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Structure of cholesteric gels and their electrically induced light scattering and colour changes

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Networks with a helical structure containing large amounts of low mass liquid crystal molecules (gels) were produced by photopolymerization of a nematic diacrylate in the presence of low mass cholesteric mixtures. Prior to polymerization the systems selectively reflected a band of circularly polarized light. Upon polymerization, the gels obtained gave rise to two reflection peaks which were subsequently associated with polymer rich and polymer poor phases. At high network concentrations (>40 per cent w/w) one of the peaks did not appear, indicating that the behaviour of the molecules which were not chemically attached to the network was totally dominated by the network. From the gap required for the suppression of the rotation of the director, it was estimated that the molecules, which were not crosslinked, were confined in layers thinner than 85 nm. The gels were very transparent and did not give rise to excess light scattering as compared with the monomeric state. Upon application of an electric field, colour changes as well as light scattering were induced. These efffects were found to be highly dependent on the state of the polarization of the light as well as the kind of field applied. The response times were very short and they depended strongly on the structure of the network.

1. Introduction

Anisotropic gels and plasticized networks are a new class of materials [1–3] which can be used in the production of passive [4] as well as active [5, 6] optical systems. These materials are obtained by *in situ* polymerization of reactive liquid crystal molecules in the presence of conventional liquid crystal molecules. In this way anisotropic polymer networks containing free molecules (molecules which are not chemically attached to the network) are produced. In our previous studies [1, 2] concerning uniaxially oriented systems it was shown that the first order nematic to isotropic transition of the free molecules was suppressed with increasing network concentration up to a point above which no first order transition was observed. This behaviour was associated with the presence of a distribution of domain sizes within the system with a critical value below which no first order transition was to be observed, as predicted by theoretical considerations.

Apart from the thermal behaviour the electro-optic characteristics of the free molecules were also influenced to a large extent by the inclusion of the network molecules. It was found that [5, 6] when a sufficiently high electric field was applied to these transparent systems they turned translucent and light scattering could be induced. As compared with the monomeric state in a cell, much faster decay times were obtained upon creation of the network. However, the threshold voltage required to

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induce light scattering could be ten times higher in a system containing a small amount of network molecules than the Frederiks threshold in the absence of the network, showing further the large influence of the network on the free molecules. Even though the structure of the gels and plasticized networks has not been directly observed, there is evidence to suggest that the network molecules form a continuous rather than a discontinuous polymer phase. The results from our previous study [2] on cholesteric networks containing free molecules indicated that the free molecules are confined between layers of network molecules which dominated to a large extent the behaviour of the free molecules.

Here we describe the cholesteric gels in which a large amount of free molecules with a chiral component are contained in a network with a helical structure. The effect of the network on the cholesteric phase of the free molecules and the influence of direct and alternating electric fields on the scattering behaviour of various gels is described.

2. Experimental

The cholesteric dopant used in the studies was the chiral CB15 (Merck, Darmstadt). Desired amounts of the dopant were mixed together with the commercial mixture E44 (Merck, Poole) to form a chiral mixture. In the text we shall further refer to the concentration of CB15 in chiral mixtures by the digits placed after the letters CM. The desired quantity of the polymerizable liquid crystal diacrylate C6M described in [3] was then added to the chiral mixture to form a polymerizable mixture which was then provided with 1 per cent photoinitiator Irgacure 651 (Ciba-Geigy). Display cells with a gap of 6·5 μm containing rubbed polyimide layers and transparent indium tin oxide electrodes were filled with the mixtures. After obtaining a uniform Grandjean texture polymerization was initiated using a high pressure mercury lamp; the intensity used was 1·5 mW cm^{-2} (366 nm) unless stated otherwise.

UV-VIS spectrometry was carried out using a Philips PU 8740 UV-VIS spectrophotometer. Electro-optic responses of the gels were measured using a Helium–Neon 5 mW laser ($\lambda = 633$ nm) and a photomultiplier at a collection angle of 0·2°. Some measurements were also carried out using a microscope provided with the photomultiplier. An Abbe refractometer which could be heated was used for the refractive index measurements. For cyclic voltammogram measurements a Keithley 617 electrometer was used.

3. Results and discussion

3.1. *Properties of cholesterics*

3.1.1. *Monomeric cholesteric mixture*

Before investigating the effect of the network on the cholesteric phase of the free molecules we investigated the behaviour of the cholesteric mixture containing 40 per cent w/w CB15 molecules (CM40). The reason for the choice of this composition for the mixture will become clearer later. In figure 1 transmission spectra through CM40 obtained using right handed circularly polarized light are shown at various temperatures. This figure shows a typical behaviour for cholesterics where a band of circularly polarized light is selectively reflected. The width of the reflected band ($\Delta\lambda$) decreases as the mean (λ_m) shifts to larger wavelengths with increasing temperature before becoming isotropic at about 53°C.

For a cholesteric structure λ_m is given by [7]

$$\lambda_m = p n_{c,o}, \tag{1}$$

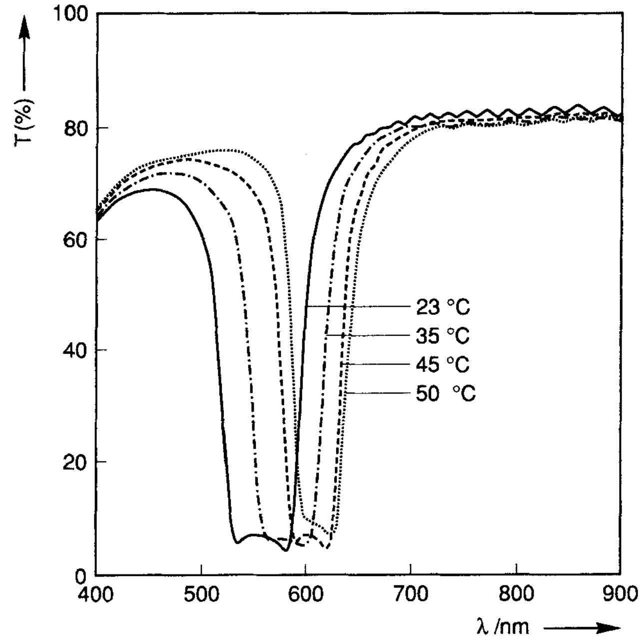


Figure 1. Transmittance as a function of wavelength for CM40 at various temperatures.

where ($n_{c,o}$) is the cholesteric ordinary refractive index and p is the pitch. Cholesteric ordinary and extraordinary ($n_{c,e}$) refractive indices of the material can be measured directly using a refractometer. These indices are related to the refractive indices (n_o, n_e) of a uniaxially oriented nematic phase by [8]

$$n_o = n_{c,e}, \tag{2}$$

$$n_e = [2n_{c,o}^2 - n_o^2]^{1/2}. \tag{3}$$

The width of the reflected band is given by

$$\Delta\lambda = p(n_e - n_o) = p\Delta n. \tag{4}$$

In the table refractive indices at various temperatures are given together with the pitch calculated using the values of λ_{max} in equation (1). It can be seen that with increasing temperature Δn also decreases showing that the decrease in $\Delta\lambda$ is associated with the decrease in the birefringence. Furthermore, it shows that the increase in λ_m with temperature is associated with the increase in the pitch.

