This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

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

Dye guest-host effects in ferroelectric liquid crystals

H. J. Coles[a]; H. F. Gleeson[a]; J. S. Kang[a]
[a] Liquid Crystal Group, Physics Department, The University, Manchester, England

To cite this Article Coles, H. J. , Gleeson, H. F. and Kang, J. S.(1989) 'Dye guest-host effects in ferroelectric liquid crystals', Liquid Crystals, 5: 4, 1243 — 1252
To link to this Article: DOI: 10.1080/02678298908026430
URL: http://dx.doi.org/10.1080/02678298908026430

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1989, VOL. 5, NO. 4, 1243–1252

Dye guest–host effects in ferroelectric liquid crystals

by H. J. COLES, H. F. GLEESON and J. S. KANG
Liquid Crystal Group, Physics Department, The University,
Manchester M13 9PL, England

Here we present the optic and electro-optic characteristics of ferroelectric dye guest–host devices incorporating different dye and S_C^* host materials. We demonstrate fast response time ($< 100\,\mu s$) single polarizer and zero-polarizer device configurations for high order parameter dichroic dyes and single polarizer fluorescent dye devices. The dynamic data include measurements of response times as functions of voltage, temperature and dye concentration, from which we conclude that the inclusion of certain dyes does not adversely affect the ferroelectric phase. The contrast ratios of these novel guest–host devices are also presented and are shown, as expected, to be functions of tilt angle (and therefore temperature). However, we demonstrate that the high tilt angle of 45° is not necessary for high contrast devices, and in fact for certain devices configurations $\theta = 22\frac{1}{2}°$ is optimum. These results are discussed.

1. Introduction

Since the concept of ferroelectric liquid crystal displays was first introduced by Meyer *et al.* [1] and demonstrated by Clark and Lagerwall [2], there has been a considerable investment of research and development resources aimed at producing commercially viable complex ferroelectric devices. Much of this effort has been extremely fruitful; wide range ferroelectric liquid crystals are now commercially available [3], surface [4] and A.C. stabilized [5] alignment techniques have overcome many of the original difficulties experienced in producing good surface alignment and bistability, and novel electrical addressing schemes for displays have been developed [6]. The major remaining obstacle preventing large scale production of ferroelectric devices is fabrication of the devices themselves. The optical properties of ferroelectric materials used in a birefringence device constrain the device thickness to be typically $2\,\mu m$. This has been achieved over relatively small areas (3 cm × 3 cm), but severe difficulties are experienced in scaling up to A4 size (210 mm × 297 mm) or larger area displays. In addition the viewing angle characteristics of the birefringence displays are poor, as different birefringence colours are observed at different angles.

The possibility of relieving some of these device fabrication constraints and improving the optical performance of ferroelectric liquid crystal devices led us [7, 8] and others [9] to examine the dyed guest–host ferroelectric (DGHFE) device. The use of a dye dissolved in a ferroelectric host offers, in principle, a device which does not suffer the thickness constraints or poor viewing angle characteristics of the birefringence device. However, it is important to examine the effect that the addition of a dye has on the other device parameters (response time (τ_R), tilt angle (θ), spontaneous polarization (P_S), and phase range) in parallel with the optical properties. In this paper we describe single polarizer DGHFE devices using a black dye and two commercially available ferroelectric hosts. We consider the performance of the devices in terms of the relevant parameters (τ_R, θ, etc.) and compare the influence of

0267-8292/89 $3.00

the dye on the properties of the two different host materials. We also describe, briefly, two other device geometries, a zero polarizer and fluorescent DGHFE device, and consider their potential for use as commercial displays.

