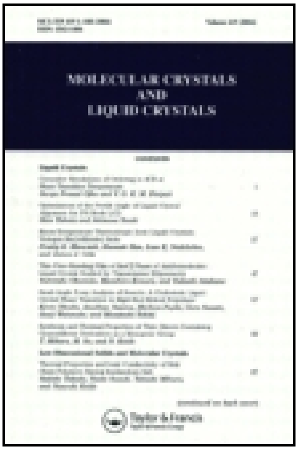

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Orientation-Control of Liquid Crystal Molecules by Photochromism of Azobenzene

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ORIENTATION-CONTROL OF LIQUID CRYSTAL MOLECULES BY PHOTOCHROMISM OF AZOBENZENE

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Langmuir-Blodgett films of amphiphilic azobenzene were prepared on a glass plate as a substrate of liquid crystal (LC) cell. Photochemical regulation of LC alignment was dependent on adsorption structure of azobenzene on a glass plate. When the amphiphilic LC molecules were sandwiched with two glass plates covered with hydrophobic surface of azobenzene, the transmittance change of the cell did not occur by UV and/or visible light irradiation. On the other hand, the relative transmittance of the cell in which the amphiphilic LC molecules were sandwiched with hydrophobic and hydrophilic surfaces of azobenzene film was changed reversibly by UV and visible light irradiation. Similar behavior was observed in the cell constructed with hydrophobic azobenzene surface/hydrophobic LC/hydrophobic azobenzene surface.

Keywords: azobenzene LB film; nematic liquid crystal; orientation control

INTRODUCTION

The studies of induced mechanical effects in photochromic molecules had been an area of great interest. Azobenzenes are one of the most extensively studied groups of photochromic materials due to their potential use as photoactive media for information storage and processing [1,2]. The Langmuire-Blodgett (LB) technique has been shown to be a powerful and convenient method for the preparation of ultra thin, uniform, and controllable films. There are many reports on structures [3,4] and properties

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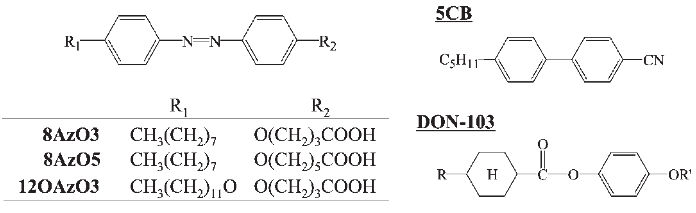
such as aggregate formation [5], molecular switching of amphiphilic azobenzene derivatives in LB films [6]. Ichimura *et al* have reported that the orientation of liquid crystal (LC) was changed reversibly by conformational changes in the *trans-cis* isomerization process of azobenzene LB film [7]. However, detailed relationship between the adsorption structure of azobenzene against to the substrate and the orientation of LC isn't clear.

In this study, LB films of azobenzene derivatives taking various adsorption structures were prepared. Orientation change of LC molecules induced by photochromism of azobenzene in azobenzene/LC/azobenzene cell is discussed based on the adsorption structure of azobenzene molecules against to the substrate.

EXPERIMENTAL

Glass plates and fused silica plates were used as a substrate for preparation of LB film. They were cleaned ultrasonically with detergent for 15 minutes, with distilled water for 15 minutes, and with methanol for 15 minutes. The surface of cleaned substrate was sufficiently hydrophilic after dipping into distearyldimethylammonium chloride (0.5 wt%) aqueous solution. Hydrophobilized substrates were obtained by dipping into sodiumdialkylsulfosuccinate aqueous solution.

