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Evidence for the non-uniform distribution of polymer networks formed in liquid crystal devices

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The electro-optic properties of liquid crystal devices are modified by the presence of a polymer network formed by the exposure to UV light of reactive mesogen molecules dissolved within the liquid crystal host. The effect of the polymer network depends on its density, and knowledge of this through the liquid crystal layer is necessary to understand qualitatively, and to model quantitatively, the electro-optic properties of liquid crystal devices containing polymer networks. Various techniques have been used to study the distribution of the polymer network and these show an increased concentration of the network near the surface closest to the UV light. Evidence is presented that the polymer network distribution becomes more uniform when non-UV absorbing liquid crystals are used.

1. Introduction

The electro-optic properties of a liquid crystal device are modified by the presence of a polymer network (PN) formed by the exposure to UV light of reactive mesogen (RM) molecules [1] dissolved within the liquid crystal (LC) host. The polymer network imposes an extra alignment force on the LC molecules with a direction equivalent to that of the LC during exposure [2–4] and a strength related to the density of the polymer network [5]. This density is related both to the initial concentration of RM and to the subsequent PN distribution following polymerization. Knowledge of the polymer network distribution through the LC layer is therefore necessary to understand qualitatively, and to model quantitatively, the influence of PNs on the electro-optic properties of LC devices.

Analysis of capacitance measurements [6] suggests that the PN might be concentrated close to both cell surfaces, possibly as a result of the attraction of the reactive species to the surfaces. A similar conclusion has been drawn from the influence on the LC alignment of PNs formed when high voltages are applied across the device. A large difference was found [5] in the alignment present in devices polymerized at applied voltages of 10 and 15 V, when the average bulk LC alignment is expected to be similar and differences in the alignment should only exist near the two surfaces. The formation of diffraction gratings in PN/LC combinations exposed to interfering UV beams [7, 8] also suggests that the

intensity of the UV light can influence the distribution of the PNs formed. It also has been reported [9] that a UV intensity gradient, together with differences in reactivity, can influence the molecular architecture in chiral nematic polymers. Many LC materials absorb UV light quite strongly and it has recently been speculated that this absorption may be strong enough to influence the distribution of the PN, producing a higher concentration near the surface closest to the UV light [10].

In this paper structural, optical and electro-optical observations are reported which provide qualitative evidence for the non-uniform distribution of PNs in LC devices and for the influence of the UV absorbing properties of the LC host.

2. Materials, absorption spectra and device processing

Two host nematic liquid crystal (NLC) mixtures that were expected to show quite different UV absorbing properties were used. E7 should absorb UV light strongly because it contains absorbing materials [11], cyanobiphenyls (CB) and a cyanoterphenyl (CT) (figure 1); whereas ML1001 contains phenylcyclohexane (PCH) materials (figure 2) and should be non-absorbing for the wavelengths of interest [11]. Both LC mixtures were supplied by Merck Specialty Chemicals Ltd.

The polarized UV absorption spectra of both LC mixtures were measured parallel and perpendicular to the LC director using 5 μm cell gap antiparallel aligned glass devices and a UV/visible spectrophotometer (UV/Vis/NIR Lambda 19 Spectrometer, Perkin Elmer) with an equivalent empty device as reference. The spectra are shown in figure 3. Interference in the empty reference

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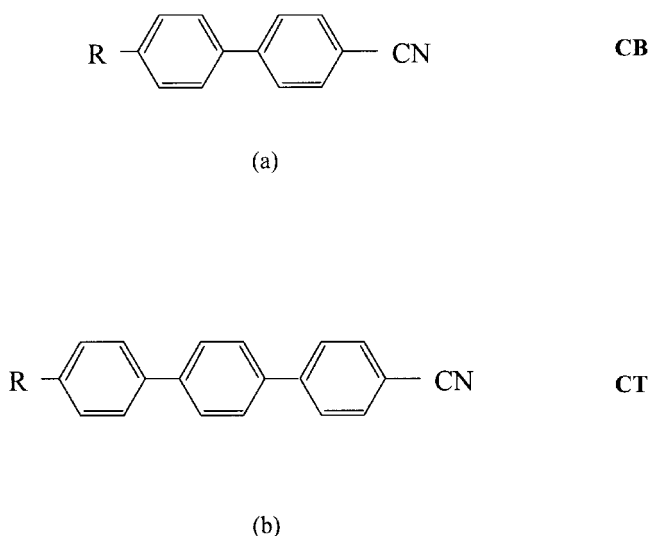


Figure 1. Chemical structure of (a) a cyanobiphenyl (CB) and (b) a cyanoterphenyl (CT) material.