3.1.2. *Cholesteric gels*

Polymerizable mixtures were formed by adding various amounts of C6M to CM40. Gels were obtained after the polymerization of the mixtures at room temperature. In figure 2 transmission spectra using right handed circular polarized light for a gel mixture containing 80 per cent w/w CM40 are shown before and after polymerization together with the spectrum of CM40 at room temperature. In this figure it can be seen that λ_m for the polymerizable mixtures before polymerization appears at a higher wavelength than that for CM40. This effect is partly due to the increase of $n_{c,o}$ and partly due to the reduction in the effective concentration of the chiral CB15 in the polymerizable mixtures giving rise to a larger pitch. Upon polymerization it can be seen

Pitch of the CM40 mixture as a function of temperature.

$T/°C$	n_o	n_e	p(mon)/nm
30	1·542	1·72	340
40	1·545	1·70	356
45	1·550	1·68	363

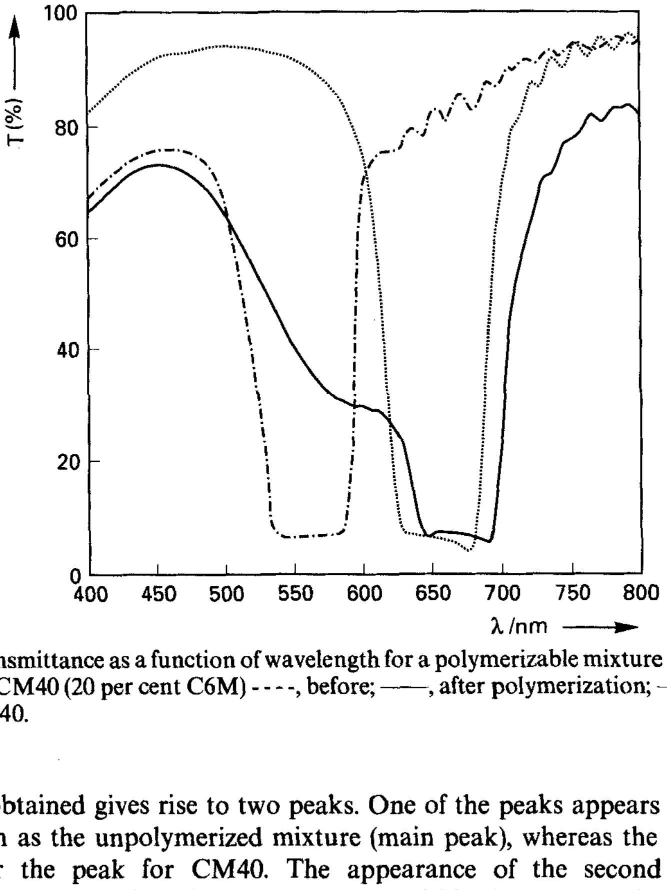


Figure 2. Transmittance as a function of wavelength for a polymerizable mixture containing 80 per cent CM40 (20 per cent C6M) - - - -, before; ——, after polymerization; — · — · —, 100 per cent CM40.

that the gel obtained gives rise to two peaks. One of the peaks appears at about the same position as the unpolymerized mixture (main peak), whereas the second peak appears near the peak for CM40. The appearance of the second peak upon polymerization is indicative of phase separation within the system. The fact that the main peak showed only a small change in its position upon polymerization indicates that it corresponds to the initial structure preserved by the network. Since only 20 per cent w/w of the system is the network the structure giving rise to the main peak probably contains a large percentage of CM40 molecules which are not chemically attached to the network but nevertheless their behaviour is influenced to a large extent by the network. The influence of the network is probably exerted on CM40 molecules by 'trapping' them between and/or within layers containing the network. In order to study this phase separation behaviour gels containing various amounts of CM40 were made and transmission spectra through the gels were measured as a function of temperature. The results are shown in figures 3(*a*), (*b*) and (*c*) corresponding to gels containing 90, 80 and 60 per cent w/w CM40 (10, 20, 40 per cent network) molecules, respectively. Here it is important to note that in these figures the gels containing 10 and

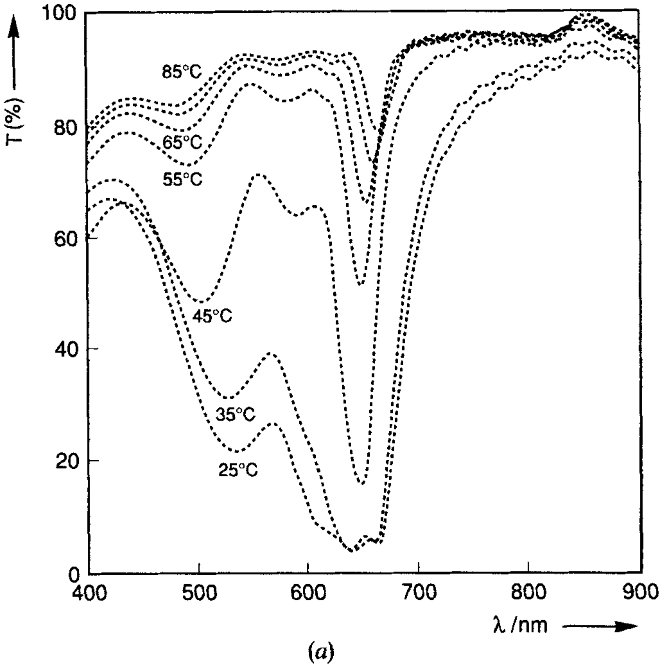
20 per cent w/w network show multiple peaks whereas the gel containing 40 per cent w/w network shows a single peak.

