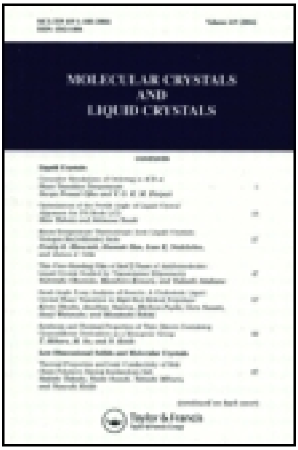


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Formation of Polymer Walls by Phase Separation of Lc-Polymer Binary Mixtures in a Nonuniform Electric Field

Volodymyr H. Bodnar [b], Yoan Kim [a], Bahman Taheri [a] & John L. West [b]

[a] Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242

[b] Chemical Physics Interdisciplinary Program

Version of record first published: 24 Sep 2006

To cite this article: Volodymyr H. Bodnar, Yoan Kim, Bahman Taheri & John L. West (1999): Formation of Polymer Walls by Phase Separation of Lc-Polymer Binary Mixtures in a Nonuniform Electric Field, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 329:1, 405-412

To link to this article: http://dx.doi.org/10.1080/10587259908025963

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 405-412
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Formation of Polymer Walls by Phase Separation of Lc-Polymer Binary Mixtures in a Nonuniform Electric Field

VOLODYMYR H. BODNAR[b*], YOAN KIM[a], BAHMAN TAHERI[a] and JOHN L. WEST[b†]

[a]*Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 and* [b]*Also with Chemical Physics Interdisciplinary Program*

We investigated the mechanism of polymer wall formation induced by an inhomogeneous electric field. The patterned electric field drives the phase separation of a liquid crystal-polymer mixture. By proper selection of polymer and liquid crystal, polymer walls can be formed in the interpixel region of a multiplex display. We found that difference in the dielectric properties of the LC and polymer components of the mixtures in conjunction with gradient of the electric field results in formation of the polymer walls. We discuss factors controlling the phase separation process such as concentration, temperature and electric field.

Keywords: liquid crystal – polymer mixtures; field induced phase separation

INTRODUCTION

In recent years, liquid crystal (LC) formulations with various polymers included have been of great interest for display applications. The first bistable, polymer stabilized cholesteric texture (PSCT) devices utilized a low concentration of photocurable monomer dispersed in a cholesteric liquid crystal mixture.[1-3]

At the same time, using relatively high polymer content formulations to produce bistable PSCT displays[4-6] provides some additional advantages over no or low polymer content formulations, making possible fabrication of large area flexible devices. However, the polymer networks produced using high polymer content formulations can reduce significantly the contrast and brightness of a display due to light scattering.

To overcome the drawbacks of displays made by using high polymer content formulations, while maintaining the structural advantages of polymer networks, polymer walls have been formed in PSCT displays[7]. Irradiation of

---

* E-mail: vbodnar@kentvm.kent.edu.
† E-mail: johnwest@scorpio.kent.edu.

selective areas of a cell with ultraviolet (UV) light using a photo-mask forms polymer walls through phase separation induced by photo-polymerization.[8]

Recently polymer walls have been formed by applying a patterned electric field during the phase separation process of a LC-monomer solution.[9] Generally, cooling a LC-monomer mixture results in passing from the one phase region into the miscibility gap, causing the phase separation. Application of a patterned electric field during the separation process forms a patterned distribution of the mixture components that can be fixed by UV light irradiation.

In this paper we report results of polarizing microscopy studies and analysis of the mechanism of polymer wall formation in a patterned electric field.

EXPERIMENTAL

In this study we used a mixture of a nematic liquid crystal, E48, and photo-polymerizable monomer, Norland Optical Adhesive 81 (NOA 81). E48 is a nematic mixture of BDH, Ltd. with positive dielectric anisotropy, $\Delta\varepsilon = 15.1$ with $\varepsilon_{\parallel} = 20.5$ (at 20°C, 1 kHz). NOA 81 is a single component liquid adhesive of Norland Products, Inc. which cures in seconds to a tough, hard polymer when exposed to UV light. The dielectric constant of NOA 81 is about 5.2. The phase behavior of E48 and NOA 81 mixtures is shown in Figure 1.

