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Electrically Induced Light Scattering from Anisotropic Gels with Negative Dielectric Anisotropy

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Homeotropically aligned gels were obtained by photo-induced crosslinking of a liquid crystalline (LC) mixture containing LC diacrylates and conventional LC molecules with negative dielectric anisotropy. The gels produced in this way were very clear as observed from all directions. When an electric field was applied across the gel, its appearance changed and a light scattering texture was formed. The intensity of the scattered light increased non-linearly with increasing voltage in a reversible way. Light scattered by the gels was not polarised and, especially at high voltages, the scattering efficiency of the gels was found to be independent of the direction of the incident light. In the case of gels containing dye molecules, scattering was combined with absorption. In this way grey levels for dye absorption could be obtained.

INTRODUCTION

Liquid crystalline (LC) systems working on the principle of light scattering are of great interest, since they require no polarizers to produce the contrast. In these systems the optical anisotropy of LC molecules in small domains is used to induce light scattering. The earliest form of this kind of display, the dynamic scattering display,[1,2] was described long before the commonly used twisted nematic display.[3] In the dynamic scattering mode, application of a sufficiently high electric field induces turbulence caused by the flow of ionic impurities or dopants, leading to scattering of light. Hence there is a difference in the transmitted light intensities between the on and off states. Another system which works on a similar principle uses smectic LC and shows bistable characteristics.[4,5] In this system a smectic LC with positive dielectric anisotropy is used. At low frequencies, flow of ions results in the breaking up of the smectic layers to form a scattering texture which remains stable after the removal of the electric field. Upon application of a high-frequency electric field, clear homeotropic orientation of the molecules is obtained. This system however has long response times. In another invention[6] which also uses smectic LC materials, switching between scattering and non-scattering is initiated by the coordinated use of heat and an electric field. In this way very short response times can be obtained. Cholesteric systems[7] are also used in the production of

scattering effects. In the on state, the cholesteric helix unwinds, giving a clear homeotropic orientation. Upon removal of the electric field, a scattering texture formed by the randomly oriented cholesteric structure is obtained. Recently LC dispersed polymer films have been suggested as display units.[8,9] In such systems, sub-micron droplets of LC molecules are dispersed in a polymer matrix. In the off state, mismatch in the refractive indices of the polymer and the LC molecules causes scattering. Application of an electric field to such a two-phase system containing LC molecules with positive dielectric anisotropy aligns the molecules in the direction of the applied field. When the ordinary refractive index of the LC molecules is matched with the refractive index of the polymer, the intensity of the light travelling parallel to the electric field can be altered by the electric field. Many applications have been suggested for this novel display system which requires no polarizers. They range from large-area displays and switchable coatings for windows to projection displays. Indeed, the use of such a display in a colour projection television system has already been demonstrated.[10]

In a recent publication,[11] a novel gel system formed by interconnected phases of free LC molecules and cross-linked polymer molecules which can be used for electrically induced light scattering was described. The anisotropic gel was produced[12] by photopolymerising an LC mixture containing LC diacrylates in a planar uniaxially oriented state. In the absence of an electric field, no scattering was observed. Upon application of an electric field across the uniaxially oriented gel system, containing LC molecules with positive dielectric anisotropy, light scattering could be induced. However, such a uniaxially oriented system was found to scatter only one of the polarisation directions effectively. In the present publication, in order to induce isotropic light scattering, a homeotropically oriented gel system containing LC molecules with negative dielectric anisotropy has been used. Here the production of these homeotropically oriented gels and the effect of the structure and the concentration of the anisotropic network molecules on the electrically induced light scattering from these gels are described. Furthermore, the effect of inclusion of dichroic dye molecules in these gels is discussed.

EXPERIMENTAL

Materials and Sample Preparation

The structure of the diacrylate (C6H) used in the study is shown in Figure 1. The other LC material used in the study is a commercially available mixture ZLI4788 (Merck, Darmstadt) with room temperature refractive indices of $n_o = 1.486$, $n_e = 1.650$. The dichroic black dye (S409) which shows a high absorbance from 420–700 nm was obtained from Mitsui Toatsu Chem. Inc. (Japan). The photoinitiator used was Irgacure 651 supplied by Ciba Geigy. In order to produce homeotropically oriented gels the following procedure was used. The desired amount of C6H was

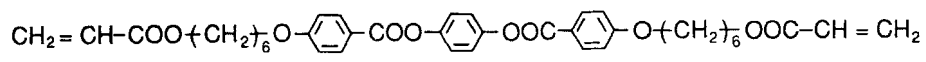

FIGURE 1 The liquid crystalline diacrylate.

mixed with the LC mixture, and 1% w/w of photoinitiator was added to the total mixture. Common LC display cells provided with transparent electrodes and 3-*N*,*N*-dimethyl-*N*-octadecylaminopropyltrimethoxysilyl chloride (DMOAP) aligning layers for inducing homeotropic orientation were filled with the polymerisable mixtures. After obtaining homeotropic orientation of the molecules, polymerisation was initiated by UV radiation from a high-pressure mercury source. The intensity of the radiation could be controlled by varying the distance between the source and the object. The cell thicknesses used were 8 μm unless stated otherwise.

