This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 18 February 2013, At: 12:12

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



# Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/gmcl19

## New Chiral Monomers for Polymer Stabilized Cholesteric Textures

N. Leroux <sup>a</sup>, W. J. Fritz <sup>a</sup>, J. W. Doane <sup>a</sup> & L.-C. Chien <sup>a</sup> Liquid Crystal Institute and NSF ALCOM Center, Kent State University, Kent, OH, 44242, U.S.A. Version of record first published: 23 Sep 2006.

To cite this article: N. Leroux, W. J. Fritz, J. W. Doane & L.-C. Chien (1995): New Chiral Monomers for Polymer Stabilized Cholesteric Textures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 261:1, 465-480

To link to this article: <a href="http://dx.doi.org/10.1080/10587259508033490">http://dx.doi.org/10.1080/10587259508033490</a>

#### PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, 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.

**NEW CHIRAL MONOMERS FOR** POLYMER STABILIZED CHOLESTERIC TEXTURES

N. LEROUX, W. J. FRITZ, J. W. DOANE and L.-C. CHIEN\* Liquid Crystal Institute and NSF ALCOM Center, Kent State University, Kent OH 44242, U. S. A.

Abstract New mesomorphic chiral acrylates were synthesized. Their additions to a nematic liquid crystalline mixture cause the director of the nematogens molecules to adopt a helically twisted orientation. The pitch of the resulting helicoidal structure is determined by the concentration of the chiral dopant. Mesomorphic properties and actual pitches of several mixtures of these chiral dopants with nematic or cholesteric liquid crystalline solvents were studied. Photochemical polymerizations of these mixtures were performed in thin films which resulted in cross-linked polymer networks with a twisted superstructure. The use of such specific chiral additives in polymer stabilized cholesteric texture material resulted in white reflective displays. The electro-optical properties of such devices were investigated.

#### INTRODUCTION

There is a great deal of interest in developing reflective displays because they do not require a back-light which results in a more compact, light-weight display as compared to current backlit displays. One type of reflective display, polymer stabilized cholesteric texture (PSCT), incorporates a polymer network into chiral liquid crystal material<sup>1,2</sup>. The polymer network improves the viewing angle and uniformity in addition to making the display bistable. However, this material results in a display that operates with only one color in the reflecting state and black in the scattering state. It is desirable to produce a display that is white in the reflecting state. The addition of a chiral material to a nematic liquid crystalline mixture causes the director of the nematogenic molecules to adopt a helically twisted orientation<sup>3,4</sup>. The pitch of the resulting helicoidal structure is determined by the concentration of the \* Author for whom correspondance should be addressed.

chiral dopant. The chirality of a designed mixture may also be modified by the addition of small amounts of a chiral molecule. On the other hand, photoinitiated polymerization of a liquid crystalline acrylate monomer in its macroscopically oriented state leads to a highly ordered liquid crystalline side-chain polymer film<sup>4,5</sup>. When the same method is used to polymerize a chiral acrylate and a diacrylate moiety together in a designed cholesteric mixture, one obtains an oriented cross-linked polymer network with a helicoidal superstructure.

It is the aim of this work to produce a white reflective display by adding the chiral monomer to a chiral nematic mixture. A chiral nematic diacrylate (AAMP), (4-(2-(acryloyloxy)ethyloxy)-4'-(2'-(acryloyloxy)-(S)-1-methyl-ethyloxy)) phenylbenzoate, was added to a chiral nematic mixture and the resultant material was then polymerized photochemically in thin films. In the case of binaphthol acrylate (BNA), (R)-2hydroxy-2'-(4(acryloyloxy)butoxy)-1,1'-binaphthalene, a cross-linker 4,4'-bisacryloy -loxybiphenyl (BAB) was added together with a chiral nematic mixture. Under ultraviolet (UV) radiation, the chiral acrylate can be incorporated into the cross-linked polymer. As the polymer network forms via one component system (AAMP) or two components system (BNA and BAB), the chiral acrylate will be separated out from the solution. Consequently, there will be a greater chiral concentration in the vicinity of the polymer network than in the bulk. This can lead to a distribution of two areas with different pitch as a result of the chiral concentration difference within a given volume element. A judicious choice of chiral concentration can lead to two colors that additively combine to give white (e.g., blue and yellow) or there will be an overlap in the reflected spectrum from the two different pitch areas such that the reflected spectrum is sufficiently broadened to produce white. The electro-optical properties of these thin films were investigated.

