

# Reversible Light-Induced Morphological Change in Langmuir–Blodgett Films

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**Abstract:** An amphiphilic anionic azobenzene derivative, soluble in water, formed a monolayer on an aqueous subphase containing a water-soluble polycation. The monolayers were transferred onto solid substrate by the Langmuir–Blodgett (LB) technique. XPS measurements showed that ion exchange reaction proceeded almost completely at the air–water interface and that the ratio of the monomer unit of the polycation to the azobenzene was almost unity. UV/vis absorption and IR measurements indicated that the azobenzene photoisomerized reversibly in the LB films on alternate illumination with UV and vis light. Furthermore, a reversible morphological change induced by light was observed in the LB films with AFM. Before illumination, the surface of the single-layer LB film was very smooth with a surface undulation of less than 1 nm. On illumination with UV light, however, a number of hills, with the height of ca. 5 nm and the diameter of the base of ca. 100 nm, appeared on the film surface. These structures almost disappeared on illumination with vis light. This indicates that the widely accepted assumption that photoisomerization should not change the two-dimensional structures significantly does not hold in the present case.

## Introduction

Photoisomerization of a chromophore is related to the biological activities of living creatures<sup>1</sup> and has been investigated extensively in Langmuir–Blodgett (LB) films.<sup>2–17</sup> The im-

portant aspect of photoisomerization is that molecular conformation also changes with the absorption spectrum. The conformational change caused by photoisomerization of azobenzene has been utilized to functionalize LB films. Photoisomerization has been used to control the electrical conductivity of the LB films of multifunctional molecules,<sup>2</sup> the alignment of liquid crystals lying on the monolayer of azobenzene,<sup>3</sup> and the aggregate state of dye molecules coexisting in the LB films.<sup>4</sup> The concept of free volume has been widely accepted: cis-to-trans photoisomerization proceeds in LB films, whereas trans-to-cis photoisomerization is prohibited since the latter process is accompanied by an increase in cross-sectional area of the molecule, which is not allowed in closely packed LB films.<sup>2–10</sup> Several strategies have been employed to confer free volume to the azobenzene moieties to facilitate photoisomerization in LB films. Azobenzenes have been included in the cavity of amphiphilic cyclodextrins,<sup>5</sup> coupled with bulky hydrophilic moieties<sup>2,4</sup> or bulky hydrophobic moieties,<sup>6</sup> and tethered to polymers.<sup>3,7–9</sup> The basic assumption here is that photoisomerization should not change the two-dimensional structures significantly though in some cases the morphology of the LB film surface changes slightly.<sup>11–14</sup> In other words, the molecules should stay in the same layer during photoisomerization, thereby inhibiting the process in which cross-sectional area of the

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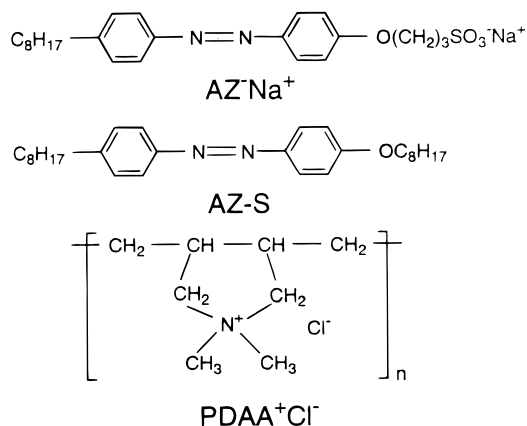
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**Figure 1.** Chemical structures of the molecules used in this study.

molecule increases unless there is enough free volume available. As a counter example, we will present a case where the morphology of the LB films changes reversibly by the alternate illumination, which is associated with photoisomerization of azobenzene. The results suggest that the LB films experience substantial modification of the two-dimensional film structures to accommodate the increase in area of azobenzene when trans-cis photoisomerization proceeds.

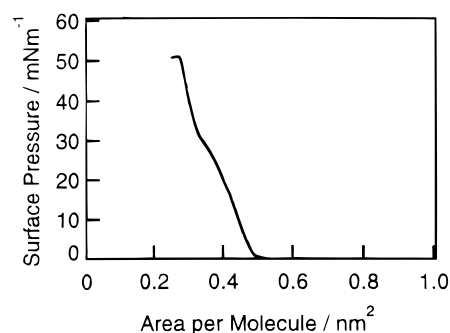
## Experimental Section

**Materials.** The molecules used in this study are shown in Figure 1. AZ<sup>-</sup>Na<sup>+</sup> was synthesized as follows: 4-hydroxy-4'-octylazobenzene was synthesized by the coupling reaction of 4-octylaniline and phenol. The azo dye was refluxed for 15 min in butanol in the presence of potassium *tert*-butoxide and dicyclohexyl-18-crown-6 and reacted with sodium 3-bromopropanesulfonate under reflux. The reaction mixture was put in water, neutralized with 1 N hydrochloric acid, filtered, washed, and dried. AZ<sup>-</sup>Na<sup>+</sup> was recrystallized from methanol. AZ-S was synthesized similarly. Poly(diallyldimethylammonium chloride), abbreviated as PDAA<sup>+</sup>Cl<sup>-</sup> hereafter, was purchased from Polysciences, Inc. as an aqueous solution (20 wt %) and used without further purification. The average molecular weight was 240 000 ( $n = 1500$ ).

