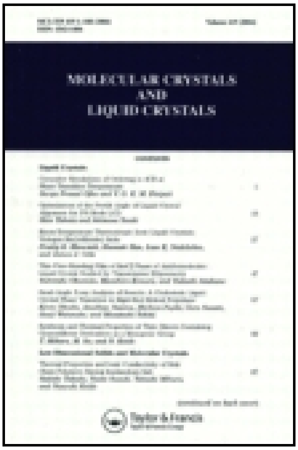

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PHOTOCHEMICAL MANIPULATION OF GLYCEROL DROPLETS IN NEMATIC LIQUID CRYSTALS

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Dynamic manipulation of glycerol droplets could be achieved by light in azobenzenedoped nematic liquid crystals. On irradiation of UV light, the trans-cis photoisomerization drives a directional motion of the droplets towards the cis-rich region and assembled close-packed two-dimensional hexagonal colloidal crystals. This behavior is mainly attributable to reduction of the droplet-LC interfacial tension, associated with the enhanced surface-activity of cis isomers. We also performed photochemical assembly of tailored droplet arrays by projection of computer-generated images on the samples. The photoinduced manipulation of droplets will provide a versatile approach to micro-structuring of LC devices.

Keywords: interfacial tension; liquid-crystal emulsions; photoisomerization; tailored droplet arrays

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INTRODUCTION

Assemblies of micro- and nano-particles or droplets have a wide range of applications in photonic materials, and bio-sensors and assay devices [1]. Sedimentation is a well known pathway to spontaneous formation of colloidal crystal structures, and is already widely employed to prepare self-oranized photonic crystals. By an additional external assist of electric fields, for example, patterned arrays of particles can also be fabricated [2]. Recently, one of the present authors (B.I.L) discovered a spontaneous formation of hexagonal crystals of micron-sized glycerol droplets suspended in a nematic LC [3]. The crystal stucture is stabilized by liquid-crystalline orientational elastic forces, and hence we can expect that by modulating the LC Properties by external stimuli, the colloidal crystal structure can also be manipulated. Here we demonstrate a photochemical assembly and disassembly of the glycerol droplets by doping the nematic emulsion with photoresponsive azobenzene derivatives.

EXPERIMENTAL

Chemical structures of compounds used in this work were shown in Figure 1. As a LC host, we employed 5CB, and doped it with an azobenzene

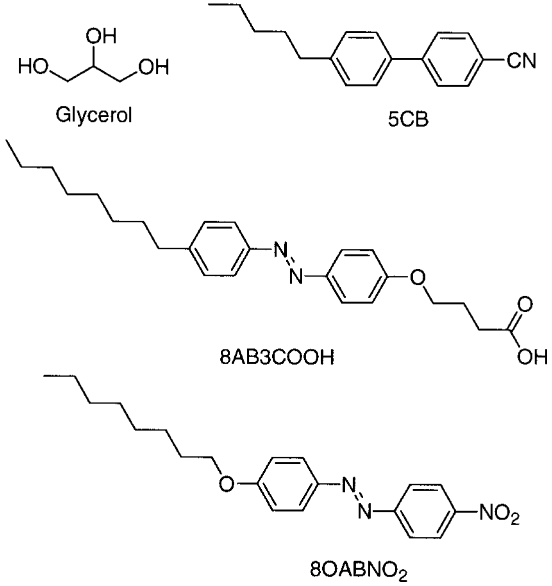

FIGURE 1 Compounds used in this work.

derivative (8AB3COOH, $\lambda_{max} \approx 350\,nm$, 1 mol%). 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-isotropic phase transition temperature (37°C), and kept there for 60 min. Substantial amount of glycerol could diffuse into the LC host 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.

Photochemical manipulation was investigated with a fluorescent/polarizing microscope (Eclipse E-800, Nikon, Japan). Schematic illustration of the experimental system was shown in Figure 2. Photochemical assembly of tailored droplet arrays was performed with “Maskless Projection System” (NewCreation Co. Ltd., Japan). Sample temperature was maintained with a hot stage (Themoplate MATS-2002ST, Tokai Hit, Japan).

RESULTS AND DISCUSSION

Uniformly dispersed glycerol droplets with the typical diameter of 3 μm appeared after the preparation was kept in the nematic phase overnight

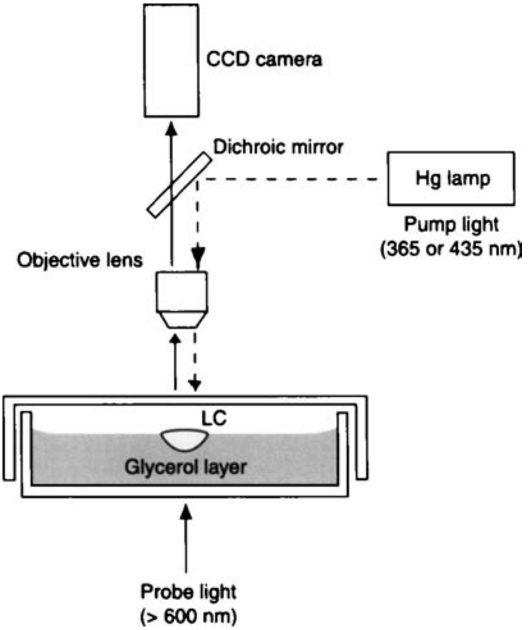

FIGURE 2 Schematic illustration of the experimental setup. The host LC was floating in the glycerol layer with lens shape. Glycerol droplets were suspended right beneath the air-LC interface.

