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Liquid Crystals

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Photomechanically induced ferroelectricity in smectic liquid crystals

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We report new photomechanical effects in the ferroelectric liquid crystal SCE13 doped with a photoisomerizing guest azo dye. Low concentrations of dye (~5 per cent wt:wt) are shown to cause an isothermal, reversible disruption of smectic phases when the system is illuminated with low power density ($\sim 1 \text{ mW cm}^{-2}$) UV light. In the case of a sample initially in the S_C^* phase, this results in a fall in the magnitude of spontaneous electrical polarization (P_s) and changes in electro-optic switching characteristics. If the sample is illuminated in the S_A phase, the electroclinic switching decreases. In contrast to this, when systems containing higher concentrations of dye (≥ 10 per cent wt:wt) are UV illuminated in the S_A phase, a reversible, isothermal transition to a biphasic $S_C^*/$ isotropic state occurs. In this case, the P_s is seen to rise from zero in the S_A phase to a finite value ($\sim 2 \text{ nC cm}^{-2}$) in the biphasic mixture and hysteresis occurs in the electro-optic switching. When these higher dye concentration mixtures are held initially in the S_C^* phase and UV illuminated, a more complicated variation of P_s occurs with the sample again undergoing a transition to a biphasic $S_C^*/$ isotropic state. Possible mechanisms for the transition are discussed.

1. Introduction

Liquid crystals have attracted ever increasing interest over recent decades because of their ability, which their ordered structure conveys upon them, to alter dramatically the properties of light reflected from or transmitted through them. The ease with which the molecular ordering, and hence the optical properties, of liquid crystals is altered by applied electric fields, makes liquid crystals natural candidates for use in electro-optic displays and data storage devices. Optical properties such as birefringence, dichroism, fluorescence, light scattering and specular reflection have all provided the impetus for the development of new devices. In all these cases however, it is the changes that occur in the incident light (i.e. changes in polarization state, spectral content etc.), rather than any changes that may occur in the liquid crystal itself, that are of primary importance to the operation of the device. Recently however, interest has grown in just such photomechanical counter-processes, in which it is incident light itself which brings about molecular reordering of the liquid crystal.

Photomechanical molecular reordering processes are best achieved by incorpor-

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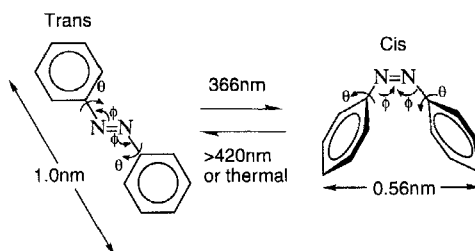


Figure 1. The isomerization of azobenzene. *Trans*: $\phi = 114^\circ$, $\theta = 15^\circ$; *Cis*: $\phi = 121^\circ$, $\theta = 56^\circ$.

ating some photoisomerizing molecule into an anisotropic system. This can be achieved by simply dissolving a proportion of such molecules into the system, or by building in the isomerizing units directly, as side group moieties in a polymer system for example. In either case, illumination by light of correctly chosen wavelength brings about isomerization of the added molecules and a consequent change in their steric and electronic properties. Since the bulk ordering of a liquid crystalline system depends intimately upon the microscopic steric and electrostatic interactions of the constituent molecules, even small changes in molecular properties can be thus *amplified* to produce dramatic changes in macroscopic properties. The literature contains examples of the photonic control of polymer solubility [1], droplet surface-wetting [2], the osmotic potential of gels [3] and the electrical properties of Langmuir–Blodgett films [4]. In addition, light induced texture changes in polymer films have enabled several groups [5,6] to demonstrate holographic image storage, with obvious applications for optical data storage devices. Interest is also growing in using photoresponsive Langmuir–Blodgett films [7] and polymers [8] as alignment surfaces for liquid crystals. The photosensitive membranes found in the eye [9] are a beautiful illustration of nature utilizing photomechanical effects, and the biological photochrome bacteriorhodopsin has been used in the construction of novel spatial light modulators and optical data storage devices [10].

Working with liquid crystals, several groups [11,12,13] have demonstrated the ability of photoisomerizing azo-molecules dissolved in host liquid crystals in the nematic phase to induce an isothermal transition to the isotropic phase upon conversion of the azo molecules from their *trans*-isomeric state to the *cis*-state. The assumption is that the bent *cis*-isomer is less easily packed into the nematic matrix than the linear *trans*-form, and tends to disrupt the packing of neighbouring liquid crystal molecules. An increase in *cis*-isomer population produces a corresponding reduction in the order of the system, eventually giving rise to complete isotropy. Azo-molecules are good candidates for studying photomechanical effects because of the large steric change (see figure 1) in going from the *trans*- to the *cis*-state, and also because of the reversible nature of the isomerization, the *cis*- to *trans*-conversion being effected either photonically or thermally.

We were recently able to verify that phases other than the nematic could be disordered in this fashion, by showing that the magnitude of the ferroelectric spontaneous electrical polarization of a single component host liquid crystal in its smectic C^* (S_C^*) phase could be isothermally reduced by low input power density ($\sim 0.8 \text{ mW cm}^{-2}$) UV-excitation of guest azo-molecules [14]. As was originally predicted by Meyer [15] in 1975, any smectic phase composed of tilted, chiral molecules must, by symmetry arguments, exhibit a ferroelectric spontaneous polarization (P_s). The

S_C^* phase is of great technological interest for display devices, because the molecules can be made to switch between two tilted positions by the application of electric fields. When switching, each molecule moves around the perimeter of a cone (so-called Goldstone mode switching). In the non-ferroelectric S_A phase, only soft-mode or electroclinic switching is allowed, with the electric field inducing a small or moderate tilt of the molecules. The soft mode is also present in the S_C^* phase, but it usually masked by the much larger Goldstone switching. Because the ferroelectricity in the S_C^* phase is purely a consequence of the symmetry of the system, a fall in the magnitude of P_s corresponds to a reduction of the system's order. The fall in P_s upon UV illumination as described above is therefore a demonstration of optically induced reordering of a S_C^* phase. Ikeda *et al.* [16], were also able photomechanically to reduce P_s in the S_C^* phase of a second liquid crystal material using a pulsed YAG laser operating in the UV region. Most recently, however, we have been able to give a full demonstration of complete phase transitions between several different smectic phases [17, 18]. Using only low input power densities ($\sim 0.8 \text{ mW cm}^{-2}$) of UV light to irradiate a single component liquid crystal doped with a mesomorphic azo-dye, we were able to induce isothermal, reversible transitions from a S_I^* to a S_C^* phase and from a S_C^* to S_A phase, with corresponding changes in the magnitude of P_s and optical tilt angle.