**Monolayer Measurements.** All the monolayer measurements were made on a Lauda film balance at 290 K. AZ<sup>-</sup>Na<sup>+</sup> was spread either on a pure water subphase or on a water subphase containing 10<sup>-4</sup> M of PDAA<sup>+</sup>Cl<sup>-</sup> (calculation based on monomer unit) using chloroform/methanol = 7/3 (v/v) as the spreading solvent. The compression was made 30 min after the spreading for relaxation. Prolonged relaxation time up to 1 h did not cause significant change in the surface pressure–area isotherm. The vertical dipping method was employed throughout the measurements. Monolayers were transferred at 25 mN m<sup>-1</sup> onto hydrophilic substrates: quartz plates for UV/vis absorption spectroscopic measurements, glass and quartz plates for XPS measurements, CaF<sub>2</sub> and Au-evaporated glass plates for IR measurements, and freshly cleaved mica for AFM measurements.

**Photoisomerization of Azobenzene.** The photoisomerization of AZ-S in chloroform was induced by alternate illumination with monochromatic UV light at 365 nm and vis light at 436 nm from a 500-W high-pressure mercury lamp. The photoisomerization of AZ<sup>-</sup> in the LB films was also induced by alternate irradiation with UV and vis light.

**Instruments.** XPS spectra were taken with a Perkin-Elmer PHI5600ci ESCA system. The source was Al K $\alpha$  X-rays at 1464.6 eV. The base pressure in the sample chamber was 6–7  $\times$  10<sup>-10</sup> Torr. UV/vis absorption spectra were taken with a JASCO HSSP-1 spectrophotometer. All IR spectra were taken with a Perkin-Elmer Spectrum 2000 Fourier transform infrared spectrophotometer. Two modes were employed: transmission IR (TIR) spectroscopy and reflection–absorption IR (RAIR) spectroscopy. TIR and RAIR spectra of the LB films were recorded at 4 cm<sup>-1</sup> resolution with an MCT detector with the coaddition of 128 and 256 scans, respectively. The incident angle



**Figure 2.** Surface pressure–area isotherms of AZ<sup>-</sup>Na<sup>+</sup> on a water subphase containing PDAA<sup>+</sup>Cl<sup>-</sup>.

of 80° was employed for RAIR spectroscopic measurements. The AFM image was taken by a Seiko SPA 300 with an SPI 3700 probe station with a noncontact mode (dynamic force mode) at 27 kHz. Commercially available Si cantilevers with a force constant of 1.5 N m<sup>-1</sup> were used. In addition to the usual ex-situ AFM measurements in which the samples were removed from the AFM sample holder for illumination, we also performed in-situ measurements. For in-situ measurements, the samples were placed in the AFM sample holder and illuminated through an optical fiber without removing the samples from the holder. The illumination was done from the vertical and oblique directions. For the oblique illumination, the scanning position did not change significantly, while for the vertical illumination, the monitoring laser and the detector unit were removed during the illumination, which made it difficult to return to the same scanning position after illumination.

