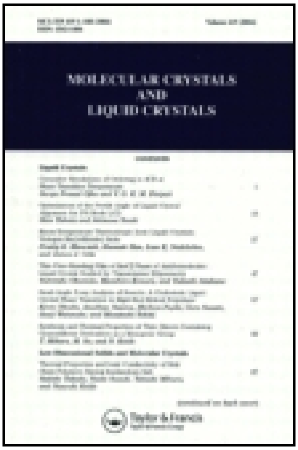

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Self-Organization and Photochromic Reaction in the Langmuir-Blodgett Films of Amphiphilic Azobenzene Complexed with Polyallylamine

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Self-Organization and Photochromic Reaction in the Langmuir-Blodgett Films of Amphiphilic Azobenzene Complexed with Polyallylamine

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The molecular area of an amphiphilic azobenzene (AZ) bearing a carboxylic group was larger on aqueous subphase containing polyallylamine (PAA) than on the subphase containing Cd^{2+}. In AZ/PAA LB films, AZ was deprotonated and PAA was protonated, indicating the salt formation of the two components. When the AZ/PAA LB films were stored in the dark, the absorption spectra of the LB films changed due to the variations in the orientation and the electronic structure of AZ. The LB films of AZ/Cd^{2+} showed similar structural changes and, in the final state, took almost the same structures with those of AZ/PAA LB films although the initial structures were different. AZ showed reversible photoisomerization in the AZ/PAA LB films both in the initial and the saturated state. Photoisomerization of AZ did not proceed in the AZ/Cd^{2+} LB films either of the initial and the saturated state probably due to the lack in free volume.

Keywords: azobenzene; Langmuir-Blodgett films; self-organization; H-aggregate

INTRODUCTION

Polyion complex method coupled with Langmuir-Blodgett (LB) technique has been attracting considerable interest form the view point of the modification of the structures and functions of the LB film. Recently, several interesting phenomena have been found in the LB films of amphiphilic azobenzene complexed with polycations. Photochemical reaction of azobenzene can be controlled by varying the polycation species incorporated in the LB films[1]. In other polyion complex LB films, reversible morphological changes involving 2D to 3D transformation and vice verse can be induced by cis-trans photoisomerization of azobenzene[2]. The polyion complex method has also been applied to fabricate inorganic-organic hybrid LB films[3]. Highly conductive LB films has been realized in the hybrid LB film based on transition metal dichalcogenide, MoS_2[4]. In this paper, we will report on the effect of water-soluble polyallylamine (PAA) on the self-organization and photochromic reaction of the LB films of an amphiphilic azobenzene.

EXPERIMENTAL

3-[4-(4-octylphenylazo)phenoxy]propanoic acid (AZ) was dissolved in chloroform and spread on a 0.1 mM polyallylamine (PAA, $Mw=1x10^4$) aqueous subphase or an aqueous subphase of 4×10^{-4} M $CdCl_2$ and 5×10^{-5} M $KHCO_3$. AZ and PAA used in this study is shown in Figure 1. The monolayers was transferred at 25 mNm^{-1} using the vertical dipping method. The AZ complexed with PAA and Cd^{2+} are referred to as AZ/PAA and AZ/Cd^{2+}, respectively. Monochromatic light at 365 and 436 nm from a 500 W high-pressure mercury lamp was used as the UV and visible light source for the photoreaction of AZ, respectively.

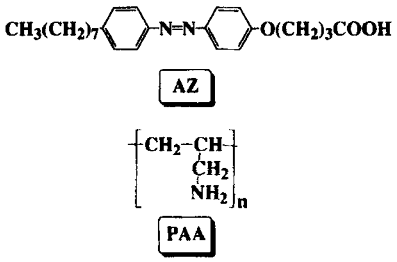

FIGURE 1 Chemical structures of molecules used in this study.

