Soft Matter

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Journal:	Soft Matter
Manuscript ID	SM-COM-07-2018-001426.R3
Article Type:	Communication
Date Submitted by the Author:	30-Aug-2018
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Optically induced motion of liquid crystalline droplets

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Controlled motion of a liquid crystalline active droplet was demonstrated in a surfactant solution and by irradiation of UV light. Droplet could be induced to roll on a glass substrate toward the UV light source. This was explained by the Marangoni flow induced by the UV-induced desorption of surfactants.

Small objects moving around spontaneously by chemically and biologically generated energy sources are referred to as active matter, and this phenomenon has been studied extensively. Many types of active matter have been introduced;[1] stress difference due to the concentration gradient of chemicals,[2] motor proteins activated by biological energy,[3] gas bubble formation due to chemical reactions on a surface,[4,5] and a flow induced by the surface tension gradient have been utilized for the demonstration of active matters. Recently, 3D motion control was demonstrated by intentionally generating a surface tension gradient using photochemical reactions.[6] Because inhomogeneous force is necessary to induce the active motion, Janus particles have frequently been utilized for this application.[7,8] Not only hard objects but also soft objects have been used as active matters. Liquid crystals (LCs) have been especially utilized because these enable long-range molecular interactions, which can induce macroscopic motion, flow, and a change in shape.[9,10]

In the form of droplets made of LCs, molecules are aligned depending on the boundary condition of the molecules at the interfaces, and the droplets also have topological defects, which indicate the singular point of the molecular alignment.[11,12] The long-range molecular interactions can induce various macroscopic motions and shape changes. In recent years, a new type of active LC droplets has been reported. A self-propelled motion was induced by the

convective flow inside an LC droplet when the LC droplet is in an ionic surfactant solution whose concentration is higher than the critical micellar concentration (CMC).[13] The motion mechanism was well-described based on the melting of LC molecules, which are taken into the micelles of surfactants and, as a result, the gradient of the surface tension on the surface of an LC droplet is induced, which causes the Marangoni flow inside and outside the LC droplet.[14] It was demonstrated that this flow helped the formation of collective motion of multiple LC droplets, as well as the aggregation or packed-form of LC droplets.[15] As another example, in a maze consisting of microfluidic channels, a chemotaxis-like motion of LC particles was demonstrated using the concentration gradient inside the microfluidic channel.[16] Furthermore, a helical motion was reported for a nematic droplet when the coupling between the director and the convective flow induces the symmetry breaking [17] and also for an LC droplet with a helical director made of cholesteric liquid crystal including chiral dopants.[18]

Light-induced changes in the particles consisted of LC have also been well-studied, and various stimuli-responsive arrangements of the LC molecules in the particles were demonstrated.[19] Notably, the control of the color and color pattern have been demonstrated by adding photo-responsive chiral molecules and by controlling the pitch of the cholesteric liquid crystals.[20] This application was possible thanks to the preparation of mono-disperse particles using a microfluidic device and capillaries with tiny tips.[21]

We have studied the molecular orientation/ordering change with a time-resolved method after a pulse light irradiation for photo-responsive LCs,[22,23] and recently we could prepare photo-responsive LC droplets and emulsions that were prepared using a microfluidic device similar to that described above.[24] The orientational or phase change was observed, and we found that the change occurred from the center of the topological defects. Also, we clarified that the photo-response is different from the thermally-induced change.

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In previous works, the motion of LC droplets has been activated in random directions. Here, we combined the active motion in an amphipathic solution and the photo-response of LC droplets to control the direction and speed of the motion. In this study, we could successfully induce the macroscopic motion of the photo-responsive LC droplets by irradiation of UV light.

Photo-responsive LC droplets were prepared by a microfluidic device, consisted of a tapered glass capillary inside a square capillary.[21] A schematic drawing of the setup of the microfluidic device for the formation of the LC droplets is shown in Figures S1 and S2 in the Supporting Information (SI). A tapered cylindrical capillary was inserted into a square glass capillary from the outlet side, and two immiscible solutions were introduced: the inner fluid (liquid crystal) from the inlet side flows into the outlet tapered cylindrical capillary, and the outer fluid (surfactant solution) shears the inner fluid near the tip of the tapered cylindrical capillary. Since hydrophilic treatment was applied to the outside and inside of the capillary, the adhesion of the droplets was prevented on the capillary surface.

