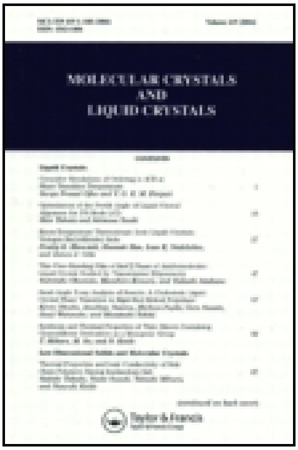

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Large LC Droplets in Polymer Matrix

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Version of record first published: 18 Oct 2010

To cite this article: S. J. Kłosowicz, A. Walczak, E. Nowinowski-Kruszelnicki & D. Manaila-Maximean (2004): Large LC Droplets in Polymer Matrix, Molecular Crystals and Liquid Crystals, 412:1, 453-459

To link to this article: http://dx.doi.org/10.1080/15421400490431976

Mol. Cryst. Liq. Cryst., Vol. 412, pp. 453/[2063]–459/[2069], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490431976

LARGE LC DROPLETS IN POLYMER MATRIX

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The methods of preparation of PDLC containing liquid crystals droplets of size larger than 15 μm in planar cells are presented. The morphology of such systems is discussed. The essential properties of electro-optical switching in large LC droplets are presented. The possibility of an application of such systems to measure elastic properties of confined LC is shown.

Keywords: director field; electro-optical switching; phase separation; polymer-dispersed liquid crystals

INTRODUCTION

Relatively large liquid crystal (LC) droplets can be interesting for studies of director field, optical properties and anchoring effects in those materials. Polymer-dispersed liquid crystals (PDLC) contain LC droplets, however their size is usually small, order of 1 μm [1] or even lower. For this reason the anchoring effects are profound, moreover it is difficult to adopt light beam as a measuring probe. In this paper we present the way of preparation large LC droplets in a polymer binder, their electro-optical properties and the method of director field determination in those droplets, which can lead to estimation of elastic constants in such systems.

This work has been supported by the Polish State Committee for Scientific Research (MUT Statutory Task PBS637).

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METHOD OF DIRECTOR FIELD MEASUREMENT

Let us consider a planar waveguide (shown in the Figure 1 between glass prism and plane parallel plate) in which the refractive index is a function n(z)where z-axis is perpendicular to the guiding layer.

The condition for wave propagation in the guide requires that total phase change measured along the beam path must be 2π multiplicity. This resonance condition is [2]:

$$2k_0 \int_0^{z_m} (n^2(z) - N_m^2)^{1/2} dz + 2\varphi_{ca} + 2\varphi_{cb} = 2\pi m. \tag{1}$$

The turning point Z_m is defined by $n(Z_m) = N_m$, where N_m is the effective refractive index for a mode propagating along the guide. In Equation (1) the m is an integer numbering the modes, while k_0 is the wave vector in the free space. Phase shifts φ_{ca} and φ_{cb} are described by Fresnel rules [2]:

$$\varphi_{ca,cb} = \operatorname{arctg}\left(\frac{n(z_m)}{n_{a,b}}\right)^{\rho} \sqrt{\frac{N_m^2 - n_{a,b}^2}{n^2(z_m) - N_m^2}}, \tag{2}$$

where ρ equals 0 for a wave polarized perpendicularly to the plane of incidence, or 1 for a wave polarized in plane of incidence. Subscripts a, b, c

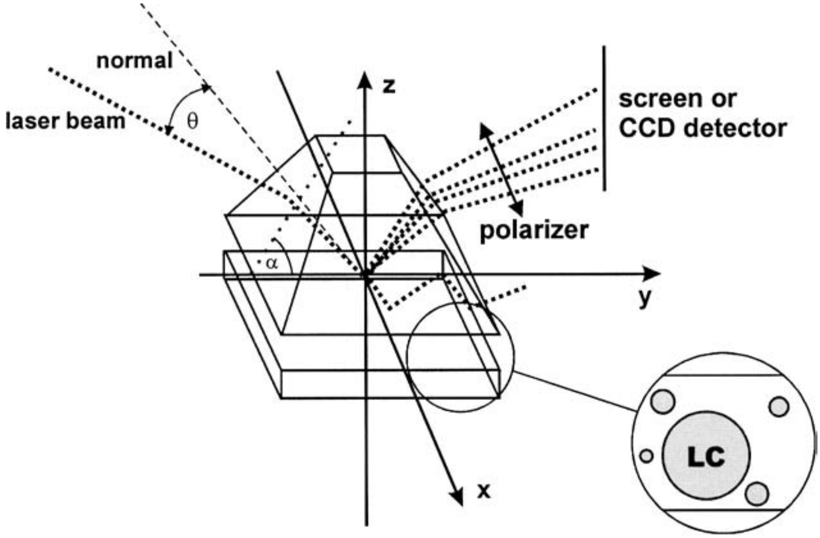

FIGURE 1 Measuring device cross-section and the scheme of modal lines visualization.

stand for waveguide regions (compare Figure 1), where "c" is the region of the guide while "b" and "a" are regions of the optical buffer ITO/SiO_2/polyimide on both boundaries of the waveguide.

