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Electric Field Effects and Two Frequency Colour Switching in the Cholesteric and Blue Phases of Nematic/Cholesteric Mixtures

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Colour switching has been studied in the blue phases of a chiral nematic system as a function of the voltage and frequency of an applied electric field. In the BPI two effects were observed. Above a critical frequency, small wavelength shifts ($\sim 50\text{nm}$) were observed whilst, below this frequency, a cholesteric fan structure was induced. This fan texture was stored on removal of the field and reapplication of an a.c. signal induced a change in the reflected colour from blue to red. In the BPII, a voltage dependent critical frequency was also observed. Above this frequency, the selectively reflected colour could be switched reversibly from orange to blue or green in a time faster than 40 ms. Below the critical frequency, a turbulent scattering texture was induced and this provided an erasure mechanism for the colour switch.

INTRODUCTION

Cholesteric liquid crystals have excited considerable interest as thermometry devices over the last two decades or so because of their temperature dependent wavelength selective reflection of circularly polarised light. It has been shown recently¹ that electric fields applied across such cholesteric materials may also change the wavelength of the selective reflection of a sample held at constant temperature. This suggests a new domain of colour switching devices. The main drawback to such cholesteric phase electric field switching appears to be in the small wavelength shifts (10-20 nm) and the slow relaxation

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times reported. If, however, electric fields are applied in the so called 'blue phases' exhibited by some cholesteric liquid crystals, then it would appear that much larger wavelength changes ($\sim 100\text{--}200\text{nm}$) can be recorded.²⁻⁴

The cholesteric blue phases, reviewed recently,⁵ appear to be due to pretransitional phenomena in between the isotropic and cholesteric phases. Generally such phases, which occur just below the clearing temperature, are known as BPI, BPII, etc. (in order of their appearance with increasing temperature). These blue phases tend to be exhibited by cholesteric materials having a short pitch and they have all the usual cholesteric phase reflection properties (i.e. strong optical rotation and Bragg like scattering of circularly polarised light) over a limited temperature range ($1\text{--}2^\circ\text{C}$) before the cholesteric phase itself is manifest.⁶ Macroscopically the blue phase is isotropic and its structure, although not clearly understood, is thought to have cubic symmetry.⁵⁻⁷ In the previously published research²⁻⁴ aimed at a better understanding of this structure, it has been shown that electric fields may (i) induce a phase transition from the blue phase to either a cholesteric phase or to an unwound cholesteric-nematic state and (ii) vary the wavelength of the reflection as a function of applied voltage.

In the current work, carried out as part of a programme on the influence of external fields on cholesteric phases, we have examined the influence of electric fields in the blue phases of chiral nematic materials. For the materials used we have (i) demonstrated colour switching within the field induced cholesteric structure in BPI, (ii) observed a two frequency colour switching effect in BPII, and (iii) shown that the colour changes are rapid (less than 40ms). For the two frequency case it has been shown that the colours may be switched reversibly from orange to blue, or orange to green, or removed using field induced turbulence.

EXPERIMENTAL

A number of cholesteric systems were studied using mixtures of the chiral nematics, TM74A (8.2%), TM74B (8.2%), TM75A (41.8%), TM75B (41.8%), and the eutectic nematic E49. These materials were supplied by BDH (Ltd) and the percentage numbers refer to the weight concentrations of the TM compounds used to prepare a stock twisting agent denoted TS hereafter. When added to TS, the maximum weight concentration of E49 used was 40% g/g (the nomencla-

ture for these materials is that used in the BDH literature). The optical properties of the mesomorphic mixtures were studied using glass cells with In/SnO₂ transparent electrodes and a rubbed polyvinyl alcohol (PVA) alignment layer. Fields were applied across the cell (i.e. in the viewing direction) and the cell thickness was $23(\pm 2)\mu\text{m}$. The cells were constructed so that they could be observed either using the microscope or the uv/visible spectrometer.

A schematic of the apparatus is given in Figure 1. The photo microscopy part of the apparatus was based on an Olympus BH2 polarising microscope which allowed observation of the blue phase both in reflection and transmission. Photographs were taken using an Olympus OM1 camera. This could be replaced with a video camera and recorder thus enabling the switching effects observed in the blue phase to be measured to within a frame time, i.e. 40ms. A Mettler FP82 hotstage and controller were used in the determination of the phase transitions of the samples, as well as to maintain the samples at specific temperatures in the blue phase.

A.C. fields of up to 300V rms at frequencies between 5Hz and 5kHz were applied to the samples. The a.c. signal, derived from a Linstead low voltage signal generator, was amplified and then monitored using an oscilloscope and voltmeter. In this way the rms value of the applied voltage could be determined and the signal checked for distortion while the a.c. field was applied to the sample. Relays were included in the circuit to ensure bounce-free switching and thus avoiding the possibility of high voltage transients which might otherwise lead to spurious colour switching. As well as the direct visual observation and recording of field induced changes the absorption spectra were obtained using an adapted Pye-Unicorn SP 8000 uv/visible recording spectrometer. A specially constructed cell assembly allowed fields to be applied, during measurement of the spectra, at the required constant temperature.

