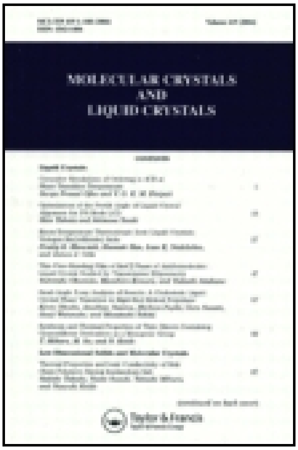

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PHOTOISOMERISING EFFECTS IN NITROAZO FERROELECTRIC DYE GUEST HOST SYSTEMS

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Photoisomerising Effects in Nitroazo Ferroelectric Dye Guest Host Systems

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The effect of a photoisomerising dye in a ferroelectric liquid crystal host has been investigated. A nitroazo dye incorporating the same three-siloxane unit as an organosiloxane ferroelectric host has been used to insure good miscibility and high dye concentrations. The effect of photoisomerisation by 300-400 nm UV of up to 430 mW.cm^{-2} has been investigated in two mixtures with 25% and 50% molar weight of dye. The 25% mixture has an I-SmC*-crystal phase sequence, while the 50% mixture has I-SmA*-SmC*-crystal. Transition temperatures of both the mixtures are reduced by increased UV illumination. For the first mixture at a constant temperature, the spontaneous polarisation in the ferroelectric phase is reduced by UV illumination. For the second mixture both the spontaneous polarisation and tilt angle of the SmC* phase are reduced by UV illumination and the phase is changed from SmC* to SmA* at temperatures close to the transition. The change of tilt angle and observations of micrograph textures indicate that this is a macroscopic change of the material rather than any phase separation of the dye and host materials.

Keywords: ferroelectric; dye guest host; photoisomerising; nitroazo

INTRODUCTION

There has been much interest in the photoisomerising effects observed in liquid crystals containing azobenzene molecules[1,2]. In this study, a ferroelectric organosiloxane host and nitroazo dye molecule with the same three siloxane unit have been investigated because their complete miscibility allows a wide range of dye concentrations[3]. The ferroelectric benzoate host[4,5] and nitroazo dyes are shown schematically in figure 1. By choosing two mixtures, at 25% and 50% molar dye concentration, we can compare and contrast the behaviour of two molecularly similar systems exhibiting an I-SmC* and an I-SmA*-SmC* phase sequence. The effect on the macroscopic ferroelectric and electroclinic properties of the mixtures will be investigated in terms of the conformational change of the nitroazo dye molecules on UV illumination.

MATERIALS

The host material is a member of a family of Low Molar Mass Organosiloxanes (LMMO). Synthesised in house, these LMMOs are based around a central siloxane core and generate highly tilted ferroelectric phases with temperature independent spontaneous polarisation and tilt angle[4,5]. The mesogens consist of a chiral moiety with a laterally substituted halogen, in this case bromine. This is hydrosilylated onto the siloxane end group by a C11 alkyl chain, see figure 1 and denoted Br11-Si3. The addition of a single nitroazo moiety to the siloxane core, as for NA11-Si3, gives photoisomerising mesogens, with an I-SmA-crystal phase sequence, mimicking the host structure.

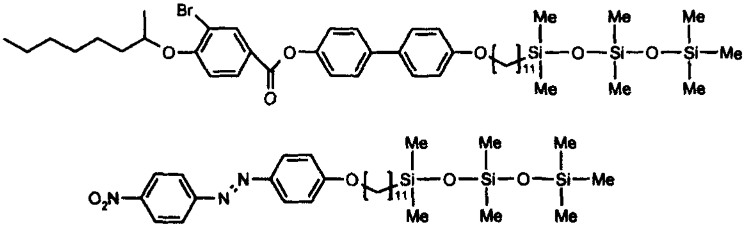

FIGURE 1 Schematic diagram of host, Br11-Si3, and dye, NA11-Si3, materials.

