

Photopolymerization of Diacetylene Langmuir–Blodgett Films on an Azobenzene-Containing Monolayer

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ABSTRACT: Single layered Langmuir–Blodgett (LB) films of 10,12-pentacosadiyonic acid (PDA) were prepared on a monolayer comprised of an azobenzene (Az) containing polymeric amphiphile. The photopolymerization process of this PDA LB film on ultraviolet (UV) light (254 nm) irradiation was followed by UV-Vis absorption spectroscopy. The conjugation state of the resulting polydiacetylene was dependent on the initial isomerization form of the Az monolayer beneath the diacetylene LB film. The *trans*- and *cis*-Az surfaces led to a blue and red colored polydiacetylene film, respectively. Atomic force microscopic observation revealed that the photopolymerization of PDA enlarges the surface roughness within the molecular length of the amphiphiles, indicating that the molecular layer structure is preserved on polymerization. The polymerization behavior in this system was highly sensitive to humidity. This can probably be correlated to an enhanced molecular mobility of 6Az10-poly(vinyl alcohol) (PVA) monolayer in a humid atmosphere.

KEY WORDS Azobenzene Monolayer / Photopolymerization Controls / Diacetylene Langmuir–Blodgett Film / UV-Vis Absorption Spectroscopy / Atomic Force Microscopy /

The topochemical polymerization of diacetylenes proceeds with retention of molecular packing of the crystal structure.^{1–4} The reactivity strongly depends on the molecular packing which can be characterized by two parameters, the stacking distance of the monomers and the angle between the diacetylene rod and the stacking axis. In these solid state topochemical systems, a subtle environmental change in the polymerization conditions leads to a drastic change in the conjugation state of the resulting polydiacetylene. The conjugation results in a strong π – π^* absorption in the visible region. Most commonly the polymer is blue in color whereas the monomer is colorless. The blue polymer undergoes a chromic change to red upon heating or prolonged exposure to ultraviolet (UV) light. The most widely accepted explanation for the color change from blue to red is due to a rearrangement of the side chains, which causes a stress and distortion to the conjugated backbone of the polymer causing a shift of the π – π^* electronic energy levels.⁵ This packing-state dependent polymerization behavior provides characteristic chromic molecular systems in ultrathin films such as Langmuir–Blodgett (LB) films⁴ and self-assembled monolayers.⁶ Color changes between blue and red phases of diacetylene monolayers on a water surface and transferred mono- and multilayered LB films have been widely observed. Chromic behavior is coupled with environmental changes such as the surface pressure,^{7–10} pH,¹¹ temperature,¹² substrate interactions,¹³ and a biological receptor–ligand interaction.¹⁴

Due to such highly sensitive nature of the polymerization behavior of diacetylenes, it seemed of particular interest to pursue the possibility if a photochromic reaction on a substrate surface is able to change this reactivity in LB systems. We have heretofore accumulated a great deal of knowledge on the orientational photoregulation of liquid crystal molecules by photo-

chromic molecular layers terms as command surfaces or command layers.^{15–17} The most typical photochromic unit for this purpose is azobenzene (Az). Within a framework of this concept, it was anticipated that the *trans/cis* photoisomerization of Az command layer influences the packing state of successively deposited diacetylene monomer layer, and consequently modifies the polymerization behavior.

The motivation of this investigation is attributed in part to the work of Peterson and coworkers^{18,19} demonstrating that the packing structure of LB layers of 22-tricosenoic acid develop epitaxially following the crystallite structure of an initially deposited monolayer to a large thickness. For this reason, it was anticipated that the packing state of the overall LB film may be modified if the first monolayer possesses the light-switching functionality. Very recently, Kawai²⁰ in fact demonstrated that the orientation of a mixed LB film of 4'-dodecyl-4-cyanobiphenyl (12CB) and deuterated stearic acid is changed in a reversible fashion by the surface *trans/cis* photoisomerization in a polyion complex-type Az derivative monolayer on the substrate.

