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Helical filamentary growth in liquid crystals consisting of banana-shaped molecules

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The formation of coils is common in nature when achiral symmetry breaking occurs. Here we describe spectacular examples of single, double and triple coils observed in smectic liquid crystal phases of achiral banana-shaped molecules. Such molecules form chiral smectic phases due to two symmetry-breaking instabilities: polar molecular packing, and molecular tilt. The appearance of helical filaments at the isotropic–smectic transition is therefore a direct indication of the achiral symmetry-breaking of the smectic structures. The number of observed left- and right-handed domains is equal, reflecting the achiral nature of the constituent molecules. Our studies indicate that the helical filaments consist of concentric smectic layers. The coiling stabilizes the growth process and suppresses the penetration of molecules from the isotropic phase, leading to moving of the tip with constant speed.

1. Introduction

When smectic liquid crystals grow from anisotropic phase a rich variety of spatial pattern can be observed. Usually a smectic phase separates from the isotropic liquid in form of 'bâtonnets', which are elongated structures consisting of focal-conic domains [1]. In some cases (probably when the surface tension measured along the smectic layers is smaller than perpendicular to them), the smectic phase grows in interesting filamentary shapes [2–5]. Helical coils were observed in lyotropic systems originating either from chiral molecular structure [6–10] or from spontaneous achiral symmetry breaking [11].

Recently various helical super-structures were observed in thermotropic smectic phases of achiral banana-shaped molecules [12, 13]. These molecules may form chiral smectic phases due to two symmetry-breaking instabilities: a polar molecular orientation ordering along the smectic layers and a molecular tilt [14]. The appearance of helical structures therefore is a spectacular indication of the achiral symmetry breaking of the smectic structures. In this paper we describe studies on initial individual single, double and triple coils, since their properties are not influenced by interactions with each other. Our aim was to reveal how the chirality affects the shape and dynamics of the growing smectic domains.

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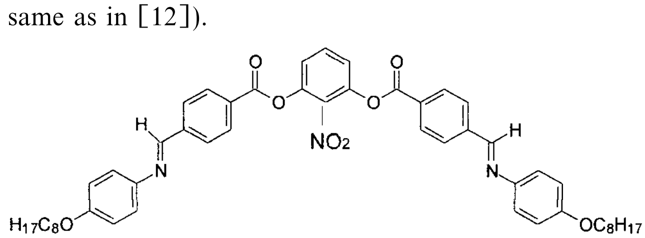
2. Experimental results

Measurements were carried out on 2-nitro-1-3-phenylene bis[4-(4-*n*-alkyloxyphenyliminomethyl)benzoates] (the same as in [12]).



It has an isotropic–B_7 phase transition at 177°C, where B_7 is a tilted smectic phase, but its detailed structure has not yet been determined [12]. Recent X-ray observations on freely suspended filaments in the B_7 phase indicate a complex order within the plane of the smectic layers [15]. In our measurements the textures were observed by a polarizing microscope and recorded by a video camera during cooling the sample from the isotropic phase with slow (0.2–0.5°C min^{-1}), and with fast (> 1°C min^{-1}) rates.

During slow cooling we studied 50 individual smectic domains growing into the isotropic phase. We identified 44 single (22 right-handed and 22 left-handed) helices resembling corkscrews, 5 double helices resembling the structure of DNA, and 1 triple helix, similar to a braid. Typical corkscrew and DNA-like domains are shown in figure 1(*a*). Sometimes a second coil nucleates and grows on an existing coil, figure 1(*b*). In a few cases an apparently smooth tube forms around a corkscrew. In

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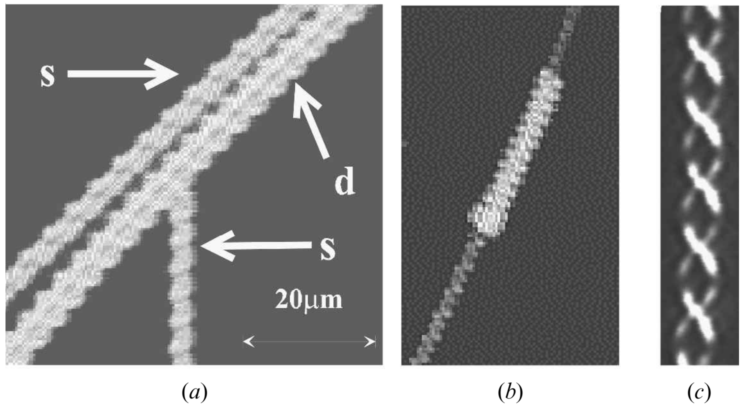


