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Microscopic structures of the B_7 phase: AFM and electron microscopy studies

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A wide variety of morphologies, such as screw-like filaments, ribbons, etc., have been observed in polarizing microscopy studies of the B_7 phase in a melt or with free surface. In this paper, we present the results of AFM and scanning electron microscopy measurements of structures formed by a columnar-type B_7 phase. These measurements are aimed at elucidating the three-dimensional structure of the observed patterns.

1. Introduction

For several years, mesophases formed by bent-shaped molecules have attracted particular attention in liquid crystal research. Interplay between the polar properties of the molecules and chirality of the phase structure results in a broad new class of polar phases of unexpected richness [1, 2]. Lamellar as well as columnar structures are encountered among the bent core ('banana') compounds. It has been shown that several mesophases such as SmCP (where P stands for polar), PM-SmCP (polarization modulated SmC) and B_7 can also form free-standing fibres [3–6].

Until now, microscopic textures associated with the B_7 phase ('B_7 texture') remained among the most mysterious patterns of the 'banana phases'. Extensive experimental studies showed at least two different mesophase modifications exhibiting similar microscopic patterns [2, 7, 8]. A PM-SmCP structure has been suggested for the layered version of the B_7 phase [9, 10]. In the PM-SmCP phase, the molecules are tilted within the layers and the local polarization experiences spontaneous splay. As a result of the coupling between the divergence of the spontaneous polarization (director) and the layer curvature, the layers become modulated. This modulation is responsible for satellite reflections in the X-ray diagrams of PM-SmCP. On the other hand, another phase shows a similar microscopic texture; this phase (initially designated as B_7 [2]) has additional reflections that cannot be explained in the frame of a simple lamellar structure. It has been suggested that the orientation frustration at the splay defect planes may be relieved not only by the layer expansion but also by interdigitation of the layers, yielding a columnar-like two-dimensional structure [9]. Exactly this type of the mesophase is discussed in this paper.

The frustrated structure of the B_7 phase is reflected in a variety of microscopic textures observed in polarizing optical microscopy (POM). Several papers discuss the structure and topological properties of screw-like filaments (or helical ribbons) based on POM observations [11–14]. On the other hand, higher resolution techniques are required to capture the real three-dimensional morphology of the filaments. Only few atomic force microscopy (AFM) studies of the focal conic structures in the B_7 and B_2 (SmCP) phases have been reported [15–17]. Freeze-fracture studies of the PM-SmCP phase have revealed the presence of three-dimensional filaments forming different kinds of focal-conic and maze-like patterns [9].

In this paper, we present the results of scanning electron microscopy (SEM) and AFM measurements that are aimed to elucidate the structure of the screw filaments and ribbon microscopic patterns observed in the 2D-type B_7 phase.

2. Experimental

We have studied the liquid crystalline compound 2-nitro-1,3-phenylene bis[4′-(9-decen-1-yl-oxy)-1,

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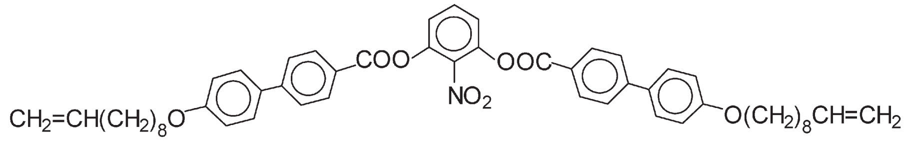


Figure 1. Chemical formula of 10NO2PBBC.

1′-biphenyl-4-carboxylate] (10NO2PBBC) (see figure 1), which exhibits the following phase behaviour:

$$\text{on heating Cr}\xrightarrow[\left[3.97\,\text{kcal mol}^{-1}\right]]{74.9^{\circ}\text{C}}\text{B}_7\xrightarrow[\left[10.84\,\text{kcal mol}^{-1}\right]]{119.2^{\circ}\text{C}}\text{I}$$

(on cooling: $\text{I}\xrightarrow[\left[5.27\,\text{kcal mol}^{-1}\right]]{111.3^{\circ}\text{C}}\text{B}_7\xrightarrow[\left[0.192\,\text{kcal mol}^{-1}\right]]{78.0^{\circ}\text{C}}\text{Cr}$)

The B_7 phase is monotropic and occurs on cooling from the isotropic state. The synthesis of 10NO2PBBC mesogen and its analytical data have previously been presented in ref. [18].