Three amphiphilic azobenzene derivatives used here were 4-octhyl-4′-(3-corboxy-trimetyleneoxy)azobenzene (8AzO3), 4-octhl-4′-(5-corboxy-penta-metyleneoxy)azobenzene (8AzO5), and 4-dodecyloxy-4′-(3-corboxy-trimetyleneoxy)azobenzene (12OAzO3). Their molecular structures are shown in Figure 1. These samples were purchased from Dojindo laboratory. LB films of azobenzene derivatives were prepared on air-water interface of a LB trough (Kyowa kaimen kagaku). A chloroform solution of azobenzene derivatives (3×10^{-4}mol/l) was spread on deionized and distilled water. The molecules were compressed with a moving barrier at the speed at 15 cm^2/min. A single monolayer was transferred onto hydrophililized and



	R_1	R_2
8AzO3	$CH_3(CH_2)_7$	$O(CH_2)_3COOH$
8AzO5	$CH_3(CH_2)_7$	$O(CH_2)_5COOH$
12OAzO3	$CH_3(CH_2)_{11}O$	$O(CH_2)_3COOH$

FIGURE 1 Molecular structures of azobenzene derivatives and liquid crystal molecules.

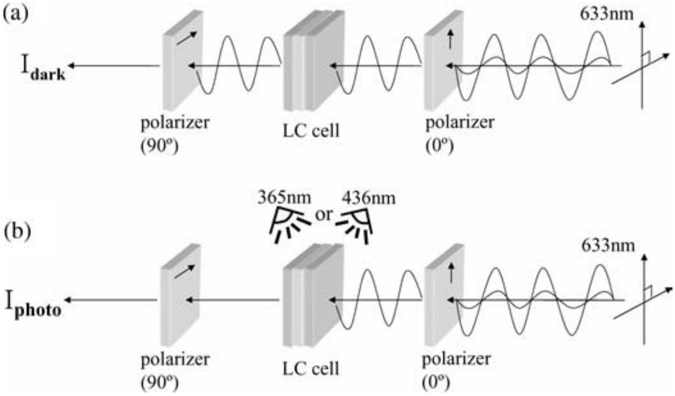


FIGURE 2 Schematic drawing of optical setup for transmittance measurement of LC cell.

hydorophobilized glass plates by vertical dipping method and horizontal lifting one, respectively.

Two kinds of rod-like nematic LCs were used for LC cells. 5CB is amphiphilic and DON-103 has hydrophobic groups at both ends of molecule (Fig. 1). The LCs were sandwiched between two glass plates covered with azobenzene monolayer. The LC cell was set between two crossed polarizers and exposed alternately to UV(365 nm) and visible(436 nm) light as shown in Figure 2. Transmittance change of LC cell with UV and visible light irradiation was defined by following equation.

$$\text{Transmittance change} = I_{\text{photo}}/I_{\text{dark}}$$

Here, I_{dark} is the light intensity passed through two crossed polarizers with a LC cell and I_{photo} is the light intensity after UV or visible light irradiation.

UV-visible spectra and transmittance change were recorded on a Shimadzu UV-2200 spectrophotometer at room temperature (20–23°C).

RESULTS AND DISCUSSION

Figure 3(a) shows the UV-vis absorption spectra of the 8AzO3 chloroform solution. The band region from 400 nm to 500 nm is the feature of n-π^* transition of azobenzene compound. The π-π^* transition along the long axis of trans-azobenzene chromophore is located at 355 nm. The short wavelength absorption found at 245 nm is the electronic transition with the transition moment roughly parallel to the short axis of the trans-azobenzene chromophore. After UV irradiation, the absorption intensity of n-π^* transition increased slightly, as shown in Figure 3(b). Moreover, it comes into notice

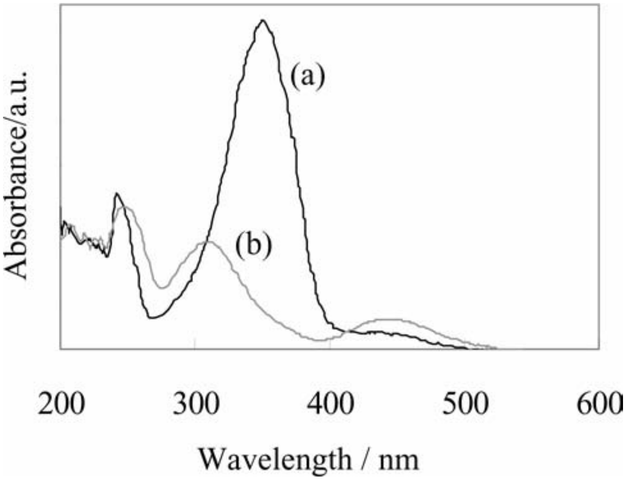


FIGURE 3 UV-vis absorption spectra of the 8AzO3 in chloroform solution before (a) and after UV (365 nm) light irradiation (b).