Electro-Optic Measurements

The optical properties and electro-optic responses of the gels were measured using a Helium-Neon 5 mW laser and a photo-detector. A circular aperture positioned in front of the detector ensured a collection angle of 0.2° for the transmitted light. The electric pulse applied was a sinusoidal wave (1 kHz) modulated with a square wave. Electrical pulses from the signal generator and the response of the photo-detector were fed into a storage oscilloscope. Results could then be plotted on an X-Y recorder. The set-up and the definition of the angles are shown in Figure 2. The wavelength dependence of the scattered light was measured using a Philips PU8740 UV-Visible spectrometer.

RESULTS AND DISCUSSION

Scattering Characteristics of the Gels

As described before,[11] anisotropic gels were produced by filling a cell and by polymerising the acrylate monomer after obtaining homeotropic orientation of the

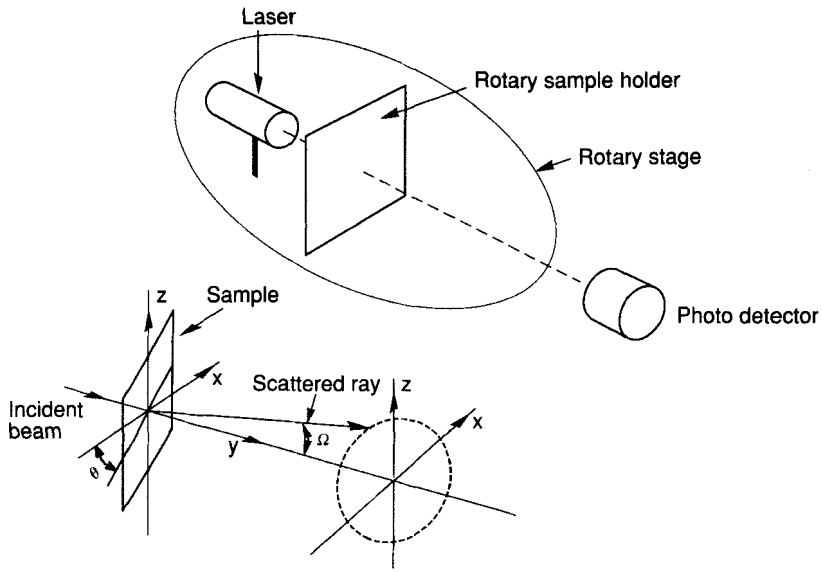

FIGURE 2 Schematic representation of the set-up used for studying the light scattering and the angles defining the scattering.

molecules. After completion of the polymerisation, the system remained clear. When a sufficiently high electric field was applied across the gels they became translucent. The previously described system with a positive dielectric anisotropy[11] had a uniaxial planar orientation and a strong birefringence. As a result, the scattering obtained from the system was highly polarised. In the present case however, the scattered light was found to be unpolarised. When the gels were observed between crossed polarisers, the areas which did not cause scattering appeared dark, whereas the areas giving rise to depolarisation of light by scattering appeared bright. When the system was observed under normal back lighting, the scattering areas in the gels appeared darker. A photograph of a projected image of a gel by an overhead projector is shown in Figure 3. In this figure the scattering areas appear darker than the rest.

As shown before,[11] the scattering observed from the gels is a result of the domains created between the network molecules. In the homeotropic orientation, the molecules have no sense of tilt direction, and therefore upon application of an electric field, they all orient in different directions creating domains. However, the domains which form in the absence of the network are too large to give rise to effective scattering of light. Creation of a network however changes the situation, giving rise to smaller domains to induce more effective scattering of light. The effect of the network on the voltage-scattering characteristics of a gel system is best demonstrated in Figure 4, where the transmitted intensity is plotted as a function of root mean square (rms) voltage for gels containing various amounts of network molecules obtained under two different UV intensities. When the gels containing 5 and 10% w/w of network molecules, polymerised under 3 mW/cm^2, are compared,

