

# Observation of Direct Phase Transition Smectic A $\leftrightarrow$ Blue Phase in a Liquid Crystalline Mixed System

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Hitherto, for all liquid-crystalline samples exhibiting Blue Phases (BP) it has been found that these phases occur between the cholesteric and the isotropic state. In the mixed system of cholesteryl myristate and an azoxybenzene derivative a phase transition from the smectic A phase directly to the BP has been observed. The phase diagram has been obtained by differential scanning calorimetry and is discussed together with the helical pitch behaviour.

## 1. Introduction

It is well known that cholesteric systems of sufficiently short pitch show additional mesophases called Blue Phases (BP) just below the clearing point in a temperature range of only a few tenths of a Kelvin. These mesophases show selective reflection (SR) of circularly polarized light and anomalous optical rotatory dispersion (ORD) like the ordinary cholesteric phase, but no birefringence ( $\Delta n = 0$ ) [1].

A structure proposal, based upon the ORD and the lack of birefringence was first made by Saupe [2] who suggested at cubic structure for the BP. By extending the Landau theory approach into three dimensions, Hornreich and Shtrikman [3] were able to show that cubic structures are thermodynamically stable for compounds with a high chirality close below the clearing point. Evidence for cubic lattices in the BP has been obtained by investigation of Bragg reflections [4], by growth of cubic liquid single crystals of BP [5, 6] and by observation of paramorphic quadratic cholesteric textures arising from supercooled BP [7].

In polymorphic liquid crystals generally the phase sequence smectic A  $\rightarrow$  cholesteric  $\rightarrow$  BP  $\rightarrow$  isotropic has been found on increasing temperature. If the helical pitch of the cholesteric phase in mixed systems will be increased above a critical value by a composition change the BP will become unstable resulting in a direct phase transition cholesteric

$\rightarrow$  isotropic. In this paper we will show that also a direct phase transition smectic A  $\rightarrow$  BP can occur in an appropriated mixed system.

## 2. Experimental

The investigations regarding phase stability were carried out in a mixed system of cholesteryl myristate (CM) and 4,4'-di-n-decyl azoxybenzene ( $C_{10}$ ). Whereas  $C_{10}$  exhibits only a smectic A phase, additionally a cholesteric and two BPs occur in CM.

The phase diagram of the mixed system was obtained by DSC measurements (Perkin-Elmer DSC 2) and by polarizing microscopy (Leitz-Ortholux-Pol with Mettler FP 52 heating stage). To obtain DSC thermograms of very high resolution, the DSC measurements were carried out in gold pans with a heating rate of 0.31 K/min. Because of the self absorption of the  $C_{10}$  molecules, the cholesteric pitch cannot be determined by SR measurement. Instead, we measured the dispersion of the optical rotatory power in the cholesteric phase, using a JASCO J-20 spectropolarimeter, which has been equipped with a LORD-I device.

## 3. Results

### 3.1 Phase diagram

In Fig. 1 the phase diagram of the mixed system is given. The diagram shows that the cholesteric phase is only stable over a small composition range. To study the phase behaviour of the BP in more detail, a section of Fig. 1 is enlarged in Figure 2.

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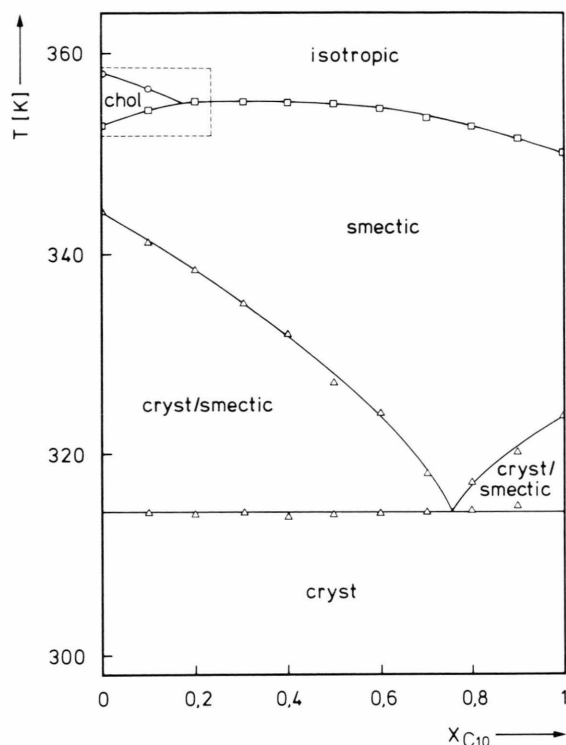


