

FT-IR External Reflection Spectroscopy Study on Photochromic Monolayers at the Air-Water Interface

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Photoresponse behavior of azobenzene containing fatty acid in Langmuir (L) film was investigated using FT-IR and UV-vis spectra. Irradiation of UV or visible light resulted in reversible photoisomerization of the fatty acid in L film. The orientational change in the alkyl chain of the fatty acid in L film was determined *in situ* by FT-IR external reflection spectra, and the effect of the surface area on these changes is discussed.

Photochromism and photomechanical response in Langmuir (L) film at the air-water interface have been extensively investigated, and surface pressure changes or photoinduced morphological and rheological changes of photochromic L films have been revealed by surface pressure measurements, UV-vis spectroscopy and Brewster angle microscopy.¹⁻⁸ In photomechanical response in L films, the alkyl chain moiety as well as the chromophore moiety of photochromic molecules plays a crucial role; however, details of photoinduced orientation change in the alkyl chain is still not fully understood. For such analysis, infrared external reflection (IER) spectroscopy is a powerful tool, because IER spectra provide information on each functional group of L films.⁹⁻¹¹

In the present study, L film of a long-chain azobenzene derivative on pure water is irradiated using UV or visible light and IER spectroscopy is used to evaluate the orientational changes in the alkyl chain that are induced by the photoisomerization.

4-octyl-4'-(5-carboxypentamethyleneoxy)azobenzene (8A5) was purchased from Dojindo Laboratories Co. Ltd. Chloroform solution of 8A5 (1.0×10^{-3} mol/dm³) was spread on pure water contained in a homemade Teflon trough (150×30×5 mm). The surface pressure was measured using the Wilhelmy technique and a glass plate attached to an HBM film balance (Kyowa Interface Co. Ltd.).

L film was irradiated from the top-side through a quartz optical fiber connected to a 150 W Xe lamp. Optical glass filters of UV-360 and L-42 (Toshiba) were used for selecting UV and visible lights, respectively.

UV-vis spectra were obtained using a spectrophotometer (JASCO, V-500). Probe light for UV-vis measurements was incident to the L film at an angle of 45°. IER spectroscopy was performed using a Nicolet 510 M spectrometer equipped with an MCT detector and a modified attenuated total reflectance attachment (Spectra-Tech Inc.). An s-polarized beam at an incident angle of 30° was used to obtain interferograms, which were accumulated 500 times and had a resolution of 4 cm⁻¹. The reflection spectrum is defined as $-\log(R/R_0)$, where R_0 and R are the reflectivity of the pure and film-covered water surfaces, respectively.

Photoinduced response of 8A5 in L film was initially examined by measuring changes in surface pressure. Figure 1 shows changes in the surface pressure of the 8A5 monolayer under alternating irradiation using UV and visible lights at various surface areas per molecule, A_s . The surface pressure increased

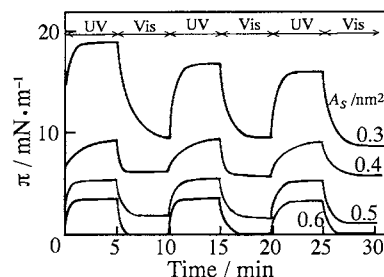


Figure 1. Surface pressure changes of L film of 8A5 upon alternating irradiation using UV and visible light at 20 °C.

after continuous UV light irradiation, and reverted to the original value upon irradiation using visible light. At $A_s > 0.40$ nm², high reproducibility of the surface pressure change was induced by alternating irradiation using UV and visible lights, whereas poor reversibility was observed when $A_s < 0.3$ nm², because the 8A5 monolayer was unstable and collapsed easily at higher surface pressures.

The change in surface pressure is due to the trans-cis photoisomerization of 8A5, which was confirmed by measuring the UV-vis spectra of the L film of 8A5. In other words, upon irradiation using UV light, the intensity of the π - π^* band of trans-azobenzene at approximately 330 nm decreased, and the n- π band of cis-azobenzene at 450 nm appeared,^{3,8} as shown in Figure 2.

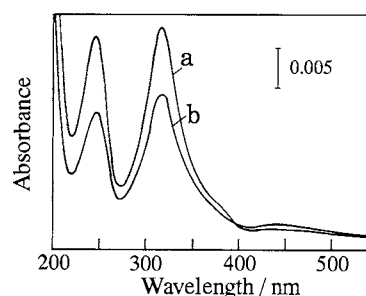


Figure 2. UV-vis spectra of L film of 8A5 under continual irradiation using visible (a) and UV (b) lights. $A_s = 0.45$ nm².

From the decrease in the π - π^* band intensity in Figure 2, the conversion of trans-to-cis isomerization at $A_s = 0.45$ nm² was estimated to be ca. 25% (trans:cis=75:25). Estimated conversions at $A_s = 0.35, 0.40, 0.50$ and 0.60 nm² were ca. 20, 20, 30 and 45%, respectively.

