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Communication: Orientational structure manipulation in nematic liquid crystal droplets induced by light excitation of azodendrimer dopant

Sergey A. Shvetsov,^{1,a)} Alexander V. Emelyanenko,¹ Natalia I. Boiko,¹ Jui-Hsiang Liu,² and Alexei R. Khokhlov¹

¹M.V. Lomonosov Moscow State University, Moscow, Russia ²National Cheng Kung University, Tainan, Taiwan

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Reversible orientational transitions in the droplets of a nematic liquid crystal (NLC) caused by the change of boundary conditions under the low intensity diode illumination are investigated. Photosensitivity of NLC is achieved by the addition of the dendrimer compound with azobenzene terminal groups. Two types of NLC droplets in glycerol are considered: the spherical droplets in the bulk of glycerol and the droplets laid-down onto the solid substrate. In the second case, the first order phase transition is revealed. The effects described can be useful for the development of highly sensitive chemical detectors and microsized photo-tunable optical devices. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4984984]

Dispersions of nematic liquid crystals (NLCs) are of great interest in different research fields, such as electro-¹⁻³ and nonlinear⁴ optics, medical applications,⁵ and sensor devices⁶ of various inclusions from ions⁷ to bacteria and viruses.⁸

For this reason, several approaches for the control and modulation of a NLC droplet structure have been developed. Bipolar-to-radial structure transformation in spherical droplets was first described in Ref. 9. NLC droplets in glycerol have a bipolar structure with two point defects at the surface due to planar surface conditions. Using a mixture of lecithin and glycerol, it is possible to change the surface conditions from planar to homeotropic by the variation of the sample temperature.

Another technique is an electrically controlled NLC droplet structure modification.^{10–12} The sensitivity of the NLC surface anchoring to the electric field has been achieved by doping the ion-forming compounds into the NLC. The rearrangement of positive and negative ions under the action of electric field caused significant changes in the surface anchoring conditions at some part of a droplet interface. In the initially bipolar NLC droplets encapsulated into a polymer matrix, one of the surface defects was collapsing, whereas, in the initially radial NLC droplet, the point defect was shifting from the center to the surface of the droplet.

Macromolecules have a tendency to self-organise and order their environment,¹³ specifying the biological structure formation.^{14,15} Thus, it was shown that some macromolecular additives (dendrimers with azobenzene terminal fragments) can modify the orientational structure of liquid crystalline droplets in glycerol.¹⁶ In particular, the droplet structure of NLC doped with azodendrimer becomes radial instead of the bipolar one. The effect is explained by adsorption of dendrimer molecules on the NLC-glycerol interface that causes the change of the surface anchoring condition. The formation

of *cis*-isomers of dendrimer chromophores under ultraviolet (UV) light illumination leads to the bipolar droplet structure.

Recently, the different geometry, when the NLC droplets were laid-down onto the solid substrate,¹⁷ was investigated, especially from the point of view of chemical sensor applications.^{7,18–20} Depending on the surface layer coating, different droplet structures can be realized, which can also be affected by the external impurity in the solvent. The main problem is that the NLC director distribution and the orientational transitions within these droplets are not clearly understood up to now.

In the present study, we obtained and investigated the orientational transitions in azodendrimer-doped NLC droplets under the light illumination. We considered two configurations of NLC droplets: in the bulk of glycerol and in contact with a solid substrate. The aim of this study is to reveal the features of optical structure manipulation in the NLC droplets with a different geometry.

We used the MLC6816 (Merck Ltd.) nematic liquid crystalline matrix based on cyclohexane derivatives, which is transparent to UV-light. The isotropization temperature of the matrix is 76.5 °C. NLC was doped with (0.08 wt. %) G5 carbosilane dendrimer of the fifth generation with azobenzene terminal groups (Fig. 1).

The influence of light illumination on the isomerization activity of dendrimer azo-fragments was investigated in the case of a planar 100 μ m film of NLC doped with 0.08% G5. The absorption spectrum of an extraordinary wave (measured by the MS-122 spectrophotometer, Proscan Special Instruments) is shown in Fig. 2 (curve 1) and corresponds to *trans*-isomers. To induce the *trans* \rightarrow *cis* and *cis* \rightarrow *trans* photoisomerization processes of dendrimer azofragments, two light diodes (LDs) were used: LD-1 with the luminescence maximum at $\lambda_{max} = 400$ nm (Fig. 2, curve 4) and LD-2 with the maximum at $\lambda_{max} = 467$ nm (Fig. 2, curve 5) (the spectra were obtained with the aid of Ocean Optics Maya 2000 Pro). Thus, LD-1 preferably induces the π - π^* transition which

^{a)}Electronic mail: shvetsov@lebedev.ru. Also at P.N. Lebedev Physical Institute, Moscow, Russia.