Droplets of liquid crystalline material were placed on a glass substrate and heated to the isotropic state (Linkam T60 heating stage); they were then slowly cooled (0.1 K min^{-1}) into the B_7 phase. The microscopic textures were observed in a reflection polarizing microscope (Axioscope 40 Pol, Carl Zeiss GmbH). After the optical observations revealed the desired textures, the sample was rapidly cooled to room temperature by a manually placing the sample on a cool (room temperature) brass plate; on some occasions liquid nitrogen was used to cool the heating stage. Despite the fact that we have not explicitly studied the dynamic properties of the final state, we can assume that this cooling leads to a transition into a glassy state, as often happens with similar bent-core compounds. In contrast to the transition at a slow cooling rate, the texture remains intact after the fast cooling procedure. Additional optical observation was made to ensure that the texture remained intact upon cooling.

Electron microscopy studies were made with an Oxford LEO 1550VP field emission scanning electron microscope. Using this technique, resolutions of the order of 5 nm are possible. To improve the contrast and spatial resolution of the images, a thin carbon coating was applied to the probes. For coating we used carbon plating by Edwards Sputter Coater S150B with a work distance of around 50 mm.

AFM measurements were performed using a Nanoscope IIIa (scanning probe microscope controller, Model no. MMAFMLN) (Veeco Metrology Group) in Tapping mode at 300 kHz with silicon-tips. The *maximum* scan rate was 0.2–0.4 Hz. The sample was measured at room temperature and ambient conditions. The position of the cantilever against the microscopic texture was controlled by a built-in microscope.

3. Results and discussion

On slow cooling of an isotropic droplet, the transition into the B_7 phase is marked by formation of complex patterns containing screws and coils as well as ribbon domains coiled into a maze pattern. The diameter of the screws is around 3.5 µm and the period of the ribbons in the ribbon maze pattern is approximately 1.2 µm (figure 2). With special care during cooling, it is possible to obtain droplets in which a single coil grows slowly, 'reflecting' from the boundaries. When a screw-like filament meets the boundary of the droplet, the mechanical stress exerted along the filament can slightly deform the screw, revealing that its structure is formed by fine fibres coiled into a screw (figure 3). Growing fibres buckle when the droplet boundary obstructs the growth of the screw, as shown in figure 3. Unfortunately, the low spatial resolution of light microscopy does not allow us to see the features of these fibres in close-up, and techniques such as AFM and electron microscopy are needed. In order to isolate single screws, we spread a small droplet across the substrate surface. On several occasions, we were able to obtain a single screw or a flat maze on the substrate surface out of the bulk. It is important to mention that the microscopic pattern could be observed both in polarizing and in bright-field microscopy, suggesting that the textures represent true three-dimensional

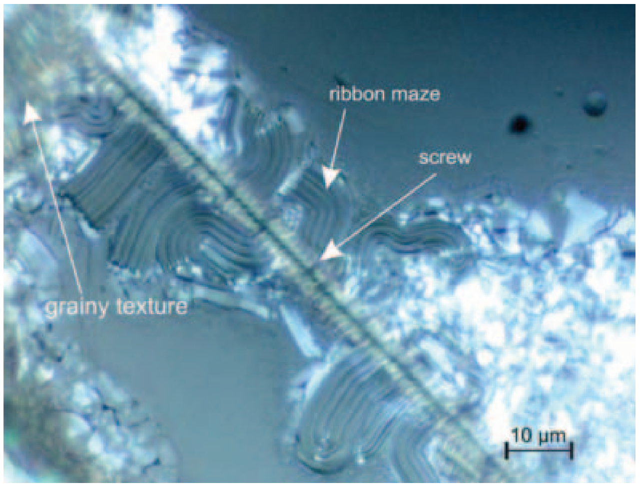


Figure 2. Typical morphologies observed in polarizing microscopy of the B_7 droplets.

