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Chiral induction of micellar cholesterics from lamellar phases

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It is shown for the first time that induced micellar cholesterics can be obtained from lamellar phases within the sequence: lamellar → micellar nematic → micellar cholesteric → biphasic region → isotropic phase. The pitch is shortened by over 50 per cent when the temperature is raised within the cholesteric range of about 15 K.

Induced micellar cholesterics were discovered by Radley and Saupe in 1978 by adding optically active compounds to micellar nematics [1]. In 1980, Acimis and Reeves found that optically active amphiphiles also form micellar cholesterics (intrinsic cholesterics) and that their racemates give a micellar nematic phase [2]. Both papers provided the basis for the development of micellar cholesterics. The phenomena thereby observed are in many ways analogous to the phenomena already known for thermotropic liquid crystals.

For the past 13 years, the papers published by various research groups have concentrated on developing materials forming intrinsic [3–7] and induced micellar cholesterics [8, 9]. Though these works have led to a better understanding of various cholesteric systems, some problems concerning the mechanism of the chiral inductions remained unsatisfactorily answered [3, 6].

The phase transition sequence smectic–cholesteric, obtained by raising the temperature in thermotropic liquid crystals, was discovered over a century ago [10, 11]. An analogous phase transition from optically lamellar phases has not yet been reported. Therefore, we regard the induction of micellar cholesterics from lamellar phases as a completion of the systematics of obtaining micellar cholesterics. In this preliminary communication we present polarizing microscopic results portraying the phase transition sequence, lamellar–micellar nematic (N_D)–micellar cholesteric (Ch_D)–unassignable biphasic region–istropic phase.

The system analysed consisted of decylammonium chloride (DACl), ammonium chloride (NH_4Cl), cholesteryl 2-ethoxyethoxyethyl carbonate (CEEC) and heavy water (D_2O). The ingredients were weighed into test tubes which were sealed off and the contents homogenized by keeping them in a water bath (50°C) and centrifuging occasionally. A small amount of the liquid crystal was transferred into a microslide (CAMLAB, UK) of thickness 0·1 mm by capillary forces and both ends of the microslide were fused by heating.

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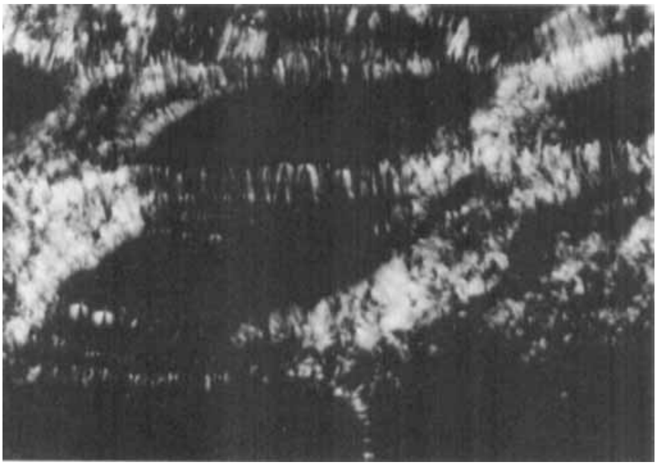

Figure 1. Oily streak texture of the lamellar phase at 22°C (× 100).

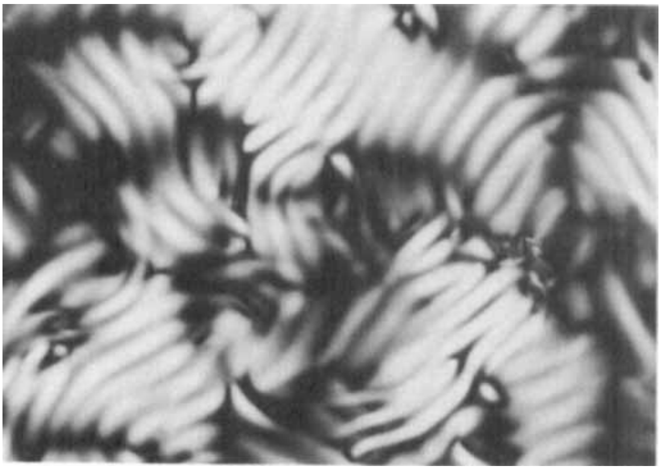

Figure 2. Finger print texture at 35°C.

