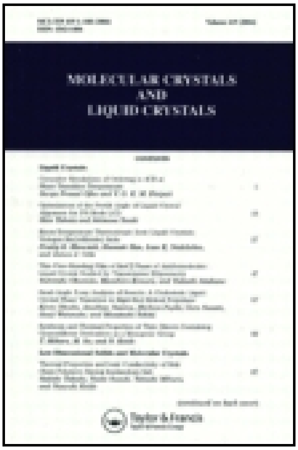

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Light-Induced Transformation of Defect Structures in Photochromic Liquid-Crystal Emulsions

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We investigated photoresponsive behavior of azobenzene-containing liquid crystals dispersed with glycerol or water droplets. At an initial state, Saturn ring and hedgehog defects were formed around the glycerol and water droplets, respectively, indicating that homeotropic anchoring was induced by adsorption of the azobenzene molecules onto the droplets. For the glycerol droplets, we observed structural transformation between Saturn ring and boojums on irradiation with ultra-violet and visible light. For the water droplets, an inter-droplet distance varied by changes of the defect size on the irradiation. These phenomena would result from modulation of anchoring conditions by the photoisomerization of the adsorbed dyes.

Keywords: azobenzene; boojums; hedgehog; liquid-crystal colloid; Saturn ring

1. INTRODUCTION

Over recent decades, liquid-crystal colloids, colloidal systems using liquid crystals as the continuous phase, have been recognized as a new class of soft materials and extensively investigated owing to their scientific and industrial points of view [1–18]. In liquid-crystal

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colloids, we can observe a variety of colloidal structures and properties governed by boundary conditions between dispersed colloidal particles and host liquid crystals. If surface anchoring of a particle is strong enough to induce definite molecular alignment on the particle surface, a nearby director field will be in conflict with the uniform alignment of the bulk liquid crystal. As a result, topological defects are formed close to the particle. When the liquid-crystal molecules are aligned perpendicular to a particle surface (homeotropic anchoring), a point-like defect called hedgehog (Fig. 1(A)) [4,5] or a disclination loop (Saturn ring, Fig. 1(B)) [6,7] can be observed in various liquid-crystal colloids. On the other hand, two surface defects referred to as boojums are formed in the case that the molecules are aligned parallel to the surface (planar anchoring) [5]. If several particles are dispersed in the systems, the elastic nature of liquid crystals brings about anisotropic interactions with both attractive and repulsive components between the colloidal particles. Consequently, self-organized structures of colloidal particles can be found in the liquid-crystal colloids. For instance, the particle carrying the hedgehog defect has a dipolar character, resulting in a formation of one-dimensional chain-like structures [4,5,8,9]. It has been found that colloidal particles having the Saturn ring or the boojums defects form two-dimensional closely packed structures as well as the one-dimensional structures due to a quadrupolar character [5,10].

Although a great number of studies on static behavior of the liquid-crystal colloids have been performed, their dynamic properties in the presence of external fields have not been appreciably investigated. With the characteristics of the self-organized structures in liquid-crystal colloids in mind, it is expected that the colloidal structures can be manipulated by modulating the defect structures. So far, a structural transformation of the topological defects between the hedgehog and the Saturn ring has been reported by applying magnetic

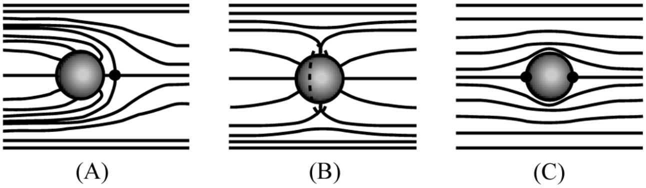


FIGURE 1 Schematic representation of director fields and defect structures formed around a colloidal particle immersed in a nematic liquid crystal: (A) Hedgehog; (B) Saturn ring; (C) Boojums.

or electric fields [11–13], whereas no other transformations such as hedgehog-boojums and Saturn ring-boojums have been observed. In order to achieve these structural changes of the topological defects, it will be essential to modulate the liquid-crystal anchoring of the particles. In this point of view, we paid attention to the photochemical control of the liquid-crystal anchoring on azobenzene-modified substrates, since the liquid-crystal anchoring between homeotropic and planar alignments are reversibly controlled by *cis-trans* photoisomerization of the modified azobenzene moieties [19,20]. By means of the photonic modulation of the anchoring conditions, we report the novel structural transformation of the defect structures and a modulation of colloidal chains in the liquid-crystal emulsions in which glycerol or water droplets are dispersed.

2. EXPERIMENTAL PART

2.1. Materials

Chemical structures of azobenzene and liquid-crystalline materials used in this study are shown in Figure 2. Two kinds of azobenzene derivatives were employed: one is an amphiphilic derivative (8ABO5COOH); another is a hydrophobic dye (8ABO6). We used 5CB containing a small amount of each azobenzene dye (0.5 mol%) as host liquid crystals (8ABO5COOH/5CB and 8ABO6/5CB).

