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## Liquid Crystals

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# Ferroelectric lyo-mesophase of banana-shaped molecules

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Preliminary results are reported on the first ferroelectric ‘lyo-mesophases’ of banana-shaped molecules. We studied the effect of the non-polar solvents *p*-xylene and *m*-xylene on the macroscopic properties of banana-shaped molecules having a B<sub>7</sub> phase. It was observed that by adding only 15% of solvent the isotropic–B<sub>7</sub> transition temperature was lowered from 130°C to 70°C and the ferroelectric electro-optical switching range was extended from 1–2°C to more than 50°C, thus maintaining the switching even at room temperature. The xylene molecules act as spacers, maintaining larger separations between the banana-molecules, thus reducing the polar packing order. These observations provide unique opportunities for tuning the intermolecular interactions of banana-shaped molecules and modifying their macroscopic properties.

## 1. Introduction

Recently it was shown that by dissolving polar disc-shaped molecules in apolar organic solvents ferroelectric lyotropic liquid crystals could be produced [1]. The electro-optical switching properties of the solution are some extent better than those of the pure columnar liquid crystals, since the switching threshold and phase transition temperatures are lowered [2]. These results imply that lyo-mesophases in non-aqueous solvents could be used in electro-optical devices; this motivated us to explore similar lyo-mesophases in polar ‘banana-shaped’ molecules. Banana-shaped mesogens comprise a new class of materials. Although more than sixty years ago Vorländer already reported the synthesis of bent-shaped liquid crystals [3], they did not attract much interest until Matsunaga *et al.* [4] synthesized new mesogenic compounds with ‘banana-shaped’ molecular structures. Later Niori *et al.* [5] synthesized the corresponding octyl derivatives and observed ferroelectric polarization without any electro-optical switching. First it was suggested [5, 6] that these compounds have a polar smectic A type structure with C<sub>2v</sub> symmetry in layers. Later Heppke *et al.* [7] found that the electrically switchable phase shows electro-optic effects, and it has a tilted SmC-like texture. Link *et al.* gave the first evidence for the antiferroelectric SmC-type structure [8]. They also pointed out that, due to the simultaneous director tilt and polar order, each smectic layer loses its inversion symmetry and becomes chiral, although the

molecules contain no chiral carbons. Depending on the relative orientations of the two-fold symmetry axis and the tilt direction, the layers can be right- or left-handed. There are a number of ‘banana’ phases [9, 10], which are tentatively labelled as B<sub>1</sub>–B<sub>7</sub> [11]. Among them B<sub>2</sub>, B<sub>5</sub> and B<sub>7</sub> are switchable ferroelectric smectic phases, but the exact structure of B<sub>5</sub> and B<sub>7</sub> are not yet known. Although the thermotropic ferroelectric and antiferroelectric aspects of these materials are extremely interesting from the academic point of view, their practical applications are strongly restricted by the high temperature ranges (well above 100°C) of the switchable phases, and by the difficulty in achieving uniform alignment. Based on the results on disc-shaped molecules it could be anticipated that the ferroelectric phase of the banana-shaped molecules would be maintained when dissolved in a non-polar solvent, but with considerably lower phase transition temperatures.

## 2. Experimental results

For our studies we chose the material 1,3-phenylene bis[4-chloro-(4-*n*-octyloxyphenyliminomethyl)benzoate] (PBCOB) [12]. This material has a B<sub>7</sub> phase between 133°C and 90°C. It has a smectic structure with a layer spacing of 3.85 nm and with a complex in-layer structure [11]. The hallmark of the B<sub>7</sub> phase is the formation of helical filaments [13, 14] at the transition from the isotropic phase.

