

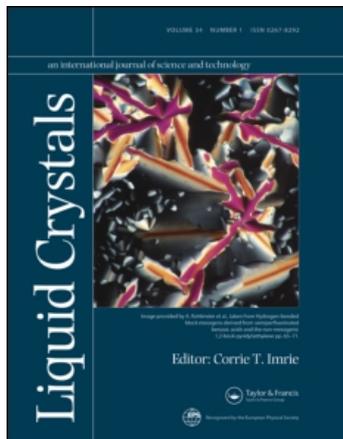
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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Jakli, A. , Lischka, Ch. , Weissflog, W. and Pelzl, G.(2000) 'Textural transformations of a smectic phase with asymmetric banana-shaped molecules', *Liquid Crystals*, 27: 6, 715 – 719

To link to this Article: DOI: 10.1080/026782900202174

URL: <http://dx.doi.org/10.1080/026782900202174>

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Textural transformations of a smectic phase with asymmetric banana-shaped molecules

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(Received 22 September 1999; accepted 20 December 1999)

Materials consisting of asymmetric banana-shaped molecules may form a smectic C_G phase having C_1 symmetry. We have studied textural transformations in a smectic phase of an asymmetric chlorine-substituted banana-shaped material under electric and mechanical fields. We observed two novel features that have not been observed so far on corresponding materials with symmetric banana-shaped molecules. These observations, however, could be explained by the same arguments as were used for the symmetric molecules. Although our studies do not exclude the possibility that the material has C_1 symmetry, we suggest that the chlorine molecules are positioned arbitrarily and the bulk has C_2 symmetry.

1. Introduction

The polar tilted smectic (B_2) phase of achiral banana-shaped molecules [1] represents a new class of soft materials. It usually appears from the isotropic liquid and has C_2 symmetry due to the simultaneous appearance of two symmetry-breaking transitions: a polar packing of the bent-core molecules, and a tilt of the molecular plane. Bulk samples generally contain both 'chiral' and 'racemic' domains [2]. In the chiral state the chirality of neighbouring layers is the same, whereas in the racemic state the chirality alternates in subsequent layers. These molecular structures may form various macroscopic textures that are sensitive to a number of external factors. The main features of textural transformations observed so far are the following. Cooling from the isotropic phase the texture tends to be racemic, but heating from lower temperature phases the chiral domains become dominating. The relaxed ground state is antiferroelectric [2, 3], which can be switched to ferroelectric. Voltage dependence of the net polarization indicates [4, 5] that the antiferroelectric ground state of banana-shaped molecules is much softer than that of chiral antiferroelectric smectic materials [6]. Although the chirality of the layers tends to remain constant during switching [4], the long term application of fields

may lead to changes in the chirality [5]. In one material of symmetric banana-shaped molecules it was observed that under rectangular fields the sample becomes fully chiral, whereas triangular fields transform it to racemic. In zero electric fields both the racemic and the chiral states were stable.

In principle, banana-shaped molecules may also form the so-called smectic C_G phase [7, 8] with C_1 symmetry (the molecular long axis is tilted in the plane of the bent molecules), but no experimental evidence of such a phase has yet been found. In monochlorine-substituted banana-shaped compounds the central part of the molecule is asymmetric due to the position of the chlorine. If the molecules were packed with chlorine showing arbitrarily up or down, the symmetry of the materials would be the same C_2 as of symmetric molecules, see figure 1(a). It might happen however, that the interactions between neighbouring Cl–C bonds favour molecular packing with the chlorine atoms on the same side. In this case the molecules may prefer to tilt with respect to the layer normal in the plane of the molecules, see figure 1(b). NMR studies indicate that the conformation of the mono-substituted materials really deviate from the respective di- and non-substituted symmetric molecules. Electro-optical studies [9] on 4-chloro-1,3-phenylene bis-[4-(4-alkoxyphenyl)liminomethyl]benzoates also showed a complicated switching behaviour, which would be an indication for C_1 symmetry.

