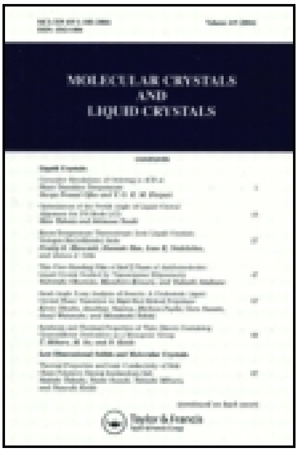

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Surface-Mediated Modification of the Polymerization Process of Diacetylene LB Films by Photochromic Azobenzene Monolayers

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SURFACE-MEDIATED MODIFICATION OF THE POLYMERIZATION PROCESS OF DIACETYLENE LB FILMS BY PHOTOCHROMIC AZOBENZENE MONOLAYERS

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Abstract Photopolymerization of a diacetylene Langmuir-Blodgett (LB) film was achieved on an azobenzene (Az) containing monolayer. The color of the polydiacetylene obtained was found to be dependent on the photoisomerized form of the Az monolayer beneath the diacetylene LB film. The phenomenon observed here can be a new example of the photochemical molecular switching mediated by surface photochromism.

INTRODUCTION

Most of our recent efforts have been devoted to photochemical orientational arrangements of molecular assemblies such as nematic liquid crystals (LCs)[1,2] and dye aggregates[3] which are assisted by the photochromic reaction of azobenzene (Az) surface layers (command surfaces[2]). On the other hand, Peterson et al.[4,5] reported more than ten year ago that the structure of Langmuir-Blodgett (LB) layers of 22-tricosenoic acid develop epitaxially following the crystallite structure of an initially deposited monolayer to a thickness for optical observation. Above two aspects inspired us to examine a possibility that, if one adopt a photochromic Az monolayer as the initial layer, the photochemical information possessed by the first layer may be transferred and reflected to the structure of successively deposited LB layers. A diacetylene LB film seemed to us the most appealing candidate for the successively depositing material because (i) the polymerization behavior is highly sensitive to the molecular packing state as will be mentioned just below, and (ii) the polymer obtained can be readily observable by the UV-visible absorption spectroscopy at wavelengths which do not essentially overlap those of the photochromic Az unit.

The photopolymerization of diacetylene derivatives in LB multilayers has extensively been studied[6]since the first report of Tieke et al.[7] Particular attention has been paid in its topochemical polymerization behavior. Diacetylenes undergo rapid polymerization when exposed to UV light. The polydiacetylene formed has a rigid, one dimensional, conjugated backbone. This 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 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 resulting in a shift of the π - π * electronic energy levels.[8]

This paper presents our preliminary results of the polymerization behavior of 10,12-pentacosadiyonic acid (PDA) LB film placed on a photochromic 6Az10-PVA LB monolayer (Figure 1). We demonstrate here that the surface photochromic reaction is actually able to control the conjugated state of the polydiacetylene backbone in the LB film.