We have studied the effect of *para*- and *meta*-xylenes on the properties of PBCOB. The molecular mass of

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the xylene molecules is only 108; they do not contain any polar groups, i.e. they are basically non-polar. The interaction force between xylene molecules is a London-type dispersion force, explaining the low (138°C) boiling point. We studied both *m*-xylene and *p*-xylene, which differ only in the position of the methyl group: *p*-xylene is linear whereas *m*-xylene has a bent-shape. The bent shape renders *m*-xylene a permanent dipole, but this is so small that the intermolecular interaction is still mainly London-type as evidenced by their almost identical boiling points. The structures of the banana-shaped liquid crystal and the xylene molecules are illustrated in figure 1.

Our main observations are summarized in the following paragraphs.

The pure liquid crystal forms helical filaments ('telephone-wire-like structure') typical for the B<sub>7</sub> phases. Very near to the clearing point (within about 1°C) we observed a weak electro-optical response of the material above 10 V μm<sup>-1</sup> fields.

On adding a small amount (3–10 wt %) of xylene to the banana-shaped molecules, an interesting alignment effect appears. Instead of forming helical filaments, wide smooth and weakly birefringent stripes form and grow straight at the transition to the B<sub>7</sub> phase. During growth they also widen, and the adjacent stripes tend to grow parallel to each other. As a result, fairly uniform weakly birefringent textures appear indicating that the smectic layers are mainly parallel to the substrates; see figure 2(a). On cooling further by a few degrees, the texture gradually transforms to uniform, highly birefringent regions corresponding to bookshelf-type layer structures; see figure 2(b). Under electric fields the switching is similar to the pure

## 'banana-shaped' molecule

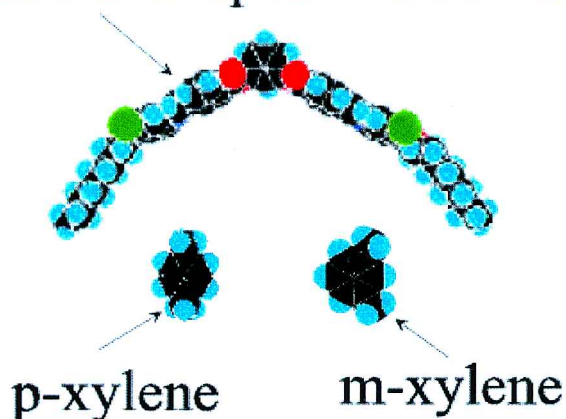


Figure 1. Structures of the materials used. The banana-shaped liquid crystal is 1,3-phenylene bis[4-chloro-4-*n*-octyloxy-phenyliminomethyl]benzoate (PBCOB), the apolar solvents are *p*-xylene and *m*-xylene.

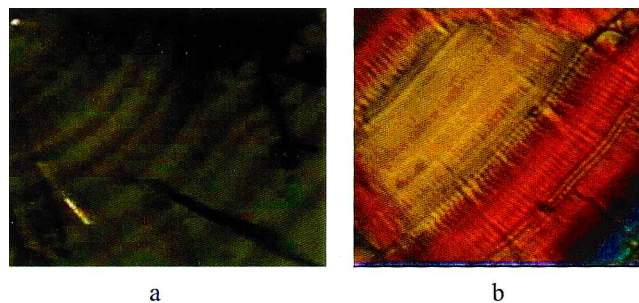


Figure 2. Typical textures in the B<sub>7</sub> phase of the mixture of 5 wt % *p*-xylene and 95 wt % PBCOB. (a) Initial homeotropic texture; (b) the same area at 5°C lower temperatures. The pictures represent 0.5 × 0.4 mm<sup>2</sup> areas.

material, but with slightly decreased threshold (8 V μm<sup>-1</sup>) and with widened temperature range for the switchable region (~5°C).