FIG. 1. Structural formula of the G5 carbosilane dendrimer of the fifth generation.

effectively switches the azo-fragments into cis-isomers, whereas LD-2 induces the $n - \pi^*$ transition and partially recovers *trans*-isomers.²¹ The luminance of LD-1 and LD-2 was 340 cn/m² and 2000 cn/m², respectively. The saturation of photoisomerization, at which the mutual concentrations of cis- and trans-isomers stopped changing in time, was reached during 30 s at LD-1 illumination and 120 s at LD-2 illumination. The main absorption peaks of saturation spectra at 360 nm (Fig. 2, curves 2 and 3) are lower than those before LD illumination due to the weaker absorption of cis-isomers with respect to that of trans-isomers. These changes in absorption spectra allowed us to evaluate²² the relative concentrations of trans- and cis-isomers in the saturation state: $X_{trans} = 0.1$, $X_{cis} = 0.9$ for LD-1 illumination and $X_{trans} = 0.7$, $X_{cis} = 0.3$ for LD-2 illumination. It should be noted that our estimations were made in the assumption that photoisomerization processes are not accompanied by a



FIG. 2. Absorption spectra of an extraordinary wave for planar NLC doped with 0.08% of G5: before light diode illumination (1), after LD-1 illumination (2), after LD-2 illumination (3), and normalized luminescence spectra of light diodes LD-1 (4) and LD-2 (5).



FIG. 3. Polarized optical microscopy (POM) image of NLC + 0.08% of G5 dispersion in glycerol: spherical nematic droplets in the bulk of glycerol (1) and NLC droplets at the cell substrate (2).

change of the NLC order parameter if the concentration of the dopant is small.^{23,24}

The nematic droplets were obtained by mixing the dendrimer doped NLC with glycerol. The mixture was filled into the 100 μ m-thick plane-parallel glass cell. Both inner surfaces of the cell were covered with a chromium stearyl chloride layer providing the strong homeotropic orientation of NLC.

This approach allowed us to distinguish the spherical NLC droplets located in the bulk of glycerol from the NLC droplets spontaneously laid-down onto the cell substrate. As one can see from the microphotograph (Fig. 3) of the sample placed between crossed polarizers, the spherical droplets of NLC located in the bulk of glycerol have a bipolar structure [Fig. 4(a)] with two point defects (boojums), while the droplets at the cell substrate have axial symmetry and contain one boojum in the middle [at the top of the droplet, see Fig. 4(b)]. Inhomogeneity of the surfaces causes the shape deviation of some droplets. The diameter *d* of the spherical droplets located in the bulk of glycerol varies between 5 and 50 μ m, while the diameter *D* of the droplets laid-down onto the cell substrate



FIG. 4. Schematic illustration of the NLC director distribution in spherical droplets located in the bulk of glycerol [(a) and (c)] and in droplets laid-down onto the cell substrate [(b) and (d)] in the cases of planar [(a) and (b)] and homeotropic [(c) and (d)] anchoring at the surface between NLC and glycerol. Dashed lines show the local director orientation.



FIG. 5. POM images of the spherical NLC droplet (MLC6816 + 0.08% G5) in glycerol at illumination of LD-1 during exposure time τ_{exp} : 0 s (a), 30 s (b), 40 s (c), 50 s (d), 70 s (e) and subsequent illumination of LD-2 during τ_{exp} : 0 s (f), 70 s (g), 90 s (h), 110 s (i), 130 s (j).

is significantly larger because of the wetting effect and varies between 40 and 150 μ m. The average ratio of droplet height *h* to diameter *D* was about 0.2.

Let us focus on the two droplets, one located in the bulk of glycerol and another one laid-down onto the cell substrate (1 and 2 in Fig. 3, respectively), and describe an influence of the LD illumination. In the case of a spherical droplet located in the bulk, the LD-1 light (with exposure time $\tau_{exp} \sim 70$ s) causes a transformation of its structure from bipolar to radial (hedgehog) [see Figs. 5(a)-5(e)]. The latter one is accompanied by the presence of a point defect in the center of a droplet [see the schematic illustration in Fig. 4(c)]. Illumination of LD-2 during $\tau_{exp} \sim 130$ s restores the initial bipolar structure of the droplet [see Figs. 5(f)-5(g)]. The bipolar structure restores also without any LD illumination because of the thermal cis \rightarrow trans relaxation of dendrimer azobenzene fragments, but it takes much longer time (~ 2000 s). Thus, the changes of a droplet structure should be associated with either *trans* \rightarrow *cis* or $cis \rightarrow trans$ isomerization processes of dendrimer azobenzene fragments.

It is interesting to note that, in the opposite way to the previous study of ordering transition in NLC droplets,¹⁶ the initial bipolar NLC droplet structure in glycerol, in our case, remains the same in the probe light by addition of azodendrimer dopants, while sufficient near-UV light illumination causes the radial structure formation. This can be associated with the specific dopant structure, which can promote the different anchoring types at the interface between NLC and glycerol molecules.