## **EXPERIMENTAL**

#### Materials

The synthesis of a right-handed chiral diacrylate (AAMP) and a left-handed chiral monoacrylate (BNA) are shown in scheme 1 and 2, respectively.

The NMR spectra were run on a Varian 200MHZ Spectrometer and the infrared spectra were obtained using a Nicolet Magna IR Spectrometer 550. The specific rotations of the optically active compounds were measured using a digital polarimeter

Jasco DP 360 and an automatic polarimeter AA-10 from Optical Activity Limited. The purities of compounds were examined using a reverse phse Waters 600E HPLC with a 994 photo diode array detector. A Perkin-Elmer DSC7 was used to determine the transition temperatures and the anisotropic textures are observed under a Leitz Laborlux S polarizing microscope fitted with a Mettler FP5 heating stage.

Synthesis of the chiral diacrylate

Scheme 1

Ethyl 4-(2-bromoethyloxy)benzoate (I)<sup>5</sup> Dibromoethane (20.7g, 0.110mol) was added to a stirred mixture of 1-hydroxy-4-ethylbenzoate (8.30g, 0.050mol) and potassium carbonate (13.8g, 0.100mol) in dried acetone. The reaction mixture was stirred under reflux for 20 hours. Then it was cooled to room temperature and filtered to remove the potassium bromide and the excess of potassium carbonate. The solvent was removed from the filtrate and the crude product purified by flash chromatography using dichloromethane as the eluant. Yield: 8.00g (58.6 per cent). IR (Nujol): 1740 cm<sup>-1</sup> (ester), 1600 and 1480cm<sup>-1</sup> (aromatic C – C), 1250cm<sup>-1</sup> (COPh). NMR (CDCl<sub>3</sub>):  $\delta$  8.00 (d, 2H, Ar), 6.92 (d, 2H, Ar), 4.34 (m, 4H, CH<sub>2</sub>OCO and CH<sub>2</sub>O), 3.65 (t, 2H, CH<sub>2</sub>Br), 1.37 (t, 3H, CH<sub>3</sub>). Melting point: 74 °C.

4-(2-Bromoethyloxy)benzoique acid (2) Ethyl 4-(2-bromoethyloxy)benzoate (1) (8.00g, 0.029mol) was dissolved in 60ml ethanol and a solution of potassium hydroxide (18.7g, 0.334mol) in 130ml ethanol was added. The reaction mixture was stirred in a hot water bath overnight. The potassium salt was dissolved with 150ml water and the mixture was acidified with hydrochloric acid. The acid was then filtrated, washed with water and dried in vacuum under phosphorus pentoxide. Yield: 5.00g (70 per cent). IR

(Nujol):  $3000cm^{-1}$  (acid), 1600 and  $1480cm^{-1}$  (aromatic C – C),  $1250cm^{-1}$  (COPh). NMR (DMSO):  $\delta$  7.90 (d, 2H, Ar), 7.03 (d, 2H, Ar), 4.39 (t, 2H, CH<sub>2</sub>O), 3.83 (t, 2H, CH<sub>2</sub>Br). Melting point: 174 °C.