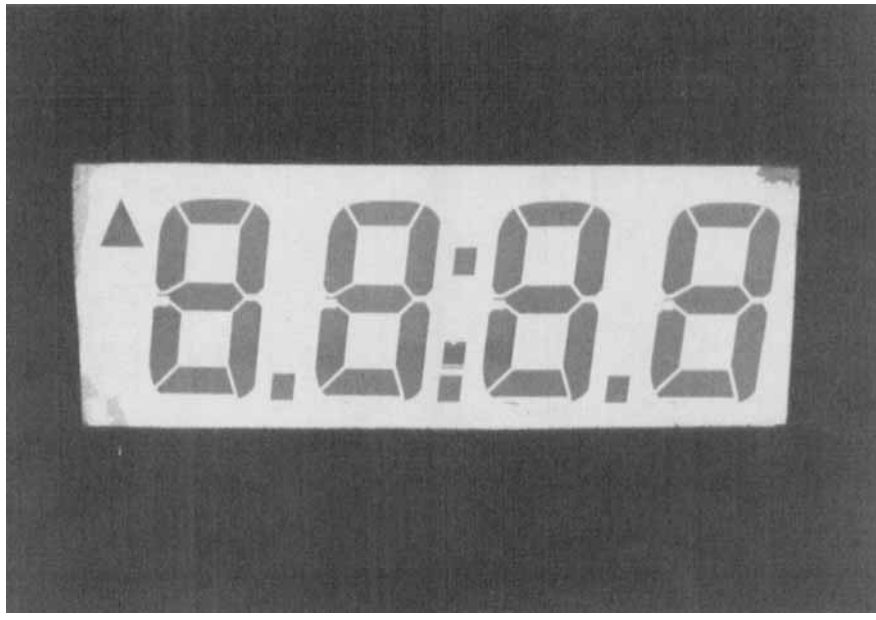

FIGURE 3 Photograph of a projected image of a gel by an overhead projector.

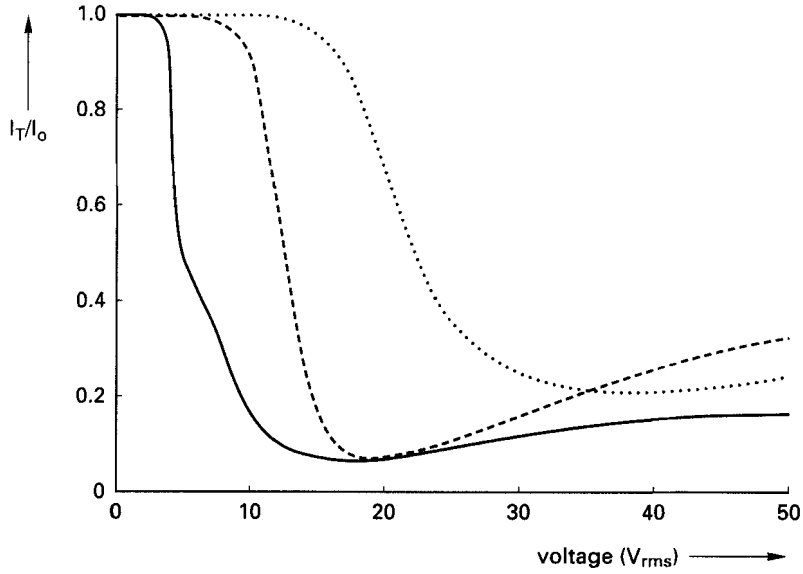

FIGURE 4 Normalised transmitted intensity as a function of rms voltage for various gels. —— = 5% w/w of network, 60 μW/cm²; – – – = 5% w/w of network, 3 mW/cm²; ···· = 10% w/w of network 3 mW/cm².

it can be seen that the threshold voltage to cause scattering decreases with decreasing network concentration and the voltage-transmission curve becomes steeper. Furthermore, both curves pass through a minimum. These effects will be dealt with separately as follows.

The threshold V_{th} voltage for distorting the homeotropic orientation is given by[13]

$$V_{th} = \pi \sqrt{\frac{K_{33}}{\varepsilon_o |\Delta\varepsilon|}} \tag{1}$$

where K_{33} is the bend elastic constant, $\Delta\varepsilon$ is the dielectric anisotropy of the system and ε_o is the permittivity of free space. The threshold voltage for ZLI4788 is about 1.7 V. In Figure 4, it can be seen that a large increase in V_{th} is obtained upon inclusion of a small percentage of a network. This effect is similar to those seen in PDLC systems where the threshold voltage increases dramatically with decreasing size and shape of the LC droplets.[14] In the present case the domain size is expected to decrease with increasing network concentration and that there will also be an increase in V_{th}. The effect of the network structure on the behaviour of the free molecules was investigated by polymerising a mixture containing 95% w/w of ZLI4788 under two different UV intensities (60 μW, 3 mW/cm²) in order to control the speed of polymerisation. In the case of the gel formed under the low UV intensity, the periodicity between the network and free molecules was expected to be larger than that for the gel formed under a high intensity. Under both UV intensities, exposure times were long enough (~15 min) such that no unreacted

acrylate molecules were expected to be present in the resultant gels. Photographs of the two gels under electric fields are shown in Figure 5. It is quite clear that the gel obtained under the high intensity (Figure 5(*b*)) shows a denser texture than the gel obtained under the low intensity (Figure 5(*a*)), conforming well with expectations. Figure 4 shows a comparison of the response of the gels formed under these two different UV intensities to the electric field. Here again it can be seen that the threshold voltage and the maximum scattering obtained are higher for the gel formed under intense lighting.