First we wish to discuss the behaviour of the main peak in figures 3 (*a*), (*b*) and (*c*). When the magnitude of the main peaks at a given temperature is compared, it can be seen that, especially at high temperatures, the magnitude of the peak increases with increasing network concentration. These results support our earlier suggestion that the main peak corresponds to the cholesteric structure dominated by the network. The fact that the system containing 40 per cent w/w network showed a single peak indicates that at high concentrations of the network the behaviour of the free molecules is totally determined by the network structure. In order for this to happen, assuming that the CM40 molecules are between layers of network molecules, rotation of the director, i.e. the pitch of CM40 (p_{cm40}) must be suppressed. Therefore the distance (d) between the network layers needs to be $d < p_{\mathrm{cm40}}/4 = 85$ nm (see the table). Here it is also important to note that the network concentration of 40 per cent observed here for the disappearance of the second peak, agrees well with our earlier observations [1, 3] where at about the same network concentrations the first order nematic to isotropic transition also disappeared.

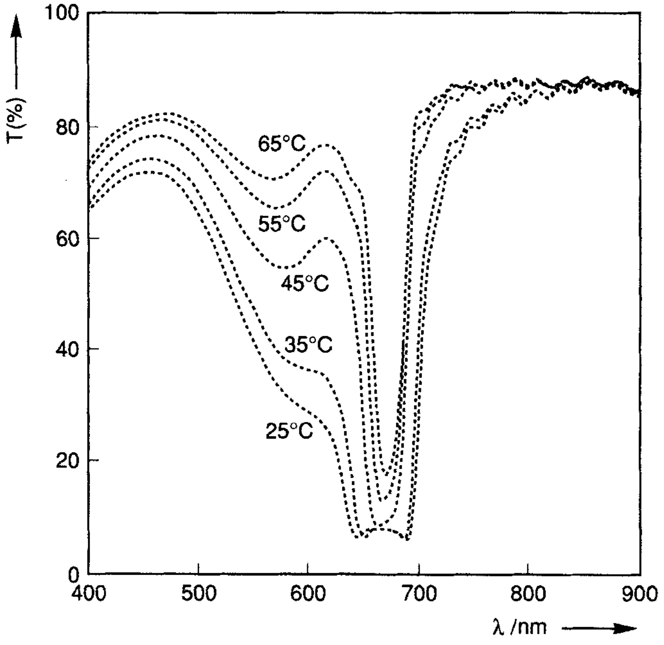
The other points to be emphasized in these figures are as follows: (i) The width of the main peak shows a decrease with increasing temperature indicating a decrease in Δn. In the case of gels containing higher amounts of network this decrease is smaller indicating the influence of the network on Δn within the structure. (ii) The magnitude of the main peak shows a decrease with increasing temperature which is most evident in figure 3 (*a*). It is known that the magnitude of the reflection peak is determined by the number of cholesteric pitches along the path of the light and according to theoretical calculations [9] for cholesteric layers thinner than ten pitch lengths the reflectance starts to decrease. Therefore the decrease in the reflected intensity observed here indicates a decrease in the number of pitches with increasing temperature.

Apart from the main peak in figures 3 (*a*) and (*b*) the existence of secondary broad peaks is clear. These secondary peaks appear in the region which corresponds to the reflection band of CM40. It is tempting therefore, to associate these peaks with the cholesteric structure dominated by the CM40 molecules since the secondary peak decreases in magnitude much faster than the main peak with increasing temperature (see figure 3 (*b*)) and it is totally absent in the gel containing 40 per cent network. In the case of pure CM40 the isotropic transition temperature at about 53°C coincides with the disappearance of the reflection band. However, for the gels the secondary peaks do not disappear completely above the isotropic transition temperature of CM40. It can also be seen most clearly in figure 3 (*a*) that unlike CM40 (see figure 1) the secondary peak moves towards smaller wavelengths with increasing temperature. This indicates that even though the behaviour of the secondary peaks is dominated by the chiral structure of CM40 molecules the structure probably also includes some pendant network molecules and its composition might even be different to that of CM40 in the bulk.

It has already been shown that in electric fields the behaviour of the molecules which are not chemically attached to the network molecules is influenced to a large extent by the network [2, 5, 6]. In order to investigate the behaviour of the two different populations of molecules which are not chemically attached to the network (two reflection bands) in electric fields we used the gel containing 90 per cent CM40. The effect of applying an alternating electric field was minimal and at a root mean square (rms) voltage of 60 V (1 kHz) a shift of a few nanometres in the position of the secondary


T (%)
100
80
60
40
20
0
400
500
600
700
800
900
λ /nm
85°C
65°C
55°C
45°C
35°C
25°C

(*a*)


T (%)
100
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λ /nm
65°C
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45°C
35°C
25°C

(*b*)

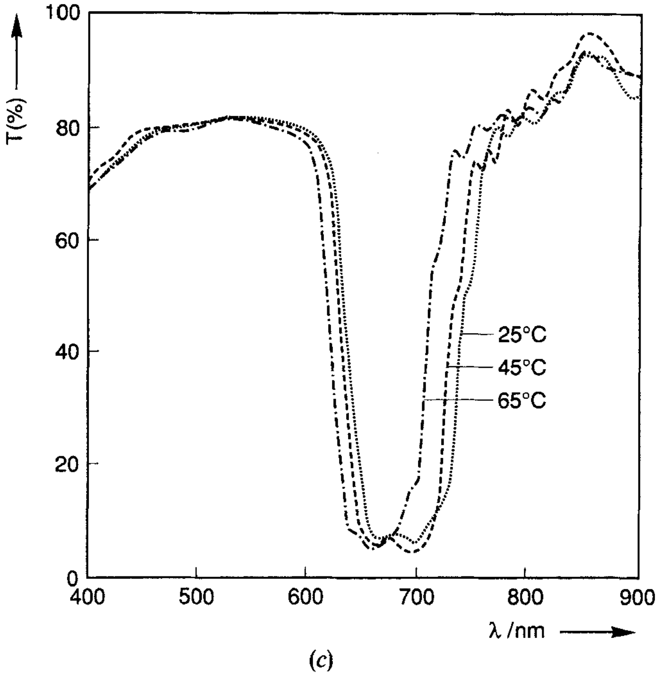


Figure 3. Transmittance as a function of wavelength measured at various temperatures for gels containing (*a*) 90 per cent, (*b*) 80 per cent, (*c*) 60 per cent CM40 molecules.

peak and almost no change in the position of the main peak was to be seen. For cholesteric low mass liquid crystals with a positive dielectric anisotropy the effect of an electric field applied along the helical axis is first to rotate the helical axis by $\pi/2$ and then to unwind the helix. The threshold voltage for the helix unwinding is (10)

$$V_c=\frac{2\pi d}{p}\left[\frac{k_{22}}{\varepsilon_0\Delta\varepsilon}\right]^{1/2}, \tag{5}$$

where $\Delta\varepsilon$ is the dielectric anisotropy, ε_0 is the permittivity of free space and k_{22} is the twist elastic constant. In the present case the absence of almost any change in the position of the main peak is not surprising since the rotation of the cholesteric helix is hindered to a large extent due to the presence of the polymer network. In the case of the secondary peak which is attributed to the phase containing CM40 molecules the small change indicates the large influence of the confinement imposed by the phase containing the polymer network since the threshold voltage of helical rotation for CM40 molecules in the absence of the network was found to be of the order of 9 V (rms).