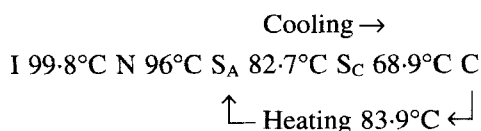
In the present work, we will study photomechanical phenomena in the room temperature ferroelectric mixture SCE13 (Merck Ltd, U.K.) incorporating a novel mesomorphic guest azo-dye, as a function of dye concentration. These phenomena will be studied for both the S_C^* and S_A phases. At low dye concentration (~ 5 per cent wt: wt), we will show that the *cis*-isomeric change reduces the ferroelectric order in the system, whilst at high concentration (≥ 10 per cent wt:wt dye), we will demonstrate an isothermal, reversible, photomechanically induced transition from a non-ferroelectric S_A phase to a biphasic ferroelectric $S_C^*/$ isotropic state with a consequent *rise* in the P_s from zero to a finite value. The transitions are induced using only low input power density ($\sim 1 \text{ mW cm}^{-2}$) UV illumination.

2. Experimental

2.1. Materials

In all the work described here, the host liquid crystal used is the commercial mixture SCE13 (Merck Ltd, U.K.), chosen for its broad room temperature range S_C^* phase and for its excellent ease of alignment. The phase sequence of SCE13 as a function of temperature is given in the table.

The chemical structure of the photoisomerizing guest azo-dye, hereafter denoted N5, used as a dopant is shown in figure 2. Individual N5 molecules have a chiral centre carrying a methyl group, but bulk samples used were racemic. The N5 has the novel property, for a guest dopant, of itself being liquid crystalline, exhibiting N, S_A and S_C mesophases. This liquid crystallinity was used to ensure good miscibility and high solubility of N5 in the host SCE13. The phase sequence of N5, as determined by DSC and polarising microscopy, is shown below.



The effect of addition of N5 to SCE13 on the transition temperatures of SCE13, on

Liquid crystalline phase transitions of N5/SCE13 mixtures as a function of concentration.

Per cent N5 in SCE13 (wt:wt)	$S_C^*/S_A/^\circ\text{C}$	$S_A/N^*/^\circ\text{C}$	$N^*/\text{isotropic}/^\circ\text{C}$
0	60.0	84.5	101.6
5	60.2	84.6	101.7
10	60.9	85.2	101.1
20	62.1	86.1	100.8

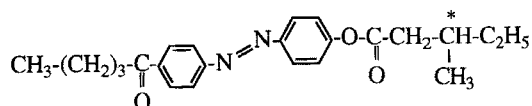


Figure 2. The chemical structure of the azo-dopant N5.

heating or cooling, was slight and this is shown in the table. The melting temperatures (crystal to S_C^*) of the mixtures are not shown as these were $< -10^\circ\text{C}$ and not important for the present discussion. There was no evidence of biphasic behaviour under normal viewing (i.e. when not UV irradiating samples) within the temperature resolution (0.1°C) of the experiment.

The occurrence of a reversible *trans*-/*cis*-isomerization for N5 was confirmed by UV/visible spectroscopy. The maximum absorption for the *trans*- to *cis*-isomerization occurred at 350 nm, and at 450 nm for the reverse *cis*- to *trans*-conversion. Changes in the ratio of the number of *cis*- to *trans*-isomer molecules for N5 in solution could be followed by observing the changes in the strength of the absorption peaks for the two isomers. If N5 was dissolved in toluene and the *cis*-/*trans*-population ratio given time to reach an equilibrium value under UV illumination, the solution subsequently took several hours at room temperature to relax to a new equilibrium state (with the majority of N5 molecules in the thermally favoured *trans*-state) following removal of the UV light thereby leaving the sample in darkness.

Samples were contained in glass cells of $7.5\ \mu\text{m}$ thickness, with a $25\ \text{mm}^2$ area patterned with transparent ITO film to enable electric fields to be applied across the cell, and with the inner glass surfaces coated with a polyimide alignment layer which helped induce excellent planar alignment in the sample. Alignment was obtained by cooling the sample slowly ($< 1^\circ\text{C}\ \text{min}^{-1}$) down from the isotropic phase, through the long pitch chiral nematic phase and into the required smectic phase. A hot stage allowed the sample temperature to be maintained to within 0.1°C . The UV illumination of samples was by a Hg-arc lamp with its output filtered to select light in the 300 to 400 nm range with a maximum output at 350 nm. The glass of the sample cell was essentially transparent over this range of wavelengths. The power density of the UV light at the sample cell was always $1.4\ \text{mW}\ \text{cm}^{-2}$. It was confirmed that UV illumination caused no temperature jumps in the irradiated sample that could account for the effects discussed herein. When not illuminating the sample with UV light, the cell was kept in darkness.

Measurement of the magnitude of the sample P_s in the S_C^* phase was made by the well-known current pulse technique [19]. A triangular-wave driving voltage induces the liquid crystal molecules to flip between their two switched states. There is a short flow of current, which is measured as a function of time, as each molecule's polarization dipole vector reverses direction. The area under the current pulse produced is then calculated (by an on-line microcomputer in the present work) to yield the value of P_s .

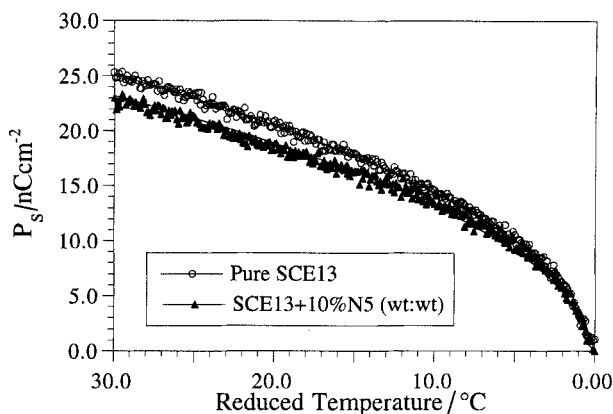


Figure 3. The effect of the dopant N5 on the P_s of SCE13. For clarity only the effect of 10 per cent N5 (wt:wt) is shown. The theoretical curve-fits from mean field theory (see equation (1)) are also shown.

