Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: Nagappa, J Mahadeva, R H Nayak & P R Alapati (1997): Twisted Grain Boundary Phase in the Binary Mixture of Neuatic and Ceolesteryl Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 304:1, 409-414

To link to this article: http://dx.doi.org/10.1080/10587259708046989

Mol. Cryst. Liq. Cryst., 1997, Vol. 304, pp. 409–414
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TWISTED GRAIN BOUNDARY PHASE IN THE BINARY MIXTURE OF NEMATIC AND CHOLESTERYL COMPOUNDS.

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Abstract: The binary mixture of cholesteryl nonanoate(CN) and 4,4'-hexyloxy azoxy benzene (HOB) exhibit a very interesting mesophases like blue phase, twisted grain boundary (TGB) phase, induced smectic A, smectic C and smectic B phases at different temperatures when the mixture is cooled from isotropic phase. The existence of TGB phase is confirmed by DSC and optical microscopic studies. The mixtures with concentration 30 to 45% of CN exhibit TGB phase at higher temperature. The optical anisotropy of cholesteric phase is estimated. Numerous interesting optical textures are also illustrated.

INTRODUCTION

The novel new liquid crystalline twisted grain boundary(TGB) phase was first theoritically predicted by Renn and Lubensky[1] which is analog of the Abrikosov phase in superconductors[2]. This phase is a helical smectic A (S_A) or TGB which intervene between the low temperature S_A phase and high temperature cholesteric phase. This new phase is recognised by a rotated blocks of a S_A layers, in which long molecular axes are arranged normally to the layer planes. The twist in the molecular axes are expected in the direction of the layer planes. Hence the helical axes of a TGB phase is perpendicular to the molecular axes and parallel to the smectic planes. The relative rotations of the individual smectic blocks are considered as the net work of screw dislocation. The

existence of TGB phase in the mixtures of nematic and cholesteric compounds was studied by an earlier authors[3,4]. Renn and Lubensky[5] theoritical prediction of TGB-S_A phase, is always appear if the molecular chirality is introduced near the nematic-S_A-Sc (NAC) multicritical point in the phase diagram[6]. In the case of TGB-S_A phase the temperature span of it should increase with increase in chirality of the system. The TGB-Sc^* phase close to NAC point composed of twisted stacks of helical Sc^* phase is also predicted[7,8].

In the light of the above facts we consider the mixture of two component system exhibiting Ch-S_A-Sc point which is shown in phase diagram. The liquid crystals used in this investigation are nematic compound HOB and cholesteryl compound CN. The mixture exhibit a blue phase III, II and I-c^1-TGB-S_A-Sc-S_B phases sequentially, While cooling the specimen from isotropic phase. DSC, Optical and X-ray studies have been carried out at different temperatures.

EXPERIMENTAL

Mixtures of ten different concentrations were prepared and the phase transitions of the mixtures were determined using Leitz polarizing microscope and hot stage. The DSC thermograms were taken for all the concentrations using the Perkin-Elmer DSC II instrument facility available at Raman Research Institute. The DSC thermogram which is obtained for the 40% of CN exhibits, Iso 121°C-BP118°C - $Ch_1$116°C - Ch_2 110°C - TGB_1 103°C - TGB_2 71°C -S_A 59°C - Sc 25°C - S_B. The DSC curve is shown in fig(2).

The phase diagram shown in the fig(1) illustrates that the concentration from 1 to 30% of CN in HOB and from 46 to 100% of CN exhibit cholesteric, S_A and S_B phases respectively. The concentrations between 31 to 45%

of CN exhibits Iso-BP-Ch-TGB-S_A-S_B phases sequentially when the specimen is cooled from isotropic phase.

OPTICAL TEXTURE STUDIES

The textures obtained in the present study were similar to that observed in the literature[9,10,11]. When the specimen is cooled from isotropic state, it exhibit blue phase and then non ringed sphurulitic textures at 118°C which is the characteristics of cholesteric phase as shown in fig.3(a). At 116°C ringed sphurulites were developed and which are shown in fig.3(b). Further when the transition takes place from cholesteric to TGB phase, ringed sphurulites grow in size and rings develop in the form of spiral filament at 110°C which is shown in fig.3(c). This texture is the characteristics of TGB phase. These spirals slowly unwinding at 103°C and the filament texture is appeared as shown in fig.3(d). This filament texture of the TGB phase remains for long range of temperature from 103 to 71°C. The helical structure of the TGB phase which is exhibiting plane texture has a helical axis lie in a direction parallel to the layer of the phase[8,12]. On further cooling the specimen it exhibits focal conic texture upto 54°C which is characteristic of S_A phase as shown in fig.3(e). This S_A phase is unstable and on further cooling the S_A phase is transformed to S_C phase and then to S_B phase at room temperature.

