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## Liquid Crystals

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## INVITED TOPICAL REVIEW

### Thermochromic liquid crystals

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Thermochromic liquid crystals have been exploited in novelties and in high-technology applications alike since the earliest years of liquid crystal technology. They have also played a central role in the elucidation of the structures of liquid crystal phases and their inter-relationship, the optics of mesophases, the nature of phase transitions and their static and dynamic continuum theory. Despite this long history, many of the materials and applications have been continually exploited for several decades, indicating an early achievement of maturity in this area of liquid crystal technology. This article briefly reviews the main materials, applications and devices, and attempts to place them in the context of related developments in liquid crystal science.

**Keywords:** chiral nematic; cholesteric; thermography; microencapsulation; applications

#### 1. Introduction

If in the field of liquid crystal science a single material can be said to have changed the world, a strong case can be made for that material being cholesteryl benzoate. It was Reinitzer's study of the properties of cholesterol esters [1] which led to the recognition of liquid crystals as distinct phases of matter, and although his early communications to Lehman described both cholesteryl acetate and benzoate, the enantiotropic liquid crystalline behaviour of the benzoate derivative with its prominent display of what we now recognise as cholesteric colour play and blue phase formation meant that the latter compound commanded the principal attention. The short-pitch chiral nematic phases which display these colour reflection effects show microscopic textures and flow properties which resemble those of smectic liquid crystals rather than N materials. Before the elucidation of the structures of the various liquid crystalline phases, the liquid crystals observed by Reinitzer in cholesterol derivatives were assigned to a distinct phase type, designated the cholesteric (Ch) phase. The relationship of the materials is now understood and the terms cholesteric and chiral nematic, along with the abbreviations Ch and N\*, are used interchangeably. Understanding of the relationships between these phase structures represented one of the landmark achievements in the early development of liquid crystal science. The chiral nematic phase likewise played a central role in the understanding of liquid crystal optics.

In the early period of exploitation and commercialisation of liquid crystalline phenomena, cholesteric and thermochromic liquid crystals likewise played a prominent role: thermochromic systems were not reliant on the development or application of then-costly microelectronics. The thermochromic liquid crystal thermometer became a popular and affordable item well before liquid crystal displays were widespread. Their use continues to the present day, and many innovations in materials, processing and device fabrication have been driven by the application of these materials.

This article seeks to place some of these key developments in their proper context and to examine the current status and applications of thermochromic materials.

#### 2. Chiral nematic liquid crystal structure and selective reflection

Thermochromic liquid crystal devices exploit the optical properties of the chiral nematic phase. The structure of this phase is well established; as in the nematic phase, the constituent calamitic ('rod-shaped') molecules show only orientational order. The order is imperfect and is quantified by an order parameter  $S$ . If the angular distribution of the long molecular axes of the molecules is expanded in terms of Legendre polynomials,  $S$  represents the weight of  $\langle P_2(\cos \theta) \rangle$ , the polynomial which has the symmetry of the nematic phase. In a local volume of nematic liquid, the most

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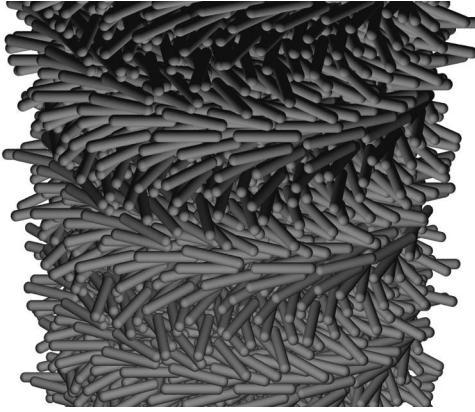


Figure 1. Illustrative structure of the chiral nematic phase.

probable direction of the molecular long axes defines the director, and also coincides with the principal optic axis of the uniaxial phase.

In a chiral nematic phase, the director spirals about a helical axis to which it is everywhere perpendicular (Figure 1), and the optical properties are symmetric about this axis. The nematic phase is (almost invariably [2]) optically a positive uniaxial material, that is:

$$n_e > n_o$$

where  $n_e$  and  $n_o$  are refractive indices measured with the electric vector polarised respectively parallel and perpendicular to the molecular long axis. However, in the tightly twisted phases considered here, the unique optical axis is generally taken along the helical direction and the phase is then optically negative.

The optical properties of the chiral nematic phase for the case where the chiral pitch length  $p$  is comparable with the wavelength of light are remarkable and have served as a test case for understanding and analysis of the liquid crystalline state, and for the development of optical modelling techniques. For the case of light incident parallel to the helical axis, an analytical solution to the Maxwell equations can be derived [3], while for most practical situations numerical modelling is used and provides essentially exact agreement with experiment – provided the latter is conducted with sufficient care, particularly with regard to perfecting the alignment of the sample. The essential features of the optical behaviour are:

- Within a band of wavelength, circularly polarised light is reflected from the helical liquid crystal structure. The reflected light has the same sense of twist as the liquid crystal phase and does not undergo the change in handedness experienced by circular polarised light on ordinary reflection. The reflection [4, 5] is centred at a wavelength

$$\lambda = p \cdot (n_e + n_o)/2$$

and occurs over a band of width

$$\Delta\lambda = 2\lambda \cdot (n_e - n_o)/(n_e + n_o)$$

As the opposite sense of circular polarisation is not reflected, the reflectivity of the liquid crystal to unpolarised light is limited to 50%.

