Liquid Crystals

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

Ferroelectric liquid crystal gels Network stabilized ferroelectric display

R. A. M. Hikmet[a]; H. M. J. Boots[a]; M. Michielsen[a]
[a] Philips Research, Prof. Holstlaan 4, Eindhoven, The Netherlands

To cite this Article Hikmet, R. A. M. , Boots, H. M. J. and Michielsen, M.(1995) 'Ferroelectric liquid crystal gels Network stabilized ferroelectric display', Liquid Crystals, 19: 1, 65 — 76

To link to this Article: DOI: 10.1080/02678299508036721

URL: http://dx.doi.org/10.1080/02678299508036721

LIQUID CRYSTALS, 1995, VOL. 19, NO. 1, 65–76

Ferroelectric liquid crystal gels
Network stabilized ferroelectric displays

by R. A. M. HIKMET*, H. M. J. BOOTS, M. MICHIELSEN
Philips Research, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

(*Received 13 October 1994; accepted 22 December 1994*)

Liquid crystal (LC) mixtures of a reactive diacrylate and a commercial ferroelectric liquid crystal (FLC) mixture were produced. The mixtures were brought into cells provided with orientation layers in which various orientations such as uniaxial and twisted orientations, could be induced. When the desired orientation had been obtained, the polymerization of the reactive molecules was induced creating a three-dimensional anisotropic network containing the FLC molecules which were not chemically attached to the network (*ferroelectric gels*). The presence of the anisotropic network was found to have a large effect on various properties of the FLC molecules. For example, complex orientations (for example, 180° twisted) obtained by polymerization (formation of the gel) in the nematic phase remained unchanged when the gel was cooled to the FLC phase. Likewise uniaxial orientation, which cannot be realised in thick cells containing the pure FLC, could be realised when ferroelectric gels were used. For this reason the ferroelectric gels will be referred to as an *anisotropic network-stabilized FLC*. Optical properties such as effective birefringence and tilt angle were also influenced by the network. When use was made of a network with a lower birefringence than the FLC, a reduced effective birefringence in gels was observed. This is important for technologies involving thicker cells. The switching covered a range of voltages in the case of the gels, instead of showing a well-defined threshold voltage as in the bulk. The possibility of using this effect to obtain grey scales in cells during passive addressing has also been demonstrated.

1. Introduction

After ferroelectricity in liquid crystals (LC) has been predicted by Meyer [1] in 1974, the first ferroelectric liquid crystal (FLC) was soon synthesized [2]. However, the first use of FLC in displays using the surface stabilization concept [3] was to follow only in 1980. In the case of surface-stabilized ferroelectric liquid crystal displays (SSFLCD), the FLC is placed in a cell with a thin gap (of only a few microns). The pitch in the nematic phase is then suppressed and the LC molecules become uniaxially oriented in the nematic phase. Subsequently the FLC is cooled, preferably via the smectic A phase to the ferroelectric chiral smectic C phase (S_C^*). Various devices [4, 5], such as flat-panel screens for video and data graphic applications and high-speed shutters, have been developed on the basis the surface stabilized concept. The advantages of FLC are the high speed of switching, the bistability in the case of passive addressed displays and the viewing angle independence of the contrast. However, the SSFLCD also have various problems, such as the difficulty of obtaining the desirable orientation and preserving it during the lifetime of the display, the poor shock sensitivity, the difficulty of obtaining grey levels and the small cell gap technology. The requirement of the small cell gap is due to the high birefringence of the FLC. In FLC displays use is made of the retardation mode, in which the incoming polarized light is rotated 90° as a result of the $\lambda/2$ retardation. However, due to the dispersion in birefringence, the retardation has to be of the first order, which limits the cell thickness to the order of $2\,\mu$m. The possibility of using FLC–PDLC has been suggested [6] to solve these problems. However, due to the shearing required during the polymerization to induce orientation, this method has its limitations. The use of small amounts of non-LC acrylates in the production of networks has also been investigated [7]. Here we would like to present some experimental results on a new concept of network stabilization of FLC [8]. In this method, a mixture of reactive LC and non-reactive LC is produced. *In situ* photo-induced polymerization of the mixture in the oriented state leads to the formation of anisotropic gels and plasticized networks. In these systems an ordered anisotropic polymer network contains LC molecules which are not chemically attached to the network. In our earlier studies, in which nematic [9–11], cholesteric [12, 13] and smectic A [14] LC molecules were investigated, it was shown that the behaviour of the LC molecules which are not chemically attached to the network is

---

* Author for correspondence.

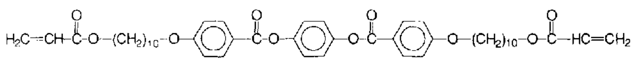


Figure 1. Structure of the LC diacrylate used in the experiments.

determined by the network rather than by the cell surfaces. In this study, we have used a commercially available ferroelectric mixture to produce ferroelectric gels. Ferroelectric gels with a compensated pitch for FLC without a smectic A phase [15] and active addressing [16] have been described in other publications. Here we will describe the thermal, optical and switching behaviour and the passive addressing of the ferroelectric gels in the concept of network stabilization.

2. Experimental

The structure of the reactive LC diacrylate C10 used in the experiments is shown in figure 1. The FLC material used in the experiments was a commercial mixture ZLI 3654 purchased from Merck (Darmstadt). Mixtures of non reactive FLC and diacrylates were provided with about 0·5 % w/w Irgacure 651 photoinitiator. The polymerization of the reactive diacrylates in the mixtures was initiated using 2 mW cm^{-2} UV radiation from a high-pressure mercury source. The molecules were uniaxially oriented in 2 μm thick cells containing uniaxially rubbed SiPVA orientation layers, unless otherwise indicated. A Keithley 617 electrometer and a Philips 5167 wave generator were used for the current–voltage measurements. An optical microscope provided with a photomultiplier and a compensator was used for the optical measurements. Various signals were stored in a Philips 3350A digital storage oscilloscope and transferred to a computer. The X-ray diffraction measurements were carried out using a Statton camera and Ni filtered Cu K$_\alpha$ radiation.

3. Results and discussion

3.1. *Monomeric mixtures*

A composition/temperature diagram of state for ZLI-C10 is shown in figure 2. It can be seen that the inclusion of reactive diacrylate causes changes in the transition temperatures of the FLC ZLI. At low concentrations of C10, the smectic A (S$_A$) and the chiral smectic C (S$_C^*$) phases are also visible in addition to the chiral nematic phase. At intermediate concentrations of C10, the nematic phase only is observed. At very high concentrations of C10, the smectic C phase appears again. The induction of different phases, changing the transition temperatures and compensation of the pitch using reactive molecules have already been described [16]. These changes are important in obtaining a uniaxial orientation in cells which is not possible in the case of pure-non reactive ZLI:

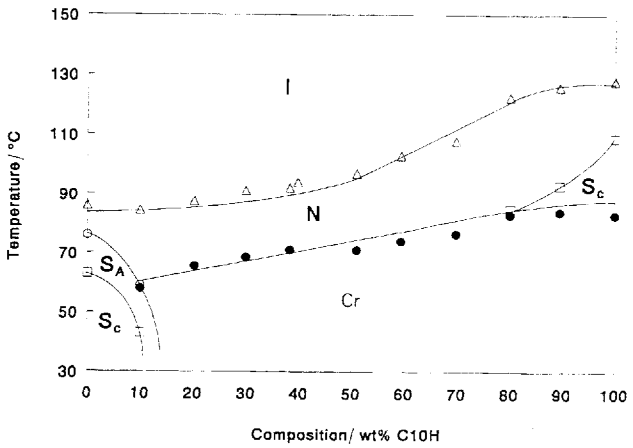


Figure 2. Temperature/composition diagram of monomeric C10 and ZLI.

