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Twisted Grain Boundary Phases in Binary Mixture of Smectic and Cholesteryl Compounds

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A binary mixture of cholesteryl ethyl corbonate (CEC) and terephthal-bis-p-n-tetradecylaniline (T_{B14A}) exhibits a twisted grain boundary (TGB) phase and smectic polymorphic phases. The mixture exhibits TGB-A and TGB-C phases at different concentrations and at different temperatures. Mixtures with higher concentrations of T_{B14A} exhibit I – Ch – TGB-A – TGB-C – Sm A – Sm I – Sm F phases sequentially when the specimen is cooled from its isotropic melt. The existence of different TGB phases and polymorphic smectic phases are confirmed by differential scanning calorimetric (DSC) and optical microscopic studies. The phase diagram is in accordance with the Renn and Lubbensky model.

Keywords TGB phase; smectic and cholestric mixture; Renn and Lubbensky model

Introduction

Liquid crystals are widely used in electro-optic display devices such as optical switches, light modulators, and image devices [1–3]. The use of liquid crystals in these devices depends on the kinds of mesophases exhibited by the liquid crystals, the transition temperature (T_C), and optical anisotropies.

The phenomenon associated with chiral liquid crystals has shown increasing importance with respect to both the crystals' fundamental scientific significance and their applicability to electro-optics and opto-electronics. The nature of chiral smectic phases that are exhibited in the mixture when there is a phase transition from cholesteric to smectic is clearly investigated. The existence of a twisted grain boundary (TGB) phase, near a virtual NAC point, in a binary mixture of liquid crystalline compounds [4] has been well investigated by earlier investigators.

The theoretical prediction by Renn and Lubbensky was a remarkable development in the field of liquid crystals to understand the effect of chirality on smectic-A liquid crystals [5,6]. The theoretical basis for this prediction was the de Gennes model for the

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nematic to smectic-A (Sm A) transition, which is analogous to super-conducting transition [7]. According to the de Gennes model, the TGB phase, which occurred on the smectic-A side, i.e., TGB-A phase, is the analog of the Abrikosov [8] vortex lattice of Type II superconductors. At the same time, Goodby et al. [9,10] discovered the Sm A* phase in highly chiral homologous series. X-ray studies on non-aligned samples reveal that the Sm A* phase exhibits both smectic layering and cholesteric textures simultaneously. Thus, the Sm A* phase is nothing but a TGB phase. The TGB phase is characterized by the non-vanishing twist and long-range smectic correlations within this plane perpendicular to the pitch axis. It has formed several remarkable features of the Sm A – Sm A* – Sm C* multicritical point [11]. Nagappa et al. [12] have observed the TGB-A phase in mixtures of cholesteric and nematic compounds. Sadashiva [13] and Pramod et al. [14] have observed a transition from TGB-A to TGB-C* in some pure chiral liquid crystals and in mixtures of chiral liquid crystals.

In the present investigation, we have considered a binary mixture of smectic and cholesteric compounds. A pure smectic compound exhibits I – Sm C – Sm I – Sm G – Sm F crystal phases. At very low concentrations of the cholesteric, the mixture exhibits transitions Cho – TGB-A and TGB-A – TGB-C at higher temperatures. The differential scanning calorimetric (DSC) and optical texture studies lend support to the above results.

Experimental Studies

In the present investigation, we have used a binary mixture of smectic and cholesteric liquid crystals, viz., terephthal-bis-p-n-tetradecylaniline (T_{B14A}) and cholesteryl ethyl corbonate (CEC). These chemicals are obtained from M/s Eastman Organic Chemicals, USA, at a given purity of 98% minimum. In the case of T_{B14A}, the isotropic liquid crystalline phase transition temperature is 160°C, and for CEC, it is 103°C, both of which are measured using a polarizing microscope in conjunction with a specially constructed hot stage.

For the optical texture studies, the sample was sandwiched between a slide and a cover slip and melted by keeping it in a conventional hot stage, the temperature of which can be controlled. The textures were observed using a Leitz polarizing microscope by varying the temperature of the hot stage; the thickness of the samples was usually of the order of 25–50 μm.

The isotropic liquid crystalline phase transition temperatures of T_{B14A} and CEC are compared with the values obtained from the DSC thermograms. The DSC thermograms are obtained from a DSC II instrument facility available at the Raman Research Institute, Bangalore, India. The structural formulae for these compounds are as shown in Figs. 1(a) and (b). The binary mixture of 20 different concentrations of T_{B14A} and CEC by weight percentage were prepared and mixed very well in the molten state.