Figure 1. Smectic domains growing in the isotropic phase. (*a*) Two single (**s**) helices and one double (**d**) helix containing two right-handed single helices; (*b*) an example of when a second coil nucleates and grows around an existing coil; (*c*) a loose double helix consisting of two left-handed helices. Diameter of the filament is $d = 1.7\,\mu m$, the diameter of the coil is $D = 4.5\,\mu m$ and the pitch is $p = 6.7\,\mu m$.

figure 1 (*c*) we show a loose double helix. The main features of the growing domains appear to be independent of the cell thickness in the 10–50 μm range, and are also insensitive to the surface treatment. This indicates that the domains do not touch the substrates. When cork-screws meet they may cross each other indicating that their vertical positions are different.

By varying the focus and magnification, and following the shape of the growing tip, we revealed that the observed objects are single, double and triple coils of smectic filaments. The filaments are typically 2–3 μm thick, just like non-helical smectic A filaments [3]. This and the observed textural similarities indicate that the local structure of the filaments is the same as that of non-helical filaments. Accordingly the smectic layers form concentric cylinders [3] ('myelinic' structure [1]). Model structures of single (right- and left-handed) coils are represented in figure 2. The pitch of the helix (p), the diameter of the constituent filament (d), and the diameter of the coil (D) can describe each coil. The tightness of the coils can be characterized by the parameters a and b ($a = D - 2d$ and $b = p - d$). The gradient angle ψ of the helix can be expressed as

$$\tan \psi = \frac{p/2}{D - d} = \frac{1}{2}\frac{d + b}{d + a}.$$

We observed that $4\,\mu m < D < 8\,\mu m$, and $\psi \sim 30°$, i.e. $a \sim b$. Coils of the same diameter D had different brightness indicating varying diameter d of the constituent filaments. Faint domains mean that $d \ll D$, while for bright domains $d = 1/2D$, which means $a = b \sim 0$, i.e. the cylinders are tightly wound. We observed that thicker and brighter domains (i.e. tighter helices) stay straight even up to a few millimeter lengths, whereas looser and thinner helices tend to bend.

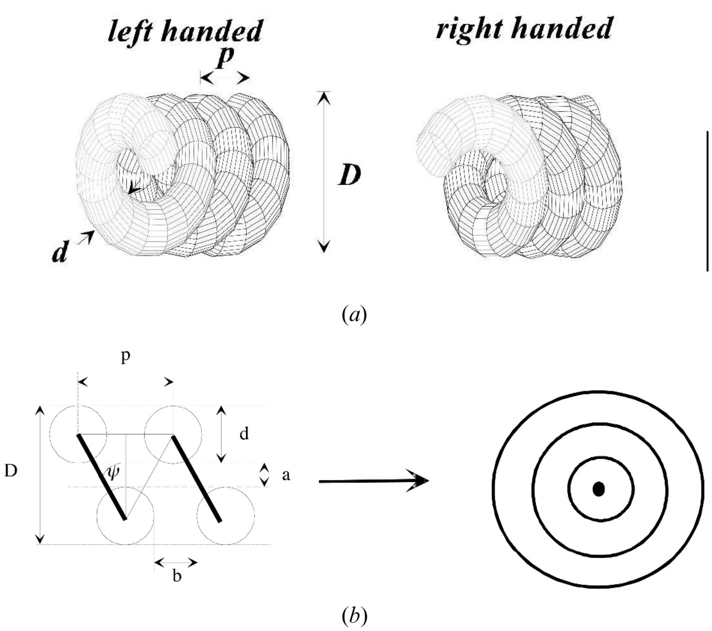


Figure 2. Model for the single helical filaments. (*a*) 3D structures; (*b*) cross-section of the helical filaments along the helical axis; p = pitch of the helix, d = diameter of the constituent filament, D = diameter of the coil. $a = D - 2d$ and $b = p - d$.

In figure 3 we plot the speed of growth as a function of the diameter of the individual filaments. It can be seen that the growth speed of the tip is approximately inversely proportional to the diameter.

The tightness of the helix seems to be correlated with the cooling rate: the higher the cooling-rate the looser the helix. Under fast cooling thin (~2 μm) filaments form, appearing like threaded beads. We will refer to them as beaded filaments. These filaments grow much faster than the coils and via local elongation, just as do the non-helical filaments [4]. A web of beaded filaments that grew in area of the already present helices (screws) is seen in figure 4 (*a*). The beaded filaments are not straight but they often bend. When two fragments of the same filament cross each other the filaments prefer to writhe and a supercoil appears. In figure 4 (*b*) we show an enlarged and edge-enhanced part of the beaded filaments. It can be seen that the beaded filaments also have a helical structure, although they are not as tight as in the screw-like filaments.

