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Estimation of size of nano-aggregates in binary mixture of two liquid crystals

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ABSTRACT

In the present investigation estimation of the size of nano-aggregation has been carried out in the binary mixture of cholesteric and nematic compounds, namely, cholesteryl nonanoate (CN) and p-methoxybenzylidene-p-ethylaniline (MBEA), which exhibits a very interesting liquid crystalline twisted grain boundary (TGB) phase and reentrant smectic-A phase. The chiral liquid crystalline TGB phases and reentrant smectic-A phases have been observed at different concentrations and at different temperatures. The existence of TGB and reentrant smectic-A phases is confirmed by DSC and optical microscopic studies. The variation of optical anisotropy has been discussed. Present study clearly illustrates that, the nano aggregated size of the given molecules decreases with increasing the temperature. In SmB phase, small nano aggregated size of the molecules (35 nm - 40 nm) are observed. But in SmE phase, nano aggregated size of the molecules are bit large enough to show the value of 49 nm.

KEYWORDS

Nano-aggregates;
XRD traces;
Reentrant smectic phase;
Phase transition;
TGB phase.

INTRODUCTION

The twisted grain boundary (TGB) phase of a chiral liquid crystal exhibits long-range order that combines a helical twist and smectic layering[1]. This TGB phase, which is an intermediate structure between smectic-A and cholesteric phases, is an analog of Abrikosov[2] flux vortex lattice in type-II superconductors, whereas the smectic-A phase is analogous to the Meissner phase. Indeed, Kamien and Lubbensky[3] have predicted a significant short-range TGB structure in the cholesteric phase at low temperatures, corresponding to a liquid of screw dislocations[4] to be called a chiral liquid. Therefore, it is recognized as rotated blocks of SmA layers, in which the long molecular axes are arranged normal to the layer planes. Hence, the chiral smectic layers twisted in the molecular axes are expected in the direction of the layer planes[5], and hence the helical axes of TGB phase are perpendicular to the molecular axes and parallel to the smectic planes.

Some of the investigators[6–8] have studied the TGB phase in the mixture of cholesteric and nematic compounds. Lubbensky and Renn[7] have made theoretical predictions in case of TGB-SmA phase transition that it always appears, if the molecular chirality is introduced near the nematic-smectic-A-smectic-C (NAC) multicritical point[8]. In case of TGB-SmA phase, the temperature span Δt should increase with increase in

chirality of the system. The TGB-SmC* phase has also been close to the NAC point, which is composed of twisted stacks of helical, SmC* phase is also predicted[9].

In the present investigation, our aim is to carry out the study of optical and thermal properties of the binary mixture of nematic and cholesteric liquid crystalline compounds. Some of the concentrations of the mixture exhibit I-Ch-TGB-SmA-SmC-SmB-SmE phases sequentially when they are cooled from isotropic phase. Optical, thermal and X-ray studies have been carried out to understand the intermolecular interactions in the mixture.

EXPERIMENTAL SECTION

In the present investigation, we have studied binary mixtures of liquid crystals, namely, cholesteryl nonanoate (CN) and p-methoxybenzylidene-p-ethylaniline (MBEA), which are obtained from M/s Eastman Organic Chemicals, USA. The chemicals are purified twice with benzene. Mixtures of twenty five different concentrations of CN in MBEA were prepared and were mixed thoroughly. These mixtures of various concentrations of CN in MBEA 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 a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The differential scanning calorimetry (DSC) thermograms were taken for the mixtures of all concentrations using Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. 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[10,11].

RESULTS AND DISCUSSION

Phase diagram

The binary mixture of CN in MBEA exhibits a very interesting different liquid crystalline phase and the phase transition temperatures are measured by using Leitz-polarizing microscopic technique[12]. The phase diagram

