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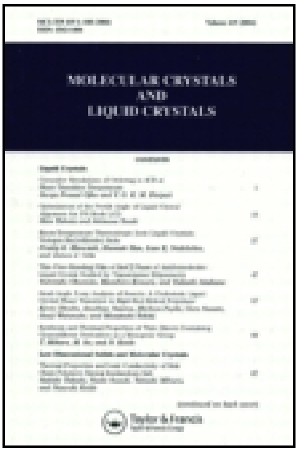

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Twisted Grain Boundary Phase in Binary Mixture of Liquid Crystals

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In the present work, our investigation is to study the optical and thermal properties of the binary mixture of cholesteric and nematic compounds, namely, cholesteryl chloride and 4,4′-hexyloxy azoxy benzene, which exhibits a very interesting liquid crystalline twisted grain boundary (TGB) phase and induced smectic phases like SmA, SmC, SmE, and SmB phases. The chiral liquid crystalline TGB phases have been observed at different concentrations and at different temperatures. The mixture with concentration from 26% to 37% of shows I-Ch-TGB-SmA-SmC*-SmE-SmB phases sequentially when the specimen cooled from isotropic phase. The existence of TGB phase is confirmed by DSC and optical microscopic studies. The temperature variation of optical anisotropy is also discussed. X-ray studies have been carried out to understand the intermolecular interactions in the mixture. With the help of phase diagram, the phase behavior has also been discussed.*

Keywords Binary mixture; induced smectic phases; phase transition; TGB phase

Introduction

The twisted grain boundary (TGB) phase of a chiral liquid crystal exhibits long-range order that combines a helical twist and smectic layering [1]. This TGB phase, which is an intermediate structure between smectic-A and cholesteric phases, is an analog of Abrikosov [2] flux vortex lattice in type-II superconductors, whereas the smectic-A phase is analogous to the Meissner phase. Indeed, Kamien and Lubbensky [3] have predicted a significant short-range TGB structure in the cholesteric phase at low temperatures, corresponding to a liquid of screw dislocations [4] to be called a chiral line liquid. Therefore, it is recognized as rotated blocks of SmA layers, in which the long molecular axes are arranged normal to the layer planes. Hence, the chiral smectic layers twisted in the molecular axes are expected in the direction of the layer planes [5], and hence the helical axes of TGB phase are perpendicular to the molecular axes and parallel to the smectic planes.

Some of the investigators [6–8] have studied the TGB phase in the mixture of cholesteric and nematic compounds. Lubbensky and Renn [7] have made theoretical predictions in case

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of TGB-SmA phase transition that it always appears, if the molecular chirality is introduced near the nematic-smectic-A-smectic-C (NAC) multicritical point [8]. In case of TGB-SmA phase, the temperature span Δt should increase with increase in chirality of the system. The TGB-SmC* phase has also been close to the NAC point, which is composed of twisted stacks of helical, SmC* phase is also predicted [9].

In the present investigation, our aim is to carry out the study of optical and thermal properties of the binary mixture of cholesteric and nematic liquid crystalline compounds. Some of the concentrations of the mixture exhibit I-Ch-TGB-SmA-SmC*-SmE-SmB phases sequentially when they are cooled from isotropic phase. Optical, DSC, thermal, and X-ray studies have been carried out to understand the intermolecular interactions in the mixture.

Experimental Studies

In the present investigation, we have studied binary mixtures of liquid crystals, namely, cholesteryl chloride (CCl) and 4,4′-hexyloxy azoxy benzene (HOB), which are obtained from M/s Eastmann Organic Chemicals, USA. The chemicals are purified twice with benzene. Mixtures of 20 different concentrations of HOB in CCl were prepared. The phase transition temperatures of the mixtures were determined using Leitz-polarizing microscope in conjunction with hot stage. Refractive indices n_1 and n_2 for 5893 Å in cholesteric phase of the mixture were measured using Abbe refractometer and also goniometer spectrometer at different temperatures [10]. DSC thermograms were taken for all concentrations of the given mixture using Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The values of phase transition temperatures of the mixtures were found to be in good agreement with the values obtained from the optical texture studies. The DSC thermograms of 30% of HOB in CCl are shown in Fig. 1, which illustrate that the different sequences of phases are as follows:

I → 97.9°C, Ch → 95.08°C, TGB$_1$ → 94.82°C, TGB$_2$ → 93.3°C, SmA → 65.6°C,
SmC* → 51.7°C, SmE → 39.8°C, SmB → 29°C

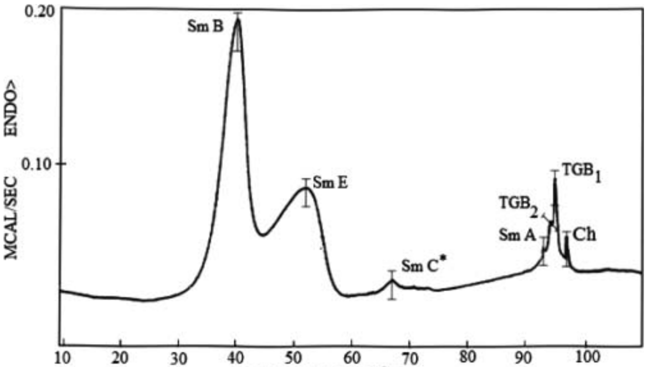

Figure 1. DSC thermogram for the sample of 30% of HOB in CCl.

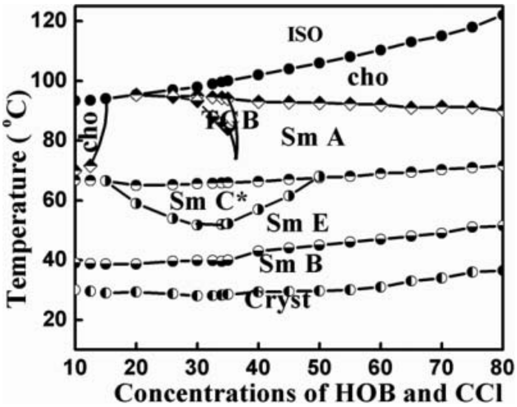

Figure 2. Partial phase diagram for the mixture of HOB and CCl.

Results and Discussions

Phase Diagram

The binary mixture of cholesteric and nematic compounds exhibits different liquid crystalline phases, and the phase transition temperatures are measured by using Leitz-polarizing microscopic. The partial phase diagram is shown in Fig. 2. It illustrates that the mixture of lower and higher concentrations of HOB in CCl exhibits cholesteric, smectic-A, smectic-C*, smectic-E, and smectic-B phases, and the middle concentrations show a very interesting TGB phase along with the chiral smectic (SmC*) phase. For example, the concentrations from 40% to 55% of this mixture exhibit cholesteric, smectic-A, smectic-C*, smectic-E, and smectic-B phases, whereas the concentrations from 10% to 15% and 56% to 80% of the mixture exhibit cholesteric, smectic-A, smectic-E, and smectic-B phases. But the concentrations from 26% to 37% of the mixture exhibit I-Ch-TGB-SmA-SmC*-SmE-SmB phases sequentially when the specimen is cooled from its isotropic liquid phase. The concentrations from 15.5% to 19.5% of the given mixture show only the smectic-A, smectic-C*, smectic-E, and smectic-B phases. The strong peak in the DSC thermogram is associated with the first-order transition and the weak peak for the second-order transition, whereas the transition from cholesteric phase to TGB phase is second order, and the transition involves changes in specific heat.

The molecules in chiral smectic phase form a layered structure, the thickness of each layer being typically of the order 20–30 Å. X-ray studies have shown that the molecular centers are packed randomly within the layers. The molecules are tilted from the layer normal by an angle. The density and refractive indices n_e and n_o in the different phases were measured, and the optical anisotropy of the different phases was estimated. It is also observed that wherever there is change in phase there is drastic change in the values of n_e, n_o, and optical anisotropy.

Optical Anisotropy

To understand the additivity of polarizability in the given mixture of cholesteric phase, we have estimated the optical anisotropy of the mixture in cholesteric phase, using refractive index and density data. Densities were measured for different concentrations of the mixture at various temperatures, using the sensitive traveling microscope with capillarity. These measurements of refractive indices n_1 and n_2 were carried out for the mixture of 50% HOB in cholesteric phase. The refractive index n_1 corresponding to ordinary ray is greater than ($n_1 > n_2$) refractive index n_2 corresponding to the extraordinary ray indicating that the material is uniaxial negative.