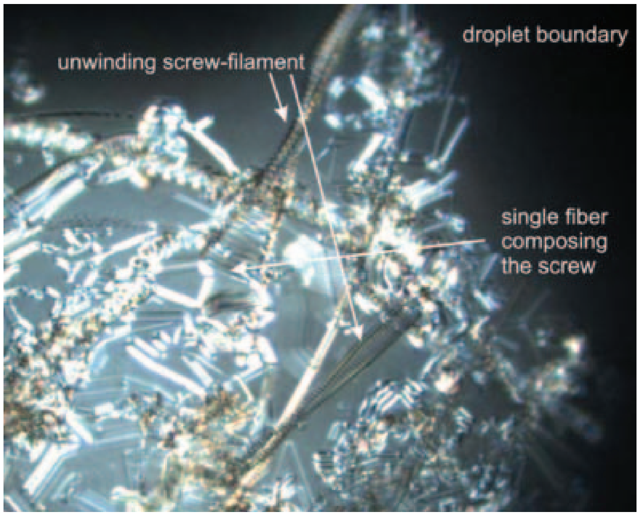


Figure 3. Optical image of a screw-like filament growing in an isotropic droplet (crossed polarizers). As soon as it touches the boundary, a longitudinal stress along the screw leads to unwinding of the small fibres of the structure.

structures of interfaces and not just a configuration of the director field.

Figure 4 depicts the SEM image of an isolated screw filament emanating from a single droplet. The electron microscopy images provide a far better spatial resolution than the optical images in figure 3, and they explicitly show that the screws are formed by tightly coiled fibres. The fibre structure is particularly well seen when a crack occurs within the screw and the fibre coils become separated, as shown in figure 5. Unfortunately, little can be said about the cross-section of the fibres: the large thickness of the screws (several μm) does not allow us to map the screw fully using AFM. Instead, we managed to scan a fragment of the upper surface of the screw. The AFM image of this area yields an undulated profile of period 1.2 μm and height 250 nm (figure 6). These images suggest that the fibres do not have a circular cross-section but have a polygonal form.

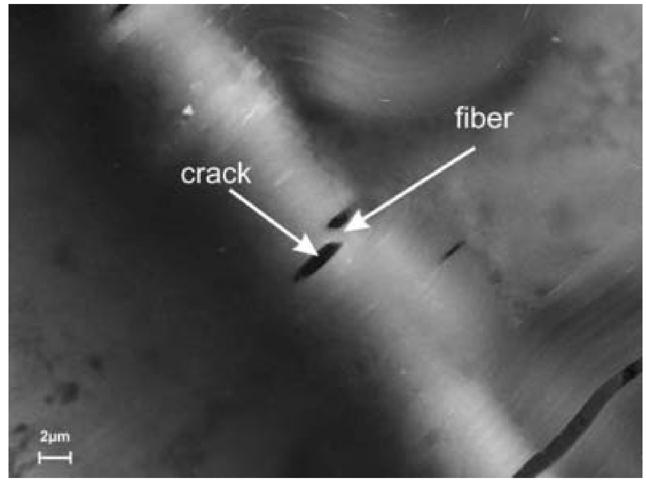


Figure 5. 'Defect' cracks occur in the screw filament. These cracks show that the filament is composed of a tightly coiled fibre. The scale bar is 2 μm.