In the previous study,[11] due to the uniaxially planar orientation of the gels, only 50% scattering of the light could be induced. In the present case, despite the

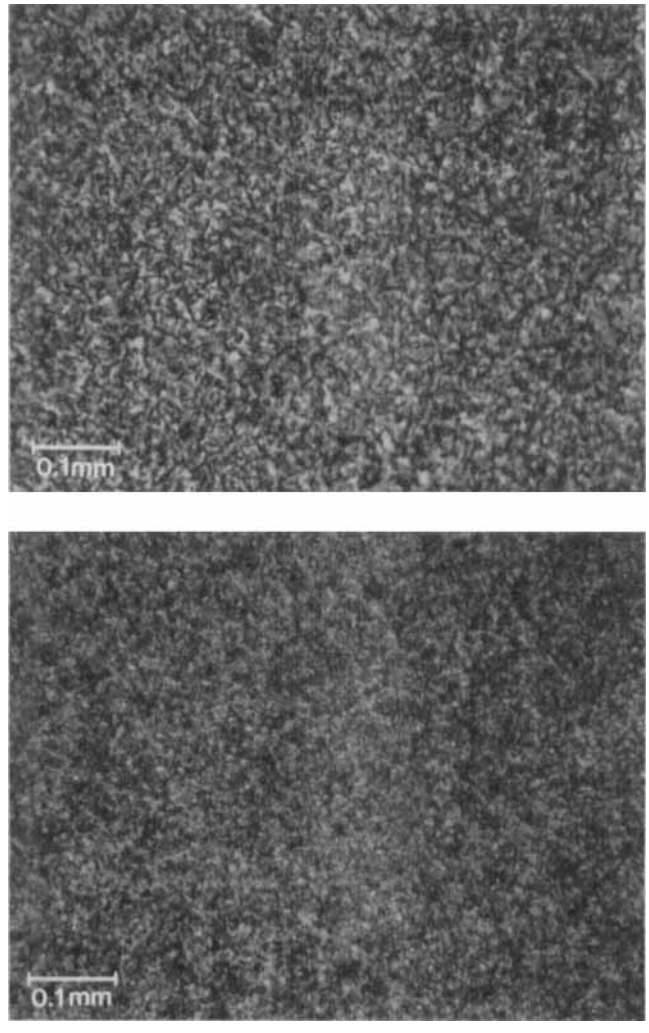

FIGURE 5 Optical micrographs of gels containing 5% w/w of network molecules in the scattering state as observed between cross polarisers. *a*) obtained under 60 μW/cm² UV; *b*) obtained under 3 mW/cm². See Color Plate I.

isotropic scattering, 100% scattering was still not possible. This behaviour is probably due to the shape of the scattering domains as well as the number along the light path. In Figure 6, the effect of the cell thickness on the light scattering from gels containing 5% w/w network molecules produced under 60 $\mu W/cm^2$ is plotted as a function of rms voltage. Here it can be seen that indeed with increasing cell thickness the maximum transmitted intensity does decrease, all be it a non-linear way. In the case of the 8 μm cell, the transmitted intensity passes through a minimum as a function of rms voltage. This indicates that the relative orientation of the molecules is optimal at a given voltage. This point was investigated further by measuring the intensity of the transmitted light as a function of the angle of incidence. For this purpose, the gel containing 5% w/w of network molecules formed under 60 $\mu W/cm^2$ UV intensity was rotated about an axis parallel to the surfaces of the cell so that the angle θ between the light beam and the normal to the cell surface could be varied (see Figure 2). In Figure 7, the normalised transmitted intensity is plotted as a function of θ at various rms voltages. It can be seen that at 5 and 30 V, the transmitted intensity decreases with increasing angle, whereas at 10 V, the transmitted intensity is almost independent of the angle. With increasing angle, the effective path length of the light within the gel increases; therefore more of the light is expected to be scattered with increasing angle if the relative orientation of the molecules does not show angular dependence. The fact that at 10 V the transmitted intensity remains independent of angular incidence indicates that the relative orientations of the molecules in domains are highly angular dependent and that increasing θ decreases the refractive index variation in domains along the path of the light.

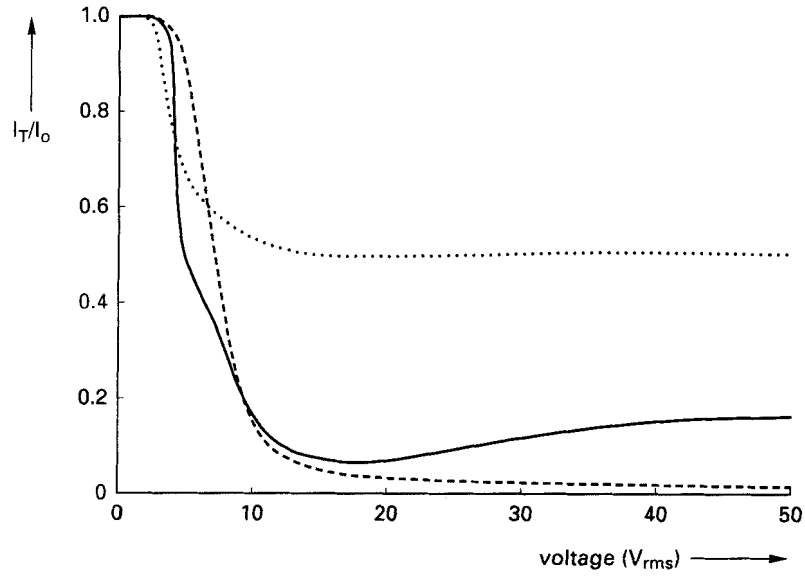

FIGURE 6 Normalised transmitted intensity as a function of rms voltage for a gel containing 5% w/w of network obtained under 60 $\mu W/cm^2$ for various thicknesses. - - - = 15 μm; —— = 8 μm; ···· = 4 μm.