This paper presents the details of our study on the polymerization behavior of diacetylene LB film on an Az derivative monolayer.²¹ A schematic illustration of the double layered hybrid LB film system employed in this study is shown in Figure 1. We will show here that the photoisomerization behavior of 10,12-pentacosadiyonic acid (PDA) LB layer is effectively governed by the *trans/cis* state of Az in the monolayer of poly(vinyl alcohol) having an Az side chain denoted as 6Az10-PVA. The molecular structure of these compounds is indicated in Chart 1. Evaluations of the photopolymerization process and molecular orientations are carried out by UV-Vis absorption spectroscopy and contact angle measurements, and the film morphologies were observed by atomic force microscopy (AFM).

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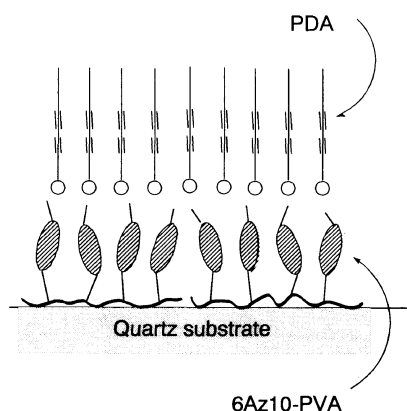


Figure 1. Schematic illustration of the molecular system employed in this study.

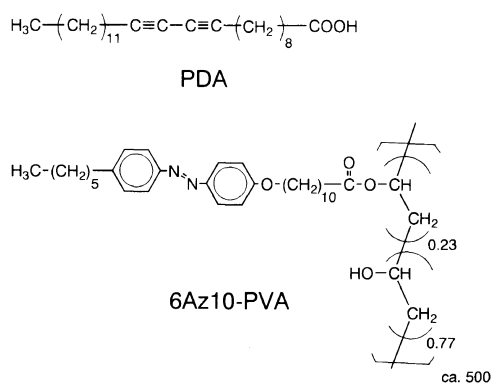


Chart 1.

EXPERIMENTAL

PDA was purchased from Tokyo Chemical Industry Co., Ltd. The synthetic procedure of 6Az10-PVA was described previously.²²

All measurements except for AFM observation were achieved in dimmed red light.

Preparation of 6Az10-PVA LB monolayer was achieved as follows. A chloroform solution dissolving 6Az10-PVA (1×10^{-3} mol dm⁻³) was first exposed to UV (365 nm) light (ca. 90% *cis* isomer content), and spread on pure water (Millipore-Q grade, 18 M Ω cm⁻¹, pH 5.7) filled in a Lauda FW1 film balance at $20 \pm 0.5^\circ\text{C}$. After evaporation of the solvent, the monolayer was compressed at a speed of 20 cm min⁻¹. This monolayer was transferred onto a pair of clean quartz plates at 13 mN m⁻¹. Transfer in the *cis* form was essential for obtaining a homogeneous 6Az10-PVA LB monolayer with a transfer ratio of unity. These samples were stored in the dark at room temperature for four days to allow the thermal conversion to the *trans* Az form. This dark adaptation of 6Az10-PVA films was achieved in dry atmosphere on silica gel. The humidity condition of storage was found to be of particular importance in this work as will be stated below.

A pair of *trans*-6Az10-PVA monolayers on the quartz plate prepared as stated above (*trans*-Az surface) and one of them was exposed to 365 nm light to allow the photoisomerization to the *cis* form (ca. 70% content, *cis*-Az surface). Onto these *trans*- and *cis*-Az surfaces, a single PDA LB layer was transferred in the following procedures. A PDA chloroform solution (1×10^{-3} mol

dm⁻³) was spread onto pure water at 9°C filled in a USI FSD-110 Langmuir trough. The spread film was compressed at a speed of 5 mm min⁻¹, and the upstroke transfer was achieved at a surface pressure of 3 mN m⁻¹ and a speed of 1 mm min⁻¹.

Photoirradiation for polymerization (254 nm) was performed with a JASCO CRM-FD irradiator equipped with a 300 W xenon lamp in an ambient atmosphere.²³ Light power was determined by a chemical actinometer using Fe(3+) trioxalate solutions. The light intensity at 254 nm for photopolymerization was determined to be 0.7 mW cm⁻².

