Photo-induced Orientational Change in Langmuir-Blodgett Films of Azobenzene Complexed with Polyviologen

Hiroaki Tachibana,* Norio Yoshino†, and Mutsuyoshi Matsumoto
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305-8565
†Faculty of Engineering, Science University of Tokyo, Tokyo 162-0825

(Received November 17, 1999; CL-990979)

We have demonstrated a new type of cis-trans isomerization of azobenzene in the complex LB films of amphiphilic azobenzene and polyviologen. This was accompanied by the changes in the orientation and the electronic state of azobenzene. The molecular orientation of azobenzene can be controlled by cis-trans photoisomerization.

Polyion complex method has been applied to the fabrication of Langmuir-Blodgett (LB) films and has been attracting considerable interest as a means to prepare functionalized materials.[1-10] The advantage of the polyion complex method is that it gives us the opportunity of transferring monolayers onto solid substrates when the monolayers are not suitable for the transfer by the conventional LB technique. Further, the polyion complex methodology allows us to control the structures of the monolayers by selecting suitable polyion species. In this sense some of the synthetic difficulties will be avoided by using this method especially when functional units are to be introduced in the LB films.

In this letter, we demonstrate that the orientation and the electronic structure of azobenzene can be controlled by the cis-trans photoisomerization in the LB films prepared by the polyion complex method. Furthermore, an unusual spectral change was observed on photoisomerization of azobenzene in the LB films. We used an anionic amphiphile bearing two azobenzene units, AZ, and polyviologen, PV12, as an amphiphilic azobenzene and polycation, respectively. The chemical structures are shown in Figure 1.

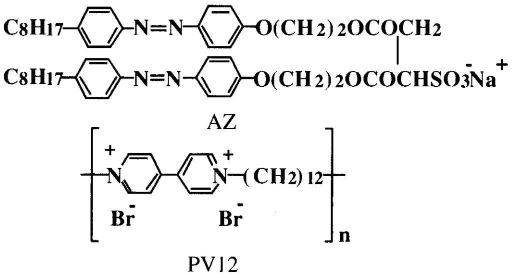

Figure 1. Molecular structures of the amphiphilic azobenzene, AZ and the polycation, PV12.

AZ and PV12 were synthesized in a similar way as reported in the literature.[11,12] Chloroform solution of AZ was spread onto a subphase containing 1x10^{-4} M of PV12. Surface pressure-area (π-A) isotherms were measured using a Lauda film balance at 17 °C. The monolayer was transferred at 25 mN m^{-1} on hydrophobized quartz plate by the vertical dipping method. Monochromatic UV (365 nm) and visible (436 nm) light from a 500 W high-pressure mercury lamp was used as the light source for the photoisomerization of azobenzene.

Figure 2 shows a change in the absorption spectrum of the LB film of the AZ/PV12 polyion complex on alternate irradiation with UV and visible light. Before photoirradiation, the absorption band of the trans-azobenzene around 340 nm is small in the absorption spectrum. Dotted line represents the absorption spectrum after irradiation with UV light. An absorption band of the cis isomer is visible around 450 nm. The 340-nm band is absent although the baseline is shifted upward. This means that trans-to-cis isomerization of azobenzene occurred in the AZ/PV12 complex LB films. On irradiation with visible light, the absorption band of the cis azobenzene disappeared whereas the 340-nm band became larger than in the film before irradiation. This spectral change on photoirradiation indicates that cis-to-trans photoisomerization of azobenzene proceeded in the complex LB films. The increase in intensity of the 340-nm band will be discussed later. On repeating alternate irradiation of UV and visible light, the spectrum after UV light irradiation was essentially the same while the one after visible light irradiation changed in such a manner that the absorption of the 340-nm band increased. In the inset of Figure 2, we plot the change in absorbance at 340 nm on alternate irradiation of UV and visible light. The absorbance of trans-azobenzene after irradiation with visible light became constant when the irradiation cycle was repeated more than ten times. In the further irradiation cycles, usual reversible cis-trans photoisomerization of azobenzene was observed.

