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Field-induced periodic chiral pattern in the N_x phase of achiral bimesogens

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Some hydrocarbon-linked mesogenic dimers are known to exhibit an additional nematic phase (N_x) in the temperature range below the conventional nematic (N_u) phase. One of the features of this phase is the presence of optical response typically found in chiral systems, while the involved molecules are non-chiral. We demonstrate that the two domains of opposite handedness found in planar cells can be controlled/induced by the external electric field and these form periodic striped patterns. The effect of frequency and amplitude of the electric field on the periodicity and formation of the domain pattern is investigated. © *2012 American Institute of Physics*.
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Hydrocarbon linked mesogenic dimers (Fig. 1) have recently attracted significant attention due to a number of unique and promising properties.[1–3] The list includes an additional nematic phase (N_x) found below the conventional uniaxial nematic phase, the spontaneous self-deformation domains appearing in the absence of electric field,[1] microsecond linear optical response,[2] etc. One of the possible explanations of the unusual properties of the N_x phase is based on a prediction[5] of a twist-bend helical structure induced by the bended molecular shape of the odd dimers.[3,6,7] Another possible explanation involves clustering of the molecules, which leads to multiplication of the quadrupolar moment thus producing unusually high flexoelectric coefficients.[8,9] Externally induced ("top-down") deracemisation is promising potential for both basic science and applications. It has already been shown that a deracemisation can be induced by a mechanical strain.[4] In this work, we show that an external electric field is able not only to cause such a deracemisation by inducing neighbouring domains of opposite handedness reported earlier[2] but also to control the parameters of the periodic micro-pattern formed by the domains.

Periodic patterns caused by the phenomenon of self-assembly have attracted attention due to potential applications in variable grating mode devices, in structured nano-composite materials and in nano-patterning required for advanced microchip fabrication. Measuring the parameters of a pattern (such as the periodicity etc.) is a precise and convenient tool of determining the intrinsic properties of the material.

One type of such patterns in the liquid crystalline phase under investigation has already been reported earlier.[1] This was referred to a *self-deformation* (or *spontaneous deformation*) striped pattern. This is not to be confused with the pattern formed by the *domains* of opposite switching presented in this work. Both of the two patterns are striped textures with comparable spatial periodicity; they appear in the same confining cells. However, their appearance (compare Fig. 2 with Fig. 3) is obviously different as are the conditions required for observation.

Although composed of non-chiral molecules, the N_x phase is found to exhibit switching sensitive to the sign of the applied electric field. This is normally observed in the systems containing chirality. This switching is found to have remarkably low response time of the order of a few microseconds. Uniformly lying helix (ULH), electroclinic, and flexoelectric effects, normally found in chiral systems,[10–12] were proposed as possible causes for this intriguing phenomenon.[2] Splitting of nuclear magnetic resonance (NMR) spectral lines, typical for chiral systems, were also reported in the N_x phase.[13] Two domains with opposite handedness and, consequently, opposite responses are found in planar cells.[2] Such a spontaneous symmetry breaking with domain formation was previously theoretically discussed[14] and experimentally reported[15] in bent-core materials.

The molecular structures of the material under investigation are shown in Fig. 1. 35 wt. % of a monomer was added in an attempt to reduce the viscosity and to achieve more convenient working temperatures. The material has negative dielectric anisotropy ($\Delta\varepsilon < 0$), and this allows the use of high electric fields in planar sandwich cells without causing Freedericksz transition. A number of cells with cell gaps varying from 2 to 7 μm and with different alignment layers have been used. These include planar commercial cells (EHC. Co., KSRP-XX-A2||P1NSS), homemade cells (planar aligning agent RN1175, Nissan Chemicals, Japan) and cells with asymmetric alignment (planar rubbed on one surface and bare indium tin oxide (ITO) in the other).

It has been shown earlier[2] that in planar cells, the materials possessing the N_x phase exhibit linear deviation of the optical axis away from the rubbing direction to the applied electric field. This is similar to the electroclinic effect or ULH switching.[10–12] In planar cells, domains exhibiting both

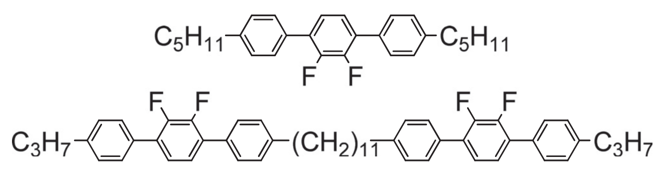

FIG. 1. Liquid crystalline mixture used: 35 wt. % monomer (top), 65 wt. % dimer(bottom). Cr (59 °C) N_x (87.5 °C) N_u (160 °C) Iso.

