Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: T. N. Govindaiah (2015) TGB and Re-entrant Smectic-A Phases in Ternary Mixture of Liquid Crystalline Materials, Molecular Crystals and Liquid Crystals, 623:1, 80-86, DOI: 10.1080/15421406.2015.1010864

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1010864

Published online: 21 Dec 2015.

Mol. Cryst. Liq. Cryst., Vol. 623: pp. 80–86, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1010864

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TGB and Re-entrant Smectic-A Phases in Ternary Mixture of Liquid Crystalline Materials

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The ternary system of 4-cyano-4'-heptyl biphenyl (7CB), 4'-n-octyloxy-4-cyanobiphenyl (80CB), and Cholesteryl chloride (ChCl) exhibits very interesting unusual liquid crystalline phase of cholesteric, twisted grain boundary phase and re-entrant smectic-A 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 and pitch of the cholesteric phase have been discussed.

Keywords Molecular orientation; nano segregation; pitch; 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 kind of mesophases exhibited by 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] have been well investigated by earlier investigators.

In the present study, we have considered three compounds, viz. (4-cyano-4'-heptyl biphenyl (7CB), 4'-n-octyloxy-4-cyanobiphenyl (80CB), and cholesteryl chloride (ChCl). Some concentrations of the mixture show Iso→Cho→TGB→SmA→SmC→RSmA→SmB→Cryst phases sequentially when these are cooled from isotropic phase. The optical and X-ray studies have been carried out to understand the intermolecular interactions of the mixture.

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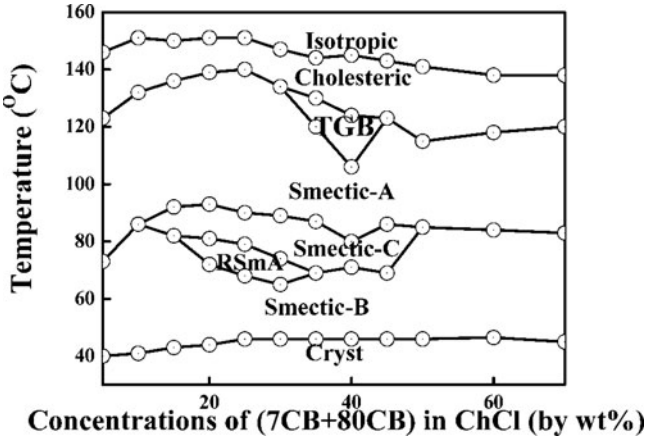


Figure 1. Partial phase diagram for the mixture of (7CB + 80CB) in ChCl.

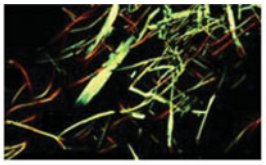
Experimental

In the present investigation, we have studied binary mixtures of liquid crystals, namely ChCl and (4-cyano-4'-heptyl biphenyl (7CB), 4'-n-octyloxy-4-cyanobiphenyl (80CB) (obtained from M/s Eastman Organic Chemicals, USA). The chemicals are purified twice with benzene. Mixtures of 25 different concentrations of (7CB + 80CB) in ChCl were prepared and mixed thoroughly. These mixtures of different concentrations of (7CB + 80CB) in ChCl 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 earlier investigators [9, 10]. Electrical conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

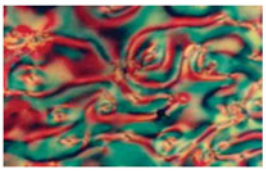
Results and Discussion

Phase Diagram

The multi-component system of (7CB + 80CB) in ChCl 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 concentrations against phase transition temperatures of the given mixture, which clearly illustrates that the mixture of all concentrations of (7CB + 80CB) in ChCl exhibits Cho, SmA, SmC, and SmB phases at different temperatures when the specimen is cooled from its isotropic liquid phase. The concentrations of the mixture from 30 to 45% and 15 to 35% of (7CB + 80CB) in ChCl show TGB and re-entrant smectic-A phases in addition to cholesteric, smectic-C, and smectic-B phases at different temperatures.



a) Mobile thread like filament texture of TGB phase (250X).



b) Schlieren texture of SmC phase (250X).

Figure 2. Microphotographs obtained in-between the crossed polars. (a) Mobile thread-like filament texture of TGB phase (250x). (b) Schlieren texture of SmC phase (250x).

