

Light-Induced Dynamic Behaviors and Tailored Droplet Arrays of Micro-Droplets in Photoresponsive Liquid Crystal Emulsions

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Glycerol micro-droplets ($\phi \sim 3 \mu\text{m}$) exhibited directional motions in liquid-crystal (LC) emulsions doped with azobenzene derivatives on photoirradiation. When the samples were locally irradiated with ultra-violet (UV) light ($\lambda = 365 \text{ nm}$), in which azobenzene derivatives in *trans* form were converted into *cis* one, the micro-droplets migrated inside the irradiated area resulting in forming a condensed two-dimensional hexagonal structure. To the contrary, the droplets in the condensed state showed drastic backward motion on irradiation of visible light ($\lambda = 435 \text{ nm}$) that induces the preferential *cis*-to-*trans* isomerization. Contact angle measurement indicated that glycerol-LC interfacial tension was reduced by irradiation of UV light. This will be attributable to adsorption of the *cis* isomers having the enhanced surface activity on the glycerol-LC interface. According to a concentration gradient of the *cis* isomers formed in the system, a spatial inhomogeneity of the interfacial energy around the droplets will be created and drive the droplet condensation so as to reduce the droplet-LC interfacial energy. On the basis of the discovered photokinetic effects, we attempted photochemical addressing of the micro-droplets with an aim to providing a versatile approach to construction of LC micro-devices.

Keywords: Liquid crystals, Colloids, Azobenzene, Interfacial tension

1. INTRODUCTION

Dispersions of small substances in continuous phases, colloidal suspensions and emulsions, are of considerable technological importance and ubiquitous in our everyday life.[1] Especially, over recent decades, colloidal systems employed liquid crystals (LCs) as the continuous phases have been recognized as a new class of materials and extensively explored owing to their scientific and technological interests.[2-7] In the LC colloids, orientational elasticity of LCs gives rise to anisotropic interactions between the particles with both repulsive and attractive components. Nature of LCs plays important roles in determining droplet configuration.

In this paper, we attempted manipulation of glycerol micro-droplets dispersed in LCs (LC emulsions) by modulating the physical properties of the systems. Alignment and physical properties of LCs are known to be quite sensitive to a variety of external fields. For instance, LCs readily change their macroscopic molecular alignment by applying electric and magnetic fields as well as temperature. On the other hand, by introducing photochromic compounds, the LCs can be modulated by optical fields. Azobenzene derivatives, which show *trans-cis* photoisomerization by absorbing appropriate light, are frequently employed in optical modulation of LCs.[8-14]

We will report here photochemically-induced dynamic behaviors (condensation and dispersion) of glycerol droplets in LC emulsions doped with azobenzene derivatives.[15] We also demonstrated

assembly of tailored droplet arrays.

2. EXPERIMENTAL

2.1 Materials

Chemical structures of compounds used in this study were shown in Figure 1. As a LC host, we employed 5CB, and doped it with an azobenzene derivative (8AB3COOH, $\lambda_{\text{max}} = 350 \text{ nm}$, 1 mol%).

2.2 Preparation of LC emulsion

A drop of the host LC was first placed on a purified glycerol layer to form a lens of 2 mm-thickness and 6 mm-diameter. It was then heated to 60 °C, well above its nematic-to-isotropic phase transition temperature (37

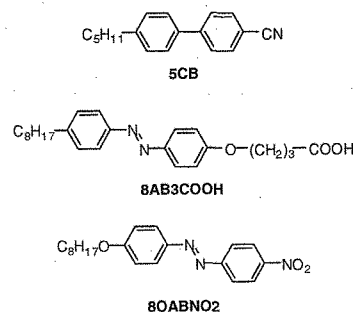


Figure 1. Chemical structures of liquid crystal and azobenzene derivative used in this study.

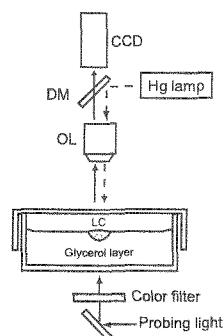


Figure 2. Schematic illustration of the experimental setup used in photoresponsive behavior of LC emulsion: DM, dichroic mirror; OL, objective lens.