- Outside but in the vicinity of the reflected band, the phase shows very large optical rotatory power to incident linear polarised light. The rotation [6] in a layer of thickness  $d$  follows the equation

$$R = d \cdot \frac{\pi}{16} \cdot \left[ \frac{(n_e^2 - n_o^2)}{(n_e^2 + n_o^2)} \right]^2 \frac{p^3}{\Lambda^2 (p^2 - \Lambda^2)}$$

where  $\Lambda$  is the wavelength of light in the liquid crystal phase. The expression holds only for wavelengths well outside the reflection band. Note that for wavelengths shorter than the reflection band, the optical rotation has the same sense as the helical pitch of the liquid crystal, while the sense of rotation is reversed at long wavelengths. Simpler expressions have been derived [7] for the rotatory power on each side of the reflection band. At shorter wavelengths

$$R = \frac{-\pi \cdot \Delta n^2 \cdot p}{4\Lambda^2}$$

and at long wavelengths

$$R = \frac{\pi \cdot n^2 \cdot \Delta n^2 \cdot p^3}{4\Lambda^4}$$

For the purposes of examining the properties and applications of thermochromic liquid crystals, the selective reflection is of dominant importance and the rotatory power will not be discussed further.

Analysis of the selective reflection of light from a carefully aligned monodomain sample of chiral nematic liquid crystal has been examined in detail at both normal and oblique incidence, and provides a classic demonstration of the power of the now standard  $4 \times 4$  matrix method for the numerical modelling of liquid crystalline optical properties [8]. This study refines earlier work [4] and shows the key details of the selective reflection in detail:

- The reflection is analogous to Bragg reflection from a layered structure.
- At oblique angles of incidence (and reflection) the reflected light shifts to shorter wavelength according to a  $\cos\theta$  law.

- At oblique incidence, the reflected light becomes elliptically polarised.
- Only first order reflection is observed at normal incidence, while at oblique incidence higher order reflections can be obtained; the latter are generally rather weak.
- For liquid crystal films of finite thickness, optical interference fringes are superimposed on the reflection band.

The analysis of selective reflection from a chiral nematic layer has been extended to consider multidomain samples [9, 10]; in practice, chiral nematic samples with imperfect alignment show reduced saturation of the reflected colours, and in extreme cases appear as scattering media rather than Bragg reflectors.

The structure adopted by a short-pitch chiral nematic phase in a spherical droplet is of considerable importance for devices and other practical applications. The alignment adopted in the case of tangential boundary conditions is illustrated in Figure 2.

In this structure, a line singularity penetrates the droplet, shown aligned with the  $x$ -axis; elsewhere the director configuration is described by reference to a series of concentric spherical shells. The liquid crystal director in each shell forms a series of circular arcs which are cotangent at the  $x$ -axis. On passing from one shell of radius  $r$  to another of radius  $r - \delta r$ , there is a rotation  $\phi$  about the  $x$ -axis representative of the pitch length, so that  $\phi = \delta r/p$ . The liquid crystal directors in the two shells now intersect at a constant angle  $\phi$  at all points on the surface, when viewed from normal incidence. The normal incidence condition, however, is only satisfied for a ray of light directed at the precise centre of the droplet. Rays of

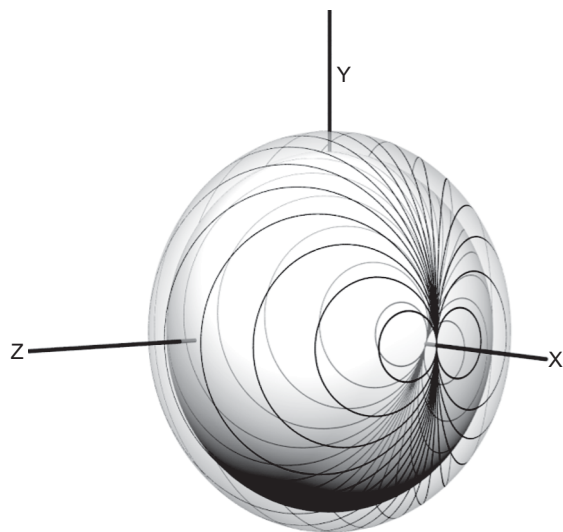


Figure 2. Liquid crystal director configuration in a spherical droplet of chiral nematic fluid.

light striking other regions of the drop are not only reflected at an angle, but experience a varying effective pitch length. Observationally, a chiral nematic droplet with this structure provides bright selective reflection of coloured light only from a small region close to its centre. The requirements on alignment of material in thermochromic devices will be returned to below.

Given knowledge of the reflection spectrum of a chiral liquid crystal sample, the array of colours which can be observed can be predicted by reference [11] to the standard observers and colour spaces defined by the CIE. In general, liquid crystal phases with a relatively high birefringence display brighter colours in consequence of their broader reflection bands. The colour saturation may be lower for the same reason, but also because the largely achromatic light scattering noted above also occurs from small imperfections in the alignment of the sample, and increases rapidly as the birefringence is raised.

In the chiral nematic phase described above, the helical axis develops along a unique direction perpendicular to the nematic director. On a microscopic scale, there is no reason to favour a particular helical axis; it is possible for a twist to develop uniformly along all directions perpendicular to the director, and locally this is the lowest energy configuration. The resulting structures are known as twist cylinders and they can pack into cubic structures which are the basis of the liquid crystal blue phases (BP). Partial long-range continuity of the director is achieved when the diameter of the twist cylinder corresponds to a quarter pitch length of the liquid crystal helix, but in a macroscopic volume of the phase the director continuity is inevitably broken by generation of an array of linear disclinations. The packing arrangements of twist cylinders in BP1 and BP2 are shown in Figure 3.

