Influence of Packing in LB Films on Photoisomerization of Azobenzene Derivative

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In this work, we investigated the influence of packing state of azobenzene chromophore on the cis-trans reverse photoisomerization in the Langmuir-Blodgett (LB) film. For this purpose, a long-chain azobenzene derivative of p-(ω-trimethylammoniodecyloxy)-p'-octyloxyazobenzene bromide (TAOAB), employed as the photoactive film material, was mixed with methyl stearate (MeSt) at various molar fractions. Fabrication of the TAOAB/MeSt mixed LB films was carried out by using polyion-complex technique, followed by structural characterizations by means of FTIR and UV-vis spectroscopy. The results obtained showed that as the degree of packing in the LB films increases, both the azobenzene chromophore and the hydrocarbon chain orient more perpendicularly to the film surface. Reversible cis-trans photoisomerization of TAOAB was induced by alternate irradiation with UV and visible light even in the mixed LB films with dense packing of the chromophore. In the process of thermal cis-to-trans isomerization, we found that more closely packed chromophore presented slower reaction rate at 20 °C, reflecting the difference in the steric hindrance at various contents of MeSt in the LB films.

Key words: LB film, azobenzene derivative, photoisomerization, polyion-complex technique, isomerization kinetics

1. INTRODUCTION

Reversible photochromism based on a cis-trans isomerization has been extensively studied for azo dyes in solutions, polymer matrixes, organized molecular assemblies including alternate layer-by-layer assemblies and LB films.[1-9] Owing to the potential applications for optical information storage media and light switching devices, long-chain azobenzene derivatives have been of immense interest as one of the functional film-forming materials. In particular, their LB films are very attractive molecular design option for the possibility of controlling orientation, density and packing of the azobenzene chromophore in the thin layer system. At present, several techniques to introduce azo chromophore into LB film are available, e.g., simply employing water-insoluble amphiphilic azobenzene derivatives or side-chain polymers containing azobenzene group as a film material, applying polyion-complex technique and so on. In previous works,[10-12] we proposed an adsorption technique, that is, the water-soluble azo dyes are incorporated in the cationic LB films via adsorption process by the electrostatic interaction. We also showed that the orientation of chromophores embedded in the LB film could be controlled by designing molecular structure of the adsorbates.

When isomerization reaction takes place in an active site of the molecule, factors such as the molecular mobility and the free volume strongly influence the reaction kinetics.[1-5] For instance, stacking of the azobenzene chromophores remarkably prevents the cis-trans reverse photoisomerization, while the chromophores, being in the polymer side chains,[2] cyclodextrin cavity,[3] and polyion complex LB films[5,6] are advantageous for the photoisomerization reaction. However, because the microenvironment favorable for the photoisomerization simultaneously induces the thermal reaction to the more stable trans-isomer even at an ambient temperature, a relatively large energy barrier for the isomerization would be required for the potential application of the LB film to optical memories. Therefore, it would be of increasing importance to study the kinetics of the cis-trans isomerization quantitatively for the azobenzene derivatives in the LB films.

In this study, we report the effects of packing on the cis-trans isomerization reaction of azobenzene in the LB films. An amphiphilic azobenzene derivative of TAOAB was deposited by polyion-complex technique[13] not only to facilitate the transfer of monolayer on the solid substrate but also to give an efficient free volume around the azobenzene chromophore, being required for the reversible photoisomerization. We continuously changed packing state of the polyion-complex LB films by mixing MeSt with TAOAB at various molar fractions. The structure of the LB films and their thermal cis-to-trans isomerization kinetics were characterized by spectroscopic methods. We particularly focus on the changes in molecular orientations and reactivity with packing state in the LB films.

2. EXPERIMENTAL

The cationic long-chain azobenzene derivative of TAOAB was purchased from Sogo Pharmaceutical Co., Ltd. MeSt and water-soluble polymer of poly(sodium 4-styrenesulfonate) (PSSS) were supplied by Aldrich Chemical Co., Inc. These substances were used without further purification. The structural formulae for TAOAB and PSSS are exhibited in Chart 1.

Spreading solutions were prepared by mixing chloroform solutions of TAOAB and MeSt at various ratios. Total concentration was adjusted to ca. 1.0×10^{-3} mol dm^{-3}. TAOAB/MeSt monolayer was formed on the aqueous 4.0×10^{-5} mol dm^{-3} PSSS subphase by spreading the chloroform solution. The measurements of surface pressure-area (π-A) isotherms and the multilayer depositions of the monolayer were carried out by a FSD-300 LB film balance of U. S. I. System, Co., Ltd.