RESULTS AND DISCUSSION

The phase transitions were determined for each of the mixtures using the polarising microscope and hotstage. Figure 2(a) shows the variation of transition temperature with respect to weight percentage of E49 in the mixture (TS + E49) on heating the sample at 1°C/min. Figure 2(b) similarly shows the transition temperatures on cooling at 1°C/min. None of the mixtures containing more than 14% of E49 exhibited a blue phase.

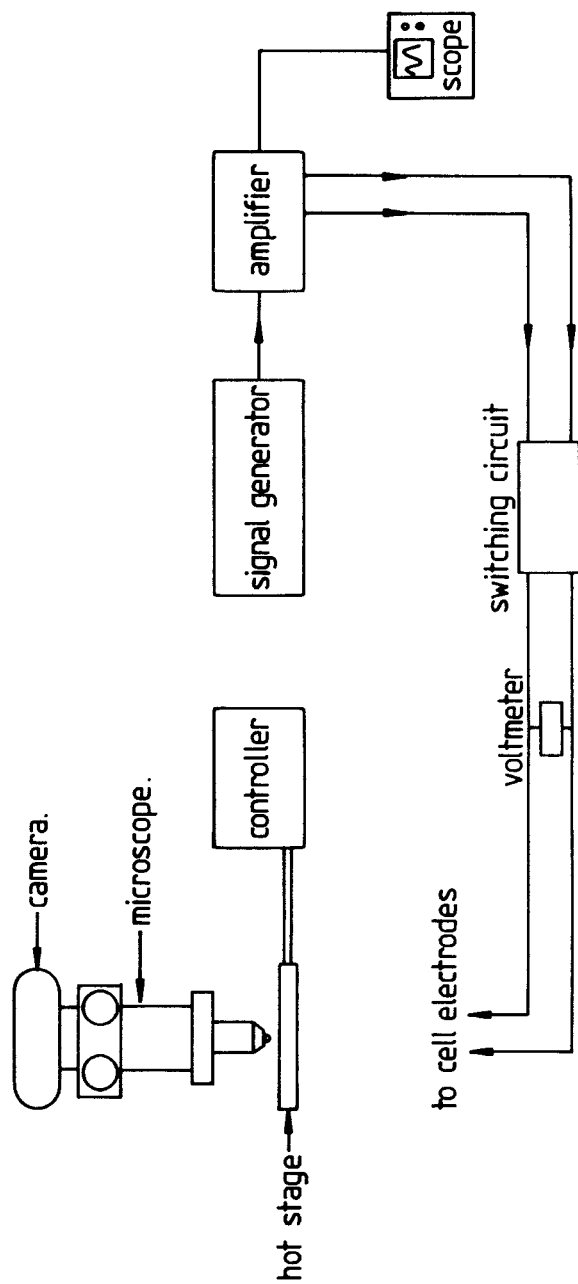


FIGURE 1 Schematic of the experimental arrangement.

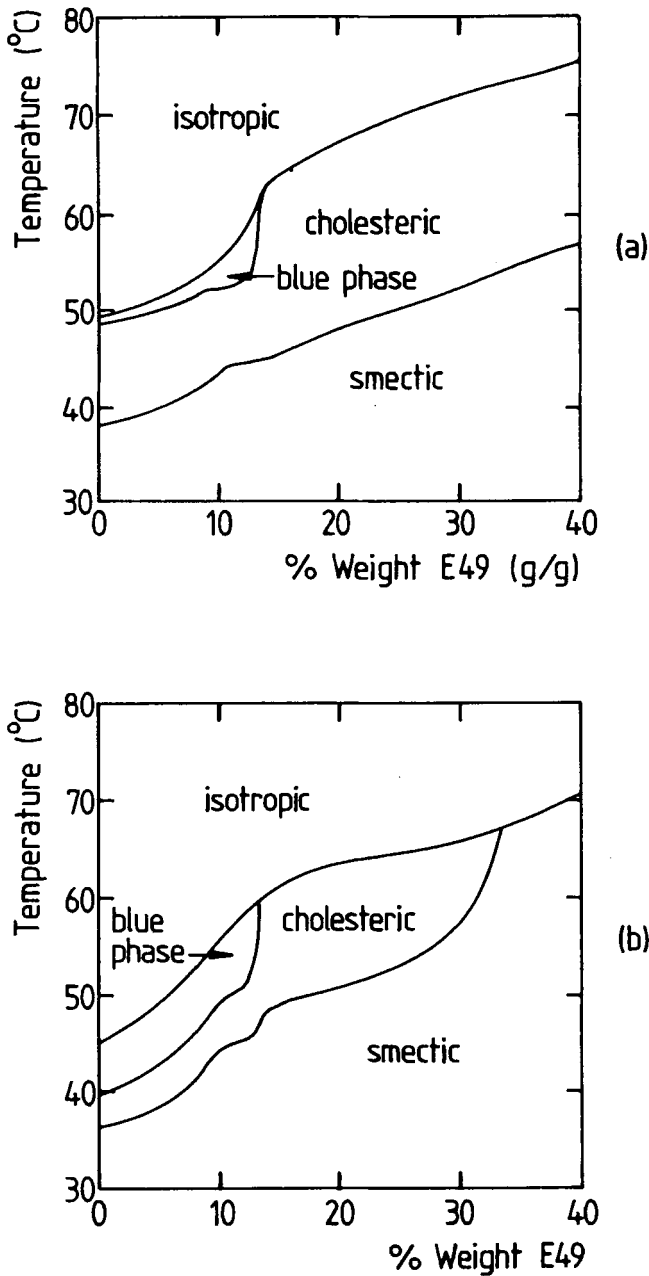
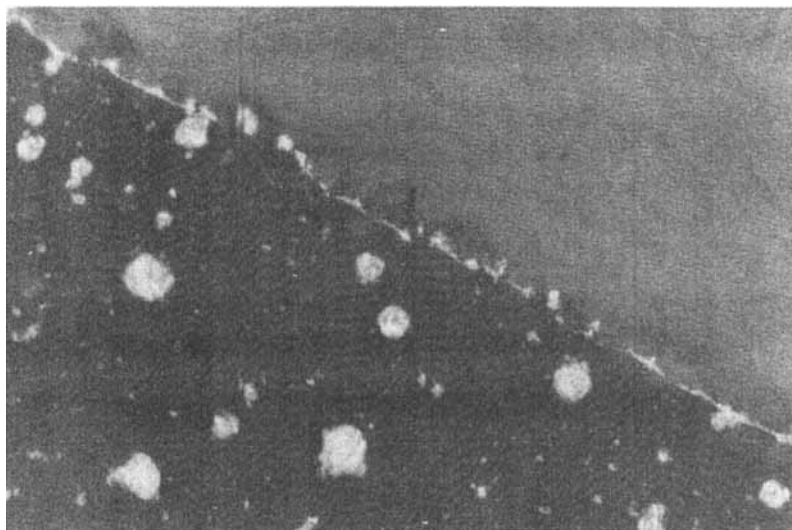