CHARACTERISATION

The phase sequence and transition temperatures of the mixtures were determined by optical microscopy. The spontaneous polarisation was calculated using the current pulse technique [6]. The tilt angles were determined by crossed polariser optical microscopy. The samples were analysed in 5μm cells with an anti-parallel rubbed polyimide alignment. They were aligned by cooling just below their isotropic transition and then adjusting the frequency and amplitude of the applied waveform until good alignment was achieved, then cooled into the smectic phase at rates between 0.1 and 0.5 °C per minute. The samples were illuminated by ultra violet light of 300 - 400 nm and up to 430 mW.cm^{-2} from a mercury lamp fitted to a side arm assembly of the microscope.

RESULTS

The dye is completely miscible with the host material allowing large dye concentrations. The ferroelectric SmC* behaviour is retained for dye concentrations of up to 80%, as shown in the phase diagram of figure 2. As has been reported before[3] both the spontaneous polarisation and tilt angle are reduced by increasing dye concentration, while the response time is slightly reduced by dye addition. For dye concentrations between 30% and 80% a SmA* phase is present at temperatures above that of the SmC* phase. This phase improves the alignment of the SmC* phase and shows a marked electroclinic effect. Photoisomerising effects will be investigated in two mixtures, the 25% dye concentration with the phase sequence I - 88°C -SmC* - 40° - crystal and the 50% dye concentration with the phase sequence I – 98°C - SmA* - 78°C - SmC* - 30°C - crystal.

The effect of UV illumination on the spontaneous polarisation and tilt angle of both the samples was reversible. The I–SmC* transition temperatures of the 25% dye mixture have been measured by observing the transmitted optical intensity through crossed polarisers against temperature. These transition temperatures are reduced by increased intensity of ultra violet illumination as shown in table 1. The magnitude of the spontaneous polarisation is isothermally decreased by ultra violet illumination as shown in figure 3.

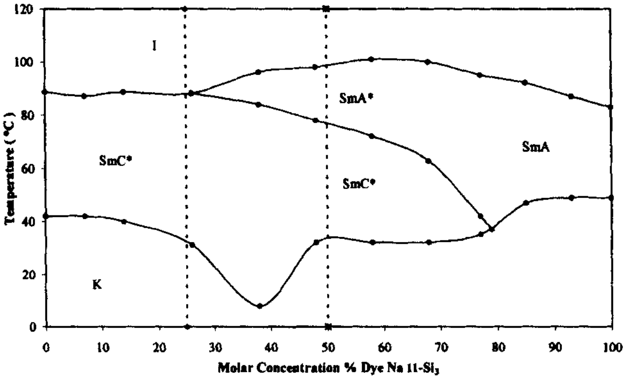

FIGURE 2 Phase diagram of NA11-Si3 dye addition against temperature

The optical micrographs shown in figure 4 show how the application of ultra violet illumination affects the focal conic texture of the material. Figure 4a shows the SmC* texture of the sample before illumination at 60°C. Figure 4b shows the same sample area illuminated by 286 $mW.cm^{-2}$of UV. The birefringence has changed and a striped texture has appeared across the focal conic fans. A greater intensity of UV illumination adds defects to the texture. For comparison, figure 4c shows the sample at 80°C without UV illumination, with an equivalent lowered value of polarisation showing a similar birefringence. This indicates that the tilt of the system is changed leading to the change of spontaneous polarisation. There is no optical evidence of any phase separation between the host and dye materials upon application of ultra violet illumination. A biphasic region only appears at lower values of polarisation corresponding to those at higher temperatures in the mixture before illumination. In both cases this is very close to the SmC* isotropic transition.

UV intensity (mWcm^{-2})	**I - SmC* transition (°C)**
0	88
72	87.5
143	86
286	84.5
430	82.5

TABLE 1 Transition temperatures of the 25% NA11-Si3 dye concentration for ultra violet illumination.