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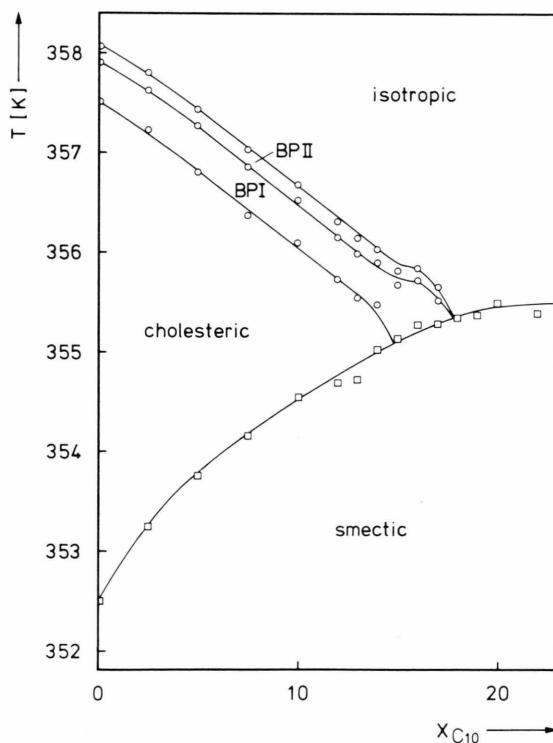
Fig. 1. Phase diagram of the mixed system CM/C<sub>10</sub>.

Except for the transition BP I → BP II in the 17 mol % C<sub>10</sub> mixture, which was only obtained by polarizing microscopy, all transition temperatures were obtained as well by DSC as by polarizing microscopy. Although the cholesteric range decreases rapidly with increasing C<sub>10</sub> proportion, the BP temperature range remains approximately constant. At 15 mol % C<sub>10</sub> the cholesteric phase vanishes, but the BPs exist still up to 18 mol % C<sub>10</sub>. The result is a transition smectic A → BP in the range 15 to 18 mol % C<sub>10</sub>. In Fig. 3 four very high resolved DSC thermograms of different CM/C<sub>10</sub> mixtures are shown. Figure 3 A shows the transitions smectic A → cholesteric → BP I → BP II → isotropic. In Fig. 3B only the transitions smectic A → BP II → isotropic occur. In the scan given in Fig. 3C only two transition peaks can be seen assigned to the transitions smectic A → BP and BP → isotropic. In this mixture with 17 mol % C<sub>10</sub> we observed the transitions smectic A → BP I → BP II → isotropic by polarizing microscopy. The temperature range of the

BPs, however, is so small (> 0.4 K) that the DSC cannot resolve these transitions. Only one large transition peak is shown in Fig. 3D, caused by transition smectic A → isotropic. Because the peak is approximately 0.5 K wide, it may be that hidden BP transitions cannot be resolved. But microscopic and ORD measurements reveal no BP in this mixture. Notice in Fig. 2 that the BP range is nearly constant in all mixtures showing a cholesteric phase. In Fig. 4 the BP ranges of the different mixtures are given, and indeed the BP ranges of the mixtures with a cholesteric phase (up to 15 mol % C<sub>10</sub>) are constant within the accuracy of these measurements. For the mixtures with a smectic A → BP transition, we find a strong decrease of the BP range with increasing mole fraction of C<sub>10</sub>.

### 3.2 Pitch behaviour

Because of the well-known dependence of the BP range on the cholesteric pitch at the transition temperature cholesteric → BP [8], together with the

Fig. 2. Section of the phase diagram of the mixed system CM/C<sub>10</sub>.

results of Fig. 4 we expect that the pitch will be approximately the same in all mixtures with a cholesteric phase. To verify this, the pitch of the cholesteric phase was determined by measurement of the ORD spectrum.

The inversion wavelength  $\lambda_0$  is proportional to the pitch ( $\lambda_0 = \bar{n} \cdot p$ ) [9]. In Fig. 5  $\lambda_0$  of the cholesteric phase is shown as a function of concentration of  $C_{10}$  at the transitions cholesteric  $\rightarrow$  BP and cholesteric  $\rightarrow$  smectic A. Figure 5 shows that  $\lambda_0$  depends only slightly on  $x_{C_{10}}$  at the transition cholesteric  $\rightarrow$  BP running through a flat minimum with deviation of only 5%. We can therefore understand why the BP range in these mixtures with a cholesteric phase is approximately constant.

An unusual result, however, is found for the pitch at the transition cholesteric  $\rightarrow$  smectic A, i.e., the pitch decreases with increasing proportion of  $C_{10}$ . At about 15 mol %  $C_{10}$  the decreasing pitch at the transition cholesteric  $\rightarrow$  smectic A intersects the ap-

