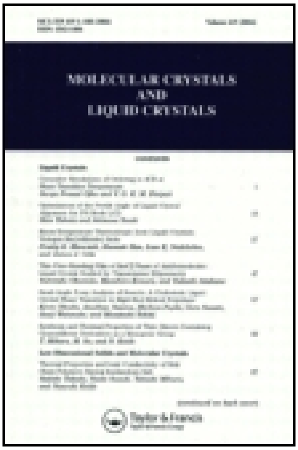

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Manipulation of Defect Structures and Colloidal Chains in Liquid Crystals by Means of Photochemical Reactions of Azobenzene Compounds

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Photonic control of defect structures and colloidal chains has been performed in azobenzene-containing liquid crystals dispersed with glycerol or water droplets. When we dispersed the colloidal droplets into the host liquid crystals, we could observe, at an initial state, Saturn ring and hedgehog around the glycerol and water droplets, respectively, indicating that normal alignment of liquid crystal molecules was induced on the droplets by the adsorption of the azobenzene molecules onto the droplets. In the case of the glycerol droplets, we achieved photochemical manipulation of the defect structures between Saturn ring and boojums on irradiation with ultra-violet and visible light. For the water droplets, an inter-droplet distance of the self-organized colloidal chain could be controlled by changes of the defect size on the photoirradiation. Photoinduced structural changes in the topological defects can be explained by the modulation of surface anchoring of the droplets by means of the cis-trans *photoisomerization of the adsorbed azobenzene molecules.*

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

INTRODUCTION

Colloidal suspensions and emulsions in which small particles or droplets are dispersed in continuous phases are ubiquitous and of

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considerable importance in various industrial fields [1]. Colloidal materials can be found in many familiar substances, including butter, milk, cream, asphalt, paints, glues, and drugs. In recent decades, liquid-crystal colloids, colloidal dispersions using liquid crystals as the continuous phase, have been recognized as a new class of materials and extensively explored owing to their scientific interests [2–13].

In liquid-crystal colloids, we can observe a variety of colloidal behaviors governed by boundary conditions between the host liquid crystals and the dispersed particles. If the surface anchoring of the colloidal particles is strong enough to induce specific molecular arrangement on the particle, a nearby director field will be conflict with the uniform orientation of the bulk liquid crystal. As a result, topological defects are created in the vicinity of the particle. When the molecules are anchored normally to a surface of the particle, a point-like defect (hedgehog, Fig. 1(A)) [2,3] or a disclination loop (Saturn ring, Fig. 1(B)) [4,5] have been observed in various liquid-crystal colloids. While in the case of planar anchoring, two surface defects referred to as boojums have been created around the particle (Fig. 1(C)) [3]. With the existence of several particles in the systems, the orientational elasticity of liquid crystals gives rise to anisotropic interactions with both repulsive and attractive components between the spheres. Consequently, self-organization of colloidal superstructures can be found in liquid-crystal colloids. For example, the particles possessing the hedgehog have a dipolar character, resulting in a formation of one-dimensional chain-like structures [2,3,6,7]. It has been reported that colloidal particles having the Saturn ring or the boojums form two-dimensional closely-packed structures as well as the one-dimensional structures due to a quadrupolar character [3,8,12].

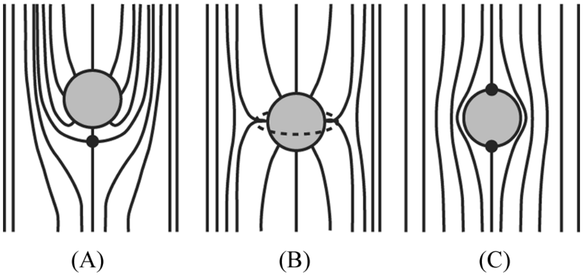


FIGURE 1 Schematic representation of director fields and defect structures formed around a colloidal sphere in nematic liquid crystals: (A) hedgehog; (B) Saturn ring; (C) boojums.