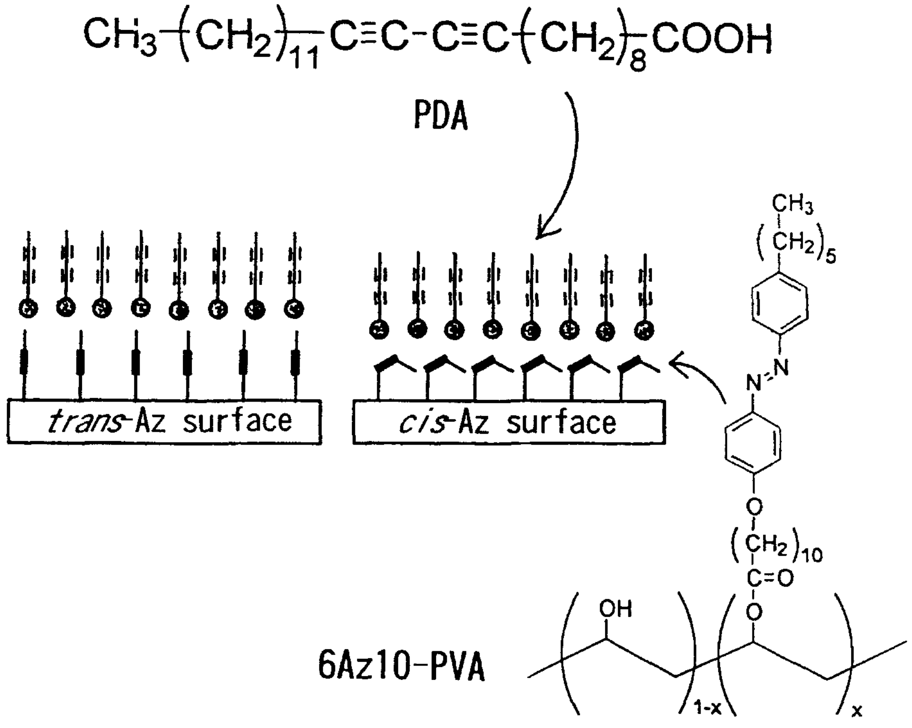

FIGURE 1 Molecular architecture in this study.

EXPERIMENTAL

The synthesis of 6Az10-PVA was described previously.[9] PDA was purchased from Tokyo Kasei Kogyo. Co. Ltd, and recrystallized from diethylether before use.

Preparation of the 6Az10-PVA/PDA composite layer was achieved as follows (see Figure 2). UV light-irradiated 6Az10-PVA in chloroform (1×10^{-3} mol dm^{-3}) containing ca. 90 % *cis* isomer was spread on pure water (Milli-Q SP grade) filled in a Lauda FW-1 film balance at 20 ℃ , and transferred onto a pair of quartz plates at 13 mN m^{-1} as described previously.[9] Transfer in the *cis* form is preferable to obtain a homogeneous 6Az10-PVA LB monolayer with a transfer ratio of unity. These Az modified plates were stored in the dark at room temperature for four days to allow the thermal conversion to the *trans* Az form (*trans*-Az surface). One of the two plate was then exposed to 365 nm light (*cis*-Az surface). Onto these *trans*- and *cis*-Az surfaces, a PDA LB monolayer was overlayered. A PDA chloroform solution (1×10^{-3} mol dm^{-3}) was spread onto pure water at 9 ℃ filled in a USI FSD-110 Langmuir trough. The upstroke transfer was achieved at a surface pressure of 3 mN m^{-1} and a speed of 1 mm min^{-1}. The transfer ratio was satisfactory giving 0.95 and 1.0 for the *trans*- and *cis*- films, respectively. These composite LB films were then immediately exposed to UV light (254 nm) for photopolymerization.

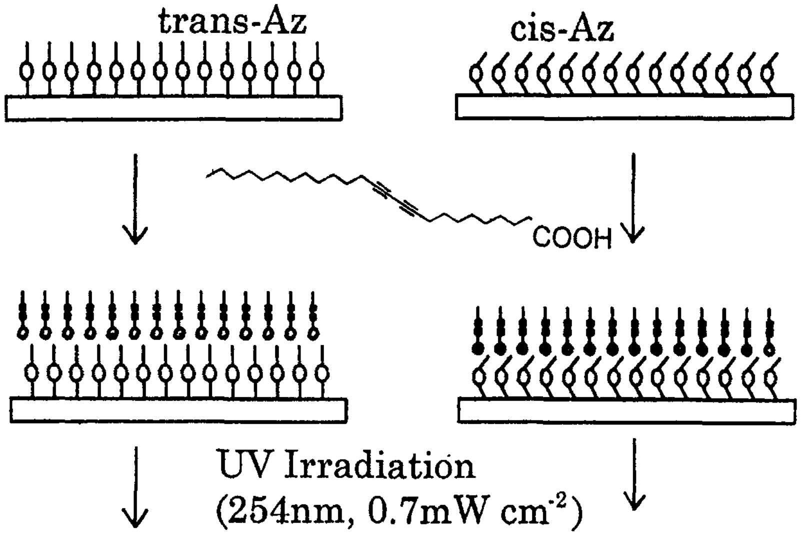

FIGURE 2 Preparation of hybrid LB films composed of the *trans*- and *cis*-Az monolayers overlayerd by a PDA monolayer.