The mean polarizabilities ($\bar{\alpha}_{mix}$) of cholesteric phase for different concentrations were calculated using Lorentz–Lorentz relations:

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi N \alpha_{mix}}{3} \tag{1}$$

where $\bar{n} = \frac{(n_1^2 + 2n_2^2)}{3}$, $N(\alpha_{\mathrm{mix}}) = N_a\alpha_a + N_b\alpha_b$ and $N = N_a + N_b$, N_a and N_b are the number of molecules per unit volume of CCl and HOB, respectively.

Here

$$N_a = \frac{x_a}{x_a + x_b}\left(\frac{N_A \rho_{mix}}{M_a}\right) \tag{2}$$

$$N_b = \frac{x_b}{x_a + x_b}\left(\frac{N_A \rho_{mix}}{M_b}\right) \tag{3}$$

where M_a is the molecular weight and N_A is the Avogadro number. Similarly, N_b can also be calculated by taking M_b, the molecular weight of HOB. ρ_{mix}, density of the mixture.

The effective polarizabilities α_1 and α_2 of the cholesteric phase of the mixtures were calculated using the relation:

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi N (\alpha_i)_{mix}}{3}, \quad i = 1, 2 \tag{4}$$

The mean polarizability ($\bar{\alpha}_{mix}$) is calculated by using the relation:

$$(\overline{\alpha}_{mix})_{\mathrm{exp}} = \frac{(\alpha_1 + 2\alpha_2)}{3} \tag{5}$$

Here $(\overline{\alpha}_{mix})_{\mathrm{exp}}$ values are also calculated using additivity relation:

$$(\bar{\alpha}_{mix})_{cal} = \frac{(N_a\alpha_a + N_b\alpha_b)}{(N_a + N_b)} \tag{6}$$

The experimental and calculated values of mean polarizability ($\bar{\alpha}_{mix}$) are potted against $N_a/(N_a + N_b)$ at $(T_c - T) = 3$°C. The experimental values of ($\bar{\alpha}_{mix}$) are in good agreement with the theoretical values, and the same is shown in Fig. 3.

The optical anisotropy of the polarizabilities $(\alpha_1 - \alpha_2)_{mix} = (\Delta\alpha)_{mix}$ is given by additivity relation [11].

$$\Delta\alpha_{mix} = \frac{[N_a(\Delta\alpha)_a + N_b(\Delta\alpha)_b]}{N_a + N_b} \tag{7}$$

$(\Delta\alpha)_a$ and $(\Delta\alpha)_b$ are the anisotropy of the polarizabilities of CCl and HOB, respectively. $(\Delta\alpha)_b$ is equal to $(\alpha_e - \alpha_o)/2$ at a corresponding temperature of nematic phase and $(\Delta\alpha)_a$

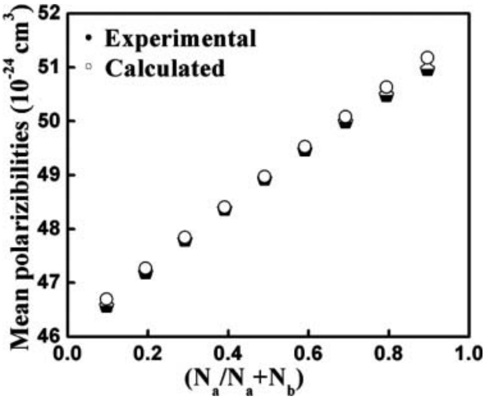

Figure 3. Mean polarizabilities as a function of ($N_a/N_a + N_b$) at a temperature ($T_c - T$) = 3°C.

is equal to ($\alpha_1 - \alpha_2$) of CCl. From equation 7, it follows that

$$\Delta\alpha_{mix} - \frac{N_a(\Delta\alpha)_a}{N_a + N_b} = \frac{N_b(\Delta\alpha)_b}{N_a + N_b} \tag{8}$$

The left-hand side of the above equation is plotted against the mole fraction should linear, and this is actually the case in Fig. 4. The slope of the straight line is equal to 13.7 × 10^{-24} cm^3, which is equal to the anisotropy of the nematic, which is being half of the values of ($\alpha_{e-}\alpha_o$) = 6.862 × 10^{-24} cm^3 for HOB at ($T_{C-}T$) = 3°C.