Chart 1

$H_3C-(CH_2)_7-O$—⟨⟩—N≈N—⟨⟩—O-$(CH_2)_{10}$-$N^+(CH_3)_3$ Br$^-$

TAOAB

—$(CH$-$CH_2)_n$—
⟨⟩
SO_3Na
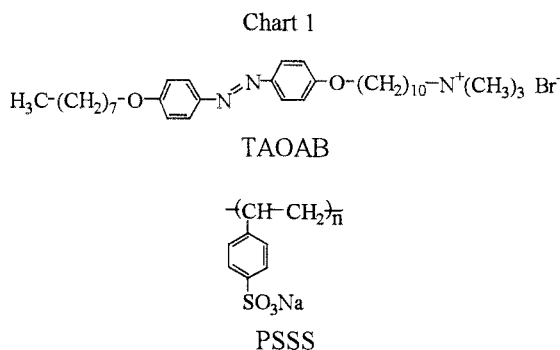
PSSS

The compression rate (the barrier speed) used was 10 mm min^{-1}. Using the conventional vertical dipping (LB) method, the fabrication of the polyion-complex LB films of TAOAB/MeSt-PSSS was performed at a surface pressure of 30-35 mN m^{-1}. The dipping and withdrawal speeds were kept at 7 mm min^{-1}. Solid substrates such as gold-coated brass plate, calcium fluoride plate and quartz plate were used for the most appropriate measurements.

Irradiation with UV and visible light was carried out by using an Usio SX-UI500XQ optical moduleX with a Xe lamp (500 W) as a light source. The sample was exposed with the light passing through a glass band-pass filter (365 or 400 nm) and an IR cut filter for 10 min.

UV-vis and FTIR spectra of the LB films were measured with a Shimadzu UV-3100PC UV-vis-near-IR scanning spectrophotometer and a JASCO FT/IR-8900 spectrometer equipped with an MCT detector, respectively. In the measurements of FTIR-reflection absorption (RA) spectra, an incident angle of 80° and a p-polarized direction of the incident light were employed.

3. RESULTS AND DISCUSSION

Mixed monolayer properties of TAOAB/MeSt were examined by measuring π-A isotherms on distilled water and a PSSS containing subphase at various molar fractions of TAOAB (X_{TAOAB}) at 20 °C. As shown in Fig.1, TAOAB on the water subphase forms an expanded monolayer (isotherm i). On the other hand,
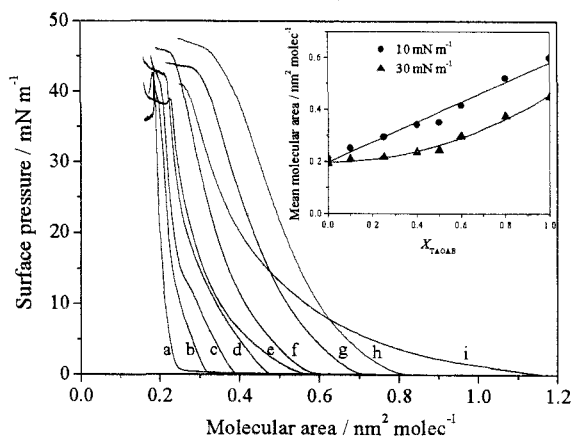
π-A isotherm on the PSSS subphase (isotherm h) shows rather steep rising of the surface pressure, indicating formation of more condensed monolayer by complxation with PSSS. In this monolayer, the molecular area of TAOAB is governed by the surface density of sulfonate anions of PSSS rather than the size of TAOAB itself because the limiting area was fairly larger than expected from the cross sectional area of TAOAB.

The isotherms of mixed TAOAB/MeSt monolayers (isotherms a-g) are gradually condensed with decreasing X_{TAOAB}. Inset in the figure shows the plots of mean molecular area of the TAOAB/MeSt monolayer at a constant surface pressure against X_{TAOAB}. The areas at 10 mN m^{-1} follow a straight line, while those at 30 mN m^{-1} deviate downward from linearity. This means that TAOAB slightly interacts with MeSt in the monolayer at higher surface pressure.

