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TGB Phases in the Binary Mixtures of Nematic and Cholesteric Compounds

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We report here some interesting optical textures and phase behavior exhibited by the binary mixtures of Cholestryl 5-(4-((4-hexylphenylimino) methyl)-3-hydroxyphenoxy) pentanoate (C74) and n-Butyloxybenzylidene-p-pentylaniline (BBPA). The samples with 1% to 30% of BBPA exhibit smectic and cholesteric phases. The intermediate concentrations ranging from 30% to 70% of BBPA exhibit smectic A, smectic C, smectic G, smectic F and smectic B phases. The mixtures with higher concentrations from 71% to 99% of BBPA show Blue phase – N* – TGBA – TGBC – TGBC* – UTGBC* – Sm A phases, Sequentially. The phase behavior exhibited by the samples of different concentrations of BBPA has been studied using polarizing microscope and from the DSC recordings.*

Keywords: liquid crystals; phase transition; TGB; TGBC*; UTGBC*

INTRODUCTION

The TGBC* phase was observed for the first time by Kuczynski and Stegemeyer in the binary mixtures of cholesteryl benzoate (ChB) and di-heptyloxyazoxybenzene (HOAB) [1,2]. Later it was studied in the pure systems as well [3,4]. In 1997 Pramode *et al*. [5] have observed a new phase in a binary mixture of CE8 and 7CN5 and later called that as undulating twist grain boundary (UTGBC*) phase. This phase was not anticipated by the theoretical work of Renn [6].

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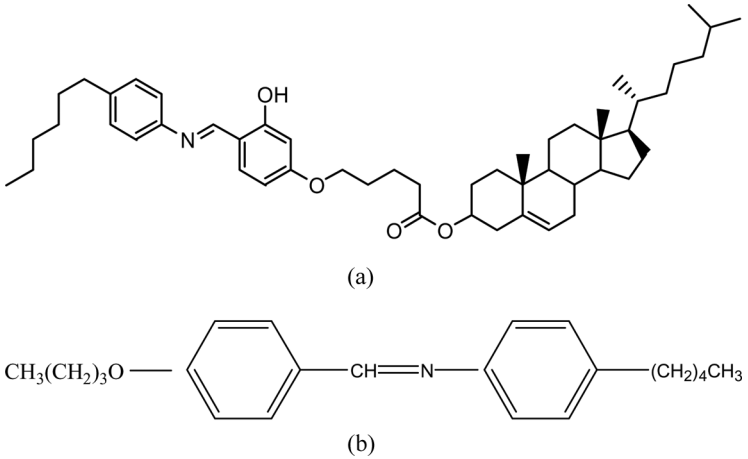

FIGURE 1 The molecular structure of (a) C74 and (b) BBPA.

Subashree and Sadashiva [7] have realized UTGBC* phase in the single-component system. Yelamaggad *et al*. [8] also observed UTGBC* phase in the trimesogenic system.

The structural characteristics of this undulating twist grain boundary (UTGBC*) phase is based on the following results. The smectic blocks as well as the blocks themselves have periodic undulations in the form of square lattice. All the grain boundaries and blocks undulate along two orthogonal directions normal to the TGB helical axis.

In this paper we present only the results of our optical observations in the binary mixtures of chiral "Cholestryl5-(4-((4-hexylphenylimino)methyl)-3-hydroxyphenoxy) pentanoate (C74)" and nematic "n-Butyloxybenzylidene-p-pentylaniline (BBPA)". The molecular structures of these compounds are given in Figure 1.

EXPERIMENTAL

About 20 samples of different concentrations of BPPA in the total mixture were prepared by mixing the suitable quantities of C74 and BBPA. The transition temperatures of these samples were determined using Leitz polarizing microscope in conjunction with a Mettler hot stage and also with the DSC. The phase diagram is drawn considering phase transition temperatures against various concentrations of the mixed samples, which is shown in Figure 2. The phase diagram illustrates that 1% to 20% of C74 in BBPA exhibit N* phase at higher temperature and smectic phase at lower temperatures. The concentrations