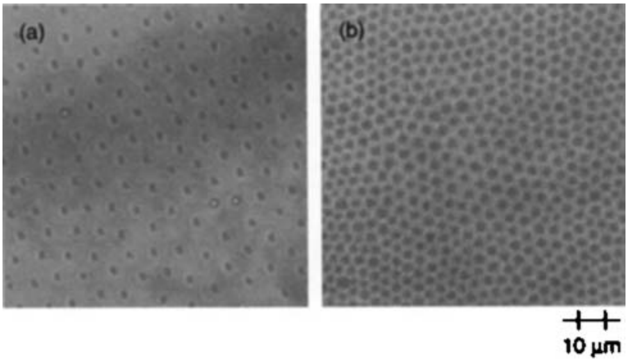

FIGURE 3 Polarizing photographs of the LC emulsion (a) before and (b) after irradiation of circular-shaped beam at 30°C (365 nm, 50 m,W/cm^2, 300 s).

(Fig. 3(a)). Although the glycerol has a higher density than the LC, the Van der Waals forces keep the glycerol droplets trapped right beneath the LC-air interface [3]. For the photochemical manipulation of droplets, we irradiated the nematic emulsion at 30°C with a 160 μm-diameter circular beam of UV light (365 nm, 50 mW/cm^2) that preferentially induces the *trans→cis* isomerization. Right after the irradiation, the droplets near the periphery of the light beam started to move toward inside the beam. The droplets far from the beam were also gradually attracted to make the irradiated region more condensed with the droplets. Typical velocity of the droplet motion was roughly estimated as ≈ 0.5 μm/s. It took about 300 s for this process to virtually come to an end with closely packed droplets (Fig. 3(b)). When the irradiation was terminated, the droplets began to slowly diffuse back to the initial state with a relaxation time of the order of hours, presumably associated with the thermal conversion of *cis*-isomers. However, by shining the close-packed colloidal crystal with a visible light (435 nm) that causes the rapid *cis→trans* conversion, we could induce a dramatically swift backward dispersion of the droplets out of the irradiated region. In contrast to the condensation process driven by UV light, the backward motion is not preferentially initiated at the edge of the light beam, but takes place uniformly even from inside the close-packed droplet crystal like an explosion. These wavelength-dependent behaviors prove that the directional motion of droplets is photochemical rather than photothermal in nature. We also confirmed by monitoring the motion of floating fine solid particles that no macroscopic convective flow was involved at least up to ten times of the light intensity used.

In general, tailored assemblies of micro-particles have potential applicability to photonic crystal circuits and array-based bio-assay devices [1].

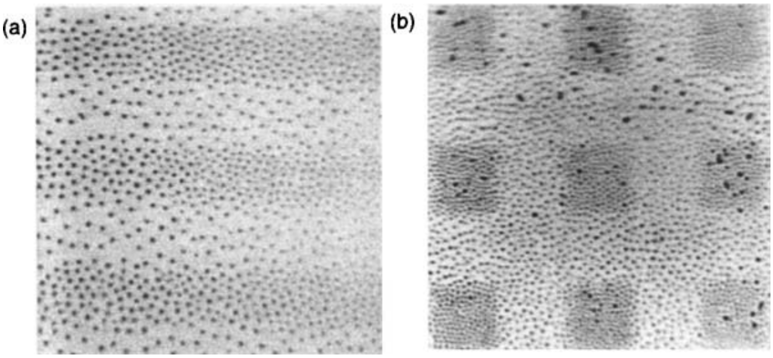

FIGURE 4 Photo-addressed droplet arrays in the LC emulsion: (a) grating and (b) 2-D square array.

Based on the photokinetic effect, we attempted a photo-addressed patterning of droplet arays as shown in Figure 4. Here, patterns of a grating structure (Fig. 4(a)) and a two-dimensional square array (Fig. 4(b)) were computer-generated, and their PC projector images were optically reduced and projected onto the LC emulsion with the Maskless Projection System. Since the PC projector used had no emission in the near UV region, a distinct azobenzene derivative that is sensitive to violet light (8OABNO$_2$ shown in Figure 1, $\lambda_{\max} \approx 380\,\mathrm{nm}$, 1 mol%) was synthesized for this purpose and doped into the nematic LC. As clearly shown in Figure 4, the photo-patterning of droplets could be achieved quite neatly within a few minutes of irradiation. Once such a patterning is complete, it is easy to fix the structure by polymerizing or gelating the LC host for use in two-dimensional photonic devices, etc.