FIGURE 2 Phase transitions of the E49/TS mixtures as determined by optical microscopy on (a) *heating* at 1°C/min and (b) *cooling* at 1°C/min. The ordinate refers to the weight percentage of E49 in the total mixture E49 + TS.

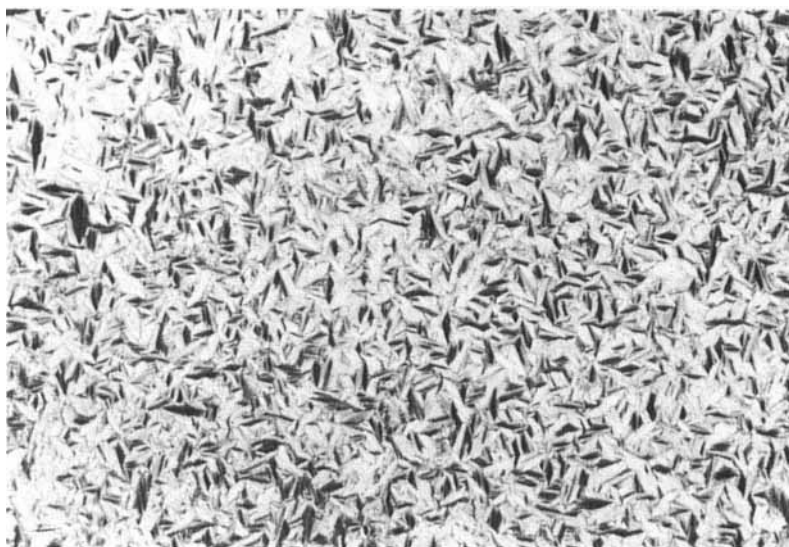
Each of the samples which showed a blue phase was heated, firstly into BPI and subsequently into BPII. Electric fields were applied in each blue phase and various optical switching effects were observed as described below. Similar switching effects were seen in each sample, but with some changes in the voltage and frequency at which they occurred depending on the sample composition. All of the figures given below are for a chiral nematic mixture containing 7.25% by weight of E49.

In the BPI, application of an electric field had one of two effects, depending on the frequency and rms voltage of the applied field. At voltages below $\sim 100\text{V}$ rms, a small wavelength shift ($\sim < 50\text{nm}$) was observed. This was the only change seen in BPI at lower voltages, and was reversible. A small wavelength shift was also induced at higher voltages, provided the frequency of the applied field was above a threshold value. This was 50Hz at 100V and increased with increasing voltage. Below this threshold frequency, a cholesteric fan struc-