(Ethyl-1-(4'-benzyloxyphenoxy)) (S)-1-methyl acetate (3) <sup>6</sup> Benzyloxyphenol (5g, 0.025mol) and ethyl(S)-(-)lactate (2.95g, 0.025mol) were dissolved in 150 ml anhydrous tetrahydrofuran with thriphenylphosphine (6.55g, 0.025mol) at room temperature. The mixture was then cooled with an ice bath and a solution of diethyl azodicarboxylate (4.35g, 0.025mol) in 10ml anhydrous tetrahydrofuran was added dropwise. The reaction mixture was stirred at room temperature overnight. The solvent was removed with a rotavapor and the obtained residue was purified by flash chromatography on silica gel using dichloromethane as the eluant. Yield: 6.9 (91 per cent); ( $\alpha$ ) = +35.80 (CH<sub>2</sub>CL<sub>2</sub>). IR (Nujol): 1750cm<sup>-1</sup> (ester), 1600 and 1480cm<sup>-1</sup> (aromatic C - C), 1250cm<sup>-1</sup> (COPh). NMR (CDCl<sub>3</sub>):  $\delta$  7.35 (m, 5H, Ar), 6.85 (m, 4H, Ar), 5.00 (s, 2H, CH<sub>2</sub>Ph), 4.65 (q, 1H, C\*H), 4.20 (q, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.59 (d, 3H, CH<sub>3</sub>CH), 1.24 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>).

(2-Hydroxy-(4'-benzyloxyphenoxy)) (S)-1-methyl-ethane (4)  $^7$  To a cold (0°C) solution of lithium aluminum hydride (1.05g, 0.028mol) in 150 ml dried diethylether was added a solution of the ester 3 (6.9g, 0.023mol) in 100ml dried diethylether over two hours . The ice bath was removed and the reaction mixture was then gently refluxed for 24 hours. The mixture was cautionary hydrolyzed with water until no more hydrogen was evolved. Then some concentrated sulfuric acid was added dropwise to dissolve the white precipitated aluminum hydroxide. The two phases are separated and the aqueous phase is washed twice with diethylether, the combined ether extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and then filtered. Yield: 5.25g (90per cent); ( $\alpha$ ) =  $^-$ 1.34  $^0$  (CH<sub>2</sub>CL<sub>2</sub>). IR (Nujol): 3450cm<sup>-1</sup> (alcohol), 1600 and 1480cm<sup>-1</sup> (aromatic C - C), 1280cm<sup>-1</sup> (COPh). NMR (Acetone D4):  $\delta$  7.40 (m, 5H, Ar), 6.90 (m, 4H, Ar), 5.06 (s, 2H, CH<sub>2</sub>Ph), 4.35 (q, 1H, C\*H), 3.62 (m, 2H, CH<sub>2</sub>OH), 1.23 (d, 3H, CH<sub>3</sub>). Melting point: 68°C.

(2-Bromo-(4'-benzyloxyphenoxy)) (S)-1-methyl-ethane (5) <sup>8,9</sup> The alcohol 4 (5.25g, 0.020mol) was dissolved in 150 ml anhydrous tetrahydrofuran with imidazole (4.49g, 0.082mol) and carbon tetrabromide (20.3g, 0.061mol). The mixture was cooled with an ice bath (0°C) and a solution of triphenylphosphine (10.7g, 0.040mol) in 20 ml

anhydrous tetrahydrofuran was slowly added. Then the reaction mixture was stirred at room temperature for 14 hours. The precipitate was removed by filtration and then the solvent was removed with a rotavapor. The obtained residue was purified by flash chromatography on silica gel using dichloromethane as the eluant. The final product is an oil at room temperature. Yield: 5.23g (80 per cent). IR (pure): 1600, 1510 and 1460cm<sup>-1</sup> (aromatic C - C), 1240cm<sup>-1</sup> (COPh). NMR (DMSO): δ 7.42 (m, 5H, Ar), 6.94 (m, 4H, Ar), 5.05 (s, 2H, CH<sub>2</sub>Ph), 4.53 (q, 1H, C\*H), 3.65 (m, 2H, CH<sub>2</sub>Br), 1.31 (d, 3H, CH<sub>3</sub>).