True Bragg reflection from the cubic structure of BP samples provides selective reflection of coloured light – which is not necessarily in the blue region of the spectrum. Compared with the common helical chiral nematic phase [12], the reflection occurs as a narrow peak in wavelength. Bragg reflections can, however, be observed at different wavelengths from different crystal planes of one sample. In most chiral liquid crystal systems, the BPs persist over a very short range of temperature close to the clearing point, and although BP optical effects are clearly visible in cholesteric samples and were described by Reinitzer, they are not commonly exploited in devices.

A matter of central importance in the use of colour-reflecting liquid crystals is that the light which is not reflected by the liquid crystal layer is transmitted with little change. If the liquid crystal is viewed against a white background, the liquid crystal and the background between them reflect all wavelengths and

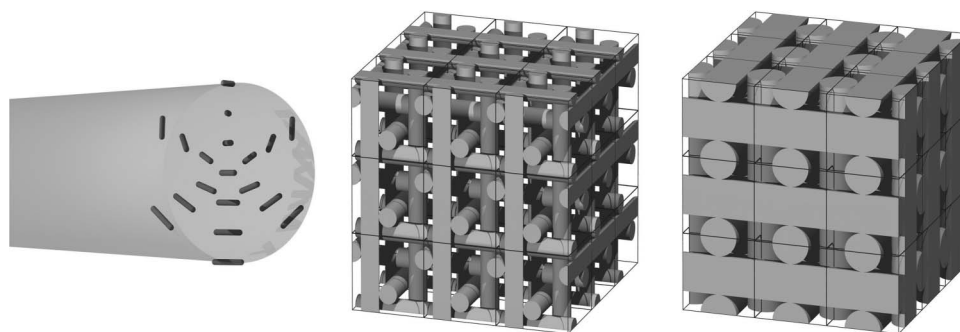


Figure 3. The structure of a twist cylinder and the packing order of such cylinders in BP1 (body centred cubic) and BP2 (simple cubic). The twist cylinder is depicted at the critical diameter where the director is continuous at the boundaries of adjacent cubic packed cylinders.

the colour is lost. Only by providing a dark or preferably black background can the liquid crystal selective reflection be seen to advantage. Thermochromic liquid crystal devices are invariably provided with a printed black background to maximise the colour contrast from the active layer.

### 3. Thermochromism in chiral nematic liquid crystals

The preceding paragraph describes the origin of the selective reflection of coloured light from chiral liquid crystal layers, which depends on the helical pitch length. In order to obtain a thermochromic effect, it is necessary for the pitch to vary rapidly as a function of temperature. Chiral nematic materials in general show a small variation in reflected colour with temperature which can be attributed to changes in intermolecular potentials and density, and these changes are hardly noticeable under ordinary conditions. Thermochromic liquid crystals conventionally exploit phase transitions to mediate an abrupt and dramatic colour change, and two transitions are commonly exploited:

- The  $N^*$ -I transition can be used to provide a device which shows an almost constant coloured reflection up to a target temperature. Above this temperature the colour disappears and is replaced by that of the black background. On cooling again the colour may return quickly or alignment effects can provide a pseudo-irreversible colour change.
- Most commonly, a  $N^*$ -S transition is exploited. Above but close to the transition temperature the pitch of the  $N^*$  phase is lengthened, resulting (Figure 4) in a reflected colour which progressively moves from the blue toward the red end of the spectrum and finally to black (infrared reflection) as the temperature is lowered.

The well-known liquid crystal thermometers and novelties which pass from black at low temperature to red and progressively through the spectrum to

blue as they are warmed rely on a S- $N^*$  transition. Overwhelmingly, the underlying phase is smectic A, as this phase is common in the materials used and the low enthalpy of the transition provides pre-transitional effects which extend up to 10°C or more above the phase change. Materials can be formulated which have other underlying phases; a  $S_C$ - $N^*$  transition provides a thermochromic effect essentially indistinguishable from the  $S_A$ - $N^*$  case. Selective reflection from the  $S_C^*$  has not been used in devices: even if the pitch length of the  $S_C$  phase is short enough to reflect light, its alignment is usually such as to give little selective reflection below the S- $N^*$  transition. Materials also exist in which a hexatic phase underlies the  $N^*$ . The large enthalpy of transition [13] then provides a rapid loss of colour reflection on cooling into the smectic, with little pre-transitional colour change. This effect has likewise been little exploited in devices and products.

As can be seen from Figure 4, the variation of peak-reflected wavelength as the temperature is changed above a  $S_A$ - $N^*$  transition is markedly non-linear. The shape of the curve is mediated by the pre-transitional effects in the chiral nematic phase [5], which are determined by the thermodynamic and elastic properties of the liquid crystal and by the limiting pitch of the material – that is, the pitch in the absence of any pre-transitional unwinding. The functional form of the temperature dependence of pitch in the vicinity of the transition has been analysed using various assumptions about the mechanism of unwinding [14, 15], but either analysis provides an equivalent fit to experimental results [16]. Alben's expression [15] of the form:

$$p = p_0 + \frac{a}{(T - T_0)^{\nu}}$$

with  $\nu \sim 2$  provides a simple and adequate fitting function. As shown in Figure 4, as the temperature is raised the reflection passes rapidly through the red region of