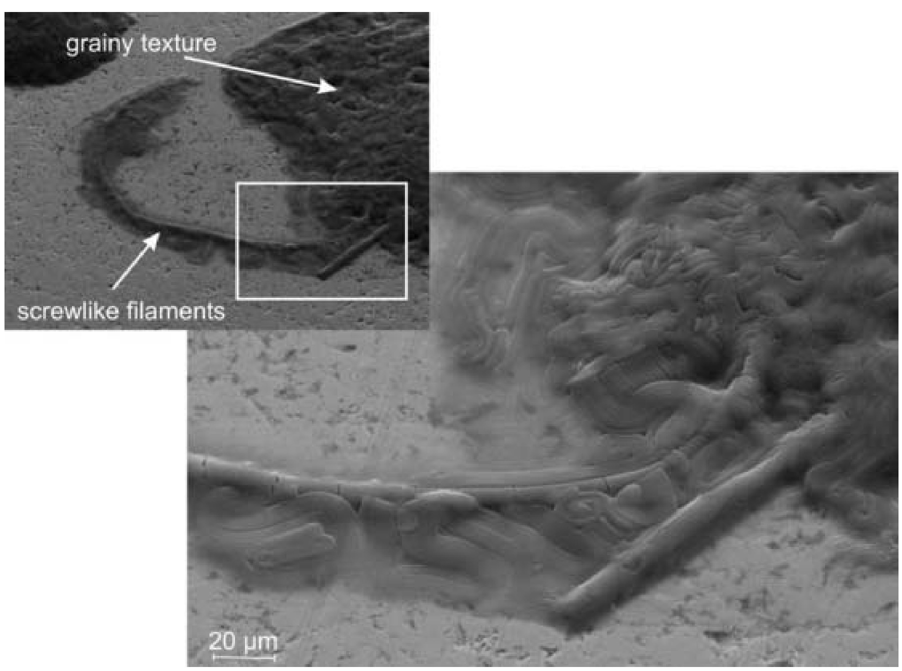


Figure 4. Scanning electron microscopy image of a droplet with an isolated screw filament and the grainy texture in the bulk.

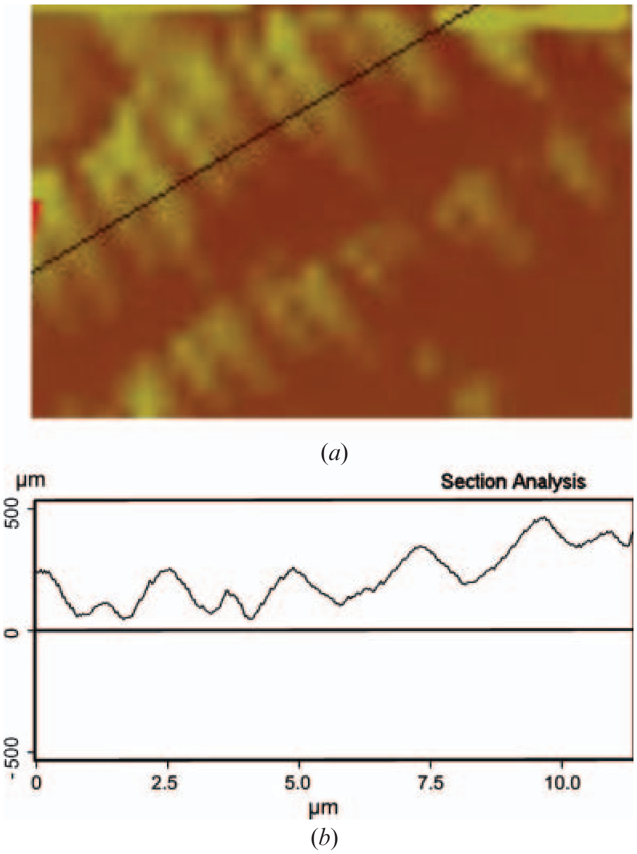


Figure 6. AFM image of a single screw-like filament. The profile shows undulations with period $\approx$1.2 µm and height $\approx$0.25 µm.

On some occasions the coiling of fibres into screws is obstructed by interaction with a glass substrate. Instead, the fibres become trapped on the surface, and form a flattened structure rather than a cylindrical coil (figure 7).

