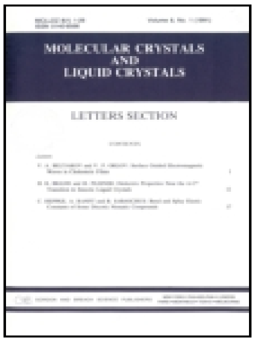

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Temperature-dependent Anisotropic Nano-Molecular Orientations of Liquid Crystalline Materials

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ABSTRACT
In the present work, our investigation is to study the optical anisotropic properties of the binary mixture of cyano-benzilidene-p-n-octyl-oxy-aniline (CBOOA), cholesteryl nonanoate (CN), which exhibits a very interesting liquid crystalline Cho-TGB-SmC-SmA-SmB phases sequentially when the specimen cooled from its isotropic phase. These phases have been characterized by using microscopic and optical anisotropic technique. The temperature variations of optical anisotropy and electrical conductivity have been discussed. X-ray studies are supported to calculate the nano-aggregated grain size of the molecules.

KEYWORDS
Molecular orientation; optical anisotropy; optical texture; twisted grain boundary; X-ray studies

Introduction

Molecules are in a solid, generally posses both positional and orientational order. That means to say that the centre of mass of the molecules occupies specific locations and the molecular axes point in certain directions. Thus it possesses an anisotropic property, which is direction dependent. When the solid melts into a liquid, then both the positional and orientational order disappear. In this state, there will not be any preferred locations for the centre of mass or preferred direction of orientation for the molecular axes. Thus, in the liquid state, the molecules diffuse freely throughout the sample and the centers of mass move in random directions. Thus, it is said to be an isotropic phase. In addition to the solid and liquid phases, there are condensed phases which exhibit intermediate order. The simplest case is the one in which the molecules are generally fixed at lattice points wherein, in addition to vibrations it may freely rotate. This type of material is known as plastic crystal. However, If one axis of a molecule is much longer or shorter than the other two axes, then it is possible for additional phases to form in which there is some positional and orientational order, but much less than that found in solids and plastic crystals. These are known as liquid crystal phases, in which the molecules diffuse throughout the sample while maintaining some short-ranged positional and orientational order. In this case, the ability of the molecules to move among the various lattice sites brings in fluidity to these structures. But since all directions within the phase are not identical, they are said to be anisotropic rather than isotropic fluids. Thus liquid crystals combine the anisotropic properties of solids and fluidity of liquids. Hence, these anisotropic ordered fluids lie in between solids and

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liquids and possess properties of both and thus they are called as intermediate phases or mesophases.

Twisted grain boundary phase was theoretically predicted by Renn and Lubbensky [1] which is analogous to deGennes model of the Abrikosov phase in superconductors [2]. This phase is called as helical smectic-A or TGB phase. This oscillates between the low temperature Smectic-A phase and high temperature chiral nematic phase. This phase will be recognized by rotated blocks of smectic-A layers in which long molecular axes are arranged normally to the layer planes. Hence the helical axis of TGB phase is perpendicular to the molecular axis and parallel to the smectic planes. The re-entrant phenomenon of liquid crystalline phases is peculiar in pure compounds as well as mixed systems [3–5]. This is also peculiar with TGB phase. For example re-entrant phenomenon of TGB-A phase along with re-entrant cholesteric phase has been reported in the mixtures and the cholesteric based nonsymmetrical dimmers. Also, such phases have also been reported in pressure-temperature based phase diagrams [6–8]. In the case of TGB and SmA phase, the temperature of this region should increase with increase in chirality of the system. The TGB and chiral SmC* phase has also been close to the NAC multi-critical point, which is composed of twisted stacks of helical SmC* phase which was predicted by the theoretical studies of Lubbensky and Renn [9].

In the present work, our aim is carried out to study on different properties of binary mixture of liquid crystalline materials. Some concentrations of the given mixture exhibit a liquid crystalline phases of cholesteric, twisted grain boundary (TGB) and induced smectic phases sequentially when the specimen cooled from its isotropic phase. Optical, thermal and X-ray studies have been carried out to understand the intermolecular interactions of the given mixture.