UV-Vis absorption spectra were taken on a JASCO MAC-1 spectrophotometer. The polarized absorption spectra were obtained on the same instruments equipped with a Glan-Thomson type polarizer in front of the specimen.

AFM observation was carried out on a Seiko Instruments SPA300/SPI3700 system in the contact mode in an ambient atmosphere (ca. 20°C, relative humidity of 30–40%).

Contact angle measurements were performed with a CA-X of Kyowa Interface Science Co. in an ambient atmosphere. Pure water used for this experiment was of Milipore grade.

RESULTS AND DISCUSSION

Preparation of the Double Layered Hybrid LB Film

Veagle and Peterson¹⁹ pointed out that interlayer structural correlation of the 22-tricosenoic acid is impaired when the divalent cations such as cadmium and calcium are present in the subphase. Therefore, we prepared PDA monolayers on pure water despite that the mechanical stability of this monolayers for transfer was considerably decreased.

The compressive surface pressure–area (π -A) isotherms of PDA monolayer at 9, 14, and 20°C on pure water were indicated in Figure 2. With lowering the temperature, the limiting area around 0.3 nm² (extrapolation of the steepest slope to zero pressure), and the collapse pressure increased. The π -A curves were essentially in consistent with those reported by Tieke *et al.*²⁴ The monolayer on pure water was not sufficiently stable when applied pressures of more than 5 mN m⁻¹. At these higher pressures, a notable collapse started after 30 min, and the area reduced nearly to half of the initial one after 90 min. In consideration of the above results, we adopted the transfer conditions of the PDA monolayer as a pressure of 3 mN m⁻¹ and temperature of 9°C. Unfortunately, deposition to multilayers under these conditions was difficult. Therefore, the present work was limited to investigation of single layered PDA on 6Az10-PVA monolayer. As for a single layer, the PDA monolayer was readily and satisfactorily transferred on both the *trans*- and *cis*-6Az10-PVA monolayers. The transfer ratios of PDA monolayer on the *trans*- and *cis*-6Az10-PVA monolayer were essentially unity, 0.95 and 1.0, respectively.

Photopolymerization Behavior of PDA Film on the Azobenzene Layer

Figure 3 indicates the changes in the UV-Vis ab-

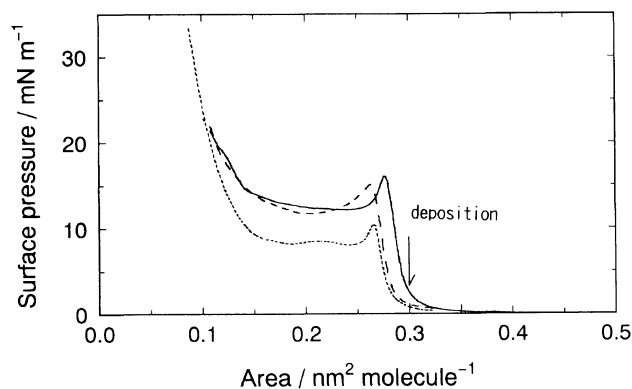


Figure 2. Surface pressure–area isotherms of the PDA monolayer on pure water at 9 (solid line), 15 (dashed line), and 23°C (dotted line). The deposition condition is indicated by an arrow.

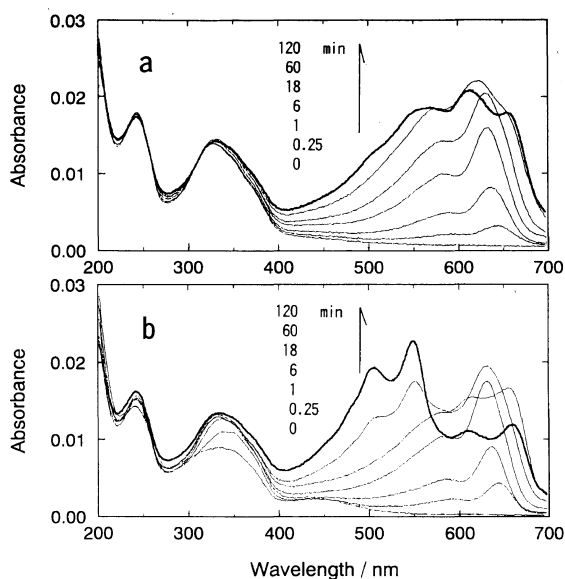


Figure 3. Changes in UV-Vis absorption spectrum of the PDA/6Az10-PVA hybrid LB film upon UV light (245 nm, 0.7 mW cm⁻²) irradiation. The PDA monolayer was deposited onto the *trans* (a) and *cis* (b) form of 6Az10-PVA monolayer.

