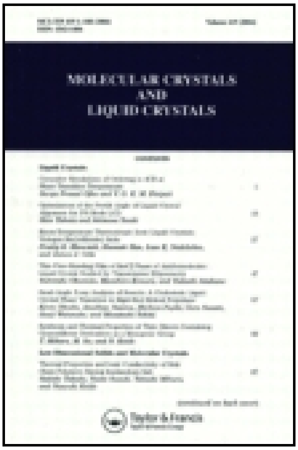

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Micro Manipulation with Optical Responsive Cholesteric and Compensated Nematic Liquid Crystal

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Micro Manipulation with Optical Responsive Cholesteric and Compensated Nematic Liquid Crystal

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We have developed photoresponsive liquid crystalline films (cholesteric liquid crystal and compensated nematic liquid crystal) having azobenzene compound to manipulate micro particles on the surface by light irradiation. When few solid particles (polystyrene bead) were placed on the surface of the film, movement of the solid particles was observed upon irradiation of UV (365 nm) or visible light (>420 nm). Only rotational motion of the particles was observed on the cholesteric liquid crystal film. Both translation and rotation was observed on the compensated nematic liquid crystal film. So the mode of motion (either rotation or both translation and rotation) was changed by changing the film from cholesteric film to compensated liquid crystal film. The rotational direction of the solid was controlled by using chiral azobenzene compound with right or left handed twisting ability.

Keywords: chirality of azobenzene compound; liquid crystalline film; micro manipulation; photo responsive; transfer of particles

INTRODUCTION

Recently, manipulation of micro materials using fluids is attracting a lot of attention, because of being expected application to micromachine and biochip, etc. [1]. If liquid crystals (LC) are utilized as a working fluid for micro manipulation, it can be expected that several micro materials can be manipulated at micro scale by external stimuli such as light, electric field, magnetic field, temperature, and so on. It is well known that cholesteric LC doped azobenzene molecules with chirality

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shows transformation of the pitch by the change of helical twisting power (HTP) with trans-form and cis-form of azobenzene groups induced by the photoisomerization [2].

Several attempts have been reported to manipulate small scale material induced by light on surface. Ichimura *et al.* [3] first demonstrated the ability of azobenzene molecular switches to manipulate (translate) liquid droplet by generating surface energy gradient by alternating irradiation of ultraviolet and blue light. Eelkema *et al.* [4] used the rotational reorganization of the LC film to rotate microscopic objects four orders of magnitude larger than the bistable dopants in the film.

In this study, we prepared azobenzene doped cholesteric LC and compensated nematic LC films and investigated the movement behaviors of micro particles on surface of these LC films by irradiation of ultraviolet (UV) or visible (VIS) light.

EXPERIMENTAL

Synthesis of Azobenzene Derivatives

First, 4-aminobenzoic acid (12.5 g) was dissolved in 100 cm^3 *conc.* HCl (about 18% v/v) and cooled to 0°C, and an aqueous solution of sodium nitrite (6.8 g in 70 cm^3 of water) was added dropwise under constant stirring. To the resulting solution, phenol (9.5 g) in 4 N sodium hydroxide was added dropwise under constant stirring. After stirring for another 1 h at RT, *dil.* HCl was added to the solution until acidic condition and the mixture was stirred for 6 h at RT. The solution was filtered. After drying, the solid was purified by recrystallization from ethanol-hexane mixture to get pure 4-(4-hydroxyphenylazo)benzoic acid.

Yield: 60%, mp 278.0°C.

Next, 4-(4-hydroxyphenylazo)benzoic acid (4.8 g) and potassium hydroxide (3.0 g) were dissolved in ethanol (100 cm^3). To this solution small amount of potassium iodide and 1-chlorohexane (10 g) was added, and then refluxed at 80°C for 24 h. This mixture was acidified by *conc.* HCl, and then filtered. After removing the solvent by evaporation, the solid was washed with aqueous solution of acetic acid. After washing, 4-(4-hexyloxyphenylazo)benzoic acid was purified by recrystallization from ethanol.

Yield: 40%, mp 230°C.