As revealed in Figure 1, the response of the pressure increment at $A_s = 0.4$ nm² is slower than those at the other A_s values. This is a result of the presence of a plateau region at 0.40 nm² in the π - A curve,¹² i.e., in the plateau region the increase in the cross section of 8A5,^{1,3} which is brought by trans-

to-cis photoisomerization, does not effectively produce the increment in surface pressure.

Thus, UV irradiation results in the photoisomerization of 8A5 in L film, even though the conversion is not high. Next, the orientation of the alkyl chain of 8A5 is examined. IER spectra of 8A5 in L film are depicted in Figure 3. Bands at 2922

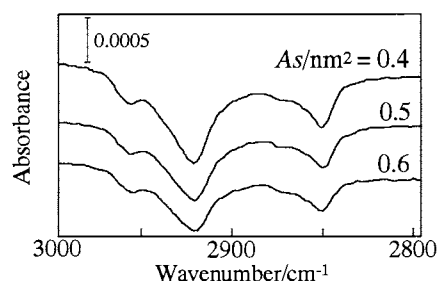


Figure 3. IER spectra of 8A5 monolayer upon irradiation using visible light.

cm^{-1} and 2852 cm^{-1} corresponding to the antisymmetric and symmetric CH_2 stretching modes, respectively,^{10,11} appeared clearly and the intensity of these bands increased with decreasing A_s . As reported by Mao et al.,¹³ the band intensity (I_{obs}) observed in the IER spectrum depends both on the surface density of the molecule ($D_s=1/A_s$; number of molecules/ nm^2) and on the orientation of the transition moments of the band. Thus, the band intensity normalized by the molecular density, i.e., I_{Nor}/D_s , is useful for the investigation of molecular orientation changes. Figure 4 shows the normalized intensity I_{Nor} ($=I_{\text{obs}}/D_s$)

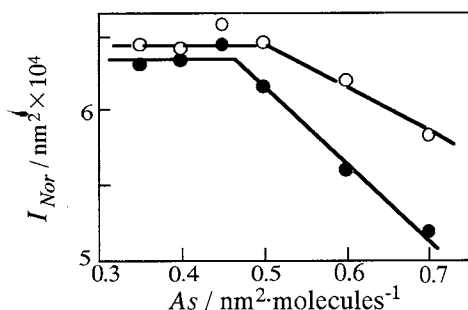


Figure 4. Normalized IER intensity (I_{Nor}) of antisymmetric CH_2 stretching band upon irradiation using visible (open) and UV (closed) lights as a function of A_s .

of the antisymmetric CH_2 stretching band upon irradiation using visible and UV lights as a function of A_s . At $A_s > 0.50 \text{ nm}^2$, I_{Nor} increased with decreasing A_s and decreased upon irradiation using UV light. At $A_s < 0.50 \text{ nm}^2$, the intensity changes

relatively became small. A similar dependency was observed in I_{Nor} values of the symmetric CH_2 stretching band.

If no orientation changes occur, I_{Nor} should remain constant, irrespective of A_s .¹³ The band intensity increases as the transition moment becomes parallel to the water surface, because an s-polarized IR beam was used to measure IER spectra.^{10,11} Furthermore, since the transition moments of the antisymmetric and symmetric CH_2 stretching bands and the long axis of the alkyl chain are mutually orthogonal,¹¹ increases in both of the band intensities result in a more perpendicular orientation of the alkyl-chain to the water surface. Thus, Figure 4 shows that at $A_s > 0.5 \text{ nm}^2$ the alkyl chain tends to orient perpendicular with the decrease in A_s , and the tilt angle increases due to UV irradiation. In addition, at $A_s < 0.5 \text{ nm}^2$, change in A_s and UV irradiation have a slight effect on the alkyl chain orientation. This finding contrasts that for a similar azobenzene derivative system reported by Seki et al.^{1,3} In their proposed model, the alkyl chain orientation is perturbed considerably by photoisomerization, even though their experiments were conducted under a fixed surface pressure condition.

In the present study, the critical A_s value of 0.5 nm^2 is consistent with the area at which surface pressure increases in the π -A curve of 8A5,¹² suggesting that the alkyl chains at $A_s < 0.50 \text{ nm}^2$ are packed closely together in the L film. At $A_s < 0.50 \text{ nm}^2$, the slight orientation change under fixed area conditions, which is induced by photoisomerization or change in A_s , is considered to be due to the closely packed alkyl chains.

In conclusion, IER spectroscopy was demonstrated to be an extremely valuable method in elucidating orientational information on the alkyl chain in L film, and that the photoisomerization and A_s change of 8A5 monolayer at high surface pressure has no effect on alkyl chain orientation under fixed area conditions. Photoisomerization of 8A5 monolayer at high surface pressure leads to orientational and conformational changes in only the azobenzene moiety of 8A5.

References and Notes

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