Finally, we discussed the mechanism of the photo-induced assembly of the droplets. Among Possible consequences of *trans*→*cis* isomerization, we point out here its effect on the interfacial tensions between the LC, glycerol and air. We experimentally confirmed that the azo-doped LC undergoes a drastic flattening of its lens shape on glycerol layer, when the whole droplet region was irradiated with the UV light at 30°C. This observation clearly indicates the relative reduction of the LC glycerol and/or the LC -air interfacial tensions. Such a decrease in interfacial tension can occur as a result of preferential adsorption of the generated *cis* isomers due to its enhanced polarity relative to the *trans* form [4].

As soon as the azobenzene-doped LC is locally illuminated with UV light, virtually all azobenzene molecules are almost instantaneously converted to the *cis* isomer, resulting in the formation of concentration gradient of *cis* isomer toward the edge of the lens (see Fig. 5). In the absence of macroscopic convective or Marangoni flows, as presently

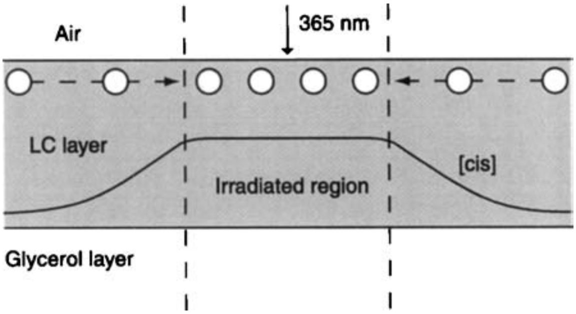

FIGURE 5 Schematic illustration for the cross-section of the system during irradiation of 365-nm light. Open circles are the droplets. Curved line indicates the concentration gradient of the *cis* isomer. Dashed arrows denote the direction of the droplet motion.

confirmed experimentally, the gradient can relax only through the diffusion and the thermal back conversion of the *cis* isomer. Let D and τ be the diffusion coefficient and the time constant of thermal back conversion of *cis* isomer, respectively, then the stationary decay length of the *cis* isomer concentration is given by $\sqrt{D\tau}$ and the characteristic time necessary for the initial abrupt gradient to relax into the stationary one is given by τ. If we put glycerol droplets in such a transient *cis* isomer gradient, the droplets tend to move along the gradient toward the higher *cis* concentration in such a way that the LC-glycerol interfacial tension be more reduced [5,6]. Although it is difficult to evaluate the interfacial tension as a function of the *cis* concentration with both orientationally isotropic and anisotropic contributions, a rough estimate of the droplet speed can still be obtained by simply equating the viscous drag on the droplet (in negligence of orientational correction [7] and the thermodynamic force due to the decreasing interfacial tension [6]:

$$4\pi R^2 \nabla\gamma_{eff} = 2\pi R \mu_{LC} v \left(\frac{3\mu_g + 2\mu_{LC}}{\mu_g + \mu_{LC}}\right),$$

where R and v are the radius and the traveling speed of the droplet, γ_{eff} is the effective interfacial tension between glycerol and the LC including both the isotropic and anisotropic contributions, and $\boldsymbol{\mu}_{LC}$ and $\boldsymbol{\mu}_g$ are the viscosities of the LC host and glycerol. Noting $\boldsymbol{\mu}_g > 100\,\mathrm{mPa\cdot s}$, $\boldsymbol{\mu}_{LC} \approx \mathrm{mPa\cdot s}$ and $R \approx 1.5\,\mu\mathrm{m}$ we find $v \approx 10\,\mu\mathrm{m/s}$ even for a very modest assumption of $\nabla\gamma_{eff} \approx 10\,\mathrm{mN/m^2}$, corresponding to a minute change in surface tension as $10^{-2}\,\mathrm{mN/m}$ over 1 mm-distance. This estimate is sufficiently large to account for the observed motion of the droplets ($\approx 0.5\,\mu\mathrm{m/s}$). Along with the ordinary isotropic contribution, γ_{eff} contains an anisotropic contribution from the orientational strain around the droplet. In terms of the surface anchoring energy W and the Frank elastic constant K of the LC, the anisotropic part of γ_{eff} may be approximately written as $K/(KW^{-1}+R)$. Since the anchoring energy is likely to be a decreasing function of the *cis*-isomer concentration, the anisotropic contribution also drives the particles toward the illuminated region along the anchoring energy gradient. Even assuming a rather weak anchoring energy of $W \approx 10^{-3}\,\mathrm{mN/m}$ in dark that satisfies $KW^{-1} >> R$ for $K \approx 10^{-11}$ N, we still find that the droplet speed by this anisotropic effect amounts to $\approx 1\,\mu\mathrm{m/s}$, indicating the potentially significant role of the LC anchoring in the photokinetic effect.

CONCLUSION

We have demonstrated photo-manipulation of colloidal crystal structure in nematic emulsions on the basis of the photoisomerization of azobenzene derivatives. The wavelength-sensitive directional motion of the droplets clearly indicates that the observed phenomena are a photochemical event, and may be mainly attributable to the decrease of the interfacial tension at the droplet-LC interface in the presence of *cis* isomer. Given the established utility of LCs in various applications, we believe that the photochemical droplet assembly in LC hosts should serve as an efficient and versatile approach to micro-structuring of LC devices.

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