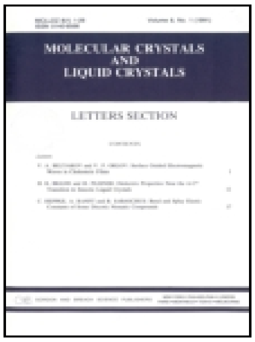

Molecular Crystals and Liquid Crystals

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 (2016) Optical and electro-optical characterizations of thermal stability of induced smectic phases, Molecular Crystals and Liquid Crystals, 631:1, 99-106, DOI: 10.1080/15421406.2016.1149024

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1149024

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 631, 99–106
http://dx.doi.org/10.1080/15421406.2016.1149024

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Optical and electro-optical characterizations of thermal stability of induced smectic phases

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ABSTRACT
In the present work, our investigation is to study the optical and electric properties of the binary mixture of heptyl-oxy-benzilidene-p-n-heptyl-aniline and cholesteryl laurate, which exhibit very interesting liquid crystalline Cho–TGB–SmA–SmC-ReSmA–SmE phases sequentially when the specimen is cooled from its isotropic phase. These phases have been characterized by using microscopic and optical anisotropic technique. Temperature variations of optical anisotropy and X-ray studies have been discussed. An electro-optical measurement has also been discussed.

KEYWORDS
Twisted grain boundary; re-entrant smectic-A; molecular orientation; optical texture; electro-optical studies

Introduction

Liquid crystals are a meso-state between solids and liquids. These share anisotropic properties of optical (uniaxial and biaxial) crystals and the fluid properties of isotropic liquids [1, 2]. These materials are extremely sensitive to small external factors (electric and magnetic fields, surface effects, temperature, etc.) and possess order and mobility at microscopic and macroscopic levels [3]. Thermotropic liquid crystals are technologically most important among all liquid crystalline mesophases, and the nematic mesophase is one of these, which has broad applications in many engineering devices. The remarkable advances in liquid crystal technology have led to the appearance of liquid crystal-based spatial light modulators and display applications [3]. The correct performance of devices requires liquid crystal materials that are stable over a long period, have high thermal stability and thermal range, high dielectric and optical anisotropy, and low switching voltage and switching time. These various requirements are achieved by using chemical synthesis and carefully designed mixtures of different liquid crystalline materials such as dye, polymer, and nano-particle [4, 5].

In the present investigation, our aim is to study the different properties of binary mixtures of liquid crystalline materials [6]. Some different concentrations of given mixtures show the existence of twisted grain boundary (TGB) and re-entrant smectic-A (ReSmA) phases and they have been microscopically observed in addition to the conventional liquid crystalline phases such as cholesteric, smectic-A, smectic-C, smectic-B, and smectic-E phases sequentially when they are cooled from their isotropic melt. Optical, electrical, X-ray studies of the samples taken for investigation have been discussed.

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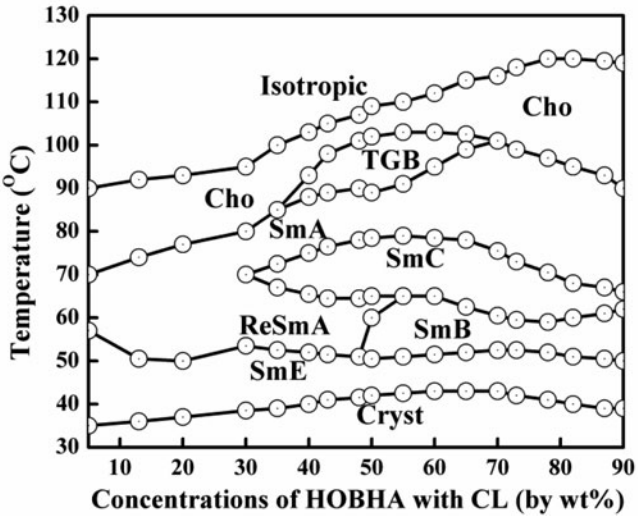

Figure 1. Partial phase diagram of mixture of HOBHA in CL.

Experimental

Compound heptyl-oxy-benzilidene-p-n-heptyl-aniline (HOBHA) used in this investigation was obtained from the Basic Pharma Life Science Pvt. Ltd., India, and it was further purified twice by a recrystallization method using benzene as a solvent. The cholesteryl laurate (CL) was obtained from M/s East Mann Organic Chemicals, USA. Mixtures of different concentrations of HOBHA in CL were prepared and mixed thoroughly. The mixtures of different concentrations of HOBHA in CL were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. Phase transition temperatures of these mixtures with different concentrations were measured using Leitz-polarizing microscope and conventional hot stage. The sample was sandwiched between slide and cover slip, which was sealed for microscopic observation. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [7–9]. The X-ray broadening peaks were obtained at 59°C using JEOL diffractometer. Electro-optical measurements were carried out by the usual experimental setup of Williams [10]. It consists of tin oxide-coated transparent conducting glass plate and the sample sandwiched between these two glass plates. Teflon spacers having a thickness of $d = 39 \pm 1\ \mu$m were used, and observations were made at 90°C using polarizing microscope in conjunction with a hot stage.