sorption spectrum upon 254 nm light irradiation onto the PDA/6Az10-PVA hybrid LB film. The figure shows the spectral changes observed on the *trans*- (a) and *cis*-Az surfaces (b). Before irradiation, the spectra of the hybrid LB films were virtually equivalent to those of 6Az10-PVA films alone because the PDA monomer absorbs light at wavelengths below *ca.* 260 nm with low absorptivity.

In both film systems, the spectral changes virtually ceased within 120 min under the irradiation conditions employed. As seen in the figure, there observed a marked difference in the conjugation state of the resulting polydiacetylene main chain for the *trans* and *cis* Az surfaces. Upon 254 nm light illumination, new absorption bands appeared in the visible regions above 400 nm, indicating the growth of the conjugated diacetylene polymer. A band peaked at 630 nm giving a blue form enhanced rapidly, followed by a secondary change depending on the isomerization state of the initial Az surface beneath the PDA film. On the *trans*-Az surface, the spectrum was somewhat broadened after 120 min maintaining the blue form. On the *cis*-Az surface, in contrast, prolonged irradiation led to an appearance of

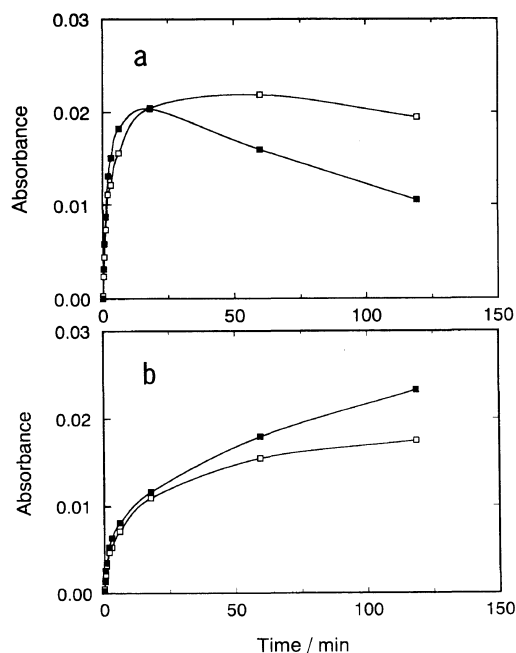


Figure 4. The time course of absorbance changes at 630 (a) and 550 nm (b) upon UV light illumination obtained from the spectral data indicated in Figure 3. The open and closed squares show the data for the *trans*-Az layer and *cis*-Az layer, respectively.

hypsochromic bands peaking at 550 nm to give a red form. Also for this surface, the spectral changes ceased in 120 min. Simultaneous preparation of PDA LB films onto the *trans*- and *cis*-Az surfaces from one batch of PDA monolayer led to the same results, indicating the reliability of this phototropic surface control. A PDA LB monolayer on a quartz plate without 6Az10-PVA gave a blue state likewise to that on the *trans*-Az surface with smaller absorbances under the same polymerization conditions. The spectral shape of the final state is shown in Figure 5c.

