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J. Mahadeva^a, Nagappa^b, K. Rajashekara Prasad^c & P. R. Alapati^d

^a Department of Physics, PES College of Science, Mandya, INDIA

^b Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, 570 006, INDIA

^c Department of Chemistry, University of Mysore, Manasagangotri, Mysore, 570 006, INDIA

^d Department of Physics, N E R I S T, Itanagar, INDIA

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Twist Grain Boundary Phases in the Binary Mixtures of Smectic and Cholesteryl Compounds

J. MAHADEVA^a, NAGAPPA^b, K. RAJASHEKARA PRASAD^c and
P.R. ALAPATI^d

^a*Department of Physics, PES College of Science, Mandya, INDIA*, ^b*Department of Studies in Physics and* ^c*Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, INDIA* and ^d*Department of Physics, N E R I S T, Itanagar, INDIA*

The binary mixture of Terephthal-bis-p-n-hexadecylaniline (TB16A) and cholesteryl nonanoate (CN) exhibits $I - N^* - TGB_A - TGB_{C*} - Sm A - Sm I - Sm F - Sm G - K$ phases in the concentration region between 95 to 98% of TB16A at higher temperature range. The 90% of TB16A exhibits $I - N^* - TGB_A - TGB_C - Sm A - Sm I - Sm F - K$ phases. The mixtures of concentration between 50 to 80% of TB16A exhibits $I - Sm A - Sm I - K$ phases. The frustrated blue phase is also observed in the mixtures of lower concentration of TB16A in CN at higher temperature. Optical, DSC and X-ray studies were carried out for the identification of the different phases. The phase diagram of the Chen-Lubensky model in this context is discussed.

Keywords: TGB phase; Binary Mixtures; Smectic and Cholesteryl Compounds

INTRODUCTION

The theoretical prediction of the Renn and Lubensky coined a remarkable development in the field of liquid crystal to understand

the effect of chirality on smectic A liquid crystal^[1,2]. The theoretical basis for this prediction was the de Gennes model for the Nematic to Smectic A (Sm A) transition, which is analogous to normal to superconducting transition^[2]. According to the de Gennes model the twist grain boundary phase (TGB) which occurred on smectic A side i.e. TGB_A phase is the analog of the Abrikosov^[3] vortex lattice in type II superconductors. At the same time Goodby *et al.*^[4] discovered the Sm A* phase in a highly chiral homologous series. X-ray studies on non aligned samples reveal that the Sm A* exhibited both smectic layering and cholesteric like textures simultaneously and Sm A* phase is nothing but a TGB phase. TGB phase is characterized by a nonvanishing twist and long range smectic correlations with in this plane perpendicular to the pitch axis.

It has been formed several remarkable features of the Sm A- Sm A*- Sm C* multicritical point^[5].

The phase diagram obtained for chiral liquid crystal from, Chen-Lubensky model illustrates that the Sm C* phase can exhibit transition to the TGB_A, TGB_C or TGB_C*. In addition to this N*- TGB_A and N*- TGB_C is possible, But N*- TGB_C* is not possible^[2].

The TGB_C - TGB_C* phase is first order near the TGB_A- TGB_C - TGB_C* bicritical point and the N*- TGB_C phase transition are second order. The transition from TGB_A - TGB_C* is possible when the cholesteric pitch increases beyond $2P_c/2$ where P_c is the pitch of the Sm C* phase. Nagappa *et al.* observed TGB_A phase in the mixture nematic and the cholesteric compounds^[6]. Sadashiva^[7] observed a transition from TGB_A - TGB_C* in some pure and mixtures of chiral liquid crystals.

TGB_C and TGB_C* phases are also consists of a twisted array of two dimensional smectic slabs stacked along the pitch axis similar to TGB_A phase. TGB_A, TGB_C and TGB_C* phases consists of Sm

A, Sm C and Sm C* slabs respectively^[8]. In the present investigation we have consider the smectic and cholesteric mixtures and the pure smectic exhibits I - Sm C - Sm I - Sm F - Sm G - K phases. At very low concentration of the cholesteric, the mixture exhibits N* - TGB_C* and N* - TGB_C at higher temperature. The DSC, Optical texture and X-ray studies lend support to the above results.

Experimental

In the present investigation we here consider the binary mixtures of liquid crystals, viz Terephthal-bis-p-n-hexadecylaniline (TB16A) is smectic and cholesteryl nonanoate (CN). The binary mixtures of different concentration from 95 to 98% of TB16A in CN by weight fraction were prepared and mixed well in molten state. The transition temperatures of the different concentrations were determined using hotstage and polarizing microscope. The phase diagram illustrates that TGB_A, TGB_C* and TGB_C phases are obtained at higher concentration and at high temperatures. The concentration with 95% of TB16A exhibits I - N* - TGB_A - TGB_C* - Sm A - Sm I - Sm F - Sm G - K phases, and sample with 90% of TB16A exhibits I - N* - TGB_A - TGB_C - Sm A - Sm I - Sm F - K phases sequentially. Here it is very interesting to note that there is phase transition from TGB_A - TGB_C* in the case of 95% of TB16A and TGB_A - TGB_C in the case 90% of TB16A. The twist grain boundary phases are observed only in higher concentration of TB16A in the range from 90 to 98%. The intermediate concentration of TB16A exhibits I - Sm A - Sm I - K phases. The lower concentration from 10 to 20% of TB16A shows only cholesteric phases. All these change of phases with respect to temperature are shown in the phase diagram, Fig.1(a.b).

