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

Tunable chiral materials for multicolour reflective cholesteric displays

Frederic Vicentini; Julie Cho; Liang-Chy Chien

Online publication date: 06 August 2010

To cite this Article Vicentini, Frederic , Cho, Julie and Chien, Liang-Chy(1998) 'Tunable chiral materials for multicolour reflective cholesteric displays', Liquid Crystals, 24: 4, 483 — 488
To link to this Article: DOI: 10.1080/026782998206939
URL: http://dx.doi.org/10.1080/026782998206939

LIQUID CRYSTALS, 1998, VOL. 24, NO. 4, 483–488

Tunable chiral materials for multicolour reflective cholesteric displays

by FRÉDÉRIC VICENTINI, JULIE CHO and LIANG-CHY CHIEN*
Liquid Crystal Institute, Chemical Physics and NSF ALCOM Center,
Kent State University, Kent, Ohio 44242, USA

(*Received 18 October 1996; in final form 1 September 1997; accepted 8 September 1997*)

A polymerizable tunable chiral material (TCM) has been prepared for the fabrication of multicolour reflective cholesteric displays. This photosensitive chiral material, whose chirality is adjustable upon UV irradiation, enables us to adjust the pitch of a cholesteric material and thus to produce the three reflected colours (red, green and blue) for a multicolour reflective cholesteric display. Furthermore, the possibility of linking this compound to a polymer network helped to solve the problem of colour diffusion. Reflection spectra of the corresponding cells show broad reflection peaks, because of scattering from the large amount of polymerizable compound. We also report the difference of response under UV irradiation between this polymerizable tunable chiral material and a non-polymerizable material.

1. Introduction

Reflective displays based on cholesteric liquid crystals are very attractive for information and video display applications since they produce bright reflective pictures without a back-light. Cholesteric liquid crystals represent a unique class of materials; they are good candidates for reflective displays in that a highly coloured material does not absorb incident ray but reflects in planar texture and scatters light weakly in focal-conic texture. Recently, a considerable improvement which has been achieved in this field is the introduction of a low concentration of polymer network material into the liquid crystal [1–3]. The resulting displays, based on polymer stabilized cholesteric texture (PSCT), exhibit a wide viewing angle, grey scale and low power consumption as well as zero field bistability.

A practical challenge of the cholesteric LCD has been to provide a full colour reflective display. A method of preparing a multicolour reflective display has been reported recently by this laboratory [4]. This method provides the three primary colours in a sequential array from the same original cholesteric stock solution formed from a mixture of a nematic host, a chiral dopant and tunable chiral material (TCM), a chiral compound whose chiral centre is linked to a photosensitive group. The resulting mixture is in the cholesteric phase with a selected pitch, and the wavelength of the reflected light λ_R is governed by the Bragg reflection law:

$$\lambda_R = p n_{avg} \tag{1}$$

where p is the pitch of the cholesteric phase and n_{avg} is the average refractive index. The pitch of the cholesteric mixture can be controlled by varying the concentration of chiral dopant and is given by the following equation (only at concentration under 10%) [5]:

$$p = \frac{1}{\beta_0 . c_0 + \beta_{TCM} . c_{TCM}}. \tag{2}$$

It is thus possible by adjusting c_0 and c_{TCM} to provide a colour display reflecting the three basic colours: blue, green and red. By irradiating the mixture with UV light, the concentration of TCM (c_{TCM}) is decreased, resulting in a change of the pitch p and thus a change of the reflected wavelength λ_R.

In a reflective cholesteric display cell, the colour pixelation is achieved '*in situ*', using UV light irradiation and photolithography techniques. This concept is very attractive since it does not require any stacked multiple-cells, separated pixels filling, dyes or colour filter. However, since the cholesteric compounds used so far are low molecular weight liquid crystals, they diffuse across the cell resulting in colour mixing between adjacent pixels. This paper presents an alternative approach to prevent this colour diffusion.

