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Some Experimental Investigations on Type II Chiral Liquid Crystals

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We report the following new experimental results on binary mixtures which exhibit the TGB_A and $UTGB_C*$ phases: (i) optical reflectivity measurements in the cholesteric phase to confirm that the chiral strength decreases as the concentration of the nonchiral compound is increased (ii) electroclinic measurements in the SmA phase to demonstrate that the tilt elastic constant decreases rapidly with concentration, thus enhancing the type II character of the mixture (iii) an irreversible transition from TGB_A phase to SmA phase under the action of a low frequency electric field and (iv) occurrence of a new type of periodic radial structure in the meniscus region of free standing films. It is suggested that this structure arises from the type II character of the material.

Keywords: type II materials; tilt elastic constant; electroclinic effect; edge dislocations.

INTRODUCTION

The formal similarity between smectic liquid crystals and superconductors was pointed out by de Gennes [1]. He predicted the possibility of an intermediate phase in which a defect lattice generates bend or twist of the director in analogy with type II superconductors in a magnetic field. Renn and Lubensky [2] showed that in the intermediate phase of highly chiral type II materials smectic blocks are separated by twist grain boundaries(TGB) made of screw dislocations. The smectic blocks then form a helical structure. Goodby *et al.* [3] reported the observation of such a phase in some highly chiral compounds. The TGB phase with SmC-like blocks (TGB_C) has also been experimentally charcterised [4]. Pramod *et al.* [5] reported the discovery of a new twist grain boundary phase called $UTGB_{C*}$

which is characterised by a 2D undulation of SmC* -like blocks in the form of a square lattice in a binary mixture of the chiral compound 4-(2-methyl butyl)phenyl 4'-n-octylbiphenyl-4-carboxylate (CE8) and the nonchiral compound 2 - cyano 4 - heptylphenyl 4' – pentyl 4 – biphenyl carboxylate (7(CN)5). Several physical studies have been made to characterise this new liquid crystalline phase [6]. In this paper we report some new experiments on the above binary system whose phase diagram is shown in fig.1.

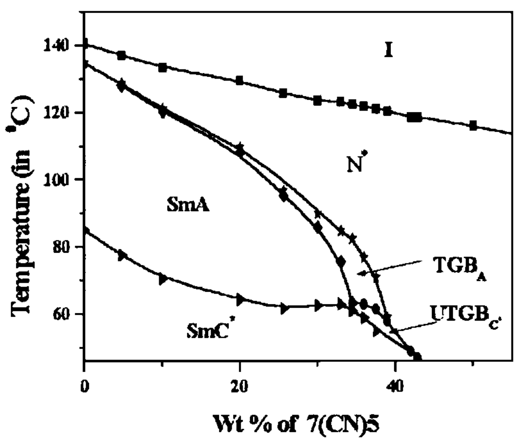

FIGURE 1. Part of the phase diagram containing the TGB phases in binary mixtures of CE8 and 7(CN)5 (adapted from [5]).

The temperature range of TGB_A phase is found to increase with the concentration of the *nonchiral* compound and above 34wt% the $UTGB_C$* phase is also induced. The CE8 sample obtained from Merck does not by itself exhibit the TGB_A phase, even though recently Wilson et al. [7] have reported that in a highly purified sample it shows the TGB_A phase with a range of ~0.5 ^{0}C. However this is not expected to change the main features of the phase diagram. We report measurements of the optical reflection band in the cholesteric phase of a few mixtures to show that the chiral strength decreases as the concentration of 7(CN)5 is increased. Apart from having a sufficiently large chiral strength the material must have type II character to exhibit the TGB_A phase[1,2]. The Ginzburg parameter κ_2

= λ_2/ξ must be greater than $1/\sqrt{2}$, where λ_2 is the twist penetration length defined by $\sqrt{(K_{22}/D)}$ [8], K_{22} and D being the elastic constants for the director twist and tilt in the layer respectively and ξ the smectic order parameter coherence length. We report an electroclinic measurement of D to demonstrate that κ_2 increases with the concentration of 7(CN)5. We describe the effect of low frequency electric fields on the stability of the TGB_A and $UTGB_C$* phases. We also report the observation of a new type of periodic radial structure in the meniscus region of free standing films of the mixtures in the smectic and TGB_A phases. We suggest that the occurrence of this structure depends on the type II character of the materials.