6AzMent(+)

4-(4-hexyloxyphenylazo)benzoic acid (2.0 g), (+)-menthol (1.1 g) and *N,N*-dimethylaminoaminopyridine (0.12 g) were added to dried methylene chloride (100 cm^3) with dicyclohexylcarbodiimide (1.5 g) and stirred at room temperature for 96 h. After stirring, insoluble byproduct was removed by filtration and the filtrate was concentrated by evaporation. Residue was purified by column chromatography with dichloromethane and following recrystallization from ethanol.

Yield: 12%, mp 74.3°C, ^{1}H-NMR ($CDCl_3$-d_6, δ): 4.1 (t, 2 H, CH_2OPh); 4.9 (m, 1 H, COOCH); 7.0–8.2 (m, 8 H, aromatic), Helical sense: right-handed, HTP; $49.4 \times 10^8\,m^{-1}mol^{-1}$ g-E-host (trans-cis) and 10.4×10^8 $m^{-1}\,mol^{-1}$ g-E-host (cis-trans).

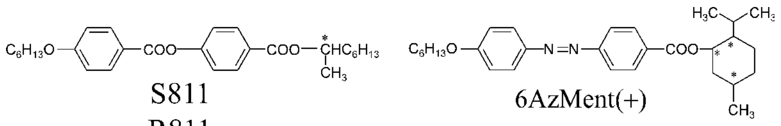
6AzMent(−)

6AzMent(−) was synthesized with (−)-menthol in the same way as 6AzMent(+).

Yield: 10%, mp 75.5°C, ^{1}H-NMR ($CDCl_3$-d_6, δ): 4.0 (t, 2 H, CH_2OPh); 5.0 (m, 1 H, COOCH); 7.0–8.2 (m, 8 H, aromatic), Helical sense: left-handed, HTP; $49.0 \times 10^8\,m^{-1}\,mol^{-1}$ g-E-host (trans-cis) and $10.8 \times 10^8\,m^{-1}\,mol^{-1}$ g-E-host (cis-trans).

FABRICATION OF LC FILMS

LC films were prepared by mixing accurately weighed mixture of **E-host** as low molecular weight host nematic LC and synthesized azobenzene derivatives (**6AzMent(+)**/**6AzMent(−)**/**R-811**/**S-811**). The thermal behavior of pure **E-host** and the mixture is given in Figure 1. The phase transition temperature decreased in the case of mixed material compared to the pure **E-host**. Photoisomerization of **6AzMent(+)** compound in methanol solvent and in E-host matrix is given in Figure 2. **6AzMent(−)** compound showed similar photoisomerization behavior. To make film, THF solution of the mixtures was dropped on glass substrates with oriented polyimide coating and allowed to evaporate the solvent. Thickness of the film was estimated using Beer-Lambart law. It was about 25 ± 5 μm. To observe motion, polysterene (PS) particles with diameter about 5 μm [5] were dispersed



S811
R811

6AzMent(+)
6AzMent(−)

SCHEME 1 Nonphotochromic chiral compound, **S811** and **R811** and synthesized chiral azobenzene compounds, **6AzMent(+)** and **6AzMent(−)**.

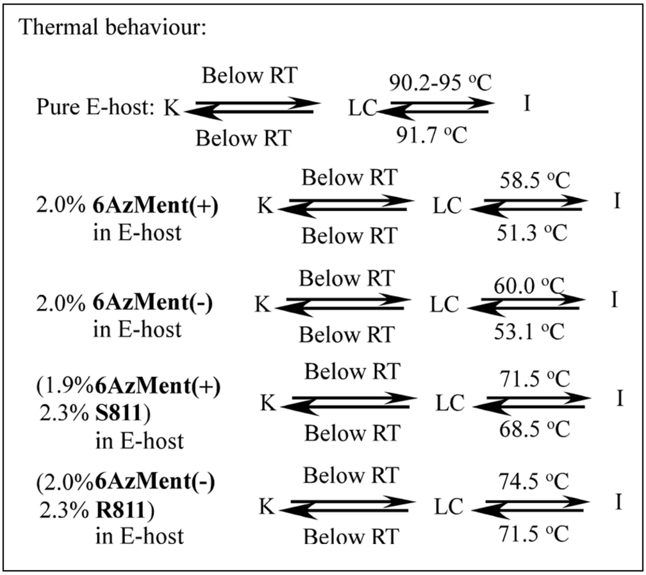


FIGURE 1 Thermal behavior of pure **E-host** and mixed material used to make films.

on the surface of the LC film. The movement of the PS particles with photoisomerization was observed by polarizing microscope under irradiation of UV light (365 nm) or VIS light (>420 nm).