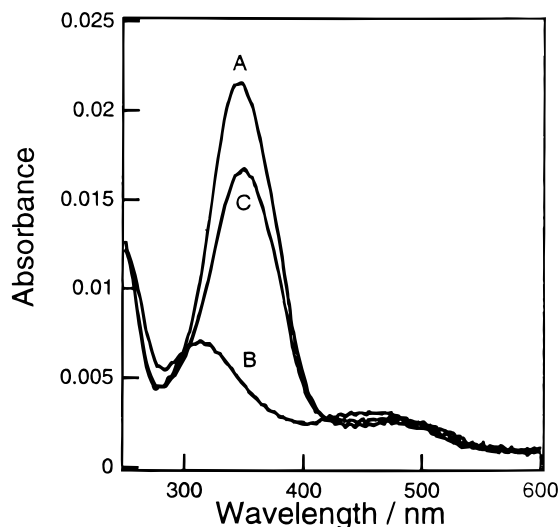
## Results and Discussion

**Monolayer Formation at the Air–Water Interface.** Figure 2 shows the surface pressure–area isotherms of AZ<sup>-</sup>Na<sup>+</sup> on a water subphase containing PDAA<sup>+</sup>Cl<sup>-</sup>. AZ<sup>-</sup>Na<sup>+</sup> on a pure water subphase did not show any onset pressure at an area per molecule as small as 0.05 nm<sup>2</sup>. This is understandable since AZ<sup>-</sup>Na<sup>+</sup> is soluble in water. On the other hand, on a water subphase containing PDAA<sup>+</sup>Cl<sup>-</sup>, the surface pressure of AZ<sup>-</sup>Na<sup>+</sup> increased from an area per molecule of around 0.53 nm<sup>2</sup>. This suggests the formation of a polyion complex of AZ<sup>-</sup> and PDAA<sup>+</sup> at the air–water interface.<sup>7,9,18</sup> In other words, a water-insoluble salt of AZ<sup>-</sup> and PDAA<sup>+</sup> was formed at the air–water interface, which enabled the monolayer formation, leading to a surface pressure increase at a large area per molecule. Hereafter, AZ<sup>-</sup> complexed with PDAA<sup>+</sup> is referred to as AZ<sup>-</sup>/PDAA<sup>+</sup>.

**Fabrication of LB Films.** The AZ<sup>-</sup>/PDAA<sup>+</sup> monolayer was easily transferred onto solid substrates during the upward strokes (transfer ratio was almost unity). As for the downward strokes, the transfer ratio was ca. 0.1 until the third downward stroke, but it jumped to ca. 0.5 on the fourth downward stroke, increasing gradually for further strokes. Hence, the monolayer transfer was Z-type until the third upward and downward cycles, while for the further cycles the deposition became more like the Y type. We limit our experiments to the Z-type deposition region for simplicity, and all the data presented in this study were obtained for the layer number up to three. The transfer of the monolayer of AZ<sup>-</sup>Na<sup>+</sup> on a pure water subphase was not tried.

XPS measurements were made to obtain information on the ratio of (PDAA<sup>+</sup>)<sub>unit</sub> to AZ<sup>-</sup> in the LB films, where (PDAA<sup>+</sup>)<sub>unit</sub> denotes the monomer unit of PDAA<sup>+</sup> having a single positive

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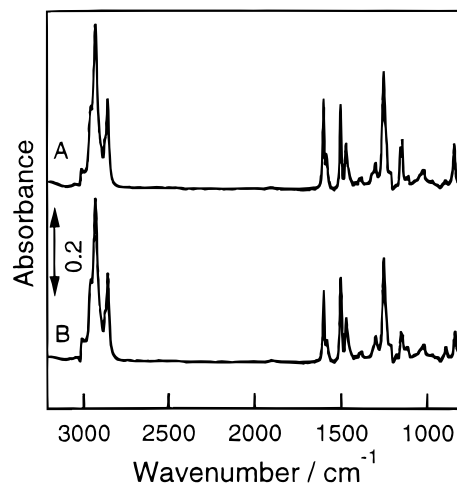


**Figure 3.** Change of absorption spectrum of a single-layer LB film of  $AZ^-/PDAA^+$  on quartz before (A) and after illumination with UV light for 4 min (B) and vis light for 3 min (C).

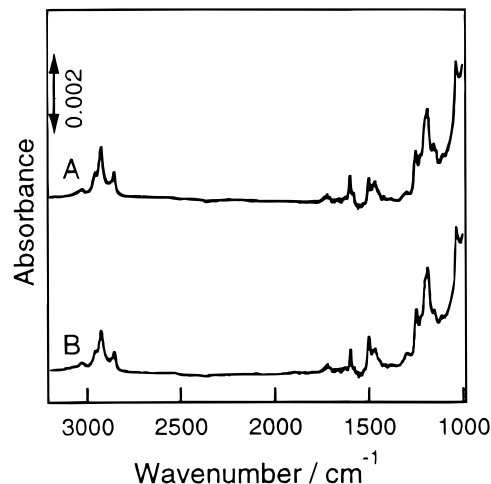
charge. The ratios of N, S, Na, and Cl atoms normalized to the number of C atoms in the LB films were obtained by integrating the bands of  $C_{1s}$ ,  $N_{1s}$ ,  $S_{2p}$ ,  $Na_{1s}$ , and  $Cl_{2p}$  in the XPS spectra. We obtained C:N:S:Na:Cl = 1:0.095:0.044:0.002:0.001 by averaging the values for 2-layer and 3-layer LB films. The calculated values assuming  $AZ^-(PDAA^+)_{unit} = 1:1$  are C:N:S:Na:Cl = 1:0.097:0.032:0:0. The observed values agree well with the calculated ones although the number of S atoms is slightly too large. Assuming that the counterions of  $AZ^-$  are only  $PDAA^+$  and  $Na^+$ , we obtain  $AZ^-(PDAA^+)_{unit}:Na^+ = 1:0.94:0.06$  for the observed values. The results show that most of the  $Na^+$  has been replaced by  $PDAA^+$  at the air–water interface. Therefore, the ion exchange reaction proceeded almost completely at the air–water interface.