that the absorption due to the transition of the long axis blue-shifted to 310 nm and that of the short axis red-shifted to 255 nm, respectively. The absorption spectrum after UV irradiation was assigned to cis-azobenzene. By visible light irradiation, the photoisomerization from cis-azobenzene to trans-azobenzene occurred quantitatively. 8AzO5 and 12OAzO3 molecules in chloroform also indicated similar reversible photoisomerization. Figure 4 shows the UV-vis absorption spectra of the 8AzO3 monolayer film transferred on both sides of the fused silica plates by vertical dipping method. The absorption peaks due to the π-π^* transition of trans- azobenzene form appear at 330 nm and 250 nm. The absorption intensity at 330 nm decreased and the absorption peak shifted slightly to the short wavelength region by UV irradiation. Subsequent visible light exposure regenerated the trans-form. This phenomenon indicates that 8AzO3 molecules photoisomerize reversibly even in solid state. On the other hand, such photoisomerization was not observed in the 8AzO3 five-layers film transferred on the fused silica plate by horizontal lifting method (Absorbance intensity of monolayer on one side of substrate was too small to confirm whether photoisomerization was occurred). The LB technique by vertical dipping method possesses, besides its utility in molecular tailing, a superior feature that in-plane structural anisotropy may be imprinted during the dipping process. This leads frequently the molecular orientation along the dipping direction. It seems that azobenzene molecules transferred by vertical dipping method adsorb obliquely to the substrate surface. Therefore, it is reasonable to consider the occupied area per one molecule in

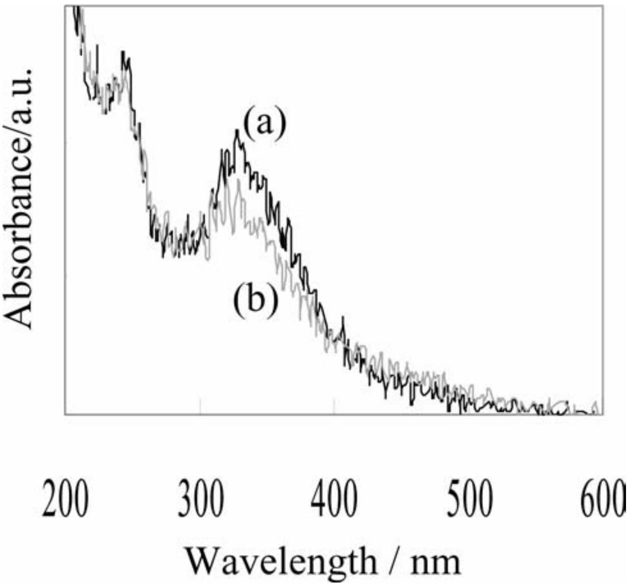


FIGURE 4 UV-vis absorption spectra of monolayer of 8AzO3 deposited on a fused silica plate by vertical dipping method before (a) and after UV (365 nm) light irradiation (b).

solid state is larger than that on the water. In-plane structural anisotropy, on the other hand, dose not expect with horizontal lifting method. The molecular packing of 8AzO3 in the film transferred by horizontal lifting method seems to be denser than in the film transferred by vertical dipping method. At present, we are not able to elucidate the detailed.