The effect of DC fields was also investigated by keeping one of the electrodes at zero potential and applying a positive or a negative potential to the other. The results are shown in figure 4 where the transmission spectra for the gel are plotted at various potentials. For the positive potential it can be seen that both peaks move towards higher wavelengths as they decrease slightly in magnitude. The shift towards higher wavelengths cannot be attributed to the rotation of the pitch or decrease in the birefringence since the result would be a shift towards shorter wavelengths. The only feasible explanation, therefore, is the expansion of the cholesteric pitch upon application of a positive potential. The effect of reversing the direction of the applied field is also shown in figure 4. It can be seen that while the main peak as in the previous

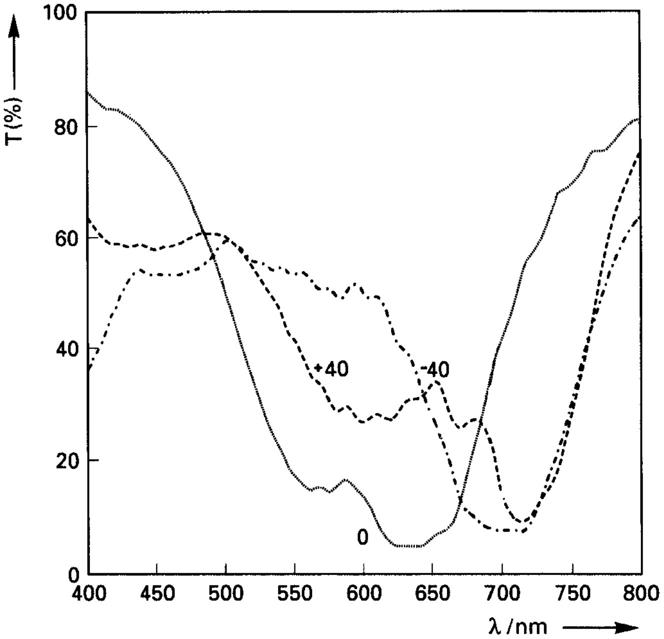


Figure 4. Transmittance as a function of wavelength at various DC voltages for a gel containing 90 per cent /w CM40 molecules at positive and negative DC voltages.

case shifted towards higher wavelengths the secondary peak tended to disappear leaving behind a scattering background indicating a helical rotation. The fact that the secondary peak is influenced to a larger extent by the electric field supports our earlier suggestion that is corresponds to the phase dominated by the molecules of the cholesteric mixture.

However different response of the gel to different fields is difficult to explain. A reason for the observed behaviour may be the existence of polarity within the system. In order to check this possibility a cyclic voltammogram was obtained by applying a triangular alternating potential across the sample. However, the voltammogram curve was quite symmetrical about the zero point showing that the direction of the current flow did not influence its magnitude. This indicated that the phase giving rise to the secondary peak was sensitive to the direction of flow of the charges whereas the phase containing the network was influenced to a much smaller extent by the flow. The observed response of the gel to DC fields may also be attributed to the piezoelectricity of cholesteric structures proposed by Brand [11]. However it will not be discussed further as it goes beyond the scope of this paper.

3.2. *Electrically induced scattering and colour change of the gels*

3.2.1. *Electrically induced colour changes*

In the previous section it has been shown that the gels contain polymer poor and polymer rich regions. It has also been shown that already at 10 per cent w/w network concentration the response of the gel especially using alternating fields was influenced to a large extent by the network and only small effects could be observed. Therefore, in this section we have used gels containing 5 per cent w/w network. In order to change the pitch we changed the CB15 concentration of the cholesteric mixtures. First, we show the effect of an applied field on gels which reflect a band of light in the visible region. In figure 5 transmission spectra using circularly polarized light for the gel containing CM40 molecules are shown at various applied rms voltages (1 kHz). All of the spectra were obtained using right handed circularly polarized light except for the spectra for 35 V which was obtained using left handed circularly polarized light. It can be seen that the effect of the field is to shift the reflection peak towards shorter wavelengths, while decreasing its magnitude and causing a background scattering. This is quite different to the behaviour observed for the gel containing 10 per cent w/w network (see figure 4), where the application of a DC field caused the shift of the reflection peak towards higher wavelengths. The shift towards shorter wavelengths can either be caused by a decrease in the $n_{c,o}$ or rotation of the axis of the cholesteric helix. However, a decrease in $n_{c,o}$ would also result in a decrease in Δn, hence $\Delta\lambda$. The fact that only the position and not the width of the reflection peak changes indicates that the observed shift is probably caused by the rotation of the helix. The effect of background scattering is best demonstrated in figure 5 where a spectrum for left handed polarized light is also shown. The speed of the colour change was studied by measuring the reflection from the gel containing 95 per cent CM40 molecules at 589 nm and the results are shown in figure 6. It can be seen that the reflected intensity decreases with increasing voltage caused by the shifting of the reflection maximum towards lower wavelengths as shown in figure 5. However above 35 V no further change in the reflected intensity was observed as the systems become more scattering. Furthermore in figure 6 it can also be seen that the decay times are very fast. For cholesterics in the absence of the network, electric field induced scattering is caused by the rotation of the cholesteric helix [12]. Upon removal of the field the scattering state persists for several minutes while it gradually disappears.

