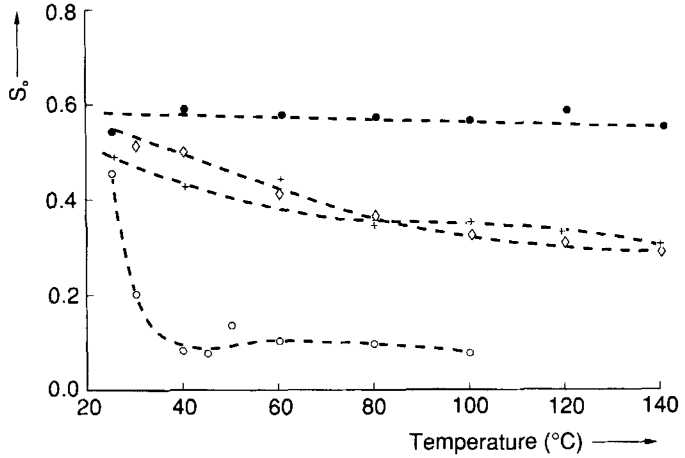

FIGURE 7 Order parameter S_o of K15 molecules in various networks estimated from IR dichroism. ● = 90% w/w C6M, + = 70% C6M, ◇ = 30% C6M, ○ = 10% C6M.

their birefringence accompanied with a drop in the order parameter of the K15 molecules at around 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 first order nematic to isotropic ($N \rightarrow I$) transition, whereas the other population behaves like the bulk K15. In order to check these possibilities further, DSC measurements were performed. Small quantities of samples were polymerized in DSC pans and the transition enthalpy involved in $N \rightarrow I$ transition (ΔH_{NI}) was recorded for various gels containing various amounts of network molecules. In Figure 8 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 concen-

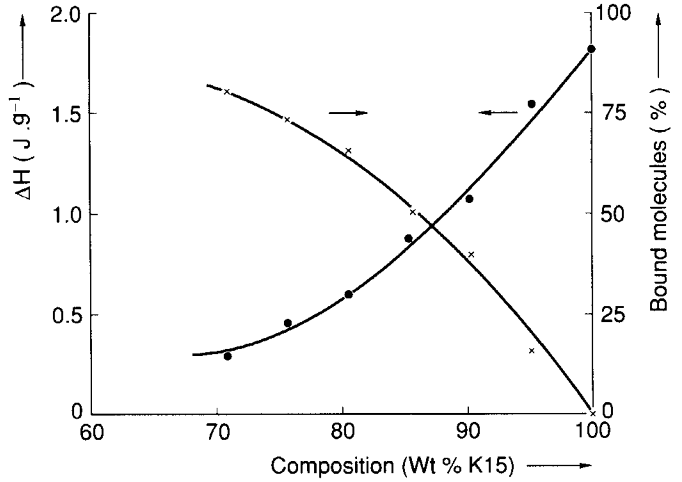

FIGURE 8 Heat of nematic to isotropic transition for K15 molecules and the fraction of bound K15 molecules in gels containing various amount of K15 molecules.

tration the ΔH_{NI} decreases and above 30% w/w network content the transition falls below the detection limit of the DSC. This result supports earlier observations and indicates that in these systems there are to 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 $N \rightarrow I$ transition with the enthalpy observed for the bulk K15 we calculated the fraction of the molecules bound by the network. The results are plotted in Figure 8. Here it can be seen that, as expected, with increasing network fraction more K15 molecules become bound. In the gel containing 70% w/w K15 molecules according to this figure almost 80% w/w of these molecules are bound by the network.

Structure of the Gels

In order to study the study the microscopic structure of the gels X-ray scattering was used. The pattern shown in Figure 9(a), which was obtained using a mixture composed of C6 and E7 (30% w/w C6), is a typical pattern obtained for all the nematic mixtures studied before polymerization. Broad equatorial wide angle peaks and the absence of any sharp low angle peaks in these patterns are indicative of the nematic phase. In Figure 9(b) the pattern obtained for a gel composed of C6M and K15 (30% w/w C6M) is shown. This pattern is very similar to the pattern obtained before polymerization indicating that the nematic structure became frozen in by photopolymerization. The diffraction pattern obtained for a gel composed of C6 and E7 (30% w/w C6) is shown in Figure 9(c). In this pattern as opposed to the ones shown in Figures 9(a) and (b) the existence of small angle peaks in addition to the wide angle peaks is clear. These peaks indicate that there is a lateral periodic smectic like structure within the system which was not present before polymerization (Figure 9a). The fact that the small angle peaks were also absent for gels which were made using C6M with E7 and C6 with K15 indicate that the formation

