

## Macroscopic chirality of a liquid crystal from nonchiral molecules

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The transfer of chirality from nonchiral polymer networks to the racemic  $B_2$  phase of nonchiral banana-shaped molecules is demonstrated. This corresponds to the transfer of chirality from an achiral material to another achiral material. There are two levels of chirality transfers. (a) On a microscopic level the presence of a polymer network (chiral or nonchiral) favors a chiral state over a thermodynamically stable racemic state due to the inversion symmetry breaking at the polymer-liquid crystal interfaces. (b) A macroscopically chiral (enantiomerically enriched) sample can be produced if the polymer network has a helical structure, and/or contains chemically chiral groups. The chirality transfer can be locally suppressed by exposing the liquid crystal to a strong electric field treatment.

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### INTRODUCTION

Many liquid crystal phases [e.g., cholesteric, blue, twisted grain boundary (TGB) and chiral smectic- $C$  ( $Sm-C^*$ ) phases] are chiral due to the introduction of chirality by molecules containing chiral carbons. The long-range orientation order and the chirality of the molecules result in a spontaneous twist over the micrometer range, i.e., the chirality transfers from the molecular range to the “mesoscopic” [1] range, and the phase becomes chiral. Chiral phases can also occur without chiral molecules by spontaneous symmetry breaking [2]. Recently, a fascinating example of achiral symmetry breaking was found [3] in tilted smectic phases of bent-core (banana-shaped) molecules [4]. In the so-called  $B_2$  phase [5], banana-shaped molecules pack into polar layers. Due to the simultaneous director tilt and the polar order, each smectic layer loses its inversion symmetry and becomes chiral, although the molecules contain no chiral carbons. The chirality of the subsequent layers can alternate (racemic) or can be the same (chiral) over several microns. These structures and their behavior in electric fields are shown in Fig. 1. When no field is applied, both the racemic and chiral structures form antiferroelectric states, i.e., the polarization alternates in subsequent layers. The antiferroelectric racemic state is “synclinic,” i.e., in subsequent layers the molecular planes are all tilted in the same direction. The structure of the racemic state therefore can be described as  $Sm-C_s P_A$ , where  $P$  designates the polar order, subscript  $A$  stands for “antiferroelectric,” and subscript  $s$  for “synclinic.” In bulk the tilt directions are equivalent, resulting in few-micron-wide stripes. In subsequent stripes the tilt directions are opposite, leading to a modulation of the optical axis by  $\pm\theta$  ( $\theta$  is the director tilt angle). The chiral domains are “anticlinic,” i.e., the director tilt is opposite in subsequent layers, and the optical axis is parallel to the layer normal. They have a  $Sm-C_a P_A$  structure, where the subscript  $a$  stands for “anticlinic.” Strong electric fields ( $E > 3 \text{ V}/\mu\text{m}$ ) cause an antiferroelectric to ferroelectric (AFE  $\rightarrow$  FE) transition, but the individual layer chirality does not change [3]. The corre-

sponding structural changes can be described by  $Sm-C_s P_A \rightarrow Sm-C_a P_F$  and  $Sm-C_a P_A \rightarrow Sm-C_s P_F$  (the subscript  $F$  stands for ferroelectric) transitions. In the ferroelectric racemic state the optical axis is parallel to the layer normal independent of the sign of the electric field, i.e., no optical switching occurs under square-wave electric fields. In the chiral domains the optical axes are tilted with respect to the layer normal, and their directions change at field reversals (optical switching occurs under square-wave electric fields). This property gives us an easy way to distinguish between racemic and chiral domains.

In some materials it was observed that a square-wave

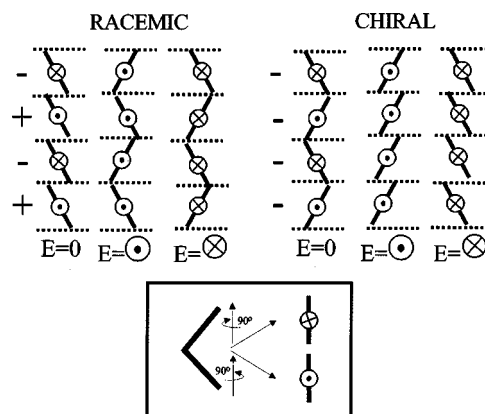


FIG. 1. The Boulder model [3] for the electro-optical switching of the  $B_2$  phase of banana-shaped molecules for racemic and chiral domains. Dotted lines represent the smectic layers. At  $E=0$  the structure is antiferroelectric. On application of an electric field  $E > E_{th}$ , where  $E_{th}$  is the threshold field required for switching, the structure changes over to ferroelectric. The sign to the left of each layer indicates the chirality descriptor for that layer. In the racemic state the optic axis is parallel to the layer normal both when the electric field points out ( $E=\bullet$ ) or in ( $E=\otimes$ ) at the plane of the page. In the case of chiral domains the optic axis depends on the field direction, and rotates to the left or right as determined by the director tilt angle.