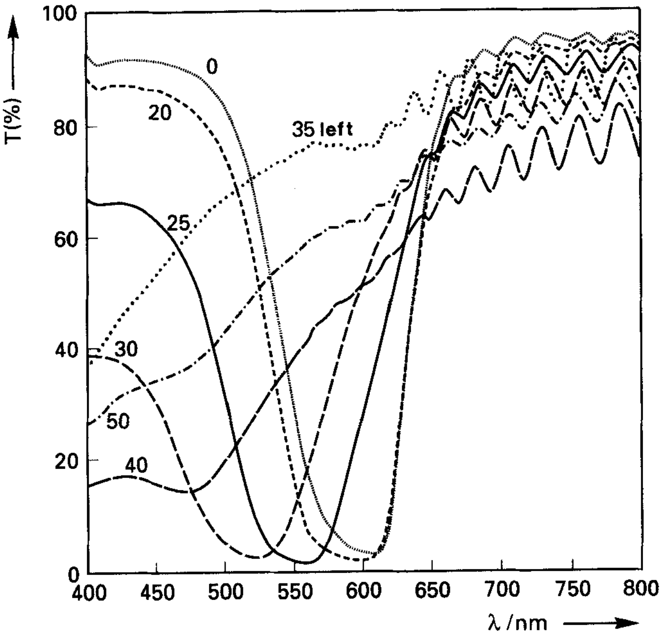


Figure 5. Transmittance as a function of wavelength obtained for a gel containing 95 per cent w/w CM40 molecules at various rms voltages using right handed circularly polarized light; ····, 35 V left handed circularly polarized light.

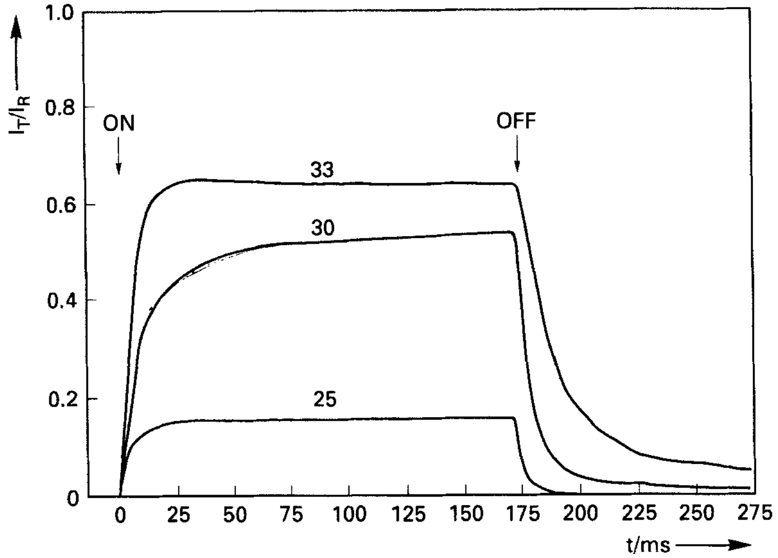


Figure 6. Normalized transmitted intensity with respect to 100 per cent reflectance as a function of time at various rms voltages for a gel containing 95 per cent w/w CM40 molecules.

Here the presence of the network makes it possible for a gradual rotation of the cholesteric helix and shift of the reflection band. However, it should also be noted that the colour change observed here is not only confined to gels but it has also been observed for various cholesteric systems [13]. The most important purpose served by the network is to bring the molecules back to the initial state at a high rate.

3.2.2. *Electricity induced light scattering*

Scattering effects in cholesteric systems have been known for a long time [12, 13]. For the so-called storage mode an electric field is applied across a cholesteric sample with the Grandjean texture to induce a light scattering focal conic texture which persists upon removal of the field. Since both Grandjean and focal conic textures can be stable the system is suggested for display applications [14]. In order to study the effect of electrically induced light scattering further we used the gel containing 95 per cent CM5 molecules. The pitch induced by this mixture was estimated to be 3 μm using the Cano wedge method [15]. The gels were produced under two different UV intensities. It is already known [6] that the UV intensity controls the speed of polymerization and so influencing the structure of the network formed. As a result different response characteristics are expected. Transmission spectra for gels using left and right handed circularly polarized light at an AC (1 kHz) field as well as at plus and minus DC fields using left handed circularly polarized light are shown in figures 7 and 8 for gels obtained at UV intensities of 1·5 and 0·15 mW cm^{-2}, respectively. In these figures the voltages correspond to a high scattering state for different fields. One of the effects to be seen is that the left handed circularly polarized light is scattered to a larger extent than right handed circularly polarized light. In our previous publications [5, 6] it was shown that the scattering is caused by the domains between the network molecules which change their orientation upon application of an electric field. For the uniaxially planar oriented system light polarized in the direction along the molecular orientation was

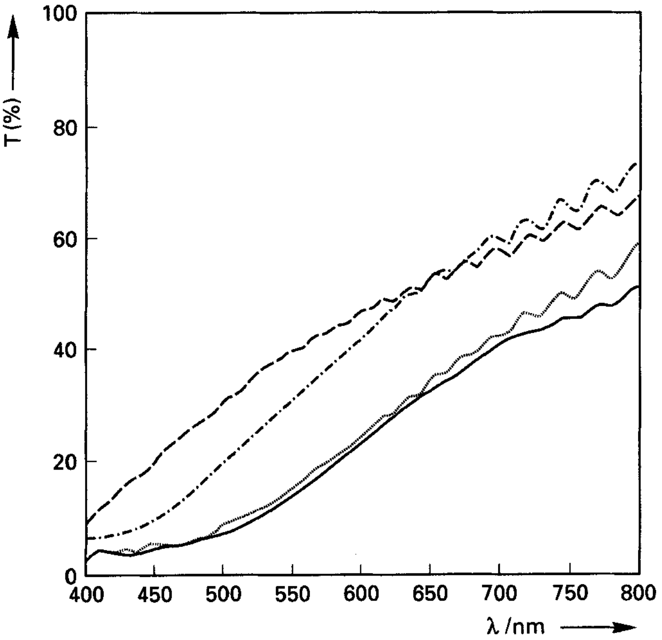


Figure 7. Transmittance as a function of wavelength for a gel containing 95 per cent w/w CM5 molecules produced under 1·5 mW cm^{-2} UV intensity. Spectra obtained: – – –, 20 V (rms) right circular; - - - -, 20 V (rms) left circular; ——, −40 V (DC) left circular; –·–·–, 40 V (DC) left handed circularly polarized light.