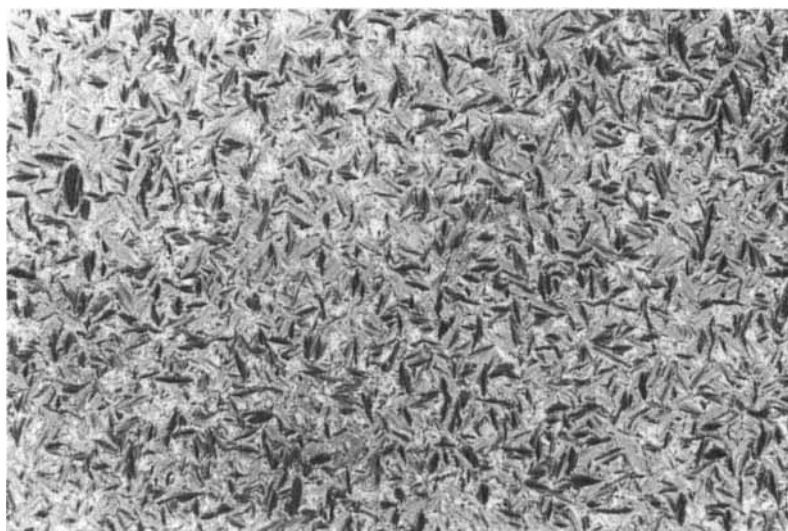
a

FIGURE 3 (a) Texture formed in BPI for an applied voltage of 100V rms at 50Hz . The electrode runs diagonally across the figure and the field was applied across the lower left-hand area. The large light regions show nucleation growth of a cholesteric fan texture as the field is applied. (b) This figure shows the induced cholesteric fan texture after the field has been applied for 5 seconds or more and then removed. In figure (c) a 50V rms 500Hz a.c. signal has been applied across the cell to induce a colour switch in the stored cholesteric fan texture. All figures were taken on reflection at $125\times$ magnification; figures (b) and (c) show only the electrode area. See Color Plate XXXI, in this issue.



b

See Color Plate XXXII , in this issue.



c

FIGURE 3 Continued. See Color Plate XXXIII, in this issue.

ture was induced. The fan texture was formed first of all as cholesteric nuclei as shown in figure 3(a). If the a.c. field was left on for several seconds, the fan structure extended to cover the whole electrode area. The extended cholesteric fan structure is shown in figure 3(b); note that the electrode edge no longer appears in the photograph but that

this nucleation and growth effect occurs only in the electrode area. The fan texture was stored on removing the field, the storage occurring irrespective of how much of the electrode area had been affected at the time of the removal of the field. Once the cholesteric phase had been induced, colour switching within the texture was possible with smaller voltages. Figure 3(c) shows a switch from blue to red on application of 50V rms at 500Hz.

In the BPII a number of switching effects were observed depending on the voltage and frequency of the applied a.c. signal. For a given voltage a critical frequency was determined below which a scattering turbulent texture was induced and above which colour switching was achieved, Figure 4. At voltages lower than 100V rms, observation of a colour switching effect was difficult due to the small wavelength changes although these could be determined using the spectrometer (see below). However, under these voltage conditions, the switch with frequency from a coloured reflecting to a turbulent scattering texture was readily observed. Above 100V rms and the critical frequency, for that voltage, a marked change in the reflected colour of

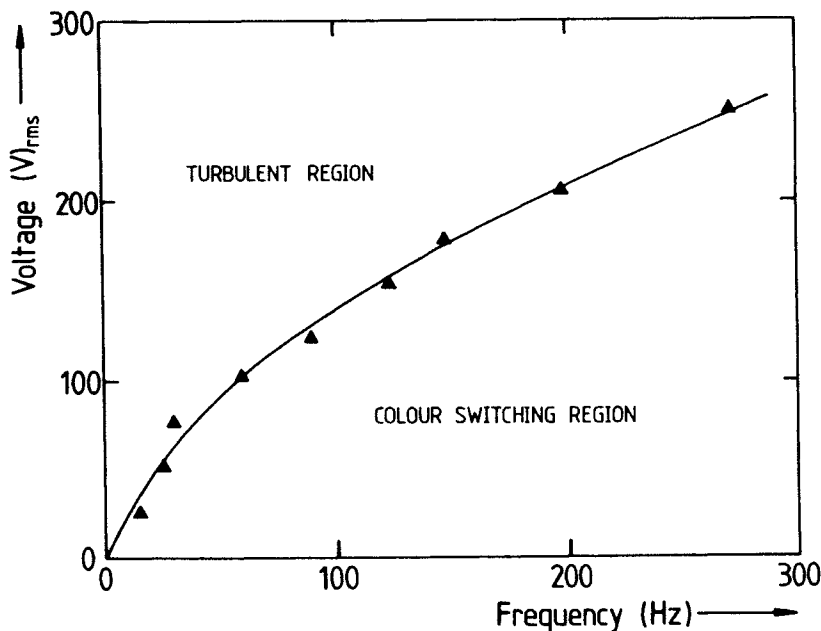
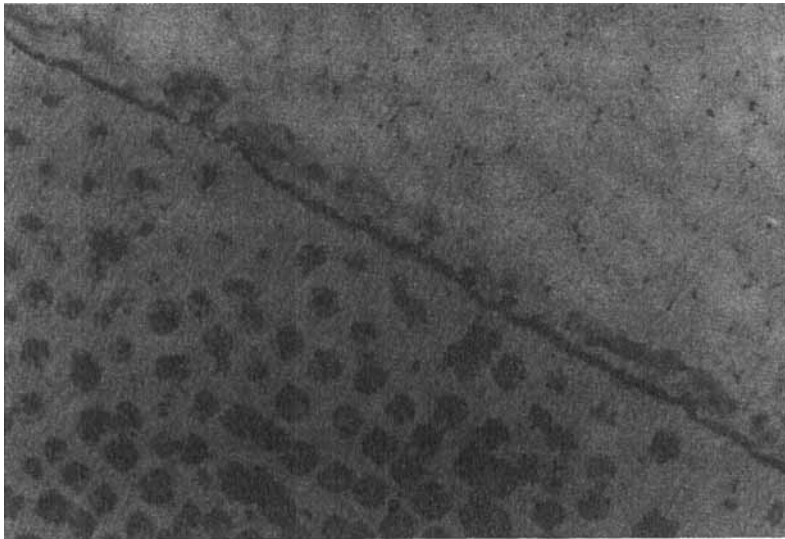


FIGURE 4. Dependence of the onset of turbulence in BPII on applied voltage and frequency for the sample containing 7.25% of E49 (by weight) and at a temperature of 51.7°C.