3. Results

3.1. Properties of N5/SCE13 mixtures before UV illumination

Addition of N5 to SCE13 has only a small effect on the transition temperatures (c.f. the table), P_s and tilt angle of the host. The variation of P_s for the S_C^* phase of SCE13 doped with N5 plotted against the reduced temperature, T_{red} , of the sample below the transition to the S_A phase is given in figure 3. In taking the data for these plots, the sample was kept in darkness. According to Landau–de Gennes mean field theory [20], the P_s in the S_C^* phase should obey the following temperature relation:

$$P_s = K_{P_s} \left(\frac{T - T^*}{T^*} \right)^\beta \quad (1)$$

where T is the temperature and β is a critical exponent with a value of 0.5 in mean field theories. Experimental determination of exact values of β is an involved procedure; however for most purposes the mean field value of 0.5 gives an excellent fit for the variation of P_s with temperature except within a few mK of the transition to the S_A phase. The constant T^* has units of temperature and is normally very close to the S_C^* to S_A transition temperature (see the table). The constant K_{P_s} [nC cm^{-2}] determines the value towards which the P_s tends at temperatures far below the transition from the S_A phase. The P_s data given in figure 3 yields values of $K_{P_s} = 38.8$ and 33.7 for SCE13 and for SCE13 + 10 per cent N5 (wt: wt), respectively, when the data are fitted to equation (1). This reduction in the K_{P_s} value of SCE13 when 10 per cent N5 (wt: wt) is added indicates the reduction in the magnitude of P_s , at a given reduced temperature, upon addition of racemic N5. This trend of a reduction in P_s upon addition of increasing amounts of racemic N5 is apparent as a decreasing trend in the K_{P_s} values plotted in figure 4.

The variation of tilt angle, θ , with temperature can also be well fitted to an equation of the type (1), with, of course, the quantities P_s replaced by θ and K_{P_s} by K_θ . Figure 4 also shows the K_θ values plotted against N5 concentration. In contrast to the trend of decreasing P_s with increasing N5 concentration, the optical tilt angle, θ , of molecules in the S_C^* phase is found to *increase* upon addition to N5. The probable explanation here is that whilst an increase in the tilt of a chiral molecule in a smectic phase should, by Meyer's symmetry arguments [15], result in an increase in the local P_s , we must

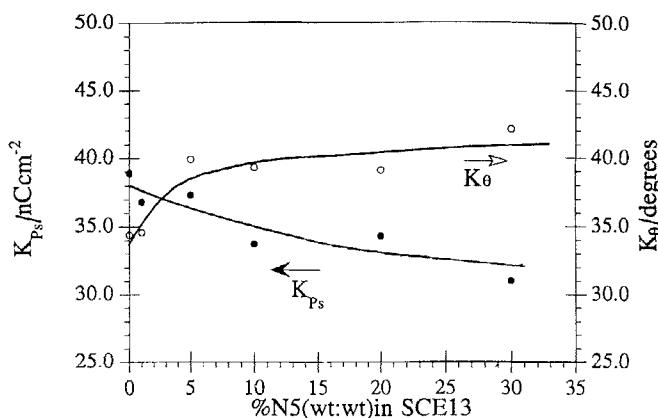


Figure 4. Variation of K values (see equation (1)) with concentration of N5, for P_s (●) and for optical tilt angle (○).

remember that in order to induce this change in tilt angle, we have replaced a given quantity of the chiral host molecules with molecules of the racemic guest azo dye which do not contribute to P_s . This will act to reduce the P_s observed in the bulk sample even though the guest azo increases tilt angle (c.f. figure 4). The important result here is that whilst we have shown that definite trends exist in the magnitude of P_s and θ when SCE13 is doped with the azo guest N5, the changes are slight. In the absence of UV illumination the guest N5 molecules are in their linear *trans*-form and that in this state they cause little disruption of the ordering of the host smectic and if anything improve the ferroelectric order by increasing slightly both the optical tilt angle and the temperature of the S_C^* to S_A phase transition (c.f. the table). In contrast to the small effects that addition of N5 to SCE13 has on the behaviour of the host SCE13 in the absence of UV illumination, the following sections will discuss the dramatic consequences of subsequently exposing such systems to UV illumination.

3.2. Photomechanical changes in P_s

3.2.1. Low concentration N5/SCE13 mixtures (~5 per cent wt:wt) in the S_C^* phase

We have previously demonstrated [17] using the single component host liquid crystal 4-(2'-methylbutyl)phenyl 4'-*n*-octylbiphenyl-4-carboxylate (CE8, Merck Ltd, UK) doped with low concentrations of N5 (~5 per cent wt:wt), that it is possible optically to induce isothermal, reversible phase transitions between the S_C^* , S_C^* and S_A phases with illumination by UV light. The result of exposure to UV light is a transition from a more ordered to a less ordered smectic phase. By arranging that the system be initially in its ferroelectric S_C^* phase, the magnitude of P_s can therefore be reversibly and isothermally reduced by driving the system towards the less ordered and non-ferroelectric S_A phase using low power density UV illumination. In this section we show that the P_s of the commercial mixture SCE13, acting as a host for the N5 azo-dopant, can be similarly reduced by UV illumination of the sample held initially in its S_C^* phase.