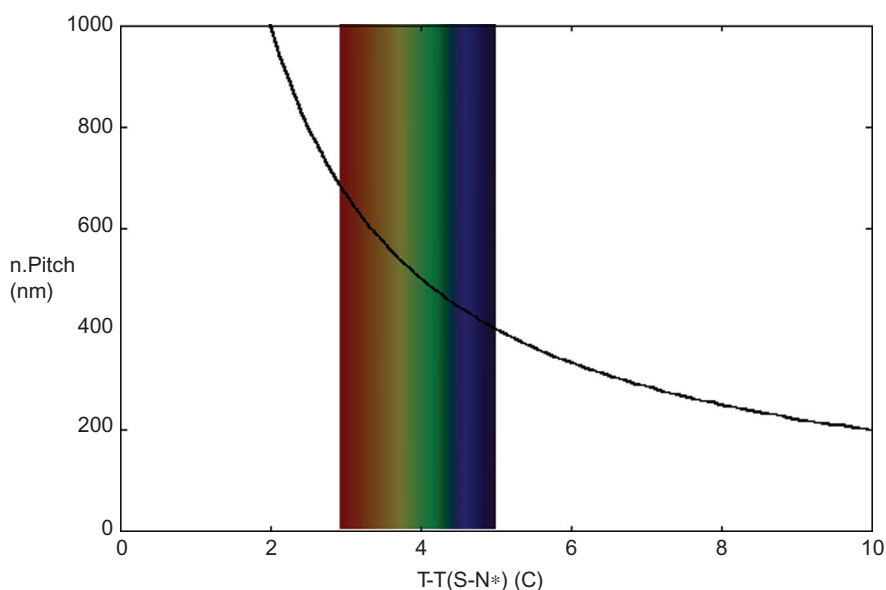


Figure 4. Illustrative change of pitch and reflected colour in a chiral nematic phase above a  $S_A-N^*$  transition.

the spectrum, and more gradually through the blue. Experimentally, different classes of thermochromic liquid crystals show this non-linearity to appreciably differing degrees resulting, in some formulations, in compression of the red colours into a very narrow band. The form of the curve has a fundamental and important consequence: by adjusting the limiting pitch of a  $N^*$  formulation while leaving the  $S_A-N^*$  transition temperature unchanged, the temperature range over which the formulation passes through the visible spectrum can be adjusted. This issue will be returned to below, in the section on materials.

Thermochromism at the  $N^*-I$  transition relies on the destruction of the special optical properties of the material on passing through the clearing point. A well-aligned planar sample of  $N^*$  material with a pitch appropriate to selective reflection of visible light can show an abrupt disappearance of the reflected colour at the clearing point. Poorly formulated materials can show a significant width of biphasic behaviour at the transition, resulting in an indistinct colour change. Formation of BPs is also common in compositions with a biphasic range and can result in additional colour transition. Typically the reflection colour of the formulation is adjusted into the green or red regions of the spectrum, these colours being indicative of a safe or undesired condition below the clearing temperature, according to the application. For example, a formulation may be used which is green below about  $5^\circ\text{C}$ , indicating a safe working temperature for a domestic refrigerator.

If such a mixture is cooled from the isotropic phase to the  $N^*$  phase, the resulting alignment of the liquid

crystal helices may not be in the uniform planar structure which provides bright reflection: either a focal conic or a multidomain structure can be formed and result in a scattering, largely colourless state on cooling. The well-aligned state is normally recovered over a period of time, which can be seconds or months in duration. Control of this alignment period provides routes to the manufacture of devices in which the colour transition is fully reversible, such as might be required for the fridge temperature indicator described above, or to irreversible devices in which the colour is lost more or less permanently when the clearing point is exceeded. These irreversible devices may, for example, be used to show when perishable goods have not been stored correctly, providing a permanent record of their history. The materials and methods used to achieve reversible or irreversible behaviour are well founded in liquid crystal technology, but are generally regarded as proprietary by device manufacturers.

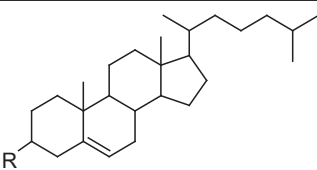
#### 4. Materials for thermochromic devices

As outlined above, the basic requirements for a thermochromic liquid crystal include a short-pitch chiral nematic phase with – in most cases – an underlying smectic phase. The temperature of the  $S_A-N^*$  transition determines the lower limit of temperature at which thermochromic effects can commence, while the temperature range of the colour play depends on the intrinsic  $N^*$  pitch length and the details of the pre-transitional effects which lengthen the pitch. It will be apparent that a huge range of chemical structures is capable of providing these properties, since most

nematogenic liquid crystal series can be induced to show a smectic phase by substitution of long-chain terminal groups, and a wide range of chiral branched substituents will provide the necessary twisting power to yield a pitch length in the optical wavelength range. Despite this apparent wealth of possibilities, only two basic series of liquid crystals have ever achieved considerable importance as thermochromic liquid crystals, these being, respectively, esters of cholesterol, and ester derivatives of (S)-4-(2-methylbutyl)phenol. The reason for this lies in the relatively simple requirements of the liquid crystalline properties of the materials, which offers little incentive to explore more complex structures, and the dominant place of the cost of liquid crystal materials in the production of the final device. It is therefore more pertinent to examine these established systems and the contrasts between them, than to review a large range of compounds which might theoretically be exploited in thermochromic applications. It should also be understood that closely analogous phases and optical effects can be achieved in discotic liquid crystal systems [17]. The phase properties of some key materials are summarised in Tables 1 to 5 below.

