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Stabilization of TGB Phase in the Binary Mixture of Rod-Shaped Compounds

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*A miscibility study of two cholesterol based rod-shaped compounds (**R1** and **R2**) is presented. Both the compounds possess in common enantiotropic liquid crystalline phase sequence $Cr \rightarrow SmA \rightarrow N^* \rightarrow Isotropic$, which is generally exhibited by cholesterol-based compounds. Additionally, one of the rod-shaped compounds (**R1**) possesses a twist-grain boundary (TGB) phase over a short temperature range. In the binary mixture of these two rod-shaped compounds the TGB phase was stabilized over a long temperature range compared to that in the individual molecule **R1**. In the binary mixture up to 20% (w/w) of compound **R1** possessing the TGB phase exhibited enhancement of the temperature range of the TGB phase compared to that of individual compound **R1**. Further gradual increase of percentage of **R1** in the binary mixture did not show any enhancement of the TGB phase compared to that of individual **R1**.*

Keywords Binary mixture; phase diagram; phase induction; rod-shaped molecules; TGB phase

Introduction

Twist-grain boundary (TGB) phases are commonly observed in chiral materials and the phases are generally located between the cholesteric and the respective smectic phase [1]. The temperature range of this phase is generally small (~1°C) in a single-component system but sometimes in mixtures the ranges of existence of the TGB phase are greatly enhanced. A twist that is observed in the cholesteric phase is for elastic reasons in general not compatible with the layered structure of the smectic A^* phase. If, on the other hand, the tendency to helical superstructure formation is very strong, the competition between twist formation and smectic layer formation can result in a defect-stabilized, frustrated structure. Grains with a local SmA^* layer structure are separated by regular arrays of screw dislocations. The basic structural parameters of the $TGBA^*$ phase are the smectic layer thickness l; the helical pitch P; the thickness of smectic layer blocks l_b, *i.e.*, the distance between adjacent grain boundaries; the distance between dislocation lines within a grain boundary l_d;

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and twist between consecutive blocks $\Delta\alpha$ [1]. These parameters are related by the following relationships:

$$\Delta\alpha \approx \frac{l}{l_d}$$

$$\Delta\alpha = \frac{2\pi d_b l_d}{P}$$

Combination of these two equations gives

$$P = \frac{2\pi d_b l_d}{l}$$

The analogy between liquid crystals and superconductors was proposed by de Gennes [2,3]. Due to this analogy, de Gennes predicted that the regular defect structure should occur in smectic phases close to the smectic-nematic (Sm-N) when a twist or bend deformation is exerted on the director field of the Sm phase. This defect structure is analogous to the mixed state in type II superconductors, which exhibits a lattice of magnetic flux lines. A schematic phase diagram representation is shown in Fig. 1, which illustrates the analogy of the Abrikosov flux lattice phase and the twist-grain boundary TGBA* phase. Renn and Lubensky theoretically predicted the chiral smectic A (SmA*) phase [4], which is now known as the TGBA phase. The smectic A* phase predicted by Renn and Lubensky was first observed by Goodby *et al.* in 1989 in a highly chiral ferroelectcrtic liquid-crystal material [5]. This identification has been confirmed by a high-resolution X-ray study on aligned samples by Srajer *et al.* [6]. Almost simultaneously this phase was observed by Lavrentovich *et al.* [7] in binary mixtures of cholesteryl nonanoate and nonyloxybenzoic acid. We have