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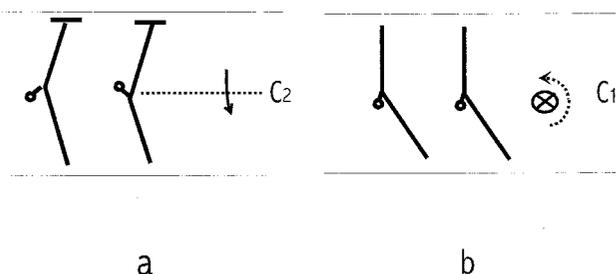


Figure 1. Possible arrangements of asymmetric (mono-substituted) bent-core molecules. (a) The substituted molecules are positioned arbitrarily up and down and the plane of the bent-core molecules is tilted with respect to the layer normal (nails indicate the parts of the molecules that are closer to the observer). The material has C_2 symmetry and the polarization is along the symmetry axis. (b) The asymmetric part of each molecule is positioned in the same direction, and energetically a tilt is favoured along the plane of the molecules (a tilt with respect to the layer normal may also exist). In this case the material has a C_1 symmetry and is polar with random polarization direction.

In this paper we present detailed textural studies of the above mono-substituted material under various electric and mechanical treatments. In order to find an indication of the bulk symmetry we compare the textural transformations with those of symmetric banana-shaped molecules.

2. Results

Textures that appear on cooling from the isotropic phase show racemic-type switching below $E_{th} \cong 2.8 \text{ V } \mu\text{m}^{-1}$ fields (grainy texture, which is not sensitive to the sign of the electric field). Textures formed after heating from the lower temperature phase are brighter and possess larger domains. This state shows a rotation of the average optic axis without a threshold (see figure 2) indicating the presence of both chiral and racemic domains. The variation of the optic axis increases abruptly at $E_{ch} = 3 \text{ V } \mu\text{m}^{-1}$ and a purely chiral-type switching appears (different domains exist, which switch oppositely). Similar behaviour was found in some symmetric banana-shaped molecules [5], but in the present case the chiral state relaxes back to the racemic structure after field removal. The relaxation process is represented in figure 3, where the time dependence of the transmitted light intensity under a field and after field removal is plotted. Under alternating fields small domains of different chirality switch oppositely and the time average of the transmitted light intensity is low. Immediately after field removal the sample quickly assumes a bright greenish fan-shaped texture, which can be assigned to an antiferroelectric anticlinic chiral state. This gradually

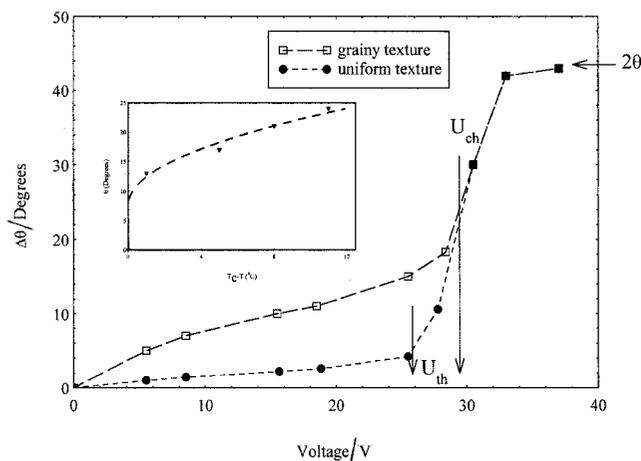


Figure 2. Voltage dependence of the modulation of the optical axis for initially grainy texture (\square) and for uniform textures induced by shear (\bullet) of $10 \mu\text{m}$ films. At U_{zz} the uniform texture starts to modulate (threshold for zigzag layer deformation) and stripes form perpendicular to the smectic layers. At U_{ch} the sample becomes completely chiral consisting of domains with opposite chirality. The insert shows the temperature dependence of the tilt angle (half of the maximum modulation angle).