MEASUREMENTS

^{1}H-NMR spectra of synthesized compound were taken on a JEOL JNM-EX400; 400 MHz. Diameter of a polystyrene particle was measured by using SEM (JEOL JSM-T-2001). The phase transition behavior of the samples was explored by the polarizing microscope (Olympus BH-2) with hot stage (Mettler FP-82HT) which was controlled to 5°C/min by the central processor (Mettler FP-80HT). UV (365 nm) light and VIS (>420 nm) light were irradiated using high pressure mercury lamp (Ushio SX-U1500H) combined with UV filter (Sigma UTVAF35U) and sharp cut filter (Sigma SCF-50S-42L), respectively.

RESULTS AND DISCUSSION

The polarizing optical micrograph of the cholesteric LC films (E-host/**6AzMent(+)** = 98.0/2.0 wt%) and (E-host/**6AzMent(−)** = 98.0/2.0 wt%)

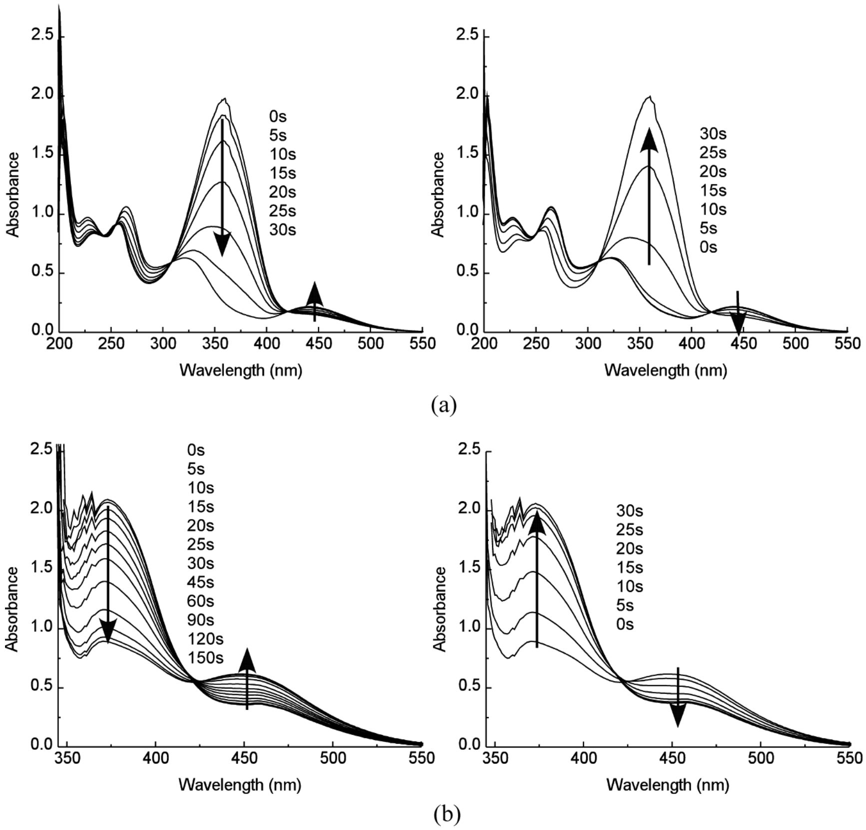
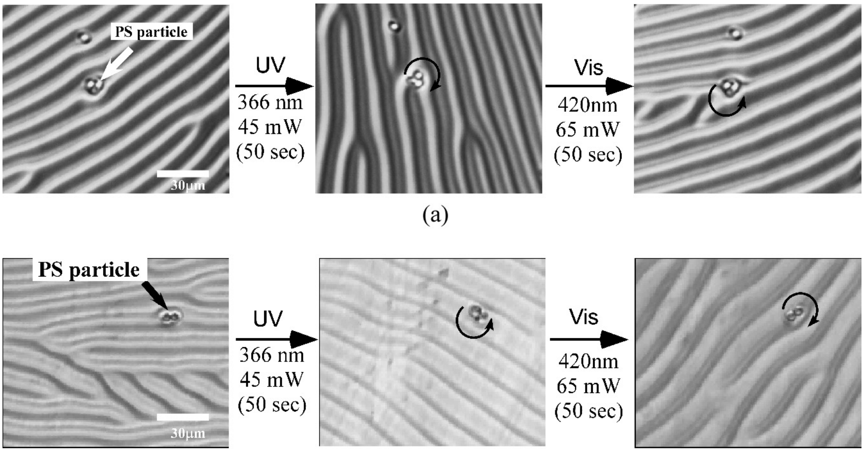