**Photoisomerization of  $AZ^-$  in the LB Films.** Figure 3 shows the absorption spectra of the LB films of  $AZ^-/PDAA^+$  before and after illumination. It is clearly seen that the trans-to-cis photoisomerization of  $AZ^-$  proceeds on illumination with UV light and that the illumination with vis light causes the cis-to-trans photoisomerization of  $AZ^-$ . On further alternate illumination with UV and vis light, the spectrum changes from curve C to B and curve B to C, respectively. Similar results have been reported for other polyion complex LB films.<sup>9</sup> The fraction of the cis isomer of  $AZ^-$  at the photostationary state under UV illumination was estimated at ca. 0.9 by using a calculation based on the difference spectra.<sup>19</sup>

IR spectroscopy has been used to investigate the photoisomerization of amphiphilic azobenzene derivatives.<sup>16,17</sup> First, we have investigated a change in the TIR spectrum of an azobenzene derivative in solution accompanied by photoisomerization. Figure 4 shows TIR spectra of AZ-S in chloroform when AZ-S takes the trans and the cis forms (at the photostationary state under vis and UV illumination, respectively). AZ-S was employed because we could not find an appropriate solvent for  $AZ^-Na^+$ . The bands are assigned according to the literature:<sup>17</sup> the band at ca. 2920  $cm^{-1}$  to the  $CH_2$  asymmetric stretch, the one at ca. 2850  $cm^{-1}$  to the  $CH_2$  symmetric stretch, the one at ca. 1600  $cm^{-1}$  to the ring C–C stretch ( $\nu_{8a}$ ), the one at ca. 1580  $cm^{-1}$  to the ring C–C stretch ( $\nu_{8b}$ ), the one at ca. 1500  $cm^{-1}$  to the ring C–C stretch ( $\nu_{19a}$ ), the one at ca. 1470  $cm^{-1}$  to the  $CH_2$  asymmetric bend, the one at ca. 1250  $cm^{-1}$  to the ring–O–C asymmetric stretch, the one at ca. 1150  $cm^{-1}$  to the ring–N stretch, the one at 1140  $cm^{-1}$  to the ring–N stretch



**Figure 4.** TIR spectra of AZ-S in chloroform solution when AZ-S takes the trans (A) and the cis (B) forms (at the photostationary state under illumination with vis light for 25 min and UV light for 15 min, respectively).



**Figure 5.** TIR spectra of a 3-layer LB film of  $AZ^-/PDAA^+$  on  $CaF_2$  when  $AZ^-$  takes the trans (A) and the cis (B) forms (at the photostationary state under illumination with vis light for 25 min and UV light for 15 min, respectively).

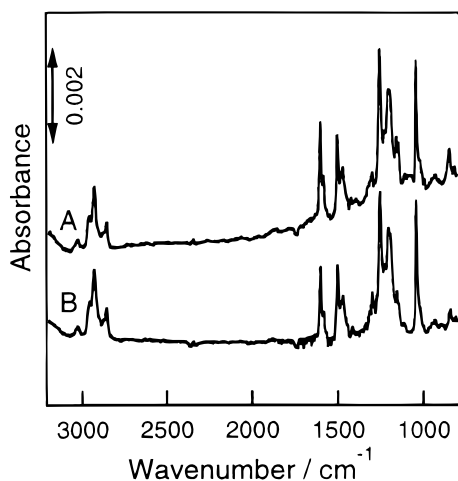
and the ring C–C stretch ( $\nu_{13}/\nu_{9a}$ ),<sup>20</sup> the one at ca. 1050  $cm^{-1}$  to the ring–O–C symmetric stretch, and the one at ca. 840  $cm^{-1}$  to the ring–CH out-of-plane stretch. It is seen that the absorption bands at ca. 1600, 1580, 1250, 1140, and 840  $cm^{-1}$  become weaker with trans-to-cis photoisomerization. Similar results have been reported for another azobenzene derivative.<sup>17</sup> However, the broadening of the band at ca. 1500  $cm^{-1}$  reported in the literature was not observed in our study.

Next, we have investigated the change in IR spectra of the LB films of  $AZ^-/PDAA^+$  during the photoisomerization. Figure 5 shows the TIR spectra of a 3-layer LB film of  $AZ^-/PDAA^+$  on  $CaF_2$  when  $AZ^-$  takes the trans and the cis forms (at the photostationary state under vis and UV illumination, respectively). The band at ca. 1190  $cm^{-1}$ , which is not seen in Figure 4, is assigned to the S=O asymmetric stretch.<sup>21</sup> On going from the trans to the cis isomer, the intensities of the bands at ca.