Thus far, the observation and the theoretical analysis of the topological defects formed around colloidal particles and resultant colloidal structures have been extensively performed. However, manipulation of the defects and the colloidal structures by means of external fields has not been appreciably investigated. In this study, we investigated dynamic control of defect structures formed around colloidal droplets by means of photochemical reactions of azobenzene derivatives introduced in liquid-crystal emulsions. In addition, by using the photoinduced changes of the topological defects, we could achieve the reversible manipulation of the inter-droplets distance of the one-dimensional droplet chains.

EXPERIMENTAL SECTION

Materials and Sample Preparation

Chemical structures of a nematic liquid crystal and azobenzene compounds used in this study are shown in Figure 2. Two kinds of azobenzene derivatives were employed: one is an amphiphilic derivative (AB1); another is a hydrophobic dye (AB2). We used 5CB containing a small amount of each azobenzene compound (0.5 mol%) as host liquid crystals (AB1/5CB and AB2/5CB).

Liquid-crystal emulsions dispersed with the glycerol droplets are prepared as follows [14]. At first, we put a drop of the host liquid crystals on a glycerol layer at room temperature. Then it was heated to 60°C in which the host liquid crystals are in the isotropic phase, and kept there for 60 min. After heating, the sample was slowly cooled to

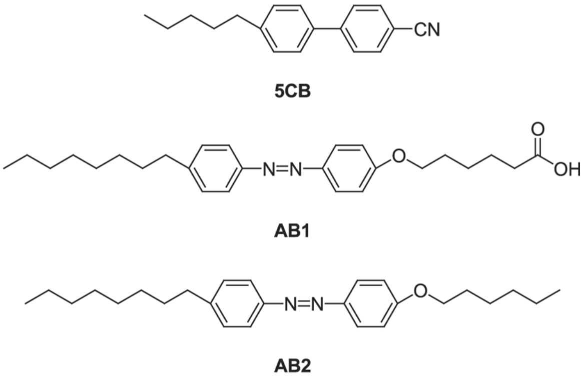


FIGURE 2 Chemical structures of the liquid crystal and the azobenzene compounds.

room temperature, resulting in the formation of glycerol droplets at an interface between air and the host liquid crystals. In the case of 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 molecules by ionization of AB1.

Observation and Photochemical Manipulation of Defect Structures and Colloidal Chains

After the preparation, the liquid-crystal emulsions were sandwiched between two glass plates, the surfaces of which were covered with a polyimide film and rubbed in a unidirectional way to impose uniform molecular arrangement of the bulk liquid-crystal molecules. Photoresponsive behavior of the defect structures and the colloidal chains were investigated in a polarized light microscope equipped with an ultra-high-pressure mercury lamp as a light source for the excitation of the azobenzene dyes. Wavelengths of ultra-violet (UV, $\lambda = 365\,\mathrm{nm}$) and visible (VIS, $\lambda = 435\,\mathrm{nm}$) light were selected with dichroic mirrors. Sample temperature was adjusted with the temperature controller (MATS-2002ST, Tokai Hit Co., Ltd., Japan). All the experiments were conducted at 25°C.

RESULTS AND DISCUSSION

Defect Structures Formed around the Colloidal Droplets in Different Host Liquid Crystals

Firstly, we investigated initial structures of topological defects formed around the colloidal droplets dispersed in the different host liquid crystals. Figure 3 shows photographs of the defect structures observed with the polarized light microscope. The liquid-crystal molecules far from the droplet are uniformly aligned along the horizontal axis. When the glycerol droplets are dispersed in 5CB, two strongly birefringent regions that are aligned along the horizontal axis can be observed around the droplet (Fig. 3(A)). This defect structure can be assigned to the boojums shown in Figure 1(C) in which the liquid-crystal molecules should be align planar to an interface between the droplet and 5CB [3]. On the other hand, the birefringent regions which are located perpendicular to the bulk liquid-crystal alignment can be observed around the droplet in glycerol-droplet/AB1/5CB (Fig. 3(B)), indicating a formation of the Saturn ring shown in Figure 1(B). In this