FIGURE 2 UV-visible spectra of **6AzMent(+)** and changes observed in the absorption spectra during UV and visible light irradiation (a) in methanol solution (b) doped in E-host (injected in 25 μm cell).

were shown in Figure 3. The helical axis of the cholesteric LC is parallel to the glass plane, because a fingerprint texture was observed. It is known that the fingerprint texture can be observed when the helical axis of the cholesteric LC is parallel to the glass plane; where the column of cholesteric LC aligns parallel to the glass substrate. The change in HTP of the chiral azobenzene compound due to the photoisomerization from trans- to cis-form was found to cause reorientation of fingerprint texture of the cholesteric LC by irradiation of UV or VIS light. After putting PS particles on the surface of the LC films, rotational motion of PS particles was induced by photo irradiation as shown in Figure 3. The direction of the rotation was changed



(a)

(b)

FIGURE 3 Movement of PS particle on cholesteric liquid crystalline films (a) (**E-host**/**6AzMent**(+) = 98/2) and (b) (**E-host**/**6AzMent**(−) = 98/2) after UV-Vis light irradiation.

alternately by UV or VIS light irradiation. It was reported about this rotational motion by Feringa *et al*. [2,6].

Knowing helical pitch (P) is important to determine optical property of cholesteric LC. Then, right-handed helical structure was regarded as $P > 0$, and left-handed helical structure was regarded as $P < 0$. By mixing right-handed chiral (**6AzMent**(+) or R-811) compound and left-handed chiral (**S-811** or **6AzMent**(−)) compound to compensate the helical pitch value to be zero ($P = 0$), compensated nematic LCs were made. And, the movement of the PS particles on the compensated nematic LC films (E-host/**6AzMent**(+)/**S811** = 95.8/1.9/2.3 wt%) and (E-host/**6AzMent**(−)/**R811** = 95.7/2.0/2.3 wt%) were examined under UV light irradiation, resulting the phase transition from compensated nematic phase to cholesteric phase due to the change in HTP [7,8]. The particles exhibited both rotational and linearly motion during the phase transition from nematic phase to cholesteric phase (Fig. 4). On the compensated nematic liquid crystal film made by **6AzMent**(+) and **S811**, upon UV irradiation initially the particles translated with slight rotation (clockwise), when cholesteric textures appeared the particles rotated clockwise with little translation, the particles rotated counterclockwise by VIS light irradiation, when the fingerprint texture disappeared the particles translated opposite direction with little or no rotation. The direction of rotation was