The time profiles of absorbance changes in the above processes are shown in Figure 4. As indicated, the photopolymerization at early stages occurred at almost the same rate, and discrepancies start to appear after *ca.* 20 min irradiation. On the *cis*-Az surface, absorbance at 630 nm substantially decreased after 20 min (a, closed squares), and that at 550 nm grew accordingly (b). It is worth mentioning that, in the *cis*-Az surface system, 254 nm light irradiation also caused the *cis* to *trans* photoisomerization of the Az unit simultaneously to the PDA polymerization. This can be obviously seen in the changes of the π - π^* band of the Az unit ranging 300–400 nm (Figure 3b). The Az photoisomerization reached the photostational state at an early stage within 10 min. Interestingly, the polymerization process giving rise to the red form is considerably delayed, after 20 min. This fact implies that the discrimination of the final conjugation state of polymerized PDA is imposed during the LB deposition of PDA monolayer or by the simultaneously occurring *cis* to *trans* photoisomerization in the command layer at the early stage. The two final spectra in Figure 3 show that the final films contains the mixture of blue and red forms. A complete transition of the conjugation state which is often observed in crystals² on prolonged irradiation or heating

was not attained in our system.

The actual origin of the color change is still unclear. Probably conformational transitions and/or aggregation phenomena are involved in the chromic process. If we accept an explanation that the hypsochromic shift of the polydiacetylene chain is caused by stress or strain at the later stages of photopolymerization in the solid state,^{2,4} it can be assumed that the *cis*-Az surface provides a more favorable environment for the PDA polymerization.

Furthermore, UV light irradiation for Az photoisomerization (365 nm, 4 mW cm⁻²) was performed for the pre-polymerized film of PDA/*trans*-6Az10-PVA system (corresponding to the film final spectrum of Figure 3a). This attempt was undertaken to examine the workability whether reversible conjugation changes of the blue \rightleftharpoons red forms of the polydiacetylene film can be performed. As a consequence, no appreciable spectral change was observed. Thus, once the PDA LB film was polymerized, it can not be "commanded" by consecutive light irradiation under conditions employed.

Azimuthal Anisotropy of the Conjugated Backbone

LB film preparation by the vertical dipping method frequently impose azimuthal structural anisotropies in the transferred LB film. This arose our interest to carry out the spectroscopic observation with linearly polarized light. Figure 5 displays the polarized UV-Vis absorption spectra for the polymerized film on the *trans*-Az surface (blue form, a), the *cis*-Az surface (red form, b), and a bare hydrophilic quartz (c) taken with polarized light set parallel (//) and perpendicular (\perp) to the lifting direction of LB film preparation. In all cases, absorbance obtained with the perpendicular direction was larger than that with parallel polarization in the band region of the conjugated polydiacetylene. These results indicate that the conjugated polymer aligns perpendicular to the lifting direction to some extents. However, the in-plane anisotropy was not obvious. The dichroic ratio defined as Abs.(\perp)/Abs.(//) was 1.1–1.2. Judging from the fact that the chain orientation of the polydiacetylene on 6Az10-PVA monolayers (a and b) and on the bare quartz surface (c) gave no appreciable differences, the anisotropic feature can be ascribed to the intrinsic property of PDA monolayer and the deposition conditions adopted in this study.

Surface Wettability and Morphology

The hybrid layer structure cartooned in Figure 1 is based on the assumption that, in the upper PDA layer, the hydrophobic hydrocarbon chains are likely to direct toward the air due to energetic requirements. To confirm this, we evaluated the static contact angle of water droplet for the hybrid LB film surface, which provides profitable sets of data for the molecular orientation of the amphiphile. The static contact angle measurements were carried out for polymerized film on the *trans*-Az surface monolayer. The average contact angle value of more than ten measurements at different positions was $98 \pm 2^\circ$. The value approaching to 100° shows the coverage of hydrocarbons at the outermost surface. Thus, the lipophilic tail ends of PDA layer should be exposed to the air, and formation of a head to tail arrangement as