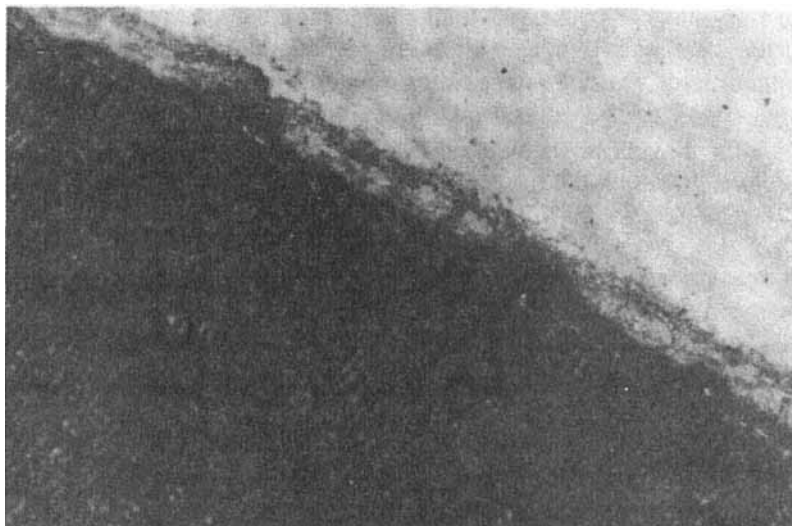
the blue phase was observed. This change in reflection then depended on the starting colour as well as the voltage and frequency of the applied field. The following plates refer to the textures observed in reflection using the optical microscope under weak magnification.

Figure 5(a) shows the effect of applying 140V at 500Hz to the BP11, switching the colour from blue/green, as seen in the upper right hand half of the photograph, to green in the electrode area. The electrode edge runs diagonally across the photograph. The frequency of the electric field was changed to 50Hz without removal of the field. This induced turbulence in the electrode area, as seen in figure 5(b). The frequency was then changed back to 500Hz, again while maintaining the same rms field, causing the electrode area to become bright orange, as shown in figure 5(c). Switching the field off from 140V and 500Hz resulted in the appearance shown in figure 5(d). The blue/



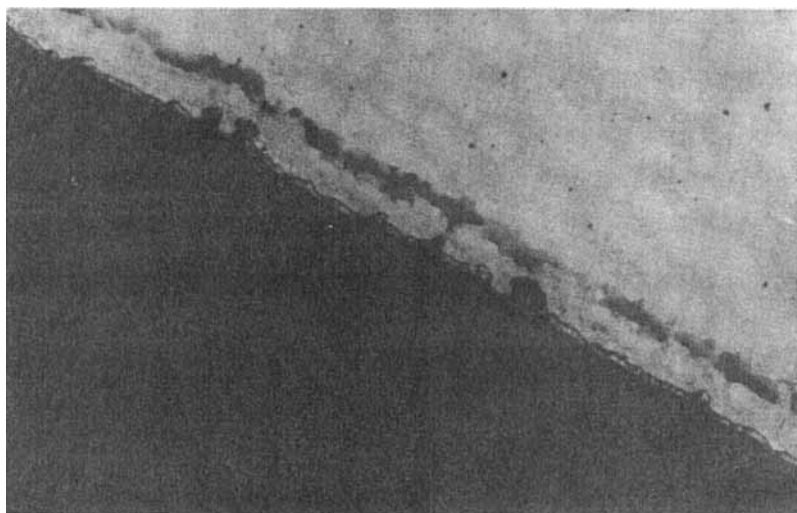
a

FIGURE 5 These figures show the effects of switching the frequency of the applied constant field (140V rms) in BP11 (a) The field free region showing the blue/green blue phase is in the top right-hand corner of the figure. The bottom left-hand corner of the figure shows the switching effect induced at 500Hz. Figure 5(b) shows the turbulent texture induced by a 50Hz signal and figure 5(c) shows the bright orange texture induced on increasing the frequency to 500Hz. Removal of the 500Hz signal results in a slowly decaying coloured texture. This is shown in figure 5(d) where the green texture can be seen in the electrode area at the top left-hand corner. Figure 5(e) shows the effect of removing the 140V 50Hz signal, i.e. switching off the turbulent texture. The electrode area appears faintly green and returns to the original blue/green BP11 texture after about 10 minutes. All photos were taken on reflection at 125x magnification. See Color Plate XXXIV, in this issue.