At higher xylene concentrations (10–35 wt %) the formation of helical filaments, similar to those observed in the pure 'banana' materials [13] can again be observed. Photographs of a growing filament are shown in figure 3. When the phase transition is complete the filaments coalesce into small fan-shaped domains. This concentration region proves to be the most important regarding electro-optical behaviour. Samples with xylene concentrations in the region of 15 wt % can be switched

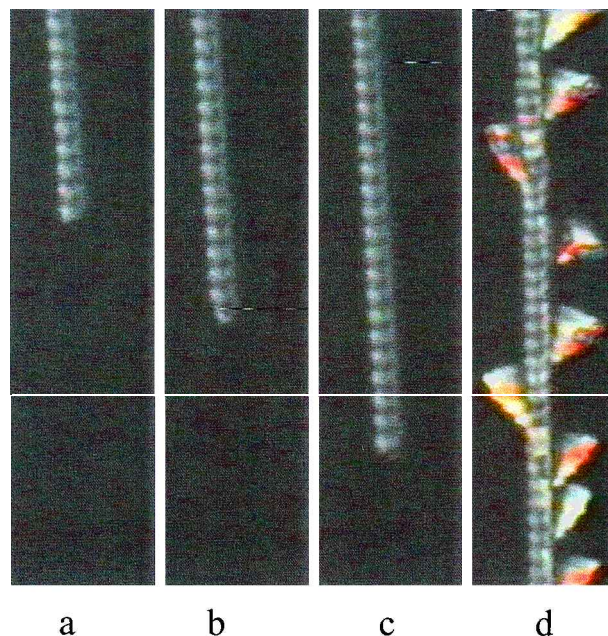


Figure 3. Helical filamentary structures forming at 69°C on cooling from the isotropic state of the system 83 wt % PBCOB + 17 wt % *p*-xylene. (a) A growing telephone-wire-like helical filament; (b) same as (a) after 5 s; (c) same as (a) after 10 s; (d) a 'blooming' filament formed before coalescing to fan-shaped domains. Each picture represents 40 × 200 μm<sup>2</sup> areas.

over a wide temperature range, down to room temperature. The threshold voltage for switching is  $4 \text{ V } \mu\text{m}^{-1}$  at  $1^\circ\text{C}$  below the clearing point and is  $10 \text{ V } \mu\text{m}^{-1}$  at room temperature. Such textures show an isotropic  $B_7$  phase transition at around  $70^\circ\text{C}$ . The switching is represented in figure 4, which shows the rotation of the optical axis of fan-shaped domains by  $\pm 10^\circ$  from the zero-field direction. The switching indicates a chiral structure that switches between two ferroelectric states.

We measured the polarization current during switching (figure 5). Although the conductivity of the material is relatively high, it is clearly seen that there is only one

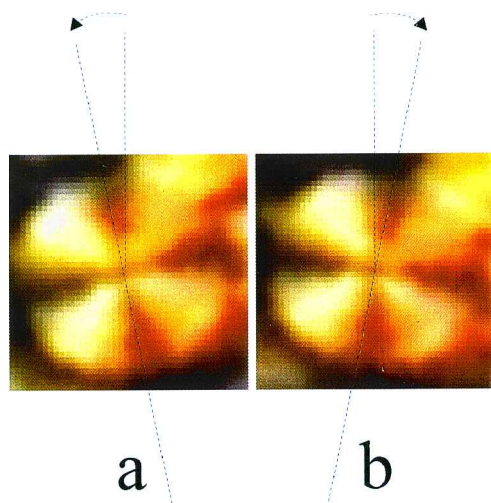


Figure 4. Switching of a fan-shaped domain at room temperature under  $\pm 5 \text{ V } \mu\text{m}^{-1}$  fields of the system 83 wt % PBCOB + 17 wt % *p*-xylene. The pictures represent  $50 \times 50 \mu\text{m}^2$  areas.

