Phase Separation Induced Polar Electrooptical Effect in a Doped Nematic Liquid Crystal Cell

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Abstract

A cell prepared for vertical alignment was filled with a mixture of the liquid crystal octylcyano biphenyl, doped with a three-legged molecule, in the isotropic phase in the presence of an imposed temperature gradient perpendicular to the substrates. After cooling the cell through the nematic phase and restoring the temperature uniformity, an electrooptic response was observed on applying an electric field across the cell in one direction but not in the other. This unipolar effect was absent for cells prepared in the absence of a temperature gradient. The results are discussed in terms of phase separation and preferential adsorption of the tripod molecule.

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Polar effects at liquid crystal / substrate interfaces have received considerable attention over the years. It was realized that the absence of inversion symmetry leads to a spontaneous polarization normal to the surface\textsuperscript{1,2,3} that may result in surface-specific phenomena such as a field induced orientational instability. Thirty years ago Derzhanski, \textit{et al.} demonstrated an electrooptic effect for asymmetric surfaces treated for planar alignment\textsuperscript{4)}. Using a vertically-aligned nematic cell, Monkade, \textit{et al.} demonstrated\textsuperscript{5)} an effect predicted by Helfrich\textsuperscript{6)}, \textit{viz.}, that an elastic deformation at the surface can arise because of flexoelectric and surface polarization effects. Lavrentovich, \textit{et al.}\textsuperscript{7)} and Nazerenko, \textit{et al.}\textsuperscript{8)} later showed that the absence of inversion symmetry can be exploited to create an “optical diode,” wherein a surface instability occurs for one orientation of an electric field but not for the antiparallel orientation. A number of other workers also have demonstrated electric field polarity switching effects in nematic liquid crystals\textsuperscript{9,10,11,12,13)}, some of which may be exploited in the development of polarity-dependent electrooptical devices. All of these effects have involved non-identical preparation of the two substrates before the cell is assembled. In this paper we show that polarity sensitive switching can be obtained with \textit{identically-prepared} substrates by doping the liquid crystal with a highly polar molecule that preferentially adsorbs at one substrate in the biphasic temperature region in the presence of a temperature gradient. This \textit{in situ} technique obviates the need to chemically/mechanically prepare two different substrates prior to cell construction.

Cells were prepared using indium-tin-oxide (ITO) coated glass of thickness 1.1 mm that was cleaned and spin coated with the polyamic acid SE-1211 (Nissan Chemical Industries). The slides were baked according to the manufacturer’s specification for 60 min at 180° C, which provides vertical (homeotropic) orientation of the nematic director. The slides were placed together, separated by 4 µm glass spacers, and cemented. The cell gap $d$ was measured using an interferometric technique and found to be $d = 4.0 \pm 0.1 \mu m$. Wires were then attached to the
conducting ITO surfaces and the cell was placed onto a hot stage. A 5 wt.-% mixture of the three-legged dopant molecule triallyl-1,3,5-triazine-1,4,6(1h,3h,5h)-trione\textsuperscript{14}) in the liquid crystal octylcyano biphenyl (“8CB,” Merck) was prepared (Fig. 1). It has been suggested\textsuperscript{14}) that each leg of the dopant physically associates with one 8CB molecule, becoming a “tripod”, as shown schematically in Fig. 1c. Polarized optical microscopy determined that the mixture exhibits a homogeneous isotropic phase for $T > 27.8^\circ$ C, a biphasic region for $26.4^\circ < T < 27.8^\circ$ C and a nematic for $T < 26.4^\circ$ C; thus the width of the biphasic region $\delta T = 1.4$ K. The mixture was injected under three different conditions into three identically prepared cells. In all cases the bottom substrate was held at $60^\circ$ C. A second thermally controlled stage was in contact with the top surface, with the stage held at temperatures $T = 15^\circ$ (i), $26^\circ$ (ii), and $60^\circ$ C (iii). These correspond to temperature differentials of 45, 34, and 0 K, respectively, from one thermally controlled stage to the other; the actual temperature gradients across the interior of the cell were estimated to be $2 \times 10^4$, $1.5 \times 10^4$, and 0 K m$^{-1}$. The samples then were cooled to the nematic phase with a different protocol used for each cell. For cell i the bottom unit was turned off and cooled at a rate of approximately 5 K min$^{-1}$ — this occurred while the top unit was maintained at $15^\circ$ C. After the bottom unit reached $26^\circ$ C the nematic phase sample was removed and equilibrated at $26^\circ$ C. For cell ii the bottom heating unit was turned off, cooling at a rate of approximately 4.5 K min$^{-1}$ while the top unit was maintained at $26^\circ$ C. The sample then was removed. Finally, for cell iii both top and bottom heating units were turned off and the cell cooled through the nematic – isotropic (NI) phase transition at a rate of approximately 3 K min$^{-1}$, eventually stabilizing at approximately $26^\circ$ C.