(2-Bromo-(4'-hydroxyphenoxy)) (S)-1-methyl-ethane (6) A solution of compound (5) (5.23g, 0.016mol) in ethylacetate (30 ml) containing 10 % Pd/C (0.52g) was hydrogenated at 55 psi at 40°C during 48 hours. The catalyst was removed by filtration through Celite and the filtrate was purified by flash chromatography on silica gel using dichloromethane as the eluant. Yield: 3.54g (94 per cent). IR (pure): 3390cm<sup>-1</sup> (alcohol), 1600, 1520 and 1430cm<sup>-1</sup> (aromatic C – C), 1220cm<sup>-1</sup> (COPh). NMR (DMSO):  $\delta$  6.75 (m, 4H, Ar), 4.40 (q, 1H, C\*H), 3.62 (m, 2H, CH<sub>2</sub>Br), 1.28 (d, 3H, CH<sub>3</sub>).

(4-(2-Bromoethyloxy)-4'((2'-bromo-(S)-1'-methyl)ethyloxy))phenylbenzoate (7) Dicyclohexylcarbodiimide (3.15g, 0.015mol) and dimethylaminepyridine (0.1g) were added to a stirred mixture of alcohol (6) (3.54g, 0.015mol) and acid (2) (3.75g, 0.015mol) in anhydrous tetrahydrofurane (50ml). The reaction mixture was stirred at room temperature for 3 hours and the white precipitate is removed by filtration. The solvent is then removed with rotavapor and the crude product is purified by flash chromatography on silica gel using dichloromethane as the eluant. Yield: 5.13 (73 per cent); ( $\alpha$ ) = + 2.74 $^{0}$  (CH<sub>2</sub>CL<sub>2</sub>). IR (Nujol): 1740cm<sup>-1</sup> (ester), 1620, 1500 and 1460cm<sup>-1</sup> (aromatic C - C), 1290 and 1260cm<sup>-1</sup> (COPh). NMR (CDCL<sub>3</sub>):  $\delta$  8.15 (d, 2H, Ar), 7.12 (d, 2H, Ar), 7.00 (m, 4H, Ar), 4.52 (q, 1H, C\*H), 4.37 (t, 2H, CH<sub>2</sub>OPh), 3.67 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>Br), 3.49 (m, 2H, CH<u>CH<sub>2</sub>Br</u>), 1.47 (d, 3H, CH<sub>3</sub>). Melting point:79°C.

(4-(2-(Iodo)ethyloxy)-4'((2'-iodo-(S)-1'-methyl)ethyloxy))phenylbenzoate (8) <sup>10</sup> The mixture of sodium iodide (6.72g, 0.0448mol) and dried acetone (200ml) was cooled with an ice bath and the dibromo (7) (5.13g, 0.0112mol) diluted in ml dried acetone was added dropwise. Then the reaction mixture is stirred at room temperature

for 16 hours. The sodium bromide precipitate was filtered and washed with acetone. The solvent was removed from the filtrate and the product was dried in vacuo at  $60^{\circ}$ C. Yield: 3.5g (56 per cent). IR (Nujol): 1720cm<sup>-1</sup> (ester), 1600, 1520 and 1470cm<sup>-1</sup> (aromatic C - C), 1260cm<sup>-1</sup> (COPh). NMR (CDCL<sub>3</sub>):  $\delta$  8.13 (d, 2H, Ar), 7.10 (d, 2H, Ar), 6.95 (m, 4H, Ar), 4.50 (q, 1H, C\*H), 4.30 (t, 2H, CH<sub>2</sub>OPh), 3.45 (m, 4H,CH<sub>2</sub>I), 1.47 (d, 3H, CH<sub>3</sub>). Melting point: 82°C.