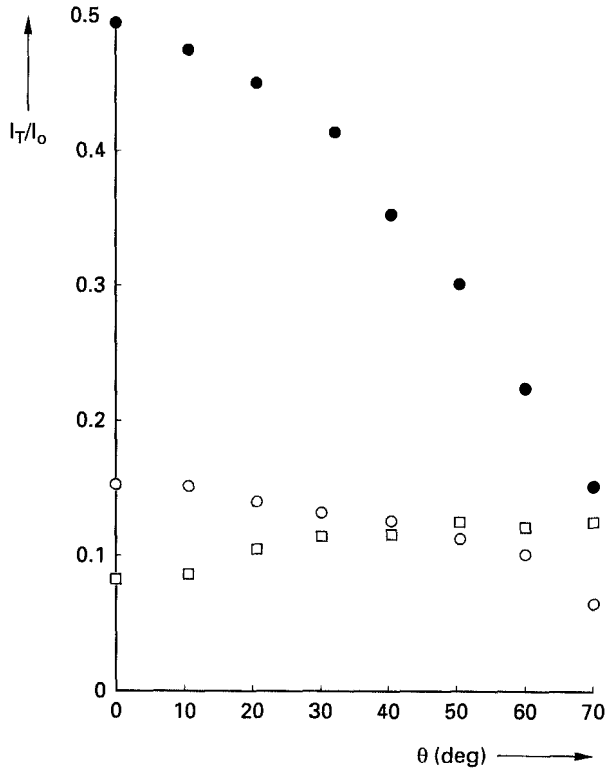

FIGURE 7 Normalised transmitted intensity as a function of angle, θ, for a gel containing 5% w/w of network molecules; 60 μW/cm² at various rms voltages: ● = 5 V; □ = 10 V; ○ = 30 V.

The distribution of the scattered light intensity was also investigated. Figure 8 shows the intensity of the scattered light as a function of angle Ω, as defined in Figure 2, for the gel containing 5% w/w of network molecules formed under 60 μW/cm² UV intensity at various rms voltages. In this figure, it is clear that most of the scattering occurs at small angles and almost no scattering is to be seen at angles above 30°. Such a central scattering indicates that the domains along the path of the light have shapes and sizes such that the light is not deviated to a large extent from its original path as it passes through the gel. Due to the structure of the network, upon application of an electric field across the gel, the creation of layers with various refractive indices along the path of the light is expected. Such a layered structure is likely to give a periodic interference pattern as a function of wavelength. In Figure 9, transmitted intensity as a function of wavelength for a gel containing 5% w/w of network molecules formed under 60 μW/cm² UV intensity is shown at various rms voltages. It can be seen that the spectrum contains a series of minima and maxima. The intensity of a beam of light at normal incidence travelling through a film with a thickness d and a refractive index n varies[15] with the wavelength as

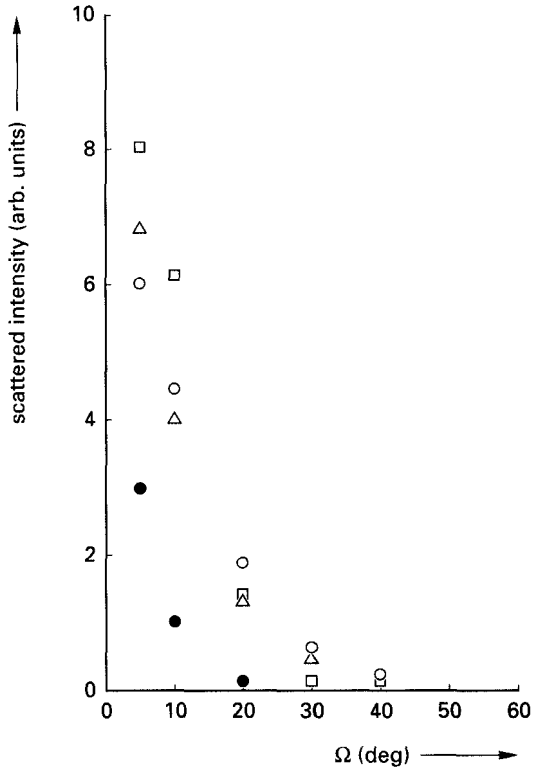

FIGURE 8 Scattered intensity as a function of angle, Ω, for a gel containing 5% w/w of network molecules; 60 μW/cm² at various rms voltages: ● = 0 V; □ = 5 V; △ = 10 V; ○ = 20 V.