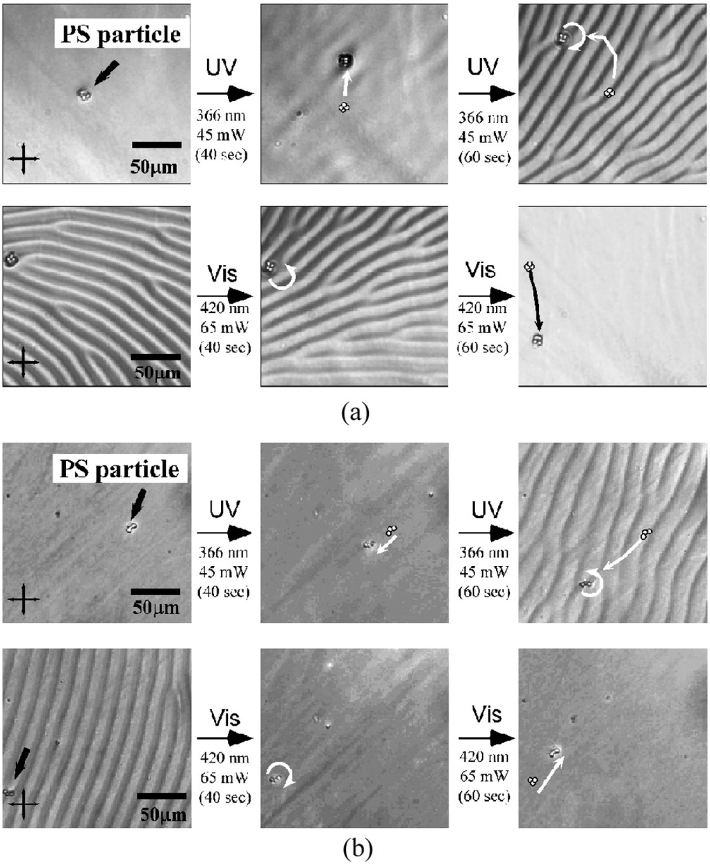


FIGURE 4 Movement of PS particle on compensated nematic liquid crystalline films (a) (**E-host**/**6AzMent(+)**/**S-811** $= 95.8/1.9/2.3$) and (b) (**E-host**/**6AzMent(−)**/**R-811** $= 95.7/2.0/2.3$) during UV-Vis light irradiation.

reversed on the films made by **6AzMent(−)** and **R-811**. So, the movement direction of the solid was controlled by using chiral azobenzene compound with right or left handed twisting ability.

According to these results, it seemed that the driving force would be generated by reorientation of LC molecules from out-of-plane alignment to in-plane alignment (Fig. 5). Although the driving force for the movement of the PS particles on the LC films is not clear at the present stage, the change in the orientation of the LC molecules may be closely related to the photo transfer on the LC films.

As for the rotational movement of particles on cholesteric LC film, it may be based on the reorientation of the column structure of

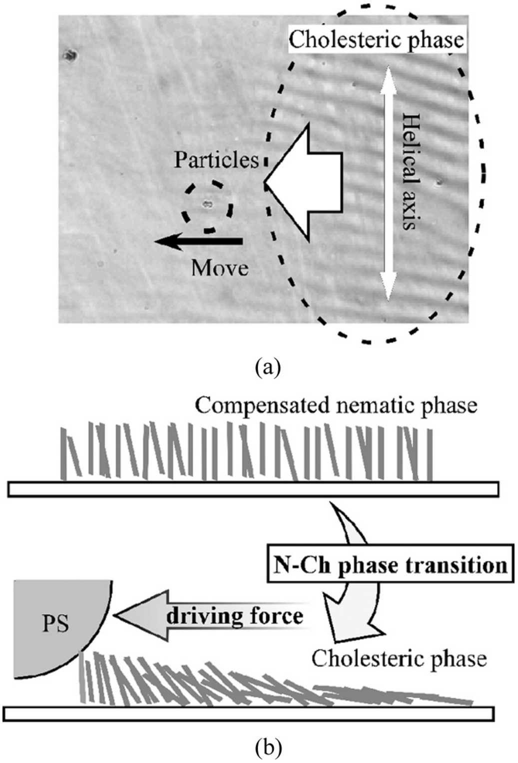


FIGURE 5 (a) In optical micrograph of compensated nematic film, the moment of developing cholesteric phase (b) illustration of driving force.

cholesteric LC due to change of pitch (P). And the linearly motion on surface of the compensated nematic LC films may be due to change of orientation of LC molecules induced by light.

CONCLUSIONS

As for these movements of micro particles on surface of the LC films with azobenzene compound induced by light, it seems that the orientation of the LC molecules was changed by the photoisomerization of the azobenzene compound, and generated movement as a driving force. The movement would make particles to transfer. Although these structural changes are not clear, we were able to make particles to rotate, move linearly, or the both at the same time on a LC surface by light.

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