(4-(2-(acryloyloxy)ethyloxy)-4'-(2'-(acryloyloxy)-(S)-1-methyl-ethyloxy)) phenyl Potassium fluoride (1.6g, 0.0276mol) and diiodo (8) (3.5g. -benzoate (9) 11 0.0063mol) were stirred together in N,N-dimethylformamide (100ml) at room temperature for one minute. Acrylic acid (0.1g, 0.014mol) was then added to the reaction mixture and the whole stirred at room temperature for 48 hours. The product was extracted from the reaction mixture with diethylether, the ethereal extracts washed three times with equal volumes of water to remove the N,N-dimethylformamide and dried under Na<sub>2</sub>SO<sub>4</sub>. The solvent is removed with rotavapor at room temperature and the product is purified by flash chromatography on silica gel using dichloromethane as the eluant. Yield: 2.25g (80 per cent); ( $\alpha$ ) = -2.762° (CH<sub>2</sub>CL<sub>2</sub>). IR (Nujol): 1732 cm<sup>-1</sup> (ester), 1618, 1517 and 1463 cm<sup>-1</sup> (aromatic C - C), 1288 and 1254 cm<sup>-1</sup> (COPh), 1645, 995 and 910 cm<sup>-1</sup> (vinyl groups). NMR (CDCL<sub>3</sub>): δ 8.15 (d, 2H, Ar), 7.12 (d, 2H, Ar), 6.98 (m, 4H, Ar), (6.50 (2d, 2H), 6.19 (2d, 2H), 5.90 (2d, 2H), vinyl protons), 4.57 (m, 3H,  $C^*H$  and  $CH_2\underline{CH_2}OCO$ ), 4.30 (t, 2H,  $\underline{CH_2}OPh$ ), (m, 2H, CHCH2OCO), 1.47 (d, 3H, CH3). HPLC (MeOH): 100% pure. Elemental analysis: C 65.02, H 5.06 (theory C 65.45, H 5.45). Mesomorphic properties: Crystal 1 - 58°C - Crystal 2 - 63°C - Cholesteric - 67°C - Isotrope.

## Synthesis of the binaphthol acrylate

### Scheme 2

(R)-(+)-1,1'-Bi-2-naphthol (10.0g, 0.036 mol) and 4-hydroxybutyl acrylate (5.28g, 0.036 mol) were dissolved in 200 ml anhydrous tetrahydrofuran with

triphenylphosphine (9.35g, 0.0357mol) at room temperature. The mixture was then cooled with an ice bath and a solution of diethyl azodicarboxylate (5.8ml, 0.0357mol) in 10ml anhydrous tetrahydrofuran was added dropwise. The reaction mixture was stirred at room temperature overnight. The solvent was removed with a rotavapor at room temperature and the obtained residue was purified with one flash chromatography in dichloromethane and one flash chromatography dichloromethane / ethylacetate (95/5). The monoacrylate was dried under phosphorous pentoxyde with vacuum 5 days. Yield: 60% (8.3g). ( $\alpha$ ) = + 0.634 ° (CH<sub>2</sub>CL<sub>2</sub>). IR: 3436 cm<sup>-1</sup> (phenol), 1728.5cm<sup>-1</sup> (cetone). NMR (CDCL<sub>3</sub>): 8.01 (d, 1H), 7.87 (m, 3H), 7.30 (m, 1H), 7.05 (d, 7H), 6.29 (d, 1H vinyl), 6.02 (q, 1H, vinyl), 5.75 (d, 1H, vinyl), 5.04 (s, 1H, OH), 4.02 (m, 2H, CH2OCO), 3.82 (m, 2H, CH2OPH), 1.51 (m, 2H, -CH<sub>2</sub>OCO-), 1.25 (m, 2H,-CH<sub>2</sub>-CH<sub>2</sub>-OCO). HPLC (MeOH): 100% pure.

The cross-linker BAB structure is given in scheme 3.

$$CH_2$$
= $CHCOO$ — $\bigcirc$ — $\bigcirc$ — $\bigcirc$ OOCCH= $CH_2$ 
Scheme 3

## Preparation of the polymers/liquid crystal composites and cells

To investigate the mesomorphic and electro-optic properties, samples of nematic or cholesteric mixtures with various amounts of the chiral monomer and the diacrylate cross-linker were prepared by vacuum filling ITO coated, rubbed polyimide surface glass cells that were separated by 5 micron spacers. The samples were irradiated with UV light while an electric field was applied to place the liquid crystal/monomer mixture in the homeotropic state. We varied the UV irradiation time for several samples made with both BNA and BAB.