electric field eventually (in a few minutes) could change racemic domains to chiral domains [6]. On a macroscopic scale the number of left- and right-handed domains is the same, i.e., the entire film is still racemic. However it was found [3] that very small (~1 wt%) amount of chiral dopants, added to the achiral banana-shaped molecules, can induce a uniform chirality in the whole sample.

These experiments illustrate that chiral and racemic states are very close energetically, and motivated us to explore whether chirality could be introduced by surface interactions as well. In this paper we show that polymer networks can transfer chirality to the ferroelectric liquid crystal phase of banana-shaped molecules both at microscopic and macroscopic levels.

**EXPERIMENTAL RESULTS**

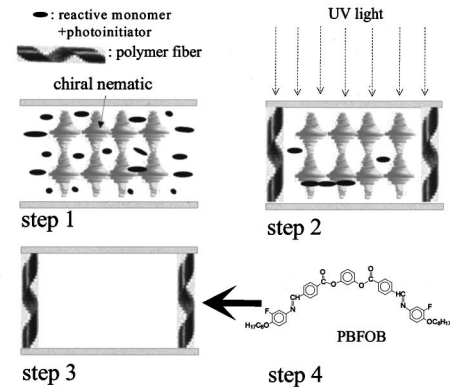
For our studies we chose a liquid crystalline material of banana-shaped molecules 1, 3-phenylene bis[3-fluoro-4-*n*-octyloxyphenyliminomethyl] benzoate] (PBFOB) [7], because it forms completely racemic textures when it is filled into 5- $\mu$ m-thick empty cells. This can be judged by the presence of fine stripes in the antiferroelectric ground state, and by the electro-optical response that is not sensitive to the sign of the electric field. PBFOB has a *B2* phase between 110 and 161 °C. The electrical and optical properties of the material were described in Ref. [8].

The properties of this material were studied in three types of polymer networks. Type 1 cells were prepared from non-chiral monomers (nc) dissolved in nonchiral nematic liquid crystals. In type 2 samples the nonchiral monomers were dissolved in a chiral nematic liquid crystal. Type 3 cells contain chiral monomers (cm) dissolved in nematic liquid crystals. Obviously type 1 cells are nonchiral on neither molecular nor macroscopic levels. Type 2 cells are nonchiral on the molecular level, but presumably are chiral on the macroscopic level. Type 3 cells are chiral both on molecular and macroscopic levels. The macroscopic chirality of a polymer network formed in a chiral liquid crystal was predicted by de Gennes [9], and experimentally verified [10,11]. We made attempts to see the helix by UV-visible spectroscopy, but the reflections were not strong enough to draw definite conclusions. All cells were prepared by the following steps.

*Step 1:* The mixtures of preparation liquid crystal, reactive monomers, and photoinitiators were capillary filled into 5- $\mu$ m cells consisting of two glass plates with inner surfaces coated by transparent conductive indium tin oxide and by unidirectionally rubbed polyimide alignment layers that promote uniform alignment of rod-shaped liquid crystal molecules parallel to the glass plates.

*Step 2:* The samples were irradiated by UV light that induced a free-radical polymerization of the reactive monomer. The polymers separated out and formed a physical network.

*Step 3:* The liquid crystal and the dissolved low mass components were removed by immersing the cells into pure acetone. The removal was considered to be complete only when the samples were optically isotropic (black between crossed polarizers).



