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Nano segregation and thermal stability of TGB and re-entrant smectic-A phases in a ternary mixture of liquid crystalline materials

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ABSTRACT

The ternary system of 4′-n-octyloxy-4-cyanobiphenyl (8OCB), 4-cyano-4′-Pentyl teraphenyl (5CT), and cholesteryl nonanoate (CN) exhibits very interesting unusual liquid crystalline phase of N* (cholesteric), twisted grain boundary (TGB) phase, and re-entrant smectic-A (ReSmA) phases and it is obtained sequentially when the specimen is cooled from isotropic phase. These phases have been characterized by using X-ray and optical texture studies. The temperature variations of electrical conductivity have been discussed.

KEYWORDS

Molecular orientation; nano segregation; re-entrant smectic-A; temperature dependence; TGB phase

Introduction

Liquid crystals are widely used in electro-optic display devices such as optical switches, light modulators, and image devices [1–4]. The use of liquid crystals in these devices depends on the kinds of mesophases exhibited by the liquid crystals, the transition temperature, 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 twisted grain boundary (TGB) and re-entrant smectic-A phase in a binary mixture of liquid crystalline compounds [5–8] has been well investigated by earlier investigators [9–11].

In the present study, we have considered the mixture of three compounds, viz., 4'-n-octyloxy-4-cyanobiphenyl (8OCB), 4-cyano-4'-Pentyl teraphenyl (5CT), and cholesteryl nonanoate (CN). Some concentrations of the mixture show Iso→N*→TGB→SmA→SmC→ReSmA→SmB→Cryst phases sequentially when they are cooled from isotropic phase. The optical and X-ray studies have been carried out to understand the intermolecular interactions of the mixture.

Experimental section

In the present investigation, we have studied binary mixtures of liquid crystals, namely, 4'-n-octyloxy-4-cyanobiphenyl (80CB), 4-cyano-4'-Pentyl teraphenyl (5CT), and cholesteryl

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nonanoate (CN) are obtained from M/s Eastman Organic Chemicals, USA. The chemicals are purified twice with benzene. Mixtures of 25 different concentrations of (8OCB+5CT) in CN were prepared and were mixed thoroughly. These mixtures of different concentrations of (8OCB+5CT) in CN were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. The phase transition temperatures of these concentrations were measured with the help of Leitz-polarizing microscope in conjunction with hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The X-ray peaks were obtained at different temperatures using JEOL diffractometer. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [12,13]. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

Results and discussion

Phase diagram

The binary mixture of (8OCB+5CT) in CN 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. 1, which is obtained by plotting the concentrations against phase transition temperatures of given mixture, which clearly illustrates that the mixture of all concentrations of (8OCB+5CT) in CN exhibits N*, SmA, SmC, and SmB phases, respectively, at different temperatures, when the specimen is cooled from isotropic phase. The concentrations of the mixture from 35% to 50% and 20% to 60% of (8OCB+5CT) shows twisted grain boundary and re-entrant smectic-A phases in addition of N*, smectic-C, and smectic-B phases, respectively, at different temperature.

Optical texture studies

For the purpose of optical texture studies, the sample was sandwiched between slide and cover glass and then the optical textures were observed using a Leitz polarizing microscope

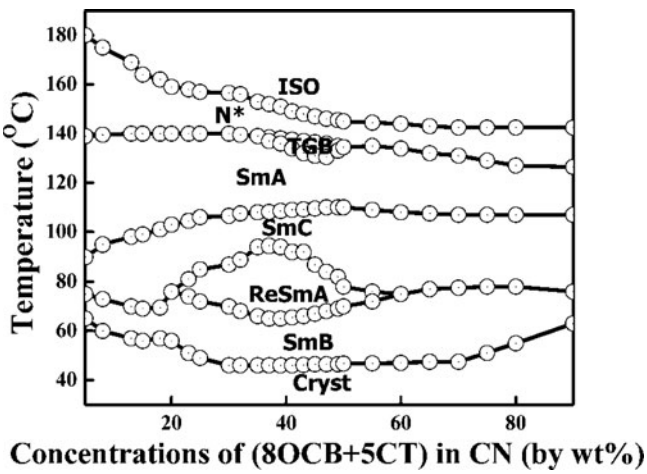

Figure 1. Partial phase diagram for the mixture of (8OCB + 5CT) in CN.