Each cell was mounted between a pair of crossed polarizers. Light from a He-Ne laser passed through the polarizer, the sample, the analyzer, and into a photodiode detector. A dc voltage was applied across each cell, starting at 0 V and increasing in 0.25 V steps up to 5 V; a similar scan was made over the range 0 V through -5 V. The intensity vs. applied voltage for the three cells is
shown in Fig. 2. In a separate measurement the intensity was measured for both increasing and
decreasing voltage over the same voltage range, and no significant difference was observed between
the two scanning directions, indicating no voltage hysteresis.

The qualitative difference between the cell cooled symmetrically and those cooled
asymmetrically is striking. For the thermally symmetric cell (iii) we observed nearly symmetric
peaks in the intensity at $\sim \pm 2.5$ V; for cells i and ii that were cooled asymmetrically, peaks are
observed for a positive applied voltage only, and the peak for the more asymmetric cell i is both
sharper and occurs at a lower applied voltage. Because 8CB has a positive dielectric anisotropy,
one would expect no observable optical transmittance for a pure 8CB cell when only dielectric
phenomena are considered. However, a weak surface-based distortion may occur when surface
polarizations are taken into account. The presence of the tripod apparently has a marked
impact on the electrooptic effect. For the thermally symmetric cell iii the appearance of nearly
symmetric peaks is indicative of an increased surface polarization due to the approximate equal
adsorption of tripod molecules at the substrate. When a cell of pure 8CB (without tripod dopant) is
prepared the same way, no variation in the intensity is observed out to $\pm 5$ V. The asymmetric
behavior observed for cells i and ii is consistent with that observed in Refs. 8 and 9, where the
polarizations at the two surfaces are different. This polarization difference in our experiment
clearly is due to the thermal treatment of the cells, causing a differential adsorption of tripod at the
two substrates. But does this behavior arise from the presence of a temperature gradient $\nabla T$ during
the cooling process, or is it due to phase separation over the range $\delta T$?

To answer this question we then prepared two additional cells iv and v and used the thermal
protocol of cell ii, except in these two cases the bottom stage of cell iv was held at $40^\circ$ C and that of
cell v at $80^\circ$ C prior to cooling. After cooling and equilibrating at $26^\circ$ C, the intensity vs. voltage
measurements were found to be identical for cells ii, iv, and v (Fig. 3). Thus, it is clear that the
presence of a temperature gradient in the isotropic phase alone does not cause the differential adsorption of tripod at the two surfaces. Instead, as the sample is cooled, just above the final equilibration temperature of 26° C a biphasic region of width $\delta T = 1.4$ K occurs. The additional presence of the imposed temperature gradient results in the nematic phase, which is poor in tripod concentration relative to the isotropic phase, to nucleate at the cooler top substrate; the warmer bottom substrate is in contact with the tripod-rich isotropic phase. Thus, just above the equilibration temperature there is a range of temperature $\delta T$ over which the bottom substrate is in contact with a high concentration of the polar tripod molecules. When the entire sample finally is cooled into the nematic phase, some of the tripod molecules near the bottom substrate precipitate out — they are relatively insoluble in the nematic phase — and adsorb at this surface due to their relative high concentration there. The resulting polarization difference is precisely the condition observed in Refs. 8 and 9. In particular, Nazerenko, et al. observed that this asymmetry of the substrates gives rise to a unipolar optical effect$^8$), which is observed for all of our cells except the symmetric cell iii. Moreover, by increasing the polarization of one substrate relative to the other, they found that the threshold voltage for the instability decreases, with an increase in $dI/dV$ above the threshold voltage. This is exactly what is observed in our cell i (Fig. 2): a narrow unipolar peak occurs at a smaller voltage than that observed with a smaller applied temperature gradient.