2. Single polarizer dichroic DGHFE device

2.1. *Materials*

Two commercially available ferroelectric materials, SCE4 and SCE6, supplied by B.D.H. Chemicals Ltd [3] were used as hosts for the black dichroic dye, S304, provided by Mitsui Toatsu Chemical Inc. The dye was dissolved in SCE4 and SCE6 in concentrations of up to 4 and 2 wt %, respectively. The dye proved to be less soluble in SCE6, and at concentrations greater than 2 per cent crystallized out of solution. Addition of the dye lowered the $S_C^* \rightarrow S_A$ transition temperatures to different extents in each of the hosts. The effect was least marked in SCE6 where the transition temperature was depressed by only 3°C in the 2 per cent solution; the 2 and 4 per cent SCE4 solutions suffered 7 and 13°C reductions, respectively.

Test cells of thickness 5 and 14 μm were used to determine the device characteristics of the guest–host materials. The transparent indium–tin oxide (ITO) electrodes were coated with a rubbed polyimide alignment layer. The rubbing directions on the upper and lower surfaces were antiparallel in the assembled device. Both SCE4 and SCE6 have the phase sequence $S_C^* \rightarrow S_A \rightarrow N^* \rightarrow I$, and the helical pitch is compensated above the $S_A \rightarrow N^*$ transition. The pitch compensation was unaffected by the addition of small quantities of the dye, and planar alignment in the S_C^* phase was achieved by heating the devices into the N* phase regime and slowly cooling through the S_A to the S_C^* phase.

2.2. *Device operation*

The operation of the single polarizer DGHFE device relies on the cooperative orientation of the dichroic dye by the ferroelectric hosts. If a polarizer is aligned at an angle ϕ with respect to the dye absorption moment (see figure 1), the intensity of transmitted light, I_T, relative to some initial intensity, I_0, is [8]

$$\frac{I_T}{I_0} = 10^{-A_\parallel}\cos^2\phi + 10^{-A_\perp}\sin^2\phi + 10^{-(A_\parallel+A_\perp)/2}\sin 2\phi.$$

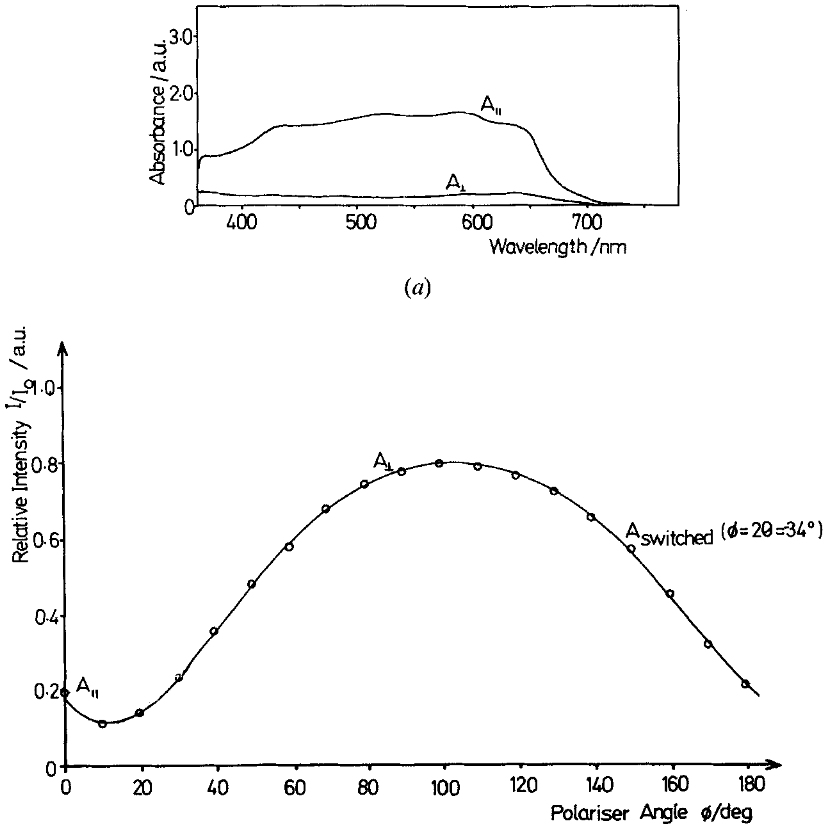
Here $A_\parallel$ and $A_\perp$ are the absorbances of the device parallel and perpendicular to the dye absorption moment. For a dye dissolved in a ferroelectric host in a single polarizer device, the orientation is rotated through twice the tilt angle (2θ) of the guest–host material on changing from one switched state to the other. If the polarizer is aligned with the dye direction to give maximum absorption (dark state), the switched state ($\phi = 2\theta$) is then lighter. For maximum contrast a tilt angle of 45° is required. However, relatively few ferroelectric host materials exist with such high tilt angles, so it is important to realize that a 10–90 per cent change in intensity may be achieved