The DSC recording also lend support to the change of phases as observed in phase transition studies using polarizing microscope.

The DSC traces for 95% of TB16A are shown in Fig.2.

Results and discussion

Texture studies

The texture studies were carried out using Leitz polarizing microscope, by sandwiching the sample between slide and the coverslip. The transition temperatures for all the concentrations were measured accurately. When the sample of 95% is cooled from its isotropic melt a genesis of nucleation starts in the form of small bubbles and immediately these bubbles are transform into a N^* phase. A small change in temperature results to the phase transition from N^* to TGB_A phase showing the smectic drop like texture, as shown in Fig.3(a). It is interesting to note here that these drops are arranged in hexagonal grid pattern form. On further cooling the specimen, the hexagonal drop pattern change over to the fringe pattern which is characteristics of TGB_C^* as shown in Fig.3(b). This phase is further change over to Sm A phase. On further cooling the mixture undergoes a polymorphic phase transitions, sequentially Sm A - Sm I - Sm F - Sm G - K phases.

When the unaligned sample of 90% of TB16A cools from isotropic phase, it exhibits the I - N^* - TGB_A - TGB_C - Sm A - Sm I - Sm F - K sequentially. In this concentration TGB_A phase changes to TGB_C phase giving rise to a Schliere texture as shown Fig. 4(a). TGB_C phase further change over to Sm A phase exhibiting focal conic fan shaped texture as shown Fig. 4(b). Later this texture followed by broken focal conic Schliere texture and Schliere mosaic texture which are characterised by Sm I and Sm F phases are shown in Fig.4(c) and 4(d) respectively. The smectic I phase is a tilted biaxial phase^[9], the molecular structure in the Sm I phase is identified by the pseudo-hexagonal molecular packing and phase is hexatic

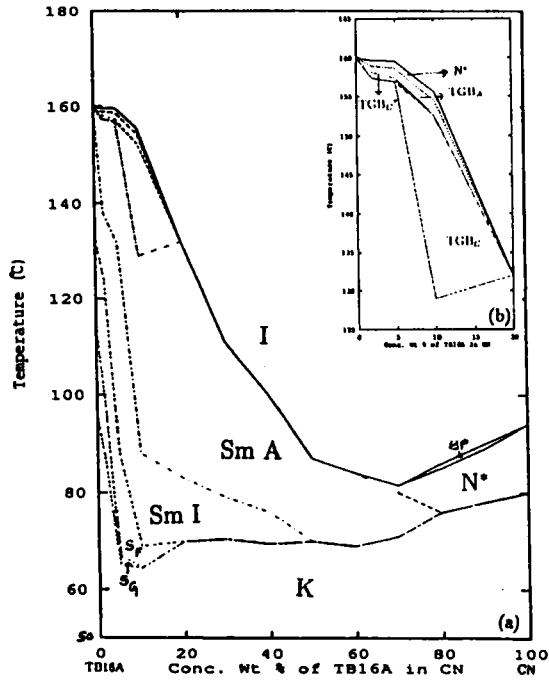


Fig.1 Phase diagram of (a) Wt % of TB16A in CN (b) (Inset) 80 - 100% of TB16A in CN