relaxes to a grainy texture corresponding to an antiferroelectric racemic state. The field-induced racemic-to-chiral transition can be understood by assuming that the synclinc structures have smaller free energy than the anticlinic states [5]. In zero fields the antiferroelectric racemic state is synclinc, whereas at high fields, when the ferroelectric state is induced, the chiral state becomes synclinc, i.e. energetically favourable. Turning the field off, the antiferroelectric arrangement returns, making the racemic state preferable again. In the previous example of symmetric molecules, the racemic state did not reform spontaneously by a relaxation process, but could be induced only by triangular fields. This indicated that the induced chiral state was metastable and the potential barrier to reach the more stable state was much larger than the thermal energy. It follows that the observation of the relaxation in the present case indicates a smaller potential barrier.

The relaxation time τ depends on the surface properties. For films with rubbed polyimide surface $\tau \sim 1 \text{ h}$, whereas for films on clean ITO surfaces $\tau < 10 \text{ s}$ was found (figure 3 refers to this situation). This observation shows that the depth of the metastable state is greatly influenced by surface interactions. Polyimide coating provides a stronger anchoring, thus impeding the nucleation. In figure 4 relaxation time is plotted as a function of temperature. From the slope of $\ln \tau$ vs. $1/T$ we obtain an activation energy $U = 6 \times 10^{-19} \text{ J}$. From the molecular weight (~ 700)

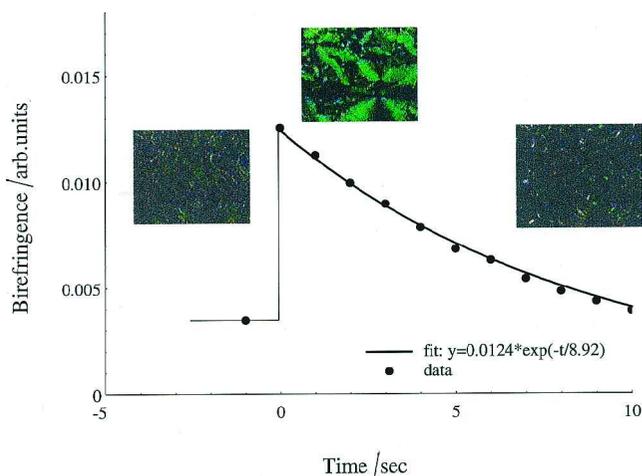


Figure 3. Typical textures of a $10\ \mu\text{m}$ ITO coated film when switching the film with voltages larger than U_{ch} , and after removing the field. During application of the field the sample consists of oppositely switching domains. Immediately after field removal the sample turns quickly to a greenish fan shaped texture, then gradually relaxes to a grainy texture.

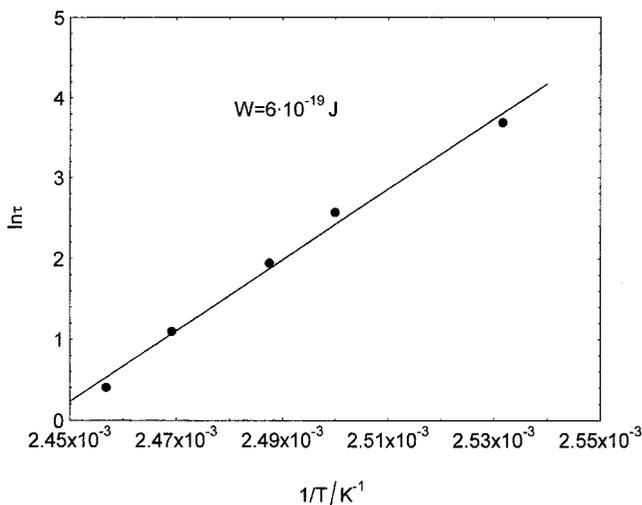


Figure 4. Temperature dependence of the relaxation time of a $10\ \mu\text{m}$ ITO coated film (corresponding to figure 3). The activation energy W is calculated from the slope of the linear fit to $\ln \tau$ vs. $1/T$.

and the mass density ($\sim 10^3\ \text{kg m}^{-3}$) we estimate that the number density of the molecules is $10^{27}\ \text{m}^{-3}$. As planar alignment is favoured the effective area occupied by a molecule is $A \sim 10^{-17}\ \text{m}^2$. Taking into account that the surface anchoring energy is typically $W \sim 10^{-2}\ \text{J m}^{-2}$, we obtain an adhesion energy for a surface molecule of $W \times A \sim 10^{-19}\ \text{J}$. This is comparable to the activation energy, indicating that the chiral phase is stabilized mainly by surface anchoring.