$$\text{maxima at } 2dn = m\lambda \tag{2}$$

$$\text{minima at } 2dn = (m - \tfrac{1}{2})\lambda \tag{3}$$

where m is an integer. The layer thickness can be calculated as

$$d = \frac{\lambda_1\lambda_2(m_1 - m_2)}{2n(\lambda_1 - \lambda_2)} \tag{4}$$

where $(m_1 - m_2)$ corresponds to the number of maxima or minima between the first and the last minimum or maximum corresponding to the wavelengths of λ_1 and λ_2, respectively. In Figure 10, assuming an average refractive of 1.6 for the layers, the layer thickness was estimated as a function of applied rms voltage. In the calculations, various peaks were used, and the results shown in Figure 10 indicate that a periodicity in the order of 700 nm is present within the scattering gels. It can also be seen that in all cases, with increasing voltage the average layer thickness decreases. This cannot be associated with a change in the average refractive index since increased voltage gives rise to an increase in the refractive

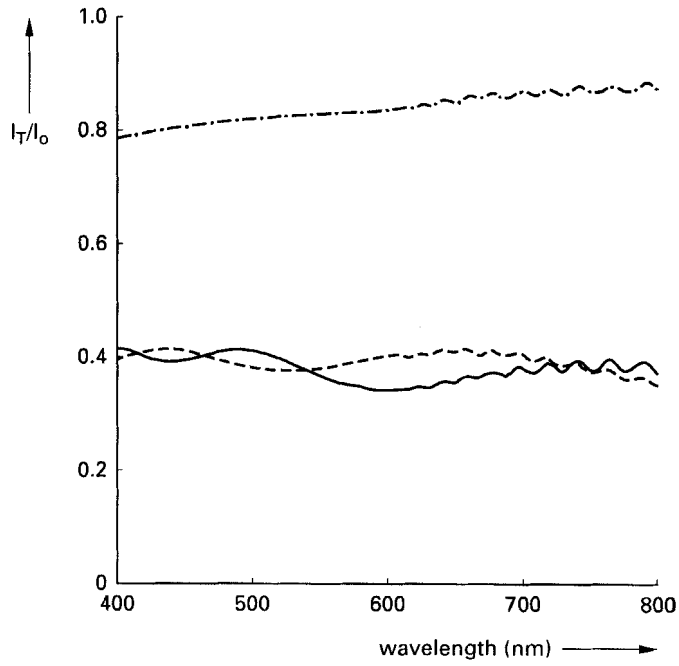

FIGURE 9 Normalised transmitted intensity as a function of wavelength for a gel containing 5% w/w of network molecules; 60 μW/cm² at various voltages: -·-·- = 5 V; - - - = 10 V; —— = 15 V.

index and the opposite of what is observed would result. The observed result is therefore probably due to the inadequacy of the simple model to explain the complex system.

The effect of the network on the response times of the LC molecules was also investigated using gels containing different amounts of network molecules, polymerised under various intensities. The results are shown in Figure 11. It can be seen that in all the cases, with increasing voltage, rise times also increase, whereas the decay times remain almost independent of the applied voltage. This is typical behaviour which is also observed for TN cells. When the gels formed under different UV intensity, containing 5% w/w of network molecules, are compared (Figures 11*a* and *b*), it can be seen that at a given voltage, the gel formed under high UV intensity shows longer rise times than the gel obtained under low UV intensity. When the decay times are compared, exactly the opposite behaviour can be seen. This must be associated with the degree of interaction between LC and network molecules. In the case of the sample polymerised under high UV intensity, the distance between the areas containing network molecules and LC molecules is probably smaller. As a result a higher degree of interaction between the LC and the network molecules occurs, explaining the observed behaviour. When the gels produced under 3 mW/cm² UV intensity, containing 5 and 10% w/w of network molecules (Figures 11(*b*) and (*c*)), are compared, it can be seen that the rise and the decay times of both gels are very similar. This behaviour is quite different to the behaviour observed in Figure 4, where the increase in the network concentration causes a large increase in the threshold voltage. As in the previous case, an increase

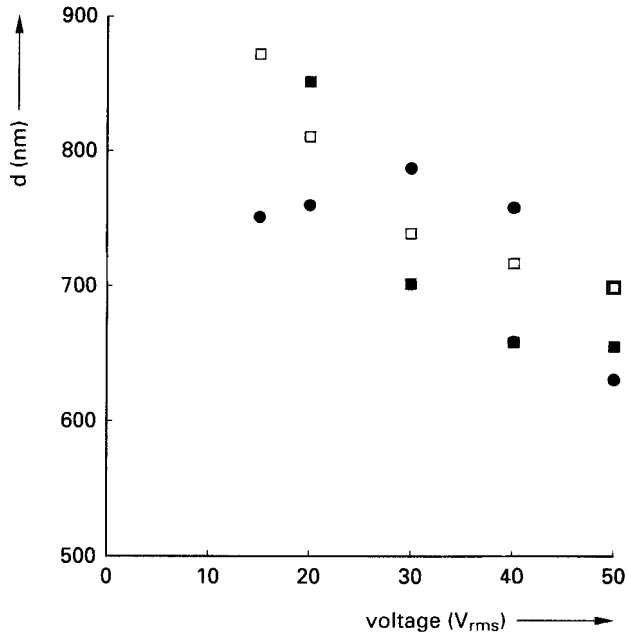

FIGURE 10 The average distance (d) between scattering layers as a function of rms voltage. Different symbols correspond to various minima and maxima (as in Figure 9) which were used in Equation 4 for calculating d.

in the network concentration would also be expected to increase the interaction between the LC and the network molecules and to decrease the response times. On close inspection, however, it can be seen that for the gel containing 10% w/w of network molecules, initially the rate of decay is higher than that for the gel containing 5% w/w of network. This shows that the effect of the network structure and the concentration is a complicated parameter influencing the response of the LC molecules to applied electric fields.