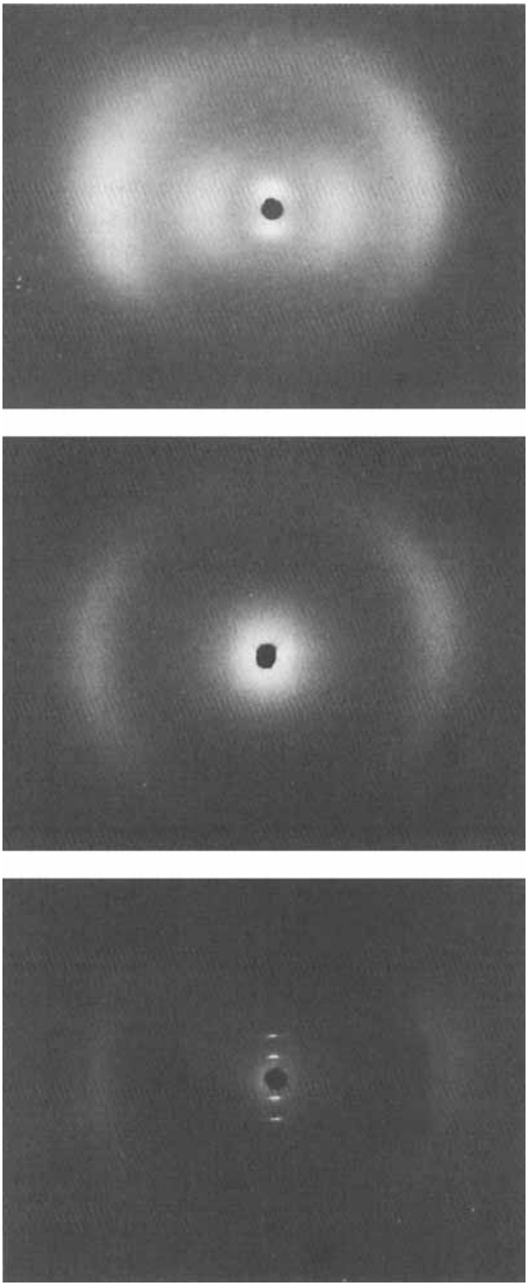

FIGURE 9 X-ray diffraction patterns of: a) Unpolymerized mixture containing 30% C6 in E7; b) Gel containing 30% C6M in K15; c) Gel containing 30% C6 in E7.

of the layered structures very much depend on the structure of the components making up the gel.

Electrically Induced Light Scattering

As described before, uniaxially oriented gels were produced in cells containing transparent electrodes. The orientation of the molecules induced by rubbed polyimide layers were parallel to the surfaces of the cells. In the scattering experiments C6 and E7 were used. When a transparent gel was subjected to an electric field the system became increasingly translucent with increased applied voltage. This effect is demonstrated in Figure 10, where the applied voltage across a 6 μm cell is plotted as a function of transmitted intensity for gels containing various amounts of E7. At low network content the system starts to scatter at around 14 volts, and at higher fields the scattering rapidly reaches a maximum level above which the scattered intensity decreases slightly. The decrease in the scattering is probably due to the relative orientation of the molecules within the scattering units, and this will be considered together with other related effects later in the text. The threshold voltage to cause scattering, however, increases rapidly with increasing network fraction, and the slope to reach the maximum level becomes less steep. The results observed here are in good agreement with the earlier suggestion that the high voltages required here to obtain reorientation of the molecules are due to the high degree of anchoring created by the oriented network molecules. As more and more network molecules are incorporated within the system the binding force on the free molecules becomes, larger and therefore higher voltages become necessary for reorientation. The effect of the applied field on the rise and fall times is shown in Figure 11. Here it can be seen that the rise times decrease with increasing applied

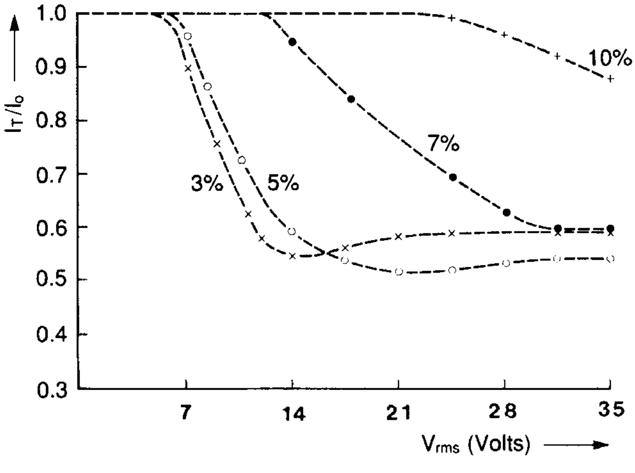

FIGURE 10 Normalized transmitted intensity as a function of voltage for gels containing various amounts of network molecules. × = 3% w/w, ○ = 5% w/w, ● = 7% w/w, + = 10% w/w.

