Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 05 Oct 2009

To cite this article: Anjuli Khandelwal, S. S. Bawa & Maneesha Yadav (2009): Optical Investigations of Twist Grain Boundary Phases Exhibiting Cylindrical and Cone-Like Domain Textures, Molecular Crystals and Liquid Crystals, 511:1, 59/[1529]-74/[1544]

To link to this article: http://dx.doi.org/10.1080/15421400903048594

Mol. Cryst. Liq. Cryst., Vol. 511, pp. 59/[1529]–74/[1544], 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903048594

Optical Investigations of Twist Grain Boundary Phases Exhibiting Cylindrical and Cone-Like Domain Textures

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Polarized optical microscopy observations performed on mixtures of Liquid crystals reveal developable domain textures for Twist Grain Boundary (TGB) phases. In these structures, the smectic blocks, the grain boundaries and the layers of helical structure of TGB phase are coiled in a double-twist manner. The energy considerations require that the blocks can just be folded in cones and cylinders, the only surfaces that may be unrolled without elongations. The cones need defects to build up; in particular, a disclination is necessary all along the cone axis. In the N^* phase, the field of the χ-director that emanates from the center of the spherulite has the geometry of a hedgehog point defect. The disclination lines of strength $k = 2$ escape into third dimension with no singularity remaining and the χ-director is not materialized. However in TGBA the χ-singularities are materialized as singularities of the slabs.

Keywords: CC domains; liquid crystals; TGB; χ-singularities

INTRODUCTION

Polarizing microscopy, it is most powerful tool for the identification of liquid crystals and it has been used to study the textural behavior of liquid crystals (LCs) and to photographs the imperfections in LCs. The basic information in structure investigations is the description of the 'texture', the term being defined as the sum of topological elements, which are enough to be observed under the polarizing microscope.

Anjuli Khandelwal wants to thank Prof. S. D. Lee for partial support to attend ILCC08.

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Twist Grain Boundary (TGB) phases are frustrated phases and are among the very few phases in nature in which there is an equilibrium distribution of topological defects. The analogy between the nematic (N) to smectic A (SmA) transition in liquid crystals and the normal to superconductor transition in metals was first recognized by de Gennes in 1972 [1]. According to it, a transition between the cholesteric (N^*) and SmA phases would occur either directly or would proceed through an intermediate phase characterized by a twisted lattice of screw dislocations. This intermediate phase is the analog of Abrikosov's triangular flux vortex lattice [2,3], which occurs in type II, superconductors in an externally imposed magnetic field. Like Abrikosov's flux lattice, the TGB would occur if $\kappa \equiv \lambda/\xi$, the ratio of the twist penetration depth and the smectic coherence length, exceeded $1/\sqrt{2}$. From different studies it has become clear that these phases are helical stack of smectic blocks; the helical axis being parallel to the smectic layers. Any two smectic blocks are connected through a twist grain boundary. The twist grain boundary is a periodic array of screw dislocations. Further the smectic blocks could be of smectic A, smectic C (Sm C), smectic C^* (Sm C^*) structure. The TGB phases are then designated as TGBA, TGBC, TGBC^* respectively.

The TGBA and the TGBC mesophases, respectively predicted by Renn and Lubensky in 1988 [2] and by Renn in 1992 [3], were experimentally observed for the first time in 1989 by Goodby *et al.* [4] and in 1992 by Nguyen *et al.* [5]. In 1994, Rebeiro *et al.* [6] reported for the first time the characterization of a mesogenic compound with two chiral centres, exhibiting a TGBA mesophase and showing simultaneously different optical textures, usually observed in the separate cases of helical and columnar ordering. Rebeiro *et al.* reported in 1998 [7] the characterization of two new diastereomers showing TGBA and TGBC phases. With both diastereomers and in both mesophases, it was possible to observe the coexistence of two different types of optical textures, namely planar helical textures usually observed in planar aligned cholesteric samples and textures apparently similar to the developable domains textures observed in the columnar mesophases and first described in this way by Kleman [8]. The theoretical interpretation concerning the observation of developable domain textures in the TGB mesophases was also presented in [7]. These types of textures are more precisely made of cylindrical (or marginal cone-like) domains (CC) which may be seen as particular focal – conics, but also as developable domains [7]. Rebeiro *et al.* reported in 2000 [9] that simultaneous observation of helical textures and CC textures could be considered as a new criterion for the identification of TGBA mesophase.