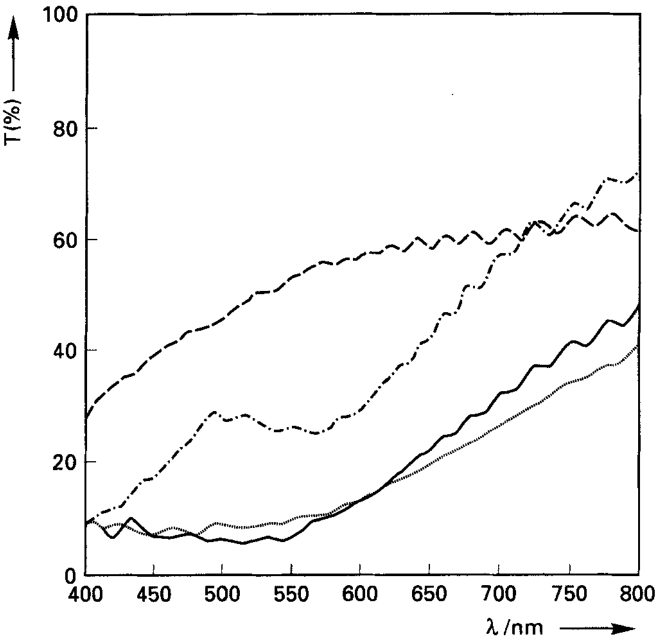


Figure 8. Transmittance as a function of wavelength for a gel containing 95 per cent w/w CM5 molecules produced under 0·15 mW cm^{-2} UV intensity. Spectra obtained: – – –, 15 V (rms) right circular; - - - -, 15 V (rms) left circular; –·–·–, −10 V (DC) left circular; ——, 40 V (DC) left handed circularly polarized light.

scattered to a much larger extent than the light polarized in the perpendicular direction. In the present case the fact that left handed circularly polarized light is scattered to a larger extent indicates that the left handed circularly polarized light realizes a larger refractive index variation along its path than right handed circularly polarized light. However, it is also important to note that neither of the polarizations of the light are fully scattered. This is probably partly due to the magnitude of refractive index variation along the light path. For example, the circular polarized component of light with a sense opposite to that of the cholesteric helix (in the present case left handed circularly polarized) in the field-off state, experiences an average refractive index of $n_{c,o}$ as it passes through the system. In the field-on state therefore the maximum refractive index variation possible along the path of the light is $n_{c,o}-n_{c,e}$; for the gel containing 95 per cent CM5 molecules $n_{c,o}-n_{c,e}=0{\cdot}136$. The magnitude of the refractive index anisotropy within a gel is known [5] to have a large influence on the scattering efficiency and it has been shown that the refractive index anisotropy of 0·262 caused more than 90 per cent of the light to scatter as compared with the scattering efficiency of about 60 per cent for the system with a refractive index anisotropy of 0·146. Therefore, the low scattering efficiency observed here is probably partially associated with the refractive index anisotropy within the gel. Due to normal dispersion the refractive index anisotropy increases with increasing wavelength and in figures 7 and 8 it can be seen that at shorter wavelengths the scattering increases. However, how much of this effect is due to the refractive index anisotropy and how much of it is due to the wavelength dependence of the scattered intensity is not clear. Nevertheless it can be seen that the scattered intensity is not proportional to $1/\lambda^4$ as would be expected from Rayleigh scattering indicating the complex nature of the scattering induced by the gels. The influence of other factors such as the domain size and the structure will be demonstrated later.

As before, we also studied the effect of AC and DC voltages on the system using the helium–neon laser (633 nm). Figure 9 shows the transmitted intensity for left and right handed circularly polarized light as a function of rms voltage (1 kHz) and figure 10 shows the transmitted intensity as a function of positive and negative DC voltages for gels containing 95 per cent w/w CM5 molecules polymerized under 0·15 and 1·5 mW cm^{-2}. It can be seen that for a certain polarization the kind of voltage applied has an important effect on the shape of the intensity versus voltage curve. For example, in figure 9 it can be seen that for different polarizations of light the maximum scattering occurs at different voltages. This indicates that the efficiency of scattering does not depend only on the sense of polarization of light but each polarization sense is influenced in a different way by the domain structure formed by the kind of applied field. Here it is interesting to note that in each case for a given polarity of the applied field the maximum scattering obtained is also different. At the AC frequency of 1 kHz used here the influence of the ionic impurities is minimal therefore the scattering is due to the reorientation of molecules under the electric field. This indicates that the kind of domain formation is not only dependent on the field being AC or DC, but it also depends on the sign of the DC voltage, i.e. the direction of the current flow as well. Furthermore, the voltage for inducing scattering is higher for the gel produced under high UV intensity. As previously shown [6], we attribute this effect to the size of the 'domains' containing CM5 molecules which form during polymerization. In the case of the gels formed under high UV intensity, polymerization proceeds at a high rate giving rise to smaller domains. In smaller domains a higher degree of interaction between the polymer network and liquid crystal molecules in turn causes higher threshold voltages

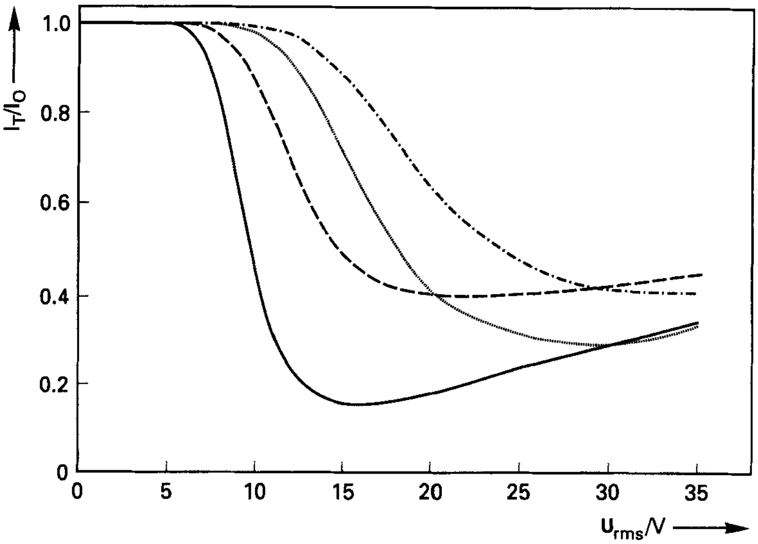


Figure 9. Normalized transmitted intensity (633 nm) as a function of rms voltage for a gel containing 95 per cent w/w CM5 molecules using ——, left; – – –, right handed circularly polarized light for gel obtained under 0·15 mW cm^{-2} UV intensity. - - - -, left; —·—·—, right handed circular polarized light for gel obtained under 1·5 mW cm^{-2} UV intensity.