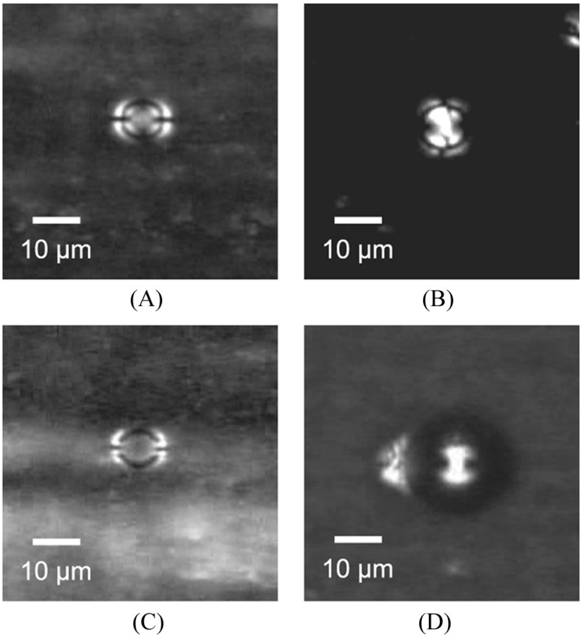


FIGURE 3 Polarized light microscope images of defect structures created around colloidal droplets dispersed in different host liquid crystals: (A) glycerol-droplet/5CB; (B) glycerol-droplet/AB1/5CB; (C) glycerol-droplet/AB2/5CB; (D) water-droplet/AB1/5CB. In the water droplet, a small amount of sodium hydroxide was dissolved. The 5CB molecules in bulk region are uniformly aligned in horizontal axis.

case, we can expect that the amphiphilic azobenzene molecules would be adsorbed on the droplet through a hydrophilic interaction and induce the normal surface anchoring. The importance of the hydrophilic interaction can be confirmed with the result for glycerol-droplet/AB2/5CB. When the azobenzene derivative is hydrophobic AB2, the boojums defect is formed around the droplet as shown in Figure 3(C), since the hydrophobic azobenzene molecules should exhibit no specific interactions with the surface of the hydrophilic glycerol droplet. In the previous studies [3,4], it has been reported that the Saturn ring defect can be observed in the case of relatively weak normal anchoring. In order to create the hedgehog which is illustrated in Figure 1(A), we should enhance the anchoring strength of the droplets. 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 liquid-crystal alignment spontaneously. In addition, the amphiphilic azobenzene dye, AB1, will be ionized by contact with the water droplet, resulting in an enhancement of the dye adsorption and the anchoring strength. As we expected, the hedgehog defect could be found around the droplet at the initial state as shown in Figure 3(D).

Photochemical Manipulation of the Defect Structures

Next, we performed photonic control of the defect structures formed around the colloidal droplets by the irradiation with UV or VIS light. Figure 4 exhibits photoresponsive phenomena of the topological defects in the photochromic liquid-crystal emulsions. As shown in Figure 4(A), we could observe light-induced reversible changes of the defect structures formed around the glycerol droplet in AB1/5CB. On irradiation with UV light in which the *trans*-to-*cis* photoisomerization should be induced, the Saturn ring was transformed into the