The cholesterol derivatives shown in Tables 1, 2 and 3 below are representative of materials used since the first manufacture of thermochromic devices, and still in use today. The 2-methylbutylphenol derivatives in Tables 4 and 5 were introduced [19] as alternative materials which have higher birefringence. This allows use of thinner layers of material, and can provide brighter colours and allow the use of faster coating methods when devices are manufactured. They may also show better environmental stability than cholesterol derivatives. As for other liquid crystal

Table 1. Phase properties of some cholesterol esters, etc.



R	Phase transitions
CH <sub>3</sub> CO <sub>2</sub>	Cr97.5(N*94.5)I
C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub>	Cr95.2N*111.8I
C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub>	Cr102.0N*113.0I
C <sub>4</sub> H <sub>9</sub> CO <sub>2</sub>	Cr93.0N*101.5I
C <sub>5</sub> H <sub>11</sub> CO <sub>2</sub>	Cr99.5N*101.5I
C <sub>6</sub> H <sub>13</sub> CO <sub>2</sub>	Cr114.0(SmA92.5N*95.5)I
C <sub>7</sub> H <sub>15</sub> CO <sub>2</sub>	Cr110.0(SmA69.5N*96.5)I
C <sub>8</sub> H <sub>17</sub> CO <sub>2</sub>	Cr80.5(SmA 77.5)N*92.0I
Benzoate	Cr150.5N*182.6I
Cl	Cr96(N*88.7)I

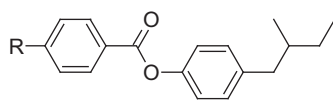
Table 2. Phase properties of some cholesterol alkylcarbonates.

R	Phase transitions
CH <sub>3</sub> OCO <sub>2</sub>	Cr114.0(N*110.9)I
C <sub>2</sub> H <sub>5</sub> OCO <sub>2</sub>	Cr83.9N*105.8I
C <sub>3</sub> H <sub>7</sub> OCO <sub>2</sub>	Cr98.8N*101.0I
C <sub>4</sub> H <sub>9</sub> OCO <sub>2</sub>	Cr80.2N*94.0I
C <sub>5</sub> H <sub>11</sub> OCO <sub>2</sub>	Cr106.3I
C <sub>6</sub> H <sub>13</sub> OCO <sub>2</sub>	Cr108.3I
C <sub>7</sub> H <sub>15</sub> OCO <sub>2</sub>	Cr88.0(N*81.3)I
C <sub>8</sub> H <sub>17</sub> OCO <sub>2</sub>	Cr54.8(SmA 35.4)N*78.9I
C <sub>9</sub> H <sub>19</sub> OCO <sub>2</sub>	Cr79.3(SmA 45.1)N*77.2I

Table 3. Phase properties of some low melting point cholesterol derivatives.

R	Phase transitions
Oleate/(Z)-octadec-9-enoate	Cr48.5(SmA 39.3N*45.2)I
Oleylcarbonate/(Z)-octadec-9-enylcarbonate	Cr26.7(SmA 20.0)N*34I
Isostearylcarbonate/16-methylheptadecan-1-ylcarbonate	Detailed data unpublished [18]

Table 4. Phase properties of some two-ring esters of 2-methylbutyl phenol.

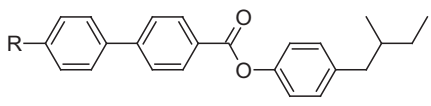


R	Phase transitions
C <sub>5</sub> H <sub>11</sub>	Cr6(N*-1)I
C <sub>8</sub> H <sub>17</sub>	Cr17(N*-3)I
C <sub>6</sub> H <sub>13</sub> O	Cr38(N*36.7)I
C <sub>7</sub> H <sub>15</sub> O	Cr45.5(N*36.3)I
C <sub>8</sub> H <sub>17</sub> O	Cr47.5(N*42)I
C <sub>9</sub> H <sub>19</sub> O	Cr49.5(SmA 37.2N*42.7)I
C <sub>10</sub> H <sub>21</sub> O	Cr41.8 SmA 42.2N*45.3I

devices, the materials used in thermochromic systems are generally multi-component mixtures which are carefully formulated to simultaneously satisfy several requirements on their physical properties, the key properties for thermochromic applications being the phase transition temperatures and pitch length.

It is convenient to consider first the synthetic derivatives of 4-(2-methylbutyl)phenol. As can be seen in Table 4, the esters of this compound provide several 2-ring derivatives which melt somewhat above room temperature and provide enantiotropic N\* phases. Formulation of multi-component mixtures is used to

Table 5. Phase properties of some three-ring esters of 2-methylbutyl phenol.



R	Phase transitions
C <sub>5</sub> H <sub>11</sub>	Cr66.0SB77.3 SmA 133.9N*156.0I
C <sub>6</sub> H <sub>13</sub>	Cr81.0(SmB 71.0) SmA 132.6N*146.2I
C <sub>7</sub> H <sub>15</sub>	Cr74.6 SmB 75.0 SmA 138.4N*147.6I
C <sub>8</sub> H <sub>17</sub> O	Cr78.0SmI80.0SmC*128.3 SmA 171.0N*174.2I

depress the melting point well below room temperature by approaching a eutectic point. The Schroeder–van Laar equation:

$$\ln[X_i] = \frac{\Delta H_{fi}}{R} \left[ \frac{1}{T_{mi}} - \frac{1}{T} \right]$$

relates the solubility of each component at a set temperature  $T$ , to its heat of fusion and melting point and provides a useful guide to the eutectic temperature and to the melting point of non-eutectic compositions. The S<sub>A</sub>–N\* transition temperature and the N\*–I transition may be raised by addition of a three-ring derivative such as those shown in Table 5, and the S<sub>A</sub>–N\* temperature is ‘fine-tuned’ by a suitable choice of substituent chain lengths.