Figure 1. The definition of the polarizer angle, ϕ, with respect to the parallel and perpendicular absorbances of the dye molecule.

with a tilt angle of only 27°. This observation indicates that commercially available ferroelectric liquid crystals with tilt angles of typically 22–25° may indeed be useful host materials; this is confirmed by the following experimental results.

2.3. *Absorption spectra and order parameters*

The absorption spectra measured in a dual beam spectrophotometer for the 2 per cent solution of S304 in SCE4 in a 14 μm thick device at 30°C are shown in figure 2 (*a*). The figure includes the spectrum determined with the dye absorption direction parallel to the polarization direction (off-state) and the perpendicular orientation ($\phi = 90°$). Figure 2 (*b*) shows the change in relative intensity transmitted by the SCE4–2 per cent S304 guest-host cell with respect to the polarizer angle, ϕ. The positions corresponding to $A_{\parallel}$, $A_{\perp}$ and A_{switched} are marked on the figure. It can be seen that there is a distinct change in transmitted light intensity between the off (dark) and on (bright) states, confirming that the dye has been cooperatively oriented by the ferroelectric host. The contrast ratio of the actual device is about 3 : 1 compared with an optimum possible value of 8 : 1 for S304 in SCE4, although it should be noted that the device contrast ratio may be varied by suitable orientation of the polarizer with respect to the device. The same dye in SCE6 also has a contrast ratio of about 3 : 1.



(*a*)

(*b*)

Figure 2. (*a*) The absorption spectra of 2 per cent S304 in SCE4 corresponding to $A_{\parallel}$ and $A_{\perp}$. (*b*) Variation in the relative transmitted light intensity at 589·6 nm for the 14 μm thick 2 per cent S304–SCE4 DGHFE cell.

Both of these values are lower than the contrast ratio of 15 : 1 determined for the Mitsui Toatsu dye M483 in SCE6 reported previously [8].

The order parameter of the dye in each host was determined from the absorption spectra via

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}.$$

Preliminary measurements recorded dye order parameters of 0·75 at 30°C for the 2 per cent solutions of S304 in SCE4 and SCE6; this is higher than that measured for the single component blue azo dye, M483, in SCE6 (0·56) [8]. The dye order parameter decreased to 0·57 at the maximum concentration of 4 per cent, in contrast with our previous measurements [8], and nematic guest–host systems [10] where no concentration dependence of the order parameter was observed. Because the previously reported dye, M483, had a significantly higher contrast ratio, but lower order parameter than 2 per cent S304 in SCE6, we observe that a high dye order parameter does not necessarily indicate a high contrast ratio. Further, appropriate selection of the dichroic dye and ferroelectric host may have a greater influence on the contrast ratio of the device than an increase in tilt angle to an optimum 45°. However, in a thorough comparison of the contrast ratios of the different systems, the actual tilt angles of the dye guest–host mixtures must clearly be taken into account, and this parameter is considered in the following section.