Samples were prepared with commercially available chiral materials E48, CB15, CE1 and R1011, and particularly with the standard chiral materials at concentrations of 28% and 30% which resulted in a green and blue reflected color, respectively. The sample were examined optically after exposure to 30 minutes UV irradiation (12.6 doses  $J/cm^2$ ). The average refractive indices ( $n_{average}$ ) were determined in the isotropic state with an Abbe refractometer. In the case of cells in the transparent medium, the pitch (p) was determined with the Cano-Wedge method. In other cases, the pitch (p) was calculated from the wavelength at maximum reflection ( $\lambda_0$ ) using the equation:

 $p = \lambda_o / n_{average}$ .

#### **RESULT AND DISCUSSIONS**

The experimental results are summarized in the following tables (table 1 to table 3).

#### One component system (AAMP)

Samples in the near infrared range:

TABLE 1 Physical data for the samples with the chiral diacrylate (AAMP) in the near infrared range. All pitch values were determined with the Cano-Wedge method.

	'ENTS Weight)	E4 (1)	-	E48 / CB15 (72% / 28%) (N*)		
San	nple	la	Ib	lc	1d	
% Chiral Diacrylate (Weight)		2	10	2	10	
Before	T <sub>N-I</sub> / T <sub>N*-I</sub> ( °C)	89.2	80.0	59.7	48.0	
Irradiation	Pitch* (micron)	4.960	4.782	0.406	0.380	
After	T <sub>N-I</sub> / T <sub>N*-I</sub>	70.4	69.9	43.2	41.0	
	( °C)	79.0	82.0	56.0	57.0	
Irradiation	Pitch* (micron)	4.425	2.851	0.365	0.370	

In the table 1, we notice that the higher is the chiral concentration, the shorter is the pitch.

Regarding to the transition temperatures, the introduction of a chiral dopant in a nematic material reduces the clearing temperatures before polymerization. After photopolymerization, the effect of the chirality of the additive (which leads to decrease the clarifications temperatures) is counterbalance with the effect of the cross-linked structure (due to the diacrylate moitie) which stabilizes the cholesteric state.

And logically, higher is the diacrylate concentration, higher is the gel transition temperature.

Samples in the visible range:

TABLE 2 Physical data for the samples with the chiral diacrylate in the visible range.

Solven (% in W		E48 // 0	reen mixtur CB15 / CE1 / 72 % // 28%)	R1011	Green mixture E48 // CB15 / CE1 / R1011 (70 % // 28%) + 0.8% BAB			
Sam	ple	2a	2b	2c	2d	2e	2f	
% of Chiral Diacrylate (% in Weight)		2	10	20	2	10	20	
Before	T <sub>N*-I</sub> (°C)	81.0	74.5	66.0	81.4	71.0	64.0	
UV	Cell	green	green	yellow	green	green	yellow	
Irradiation	λο (nm)	547.3	561.8	569.1	543.6	550.9	587.7	
	n average	1.566	1.565	1.564	1.567	1.5665	1.565	
	Pitch (micron)	0.349	0.359	0.364	0.347	0.352	0.375	
After	Tg and T <sub>N*-I</sub>	70.7	53.7	67.4	71.0	67.5	68.7	
1137	( °C)	81.0	78.0	78.0	80.0	73.0	79.0	
UV	Cell	bluish white	yellowish green	white	green	yellowish green	white	
Irradiation	λο (nm)	537.5	525.8	-	527.9	525.4	-	
	n average	1.567	1.567	1.567	1.569	1.569	1.569	
	Pitch (micron)	0.343	0.336	-	0.336	0.334	-	

In the table 2, we notice that the evolution of the pitch values in the monomeric state is opposite to the previous examples because in this case the solvent mixture is a right handed chiral material. A whitish color is then observed for the concentration of 20%

of the chiral diacrylate which is probably due to the scattering of the polymer network. In fact, a high scattering is observed in the focal conic state of the 20% samples. Moreover, for all the studied samples we observed a decrease in the pitch after UV polymerization because of the polymer network formation.

## Two components system (BNA and BAB)

TABLE 3 Physical data for the samples with the binaphthol acrylate in the visible range.