In the TGBC structure proposed by Renn and Lubensky [10], directors of the molecules in the smectic slabs are tilted with respect to the smectic layer normal. In TGBC*, slab are filled by SmC* structure and thus TGBC* has two helices mutually perpendicular to each other. Several structures have been proposed for TGBC and TGBC* [11,12]. A complete review on TGB can be seen in the articles of Goodby [13] and Kitzerow [14].

Dhar [15] and Pandey *et al.* [16] have reported TGB phases in mixtures of Liquid Crystals. We have reported TGBA and TGBC* phases giving cylindrical and cone-like domain textures (CC type textures) in mixtures of liquid crystals [17,18]

The present paper reports existence of TGBA phase in a thin film of cholesteryl nonanoate and other TGB phases in binary mixtures of Cholesteryl Nonanoate (CN) and N-(4-Ethoxy benzylidine)-4-butyl aniline (EBBA).

EXPERIMENTAL

Binary mixtures of Cholesteryl Nonanoate (CN) and N-(4-Ethoxy benzylidine)-4-butyl aniline (EBBA) were prepared by weighing out pure samples using electro balance of Precisa (Model ACS-205) having an accuracy ± 0.1 mg. In all nine samples were prepared in weight proportion namely CN10 (CN: EBBA:: 9:1), CN20 (8:2), CN30 (7:3), CN40 (6:4), CN50 (5:5), CN60 (4:6), CN70 (3: 7), CN80 (2:8), CN90 (1: 9). A transmitted light polarizing microscope, OLYMPUS BX 51P, was used to identify the textures of different mesophases. TGB phases have been recorded in CN, CN10, CN20, CN30 and CN70. The transition temperatures recorded by polarizing microscopy observations were confirmed [18] by using a Differential Scanning Calorimeter (DSC) of Mettler Toledo (Model DSC822 with STAR software).

RESULTS AND DISCUSSION

The optical microscopy observations show nice textures apparently associated with different kinds of structures. The optical textures of different TGB phases and other liquid crystalline phase have been recorded in a sample thickness of 6 μm.

Textural Investigations of CN

When molten CN is cooled, the separation of cholesteric phase (Fig. 1) from isotropic phase is marked at 88°C by genesis of nucleation at

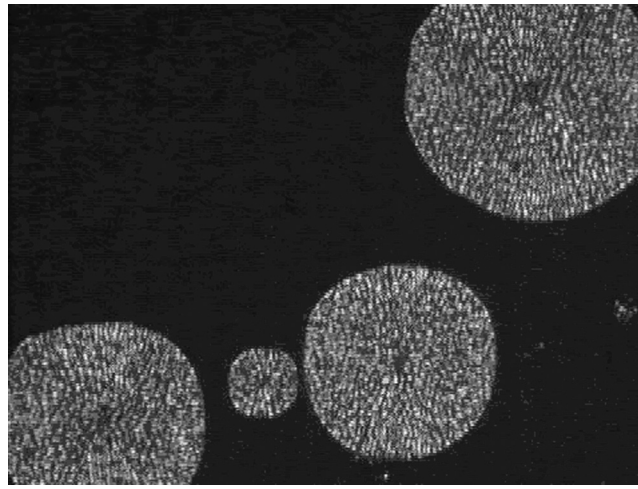

FIGURE 1 Separation of N^* phase from the molten sample of CN (×100), 88°C.

several points which appear minute bubbles initially (spherulites), but which progressively grow radially. Figure 2 shows perfectly grown cholesteric phase at 80°C. Figure 3 shown at 78°C witness a transformation $N^* \rightarrow$ TGBA with origin of black brushes from the centers of the spherulites. Figure 4 gives TGBA cylindrical and cone like domain

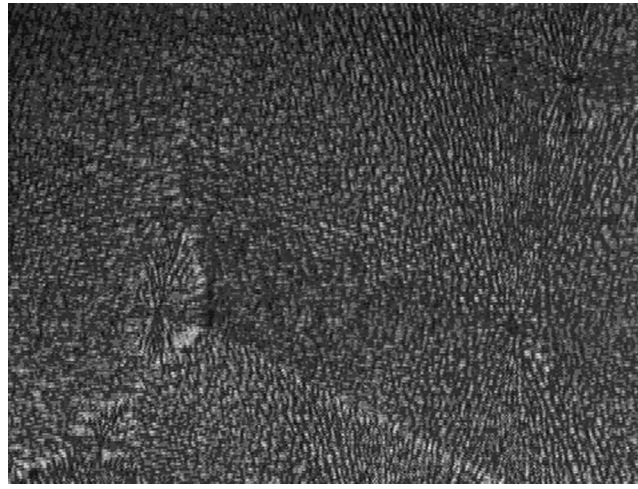

FIGURE 2 Texture of cholesteric phase of CN. (×100), 80°C.