°C), and kept there for 60 min. Substantial amount of glycerol could diffuse into the host LC at this elevated temperature. Then, the system was cooled to 30 °C well inside the nematic phase at the rate of about 0.5 °C/min.

2.3 Photoresponsive behaviors of LC emulsion

Photoresponsive behaviors were investigated with a fluorescent/polarizing microscope (Eclipse E-800, Nikon, Japan) equipped with an ultra-high-pressure mercury lamp as a light source of pumping light. The wavelengths of ultra-violet (UV, $\lambda = 365$ nm) and visible ($\lambda = 435$ nm) light were selected with a dichroic mirror. Sample temperature was controlled with a hot stage (Thermoplate MATS-2002ST, Tokai Hit, Japan). The experimental setup was shown in Figure 2.

Photochemical assembly of tailored droplet arrays was performed with "Maskless Projection System" (NewCreation Co. Ltd., Japan) equipped with a commercially available projector as a light source. On the hot stage, geometrical patterns were optically reduced and projected on the sample. Since the projector had no emission in the near-UV region, a distinct azobenzene derivative (8OABNO₂, 1 mol%, Fig. 2) that is sensitive to violet light was doped into the host LC.

2.4 Confocal fluorescence microscopy

A vertical position of the micro-droplets in the samples was investigated in an optical microscope (Eclipse model E600POL, Nikon) equipped with an image intensifier (model C8600, Hamamatsu), a confocal scanner unit (model CSU10, Yokogawa), and a digital camera (model C4742-95, Hamamatsu) at room temperature. In this experiment, a small amount of Safranin O (1 wt%, $\lambda_{ex} = 495$ nm, $\lambda_{em} = 565$ nm) was dissolved in glycerol as a fluorescence probe for the droplets. Excitation of the probe was conducted with 488-nm light from an Ar⁺ laser (Melles Griot, models 175B-100B for a laser power supply, and 532-BS-AO4 for a laser head).

3. RESULTS AND DISCUSSION

3.1 Condensation and dispersion of micro-droplets

Figure 3 shows polarizing microscope images of the sample before (A) and after (B) irradiation of UV light at 30 °C. Glycerol droplets were dispersed with a

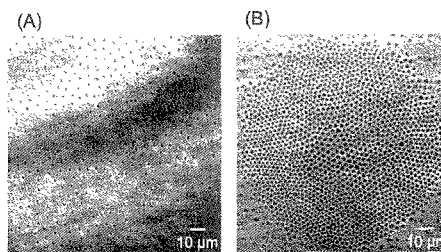


Figure 3. Polarizing optical microscope images of a LC colloid before (A) and after (B) irradiation of focused UV beam ($\phi \sim 160$ μm , $\lambda = 365$ nm, 50 mW/cm²). The irradiation was conducted at 30 °C where the host LC shows nematic phase for 300 s.

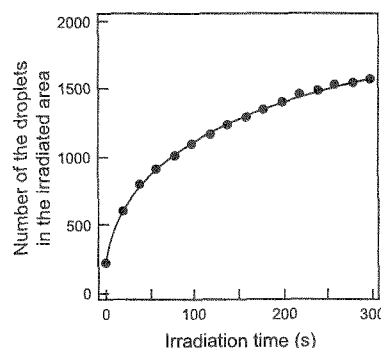


Figure 4. Typical growth of the droplet number in the irradiated area during the condensation process. Experimental conditions are the same as those shown in figure 3.

typical diameter of 3 μm after the prepared sample was kept in the nematic phase overnight (Fig. 3(A)). In this state, an inter-droplet distance was estimated as 6.8 ± 0.9 μm . In order to explore photoresponsive behavior of the droplets, we at first irradiated the sample with a focused UV beam (160 μm -diameter, 50 mW/cm²) that preferentially induces *trans*-to-*cis* isomerization of the doped azobenzene derivative. Right after the irradiation, the droplets near the periphery of the light beam started to move toward the inside the beam. The droplets far from the beam were also gradually attracted to make the irradiated area more condensed with the droplets (Fig.3(B)). In Figure 4 shown is a typical profile of the droplet condensation process. It is found that the condensation process takes about 300 s to virtually come to an end with closely packed droplets. In this state, the inter-droplet distance was evaluated as 3.8 ± 0.2 μm .