Dye-Containing Gels

The gels containing 5% w/w of network and 5% w/w of dye molecules were produced under 3 mW/cm^2 UV radiation. The exposure time was 30 min and the sample was regularly rotated for even exposure of both sides. Following the polymerisation, gels containing dye molecules remained homeotropically oriented. Upon application of an electric field, gels became scattering and showed a tendency to absorb more of the incident light. In Figure 12, the normalised transmitted light intensity through the gel containing dye molecules is compared to that through the gel containing no dye molecules, at two different collection angles. When the transmitted light intensities at the collection angle of 0.2° are compared, it can be seen that both systems show similar behaviour at low voltages. At higher voltages, however, for the gel without dye molecules, the transmitted intensity increases with increasing rms voltage, whereas for the gel containing dye molecules, the transmitted intensity keeps decreasing. This behaviour is due to the presence of

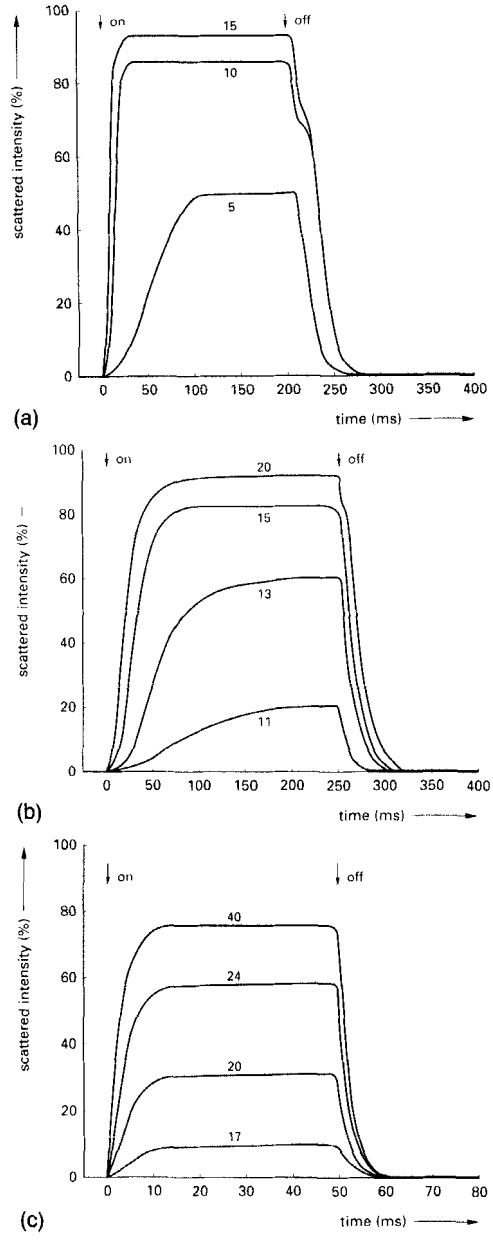

FIGURE 11 Scattered intensity as a function of time for gels at various rms voltages: *a*) 5% w/w of network; 60 μW/cm², *b*) 5% w/w of network; 3 mW/cm², *c*) 10% w/w of network; 3 mW/cm².

dichroic dye molecules which absorb more of the incident light as they assume a planar orientation with increasing voltage. Figure 12 also shows the transmitted intensity through the gels as measured by placing the photo-detector directly behind the gel without an aperture. In the case of the gel containing no dye molecules, the maximum transmitted intensity is 85%, indicating that 15% of the light is