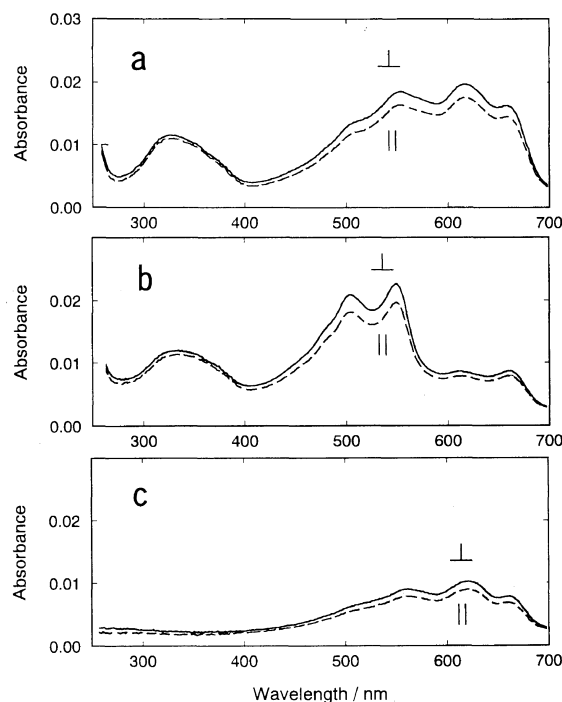


Figure 5. Polarized UV-Vis absorption spectra of the photo-polymerized PDA LB films on *trans*-6Az10-PVA (a), on *cis* 6Az10-PVA (b), and on a bare quartz plate (c). The polarizer was set parallel (dashed line) and perpendicular (\perp) to the lifting direction of PDA transfer.

illustrated in Figure 1 is rationalized. The contact angle value can be compared to those obtained for LB film surfaces of arachidic acid. The value of as-deposited arachidic acid LB film is reported to be $108 \pm 2^\circ$, and it is lowered to $100 \pm 2^\circ$ after annealing.²⁵ The lowered value reflects thermally induced disordering of the array of hydrocarbon chains. The wettability of water for our hybrid film is corresponding to that observed for the annealed film. The measurements were also carried out for the film before polymerization, however, the values were not reproducible but time dependent. It seems that, in the monomeric state, contact of water to the PDA layer probably induces a flip-flop reorientation of the amphiphile or removal from the surface.

Figure 6 shows the surface topographical AFM images before and after photopolymerization of PDA film on the *trans*-6Az10-PVA layer deposited on mica. The *cis*-Az surface essentially gave the same results. Before irradiation, the surface of the hybrid film was adequately smooth, the roughness being within 0.5 nm. This indicates that the hybrid film is prepared without appreciable collapse of the PDA monolayer. After UV light (254 nm) irradiation for 120 min, the surface roughness became substantially large, indicating increased disordering and distortion of packed hydrocarbon chains. Nevertheless, the surface roughness was still within 1 nm which is smaller than the molecular length of PDA (ca. 3 nm). It can be concluded that the photopolymerization of PDA on 6Az10-PVA monolayer proceeds with retention of the two dimensional state, and that no appreciable three dimensional crystallization or collapse is involved.

The above facts strongly suggest that the surface-mediated control of the polymerization process of PDA