Subsequently, the LB deposition was applied to the TAOAB/MeSt-PSSS monolayers, and regular transfer on the solid supports was successfully achieved at 10 °C. For the LB films obtained, photoisomerization reaction was examined by irradiating with UV and visible light. Fig.2 shows the change in UV-vis absorption bands of TAOAB upon the irradiation for the LB film at X_{TAOAB}=0.5. In the spectrum for the as-deposited film, absorption band of the π-π^* transition moment of the trans-azobenzene chromophore is observed at around 350 nm. On irradiation with UV light, the band at 350 nm become smaller, whereas absorption bands due to cis-isomer appear at 320 and 460 nm. While the spectrum does not recover completely with visible light for 10 min to that before UV irradiation, the spectral change between Fig.2 (b) and (c) was confirmed to take place reversibly by alternate irradiation with UV and visible light over and over again. Similarly, the cis-trans reverse photoisomerization of TAOAB was observed for the LB films at the other X_{TAOAB} as well.

To get information on the structural changes with mixing of MeSt and photoirradiation, spectroscopic measurements were carried out for the TAOAB/MeSt-PSSS LB films. Tilt angle of the azobenzene chromophore in the LB films was estimated from polarized UV-vis spectra. As shown in Fig.3, the
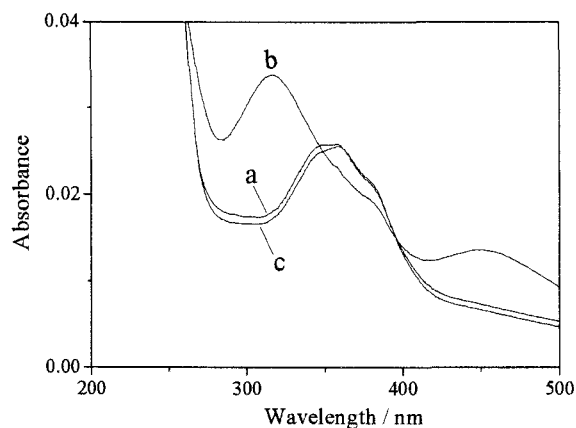

Fig.1. π-A isotherms of the TAOAB/MeSt monolayers at various X_{TAOAB} on an aqueous PSSS solution at 20 °C; X_{TAOAB}: a, 0; b, 0.1; c, 0.25; d, 0.4; e, 0.5; f, 0.6; g, 0.8; h, 1.0. Curve i is an isotherm of the TAOAB monolayer on distilled water. The inset indicates the plots of molecular area at 10 and 30 mN m^{-1} vs. X_{TAOAB}.

Fig.2. Change in UV-vis spectra of the TAOAB/MeSt-PSSS LB film at X_{TAOAB}=0.5 on alternate irradiation with UV and visible light; a, as-deposited; b, after UV light irradiation; c, after visible light irradiation.

9-layer LB film of X_{TAOAB}=0.5 exhibits the anisotropic spectra at incident angles (α) of 60°, i.e., the absorption band at around 350 nm appears stronger in the p-polarized spectrum than that in the s-polarized spectrum. In addition, the result that in-plane anisotropy was not admitted in the spectra at the normal incidence (spectra are not shown) reveals uniaxial distribution of the azobenzene chromophore around the surface normal. From a dichroic ratio of the bands at α=60°, we estimated the tilt angle of the long axis of azobenzene chromophore in the LB film by assuming the refractive index of the LB film to be 1.50 (the calculated value is given in Table 1).[14] In addition, the band in the p-polarized spectrum is slightly shifted to the shorter wavelength (331 nm) due to parallel aggregation of trans-azobenzene.[1] Since this blue-shifted peak was absent in the spectrum at normal incidence, the aggregates are supposed to orient almost vertically with respect to the film surface.[15]