The 8AzO5 monolayer film transferred by vertical dipping method and the five-layers film transferred by horizontal lifting method showed good photoisomerization. In the case of 12OAzO3, LB films transferred by vertical dipping and horizontal lifting methods did not show the photoisomerization. Figure 5 shows the UV-vis absorption spectra of the 12OAzO3 in chloroform solution and its monolayer film prepared by vertical dipping method. The absorption peak due to the π-π^* transition of trans-azobenzene chromophore appears at 360 nm in solution and at 305 nm in the film. Generally, the π-π^* transition peak of azobenzene chromophore is used to research the aggregation of the molecule for which its transition dipole is directed along the long axis of the azobenzene molecule. The peak position of the film is blue-shifted to 55 nm in comparison with that in solution. The blue shift occurs when the dipole moments of molecules in aggregates are parallel. The parallel aggregates are known as H-aggregates. Although the π-π^* transition peaks of 8AzO3 film and 8AzO5 film are blue shifted

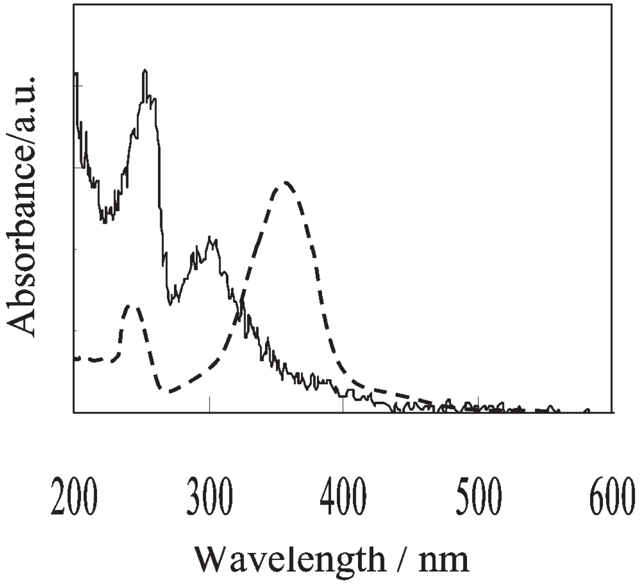


FIGURE 5 UV-vis absorption spectra of 12OAzO3 chloroform solution (dash line) and of monolayer deposited on a fused silica substrate by vertical dipping method (solid line).

approximately 20 nm in comparison with the peak position observed in solution, the blue shift of 12OAzO3 is bigger than those of 8AzO3 and 8AzO5. This result is attributed to strong molecular interaction of 12OAzO3 because 12OAzO3 has strong hydrophobic group and ether linkage. Therefore, 12OAzO3 didn't show photoisomerization because it was densely packed with the long axis parallel to each other and formed already rigid H-aggregate on water surface.

The 8AzO5-coated glass plate was used as a substrate for LC cell because 8AzO5 films transferred by vertical dipping method and horizontal lifting method showed photochromism. Hydrophobic surface of 8AzO5 on the glass plate was obtained by vertical dipping method, and hydrophilic one was obtained by horizontal lifting method. When 5CB was sandwiched with two glass plates covered with hydrophobic surface of 8AzO5, the transmittance of the cell did not change by UV and/or visible light irradiation (Figure 6(a)). On the other hand, the transmittance of the cell changed reversibly by UV and visible light irradiation when 5CB was sandwiched with hydrophobic and hydrophilic surface of 8AzO5, as shown in Figure 6(b). In the case of DON-103, no transmittance changes revealed in the cells constructed with hydrophilic 8AzO5 surface/DON-103/hydrophilic 8AzO5