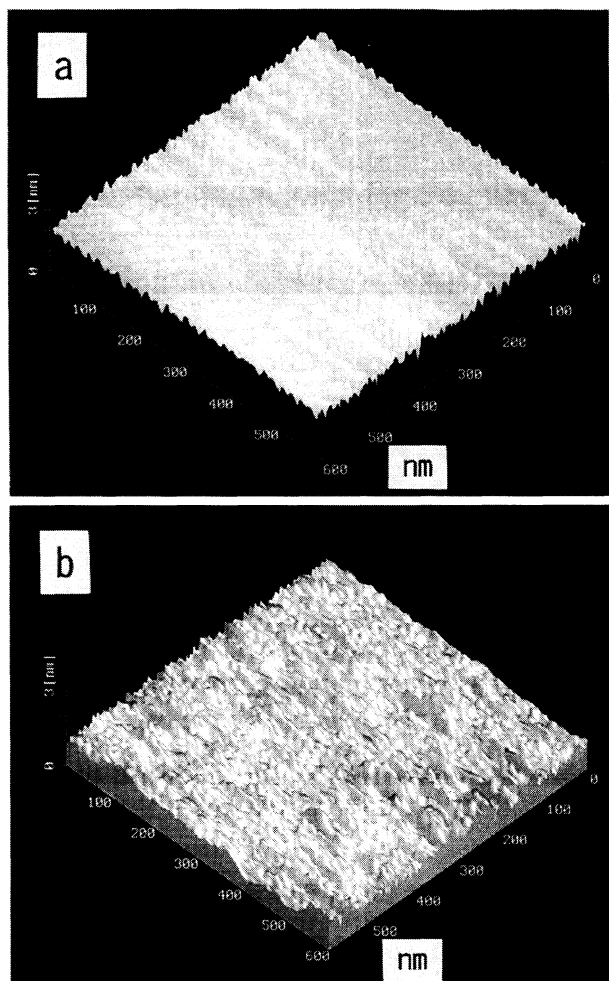


Figure 6. Topographical atomic force microscopic images of the PDA/*trans*-6Az10-PVA hybrid film before (a) and after (b) UV light irradiation (254 nm, 0.7 mW cm^{-2} for 120 min).

stems from the difference in molecular packing state of PDA array. Since the transfer ratio was essentially identical for the both *trans*- and *cis*-Az surfaces, the average lateral density is the same. It can lead to an assumption that the observed modification of photoisomerization behavior is brought about by a tilt angle change of packed PDA molecules rather than a change in molecular distance. In another LB film system, Kawai²⁰ confirmed surface-triggered tilt changes of amphiphilic molecules by Fourier transform infrared spectroscopy. Such tilt changes may be caused either by the change in the molecular geometry of Az unit or variations in the surface energy.²⁶ We have not elucidated the major contribution at moment for the present LB film system, however, in the alignment switching of nematic liquid crystals, the geometrical factor is found to be predominant.²²

Spectroscopic Evidence for the Interlayer Molecular Interaction

It is already conceived that contact of liquid crystal molecules to an Az command layer induces reorientation of the surface Az side chain to normal direction of the substrate plane.^{22,26} The orientational change is readily detectable by the UV-Vis absorption spectroscopy. In observation of the π - π^* band of the *trans* Az unit in

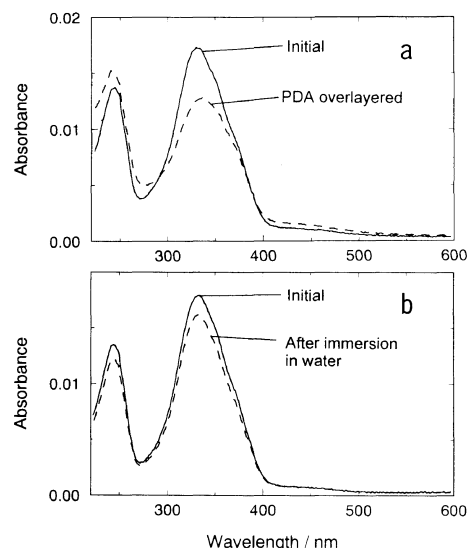


Figure 7. UV-Vis absorption spectra of the 6Az10-PVA monolayer on both sides of a quartz plate. The “initial” film was taken after 4 days after deposition. On this film, PDA monolayer was overlayered (a, dashed line). As a control experiment, immersion into water without PDA monolayer was also achieved (b, dashed line).

the transmission mode, the spectral modulation reflects the out-of-plane orientational change of the Az side chain. In this examination, the *trans*-Az unit can be used as a dichroic dye. Induction of perpendicular orientation of the Az-side chain is detected by a decrease of the π - π^* band of long axis transition (typically positioned at 300–400 nm) with a concurrent increase of the short axis transition band (*ca.* 250 nm).

Figure 7a depicts the UV-Vis absorption spectra of pure 6Az10-PVA monolayer (solid line) and with overlayered PDA monolayer (dashed line). As a control experiment, spectra before and after immersion into water were also compared (Figure 7b). Similarly to the spectral changes observed for liquid crystal molecules, deposition of the single PDA monolayer onto the 6Az10-PVA monolayer induced a clear spectral change of Az unit (a). The absorbances at 330 nm (long axis) and 248 nm (short axis) decreased and increased, respectively, upon contact with the PDA monolayer. These changes clearly show the reorientation of the Az side chain to the substrate normal. Since immersion procedure into water alone without PDA monolayer did not cause a significant spectral change (b), it can be verified that the reorientation of 6Az10-side chain is certainly brought about by the contact of PDA monolayer. We believe that these facts provide a strong evidence for existence of mutual interactions between the 6Az10-PVA and PDA layers which would play an essential role in achievement of the polymerization control.

