Microsecond linear optical response in the unusual nematic phase of achiral bimesogens

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Some hydrocarbon linked mesogenic dimers are known to exhibit an additional nematic phase (N_x) below a conventional uniaxial nematic (N_u) phase. Although composed of non-chiral molecules, the N_x phase is found to exhibit linear (polar) switching under applied electric field. This switching has remarkably low response time of the order of a few microseconds. Two chiral domains with opposite handedness and consequently opposite responses are found in planar cells. Uniformly lying helix, electroclinic, and flexoelectric effects are given as possible causes for this intriguing phenomenon. © 2011 American Institute of Physics. [doi:10.1063/1.3671996]

A change in the direction of the optical axis by a moderate electric field is the basis of the use of liquid crystals (LCs) in contemporary display technologies. However, further exploitation of this property in optical telecommunication technologies is hindered by the limited speed of the optical axis switching. Amongst the fastest electro-optic effects in LCs are surface stabilized ferroelectric smectic LCs,[1] uniformly lying helix (ULH) geometry in flexoelectric cholesteric LCs,[2] electro-optic effect in blue phases,[3] and the electroclinic effect[4] found in both chiral smectic and cholesteric LCs. These switching modes are defined by the asymmetry of the chiral molecules forming the corresponding LC phases.

Meanwhile, non-chiral dimers of mesogenic molecules linked with a flexible hydrocarbon chain with odd number of alkyl units have recently attracted attention due to the presence of an unusual liquid crystalline phase (currently designated as N_x) in the temperature range below the classical nematic phase (N_u).[5–7] Although identified as a nematic phase by x-ray diffraction studies, the phase exhibits clearly different patterns in polarised optical microscopy (POM) observations as well as a difference in the enthalpy from N_u measured by the differential scanning calorimetry.[5] The ability of this class of materials to spontaneously form unusual stripe patterns with periodicity defined by the gap between containing surfaces is promising for applications in photonics. A theoretical explanation connecting the molecular properties to the macroscopic self-assembly properties is still to be developed.

In this Letter, we report one more intriguing property of the N_x phase: it exhibits polar switching with remarkably low switching time under electric field in a similar manner as the above mentioned materials involving chirality.

The molecular structures of materials under investigation are shown in Fig. 1. We have investigated both pure dimers (*M1-3*) and mixtures of *M4* with 4-4′pentyl-cyano-biphenyl (5CB) (70/30% w/w) and of *M2* with its monomer (65/35% w/w). A number of cells with cell gaps varying from 2 to 25 μm and with different alignment layers have been used. These include anti-parallel planar commercial cells (EHC. Co., KSRP-XX-A2 ‖ P1NSS), homemade planar cells (planar aligning agent RN1175, Nissan Chemicals, Japan), and homemade hybrid aligned cells (homeotropic aligning agent AL60702 JSR, Korea). The experimental set-up for the investigation of the electro-optical properties of liquid crystals includes an optical microscope with crossed polarizers (POM), a photodiode with I-V converter, an oscilloscope, and a data acquisition board (NI-USB 6216).[8] A lock-in amplifier algorithm allows for the extraction of the DC component and the first four harmonics of the photodiode signal. This is an extensive modification of the technique given earlier.[9] This highly sensitive optical contrast spectroscopic technique detects switching properties that are not ordinarily observed during the previous experiments.

When a cell is fixed with the rubbing direction at an angle of at 22.5° to the POM polarizer direction and a periodic electric field is applied normal to the cell plane, a linear (polar) optical response from the LC can be detected in the photodiode signal by the presence of the first (fundamental) harmonic of the applied frequency. If the response is linear and its switching time is much lower than the period of the applied wave, the amplitude ratio between the first (V_{1F}) and the third (V_{3F}) harmonics should remain the same as in the applied wave (i.e., $3V_{3F} = V_{1F}$ for a square wave). Alternatively, when the material does not show fast enough response (and, therefore, behaves as a low-pass filter), the level of the higher harmonics must be lower than in the original waveform.
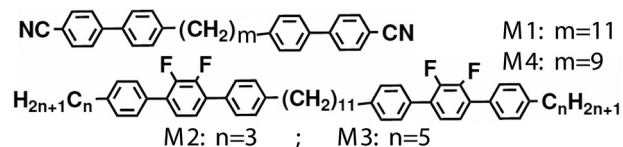

FIG. 1. Liquid crystalline materials used. *M1*: Cr (91 °C) N_x (109 °C) N_u (127 °C) Iso; *M2*: Cr (95 °C) N_x (124.9 °C) N_u (180 °C) Iso; and *M3*: Cr (85 °C) N_x (123 °C) N_u (170 °C) Iso. *M2*+ monomer: Cr (59.3 °C) N_x (102 °C) N_u (154 °C) Iso.

a)Electronic mail: jvij@tcd.ie.

