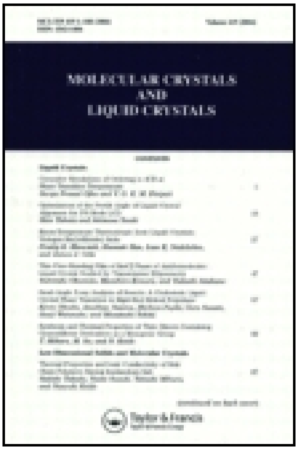

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# Thermochromism in Chiral Mixtures Exhibiting Injected Smectic Phases

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# Thermochromism in Chiral Mixtures Exhibiting Injected Smectic Phases†

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Despite their advantages, most synthetic chiral nematic systems are not useful for thermochromic applications because of their low smectic transition temperatures. To overcome this problem, chiral "hybrid" mixtures of polar and nonpolar liquid crystals, which exhibit injected smectic phases, have been investigated. The thermochromic properties of hybrid mixtures for a range of chiral nematics are described.

*Keywords: cholesteric liquid crystals, thermochronism, injected smectics*

## INTRODUCTION

Thermochromism in cholesteric liquid crystals occurs as a result of the pretransitional unwinding of the helix just above a smectic phase[1] and this property has found widespread use in a range of thermometric and thermographic devices.[2] These applications demand materials with low melting points, short pitch lengths and smectic transitions just below the sensing temperature. Mixtures are needed to satisfy these requirements over a wide operating temperature range (≈ −50°C to ≈ 150°C). For a number of years the only available materials were cholesteryl esters, which are not satisfactory because of their limited chemical/photochemical stability and range of physical properties. However, in recent years the need for stable chiral additives for electro-optical displays has stimulated the development of synthetic chiral nematic materials and several of these are now available in commercial thermochromic mixtures.[3] Despite their advantages, many synthetic chiral nematic liquid crystals are not useful for ther

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mochromic applications because of their low smectic transition temperatures. In an attempt to overcome this problem, we have investigated the enhanced smectic transitions found for the injected smectic phases[4] of 'hybrid' mixtures exhibiting chiral nematic liquid crystal phases and consisting of strongly polar and nonpolar† materials.

## EXPERIMENTAL

Transition temperatures were measured by optical microscopy using a Mettler heating stage (FP52) and control unit (FP5). Enthalpies were obtained using a Mettler TA3000 DSC.

Selective reflection studies were made on samples mounted in glass cells 10 μm thick with rubbed polyimide alignment[5] on the inner surfaces. The spectra were recorded in transmission using a Perkin Elmer 554 UV/visible spectrometer.

The pitch length ($P$) is defined as the thickness for a 360° rotation of the director and is related to the wavelength of selective reflection ($\lambda$) by:

$$\lambda = \bar{n} P$$

where

$$\bar{n} = (n_e + n_o)/2$$

## RESULTS AND DISCUSSION

S-(+)-4-(2″-methylbutyl)-4′-cyanobiphenyl[6] is a short pitch length (0.15 μm) chiral nematic material which is commercially available as CB15 from BDH Ltd. Although it has a low cholesteric to isotropic transition temperature (−30°C) it can readily be mixed with commercial nematic liquid crystal mixtures to produce room temperature cholesteric phases selectively reflecting in the visible. In Figure 1, the wavelength of selective reflection ($\lambda$) as a function of reduced temperature ($T/T_{\text{Ch-I}}$) is shown for mixtures containing 50% by weight of CB15 in nematic hosts comprising cyanobiphenyls (BDH E44), phenylcyclohexanes—PCH's, (Merck ZLI 1132) and cyclohexylcyclohexanes—CCH's, (Merck ZLI 1695). The cholesteric to isotropic transition temperatures for these mixtures are 41°C, 28°C and 26°C

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†Materials are referred to as nonpolar if they do *not* contain a strongly polar terminal group such as a cyano-group.