The pitch can also be compensated by adding chiral reactive molecules [15].

3.2. *Polymerized mixtures*

3.2.1. *Thermal properties*

Various mixtures provided with the photoinitiator were brought into cells. After the desired orientation has been included in the cells in the nematic phase, the mixtures were polymerized using the high-pressure UV source to obtain anisotropic gels and plasticized networks. In the experiments described below, uniaxially oriented samples in 2 µm cells were used unless otherwise indicated. Figure 3 shows the birefringence of various gels and plasticized mixtures as a function of temperature. Here it is important to note that the diagram shown in figure 2 applies to the monomeric mixtures. After

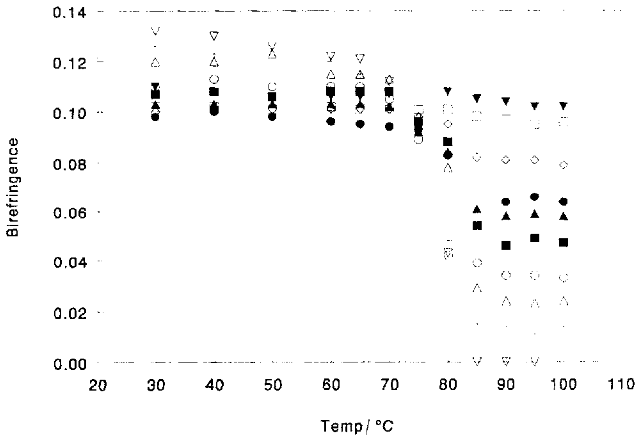


Figure 3. Birefringence of gels containing various amounts of network as a function of temperature. ▽ = 0 per cent, + = 10 per cent, △ = 20 per cent, ○ = 30 per cent, ■ = 40 per cent, ▲ = 50 per cent, ● = 60 per cent, ◇ = 70 per cent, □ = 80 per cent, ▼ = 90 per cent.

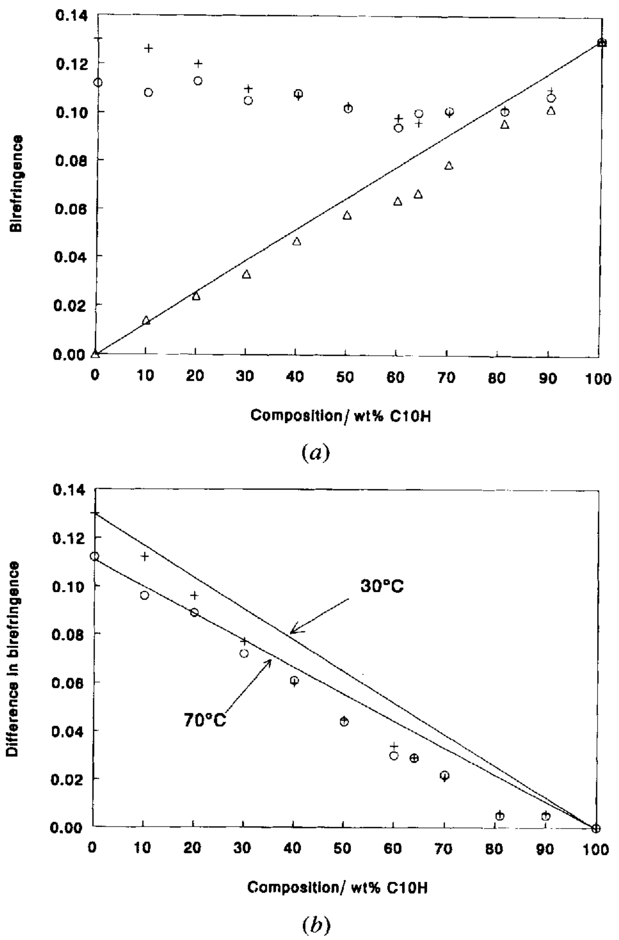


Figure 4. (a) Birefringence as a function of the composition measured at various temperatures. + = 30°C, ○ = 70°C, △ = 100°C. (b) Difference in birefringence as a function of the composition measured at + = 30 and 100°C, ○ = 70 and 100°C. The solid lines define the theoretically expected values.

polymerization (creation of a network) phase transitions temperatures in gels correspond to those of ZLI. Therefore in figure 3, in all cases, a moderate decrease in birefringence in the temperature range corresponding to that of the smectic C and smectic A phases of the ZLI, followed by a rapid decrease in the nematic phase of the ZLI is observed. However, a residual birefringence is observable above the isotropic transition temperature of the ZLI. The residual birefringence can be associated with the anisotropic network formed upon the polymerization of the reactive LC diacrylate. As the anisotropic acrylate network is highly cross-linked, it stays oriented and does not become isotropic. In figure 4(*a*), the birefringence measured at various temperatures is plotted as a function of the composition for various systems. The curves representing the results of the birefringence measurements performed at 30°C and 70°C (corresponding to the C and A phases of ZLI, respectively) show a minimum. The minimum can be associated with the tilted orientation of the molecules with respect to the cell surface in the S_C phase. However the S_C phase cannot be the only cause of the minimum, because a similar behaviour was also observed in the smectic A phase in measurements at 70°C. In the case of the values measured at 100°C, however, the birefringence increases almost linearly with the network (polymerized C10) concentration. In figure 4(*a*), the increase in the residual birefringence (the birefringence measured at 100°C) with increasing C10 indicates that the residual birefringence is due to the anisotropic network. However, the fact that linearity is not observed (as indicated by the solid line in figure 4(*a*) extrapolated from the value measured for 100 per cent C10) indicates that the networks produced in different compositions have different birefringence values. In order to obtain a better understanding of the observed effect, we plotted the difference between the birefringence values measured at 30°C and 100°C, together with the difference in the birefringence values measured at 70°C and 100°C, for various compositions in figure 4(*b*). The solid lines in figure 4(*b*) represent the decrease in birefringence theoretically expected on the assumption that all of ZLI molecules within the gels become isotropic at 100°C. It can be seen that the experimentally determined values lie below the theoretical line [5]. This indicates that a fraction of the ZLI molecules does not become isotropic above the isotropic transition temperature. We tried to estimate the bound fraction from this figure using the data for the changes in birefringence between 30°C and 100°C. The difference between the theoretical values and the measured values was assumed to be caused by the bound fraction which does not become isotropic at 100°C. In figure 5 this bound fraction is plotted as a function of the