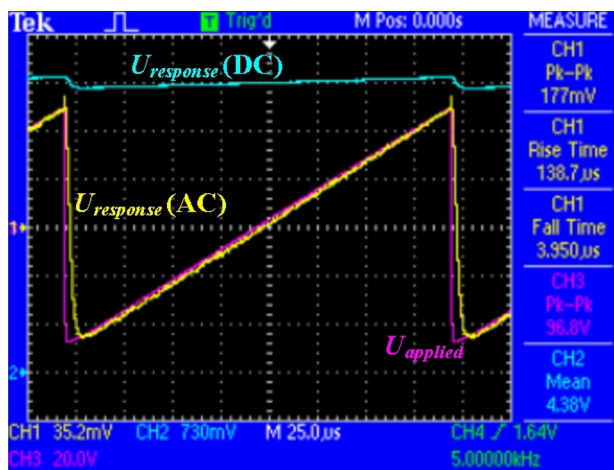FIG. 2. (Color online) Oscillogram of the optical response in N_x phase of *M2*. $U_{applied} = 96.8$ V$_{Pk-Pk}$.

FIG. 3. (Color online) POM textures of *M2* in planar cells of 2 μm (a) and 5 μm (b,c,d) thickness. Domain boundary at 0 V(a,b), +200 V$_{DC}$ (c,e), and −200 V$_{DC}$ (d,f). White bar length is 100 μm. In (e,f), n_1 and n_2 are the optical axes in the neighboring domains deviated in the opposite directions and the dotted red line corresponds to the domain boundary

This experiment shows clear difference in the behaviour between N_u and N_x phases. In contrast to the N_u phase, the response in the N_x phase meets the above odd harmonic criteria for the fast polar switching in the entire temperature range. The polar switching is being detected in all of the above materials and mixtures in the cells with planar alignment on at least one of the surfaces.

The appearance of the striped spontaneous periodic deformations[5] at lower temperatures in the N_x phase does not show conclusive influence on the observed switching, although the amplitudes of the optical transmittance signals are modified by the presence of this pattern. Moreover, the striped pattern vanishes at rather moderate fields for both positive and negative dielectric anisotropy materials, whereas the odd-harmonic response continues to be present.

For the materials with positive dielectric anisotropy ($\Delta\epsilon > 0$: *M1*, *M4* and their mixtures with 5CB), the polar response degrades rapidly when the applied voltage induces Freedericksz transition to a homeotropic state. In the materials with negative dielectric anisotropy ($\Delta\epsilon < 0$: *M2*, *M3* and mixtures), the fast response remains linear up to the breakdown fields, reaching visible director deviation angles. The oscilloscope screenshot (Fig. 2) demonstrates the switching time and linearity of the optical response in a 5 μm cell filled with (*M2*) in the N_x phase. Here, channel 3 (pink) is the applied voltage, channel 1 (yellow) is the optical response magnified utilizing AC input mode of the oscilloscope, and channel 2 (blue) is the same response signal acquired with DC mode. One can see a perfect linear response and the switching time is of the order of 4 μs.

Thus, there are two types of electro-optical responses in the N_x phase (planar cell, $\Delta\epsilon > 0$): the linear response as reported above with a microsecond characteristic time and the Freedericksz transition with a characteristic time of about 1 min seen in cells under the same conditions. This difference is challenging to explain. Even bigger challenge is to explain the linear nature of the response. It is not obvious as to why the polar switching can be observed in symmetric cells filled with a non-chiral material.

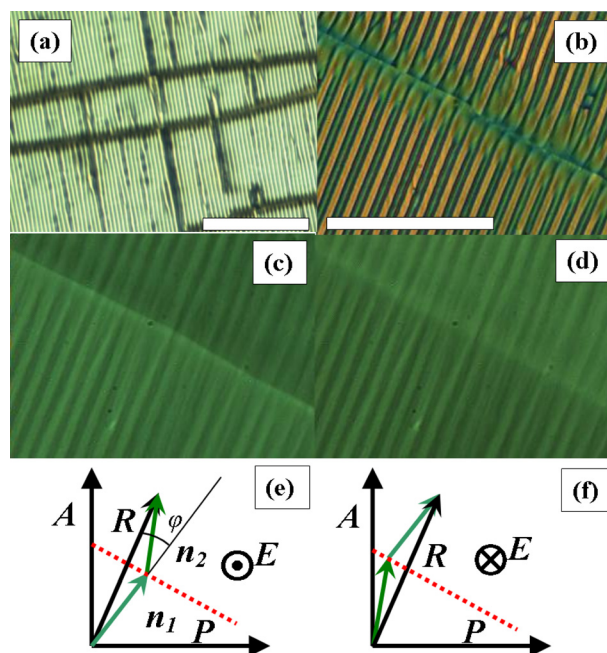More detailed investigation revealed the presence of wide-area domains separated by a discontinuity in the striped pattern [Figs. 3(a) and 3(b)]. The domains remain stable in the N_x phase. However, on heating of the sample to the N_u phase, these disappear and on cooling back the sample these re-appear randomly. The domains do not exhibit visible difference without application of an external field. However, on applying DC electric field, one can observe [Figs. 3(c) and 3(d)] that the optical axis in neighboring domains (n_1, n_2) deviates from the rubbing axis (R) in opposite directions [Figs. 3(e) and 3(f)].