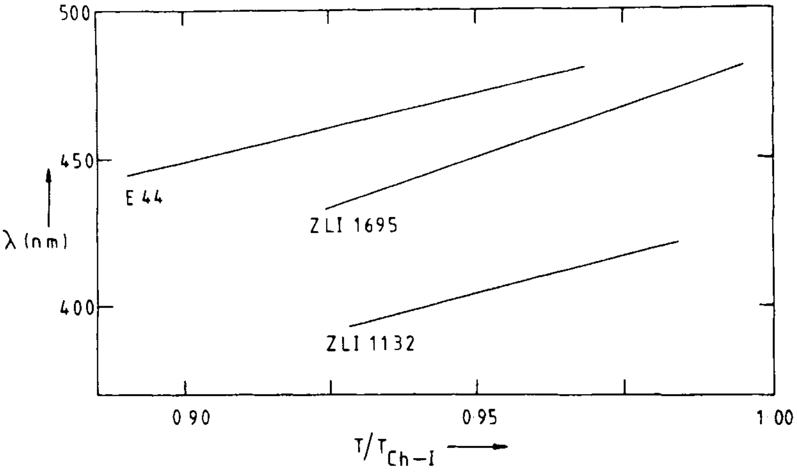


FIGURE 1 Temperature dependence of selective reflection wavelengths for mixtures containing 50% by weight of CB15.

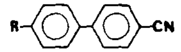
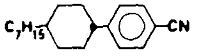
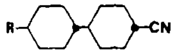
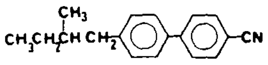
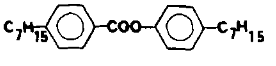
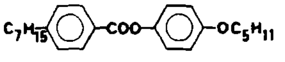
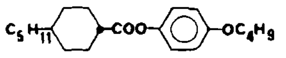
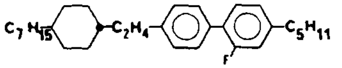
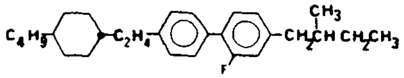
respectively. It is interesting to note that, in these mixtures and other similar mixtures[7] based on materials with terminal cyano-groups, the wavelength increases with temperature. This is opposite to that normally found for nonpolar materials such as the cholesteryl esters.

Although room temperature short pitch length cholesterogens can readily be produced in this way, the rapid divergence of the pitch needed for thermochromic applications also requires the presence of a smectic phase. In the above mixtures this occurs only at temperatures below −20°C. Previous work[4] on multiplexing mixtures for twisted nematic devices showed that hybrid mixtures of polar cyanobiphenyls and nonpolar benzoate esters usually exhibit injected smectic phases. The thermal stability of these smectic phases is enhanced by long alkyl chains and materials with benzene rings.[8] Therefore we studied mixtures of 40 wt % of CB15 in S2 (BDH long chain biphenyl smectic mixture $S_A$—$\tilde{N}$, 48°C, N—I, 49°C) and 40 wt % of CB15 in the benzoate ester ME77 (see Table I). The phase diagram of this mixture is shown in Figure 2. It should be noted that the right hand side of the diagram is not 100% nonpolar material because of the presence of the polar CB15.

The temperature dependence of the wavelength of selective reflection for mixtures at four positions on this phase diagram are shown in Figure 3. There are two important conclusions:

(*a*) the twisting power of CB15 is greater in the nonpolar ME77 host;

TABLE I

| POLAR | | mpt °C | S–N/Ch °C | N/Ch–I °C | Δn |
|---|---|---|---|---|---|
| BDH S2 |  | −10 | 48 | 49 | 0.23 |
| PCH 7 |  | 30 | – | 57 | 0.12 |
| ZLI 1167 |  | 8 | 32 | 83 | 0.06 |
| CB 15 |  | 4 | – | (−30) | 0.23 |
| | (Pitch = 0.15 μm) | | | | |
| NON-POLAR | | | | | |
| ME 77 |  | 24 | – | 32 | 0.14 |
| ME 705 |  | 45 | | 61 | 0.15 |
| OE 504 |  | 49 | – | 81 | 0.08 |
| I 75 |  | – | 80 | 106.5 | 0.14 |
| I 42MB |  | – | 6 | 72 | 0.14 |
| | (Pitch = 0.22 μm) | | | | |

(*b*) the divergence of the pitch ($dP/dT$) increases with increasing concentration of the non polar ME77.