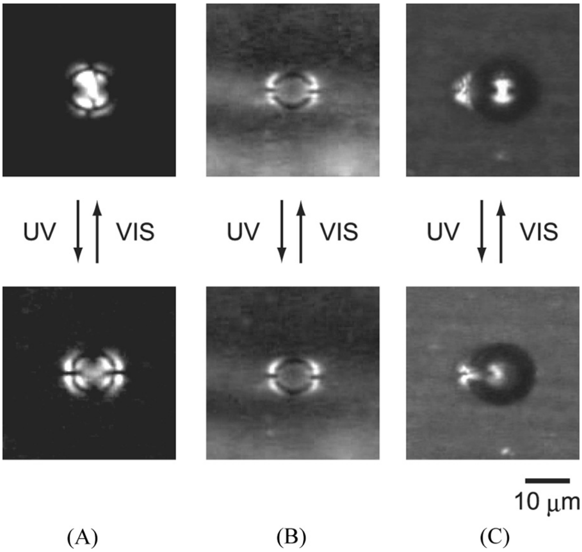


FIGURE 4 Photoresponse of the topological defects formed around the droplets in liquid-crystal emulsions containing the azobenzene compounds: (A) glycerol-droplet/AB1/5CB; glycerol-droplet/AB2/5CB; (C) water-droplet/AB1/5CB. In the water droplet, a small amount of sodium hydroxide was dissolved. Light intensities were adjusted at 2.1 and 2.6 mW/cm^2 for UV and VIS light, respectively. The 5CB molecules in bulk region are uniformly aligned in horizontal axis.

boojums [15]. When the wavelength of the irradiated light was changed to the VIS region, the boojums went back to the initial structure by the *cis*-to-*trans* photoisomerization. Although the photochromic reactions of azobenzene derivatives are known to have an influence on a variety of physical properties of liquid crystals as well as the surface anchoring [16], the observed transformations of the topological defects are principally caused by the changes of the surface anchoring. Because, when we examined the photoresponse of the defect structure formed around the glycerol droplet in AB2/5CB (Fig. 4(B)), the defect structure exhibited no structural changes on irradiation with UV or VIS light while the bulk liquid-crystal alignment was slightly affected by the photoisomerization of the hydrophobic azobenzene molecules. These results suggest that the light-induced changes of the topological defects observed in this study are attributable to the anchoring changes by means of the *cis-trans* photoisomerization of the azobenzene molecules adsorbed on the droplet [16]. In the case of the water droplet dispersed in AB1/5CB, we observed photoinduced changes of a size of the hedgehog in stead of the transformations into the other topological defects by the irradiation. As shown in Figure 4(C), the defect size shrank by the irradiation with UV light and returned to the original size when VIS light was irradiated. In this stage, we speculate that the shrinkage of the defect size will also result from the photochemical change in the surface anchoring of the droplet.

Photochemical Control of the Inter-Droplet Distance of the Colloidal Chain

As mentioned before, when several colloidal particles having the hedgehog defect are dispersed in nematic liquid crystals, it has been reported that the particles form one-dimensional chain-like structures [5]. Utilizing the photoinduced changes of the defect size shown in Figure 4(C), we achieved manipulation of inter-droplet distance of the colloidal chain as shown in Figure 5. On the irradiation with UV light, the inter-droplet distance was decreased by the shrinkage of the defect size. When VIS light was irradiated, the distance was increased by the recovery of the defect size. These photoinduced changes could be performed reversibly by changing the wavelength of the irradiated light. Figure 6 shows the time course of the changes of the inter-droplet distance on irradiation with UV (A) or VIS light (B). The photoinduced changes completed within 10 sec in the both processes. The response time will be improved by increasing the intensity of the irradiated light. Although the detailed phenomena on the droplet

