Electro-Optical and Thermodynamic Response of Twisted Grain Boundary Phase

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Abstract: In the present work, our investigation is to study on the optical and electrical properties of binary mixture of cholesteryl chloride (ChCl) and 4, 4'-hexyloxy azoxy benzene (HOB). Mixtures of these molecules exhibits cholesteric, twisted grain boundary and induced smectic phases sequentially when the specimen cooled from its isotropic phase. These phases have been characterized by using microscopic technique. Thermodynamical response of birefringence of given molecules have been discussed to understand the phase stability, chemical structure and molecular dynamics of the binary mixture of liquid crystalline materials. Temperature dependent electro-optical phase transition behaviors of the given molecules have also been discussed.

Keywords: Molecular orientation; Filament texture of TGB; Electro-Optical Studies; Thermodynamical studies; Molecular segregation

1. Introduction

Chirality in functional molecular materials is a powerful tool for inducing properties and molecular organizations absent in non-chiral materials. This is particularly true in mesogenic materials. For instance, the twist-grain boundary (TGB) phase is a type of frustrated phases with absorbing physical and structural features, which are found exclusively in optically active systems. TGB phases have been known since 1988 [1] and have attracted great consideration during the last two decades. Chiral liquid crystals have the tendency to form a cholesteric-like helical director field. On the other hand, the molecular interactions may favor a smectic layer structure. However, it is impossible to realize a continuous structure which exhibits both a cholesteric director field and a smectic layer structure at the same time. The competition between these two structural features can result in frustrated structures containing a regular lattice of grain boundaries, which in turn consist of a lattice of screw dislocations. This defect structure exhibits an interesting theoretical analogy to the flux line lattice which occurs in the Shubnikov phase of type II superconductors. However, the range of parameters determining the structure is larger in liquid crystals than in superconductors. A large variety of new phases, such as the TGB-A [1], TGB-C [2], TGB-C* [3], melted grain boundary [4] phases, a defect line liquid (N*L) [5], antiferroelectric crystals of twist grain boundaries [6], and smectic blue phases [7] have been predicted and/or experimentally observed. The first experimental observation of TGBA phase was reported by Goodby et al., [8, 9]. The observations of TGB-A phase consists of smectic slabs, separated by defect walls (grain boundaries) consisting of defect lines (twist dislocations). In the slabs, molecules are arranged in layers with their director normal to the smectic layers. Neighboring slabs (and hence molecular director in the slabs) are twisted with respect to each other by an angle $\chi$, thereby forming a helical structure with the helix axis normal to the molecular director [10, 11].

In the present investigation, our aim is to carry out the study of optical and electrical properties of the binary mixture of cholesteric and nematic compounds namely: cholesteryl chloride (ChCl) and 4, 4'-hexyloxy azoxy benzene (HOB). The mixture of these molecules exhibits a very interesting cholesteric, twisted grain boundary and induced smectic phases such as SmA, SmC*, SmE, and SmB phases sequentially when they are cooled from its isotropic phase. These phases were observed using microscopic and optical anisotropic technique. The temperature dependent electro-optical phase transition behavior twisted grain boundary phase has been discussed, in order to understand the irregularity of molecular re-orientations of liquid crystalline phase.

2. Experimental Studies

In the present investigation, we have studied binary mixtures of liquid crystals, namely, cholesteryl chloride (ChCl) 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 different concentrations of HOB in ChCl were prepared. The phase transition temperatures of these mixtures were...
determined using Leitz-polarizing microscope in conjunction with hot stage. Electrical conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit. Electro optical measurements were carried out by the usual experimental setup of Williams [12]. It consists of tin oxide coated transparent conducting glass plate and the sample sandwiched between these two glass plates. Teflon spacers having thickness of d=39 ±1 μm were used and observations were made at 93 °C using polarizing microscope in conjunction with a hot stage.

3. Optical Texture Studies

In the present study, optical textures exhibited by the samples were observed and recorded using Leitz polarizing microscope and constructed hot stage. The specimen was taken in the form of thin film and sandwiched between slide and cover glass. Concentrations of 30% and 35% of binary mixture of ChCl and HOB have been considered for the experimental studies. 30% and 35% of given 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 spherulitic texture of cholesteric phase at temperature 95.08 °C with large values of pitch [13-15] and the same is shown in Figure 1(a). 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 and it as shown in Figure 1(b). The helical axes of the TGB phase lies in a direction parallel to the smectic layer planes [16, 17]. On further cooling the specimen, the filamentary texture of TGB phase changes over to a focal conic fan-shaped texture at temperature 65.6°C, which is the characteristic of smectic-A phase, as shown in Figure 1(c) 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 phase. 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 [18, 19]. 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, meta-stable 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 Figure 1(d). 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 zig-zag conformation in successive layer planes [20, 21] and finally the specimen crystallizes with smectic-B phase. The detail of this paper has been reported by T. N. Govindaiah et al. [22].

