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Formation of Photo-Responsive Liquid Crystalline Emulsion by Using Microfluidics Device

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Abstract: Photo-responsive double emulsions made of liquid crystal (LC) were prepared by a microfluidic device, and the light-induced processes were studied. The phase transition was induced from the center of the topological defect for an emulsion made of (*N*-(4-methoxybenzylidene)-4-butylaniline (MBBA), and strange texture change was observed for an emulsion made of 4-cyano-4′-pentylbiphenyl (5CB) doped with azobenzene. The results suggest that there are defect-involved processes in the phase change of LC double emulsions.

Keywords: photo-responsive liquid crystal; double emulsion; phase change

1. Introduction

There are various particles that can show various optical, electrical, and chemical properties, and they are used as raw materials for pharmaceuticals, cosmetics, semiconductor materials, etc. Research on improvement of functionality and formation of uniform and/or homogeneous particles has been made. These days, "active matter" has become one of the topics in this field of study. In a broad sense, active matter is an object with spontaneous motion induced by chemically/biologically generated force. The control of the motion would open application for transport of chemicals such as drug delivery. As an external energy source, pressure difference due to the concentration gradient of chemicals, pressure induced by bubble formation due to chemical reaction on particle surfaces, and the difference of the surface tension on the particle surface have been utilized [1]. Many different types of particles and/or rods have been utilized, and many of them have asymmetric structure to induce the unbalance of the force induced on each surface. Typical examples are a rod made of different materials on both ends, and a Janus particle with different materials on each side [2,3].

In the series of research on "active matter", liquid crystal (LC) has been utilized frequently. LC is an intermediate state of liquid and solid, and it keeps its fluidity but has at least one direction of orientational order. Due to its optical anisotropy, it has been used for the display material. In addition, LC can be found on cell membranes, and highly concentrated protein or DNA solutions show a LC state, too. The LC features softness, although it keeps a molecular interaction for a long distance. For the application of active matters, this long-ranged molecular interaction could be well utilized. For example, a micro object with photo-active molecules was put into a LC media, and it can be moved by a macroscopic flow induced by the structural change of the molecules on the surface [4]. Another example is that a macroscopic flow was induced in LC by putting bacteria in it, because it can only move in the orientation direction of the LC [5]. Moreover, the LC flow was successfully controlled by a photo-patterned alignment layer. When the LC is made into a droplet or capsule form, and mobile molecules are included into it, the LC droplet starts motion [6], the motion can be controlled by a couple of defects formed on the LC capsule [7]. In some studies, the motion can be

controlled by such topological defects. When solid particles are put into LC medium, defect points are formed on the boundary of the particle and the LC, and electrophorestic motion was induced by applying AC voltage [8,9].

For the functionality of micron-sized particles, it is expected to mix materials and to change the material inside and outside such as a core–shell structure. It is also required to be uniform in size, where a microfluidic device is a promising platform, because the experimental conditions such as the temperature and flow rate can be easily maintained. Many studies on particle syntheses have been reported. Since Weitz et al. reported one of the microfluidics devices to make double emulsions, where different inner and outer fluids can be controlled, the number of reports using this device has increased drastically [10]. In this method, an arbitrary liquid droplets can be formed by the control of the counter-propagating two/three fluids. There is a report on the formation of the LC droplet using this method [11]. Moreover, the color control of a cholesteric liquid crystal droplet with photo-responsive chiral dopant was reported, and the color ranged from blue to red [12,13], and also it was demonstrated for the lasing application [14]. By encapsulating this LC droplet with a polymer core, the coloring particle was successfully developed [15].

As described in the above, LC is a promising material to possess functionality and mobility, which could be remotely controlled. For this application, the microfluidic device offers a good platform to make uniform and complex droplets. In this research, we report on the formation of LC droplets or double emulsions which include photo-responsive molecules by a microfluidics device, and the photo-response of these materials were studied. By mixing LC with guest dyes, the photo-induced structural change was induced, and change in the host LC molecules was investigated.