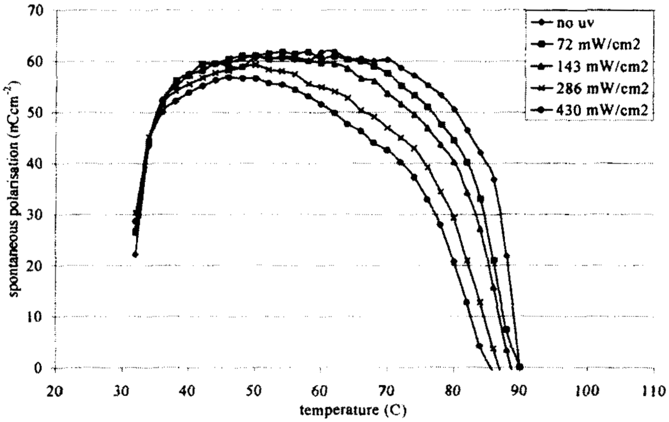

FIGURE 3 Spontaneous polarisation against temperature for the 25% NA11-Si3 mixture as it is UV illuminated.

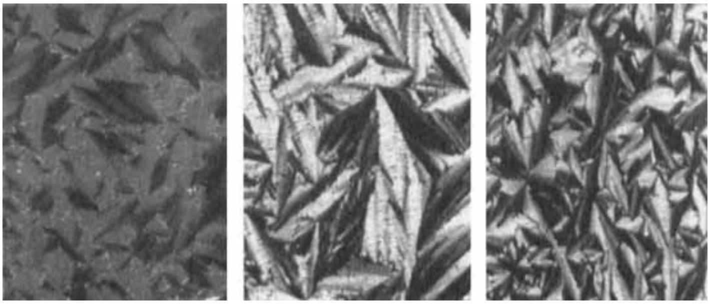

FIGURE 4 25% NA11-Si3 a) SmC* texture for no illumination at 60°C;b) 286 mW.cm^{-2} at 60°C; c) no illumination at 80°C. See Color Plate XVI at the back of this issue.

The I- SmA* and SmA*-SmC* transition temperatures of the 50% dye mixture were also measured by the change in transmitted intensity through crossed polarisers. The reduction in both these transition temperatures with ultra violet illumination is recorded in table 2.

UV intensity ($mW.cm^{-2}$)	**I-SmA* transition (°C)**	**SmA*-SmC* (°C)**
0	95.5	74
72	93.5	71
143	92	69
286	90	65
430	89	59

TABLE 2 Transition temperatures for the 50% dye mixture for UV illumination.

Both the spontaneous polarisation and tilt angle are reduced by ultra violet illumination as shown in figures 5 and 6. In order to demonstrate that the reduction in spontaneous polarisation is related to the primary order parameter, θ, and not, initially, due to microphase separation we consider the ratio of the spontaneous polarisation to the tilt. This ratio is constant for lower magnitudes of illumination as shown in figure 7. It appears to become sinusoidal with temperature for higher illuminating power densities. From the sequence of textures and optical hysteresis loops, it is clear that the material is moving from a SmC* phase to a SmA* phase and that the electro-optic switching changes from ferroelectric to electroclinic. The optical micrographs and hysteresis loops of figure 8 show the changes in the 50% mixture upon UV illumination. The material changes from the SmC* phase(figure 8a), to a SmC* phase with a striped appearance and a birefringence similar to that of the SmA* material(figures 8b and 8c). Upon further illumination this is transformed to the SmA* phase(figure 8d).