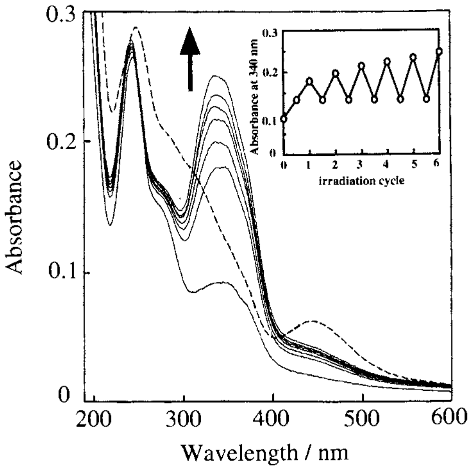

Figure 2. Change in absorption spectrum of 18-layer polyion complex LB film of AZ/PV12 system on alternate irradiation with UV (365 nm) and visible (436 nm) light. The dashed line represents the absorption spectrum after irradiation with UV light. The insert shows the change in absorbance at 340 nm on alternate irradiation.

The above unusual photoisomerization phenomena should be due to a change in orientation of highly oriented azobenzene molecules since the number of azobenzene molecules should

Copyright © 2000 The Chemical Society of Japan

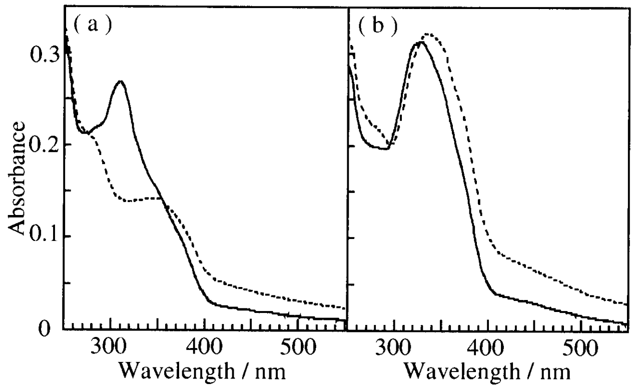

Figure 3. Polarized absorption spectra of 18-layer AZ/PV12 complex LB film with an incident angle of 45° (a) before and (b) after ten times of alternate irradiation with UV and visible light. Solid and dotted lines represent p- and s-polarized absorption spectra, respectively.

remain unchanged during the isomerization. To obtain the information on the orientation and the intermolecular electronic interaction of the azobenzene, we have measured polarized absorption spectra with oblique incidence. Figure 3 shows the polarized absorption spectra of the AZ/PV12 polyion complex LB films with an incident angle of 45° before and after ten cycles of alternate irradiation with UV and visible light. Before photoirradiation, an intense band is seen at ca. 310 nm due to H-aggregates of trans-azobenzene[13,14] in the p-polarized spectrum (see Figure 3(a)) while this band is absent in the s-polarized spectrum. A broad band at ca. 350 nm due to monomeric azobenzene is seen in both the spectra. This indicates that there are two components of azobenzene: the major one in H-aggregated state with nearly vertical orientation with respect to the film surface and the minor one in monomeric state with oblique orientation. The nearly vertical orientation of the former indicates that this component does not contribute to the absorption spectrum at normal incidence. This is the reason why the intensity of the 340-nm band is small and the 310-nm band is absent in Figure 2 before photoirradiation.

Figure 3(b) shows the polarized absorption spectra of the film after ten illumination cycles. The absorption band at 350 nm due to trans-azobenzene are seen in both the s-polarized and the p-polarized spectrum, which means that the long axis of the trans-azobenzene is tilted with respect to the film normal. The 310-nm band is absent in both the spectra. From these results, the increase in the absorbance of trans-azobenzene with illumination cycles is due to an increase in the number of the trans-azobenzene in monomeric state with oblique or random orientation. This is compensated by the decrease in the number of the trans-azobenzene in H-aggregates with vertical orientation. The results indicate that the repetition of alternate irradiation with UV and visible light changes the population of the two states, thereby controlling the electronic state and the orientation of the azobenzene in the LB films.