2.4. *Tilt angle*

Although we have shown that it is possible to achieve good contrast ratios in DGHFE devices with tilt angles as low as 20–25°, it is clearly important to ensure that the addition of a dye does not reduce the tilt angle further. We have therefore measured the tilt angles of the ferroelectric guest–host solutions using a polarizing microscope and with a switching field applied to the sample. Figure 3 shows the

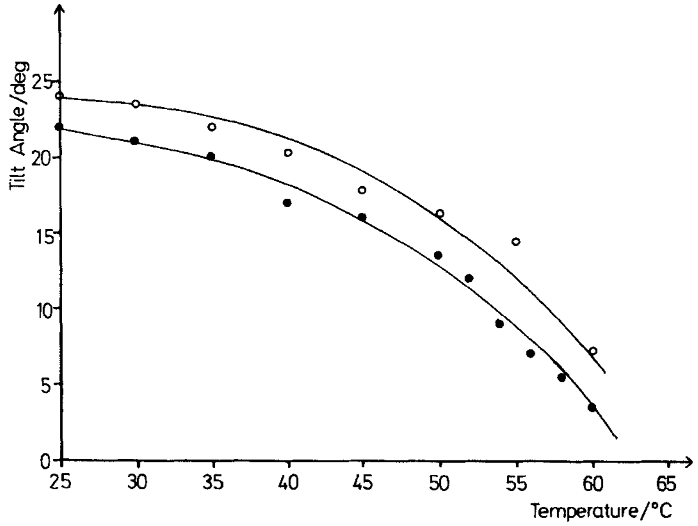
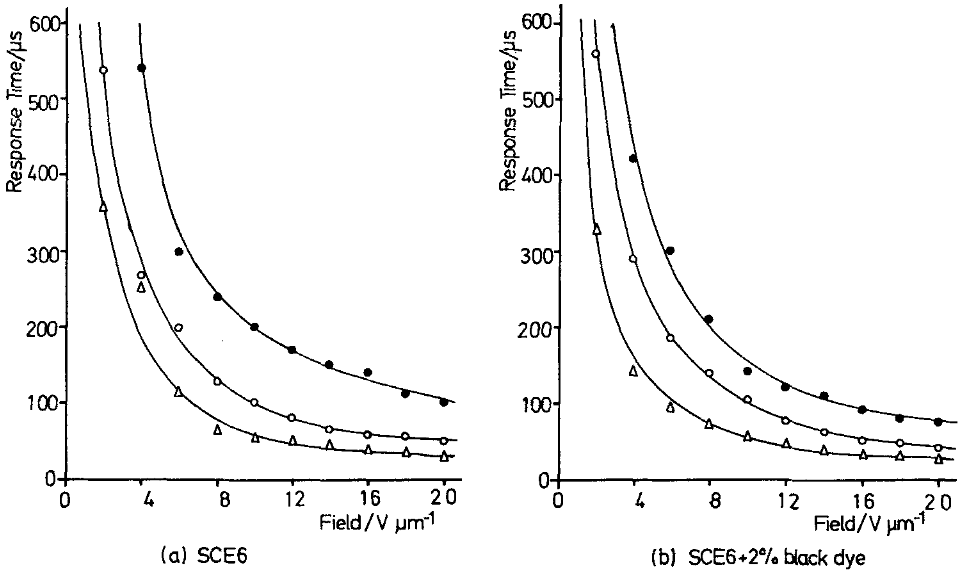


Figure 3. The variation of the tilt angle with temperature for (○) SCE6 and (●) the 2 per cent mixture of S304 and SCE6.

comparison of tilt angle for pure SCE6 and the SCE6–2 per cent S304 dye solution. It can be seen that addition of the dye reduces the tilt angle by approximately 2° over the S_C^* mesophase range. For mixtures of 2 and 4 per cent S304 in SCE4 the tilt angle was reduced by at most 1° from the host values at temperatures within 10°C of the $S_C^* \rightarrow S_A$ transition. However, this reduction was greater at lower temperatures, and at $T - T_{S_C^*S_A}$ of -20°C the tilt angles of the 2 and 4 per cent mixtures were lowered by 2 and 4°, respectively. We may conclude that the dye S304 has a small negative influence on the tilt angles of SCE4 and SCE6.