2. Experimental

2.1. *Instrumentation*

^{1}H NMR spectra were performed with a Varian 200 MHz spectrometer; infrared spectra were obtained from a Nicolet Magna IR spectrometer 550. Optical rotation power was measured with a polarimeter AA-10 from Optical Activity Ltd. The molecular weight of the

*Author for correspondence.

synthesized polymer was determined on a Waters GPC, using polystyrene standard as a reference. A Nuarc NL22-8C metal halide UV lamp of 900 W was used as the UV source for initiating the polymerization and colour patterning. The reflection spectra were obtained with a RSA-HP-84 reflectance accessory from Labsphere Inc. on a HP8452A diode array spectrophotometer.

2.2. *Synthesis of the TCM*

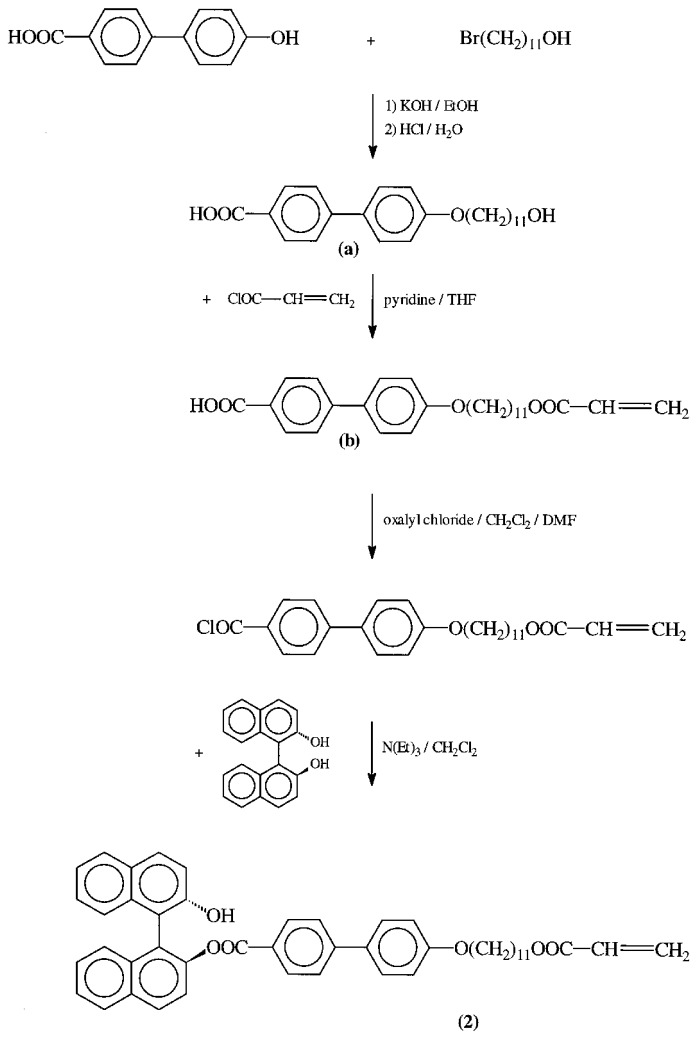
The synthetic route to compounds **a**, **b** and **2** (TCM **2**) is shown in the scheme.

2.2.1. *Synthesis of 4′-(ω-hydroxyundecyloxy)biphenyl-4-carboxylic acid (**a**)*

In a 100 ml round-bottom flask, 3·89 g (18·18 mmol) of 4-(4-hydroxyphenyl)benzoic acid was dissolved in 100 ml of ethanol and 20 ml of water and the mixture was heated to 110°C. 2·24 g (40 mmol) of KOH dissolved in 30 ml of ethanol was added in one portion. Under reflux, 5 g (20 mmol) of 11-bromo-1-undecanol dissolved in 50 ml of ethanol was added dropwise. The mixture was reflux heated under with stirring for 24 h. The solvent was evaporated and the residue acidified with 5% aqueous HCl until pH = 2. The resulting precipitate was filtered, washed with water, and recrystallized from ethanol. Yield 6·2 g (89%), m.p. >300°C (decomp.). IR (nujol): 3392, 2925, 2861, 1695, 1612, 1535, 1298, 1260, 1209, 1132. NMR ^{1}H (DMSO, ppm) δ: 8 (d, 2H), 7·75 (m, 4H), 7·05 (d, 2H), 4·4 (br, 1H), 4 (t, 2H), 3·4 (t, 2H), 1·7 (m, 2H), 1·25–1·4 (m, 16H).