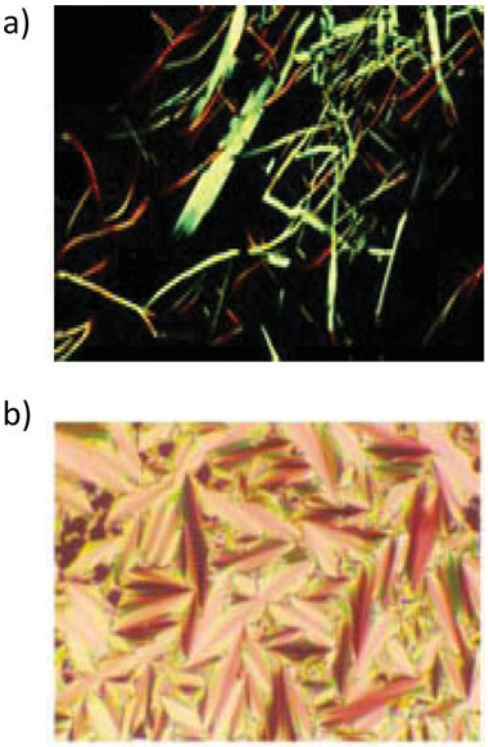

Figure 2. Microphotographs obtained in between the crossed polars. (a) Mobile thread like filament texture of TGB phase (250X). (b) Focal conic fan-shaped texture of SmA phase (250X).

in conjunction with a specially constructed hot stage. The concentrations ranging from 35% to 50% of mixture are slowly cooled from its isotropic melt, the genesis of nucleation starts in the form of small bubbles and slowly grow radially, which form spherulitic texture of N* phase with large values of pitch [14,15]. On further cooling the specimen, the N* phase slowly changes over to mobile thread like filament texture, which is the characteristic of twisted grain boundary phase as shown in Fig. 2(a). The helical axes of twisted grain boundary phase lie in a direction parallel to the smectic layer planes [16,17]. On further cooling, the twisted grain boundary phase of filamentary texture slowly changes over to focal conic fan-shaped texture of smectic-A phase and then this phase changes over to schlieren texture of smectic-C. On further cooling the specimen, unstable schlieren texture of smectic-C phase slowly changes over well-defined focal conic fan texture of re-entrant smectic-A phase and the texture is shown in Fig. 2(b). In this system, the microscopic observations clearly indicate that the given mixture exhibits a very interesting re-entrant smectic-A phase [18]. The lowest temperature mesophase of some certain compounds exhibits two or more mesophases of the same type, over different temperature ranges. Re-entrant mesophases are most commonly observed when the molecules have strong longitudinal dipole moments. The sequences of re-entrant mesophases have also been found in binary mixtures of non-polar liquid crystalline compounds [19]. In the given mixture, some of middle concentrations of (8OCB+5CT) at lower temperatures did not show the molecular aggregates in preferred direction of alignment toward the crystalline phase, but it randomly oriented to form a re-entrant smectic-A phase and then this phase changes over to the crystalline smectic-B phase, which remains stable at room temperature [8].

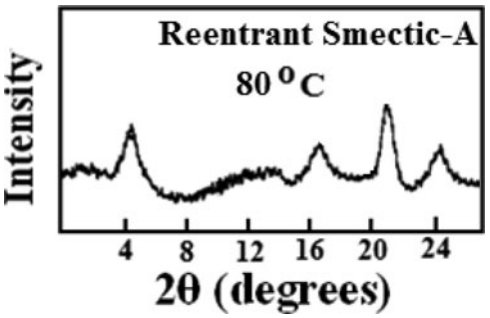

Figure 3. X-ray broadening spectrum for the mixture of 43% (8OCB + 5CT) in CN at 80°C temperature of ReSmA phase.

Characterization of nano aggregated grains

The X-ray diffractometer traces obtained for the mixture of 43% (8OCB+5CT) in CN at temperature 80°C are shown in Fig. 3. The diffraction peaks at this temperature correspond to RSmA phase (by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å). X-ray diffraction study is an important method to determine the nano aggregated size of the molecules for different liquid crystalline phases [20,21]. The X-ray traces obtained for the Perfect liquid crystals would extend in all directions to infinity, so we can say that no crystal is perfect due to its finite size. The deviation from perfect liquid crystallinity leads to a broadening of the diffraction peaks. In order to estimate nano aggregated size of the molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks, we have used the Scherrer's formula

$$L = K\lambda/\beta\cos\theta,$$

where L is the nano aggregated size, λ is the wave length of X-ray radiation (1.934 Å), K is usually taken as 0.89, β is the line width at half maximum, and &thetas; is the diffraction angle. The phase transition temperature increases as it moves from crystalline phase to amorphous region [22,23], which clearly illustrates that nano aggregated size of the phase transition behavior of the molecules decreases with increasing the temperature. In Fig. 3, if we have observed that the structure of molecular orientation for re-entrant smectic-A phase is energetically more stable, molecular ordering of this phase shows intense four peaks. The nano aggregated size of liquid crystalline material for re-entrant smectic-A phase comes out to be 46.13 nm. From this study, we have observed that the phase transition behavior of molecular ordering of the liquid crystalline materials is increasing as we move toward lower temperature. This clearly illustrates that nano aggregated size of liquid crystalline materials of different phases are big enough to indicate that the molecular ordering [24] of layer structure increases with decrease in the temperature.