Fig.4 gives FTIR-transmission and -RA spectra measured for a 9-layer LB film at X_{TAOAB}=0.5 in the C-H stretching vibration range. In the transmission spectrum, CH₂ symmetric and antisymmetric stretching vibration bands, originating from the methylene groups in both TAOAB and MeSt molecules, are observed at 2852 and 2922 cm⁻¹, respectively. This suggests that a gauche conformation is involved to some extent in the hydrocarbon chains.[16] These peaks shift to larger wavenumber if X_{TAOAB} increases. This result shows that the gauche conformation originates from the TAOAB molecule. In addition, intensities of these bands in the transmission spectrum are stronger than those in the RA spectrum. Since an electrical field vector of the incident light is perpendicular to the film surface in the RA measurements, this result shows that the transition dipole moments of both CH₂ symmetric and antisymmetric stretching vibration bands are oriented almost parallel to the film surface. This qualitatively means that the hydrocarbon chain is fairly perpendicular to the film surface. The intensity ratios of transmission absorbance to RA absorbance allow us to estimate the tilt angle of the hydrocarbon chain in the TAOAB/MeSt-PSSS LB films.[17] The calculated values at various X_{TAOAB} are listed in Table 1, along with the orientation angles of the azobenzene chromophore. As seen in the table, tilt angles of the hydrocarbon chain before UV light irradiation are ca. 9-16° from the surface normal, pointing to a nearly perpendicular orientation to the film surface. Also, incorporation of MeSt seems to improve the packing state of the LB films. In particular, the smallest tilt angle is found at X_{TAOAB}=0.5. In this LB film, dense packing of the hydrocarbon chains would be expected from the result of π-A isotherms, suggesting stronger hydrophobic interaction between TAOAB and MeSt at 30 mN m⁻¹. On the other hand, tilt angle of
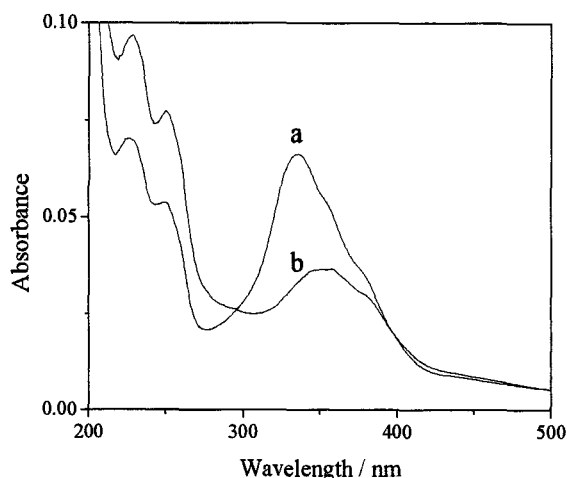

Fig.3. Polarized UV-vis spectra of the TAOAB/MeSt-PSSS LB film at X_{TAOAB}=0.5. The spectra were measured at α=60° with p-polarized light (a) and s-polarized light (b).
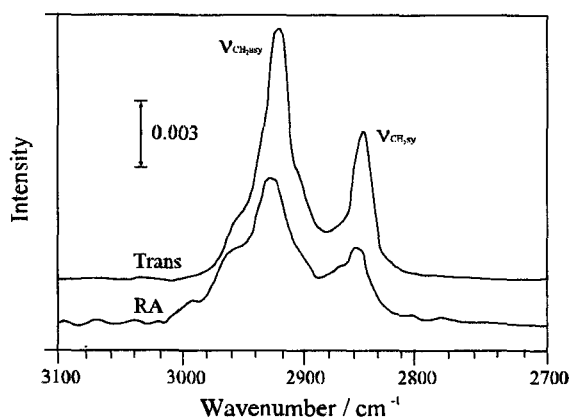

Fig.4. FTIR-transmission and -RA spectra for a 9-layer TAOAB/MeSt-PSSS LB film at X_{TAOAB}=0.5 in the C-H stretching vibration range.

azobenzene chromophore is sufficiently influenced by the packing state. Typically, the tilt angle at X_{TAOAB}=1.0 was calculated to be 62°, which indicates fairly flat-lying orientation, whereas the angle at X_{TAOAB}=0.4 to be 18°, which means almost edge-on orientation. These results clearly show that when the free volume around the TAOAB molecule is filled with MeSt, TAOAB is required to take an orientation with compact packing, so that the chromophore could be no longer oriented with a large tilt angle.

On irradiation with UV light, conformational change of the azobenzene chromophore is accompanied by an increase in the tilt angle of the hydrocarbon chains. Considering the result that the changes in tilt angle are enhanced especially at X_{TAOAB}=0.5, it is most likely the

Table 1. Tilt angles (degree) of the hydrocarbon chain and the azobenzene chromophore in the LB films.

X_{TAOAB}	0.25	0.4	0.5	0.6	0.8	1.0
azobenzene chromophore	22	18	30	29	46	62
hydrocarbon chain						
as-deposited	14	12	9	10	15	16
after UV light irradiation	15	16	17	15	16	18
after visible light irradiation	15	12	14	9	14	17

configurational change from trans to cis-form disturbs arrangement of neighboring hydrocarbon chain of MeSt as well as that of TAOAB itself. In addition, subsequent irradiation with visible light recovers the tilt angle of the hydrocarbon chain, but the angle does not necessarily return to the initial value.