2.2.2. *Synthesis of 4′-(ω-acrylylundecyloxy)biphenyl-4-carboxylic acid (**b**)*

In a 100 ml round-bottom flask, 6·2 g (16·15 mmol) of compound **a** and 1·58 g (20 mmol) of pyridine were dissolved in 100 ml of THF; the mixture was heated under reflux for 10 min, then cooled to room temperature. 1·8 g (20 mmol) of acryloyl chloride dissolved in 80 ml of THF was added dropwise, and the mixture (a heterogeneous solution) was stirred overnight at room



Scheme. Synthetic scheme for TCM **2**.

temperature. The crude mixture was extracted with ethyl acetate; the extract was washed with 5% aqueous HCl, saturated aqueous $NaHCO_3$ and water, and dried over Na_2SO_4. The solvent was then evaporated. The final compound was purified by a flash chromatography column on silica gel using hexane/ethyl acetate (3/7) as eluent. Yield 3·3 g (46%), m.p. 203°C. IR (nujol): 3420, 2927, 2861, 1729, 1683, 1604, 1565, 1301, 1249, 1196, 1124, 986 (vinyl). NMR ^{1}H ($CDCl_3$, ppm) δ: 8·15 (d, 2H), 7·65 (quad, 4H), 7 (d, 2H), 6·4 (dd, 1H), 6·15 (dd, 1H), 5·85 (dd, 1H), 4·15 (t, 2H), 4 (t, 2H), 1·6–1·8 (m, 4H), 1·3 (m, 14H).

2.2.3. *Synthesis of (S)-(-)-2-hydroxy-2′-[4′-(ω-acryloylundecyloxy)biphenyl-4-carboxy]-1,1′-binaphthalene (**2**)*

In a 100 ml round-bottom flask, 3·3 g (7·53 mmol) of compound **b** was dissolved in 80 ml of dichloromethane and few drops of DMF. The mixture was cooled in an ice bath and 8·9 g (70 mmol) of oxalyl chloride in 50 ml of dichloromethane was added dropwise. This mixture was stirred for 1 h, resulting in a homogeneous solution. The solvents were evaporated under vacuum, and the resulting acid chloride was used without further purification. 2·17 g (7·6 mmol) of (*S*)-(-)-2,2′-dihydroxy-1,1′-binaphthalene and 0·81 g (8 mmol) of triethylamine were dissolved in 50 ml of dichloromethane with stirring at 0°C. At this temperature, the acid chloride of compound **b**, dissolved in 50 ml of dichloromethane, was added dropwise and the mixture was stirred overnight. The final compound was purified by three successive flash chromatography columns on silica gel using hexane/ethyl acetate (8/2) as eluent. Yield 1·45 g (27·5%). IR (nujol): 3414, 3070, 2934, 2861, 1736, 1723, 1656, 1611, 1565, 1505, 1282, 1223, 1190, 1085, 986 (vinyl). NMR ^{1}H ($CDCl_3$, ppm) δ: 8·15 (d, 1H), 8(d, 1H), 7·75 (m, 4H), 7·2–7·6 (m, 12H), 6·95 (d, 2H), 6·4 (dd, 1H), 6·15 (dd, 1H), 5·8 (dd, 1H), 5·4 (s, 1H), 4·15 (t, 2H), 4 (t, 2H), 1·6–1·8 (m, 4H), 1·3 (m, 14H). Elemental analysis: calculated, C 79·88, H 6·52; found, C 79·52, H 6·55. $[\alpha]_D = -135{\cdot}0°$ (in CH_2Cl_2).

2.3. *Solution polymerization of compound **2***

In a polymerization tube, 210 mg (0·3 mmol) of **2** and 1 mg (0·006 mmol) of AIBN were dissolved in 2 ml of toluene under nitrogen and heated at 70°C with stirring for 24 h. The polymer was precipitated by adding to 100 ml of methanol; it was filtered off, washed with methanol, and dried under vacuum. Yield 95 mg (45%). ^{1}H NMR ($CDCl_3$, ppm) δ: 8·1–7·9 (2H), 7·7–6·8 (18H), 5·45 (1H), 4·15–3·9 (4H), 1·5–1·8 (4H), 1·3 (14H). $[\alpha]_D = -76{\cdot}2°$ (in CH_2Cl_2).