We next examined the photoresponsive behavior of the condensed droplets with visible light that induces *cis*-to-*trans* photoisomerization. Figure 5 shows light-induced droplet dispersion at 30 °C. The condensed droplets exhibited a dramatically swift backward motion out of the irradiated area. An average inter-droplet distance went up to 6.0 ± 0.3 as an equilibrium value within several tens of seconds. In contrast to the condensation process, the dispersion process is not preferentially initiated at the edge of the irradiated area, but takes place uniformly even inside the close-packed droplet structures like an explosion. These wavelength-dependent behaviors clearly prove that the droplet motion is photochemical rather than photothermal in nature.

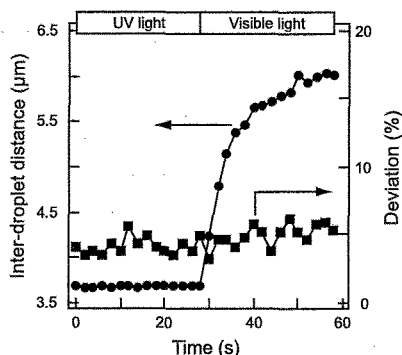


Figure 5. Light-induced dispersion of the condensed droplets. Light intensities were 50 and 100 mW/cm² for UV and visible light, respectively. The experiment was performed at 30 °C.

3.2 Effects of the photochemical reactions on the LC emulsion

As mentioned before, photo-generated *cis* azobenzene molecules have striking effects on various properties of LCs. Indeed, upon the *trans*-to-*cis* photoisomerization, the nematic-to-isotropic phase transition temperature was found in this study to be reduced from 37 to 33 °C although this is unlikely to be directly responsible for the observed photoresponsive behaviors. Among other possible consequences of the photoisomerization, we paid attention to its effects on the interfacial tensions between the LC, glycerol, and air. Figure 6 exhibits a change of contact angle at the glycerol-LC interface. In this study, we defined the contact angle as shown in the inset. When the whole sample region was irradiated with UV light, the LC is spread out on the glycerol layer and the contact angle typically decreased from 65 ± 3 to $9 \pm 1^\circ$. This indicates a reduction of glycerol-LC interfacial tension. Azobenzene derivatives exhibit changes in net dipole moments as well as their molecular shapes on the photoisomerization: *cis* isomers have enhanced polarity compared to *trans* isomers.[12] Thus, such a reduction of the interfacial tension will occur as a result of preferential adsorption of the *cis* isomers on glycerol. In this stage, we consider that the azobenzene molecules should not be distributed in the

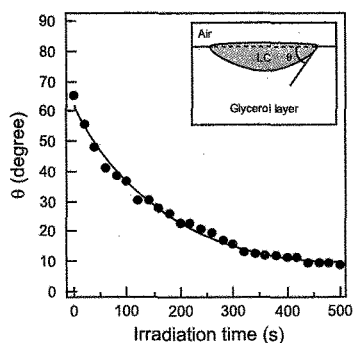


Figure 6. Time course of a contact angle at glycerol-LC interface during irradiation of UV light. The experiment was performed at 30 °C. In this experiment, the whole sample region was irradiated. The light intensity was adjusted at 50 mW/cm². Contact angle was defined as shown in the inset.

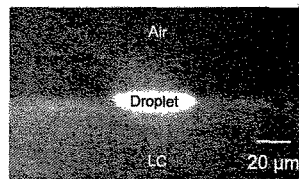


Figure 7. A confocal fluorescence microscope image of the micro-droplet in the sample. Excitation of the fluorescence probe (Safranin O) was performed with 488-nm light from Ar⁺ laser at room temperature.

glycerol layer and the droplets. The molecules will be present in the LC and at the glycerol-LC interface.