Besides, the cis-to-trans isomerization of azobenzene was admitted to proceed spontaneously without irradiation of light. To evaluate the reaction rate, the TAOAB/MeSt-PSSS LB films, irradiated with UV light to convert trans-TAOAB to cis-isomer, were left in the dark; afterward the UV-vis spectra were recorded over different time intervals. After a series of measurements, cis-TAOAB, which remains in the LB film, was completely changed to stable trans-form by the visible light irradiation. This LB film is regarded much the same as that with infinite elapsed time in the dark. From the time-dependent recovery of absorbance A_t in these spectra, isomerization ratio θ, i.e., molar fraction of trans-TAOAB in the LB film, was calculated by

$$\theta = (A_0 - A_t)/(A_0 - A_\infty)$$

where A_0 and A_∞ denote the absorbances at t=0 and infinity, respectively. Fig.5 shows the time-dependence of θ for the TAOAB/MeSt-PSSS LB films at 20 °C. In this figure, the difference in kinetics of thermal isomerization is found among X_{TAOAB}=0.25, 0.50 and 1.0, that is, the reaction rate decreased with decreasing X_{TAOAB}. This would be interpreted as microenvironmental properties around the azobenzene chromophore. Since the terminal position of the TAOAB molecule is separately bonded to the polymer chain of PSSS, the free volumes in the layer structure, which allows the isomerization reaction, are considered to be sufficient for the LB film at X_{TAOAB}=1.0. When TAOAB is densely packed with MeSt, the lack of free volume, namely large steric hindrance, results in the restriction on spontaneous cis-to-trans isomerization. Such a molecular design would be favorable for the applications to the optical devices such as optical information storage and light switching. As a reference, data obtained for the TAOAB chloroform solution are also plotted in Fig.5. Comparing the reaction rate for the chloroform solution with those for the LB films, it is possible to see how the kinetics is influenced by the LB deposition. The result emphasizes that the cis-to-trans isomerization proceeds much faster when the mobility of TAOAB is less restricted. Similarly, the isomerization rate was evaluated at 30 and 40 °C for the LB films at various X_{TAOAB}. It was found that the reaction rate become faster with the rise of temperature. However, no significant difference in the reaction rate was observed in the LB films with different X_{TAOAB} above 30 °C.

CONCLUSIONS

The environmental control of the cis-trans isomerization reaction for TAOAB was demonstrated in the matrix of polyion-complex LB films by using MeSt as a filler material. As the degree of packing in the LB films increased, both the azobenzene chromophore and the hydrocarbon chain oriented more perpendicularly to the film surface. The cis-trans reverse photoisomerization of TAOAB was confirmed to take place with alternate irradiation with UV and visible light even in the dense mixed LB films. The thermal
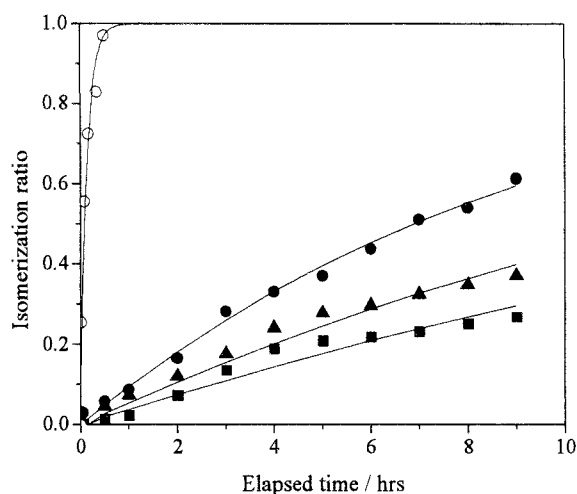

Fig.5. Time-dependence of isomerization ratio for the TAOAB/MeSt-PSSS LB films at 20 °C; X_{TAOAB}: ●, 1.0; ▲, 0.5; ■, 0.25. Data for TAOAB in the chloroform solution (○) are also shown in the figure.

cis-to-trans isomerization kinetics of TAOAB was examined for the LB films and the chloroform solution. It was found that compared to TAOAB in the chloroform solution, the reaction rates were markedly slow in the LB films, and the LB film with more closely packed chromophore presented slower reaction rate.

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