2.4. *Liquid crystal mixtures and cells*

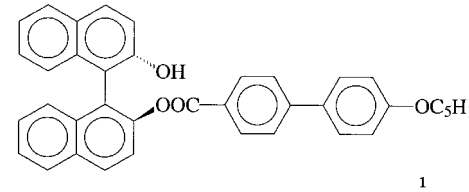
Nematic liquid crystal E48 and chiral dopants CB15, CE1 and R1011 were purchased from Merck Ltd (England). The crosslinker BAB (4,4′-bisacryloyloxybiphenyl) was synthesized in this laboratory [6]. A red cholesteric stock solution ($\lambda_R = 680$ nm) was prepared by mixing E48 (76·8 wt %) with chiral dopants (23·2 wt % of dopants CB15 : CE1 : R1011 = 3 : 3 : 1). A red stock solution was mixed with TCM **1** at 80°C to form a blue mixture ($\lambda_R = 480$ nm), whereas a blue mixture of the TCM **2** and red stock solution was mixed in dichloromethane and followed by evaporating the solvent under reduced pressure. These mixtures were introduced into display cells by vacuum filling. The display cells, obtained from Crystalloid Electronics (Hudson, Ohio), were constructed and assembled with ITO coated glass, rubbed polyimide coated surface and 5 μm glass spacers.

2.5. *Colour patterning*

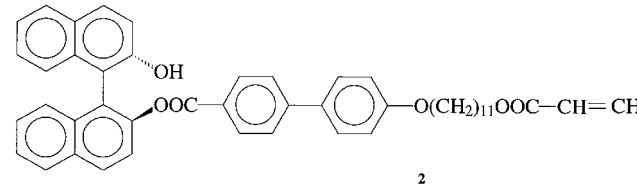
A metal halide lamp with a Pyrex filter ($\lambda \geqslant 330$ nm) was used for the photopolymerization and colour patterning of sample cells. Photopolymerization was performed by exposing the cells to UV light directly, while colour patterning was performed by exposing the cells to UV light through masks.

3. Results and discussion

The compounds used in this study as tunable chiral materials are the binaphthol derivatives:



1



2

Esters of binaphthol have already been reported as compounds with high helical twisting power [7, 8]. Binaphthols have been reported to exhibit a strong photosensitivity to UV irradiation, giving rise to radical species [9]. Although the recombination of these species in the bulk has not yet been studied, it appears that the resulting compounds show no chirality after irradiation. We used a mono-esterified *s*-binaphthol to increase the solubility of these compounds in the nematic host. Nevertheless, the binaphthol derivative **1** was found

to have a sufficiently high helical twisting power as a chiral additive in a nematic host to form a short pitch cholesteric mixture. The use of a low concentration of chiral additive is significant in reducing the threshold voltage of the corresponding cholesteric displays.

In a previous study [10], TCM **1** has shown promising results in achieving multicolour pixels in one cell. However, the occurrence of colour diffusion can be observed after a few days, due to the diffusion of TCM **1** following the concentration gradient in the patterned cell. A possible method to prevent this diffusion could be the linkage of the TCM molecule to this network via an acrylate function, following the use of polyacrylate network in polymer stabilized reflective cholesteric displays. Hence the synthesis of TCM **2** which followed the synthetic route as shown in the scheme. The introduction of a long aliphatic chain between the acrylate functional group and the biphenyl moiety preserves the high helical twisting power of the binaphthol ester side chain when TCM **2** is linked to the polymer network.

The compositions of blue mixtures for cells A and B are given in the table. To standard red cholesteric stock solution was added a diacrylate monomer (BAB) and the required concentration of TCM to reflect the blue colour. We noticed that it required the addition of 7% of TCM **2** by the weight of liquid crystal, compared with 5·5% of TCM **1**, to reflect the blue colour. In fact, TCM **1** has a higher value of helical twisting power than that of TCM **2** whose behaviour parallels the corresponding optical rotation power values: $-135{\cdot}0°$ for TCM **2** and $-187{\cdot}2°$ for TCM **1**.