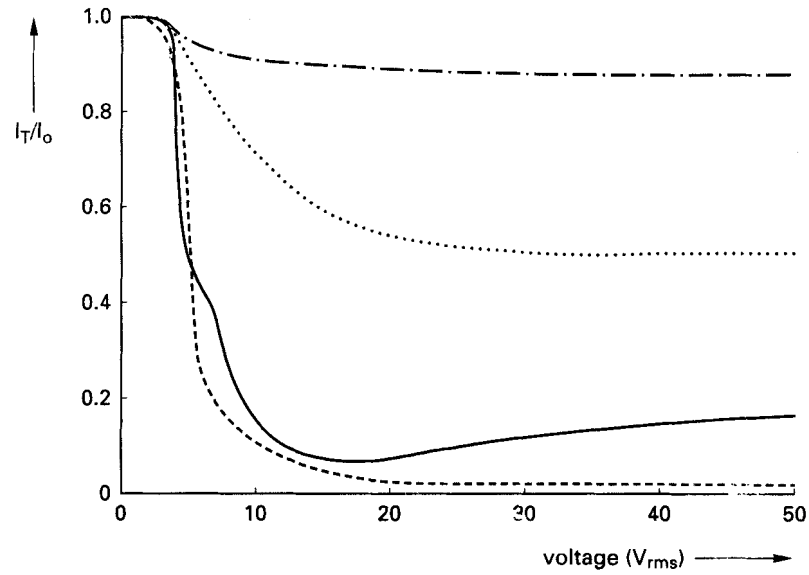

FIGURE 12 Normalised transmitted intensity as a function of rms voltage for gels containing 5% w/w of network molecules ·–·–· without a dye, forward scattering; ···· = with dye, forward scattering; —— = without dye at a collection angle of 0.2°; – – – = with dye at a collection angle of 0.2°.

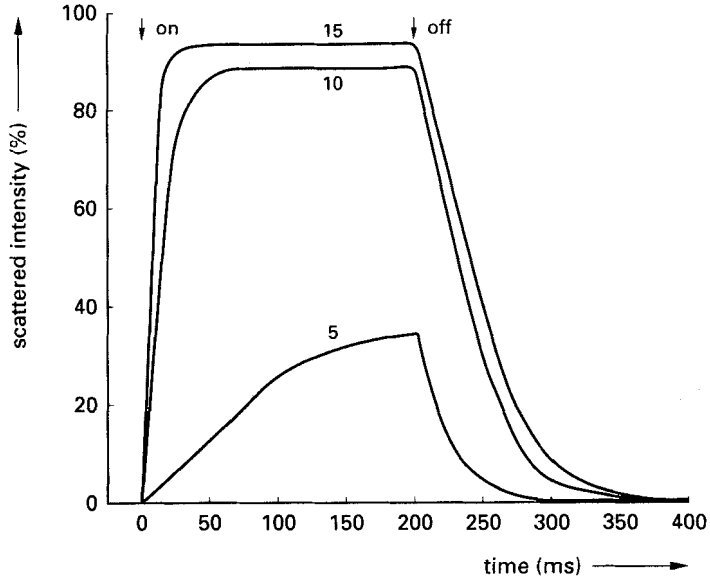

FIGURE 13 Scattered intensity as a function of time for a gel containing 5% w/w of network and dye molecules at various rms voltages.

backwards scattered. In the case of the gel containing dye molecules, the maximum transmitted intensity was around 60%. Assuming that 15% of this is due to backward scattering, only 25% of the intensity decrease is caused by the absorbance of the dye molecules. In the absence of network molecules, such a cell containing

the same percentage of dye molecules would give a transmittance below 3%. In the present case, the low absorbance caused by the dye molecules indicates that upon application of the electric field, the dye molecules do not completely assume a planar orientation. This indicates that within the gels, the interaction between the network and LC molecules is too strong so that it is difficult for the LC molecules to align themselves in the direction perpendicular to the applied field. This high degree of interaction was also detected using infra-red[12] and dielectric spectroscopy[16] and gels for which the LC molecules remained oriented at temperatures above their clearing temperature.

The response times of the gel containing dye molecules were also investigated at various rms voltages as shown in Figure 13. It can be seen that the decay times observed here are longer than those shown in Figure 11, in spite of the fact that the dye-containing gel was obtained under high UV intensity. This indicates that, even though the UV intensity was high, probably as a result of partial absorbance of the UV intensity by the dye molecules, the effective UV intensity within the gel was lower, giving rise to the observed behaviour.

Finally, it is also important to point out that a system with a homeotropic orientation and negative dielectric anisotropy shows a very sharp transition from the bright to a darker state, making it difficult to obtain grey levels. Here it has been shown that, with the inclusion of the network molecules, grey levels could also be obtained. Inclusion of the molecules with large birefringence combines scattering with absorbance. In the instances where absorbance without scattering is required, LC molecules with lower birefringence can be used. In this way a homeotropically oriented dye-containing system showing grey levels can be obtained.

CONCLUSIONS

It has been shown that gels, with a homeotropic orientation, containing LC molecules with a negative dielectric anisotropy can be produced. The gels were clear and did not give rise to scattering of light. When an electric field was applied across the gels, scattering of the light could be induced. The intensity of the transmitted light decreased with increasing voltage. The transmitted intensity, as a function of voltage, passed through a minimum, indicating that there is an optimum orientation of molecules for inducing maximum scattering of the light. The scattered intensity was found to be very central, and only about 15% of the light was back scattered. The structure and the concentration of the network was found to have a pronounced effect on the response times of the LC molecules and the resultant light scattering from the gels. Gels formed under high UV intensities showed higher threshold voltages, but their decay times were much shorter compared with gels produced at lower UV intensities.

Gels with a homeotropic orientation containing dye molecules could also be produced. In these systems, light scattering was combined with light absorption. Due to the high degree of interaction between the dye and the network molecules, total planar orientation of the dye molecules could not be induced. However, by the inclusion of the network molecules grey levels could be obtained.

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