Twist grain boundary and blue phase in binary system of liquid crystalline materials

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The behaviour of one chiral mesogenic material with another mesogen in a mixed system has been investigated. The mixture of chiral component having smectic Q phase and chiral antiferroelectric smectic C phase and non-chiral component having nematic and smectic C phases exhibits some interesting mesophases like blue phase, twist grain boundary phase, smectic A phase and smectic C phase, both on cooling the isotropic melt as well as on heating the crystalline material. The appearance of twist grain boundary phase and blue phase, which is studied by optical microscope, lies in a very narrow temperature and composition range. These phases are illustrated by their optical textures.

The novel twist grain boundary (TGB) phase was theoretically predicted by Lubensky and Renn1 which is analogous to the de Gennes model of the Abrikosov phase in superconductors2. This phase called helical smectic A or TGB phase oscillates between the low temperature smectic A (SmA) phase and high temperature chiral nematic phase. This phase is recognized by rotated blocks of SmA layers in which long molecular axes are arranged normally to the layer planes. The twist in the molecular axis is expected in the direction of 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 (a higher temperature thermodynamic phase with higher symmetry reappearing below a stable thermodynamic phase with lower symmetry) of liquid crystalline phases which is peculiar in pure components as well as in mixed systems3, 4 is also peculiar with TGB phases. For example, re-entrant phenomenon of TGBA phase along with re-entrant of cholesteric phase has been reported5. In these compounds, SmQ phase was stable in the temperature range up to 50°C whereas their respective recemates showed smectic A or chiral analog of antiferroelectric smectic C (SmCA*) phase only. Most of the known SmQ compounds have a symmetrical mesogenic core and side chain system.

In the present investigation, we report the mesomorphic properties of phase diagram in which TGB phase appears. The substances (S,S)-M7BBM7 and IS-2934 were received from Dr D Bennemann (Germany) and E Merck, Darmstadt, Germany respectively. The phase diagram shows, in addition to TGB phase, a variety of other phases like induced SmA and blue phase (BP).

Experimental
The materials used in the studies were:

4-{4-[(Methylheptyl)oxy carbonyl]phenyl}phenyl 4-{4-[(methylheptyl)oxy carbonyl]phenyl}benzoate (S,S)-M7BBM7

Levelut et al.8 have reported a new liquid crystalline phase which occurs in chiral MHTAC, [(1-methyl heptyl)-terephthaldiane-bis amino-cinnamate], over a temperature range of about 3°C. This phase, called smectic Q (SmQ), has a three-dimensional tetragonal structure superimposed on a liquid-like order of the center of mass. New compounds exhibiting SmQ phase have been reported later9. In these compounds, SmQ phase was stable in the temperature range up to 50°C whereas their respective recemates showed smectic A or chiral analog of antiferroelectric smectic C (SmCA*) phase only. Most of the known SmQ compounds have a symmetrical mesogenic core and side chain system.
The mesophases and their corresponding phase transition temperatures were primarily determined by the use of thermal optical microscopy. The Leitz POM with programmable Mettler FP82 hot stage and Mettler FP90 central processor were used to study the phase behaviour. The samples, layered between two untreated glass plates, at different compositions were investigated in the heating as well as cooling modes at uniform rate of heating of 2°C per minute first by contact method\textsuperscript{10} in which the effect of concentration gradient in the sample was monitored microscopically. Later, in the concentration method, the two compounds were weighed accurately (10^{-4}g) on a glass slide using Mettler AE 240 balance and intensively mixed with 10 weight% concentration steps until sharp change in the temperatures were observed. The temperatures at which the mesophase completely disappeared from the microscopic field were measured in the usual manner. The different phases were identified by their characteristic textures. The DSC runs were performed using Perkin Elmer thermal analyzer wherein the rate of heating and cooling was maintained at 5°C per minute.

**Results and discussion**

The mixed system IS-2934/M7BBM7 (Fig. 1) shows the induction of SmA phase between two non-smectic A components. On the right hand side of the diagram, the nematic phase and smectic C phase of pure IS-2934 and on the left hand side the SmQ phase and chiral antiferroelectric smectic C phase of pure M7BBM7 are presented. A small amount of the chiral compound added to nematic IS-2934 causes the formation of a chiral nematic phase, called cholesteric phase, which is observed at 65 wt. % of IS-2934. A blue phase is observed for concentrations between 75% and 90% of IS-2934. For textural presentation, a mixture of 85 wt% of IS-2934 was heated and then cooled from the isotropic state. In the beginning, the blue phase formed is characterized by an iridescent platelet texture (Fig. 2a). The texture is greenish but with increasing component of chiral compound progressively changes to blue. The change in the colour of the texture represents the pitch change of blue phase. The disadvantage of blue phase is that they have limiting thermal stability (0.5 – 5.0°C), as predicted theoretically and proved experimentally, between isotropic and chiral nematic phase which limits its practical application. However, liquid crystals with a wide temperature range of blue phase has recently been reported\textsuperscript{11}. On cooling from blue phase, the formation of various cells-like texture demonstrate the existence of chiral nematic phase (N* or Ch, Fig. 2b).

Optical microscopic studies further reveal that the chiral nematic phase transforms into SmA phase through an intermediate phase which is signaled by the appearance of filament texture (Fig. 2c) characteristic of TGB phase\textsuperscript{12-17}. The filaments develop from the cholesteric phase and to some extent still possess the shape and edge of cells from which they are formed. The temperature range for TGB phase is often found to be very small, particularly with respect to the method of examination. In fact, the binary system of cholesteryl benzoate and diheptyloxy azoxybenzene is one of the mixed systems which has shown the largest temperature range (~40°C) of TGBA phase\textsuperscript{16}. As the phase is essentially a frustrated phase, the parameters like surface pinning can alter its transition temperature and the actual range. In our studies, this phase was observed from about 75 – 82 wt.% of IS-2934 and that too in a very narrow temperature range which could not be shown in the binary diagram of state and, therefore, is represented simply by an arrow. As the
temperature is lowered to the SmA phase, the pattern (filament texture) vanishes resulting into fan shaped texture of SmA phase (Fig. 2d).

The induced SmA phase has been observed from ~20% to ~75% of IS-2934 whereas the SmC phase which is present in pure IS-2934 simultaneously exists in the range from ~20% of IS-2934.

The differential scanning calorimeter scan for 38.41% of IS-2934 shows that the isotropic-SmA transition is quite strong. In contrast, SmA-SmC transition is extremely weak, although clear. This fact is also concluded from optical studies of the same preparation provided the heating and cooling rate is kept very low. The microscopic studies of contact preparation shows two regions with the schlieren texture between SmC and SmC_{A*} phases. At the boundary of these regions, a helix inversion is observed.

In summary, we report the observation of a phase diagram in which a blue phase appears and the TGB phase oscillates between the cholesteric and smectic A phases. The existence of TGB phase in the phase diagram between M7BBM7 and IS-2934 validates the theoretical expectation of the model proposed by Lubensky and Renn17.

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