We also have examined the thermal stability of the cells. One unipolar cell was held at room temperature for 180 days. Because the unipolar switching characteristics were found to be unchanged over this time, we conclude that the state formed by cooling in a gradient is robust. All these results seem to be consistent with a very low solubility of the tripod molecule in the nematic phase. Cooling in a thermal gradient results in phase separation in which the tripod-rich isotropic phase is adjacent to the higher temperature surface, which in turn can result in precipitation of the tripod molecules at this warmer surface.
As a further test of this hypothesis, we turned over a previously heated cell, switching the two surfaces with respect to the temperature gradient and thereby exposing the previous “cold” surface to the hotter stage. We then brought the cell briefly (~10 min) into the isotropic phase before cooling using protocol i, and then measured the I vs. V characteristics. In the second step we again heated the cell, but for a much longer duration (~13 h) in the isotropic phase before cooling. We found that the first thermal treatment resulted in a significant decrease in intensity, but the cell still exhibited unipolar switching, whereas the second step of the treatment resulted in bipolar, nearly symmetric switching; here both substrates had now been exposed to the tripod-rich isotropic phase on cooling through the biphasic region. This result is again is consistent with the hypothesis that transport and adsorption of the tripod molecule is much easier in the isotropic phase.

To summarize, we have observed an optical diode effect analogous to that observed by Nazerenko, et al., but without the need to prepare substrates asymmetrically before cell construction. By doping the liquid crystal with a polar tripod-shaped molecule and cooling the cell through its biphasic region in the presence of a temperature gradient, we have created the required substrate asymmetry in situ. Moreover we have investigated the formation of this asymmetry and find that it depends on the history of the sample in a way that is consistent with the tripod molecule being soluble in the isotropic phase and only sparingly soluble in the nematic phase. The history dependent nature of this effect also suggests that similar phenomena could be used to configure or reconfigure electrooptic phenomena in liquid crystal cells after assembly.

Acknowledgements: J.-H.L. was supported in part by a Korean Research Foundation (KRF) grant (KRF-2007-357-C00034). D.K. was supported by the KRF under grant KRF-2007-013-D00070 and by Soongsil University. R.G.P. was supported by the Office of Naval Research under grant N00014-05-0404. C.R. was supported by the NSF’s Solid State Chemistry program under grant DMR-0804111.
Figures

1. a) Liquid crystal molecules octylcyanobiphenyl; b) tripod base triallyl-1,3,5-triazine-1,4,6(1h,3h,5h)-trione; c) cartoon of assembled tripod molecule consisting of (a) and (b).

2. Normalized intensity vs. applied voltage for cells prepared with three different thermal protocols. In all cases the bottom stage is at 60° C before it is cooled. The top stage is held at temperatures $T = 15°$ C (i, circles) and $26°$ C (ii, squares) during the cooling of the bottom stage. In trace iii (triangles) the top stage starts at $60°$ C and is cooled together with the bottom stage. Solid lines are meant as a guide for the eye.

3. Normalized intensity vs. applied voltage for cells prepared such that the bottom stage starts at $40°$ C (triangle), $60°$ C (squares), and $80°$ C (circles) before it is cooled. The top stage is held at $26°$ C throughout the three cooling protocols of the bottom stage.
Figure 1
Figure 2
Figure 3
References

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