The domain formation seems to be controllable by the cooling rate. In some cells, only one of the switching directions dominates over the field of view of the microscope. In such samples with only one domain present, we measured the in-plane position of the optical axis (Fig. 4, blue squares)
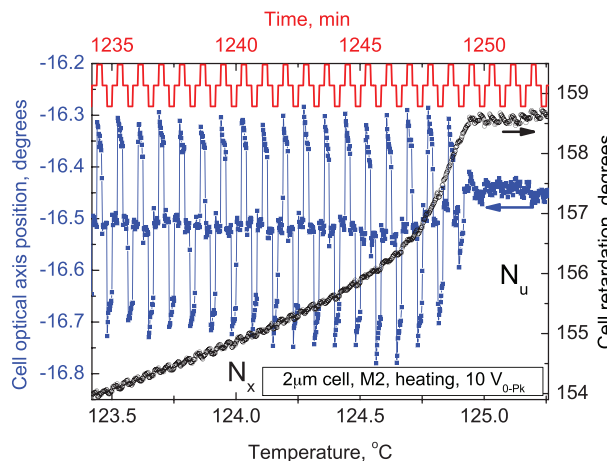

FIG. 4. (Color online) Alternating electric field of the waveform shown by the red line (top of this figure) was applied to the cell during the temperature ramp. (Applied voltage amplitude: 10 V$_{0-Pk}$, Period: 50 s, and heating rate: 0.1 °C/min). Retardation is marked to the right, and azimuthal angle to the left.

and optical retardation (black circles) using a photoelastic modulator (PEM) system.[10] Within the measurement error, the switching angle in the plane of the cell φ is proportional to the electric field applied (red line, on the top of the figure) along the cell normal. The deviation of the optical axis from the rubbing direction is approximately $\varphi \approx \pm 0.3°$ at a field of $E = 5$ V/μm. It reaches this maximum value almost immediately below the $N_u - N_x$ phase transition. At lower temperatures in the N_x phase, the deviation of the optical axis is lower. One can also see that φ slightly decreases with time after applying the field. This is probably due to a gradual formation of ionic layers which tend to compensate the external DC field. The retardation change (black circles), however, remains below the detection limit (approximately 0.2% of the total retardation), and therefore, the data in Fig. 4 does not allow us to draw conclusions about the deviation of the director out of the cell plane.

Flexoelectric polarization appears to be very promising in explaining the phenomena of stripe formation observed in the N_x phase.[7,11] One can write down the free energy as follows:

$$f = \frac{1}{2}\left(K_1 - \frac{e_1^2}{\varepsilon_{\parallel}}\right)(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2}\left(K_3 - \frac{e_3^2}{\varepsilon_{\perp}}\right)(\mathbf{n} \times \nabla \times \mathbf{n})^2.$$

Here, K, e, and $\mathbf{n}$ are the elastic constant, the flexoelectric coefficient, and the molecular director, respectively, while the indexes 1, 2, and 3 correspond to the splay, twist, and bend deformations. One can easily see that large enough e_1 with moderate value of parallel dielectric permittivity $\epsilon_{\parallel}$ can produce spontaneous deformation considered in our earlier work.[5] Moreover, a strong flexoelectric behaviour in similar materials has already been found.[12] Unfortunately, this explanation cannot predict the observed in-plane switching. The linear electric field terms are canceled out in the symmetric geometry used.

A spontaneous symmetry breaking with a formation of domains with right- and left-handed helices has already been theoretically discussed[13] and experimentally reported[14] in bent-core materials. This leads us to consider ULH as one of the potential explanations together with the formation of chiral domains.[2] In a flexoelectric material with a helical axis parallel to the cell substrates, an electric field normal to the glass surface will cause a molecular tilt φ in the cell plane. If p, γ, and E are the helical pitch, the viscosity, and the electric field, respectively, then $\tan \varphi = \frac{epE}{2\pi K}$ and the time constant

$\tau = \frac{\gamma p^2}{4\pi^2 K}$. Therefore, the switching can correspond to the presence of a very short helical pitch. However, the presence or absence of such a short pitch is impossible to confirm by optical methods. Moreover, ULH geometry is unlikely to be formed without special efforts.

The third possible explanation is the surface electroclinic effect. In this case, the observed values of the switching angle and the time constant are in good agreement with those reported for other LCs.[15] However, the electroclinic effect exists only in the presence of either molecular or surface chirality. The chirality of domains may also be important here.

Finally, this switching in the N_x phase opens up a field for further theoretical and experimental investigations of spontaneously forming chirality. In terms of applications, the switching time is sufficiently short while the optical axis deviation needs to be significantly enlarged, and a reliable technique of controlling the domain handedness needs to be developed.

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