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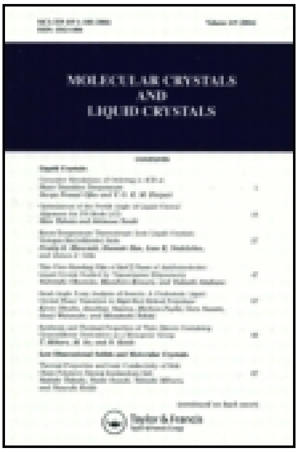

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Manipulation of Nematic Liquid Crystal Microdroplets by Pyroelectric Effect

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Published online: 02 Apr 2013.

To cite this article: Francesco Merola, Simonetta Grilli, Sara Coppola, Veronica Vespini, Sergio DeNicola, Pasquale Maddalena, Cosimo Carfagna & Pietro Ferraro (2013) Manipulation of Nematic Liquid Crystal Microdroplets by Pyroelectric Effect, Molecular Crystals and Liquid Crystals, 572:1, 66-71, DOI: 10.1080/15421406.2012.763212

To link to this article: http://dx.doi.org/10.1080/15421406.2012.763212

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Mol. Cryst. Liq. Cryst., Vol. 572: pp. 66–71, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.763212

Manipulation of Nematic Liquid Crystal Microdroplets by Pyroelectric Effect

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We present experimental results concerning liquid crystals microdroplets behavior onto functionalized lithium niobate substrates covered with Polydimethylsiloxane (PDMS) polymer. Droplets are fragmented, driven, and reassembled by electric fields generated by pyroelectric effect. We analyze the dynamics of the observed phenomena and suggest possible technological applications.

Keywords Liquid crystals, lithium niobate; polydimethylsiloxane; pyroelectric effect

1. Introduction

In recent years, liquid crystals (LCs) applications have experienced a rapid growth in many fields, ranging from display systems as well as in optics and photonics [1–9]. The major attractive feature of LCs lies in the fact that their optical properties can be modulated by electric, optical, or magnetic fields. At present, many issues are still open and further developments for manipulating and dynamically control LCs are highly demanding in many emerging fields of technology but also in fundamental research.

On the other side, ferroelectric and/or pyroelectric crystals are widely studied and employed for patterning or assembling organic and inorganic structures [10–15], also displaying different behaviors depending on the sign of the charged surface [16]. In particular, lithium niobate (LN) finds applications as selective decoration of LN domains by polystyrene microspheres [13], fabrication of silver nanowires on LN domain boundaries [17], as well as Ag deposition on periodically poled LN (PPLN) [18] and deposition of different elemental metals confined to the ferroelectric LN domain walls [19].

Lately, a novel approach has been discovered for manipulating different classes of liquids by exploiting the pyroelectric effect, where the strong electric fields pyroelectrically

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generated allow to manipulate liquids in two-dimensional on a substrate or even in three-dimensional for dispensing liquids from one liquid reservoir to a dispensable substrate. Among various applications demonstrated by taking advantage of this effect, we cite spatial modulation of the wettability (i.e., wettability patterning), fabrication of arrays of solid polymeric microlenses, realization of arrays of tunable liquid lenses, and finally liquid dispensing, patterning, and curing at nanoscale [20–25].

In this article, the behavior of LC droplets on z-cut LN wafers is reported [26,27]. The LN sample is functionalized in various configurations, in particular, by microengineering its ferroelectric domains (i.e., by spatially arranging the inverted ferroelectric domains) and covering its surface with a film of hydrophobic polymer. Very promising effects are reported and discussed. Essentially, a reversible uniform fragmentation of large LC drops has been observed [28–33]. In fact, driven by the pyroelectric fields obtained by a thermal stimulus applied to the LN substrate, the fragmented drops are self-assembled on the substrate according to the underneath ferroelectric domain patterned structures into LN. Successive coalescence of the fragmented tiny drops is observed on a longer time scale. Reversible character of the whole process has been verified. The aforementioned phenomena are deeply investigated and results of many experiments are shown.

2. Manipulating Liquid Crystal Droplets

The behavior of a nematic LC in contact with a Polydimethylsiloxane (PDMS) substrate, subject to a temperature variation, has been tested. It has to be said that, due to the PDMS nonfull wettability, it is difficult to obtain a LC homogeneous thin layer upon it; vice versa, LC arranges itself in drops. Then, thanks to the applied thermal input, a dewetting-like phenomenon occurs, in analogy with Sun et al. [33], that is, a fragmentation of drops in smaller ones. But, we also deposited the PDMS layer on a geometrical structure capable to drive these small droplets, that otherwise would be distributed on the substrate in a random configuration: a PPLN.