Experimental studies

The compound cyano-benzilidene-p-n-octyl-oxy-aniline (CBOOA) used in this investigation was obtained from the Basic Pharma Life Science Pvt., Ltd., India, and it was further purified twice by a re-crystallization method using benzene as a solvent. The cholesteryl nonanoate (CN) was obtained from M/s East Mann Organic Chemicals, USA. Mixtures of different concentrations of CBOOA in CN were prepared and were mixed thoroughly. These mixtures of various concentrations of CBOOA 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 different concentrations were measured with the help of Leitz polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The X-ray broadening 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 [10–12]. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

Result and discussion

Phase diagram

The binary mixture of CBOOA in CN exhibits a very interesting different liquid crystalline phases and the phase transition temperatures are measured by using Leitz-polarizing

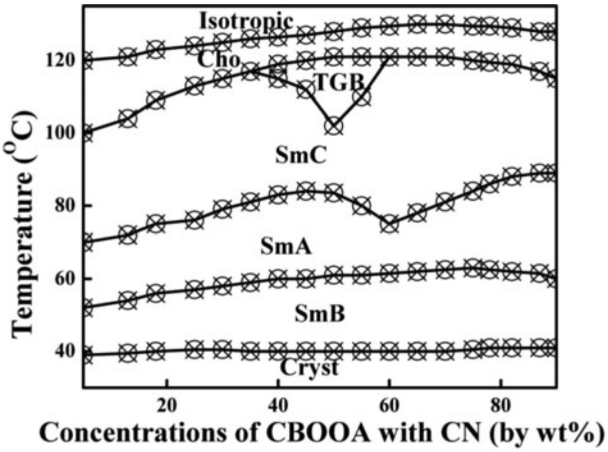


Figure 1. Partial phase diagram for the mixture of CBOOA in CN.

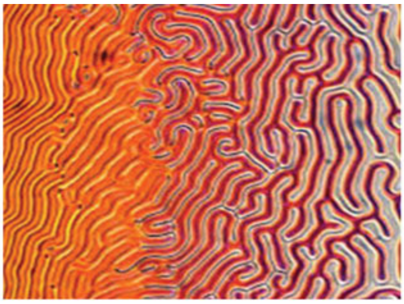
microscopic. The partial phase diagram shown in Fig. 1 and it is a very important method to determine the stability of liquid crystalline phase at different temperatures for different concentrations and it is obtained by plotting the concentrations against the phase transition temperatures of the mixture, which clearly illustrates that, the mixture of all concentrations of CBOOA in CN exhibit a cholesteric, SmC, SmA, and SmB phases, respectively, at different temperatures, when the specimen is cooled from its isotropic liquid phase. The concentrations of the mixture from 35% to 60% of CBOOA shows a TGB phase in addition of conventional phases of cholesteric SmC, SmS, and SmB phases, respectively, at different temperatures [13, 14].

Optical texture studies

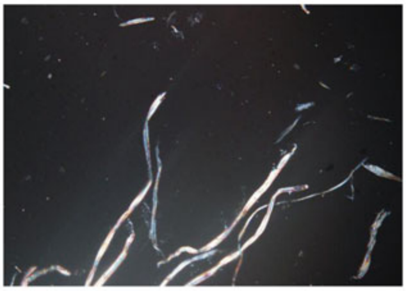
For the purpose of optical texture studies, the sample was sandwiched between a slide and cover glass, and then the optical textures were observed using a Leitz polarizing microscope in conjunction with a specially constructed hot stage. The concentrations ranges from 35% to 60 % of the mixture are slowly cooled from its isotropic melt, the genesis of nucleation starts in the form of small bubbles and slowly grow radially, which form a fingerprint pattern texture of cholesteric phase with large values of pitch is shown in Fig. 2(a) [15, 16]. On further cooling the specimen, the cholesteric phase slowly changes over to a mobile thread-like filament texture, which is characteristic of the TGB phase, as shown in Fig. 2(b). The helical axes of the TGB phase lie in a direction parallel to the smectic layer planes [17, 18]. On further cooling, the filamentary texture of TGB phase changes over to a schlieren textures of SmC as shown in Fig. 2(c). On further cooling the specimen, optical texture of SmC phase slowly transform to well-defined focal conic fan-shaped texture of the SmA phase, as shown in Fig. 2(d) and then sequentially this phase slowly changes over to a broken focal conic fan-shaped texture of the SmB phase and it remains stable at room temperature [19].

Optical anisotropic studies

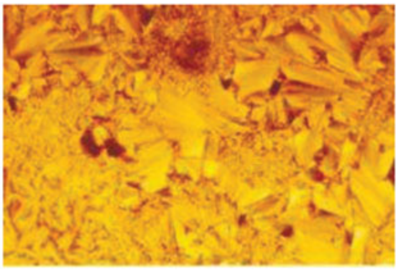
Results of this investigation are further supported by the optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the mixture were measured at different



a) Fingerprint pattern of cholesteric phase (250X).



b) Thread-like filament texture of of TGB phase (250X).



c) Focal conic fan-shaped texture of SmA phase (250X).

