Twist Grain Boundary phases in binary mixture of Liquid Crystals

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ABSTRACT

The Investigations of Twist Grain Boundary (TGB) phases in liquid crystals exhibits in different types of structural groups. In this study, these new findings present in the binary mixture of highly chiral liquid crystal, Cholesteric Nonanoate (CN) and nematic liquid crystal, N-(4-Ethoxy benzylidene)-4-butyle aniline (EBBA). The Differential Scanning Calorimeter (DSC) has shown the thermodynamic phase transition of binary mixture at different scanning rate. At the other hand Optical studies of Twist grain boundary phases has also shown different type of textures. The domain of existence of TGB has exhibited with the weight percentage of EBBA is increased in highly chiral liquid crystals. This is very excited fact that the temperature range of type of TGB (TGBA*) phase is different at the different scanning rate. In the optical investigation we found new phases in cooling cycle as compare to the heating cycle.

Keywords: Liquid crystals, TGB, TGBA*, Binary mixture

1. INTRODUCTION

Twist Grain Boundary (TGB) phases are aggravated phases. In liquid crystal area, TGB phases are less. Basically at an equilibrium distribution the topological defect is present in the Twist Grain Boundary (TGB) phases of liquid crystals. TGB phases have complex and delicate structure. de Gennes accredited brilliantly first in 1972 [1], the resemblance between the
nematic (N) to smectic A (SmA) transition in liquid crystals and the normal to superconductor transition in metals. According to this strong resemblance, a transition between the cholesteric (N*) and SmA phases would occur either directly or would proceed through an intermediate phase characterized by a twisted lattice of screw dislocations (Fig. 1). This intermediate phase is similar of Abrikosov’s triangular flux vortex lattice [2, 3], it present in type II of superconductors in an externally imposed magnetic field. Like Abrikosov’s flux lattice, the TGB would occur if \( \kappa \equiv \lambda/\xi \), the ratio of the twist penetration depth and the smectic coherence length, exceeded \( 1/\sqrt{2} \).

**Figure 1.** Schematic representation of TGBA* phase. Blocks of SmA* layers of spacing ‘d’ are separated by regularly spaced twist grain boundaries by a distance ‘\( l_b \)’. The distance between screw dislocations with in a grain boundary is ‘\( l_d \)’. The angles of the normal to the smectic planes separated by a grain boundary differ by \( \Delta \psi \approx d/l_d \). The molecular director \( n(z) \) lies in planes perpendicular to the pitch axis, P. The director executes one full turn in a distance equal to \( \lambda_0 = 2\pi l_b/\Delta \psi \). The average configuration of the director in TGB model is very similar to that of chloesteric phase [4].

On the theoretical front, Renn and Lubensky [5] predicted a specific model for the Twist Grain Boundary SmA (TGBA) phase. Its structure consists of SmA slabs of constant thickness \( l_b \) stacked in a helical fashion along an axis x parallel to the smectic layers of thickness d. Adjacent slabs are continuously connected via a twist grain boundary made of parallel screw dislocation lines analogous to magnetic vortices. The nematic director ‘\( n \)’ (or equivalently the smectic layer normal N) is rotated across each grain boundary by finite angle \( \Delta = 2 \tan^{-1}(d/2l_d) \), where d is the smectic period and \( l_d \) is the distance between parallel dislocation lines [7]. As a result, twist penetrates the smectic structure just as magnetic field penetrates the type II superconducting phase via the Abrikosov flux lattice.
In the vicinity of a cholesteric (N*) – SmA - chiral smectic C (SmC*) point (where the type II condition is expected to be met), RL [6] also predicted the existence of two new additional TGB phases, namely TGB_c and TGB_{c*} in which the smectic slabs are respectively, SmC and SmC*.

This distinction between three different Abrikosov phases is particular to liquid crystals and does not exist in superconductors [8].

Renn and Lubensky [5] showed that the nature of the TGB state depends on the value of the twist angle \(\Delta = 2\pi \alpha\). If \(\alpha\) is irrational, no periodicity exists along the pitch axis x and the state is incommensurate; If on the other hand \(\alpha\) is rational (say \(\alpha = p/q\) with p, q mutually prime integers), the structure is commensurate and x is q-fold screw axis, if this screw axis is not crystallographically allowed (i.e. if q ≠ 2, 3, 4 or 6), the TGB state has quasicrystalline rather than periodic crystalline symmetry and is commensurate in the plane y-z perpendicular to the pitch axis [9-11].

2. METHODOLOGY

A highly pure chiral liquid crystal Cholesteric Nonanoate (CN) and nematic liquid crystal N-(4-Ethoxy benzylidine)-4-butyl aniline (EBBA) was purchased from New Jersey, USA, and was procured from Aldrich chemical company respectively. Binary mixture were prepared by weighing out pure samples using electrobalance of Precisa (Model ACS-205) having an accuracy ± 0.1 mg.

Pure Cholesteric Nonanoate Binary mixtures of CN10 (90% CN and 10% EBBA) weight proportions of Cholesteric Nonanoate (CN) and N-(4-Ethoxy benzylidine)-4-butyl aniline (EBBA) were prepared by weighing out pure samples using electrobalance of Precisa (Model ACS-205). The mixtures were heated upto 100 ºC in oven; shaken well and then kept in oven for 2 hours at 100 ºC temp. After two hours these mixture are again shaken and then kept at room temp.