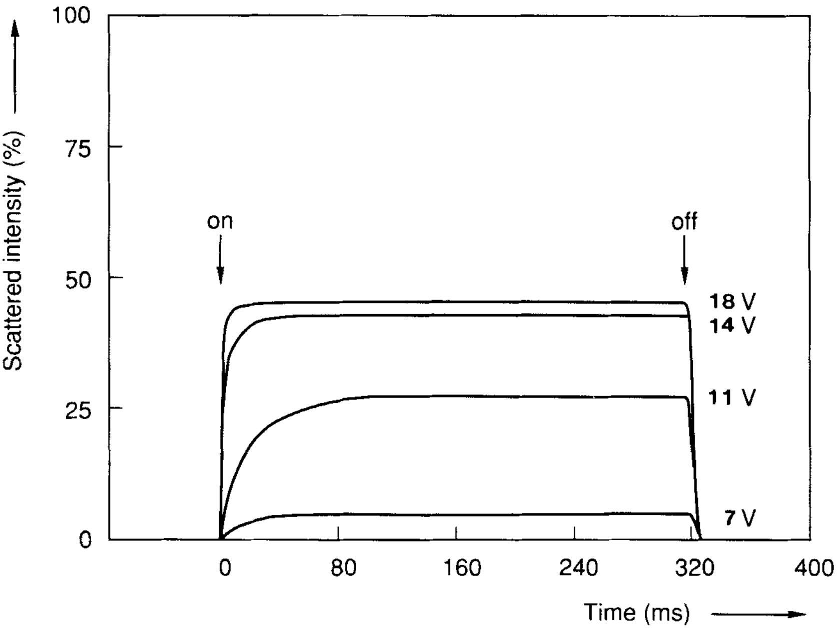

FIGURE 11 Response of 95% w/w E7 gel to various applied voltages across a 6 μm cell.

voltage as the decay times stay almost constant. For nematics the rise and fall times are represented by Equation (6)

$$T_{rise} = \eta[\Delta\varepsilon\varepsilon_o E^2 - Kq^2]^{-1} \tag{4}$$

and

$$T_{decay} = \frac{\eta}{Kq^2} \tag{5}$$

where η is the fluid viscosity, E the applied field, K the appropriate elastic constant and q the wave vector of the disturbance. For pure nematics the wave vector is approximately π/L, where L is the cell thickness.[6]

It can be seen that the rise time depends on the strength of the applied field as suggested by the theory for nematics. In order to check the effect of the cell thickness on the rise and decay times, cells with thicknesses of 6, 7.5 and 9.5 μm were used to produce a gel containing 95% w/w E7. It was found that with increasing cell thickness the rise time also increases, as suggested by Equation 4. However, the decay time remained almost constant. The effect of the network content of a gel on the decay times was also investigated. It was found that with increasing network content the decay time decreases rapidly. This implies that within the gel the disturbance vector is no longer the cell thickness but probably the average distance between the areas of the network molecules separated by the free molecules. This also explains the short decay times observed here as opposed to the long decay times (a few hundred milliseconds) observed for normal nematic cells.

It is also important to point out here that for unpolarized light the maximum transmitted intensity, regardless of the cell thickness used (6 − 10 μm), remained at about 50% of the incident intensity. The behavior can be associated with the selective scattering of one polarization direction. The effect of polarization direction on the intensity of the transmitted light is shown in Figure 12 where the transmitted intensity is plotted as a function of the angle Ω defined as the angle between the direction of molecular orientation and the plane of polarization. It can be seen in this figure that the maximum scattering is obtained when the Ω was 0°, whereas almost no scattering was observed when Ω was 90°. This means that the component of the light polarized in the direction perpendicular to the molecular orientation is transmitted almost without being scattered. This behavior can be associated with the orientation of the scattering domains and the molecules within the domains and can be accounted for in the following way. As previously suggested, before the application of the electric field the molecules are oriented uniaxially. Upon application of the field, molecules which are not strongly bound to the network reorient towards the electric field. In domains created under such a condition, it can be envisaged that the long axes of the molecules will become tilted with respect to the initial direction of molecular orientation. The ordinary refractive index n_o of a uniaxially oriented system shows no dependence on the angle between the incident beam of light and the direction of molecular orientation, whereas the effective extraordinary refractive $(n_e)_{eff}$ index is then given by

$$(n_e)_{eff} = \frac{n_e n_o}{(n_o^2 \sin^2\alpha + n_e^2 \cos^2\alpha)^{1/2}} \tag{6}$$