Optical Texture Studies

The optical textures exhibited by different concentrations of the mixture are as follows. The sample with 30% of the mixture exhibits a nonringed spherulitic texture at temperature 95.08°C, which is the characteristic of cholesteric phase, and the same is shown in Fig. 5(a). When the specimen is further cooled, transition takes place from cholesteric to TGB phase, the ringed spherulitic texture grow in size and develop in the form of spiral filament texture at 94.82°C, as shown in Fig. 5(b). This spiral filament texture is the characteristic

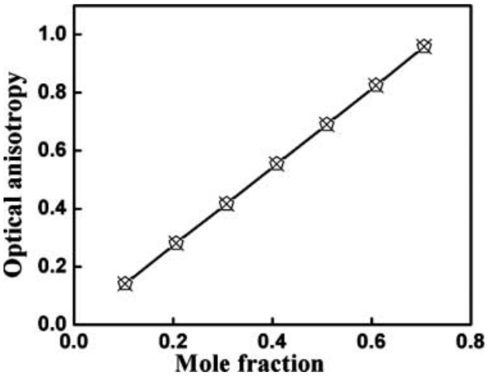

Figure 4. Variation of optical anisotropy (10^{-24} cm^3) of the mixture as a function of mole fraction at temperature ($T_c - T$) = 3°C.

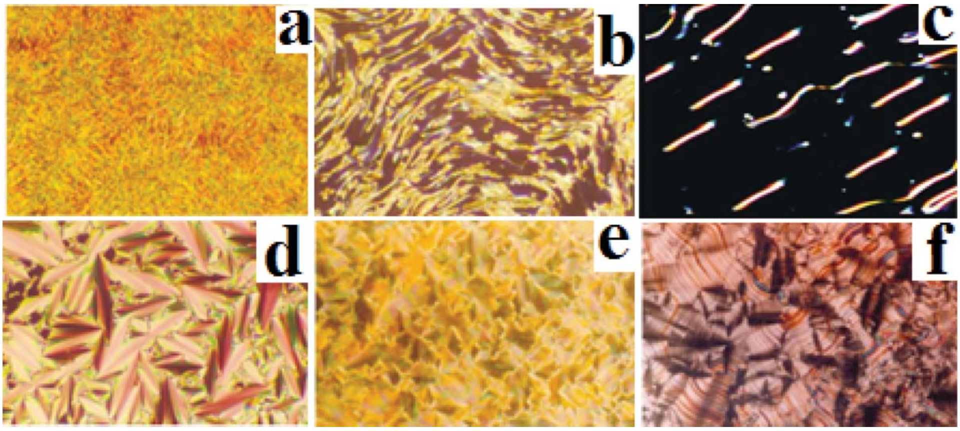

Figure 5. Microphotographs obtained in between the crossed polars. (a) Spherulite texture of cholesteric phase (185×). (b) Spiral filament texture of TGB1 phase (185×). (c) Filament texture of TGB2 phase (185×). (d) Focal conic fan-shaped texture of smectic-A phase (180×). (e) Radial fringes on the fans of focal conic fan-shaped texture of chiral smectic-C* (180×). (f) Herringbone structure of smectic-E phase (180×) (color figure available online).

of TGB_1 phase. These spirals slowly unwound at 93.3°C and then the filament texture appears, as shown in Fig. 5(c). This is the characteristic of TGB_2 phase. The helical axes of the TGB phase lies in a direction parallel to the smectic layer planes [10,11]. On further cooling, TGB_2 phase of filamentary texture changes over to a focal conic fan-shaped texture at temperature 65.6°C, which is the characteristic of smectic-A (SmA) phase, as shown in Fig. 5(d), and this phase appears to be metastable and then changes over to smectic-C* phase. This smectic-C* phase exhibits radial fringes on the fans of the focal conic textures at a temperature 51.7°C, which is the characteristic of chiral smectic-C*(SmC*) phase, and the observed texture is shown in Fig. 5(e).

The molecular twist can be of the constituent molecules in the chiral smectic-C* phase, and they posses point symmetry in relation to their asymmetric centers, when they are packed in the form of layers, where the molecular long axes are tilted with respect to the layer planes [12,13]. The stacking of the layer planes on the top of other results in the tilt normal to the layers creating macroscopic helical structures.

On further cooling the specimen, metastable chiral smectic-C* phase changes over to smectic-E phase at temperature 39.8°C, in which the fans are crossed by a number of arcs, which is the characteristic of smectic-E phase and is shown in Fig. 5(f). The optical texture and X-ray diffraction studies confirm the herringbone structure of smectic-E phase. In smectic-E phase, the molecules are arranged in zigzag conformation in successive layer planes [14,15], and finally the specimen crystallizes with smectic-B phase.