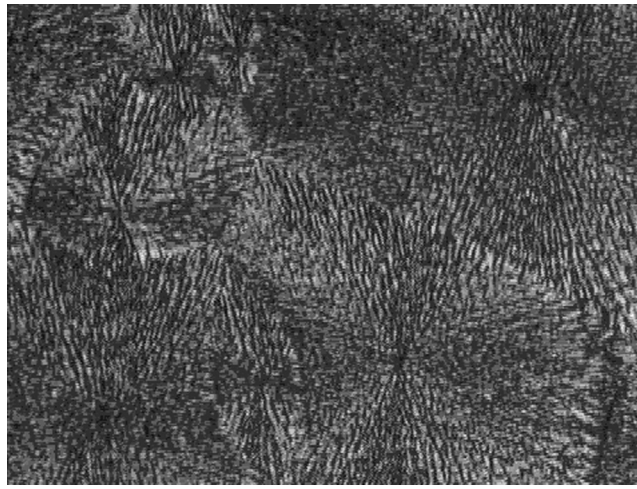

FIGURE 3 Transformation of N^* to TGBA phase of CN. (×100), 78°C.

texture (CC type texture) with a χ-line. TGBA phase transforms to SmA phase giving focal conic texture at 75.5°C (Fig. 5), which ultimately crystallizes at 23°C (Fig. 6). Figure 6 shows SmA → K transition. In the heating run, the crystal phase (Fig. 7) transforms to TGBA at 83°C (Fig. 8). The DSC thermogram shows shoulder in the

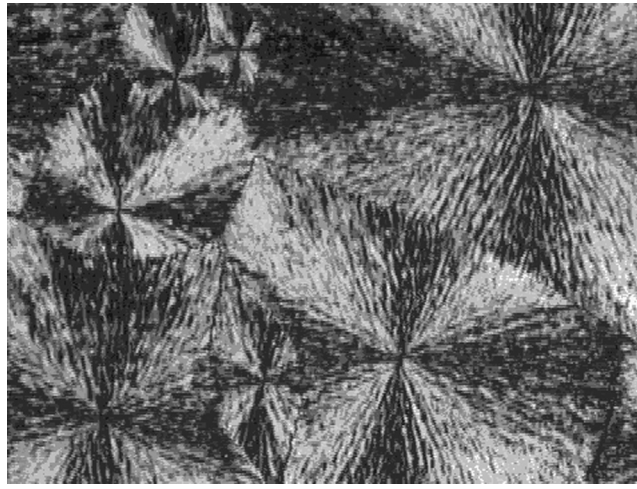

FIGURE 4 CC type texture of TGBA phase of CN. (×100), 76°C.

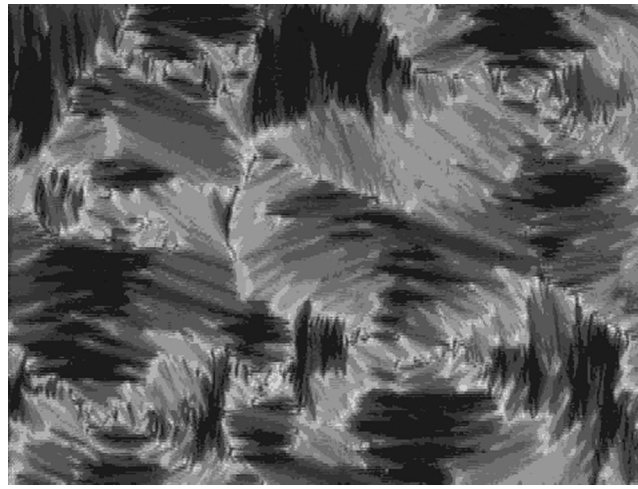

FIGURE 5 Transformation of TGBA to SmA focal conic type texture of CN. (×100), 75.5°C.

peak corresponding to TGBA-N* transition in heating cycle as well [18]. Such filamentary textures have been recorded earlier either in free standing films giving TGBA phase [4] or in homeotropic samples [19].