Results and discussions

Phase diagram

The partial phase diagram is a very important method to determine the thermal stability of different liquid crystalline phases for different concentrations of given liquid crystalline materials. The partial phase diagram is shown in Figure 1. This clearly illustrates that the mixture with concentrations ranging from 5 to 90% of HOBHA in CL exhibit cholesteric, SmA, and SmE phases sequentially when the specimen is cooled from its isotropic melt. However, the concentrations ranging from 30 to 70% of HOBHA exhibit a twisted grain boundary (TGB) and re-entrant smectic-A (ReSmA) phases respectively at different temperatures. The phase diagram is discussed with the help of phase diagram [11–13].

Optical texture studies

The optical textures exhibited by the samples were observed and recorded using the Leitz polarizing microscope and specially constructed hot stage. The specimen was taken in a form of a thin film sandwiched between slide and cover glass. The concentrations of 5 to 90% of binary mixture of HOBHA in CL were considered for experimental studies. When a specimen of 43% HOBHA in CL is cooled from its isotropic melt, it exhibits Iso–Cho–TGB–SmA–SmC-ReSmA–SmE–Cryst phases sequentially. While the sample is cooled from its isotropic phase, nucleation starts in the form of minute bubbles, and immediately the bubbles grow radially and form fingerprint pattern, which is a characteristic of cholesteric phase with large values of pitch [14]. On further cooling the specimen, the cholesteric phase slowly changes over to smectic phase, passing through an intermediate phase and is assigned by the appearance of mobile thread-like textures in homeotropic region, which is a characteristic of TGB phase as shown in Figure 2(a). The helical axes of TGB phase lies in a direction parallel of smectic layer planes [15,16]. On further cooling, thread-like TGB phase changes over to focal conic fan-shaped texture of SmA. This is shown in Figure 2(b).

Molecular structural confirmations of SmA phase at 83°C are stable. For thermal variations, the flexibility of molecular layers leads to distortions, which give rise to optical patterns known as focal-conic textures. On further cooling the specimen, SmA phase may transform into the appearance of tilting molecules relative to smectic layers and this is the characteristic of well-defined Schlieren textures of SmC as shown in Figure 2(c). If some different smectic phases are observed, these differ from one another in a way of layer formation and existing in an order inside molecular layers.

In this system, the microscopic observation clearly indicates that a given mixture with concentration ranging from 35 to 55% of HOBHA in CL exhibits a re-entrant SmA phase [17]. 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 [18]. In the present system, some of the middle concentrations of HOBHA 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 SmA phase. This phase changes over to a focal conic fan-shaped herring bone pattern of SmE phase and becomes crystalline phase, which remains stable at room temperature [19,20].

Optical anisotropy

Results of this investigation are further complemented by optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the given mixture were measured at different temperatures for different concentrations using Abbe refractometer. Variations in birefringence as a function of temperature for 43% of HOBHA in CL are shown in Figure 3. The values of electrical susceptibility for 43% of HOBHA in CL have been calculated using the Neugebauer relation [21] at different temperatures. The variation of electrical susceptibility as a function of temperature for the mixture is shown in Figure 4. It can be observed from the figure that wherever there is phase transition, the value of electrical susceptibility changes