2. Materials and Methods

The schematic drawing of the microfluidic device for the formation of the double emulsion is shown in Figure 1 [10,11]. Two tapered cylindrical capillaries were inserted into a square glass capillary, and they were faced to the side of the tapered parts. When the left cylindrical capillary was not used, and two kinds of immiscible solutions are introduced, the liquid from the left side flows into the right capillary (collection), and droplets are formed. When the capillary on the left side is used for injection (inner fluid), double emulsions whose inner fluid is encapsulated by the middle fluid are formed, similar to a bubble. For the appropriate formation condition, optimal condition for the surface tension and viscosity are required. A difference of viscosity between the outer and the middle fluid is expected, and the surface tension of the double emulsion needs to be sufficiently large.

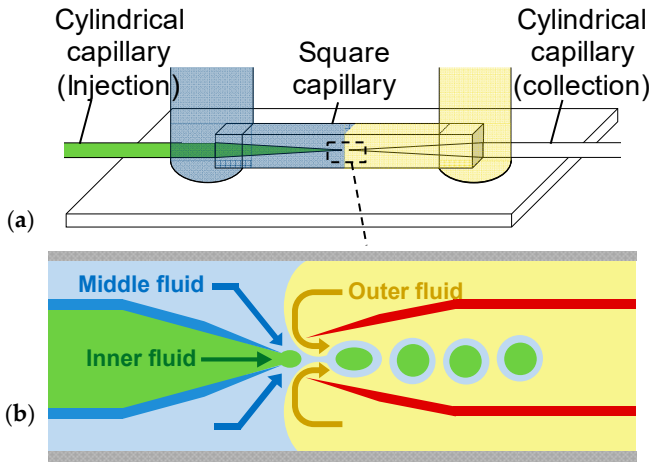

Figure 1. (**a**) Schematic drawing of the microfluidic device for the formation of double emulsions; and (**b**) the geometry of micro-capillaries and the mechanism for generating double emulsions is shown.

A picture of the microfluidic device is shown in Figure 2. A square glass capillary (inner diameter: 1.035 × 1.035 mm^2) was attached on a glass slide, and two tapered cylindrical capillaries were inserted (inner diameter: 0.70 mm, outer diameter: 0.87 mm) into it. The capillaries were prepared by a micropipette puller (P-1000, Sutter Instrument, Novato, CA, USA) to make the tips tapered, and they were fixed by an adhesive. Syringe needles were connected to the middle and the outer fluids (two needles in Figure 2a) and the liquids were introduced from there. The inner fluid was introduced from the left tapered capillary (blue solution in Figure 2a). The emulsions were collected from the right tapered capillary (yellow solution in Figure 2a). The tip diameters of the left and right capillaries were 50, and 100 μm, respectively, and the distance between their tips was 30–150 μm. The capillaries were processed for hydrophobic or hydrophilic treatment as necessary. In the hydrophilic treatment, plasma treatment was made by a plasma cleaner (PDC-32G, Harrick Plasma, Ithaca, NY, USA). For the hydrophobic treatment, 1.5 mL of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) was placed with the capillary in a sealed container. Three syringe pumps were utilized to control the inner, middle, and outer fluids. The flow rates of the inner, middle and outer fluids were 2.0, 4.0, 15.0 μL/min, respectively. Typical size of the double emulsions were 200 μm in diameter with the shell thickness about 20–30 μm. The microfluidic device was operated at room temperature (25 °C).

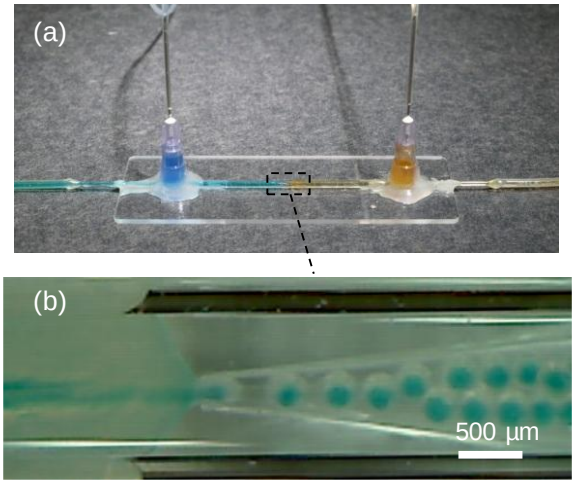

Figure 2. (**a**) A picture of microfluidic device to generate double emulsions: and (**b**) a microscopic image during the generation of water/oil/water (W/O/W) double emulsions is shown.