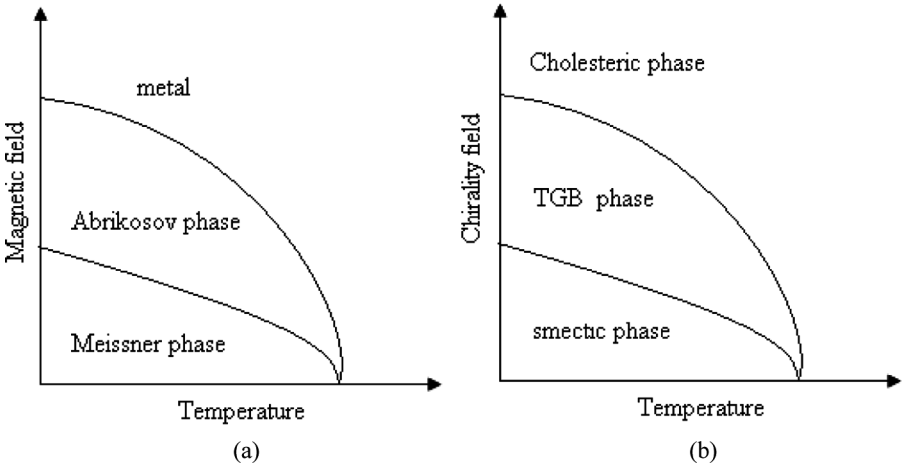


Figure 1. Schematic phase diagram of (a) a type II superconductor in an applied magnetic field and (b) a chiral liquid crystal, illustrating the analogy of the Abrikosov flux lattice phase and the twist-grain boundary TGBA* phase.

Table 1. Phase transition temperatures and enthalpies of the new mesogenic compounds

Phase transition temperature (°C) (ΔH/kJ mol^{-1})		
Compound	Heating	Cooling
R1	Cr 84.2(0.1), SmA_d 133.3(11.7), TGB 135.4(0.9), Ch 140.5(0.3) I	I 138.8(0.4), Ch 132.9(0.9), SmA_d 119.6(0.3) Cr
R2	Cr 151.6(32.6), SmA_1 154.3(4.4), Ch 158.3(2.9) I	I 157.4(3.2), Ch 151.9(0.8), SmA_1 141.1(37.3) Cr

Ch = Cholesteric, I = Isotropic.

chosen two rod-shaped molecules **R1** and **R2** for studying the liquid-crystalline phase change in binary mixtures. Both the compounds contain cholestesteryl moiety at one end [8]. The phase sequences of **R1** and **R2** are depicted in Table 1. In the phase sequence of **R2** the scarcity of the TGB phase was observed, whereas **R1** showed the presence of a TGB phase in a polarizing optical microscope (POM). **R1** possesses a partially bilayered smectic A_d (SmA_d) phase, whereas **R2** exhibits a monolayer smectic A_1 (SmA_1) phase. The results of our study on the binary mixture are reported here.

Experimental and Sample Preparation

In order to investigate the phase induction/behavior in the binary mixture of **R1** and **R2** we prepared several binary mixtures of the two (w/w). Requisite amounts of **R1** and **R2** were weighed out and mixed in a glass slide each to give binary mixtures containing 5, 10, 15, 20%, and so on, by weight of **R1**. Each binary mixture was warmed for about 30 min to melt and ensure a thorough mixing of the components in the isotropic phase and then cooled to room temperature and preserved with the lid on. A Nikon polarizing light microscope (model no. LV100POL, Tokyo, Japan), equipped with an Instec hot stage HCS302, with STC200 temperature controller configured for HSC302 (Boulder, CO, USA), was used to view the samples with objectives of various magnifications. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer Diamond DSC (Singapore) operating on Pyris software.

Results and Discussion

In this study we have used the compounds as mentioned above. The molecule **R1** exhibits $Cr \rightarrow SmA_d \rightarrow TGB \rightarrow N^* \rightarrow$ Isotropic phase sequence and the other rod-shaped molecule **R2** used in the binary mixtures exhibits $Cr \rightarrow SmA_1 \rightarrow N^* \rightarrow$ Isotropic phase sequence. The molecular structures of these compounds are shown in Fig. 2.