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**Figure 6.** RAIR spectra of a 3-layer LB film of  $AZ^-/PDAA^+$  on a Au-evaporated film on a glass substrate when  $AZ^-$  takes the trans (A) and the cis (B) forms (at the photostationary state under illumination with vis light for 30 min and UV light for 25 min, respectively).

2920, 1600, and 1140  $cm^{-1}$  decreased. The absorption of  $CaF_2$  substrates in the lower wavenumber region prevented us from obtaining reliable data for the band at ca. 840  $cm^{-1}$ . Figure 6 shows the RAIR spectra of a 3-layer LB film of  $AZ^-/PDAA^+$  on a Au-evaporated glass substrate when  $AZ^-$  takes the trans and the cis forms. The bands at ca. 1600, 1140, and 840  $cm^{-1}$  became weaker. The results are consistent with those of solution spectra, indicating the photoisomerization of  $AZ^-$  although we did not observe the weakening of the 1250- $cm^{-1}$  band in the LB films. The decreasing intensity of the 2920- $cm^{-1}$  band in the TIR spectra suggests some orientational change of the molecules accompanied by photoisomerization. However, it is difficult to address the details of the orientational change since  $AZ^-$  has two alkyl portions and  $PDAA^+$  also contributes to the intensity of this band. It is also difficult to correlate the observed increase of the band intensity at ca. 1500  $cm^{-1}$  in the RAIR spectra with a particular mode of molecular motion because this band is one of the in-plane stretches of the benzene rings.

Further, the combination of TIR and RAIR spectroscopies gives us information on the molecular orientation in the LB films.<sup>22–24</sup> The complicated structures of the molecules allow us to analyze only the relative band intensity at ca. 1250  $cm^{-1}$ , assigned to the ring–O–C asymmetric stretch. The transition moment of this band is parallel to the direction connecting the O atom and the nearest C atom in the benzene rings.<sup>25</sup> The enhancement factor  $m$  for the RAIR measurements with respect to the TIR measurement can be expressed as:

$$m = 4n_1^3 \sin^2 \theta / n_2^3 \cos \theta \quad (1)$$

where  $n_1$  and  $n_2$  are the refractive indices of air and the film, and  $\theta$  is the incident angle.<sup>22</sup> The value  $m = 6.62$  was obtained for the parameters  $n_1 = 1.0$ ,  $n_2 = 1.5$ , and  $\theta = 80^\circ$ . The average tilt angle  $\phi$  of the uniaxially oriented transition moment from the film normal is roughly described as:

$$A_T/A_R = \sin^2 \phi / 2m \cos^2 \phi \quad (2)$$

where  $A_T$  and  $A_R$  are the absorbance of the band in the TIR and RAIR spectra. We obtain the value  $\phi = 60^\circ$  for both the photostationary states under illumination with vis and UV light. The results indicate that the azobenzene moiety is tilted significantly with respect to the normal of the LB films.

**Morphological Change of the LB Films Accompanied by Photoisomerization.** AFM is a powerful tool for studying the morphology of molecular films.<sup>26</sup> AFM has been used to study the morphological change of the LB films of azobenzene, from low-molecular-weight azobenzenes to liquid crystalline copolymers with azobenzene moieties as side groups, accompanied by photoisomerization.<sup>11–14</sup> Slight morphological changes have been reported on illumination with UV light. However, they have not addressed the reversibility of the changes.

Figure 7 shows the AFM images (ex-situ measurements) of a single-layer LB film of  $AZ^-/PDAA^+$  on mica before and after illumination. Before illumination (Figure 7A), the LB film surface is rather smooth with a surface undulation of less than 1 nm, confirming the formation of a cohesive monolayer. When the film was illuminated with UV light, the morphology changed drastically as is seen in Figure 7B. There are a number of hills on the surface: the diameter of the base is ca. 100 nm and the height ca. 5 nm.<sup>27</sup> Repeated scans of the same regions produced essentially identical images. These hills almost disappeared on illumination with vis light as is shown in Figure 7C. Traces of the hills can still be seen on the surface, but the height of most of the traces is less than 0.6 nm. This change in surface morphology was observed reversibly by the alternate film illumination with UV and vis light: C to B and B to C, respectively. When the film was irradiated during a shorter time with both UV and vis light, the change in the surface morphology was less pronounced. Several minutes were enough for the spectroscopic change shown in Figure 3, while the illumination of more than 10 min was necessary for the complete morphological change. This difference indicates that thermal processes are involved in the morphological change. For single-layer LB films, some of the samples showed the morphological change from the first illumination cycle, but others needed a few illumination cycles before the morphological change could be observed. Once the morphology started to change, it continued to change reversibly.