A water/oil/water (W/O/W) emulsion was prepared using a photo-responsive LC as the shell part. A 5.0 wt % polyvinyl alcohol (PVA) solution mixed with a dye (Brilliant green, 35 μM) was used as an inner fluid for observation. Three kinds of nematic liquid crystals (*N*-(4-methoxybenzylidene)-4-butylaniline (MBBA, LC range: 22~48 °C), 4-cyano-4′-pentylbiphenyl (5CB, LC range: 22.5~35 °C), and 5CB mixed with azobenzene (40 mM)) were used for the middle fluid, and a 5.0 wt % PVA solution was used for the outer fluid. The molecular structure is given in Figure 3. MBBA has been utilized for the study on the photo-induced phase transition due to the photo-isomerization [16]. Azobenzene is also photo-isomerized in LCs to induce the phase transition [17,18], and the photo-isomerization behavior in LCs was studied before [19]. For phase transition, a non-polarized UV LED (Execure LH-1V, HOYA, Saitama, Japan) was used at 180 mW/cm^2, which was illuminated from the top side of the microscope. The double emulsions were observed by an upright polarization microscope, and a halogen lamp was used for illumination from the bottom side. The UV light was illuminated from the top side by being reflected by a dichroic mirror, while a part of the illumination light passed through the dichroic mirror to a CMOS camera.

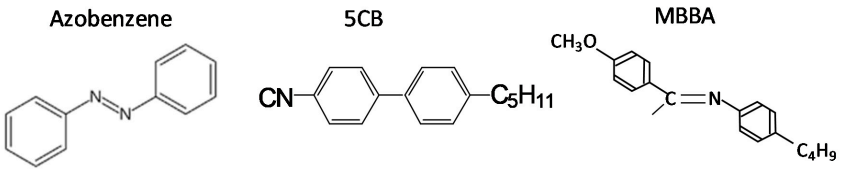

Figure 3. Molecular structures of Azobenzene, 5CB and MBBA.

3. Results

3.1. Observation of Photo-Response

After taking the double emulsions, they were observed by the microscope. Their defect patterns were randomly oriented. For observation of the photo-response of the LC double emulsions, we selected the ones which showed their defect pattern facing the top side, because the defect pattern change by a UV irradiation was easy to observe.

Before studying the photo-response, the LC alignment in the double emulsion was considered. The defect pattern of the LC emulsion made of 5CB is shown in Figure 4a. Since our experimental condition was similar as the one in a previous study [11], the alignment of LC molecules is considered based on it as well as the basics described in a review [20], and the schematic drawing of the LC alignment is given in Figure 4a. Due to the planer boundary condition, the LC molecules align parallel to the sphere interface except the defect position. At the defect position, the molecules are aligned vertically to the center of the defect. In general, a crossed pattern is observed at a defect position. In Figure 4a, two crossed patters were overlapped because two defects on the outer and inner surfaces were observed at the same time due to the thin shell. This can be confirmed by the fact that one of the crossed pattern reached the outer interface, while the other crossed pattern reached the boundary of the inner shell. We frequently observed this type of double emulsions, and it indicates that the two defects preferred to stay close, probably due to the minimization of the elastic potential.