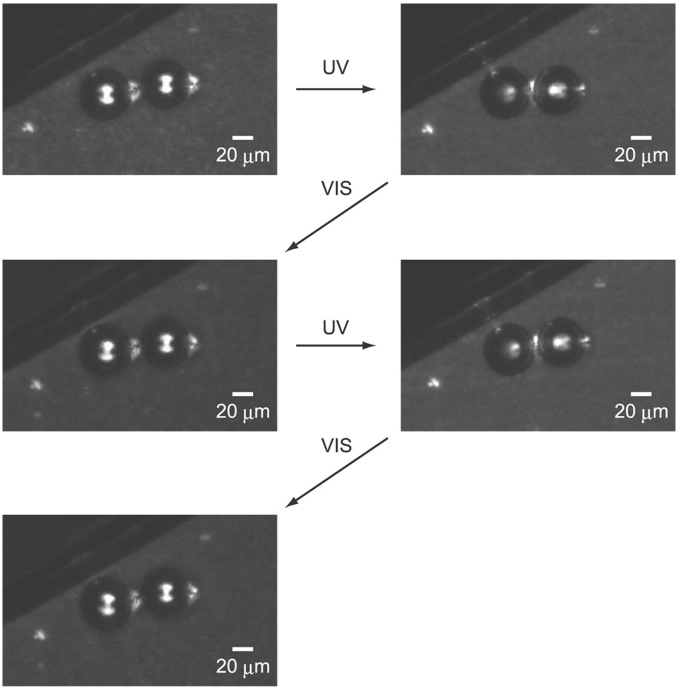
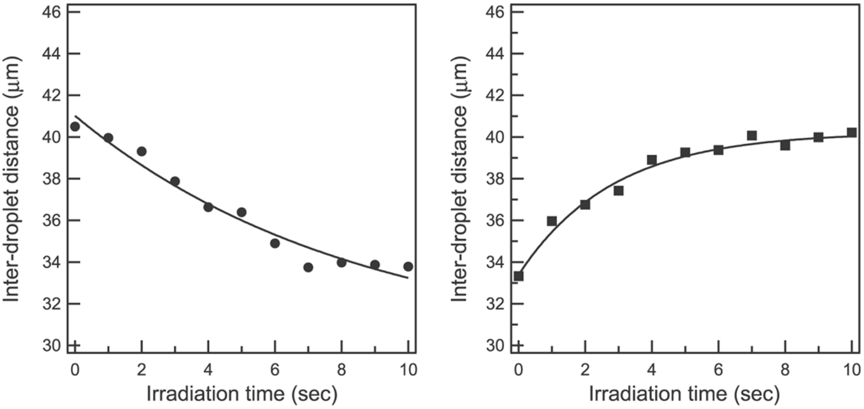


FIGURE 5 Photochemical manipulation of the inter-droplet distance of the colloidal chain. Colloidal droplets are water droplets containing a small amount of sodium hydroxide. The host liquid crystal is AB1/5CB. Light intensities are 2.1 and 2.6 mW/cm^2 for UV and VIS light, respectively.



(A) (B)

FIGURE 6 Response of photoinduced changes of the inter-droplet distance on irradiation with UV (A) and visible (B) light.

are unknown, it is clear that the reversible changes of the defect size and the inter-droplet distance resulted from the photoisomerization of ionized AB1 adsorbed on the water droplets.

CONCLUSIONS

In this study, we investigated photochemical manipulation of the defect structures and the inter-droplet distance of the colloidal chain in the liquid-crystal emulsions containing azobenzene compounds. In the emulsion dispersed with the glycerol droplets, Saturn ring could be observed at the initial state. This indicates that amphiphilic azobenzene molecules are adsorbed on the droplets and produced relatively weak normal anchoring. The *cis-trans* photoisomerization of the adsorbed azobenzene molecules caused the transitions of the surface anchoring between normal and planar conditions, and resulted in the structural change of the defect structures between the Saturn ring and the boojums. In the case of the emulsion dispersed with the water droplets containing a small amount of sodium hydroxide, the ionized azobenzene molecules contributed to the induction of strong normal anchoring and the formation of the hedgehog around the droplets. On the photoirradiation, though the hedgehog exhibited no structural transformation to the other defects, the defect size was modulated. The photoinduced changes of the defect size brought about the reversible manipulation of the inter-droplet distance of the colloidal chain.

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