In Table 1 the phase transition temperatures and associated enthalpies are shown for the individual molecules obtained by DSC. The powder X-ray diffraction pattern of individual molecules suggests a type of smectic phase in the molecules, which was described in detail in our earlier communication [8]. In the compound **R1** the appearance of bilayer SmA_d and in **R2** the monolayer Sm A_1 phase were

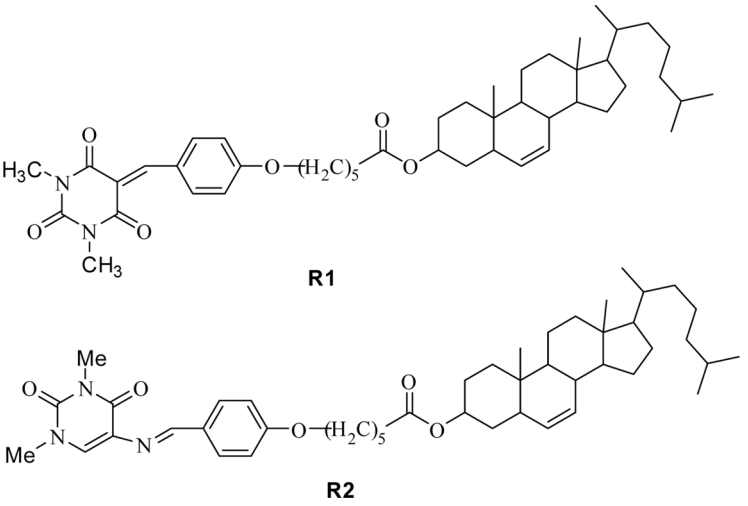
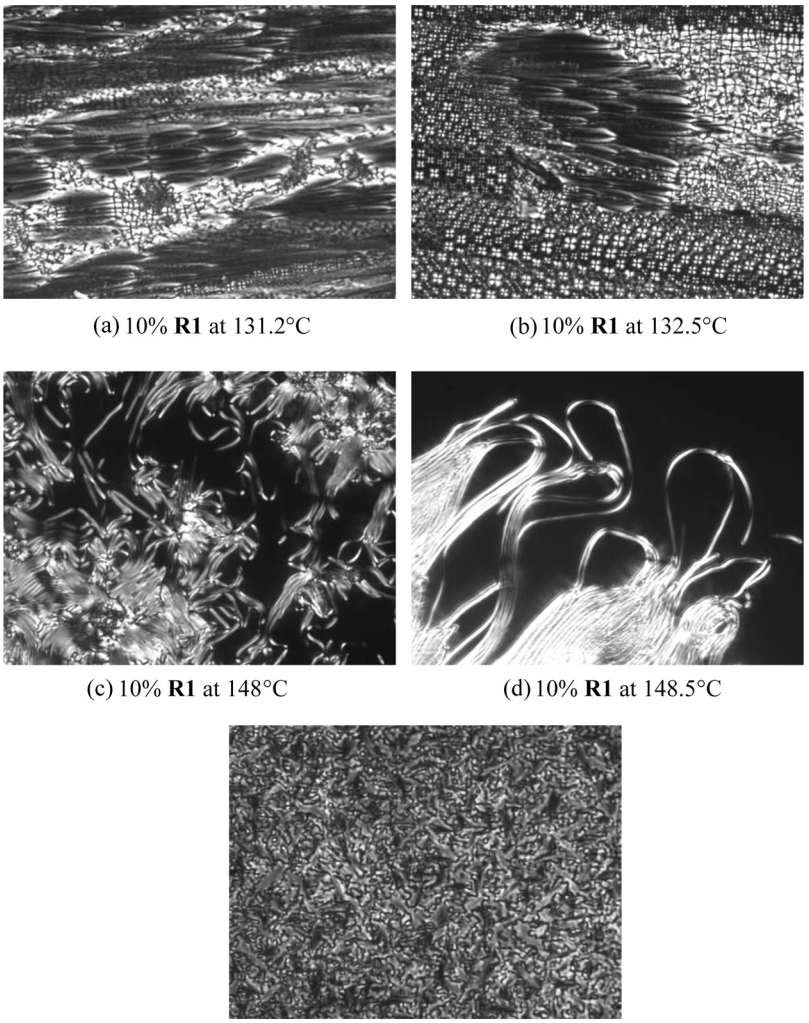


Figure 2. Molecular structure of synthesized compound **R1** and **R2**.

confirmed by general characterization technique like powder X-ray, POM, and DSC, and the TGB phase was observed in **R1** only, *i.e.*, in between cholesteric and SmA_d phase in heating cycle recorded in DSC. In this report we have attempted to observe the stabilization of the TGB phase in the binary mixture where the composition in terms of weight percentage of TGB compound is less. To achieve this we have prepared, as discussed in the Experimental section, binary mixtures of different compositions. We have taken into account that the compound that already has a TGB phase should contain less (**R1**) in the binary mixture. As in the case of binary mixture of two compounds, the miscibility study confirms the induction of a new mesophase and this new mesophase is not supposed to be present in either of the two compounds [9–15]. But we have found that the appearance of the smectic phase is different in the binary mixture from those of the individual compounds (**R1** and **R2**).