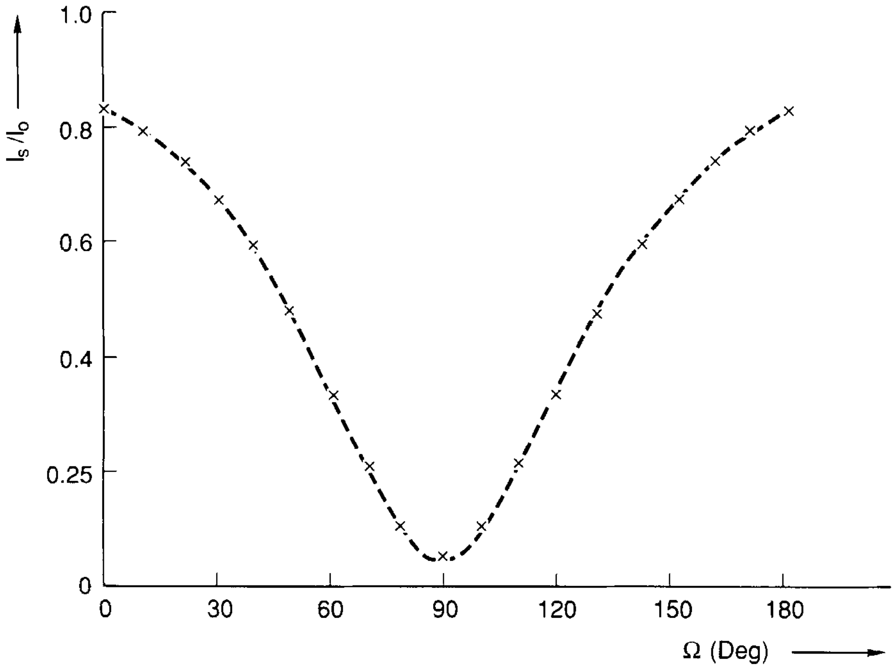

FIGURE 12 Transmitted intensity as a function of polarization angle Ω for 95% w/w E7 gel at V_{rms} = 14 V.

where α is the angle between the incident beam of light and the direction of molecular orientation and n_e is the extraordinary refractive index of the molecules.

Here it can be seen that in the above situation, for a beam of light falling perpendicular to the surfaces of the cells, the component of the light which is polarized in the direction perpendicular to the molecular orientation (horizontally polarized) will not be scattered since there is no refractive index variation along its path. The other component of the light polarized in the direction of molecular orientation (vertically polarized) on the other hand, will be scattered strongly due to large variation of refractive index along its path, explaining the observed behavior.

CONCLUSIONS

Here it was shown that anisotropic networks containing LC molecules which are not chemically attached to the network can be made. At all compositions systems did not cause any appreciable light scattering, they therefore looked very clear. In the systems the behavior of the LC molecules was found to be dominated by the network and even at temperatures much higher than the isotropic transition temperature of the LC molecules they remained partly oriented. In this way it became possible to identify two populations of LC molecules within the anisotropic networks: 1) molecules strongly bound by the network molecules which do not undergo first order nematic to isotropic phase transition, and ii) molecules free to behave like those in the bulk. At network concentrations as low as 30% w/w it was found that 80% w/w of the LC molecules within the network were bound and did not show nematic to isotropic transition. Anisotropic networks containing more than 50% w/w LC molecules did not show any detectable nematic to isotropic transition peaks or melting peaks.

It has also been shown here that anisotropic gels can be used in the production of a new display principle based on light scattering. Initially transparent gels became translucent when an electric field was applied across them. The rise time of the scattering was found to be dependent on the strength of the applied field, whereas the decay time was found to be dependent on the concentration of the network, and very short decay times could be observed. The scattered light was found to be highly polarized and the scattered intensity highly dependent on the wavelength of the incident light. The intensity of the scattered light depended on the applied voltage and with unpolarized white light 45% of the incident light could be scattered.

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