The key intermediate in the preparation of these esters is 2-methylbutanol, which is readily available as the R+ isomer as a component of fusel oil, a by-product of fermentation. A general rule exists [20] relating the absolute conformation of a chiral centre and its spacing from the mesogenic core to the twist sense of the N\* phase, and in this case the products invariably form a right-handed helix. The pitch length is typically 0.23 μm, giving a system which is well suited to providing a progressive colour play through the whole visible spectrum when the pitch is unwound by a nearby smectic phase. Experimentally it is found that a mixture composed of these esters in an enantiotropically pure form passes through the spectrum in a temperature interval of about 0.6–0.8°C. This is too narrow for many applications. For example, it is common in the design of a liquid crystal room thermometer to have a series of formulations which pass through green at intervals 2°C apart. The colour play width should then be a little over 2°, so as to provide a small overlap of the colour plays in adjacent areas. This is easily accomplished by altering the limiting pitch by addition of

the same compounds in their racemic forms, derived from synthetic, optically inactive 2-methylbutanol. The transition temperatures of the optically active and racemic forms of the esters are essentially identical (apart from the melting points), which makes these compounds particularly convenient for mixture formulation.

The same general principles apply when cholesterol derivatives are used for mixture formulation. However, there are two severe difficulties in the use of these compounds which do not arise in the former case. One is the lack of series of low-melting compounds in the cholesterol series, from which to formulate wide range eutectics. Scrutiny of Tables 1, 2 and 3 reveals only cholesteryl oleylcarbonate as a low-melting base compound. Cholesteryl isosterylcarbonate in fact has very similar phase transitions, and one or other of these compounds is used as a base component at a substantial level in almost all cholesterol-based thermochromic mixtures. The other transition temperatures are adjusted in much the same way as for methylbutyl derivatives, save that the transition temperatures of cholesteryl esters are high enough that it is not usually necessary to use further rings to raise the mesophase stability. The second difficulty in the use of cholesterol derivatives in mixture formulation is that the esters and alkylcarbonates which provide the basis of the mixtures have a uniformly left-handed sense of helical pitch. Cholesterol is not readily available in a racemic form, so adjustment of the colour play temperature range becomes problematic. The usual solution is use of the right-handed twisting cholesteryl chloride as an additive (other cholesteryl halides also have right-handed sense of twist), but the transition temperatures of cholesteryl chloride are very different from those of representative esters. The formulation of the mixture becomes more complex and subject to trial and error.

Mixtures intended for use at the N\*–I transition should be free of an underlying smectic phase in the expected temperature range of use. This is easily achieved by maximising the use of short-chain homologues in the mixtures.

## 5. Other thermochromic effects in soft matter

Although it is the thermochromism at N\*–I and N\*–S transitions which is exploited in liquid crystal devices, there are several other systems of condensed soft matter which show interesting thermochromic behaviour, or which have potential for development into thermochromic systems. Some systems which have a close relationship to conventional liquid crystals are briefly described in the following paragraphs.



Thermochromism can be observed in aqueous solutions of hydroxypropylcellulose [21]. At high solution concentrations this rigid-rod polymer forms a cholesteric liquid crystal phase which reflects light at a concentration-dependent wavelength which can be in the visible range. On heating, a phase separation occurs; the lyotropic liquid crystal phase is lost and replaced by a strongly scattering heterogeneous liquid. Application of the effect to devices appears problematic because the extremely high viscosity of the concentrated polymer solution results in very slow alignment of the liquid crystal phase into its coloured state. Colour-reflecting thermotropic liquid crystal phases are displayed by some rigid-rod polymer systems, including cellulose esters [22] and synthetic polypeptides, but are not generally strongly thermochromic.

Lamellar lyotropic liquid crystal systems in which the spacing is in the optical wavelength region are formed [23–25] by a number of amphiphiles, either in aqueous or in mixed solvent systems. The resulting phases selectively reflect coloured light without polarisation effects. The effective modulation of the refractive index is, however, rather small and the effects are best observed in substantial thicknesses of the phase, of at least millimetre dimensions. Most such phases do not show pronounced thermochromism other than destruction of the light-reflecting structure at a phase transition. A strongly thermochromic phase is, however, formed by hexadecylpyridinium salicylate [26] in dilute (ca. 0.5%) aqueous solution. The layer spacing in these lamellar phases is believed to be controlled by the charge density on the lamellae, and in this case may be affected by equilibria involving ionisation of salicylate groups or their association with the counterion. Thermochromic colour play occurs over a temperature interval of ca. 2°C in the room temperature region; because bright selective reflection requires rather large aligned domains in the fluid, the colour play is easily upset by rapid temperature changes, mechanical disturbances, etc. Lamellar phases with layer spacing in the optical wavelength range are also rather fragile in the thermodynamic sense, and are destroyed by quite small additions of ionic solutes. There may nevertheless be applications open to these materials in decorative or specialist areas.