The morphological change of a 2-layer LB film was also investigated with AFM. Figure 8 shows the in-situ AFM images of a 2-layer LB film of  $AZ^-/PDAA^+$  in the vertical illumination mode. Before illumination, a number of holes are observed, which should be associated with defects formed during the transfer process. The average depth of the holes is ca. 5 nm. When this film was illuminated with UV light, hills were also observed on the film surface as in single-layer LB films. The prominent feature is that a number of hills are situated on the "upper surface" while holes are still visible. These hills almost disappeared on illumination with vis light and the morphological change was reversibly observed by the alternate illumination with UV and vis light as in single-layer LB films. As for 2-layer LB films, some of the samples needed one illumination cycle before the morphological change started to occur. Ex-situ AFM measurements gave similar results.

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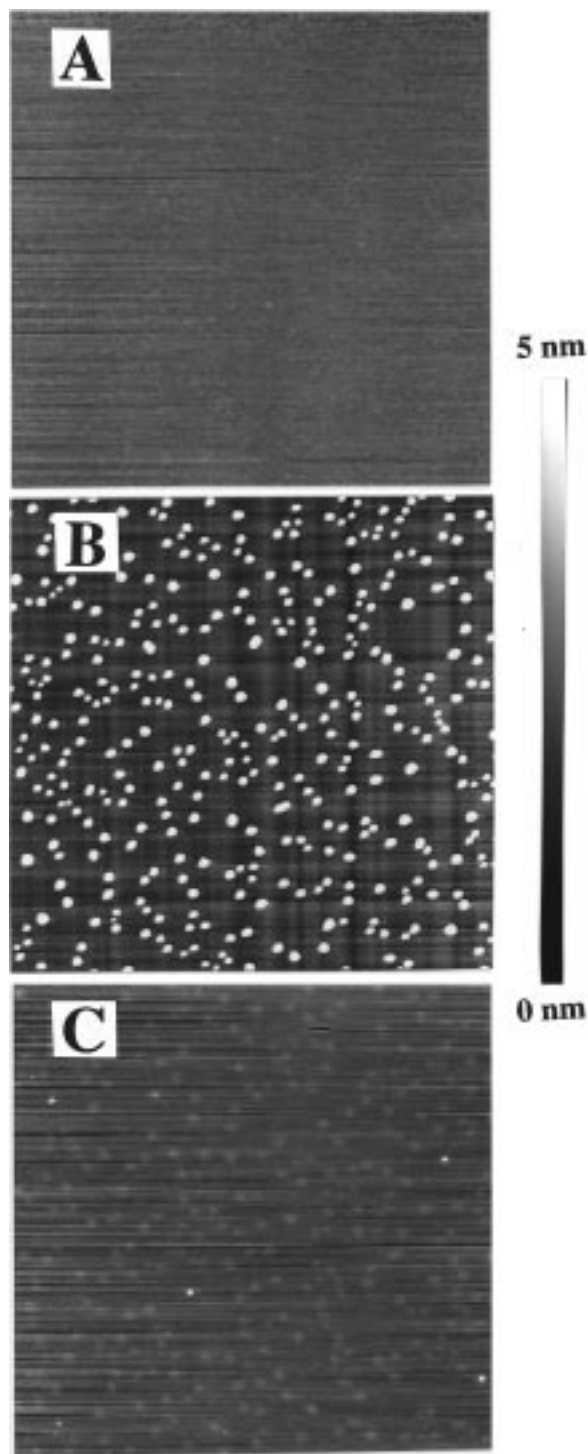
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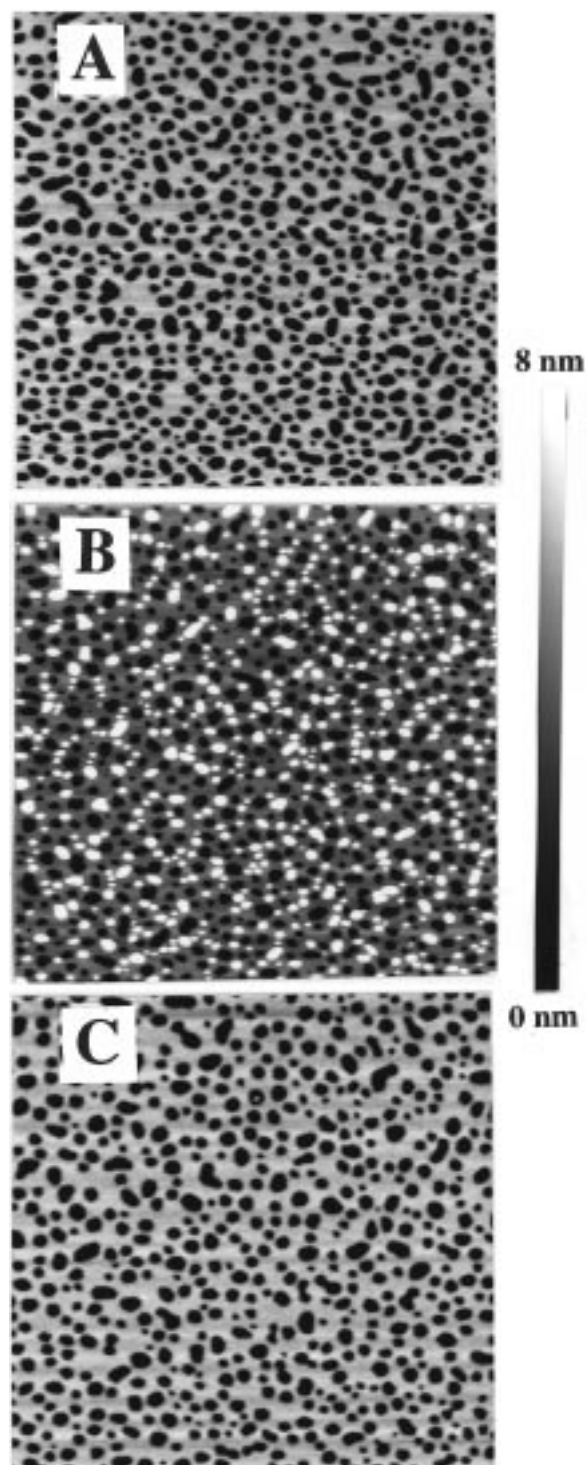
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(27) Generally the shape of the images is influenced by the shape of the AFM tip; see: Louder, D. R.; Parkinson, B. A. *Anal. Chem.* **1995**, *67*, 297A–303A. Hence, the detailed analysis on the actual shape of the hills observed in this study was not done in this paper.