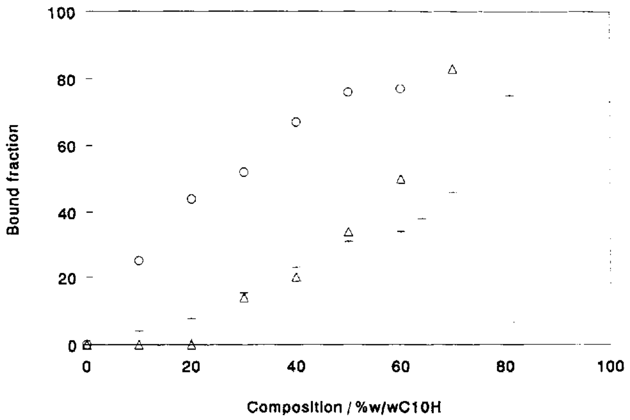


Figure 5. Bound fraction as a function of the composition estimated using various data. + = difference in birefringence measured at 30 and 100°C, △ = Effective tilt angle, ○ = spontaneous polarization.

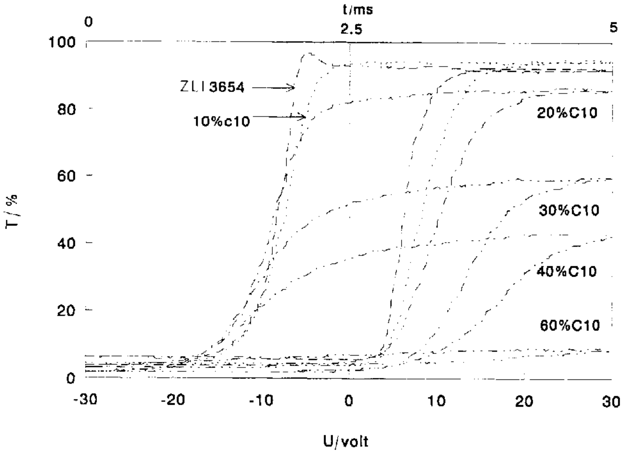


Figure 6. Transmission measured at 546 nm as a function of the voltage for various compositions.

composition. It can be seen that the bound fraction increases with increasing polymer concentration. The influence of the network is also apparent from the switching behaviour of the ZLI. The results of the electro-optic behaviour are discussed below.

3.2.2. *Optical properties*

Transmission-voltage behaviour was investigated by placing the cells between crossed polarizers so that a maximum dark state was obtained during switching. Figure 6 shows the curves obtained for ferroelectric gels containing various amounts of network (polymerized C10). It can be seen that the switching voltage increases with the polymer concentration and the switching takes place over a wide voltage range. This is a unique property of the gels and it can be used in obtaining grey levels which will be discussed later in the article. It can also be seen that the maximum transmitted intensity decreases with increasing polymer concentration. Here it is important to note that when the voltage was removed and the electrodes short-circuited, the transmission remained the same or decreased slightly. This is an indication of stable switching within the system; this will be discussed below. The transmission (T) of the wavelength λ through the crossed polarizers containing a material with a birefringence Δn and thickness d and the optic axis oriented at an angle ω with respect to one of the polarizers.

$$T = \sin^2(2\omega)\sin^2(\pi \Delta n d/\lambda). \qquad (1)$$

As can be seen in equation (1), there are two possible explanations for the decrease observed in the maximum transmission with increasing network concentration: (i) a change in the effective birefringence; (ii) a change in the effective tilt angle. Both effects are caused by the network and have therefore been studied in detail.

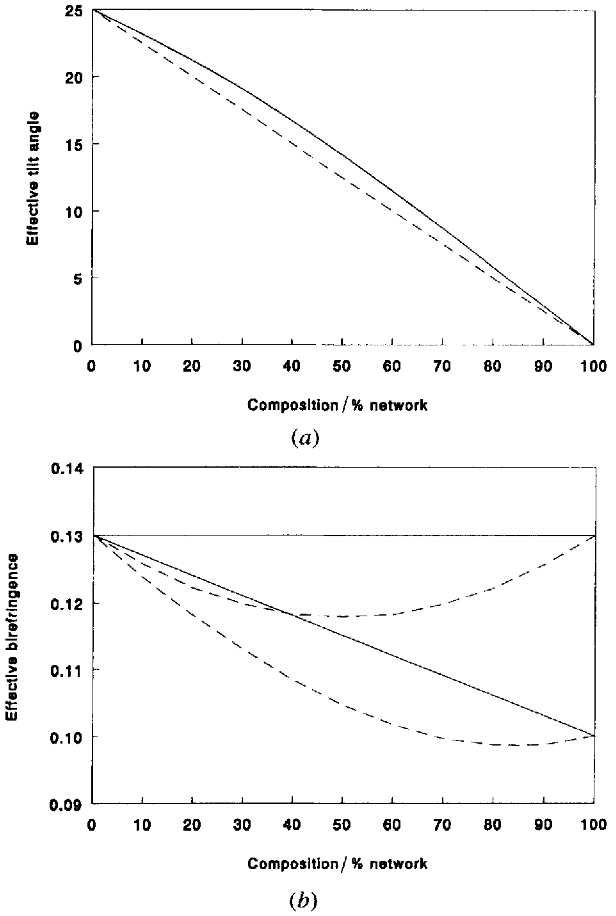
3.2.2.1. *Theoretical calculations*

We tried to simulate the optical effects caused by the anisotropic polymer network, which does not change its direction of orientation during the switching of ZLI, with the aid of a simple theoretical model. In this model the molecules were assumed to be continued in thin alternating layers containing the network and the ferroelectric molecules. The light propagating through such a system was calculated using the program developed by Mansuripur [17]. For the system to behave like a uniaxial crystal, the layers have to be smaller than the wavelength of light; the results are then independent of the layer thickness. Therefore the total thickness of each polymer–ZLI bilayer was kept constant in the calculations and the thickness of the components were varied in the same ratio as the composition. The direction of the average fast optic axis was determined by determining the direction along which the linearly polarized light remains linear. Figure 7 (*a*) shows the calculated apparent tilt angle (the angle between the direction defined by the network and the average optic axis) as a function of the composition for various Δn (0·13 and 0·1) of the network. In the calculations, the Δn of the ZLI was assumed to be 0·13 and the ZLI molecules were assumed to be oriented, at 25° with respect to the uniaxially oriented network. It can be seen that in all cases, the effective tilt angle decreases when the network concentration increases, as is also observed experimentally. Here it is also interesting to note that the decrease in effective tilt angle is larger when a higher Δn value for the network is used. In the same way, we also calculated the effective birefringence as a function of the composition; the results are shown in figure 7 (*b*). Calculations were carried out for two orientations: (i) ZLI and the polymer oriented in the same directions and (ii) ZLI and the polymer oriented at 25° with respect to each other. Here again it can be seen that in both cases the Δn decreases with increasing network concentration. In the case of the network oriented at an angle with respect to the ZLI, this decrease is larger, which shows the compensation effect.