A square glass capillary (inner diameter: 0.90×0.90 mm^2) was attached on a glass slide, and a tapered cylindrical capillary was inserted (inner diameter: 0.70 mm, outer diameter: 0.87 mm) into it. The capillary was prepared by a micropipette puller (P-1000, Sutter Instrument) to make the tip tapered, and it was fixed by an adhesive. Syringe needles were connected to the inner and outer fluids, and the liquids were introduced. The droplets were collected from the tapered capillary on the outlet side. The tip diameter of the capillary was 50 μm. For the hydrophilic treatment, plasma treatment was made using plasma cleaner (PDC-32G, Harrick Plasma). Two syringe pumps (2.0 or 10.0 μL/min) were utilized to control the flow rate of the inner and outer fluids. The typical size of the droplets was 50 μm. The microfluidic device was operated at room temperature (25°C). The formation of the LC droplets is shown in Fig. S2 in SI.

(N-(4-methoxybenzylidene)-4-butylaniline (MBBA, nematic phase: 22~48°C) was used as the inner fluid and, at the same time, works as photo-responsive LC, and the absorption spectrum of MBBA and t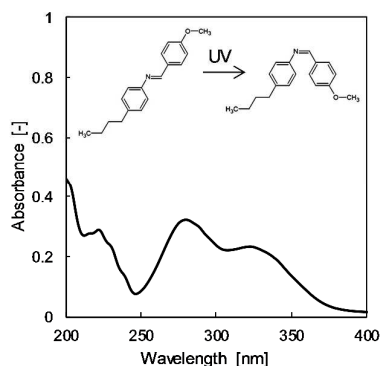he photo-isomerization reaction is shown in Figure 1. A 10 wt% sodium dodecyl sulfate solution (SDS, C_{CMC} = 0.13 wt%, 25°C) was used for the outer fluid. For a high concentration of SDS, LC droplets usually take on a radial configuration due to the homeotropic anchoring at the interface.[25] MBBA is subject to photo-isomerization by UV light irradiation, which causes disordering of alignment of LC molecules, and the phase transition is induced with high UV intensity even at room temperature.[23,26] A non-polarized UV-LED (Execure LH-1V, HOYA) with a peak wavelength of 365 nm was used as the UV light source. The behavior of the photo-responsive LC droplets was observed with an inverted optical microscope (IX71, OLYMPUS). For the motion observation of the LC droplet, a conventional mode was utilized to clearly observe the edge of the droplets, and the polarization mode was used when the defect pattern of the droplets was observed. A vessel for the observation was prepared by sandwiching a silicone rubber spacer with a thickness of 0.1 mm with two cover glasses. An open space (17×25 mm) was prepared inside the silicone rubber. After injecting the surfactant solution, including the droplets, the behavior of the droplets was observed under UV light irradiation. The UV light was irradiated with an incidence angle of 55° with a spot size of 7 mm, unless otherwise specified. The beam size was much larger than the droplet size, and the light intensity was assumed to be uniform for each droplet. The UV light intensity was 89 mW/cm^2, unless otherwise stated.

An LC droplet was identified on a glass surface, and by irradiation of UV light, it moved toward the direction of the UV light source in the plane of the sample cell. The trajectory of the droplet under the on-off operation is shown in Figure 2 (Movie S1 in the SI). The LC droplet moved under UV light irradiation and stopped immediately when it was turned off, then resumed moving when the light was turned on again. The droplet rolled on the glass surface, which can be confirmed by watching Movies S1 and S2. The droplets had a random motion without UV light illumination (see Movie S1 before UV irradiation). This is because they are in a surfactant solution