To solve the Eq. (2), the effective indices N_m for the mode of number m have to be measured. Such reconstruction of n(x) is an inverse problem and the solution has been obtained by WKB method [3].

If a photon incident along the interface between prism and PDLC layer matches the momentum of the optic mode in the waveguide, the refractive index for the mode excited at the moment is equal:

$$N_m = n_p \sin\left(\alpha + \arcsin\left(\frac{\sin(\theta_m)}{n_p}\right)\right) \tag{3}$$

This relation can be easily seen from the Figure 1. The used symbols stand for: α – prism's angle as in Figure 1, θ_m – incidence angles while guided mode is excited, n_p – refractive index of the prism, respectively. Therefore, using the device shown in Figure 1, one can easy measure propagation constant for each excited mode. Using Eq. (2) and (3) one can reconstruct the refractive index profile in waveguiding layer. Two different sets of N_m values (for ordinary and extraordinary modes, respectively) are obtained for anisotropic material (LC) placed inside the waveguide. Each set is used to reconstruct the ordinary and effective indices.

Using of values resulting from formula (3) one can also resolve n(z) profile of refractive index across the large drop body. We assumed that nematic inside the drop may be described by Ericksen-Leslie form:

$$\begin{aligned}&\left(k_{11}\cos^2\theta + k_{33}\sin^2\theta\right)\frac{\partial^2\theta}{\partial z^2} + (k_{33} - k_{11})\sin\theta\cos\theta\left(\frac{\partial\theta}{\partial z}\right)^2\\&\quad + \varepsilon_0\varepsilon_{eff}(z)E^2\sin\theta\cos\theta = 0\end{aligned} \tag{4}$$

with boundary condition:

$$k_{33}\cos^2\theta\left|\frac{\partial\theta}{\partial z}\right| + k_{11}\sin^2\theta\left|\frac{\partial\theta}{\partial z}\right| - \frac{\partial g_s}{\partial\theta} = 0 \tag{5}$$

where:

$$\varepsilon_{eff}(z) = \varepsilon_\perp + \Delta\varepsilon\, n(z)\cdot n(z) \tag{6}$$

$$n(z) = (\cos\theta(z), \sin\theta(z)) \tag{7}$$

The anchoring energy has been assumed in well-known Rapini-Popoular form [4]:

$$g_s = -\frac{1}{2}W_s(n\cdot e_0) \tag{8}$$

With known $\Delta\varepsilon$ one can determine k_{11}, k_{33} and W_s assuming electric field amplitude E uniform and steady. Similar approach for ATR measurement has been done in several Sambles and co-workers works [5–7]. The advantage of the proposed way is that none analysis of the behaviour of electromagnetic wave inside LC layer have to be done. The angular positions measured for ordinary and extraordinary modes line is quite enough to obtain the result [8].

EXPERIMENTAL

Photopolymerization-induced phase separation (PPIPS) has been chosen as the main PDLC preparation method. UV-curable polymercaptoester NOA-65 (Norland) has been adopted as a prepolymer of polymeric binder, while nematic mixture W-765 (Institute of Chemistry MUT), adjusted for this particular binder, has been chosen as a nematic LC.

Additionally the PDLC system consisting of the same LC and poly methylmethacrylate, obtained by combined solvent-induced phase separation (SIPS) and thermally-induced phase separation (TIPS) has been studied.

In the first step of PPIPS, mixtures of the components with high content of LC (from 40 to 60 per cent by weight) containing 9 μm glass spacers have been prepared. Then the measuring device (Fig. 1) has been prepared in the following way. A drop of the obtained mixture has been placed on the glass plate with conducting ITO layer, covered by the glass prism and gripped to obtain the cell thickness equal to the spacers' diameter. Then the cell has been illuminated by low-intensity UV flux (order of 0.01 W/cm^2, BondWand ElectroLite lamp), within 10 to 60 minutes securing slow PPIPS process. This procedure allowed growth of large LC drops due to the diffusion of LC from initial prepolymer-LC mixture to the nucleated droplets. The temperature of UV illumination has been usually elevated (50–70°C) to enhance LC solubility in the prepolymer, and decreased during curing process up to the room one.

In SIPS/TIPS method the polymer and the LC have been mixed (40/60 by weight, respectively) and dissolved in chloroform; the solution, with an approximate concentration of 1:9, was homogenized and spread onto ITO coated glasses, and the solvent has been slowly evaporated. After preparation the measuring cell, the dimension of the resulted droplets was reset by heating the sample up to 120 Celsius and cooling it down with a cooling rate of 0.1°C/min.

Obtained systems have been observed under polarizing microscope to register LC arrangement inside droplets and to find their location, then the described above waveguiding experiment has been performed.

The electro-optical optical properties of LC droplets have been measured by an application of bias electric field to the ordinary cell made of glass plates with ITO conductive layer. The observation of switching has been performed under polarizing microscope.