The latter is consistent with the increasing first order nature of the smectic to cholesteric transition. The proximity of the smectic to cholesteric and cholesteric to isotropic transitions did not enable accurate enthalpies for the two transitions to be resolved. However, in similar nematic mixtures without the CB15, the enthalpies of the smectic to nematic transitions varied approximately linearly across the phase diagram from a value of 0.01 J/gm for the pure biphenyl mixture to a value of 0.1 J/gm for the pure benzoate ester. This ability

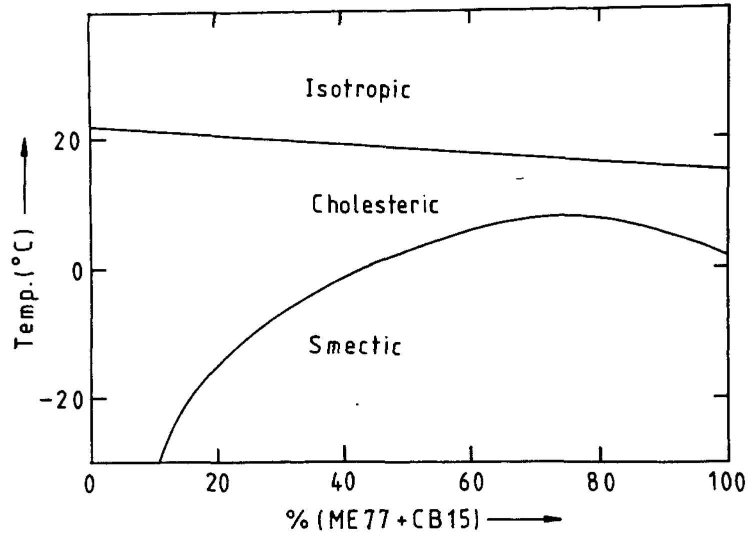


FIGURE 2 Phase diagram for mixtures made up from the components (*a*) S2 + 40% by weight of CB15 and (*b*) ME77 + 40% by weight of CB15.

to vary $dP/dT$ is important in the formulation of commercial thermochromic mixtures, and previously this has only been achieved by reducing the twisting power of the mixture by, for example, reducing the optical purity.[3] This method often has the undesirable side-effect of extending the temperature band of the blue reflection by several

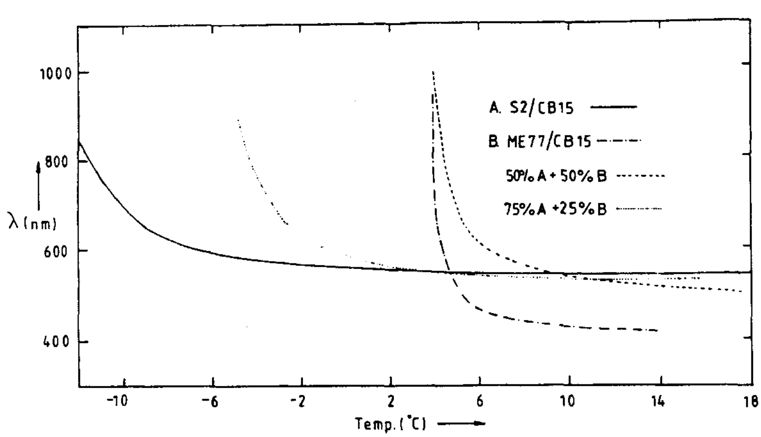


FIGURE 3 Temperature dependence of selective reflection wavelengths for hybrid mixtures of cyanobiphenyls and benzoate ester.

degrees, presenting problems of ambiguity in reading thermometer strips.

Colour purity, or breadth of the selective reflection peak ($\Delta\lambda$), is another important property affecting the appearance of thermochromic devices and is related to the birefringence ($\Delta n$) of the material

$$\Delta\lambda = \Delta n\ \lambda$$

Hybrid chiral nematic mixtures can be formulated from a wide selection of commercially available materials offering a large range of birefringence from 0.05 to 0.23 (see Table I). The thermochromic properties for selected mixtures (Table II) are shown in Figures 4 and 5. These demonstrate thermochromism in the temperature range from 0°C to 42°C, making them suitable for many thermometer applications. Access to higher temperature mixtures can also be gained by the technique, while maintaining melting points below room temperature.