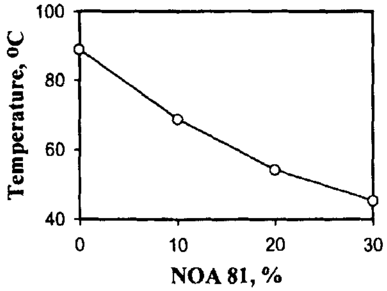


FIGURE 1 Phase separation temperatures of E48/NOA 81 mixtures.

To study phase separation and polymer wall formation under a patterned electric field action we used an E48/NOA 81 mixture with a 9:1 ratio by weight. Two glass plates with etched patterns of transparent indium tin oxide (ITO) lines were used to assemble the cells. The width of ITO electrode lines was about 300 μm and the distance between them was about 20 μm. The glass plates were sandwiched using 5-micron fiber spacers to produce patterned 80-dpi multiplexed cells. The pixel-interpixel volume ratio of the cells was 7:1. Then the cells were capillary filled with the E48/NOA 81 mixture heated to its isotropic state at 100°C.

Phase separation of the E48/NOA 81 mixture in multiplexed cells with and without an applied electric field were observed during cooling from the isotropic state at a cooling rate of 0.5°C/min. Cooling rates were controlled by a microscope hot stage system HS250-RTC-1 (Instec, Inc). The changes during the cooling process with and without an electric field were observed under a polarizing microscope, Laborlux 12 Pol (Leitz Wetzlar, GmbH), equipped with photo and video accessories.

The cells were driven by an amplified 1 kHz sine-wave AC signal from an HP 8904A Function Synthesizer and the applied voltage was measured by a Kethley 196 System DMM.

The electric potential in three dimensions for a 5 μm multiplexed cell filled with a homogeneous isotropic material of average dielectric constant $\varepsilon = 10$ were calculated using the finite difference successive overrelaxation method[10] realized in the DIGITAL Visual Fortran programming language of Digital Equipment Corporation. The results of the electric potential calculations were processed and visualized using a program in MATLAB (The MathWorks, Inc.).

RESULTS AND DISCUSSION

The phase separation process in a multiplexed cell was induced by thermal quenching of a mixture, made of 10% NOA 81 and 90% of E48, from 100°C to 25°C. Under crossed polarizers and without an electric field, the mixture exhibits formation of spherical birefringent droplets uniformly throughout the isotropic mixture. As the phase separation continues the droplets grow and start to coagulate. Finally, liquid crystal domains, separated from the monomer, fill the majority of the visual field. If an electric field is applied to the multiplexed cell before the phase separation process begins, the dynamics of the process becomes different.

When the voltage is applied to the multiplexed cell, it creates a nonuniform, fringing electric field inside the cell. The first indication of the phase separation in the E48/NOA 81 mixture under such a field is the appearance of the image of crossed ITO lines that can be seen if the polarizers are not completely crossed. This phenomenon is a result of density modulations in the mixture at the edges of the ITO lines. As the sample cools down, the image of ITO lines becomes visible even if the polarizers are crossed. At the same time the LC droplet formation begins.

In the pixel region one can see the formation of LC droplets by switching the applied voltage off for a short period of time or slightly rotating one of the polarizers from the crossed state. When the field is switching off, the droplets appear as bright spots on the dark background due to their birefringence. If the field is on, only difference of droplet refractive index from that of the surrounding allows determining, with parallel or partly crossed polarizers, the presence of the droplets. This is because the LC of the droplets is aligned normally to the cell by the strong electric field of order 10^7 V/m. As the temperature decreases the droplet size increases.

In the interpixel region LC droplets formed during the phase separation are visible or slightly visible between crossed polarizers. Their appearance depends on how close they are to the ITO edges. The droplets in the center of an interpixel gap are less visible and their brightness increases as they get closer to an edge.

As the size of LC droplets in the interpixel region increases, they begin to move toward the ITO lines. Once a droplet reaches the ITO edge, it moves into a narrow region along the edge. As more LC droplets move to the edge regions, they widen and become brighter between crossed polarizers (Figure 2a). The width of the edge regions increases near the pixel corners and decreases again in the interpixel intersection square.