The monomeric state reverted to the H-aggregated state when the films were stored in the dark (22 °C, 50 %). This thermal reaction proceeded slowly, which was confirmed by a gradual decrease in intensity of the 340-nm band. The absorption spectrum returned to that of the film before photoirradiation in one day. These structural changes were repeatable.

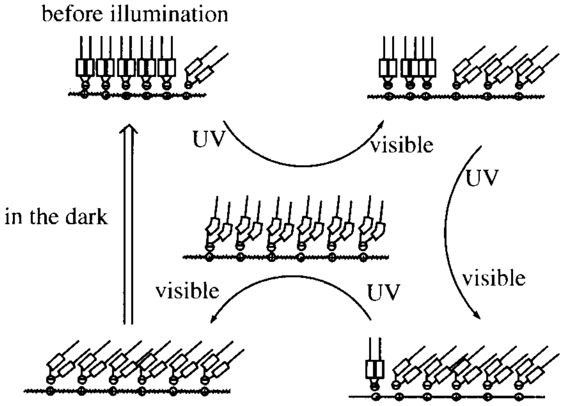

Figure 4. Scheme of orientational change on photoisomerization of azobenzene in the AZ/PV12 complex LB film.

The above results allow us to propose a scheme of the change in the structure of the polyion complex LB films as shown in Figure 4. Before irradiation, most of the azobenzene molecules are in the H-aggregated state with nearly vertical orientation and do not contribute to the absorption spectrum measured at normal incidence due to the orientation effect. The absorption spectrum reflects only the minor component in the monomeric state with oblique orientation. On alternate irradiation with UV and visible light, reversible photoisomerization of the azobenzene occurs. Some of the trans-azobenzene molecules fail to revert to the H-aggregated state on cis-to-trans isomerization. This means that the structural change occurs gradually in the LB films on repeated illumination. This structural change continues during ten illumination cycles. In the saturated state, most of the azobenzene molecules are in the monomeric state with oblique or random orientation and reversible photoisomerization of azobenzene proceeds. When the films are stored in the dark, the structures of the LB films revert to those before illumination. Such phenomena were not observed in AZ LB films complexed with other polycation.

References and Notes

1 M. Shimomura and T. Kunitake, *Thin Solid Films*, **132**, 243 (1985).
2 N. Higashi and T. Kunitake, *Chem. Lett.*, **1986**, 105.
3 K. Nishiyama and M. Fujihira, *Chem. Lett.*, **1988**, 1257.
4 J. Umemura, Y. Hishiro, T. Kawai, T. Takenaka, Y. Gotoh, and M. Fujihira, *Thin Solid Films*, **178**, 281 (1989).
5 A. T. Royappa, M. F. Rubner, *Langmuir*, **8**, 3168 (1992).
6 H. Tachibana, R. Azumi, M. Tanaka, M. Matsumoto, S. Sako, H. Sakai, M. Abe, Y. Kondo, and N. Yoshino, *Thin Solid Films*, **284**, 73 (1996).
7 R. A. Hall, M. Hara, and W. Knoll, *Langmuir*, **12**, 2551 (1996).
8 M. Matsumoto, D. Miyazaki, M. Tanaka, R. Azumi, E. Manda, Y. Kondo, N. Yoshino, and H. Tachibana, *J. Am. Chem. Soc.*, **120**, 1479 (1998).
9 M. Niwa, T. Ishida, T. Kato, and N. Higashi, *J. Mater. Chem.*, **8**, 1697 (1998).
10 T. Kawai, *J. Phys. Chem. B*, **103**, 5517 (1999).
11 N. Yoshino, A. Nagasaki, Y. Kondo, and M. Abe, *Yukagaku*, **44**, 35(1995).
12 M. Shimomura, K. Utsugi, J. Horikoshi, K. Okuyama, O. Hatozaki, and N. Oyama, *Langmuir*, **7**, 760(1991).
13 M. Kasha, H. R. Rawis, E. Ashraf, and M. Bayoumi, *Pure. Appl. Chem.*, **11**, 371 (1965).
14 M. Shimomura, R. Ando, and T. Kunitake, *Ber. Bunsenges. Phys. Chem.*, **87**, 1134 (1983).