The effect of 200 s of UV illumination on the P_s of a well-aligned sample of SCE13 + 5 per cent N5 (wt:wt) is shown in figure 5. The sample is held at a temperature $T_{red} = 5^\circ\text{C}$ below the transition to the S_A phase. The P_s when the sample is held in darkness at this temperature is $9.5 \pm 0.5 \text{ nC cm}^{-2}$. Upon exposing the sample to UV

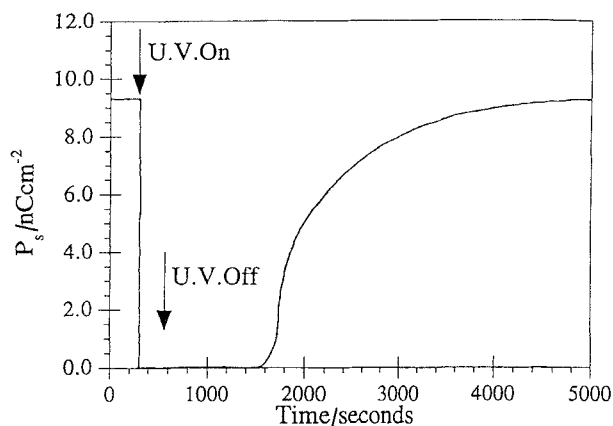


Figure 5. The UV light induced changes in the magnitude of P_s for SCE13 + 5 per cent N5 (wt: wt) in the S_C^* phase, 5°C below transition from the S_A phase.

light, the P_s is seen to fall to zero over approximately 10 s, and remain at this zero value for the duration of the UV irradiation. Upon removal of the UV leaving the cell in darkness once again, the magnitude of P_s remains at zero for a further 15 min before climbing smoothly back to its original pre-illumination value. The return to the pre-illumination value of 9.5 nC cm^{-2} indicates the reversibility of the effect and lack of sample degradation. We also note that the time for the P_s to return to its original pre-illumination value is of the same order of magnitude ($\sim 40 \text{ min}$) as for the thermal *cis*- to *trans*-relaxation of N5 in a solvent (see § 2.1) following UV excitation. This is further confirmation that the changes occurring during UV illumination of P_s cannot simply be ascribed to sample heating occurring during UV illumination, as we would then see a much faster return to thermal equilibrium in thin ($7.5 \mu\text{m}$) samples attached to a thermostatically controlled hot stage. During UV illumination of the sample, microscopy revealed that the initially well-aligned S_C^* monodomain became ‘peppered’ with many small multicoloured birefringent regions. When the UV was removed, these regions slowly disappeared and the sample returned to its well-aligned state. As a control experiment, samples of pure SCE13 showed no equivalent changes in P_s . It is apparent then, that UV illumination, which results in *trans*- to *cis*-isomerization of the guest N5 molecules present in concentrations of ~ 5 per cent (wt:wt), results in a disruption of the ordering of the sample S_C^* phase and a consequent reduction in the magnitude of ferroelectric spontaneous polarization. The effect occurs in the same manner for the commercial mixture SCE13 as it does for the single component ferroelectric CE8 discussed elsewhere [17]. As with the changes occurring in the CE8/N5 system, the disappearance of P_s results in concomitant loss of electro-optic switching hysteresis and changes in optical tilt angle. The changes in tilt angle and electro-optic switching for the CE8 and SCE13 systems are more fully discussed elsewhere [17, 18].

3.2.2. Low concentration N5/SCE13 mixtures (~ 5 per cent wt:wt) in the S_A phase

Having discussed the effects of UV illumination on the S_C^* phase of low concentration SCE13/N5 mixtures, we now study the changes which occur when samples initially in the S_A phase are UV-illuminated. In this case no changes occur in the magnitude of the ferroelectricity of the sample, which remains zero throughout.

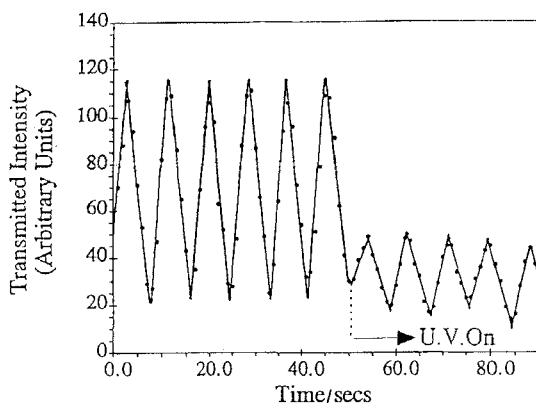


Figure 6. The UV light induced reduction in the magnitude of electroclinic switching in the S_A phase of SCE13 + 1 per cent N5 (wt:wt), 1°C above the transition from the S_C^* phase.

Changes do occur, however, in the electro-optic switching characteristics of the sample. If a liquid crystal composed of chiral molecules is held in the S_A phase and an electric field is applied in a direction normal to the director, the molecules are caused to tilt away from their equilibrium positions. The magnitude of the induced tilt is directly related to the magnitude of the applied field, and application of a time varying voltage results in electroclinic switching of the sample [21]. Figure 6 shows the transmitted intensity of a low power ($< 1 \text{ mW cm}^{-2}$) HeNe laser beam ($\lambda = 632.8 \text{ nm}$) passing through a sample of SCE13 + 1 per cent N5 (wt:wt) between crossed polarizers. The sample is initially in its S_A phase 1°C above the transition from the S_C^* phase, and undergoes electroclinic switching in response to a low frequency (1 Hz) $22 \text{ V}_{\text{p-p}}$ triangular wave applied voltage. Since the induced tilt angle, θ_{ind} , is proportional to the applied field, the optical transmission also has a triangular form of the same frequency as the applied field, as is shown in figure 6. Illumination with UV light results in a clear reduction in the amplitude of switching, but not the period or form of the switching response, showing that the ordering of the molecules in the S_A phase is disrupted by the UV light, as might be expected by the increased population of bent *cis*-N5 isomers arising from the illumination. The slight fall in the mean transmitted intensity is due to the appearance of small multicoloured birefringent regions in the sample, reducing the overall transmittance. The reduction in the magnitude of electroclinic switching is fully reversible upon removal of the UV light, with the sample showing no signs of degradation as a result of exposure to the UV light.