A mixture of DACl, NH_4Cl, CEEC and D_2O, 6·30, 2·27, 0·14 and 91·26 mol %, respectively, gave a lamellar phase which had an oily streak texture at 22°C (see figure 1). As the temperature was raised slowly a transition from lamellar phase to nematic phase, N_D, took place at about 30°C; all of the lamellar texture turned into a pseudoisotropic texture, i.e. the texture was completely extinct. Conoscopic observations showed that the director of the mesophase was aligned perpendicular to the surface of the microslide and the optical anistropy (Δn) was determined to be positive. According to the literature [12, 13], the micellar nematic phase obtained possesses a negative diamagnetic anisotropy.

At about 32°C, a cholesteric texture of low twist appeared and at about 35°C a pitch of 21 μm (see figure 2) was determined from the fingerprint texture. As the temperature was raised further, we observed a shortening of the pitch, i.e., the helical twisting power (HTP) of the CEEC increased with increasing temperature. At 50°C a pitch of 10 μm was measured. This result shows that the pitch was shortened by more than 50 per cent between 35°C and 50°C. By raising the temperature further, the cholesteric fingerprint texture became disordered. In a narrow temperature range (50 ± 1°C), a number of textures appeared to be continuously in motion. The disordered cholesteric texture passed over to a texture exhibiting cholesteric droplets [14] and in this temperature range greyish platelets or surfaces were also observed before the sample became isotropic at about 52°C. This behaviour was easily followed if the sample was cooled down from the isotropic phase. This phase region will be analysed further.

Another sample with the same relative amounts of DACl, NH_4Cl and CEEC, but with a lower water content (90·53 mol %) has also been investigated. Here, at about 41°C, a pseudoisotropic texture and at 43°C, a cholesteric phase were obtained; the pitch was 40 μm at 45°C and 20 μm at 50°C. At 55°C and at higher temperatures the pitch was extremely sensitive to temperature variation and could not be measured accurately by the present set up. Then a similar sequence of texture changes to those seen for the first sample were observed before the sample became isotropic at about 60°C. Also, a very low concentration of CEEC led to a cholesteric phase of low twist, indicating that no threshold concentration for the chiral induction is required. A lamellar phase of DACl and NH_4Cl containing cholesterol or *L*-mandelic acid also showed similar behaviour which indicates that this phenomenon is of a general nature.

The shortening of the pitch observed here is in contrast to the results obtained from other induced micellar cholesterics and also intrinsic micellar cholesterics where the pitch increases as the temperature is raised [4, 6, 15]. This shortening of the pitch is exceptionally large and in contrast to the normal findings for lyotropic phases. Thermotropic chiral smectic phases are directly transformed into a cholesteric phase [16, 17] by raising the temperature. The phase transition sequence found for the lamellar phases of DACl/NH_4/CEEC/D_2O is in contrast to the results for thermotropic systems, since the induced micellar cholesteric phase only develops after the pseudoisotropic texture. Pseudoisotropic textures are regarded as characteristics for micellar nematics [18, 19]. For the transition, lamellar–nematic–cholesteric, we may assume that in the lamellar phase, as well as at the beginning of the nematic region (pseudoisotropic texture), the micelles are large and therefore they are not affected by the chiral molecules, i.e. the large micelles are not able to develop a chiral distortion. Then by raising the temperature, the micelle size [13], as well as the interactions between the micelles, have to decrease so that the chiral interactions become important and distort the micelles to arrange in a helicoidal order. Then each distorted micelle align with its local director perpendicular on average to the optical axis of the cholesteric phase [1, 2].

A detailed study of the dependence of the pitch (induced from the lamellar phases) on temperature and on concentration of the optically active dopant and also a comparison of these results with those obtained from cholesterics (induced from nematics) will be published later.

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