2.5. *Response times*

The response times of the DGHFE devices were measured using an adapted polarizing microscope fitted with a fast photodiode. Square wave voltages corresponding to electric fields of up to 20 V μm^{-1} were applied to the test cells, and the electro-optic responses were measured using a digital storage oscilloscope. The response time was the time taken for a 10 per cent to 90 per cent change in the transmitted light intensity when the field polarity was reversed.



(a) SCE6
(b) SCE6+2% black dye

Figure 4. The 10–90 per cent response times of (*a*) SCE6 and (*b*) SCE6–2 per cent S304 measured with respect to the applied at (●) 30°C (○) 40°C and (△) 50°C. The measurements were made on a 5 μm thick device.

A comparison of the electro-optic response times of SCE6 and SCE6–2 per cent S304, measured in a 5 μm thick device, is shown in figures 4 (*a*) and 4 (*b*). It can be seen that in general the response times of the DGHFE device are slightly faster than those of the SCE6 birefringence device at all temperatures and field strengths. For solutions of S304 in SCE4, it was found that the response times of the DGHFE devices were a strong function of both dye concentration and temperature. At 20°C below the $S_C^* \rightarrow S_A$ transition the measured response times for the 2 per cent solution were approximately the same as those of pure SCE4, whereas the response times of the 4 per cent solution were a factor of 3 slower (see figure 5). The data of figure 5 were measured for a 14 μm thick device, and data measured for an equivalent device containing SCE6–2 per cent S304 is included for comparison. At higher temperatures

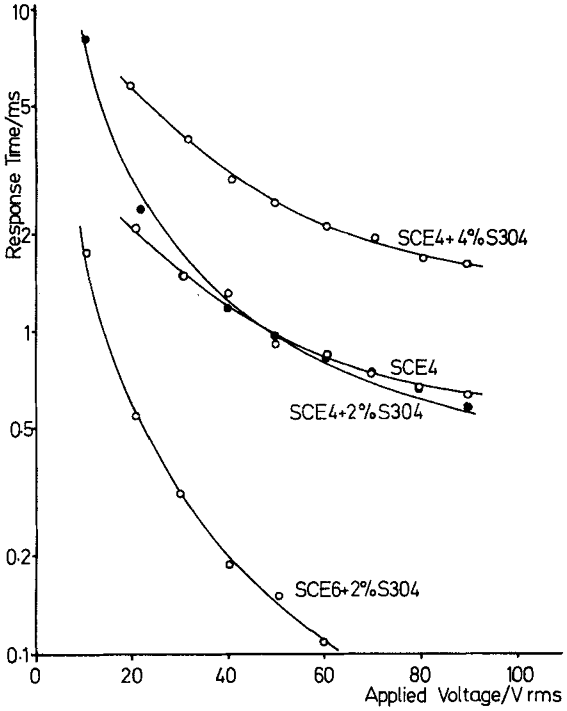


Figure 5. The 10–90 per cent response times of pure SCE4 and 2 and 4 per cent solutions of SCE4 + S304, 20°C below the $S_C^* \rightarrow S_A$ transition. Data for 2 per cent S304 in SCE6 are included for comparison.

($T - T_{S_C^*S_A} \geqslant -10°\mathrm{C}$) the response times of the SCE4 based DGHFE devices were always slower than the pure SCE4, although the 2 per cent solution was never more than a factor of 2 slower than SCE4. It appears that above a concentration of 2 per cent, inclusion of this dye has an adverse effect on the dynamic properties of the ferroelectric host SCE4. The SCE6 based mixture was found to be faster than the SCE4 mixtures in all cases, in common with the pure materials. The response times of the SCE6–S304 mixture were approximately 10 per cent slower than those of the blue dye mixture reported previously [8]; at 30°C and a field of $20\,\mathrm{V}\,\mu\mathrm{m}^{-1}$, the 10–90 per cent response times were 66 and 75 μs for the blue and black dyes, respectively. A detailed comparison between the SCE6–M483 mixture and other dyed guest–host and pure ferroelectric materials has been made elsewhere [8]. This comparison indicated that the response times were three and a half times faster than other ferroelectric materials which have been reported as being suitable for video frame rate addressing. We may conclude that the SCE6 based guest–host mixtures reported here are also suitable for video frame rate addressing.