		V 131010	. range.								
Solver (% in V		Green mixture E48 // CB15 / CE1 / R1011 (72 % // 28%) + 0.8% BAB			Blue mixture E48 // CB15 / CE1 / R1011 (70 % // 30%)						
San	ple	3a	3b	3c	3d	3e	3f	Зg	3h	31	
% of (% in V	BNA Veight)	2	5	10	.08% BAB 	2	108% BAB	5	- 0 8% BAB -7	- 0 8 4 BAB	
Before	Cell (reflective state)	yellow	yellow -ish red	red	green yellow	green yellow	yellow	yellow	pink -ish red	pink red	
UV	λο (nm)	585	650	710	540	545	592	590	618	655	
irradia -tion	Il average	1.565	1.5665	1.567	1.573	1.570	1.577	1.575	1.576	1.567	
	Pitch	0.374	0.415	0.453	0.343	0.347	0.375	0.375	0.392	0.418	
After	Cell (reflective state)	green	yellow -ish green	bluish white	green	green yellow	bluish white	bluish green	bluish white	white	
U.V	λο (nm)	506	520	-	507	512	-	512	594	-	
irradia -tion	I) average	1.570	1.566	1.5655	1.5705	1.570	1.565	1.560	1.575	1.560	
	Pitch	0.322	0.332	-	0.323	0.326	-	0.328	0.377		

BNA concentrations of 2,5,7 and 10 percent by weight of the liquid crystal were added to standard PSCT material with a BAB concentration of 0.8%. The addition of BNA resulted in an increase of pitch so that the resultant colors for the increasing BNA concentrations were green, yellow-green, reddish-yellow and red.

We observed that for both 28% and 30% cholesteric mixtures the pitch value increases regularly with the concentration of the BNA before and after UV irradiation. In those samples containing 7 and 10% BNA, the reflective state begin to exhibit a whitish color. This could be attributed to the inhomogenous distribution of the chiral concentration through the process of polymerization.

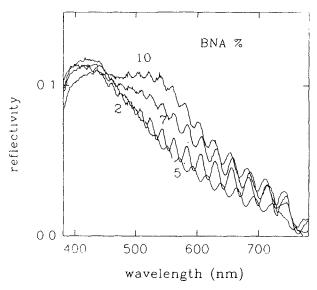


FIGURE 1 Reflectance versus wavelength in the reflecting state for the four blue samples with 0.8% BAB after UV irradiation.

The reflectance versus wavelength was mesured in the reflective state for the four blue samples with 0.8% BAB (samples 3d, 3f, 3h and 3i) after UV irradiation (see figure 1). As expected, there is a broadening in the reflected spectrum for the 7% (sample 3h) relative to the 2% (sample 3d) and the 5% (sample 3f). The broadening is further widespread in the 10% (sample 3i).

The spread in reflected wavelengths is the probable reason for the white reflection in the higher BNA concentration samples.

In the focal conic state, a slight increase in reflected intensity can be observed for the 7% (sample 3h) and the 10% (sample 3i) (see figure 2).

Moreover, the samples appeared transparent in the focal conic state indicating weak scattering which is an improvement from the whitish samples obtained with 20% AAMP with the green mixture (samples 2c and 2f) which exhibit a high scattering in the focal conic state.

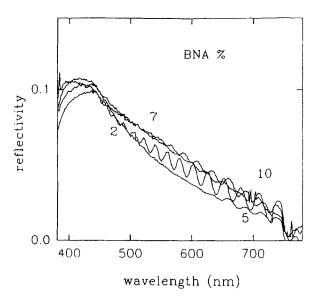


FIGURE 2 Reflectance versus wavelength for the four blue samples in the focal conic state after UV irradiation.

Figure 3 shows the reflectance versus wavelength in the reflecting state for two samples containing 2% and 5% BNA but no BAB (samples 3e and 3g) after UV irradiation. There is an increase in reflectivity over the reflected wavelength range in the 5% sample relative to the 2% sample.