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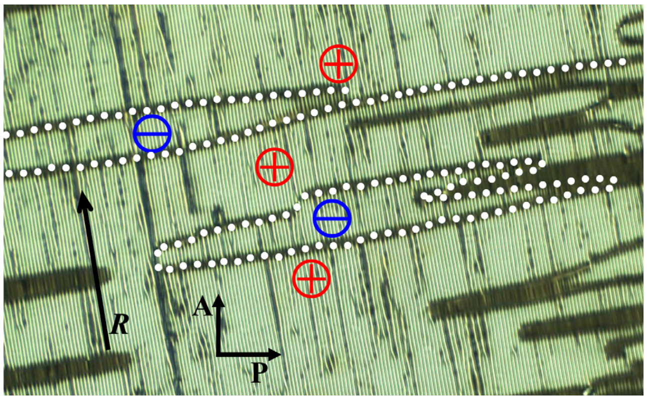

FIG. 2. A 2 μm planar cell. N_x phase. In the absence of external electric field, the boundaries of the domains with opposite switching directions (some are highlighted with white dotted line) can be identified by discontinuities in the spontaneous deformation pattern (stripes parallel to the rubbing direction ***R***). **A**, **P**—positions of the microscope polariser and analyser.

directions of deviation are usually found. The size and the shape of the domains are irregular and apparently depend on the pre-history of the cell, cooling speed and, probably, surface properties, like surface pre-tilt angle etc. Although not visually distinguishable, the domains exist at zero field, and their boundaries can be identified by discontinuities in the self-deformed striped pattern (Figure 2). Alternatively, some of the cells are found to have one of the domains large enough to cover the microscope field of view (∅2 mm). Although the positions of the domain boundaries are varying, during the experiments with moderate fields applied, they are relatively stable due to the very high viscosity of the N_x phase.

By contrast, application of high alternating current (AC) electric fields is found to affect the formation of the domains of opposite switching as shown in Figure 3. The image was taken at a temperature approximately 0.5 °C below the N_u-N_x phase transition where the viscosity is not prohibitively large as at lower temperatures, and this will allow for a visible texture changes. However, it is large enough to preserve the domain pattern under the direct current (DC) field for several seconds needed to capture the image. The pattern was formed by applying an AC electric field with zero-to-peak amplitude $U_{0-Pk} = 80$ V and frequency $f = 5$ kHz for several minutes. The image was captured with a DC field of the same amplitude applied. The difference between right and left images in Figure 3 is in the sign of the applied DC field. One can clearly see periodic striped pattern formed by the domains of opposite switching. The domain boundaries are normal to the alignment direction. The rubbing direction (long white arrow) is set at an angle of approximately 2 degrees away from the polarizer axis (parallel to the picture side) in order to demonstrate contrast between the domains. The alignment appears uniform within a particular domain with a sharp change of the in-plane deviation angle at the domain boundary. When the parameters of the applied field are changed gradually, the periodicity of the domains is changing via "sliding in" or "sliding out" of a domain along the domain boundaries as marked in Fig 3 by the circles.

When a few kHz AC field is applied to a symmetrical planar cell, the observed contrast between the domains is zero due to the persistence of the human vision or a finite exposure time of a camera. In order to overcome this difficulty in observation, we replaced the microscope light source with an ultra-bright light-emitting diode (LED) switched ON during one half-wave of the electric field applied to the cell and, correspondingly, OFF during the other half-wave period. Such a stroboscopic illumination allowed the investigation of the behaviour of the domains over a wide range of parameters of the external electric field. Figure 4 represents the frequency dependence of the domain periodicity for two values of the amplitude of the applied sine wave voltage. In order to achieve a proper equilibrium of the striped pattern, rather long waiting times (up to 1500 s/point) had to be implemented in combination with switching the field ON and OFF several times. One can see that the periodicity (distance between the two neighboring domains of the same handedness) can be controlled within the range from 2.5 μm