b

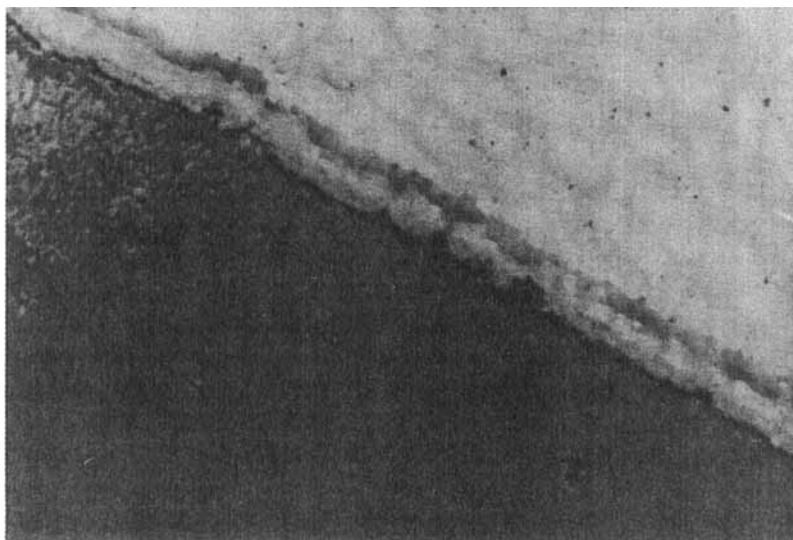
FIGURE 5 Continued. See Color Plate XXXV in this issue.



c

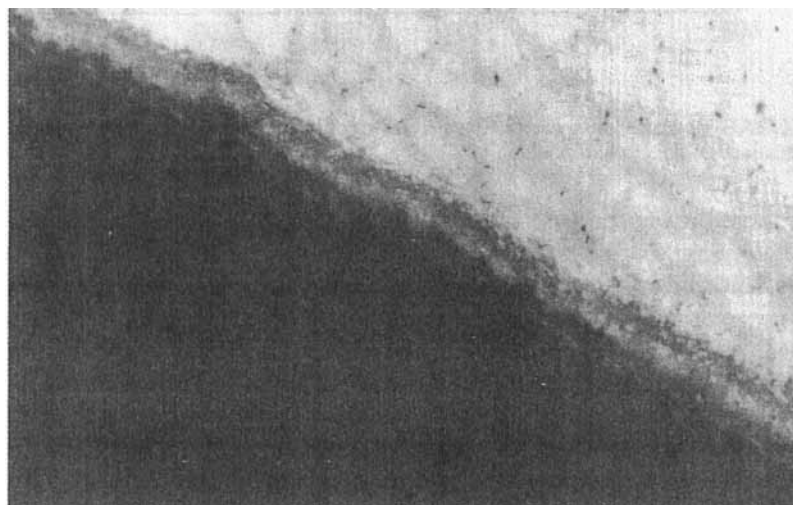
FIGURE 5 Continued. See Color Plate XXXVI, in this issue.

green colour of the original blue phase can be seen returning to the electrode area in the top left-hand corner. After 10 minutes, the whole electrode area had regained its original appearance. If the field was turned off from the turbulent state, the blue phase returned immediately to its original colour, but at a much reduced intensity, as seen



d

FIGURE 5 Continued. See Color Plate XXXVII, in this issue.



e

FIGURE 5 Continued. See Color Plate XXXVIII, in this issue.

in figure 5(e). Again, the blue phase returned to its original appearance after 10 minutes.

In the above mechanism the striking colour changes are observed by changing the frequency of the applied field and using a turbulent texture to erase between colours. These changes are then readily

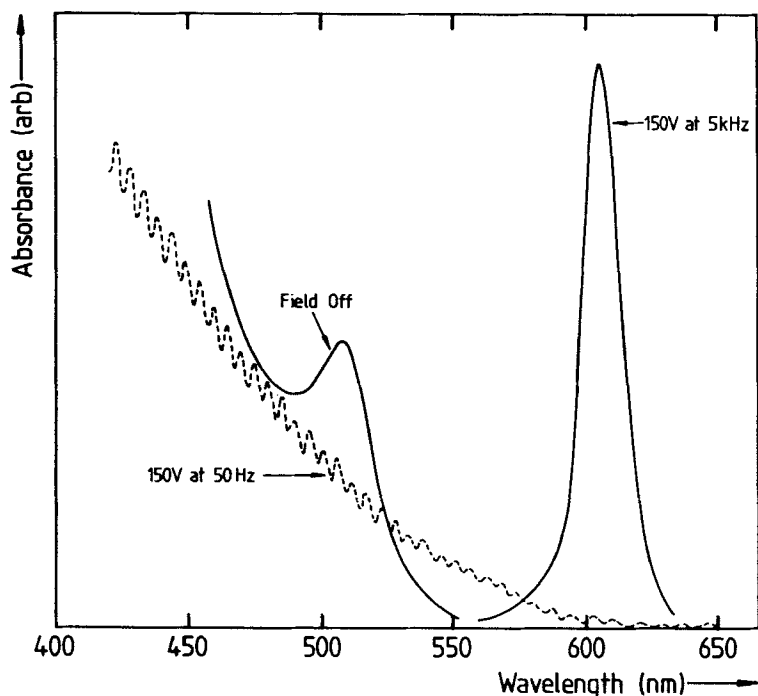


FIGURE 6 Absorption spectra for a green reflecting blue phase as a function of the frequency of the applied field.