Fig.1. The absorption spectrum of MBBA (3.7 mM) in cyclohexane. Inset shows the molecular structure of MBBA, and photo-isomerization reaction.
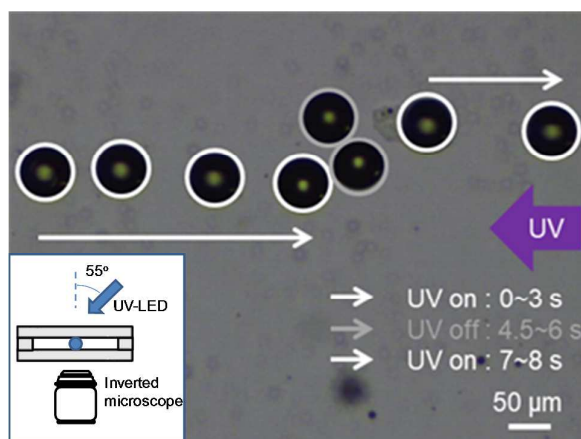

Fig.2. The trajectory of a photo-responsive LC droplet during the on-off operation of the UV light. The white and grey circles indicate the positions of the droplet under the light irradiation and non-irradiation, respectively. Inset shows the schematic drawing of the experimental setup.

with a concentration larger than the CMC and solubilization proceeded gradually, which is the same as the active motion of
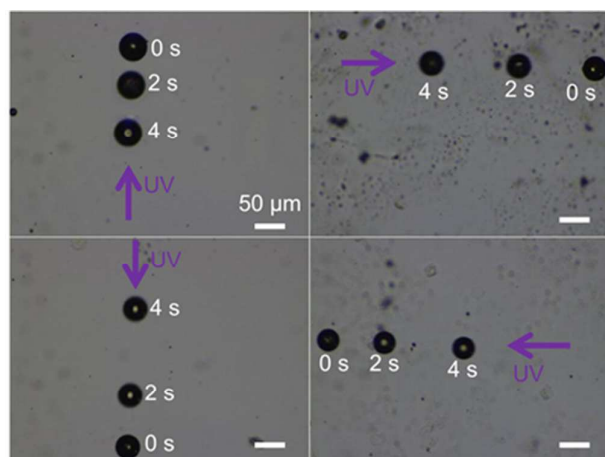

Fig.3. Observation of photo-induced motion of LC droplet by changing the UV light irradiation position under optical microscopy.

LC droplets.[13,14] The mean square distance (t = 1s) of the droplet was 180–720 μm^2, and it is smaller than the light-induced motion observed here.

The direction dependence of the UV light irradiation was investigated, and the observed motion is shown in Figure 2 (Movie S2 in the SI). Immediately after the UV light was turned on, the LC droplet moved in the plane of the sample cell toward the UV light source under all tested directions. It is evident that the motion direction of the LC droplets moved toward the light source.

The dependence of the velocity of the LC droplets on the UV light intensity was investigated. A video of the droplet motion was recorded, the video was decomposed into snapshots, and the picture frames were analyzed (example tracking data is shown in Fig. S3 in the SI). Since the speed of the droplet was saturated several seconds after the UV light irradiation, the snapshots after the speed was saturated were used for the analysis. From the calculation of the distance of the motion and the corresponding time lapse, the speed of motion was calculated. The velocity was linearly proportional to the UV intensity, as shown in Figure 5. The SDS concentration dependence was also investigated using a similar approach (Fig. 5a). The directional motion was not observed for the SDS concentration lower than the CMC (0.13 wt%), and as the concentration exceeded the CMC concentration (0.20 wt%), the droplet started to move. After this initial jump, the velocity was mostly linearly dependent on the SDS concentration (Fig. 5b). This threshold behavior of the motion and the fact that the threshold concentration is almost the same as the CMC concentration indicates that the motion can be induced only when the droplets are active due to solubilization.

The slanted incident angle dependence was studied to clarify if the slanted illumination affects the motion for an LC droplet (Fig. S4 in the SI). The droplet diameter was 50 μm, and the SDS concentration was 10 wt%. The directional motion was not observed when the light was illuminated from the

vertical position. Then, the slant angle was varied from 50 to 20°. Under the same light intensity (89 mW/cm^2), the velocities were 83.4, 74.0, and 60.8 $\mu m/s$, for 50, 30, and 20°, respectively. Slanted illumination is necessary for the motion, and the velocity was faster as the slanted illumination was made on the droplets.