Figure 2. Microphotographs obtained in between the crossed polars, (a) Fingerprint pattern of cholesteric phase (250×). (b) Thread-like filament texture of TGB phase (250×). (c) Focal conic fan-shaped texture of SmA phase (250×).

temperatures for the different concentrations using Abbe Refractometer. The variations of refractive indices as a function of temperature for 45% of CBOOA in CN are shown in Fig. 3. The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 45% of CBOOA in CN have been calculated using Neugebauer relation [20] at different temperatures. The variation of electrical susceptibility as a function of temperature for the mixture is shown in Fig. 4. From the figure, it can be observed that wherever there is phase transition, the value of electrical susceptibility changes appreciably, which indicates that the changes correspond to various smectic modifications. Further, with increase in the concentration of CBOOA, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of CBOOA also decreases.

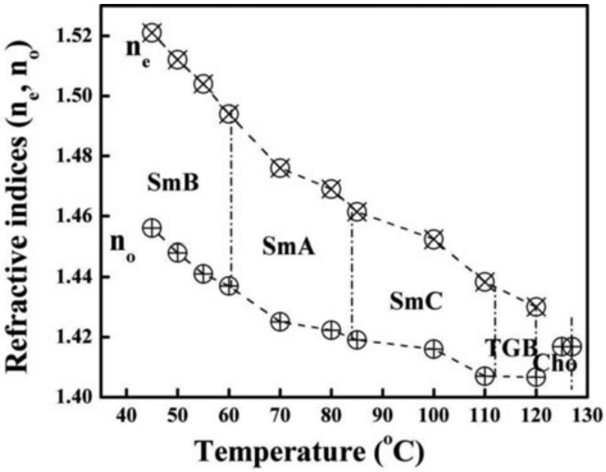


Figure 3. Temperature variations of refractive indices for the mixture of 45% of CBOOA in CN.

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 [21]. It is well known that when a cholesteric materials is added as impurity to a CBOOA molecules, 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 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 8 % to 22 % of the mixture exhibit a stripped pattern when they are cooled from its isotropic phase at the respective temperatures, which corresponds to cholesteric phase. Microscopic twisting power β of the solute in the mixture 8 % to 15 % of CN is calculated using the formula:

$$4\pi\beta C = 2\pi/P$$

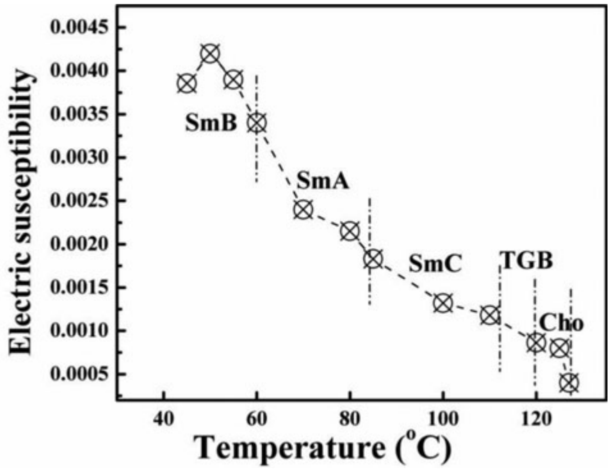


Figure 4. Temperature variation of electrical susceptibility for the mixture of 45% of CBOOA in CN.

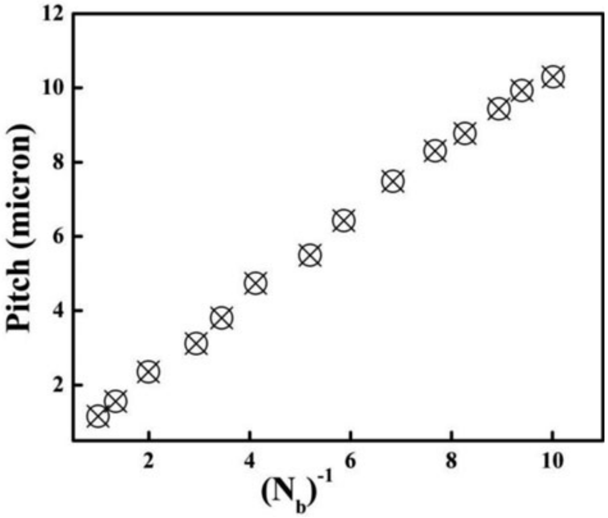


Figure 5. Variation of pitch of cholesteric phase with $(N_b)^{-1}$. Here, N_b represents the number of molecules of CBOOA per unit volume of the mixture.