3.2.2.2. *Effective birefringence and tilt angle of the gels*

In order to investigate the changes taking place during the application of the electric field in detail we used a gel containing 10 wt % of C10 in a 7·8 μm cell. In figure 8 (*a*) the change in the birefringence is shown as a function of the voltage. In this figure it can be clearly seen that the birefringence first decreases with an increasing voltage, before increasing again. Two possibilities can be considered to explain this behaviour:

(i) The initial decrease is associated with the rotation of the molecules about the cone, as mentioned before, followed by the chevrons becoming



(*a*)

(*b*)

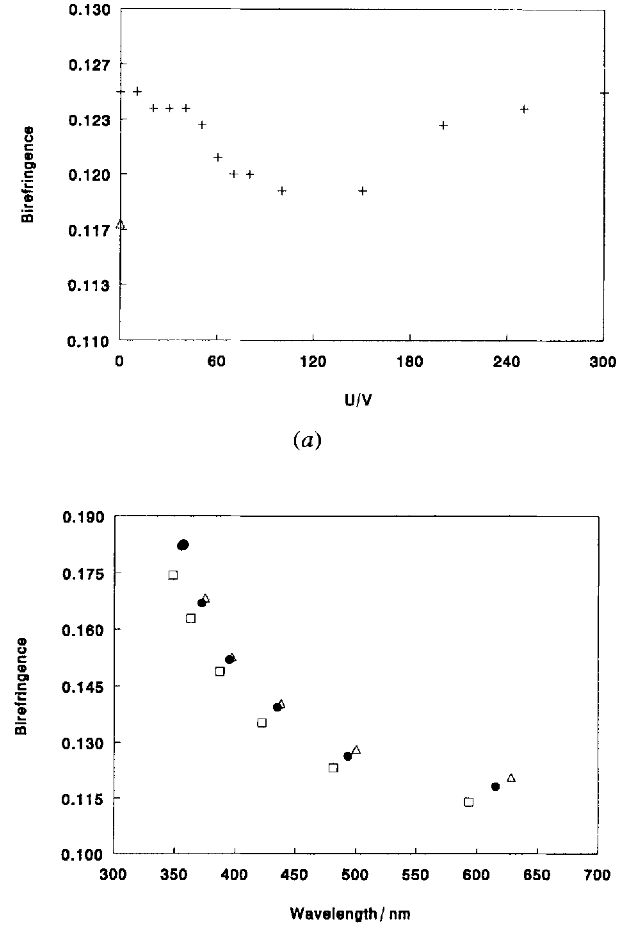
Figure 7. (*a*) Calculated effective tilt angle as a function of the composition for various Δn of the network, - - - = 0·13, —— = 0·1. The ZLI and the polymer are oriented at 25° with respect to one another. (*b*) Calculated effective birefringence as a function of the concentration of the network. Solid lines = the network and the ZLI oriented in the same direction. Broken lines = ZLI and the network oriented at 25° with respect to one another. For ZLI $\Delta n = 0{\cdot}13$ and for the network $\Delta n = 0{\cdot}13, 0{\cdot}1$.

upright. When a small potential of reverse polarity was applied across the sample, the birefringence decreased to a value lower than the initial zero voltage value. If we assume that the chevrons become upright at high voltages, the reversal of the voltage may bring the ZLI molecules to a state in which they are at an angle of 25° with respect to the surface. If the director is at an angle α with respect to the surface, the effective birefringence can be expressed as

$$\Delta n_{\text{eff}} = \frac{n_e n_o}{(n_o^2 \cos^2(\alpha) + n_e^2 \sin^2(\alpha))^{0.5}} - n_o \qquad (2)$$

where n_e and n_o are the ordinary and extraordinary refractive indices, respectively. Assuming that α equals the tilt angle and $n_o = 1{\cdot}5$, we find that Δn_{eff} is about 0·104. This is different from the measured value of 0·12.

(ii) The switching of the molecules takes place in domains and the size of the domain determines the threshold voltage for the switching. Such behaviour also explains the behaviour observed for transmission/voltage (see figure 6) where the switching of ZLI over a broad voltage range is suggested. It may be assumed that, as the concentration increases, different amounts of ZLI molecules switch from their initial orientation to an angle of 25° with respect to the initial orientation. This is also suggested by the results of the simulations shown in figure 7 (*b*), where the birefringence is plotted as a fraction of the molecules oriented at 25° with respect to each other. It can be seen that the minimum at 50 per cent yields an effective birefrin-



(*a*)

Figure 8. (*a*) Birefringence as a function of the voltage in a 7·8 µm cell measured at 546 nm + = the first run, △ = returning to −5 after 300 V. (*b*) Birefringence as a function of the wavelength measured at various voltages. △ = virgin cell 0 V, ● = 80 V, □ = going to −5 after 300 V.

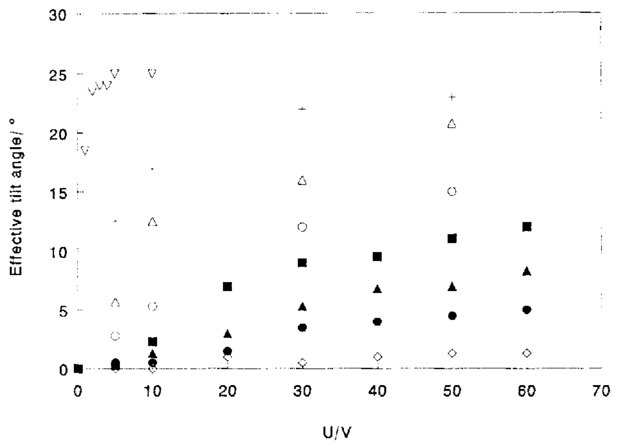


Figure 9. Effective tilt angle as a function of the voltage for various compositions. ∇ = 0 per cent, + = 10 per cent, △ = 20 per cent, ○ = 30 per cent, ■ = 40 per cent, ▲ = 50 per cent, ● = 60 per cent, ◇ = 70 per cent.

gence of about 0·118. Likewise, in figure 9 (*a*) it may be assumed that at about 120 V, 50 per cent of the ZLI is oriented at 25°. Above this voltage more of the ZLI molecules reorient and as a result the birefringence increases eventually to result in a value very close to the initial value. As the dispersion in birefringence is sensitive to the changes in the orientation in such a composite system, we measured the dispersion as the different orientations are obtained during the application of the electric field (see figure 8 (*b*)). The dispersion curve obtained for the virgin uniaxial orientation changes after the application of 80 V. It can be seen that the birefringence values at short wavelengths are very similar for these two curves, whereas the curves diverge at larger wavelengths. On the other hand the birefringence values obtained after the application of 300 V and the reversal of the field to −5 V yield a curve which appears to be vertically shifted with respect to the virgin curves. The curve obtained at 80 V shows that the birefringence at short wavelengths is very similar to that of the virgin sample. This is probably due to the wave-guiding effect, because the domains might be larger than those wavelengths. The behaviour observed at −5 V is as expected and the whole curve appears to be shifted. This might be due to the domains in which the switching takes place becoming smaller after the smectic layers had become upright during the first application of the electric field. Once the layers are upright, further switching probably takes place in domains.