TABLE II

CHIRAL 'HYBRID' MIXTURES

| A | B | A : B wt% | S–Ch °C | Ch–I °C |
|---|---|---|---|---|
| S2 60<br>CB15 40 | DE504 60<br>CB15 40 | 30 : 70 | +3 | 32 |
| PCH7 60<br>CB15 40 | ME705 60<br>CB15 40 | 30 : 70 | −1 | 25.3 |
| ZLI 1167 60<br>CB15 40 | ME705 60<br>CB15 40 | 30 : 70 | −2 | 29.5 |
| S2 60<br>CB15 40 | I 75 50<br>I 42MB 50 | 25 : 75 | +42 | 72 |

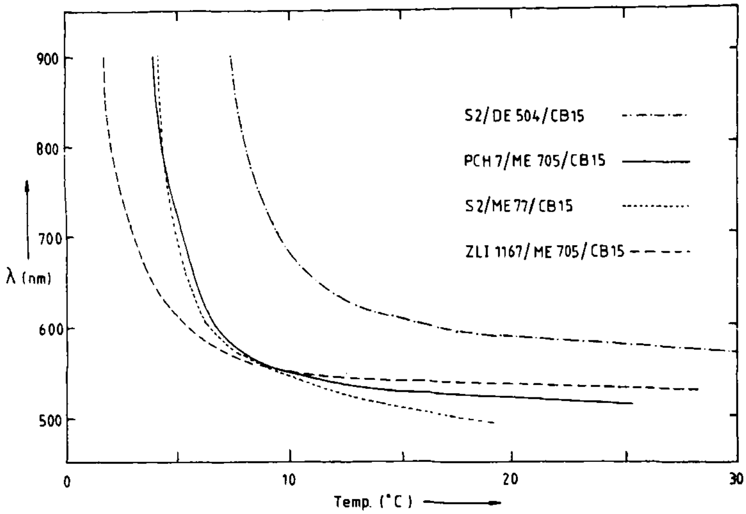


FIGURE 4 Temperature dependence of selective reflection wavelengths for hybrid mixtures from Table II.

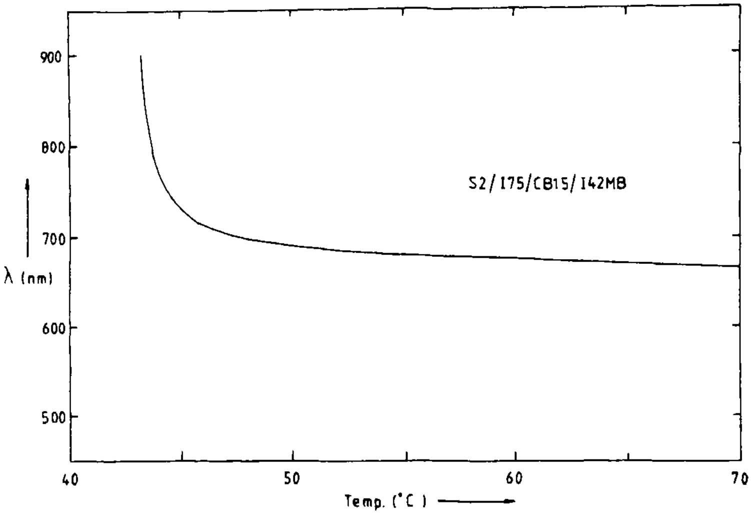


FIGURE 5 Temperature dependence of selective reflections for hybrid mixture containing I compounds (BDH Ltd)—e.g., I 75—see Table I.

## CONCLUSIONS

Thermochromism has been demonstrated in chiral mixtures exhibiting injected smectic phases. This novel technique allows a much wider selection of stable materials suitable for thermochromic mixture formulation enabling:

(*a*) wider temperature range of operation;
(*b*) wider selection of physical properties such as birefringence;
(*c*) control of $d\lambda/dT$ without extending the "blue tail."

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