On shearing (amplitude $\sim 100\ \mu\text{m}$, frequency $\sim 1\ \text{Hz}$) a uniform texture appears that shows only a weak electro-optical switching below E_{th} (figure 2). The uniform texture forms more readily for thinner films. For $5\ \mu\text{m}$ films it appears in the entire B_2 phase after a few periods of the shear, whereas for $10\ \mu\text{m}$ films it could only be induced a few degrees below the clearing point. The extinction direction of the uniform texture coincides with the direction of the shear, figure 5(a). Similar textural transformations have been observed under the simultaneous application of electric field and shear on some materials containing symmetric molecules [10]. The difference is that in the present case no electric field was applied. To understand the structure of the shear-induced uniform state in figure 6 we compare the viscosity of three different geometrical arrangements labelled as VV, VH and TH. The viscosity is smallest for a texture where the projection of the molecules onto the plane of the shear (XY) is elongated along the flow. In the VV texture both the layers and polarization are vertical and the projection of the molecules onto the plane of the

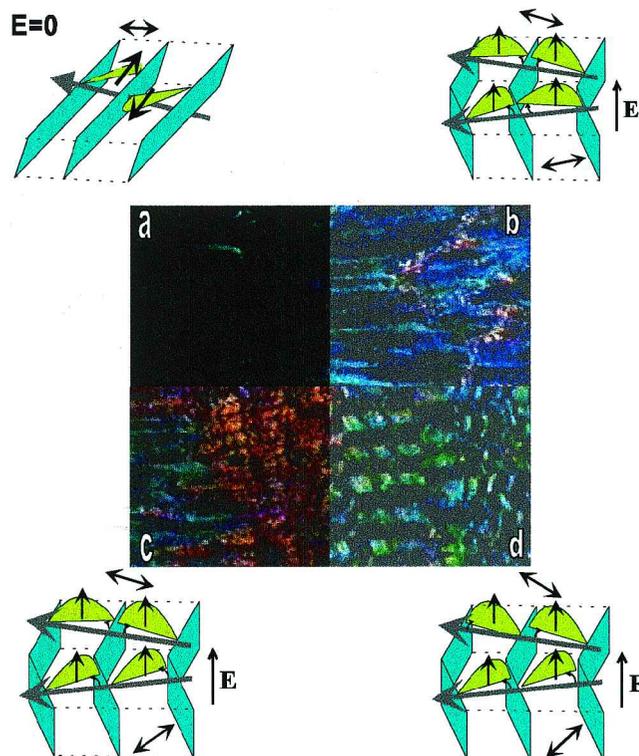


Figure 5. Electric field-induced textural transformations and their corresponding structures on a $5\ \mu\text{m}$ thick cell sheared prior to electric field treatment. (a) $U = 0\ \text{V}$, tilted racemic antiferroelectric state; (b) $U = 14\ \text{V}$, zigzag racemic ferroelectric; (c) $U = 15\ \text{V}$, mixed zigzag racemic and chiral ferroelectric; (d) $U = 16\ \text{V}$, zigzag chiral ferroelectric.