Figure 2. Chemical structure of a phenylcyclohexane (PCH) material.

cell leads to the oscillations observed and therefore ML1001 was also used as a reference for E7, figure 3 (b). The high absorption of glass below 320 nm limits the accuracy of the spectra below this wavelength.

The results in figure 3 are consistent with previous measurements [11] on the single compounds that constitute the mixtures and confirm that E7 absorbs strongly in the wavelength range of interest, whereas ML1001 is virtually non-absorbing. RM257 4-(3-acryloyloxypropyloxy)phenyl 4-[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzoate, also from Merck Specialty Chemicals Ltd., was used as the reactive mesogen (figure 4). A small amount (5–10 wt %) of the photoinitiator Irgacure 369 from Ciba Specialty Chemicals was added to the RM and this mixture was subsequently added to the host NLC mixtures (E7 or ML1001) at concentrations in the range 1–5 wt %. The final mixtures were thoroughly stirred before use and care was taken to avoid premature exposure to UV light. The absorption of the final mixtures in the 320–400 nm wavelength range is dominated by the host LC, as RM257 is non-absorbing and only a small amount of the absorbing photoinitiator is present. Polymerization was achieved by exposure to UV light (Blak-Ray Lamp, Ultra-Violet Products) of intensity 0.6 mW cm^{-2} and wavelength 365 nm for 10 min. During exposure the photoinitiator (PI) is activated and free radical polymerization of the