It is apparent from the discussions of §§ 3.2.1 and 3.2.2 that the addition of small amounts of N5 to SCE13 and illumination by UV light results in considerable changes in the ferroelectric and electro-optic properties of the sample. We have shown that the P_s of a sample in its S_C^* phase can be isothermally and reversibly reduced and electro-optic switching hysteresis reduced to zero. In addition the magnitude of the electroclinic switching of a sample in the S_A phase can also be reversibly altered. These effects open up interesting possibilities for novel photonic transducers and optical data storage devices. However in the cases so far discussed, UV illumination results in the *reduction* in magnitude of some quantity (i.e. electroclinic switching, P_s etc.). In order for photomechanical effects to find their full potential usage in devices, it is desirable to find ways in which the magnitude of such quantities can be *increased* as well as

decreased. In the following sections we show that P_s can indeed be isothermally increased and electroclinic switching isothermally transformed to ferroelectric electro-optic switching displaying hysteresis under UV illumination by once again doping SCE13 with the guest N5, but now in higher (≥ 10 per cent wt:wt) concentrations.

3.3. Photomechanical effects in high N5 concentration mixtures

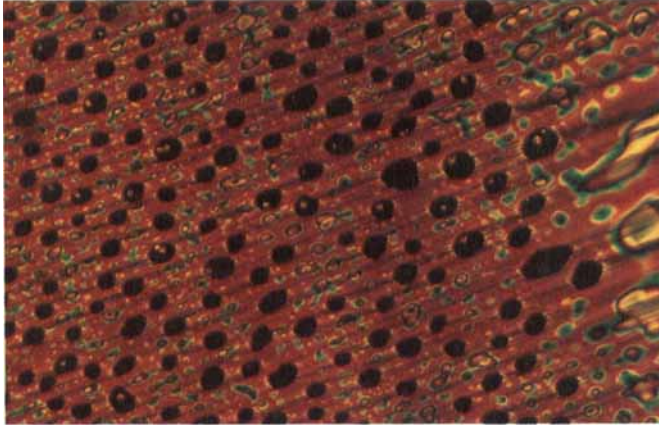
3.3.1. In the S_A phase

For samples in which the concentration of N5 in SCE13 is ≥ 10 per cent (wt:wt), UV illumination in the S_A phase results in a microscopic phase separation of the sample into an isotropic and a S_C^* phase and the dramatic *appearance* of ferroelectricity. Figure 7(a), (b) and (c) show a sample of SCE13 + 10 per cent N5 (wt:wt) before, during and after illumination, respectively, with UV light. The sample is initially well aligned in the S_A phase at a temperature 1°C above the transition from the S_C^* phase. The texture is shown in figure 7(a). When observing the sample in the polarizing microscope with a low frequency triangular wave voltage, electroclinic switching of the S_A phase was only just discernible to the naked eye. Figure 7(b) shows the dramatic consequence of exposing the same area of sample to 60 s of UV light. The sample is clearly seen to become biphasic with regions of isotropy, black between crossed polarizers, separating regions of liquid crystal showing up as multicoloured birefringent regions. It was confirmed that the black regions of the sample were indeed isotropic, and not homeotropically aligned areas, by tilting the cell out of the plane of the polarizers and observing that these regions remained optically extinct. The electro-optic switching, which prior to illuminating with UV light, had been electroclinic in nature, barely observable by the naked eye, was now easily seen and clearly recognizable as the two-state ferroelectric switching for those regions of the sample that were liquid crystalline. Figure 7(c) shows the sample following the removal of the UV light. The sample returns to its equilibrium S_A phase after ~ 5 min with a somewhat poorer alignment than initially, but otherwise no damage to the liquid crystal was seen to occur. The lower quality alignment is because the sample has not undergone the normal alignment procedure of being cooled from the long pitch N^* phase (c.f. § 2.1). Recycling the sample back through the N^* phase produced the same alignment as in figure 7(a).

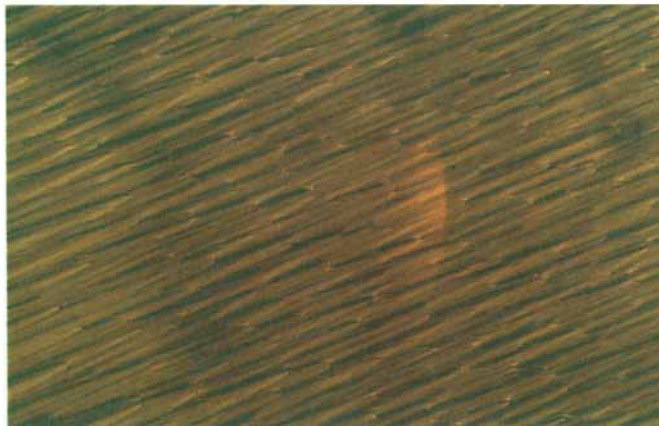
More detail regarding the UV light induced changes that occur in the electro-optic switching characteristics of a sample can be seen from figure 8. The sample is initially in its (non-ferroelectric) S_A phase at a temperature $+1^\circ\text{C}$ above the transition to S_C^* . The upper part of figure 8(a) shows a triangular wave driving voltage being applied to the sample and the optical transmission of the cell between crossed polarizers as determined by a linear response photodiode. The lower part of figure 8(a) shows the optical Lissajous figure formed by these two time dependent voltages. As expected in the S_A phase [21], a straight line Lissajous figure is produced, revealing the presence of electroclinic switching. The straight line Lissajous figure results from the induced tilt angle, θ_{ind} , being proportional to the magnitude of the applied field, E , at room temperatures of more than a few tenths of a degree above the transition from the S_C^* phase. Very close to the transition or with large applied fields, θ_{ind} has been shown to obey a $E^{1/3}$ law. Upon illumination with UV light a dramatic change is seen to occur in the switching characteristics of the sample (see figure 8(b)). The electro-optic switching is transformed from a triangular to a square wave response and the Lissajous



(a)



(b)



(c)

Figure 7. (a) SCE13 + 10 per cent N5 (wt:wt) showing excellent alignment before UV illumination in the S_A phase 1°C above the transition from the S_C^* phase; (b) biphasic S_C^* /isotropic texture during illumination; (c) ~ 5 min following removal of UV light.

