CHEMISTRY LETTERS, pp. 1257-1260, 1988. © 1988 The Chemical Society of Japan

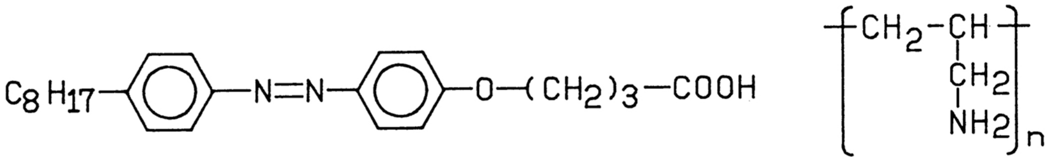
cis-trans Reversible Photoisomerization of an Amphiphilic Azobenzene Derivative in Its Pure LB Film Prepared as Polyion Complexes with Polyallylamine

Katsuhiko NISHIYAMA and Masamichi FUJIHIRA*
Department of Biomolecular Engineering, Tokyo Institute of Technology,
2-12-1 Ohokayama, Meguro-ku, Tokyo 152

By using polyallylamine (PAA) for the aqueous subphase, the pure LB films of an azobenzene derivative with a long alkyl-chain showed reversible cis-trans photoisomerization due to the relatively large cross section of the molecule determined by the surface density of the ammonium cations of protonated PAA.

The LB films of photochromic materials are of interest as possible high density information storage media and light switching devices. In the previous paper,[1)] we have reported the photochemical switching of electrochemical processes with spiropyran LB films as a biomimetic visual system. Furthermore, several groups have investigated the LB films containing azobenzene chromophores.[2-5)] The trans-cis photoisomerization of long-chain azobenzene derivatives was restricted in the case of the pure LB film. Recently, however, Yabe et al. have reported that azobenzene guest molecules in the host-guest Langmuir-Blodgett films showed photochromic behavior with complete reversibility owing to the free volume of cyclodextrin cavity.[5)] On the other hand, Kunitake et al. have already reported that monolayers of azobenzene ammonium amphiphiles are stabilized by formation of insoluble polyion complexes with potassium poly(vinylsulfonate).[3)] In addition, we have found that the cross section of the amphiphilic molecule is determined by the size of water-soluble polymer counter ions used.[6)] In this letter, we will report the reversible cis-trans photoisomerization of an azobenzene amphiphilic derivative in its pure LB film formed as polyion complexes with polyallylamine.

The azobenzene amphiphilic derivative and the water-soluble polymer used were shown in Fig. 1. 4-Octyl-4'-(3-carboxytrimethyleneoxy)azobenzene (8A3) and poly-



8A3 PAA

Fig. 1. Structural formulae of the azobenzene amphiphilic derivative 8A3 and the water-soluble polymer PAA.

allylamine (PAA) were received from Dojin Kagaku Co. and Nitto Boseki Co, respectively, and used without further purification. The measurement of surface pressure - area isotherms and automated deposition of the LB films on quartz substrates were carried out with a Langmuir trough equipped with an electronic microbalance and a glass Wilhelmy plate (Kyowa Kaimenkagaku Co.). Monolayers were obtained by spreading a chloroform solution of 8A3 on an aqueous subphase solution containing 0.4 mM PAA (1 M = 1 mol dm^{-3}, mol in the monomer unit). The 8A3 monolayers were deposited as Y-type multilayers on the quartz plates at 30 mN m^{-1} precoated with 5 layers of arachidic acid, which were prepared on the same subphase as that used for the 8A3 monolayers. The compression speed was 20 cm^2 min^{-1} and the dipping and lifting speed of the substrate was 10 mm min^{-1}. The transfer ratio was 1 ± 0.1. The photochemical processes of the LB films upon irradiation were followed by UV-visible spectroscopy. The light source was a 500 W high-pressure Hg lamp. Toshiba UV-D35 and Y-42 glass filters were used for isolating UV and visible light, respectively.

Figure 2 shows the surface - pressure isotherms of 8A3 on pure water (a) and on the PAA aqueous solution (b). On pure water, the 8A3 monolayer was not stable and collapsed below 30 mN m^{-1}. The cross section of the 8A3 molecule on pure water was 0.28 nm^2, which is larger than those of normal fatty acids such as arachidic acid and determined by the trans azobenzene moieties. On the other hand, the monolayer was stable up to 50 mN m^{-1} on the PAA subphase. In this case, the area of the 8A3 molecule was 0.39 nm^2. This means that the 8A3 carboxylate anions formed polyion complexes with the protonated PAA counter ions. In other words, the molecular area of 8A3 was determined by the surface density of the ammonium cations of the protonated PAA closely packed at the air-water interface rather than by the trans azobenzene moieties. Consequently, the free volume which allowed the

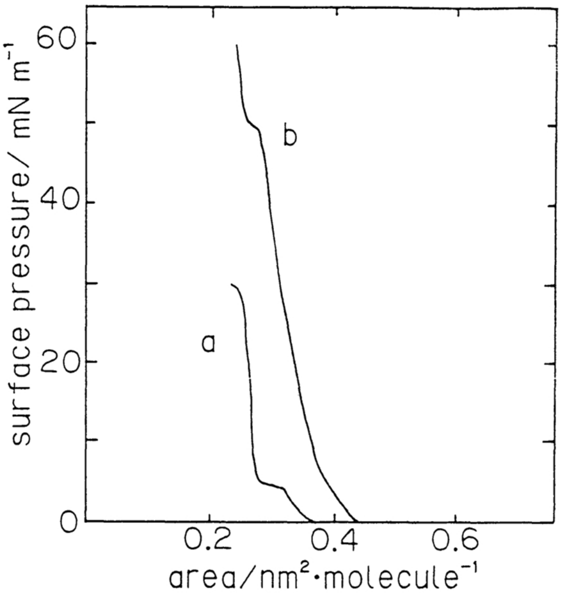


Fig. 2. Surface - pressure isotherms of 8A3 on pure water (a) and 0.4 mM PAA aqueous solution (b).