Light irradiation for the Az isomerization was performed with a 150 W mercury-xenon lamp (San-ei UVF-202S). Light of 365 nm line was selected using a set of optical filters. UV light for the photopolymerization of diacetylene was obtained from a JASCO CRM-FD irradiator equipped with a 300 W xenon lamp and a grating monochrometer. Light intensity at 254 nm was 0.7 mW cm^2. The photopolymerization was achieved in ambient air.

Monitoring the polymerization process of PDA monolayers and measurements of the polarized UV-visible absorption spectra were performed on a JASCO MAC-1 spectrophotometer.

RESULTS AND DISCUSSION

Transfer of PDA monolayer

Veale and Peterson[5] reported that the epitaxial deposition in the 22-tricosenoic acid is observed for the transfer from a pure-water subphase and existence of metal counterions inhibit this effect. Therefore, it seemed of appropriate to start with a pure water subphase also for the present material. Figure 3 shows the surface pressure-area curve of PDA monolayer. On a pure water subphase the PDA monolayer was fragile. The transfer was therefore achieved at a low surface pressure of 3 mN m^{-1}.

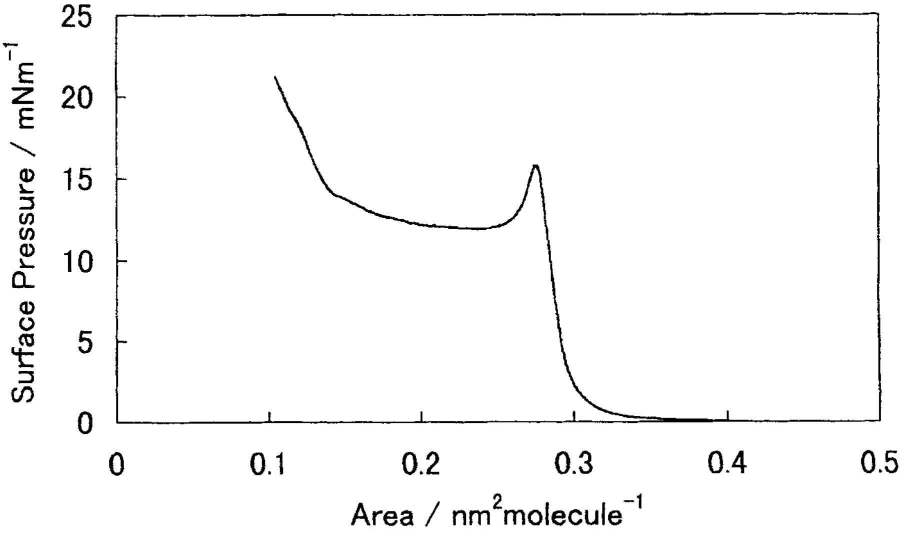

FIGURE 3 Surface pressure-area curve of PDA monolayer on pure water at 9 ℃.

Polymerization of PDA LB film

Figure 4 displays UV-visible absorption spectra of 6Az10-PVA/PDA hybrid films upon 254 nm light irradiation. Before irradiation, the spectra of the hybrid LB films were almost equivalent to those of 6Az10-PVA films because the PDA monomer absorbs at wavelengths below ca. 260 nm with low absorptivity.