Mesophase Behavior

As discussed above, the individual compounds **R1** and **R2** exhibit an identical phase sequence except that the former has a TGB phase in the phase sequence. The optical behavior was observed under POM where the 5% (w/w%) of R1 was placed on a glass slide and heated to become isotropic and then the sample was sandwiched with a cover slip. The sample was again allowed to cool to become solid and again heated slowly to observe the textural pattern. In the heating cycle the sample turned from solid to spherulite at around 115°C where in some places the polygonal texture appeared as shown in Figs. 3(a) and 3(b). This polygonal texture along with spherulites then suddenly changed to a filament-like texture at around 135°C, which persisted until around 148°C; this filament texture is characteristic of the TGBA* phase (Figs. 3(c) and 3(d)). The sample was again heated slowly. These filament textures organized themselves to form a focal conic fan texture of the cholesteric phase. At around 160°C the sample became dark under POM, indicating the isotropic nature of the sample. The sample was allowed to cool slowly, and the textural appearance



(a) 10% **R1** at 131.2°C (b) 10% **R1** at 132.5°C

(c) 10% **R1** at 148°C (d) 10% **R1** at 148.5°C

(e) 10% **R1** at 153°C

Figure 3. Polarizing optical micrograph of 10% of **R1** at different temperatures.

was the same as in the heating cycle but with reverse phase sequence, *i.e.*, isotropic to cholesteric, which changed to TGB and then polygonal texture of Sm A phase appeared. At room temperature the polygonal texture of the SmA phase persisted along with the spehrulites but brightness of the texture was diminished. The same phase sequence with similar textures was also observed in 10, 15, and 20% of **R1**. The observed textures are the same in other compositions (>20% of **R1**). However, the temperature range was much shorter for the appearance of the TGB phase and almost similar to that observed for the individual compound **R1**. The DSC profiles of 5, 10, 15, and 20% of **R1** are also different from that of pure **R1**; in pure **R1** the TGB trace was not observed in either the heating cycle or the cooling cycle, as shown in Fig. 4. Figure 5 describes the DSC profile of 10% of **R1** in both heating and cooling cycles and it clearly shows the appearance of the TGB phase in between the cholesteric and smectic A phase.

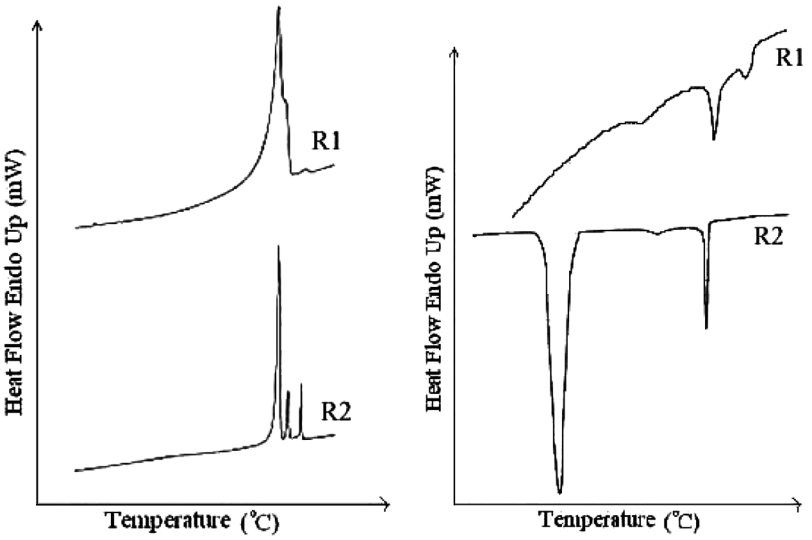


Figure 4. (a) DSC thermograms in heating cycles of **R1** and **R2**. (b) DSC thermograms in cooling cycles of **R1** and **R2**.