Optical Texture Studies

For the purpose of optical texture studies, the sample was sandwiched between slide and cover glass, and the optical textures were observed using Leitz-polarizing microscope 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 grows radially, which form spherulitic texture of cholesteric phase with large values of pitch [11, 12]. On further cooling the specimen, the cholesteric phase slowly changes over to mobile thread-like filament texture, which is the characteristic of TGB phase as shown in Fig. 2(a).The helical axes of TGB phase lies in the direction parallel to smectic layer planes [13, 14]. On further cooling, the TGB phase of filamentary texture slowly changes over to focal conic fan-shaped texture of smectic-A

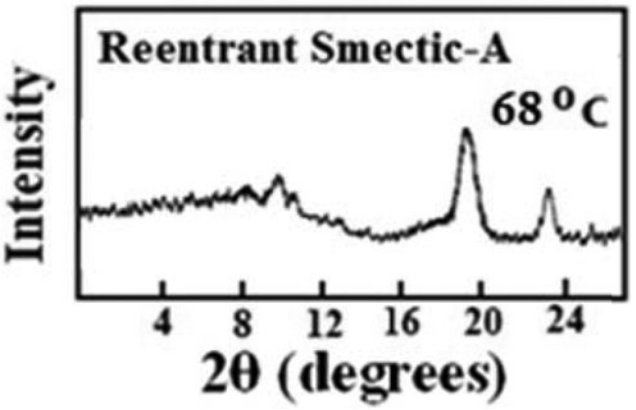


Figure 3. X-ray broadening spectrum for the sample of 32% (7CB + 80CB) in ChCl at 68°C of RSmA phase.

phase, and then this phase changes over to schlieren texture of smectic-C; the observed texture is shown in Fig. 2(b). On further cooling the specimen, unstable schlieren texture of smectic-C phase slowly changes over to well-defined focal conic fan texture of re-entrant smectic-A phase. In this system the microscopic observations clearly indicate that the given mixture exhibits a very interesting re-entrant smectic-A phase [15]. The lowest temperature mesophase of 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 [16]. In the given mixture, some of the middle concentrations of (7CB + 80CB) in ChCl at lower temperatures did not show molecular aggregates in the preferred direction of alignment toward 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].

Characterization of Nano Aggregated Grains

The X-ray diffractometer traces obtained for the mixture of 32% (7CB + 80CB) in ChCl at 68°C are shown in Fig. 3. 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 molecules for different liquid crystalline phases [17, 18]. The X-ray traces obtained for 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 the broadening of diffraction peaks. In order to estimate nano aggregated size of molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks, we used the Scherrer's formula,

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

where L is the nano aggregated size, λ is the wavelength of X-ray radiation (1.934 Å), K is usually taken as 0.89, β is the line width at half maximum, and θ is the diffraction angle. The phase transition temperature increases as it moves from crystalline phase to amorphous region [19, 20], which clearly illustrates that nano aggregated size of the phase transition behavior of molecules decreases with increasing of temperature. In Fig. 3, we observed that the structure of molecular orientation for re-entrant smectic-A phase is energetically more stable, and the molecular ordering of this phase shows intense two peaks. The nano aggregated size of liquid crystalline material for re-entrant smectic-A phase comes out to be 49.8 nm. From this study, we have observed that the phase transition behavior of molecular ordering of 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 is big enough to indicate that the molecular ordering [21] of layer structure increases with decrease in temperature.

Conductivity Measurements

Electrical conductivity measurements are helpful in the study of phase behavior with temperature. An abrupt increase or decrease in electrical conductivity with temperature relates to the phase behavior of lyotropic, thermotropic, and chromonic systems [22].

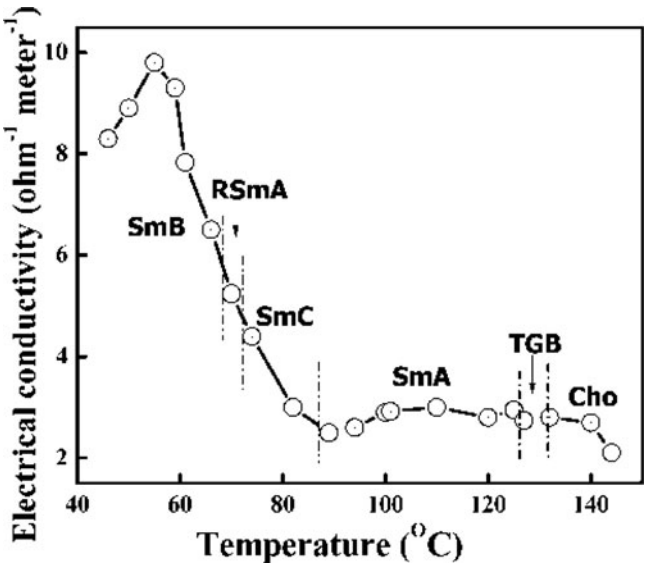


Figure 4. Temperature variation of electrical conductivity σ (Ω^{-1} m^{-1}) for a sample 32% (7CB + 80CB) in ChCl.