Conductivity measurements

The electrical conductivity measurements were carried out at different temperatures with the constant rate of scanning 2 °C min^{-1}. The temperature was stabilized using a homemade thermoelectric cooler and it was recorded by a Teflon-coated K-type thermocouple (±0.1 °C) and it was connected to the data logger thermometer centre 309 (JDC Electronic SA, Switzerland). The samples were taken in the conductometric cell having two horizontal platinum electrodes of 14 mm in diameter, with 0.5 mm inter-electrode space. Before the measurements parts of

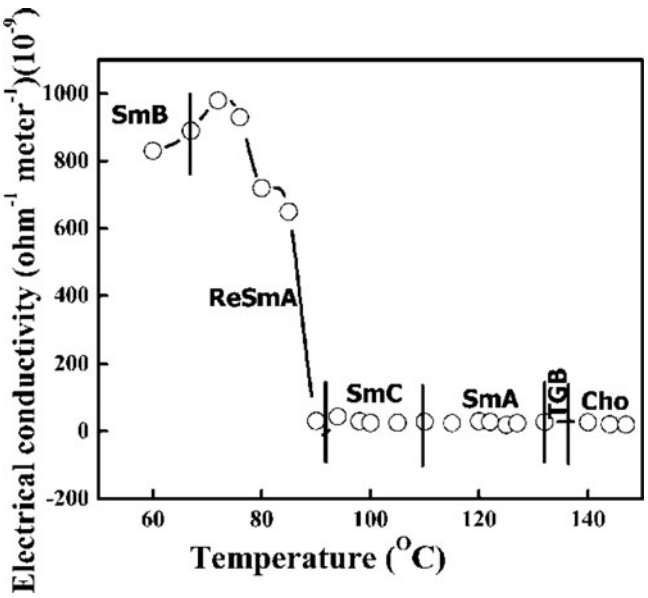

Figure 4. Temperature variation of electrical-conductivity σ (X10^{-9} Ω^{-1} m^{-1}) for the sample with 43% (8OCB + 5CT) in CN.

the cell were washed in hexane and dried at 117°C. The electrical conductivity of the samples was measured by the inductance, capacitance, and resistance (LCR) meter 819 (Instek, 12 Hz–100 kHz). The measurements were done under the applied external voltage of 1 V and frequency of 500 Hz. This frequency was selected for avoidance of significant polarization effects on the electrodes.

Electrical-conductivity measurements are helpful in the study of phase behavior with temperature. An abrupt increase or decrease of electrical conductivity with temperature relates to the phase behavior of lyotropic, thermotropic, and also chromonic systems [25]. The temperature variations of electrical conductivity are as shown in Fig. 4. The figure clearly illustrates that there is change in the value of electrical conductivity from 60°C to 147°C, while cooling from isotropic phase for the mixture of 43% (8OCB+5CT). With further decrease in temperature, the electrical conductivity starts decreasing as we move toward the room temperature. Mixture of 43% (8OCB+5CT), the sequence phase changes from N*→TGB, TGB→SmA, SmA→SmC, SmC→ReSmA, and ReSmA→SmB phases, here if there is some value of electrical conductivity goes on increasing with decreasing the temperature. Changes in electrical conductivity are observed only after further cooling the specimen. This suggests that, the size of aggregates starts growing toward decreasing temperature and the system moves toward more orderliness.

Finally, below 60°C size of aggregates becomes very large and the specimen starts moving toward crystalline nature [26–38].

Conclusions

In light of the above results, we have drawn the following conclusions. The ternary system of (8OCB + 5CT) in CN exhibits an unusual sequence of phases showing the formation of an N*, TGB, SmA, SmC, ReSmA, and SmB phases in the concentration range of 35%–50% of (8OCB + 5CT) in CN. The phase behavior is discussed with the help of phase diagram. The drastic

changes in the value of electrical conductivity with the variation of temperature unambiguously correspond to TGB, ReSmA, and N* phases. Drastic changes in electrical conductivity are expected to be due to changes in the dimension of disks along with changes in the orientation order of the arrangement. X-ray studies lend support to found the nano aggregated size of the molecules of liquid crystalline materials for ReSmA phase.

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