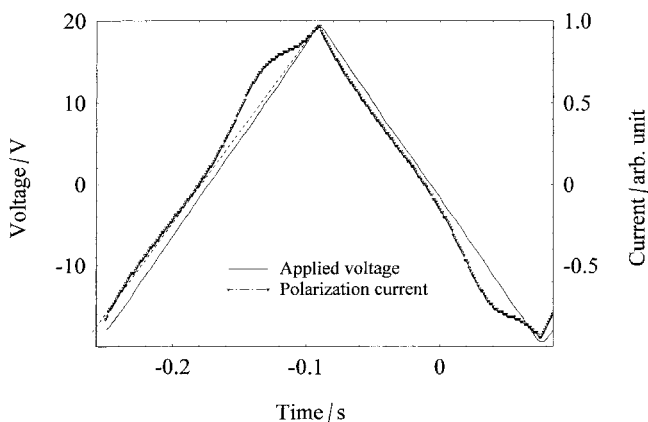


Figure 5. Time dependence of the polarization current in a  $5 \mu\text{m}$  film of the system 83 wt % PBCOB + 17 wt % *p*-xylene at  $T = 39^\circ\text{C}$ . The magnitude of the polarization ( $220 \text{ nCcm}^{-2}$ ) is calculated from the area of the polarization curve above the dotted line, which represents the background due to the conductivity.

polarization peak in each half period. This indicates a synclinc ferroelectric-type ground state ( $\text{SmC}_s\text{P}_F$ ). A ferroelectric ground state of the  $B_7$  phase of purely non-chiral banana-shaped molecules was also reported recently by Walba *et al.* [15]. The magnitude of the polarization is  $220 \text{ nCcm}^{-2}$  at  $40^\circ\text{C}$ , which is about five times larger than the value measured in the pure banana compound near to the isotropic phase [16].

When the xylene concentration is more than about 35 wt% the material remains isotropic even at room temperature. Leaving the sample unsealed, it was observed that the xylene did not evaporate completely, but an optically isotropic jelly-like substance remained. In this state the banana-shaped molecules crystallize out slowly in structures that, to some extent, resemble the filaments that appear in systems of moderate xylene concentration. Typical structures can be seen in figure 6. Although the number of separated crystal domains increases slowly the majority of the xylene molecules are trapped in the 'brownish jelly' even after 6 months.

Differential scanning calorimetry (DSC) was used to study the phase sequences. In agreement with microscopic observations, the results indicate that the two-phase range, and the difference between the isotropic- $B_7$  transitions broaden with increasing xylene concentrations. It is noticeable that on cooling the peaks are relatively narrow, indicating sharp transitions and quite uniform textures. On heating the samples from room temperature the two-phase range widens. We think that this is due to the concentration of inhomogeneities caused by segregation of the xylene and the liquid crystal

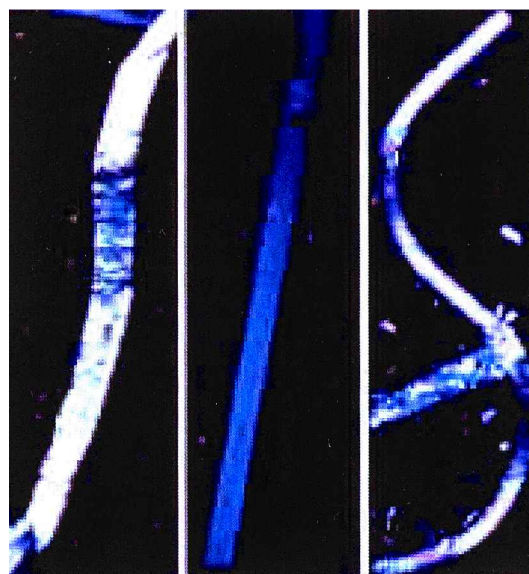


Figure 6. Crystal structures grown at room temperature in the system 50 wt % PBCOB + 50 wt % *p*-xylene. The pictures represent  $50 \times 200 \mu\text{m}^2$  areas.



molecules at low temperatures. In the isotropic phase the solution becomes uniform, i.e. the isotropic–smectic transition is again sharp on cooling. The isotropic–B<sub>7</sub> phase transitions, as deduced from the DSC measurements, are shown in figure 7. Within measurement errors the phase transition temperatures decrease linearly with increase in concentration of the xylene. The *m*-xylene has a larger effect on the suppression of the clearing point, than has the *p*-xylene. It is important to keep in mind that the molecular mass of the liquid crystal is eight times that of the xylene. Accordingly 11 wt% corresponds to about 50 mol%, and 30 wt% is to ~77 mol% concentrations.