**Figure 7.** Ex-situ AFM images of a single-layer LB film of  $AZ^-/PDAA^+$  on mica before (A) and after illumination with UV light for 15 min (B) and vis light for 15 min (C). The scanned areas are  $4 \mu\text{m} \times 4 \mu\text{m}$ .

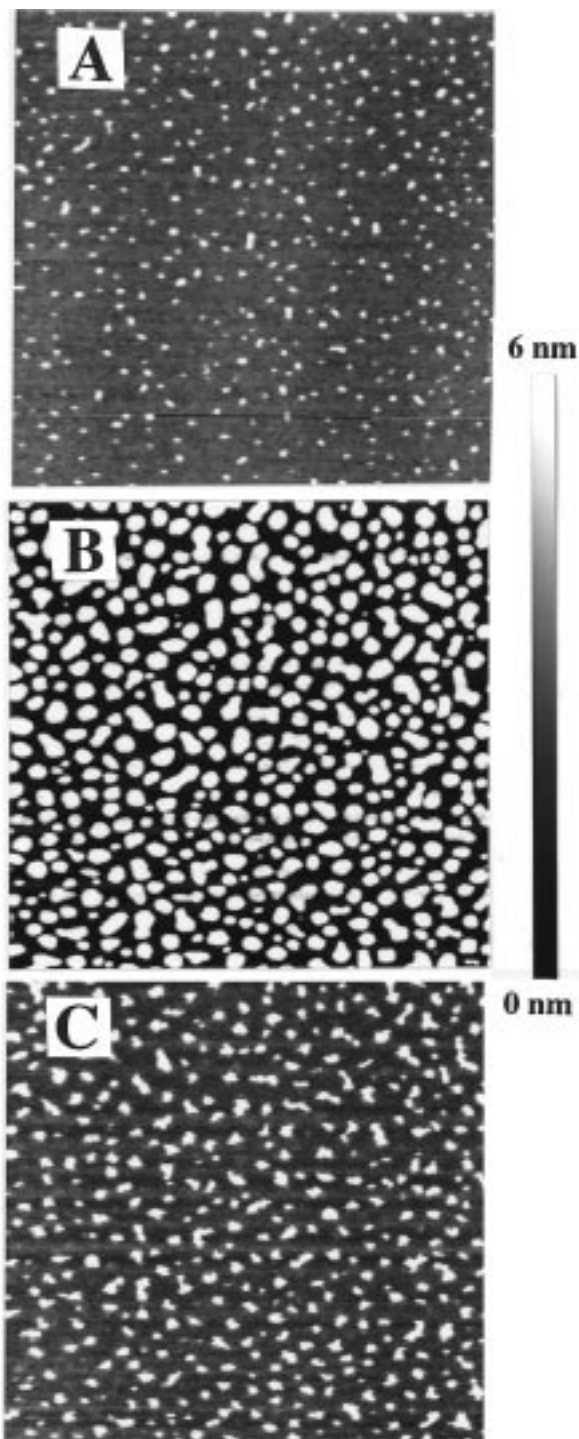
Figure 9 shows the in-situ AFM images of a 3-layer LB film of  $AZ^-/PDAA^+$  in the oblique illumination mode. Before illumination, many small hills with the height of ca. 5 nm are already seen on the surface. These hills are probably related to defects formed during the transfer process. After illumination with UV light, these hills became larger although the height did not change significantly. The formation of additional hills is also seen. They became smaller after illumination with UV light as is shown in Figure 9C. The morphological change was reversibly induced by the alternate illumination with UV and