Different mesophase transition temperatures were determined by using a Differential Scanning Calorimeter (DSC) of Mettler Toledo (Model DSC822e with STAR® software) at two scanning rates 5.0 ºC/min and 10.0 ºC/min. DSC thermograms were located with an accuracy of ± 0.2 ºC whereas the temperature reproducibility of the measurements was better than ± 0.1 ºC.

A transmitted light polarizing microscope, OLYMPUS BX 51P was used to identify the textures of different mesophases under different anchoring condition. The cell thickness was 6µm.

3. RESULTS AND DISCUSSION

3.1. Thermodynamical studies

Thermodynamic data of binary mixture of nematic and chiral liquid crystals at the ratio (90% CN and 10% EBBA) were acquired at two scanning rates.

The DSC thermograms of the binary mixture CN 10 [90 % CN and 10 % EBBA] at 5 ºC/min and 10ºC/min scanning rates in heating are shown in Fig. 2 & Fig. 3 respectively. The transition temperatures and enthalpies are given in the Table 1. Table 1 shows various transition
temperatures with respect to scanning rates. We find that the transition temperatures have a tendency to increase linearly with increase in heating rate.

**Table 1.** Variation of transition temperatures and enthalpies with scanning rate for CN10.

<table>
<thead>
<tr>
<th>Scanning Rate (°C/min) and mass (mg) of the sample</th>
<th>Phase change with transition temperatures (°C) and enthalpies (J/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 °C/min (4.9 mg)</td>
<td>K-SmA 24.6 °C (1.0 J/gm)</td>
</tr>
<tr>
<td>10 °C/min (8.2 mg)</td>
<td>K-SmA 25.4 °C (0.2 J/gm)</td>
</tr>
</tbody>
</table>

**Figure 2.** DSC thermogram of CN10 at 5 °C/min scanning rate.
Figure 3. DSC thermogram of CN10 at 10 °C/min scanning rate.

CN 10 shows SmA phase at room temperature. SmA phase on heating gives TGB phases which on further heating give rise to N* phase. The transition is reversible but the phases are super cooled on cooling and are manifested in different molecular configuration as evidenced by textural investigations.

3. 2. Characterization of Mesophases by Optical microscopy

Figure 4. Separation of N* phase from the molten sample at 85 °C
It is interesting to note that TGB phases are most easily revealed in heating cycles under DSC observations. The phases have been confirmed by microscopic observations. The N* - BP transition was not detected in DSC observations however (Fig. 4), optical microscopic observations clearly revealed the existence of Blue Phase in the mixture. Fig. 4, shows perfectly grown cholesteric phase at 84 °C obtained on cooling the Blue Phase.

The cholesteric helix axis is basically oriented in the plane of the substrate, but without any preferred in-plane direction.

![Figure 5. Texture of cholesteric phase (N*) of CN10](image)

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![Figure 6. Transformation TGBA* to TGBC* Texture of CN10](image)

Figure 6. Transformation TGBA* to TGBC* Texture of CN10
On cooling the sample from the N* phase cylindrical domain type texture with black fringes originating from the sharp eyes is observed at 69.9 °C as shown in Figure 5. This results from smectic layers being formed in a concentric fashion, with the TGBA* helix axis along the smectic layer planes and perpendicular to the long molecular axis [18]. The whole structure is coiled in a double twist cylinder as proposed by Rebeiro et. al [20].

The TGBA* phase on cooling to 67 °C gives rise to a texture as shown in Figure 6. It is possibly a TGBC* phase. Here the CC domains are decorated with fracture lines (the dielectric studies reveal existence of a Goldstone mode in this region which can be suppressed by application of high DC bias).

Figure 7. Perfect TGBC* Texture of CN10

Figure 8. Perfect SmA Texture of CN10
The helical axis orientation of the TGBA* phase in comparison to TGBC* phase is nicely demonstrated in Fig. 7 (indicated by arrows). The 90° twist of the helical axis in a SmC* block is clearly visible. The TGBC* phase transforms to SmA at 65 °C (Fig. 8).

4. CONCLUSIONS

We have presented experimental study of the TGB phases observed in binary mixtures of CN and EBBA. A phase diagram is prepared that is identical with the mean field phase diagram derived by Renn [6] within the framework of chiral Chen- Lubensky model. Phase sequence of I – BP – N* - TGBA – SmA has been observed below SmA – N* - SmC* virtual tricritical point (TCP= 70% CN and 30% EBBA) whereas the phase sequence of I – BP – N* - TGBH – TGBA – TGBC* has been observed above TCP.

Two different types of Textures namely developable domain texture – characteristic of columnar phases and planar oily-streak texture – characteristic of helical phases have been simultaneously observed [12-15]. It is interesting to note that for all the samples studied, the CC domains are formed preferentially in the cooling cycles whereas in heating cycles the planar oily streak texture or the Grandjean texture is observed in the region of TGB existence [16-19]. The observed optical textures can be interpreted in accordance with a model proposed by Rebeiro et al [20]. According to this model the observed textures result due to the coiling of the smectic blocks, the grain boundaries and the layers of the helical structure of the TGB phases around the axis of cylinder in a double twist manner.

References