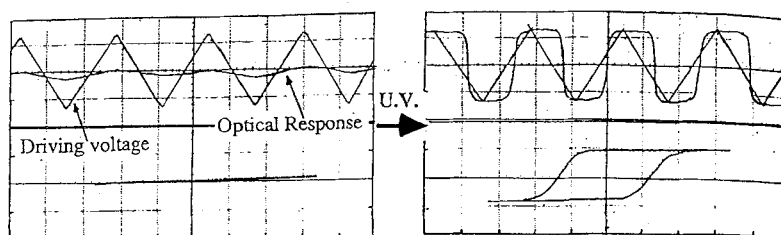


Figure 8. Photomechanically induced optical hysteresis in SCE13 + 10 per cent N5 (wt:wt): (a) before illumination, sample in S_A phase 1°C above transition from S_C^* ; (b) appearance of optical hysteresis during UV illumination. The sample is being switched with a $22\text{ V}_{\text{p-p}}$, 200 Hz triangular voltage in both cases.

figure reveals the classic optical hysteresis of ferroelectric switching, the ferroelectric switching being of much greater amplitude than the electroclinic switching.

The transformation of the sample from the non-ferroelectric S_A phase to a ferroelectric state is seen clearly from the changes in its electrical properties, monitored using the current pulse technique (see § 2.1) as is shown in figures 9 and 10. The upper part (a) of figure 9 shows a triangular wave driving voltage being applied to the same sample of SCE13 + 10 per cent N5 (wt:wt) as used above. Before irradiation with UV light, figures 9(b) and 9(c) show the current response of the sample in the S_C^* phase at reduced temperatures of 5°C and 1°C respectively, below the transition to the S_A phase. As expected, the response reveals the classic current pulses of ferroelectric S_C^* switching as the molecules are switched between their two tilted positions by the applied field. Figure 9(d) shows the sample, again before illumination with UV light, now heated into the S_A phase, 1°C above the transition from S_C^* . The transition to S_A is revealed in the current response trace by the total disappearance of the ferroelectric current pulse response. Illumination of the sample with UV light for $\sim 30\text{ s}$ at this temperature however, results in the dramatic reappearance of the current pulses (see figure 9(e)). The size of the current pulses induced during UV illumination is comparable to those seen previously, 1°C below the S_A to S_C^* transition (c.f. figure 9(c)). However, we cannot conclude that the P_s is the same in both cases, since only a certain percentage of the sample has been transformed to the S_C^* phase, whilst the remainder of the sample has become isotropic, as revealed previously in figure 7(b). Thus the magnitude of the spontaneous polarization we estimate from the size of current pulses in figure 9(e), observed when switching the bulk *biphasic* sample, will be somewhat lower than the true P_s for only those regions of sample in the S_C^* phase due to the presence of isotropic material in the active switching area of the cell. Referring to figure 9(e), we observed that the UV induced current pulses occur at approximately the same point on the driving voltage cycle as the pulses of figure 9(c) taken in the S_C^* phase 1°C below the transition to S_A , and therefore we can qualitatively assume the rotational viscosity for molecules associated with the switching in figure 9(e) to be of the same order of magnitude ($\sim 100\text{ mPa s}$) as that of the molecule in the S_C^* phase 1°C below the transition from the S_A phase. Accurate quantitative values for rotational viscosity are difficult to determine as they require the simultaneous measurement of P_s , tilt angle and switching voltage [22]. Tilt angle in particular is difficult to determine accurately for those regions of sample in the S_C^* phase, since the multi-domain texture resulting from exposure to UV (see figure 7(b)) means that the normal method of determining optical tilt angle,

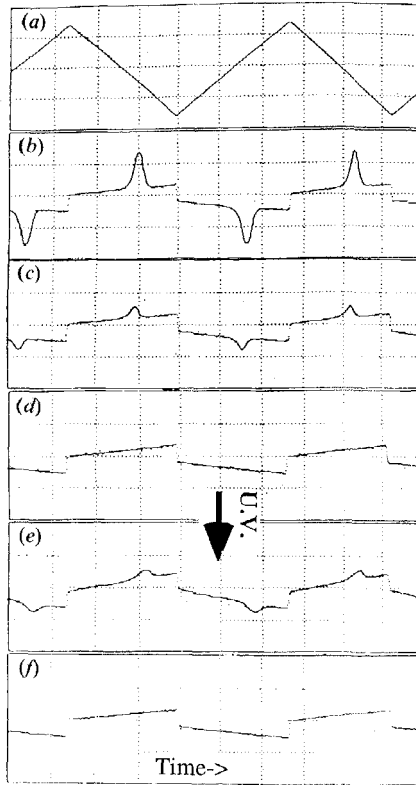


Figure 9. Photomechanically induced P_s in SCE13 + 10 per cent N5 (wt:wt): (a) driving voltage 200Hz, 22 V_{p-p}; (b) current response of sample in S_C^* phase at temperature, $T_{red} = 5^\circ\text{C}$ below S_A phase; (c) current response at $T_{red} = 1^\circ\text{C}$; (d) current response in S_A phase, 1°C above transition from S_C^* -note disappearance of current peaks; (e) reappearance of current pulses during UV illumination; (f) ~ 2 min following removal of UV light. In all frames the horizontal scale is 2 ms division⁻¹.

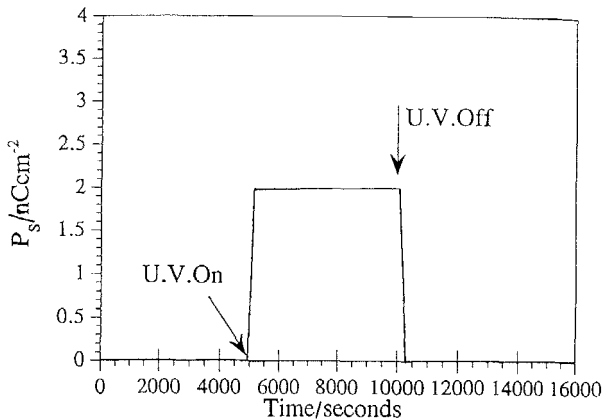


Figure 10. UV light induced variation in P_s for SCE13 + 10 per cent (wt:wt). Before UV illumination the sample is in the S_A phase, 1°C above the transition from the S_C^* phase.

namely rotation of the sample between crossed polarizers to the two positions of optical extinction, cannot be readily applied. Efforts to measure the UV light induced tilt angle in fairly well-aligned regions of sample indicate that it is of the order of 5° .