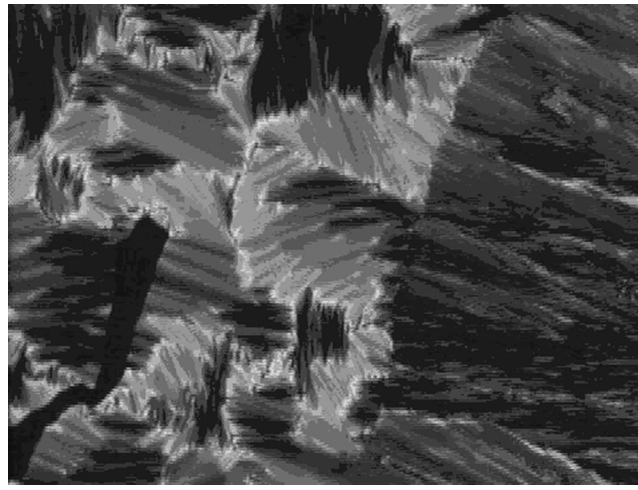

FIGURE 6 Transformation of SmA to crystal phase of CN. (×100), 23°C.

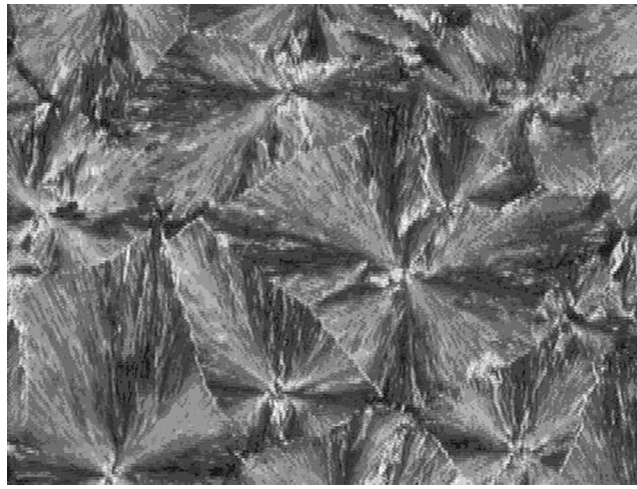

FIGURE 7 Mixed crystal phase of CN. (×100), 83°C.

The TGBA strands get separated out as the temperature is increased and at 84°C planar cholesteric texture is observed (Fig. 9) which transforms to isotropic liquid crystal giving completely dark field of view at 85°C.

FIGURE 8 Filamentary texture of TGBA phase of CN. (×100), 84°C.

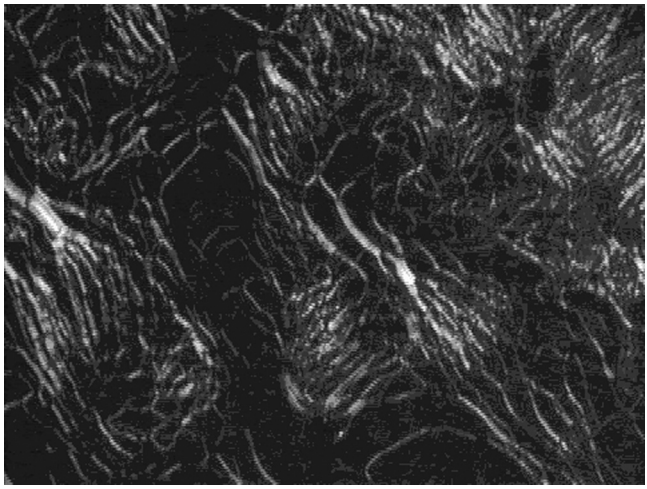

FIGURE 9 Planar cholesteric texture of CN. (×100), 85°C.