2.2. Preparation of Liquid-Crystal Emulsions

Liquid-crystal emulsions dispersed with the glycerol droplets are prepared as follows. At first, a drop of the host liquid crystals was

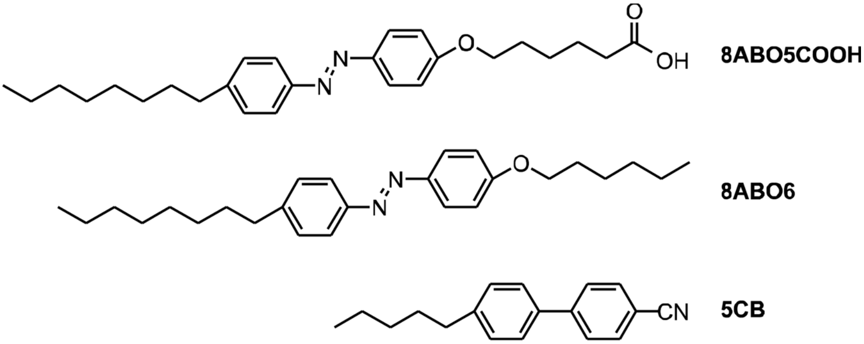


FIGURE 2 Chemical structures of azobenzene and liquid-crystalline materials used.

placed on a glycerol layer at room temperature. Then it was heated to 60°C in which the host liquid crystals are in an isotropic phase, and kept there for 60 min. After heating, the system was slowly cooled to room temperature, resulting in the formation of glycerol droplets in the host liquid crystals. On the other hand, liquid-crystal emulsions dispersed with water droplets, the host liquid crystals and appropriate amount of water were simply mixed for a while at room temperature. We added a small amount of sodium hydroxide into water to enhance an interaction between the droplets and the amphiphilic azobenzene dye by ionization of 8ABO5COOH to $8ABO5COO^{-}Na^{+}$. The prepared liquid-crystal emulsions were sandwiched between two glass plates whose surfaces were covered with a polyimide film and rubbed in a unidirectional way to impose uniform molecular arrangement of the bulk liquid crystals.

Photonic manipulation of defect structures and colloidal chains. Photoresponsive behavior of the defect structures and the colloidal structures were investigated in a polarizing optical microscope (BX51, Olympus, Japan) equipped with an ultra-high-pressure mercury lamp as a light source for an excitation of the azobenzene dyes. Wavelengths of ultra-violet ($\lambda = 365\,\text{nm}$) and visible ($\lambda = 435\,\text{nm}$) light were selected with dichroic mirrors. Sample temperature was adjusted with a temperature controller (MATS-2002ST, Tokai Hit Co., Ltd., Japan). All the experiments were conducted at 25°C.

3. RESULTS AND DISCUSSION

3.1. Photonic Transformation of Defect Structures Between Saturn Ring and Boojums

Figure 3 exhibits photoresponsive behavior of defect structures formed around the glycerol droplets in the liquid-crystal emulsions. The liquid-crystal molecules far from the droplet are uniformly aligned along the horizontal axis given by the white arrows. As shown in Figure 3(A), we could observe light-induced reversible transformations of the defect structures in 8ABO5COOH/5CB. At an initial state shown in a left photograph of Figure 3(A), two strongly birefringent regions around the droplet were found to be laid perpendicular to the bulk liquid-crystal alignment, indicating a formation of Saturn ring defect illustrated in a picture below the photograph. In the sample, the amphiphilic 8ABO5COOH molecules are expected to adsorb on the droplet through a hydrophilic interaction and induce the homeotropic surface anchoring. On irradiation with ultra-violet light where *trans*-to-*cis* photoisomerization should occur, the Saturn ring defect

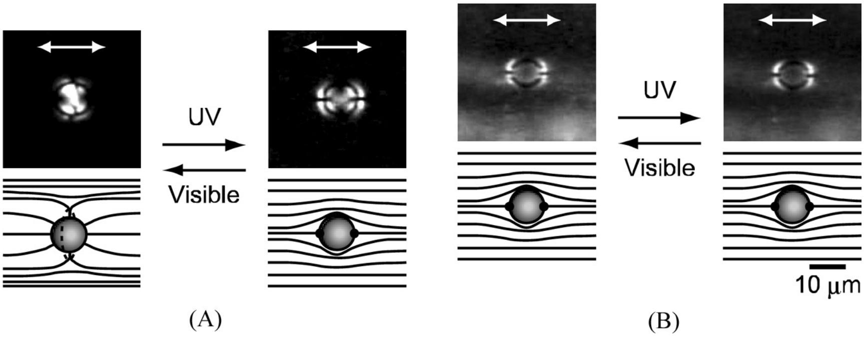
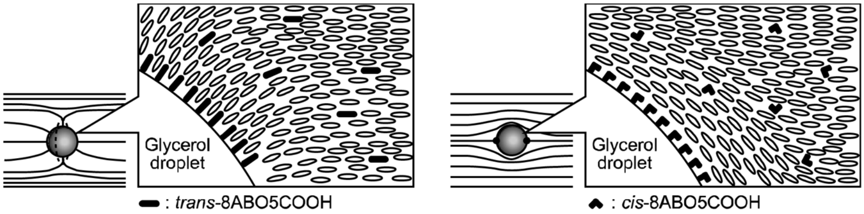