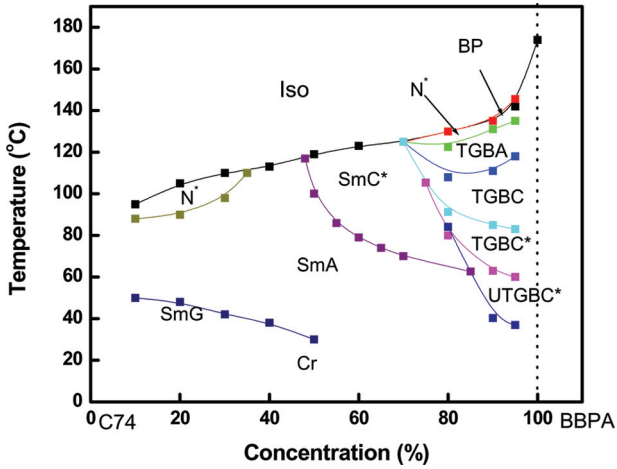

FIGURE 2 The phase diagram of the mixtures of C74 and BBPA.

from 21% to 70% C74 exhibit only smectic phase. Higher concentrations of BBPA i.e., 70% to 99% exhibit various phases sequentially from isotropic phase. For example, the sample containing 90% of C74 exhibits

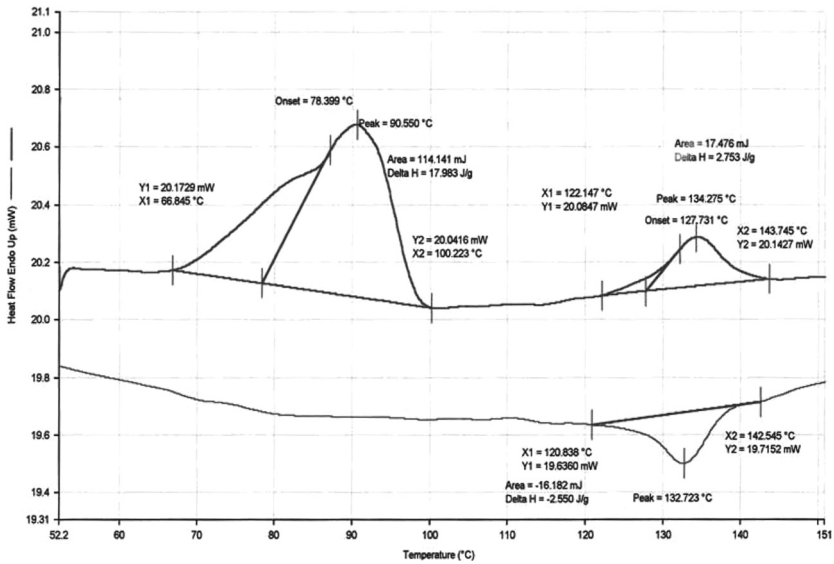

FIGURE 3 The DSC trace at 90% of BBPA in C74.

the phases sequentially as

$$I - BP - N^* - TGBA - TGBC - TGBC^* - UTGBC^* - SmA - Cry.$$

Differential Scanning Calorimeter (DSC) traces obtained from the sample containing 90% BBPA reveal that the phase changes observed at different temperatures are in agreement with that observed using polarizing microscope. The second order phase transition of $TGBC^*$ between TGBC – $UTGBC^*$ has no signature in DSC traces. The DSC trace is shown in Figure 3.

RESULTS AND DISCUSSION

Systematic investigations of the optical textures exhibited by the different binary mixtures revealed that $UTGBC^*$ phase is observed in 70% to 99% BBPA. Particular reference may be made here that Yalamaggad *et al*. [9] carried out the texture studies of pure compound C74, but they have not observed some of the texture, which we have observed in these binary mixtures. It may be seen from Figure 3 that when the sample containing 90% of BPPA in the mixture is cooled from isotropic melt, the blue phase (BP) appears first at 134.2°C. This phase is nothing but a frustrated phase, which appears in a very small temperature range just below the transition point between the isotropic and N^* phases. The medium in this phase normally will have a short pitch and very small birefringence. In BP-I we have observed hexagonal platelets of different colors and are shown in Figure 4. When the sample is cooled slowly from 131°C a spherulite texture

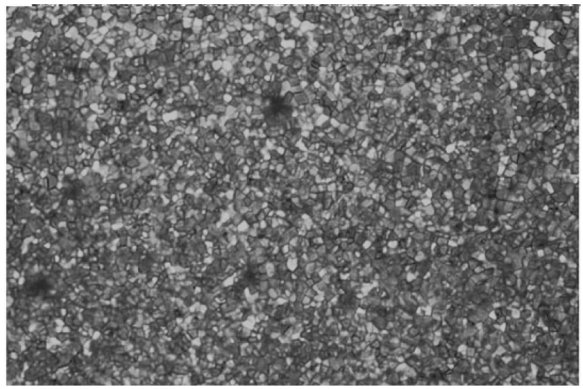

FIGURE 4 Micrographs of BP II mosaic texture at 134.2 (°C) (235X).