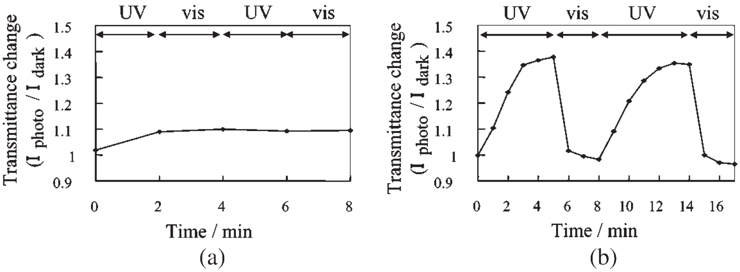


FIGURE 6 Transmittance changes at 633 nm by alternate exposure of UV and visible lights in LC cell constructed with hydrophobic 8AzO5 surface/5CB/hydrophobic 8AzO5 surface (a), and with hydrophilic 8AzO5 surface/5CB/hydrophobic 8AzO5 surface (b).

surface and with hydrophilic 8AzO5 surface/DON-103/hydrophobic 8AzO5 surface. The transmittance change was observed only in the cell in which DON-103 was sandwiched with two glass plates coated with hydrophobic 8AzO5 surface.

The mechanism of transmittance change of LC cell is shown schematically in Figure 7. When LC molecules were sandwiched with galss plates modified with azobenzene LB film, they aligne by the molecular interaction depending on the most surface structure of azobenzene film. In the cell constructed with hydrophilic 8AzO5 surface/5CB/hydrophobic 8AzO5 surface, 5CB molecules alinge by hydrophilic interaction between hydrophilic 8AzO5 surface and hydrophilic group of 5CB, and hydrophobic interaction between hydrophobic 8AzO5 surface and hydrophobic group of 5CB as shown left side in Figure 7(a). DON-103 molecules in the cell constructed

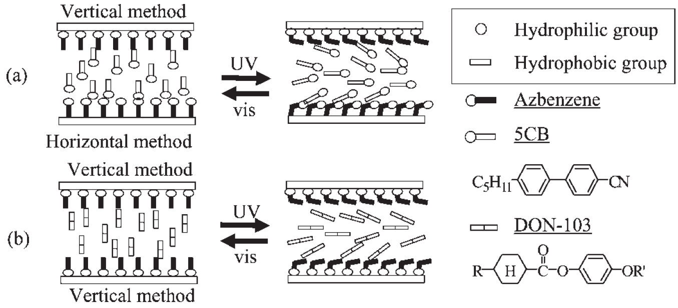


FIGURE 7 Schematic drawing of LC alignment change induced by photoisomerization of azobenzene in 5CB cell constructed with hydrophilic 8AzO5 surface/5CB/hydrophobic 8AzO5 surface (a), and in DON-103 cell constructed with hydrophobic 8AzO5 surface/DON-103/hydrophobic 8AzO5 surface (b).

with hydrophobic 8AzO5 surface/DON-103/hydrophobic 8AzO5 surface also alinge by hydrophobic interaction between hydrophobic 8AzO5 surface and hydrophobic group of DON-103 as shown left side in Figure 7(b). When the LC cell is irradiated by UV light, the trans/cis photochemical isomerization of azobenzen occurs. At that time, alignment change of LC molecules is induced by conformational change of azobenzene, as shown right in Figure 7(a) and (b)). After visible light irradiation, LC molecules are reoriented in initial state and the transmittance of LC cell is recovered.

CONCLUSION

This report provides the detailed results of the preparation of photoactive azobenzene LB film and LC alignment on the substrate coated with azobenzene LB film taking various adsorption structures. The photochromic activity of azobenzene aniphiphiles in LB film is dependent on the methylene chain length introduced as a spacer and the deposition condition. The alignment of rodlike nematic LCs can be controlled by using the hydrophililized and/or hydrophobilized substrates modified azobenzene LB films prepared with vertical dipping and/or horizontal lifting methods. When amphiphilic LC (5CB) was sandwiched with hydrophililized glass plate and hydrophobilized glass plate, the reversible transmittance change of the LC cell was observed. In the case of DON-103 which has hydrophobic groups at both ends of molecule, on the other hand, the transmittance change was obserbed only in hydrophobilized glass plate/DON-103/ hydrophobilized glass plate cell.

Photoinduced phase transitions and alignment changes of LCs are considered to have technological importance for photon-mode optical recording and transducers of optical information.

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