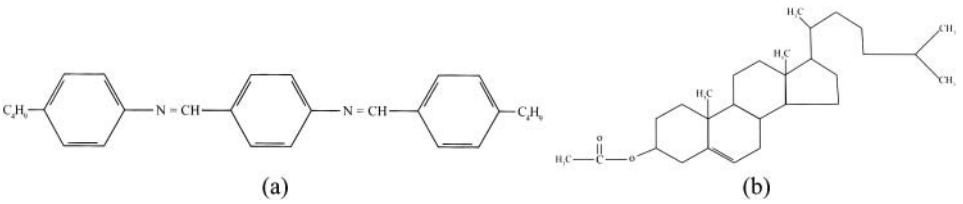

Figure 1. (a) Structural formula of the terephthal-bis-p-n-tetradecylaniline (T_{B14A}) molecule. (b) Structural formula of the cholesteryl ethyl carbonate (CEC) molecule.

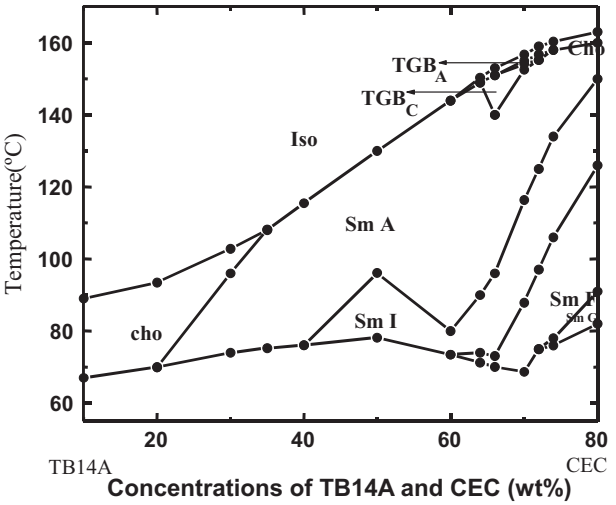

Figure 2. Partial phase diagram for the mixture of T_{B14A} and CEC.

Results and Discussions

Phase Diagram

The phase diagram is as shown in Fig. 2 and is obtained by plotting the phase transition temperatures against the concentrations of the given mixture. A concentration of 70% of T_{B14A} in CEC exhibits I – Cho – TGB-A – TGB-C – Sm A – Sm I – Sm F – crystal phases sequentially when the specimen is cooled from its isotropic melt. The chiral liquid crystalline TGB phases are observed only at higher concentrations and at higher temperatures of T_{B14A}, i.e., from 63% to 74%. The intermediate concentrations from 35% to 59% of T_{B14A} exhibit only the smectic-A and smectic-I phases. The lower concentrations from 10% to 22% of T_{B14A} show only the cholesteric phase. The change of phases observed in the DSC thermograms also lends support to the texture studies performed using a Leitz polarizing microscope. The DSC thermograms for mixtures of 70% and 50% T_{B14A} in CEC are shown in Figs. 3(a) and (b), respectively. The sequence of phases displayed at different temperatures for mixtures of 70% and 50% T_{B14A} in CEC, respectively, is

$$\mathrm{I} \rightarrow 156.7^{\circ}\mathrm{C}, \mathrm{Cho} \rightarrow 155^{\circ}\mathrm{C}, \mathrm{TGB}-\mathrm{A} \rightarrow 154.1^{\circ}\mathrm{C}, \mathrm{TGB}-\mathrm{C} \rightarrow 152.5^{\circ}\mathrm{C},$$
$$\mathrm{SmA} \rightarrow 116.4^{\circ}\mathrm{C}, \mathrm{SmI} \rightarrow 87.9^{\circ}\mathrm{C}, \mathrm{SmF} \rightarrow 68.7^{\circ}\mathrm{C}$$
$$\mathrm{I} \rightarrow 130^{\circ}\mathrm{C}, \mathrm{SmA} \rightarrow 96.2^{\circ}\mathrm{C}, \mathrm{SmF} \rightarrow 78.2^{\circ}\mathrm{C}.$$

Optical Texture Studies

A pure CEC compound exhibits a planar texture when there is phase transition from isotropic to liquid crystal. The planar texture is characterized by the specular reflection arising from the helicoidal structure of the cholesteric phase. This has a spatial periodicity in the order of the wavelength of light.