Another feature of the B_7 texture captured in figure 4 is the 'fine grainy texture' which surrounds the trapped coils. A closer examination of the electron microscope image shows that the grainy texture consists of an entangled 'spaghetti' of fibres. This finding also confirms observations in the optical microscope, revealing a disordered growth of coils on rapid cooling during the isotropic $\rightarrow$ B_7 transition.

In addition to the screw filaments, the image shows some ribbon-like structures surrounding the screws and, in some places, overlapping them. These structures are confined to the substrate surface and are usually rolled into a kind of a maze pattern (figure 2). During the formation of these structures, it is even possible to manipulate a single ribbon by pulling it. The thickness of the maze pattern varies from around 5 nm (molecular length) to several micrometers. The AFM image in figure 8 shows a cross-section of a thick pattern. The

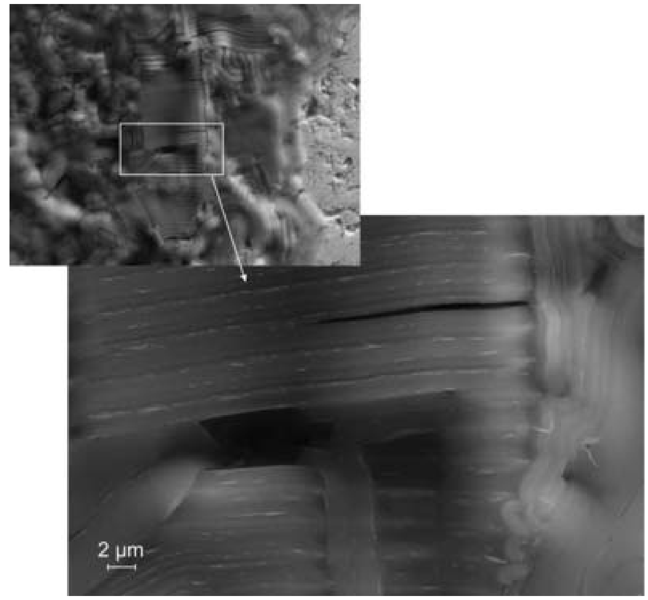


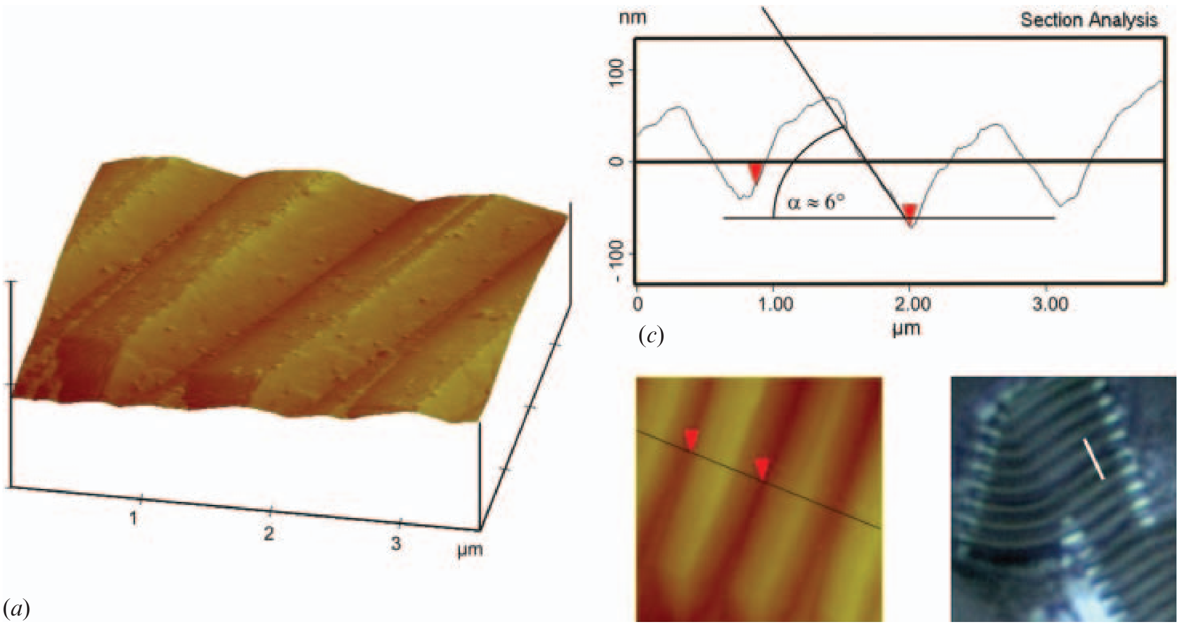
Figure 7. A filament trapped by the substrate surface (SEM image).