The reflection spectra of the photo-tuned colour cells were measured under a diffuse lighting condition using a RSA-HP-84 integrated sphere accessory from Labsphere Inc. on a HP8452A diode array spectrophotometer. Figures 1 and 2 are the reflection spectra of cells A and B, respectively. The evolution of reflection spectra was plotted as a function of UV dose. The results show that the colour patterning of the two blue mixtures provides the three basic colours (blue, green and red) for a colour display. In figure 1, after exposing cell A to a UV dose of 13·5 J cm^{-1}, a shift of 25 nm in reflective wavelength was observed (480 to 505 nm). This indicated a reduction in chirality of TCM **1** during network formation. The evolution of the red shift requires a high UV dose for cell A. The decrease in reflectance for three tuned colour pixels for cell A is negligible. For cell B (figure 2), the evolution of the red shift requires a lower UV dose. The fast red shift can be explained as a result of the photopolymerization of TCM **2** which causes a reduction in TCM **2** concentration due to its phase

Table. Composition of the blue mixtures.

	Composition/wt %						
Cell	E48	CE1	CB15	R1011	BAB	TCM **1**	TCM **2**
A	71·8	9·3	9·3	3·1	1	5·5	0
B	70·8	9·1	9·1	3·0	1	0	7

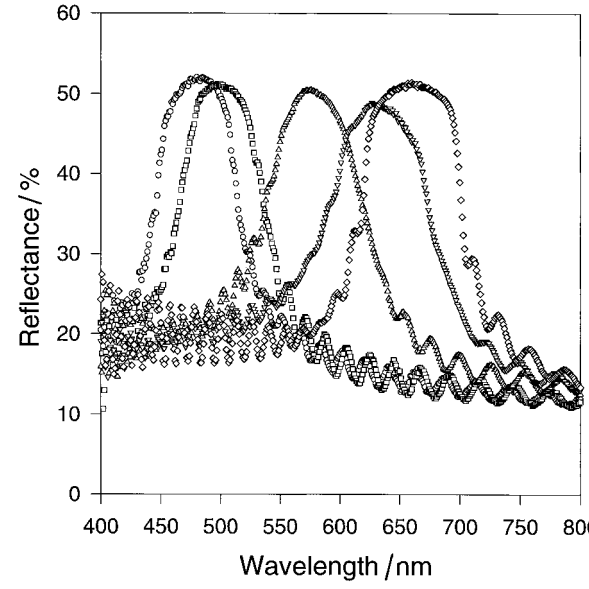


Figure 1. Reflection spectra of a cell filled with a blue mixture containing 5·5 wt % of TCM **1** (○) after a UV exposure of: (□) 13·5 J cm^{-2}, (△) 75 J cm^{-2}, and (▽) 93 J cm^{-1}. (◇) Red stock solution.

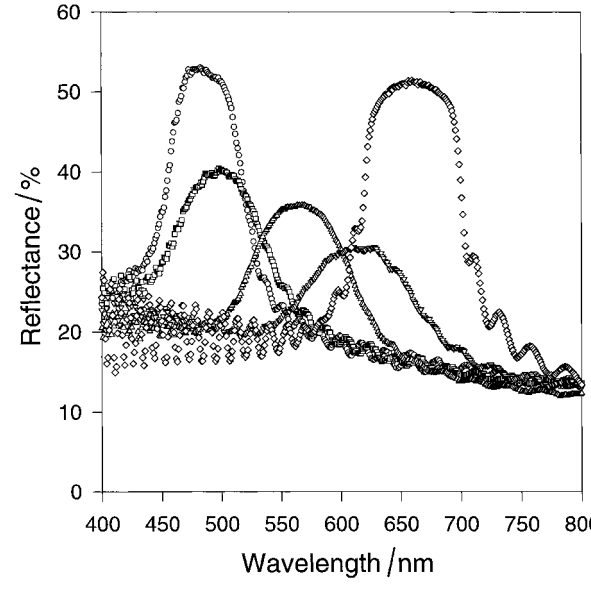


Figure 2. Reflection spectra of a cell filled with a blue mixture containing 7 wt % of TCM **2** (○) after a UV exposure of (□) 2·7 J cm^{-2}, (△) 13·5 J cm^{-2}, and (▽) 93 J cm^{-2}. (◇) Red stock solution.

separation from the cholesteric mixture and loss of chirality. Moreover, a significant loss in reflectance was observed for three tuned colour pixels in cell B.