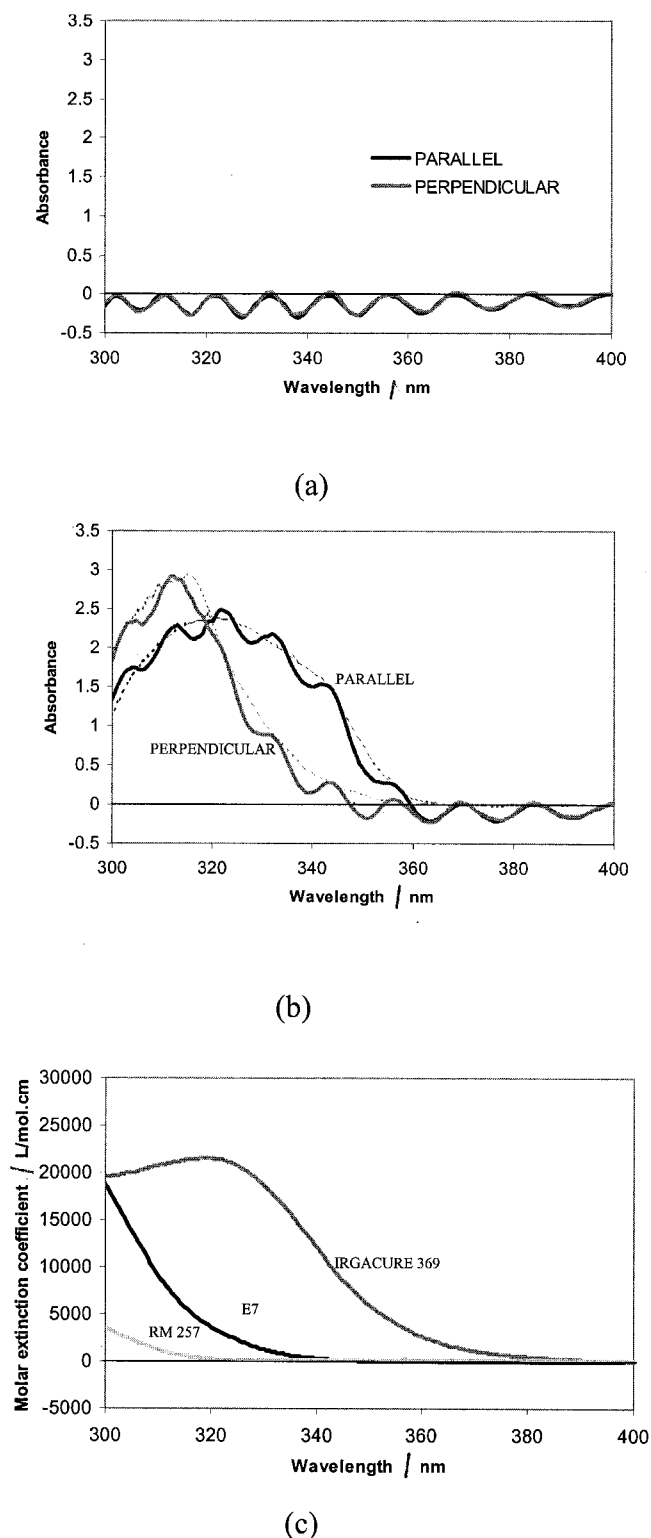


Figure 3. Polarized absorption spectra of (a) ML1001 (parallel and perpendicular) and (b) E7 (parallel and perpendicular). Reference, empty cell (solid line); ML1001 cell (dashed line). (c) Molar extinction coefficients measured in chloroform for Irgacure 369, RM 257 and E7.

Figure 4. Chemical structure of RM257.

RM molecules proceed, creating a three-dimensional polymer network.

The LC cells used were standard $5\ \mu\text{m}$ cell gap devices fabricated using glass with conventional surface alignments. Planar alignment of the LC director was achieved by rubbing a standard polyimide (PI2555) coating spun onto the glass. Devices were assembled in an antiparallel manner to produce untwisted devices or orthogonally to produce 90° twisted nematic (TN) devices. Asymmetric hybrid aligned nematic (HAN) devices were also used. In these HAN devices one surface has a planar alignment and the other a homeotropic alignment (orthogonal to the glass surface) produced by coating the glass with a standard surfactant material [12].

3. Structural observations

3.1. Direct visual observation

The quantity of polymer network attached to both surfaces was observed visually as described below and used as a rough indication of the polymer network distribution. Two microscope slides were assembled together using $6\ \mu\text{m}$ mylar spacers and clips. Mixtures containing RM, PI and host LC were introduced between the slides and exposed to UV light using two different kinds of exposure. The normal '1-sided' exposure was adapted to a '2-sided' exposure using two mirrors to direct the UV light equally onto both cell surfaces. Once exposed, the cell was unclipped, the plates were carefully separated and the LC and any un-reacted RM washed away by immersion in pentane. When the absorbing LC host E7 was used, the one-sided exposure gave a clear difference in the amount of polymer network remaining on each plate. There was a significant amount of PN apparent on the first surface encountered by the UV light whereas almost no PN was present on the other surface. Conversely, the two-sided exposure led to similar PN concentrations on both surfaces. For the non-absorbing LC host ML1001, the amount of PN was similar on both plates, even when using the one-sided exposure.

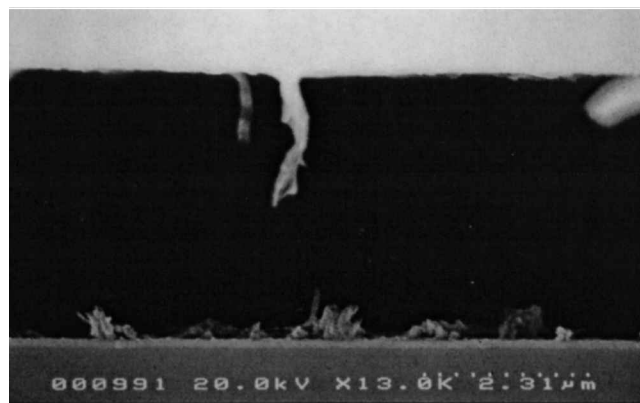
3.2. Scanning electron microscope observations

To confirm the non-uniform PN distribution when absorbing LCs are used, some scanning electron microscope (SEM) observations were carried out using a mixture of E7 and 2 wt % of RM257 and PI in a normal glass cell. The filled cell was exposed to UV light using a