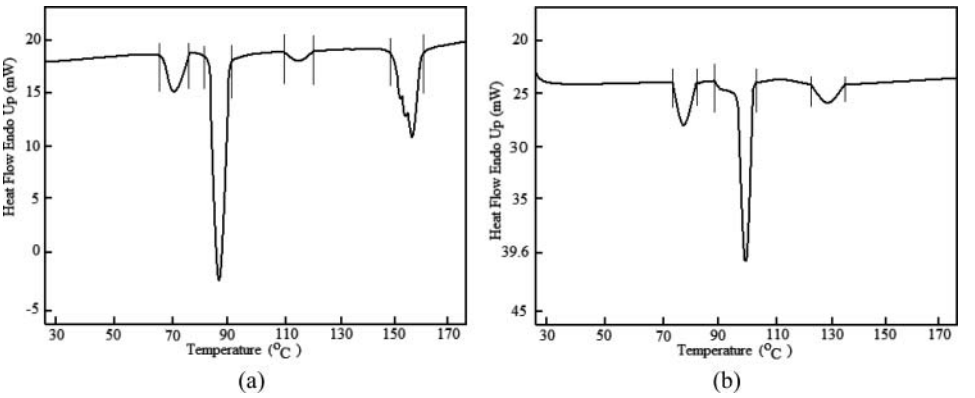

Figure 3. (a) DSC thermogram for the mixture of 70% of T_{B14A} in CEC. (b) DSC thermogram for the mixture of 50% of T_{B14A} in CEC.

When the molten sample of mixture of 70% of T_{B14A} in CEC is cooled from its isotropic liquid crystalline phase transition temperature (156.7°C), nucleation starts in the form of minute bubbles, and immediately, these bubble grow radially and form a fingerprint pattern, which is characteristic of the cholesteric phase, and the texture so obtained is shown in Fig. 4(a). With further decreasing the temperature of the sample, the cholesteric phase changes over to the smectic phase, passing through an intermediate phase. The transition to the intermediate phase is assessed by the appearance of a streak-like texture in the homeotropic region, arranged in a hexagonal form, which is characteristic of the TGB-A phase, and the same is shown in Fig. 4(b). The hexagonal grid patterned TGB (TGB-A) phase changes over to the schlieren texture at temperature 152.5°C, which is characteristic of the TGB-C phase, and is shown in Fig. 4(c). On further cooling, the schlieren texture of the TGB phase changes over to the focal conic fan-shaped texture of the smectic-A phase at temperature 116.4°C, as shown in Fig. 4(d). Ultimately, the Sm A phase undergoes a polymorphic smectic phase transition sequentially in the order Sm I – Sm F – Sm G – crystal phase at lower temperature. The molecules in the Sm G phase are packed within the layers, having their long axes tilted with respect to normal to the layer planes [15]. Whenever a TGB-C phase changes over to a smectic-A phase, this phase is followed by broken focal conic schlieren and schlieren mosaic textures, which are characterized by the Sm I and Sm F phases, as shown in Figs. 4(e) and (f), respectively. Here, the smectic-I phase is a tilted biaxial phase [16]; the pseudo hexagonal molecular packing identifies the molecular structure in the smectic-I phase, and this phase is hexatic in nature [17]. In the Sm F phase, the molecules are packed in layers, with their long axes tilted with respect to the layer planes [18]. A mixture with higher concentrations of T_{B14A} and CEC exhibits a broken, banded focal conic fan-shaped texture of the chiral smectic-G phase, as shown in Fig. 4(g). If the constituent molecules of the material, which exhibits a smectic-G phase, are of a chiral nature, then the phase itself may also be weakly optically active; it is then termed a chiral smectic-G phase. The structural studies have been carried out at that time on chiral smectic-G phases and it was originally simply presumed that the structure of the phase is similar to that of chiral smectic-C, smectic-I, and smectic-F phases. In this case, the molecules would be hexagonally closely packed in layers, within each of which the tilts must be in the same direction. The layer above and below the tilt direction will however be turned through a small angle. Thus, on passing from layer to layer, the tilt direction