3. A zero polarizer DGHFE device

It is possible [7], by placing two dichroic DGHFE devices back to back to produce a ferroelectric device which requires no polarizers. The operation of such a device is shown in the schematic given in figure 6. The vectors **n** describe the director configuration of the liquid crystal in each layer of the device for the switched states. **k** describes the direction of the smectic layer normal. The two layers of the device are arranged

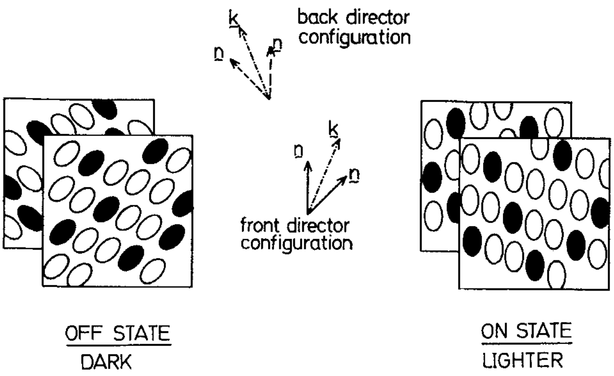


Figure 6. A schematic showing the operation of a zero polarizer dichroic DGHFE device.

so that in one switched state the directors, **n**, in the upper and lower half of the device are at right angles. Non-polarized light incident on the device will therefore be absorbed. In the other switched state the directors lie parallel so that for non-polarized incident light, only one polarization component will be influenced by the dye and the other will pass through the device unaffected. In principle, extremely high extinction is possible in such a device, although in this optimum case only half of the incident light will be transmitted in the on state. As the switch requires the directors of each layer to be parallel in one state and perpendicular in the other, each layer of the device must switch through 45°. Clearly the optimum tilt angle is therefore $22\frac{1}{2}°$, as for the birefringence device. By reducing this maximum switch, and realigning the layers of the device with respect to each other, it is also possible to increase the device response time effectively although the contrast ratio and brightness is reduced as a consequence.

4. A fluorescent DGHFE device

A further adaptation of the DGHFE device is the inclusion of an anisotropic fluorescent dye in the ferroelectric mixture. The operation of such a device is shown schematically in figure 7. In one state the absorption moment of the dye is parallel to

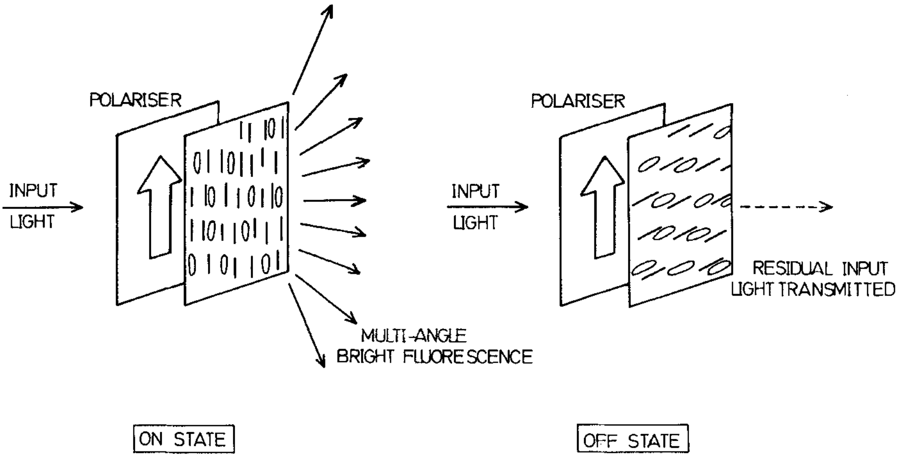


Figure 7. A schematic showing the operation of a single polarizer fluorescent DGHFE device.