Analogous to the lyotropic lamellar phases are lamellar phases, formed by monodisperse diblock copolymers in which the respective block lengths are similar. In many systems [27, 28] these phases can be swollen by addition of monodisperse homopolymers to the point where again the layer spacing is of optical dimensions. These polymers can be aligned in thin layers and annealed to provide selective reflection. Their high viscosity makes effective alignment rather

difficult, and the layer spacing is not generally highly sensitive to temperature.

The self-assembly of sub-micrometre diameter polymer and silica spheres into photonic solids which reflect visible light is well known, but the resulting structures are usually rather temperature insensitive. However, assembly of such a photonic system from highly swollen polymer gel microspheres results in a product which is not only thermochromic but sensitive to a range of other physical and chemical stimuli.

An unusual thermochromic system is also available in the form of mesogenic iron triazolylbenzamide complexes [29] which show spin transitions in the same temperature range as their mesogenic properties. A pronounced colour change accompanies the spin transition, which is also accompanied by the expected change in magnetic and other properties.

It is worth pointing out that the thermochromic systems briefly noted above are selected on the basis of their relationship to other soft matter systems and affinity with liquid crystals. However, the principal commercial competitor technology to liquid crystalline thermochromic systems is quite different to all of these, and instead relies on the reversible colouration of leuco dye systems [30]. The formulation typically comprises a leuco dye such as leuco methylene blue or crystal violet lactone in combination with a weak acid and polar solvent system. The decolouration temperature can be adjusted by altering the pK of the acid and polarity of the solvent, and the colour tone by an appropriate choice of leuco dye. Unlike liquid crystals, these thermochromic systems characteristically change from a dark to light colour on warming and are normally presented to best advantage on a light-coloured background.

## 6. Processing thermochromic liquid crystal devices

In most applications, low processing cost and efficiency of use are key requirements. Unlike electro-optic devices which are based on highly engineered glass cells, thermochromic liquid crystal products are usually fabricated by formulation of a printing ink containing droplets of liquid crystal, suspended in a binder. The ink is then deposited on a substrate by a technique such as bar or blade coating, or by screen, inkjet or flexographic printing. The details of the process must be controlled so that the liquid crystal droplet size is maintained in the ink formulation and coating steps, and to avoid contamination of the liquid crystal by organic solvents, plasticisers, etc., which would alter the transition temperatures and therefore the colour play range of the formulation. A further concern is that, as noted previously, spherical liquid crystal droplets provide a poor selective reflection of

light: in order to achieve a bright device, the droplets must be deformed into an oblate ellipsoid, or more preferably flattened against a planar surface on the viewing side of the device.

The standard route to achieve these requirements comprises microencapsulation of the liquid crystal in a coacervation process [31]. For example, thermochromic liquid crystals may be microencapsulated by first emulsifying them into a dilute solution of pigskin gelatin using a high shear mixer. Gelatin is an amphoteric polymer which is also a surfactant, and no further aid to emulsification is generally required. A dilute solution of gum acacia is then added, and the pH of the solution is adjusted to a range where the gum acacia and gelatine polymer chains carry opposite charges. A gelatin-rich phase termed a complex coacervate then separates from the aqueous solution as a separate phase which spontaneously coats the oily liquid crystal droplets. On cooling the mixture to about 10°C, the coacervate forms a hydrated gel which may be cross-linked by addition of a hardener such as formaldehyde or glutaraldehyde solution. Typically, further processes are used to remove excess water from the gelatin coacervate, to adjust the pH and to wash the dispersion free of very fine particles and contaminants. At this point, the liquid crystal droplets are enclosed and protected within permanent gelatin-walled microcapsules, which prevent droplet fusion and inhibit droplet splitting during further processing. However, microcapsules are not robust against damage by large shear or pressure forces and do not provide a barrier against contamination of the liquid crystal by low molecular weight organic compounds. Success of the microencapsulation process is highly dependent on selection of the correct grades of materials, on the emulsification method, and on control of pH and temperature within critical ranges. Many other microencapsulation techniques are available [32–35], using natural or synthetic polymers as coating materials. Those applied to thermochromic liquid crystal device manufacture must provide robust, highly transparent capsule walls and low-cost, high-throughput processing without contamination of the liquid crystal.

The microencapsulated liquid crystal dispersion is mixed into a polymer binder to convert it into a printable form which will form a durable coating on a device substrate. Because the microcapsules are permeable to low molecular mass solvents, the polymers used are generally restricted to aqueous dispersions. Either water-soluble polymers such as poly(vinyl alcohol), or proprietary emulsion polymers such as acrylic or polyurethane systems may be used; the latter generally provide more water-resistant coatings, and may incorporate cross-linkable sites allowing extra durability

and even wash-fastness in the system. The formulation of the ink depends very much on the printing or coating technique which will be used; the requirements on ink viscosity are particularly pronounced, with the low-viscosity inks required for inkjet or gravure printing contrasting with the thick paste-like formulations used in screen printing. However the ink layer is applied to the substrate, there follows a drying stage as water evaporates from the film. A successful ink remains coated uniformly on the substrate throughout the drying stage, and it follows that the drying is accompanied by a shrinkage in the film thickness. In a well-formulated ink, this shrinkage deforms the microcapsules into the desired oblate shape, improving the LC alignment and device brightness. Success depends on conformability of the capsule wall, which is limited by the capsule being under tension around the incompressible liquid contents. The volume of included liquid can be artificially reduced by, for example, adding a volatile solvent to the liquid crystal before encapsulation and allowing it to diffuse out of the capsule before the ink is formulated.