Cell	Name	Description	Structure
0	BLC	Pure banana liquid crystal (PBFOB)	racemic
1a	2%nc-PN-BLC	BLC in polymer network (PN) made from non-chiral monomer (nc) dissolved in nematic liquid crystal	~60% chiral (both signs)
1b	5%nc-PN-BLC		>90% chiral (both signs)
2a	2%nc-PN-BLC (5%cd)	BLC in PN cells made from nc in nematic liquid crystal mixed with a chiral dopant (cd)	~60% chiral (one sign)
2b	2%nc-PN-BLC (10%cd)		
2c	2%nc-PN-BLC (25%cd)		
2d	5%nc-PN-BLC (5%cd)		
3a	2%cm-PN-BLC	BLC in PN made from chiral monomer (cm) dissolved in nematic liquid crystal	~60% chiral (one sign)
3b	5%cm-PN-BLC		>90% chiral (one sign)

*nc:* 4,4'-bis[6-[(methacryloyloxy) hexoxy] benzoate]-1,1'-biphenyl (BMBB6)  
*cm:* 4,4'-bis [(S)-1-methylheptyloxy]-2,2'-diacryloxy biphenylene (BMDAB)  
*cd:* R1011 (Merck); NLC: E48 (Merck); photoinitiator: Irgacure 165 (Ciba additive)  
**PBFOB:** 1,3-phenylene bis[3-fluoro-4-noctyloxy-phenyliminomethyl] benzoate

FIG. 2. Schematics of the cell preparation procedure and a table with a list of the studied cells. Percentages refer to the weight concentration of the reactive monomers and the chiral dopants in the preparation liquid crystal. *Step 1:* A reactive monomer and a photoinitiator (10 wt % of the monomer) are dissolved in a nematic or chiral nematic liquid crystal. These mixtures are filled in 5- $\mu$ m cells. *Step 2:* The samples are irradiated by UV light with an intensity of 0.4 mW/cm<sup>2</sup>, which induces a free-radical polymerization of the reactive monomer and leads to polymer network formation. *Step 3:* The polymerized cells are immersed in pure acetone to remove the low molecular weight components (the liquid crystal, the chiral dopants, the remaining reactive monomer, and the oligomers). The cells containing only polymer networks are optically isotropic, having fibers mainly parallel to the rubbing direction. *Step 4:* The cells are refilled with banana-shaped molecules (PBFOB). In the schematics the dimensions are not proportional to the actual sizes. In reality the pitch (~1  $\mu$ m) of the helix is much smaller than the sample thickness, and the polymer network is much thicker than the molecules.

*Step 4:* The cells with polymer networks were filled with PBFOB.

This procedure and the parameters of the studied cells are shown in Fig. 2. When the banana-shaped liquid crystal materials were filled in any of the cells containing polymer networks (PN-BLC systems) the textures seen under crossed polarizers showed sensitivity to the polarity of the electric

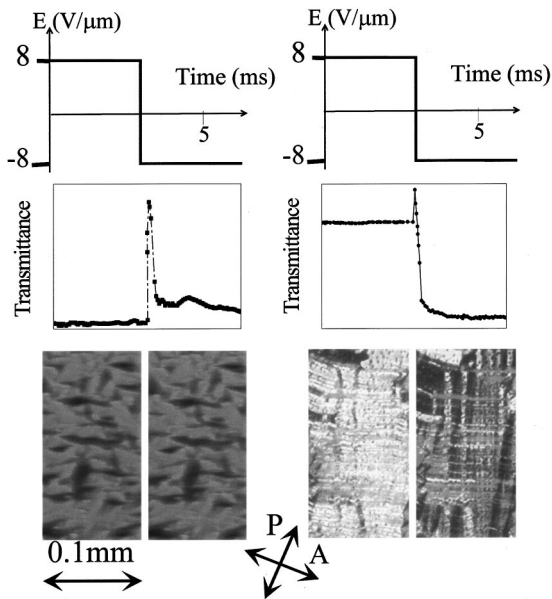


FIG. 3. Polarizing microscopic textures of  $100 \times 200\text{-}\mu\text{m}^2$  areas, and the corresponding time dependencies of the optical transmittances as measured by a photodiode placed in the eyepiece of the polarizing microscope ( $5\text{-}\mu\text{m}$  cells,  $T = 145^\circ\text{C}$ ; the monitored areas are  $1\text{ mm}^2$ ). *Left-hand side*: pure banana liquid crystal cell (BLC). *Right-hand side*: samples containing 5-wt % polymer network made from chiral molecules (5% cm-PN-BLC). Samples are rotated by between crossed polarizers by  $\sim 20^\circ$  with respect to the smectic layers.

fields. This is in contrast to the racemic-type behavior of the liquid crystal filled in an empty cell (see Fig. 3). In the 2% PN-BLC systems, still about one third of the texture possessed a racemic response, whereas more than 90% of the 5% PN-BLC textures showed chiral switching. It is very important to note that even the completely nonchiral polymer network (type 1 cell) rendered chirality to the individual domains. The only difference is that in type 1 cells there were about equal numbers of domains where the optical axis rotated oppositely during switching, whereas in type 2 and 3 samples they all rotated in the same direction.