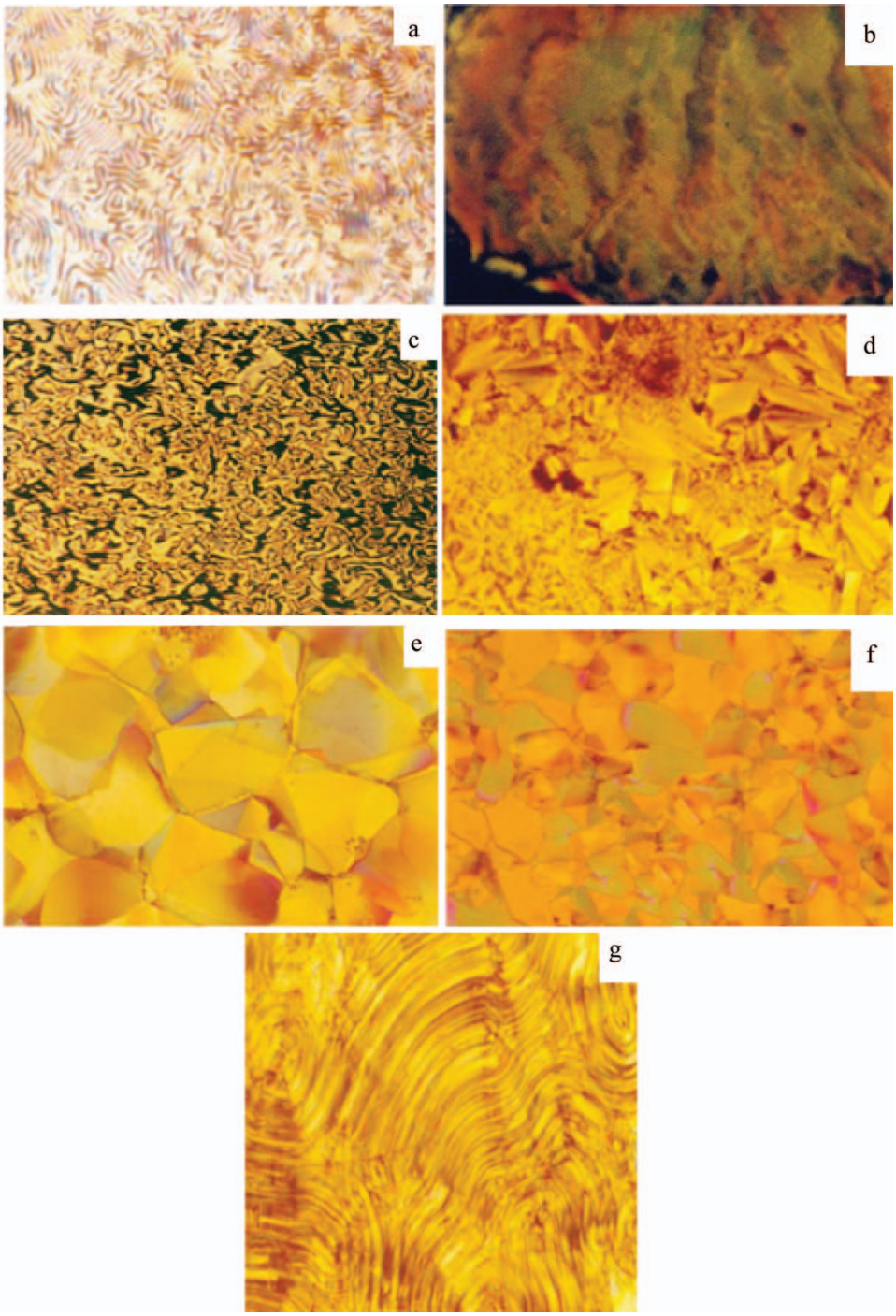

Figure 4. Microphotographs showing (a) fingerprint pattern of cholesteric phase (180X), (b) hexagonal grid pattern of TGB-A phase (360X), (c) schlieren textures of TGB-C phase (320X), (d) focal conic fan-shaped texture of smectic-A phase (320X), (e) smectic-I phase (220X), (f) smectic-F phase (220X), and (g) chiral smectic-G phase (220X).

will turn slowly either in an anti-clockwise or in a clockwise direction, depending upon the sign of the optical asymmetry of the system; this would lead to a helical change in the tilt direction, as described earlier for the Sm C and Sm F phases.

Conclusions

The salient features of this investigation are the following: we have observed the occurrence of the TGB-C phase in addition to the TGB-A phase in a binary mixture of cholesteryl ethyl corbonate (CEC) and terephthal-bis-p-n-tetradecylaniline (T_{B14A}), which is in accordance with the Renn and Lubbensky theoretical model. In addition to this, we have observed smectic phases of the mixture at different concentrations. The higher concentrations of the given smectic liquid crystals exhibit TGB-A and TGB-C phases along with polymorphic smectic phases such as Sm A, Sm I, Sm F, and chiral Sm G phases.

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