Our work shows experimental observation of TGBA phase in pure CN in thin unaligned film. Cholesteric Nonanoate (CN) is considered as a standard example of a weakly first order $N^* \rightarrow SmA$ transition exhibiting pretransitional effects at the transition. McMillan [20] gave a theory where the interaction constants of CN place it at the boundary between a first and second order transition. The Ginzburg parameter (κ) calculated for CN by Kleman [8] on the basis of its very small latent heat and of other material parameters by Mcmillan [21] and Pindak [22] is found to be practically equal to $1/\sqrt{2}$, which supported the possibility of the existence of an Abrikosov phase in the vicinity of the phase transition. The value of κ for pure CN estimated by Vigman *et al.* [23] exactly coincides with the critical value. The TGB phase has been observed and demonstrated to be located between the N^* and SmA phase in a broad temperature range in a mixture of cholesteryl nonanoate and nonyloxybenzoic acid by Lavrentovich *et al.* [24,25]. For this mixture, the Ginzburg parameter has been estimated to be larger than the critical value ($1/\sqrt{2}$) [26].

Nastishin *et al.* [27] have shown the existence of TGBA phase in CN by observing defects transformations at the $N^* \rightarrow SmA$ transition in two geometries – suspended droplets with tangential anchoring conditions and free standing films. They observed that the peak corresponding to the transition $N^* \rightarrow SmA$ was anomalously broad and its amplitude was dependent on the scanning rate. They concluded with the remark that the peak might result from several phase transformations including

the $N^* \rightarrow N_L^*$ and $N_L^* \rightarrow$ TGBA transition. Recently, Kleman *et al.* [28] have discussed theoretically topological defects of the Twist grain boundary phases and the difference between N^*, N_L^* and TGBA disclinations. They discussed the absence of focal conic domains in the TGBA phases and materialization of the helical axis (along the χ-director). The optics of TGBA phase has no qualitative distinctive features compared to N^* phase as a TGBA phase is nothing else than an N^* phase dressed with SmA layers at the microscopic scale much smaller than the wavelength of visible light. As a result, the textures corresponding to uniform and smoothly distorted director fields do not identify TGBA phase. As any other liquid crystal phase exhibiting a unique structure, TGBA has characteristic defects that are signatures of the phase. A TGBA phase is described by three directors, unit normal 'λ' common to all the layers, 'χ' a unit normal to a plane containing twist grain boundaries and $\tau = \lambda \times \chi$. The three directors λ, χ and τ form a trihedron, that rotates by an angle 'ω' between steps of length l_b[28]. Difference between N^* and TGBA disclinations are physical not topological, i.e., they arise from the energy selection of distortions governed by the materialization of the χ director and by the parallelism of smectic layers in the TGBA phase. In the N^* phase, the field of the χ-director that emanates from the center of the spherulite has the geometry of a hedgehog point defect. The disclination lines of strength $k = 2$, i.e., line defects which carry 4π rotations of the ortho-normal frame of the directors about the line, escape into third dimension with no singularity remaining. In the N^* phase the χ-director is not materialized as there is no physical singularity attached to the χ-field. However in TGBA the χ-singularities are materialized as singularities of the slabs.

Textural Investigations Performed on Binary Mixtures

Figure 10 shows perfectly grown cholesteric phase in CN10 at 70°C obtained on cooling from the Blue Phase. The cholesteric helix axis is basically oriented in the plane of the substrate, but without any preferred in-plane direction. On cooling the sample from the N^* phase cylindrical domain type texture with black fringes originating from the sharp eyes is observed at 63°C as shown in Figure 11. The TGBA phase on cooling to 62°C gives rise to $TGBC^*$ phase as shown in Figure 12. Here the CC domains are decorated with fracture lines (the dielectric studies reveal existence of a Goldstone mode in this region which can be suppressed by application of high DC bias [29]). These lines appear very faint first and get more and more visible on decreasing temperature. They seem to approach a point as the

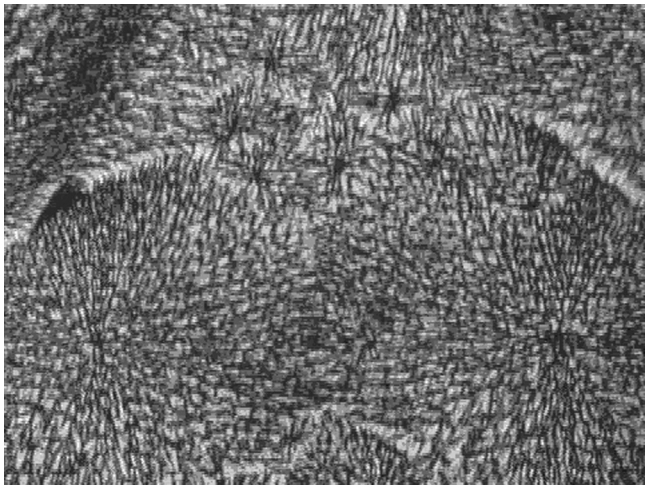

FIGURE 10 Perfectly grown N^* phase of CN 10. ($\times$100), 70°C.

temperature is lowered. This point seems to correspond to a χ-line. It appears that the helix is unwinding as the temperature is decreased.