In figure 9 the effective tilt angle (half of the angle through which the cell to be rotated between the extinction states when the polarity of the static field applied across the cell is reversed) is plotted as a function of the applied field for various compositions. Here the effect of compensation can be seen more clearly. In all cases the effective tilt angle increases with increasing voltage. This is due to the reorientation of the ZLI molecules from their initial uniaxial orientation in the direction of the polymer. If we assume that the switching of ZLI takes place in domains and increasingly more ZLI molecules get oriented at an angle of 25° with increasing voltage, then the observed behaviour is in accordance with the theoretical calculations. When the maximum effective tilt angles for various compositions are compared, it can be seen that the maximum effective tilt angle decreases with increasing network concentration. This trend is also in accordance with the theoretical calculations which also show that with increasing polymer concentration the tilt angle decreases. However on close inspection, it can be seen that the experimentally observed maximum tilt angles fall below the theoretically predicted values. The difference can be accounted for if we assume that a fraction of the ZLI is bound by the network and does not change the orientation. Using the theoretical model for the tilt angle, we also estimated the lower limit for the bound fraction on the assumption of a birefringence of 0·13 for the polymer. Using the theoretical data in figure 7 (*a*) and the maximum experimental values obtained for the effective tilt angle in figure 9, we estimated the bound fraction; the results are compared in figure 5. It can be seen that the bound fraction deduced from the birefringence measurements agrees well with the values derived from the effective tilt angle data.

3.2.3. *X-ray diffraction measurements*

X-ray diffraction was used to observe the effect of the application of the electric field on the smectic layers. Polyester films instead of glass were used as the substrates for this purpose. The geometry used in the experiments is shown in figure 10 (*a*). In the flat-on configuration, θ needs to be the same as α to obtain diffraction, whereas in the edge-on configuration the diffraction condition is satisfied for all values of θ (as long as the main beam is at an angle α with the smectic layers, satisfying the Bragg condition). The small angle diffraction peaks obtained for various samples in different directions are shown in figure 10 (*b*). The pure ZLI in the edge-on configuration shows a four-point pattern, whereas the diffraction pattern obtained in flat-on configuration shows no peaks. This indicates that the smectic layers are not parallel to the surface, but at an angle of 22° with respect to the normal to the surfaces (chevrons). In the edge-on configuration, the gels containing 10 wt% of give C10 continuous reflection between the two sharp peaks indicating that the other chevron orientations are present. In the case of the sample containing 40 wt% of C10, similar diffraction

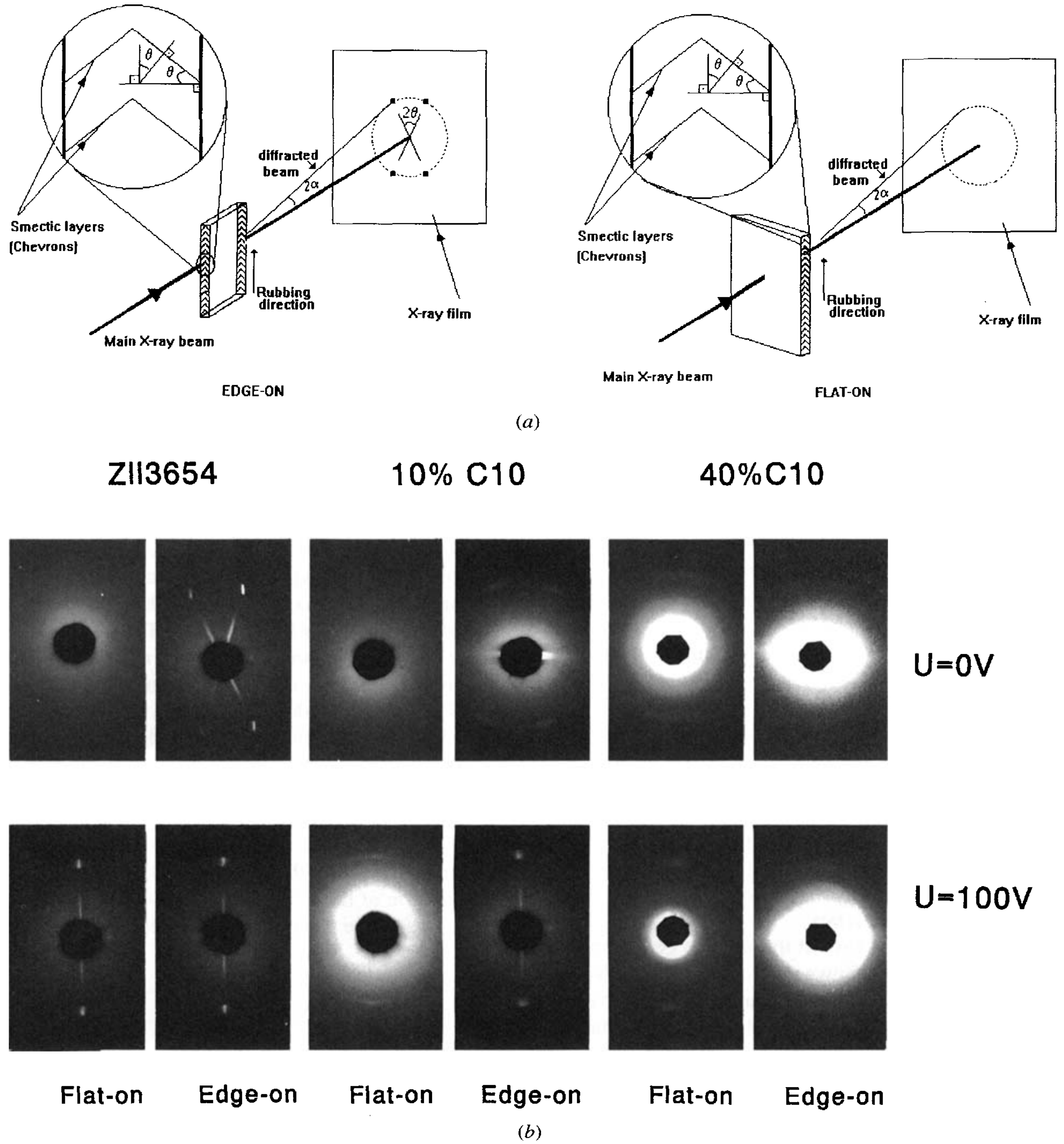
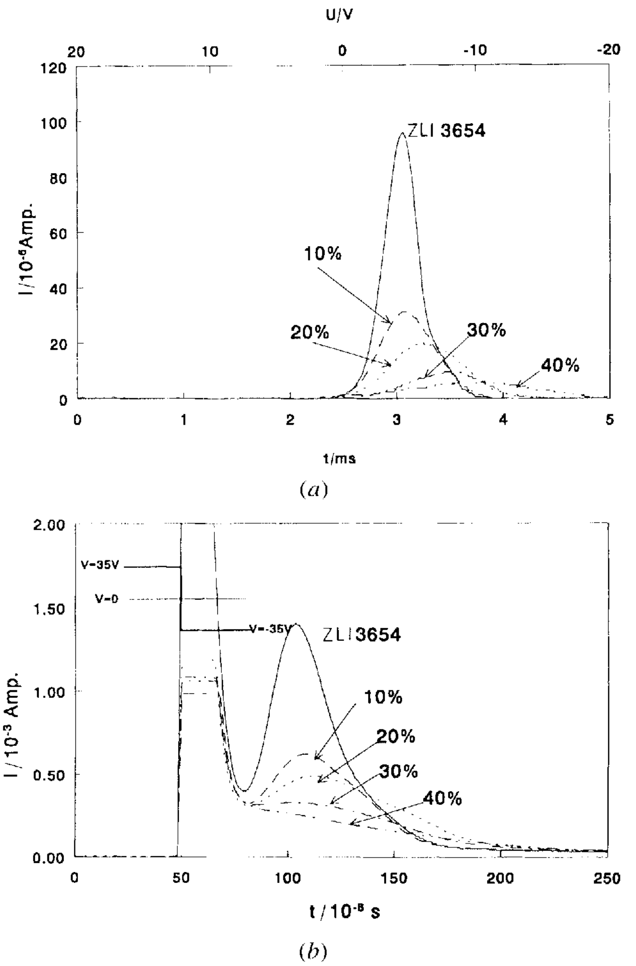