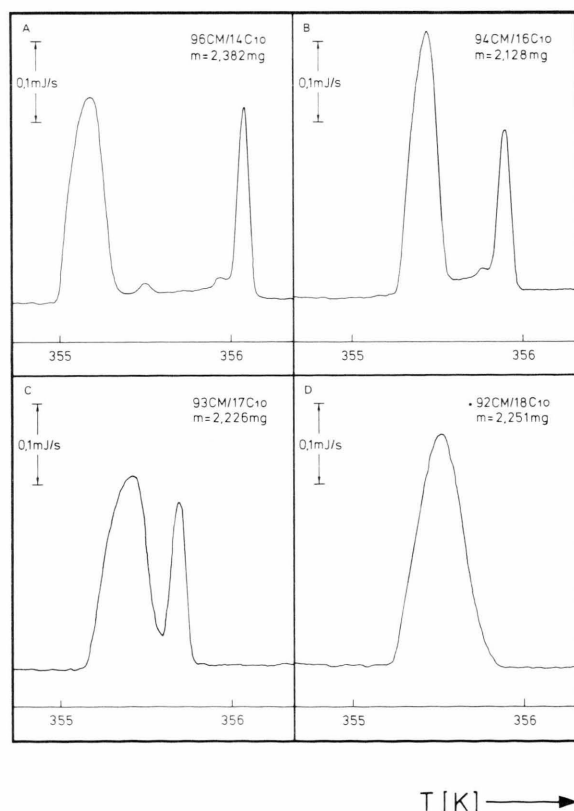


Fig. 3. DSC traces of 4 different mixtures CM/ $C_{10}$ ; heating rate 0.31 K/min.

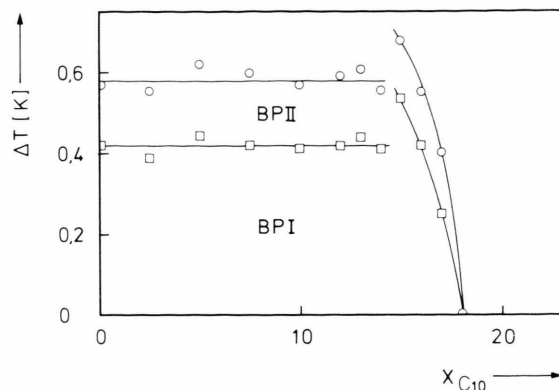


Fig. 4. Reduced phase diagram of BPs in the mixed system CM/ $C_{10}$ .  $\Delta T$ : difference between the transition temperature and either the cholesteric/BP or smectic/BP transition temperature.

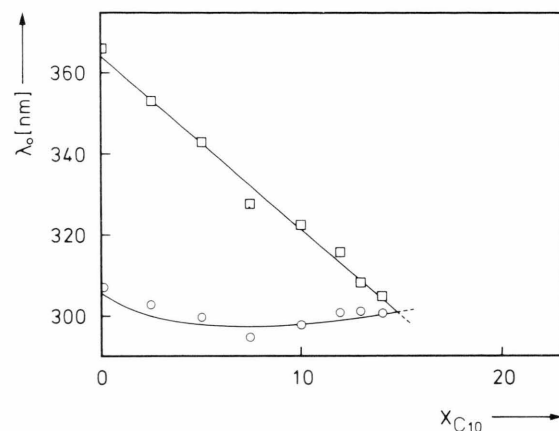


Fig. 5. Inversion wavelength  $\lambda_0$  at the transitions cholesteric/BP (○) and smectic A/cholesteric (□) vs.  $C_{10}$  mole fraction in the mixed system CM/ $C_{10}$ .

proximately constant pitch at the transition cholesteric  $\rightarrow$  BP. Just this mixture shows no cholesteric phase; the smectic A phase transforms directly into the BP.

#### 4. Discussion

As it can be seen from Fig. 2 the temperature span of the smectic A phase increases with increasing  $C_{10}$  proportion at the expense of the cholesteric phase becoming zero at 15 mol %  $C_{10}$  and  $T = 355.2$  K where the coexistence lines smectic A/cholesteric and cholesteric/BP intersect. Although the chole-

teric phase is not stable at higher contents of  $C_{10}$  the BP I and BP II is still preserved up to 18 mol %  $C_{10}$ . This result may be discussed in terms of the similarity of cholesterics and BPs with respect to their helical structure as follows:

Theoretical considerations [10] as well as experimental results [8] show that the cholesterics and BPs rely on a helical structure for their stability. In a single substance the pitch in both phases is of rather similar value. It has been shown that the enthalpy difference between the cholesterics and BPs is very small while the enthalpy difference between either phase and the isotropic phase is much larger [11]. Therefore one can argue that in a certain sense the BPs are an extension of the cholesteric phase. Increasing the proportion of the long-chain azoxybenzene derivative  $C_{10}$  which only exhibits a smectic A phase in the mixed system with CM those intermolecular forces which are responsible for the molecular organization in smectic layers will over-

come more and more the helical twisting power of the chiral molecules [12]. As in all mixtures the cholesteric pitch decreases on increasing temperature approaching the cholesteric  $\rightarrow$  BP transition whereas it is nearly independent on composition directly at this transition one would expect the cholesteric phase first to disappear during the extension of the smectic range, followed by the disappearance of the BP. In this sense the BP is the last portion of the "chiral" liquid-crystalline phase to become unstable relative to the smectic A phase.

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