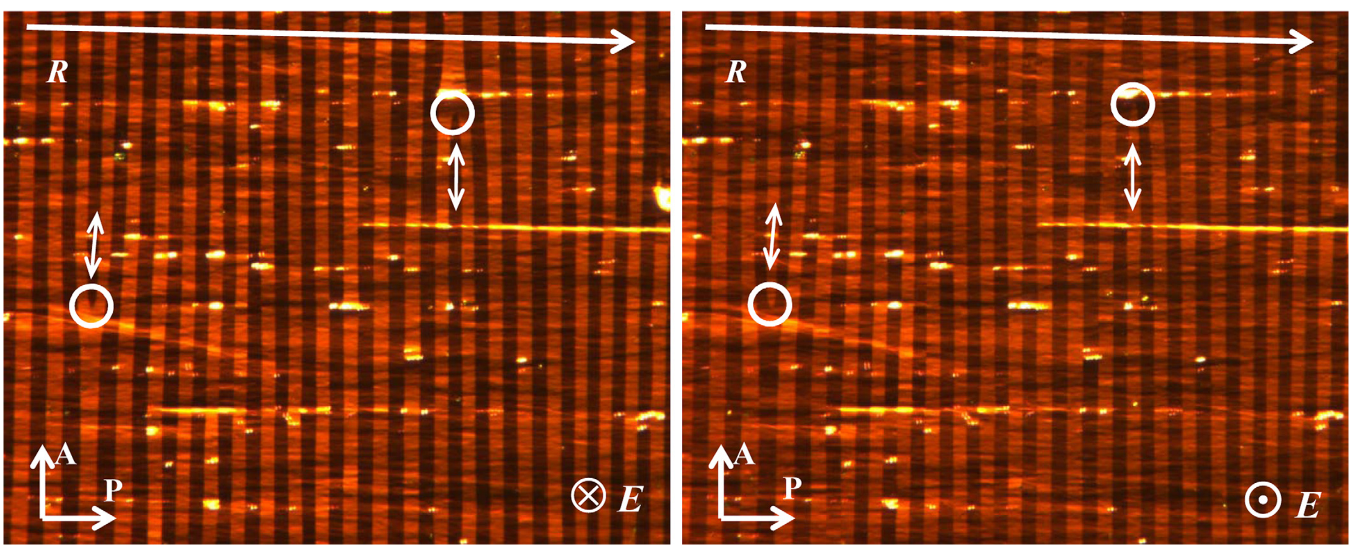

FIG. 3. Evidence of opposite switching in the domains. Polarizing optical microscope image of 5 μm EHC cell, picture height is 0.4 mm. Darker areas: the optical axis deviated from the rubbing direction (***R***) towards the polarizer axis (**P**) and is almost parallel to it. Brighter areas: the optical axis deviates in opposite direction and forms a larger angle (a few degrees) with the polarizer axis.

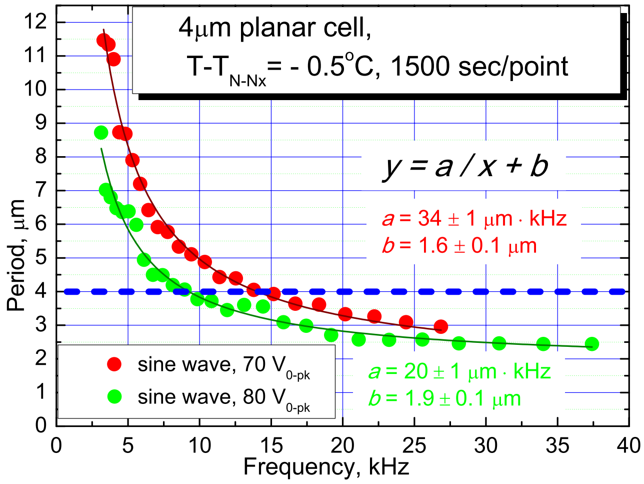

FIG. 4. Frequency dependence of the domain period obtained from images captured under the stroboscopic illumination for different applied voltages at a temperature just below the N_u-N_x phase transition. Blue dashed line denotes the cell gap size of 4 micrometers.