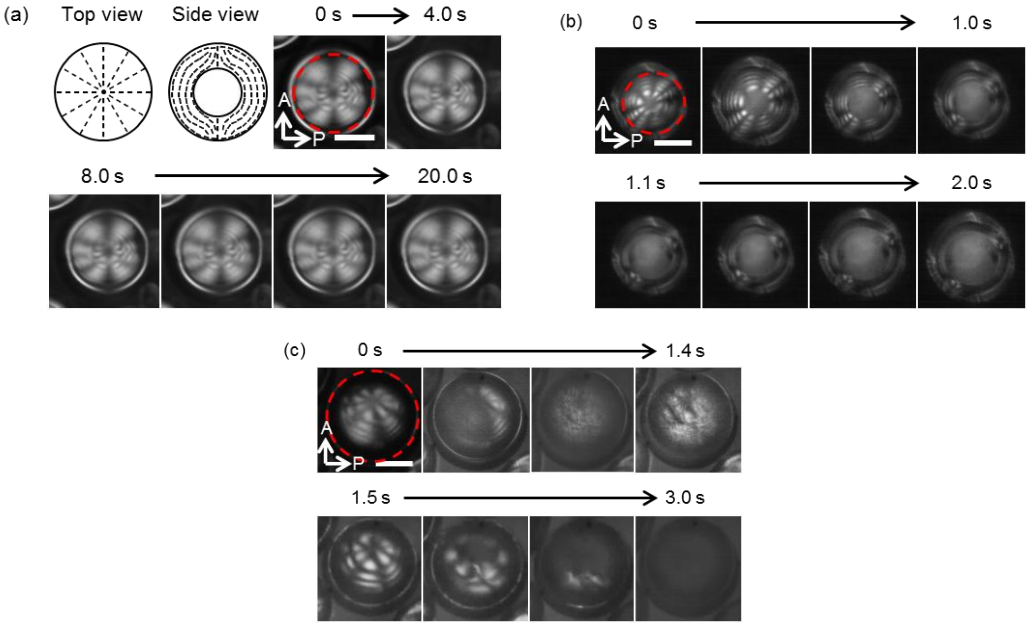

Figure 4. Polarization optical microscopy images of photoresponse of: (**a**) 5CB; (**b**) MBBA; and (**c**) azobenzene-doped 5CB by irradiation of a UV light (λ = 365 nm). The scale-bar corresponds to 100 μm. The directions of the polarizer and the analyzer are indicated with arrows. The red dotted lines indicate the inner shell boundaries for double emulsions. In (**a**), schematic drawing of the LC molecular orientation for the double emulsions is shown.

MBBA and azobenzene have C=N and N=N bonds, respectively, in the molecular structure, which is subject to photo-isomerization by a UV light. We gradually increased the UV light intensity and checked the necessary UV intensity by observing the disappearance of the defect pattern, indicating the phase change from the nematic to the isotropic phase. The observation of the photo-response by a polarization microscopy under a UV (λ =365 nm) light illumination is shown in Figure 4. The UV light was illuminated from the top side of the double emulsion. In the case of the MBBA double emulsion (Figure 4b), a uniform phase started to appear from the center position of the defect, and reached a steady state with a circle in two seconds, which was maintained as long as the UV light illumination was continued. This happened because of the photo-isomerization of MBBA from the trans to the cis isomer, causing the phase transition from the LC to the isotropic phase, and this is the reason why a homogeneous phase was observed. Although the isotropic phase should give a black image, the homogeneous circle was not totally black because the phase transition was induced only at the top part of the double emulsion. It was interesting to note that the phase transition spread from the center of the defect, and it is supposed that the defect would be the most unstable from the structural point of view, where the phase change was easy to occur. We need to study further mechanism in future.

When we observed the double emulsion made of only 5CB (Figure 4a), nothing happened under the UV illumination due to the lack of UV responsive molecules in the system. By adding azobenzene, which is subject to photo-isomerize by UV light, the photo-response of 5CB could be induced by the host (5CB)–guest (azobenzene) interaction (Figure 4c). Looking at the time course of the photo-response, the defect pattern collapsed once, and changed into an isotropic phase similar to MBBA, but the defect pattern appeared again, and finally changed into an isotropic phase. Different from MBBA, the phase transition was induced randomly in position. The observation of the defect pattern twice was unexpected, and it may be due to the pre-transitional state before the total phase transition. It is known that there is another state before the phase transition from the LC to the isotropic phase for various dye-doped LC systems [21–23], called the pre-transitional state. Under this state, a colossal refractive index change was induced, indicating an ordered state [24]. Since the phase was gradually changed from the nematic phase to the isotropic phase in our observation, and the second observed defect image showed a better contrast, indicating the larger refractive index, this might be related to this pre-transitional state, but further study on the doped dye concentration dependence is necessary in this aspect. The different photo-response for MBBA and azobenzene-doped 5CB indicates the variety of the interaction could be induced by changing the doped molecules.

3.2. Observation of Thermal Response

To clarify the feature of the photo-responses, the temperature-induced phase transition for the double emulsions was investigated. The response of each emulsion is shown in Figure 5. In this case, the phase transition was induced by the disturbance of the molecular orientation due to the increase in free energy. For all types of the double emulsions, the phase transition started from the random position when the temperature reached the phase transition temperature from the LC to the isotropic phase, and the entire region of the emulsions changed into the isotropic phase. Due to the character of the heating equipment, the phase transition was induced from one side to another because of the non-uniform heating. These changes contrasted with the photo-response of the double emulsion, as shown in Figure 4, and it indicates that the light-controlled change would give an original way to control the molecular orientation of LCs, and the light could be utilized for the macroscopic change via the long-range molecular interaction.