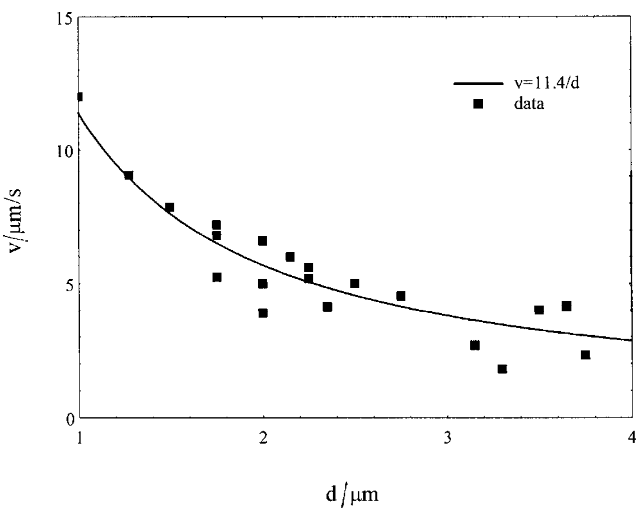
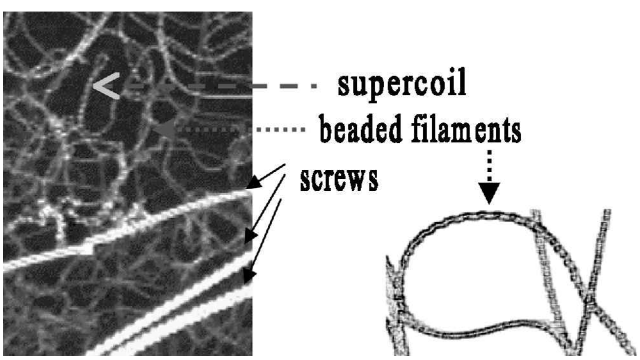


Figure 3. Speed of growth of the tips of the screw-like smectic domains as a function of their diameter.



(*a*) (*b*)

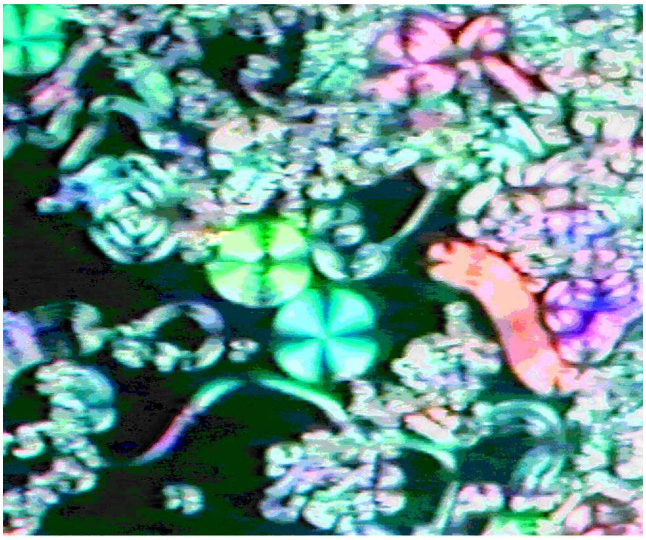
Figure 4. (*a*) Polarizing microscope texture showing the coexistence of beaded and screw-like helical filaments. Beaded filaments formed at a fast cooling rate (2°C min^{-1}), whereas the screws formed under slow cooling (0.2°C min^{-1}). The dashed arrow indicates a supercoil formed after two parts of the filaments crossed each other. (*b*) An enlarged and edge-enhanced section of beaded filaments indicating their helical structure.

On heating the sample to the isotropic liquid phase, the above-described processes repeat in reversed order. At reversals of low frequency electric fields applied normal to the cell, the coils dangle basically with the frequency of the field. Otherwise the electric field has no effect on the shape or the growing process of the domains. The minor effect of the electric field on the growing process indicates that the net polarization of the filaments is nearly zero. This supports the concentric cylinder model of the smectic layers.

When the transition to the liquid crystal phase is completed, the filaments collapse and form fans and other more complicated textures that were described in [12]. The most remarkable difference with respect to textures with the B_2 phase, is that multiple states are present at the same time. Basically four distinct birefringences corresponding to different colours such as purple, blue, yellow and green can be distinguished. A typical texture is shown in figure 5 (*a*). Under electric fields, optical switching is evident, but is too complex for quantitative conclusions to be drawn. One complication arises from mechanical motion of the domains, which indicates the contribution of ionic effects. In addition, the domains with different colours show different types of switching. In the purple fans the extinction crosses do not rotate, see figure 5 (*b*); only the birefringence is different in the ON and OFF states. In the green and yellow domains, however, the extinction brushes rotate by about ±5° depending on the sign of the field applied.