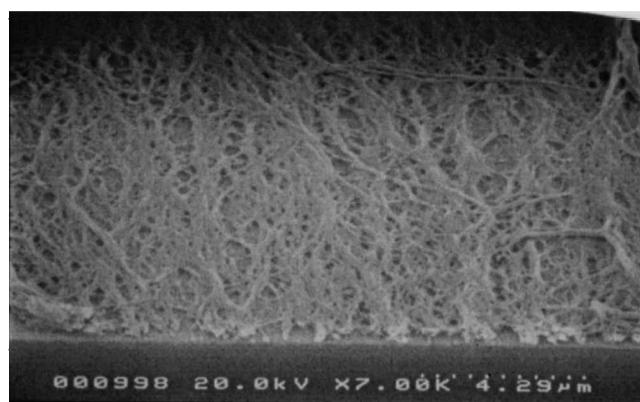
1-sided exposure and the LC and unreacted RM washed away by immersion in pentane for several days. The cell was then prepared for observation in the SEM by coating with gold. Figure 5(a) shows a section of the cell and clearly indicates that there is some PN on the surface nearest the UV light and almost nothing on the other surface. Figure 5(b) shows an oblique view of the PN structure on the exposed surface.

4. Observations using a polarizing microscope

Although the structural observations described above provide evidence that the PN distribution is non-uniform through the cell thickness, the PN could have been



(a)



(b)

Figure 5. Scanning electron microscope pictures of 2 wt % RM257 in E7: (a) side view, (b) exposed surface viewed obliquely.

affected by the pentane used to remove the LC and un-reacted RM. This may have damaged the PN by causing partial removal of the polymer in some areas, or partial collapse of the network in weaker areas. In order to confirm that the network distribution is non-uniform before immersion in pentane, observations were carried out with the LC host still present by studying the optical properties of 5 μm twisted nematic layers. In a TN layer the LC director rotates smoothly between the two surfaces with a twist angle φ relative to one surface alignment direction given by $\varphi = (\pi \times z)/(2 \times d)$, where z is the distance through the layer and d the layer thickness. The PN formed in a twisted nematic LC layer adopts the same twisted orientation. When the cell is heated above the nematic to isotropic transition temperature the birefringence of the host LC is lost, but that of the PN is retained, making the network visible between crossed polarizers. This remaining birefringence is small ($\Delta n \approx 0.01$) and is dependent upon the local density of the polymer network.

The small birefringence ($\Delta n \approx 0.01$) of the polymer network is well below the minimum value ($\Delta n \approx 0.10$) necessary to allow guiding of the polarization of visible light to occur in a 5 μm TNLC layer. Using the general expression for the transmission of light through a twisted LC layer [13], it is straightforward to show that the transmission T of light of wavelength λ through a 90° twisted layer of low and uniform birefringence ($\Delta n d \ll \lambda$) between crossed polarizers oriented at an angle θ to the surface alignment is given by

$$T = (2\Delta n d/\lambda)^2 [(\pi\Delta n d/2\lambda)^2 + \cos^2 2\theta]. \quad (1)$$

As the crossed polarizers are rotated, a minimum transmission of value

$$T_{\min} = \pi^2 (\Delta n d/\lambda)^4 \quad (2)$$

occurs at an angle $\theta_{\min} = 45^\circ$, exactly half way between the two surface alignment directions. We have used numerical modelling based on the Jones matrix [14] to show that the minimum transmission remains at $\theta_{\min} = 45^\circ$ when the birefringence (and hence the density of the polymer network) is non-uniform, provided it is symmetrical about the centre of the layer. Conversely a non-uniform asymmetric birefringence (and PN density) results in a minimum transmission at some other angle. Measurement of the angle of the polarizers for minimum transmission (θ_{\min}) therefore provides evidence for a symmetric or an asymmetric distribution of the PN. The geometry of the measurement means that minima occur every 90°.

Mixtures containing 3 wt % of RM in the two LC hosts were filled into standard 90° TN cells and exposed to UV light using 1 and 2-sided exposures. The cells were then heated into the isotropic phase and the angle

Table 1. Extinction angles for differently exposed TN cells containing 3 wt % RM257 in E7 and ML1001.

	Liquid crystal	Exposure type	Angle θ_{\min} /degrees
Cell 1	E7 (absorbing LC)	1-sided	−27/63/153/243
Cell 2	E7 (absorbing LC)	2-sided	45/135/225/315
Cell 3	ML 1001 (non-absorbing LC)	1-sided	46/136/226/316

for minimum transmission between crossed polarizers measured; the results are shown in table 1.