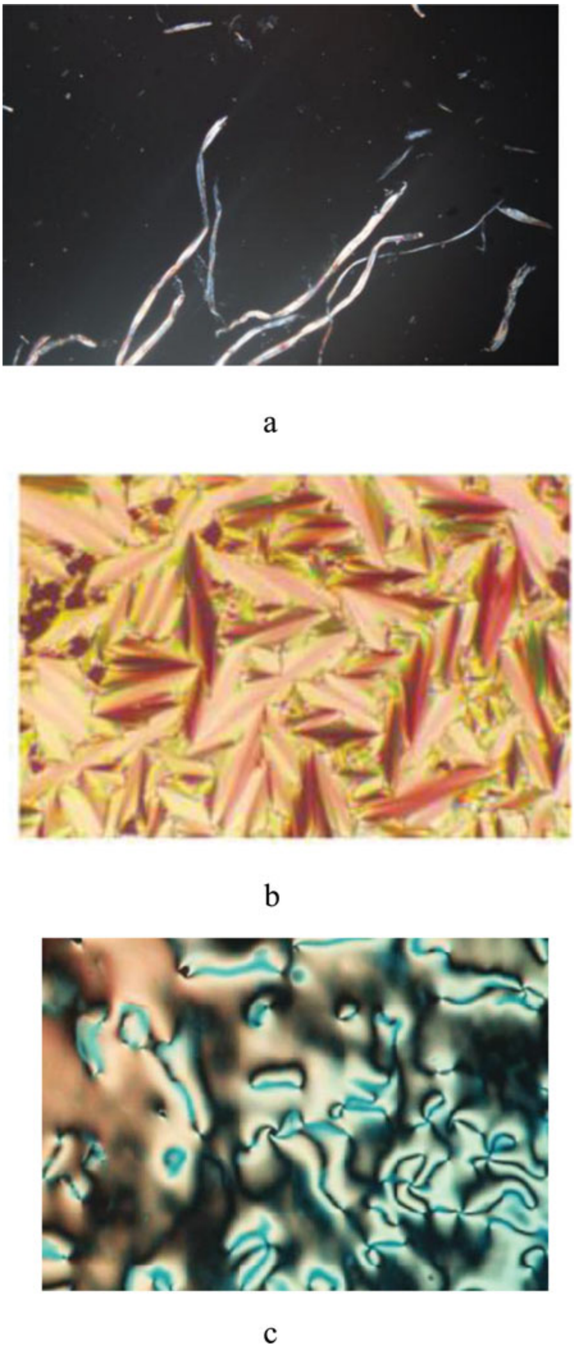

Figure 2. Microphotographs obtained in between the crossed polars: (a) streak-like texture of TGB phase (250×). (b) Focal conic fan-shaped texture of SmA phase (250×). (c) Schlieren texture of SmC phase (250×).

appreciably, which indicates that the changes correspond to different smectic modifications. Further, with increase in the concentration of HOBHA, the value of electrical susceptibility decreases with temperature because the effective optical anisotropy associated with the molecules of HOBHA also decreases.

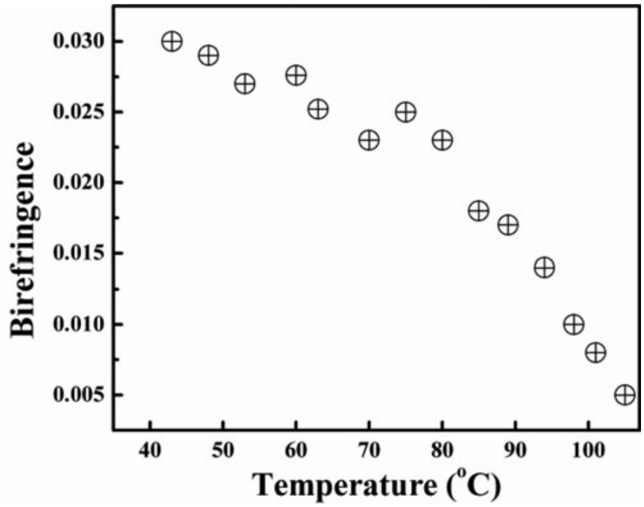

Figure 3. Variations in birefringence as a function of temperature for a mixture of 43% of HOBHA in CL.

Electro-optical studies

Electro-optical measurements are very important tools in getting better idea on the phase transition behavior of liquid crystalline phases with electric field at a constant temperature. In this study, we considered the sample for a mixture of 43% of HOBHA in CL at a constant temperature of 90°C. When the applied voltage increases, the molecular arrangements of liquid crystalline phases start to fluctuate and begin to grow, and hence it gradually deforms the original position of liquid crystalline structural formations. Remarkably, it has been observed that at a constant temperature the various aspects of low-frequency effects on a given mixture clearly show different directions of molecular orientations/reorientations, and hence it forms flow patterns, such as stripped pattern and chevron textures. The formation of zigzag and herringbone patterns are characteristic of chevron textures, and the forming time of these patterns depends on applied electric field. We observed a significant difference in the electromechanical responses of these textures, and the stripes of these textures do not have a

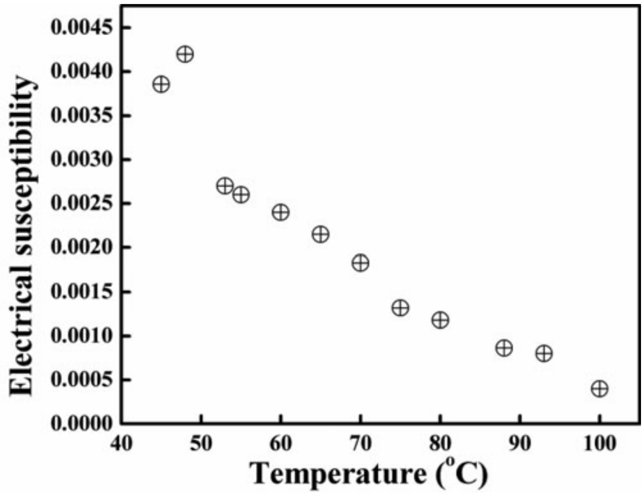

Figure 4. Temperature variation of electrical susceptibility for a mixture of 43% of HOBHA in CL.