3.3 Plausible mechanism of the dynamic behaviors

Figure 7 shows a con-focal fluorescence image of the sample excited with 488-nm light. It was found that a droplet would be partially sticking out from the LC. In such a case, it is well-known that a spatial inhomogeneity of interfacial properties can induce mass transport of liquids on substrates.[16] Such nonmechanical motion resulting from the generation of interfacial tension gradient can be created by several approaches.[17-19] Recently, a photochemical manner has also been applied to the gradient formation.[20] When a substrate whose surface was modified with an azobenzene derivative was irradiated with appropriate light possessing a gradient in light intensity, a variety of liquid drops placed on the substrate showed directional motion toward *cis*-rich region. With this light-induced process in mind, a mechanism of the droplet motion in this study can be schematically explained as shown in Figure 8. On the irradiation of UV light, the majority of *trans* azobenzene molecules in the irradiated area are almost instantaneously converted to the *cis* isomer, resulting in the formation of concentration gradient of *cis* isomer in the host LC by thermal diffusion. According to the concentration gradient, an adsorption of the *cis* isomer allows to create an imbalance of the interfacial tension acting around the droplets. In the absence of macroscopic convective or Marangoni flows, the gradient will expand only through the diffusion and thermal back isomerization of *cis* isomer. If glycerol micro-droplets are placed in such a transient gradient of *cis* isomer, the droplets will be guided along the gradient toward *cis*-rich region in such a way that the droplet-LC

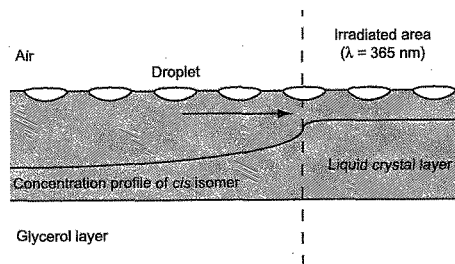


Figure 8. Schematic illustration for cross section of the LC emulsion during the condensation process. A curved line denotes a concentration profile of the photogenerated *cis* isomer. An arrow indicates a direction of the droplet motion.

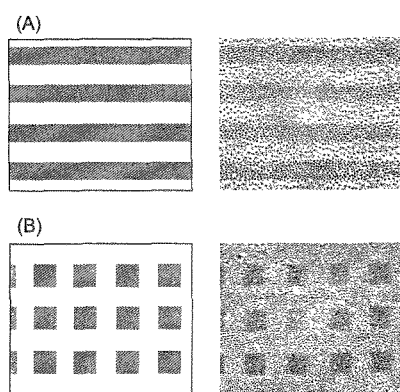


Figure 9. Photochemical addressing of the glycerol droplets by illumination of computer-generated images: (A) grating structure and (B) square array. The images were optically reduced and projected on the LC emulsion at 30 °C for 300 s.

interfacial tension be more reduced.[20,21] According to this assumption, the droplet condensation will be initiated at the edge of the irradiated area as observed experimentally.

On the other hand, the dispersion process seems to be more complicated. We can not explain this process on the basis of the imbalance in the interfacial tension solely. Although, at present, the effects of orientational elasticity and anchoring of LCs on the droplet motion are still obscure, these factors will play important roles in the dispersion process rather than the condensation process.

3.4 Tailored droplet assemblies

Recently, fabrication of two-dimensional arrays has been extensively studied for development of photonic circuits, bio-sensing chips and so on.[22-24] Finally, we attempted photo-addressed patterning of droplet arrays based on the photokinetic effects. Figure 9 shows illuminated patterns (left) and resultant assemblies (right). We employed a grating structure (A) and a square array (B). Dark areas in each pattern means illuminated areas where the *trans*-to-*cis* photoisomerization and the droplet condensation will occur. Illumination of each pattern was performed for 300 s at 30 °C. As clearly shown in Fig. 9, the patterning of droplets could be achieved quite neatly within a few minutes of illumination. In this study, the droplet condensation will be attributable to spatial inhomogeneity of the interfacial energy. It is, therefore, expected that the similar photokinetic effects can be achieved even if other particles and droplets are introduced in LCs.

4. CONCLUSION

We explored light-induced dynamic behaviors of glycerol micro-droplets in LC emulsion doped with azobenzene derivatives. The droplets exhibited condensation and dispersion on the basis of the photoisomerization of the azobenzene derivatives. The contact angle measurement and the confocal fluorescence microscopy suggested that the droplet condensation would be mainly attributable to reduction of droplet-LC interfacial tension due to adsorption of the

photogenerated *cis* isomers. A spatial inhomogeneity of interfacial energy around the droplets according to the concentration gradient of the *cis* isomers will guide the micro-droplets. Photochemical assembly of tailored droplet arrays will provide significant impacts in both scientific and technological viewpoints of LC colloidal systems.

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