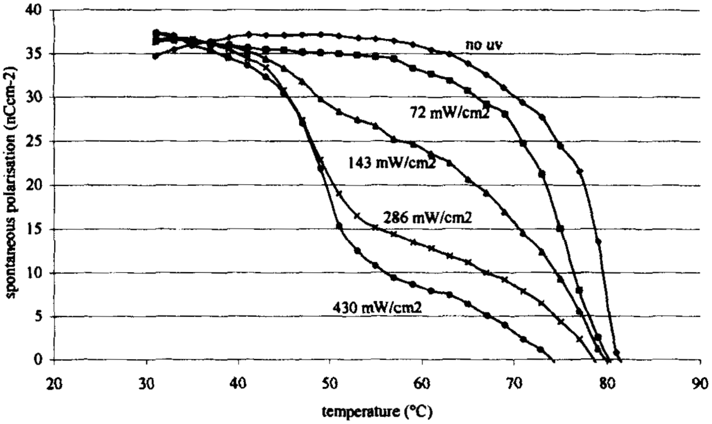

FIGURE 5 Spontaneous polarisation against temperature for the 50% mixture for a range of UV intensities.

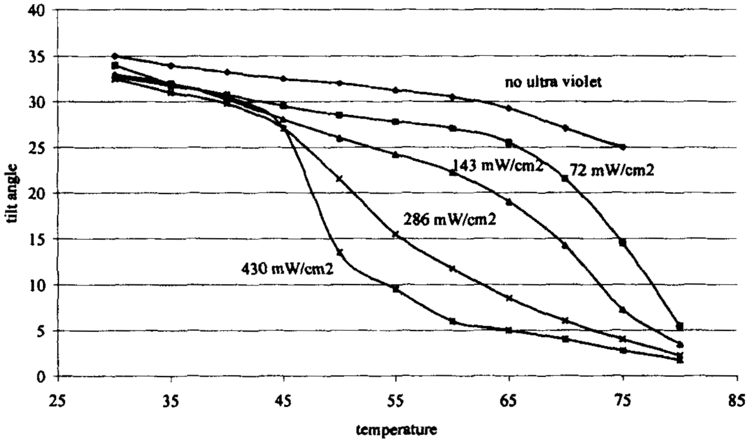

FIGURE 6 Tilt angle against temperature for the 50% mixture for a range of UV intensities.

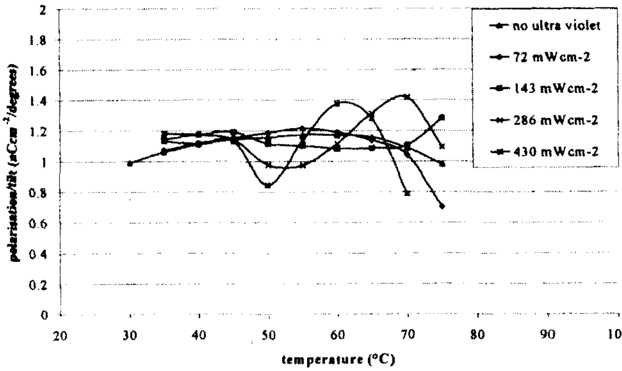

FIGURE 7 Ratio of polarisation to tilt of the 50% mixture against temperature for a range of UV intensities.

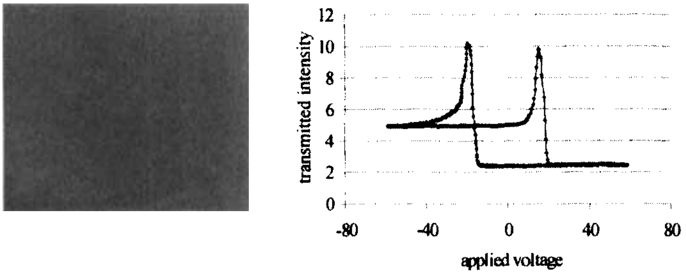

FIGURE 8a Optical texture and hysteresis loop of the 50% mixture for no illumination at 35°C
See Color Plate XVII at the back of this issue.

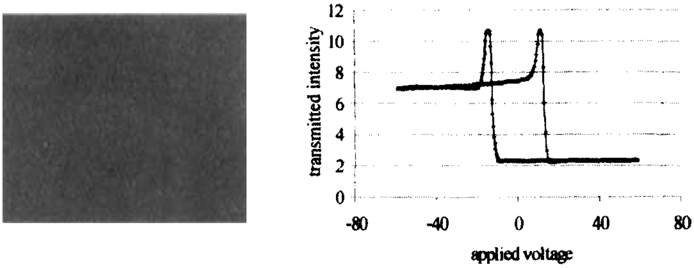

FIGURE 8b Optical texture and hysteresis loop of the 50% mixture for 72 mW.cm^{-2} illumination at 45°C
See Color Plate XVIII at the back of this issue.