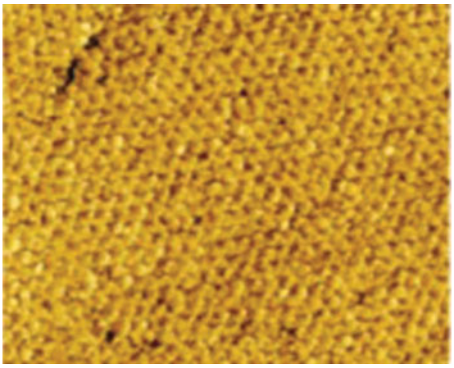

Figure 5. Hexagonal grid patterns of electro-optical texture obtained by the applied electric field.

linear electromechanical effect at low fields but at higher fields, it shows mechanical vibrations. This indicates that the spontaneous polarization has rotated and is no longer parallel to electric fields. In contrast to the direction, the molecular orientations/reorientations of layer structures are unchanged by the application of applied electric field. Sequentially, we have to increase the applied voltage above 22.20 V, the observed pattern becomes dynamic scattering mode-like, and it appeared like an irregularity of molecular reorientations of liquid crystalline phase. The new disordered regions arise probably due to the molecules not being confirmed to the orientations in the x–z plane. If the voltage is kept constant for some time, a completely stationary and regular two-dimensional hexagonal grid pattern is observed. The hexagonal grid pattern texture is as shown in Figure 5. The hexagonal grid pattern deforms gradually with increasing frequency and at some stage, it becomes indistinguishable from the chevron texture. However, the hexagonal grid pattern is rather stationary and is formed in a short time at 250 Hz and 23 V. It follows from Figure 5 that an extremely regular hexagonal grid pattern is formed when the external electric field is applied. One of the regions in the formation of hexagonal grid pattern is the electronic charge injected by applying external electric field [22–25].

Characterization of nano-aggregated grains

The X-ray diffractometer traces obtained for the mixture of 43% of HOBHA in CL at 59°C are shown in Figure 6. The diffraction peaks at this temperature correspond to ReSmA phase by using JEOL diffractometer with the following settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å. X-ray diffraction study is an important method to determine the nano-aggregated grain size of molecules for different liquid crystalline phases [26,27]. Deviation from perfect liquid crystallinity leads to broadening of diffraction peaks. In order to estimate nano-aggregated grain size of molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks, we used the following Scherrer's formula:

$$L = \mathrm{K}\lambda/\beta\cos\theta,$$

where L is the nano-aggregated grain size, λ is the wave length of X-ray radiation (Fe: 1.934 Å), K is usually taken as 0.89, β is the line width at half maximum, and θ is the diffraction angle. Usually with decrease of temperature [28,29], the nano-aggregated grain size of molecules increases. Temperature-dependent molecular orientations of focal conic fan texture of ReSmA phase is more stable, and hence the molecular ordering of this phase shows three peaks. The nano-aggregated grain size of liquid crystalline material for ReSmA phase comes out to be

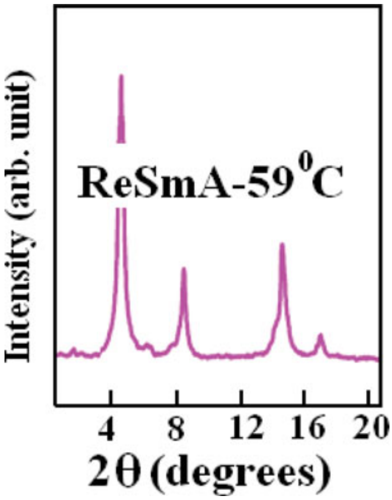

Figure 6. X-ray broadening spectrum for a mixture of 43% of HOBHA in CL at 59°C of re-entrant Smectic-A phase.

18.89 nm. We observed from the X-ray studies that the molecular ordering of the liquid crystalline phase increases with decreasing temperature. X-ray studies clearly illustrate that the nano-aggregated grain sizes are big enough to indicate that the molecular ordering [30–32] of layer structure increases and decreases the temperature.

Conclusions

The salient features of this investigation are as follows: The existence of TGB and re-entrant smectic-A phases were observed by using microscopic technique in binary mixture of HOBHA in CL. The phase behavior is discussed with the help of phase diagram. Variations of applied electrical field at constant temperature unambiguously correspond to the optical purity of liquid crystalline phases. The various aspects of frequency effects on a given mixture show different directions of molecular reorientations, which exhibit flow patterns formations such as stripped pattern, chevron textures, and hexagonal grid pattern textures, and hence these textures are observed microscopically. The X-ray study lends support to find nano-aggregated size of ReSmA phase, which comes out to be 18.89 nm.

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