EXPERIMENTAL

The electroclinic measurements were made using a standard technique [9] with an AC signal at a frequency of 417 Hz and 4.9 volts. The temperature of the cell was controlled by an Instec hot stage to an accuracy of 10 mK. The electroclinic signal was measured by using a lock in amplifier (PAR, model 5302). For the optical and electroclinic measurements, the sample was taken between two ITO coated glass plates separated by spacers of ~5μm thickness. The plates were pretreated with polyimide and unidirectionally rubbed. The thickness of the cell was measured by using an interferometric technique.The pitch in the cholesteric phase was measured using an Ocean Optics spectrometer (S2000) in the reflection mode. The free standing films were drawn in holes with diameter 2 mm, drilled in glass slides.The observations were made using a polarising microscope (Leitz, Ortholux).

RESULTS AND DISCUSSION

<u>Optical reflectivity:</u> A typical optical reflectivity spectrum is shown in fig.2. The wavelength of the maximum of the reflection band λ_o= nP where n is the refractive index with a value ≈1.5 for all the mixtures and P is pitch of the helix. In fig.3, 1/P is plotted at (i) 4 ^{0}C below the isotropic to cholesteric transition temperature and (ii) 5 ^{0}C above the TGB_A to cholesteric transition temperature respectively. In both the cases 1/P which is a measure of the chiral strength, decreases with increasing concentration of 7(CN)5, as expected.

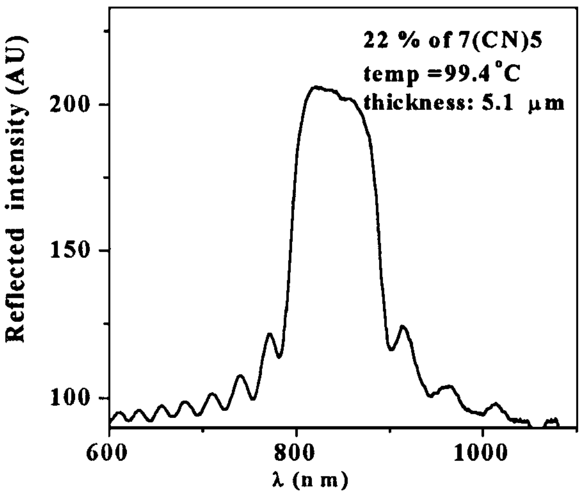

FIGURE 2. A typical reflection spectrum from cholesteric phase.The oscillations arise from the finite thickness of the sample

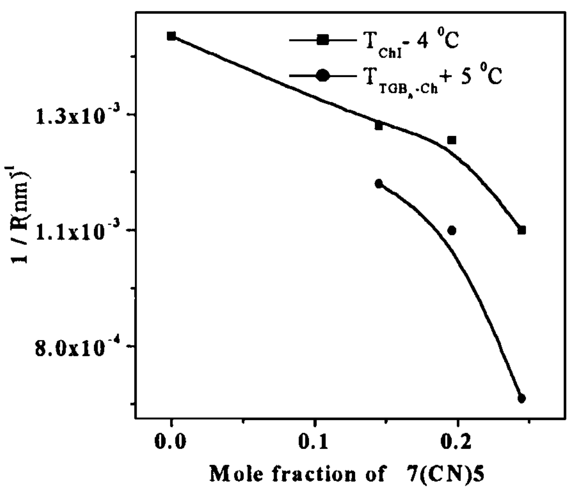

FIGURE 3. Variation of 1/P with mole fraction of 7(CN)5. The continuous lines are drawn as guides to the eye.