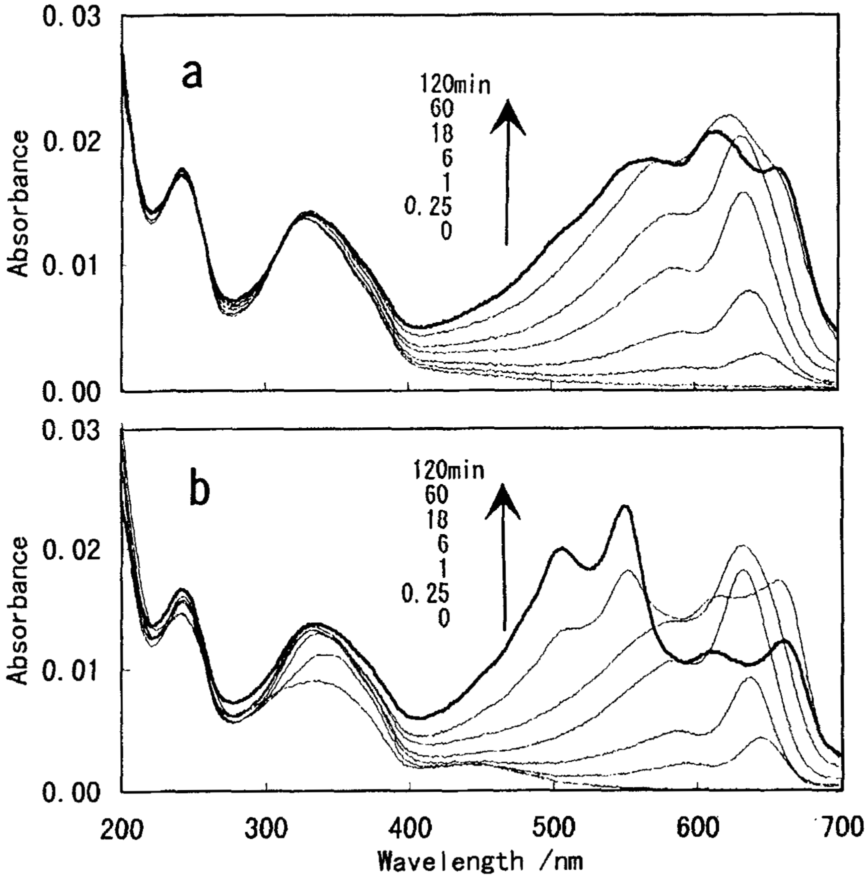

FIGURE 4 UV-visible absorption spectra following the photopolymerization process (254 nm light irradiation) of PDA monolayer deposited on the *trans-* (a) and *cis-* (b) Az surface monolayers.

On 254 nm light illumination, new absorption bands appeared in the visible regions above 400 nm, indicating formation of the conjugated diacetylene polymer. A band peaked at 630 nm appeared rapidly, which gives the film of so-called a "blue film," followed by a secondary changes depending on the isomerization state of the Az surface beneath the PDA film. On the *trans*-Az surface, the spectrum was somewhat broadened maintaining the blue state. On the *cis*-Az surface, in contrast, prolonged irradiation led to clear appearance of new shorter wavelengths-shifted bands peaking at 550 nm giving a "red film". The spectral changes almost ceased in 120 min. A PDA LB monolayer on a quartz plate without 6Az10-PVA gave a blue film likewise to that on the *trans*-Az surface with smaller absorbances under the same polymerization conditions (spectra not shown).

Absorbances at 630 nm and 550 nm for the blue and red films were plotted in Figure 5 as a function of irradiation time. These time profiles indicate that the early stage of photopolymerization occurs at almost the same rate, and discrepancies start to appear after ca. 20 min irradiation. On the *trans*-Az surface, absorbance at 630 nm gradually decreased after 20 min (a), and that at 550 nm showed a noticeable grow accordingly (b).

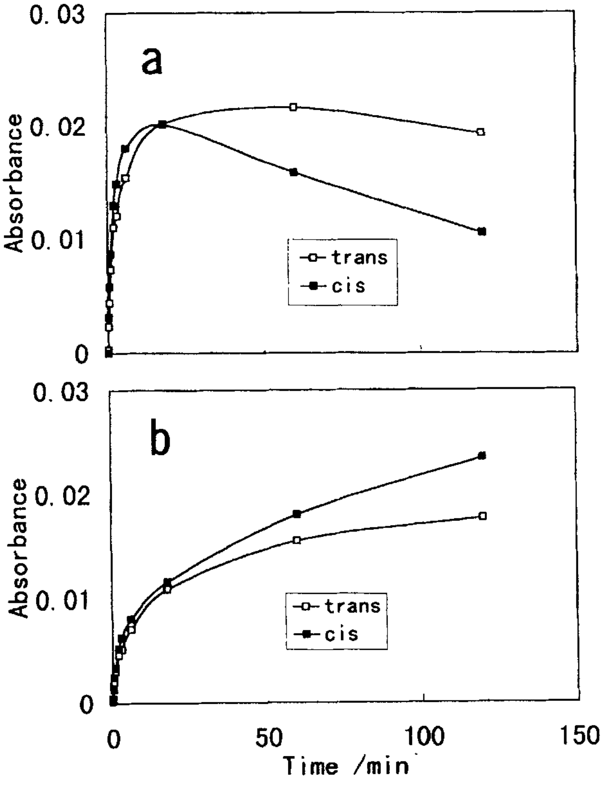

FIGURE 5 Changes in the absorbance at 630 nm (a) and 550 nm (b) as a function of irradiation time of 254 nm light.