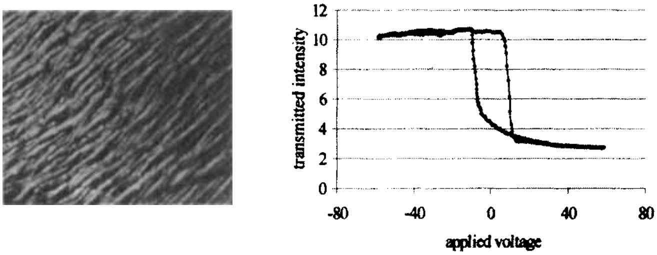

FIGURE 8c Optical texture and hysteresis loop of the 50% mixture for 286 mW.cm^{-2} illumination at 50°C.
See Color Plate XIX at the back of this issue.

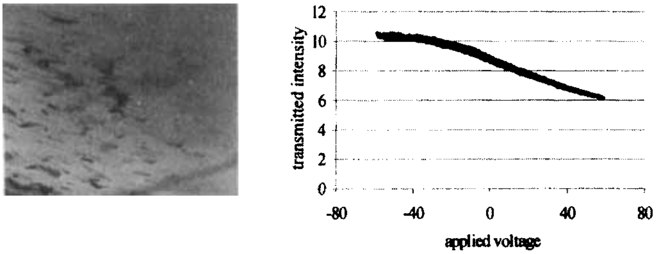

FIGURE 8d Optical texture and hysteresis loop of the 50% mixture for 286 mW.cm^{-2} illumination at 70°C
See Color Plate XX at the back of this issue.

CONCLUSION

The dye and host materials including the same three-siloxane unit were found to be completely miscible allowing a study to be made on a range of azo dye concentrations. The effect of UV illumination on the spontaneous polarisation and tilt angle of both the 25% and 50% samples was reversible but changes the of the alignment quality were observed.

The 25% dye sample had a phase sequence I-SmC*-Crystal. Illumination by UV reduced the I-SmC* transition temperature. In the ferroelectric phase the spontaneous polarisation was isothermally reduced and the optical texture was modified. These changes indicate that the steric change in the dye molecules induce a change in the bulk host material associated with the primary order parameter, θ, and not microphase separation.

The 50% dye mixture had the phase sequence I-SmA*-SmC*-crystal with decreasing temperature. Both the I-SmA* and the SmA*-SmC* transition temperatures were reduced by UV illumination. The illumination of the sample by UV isothermally reduced the magnitude of both the spontaneous polarisation and the tilt angle. The two variables are linked with respect to temperature. The microscopic textures and hysteresis loops show that illumination by UV produces a phase maintaining the ferroelectric characteristics but with a change of birefringence. These changes indicate that the change in shape of the dye molecules induces a change in the tilt, and subsequently the spontaneous polarisation and texture of the host material.

References

[1] H.G. Walton, H.J. Coles, D. Guillon, G. Poeti, *Liquid Crystals*, **17**, 333 (1994).
[2] T. Ikeda, T. Sasaki, K. Ichimura, *Nature*, **361**, 428, (1993).
[3] D.E. Shoosmith, A. Remnant, S.P. Perkins, H.J. Coles, Proc *Ferroelectrics* at press.
[4] P. Kloess, J. McComb, H.J. Coles, *Ferroelectrics*, **180**, 233, (1996).
[5] W. Robinson, C. Carboni, P. Kloess, S.P. Perkins, H.J. Coles, *Liquid Crystals*, **25(3)**, 301–307 (1998).
[6] K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, E. Kuze, *Japn J. appl Phys*, **22** L661 (1983).