FIGURE 3 Photoresponsive behavior of the defect structures formed around the glycerol droplet. The host liquid crystals are (A) 8ABO5COOH/5CB; (B) 8ABO6/5CB. Light intensities were adjusted at 2.1 and 2.6 mW/cm^2 for ultra-violet and visible light, respectively. The white arrow in each photograph indicates the molecular alignment of the bulk liquid crystal.

exhibited a structural change. In the transformed defect shown in a right photograph, the birefringent regions are located along the horizontal axis. Therefore, this defect structure can be assigned as boojums indicated in a schematic illustration below the photograph. When the wavelength of the irradiated light was changed to the visible region, the boojum defects were converted to the initial defect structure by *cis*-to-*trans* photoisomerization. On the other hand, when the droplets were dispersed in 8ABO6/5CB, we observed no structural transformations of a topological defect. In this sample, the boojums could be found around the droplet at the initial state as shown in a left photograph of Figure 3(B). This defect structure always consisted of boojums without exhibiting any structural changes on irradiation with ultra-violet or visible light while the bulk liquid-crystal alignment was slightly affected by the photoisomerization of the doped azobenzene dye. Since the hydrophobic 8ABO6 should have no specific interactions with the hydrophilic surface of the glycerol droplet, the observed transformations of the defect structures are principally caused by changes of surface properties of the droplet.

The schematic model of the photoinduced transformations is illustrated in Figure 4. In the photochromic liquid-crystal emulsions, the amphiphilic azobenzene molecules should produce the homeotropic anchoring on the glycerol droplet, since we confirmed the formation of the Saturn ring defect around the droplet at the initial state. On irradiation with ultra-violet light, the *trans*-to-*cis* photoisomerization occurs. The *cis* isomers adsorbed on the droplet play a crucial role



(A) (B)

FIGURE 4 Schematic illustration of photochemical changes of surface anchoring of the glycerol droplet in the structural transformation of the defect structures: (A) initial state and after irradiation with visible light; (B) after irradiation with ultra-violet light.

on the photoresponsive behavior of the topological defects. In a similar manner [19,20], the photoisomerization should induce anchoring transitions between homeotropic and planar molecular arrangements, and therefore leads to the transformation from the Saturn ring to the boojums. The other way round, on irradiation of the droplet having the boojums defect with the visible light, the surface anchoring and the defect structure go back to the initial condition by the *cis*-to-*trans* photoisomerization.

3.2. Photonic Modulation of Inter-Droplet Distance in Colloidal Chains

It has been reported that the Saturn ring defect could be observed in the case of relatively weak homeotropic anchoring [6,7]. In order to create the hedgehog defect, we should increase the anchoring strength of the particles. For this purpose, we next employed water droplets containing quite small amount of sodium hydroxide. We expect that the hydrophobic 5CB molecules will exhibit repulsive nature to the water droplets and adopt the homeotropic alignment intrinsically. In addition, the amphiphilic azobenzene dye, 8ABO5COOH, will be ionized to 8ABO5COO$^-$Na$^+$ by contact with the water droplet, resulting in an enhancement of the dye adsorption and the anchoring strength. Figure 5 shows photoresponsive behavior of the defect structures in 8ABO5COOH/5CB dispersed with the water droplets. As we expected, the hedgehog defect could be found around the droplet at the initial state as indicated in a left photograph. By the irradiation, the defect structure exhibited changes in its size in stead of the transformations into the other defect structures. The defect size shrank by the irradiation with the ultra-violet light and returned to the original size

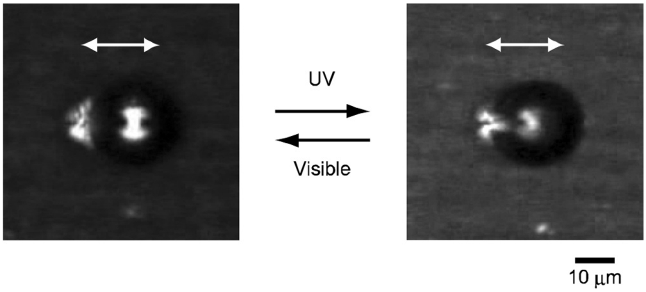


FIGURE 5 Photoresponsive behavior of the defect structures formed around the water droplet containing a small amount of sodium hydroxide. The host liquid crystal is 8ABO5COOH/5CB. Light intensities were adjusted at 2.1 and 2.6 mW/cm^2 for ultra-violet and visible light, respectively.