Figure 10. (*a*) Schematic representation of the configuration used in the X-ray diffraction experiments; (*b*) the X-ray photographs obtained for various samples in various directions before and after the application of the electric field.

patterns were observed for both configurations (cell placed flat-on and edge-on to the horizontal X-ray beam). This means that in the case of gels the smectic layers show various other orientations, instead of a well-developed chevron orientation as observed for pure ZLI. After the application of the electric field, the smectic layers in all cases tended to become oriented perpendicular to the cell surfaces. The smectic layer normal also became oriented in the direction of rubbing, and hence became oriented in the same direction as the director in the nematic phase. These results clearly indicate that when sufficiently high electric fields are applied, the smectic layers reorient in the manner suggested by the optical measurements.



(*a*)

(*b*)

Figure 11. Current as a function of time/voltage for various samples during the application of (*a*) a triangular voltage; (*b*) a step voltage.

3.2.4. *Electrical properties*

In figure 11 (*a*) the current through the cell containing the various samples is shown as a function of time/voltage during the application of a triangular voltage wave. The peaks shown in this figure are the result of the spontaneous polarization (P_s) reversal. It can be seen that with increasing polymer concentration, the onset of the peaks remains the same as the peaks become smaller and spread over a wider voltage range. The effect of the broadening of the current peaks indicates that the switching of the ferroelectric molecules spreads over a wider voltage range as the polymer concentration increases, as is also observed in figure 6 for transmission curves. The decrease in the area under the current peaks indicates that the spontaneous polarization of the samples also decreases with increasing network concentration. In order to study this effect more closely, we plotted the P_s as a function of polymer fraction in figure 12. In this figure we represent the decrease in the P_s expected on the basis of the fact that only the ZLI within the system contributes to the measured spontaneous polarization represented by the straight line. It can be seen that all the experimental points in this figure lie below the line. This indicates that some of the molecules do not switch under the electric field or that their switching is not complete (the vector defining the direction of spontaneous polarization does not become parallel to the electric field lines). The results of the birefringence and effective tilt angle experiments already indicate that some of the molecules are indeed strongly bound [14] by the network, as suggested in figure 5. In the same figure, we also plotted the bound fraction using the data from figure 12, on the assumption that the difference between the theoretical value and the measured value is caused by the molecules which are bound and do not switch. It can be seen that the bound fraction which can be derived from the birefringence (see figure 4) and the effective tilt angle measurements (see figure 9) is not large enough to account for the behaviour observed in figure 12 especially at low polymer concentrations. This indicates that the bound fraction of the ZLI contains the chiral molecules with high P_s values or that there is a certain population of molecules in ZLI within the system which are oriented in such a way that the spontaneous polarization does not become parallel to the applied field during the switching. The other possibility is that some of the pendant network molecules (molecules which are not fully cross-linked) are taken up by the ZLI and that the P_s is reduced as a result. In order to investigate the switching further, we studied the current passing through the system during the application of a step voltage. For this purpose, a 1 kΩ resistor was placed in series and the voltage drop across the resistor was measured. In figure 11 (*b*), the current through the system calculated from the results of the voltage measurements is plotted as a function of time. The initial rise in this figure is due to the capacitive discharge followed by a polarization

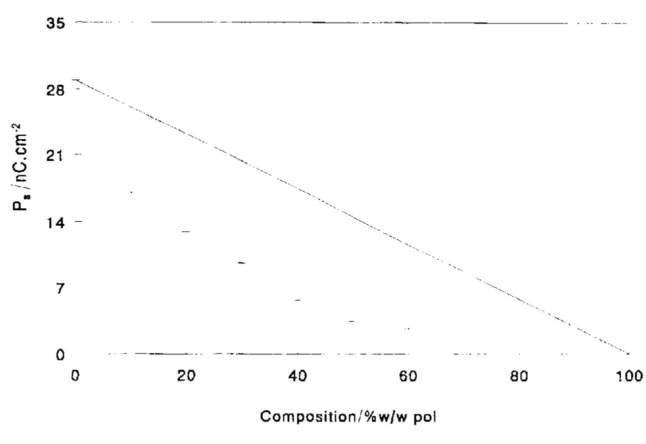


Figure 12. Spontaneous polarization + = measured, - - - = calculated for various compositions.

reversal current. The behaviour shown by the polarization reversal current is very similar to that observed in figure 11 (*a*), where the peaks also become broader. The broadening of the peaks observed in figure 11 (*b*) can be associated with the increase in the internal viscosity. The relation [18] between the rotational viscosity coefficient (γ) and t_w (the full width at half maximum) is given by

$$t_w = \frac{1 \cdot 76\gamma}{P_s E} \qquad (3)$$

where E is the applied electric field. Here the fact that the current peaks become broader indicates that the switching takes longer. This effect can be related to the increase in γ as well as the reduction in P_s. However, it is important to point out that it is not clear whether the above equation can be applied to the system studied (gels).