observed using the optical microscope. The absorption spectra corresponding to these large wavelength shifts were also obtained, using the recording spectrometer. Figure 6 shows the absorption spectra for a green reflecting blue phase, and the effect of applying 150V rms at different frequencies. When the field was applied at 5kHz, the peak in the green spectral region (at $\sim 510\text{nm}$) was shifted to the orange-red region (at $\sim 600\text{nm}$). Decreasing the frequency to 50Hz induced a turbulent texture, and then changing the frequency to 5kHz caused the absorption peak to return to $\sim 600\text{nm}$. Subtle wavelength shifts with changing voltage or frequency are not easily observed using the microscope and so further high precision measurements were carried out using a sensitive uv/visible spectrometer.

The effects of changing the applied voltage at constant a.c. frequency are illustrated by Figure 7. In these measurements the absorption spectra in transmission are equivalent to the reflection spectra observed using the microscope. The wavelength changes observed were obtained without using the turbulence erasure mechanism and

were completely repeatable and reversible, i.e. removal of the field resulted in the original absorption spectrum being attained. Maintaining the sample in the blue phase (BPII) and changing the applied voltage from zero to 200V rms, allowed a shift of $\sim 50\text{nm}$ in the position of the absorption peak to be achieved. Similar voltage switching effects in a different blue phase mixture have been observed by Heppke et al.⁴ In principle larger wavelength shifts could be obtained using a higher rms voltage as the wavelength shift is *approximately* proportional to V^2 rms, Figure 8. Unfortunately, the voltage may not be increased indefinitely as either the turbulence threshold will be reached or the high voltage will cause dielectric breakdown of the cell. However, using the frequency-colour switching mechanism described above, this would not appear to be a problem. The only limitation is that a frequency above $\sim 10\text{kHz}$ would probably cause dielectric heating. Optical switching in this red reflecting blue phase would appear to be limited to wavelength shifts of the order of 50nm . It is also interesting to note that for this red reflecting blue phase neither the lineshape of the absorption spectrum nor its peak absorption intensity appear to be altered significantly by the application of the a.c. voltages.

All of the switching effects observed were also recorded on video film and, by playing this back one frame at a time, an upper limit of 40ms could be placed on the switching times. However, this method of timing any induced changes has some limitations. There was no way to determine the reflected wavelength before and after switching while simultaneously recording the effect. Therefore, although it was apparent that the majority of the wavelength shift occurred in $<40\text{ms}$ as this could readily be seen by eye, the complete wavelength shift took a few minutes to become established. It is noteworthy that the gradual shift only corresponds to $\sim 5\text{nm}$ of the total. Therefore, this slow effect is of no consequence in the colour switching. All texture changes, from a reflecting BP to scattering turbulence, and colour switching within an induced cholesteric fan structure, occur faster than 40ms .

CONCLUSIONS

The experimental results show that a number of colour switching effects may be induced in the blue phase by application of an electric field. These colour switching effects are both voltage and frequency dependent for Blue Phase I and Blue Phase II.