Electroclinic measurements: A representative plot of electroclinic coefficient with temperature is shown in fig.4 for the mixture with 20 % 7(CN)5. In the mean field approximation [9,10] the electroclinic co-efficient e = $K/a(T-T_{AC}*)$ where K denotes the tilt-polarisation coupling constant ($P = K\,\theta$). a is the coefficient of the second order term of Landau free energy expression and in the SmA phase it is a measure of the tilt elastic constant. $T_{AC}*$ is the SmA to SmC* transition temperature .The electroclinic coefficient is fitted with the inverse of (T-$T_{AC}*$) to get the ratio of the tilt elastic constant and the tilt-polarisation coupling constant i.e *(a/K)*. Using $K \approx 10^{-4}$ C/m^2 typical for the low polarisation material, a is plotted as a function of concentration of 7(CN)5 in fig.5. It decreases more than 4 times as the mole fraction of 7(CN)5 is increased from 0 to 0.24. This means that K_2 roughly doubles in this range and increases further for the concentration at which the $UTGB_C*$ phase is induced. The enhancement of the type II character accounts for the increased temperature range of TGB_A phase with the concentration of 7(CN)5.

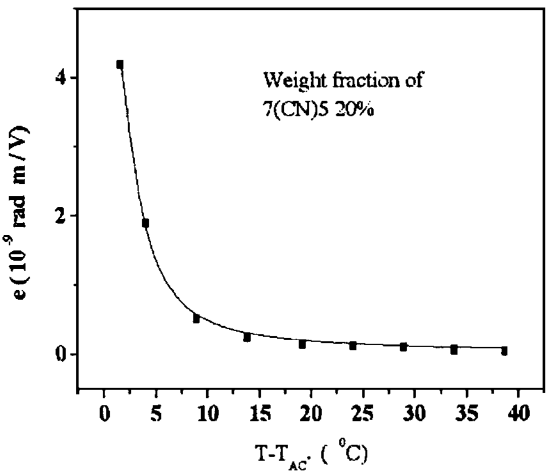

FIGURE 4. Variation of the electroclinic coefficient with temperature for the mixture with 20% of 7(CN)5. Squares: experimental data, lines: theoretical fit.

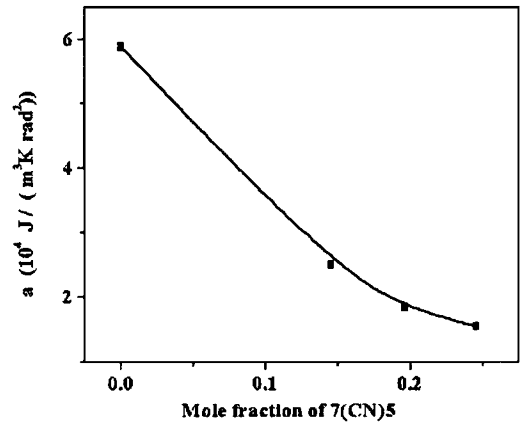

FIGURE 5. The tilt elastic constant *a* plotted as a function of mole fraction of 7(CN)5.

<u>Effect of electric field</u>: We studied the influence of a low frequency electric field along the helix axis of the TGB_A phase on its structure. In the lower temperature part of the TGB_A phase the mixtures with 20% and 25% of 7(CN)5 show an *irreversible* TGB_A to SmA transition under the action of a large (~10 V /μm) low frequency (10Hz) field. A similar effect was reported by Shao *et al.*[11]. The change of texture is shown in fig.6. The Joule heating of the system due to the application of field would have led to a transition to the cholesteric phase as it happens in the higher temperature range of TGB_A phase. The origin of the field induced unwinding of the TGB_A helix in these systems is not yet understood. It is interesting that the $UTGB_C$* undergoes a *reversible* transition to SmC* phase under a low frequency field (50Hz ;13V/μm).

<u>Freestanding Films</u>: We have studied freely suspended films of mixtures, which exhibit the TGB_A and $UTGB_C$* phases. The liquid crystalline films were suspended across a hole drilled in a glass plate. The observations reported here were made on mixtures having about 36 wt % of 7(CN)5. At a temperature corresponding to the occurrence of the TGB_A phase the structure was unwound in the central flat part of the film. The homeotropically aligned smectic layers appeared dark between crossed polarisers. Three distinct regions could be distinguished in the meniscus region. In the thicker part of the