The droplets that are formed in the interpixel square never move toward the pixel corners. First they move in the direction of the closest edge and then, along the edge and out of the interpixel region. When the pixel edge regions are saturated with the LC, they begin to grow into the pixel area, pushing still isotropic LC/monomer mixture out to the interpixel region, where the separation occurs.

The final appearance of a multiplexed cell is shown in the Figure 2b. The monomer occupies most of the interpixel region, except the part close to the pixel corners. The liquid crystal fills all the pixel and pixel edge regions, and sometime fills the interpixel intersection completely or partially (as in the Figure 2b). The behavior at the interpixel intersection depends on the difference between the volume ratio of the pixel-interpixel volume and volume ratio between the LC and monomer, which generally is lower than weight ratio 9:1 due to higher density of the monomer.

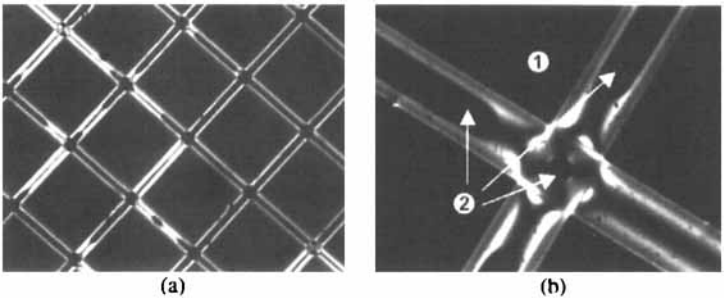


FIGURE 2 Polarizing microscopy photographs of an 80-dpi CLP cell filled with a 9:1 weight ratio mixture of E48 and NOA 81. a) Polarizers are crossed at an intermediate angle between 0 and 90 deg to facilitate the process observation. b) Polarizers are crossed at 90 deg and parallel to the photograph edges. 1 corresponds to a LC rich region in pixel area and 2 indicates monomer rich domains in the interpixel regions. (See color plate XIIat the back of this issue)

It appears that the difference in dielectric constants of the E48 and NOA 81 along with the electric field nonuniformity play an important role in the processes of polymer wall formation. We take the electrostatic field functional for the dielectric medium such as a LC-monomer isotropic mixture as

$$F=\int_V f(\Phi,\Phi'_x,\Phi'_y,\Phi'_z)dv=\int_V\left(\frac{1}{2}\varepsilon\,E^2-\rho V\right)dv. \tag{1}$$

The integrand in the first term of Eq. 1 is the volume free energy density, ε is the dielectric constant of the medium, E is the electric field strength, ρ is the density of static charges, and Φ is the electric potential. As a first approximation, an isotropic mixture of two dielectric liquids (E48 and NOA 81 at high temperatures) without static charges ($\rho=0$) is assumed to have an effective dielectric constant that depends linearly on the LC concentration:

$$\varepsilon_{mix}=(\varepsilon_{LC}-\varepsilon_m)c_{LC}+\varepsilon_m, \tag{2}$$

where c_{LC} is the concentration of the LC, ε_m and ε_{LC} are the dielectric constants of monomer and LC in its isotropic phase respectively.

Minimizing the functional we can transform the Euler equation,

$$\frac{\partial f}{\partial\Phi}-\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial\Phi'_x}\right)-\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial\Phi'_y}\right)-\frac{\partial}{\partial z}\left(\frac{\partial f}{\partial\Phi'_z}\right)=0 \tag{3}$$

into the following form:

$$\frac{\partial}{\partial x}(\varepsilon_{mix}E_x)+\frac{\partial}{\partial y}(\varepsilon_{mix}E_y)+\frac{\partial}{\partial z}(\varepsilon_{mix}E_z)=0, \tag{4}$$

which is equivalent to the Maxwell equation $\nabla\cdot\varepsilon_{mix}\mathbf{E}=\rho=0$.