A typical device such as a liquid crystal thermometer requires a series of liquid crystal inks to be deposited on different areas, each having a slightly different colour play temperature range. The coating may be achieved by bar or blade coating, or by a printing method – most commonly screen printing. The coating process can be carried out on sheets or rolls of substrate, and devices finished by cutting at right angles to the coating direction. It has been noted previously that the optimum brightness of reflection from a  $N^*$  layer is only achieved if it is in a planar alignment, while this is by no means guaranteed from the standard encapsulation/coating route to device manufacture. In general, the best results are achieved if the encapsulated liquid crystal ink is coated onto a smooth transparent plastic substrate. The planar substrate deforms the microcapsules as the film dries and improves alignment. A black backing layer may then be printed or (better) laminated onto the dried film. This device structure is not only brighter, but the liquid crystal layer is protected from contamination and from mechanical damage by the layers on each side. Alternative, lower-cost, routes to devices such as printing onto black card need great care to provide acceptable and durable results.

Finally, thermochromic devices with good performance can be obtained by exclusion of the liquid crystal from solution in a pre-polymer as the latter cures to form a binder. This is the same process used to manufacture some NCAP electro-optic devices. Although bright, durable devices can be made in this way, residual polymer dissolved in the liquid crystal and vice-versa means that precise control of



Figure 5. Temperature indicators using the S–N\* and N\*–I transitions. Photographs of Hallcrest products by kind permission of R Booth, Hallcrest.

the composition and colour play range are difficult to achieve. This route to manufacture is mainly used for novelty applications and other cases where high accuracy of temperature indication is not required.

Figure 5 shows examples of temperature indicators using the S–N\* and N\*–I transitions.

## 7. Applications

Thermochromic liquid crystal materials can be formulated to show their colour change over a wide range of temperatures from as low as  $-30^{\circ}\text{C}$  to far above  $100^{\circ}\text{C}$ . The limits to this range are defined by crystallisation and glass formation at low temperature. The upper limit tends to be set by the required stability and lifetime of the device, determined by the whole device package rather than the intrinsic stability of the liquid crystal. A vast array of products based on thermochromic temperature indicators has been produced. Some representative applications requiring different colour play temperatures are listed below in Table 6.

Thermochromic devices have considerable advantages over other thermometers in that they are cheap, flexible, virtually unbreakable and easy to read. All these advantages have made them a regular product of choice for forehead-placed fever thermometers. Elsewhere on the body, the local skin temperature is easily influenced by ambient temperature, stress, consumption of alcohol and other drugs, circulatory problems, etc. Many novelty and promotional devices have sought to use the response of body temperature to ‘mood’.

Thermography in ethical medical practice has been and to some extent is still used [36] to diagnose circulatory disorders, malignancies and inflammatory conditions. Use of liquid crystal products for this purpose was previously widespread but has, however, become relatively unimportant as infrared imaging cameras have become less expensive and more sophisticated in their capabilities.

An application area which has seen consistent focus [37] is the use of thermochromic liquid crystals

Table 6. Examples of representative applications requiring different colour play temperatures.

Colour play range ( $^{\circ}\text{C}$ )	Uses
-30–10	Freezer thermometer
-20 (irreversible change)	Frozen food overheat indicator
-10–0	Ice box refrigerator
0–10	Fridge thermometer, storage indicators for blood, vaccines etc.
5–15	Beverage ideal temperature indicator (beers, wines)
10–25	Room thermometers, energy saving initiatives, hypothermia warning
15–40	Aquarium, vivarium thermometers etc.
20–40	Novelty items, jewellery, clinical thermometers, advertising and promotional devices, ‘hidden message’ cards etc.
30–50	Bath thermometers
40–	Overheat warning for electrical, mechanical equipment
50–	Warning indicators for hot surfaces
60–100	Food heating indication, hot drink novelty mugs and packaging
> 100	Sterilisation indicator, pressure cooker thermometer etc.

in engineering applications. The ability to monitor and map the temperature of a substantial area of surface can be a great advantage in detecting a fault or localising activity. Unlike other options such as infrared imaging, liquid crystals can be used to map temperature through plastic and glass windows, and this approach does not depend on surface emissivity. In electronics, liquid crystals can be used to detect short circuits, open circuits, inoperative devices, and map operational areas in large-scale integrated circuits. Mechanical parts can be examined under an imposed thermal gradient to detect cracks, debonding and other defects which cause an interruption in thermal conductivity.

A prominent use of liquid crystal thermography has been in evaluation of thermal transfer between fluids and solid surfaces [38]. A temperature difference is maintained between the fluid (typically an airstream) and the surface, and the thermal transfer is mapped out in isotherm contours by the liquid crystal.

Liquid crystals have also proved valuable in mapping local temperature variations in a flowing fluid. The fast response of small liquid crystal droplets used as seed particles in particle image velocimetry allows rapid and small-scale temperature mapping in flow fields [39, 40], extending the value of the technique.

Many other applications of thermochromic liquid crystals have been reported which have not achieved

widespread or sustained use. For example, their use as radiation detectors has been confined to specialist devices, and equally detectors for volatile chemicals have been demonstrated but not widely used. A difficulty in many cases is that devices require rather stringent thermal management to operate over a reasonable range of ambient conditions.

Thermochromic liquid crystals were the first mesophases to be recognised, and formed the basis of the first widespread liquid crystal devices. Their striking behaviour makes them excellent educational tools and they continue to find new application in high-technology as well as novelty and consumer items. They have influenced the world since 1888, and there is every sign that they will continue to do so.

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