Figure 4 shows the reflectance versus wavelength in the scattering state. There are two peaks in the spectrum for each sample. For the 2% sample, the peaks are at 420 nm and 500 nm, while for the 5% sample, the two peaks are at 460 nm and 600 nm. The two peaks in the reflection spectra of Figure 4 indicate a chiral phase separation upon polymerization. As mentioned previously, as polymerization occurs, the chiral monomer will be pulled into the polymer network. This will create a greater chiral concentration around the polymer network than in the bulk.

Consequently, for a given volume element, there will be two regions of different pitch which will result in two different Bragg reflected wavelengths. The fact that the 5% sample had Bragg reflected peaks shifted to longer wavelength than the 2% sample is consistent with the higher chiral concentration which results in an increase in pitch.

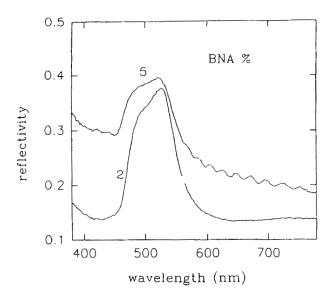


FIGURE 3 Reflectance versus wavelength in the reflecting state for two samples containing 2% and 5% BNA but no BAB after UV irradiation.

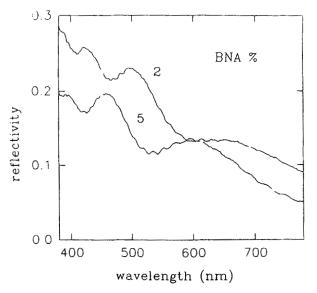


FIGURE 4 Reflectance versus wavelength in the scattering state for two samples containing 2% and 5% BNA but no BAB after UV irradiation.

In general, the double-peak spectrum occurred in most of the reflection spectra when the sample is in the focal conic state and the planar state showed a reflection spectrum that was broadened.

Measurements showed the threshold voltage to switch from the planar state to the focal conic state decreased with increasing BNA concentration. This could be due in part to the decrease in drive voltage with increasing pitch (pitch increase with BNA concentration). There also could be a decrease in drive voltage due to the formation of anisotropic polymer networks which reduce the energy required to switch from the planar state to the focal conic state.

#### CONCLUSION

A white reflective display can be made with a PSCT material and chiral monomers. The exact nature of the white reflection is not firmly established but appears to be due to broadening of the reflected spectrum. The broadening of the reflected spectrum is possibly due to the overlap of reflected spectrum from a two pitch region formed by chiral incorporation into a polymer network.

There is ongoing research to improve contrast ratio and overall white reflected intensity.

## **REFERENCES**

- 1. D. K. Yang, L.-C. Chien, J. W. Doane, <u>International Dispaly Research</u> Conference Digest, p. 49 (1970).
- 2. D. K. Yang, L.-C. Chien, J. W. Doane, Appl. Phys. Lett., 60, 3102 (1992).
- L. M. Blinov, <u>Electro-optical and Magneto-optical Properties of Liquid Crystals</u>, (Wiley, Chichester, U. K., 1983).
- 4. H. Stegemeyer, K. J. Mainusch, Chem. Phys. Lett., 3, 540, (1970).
- 5. Crivello, J. V.; Deptolla, M.; Ringsdorf, H. Liq. Cryst., 3, 235 (1988).
- Mitsunobu, O. <u>Synthesis</u> 1-28 (1981).
- 7. Ghirardelli, R. J. Am. Chem. Soc. 95, 4987 (1973).
- 8. Garegg, J.; Johansson, R.; Samuelson B. Synthesis 168 (1984).
- 9. Classon, B.; Garegg, J.; Samuelsson, B. Can. J. Chem. <u>59</u>, 339 (1981).
- 10. Finkelstein, H. Ber. Dtsch. Chem. Ges., 43, 1528 (1910).
- 11. Clark, J. H.; Miller, J. M. Tetrahedron letters, 7, 599 (1977).
- 12. R. Cano, P. C. Chatelain, R. Hebd. Seances Acad. Sci., 253B, 564, (1971).

## **AKNOWLEDGEMENT**

This work was supported in part by the NSF ALCOM Grant No DMR89-20147 and ARPA / HDDT MDA972-91-J-1020.