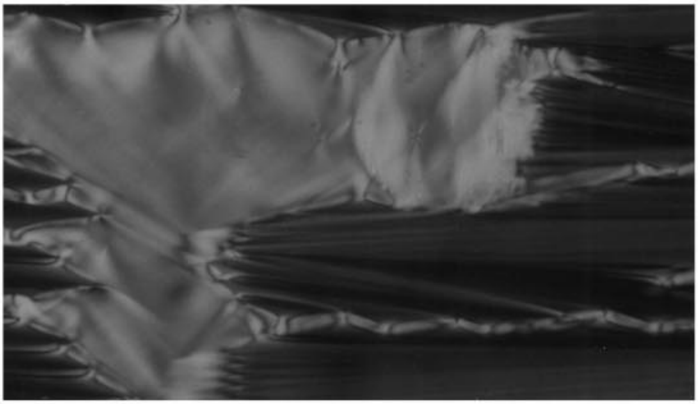

FIGURE 6 Field induced transition from the TGB_A phase (bright region) into the SmA phase in the mixture with 25 wt % of 7(CN)5 at 108.5°C. Crossed polarisers (x 500). (See Color Plate I)

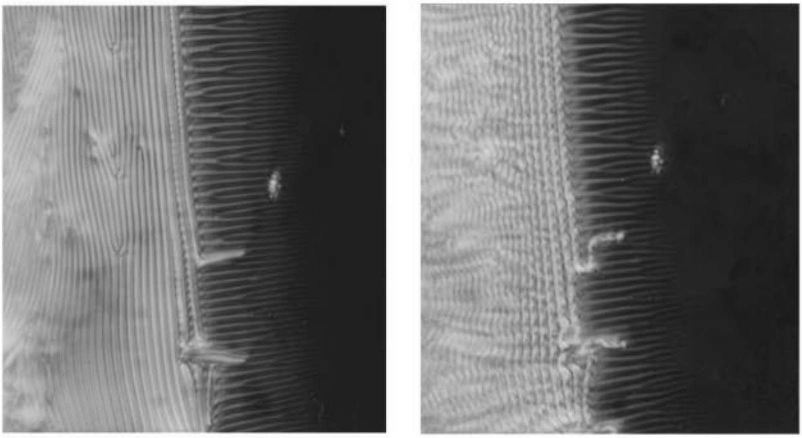

FIGURE 7 (Left) Meniscus region of the free-standing film of the mixture with 36 wt % of 7(CN)5 in the TGB_A phase at 59.8°C. Crossed polarisers, (x 400). The central flat part is at the right extreme, the radial structure is seen in the central part of the meniscus and the filaments are in the thickest part of the meniscus. (Right) Sample in the $UTGB_C^*$ phase at 57.4° C. Note the undulation of the filaments. (See Color Plate II)

meniscus, close to the periphery of the hole, filaments which are characteristic of the TGB_A liquid crystal subjected to homeotropic boundary conditions, could be observed (fig.7). The director rotates by π radians across the filament, whose width is P/2, where P is the pitch of the TGB helix. The filaments were oriented parallel to the edge of the hole. The width was independent of the local thickness. Some filaments sharply turn by 90^0 near the thinnest part in which they are seen and extend along the radial direction (fig.7). A *new* type of periodic structure was seen in the intermediate thickness region of the meniscus and was found to consist of alternate bright and dark stripes between crossed polarisers (see fig.7). The radial stripes (RS) have a low contrast in comparison to the filaments, which are very bright even when oriented along the radial direction. On rotation of the crossed polarisers, the width of the dark region of the RS decreases when the polariser axis is at 45^0 to the radial direction. Careful observations show that the bright stripes do not have a uniform intensity along their length but are marked by narrow bands of lower intensity, which are orthogonal to the radial direction. The average spatial periodicity of the radial stripes increases with film thickness, which is brought about by the introduction of edge dislocations (fig.7). The thinnest part of the meniscus region appears completely dark between crossed polarisers. The contrast of RS becomes lower as the thickness of the meniscus region is decreased. It is not clear whether the spatial periodicity of the radial structure in the thinnest part is too small to be resolved by the microscope.

When the sample was cooled into the $UTGB_C^*$ phase the filaments in the thicker part of the meniscus undulated (fig.7) as expected[5]. The periodic RS structure in the intermediate region however remained intact.