RESULTS AND DISCUSSION

First, we investigated the monolayer formation of AZ at the air-water interface. Figure 2 shows surface pressure-area (π-A) isotherms of AZ on PAA aqueous solution and Cd^{2+} buffer. For comparison, the π-A isotherm on pure water is also shown. The π-A isotherm on the Cd^{2+} buffer is almost the same with that on pure water, except for the absence of the plateau at 12 mNm^{-1}. The π-A isotherm on PAA gives a larger limiting area per molecule with a higher collapse pressure. The change in the isotherm should be due to the interaction of AZ with PAA at the air-water interface.

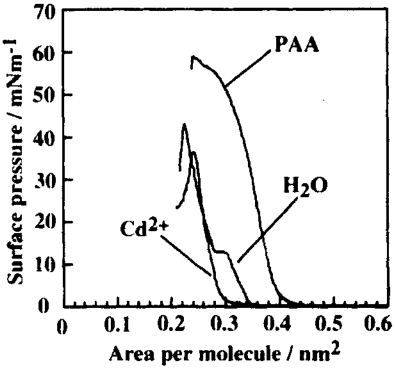

FIGURE 2 Surface pressure-area (π-A) isotherms of AZ on pure water, Cd^{2+} buffer, and aqueous solution of PAA at 17°C.

IR spectra of AZ/PAA LB films showed characteristic bands due to symmetric and antisymmetric stretching modes of COO^- at 1407 and 1586 cm^{-1}, respectively, whereas the C=O stretching mode due to COOH was absent. This strongly suggests the salt formation between AZ and PAA in the form of $COO^-NH_3^+$.

When the AZ/PAA and AZ/Cd^{2+} LB films were stored in the dark at room temperature (23°C), UV-visible absorption spectra of both LB films changed spontaneously. Figure 3 shows the spectral change of the AZ/PAA and AZ/Cd^{2+} LB films. In as-deposited AZ/PAA LB films the main absorption band of trans-azobenzene was observed at 333 nm (initial state), indicating that AZ formed dimeric state[5]. The intensity decreased with time and the band shifted to shorter wavelengths. Finally the intensity was about a third of the initial value and the absorption band was positioned at 314 nm in the saturated state. The change in absorption spectrum of the LB film was not due to the decomposition of azobenzene molecules. When the LB film was dissolved in chloroform, the absorption spectrum of the solution was essentially the same before and after the storage of the film in the dark. These results indicate that the spectral change of the LB film should be attributed to the changes in the orientation and the electronic structure of AZ.

Polarized absorption spectra of the AZ/PAA LB films at an incident angle of 45° were measured to obtain the information on the orientation of AZ. In the initial state, the absorption bands at 245 and 333 nm appeared in both of the s-polarized and p-polarized spectra. The transition moment of the former band is parallel to the short axis of azobenzene while that of the latter band is parallel to the long axis of azobenzene. The intensities of the two bands were larger in the s-polarized spectrum compared with those in the p-polarized spectrum. This indicates that the azobenzene is almost parallel to the film surface.

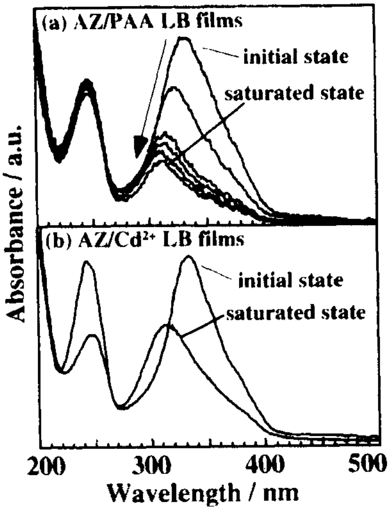

FIGURE 3 Change in UV-visible absorption spectra of 2-layer LB films of (a) AZ/PAA and (b) AZ/Cd^{2+} when the films were stored in the dark at 23°C.