To make sure that the uniform handedness was not due to any incomplete removal of the chiral molecules, we compared the alignments of the banana-shaped liquid crystals when the polymerization was carried out in the cholesteric and in the isotropic phase of the preparation liquid crystal, respectively. The polymer network formed in the cholesteric phase resulted in a uniform chirality, whereas polymerization in the isotropic phase of the same preparation material provided domains with both signs of handedness. In addition, we prepared a nonchiral polymer network, which we later filled with a chiral nematic liquid crystal. After removing the chiral nematic and filling the cell with PBO, we found equal numbers of left- and right-handed domains. These tests clearly show that the chiral additives were fully removed during the washing-out process, and that the long-range chirality transfer is due to the polymer network.

The sensitivity of the optical signal to the sign of the electric field is a hallmark of chirality [3] (see Fig. 1). For

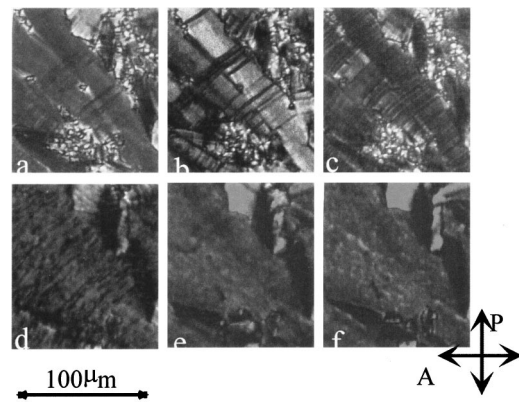


FIG. 4. Behavior of cell 1/b under different electric fields. Upper row: domains formed immediately after cooling from the isotropic phase. (a)  $U = 0\text{ V}$ , (b)  $U = +24\text{ V}$  (c)  $U = -24\text{ V}$ . Bottom row: the same domains after  $U = 40\text{ V}$  was applied for 2 min. (d)  $U = 0\text{ V}$ . (e)  $U = +24\text{ V}$ . (f)  $U = -24\text{ V}$ .

this reason we studied the electro-optical responses under a polarizing microscope. Since the quality of the alignment varies from cell to cell, electro-optical observations alone are not sufficient to compare the chirality of different materials. However, at given temperatures and polarizer-analyzer settings, the relative field dependencies can be deduced from the electro-optical responses alone. In all PN-BLC cells we observed that each domain eventually loses its sensitivity to the sign of the field. An example of this behavior for a type 1 cell is shown in Fig. 4. Virgin domains, formed spontaneously on cooling from the isotropic phase, are sensitive to the sign of the electric field, i.e., they are chiral (see the upper row). Upon application of electric field above  $5\text{ V}/\mu\text{m}$  for a few minutes, the texture lost its sensitivity to electric fields and formed fine stripes after the field removal. This texture is characteristic of racemic domains (see the bottom row of Fig. 4). The birefringence color of the virgin domains at zero fields is the same as that of the induced domains at high fields [compare Fig. 4(a) with Figs. 4(e) and 4(f)]. These observations prove that losing the sensitivity to the polarity of the field is not a misalignment effect, but is due to a field-induced racemization process. Such a behavior resembles that observed previously for nematics impregnated in porous chiral inorganic films [12,13], but there the chirality reverted after field removal. In our case the chirality is permanently suppressed as long as the sample is in the liquid crystal phase. Once the samples are heated to the isotropic phase and cooled back to the liquid crystal state, the switching is again observable under square-wave fields.

For a quantitative analysis we monitored the transmitted light intensities by a photodiode placed in the eyepiece of the polarizing microscope. In the pure liquid crystal cells there is no measurable difference in the transmitted light intensities under positive and negative fields ( $\Delta I = 0$ ), except the transient peak appearing during switching.  $\Delta I$  is also negligible in type 1 cells, provided that the monitored area is sufficiently large ( $\sim 1\text{ mm}^2$ ). In type 2 and 3 cells,  $\Delta I$  is clearly nonzero (see Fig. 3) even in large monitored areas. In sufficiently large areas  $\Delta I$  is proportional to the enantiomeric excess which is defined as the surplus of the chiral domains