Phase Diagram

Keeping in view the stabilization of the TGB phase in the binary mixtures of increasing composition of **R1** (Fig. 6), we have constructed a binary phase diagram from the experimental results of binary mixtures based on textural observations under a polarizing microscope along with DSC studies and phase sequence, X-ray diffraction study of pure **R1** and **R2** compounds.

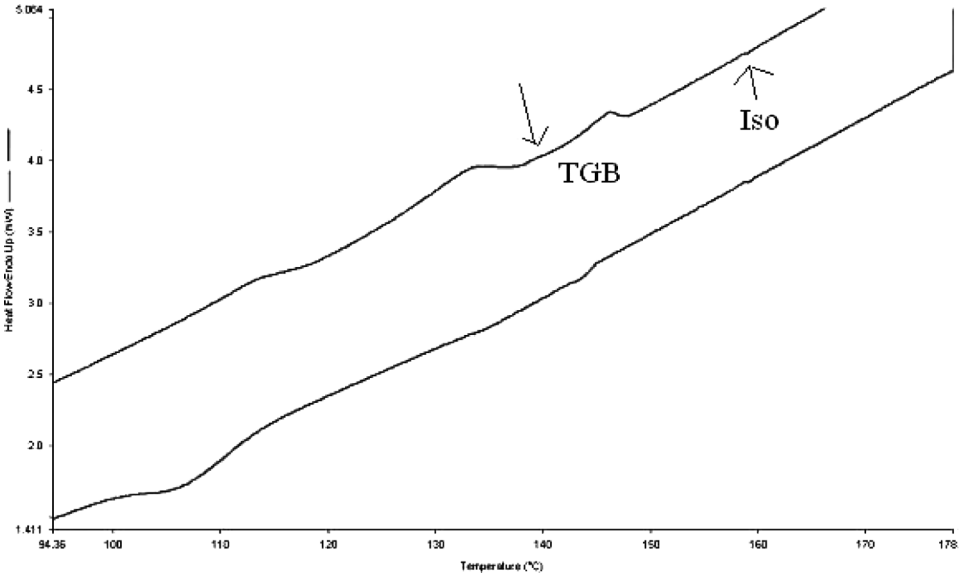


Figure 5. DSC profile of 10% **R1**.

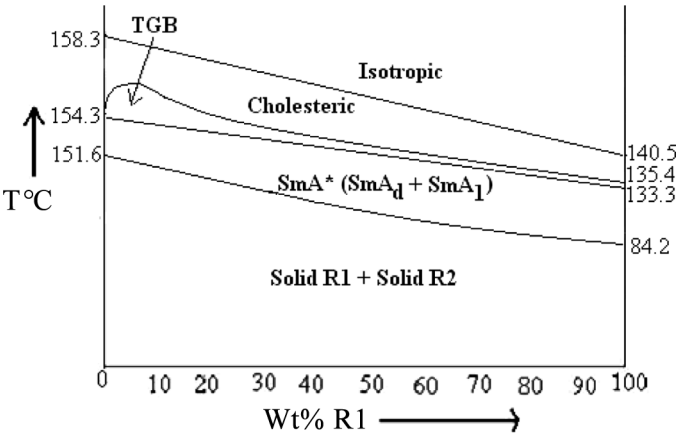


Figure 6. Phase diagram of binary mixture of **R1** and **R2**.

Conclusion

In conclusion, we have observed the stability of the TGB phase in the binary mixtures of two rod-shaped molecules in which one lacks the TGB phase. The binary mixture containing the lower composition of the compound possessing TGB phase also exhibits a TGB phase with longer temperature range than the individual compound **R1**. The observed smectic A phase in the binary mixtures is also different from the individual texture, whereas we have observed a focal conic fan texture of SmA in both the compounds [8]. It is noteworthy that the appearance of polygonal textures is recorded in the binary mixture.

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