Figure 3 shows a plot of the reflective wavelength at the maximum of the peak versus the UV dose for both cells A and B. We observed a broadening of the reflection peak in both cases which has been attributed to the formation of a polymer network and the imperfect helix of a cholesteric planar structure [11]. This broadening phenomenon appears to be more prominent in the case of cell B because of a higher concentration of polymerizable materials in the corresponding cholesteric mixture. The difference in the reflection spectra explains the lower quality of colours exhibited by cell B. There is a need to reduce the polymer concentration as low as possible and to increase the reflectivity. A solution would be to synthesize new TCMs having higher helical twisting power [12]. As shown in figures 4(*a*) and 4(*b*), the polymerizable TCM **2** gives less bright colours than does TCM **1** because the larger polymer domain results in scattering from an imperfect helix. However, the cell prepared with TCM **2** showed no colour diffusion after several days. We stopped the colour patterning when the cells showed a red colour. This does not necessarily mean it could not go to the colour of the red stock solution.

To determine the influence of polymer on the reflectance, we first prepared a polymeric TCM via the solution polymerization of TCM **2**, and then made a cell with this polymer as a TCM material. A high initiator concentration was used to obtain a polymeric TCM having a low degree of polymerization. According to the GPC measurement, this polyacrylate TCM has an average number molecular weight of 9300 g mol^{-1} and a degree of polymerization of 13. This polymer has an optical rotation power of $-76{\cdot}2°$, which is smaller than that of TCM **2**. We prepared a cholesteric mixture containing 7 wt % of polyacrylate TCM with the standard red mixture. The resulting mixture was melted as an homogeneous solution at 100°C then cooled to room temperature. This cholesteric mixture did not change colour and remained red. We examined it by polarizing optical microscopy which showed the phase separation of polymer from the cholesteric mixture; thus the polyacrylate TCM was unable to contribute to the helical twisting power of the cholesteric mixture.

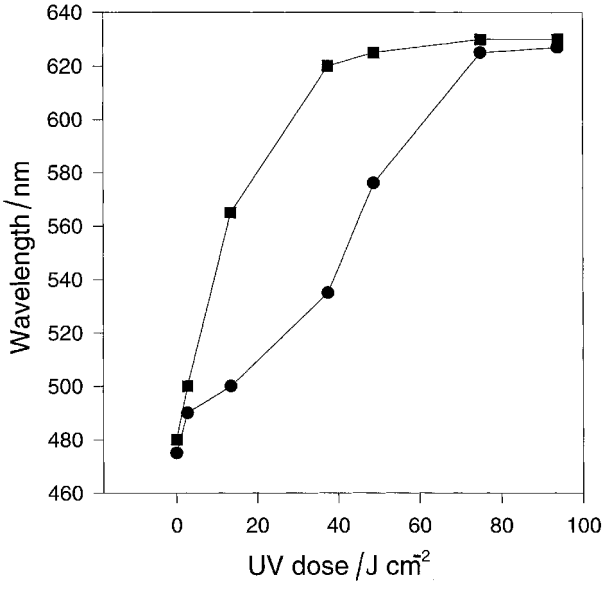
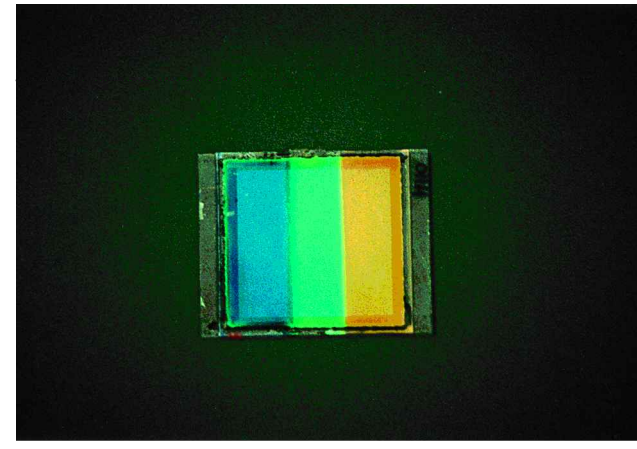
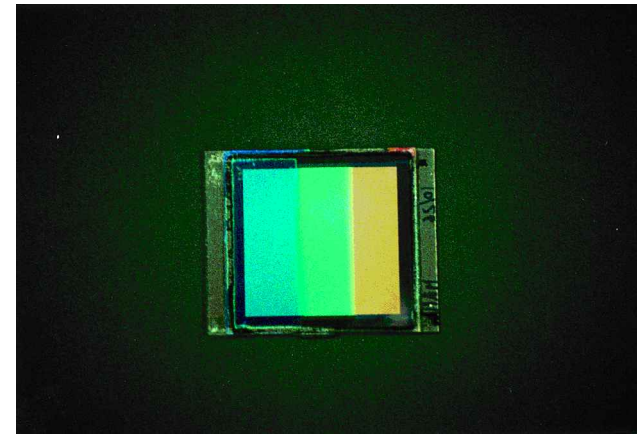