OPTICAL ANISOTROPY

For the estimation of the optical anisotropy, the density and refractive indices n_1 and n_2 for 5893A° in cholesteric phase of mixtures were measured using Abbe refractometer and Goniometer spectrometer for different temperature[13]. n_1 and n_2 correspond to the refractive

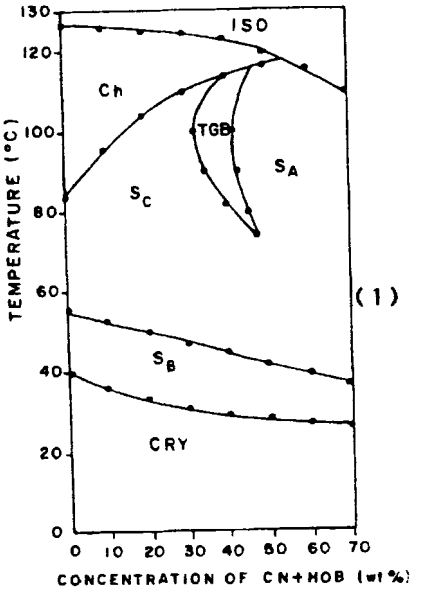
indices for ordinary and extraordinary ray respectively have $n_1 > n_2$. The mean polarizabilities α_{mix} of cholesteric phase for different concentrations were calculated using Lorentz-Lorenz relation,

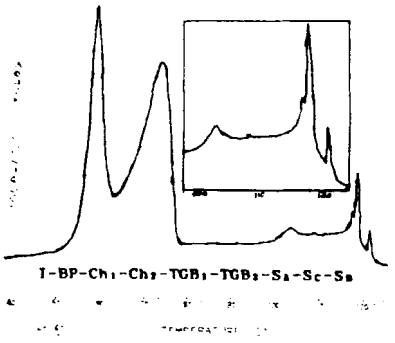
$$\bar{n}^2 - 1/\bar{n}^2 + 2 = 4\pi/3\ N\ \alpha_{mix} \quad (1)$$

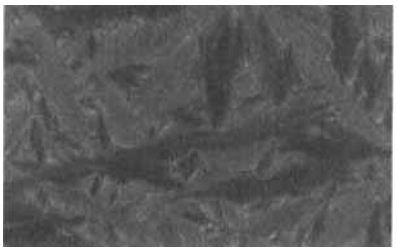
where $\bar{n} = (n_1^2 + 2n_2^2)/3$

$$N(\alpha_{mix}) = N_a\alpha_a + N_b\alpha_b \text{ and } N = N_a + N_b \quad (2)$$

N_a and N_b are number of molecules per unit volume of CN and HOB respectively. The optical anisotropy of polarisabilities







3(e)

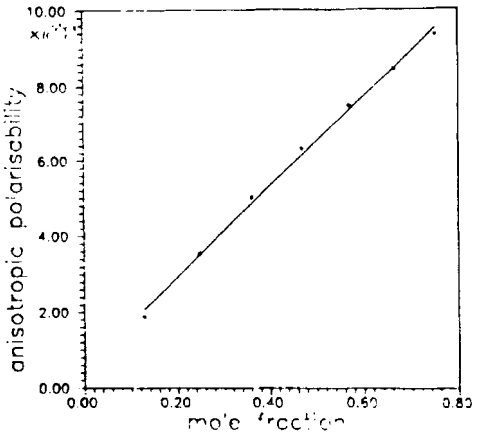


FIGURE 1 Partial phase diagram of CN + HOB
FIGURE 2 DSC Thermogram of 40 % of CN
FIGURE 4 Variation of anisotropic polarisability with mole fraction
(See Color Plate XVI).