Taking into account Eq. 2, we will arrive at

$$(\varepsilon_{LC}-\varepsilon_m)\nabla c_{LC}\cdot\mathbf{E}+((\varepsilon_{LC}-\varepsilon_m)c_{LC}+\varepsilon_m)\nabla\cdot\mathbf{E}=0. \tag{5}$$

The Eq. (5) tells us that in the case of a non-zero $\nabla\cdot\mathbf{E}$ the LC concentration in the mixture should have some gradient too. This could induce local (in the region of the electric field of high magnitude and gradient) concentration gradients of the mixture at temperatures above the phase separation point. A strong nonuniform electric field is able to increase noticebly (1-10°C) the phase separation point by changing the local concentration of liquid crystal. This phase separation would take place only in regions where the electric field is high and highly nonuniform.

The movement of LC rich droplets in the interpixel region to the ITO line edges indicates the presence of force. The nature of this force can be directly associated with the nonuniformity of the fringing field. In Figure 3 we present the results of computations of the electric field in a 5 μm muliplexed cell as the negative gradient of the 3D electric potential, Φ:

$$\mathbf{E} = -\nabla\Phi\,. \tag{6}$$

These calculations show that the electric field in the cell has the highest gradient along the electrode edges. Also the magnitude of the fringing field at the edges can exceed significantly 10^7 V/m, the value of the field inside the pixel region (Figure 3a and 3b). This is because the electrodes, as conductors, must have higher charge density at the edges to maintain unipotential.

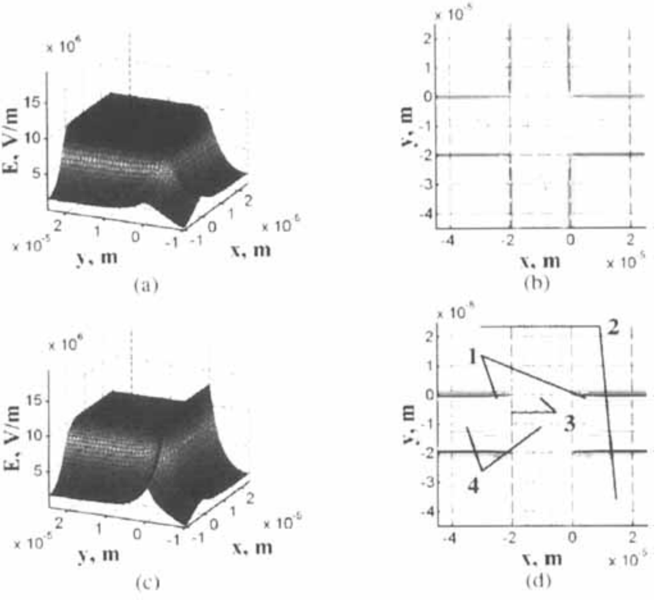


FIGURE 3 Electric field magnitude profiles and corresponding contour plots calculated for an 80-dpi multiplexed cell. The 5μm cell is filled with a homogeneous, isotropic dielectric liquid with average dielectric constant, $\varepsilon = 10$. The applied voltage is 50 V. (a) and (b) correspond to the middle plane of the cell, (c) and (d) to the distance of 1.5μm from the middle plane toward the substrate with ITO lines parallel to axis x. (See Color Plate XIII at the back of this issue)

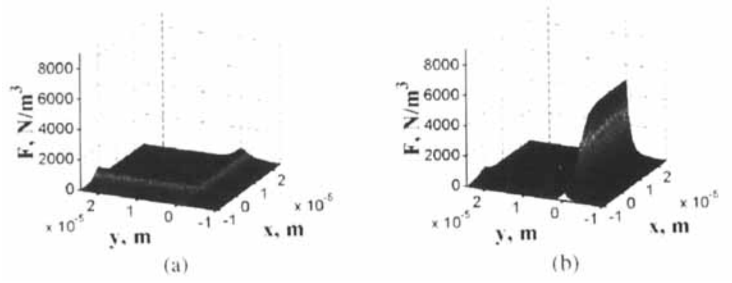
Small LC droplets formed during the phase separation in the interpixel region experience the Kelvin polarization force, the density of which can be determined as

$$\mathbf{F} = (\varepsilon_d - \varepsilon_{mix})\mathbf{E} \cdot \nabla \mathbf{E}, \tag{7}$$

where ε_d is the effective dielectric constant of the LC in droplets and ε_{mix} is the dielectric constant of the isotropic mixture. Since we use strong electric fields, the LC inside the droplets is aligned along the field direction. Therefore the value for ε_d can be assumed to be $\varepsilon_\parallel$ of the LC. ε_{mix} can be determined according to Eq. 2, assuming the effective dielectric constant of the LC in the mixture to be the average value: $\varepsilon_{LC} = (2\varepsilon_\perp + \varepsilon_\parallel)/3$. For E48 and NOA 81 the estimation is $(\varepsilon_{LC} - \varepsilon_{mix}) \approx 15$. Simple transformations produce the following formula to calculate the Kelvin force density:

$$\mathbf{F} = \frac{1}{2}(\varepsilon_d - \varepsilon_{mix})\nabla(E^2). \tag{8}$$