Figure 3. Plot of the reflected wavelength at the maximum of the peak as a function of the UV dose for: (●) cell A, (■) cell B.



(*a*)



(*b*)

Figure 4. (*a*) Cell A and (*b*) cell B having the photo-tuned three colour pixels.

4. Conclusion

The polymerizable TCM **2** is capable of providing the three basic colours for a colour reflective cholesteric display. Moreover, TCM **2** shows an improvement in

preventing colour diffusion in a patterned multicolour reflective cholesteric display. The relatively high concentration of polymer network in cell B, gives a lower reflectance than that of cell A due to light scattering from the imperfect helix. In practical applications, a layer of UV screen coating is necessary for protection of the multicolour reflective cholesteric displays.

This work was supported by ARPA Low Power Display Contract N61331-94-K-0042.

References

[1] Yang, D.-K., Chien, L.-C., and Doane, J. W., 1992, *Appl. Phys. Lett*., **60,** 3102

[2] Yang, D.-K., West, J. L., Chien, L.-C., and Doane, J. W., 1994, *J. appl. Phys*., **76,** 1331.

[3] Doane, J. W., Yang, D.-K., and Chien, L.-C., 1995, US Patent 5 437 811.

[4] Chien, L.-C., Müller, U., Nabor, M.-F., and Doane, J. W., 1995, *SID 95 Digest*, 169.

[5] Solladié, G., and Zimmermann, R. G., 1984, *Angew. Chem. int. Ed. Engl*., **23,** 348.

[6] Chien, L.-C., Boyden, M. N., Walz, A. J. and Citano, C. M., 1996, in *Liquid-Crystalline Polymer Systems: Technology and Advances*, edited by A. I. Isayev, T. Kyu, and S. Z. D. Cheng, ACS, Symposium Series 632 (Washington, DC: ACS), p. 182.

[7] Heppke, G., Lötzsch, D., and Oestreicher, F., 1986, *Z. Naturforsch. A*, **41,** 1214.

[8] Heppke, G., Kitzerow, H.-S., Lötzsch, D., and Papenfuß, Ch., 1990, *Liq. Cryst*., **8,** 407.

[9] Sur, S. K., and Colpa, J. P., 1989, *Spectrosc. Lett*., **22,** 965.

[10] Müller, U., Vicentini, F., Lin, Y., and Chien, L.-C., 1997, *Polym. Preprints*, **38,** 359.

[11] Leroux, N., Fritz, W. J., Doane, J. W., and Chien, L.-C., 1995, *Mol. Cryst. liq. Cryst*., **261,** 465.

[12] Lin, Y., and Chien, L.-C., 1998, *Tetrahedron Asymm*., in press.