Somewhat similar regularly spaced radial domains have been observed in the meniscus region of thin free-standing films of a nonchiral SmC sample[12]. This has been attributed to surface polarisation, which gives rise to a periodic splay deformation of the C-director. When such a sample is rotated between crossed polarisers the relative positions of the bright and dark domains can be expected to depend on the orientation of the polariser axis with respect to the radial direction. In the TGB_A sample studied by us there is no molecular tilt in the layers. Further, the positions of the bright and dark stripes of the periodic structure do not shift under a rotation of crossed polarisers.

The origin of the RS observed by us, cannot be the one described above.

Recent observations with a confocal microscope, on a free-standing film of the same TGB sample used by us have shown evidence for the occurrence of edge dislocations with large Burgers vectors in the smectic layers of the meniscus region [13]. The spacing between the dislocations decreases towards the thicker part of the meniscus. The sharp bands orthogonal to the radial direction of the stripes that we described earlier appear to correspond to these edge dislocations. Recent studies on the meniscus region of free-standing films of type I smectic liquid crystals (like alkyl cyanobiphenyls) have shown that the edge dislocations have Burgers vectors equal to single layer spacing in the thinnest region while larger Burgers vectors occur in the thicker parts. The latter go over to rows of focal conics[14]. On the other hand studies on swollen lamellar phases in a lyotropic system taken between a slide and a convex lens have shown that the Burgers vectors of edge dislocations are large, and increase from ten to thirty as the sample thickness is increased[15]. Our type II system appears to be similar to the latter system.

A possible arrangement of smectic layers in the meniscus region of our system is shown in fig.8. As the surface tension of smectic layers is ≈ 30 dyne / cm [14], we expect that the layers near the surface have a smooth profile. The occurrence of edge dislocations with large Burgers vectors then leads to regions with a large tensile strain (fig. 8).

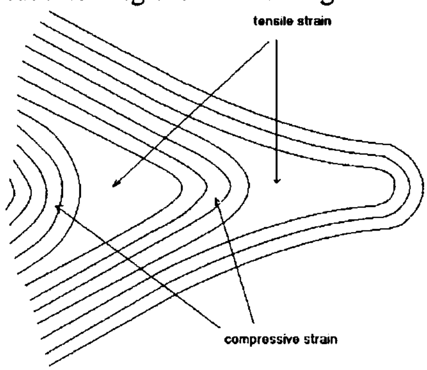

FIGURE 8 . Schematic diagram of the arrangement of smectic layers in the meniscus region. The undulation of the layers is expected to take place in the region with tensile strain, along a direction perpendicular to the plane of the paper, in which the local thickness is constant.

It is known that beyond a tensile strain $\approx 2\pi\lambda_1/d$, where λ_1 is the splay penetration length given by $\sqrt{(K_{11}/B)}$, K_{11} being the splay elastic constant and B the compression constant of the layers and d the layer spacing, the layers can undulate to fill space[1]. In the intermediate thickness region, such an instability can generate the RS seen in the experiments. The periodicity of the structure would depend on the local thickness[1] as seen in the experiment. The undulation instability is usually metastable and gives rise to other structures over a period of time [1]. On the other hand, the RS structure is indeed stable and is better formed if the sample temperature is held constant for several hours. A detailed theoretical analysis to understand this new feature is desirable.

We have also made observations on an open drop of the liquid crystal taken on a glass plate treated for homeotropic alignment. The drop has a flattened hemispherical shape. As in the free-standing film there was a decrease in thickness on moving towards the edge of the drop. The periodic radial structure was obtained in this case also with its spacing decreasing towards the periphery of the drop.

CONCLUSIONS

We have demonstrated that the type II character is enhanced in the mixtures studied by us by increasing the concentration of the nonchiral component, which in turn enlarges the temperature range of TGB phases. We have also found an unusual radial stripe texture in an intermediate thickness region of the meniscus in free-standing films of the type II material. We argue that these are generated by an undulation instability of the smectic layers in the regions of high tensile strain associated with edge dislocations with large Burgers vectors. Though the swollen lamellar phase also exhibits edge dislocations with large Burgers vectors, the orthogonal periodic stripes have not been reported in that case. Our system has a decidedly type II character and the RS structure appears to be associated with this feature.

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