irregular arcs developed in the field of view of the microscope, which is the characteristic of the cholesteric phase, and is shown in Figure 5(a). In this phase the molecules are arranged radially and perpendicular to the helical axis. These spherulites change over to leaf like pattern at 120°C on cooling and this texture is a characteristic of TGBA phase [10]; see Figure 5(b). On further cooling at 100°C the faint rings like pattern starts growing slowly from the center of leaf let and is shown in Figure 5(c). This phase is identified as TGBC phase. At 90°C the texture shown in Figure 5(c) changed to the continuous thick rings without leafs. In this texture leafs are disappear and thick rings are developed. This is characteristic of TGBC* phase sees Figure 5(d). The TGBC* phase consisting of a twisted stack of Sm C* grain boundaries which will consist of only wedge screw or heliscrew dislocations. If we cool the specimen further at 80°C the rings are unwind and change over to spiral filaments like texture, which is characteristics of an undulated twist grain boundary phase (UTGBC*). The observed undulatory nature of the filament in the absence of field is a side view of 2-D undulating structure of the medium (5). The proposed structure is non-uniform with helical axes characteristic of TGB smectic as well as in the orthogonal plane. As the smectic layer normal of the blocks

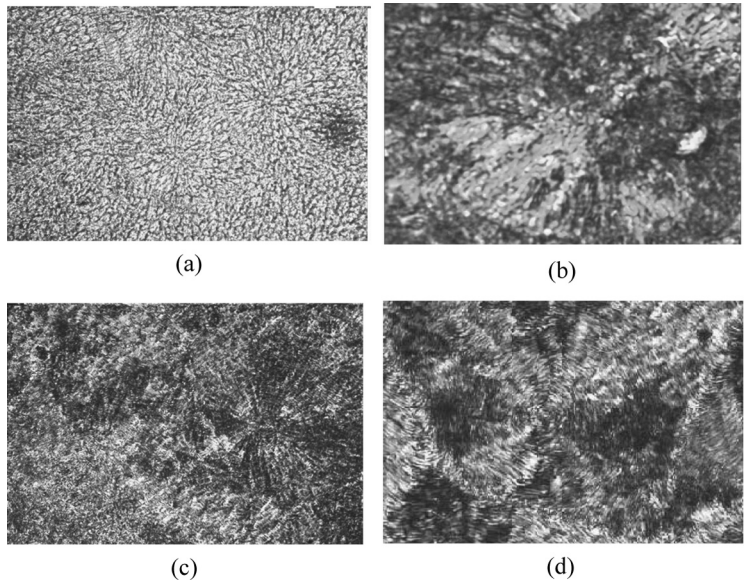

FIGURE 5 Microphotographs of (a) cholesteric phase at 131°C (180X), (b) TGBA phase at 120°C (180X), (c) TGBC Phase at 100°C (235X), and (d) TGBC* phase at 90°C (235X).

FIGURE 6 Microphotographs of UTGBC* phase at 80°C (235X).

rotates across the grain boundaries also undulates along with the entire structure. Therefore this TGBC* phase is UTGBC* phase. Pramode *et al*. [5] have explained the origin of such UTGBC* phase. In fact, TGBA phase itself has non – uniform structure, with perfect SmA blocks separated by highly defected grain boundaries with screw dislocations. Hence the UTGBC* phase is characterized by helical axes both along and normal to the SmC* layers. Finally at 50°C UTGBC* phase changes to homeotropic smectic phase and then to solid phase at 25°C.

The samples containing 71% to 99% of BBPA show similar phase change when they are cooled from isotropic melt.

The mixtures of lower concentrations (say 5% to 30 % of BPPA) exhibit N*-SmA-SmG phases sequentially when they are cooled from isotropic phase. The molecules in Sm G phase are packed in layers and within the layers molecules have their long axes tilted with respect to the layer planes. The studies of these mixtures with concentrations from 30 to 69% are of very interesting because of the fact that these mixtures exhibit SmA phase followed by SmC* and SmG phases. The samples of intermediate concentrations (i.e., 31% to 69 % of BPPA) exhibit SmA – SmC* – SmG – SmB – Crystal phases on cooling from isotropic melt. All these observed phase are represented in the phase diagram (Figure 1).

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