The motion mechanism was considered. It is clear that the motion was induced by the UV light from the dependence of the on-off operation of the light, the irradiation direction, and the irradiation intensity. In previous reports on the active
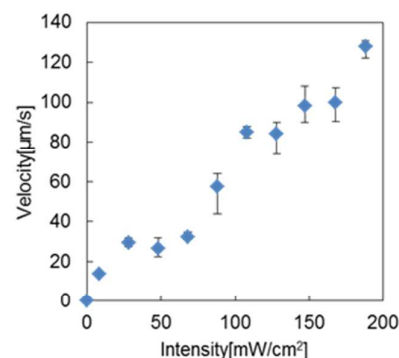

Fig.4. The velocity dependence of an LC droplet on the UV light intensity. The diameter of the LC droplet was 50 μm. The SDS concentration was 10 wt%.
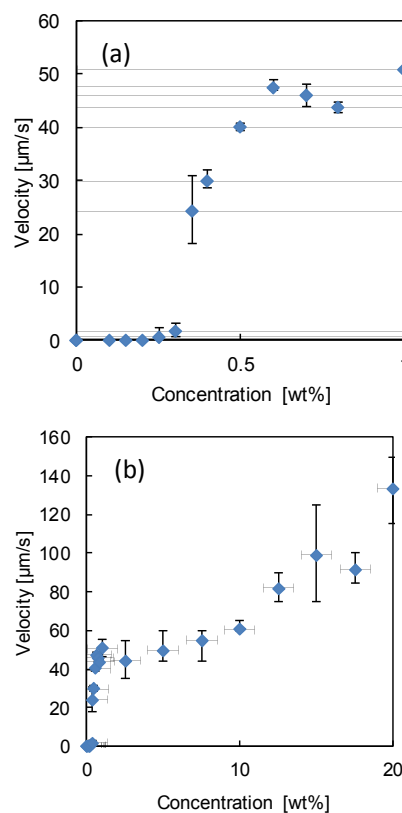

Fig.5. The velocity dependence of an LC droplet on the SDS concentration. The diameter of the LC droplet was 50 μm. The light intensity was 89 mW/cm^2. Figure 5(a) shows the dependence around the CMC concentration, and Fig.5(b) corresponds for the higher concentration.

motion of LC droplets in surfactant solutions,[13,14,16,27] it was interpreted that the solubilization of an LC droplet into a surfactant solution is induced from random positions on its surface and that the desorption of the surfactant molecules causes the inhomogeneous distribution of surfactant molecules on its surface. This causes a surface tension gradient and induces the Marangoni convective flow inside and outside the droplet. It has been proposed that these processes are the origin of the active motion of LC droplets. Our finding that no motion was induced for the SDS concentration less than the CMC indicates that solubilization is a key factor for the motion.

To clarify if similar processes occur for our system, we observed the inside change of the LC droplet by UV irradiation. In Movie S3 of the SI, the convective flow inside an LC droplet was observed during the on-off operation of UV light from the right side. The droplet was observed by adjusting the direction of the analyzer of the polarization microscope to make the inside flow visible. The flow direction on the top surface of the droplet was toward the UV light source (the LC droplet was observed from the bottom side of the droplet because of the optical configuration of the inverted microscope). In Movie S4 of the SI, the motion of the defect pattern was observed during UV light irradiation under the crossed-Nicol condition. Before the light irradiation, the topological defect pattern was confirmed at the center of the droplet. During the UV irradiation, the defect pattern moved toward the UV light source.

Based on our experimental results, we propose a motion mechanism for an LC droplet made of MBBA (Fig. 6). Since a convective flow was observed under the UV light irradiation, it is supposed that the Marangoni effect was induced because of the desorption of surfactants. From the direction of the convective flow, which was clockwise from the side view toward the UV light, and desorption should occur at the UV light side. On the side of the UV irradiation, MBBA is subject to photo-isomerization to a cis form, and we suppose that this molecular change caused the desorption of surfactant molecules. In Movie S4, within 20–30 s, a circle-like black region was formed on the light-irradiated side, corresponding to the isotropic region due to phase change. The defect

Fig.6. Proposed motion mechanism for the photo-induced motion of an LC droplet made of MBBA. The green arrow is Marangoni convective flow in the LC droplet.