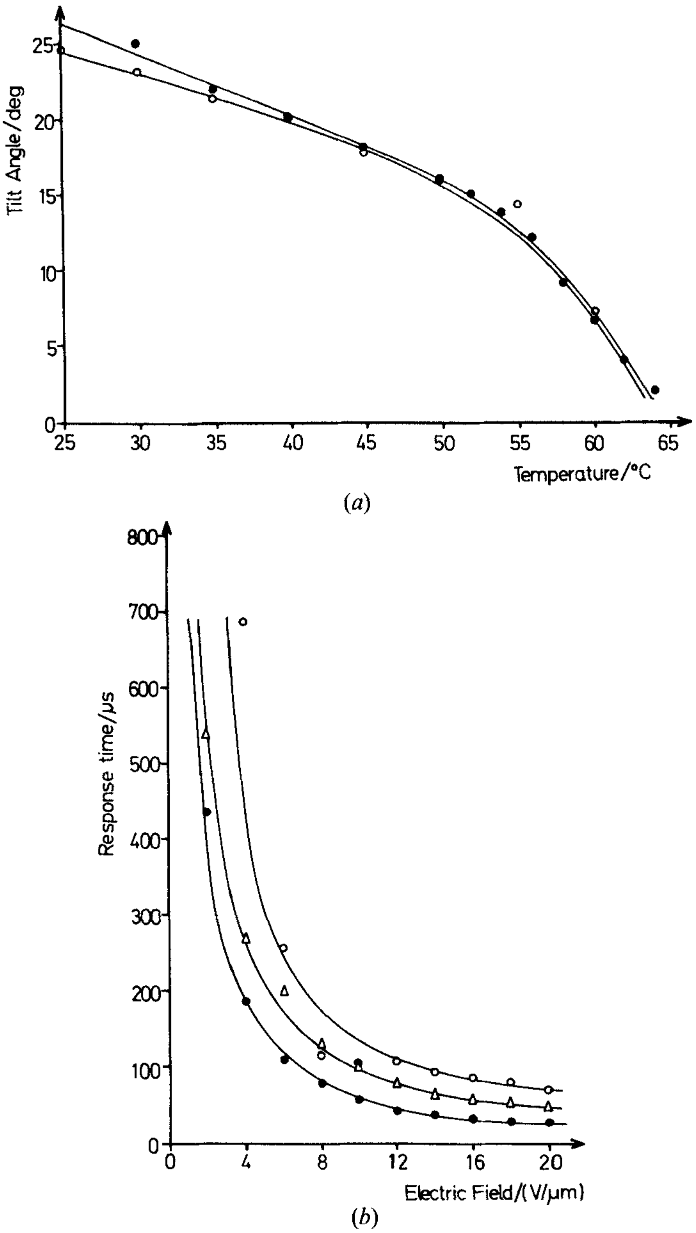


Figure 8. (*a*) The variation of the tilt angle with temperature for (●) a solution of 0·5 wt % fluorescent dye in SCE6 and for (○) SCE6. (*b*) The response time measurements, τ_R, for (●) a solution of 0·5 wt % fluorescent dye in SCE6 and for (△) SCE6. Also shown are the τ_F values for the mixture, indicated by ○.

the polarization direction. The absorbed exciting light is re-emitted at visible wavelengths and the device appears bright at all angles, even in conditions of low ambient light. In the off state the dye has been cooperatively reoriented by the ferroelectric host such that the polarization of the incident exciting light is no longer in the absorption direction. The exciting light is therefore transmitted by the device, but as its wavelength is typically in the near U.V. it is not visible and the device appears dark. The perceived contrast ratios are extremely high. Again, it is important to consider the influence that the inclusion of the dye has on the ferroelectric liquid crystal host. Figures 8 (*a*) and 8 (*b*) show the tilt angle and response time measurements for a 0·5 wt % solution of a fluorescent perylene dye in SCE6. The addition of the dye has little effect on the tilt angle or indeed the transition temperatures of the SCE6 host. Extremely fast response times were also measured (see figure 8 (*b*)). An asymmetry was observed between the measured rise and fall times in the fluorescent device, and this feature will be reported in more detail in a later paper. The 10–90 per cent rise time of the fluorescent DGHFE device was approximately half that and the fall time approximately twice that of the pure SCE6.