Figure 10 shows the temporal evolution of P_s for a sample of the mixture SCE13 + 10 per cent N5 (wt:wt). As discussed above, this is the P_s measured for the whole switching area of the cell and is a low estimate of the true P_s of the ferroelectric S_C^* areas due to the presence of regions of isotropy in the switching cell. Once again we observe that exposure to UV causes no long term degradation of the sample, with the P_s returning to its original pre-exposure value at the end of the experiment.

It was confirmed that none of the effects described above was simply pre-transitional in nature and all were observable well inside the S_A phase ($> 5^\circ\text{C}$ above the S_C^*). This is notable, because it can result in the appearance of P_s and electro-optic hysteresis in a sample at temperatures at which even pure SCE13 would be in its non-ferroelectric S_A phase in the absence of UV illumination. In this section we have reported various photomechanical phenomena for samples of SCE13 + 10 per cent N5 (wt:wt), but similar phenomena were observable for higher N5 concentrations (samples were prepared with as much as 40 per cent N5 with similar results to those discussed above). The main consequence of addition of N5 in concentrations > 10 per cent (wt:wt) is an increased number of isotropic regions in the biphasic mixtures resulting from exposure to UV light.

It is clear then that the non-ferroelectric S_A phase of SCE13 doped with fairly high concentrations (≥ 10 per cent (wt:wt)) of N5 is phase separated into a biphasic isotropic/ S_C^* mixture upon illumination with UV light. This is in sharp distinction to the process occurring for SCE13 doped with lower concentrations of dye (~ 5 per cent wt:wt), when illumination results in a straightforward lowering of system order with a consequent reduction in the magnitude of spontaneous polarization and optical hysteresis if the system begins in the S_C^* phase, or a reduction in the magnitude of electroclinic switching (with the P_s remaining zero) if the system begins in the S_A phase (§§ 3.2.1 and 3.2.2). In neither case does phase separation occur for these lower N5 concentration samples.

3.3.2. In the S_C^* phase

Having found that the exposure to UV light of a sample of SCE13 + ≥ 10 per cent N5 (wt:wt) held initially in the S_A phase results in the appearance of ferroelectric spontaneous polarization, it is obvious to proceed to explore the consequences of illuminating a sample which is held initially in the ferroelectric S_C^* phase. Figure 11 shows the results of UV illumination in this case. The sample is initially in its S_C^* phase, 5°C below the transition to the S_A phase. Upon exposing the sample to UV light, the P_s is seen to fall from 7 nC cm^{-2} to zero in approximately 10 s. This behaviour is similar to that observed for SCE13 + 5 per cent N5 (see figure 5); unlike the case of the 5 per cent N5 sample, however, the P_s does not remain at zero for the duration of the UV illumination, but instead rises to a value of $\sim 4 \text{ nC cm}^{-2}$ and remains at this level for as long as the UV light is present and for some time after its removal. Approximately 10 min after removal of the UV light, the P_s again falls to zero, remains there for ~ 25 min and only then returns to the pre-UV illumination value of 7 nC cm^{-2} . During those periods of time in which the P_s of the sample was zero (i.e. immediately following UV illumination and 10 min following the removal of the UV light), no optical hysteresis was observed for the sample. During the period of UV exposure when the P_s had a

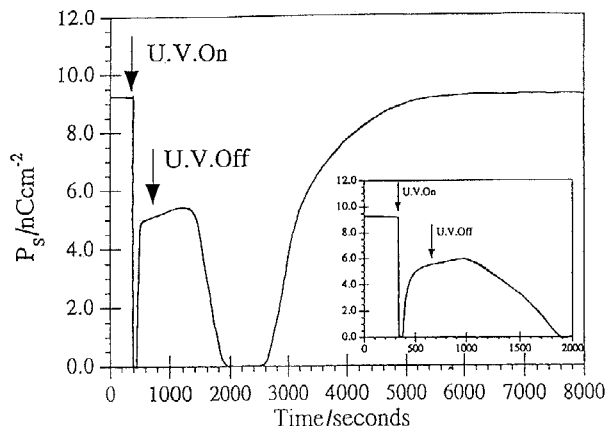


Figure 11. The UV light induced variation of P_s for SCE13 + 10 per cent N5 (wt:wt). Before UV illumination the sample is in the S_C^* phase, 5°C below the transition to the S_A .

non-zero value however, optical hysteresis was present and the optical tilt angle of the smectic areas of the biphasic sample was estimated to be $\sim 12^\circ$.

4. Discussion

We have seen that whilst addition of N5 to SCE13 produces only small changes in the behaviour of SCE13 in the absence of UV irradiation, once the system is illuminated large changes in the smectic properties occur. Two regimes of behaviour exist: a low concentration regime (~ 5 per cent N5 wt:wt) and a higher concentration regime (≥ 10 per cent N5). In mixtures containing the smaller quantities of N5, illumination with UV light results in a general disruption of the ordering of the system which is driven towards a less ordered smectic phase. If the system begins in the S_A phase, this results in a decrease in the amplitude of electroclinic switching (see § 3.1.2). If the system begins in the S_C^* phase, there is a decrease in the magnitude of P_s and of optical hysteresis (see § 3.1 and [17]). These effects are consistent with the hypothesis that the *trans*-N5 molecules pack fairly easily into the host smectic matrix (as we might expect from a linear guest molecule which itself shows liquid crystalline phases), but upon illumination with UV light and conversion of the N5 molecules to their bent *cis*-isomeric state, considerable disruption of host ordering occurs. We have demonstrated similar effects previously in the host CE8 [17], which is an important result, as it shows that the effects we have discussed here are at least to some extent independent of the nature of the host liquid crystal. When considering potential device applications, it is important to be able to choose the particular liquid crystal which optimises the performance of a device.