### 3. Discussion

Because of the bent core of the banana-shaped molecules of PBCOB, and the large dipoles of several polar groups in the core, the molecules are polar and intermolecular interactions are mainly of the dipole–dipole type. Xylene molecules are relatively small, so they can fit between the banana-shaped molecules. As they maintain a larger separation between the liquid crystal molecules, they weaken the dipole–dipole interaction. This is clearly seen in the decreased phase transition temperatures and is consistent with the observation that the more bulky *m*-xylene (see figure 1) has a larger effect on the phase transition temperatures (see figure 8). The phase separation observed at low temperature probably takes place only at a microscopic level, since the phase structure resembles lyotropic phases without a distinct phase boundary.

In summary we have developed new lyo-mesophase systems by mixing non-polar xylene and polar banana-shaped liquid crystal molecules. We observed the

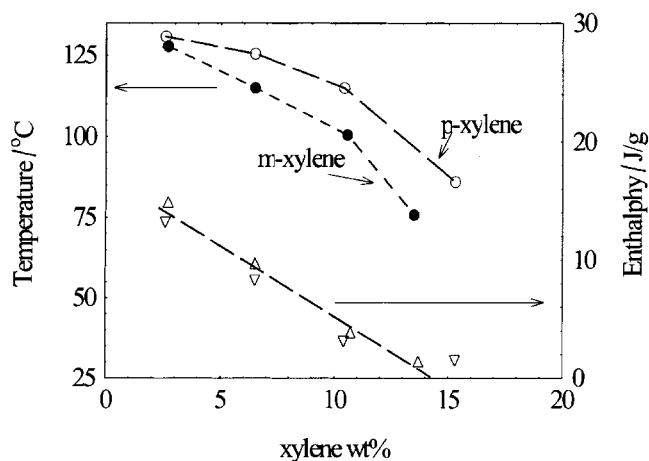


Figure 7. Clearing point and transition enthalpies of banana-shaped PBCOB as a function of xylene concentration. The solvent *m*-xylene has the same structure as *p*-xylene, but it is bent.

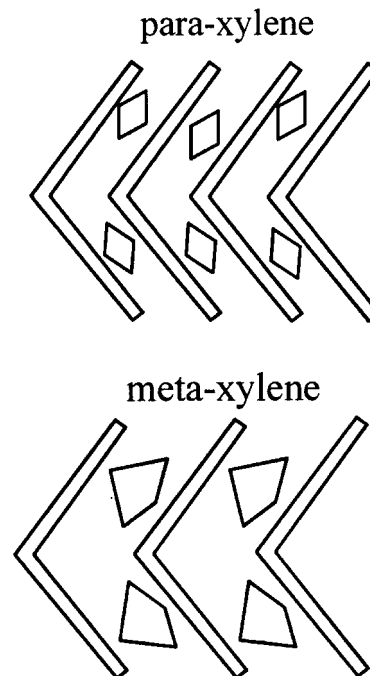


Figure 8. Illustration of the position of the *p*-xylene and *m*-xylene molecules and their effect on the banana-shaped molecules.

formation of the mesophase B<sub>7</sub> with up to 30 wt% (77.4 mol%) of xylene. The role of the apolar solvent is to soften the polar structure by keeping the banana-shaped molecules further apart. These results give the first example of a switching achiral banana-shaped liquid crystal at room temperature. Earlier attempts, mixing different banana-shaped molecules, did not result in a decrease of the phase transition or the widening of the switchable phase. These observations therefore represent a significant advance toward applications of liquid crystals formed by achiral banana-shaped molecules. Although there are a number of difficulties to overcome (e.g. suppression of the two-phase range), we believe that this kind of system deserves further investigation, even in connection with display applications. In future work we will systematically vary the structures of both the liquid crystals and the apolar solvents.

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