when the visible light was irradiated. As mentioned before, when several colloidal particles having the hedgehog defect are dispersed in nematic liquid crystals, the particles form one-dimensional chain-like structures [4,5,8,9]. Utilizing the photoinduced behavior, we achieved manipulation of inter-droplet distance of the colloidal chain as shown in Figure 6. On the irradiation with ultra-violet light, the distance between the droplet surfaces was decreased by the shrinkage of the defect size. When the visible light was irradiated, the distance was increased by the recovery of the defect size. As indicated in Figure 7, these photoinduced changes could be performed reversibly. Although the detailed phenomena on the droplet are unknown, it is clear that the reversible changes in the defect size and the inter-droplet distance resulted from the photoisomerization of 8ABO5COO$^-$Na$^+$ adsorbed on

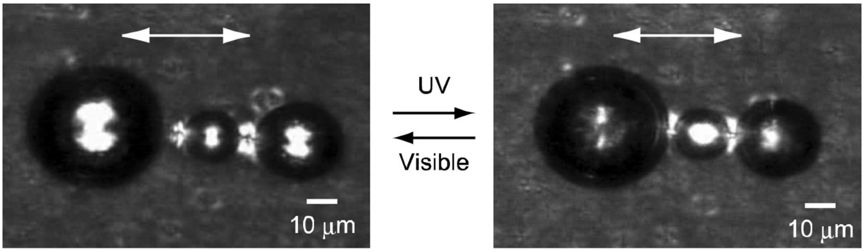


FIGURE 6 Photoinduced changes of distance between droplet surface. Colloidal droplets are water droplets containing a small amount of sodium hydroxide. The host liquid crystal is 8ABO5COOH/5CB. Light intensities are adjusted at 2.1 and 2.6 mW/cm^2 for ultra-violet and visible light, respectively.

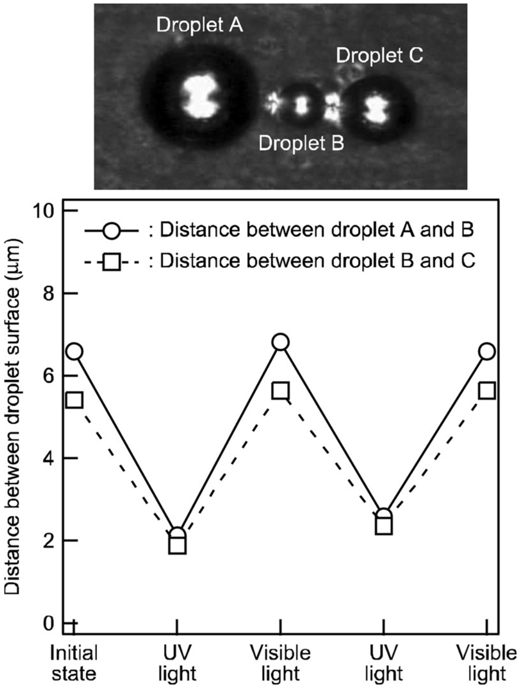


FIGURE 7 Photonic modulation of distance between droplet surface.

the water droplet. We believe that not only the surface anchoring of the droplet but also bulk properties of the liquid crystal would be affected by the photoisomerization. By an optimization of the colloidal particles and the azobenzene derivatives, the structural transformation between hedgehog and boojums and the photonic manipulation of the colloidal superstructures will be achieved.

4. CONCLUSION

We have reported photoinduced changes of the defect structures and the inter-droplet distance in the liquid-crystal emulsions doped with the amphiphilic azobenzene derivatives. In the emulsion dispersed with the glycerol droplets, Saturn ring defect could be observed at an initial condition, indicating that amphiphilic azobenzene derivative adsorbed on the droplets and produced weak homeotropic anchoring. The *cis-trans* photoisomerization of the adsorbed azo-dyes caused the transitions of the surface anchoring between homeotropic and planar alignments, and resulted in the transformations of the defect structures between the Saturn ring and the boojums. On the other hand, in the emulsion dispersed with the water droplets containing a small amount of sodium hydroxide, the ionized azobenzene dye contributed to the induction of strong homeotropic anchoring and the formation of the hedgehog defect around the droplets. On the photoirradiation, though the hedgehog defect exhibited no structural transformation to the other defects, the defect size was modulated. This would be attributable to the changes of both the surface properties of the droplet and bulk properties of the liquid crystal by the photoisomerization. The photoinduced modulation of the defect size brought about the reversible changes of the inter-droplet distance.

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