position moved toward the UV light source, and the pattern of the topological defect resembles the 'escaped radial' configuration, where LC molecules align parallel at the interface on a half surface and perpendicular on the other half interface.[28] This is reasonable if the surfactant molecules desorb and the boundary condition changes from the homeotropic to the parallel condition. Due to the surface density of the surfactants on the surface of the LC droplet (side view of Figure 6C), a free energy gradient is formed, which induces the force to the right side. On the other hand, the droplet sits on a glass substrate and is subject to friction. As a whole, the droplet has a clockwise torque, and the rolling motion occurred as a result. This scheme explains our finding that an asymmetrical illumination is necessary for motion.

To verify if the light illumination induced the solubilization of MBBA, the UV light (180 mW/cm^2) was illuminated to an MBBA included SDS aqueous solution, which was prepared by mixing an SDS solution (10 wt%, 20 mL) with a drop of MBBA (~50 μL), which was emulsified. Five-hundred microliters of the aqueous solution were sampled every 5 s, and the absorption spectrum for each sample was measured. The change in the absorption spectrum is shown in Figure S5. The absorption of MBBA increased as the UV illumination time increased. This indicates that MBBA is solubilized into the SDS solution and this result supports the mechanism of our proposal. As another possibility, hydrolysis of MBBA to p-butylaniline has been previously reported.[29] However, the absorption spectrum by UV light illumination did not show the spectral change, and this possibility can now be excluded.

There are two possible mechanisms for the light-induced desorption of surfactants. One is the change in the molecular interaction between MBBA and SDS. SDS has an ionic (SO_3^{2-}) and a hydrophobic (alkyl chain) region; the ionic region is on the outer side, while the hydrophobic side is on the inner side. Since MBBA also has an alkyl chain, it is supposed that it has an attractive interaction with the alkyl region of SDS. Due to the photo-isomerization of MBBA, the structure changed into a bent structure, and it is possible that this structural change caused the detachment between MBBA and SDS, leading to desorption of SDS from the droplet. The other mechanism is the phase change of the MBBA. When MBBA is changed into a cis form, the photochemical phase transition is induced,[26] and the isotropic domain is formed. One possibility is that the affinity of the surfactants is weaker on the isotropic phase than that on the liquid crystal phase, causing desorption of the surfactants.

The velocity's dependence on the SDS surfactant concentration can be understood if the light-induced solubilization of MBBA was increased by an increase in the surfactant concentration. Since the capacity to take MBBA molecules up into micelles increased, desorption was accelerated, and the gradient of the surface tension was increased. Thus, the convective flow and/or the exerted force increased, ultimately producing an increase in velocity.

In summary, we could observe the photo-induced motion of photo-responsive droplets made of MBBA, which were dispersed in an aqueous surfactant solution with a
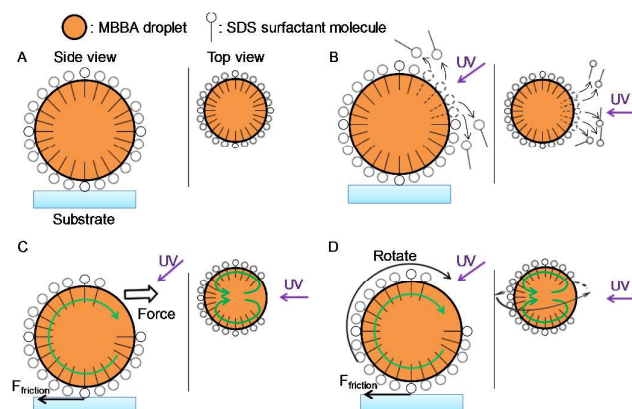
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concentration higher than the CMC. By changing the direction and the intensity of the UV light, we could control the direction and the speed of the droplet motion. We consider that the photo-isomerization of MBBA can control desorption of surfactant molecules, and the convective flow can be intentionally induced. This controlled flow can be utilized for the rolling motion of the LC droplet. This is the first demonstration of the optical motion control for an active matter consisting of liquid crystals and is a promising method for the control of active matters.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

Notes and references

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Rolling motion is activated by UV light for photo-responsive nematic droplet in a surfactant solution.