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

$$\beta = 1/2PC$$

The pitch of the cholesteric phase against concentration is drawn and shown in Fig. 5, which illustrates that at low concentrations of the cholesteric materials, the pitch is inversely proportional to the concentration of the cholesteric materials. 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 materials in CBOOA.

Conductivity measurements

Electrical-conductivity measurements help in getting better idea on the phase behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase transition behavior of lyotropic, thermotropic, and chromonic systems [22]. The temperature variations of electrical conductivity are as shown in Fig. 6. From this figure some changes are observed in the value of electrical conductivity temperature ranging from 45°C to 127°C, while the specimen cooling from its isotropic phase for the mixture of 45% of CBOOA in CN. From the microscopic observation the sequence of liquid crystalline phase changes from Cho-TGB-SmC-SmA-SmB phases respectively at different temperatures. Here it has been found that the electrical conductivity goes on increasing as the temperature decreases. This suggests that aggregated molecular size starts growing towards lower temperatures and then the system becomes more ordered [23–28].

Characterization of nano aggregated grains

The X-ray diffractometer traces obtained for the mixture of 45% of CBOOA in CN at temperature 55°C as shown in Fig. 7. The diffraction peaks at this temperature correspond to SmB phase respectively 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

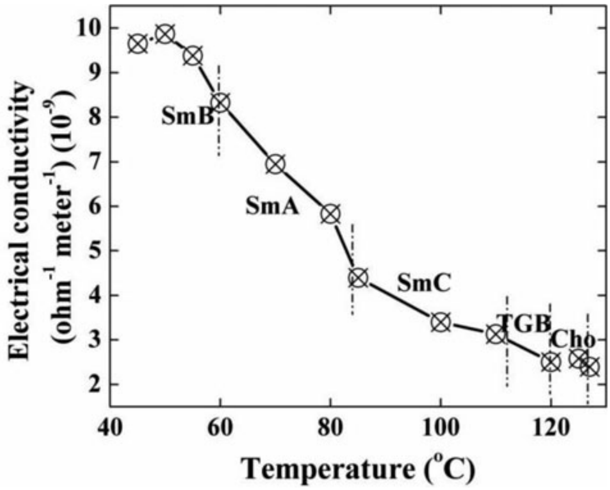


Figure 6. Temperature variation of electrical-conductivity σ (x 10^{-9} Ω^{-1} m^{-1}) for the sample of 45% of CBOOA in CN.

the nano-aggregated grain size of the molecules for different liquid crystalline phases [29, 30]. The deviation from perfect liquid crystallinity leads to broadening of the diffraction peaks. In order to estimate nano-aggregated grain 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 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 [31, 32], the nano-aggregated grain size of the molecules increases. Temperature dependent molecular orientations of broken banded focal conic fan texture of smectic-B phase is more stable and hence the molecular ordering of this phase shows two peaks. The nano-aggregated grain size of liquid crystalline material for smectic-B phase comes out to be 36.43 nm. From the X-ray studies, we have

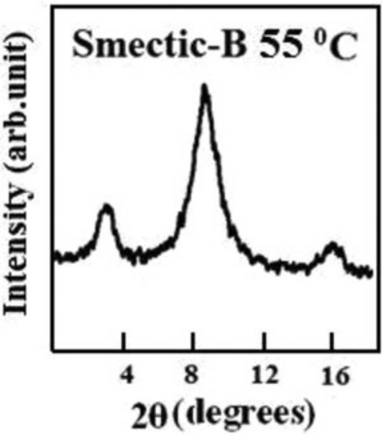


Figure 7. X-ray broadening spectrum for the mixture of 45% of CBOOA in CN at 55°C temperature of SmB phase.

been observed that, 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 [33–34] of layer structure increases as well as decrease the temperature.

Conclusions

The salient features of this investigation are the following: The existence of cho, TGB and various smectic phases have been observed by using microscopic technique in mixture of CBOOA and CN. The phase behavior is discussed with the help of phase diagram. The changes in value of electrical conductivity with temperature unambiguously correspond to smectic and cholesteric phases. With increase in the concentration of CBOOA in CN, the value of electrical susceptibility decreases with temperature since the effective optical anisotropy associated with the molecules of CBOOA also decreases. Electrical conductivity measurements reveal that below 45°C size of aggregates becomes so large that the specimen starts moving towards crystalline nature. X-ray studies help us to found the nano-aggregated grain size are 36.43 nm.

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