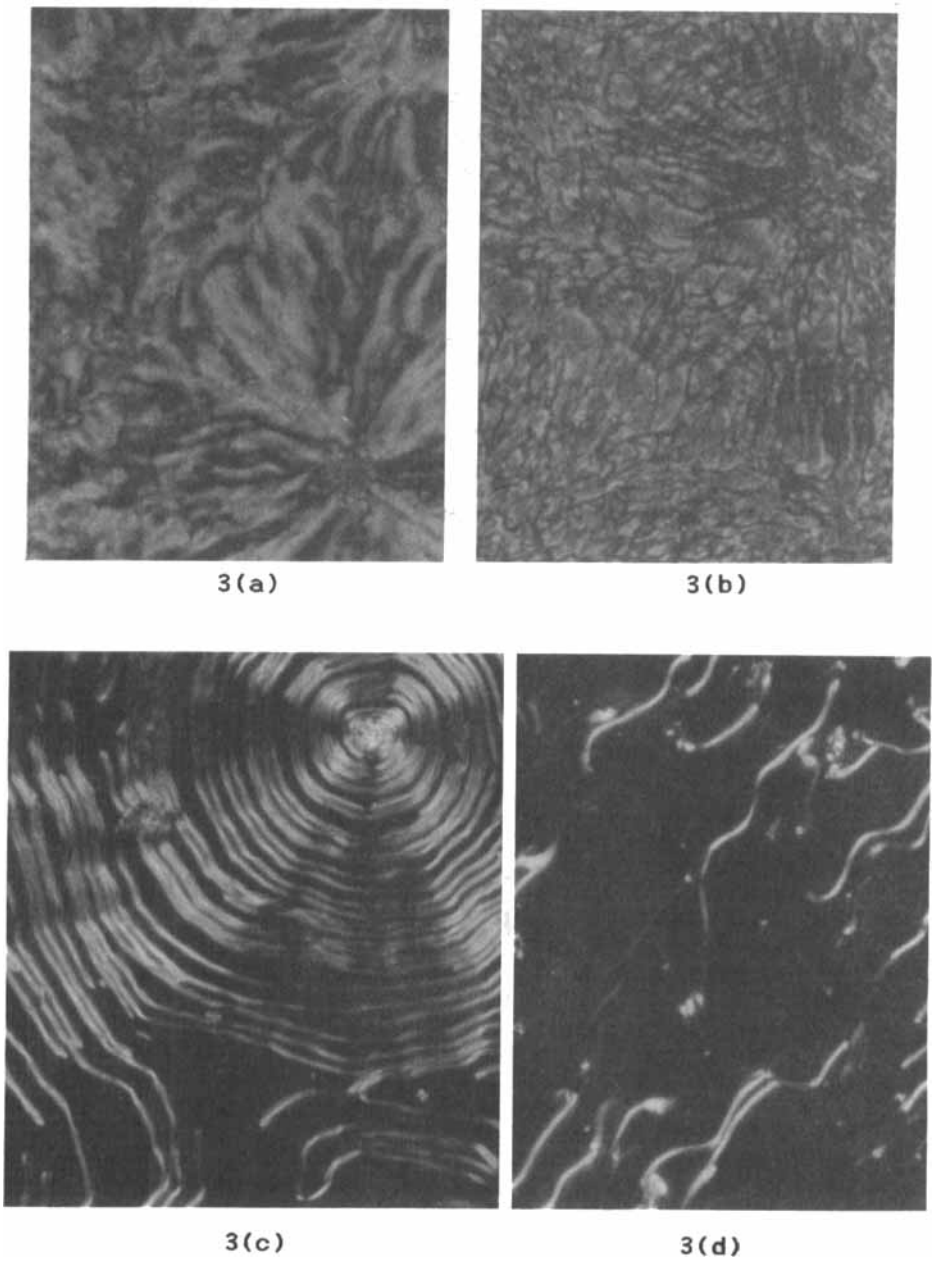


FIGURE 3 **Microphotographs of a) Cholesteric phase at 118°C (185X) b) Cholesteric phase at 116°C (185X) c) TGB Phase at 110°C (185X) d) TGB Phase at 103°C (185X) e) Smectic Phase at 59°C (160X)** (See Color Plate XVII).

$(\alpha_1-\alpha_2)_{mix} = (\Delta\alpha)_{mix}$ is given by additivity relation[14]

$$(\Delta\alpha)_{mix}=[N_a(\Delta\alpha)_a+N_b(\Delta\alpha)_b]/(N_a+N_b) \quad (3)$$

$(\Delta\alpha)_a$ and $(\Delta\alpha)_b$ are the anisotropy polarizabilities of CN and HOB respectively. $(\Delta\alpha)_b$ is equal to $(\alpha_e-\alpha_o)/2$ at corresponding temperatures of nematic phase and $(\Delta\alpha)_a$ is equal to $(\alpha_e-\alpha_o)$ of CN. The factor half involved in the expression for $(\Delta\alpha)_b$ arises because the molecules of HOB are arranged in the layers of the helicoidal structure of the cholesteric phase. Equation 3 can be written as

$$[(\Delta\alpha)_{mix}-\{N_a(\Delta\alpha)_a/(N_a+N_b)\}] = N_b(\Delta\alpha)_b/N_a+N_b) \quad (4)$$

The left hand side of the above equation is plotted against $N_b/(N_a+N_b)$ in fig.4. The slope of the straight line equal to $12.0066X10^{-24}$ cm^3 is equal to anisotropy of HOB nematic this being half of the values of $(\alpha_e-\alpha_o)$ $6.0033X10^{-24}$ cm^3 for CN at 92.2°C.

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