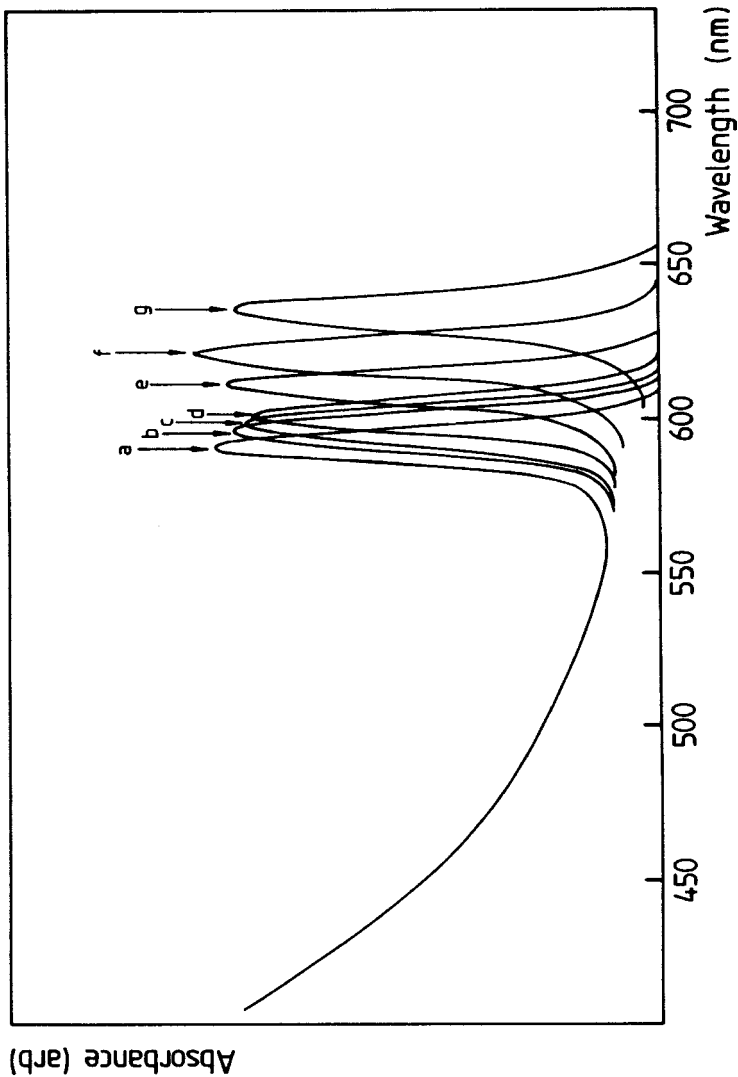


FIGURE 7 Absorption spectra obtained in BPII as a function of the applied rms voltage at a constant frequency of 500Hz. The peaks a to g correspond to 0, 80, 95, 110, 145, 166 and 193V rms respectively.

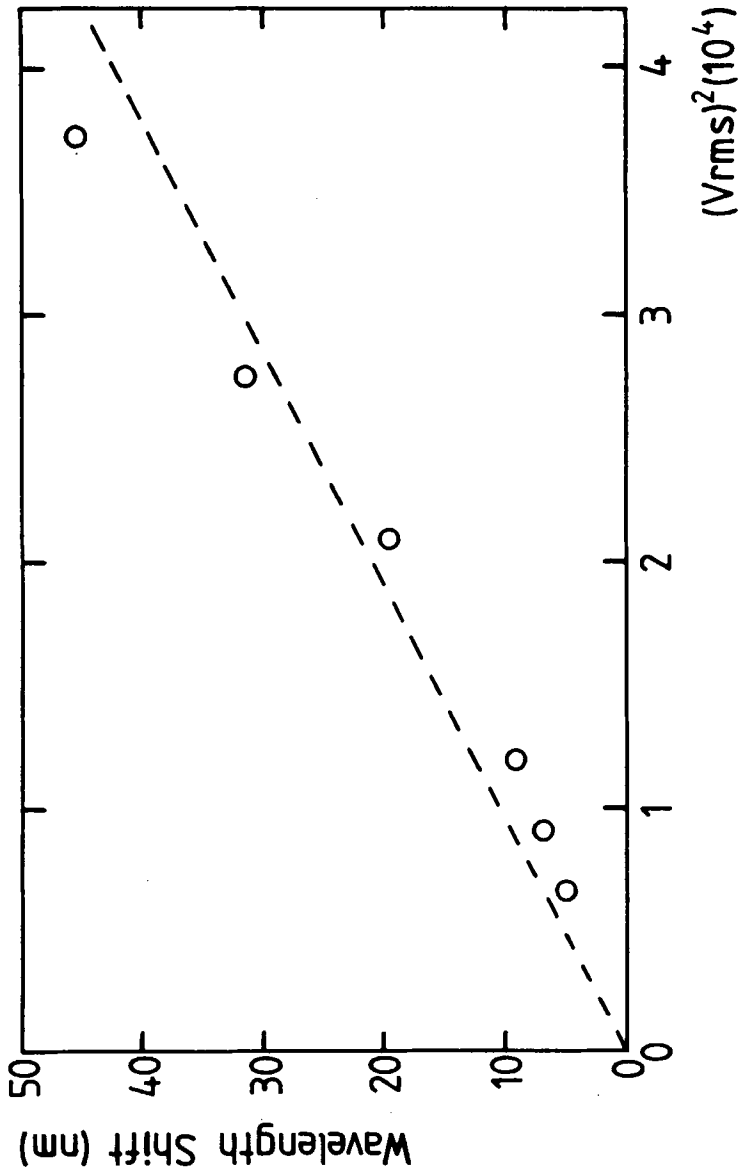


FIGURE 8 The dependence of wavelength shift on $(V_{rms})^2$ —the data refer to figure 5.

In BPI a critical frequency is observed above which small changes ($\sim 50\text{nm}$) in the peak reflectance wavelength are induced by the applied field. Below this frequency a cholesteric fan texture was induced. This texture was stored on removal of the field. Reapplication of a low voltage a.c. signal above the critical frequency induced a change in the selectively reflected colour from blue to red.

In BPII a further critical frequency was observed below which, for a fixed voltage, a turbulent scattering texture was induced. Above this frequency a fast (less than 40ms) and reversible colour switch from blue or green to orange was observed. This colour, which otherwise decays on the minutes time scale, may be removed using the turbulence mechanism. Thus, a controlled sequence of colours may be induced or erased at a constant voltage merely by switching the frequency of the applied field. Whilst the most useful switching effects were observed by changing the frequency of the applied field, the changes in the selective colour reflection could also be induced by varying the applied voltage. The reflected colours in the blue phase are very intense. However, such phases are normally only observed over a narrow temperature range and this limits their use in practical devices. In the current work we have used a eutectic nematic mixture, E49, as a host to the chiral additives. Such a eutectic appears to exhibit a broad biphasic region and this also appears to have broadened the temperature range of the blue phase to about 5°C . We are currently examining this effect for a number of different eutectic nematics and the results of this will be reported at a later date.

Acknowledgments

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