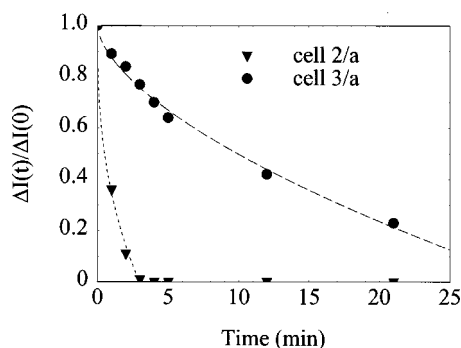


FIG. 5. Plot of  $\Delta I(t)/\Delta I(0)$  for cells 2/a and 3/a.  $\Delta I$  is the difference in the transmitted light intensities under positive and negative fields measured between crossed polarizers in  $1\text{-mm}^2$  areas. The measurements are done after square wave fields ( $E = 18\text{ V}/\mu\text{m}$ ,  $f = 4\text{ Hz}$ ) were applied for  $t$  minutes.

with one sign of the chirality. We measured  $\Delta I$  in constant fields ( $6\text{ V}/\mu\text{m}$ ) before and after high field ( $E = 18\text{ V}/\mu\text{m}$  and  $f = 4\text{ Hz}$ ) treatment. In Fig. 5 we plot the measured values of  $\Delta I(t)/\Delta I(0)$ , where  $t$  is the duration of the high field treatment and  $\Delta I(0)$  describes the virgin cell. For type 2 cells the enantiomeric excess is zero after a few minutes of high field treatment. For type 3 cells, however, the enantiomeric excess is measurable even after  $t > 20$  min. Not only the durations, but also the threshold fields, needed for suppression of the chirality are smaller in type 1 and 2 cells than in type 3 cells.

## DISCUSSION

The main result of this study is the observation that the presence of polymer networks (chiral or nonchiral) dispersed in liquid crystals of banana-shaped molecules favors a locally chiral state over the thermodynamically stable racemic state. In the bulk the nonchiral symmetry of the constituent molecules dominate. At liquid-crystal-polymer interfaces the inversion symmetry is broken, thus rendering chirality to the surface dominated areas. Surface-induced symmetry breaking effects are known in liquid crystals [14]. The local chirality of the material is determined by the interplay of the surface and bulk effects. Assuming that the surface anchoring energies  $W_s \sim 10^{-3}\text{ J}/\text{m}^2$ , which is typical for polymer-

liquid crystal interfaces [15], and the curvature elastic constant is  $K \sim 10^{-11}\text{ N}$ , the extrapolation length, i.e., the range over which the surface dominates, is  $L \approx \pi^2 K/W \sim 0.1\text{ }\mu\text{m}$ . This is very small compared to the film thickness of  $d = 5\text{ }\mu\text{m}$ . Thus the bulk effect dominates in the pure liquid crystal cells. For a polymer network containing cells the polymer mesh size  $l$  (the distance between adjacent polymer fibers) is the characteristic length for surface effects. For cells containing a few percent of polymer networks,  $l$  is typically  $0.1\text{--}1\text{ }\mu\text{m}$  (the 5% PN cells are in the lower end of the range). Accordingly,  $l \sim L$ , and the surface interactions dominate.

The diminishing electro-optical contrast after extended high field treatment is due to the suppression of chirality. The interaction between the external electric field and the permanent polarization enhances the role of the bulk in expense of the surfaces, thus favoring racemic structure. Sufficiently strong electric fields even can break the surface anchoring when the electric correlation length  $\xi_E$  is equal to the extrapolation length  $L$  [16]. Taking into account only the ferroelectric interaction,  $\xi_E = \sqrt{K/PE}$ . For the studied material [8]  $P = 5 \times 10^{-3}\text{ C}/\text{m}^2$ , and the field for chirality suppression is  $E \sim 10^7\text{ V}/\text{m}$ . These give that  $\xi_E < 0.1\text{ }\mu\text{m}$ , which is comparable to  $L$ . The reformation of the chirality preferred by the surfaces requires nucleation and growth, which is apparently a long process. The reappearance of the chirality after the sample is heated to the isotropic phase indicates that the network is fairly rigid, i.e., it has not been modified significantly by the structural changes of the liquid crystal.

The enantiomeric excess observed in type 2 and 3 cells with the helical network represents a chirality transfer on a macroscopic level. In this transfer the helix formation should play an important role. The right- and left-handed domains have the same energy, so a very small bias, given by the helical shape of the polymer fibers, can lead to the observed enantiomeric excess.

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