Effect of Humidity

In the meantime of investigation, we noticed that the polymerization behavior of PDA on 6Az10-PVA layer was highly variable from season to season. Out of the two likely affecting parameters, namely temperature and humidity, it was eventually proven that humidity influences the behavior in a crucial manner. Photopolymerization behaviors of the PDA film on the

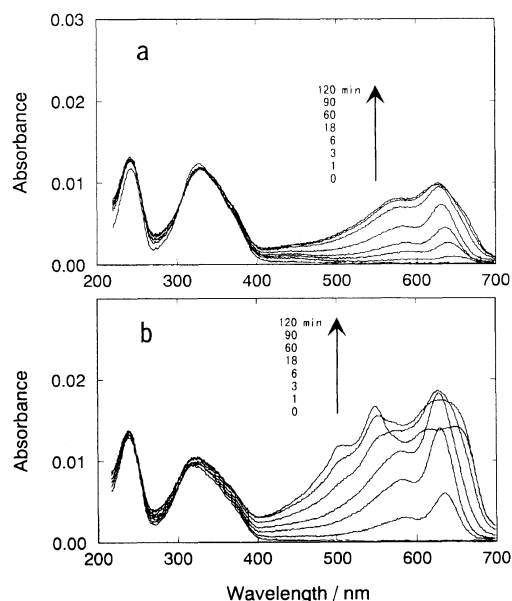


Figure 8. Changes in UV-Vis absorption spectra of the PDA/*trans*-6Az10-PVA films (*trans*-Az surface) upon 254 nm light irradiation (0.7 mW cm^{-2}) under low (a, relative humidity of below 30%) and highly (b, above 90%) humid conditions.

trans-Az surface in dry and humid atmospheres are compared in Figure 8. The dry and highly humid conditions were fulfilled in a sealed vessel in the presence of silica gels (a, relative humidity of below 30%) and a piece of wet cotton (b, relative humidity of ca. 100%), respectively. The LB films were prepared at the same time from the identical batch of LB experiment, and conditions except for humidity were strictly adapted to be equivalent. In the dry atmosphere, the photopolymerization was terminated at an earlier stage of photopolymerization which gave the blue form just as indicated in Figure 3a. On the other hand, conversion to the red form was partially observed in the same procedure under the humid condition. It is hence concluded that the phototropic control of PDA polymerization process by an Az command layer is effectively achieved only in a dry atmosphere.

We assume that the highly moisture-sensitive nature observed here can be correlated to the molecular mobility of 6Az10-PVA monolayer on the hydrophilic substrate. We recently revealed that 6Az10-PVA monolayer on a freshly cleaved mica surface becomes highly mobile under humid conditions as proven by AFM.²⁷ The UV light irradiation leads to a large morphological expansion of this monolayer under humid conditions. Such morphological changes are not observed in a dry atmosphere and hence existence of an adsorbed water layer on mica²⁸ should be responsible for the attainment of the high molecular mobility.^{29,30} We infer that the large lateral movement of 6Az10-PVA monolayer in humid atmospheres impairs the reproducible results of the polymerization behavior of the on-touched PDA layer. In this way, the surface control of the PDA photopolymerization requires dry conditions under which the mobility of 6Az10-PVA monolayer is frozen. Detailed investigation on the light-driven motion of 6Az10-PVA monolayer is now in progress.

CONCLUSIONS

It is demonstrated in this work that the photopolymerization behavior of a diacetylene LB film is controlled by the *trans/cis* photoisomerization of Az-based command layer. Achievement of this surface-mediated discrimination requires dry atmospheres in which the lateral mobility of the supporting Az layer is frozen. From a technological viewpoint, this system could be extended to micro-photopatterning of conjugated state of polydiacetylene ultrathin films, which is anticipated to provide a new tool for construction of optoelectrical devices. As shown here, the Az command layer is able to control the π -conjugation state of polydiacetylene. For an extension of this concept, our future work should involve examinations for other sorts of conjugated polymers. An attempt in this regard is now underway.

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