4. Thermodynamical Response of Birefringence

Thermodynamical variations of liquid crystalline phase at different concentrations of binary mixtures of liquid crystalline materials are estimated using Boltzmann distribution laws. Draw a graph of variations of thermodynamical response of birefringence as a function of mole fraction for the sample of ChCl in HOB at constant temperature 93 °C is presented in Figure 2, which clearly shows, the degree of microphase separations are one of the parameters to controlling a physical properties of liquid crystalline materials [27]. In this context the existence of birefringence can be varied infinitesimally small either through chemical modification or through physical modification and hence they are depends on nature of additives molecules. The figure clearly illustrates that, statistically how the birefringence of given molecules are thermodynamically changes at different concentrations in order to show the thermal stability of liquid crystalline phase. Here we noticed that: at constant temperature the given molecules are fractionally varies as increasing the concentrations of the additive molecules. In this study it is very interesting to observe the spin temperature. Due to this gradient temperature: on the surface area of the molecules of TGB phase, the degrees of freedom of molecules are thermodynamically varies with one mole fraction to the other mole fractions. If an increasing the mole fractions for the sample of ChCl in HOB; thermodynamical response of birefringence of the molecular orientations are fractionally increases/decreases, i.e., fluctuate the molecules with spin temperature, because the effective intermolecular interactions of anisotropic energy associated with the molecules of ChCl increases with the additive ones. The molecular ordering or the thermal phase stability of TGB phase at given constant temperature: the effective intermolecular interactions of optical -anisotropic energy: which are responsible for the charges of carbon and the adjacent hydrogen molecules and hence which can also shows the correct electrostatic potentials, in which they are reproduced by different partial charge distributions. If increasing / decreasing the mole fractions for the sample ChCl in HOB: it shows small variation of electrostatic potentials and which they are around the molecule. In spite of these uncertainties, the full sets of partial charges are very useful, as it can provide a detailed insight into the molecular arrangement in TGB phase and which they reproduce the electrostatic potential.
5. Electro-Optical Studies

Electro-optical measurements are a very important tool in getting better idea on the phase transition behavior with electric field at constant temperature. In this experimental study we have been considered the sample for the mixture of 30% ChCl in HOB at constant temperature 93 °C.

When the electric field applied on the sample leads to elastic deformations which become greater towards the sample surfaces because of the surface anchoring. For thin enough samples one can suppose the electric energy is accumulated into the bulk elastic energy which is balanced by the surface anchoring energy on both surfaces. For a critical field: if at constant temperature the elastic energy of the given mixture shows different directions of molecular re-orientations, which are in the form of flow patterns: such as striped pattern and chevron textures: the formations of zig-zag domains are characteristic of chevron textures: the forming time of these patterns are mainly depends on the applied electric field. If there we have been observed significant differences in the electro-mechanical responses of filament texture of twisted grain boundary phase. Stripe of this texture does not have a linear electromechanical effect at low fields; if only at higher fields it does the mechanical vibration have a component of frequency of the field. This indicates that the spontaneous polarization has rotated and is no longer parallel to the electric field. In contrast to the director re-orientations, the molecular layer structures are unchanged by the application of applied electric field and then sequentially we have to increase the applied electric field above 22.20 V, the observed pattern becomes dynamic scattering mode-like and it has been appearing like irregularity of molecular re-orientations of filament texture of twisted grain boundary phase. The new disordered regions are arises probably due to the molecules not being confirmed to the orientations in the X, Z plane. If the applied voltage is kept constant for some time, a completely stationary and regular two- dimensional hexagonal grid pattern has been observed. The hexagonal grid pattern textures are as shown in Figure 3. 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 250Hz, 23V. From the Figure 3, it follows that: an extremely regular hexagonal grid pattern is formed when the external electric field is applied. One of the regions is that: the formation of hexagonal grid pattern is the electronic charge injected by the applying external electric field [28-30].

6. Conclusion

Microscopic investigation of binary mixture of ChCl in HOB shows the existence of cholesteric, twisted grain boundary and induced smectic phases such as SmA, SmC*, SmE, and SmB phases, sequentially when they are cooled from its isotropic phase. Thermodynamical response of birefringence of twisted grain boundary phase has been discussed to understand the phase stability, chemical structure and molecular dynamics of the binary mixture of cholesteric and nematic materials. The effect of applied electric field at constant temperature unambiguously corresponds to optical purity of twisted grain boundary phase. The various aspects of low/high frequency effects on given mixture show different directions of molecular re-orientations: which exhibit a flow patterns formations such as striped pattern chevron textures and hexagonal grid pattern textures and hence these textures microscopically have been observed.

References


Figure Captions

Figure 1: Microphotographs obtained in between the crossed polars,
a) Spherulitic texture of cholesteric phase.
b) Mobile thread-like filament texture of TGB phase.
c) Focal conic fan shaped texture of smectic-A phase.
d) Focal conic fans with radial striation of smectic-E phase.

Figure 2: Thermodynamical response of birefringence as function of mole fraction for the sample of ChCl in HOB.

d) Focal conic fans with radial striation of smectic-E phase.

Figure 3: Hexagonal grid pattern electro-optical texture.
Figure 2: Thermodynamical response of birefringence as function of mole fraction for the sample of ChCl in HOB.

Figure 3: Hexagonal grid pattern electro-optical texture.