The helical axis orientation of the TGBA phase in comparison to $TGBC^*$ phase is nicely demonstrated in Figure 12. The 90° twist of

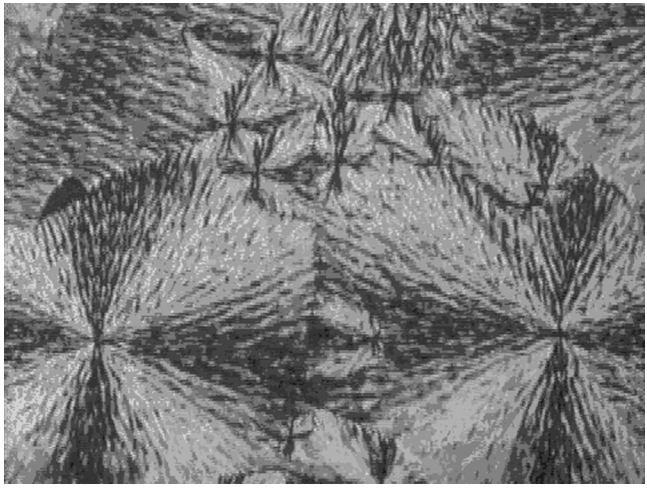

FIGURE 11 Cylindrical domain type texture with black brushes in the TGBA phase of CN 10. ($\times$100), 63°C.

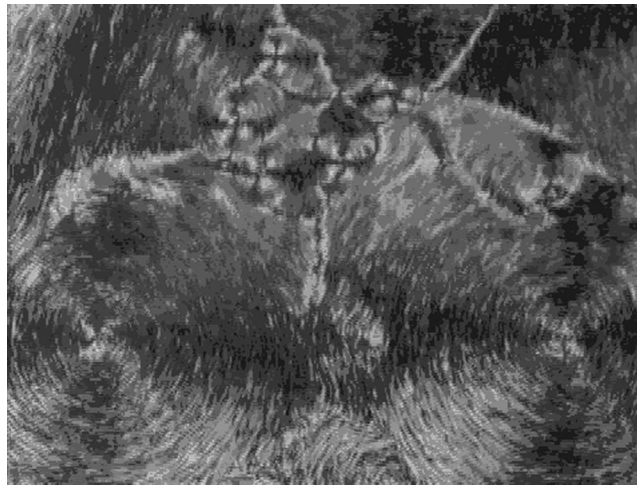

FIGURE 12 Perfect TGBC* phase of CN 10. (×100), 62°C.

the helical axis in an Sm C* block is clearly visible. The TGBC* phase transforms to SmA at 60°C (Fig. 13)

Figure 14 shows CC type texture for the TGBA phase in the mixture CN20 obtained at 46°C in the cooling run. TGBA as recorded in CN30 is displayed in Figure 15.

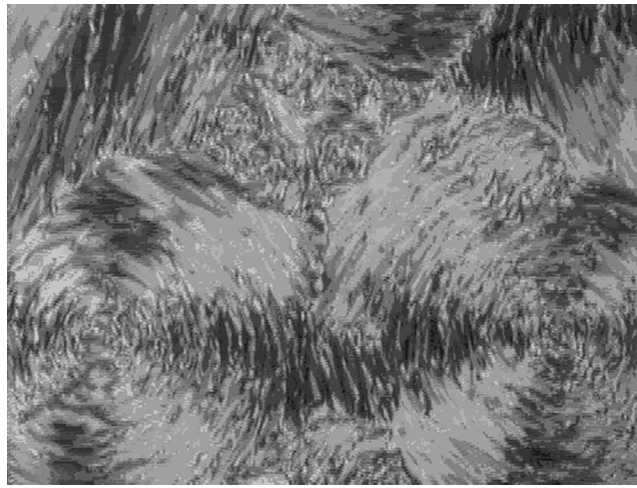

FIGURE 13 Transformation of TGBC* to SmA phase in CN 10. (×100), 60°C.