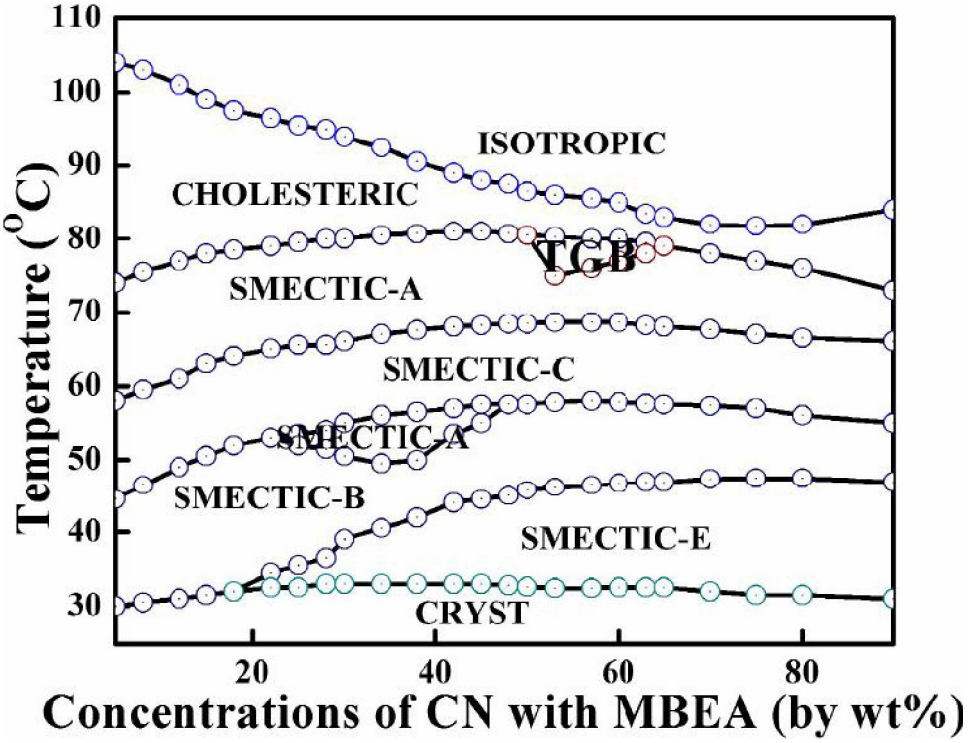

Figure 1 : Partial phase diagram for the mixture of CN in MBEA

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shown in Figure 1, is obtained by plotting phase transition temperatures against the CN concentration.

The following sequences of phases have been observed while the concentration of CN component in the mixture was increased:

- CN 5 - 22%: Cr - SmB - SmC - SmA - Ch - I
- CN 22 - 48%: Cr - SmE - SmB - SmAre - SmC - SmA - Ch - I
- CN 50 - 65%: Cr - SmE - SmB - SmC - SmA - TGB - Ch - I
- CN 65 - 90%: Cr - SmE - SmB - SmC - SmA - Ch - I

We noticed as a very interesting phenomenon the occurrence of reentrant SmA and TGB phases for CN concentrations of 22-48% and 50-65%, respectively.

Characterization of nano aggregation

The X-ray diffractometer traces obtained for the mixture of 53% of CN at temperature 43^{0}C, 50 ^{0}C, and 55 ^{0}C are as shown in the Figure 2. The diffraction peaks at these temperatures correspond to SmE and SmB phases respectively, using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for λ = 1.934 Å (With Fe - K-alpha1). XRD method is very important tool for to determine the nano aggregated size[13] of the different liquid crystalline materials. 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 complete orderliness leads to broadening of the diffraction peaks. Estimation of nano aggregated size of the given mixture from the broadening of X-ray diffraction peaks has been done by using Scherer's formula

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

where L is the crystalline 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 θ is the diffraction angle. As the temperature increases, the specimen moves from crystalline phase to amorphous phase[14,15], which clearly illustrates that, the nano aggregated size of the given molecules decreases with increasing the temperature. Because, SmB phase is energetically for small nano aggregated size of the molecules (35 nm) and (40 nm), But in SmE phase, nano aggregated size of the molecules are large enough to show the value of 49 nm. The sequence of phase transition from SmB to SmE phases respectively, when nano aggregated size of the given mixture are big enough to indicate that the molecular ordering[16] of layer structure increases as the temperature of the mixture decreases[17].

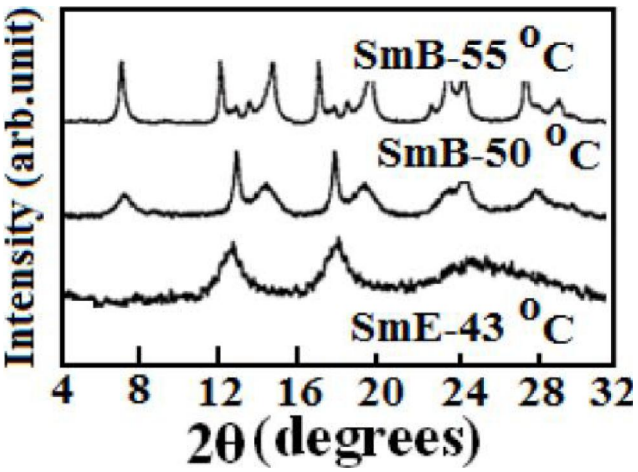

Figure 2 : X-ray broadening spectrum for the mixture of 53% of CN in MBEA at different temperatures of smectic phases

CONCLUSIONS

The binary system of the given mixture exhibits an unusual sequence of phases showing the formation of an cholesteric, TGB, SmA, SmC, reentrant SmA and SmB phases in different concentrations of CN in MBEA. As a very interesting phenomenon we have noticed the occurrence of reentrant SmA and TGB phases for CN concentrations of 22-48% and 50-65%, respectively. The drastic change in the value of density, refractive index, with the temperature unambiguously corresponds to different liquid crystalline phase transitions in the mixture. From the X-ray results we have observed the nano aggregation in the given mixture at different temperatures. Calculation of size of nano-aggregates clearly illustrates that, the nano aggregated size of the given molecules decreases with increasing the temperature. Because, SmB phase is energetically for small nano aggregated size of the molecules (35 nm) and (40 nm), But in SmE phase, nano aggregated size of the molecules are large enough to show the value of 49 nm.

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