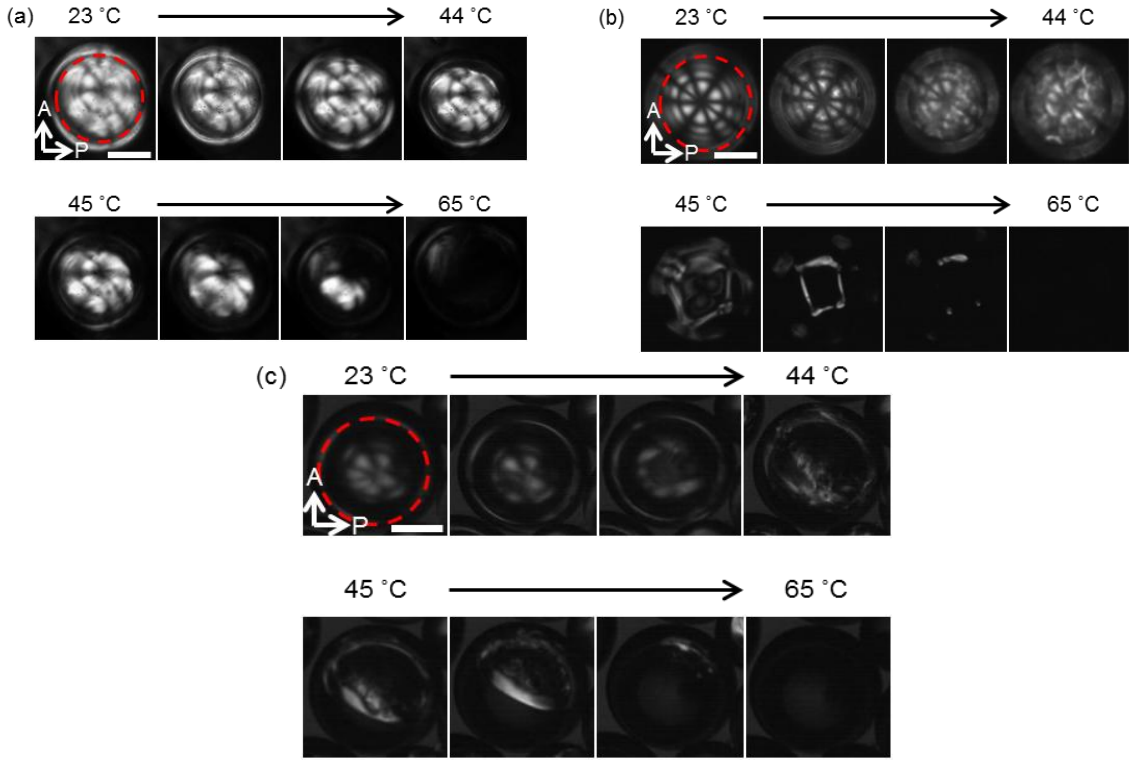

Figure 5. Polarized optical microscopy images of thermalresponse of: (**a**) MBBA; (**b**) 5CB; and (**c**) azobenzene doped 5CB. The scale-bar corresponds to 100 μm. The red dotted lines indicate the inner shell boundaries for double emulsions.

4. Conclusions

We could observe the photo-response of photo-responsive double emulsions made of LCs, prepared by a microfluidic device. By observation of the time course under the UV illumination, we could observe changes in the defect pattern in the double emulsions, which was not observed for the thermal phase transition. It would be possible to utilize the photo-control of the LC double emulsion for the purpose of active matter, in which it is expected that the force and the direction of the long-ranged molecular interaction should be controlled. To generate a larger force, a LC polymer would be a promising material, which can induce a macroscopic motion such as bending for a film [15]. Furthermore, this study would give more information on the dynamics of the defect behavior of LCs, which would be relevant to various biological phenomena on a cell membrane. This study will pave the way for understanding biological and physical phenomena and the development of a new device.

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Author Contributions: Yoshiharu Dogishi and Shun Endo performed the experiments; Woon Yong Sohn and Kenji Katayama conceived and designed the experiments; and Yoshiharu Dogishi and Shun Endo analyzed the data. All the authors wrote the paper. All authors have read and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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