FIGURE 14 CC type texture of TGBA phase of CN 20. (×100), 46°C.

The optical textures of the mixture CN 70 are shown in Figures 16–18. When the sample is cooled very slowly from the isotropic phase, TGBA phase is observed at 64°C (Fig. 16). Figure 17 shows the broken cone like domain texture of TGBA phase. The optical microscopy observations

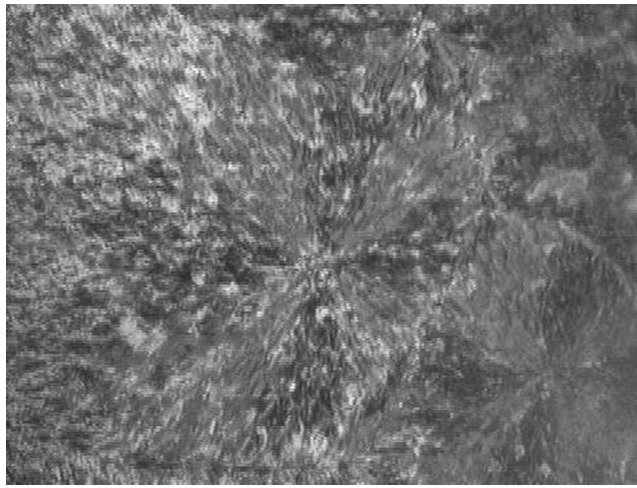

FIGURE 15 TGBA phase in a 6 μm sample in CN 30. (×100), 23°C.

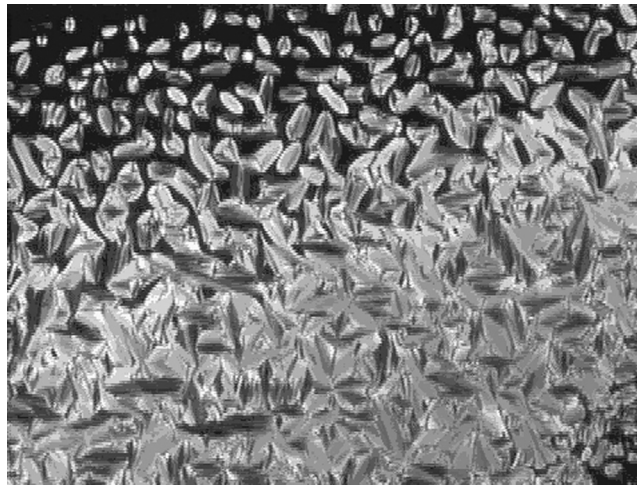

FIGURE 16 Transformation I → TGB phase for CN 70. (×100), 64°C.

performed in the transmitted mode reveal complete visible spectrum as the temperature is lowered while no change in texture is observed. At 18°C we find complete cross hatching of the structure giving indication of a TGBC* phase (Fig. 18).

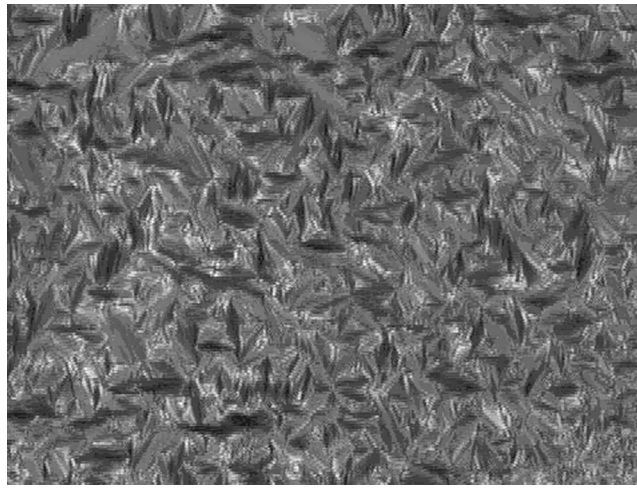

FIGURE 17 Perfect TGB phase for CN 70. (×100), 63°C.