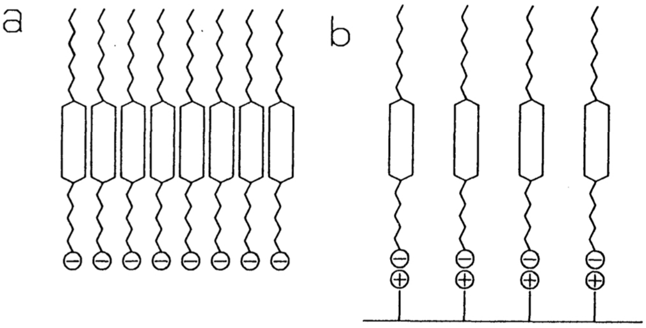


Fig. 3. The schematic representation of the 8A3 monolayer on pure water (a) and on the protonated PAA cations (b). The cross section of the molecule is determined by the molecule itself (a) and the water-soluble polymer used (b).

azobenzene moieties to photoisomerize increased as depicted in Fig. 3.

The UV-visible absorption spectra of the 8A3 multilayers (6 layers on each side) on the quartz plate are shown in Fig. 4. The spectrum (a) corresponds to the trans-isomer of 8A3 and the spectrum (b) to the partial conversion of the trans-isomer of 8A3 to the cis-isomer that was caused by irradiation of the 8A3 multilayers with UV light for 10 min. The spectrum (c) was obtained from the film showing the spectrum (b) by irradiating visible light for another 10 min, and shows that the trans-isomer was recovered. A slight difference between spectra (a) and (c) was observed in the first cycle. However, in the next five cycles with alternative irradiations for 10 min, the change in absorbance was completely reproducible, i.e. after the UV light irradiated, the spectrum coincided with curve (b) and, after visible light irradiation, curve (c) was recovered. The photoisomerization of 8A5 in the same series of azobenzene derivatives was reported by Saito et al.$^{7)}$ for the pure LB films which were deposited from the aqueous subphase containing barium or calcium salts. Under the same conditions as in Fig. 4, however, the pure 8A5 LB films deposited without PAA showed much less photoisomerization than the pure 8A5 LB film with PAA, as we would expect from their structure difference illustrated in Fig. 3.

In conclusion, the pure polyion complexed LB film of an azobenzene derivative with PAA showed reversible cis-trans photoisomerization due to the relatively large cross section determined by the surface density of the ammonium cations of the protonated PAA closely packed at the air-water interface. Further works on the rate of the photoisomerization dependence on the surface pressure of the monolayer and on other kinds of water-soluble polymer cations with different cross sections are now under investigation.

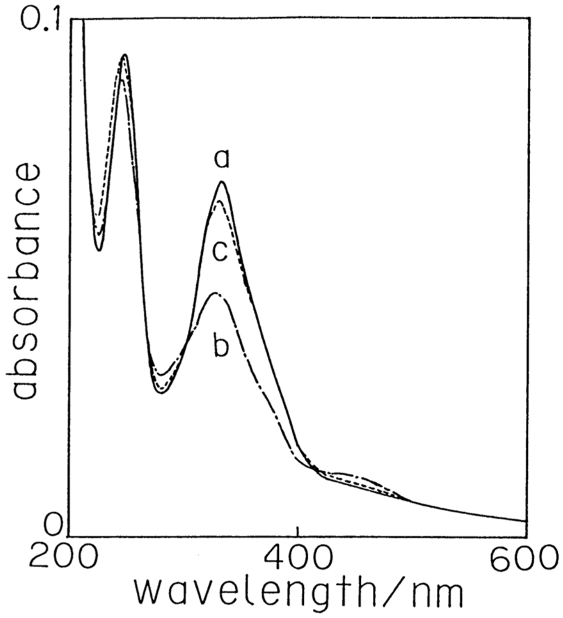


Fig. 4. Absorption spectra of the pure LB multilayer of 8A3 on the quartz plate. (a); a virgin film as deposited, (b); after UV light irradiation for 10 min, (c) after visible light irradiation for 10 min.

References

1) K. Nishiyama and M. Fujihira, Chem. Lett., 1987, 1443.

2) H. Nakahara and K. Fukuda, J. Colloid Interface Sci., 93, 530(1983); K. Fukuda and H. Nakahara, ibid., 98, 555(1984).

3) M. Shimomura and T. Kunitake, Thin Solid Films, 132, 243(1985).

4) S. S. Sandhu, Y. P. Yianni, C. G. Morgan, D. M. Taylor, and B. Zaba, Biochim. Biophys. Acta, 860, 253(1986)

5) A. Yabe, Y. Kawabata, H. Niino, M. Tanaka, A. Ouchi, H. Takahashi, S. Tamura, W. Takagi, H. Nakahara, and K. Fukuda, Chem. Lett., 1988, 1.

6) M. Fujihira and Y. Gotoh, Chem. Lett., to be submitted.

7) S. Kawamura, T. Tsutsui, and S. Saito, Abstract of Annual Fall Meeting of the Chemical Society of Japan, October, 1985, p.478.

(Received April 2, 1988)