Experimental measurements are carried out mainly on two different samples, that we named A and B and represented in Fig. 1. Details about the fabrication of samples can be found in [21,34–36].

In the following experiments [37], a small quantity of nematic LC 1-(*trans*-4-hexylcyclohexyl)-4-isothiocyanatobenzene, 6CHBT [38,39] (with phase sequence Cr 12.5°C N 43.2°C I), from Sigma Aldrich, is placed onto each sample. This LC has been chosen for the polar structure of the molecule. Successively, the sample is heated on a hot plate at 90° for 30s and then placed at room temperature under an optical microscope in transmission configuration.

The starting situation is that of many LC drops with different dimensions scattered all over the sample, as in Fig. 2(a). On heating the specimen, a quite uniform fragmentation of

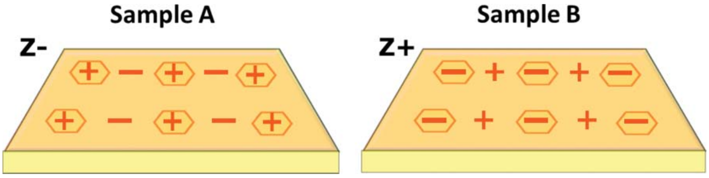

Figure 1. Fabricated samples. Sample A: PDMS film spin coated on a PPLN Z− face. Sample B: PDMS film on PPLN Z+ face. The plus and minus represent the signs of the electric charges. The pitch of the structures is about 200 μm.

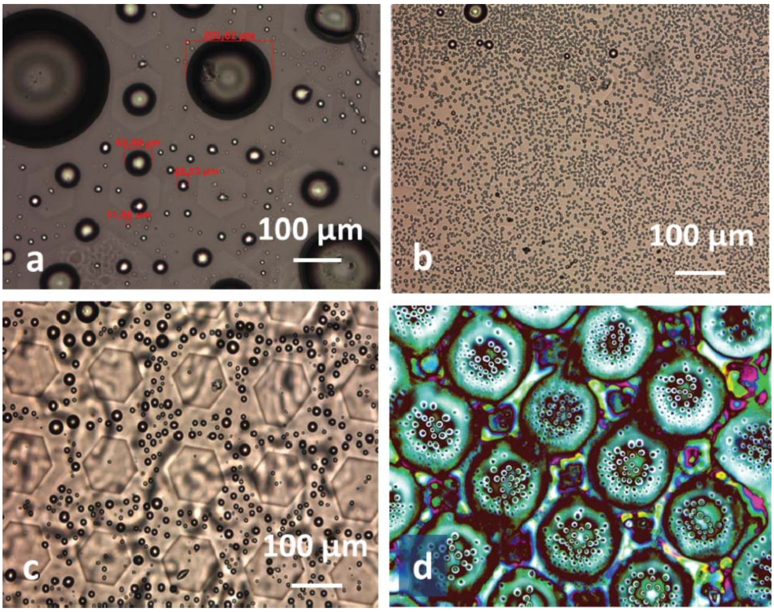

Figure 2. Temporal evolution of the experiment on samples A and B. (a) LC drops scattered on the sample without any geometry, before heating. Magnification is about 200. (b) Fragmented LC microdroplets suddenly after heating at 90°C, with dimensions much smaller than before heating. LN hexagonal domains are not well visible, covered by the droplets. (c) Sample A and (d) sample B several minutes after cooling: the droplets have been driven and assembled (c) outside and (d) inside hexagonal domains by pyroelectric effect.

the LC drops occurs; a high density of smaller droplets covers the whole sample, as reported in Fig. 2(b). This phenomenon resembles the well-known dewetting effect [20,40–45].

During the cooling step (at room temperature of 22°C), droplets are driven by the electric field pyroelectrically generated, outside (Fig. 2c, sample A) or inside (Fig. 2d, sample B) the hexagonal domains of PPLN [37].

The first evidence is that almost all of the LC drops move selectively in the areas around or onto the hexagons, depending on the side of the LN crystal, demonstrating that the phenomena are driven by the sign of the pyroelectric charge. The further significant aspect is that the fragmented drops coalesce. After 2 hours, in fact, the average size of the drops is substantially increased. This phenomenon could be probably ascribed to a reduction of the interfacial tension between nematic LC and PDMS with the decreasing of temperature [46].