In contrast to the behaviour of low N5 concentration mixtures, when the concentration of N5 in SCE13 is ≥ 10 per cent (wt:wt) UV illumination results in a phase separation of the sample leading to a state in which regions of isotropy and of S_C^* ordering coexist. For a sample which is in the S_A phase before UV illumination, this results in a transition to a biphasic $S_C^*/$ isotropic state and the dramatic appearance of P_s and optical hysteresis. We suggest that above a certain N5 concentration, the bent *cis*-isomers created during UV illumination are no longer able to remain dispersed in the host, as they were in the lower N5 concentration mixtures, and phase separate into isotropic regions. This hypothesis is supported by the observation that increasing the

concentration of N5 above 10 per cent (wt:wt) results in the appearance of a larger number of isotropic regions. Once the UV light has been removed, the *cis*-isomers begin to relax thermally back to their linear *trans*-state and slowly dissolve back into the host and the system reverts to its S_A phase. If this is taken to be the explanation behind the appearance of the isotropic regions, we have still to account for the appearance of the S_C^* ordered regions in the biphasic mixture. It is noteworthy that the UV induced transition from a S_A phase to the biphasic isotropic/ S_C^* state occurs for the high N5 concentration samples held initially in the S_A phase temperatures *above* that at which even undoped SCE13 could be in its ferroelectric S_C^* phase in the absence of UV illumination. For example a UV induced S_A to biphasic $S_C^*/$ isotropic transition can be observed at 70°C for SCE13 + 20 per cent N5 (wt:wt) and at this temperature none of the mixtures of SCE13 + N5 or even pure SCE13 would exhibit a S_C^* phase (see the table) in the absence of UV light illumination. It seems likely that preferential solvation of some component of the SCE13 mixture which normally inhibits the formation of the S_C^* phase at high temperatures results under UV illumination. The UV illumination is therefore changing the phase diagram of the N5-rich regions of the sample. It is possible that there is a second mechanism at work here, namely that the two handednesses of the *trans*-N5 racemate have a different quantum efficiency for isomerization when situated in a chiral host. Upon UV illumination therefore, an excess of one N5 stereo-isomer begins to accumulate in the host, affecting its chirality, whilst the other stereo-isomer, which isomerises to the *cis*-state more readily in the chiral host, begins to phase separate into isotropic regions. This is an intriguing possibility but further work needs to be done to confirm or deny it.

When the high N5 concentration samples are held initially in their S_C^* phase and UV illuminated, a complex temporal variation of P_s is observed (see figure 11). As before, microscopy reveals that UV light eventually causes a transition to a biphasic $S_C^*/$ isotropic state in which a non-zero spontaneous polarization can be measured. This biphasic texture is believed to arise in much the same way as was discussed in the preceding paragraph, with the UV induced *cis*-isomers agglomerating to form isotropic regions. In making the transition to this biphasic state from the initial S_C^* phase however, the system passes through a stage where its P_s is zero. Following removal of the UV light, the process is reversed and before returning to its pre-illumination value, the P_s again drops to zero. Microscopy reveals that during the periods of zero P_s , no regions of isotropy are present, but the sample is 'peppered' with multicoloured birefringent regions and has essentially the same appearance as the 5 per cent N5 + SCE13 (wt:wt) samples when illuminated. We suggest therefore that these periods of zero P_s in the ≥ 10 per cent N5 + SCE13 samples correspond to times at which the N5 molecules are present as a mixed population of *cis*- and *trans*-isomers. At these times, there is not a sufficient concentration of *cis*-isomers for full agglomeration of the N5 molecules into isotropic droplets to occur, but there are sufficient numbers of *cis*-isomer molecules to cause a disruption of the ordering of the host S_C^* matrix with a consequent loss of ferroelectricity. As time proceeds the number of *cis*-isomers either increases (if the UV light is on) and this results in a transition to the biphasic state, or the *cis*-isomer population decreases (if the lamp has been turned off) as the molecules thermally relax to their *trans*-state and are able to fit more easily back into the host S_C^* matrix. Thus there appear to be two processes involved, the first being disruption of the relevant order parameter followed secondly by a phase separation on increasing the concentration of *cis*- with respect to *trans*-isomers.

5. Conclusion

We have shown that mesomorphic azo-dyes may be incorporated into the ferroelectric liquid crystal SCE13 to give stable mixtures with a slightly reduced P_s and slightly increased tilt angle θ . We have shown that by carefully choosing the initial temperature conditions and phase sequence of the liquid crystal, it is possible photomechanically to induce reversible, isothermal phase transitions from (a) a smectic phase to a second smectic phase of higher symmetry (lower order), or (b) simply to reduce the level of order of a given smectic phase, without causing a complete transition to a higher symmetry phase (as shown for instance in the reduction of S_A electroclinic switching in § 3.2). Both effects are achieved by the UV excitation of the mesomorphic azo-molecules dissolved at concentrations of < 10 per cent (wt:wt) in the host. The photomechanical reduction of a system's molecular order will result in changes in any macroscopic property we care to probe. In the above cases, we were concerned primarily with the P_s of systems which could be reversibly and isothermally reduced, to zero if required. The ability to photonically alter P_s and electro-optic switching behaviour in a reversible and isothermal manner, using commercial ferroelectric mixtures optimised for room temperature and low powered UV illumination ($\sim 1.4 \text{ mW cm}^{-2}$) has implications for the development of new optical data storage devices and photonic transducers. We are currently studying the way in which the operating speed of such devices might be controlled by optically driving the *cis*- to *trans*-back reaction using longer wavelength light.

We have also shown that besides being able to cause a reduction in the magnitude of P_s or electroclinic coefficient by reducing the order of a S_C^* or S_A phase, respectively, it is also possible, through the addition of higher concentrations of N5 (≥ 10 per cent wt:wt), to commence with the system in its S_A phase and then induce a transition to a biphasic $S_C^*/$ isotropic phase with a consequent *appearance* of P_s and optical hysteresis. If the system is held initially in the S_C^* phase, UV illumination results in a more complex temporal variation of P_s which initially falls to zero before rising to a finite value. The process is reversible upon removal of the UV light. The precise mechanism to account for the appearance of S_C^* regions in the biphasic sample and why it is that such ordering persists at temperatures at which even the pure host SCE13 would be non-ferroelectric in the absence of UV illumination, requires further clarification. It seems likely that the UV light is isothermally changing the phase diagram of the system by preferentially solvating components of the mixture. X-ray analysis, NMR and fast time-resolved spectroscopic studies to probe the composition and mechanisms of ordering of the isotropic and S_C^* ordered regions are planned.

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