In the case of NLC droplets laid-down onto the cell substrate, the LD-1 illumination also causes the change in the droplet structure [Figs. 6(a)-6(g)]. This occurs due to the change of the boundary conditions from planar to homeotropic ones at the interface between nematic and glycerol, at which the boojum defect disappears [see the schematic illustration in Fig. 4(d)]. Because of the strong interaction of NLC molecules

with the cell substrate, the director tends to be oriented normally to the substrate surface that determines the darkening of the droplet image in crossed polarizers [Fig. 6(g)]. It is noteworthy that the areas with a different director orientation within a droplet have clear phase borders [Figs. 6(b)-6(f)]. This indicates that the change in the NLC director orientation most likely exhibits the first order phase transition, although sometimes it is difficult to distinguish between the first order phase transition and continuous transformation in small objects.²⁵ The LD-2 illumination reverses the initial director distribution. The change in the director orientation moves from the droplet periphery to its center [Figs. 6(h)-6(k)]. When the boojum is formed, it slowly shifts to the center of a droplet [Figs. 6(1)-6(n)]. The time of the direct orientational transition (under LD-1 illumination) is shorter ($\tau_{exp} \sim 20$ s), whereas the time of the reverse transition (under LD-2 illumination) is longer $(\tau_{exp} \sim 200 \text{ s})$ than in the case of spherical NLC droplets located in the bulk of glycerol. The reverse transition also occurs in the absence of LD illumination due to thermal $cis \rightarrow trans$ relaxation.

The described effects are similar to the bulk mediated photoalignment.²⁶ However, in our case, the photoactive surface layer is the interface between the NLC and isotropic liquid. The droplet structure transformations happen due to the different anisotropic interaction of NLC molecules with dendrimer molecules adsorbed at the interface between NLC and glycerol. The *trans*-state terminal fragments of dendrimer molecules tend to align along the NLC director, as the compound dissolved in NLC possesses significant dichroism in absorption spectra.²² On the contrary, when the terminal fragments turn into a *cis*-state, they are completely disordered that reduces the anisotropic anchoring of the NLC director.

Our preliminary study shows that the structural transitions can also be observed in the other nematic systems, particularly, in cyanobiphenyl-based NLC droplets with carbosilane azodendrimers of lower generations. However, the evolution



FIG. 6. POM images of the spherical NLC (MLC6816 + 0.08% G5) droplet at the cell substrate at illumination of LD-1 during exposure time τ_{exp} : 0 s (a), 2 s (b), 4 s (c), 6 s (d), 10 s (e), 15 s (f), 20 s (g) and subsequent illumination of LD-2 during τ_{exp} : 0 s (h), 120 s (i), 130 s (j), 140 s (k), 150 s (l), 160 s (m), 200 s (n).

of the droplet structures is well reproducible in both directions in the case of the cyclohexane NLC doped with G5 dendrimer. At the same time, the effect is absent in the case of low-molar mass azobenzene dopants. Thus, the possibility of the lightinduced structure transition in the NLC droplet depends on the molecular mass of the dopant. We believe that the dendritic molecular structure with long photosensitive branches embedded in NLC provides better influence on NLC molecular anchoring near the glycerol surface.

In conclusion, the orientational transitions in NLC droplets dispersed in glycerol were obtained and investigated. The NLC under study contained a small amount of azobenzene macromolecular compound (dendrimers of the fifth generation). At light illumination of the sample, which induces either $trans \rightarrow cis$ or $cis \rightarrow trans$ photoisomerization processes of dendrimer chromophores, the NLC droplets change their orientational structure. The increase of a cis-isomer concentration leads to the structure transformation of spherical droplets in the bulk of glycerol from the bipolar to the radial one. Different kinds of transformations are observed in the NLC droplets laid-down onto the solid surface: from planar having one point defect (boojum) at the top of the droplet to the defectless (almost homeotropic) director orientation. In the case of NLC droplets located on the solid surface, the structure transformation corresponds to the first order phase transition. Photo- or thermo-induced $cis \rightarrow trans$ isomer conversion recovers the initial structures of the droplets.

The effects described in this paper open a new way of the structure manipulation in liquid crystalline microparticles with the help of low-intensity light exposure. One can imitate any intermediate surface condition by simply varying the relative concentrations of *trans*- and *cis*-isomers of azobenzene-containing dopants. Features of the orientational transitions are important for further design of the low threshold chemical sensors. The NLC droplets with photocontrolled structures can be also used in the development of microsized tunable optical devices (phase plates, lenses, etc.). This study was supported by the joint project of the Russian Science Foundation (Project No. 16-43-03010) and Ministry of Science and Technology of Taiwan (Contract No. MOST 105-2923-E-006-007).

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