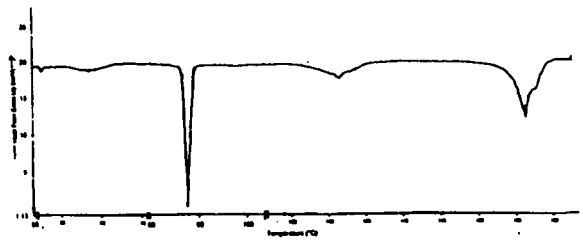


Fig.2. DSC Thermogram of 95% TB16A in CN

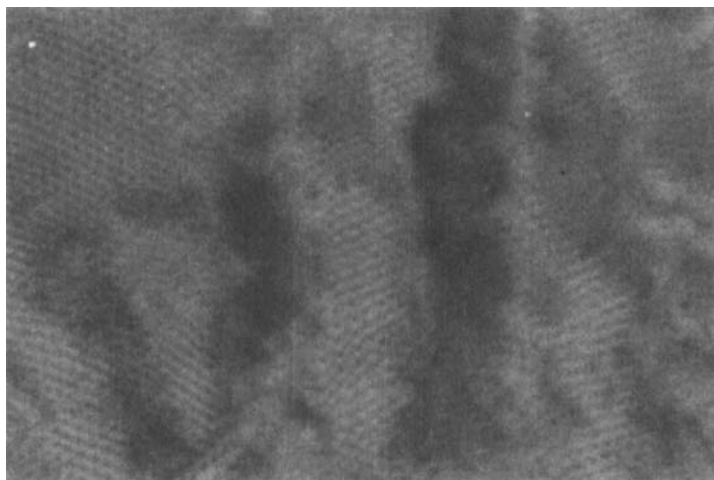
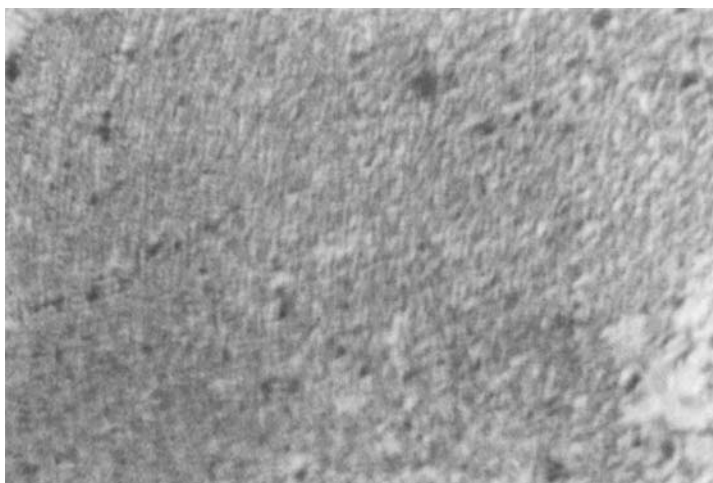
**3(a)**

Fig.3 Microphotographs of (a) TGB_A (360X) (b) TGB_c (360X)
See Color Plate XLIX at the back of this issue.

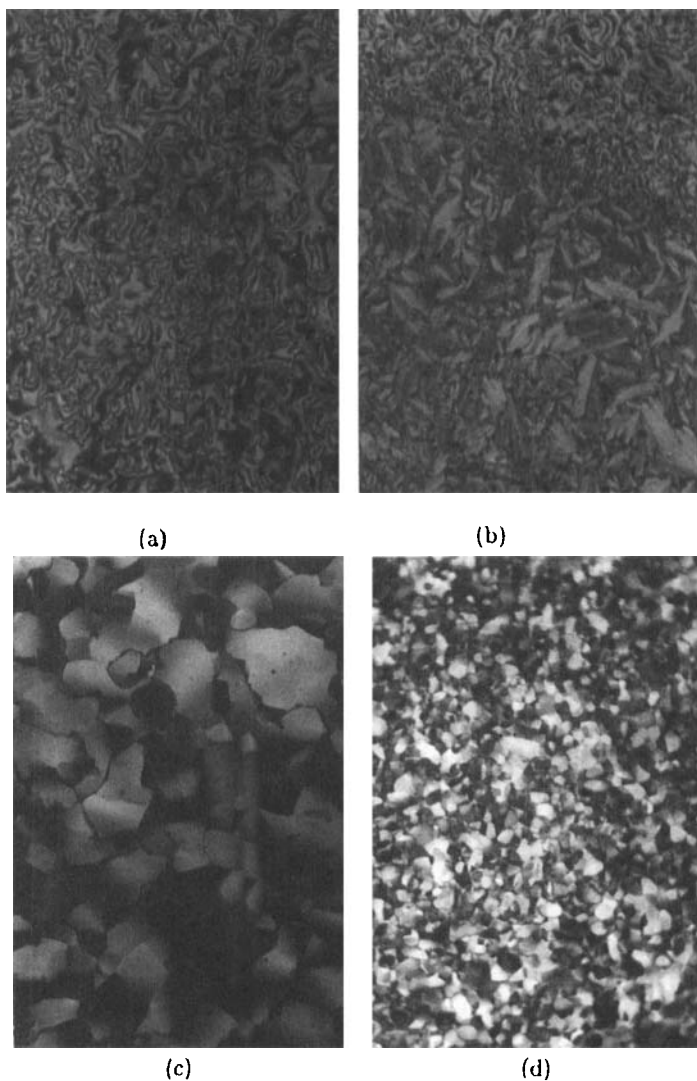


Fig.4 Microphotographs of (a) TGB_c (220X) (b) $Sm A$ (220X) (c) $Sm I$ (220X) (d) $Sm F$ (180X)

See Color Plate L at the back of this issue.

hexatic in nature^[10]. The intermediate concentrations 50 to 80% of TB16A exhibits I - Sm A - Sm I - K phases sequentially from the temperature 87°C to 132°C. The concentration 40% of TB16A exhibit Sm A phase only. In the lower concentration of TB16A we observed only cholesteric and blue phases. The X-ray diffractometer traces are obtained at various temperatures for unaligned samples. The nature of the peaks observed for Sm A and TGB_A phases are almost similar.

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