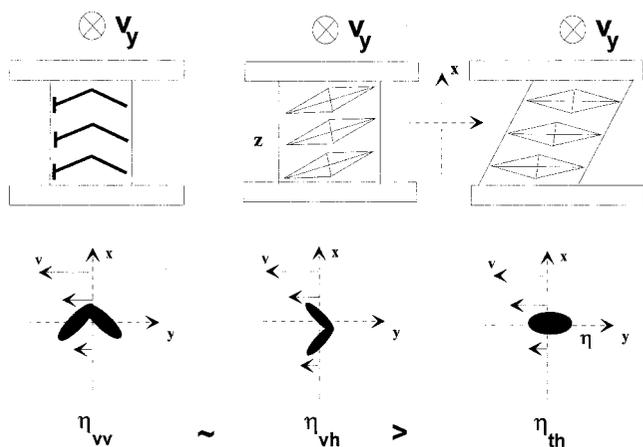


Figure 6. Viscosity of three different geometrical arrangements. (a) Vertical (bookshelf) layer structures with vertical electrical polarization (η_{vv}); (b) bookshelf texture with horizontal polarisation (η_{vh}); (c) the layers are tilted (or bent) and the polarization is horizontal (η_{th}).

shear has a bent-shape. Such a structure is favoured by strong electric fields, but it is not optimal under shear. In the VH structure the layers are vertical, but the polarization is horizontal; the projection of a molecule also has a bent-shape, but with different orientation. The most favourable situation corresponds to the TH structure, where the layers are tilted (or bent), so that the molecular plane and the polarization are horizontal. In this case the relevant projection of the molecules is elongated along the shear. Accordingly, we propose that the shear-induced uniform texture of figure 5(a) corresponds to the TH structure presented in figure 6(c). In addition the TH texture also minimizes the surface energy, since the molecular plane is along the substrate. This explains the observation that the texture appears more readily in thinner films.

Applying a field above a threshold ($\sim 2.8 \text{ V } \mu\text{m}^{-1}$) first the uniform TH texture becomes modulated, figure 5(b). This textural transformation is analogous to the chevron-to-stripped bookshelf transformation observed frequently in SmC^* materials [11] and indicates a racemic state with layers in zigzag formation. The same kind of transformation was found for a symmetric banana molecule [10]. At $E_{\text{ch}} \sim 3 \text{ V } \mu\text{m}^{-1}$ a grainy texture appears first along defect lines, then gradually fills the whole area, figure 5(c). This is a mixed state containing both racemic and chiral domains. On slightly increasing the field a chiral zigzag texture forms, figure 5(d). This texture consists of domains of reversed chirality where the optic axes rotate in opposite directions. This transformation is basically the same as that described in figure 2. The zigzag modulation of this latter case is simply due to the fact that it formed from a tilted or bent layer

structure. Under shear the zigzags disappear quickly, since the layers prefer to lie along the flow. After field removal the racemic texture reforms gradually. Interestingly a more or less uniform texture forms again when the relaxation occurs directly from the zigzag structure. This indicates that the layers remain somewhat tilted (probably near the substrates) even in the zigzag structure. Similar to the figure 3 situation, the relaxation time decreases from an hour to a few minutes as the temperature increases and the liquid crystal approaches the isotropic state.

3. Summary

We have studied textural transformations in a material consisting of asymmetric banana-shaped molecules and compared them with previous results on symmetric banana-shaped molecules. We found that the textural transformations are similar with the following minor differences:

- In the antiferroelectric racemic state the shear alone could induce a transition from a bookshelf texture to a tilted layer structure with horizontal molecular phases.
- After field removal the electric field-induced chiral state relaxed back to the racemic state.

Both features indicate that the potential barrier between the synclinic and racemic states is relatively small, but otherwise they can be explained by the same arguments as were used for symmetric molecules. Although our studies do not exclude the possibility that the material has C_1 symmetry, we propose that the chlorine molecules are positioned arbitrarily as sketched in figure 1(a), i.e. the bulk material has C_2 symmetry. The experimental verification of a ferroelectric liquid crystal material with C_1 symmetry is still an open issue.

This work was supported by the Hungarian Science Fund OTKA 023102 by a Volkswagen Stiftung between Budapest and Berlin and by the NSF ALCOM Center under Grant DMR 89-20147.

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