3. Discussion

Growth of the smectic filaments takes place via the absorption of molecules from the surrounding isotropic phase by the outmost layers. While the length is short the absorption is uniform and the growth-rate is proportional to the length [3, 4]. As the length increases an increasing number of molecules has to be pushed away by the absorbed molecules. This results in an increasing compression force and leads to undulation instability, which occurs at filament lengths of about 20 μm [4]. The advantage of the undulated shape over the straight domains is that the absorbed molecules do not have to push away all the molecules along the whole length of the filament, but only those within one period. The difference between non-helical and helical filaments becomes apparent only when the undulation appears. Non-helical filaments take a serpentine-like form, whereas helical filaments form coils. A tight coil is stable against



(a)

(b)

Figure 5. Typical texture of a 10 μm cell in the B_7 phase a few degrees below the transition to the isotropic phase. (a) Coexistence of domains with different birefringences, i.e. with different colours; (b) individual purple fan-shaped domains under electric fields of ± 6.3 V μm^{-1} and at zero fields, the birefringence at zero fields is smaller.

bending because it would require compression in one side, and a flexing in the other side of the coil. The compression increases the pressure, whereas the flexing increases the surface energy. Experimentally we indeed observed that bright and thick domains grow straight, whereas the thin beaded filaments bend, see figure 4 (a). Under slow cooling there is time to minimize the surface energy (i.e. in the liquid crystal–isotropic liquid interface) by forming tight coils. During fast cooling the growth rate is fast and there is no time to minimize the surface energy. This explains the appearance of the thin beaded filaments shown in figure 4.

Formation of coils and achiral symmetry breaking is very common in nature [16]. Chirality leads to twist deformations, which is replaced by coils, since a writhed shape has less elastic energy than the corresponding twisted one [16]. The situation is similar to a rubber band: on holding its ends taut between the thumb and forefinger of each hand and twiddling the fingers, it only twists, which is not visible. On moving the ends toward each other, the band prefers to writhe, and a coil appears. In this example the twiddling of the fingers represents the chirality of the liquid crystal, and the moving of the ends of the rubber band toward each other corresponds to the increased compression force in the growing filaments.

Tight helical filaments grow at their tips with constant speeds, and with no apparent change in thickness. Observations indicate that only the tip grows, which has not yet coiled. Denoting the length of the tip by l_t, the number of absorbed molecules by n, and the radius of filament by r, we can write that $\Delta n/\Delta t \propto r l_t$ (t = time). Assuming that the absorbed molecules penetrate through the whole radius of the filament, the increase of the length (Δl) can be expressed as $\Delta n \propto r^2 \Delta l$. The growing speed v then reads:

$$v = \frac{\Delta l}{\Delta t} \propto \frac{1}{r^2}\frac{\Delta n}{\Delta t} \propto \frac{1}{r} l_t.$$

Observations show that l_t is constant and is independent of r. Accordingly, $v \propto 1/r$, just as was observed experimentally (see figure 3).

Results on the fan-shaped domains indicate the coexistence of different structures. It is known for the B_2 phase that both racemic and chiral structures can coexist in one sample [14]. They have different colours since they are synclinic and anticlinic, respectively. It was also observed in the B_2 phase [17] that both vertical and tilted layer structures could be stable, which would double the number of the coexisting domains. However in one sample only one kind of layer alignment was observed at one time. The purple domains in figure 5 (b) might have a racemic structure with tilted layers, since the extinction crosses do not rotate under an electric field—only the colour changes. The green and yellow fans are chiral since the extinction crosses change when the polarity of the field is changed. The colour difference between these domains could indicate that chiral domains with tilted and straight layer structures can coexist in one sample. The coexistence of textures with four different colours can also indicate more complicated director structures of the B_7 phase than of B_2. It is possible that the B_7 phase has a C_1 symmetry [1, 18] as was suggested recently by Cladis et al. [19].

4. Conclusion

We have studied individual helical filaments and compared their properties with non-helical filaments. We showed that the chirality becomes important only when an undulation occurs and coils form. A coil stabilizes the growing and suppresses the penetration of molecules from the isotropic phase, leading to movement of the tip with constant speed. The mechanism of the filament to fan-shaped transitions and the electro-optics of the B_7 phase require further study.

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