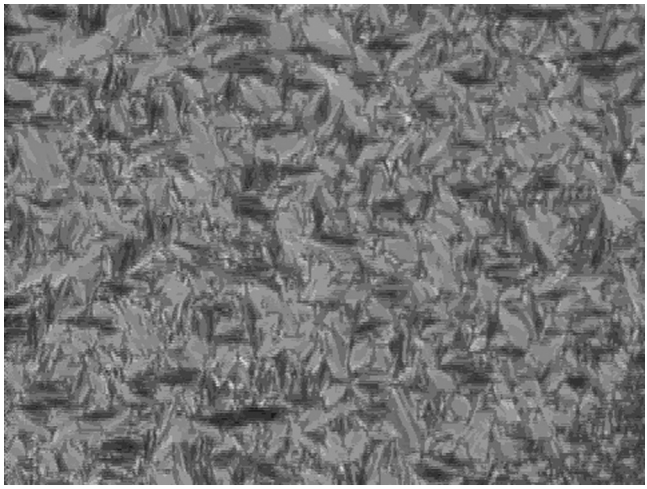

FIGURE 18 The cross hatching of the structure gives indication of a TGBC* phase in CN 70. (×100), 18°C.

CONCLUSION

It is a well-known fact now that TGB phases, that are analog of the flux phase of superconductors, consist of a twisted lattice of screw dislocations as a counterpart of the hexagonal lattice of flux lines. In this frustrated smectic phase, there are blocks of smectic layers arranged in a helical way along an axis parallel to the smectic layers. Two adjacent smectic blocks are rotated by an angle and they are separated by a grain boundary where a lattice of parallel and equidistant screw-dislocation lines exists. Thus between two adjacent slabs, which mark the place where smectic layers go continuously from one slab to the other, a kind of twisted ribbon of molecules is formed. In this structure two-dimensional columnar ordering exists only in the grain boundaries. Within the slabs, the columns are interrupted and merge back in to smectic layers. Never the less, their lateral dimensions are fixed, they have a constant density and it is possible to track them from a grain boundary to the next one. This ensures the formation of developable domains as in the classical columnar structures made of continuous columns [6].

The TGBA, TGBC* phases recorded in the present work shows well-formed developable domain textures. In these structures, the smectic blocks, the grain boundaries and the layers of helical structure of TGB phase are coiled around an axis of a cylindrical domain. In such cylindrical domains, the smectic blocks are oriented according

to the so-called double-twist [30], similarly as the molecules in the blue phases. As explained in [7] such a structure is mechanically possible provided that the smectic blocks can be bent. The bending of the smectic blocks in a plane perpendicular to smectic layers is elastically disfavored since it needs compressions and dilations of the smectic layers, involving an energy density. The TGB phases constitute layered systems, which should build focal conics. However, the smectic blocks do not behave exactly as smectic layers. They cannot be elongated locally nor continuously in the direction perpendicular to their smectic layers, because the smectic layers themselves forbid any flow in that direction. They are therefore one-dimensional liquids, with crystalline properties along the direction perpendicular to the smectic layers. This means that the blocks have metric properties in this perpendicular direction, which, due to helical twisting, extend to all the directions parallel to the block surface. This 2D metric condition prevents the block to be elongated in any manner. Therefore, like paper sheets, they cannot undergo bending with double curvatures, as involved in the sphere; in other words, they keep a zero Gaussian curvature whatever the deformations [7]. Thus the blocks can just be folded in cones and cylinders, the only surfaces that may be unrolled without elongations. These systems, made of stacks of parallel planes, cylinders or cones (CC), may be seen as particular focal conics, since they are layered systems, but also as developable domains since they are particular developable domains which have their developable surfaces restricted to axes. The cylindrical configuration does not produce any defect in both the block and helical ordering. The cone-like domains behave rather similarly as the cylindrical domains with a double twisting of the whole structure, including the TGB dislocations. However, the cones need defects to build up. Along the axes, the orderings of the helical twisting, of the blocks and of the molecular orientations is destroyed. In particular, a disclination is necessary all along the cone axis, except where the molecules are parallel to it, which occurs marginally, for one block over $N_b/2$, N_b being the number of blocks per helical pitch. The energetic cost of the complete cone-like domains could thus be heavy only parts of them could then build up. Such partial cone domains could fill the whole space when stuck together in a polycrystalline array. It is interesting to point out that CC textures were always observed on cooling slowly from the isotropic phase in the absence of any orienting field. In the present work, in CN, CN 10, CN 20 and CN 30, cone like domain textures are prominent while in CN 70 broken cone like domains are prominent.

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