The results of the calculations are shown in Figure 4. It is seen that the force density distribution has its maximum at the edges of the electrode lines and is practically zeroed in the pixel region. This means that a small LC droplet will experience the force only near the electrode edge.



(a) (b)

FIGURE 4 Kelvin polarization force density calculated for an 80-dpi multiplexed cell. a) middle plane of the cell. b) plane shifted by 1.5 μm toward the substrate with electrodes parallel axis x. (See color plate XIV at the back of this issue)

The LC, as the component with higher dielectric constant, tends to occupy the space with higher electric fields. The regions with the highest electric field are those near the pixel edges (corresponds to 1 in Figure 3d); then the pixel regions 2, then the edge regions 3 at the interpixel intersection, and finally the minimum electric field is in regions 4 in the middle of the space between adjacent pixels and in the center of the interpixel intersection. Since the LC component dominates in the mixture, it is most likely that the LC, after the phase separation is completed, will fill regions 1-3 and the monomer, as the component with low dielectric constant, will occupy regions 4. This corresponds to the experimental results (compare with Figure 2b).

CONCLUSIONS

Polymer wall formation in liquid crystal-monomer mixtures confined in a patterned electrode cell occurs due to nonuniformity of the applied field and mismatch of dielectric constants of the mixture components. The electric field in a multiplexed cell has the highest gradient and strength near the ITO lines edges. Such a field, applied to an isotropic LC-monomer mixture in a patterned electrode cell at temperatures above the phase separation point, can change locally the concentration ratio of the mixture components and can cause of phase transition temperatures to shift. As the phase separation occurs, the same nonuniformity of the applied field can drive the component with the higher dielectric constant into the high field region, and the other component into the low field region. These processes result in the space demixing of the mixture components that produces the polymer walls upon UV light irradiation.

Acknowledgments

This research is supported in part by DARPA Contract No. N61331-94K-0042, and by NSF Science & Technology Center, ALCOM, No. 89-20147. We would like also to thank Eugene C. Gartland for help with computational aspects.

References

[1] D.-K. Yang, L.-C. Chen, and J.W. Doane, *Conference record of IRDC (SID)*, **49**, (1991).
[2] D.-K. Yang, and J.W. Doane, *SID Digest of Technical Papers*, **759** (1992).
[3] J.W. Doane, D.-K. Yang, and Z. Yaniv, *Jpn. Display*, p. 73, (1992).
[4] J.L. West, R. B. Akins, J.J. Francl, and J.W. Doane, *Appl. Phys. Lett.* **63**, 1471 (1993).
[5] J.L. West, G. R. Magyar, J.J. Francl, *SID Digest of Technical Papers*, **608** (1994).
[6] J.L. West, M. Rouberol, J.J. Francl, Y. Ji, J.W. Doane, and M. Pfeiffer, *Asia Display*, **55** (1995).
[7] Y.Ji, J. Francl, W.J. Fritz, P.J. Bos, and J.L. West, *SID Digest of Technical Papers*, **611** (1996).
[8] N.A. Vaz, G.W. Smith, and G.P. Montgomery, Jr., *Liq. Cryst.* **146,** 1 (1987).
[9] Y. Kim, J. Francl, B. Taheri, and J.L. West, *Appl. Phys.Lett.* **72**(18), 2253 (1998).
[10] W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in Fortran 77: The Art of Scientific Computing* (Cambridge University Press, 1996), p. 854.
[11] H.A. Haus and J.R. Melcher, *Electromagnetic Fields and Theory* (Prentice Hall, Englewood Cliffs, New Jersey, 1989), p. 515.