surface consists of a 'massif' with horizontal spacing of about 1.2 µm and height of 130 nm. It is remarkable, that the section has an almost triangular shape. Such a massif of fine equidistant stripes produces an image of quasi-focal-conic domains under POM. Comparing the AFM profiles with electron microscopy images, we can conclude that the fibres producing the maze pattern have the same size as those forming screw filaments.

It is important to note that the formation of fibres has already been reported for several 'banana' phases such as SmCP, polarization-modulated PM-SmCP and B_7 phases. However, in those studies single fibres (or whole bundles) did not form spontaneously, but were pulled mechanically between two supports. It has been shown that in contrast to the case of a columnar-type B_7 phase, the fibres of SmCP and PM-SmCP phases have cylindrical form [6].

4. Conclusion

In this paper we present new data on different morphologies of the B_7 phase observed in droplets and thin films confined on a substrate surface. We have observed that the transition into the B_7 phase is accompanied by the growth of fibres which can either be trapped on the substrate surface or can spontaneously coil into a three-dimensional screw filament. In the case of thin films, confinement leads to the formation of flat ribbons that grow to form a maze pattern, similar to the patterns of filaments observed in freeze-fracture transmission electron microscopy by Coleman *et al.* [9]. It remains unclear what defines the



(a) (b) (c) (d)

Figure 8. Undulations of the surface in a maze pattern: (*a*) 3D image of a 'masif' measured by AFM; (*b*) contour plot of the 'massif' and (*c*) the height profile; (*d*) image in the polarizing microscope (white line shows the section path).

shape and size of the fibres. It is astonishing that the width remains almost constant for different fragments of the pattern. As to the shape, an almost triangular-shaped section of the ribbons may originate from buckling caused by a slight transversal growth of the constituent fibres perhaps reflecting the internal symmetry of the B_7 phase. On the other hand, detailed optical studies reported by Nastishin *et al.* also showed that sections of the B_7 nuclei are faceted rather than circular [13].

A particular fibre-like structure can be traced even in the disordered fine grainy texture which occurs from relatively fast cooling of the sample. In this texture, the fibres are entangled and lead to a form of 'spaghetti' texture.

By neither slow nor fast cooling could we obtain a homogeneous B_7 sample on a large scale ($>3\,\mu$m). It is not typical for most common columar phases which allow the growth of large uniformly oriented monocrystals. Our observations of the B_7 phase have shown that even the bulk droplets are formed by interface boundaries and represent a 'spaghetti' of fibres rather than a homogeneous body. What causes such a spontaneous fibre formation? This question remains unanswered and future research should shed more light on this matter. The layer structure of some mesophases could stabilize fibre structure against the collapse caused by transverse fluctuations of the fibre surface. On the other hand, fibres are seldom observed in smectics. For instance, freely-suspended fibres have been reported for polar SmCP and PM-SmCP phases but not for the ferroelectric SmC* phase. Another possibility which can contribute to fibre formation is a possible anisotropy of the surface tension [3, 19], which can induce a spontaneous curvature of the growing B_7 interface. Generally, mesophases such as the B_7 phase formed by bent-shaped molecules exhibit many symmetry breaking instabilities, and the interplay between competitive ordering tendencies contributes to the variety of morphologies observed in these phases.

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