Spiral Pitch and Helical Twisting Power

The cholesteric phase is regarded as twisted nematic phase, wherein the molecules are orientationally ordered, but at the same time they are rotationally disordered with respect to long axis [16]. It is well known that when a cholesteric compound is added as impurity to a nematic compound, the pitch of the cholesteric phase increases in dilute limit of the mixture, indeed, if the pitch is sufficiently large it is possible to observe stripes under the

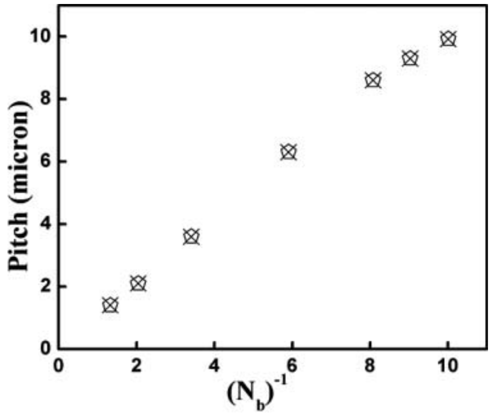

Figure 6. Variation of pitch of cholesteric phase with $(N_b)^{-1}$. Here, N_b represents the number of molecules of HOB per unit volume of the mixture.

Leitz-polarizing microscope. When the pitch is comparable to the wavelength of light, the phase becomes iridescent because of the selective reflection of light. The stripes are associated with the helicoidal structures, which clearly indicate that the mesophase is cholesteric. The mixtures with concentrations from 1% to 15% of the mixture exhibit a stripped pattern when they are cooled from isotropic phase at the respective temperatures, which corresponds to cholesteric phase. Microscopic twisting power β of the solute in the mixture 1% to 9% of HOB is calculated using the formula:

$$4\pi\beta C = \frac{2\pi}{P}$$

where P is the pitch of the helix and C is the concentration of CCl

$$\beta = \frac{1}{2PC}$$

The pitch of the cholesteric phase against concentration is drawn and shown in Fig. 6, which illustrates that at low concentrations of the cholesteric compound, the pitch is inversely proportional to the concentration of the cholesteric compound. The parameter β characterizes a helical twisting power value for the induced cholesteric phase. This result is in conformity with the rule that for a small concentration of cholesteric compounds in nematics.

X-Ray Studies

To understand the change in layer spacings in smectic-A and smectic-C* phases with respect to temperature, X-ray diffractometer traces were taken. The traces obtained for the mixture of 30% HOB in CCl at different temperatures correspond to smectic-A and smectic-C* phases. It is observed that as the temperature increases the layer spacing also increases in smectic-C* phase. But in smectic-A phase, the layer spacings are almost constant. These variations are shown in Fig. 7 [17,18].

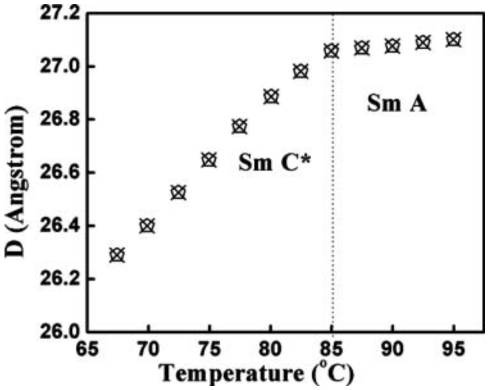

Figure 7. Variation of layer spacing with temperature.

Conclusions

The above results, apart from revealing numerous beautiful textures associated with the various cases, have enabled us to reach the following conclusions. The lower and higher concentrations of the given mixture show the mesophase, which corresponds to smectic order, and it is evidenced by various studies. For the mixture with concentrations of 15% of HOB and below, the mesophase corresponds to cholesteric phase and is typically characterized by stripped pattern. The intermediate concentrations of the given mixture exhibit a twisted TGB phase along with the induced chiral smectic phase. The mixtures with concentrations of 25% and above exhibit cholesteric phase and is evidenced by the optical texture study and optical anisotropy measurements. The temperature variation of "*d*" spacing in smectic-C* phase has also been studied.

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