In the saturated state, the intensity of the 245-nm band was larger in the s-polarized spectrum than in the p-polarized spectrum whereas the intensity of the 314-nm band was larger in the p-polarized spectrum than in the s-polarized spectrum. This shows that the tilt angle of the long axis of the azobenzene with respect to the surface normal is small and that the short axis remains almost parallel to the surface. The blue-shift of the 333-nm band indicates that the electronic interaction between the chromophores was stronger in the saturated state, resulting in the H-aggregate formation.

Similar structural change was also observed for AZ/Cd^{2+} LB films. Figure 3(b) shows the absorption spectra of the LB film in the initial and the saturated state. The main band at ca. 333 nm decreased its intensity and shifted to shorter wavelengths. The band at 245 nm increased its intensity. Polarized absorption spectra of the LB film in the initial state showed that the tilt angle of the long axis of the azobenzene was small whereas that of the short axis was large. In the saturated state, the tilt angle of the long axis was almost the same with that in the initial state and the short axis was almost parallel to the film surface. This shows that the azobenzene rotated around its long axis in such a manner that the tilt angle of the short axis decreased.

These results show that the orientation of the azobenzene in the two LB films was different in the initial state whereas the orientation was almost the same in the saturated state with almost the same aggregated state. These self-organization phenomena were observed irrespective of the layer number of each of the two LB films. The time necessary for the completion of the self-organization increased with an increase in the layer number.

Next, we studied the effect of the self-organization on the photochemical reaction of AZ/PAA and AZ/Cd^{2+} LB films. Figure 4 shows the change in UV-visible absorption spectra of AZ/PAA LB films in the initial and the saturated state on alternate irradiation of UV and visible light. In both states reversible spectral change due to cis-trans photoisomerization of azobenzene was observed. The fraction of the cis-isomer at the photostationay state under the irradiation with UV light was ca. 80% in the initial state. This value was ca. 45% in the saturated state. This decrease in the fraction of the cis-isomer is probably due to

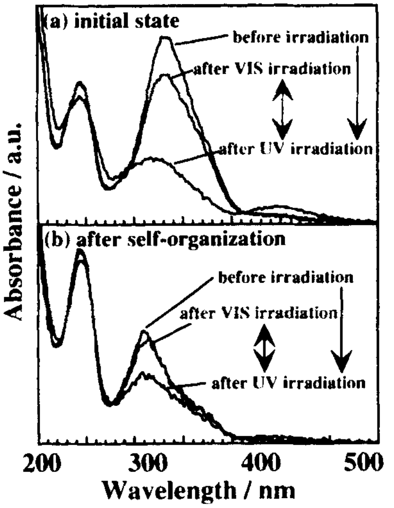

FIGURE 4 Change in UV-visible absorption spectra of a 2-layer LB film of AZ/PAA on alternate irradiation with UV and visible light: (a) before and (b) after the self-organization.

the stronger electronic interaction between the chromophores in the saturated state.

On the other hand, cis-trans isomerization of azobenzene on photoirradiation did not proceed in the AZ/Cd^{2+} LB films even in the initial state. This difference in the photochemical reaction for the AZ/PAA and the AZ/Cd^{2+} LB films will be explained in terms of free volume. Molecular area of AZ was much larger in AZ/PAA LB films than in AZ/Cd^{2+} LB films judging from the π-A isotherms shown in Figure 2. This means that free volume available for AZ is much larger in the former LB films than in the latter LB films. The salt formation of AZ with PAA is probably responsible for the presence of free volume in the AZ/PAA LB films.

In summary, we have demonstrated that the structures of the AZ/PAA and AZ/Cd^{2+} LB films changed with time due to self-organization. In the initial state, the orientation and the electronic structure of AZ was different for two LB films. In the saturated state, however, AZ took almost the same orientation and the electronic structure in the two LB films. This suggests that the main driving force of these self-organization processes is chromophoric interaction between the azobenzene, and not the structural change of PAA. The interaction of PAA with AZ gave enough free volume for the photoisomerization of AZ. These results indicate that the structures of LB films can be easily modified by the introduction of polyions in the films, thereby giving additional features and functions to the films.

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