Temperature variations in electrical conductivity are shown in Fig. 4. The figure clearly illustrates that there is a change in the value of electrical conductivity from 46 to 144°C while cooling from isotropic phase for the mixture of 32% (7CB + 80CB) in ChCl. With further decrease in temperature, the electrical conductivity starts decreasing as we move toward room temperature. The mixture of 32% (7CB + 80CB) in ChCl changes from Cho→TGB, TGB→SmA, SmA→SmC, SmC→RSmA, and RSmA→SmB phases

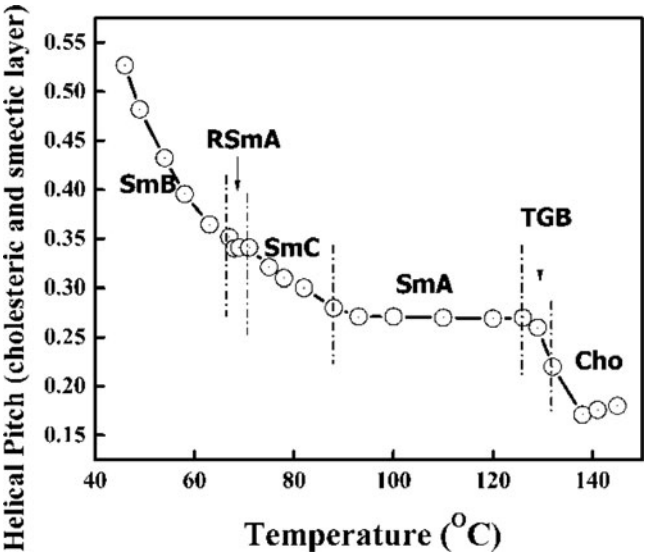


Figure 5. Temperature variations of pitch for the mixture of 32% (7CB + 80CB) in ChCl.

if some value of electrical conductivity goes on increasing with decreasing temperature. Changes in electrical conductivity are observed only after further cooling of specimen. This suggests that the size of aggregates starts growing toward decreasing temperature, and the system moves toward more orderliness. Finally, below 46°C, size of aggregates becomes so large that the specimen starts moving toward crystalline nature [23, 24].

Helical Pitch Measurements

The helical pitch measurements were performed on cholesteric phase by the well known Grandjean–Cano wedge method [25, 26]. The mixture was taken in a wedge-shaped cell treated for homogeneous alignment. The two glass plates formed a small angle at the wedge. The mixture was cooled slowly ($0.2^{\circ}C\ min^{-1}$) from isotropic phase to smectic phase, which induced an array of equidistant Grandjean–Cano lines. Pitch of the cholesteric phase was determined by measuring the distance between the Grandjean–Cano lines as a function of temperature. As the temperature was lowered from cholesteric phase to smectic phase, the spacing between the lines increased, indicating that the pitch in this phase was increasing. The temperature variation of pitch for the mixture of 32% (7CB + 80CB) in ChCl is shown in Fig. 5. From this figure, it is evident that the variation of pitch from cholesteric to smectic phase is smooth and continuous. But the value of pitch gradually increases from 0.171 to 0.19 mm upon cooling the sample from cholesteric to smectic phase. The value of pitch increased steeply and reached a maximum of 0.52 mm with transition from cholesteric to smectic phase. However, in the study we noticed that the sequence of transition is Iso→Cho→TGB→SmA→SmC→RSmA→SmB→Cryst on cooling [27]. The pitch is continuous at cholesteric to SmA transition in spite of being a rather energetic transition. It increases on cooling to smectic phase and diverges on approaching the TGB, SmA, SmC, RSmA, and SmB phases. This divergence is related to the second-order nature of transition. It exhibits a steep decrease, close to cholesteric phase, which is usually a characteristic of second-order SmA, SmC transitons.

Conclusions

In light of the above results, we have drawn the following conclusions. The multi-component system of (7CB + 80CB) in ChCl exhibits an unusual sequence of phases showing the formation of Cho, TGB, SmA, SmC, RSmA, and SmB phases in the concentration range of 15–45% of (7CB + 80CB) in ChCl. The phase behavior is discussed with the help of phase diagram. The X-ray study lends support to found nano aggregated size of molecules for re-entrant smectic-A phase to be 49.8 nm. Drastic changes in the values of electrical conductivity with the variation of temperature unambiguously correspond to Cho, TGB, SmA, SmC, RSmA, and SmB phases. Drastic changes in electrical conductivity are expected to be due to changes in the dimensions of discs along with the changes in the orientation order of the arrangement. The value of pitch increased steeply at the cholesteric to smectic phase transition.

Funding

The author thanks the University Grants Commission, New Delhi, India for financial assistance under the Minor Research Project Scheme (MRP(S)-0161/12-13/KAMY022/UGC-SWRO).

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