When the absorbing LC E7 is used with a 1-sided exposure, $\theta_{\min} = -27^\circ$, suggesting an asymmetrical distribution of PN. Using the same material with a 2-sided exposure gives $\theta_{\min} = 45^\circ$, indicating that the asymmetry present with the 1-sided exposure is removed by the symmetrical exposure. Using the non-absorbing LC host ML1001 with a 1-sided exposure gives $\theta_{\min} = 46^\circ$. This is very close to the symmetrical value of 45° , suggesting that the PN is distributed symmetrically through the layer. These results suggest that the distribution of PN across the layer is determined by the absorption of the UV light by the LC host.

5. Electro-optic measurements

The structural and optical observations reported above show that the use of an absorbing LC such as E7 results in a non-uniform PN distribution. The electro-optic properties of asymmetric devices based on the HAN configuration containing one homeotropic and one planar surface have been used to confirm the presence of a non-uniform PN distribution. HAN cells were filled with a mixture containing 1.6 wt % RM257 in E7 and exposed at a high voltage (10 V_{rms}) using two different 1-sided exposures: 1-sided-H was exposed from the homeotropically-aligned side and 1-sided-P from the planar-aligned side (figure 6).

The cell retardation for zero applied voltage was measured using a Soleil–Babinet compensator and the cell thickness used to deduce $\Delta n'$, the average birefringence. The results are shown in table 2 for both exposures,

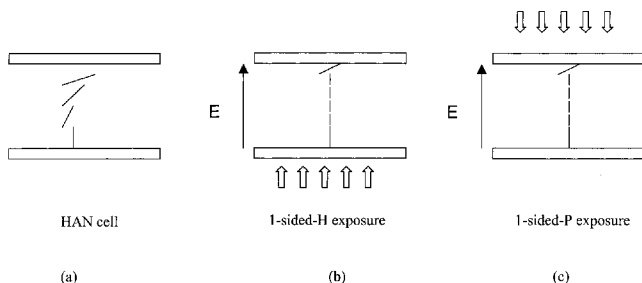


Figure 6. HAN cell and exposure conditions (a) the HAN cell, (b) 1-sided-H exposure, (c) 1-sided-P exposure.

Table 2. Average birefringence in HAN cells exposed at $10 V_{\text{rms}}$.

Cell	[RM] in E7/wt %	Exposure type	$\Delta n'$
HAN 0	0	—	0.1027
HAN 1	1.6	1-sided-P	0.0175
HAN 2	1.6	1-sided-H	0.0350

together with a reference cell (HAN 0) filled with pure E7. For this reference cell, $\Delta n' \sim 0.103$, close to half the natural birefringence of E7 ($\Delta n' \sim 0.23$), as might be expected for a HAN cell with no applied voltage. The small difference could easily be explained by inaccuracy in the thickness measurements. When $10 V_{\text{rms}}$ was applied to the reference cell, the director became virtually homeotropic throughout with a small measured average birefringence of $\Delta n' \sim 0.01$.

Exposure of a cell containing an LC/RM mixture biased at $10 V_{\text{rms}}$ will form a PN with almost complete homeotropic orientation. The cell with P-type exposure (HAN 1) showed this to be the case, with a small average birefringence of $\Delta n' \sim 0.0175$, whereas the cell with H-type exposure (HAN 2) showed a much higher average birefringence of $\Delta n' \sim 0.0175$. These results suggest that the PN is concentrated near the exposed side. In HAN 1 the homeotropic PN is concentrated near the planar aligned surface where it 'overwrites' the planar alignment producing a homeotropic layer. Conversely in HAN 2, the homeotropic PN is concentrated near the homeotropically aligned surface where it has least effect. The reduction of the average birefringence from $\Delta n' \sim 0.103$ in HAN 0 to $\Delta n' \sim 0.035$ in HAN 2 suggests that the homeotropic influence of the PN may extend to a distance of approximately $3 \mu\text{m}$ from the surface nearest the UV light source.

6. Conclusions

Using structural, optical and electro-optical measurements, we have presented qualitative evidence to show that the polymer network formed in liquid crystal layers has a non-uniform distribution when the host LC

absorbs UV light and that the PN is concentrated close to the surface nearest the source of UV light. We have also shown that the use of a non-UV absorbing LC can result in a symmetric distribution of PN across the layer. The non-uniform distribution of the PN through the layer will influence the device electro-optic properties and quantitative measures of the distribution are needed before any detailed understanding or modelling of devices can be achieved. These measurements are in progress in this laboratory.

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