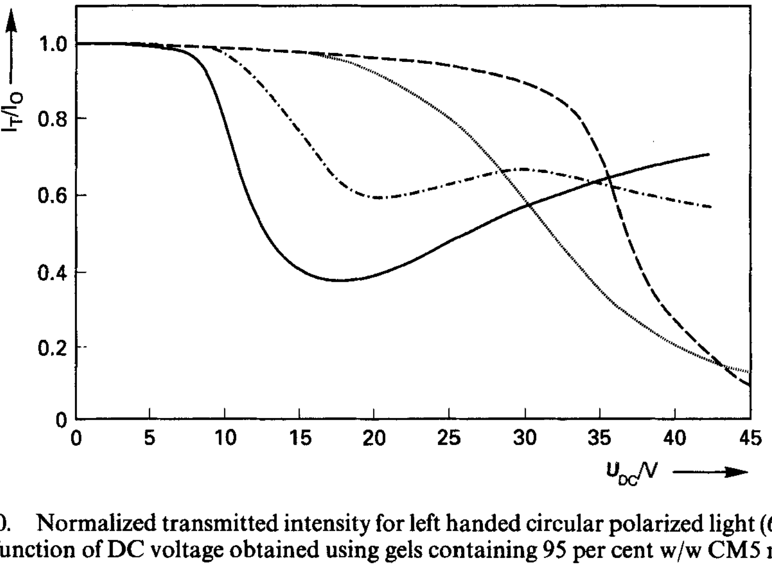
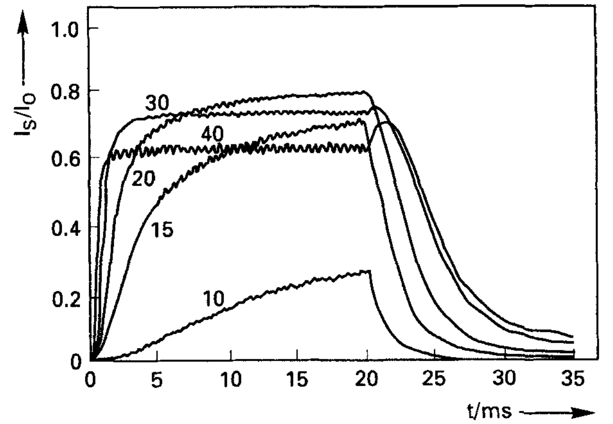


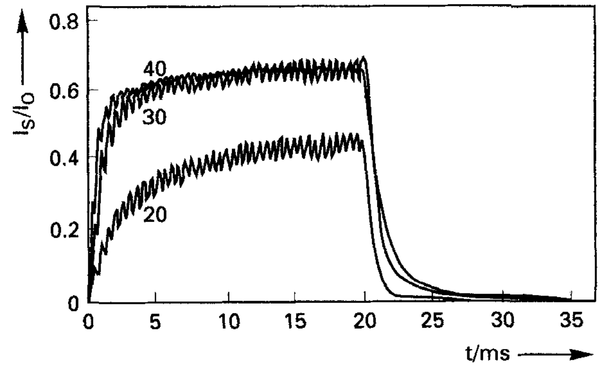
Figure 10. Normalized transmitted intensity for left handed circular polarized light (633 nm) as a function of DC voltage obtained using gels containing 95 per cent w/w CM5 molecules. - - - -, positive; ——, negative DC for the gel obtained under 0·15 mW cm^{-2} UV intensity. – – –, positive; —·—·—, negative DC for the gel obtained under 1·5 mW cm^{-2} UV intensity.

for scattering. The effect of the speed of polymerization is also evident from the maximum scattering obtained. Most clearly in figure 9 it can be seen that the maximum scattering obtained for the sample polymerized under lower UV intensity is higher. This effect is also a further manifestation of the different kind of domain structure formed in each case.

Apart from the scattered intensity, the response times of the gels were also measured by applying a block pulse of AC field (1 kHz). The response of a gel containing 95 per cent CM5 molecules obtained at 0·15 and 1·5 mW cm^{-2} UV intensities to various fields is shown in figures 11 (*a*) and (*b*). It can be seen in each figure that with increasing voltage the rise times become shorter as the decay times become longer, as was also observed for liquid crystal molecules in conventional cells. Here it is clear that at a given voltage rise times for the gel obtained under high UV intensity are longer, whereas the decay times are shorter, as was also observed for previously studied [5, 6] gel systems. As before we attribute these effects to the interaction between the polymer network and the liquid crystal molecules. Furthermore, in figure 11 a periodic high frequency change in the intensity superimposed on a background level during the duration of the AC block pulse can also be seen. This effect is attributed to the fast response of the system which can also partially follow the AC field.



(*a*)



(*b*)

Figure 11. The scattered intensity for left handed circular polarized light (633 nm) as a function of time at various rms voltages for gels containing 95 per cent w/w CM5 molecules obtained under (*a*) 0·15 mW^{-2}, (*b*) 1·5 mW cm^{-2} UV intensity.

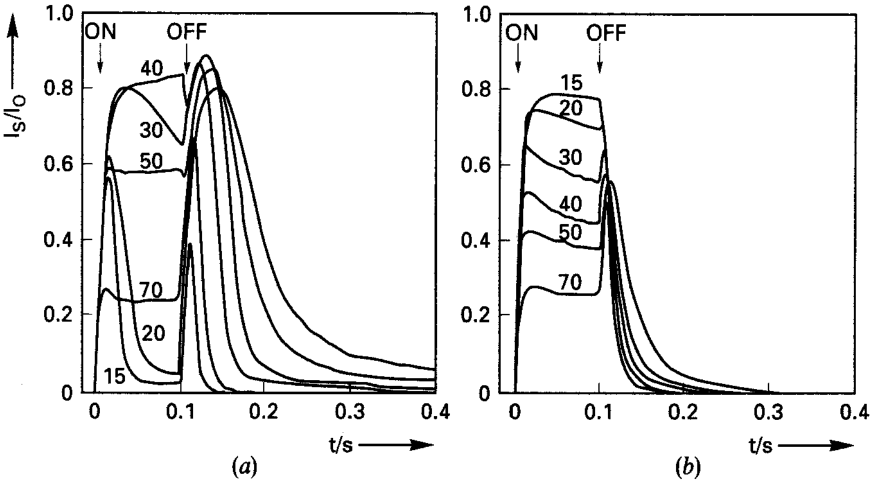


Figure 12. The scattered intensity for left handed circular polarized light (633 nm) as a function of time for a gel containing 95 per cent w/w CM5 molecules obtained under 0·15 mW cm^{-2} at various (*a*) positive, (*b*) negative DC voltages.