3.3. *Network-stabilized switching in gels*

3.3.1. *Network stabilization*

Having studied the thermal, electrical and optical properties of the gels, we also investigated their bistability. Before we say anything on the subject, we show that the orientation in these gels is determined by the network rather than by the orientation layers. This we demonstrate in two different ways:

(i) A mixture containing 5 wt% of C10 in ZLI was placed in a cell with two directly addressable segments. Before polymerization, an electric field

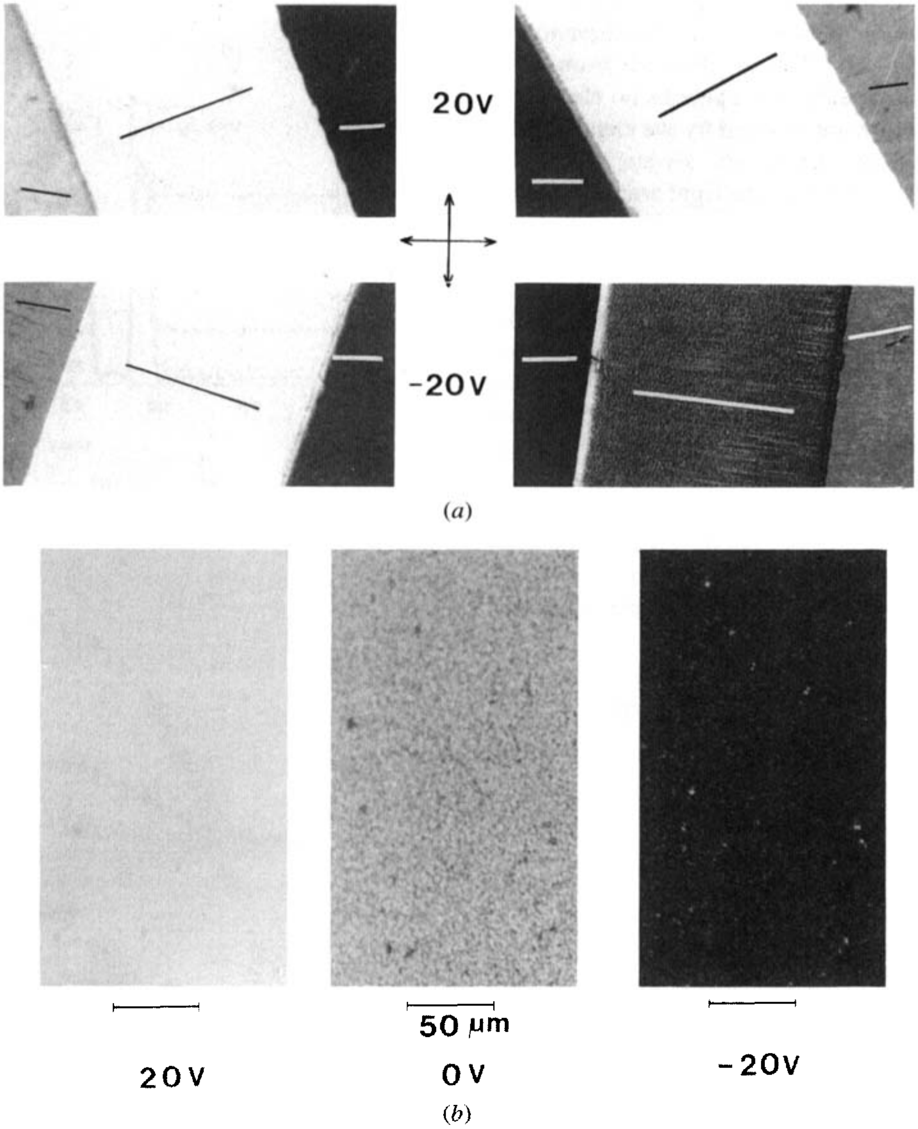


Figure 13. Photographs obtained during the application of various voltages to various samples; (*a*), (*b*)—see text for details.

was applied to cause molecules to orient at 10° with respect to the rubbing direction in one of the segments. The field was removed and polymerization was carried out. After polymerization, in the segment where the field was applied, the network was oriented at an angle of 10° with respect to the rubbing direction, while outside this segment the network orientation was in the direction of rubbing. When the electric field was re-applied to this segment upon polymerization, the ZLI molecules no longer switched about the rubbing direction, but about the direction in which the network was oriented. This effect is shown in figure 13 (*a*). Left and right areas within the cell containing the electrode segments are shown for different orientations of the cell between the crossed polarizers. The directions of the crossed polarizers are indicated in the middle of the figure. The black and white lines on the photos indicate the direction of orientation of the ZLI as derived from total extinction. The middle part contains no electrodes and it is therefore not affected by the electric field. Therefore the molecules are always uniaxially oriented in the middle. In the right area of the cell, polymerization was carried out within the field. In the right part, to obtain total extinction (photos on the left), the cell had to be rotated by the same amount in both directions with respect to the rubbing direction, as the direction of the electric field was reversed. This shows that the switching took place about the initial rubbing direction, which also defined the direction of the network orientation in this part of the cell. In the left part of the cell, polymerization was carried out under a positive electric field. This means that the polymer network was formed at an angle with respect to the rubbing direction. In figure 13 (*a*) (righthand photographs), it can be seen that the cell had to be rotated a different number of degrees in different directions about the rubbing direction in order to obtain extinction in the left part of the cell during the application of two opposite fields. This shows that the switching took place about the direction of the network which was oriented at an angle with respect to the rubbing direction.

(ii) A cell containing 20 wt% of C10 was heated to 80°C in a 4 μm cell so that the molecules became rotated by 180° from one of the surfaces to the other. The system was then polymerized. After the system had cooled to room temperature, the 180° twisted orientation remained, as opposed to the pure ZLI which would have unwound to a uniaxial orientation. An electric field did not change the twisted orientation either. The ZLI molecules

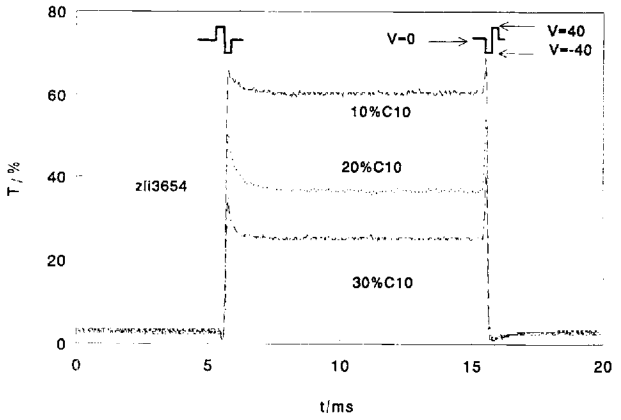


Figure 14. Transmission through crossed polarizers during the application of a bipolar pulse of ±40 V.