Let us consider the latter case, that is, sample B. The coalescence of small droplets into bigger ones, while migrating onto the center of the hexagonal domain, can be observed. It is interesting to note that LC droplets are aligned along radial directions passing through the center of each hexagonal domain. The geometrical arrangement suggests they are aligned along the lines of the electric field components in the plane of the substrate, and travel onto the domain following these lines, as shown in Fig. 3(a). Figure 3(b) represents an image taken under crossed polarizers, putting in evidence the birefringent nature of LCs.

The phenomenon at the basis of this experimental behavior is the well-known dielectrophoresis, widely described in literature [47–53]. In this case, however, the process is not induced by an external electric field, but it is due to a pyroelectric effect. So in this

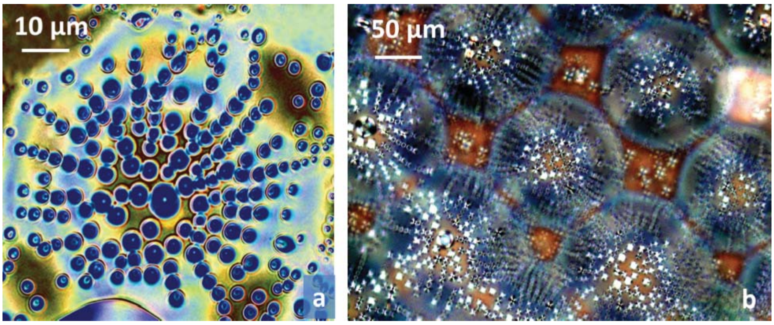

Figure 3. (a) LC droplet chains aligned along electric field lines. (b) Image taken under crossed polarizers evidencing Maltese crosses corresponding to droplets.

case, we speak of pyroelectrophoretic effect, already described in reference [34], but with different samples. The advantage of using LCs, in this case, is the birefringent behavior of these materials and their well-known ability to change the polarization of the incident polarized light and, consequently, the huge technological impact they have. Details about the pyroelectric effect in PPLN can be found in references [35,54].

Let us suppose the surface of the crystal is Z− and consider the case $\Delta T < 0$, that is, a cooling situation. As observed before, in this case, LC droplets are repulsed by inverted domains (hexagons) and place themselves among them, forming a sort of matrix, as schematized in Fig. 2(c). The LC molecules are repulsed from a positive charged region. Vice versa, if the surface under consideration is Z+, LC droplets are attracted by hexagons (in this case, negative regions), as depicted in Fig. 2(d). This behavior has to be ascribed to the strong dipole moment of the 6CHBT LC molecule [38]. In fact, analysis of electrostatic potential distribution shows that the head of the molecule exhibits negative potential, while the edges of the aromatic ring have a positive potential. The potential of the rest of the hydrocarbon chain is roughly neutral [38].

In case, this latter phenomenon could be exploited to obtain self-arrangement of small LC lenses. In fact, the coalesced LC drop produces a lens effect (Fig. 4) [37].

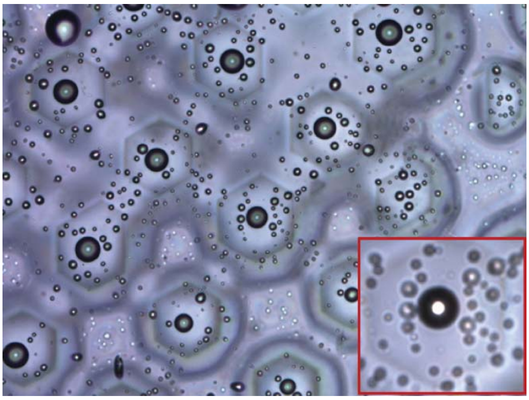

Figure 4. Microscope image of sample B after about 1 hour of cooling, in the LC lens' focal plane (from reference [37]).

3. Conclusions

In conclusion, we have been able to maneuver 6CHBT LC microdroplets exploiting the pyroelectric properties of a periodically poled LN crystal covered with PDMS polymer. Thanks to the geometrical functionalization of the substrate in inverted domains, the electric field (generated without the need of electrodes) can drive LC droplets in particular locations.

Many phenomena have been observed: fragmentation of drops in smaller ones, migration to different regions of the sample according to the geometry of the substrate (pyroelectrophoretic effect) and following the electric field lines, successive coalescence in bigger drops with the possibility of new fragmentation, square-matrix arrangements and lens effects, and planar alignment of the LC directors (Maltese crosses).

Applications can be found in the field of photonics, as the sample can be viewed as a dynamical optical element able to switch from a diffuser state (fragmentation state) to a microlens array (coalescence state). In case, the birefringent microlenses could be also tunable. Of course, for practical applications as photonic devices, the time needed for the processes should be reduced, for example by enhancing the applied gradient of temperature.

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