5. Conclusions

In this paper we have described the operation of three different DGFE device configurations. For the single polarizer dichroic DGHFE device we presented data which determined the influence of a black dye on the device characteristics of two different, commercially available ferroelectric hosts. The dye order parameter was the same in each of the hosts at equivalent dye concentrations, but was significantly reduced at a concentration of 4 per cent in SCE4. Although the order parameter of the black dye in SCE6 was higher than that of a single component blue dye reported previously, the contrast ratio was lower. The inclusion of the black dye in mixtures caused a slight reduction ($\leqslant 4°$) of the tilt angle of the host. Comparison of these data with those reported previously for the blue dye (M483) in SCE6 [8], together with the fact that the tilt angle was affected only slightly by the dye, leads us to conclude that a high dye order parameter does not necessarily imply a high contrast ratio. Further, a large contrast ratio may be attained more readily by a suitable choice of dye than by increasing the tilt angle to 45°. In SCE4, at high temperatures and dye concentrations there was an increase in the response time measured for the guest–host device when compared with the non-dyed birefringence device, though for the 2 per cent concentration at room temperature the response times were approximately the same. In SCE6 the response times of the DGHFE device were always faster than the non-dyed birefringence device. The use of a DGHFE device removes many of the constructional constraints associated with the birefringence device. Because the change in light intensity relies on a variation in the dye absorption with orientation, there is no restriction on the device thickness, other than that of achieving bistability and fast switching. The viewing angle characteristics of the device are similarly improved.

The other dyed guest–host device configurations described also offer further significant advantages over the birefringence switch. For the zero polarizer double device the optimum tilt angle is $22\frac{1}{2}°$ which, being identical to that required for the birefringence device, is already available in many commercial mixtures. Also, double devices are being produced for use in nematic guest–host and supertwist devices. The technological basis for low cost, fast and in principle high extinction, devices is therefore already available. Finally, by including a fluorescent dye in a ferroelectric host, we have demonstrated an extremely high contrast, bright, fast ferroelectric display with a single polarizer. Again, careful selection of the dye and host ensures that not only are the important device parameters not adversely affected, but they may be improved.

We thank B.D.H. Chemicals Ltd and Mitsui Toatsu Chemicals Inc. for the kind provision of materials. H.J.C. and H.F.G. thank the Wolfson Foundation for a grant which funded much of this work. J.S.K. thanks the S.E.R.C. for a studentship and financial support to attend this conference.

References

[1] Meyer, R. B., Liebert, L., Strzelski, L., and Keller, P., 1975, *J. Phys. Lett.*, **36**, L-69.
[2] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899; 1984, *Ferroelectrics*, **59**, 25.
[3 a] B.D.H. Chemicals Ltd, Poole, Dorset, England.
[3 b] E. Merck, Darmstadt, F.R. Germany.
[4] Bone, M. F., Coates, D., Crossland, W. A., Gunn, P., and Ross, P. W., 1987, *Displays*, (June) 115.
[5] Bowry, C., Mosley, A., and Nichols, B. M., 1987, *Proc. Eurodisplay*, p. 33 (IOP and SID publication).
[6] Ross, P. W., Patent Application No. 8 607 952.
[7] Coles, H. J., and Gleeson, H. F., Patent Application No. 8 709 659.
[8] Coles, H. J., and Gleeson, H. F., 1988, *Molec. Crystals liq. Crystals Lett.*, **6**, 53.
[9] Kondo, K., Era, S., Isogai, M., and Mukoh, A., 1985, *J. appl. Phys.*, **24**, 1389.
[10] Hubbard, S. D., 1986, Ph.D. thesis, Manchester University.