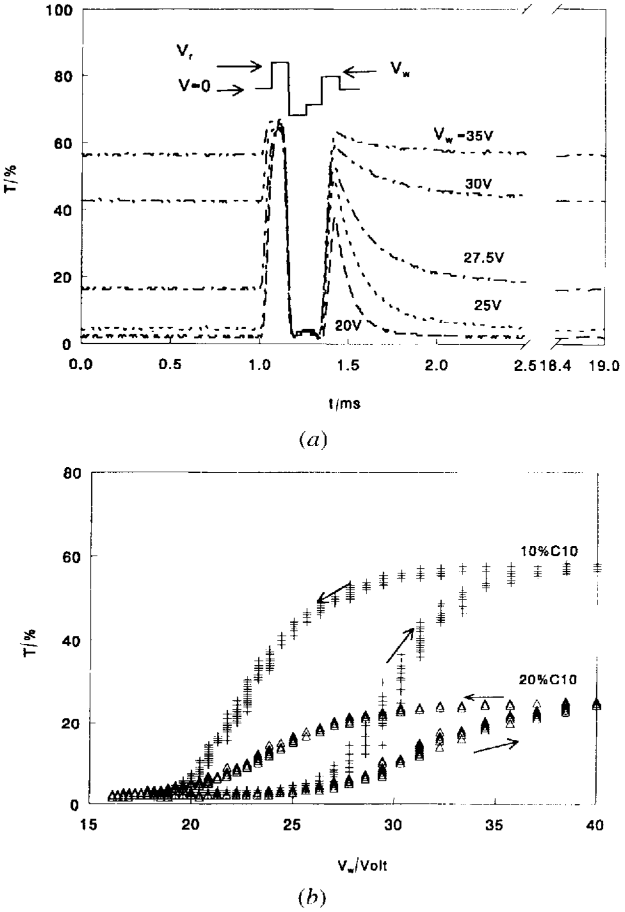


Figure 15. (*a*) Transmission through crossed polarizers during the application of a bipolar reset pulse (V_r) of ±40 V followed by write voltage pulses (V_W) of various magnitudes for a gel containing 10 wt per cent polymer. (*b*) Transmission as a function of write voltage (V_W) for two different gels. + = 10 per cent network, △ = 20 per cent network.

switched in the 180° twisted state within the anisotropic network causing the colour of the cell to change between crossed polarizers. These experiments clearly showed that the orientation in the gels was stabilized by the anisotropic network rather than by the cell surfaces.

3.3.2. *Grey levels in passive matrix addressing*

In previous sections it was shown that the ferroelectric molecules respond to the electric field in a different way from that in the surface stabilized case, and that within the gels, the switching takes place over a wider voltage range. This property of ferroelectric gels can be used to achieve grey scales in displays. For this purpose, we first studied the bistability of the ZLI molecules. In order to reorient the chevrons to the upright position (book-shelf structure), the cells containing the gels were subjected to a 10 Hz peak-to-peak 50 V square wave. Subsequently, the standard bistability test was carried out using a periodicity inverted bipolar pulse set. The results of the bistability test obtained for various compositions are shown in figure 14. It can be seen that all of the compositions used in the study showed bistable switching. We then investigated the possibility of obtaining stable grey levels. For this purpose, we used two adjacent bipolar periodic (100 Hz) pulses (bipolar pulses were used to prevent the accumulation of ionic charges within the system). The first bipolar pulse served to reset (V_r) the system; its magnitude was kept constant. The second bipolar pulse served to switch (V_w) the system to various transmission levels; its magnitude was varied. Figure 15 (*a*) shows the change in the transmission as a function of time during and after the application of such a pulse for various V_w values. It can be seen that after the reset pulse, which brought the transmission to zero, the second pulse raised the transmission. After the end of the pulse, the intensity dropped to a lower value within about 0·5 ms, where it stayed until the following pulse. This shows that grey levels can be obtained in this way. The explanation for this multi-stable switching may be switching in different domains at different voltages. The spontaneous polarization and the results of the birefringence measurements (see figure 8) both point to domain switching, which is probably also the source of grey levels. Figure 13 (*b*) shows optical photographs obtained after the application of various voltages to a sample containing 20 wt % of C10. Here it is important to note that the texture was very fine and had almost the resolution of the microscope. It is very different from the texture obtained when pure substances are used in the texture method [4, 19]. In figure 15 (*b*) we have plotted the transmission as a function of V_w during the application of a periodically varied V_w. It can be seen that in this way smooth transmission voltage curves can be obtained. The reason for the hysteresis, in spite of the reset pulse, however is not clear.

4. Conclusions

It has been shown that anisotropic networks containing ferroelectric molecules which are not chemically attached (free molecules) to the network (ferroelectric gels) can be produced by polymerizing LC diacrylates in a mixture containing the ferroelectric molecules. The orientational, thermal, optical and electrical properties of the free molecules in these gels became dominated by the network. For this reason we have also referred to these gels as network-stabilized ferroelectric gels. It has been shown that complicated orientations, such as twisted orientation can be induced in the ferroelectric material using the anisotropic network. The orientation of the network remained unaltered during the switching of the free molecules. Likewise the switching about the initially induced uniaxial orientation observed in conventional cells could be altered by the network. This was demonstrated by polymerization of the reactive molecules in a direction other than the direction of rubbing. In such a system, the switching took place about the direction in which the polymer molecules were oriented. Above the isotropic transition temperature of the free molecules, a fraction did not become isotropic and remained oriented. The apparent tilt angle decreased with the network concentration. This effect is attributed to the presence of the network, which remains uniaxially oriented during the switching. The switching was also found to spread over a range of voltages. This contrasted with the sharp transition observed for the pure material. This effect is attributed to the presence of domains of various sizes within the system. The gels also showed good bistability and stable grey scales. Variable grey levels could be obtained by changing the applied voltage levels.

References

[1] Meyer, R. B., 1974, *Presentation at the 5th International Liquid Crystal Conference, Stockholm.*

[2] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. de Phys. Lett.*, **36,** L69.

[3] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36,** 899.

[4] Hartmann, W. J. A. M., 1991, *Ferroelectrics*, **122,** 1.

[5] Maltese, P., 1992, *Molec. Crystals liq. Crystals*, **215,** 57.

[6] Kitzerow, H. S., Molsen, H., and Heppke, G., 1992, *Pol. Adv. Tech*, **3,** 231.

[7] Pris, J., Blinc, R., Martin, B., Museric, I., Pris, S., Zumer, S., and Doane, J. W., 1992, *14th International Liquid Crystal Conference, Pisa*, Poster C-P89.

[8] Hikmet, R. A. M., PHN 14.184 EP.

[9] Hikmet, R. A. M., 1991, *Liq. Crystals*, **9,** 405.

[10] Hikmet, R. A. M., and de Witz, C., 1991, *J. appl. Phys.*, **70,** 1265.

[11] Hikmet, R. A. M., and Zwerver, B. H., 1991, *Liq. Crystals*, **10,** 835.

[12] HIKMET, R. A. M., and ZWERVER, B. H., 1992, *Liq. Crystals*, **12,** 319.
[13] HIKMET, R. A. M., and ZWERVER, B. H., 1993, *Liq. Crystals*, **13,** 561.
[14] HIKMET, R. A. M., and HOWARD, R., 1993, *Phys. Rev.* E, **48,** 2752.
[15] HIKMET, R. A. M., and MICHIELSON, W., 1995, *Adv. Mater*, **7,** 300.
[16] *J. appl. Phys.*, submitted.
[17] MANSIPUR, M., 1990, *J. appl. Phys.*, **67,** 6466.
[18] KIMURA, S., NISHIYAMA, S., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1987, *Jap. J. appl. Phys*, **26,** L255.
[19] HARTMANN, W. J. A. M., VERHULST, A. G. H, LUYCKX-SMOLDERS, A. M. M., and STOMMELS, F. J., 1991, *Proc SID*, **32,** 115.