**Figure 8.** In-situ AFM images of a 2-layer LB film of  $AZ^-/PDAA^+$  on mica before (A) and after vertical illumination with UV light for 5 min (B) and vis light for 10 min (C). The scanned areas are  $4 \mu\text{m} \times 4 \mu\text{m}$ .

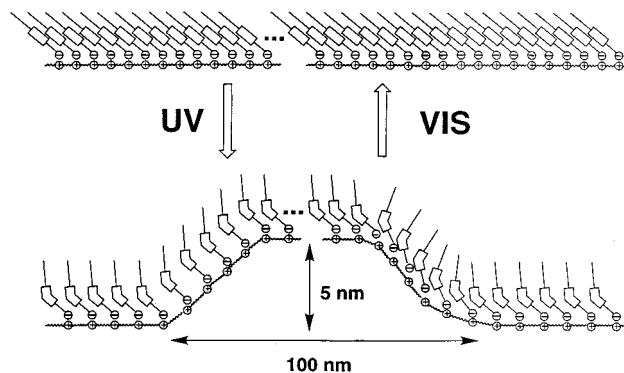
vis light as in single-layer and 2-layer LB films. All the 3-layer LB films showed the morphological change from the first illumination cycle. Ex-situ AFM measurements gave similar results.

**Structural Change of the LB Films Accompanied by Photoisomerization.** The morphological change observed in the LB films allows us to propose a model of the structural change induced by photoisomerization. We consider only single-layer LB films for simplicity since 2-layer and 3-layer LB films have defects before illumination. The reversibility



**Figure 9.** In-situ AFM images of a 3-layer LB film of AZ<sup>-</sup>/PDAA<sup>+</sup> on mica before (A) and after oblique illumination with UV light for 5 min (B) and vis light for 10 min (C). The scanned areas are 4  $\mu\text{m}$   $\times$  4  $\mu\text{m}$ .

of the morphological changes suggests the presence of ordered structures after illumination with both UV and vis light. We propose the model illustrated in Figure 10. The trans-to-cis photoisomerization gives rise to an increase in cross-sectional



**Figure 10.** Model of the structural change of a single-layer LB film of AZ<sup>-</sup>/PDAA<sup>+</sup> accompanied by photoisomerization.

area of azobenzene. When this area increase exceeds the molecular area of azobenzene in the LB films, the two-dimensional film structure should be modified. The most probable modification mechanism would include the release of stress in the film by giving curvature to the film. This means that the film comes loose at the points where the hills are formed. Another explanation of the formation of the hills may be made by assuming multilayer formation when the azobenzene takes the cis form. However, this is not likely since it seems difficult for multilayers, once formed, to return to the monolayer structures on cis-to-trans photoisomerization.

The model illustrated in Figure 10 is consistent with the morphological change of 2-layer LB films. The morphological change of 3-layer LB films suggests that the convex structures on the surface become the nucleation sites for the hills though additional hills are also formed. The reversibility of the light-induced effect in the present study suggests that the polyion has an important role in these phenomena since the electrostatic interaction between the polyion and the azobenzene will prevent the azobenzene molecules from forming thermally stable three-dimensional structures which will not return to the monolayer structures.

## Conclusion

We have found reversible morphological change of the LB films of AZ<sup>-</sup>/PDAA<sup>+</sup> on alternate illumination with UV and vis light. We believe that the reversible morphological change of the LB films is induced by the conformational change caused by photoisomerization, followed by thermal relaxation processes. Photoisomerization in LB films leads to substantial modification of the two-dimensional structures in response to the stress imposed by an increase in area per molecule induced by trans-to-cis photoisomerization of azobenzene. We suggest that the stress is released by giving curvature to the film, thereby leading to the processes in which the film comes loose at the points where the hills are formed. In this sense, the widely accepted concept of "free volume" which assumes that photoisomerization should not change the two-dimensional structures significantly does not hold in the present study. Further, the results imply that similar phenomena may be involved in other LB films in which reversible photoisomerization is observed.