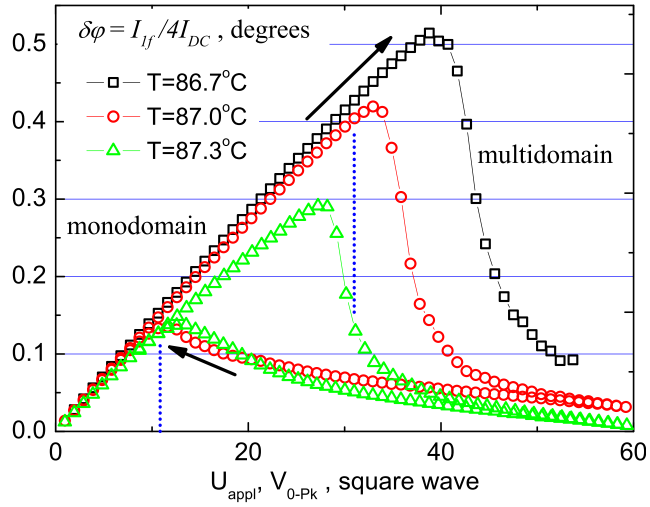

FIG. 5. Threshold behaviour of the domains, 3.1 μm cell, 100 s/point, 7 kHz, square wave. Electric field is the abscissa voltage divided by the cell thickness. Blue dotted lines denote the field values of 3.5 V/μm and 10 V/μm. The increasing and decreasing of the electric field is specified by the black arrows near the corresponding datapoints.

to 12 μm for a 4 μm cell gap. The appearance of the domains is limited at the lower frequencies by the electroconvection, while at higher frequencies, the domain visibility is gradually getting below the detection limit. Higher fields induce narrower and better defined domain patterns; however, they are also causing electroconvection and high probability of the electrical breakdown of the sample. The frequency dependence of the periodicity of the domains fits reasonably well by $y = a/x + b$ function, although the physical meaning of the fitting parameters as well as the form of the fitting function is currently a topic for theoretical investigation.

In order to investigate the condition of appearance of the domain patterns, the set-up described in our previous work was used.[2] A cell was fixed in a polarizing microscope with crossed polarizers at an angle of 22.5° between the polarizer and the rubbing direction. An AC voltage was applied to the cell and the transmitted light was measured by a Lock-in amplifier at the fundamental frequency (1*f*) of the applied signal. In the case when one single domain covers the entire field of view of the microscope, one can determine the in-plane deviation of the optical axis as $\delta\phi = \mathrm{I}_{1f}/4I_{DC}$. When a multidomain striped pattern appears, the first harmonic signals from the domains with opposite switching will cancel out and the first harmonic of the photodiode current detected by the lock-in amplified should drop to zero. This is observed experimentally as shown in Fig. 5. One can see that the applied voltage should exceed a certain threshold in order for the domains to appear. The threshold is almost 10 V/μm for the temperature close to the N_u-N_x phase transition and is increasing rapidly when cooling the sample. There is also a noticeable hysteresis: On decreasing the field, the monodomain level of the signal is restored at approximately 3.5 V/μm. The measurements were performed at a low speed, allowing for a settle time of 100 s at each voltage point. This is to negate the possible contribution to the hysteresis caused by the high viscosity of the N_x phase.

To summarize, we have observed periodic stripe domains induced by AC electric field in N_x phase of a material with negative dielectric anisotropy. It is shown that two neighboring domains show opposite direction in-plane deviation of the optical axis when an external electric field is applied across the cell. The observed periodicity ranges from 2 to 12 μm and depends on the frequency and the amplitude of the applied voltage. Narrower domains are likely to be found in thinner cells, although it would require a revision of the observation techniques and a better quality (high flatness/iniformity) of the aligning surfaces. For the periodic domain pattern to appear, rather high values of the field (10 V/μm) and frequency (>1.5 kHz) are needed. The domain boundaries are normal to the rubbing direction. This is a potential method of controlled production of periodic structures. Further work will include determining the nature of the switching phenomena associated with the domains. As previously discussed,[2] this could include electroclinic effect, uniformly lying helix, or other flexoelectricity-based switching phenomena. The opposite switching in the adjacent domains suggests the presence of opposite chiral handedness of the domains, which can now be generated in a controllable manner.

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