In addition to the response of the gels to AC fields, their response to DC fields was studied. In figures 12(*a*) and (*b*) the response of the gels to negative and positive potentials is shown. For the positive potential especially at low voltages at the start of the pulse the scattered intensity increases rapidly before starting to decrease continuously to reach a much lower level. At the end of the pulse a transient increase in the scattered intensity was seen before the sample became clear. An explanation for this behaviour is the presence of ionic impurities. Upon the application of the electric field movement of the liquid crystal molecules and the ions occur together reducing the effective field across the cell which would explain the transient increase in the scattering upon application of the pulse. Subsequent to the removal of the field opposite charges separated during the duration of the pulse move to recombine, giving rise to the observed transient increase in the scattering at the end of the pulse. The increase in the duration of the transient scattering observed at the end of the pulse, however, is probably due to the larger deviation of liquid crystal molecules as well as the charges with respect to the rest state. When the response of the gel to the negative field is considered (see figure 12(*b*)), the difference in the behaviour is apparent. In this case except for high fields there is almost no transient increase in the scattering upon application of the pulse. This indicates that the ion pairs are only present at one of the electrodes and only the positive or negative ions are mobile. Therefore, upon application of the reverse field no or a small movement of the charges occurs so that the field across the sample remains almost unchanged during the duration of the pulse. Upon the removal of the field a transient increase is observed due to the reorientation of the liquid crystal molecules. In order to investigate the behaviour of the ionic impurities a cyclic voltammogram was made. The result is shown in figure 13 where the change of current as a function of voltage is given. It can clearly be seen that the curve is not symmetric about the zero potential. This behaviour conforms with the suggestion that the ion pairs at one of the surfaces are easier to dissociate than at the other. Electrochemistry and associated behaviour in nematic solvents are frequently observed [16]. However, the origin of the behaviour of the electrodes in the present study is difficult to explain.

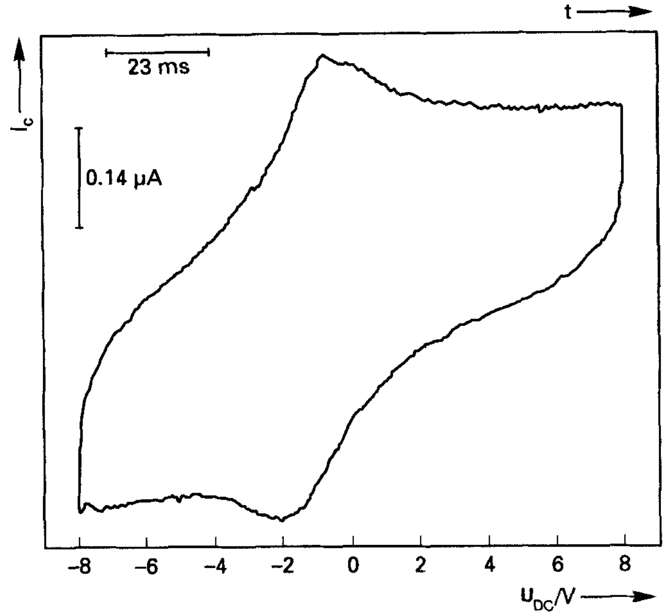


Figure 13. The cyclic voltammogram for a gel containing 95 per cent w/w CM5 molecules.

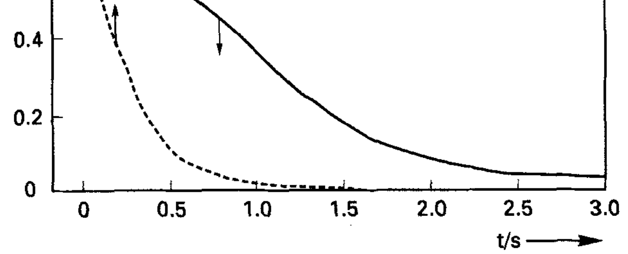


Figure 14. The normalized scattered intensity for left handed circular polarized light (633 nm) as a function of time for a gel containing 95 per cent w/w CM5 molecules obtained under 0·15 mW cm^{-2} after applying -15 V (DC) ---, short circuit; ——, open circuit state.

Finally we investigated the behaviour of the gel in the open circuit state. In figure 14 the scattered intensity upon application of a negative potential and subsequently (i) removing it leaving behind an open circuit and (ii) short circuiting the cell to zero potential are compared. In this figure it can be seen that as expected in the open circuit state the decay of the charges occurs very slowly as can be seen from the gradual decrease in the scattered intensity. As can be expected in the case of short circuiting the field across the sample the charges disappear almost instantaneously causing a rapid decrease in the scattering. The slow discharging in the open circuit state is a very important effect concerning the use of the materials in TV applications. The observed charge effects here go beyond the scope of the present paper, however they are being investigated further as a subject for future publications.

4. Conclusions

It has been shown that it is possible to produce cholesteric gels consisting of a non-chiral network with a helical structure containing low mass liquid crystal molecules having a chiral component which are not chemically attached to the network. The gels which were obtained by photopolymerization of liquid crystal diacrylates contained two populations of molecules which were not chemically attached to the network. Each population was characterized by a band of circularly polarized light which it selectively reflected. One of the populations was influenced to a large extent by the network, whereas the second population behaved much the same as in the bulk. The influence of the network on the liquid crystal molecules increased with increasing network concentration and in the gel containing 40 per cent w/w there was only one population, whose behaviour was dominated by the network molecules. For this to happen it was estimated that the molecules are confined between layers of network molecules thinner than 85 nm.

When an electric field was applied across the light scattering gels as well as for gels giving rise to a reflection band, a shift in the band position was observed. Due to the network, fast response times and reversible deformation of the cholesteric structure could be obtained. Due to the helical structure it was found that the circular polarization with a sense opposite to that of the cholesteric gel was scattered to a much higher extent than the other polarization direction. In both cases it was not possible to obtain more than 90 per cent scattering. Furthermore the scattering efficiency depended strongly on the wavelength of the light used. The structure of the gels as controlled by the speed of polymerization also affected the degree of scattering as well as the threshold voltage for scattering. The gels response to AC and positive and negative DC voltages was different, which is probably caused by the different behaviour of the ion pairs at different electrodes.

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