RESULTS AND DISCUSSION

In Figure 2 the microscopic images of large LC drops in polarized light are presented . Those drops have been highly flattened (see Figure 2d), moreover it has been observed that very large LC drops usually have non-circular cross-section due to the coalescence of few smaller droplets (see Figure 2c). Hence large LC drops are similar to thin LC layer rather than to spherical droplets in ordinary PDLC systems. This conclusion has been confirmed by a measurement of switching voltages for droplets of different size, results of which are presented in Figure 3.

As one can see, the switching voltage decreases with the increase of drop size and for sufficiently large drops it is close to that one observed for thin layer of LC (LCD geometry). In this way we obtained systems with

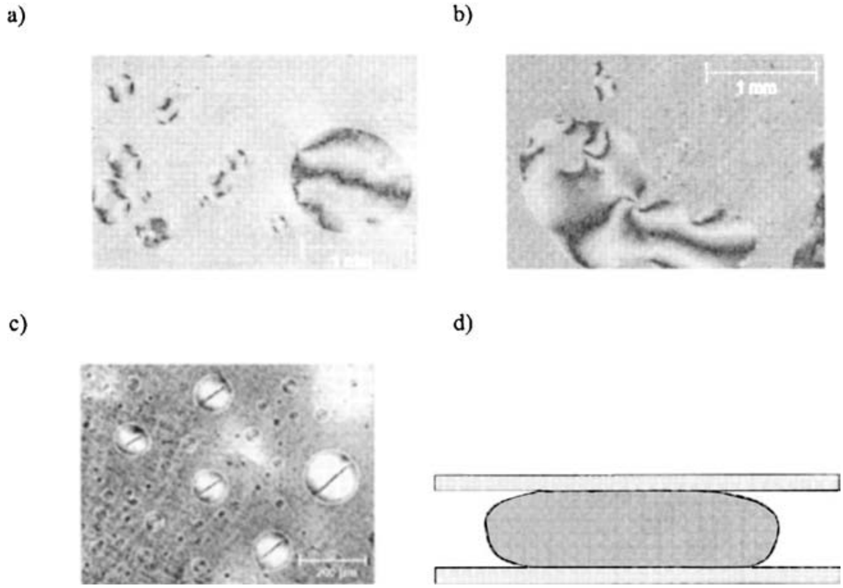

FIGURE 2 Images of large nematic droplets in polymer binder obtained under polarizing microscope: a) PPIPS-large drop of circular cross-section, b) PPIPS-the effect of drops coalescence, c) SIPS/TIPS, d) schematic cross section of the large LC drop.

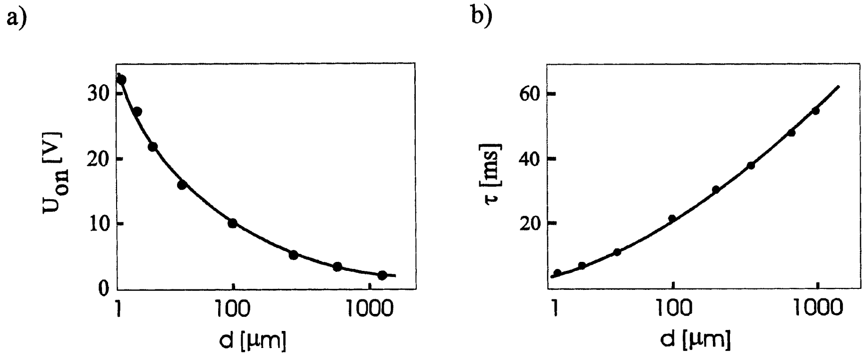

FIGURE 3 Switching voltage (a) and total switching time (b) of LC droplets as a function of their transversal size.

continuous change of properties from thin layer to droplets embedded into polymer matrix.

The director field inside large LC drops is usually more complicated than in case of small droplets, i.e. more point defects and disclination lines are observed. Moreover sometimes an intermediate layer being a classic (small droplet) PDLC surrounded large LC drop and separated it from the polymer binder. Nevertheless, usually tangential orientation of LC inside droplets has been observed.

The preliminary results of director field measurements seem to be in accordance with expectations. Elastic Frank constants obtained in waveguiding experiment are of the order of 10^{-11} N, however they are somewhat larger for LC drops than for thin layer, especially for drops of smaller size. These results are only semi-quantitative till now. The general conclusion is that small droplets, i.e. those with diameter close to the layer thickness, exhibit higher stiffness than thin planar LC layer. The contribution of the K_{13} Frank constant probably plays an important role [9]. The measuring method should be improved by reduction of beam diameter enabling measurements for smaller LC droplets.

CONCLUSIONS

1. It is possible to grown large LC drops in polymer matrix using modified induced phase separation methods.
2. The director field in such drops can be studied by waveguiding optical method. As a result, the fundamental optical and elastic properties of the LC material can be estimated.
3. Electro-optical properties of the large LC drops are similar to those ones observed for thin layer of LC.

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