It is worth mentioning that, in the *cis*-Az surface system, 254 nm light irradiation caused the *cis* to *trans* photoisomerization of the Az unit as well as 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 in the photostational state at an early stage within 10 min. Interestingly, appearance of the characteristic discrepancy leading to the red film is considerably delayed, after 20 min.

UV-visible Polarized Absorption Spectra

To evaluate the direction of the polydiacetylene backbone grown in the LB films, UV-visible polarized absorption spectra were taken in the directions parallel and orthogonal to the lifting direction of LB film transfer (Figure 6). In both *trans*- and *cis*-Az surfaces, the polydiacetylene backbone was preferentially oriented orthogonal to the lifting direction to some extents. A Polymerized PDA on an unmodified quartz plate also gave the same results, indicating that this orientational preference is not modified by the Az surface but should be attributed to the PDA deposition conditions adopted here.

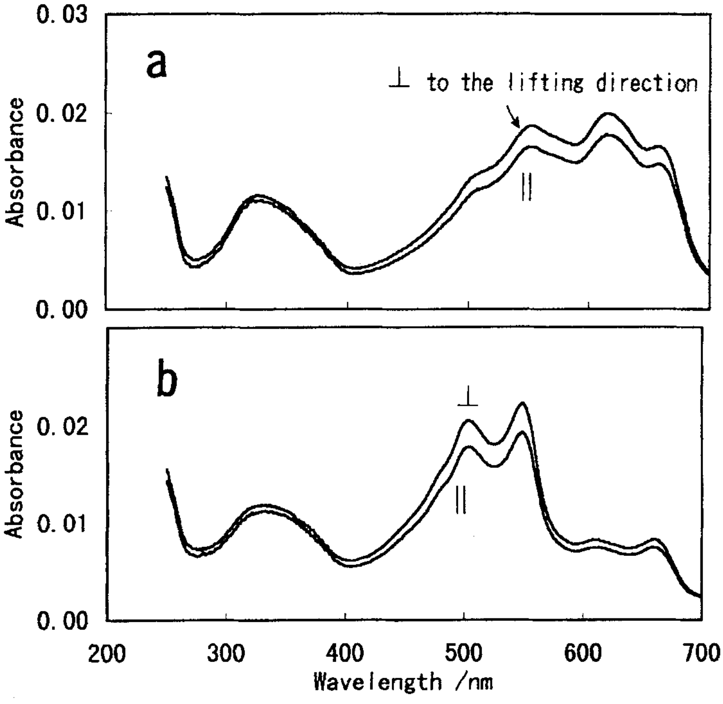

FIGURE 6 Polarized UV-visible absorption spectra of the PDA monolayer deposited on the *trans*- (a) and *cis*- (b) Az surface monolayer after sufficient 254 nm light irradiation (exposure time ≧ 120 min).

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REFERENCES

(1) For a review, K. Ichimura, T. Seki, Y. Kawanishi, Y. Suzuki, M. Sakuragi, and T. Tamaki, Photocontrols of liquid crystal alignment by command surfaces in Photo-reactive Materials for Ultrahigh Density Optical Memory, edited by M. Irie, (Elsevier, Amsterdam, 1994), pp. 55-83.

(2) K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, and K. Aoki, Langmuir, 4, 1214 (1988).

(3) K. Ichimura, M. Momose, K. Kudo, H. Akiyama, and N. Ishizuki, Langmuir, 11, 2341 (1995).

(4) I. R. Peterson, Thin Solid Films, 116, 357 (1984).

(5) G. Veale and I. R. Peterson, J. Colloid Interface Sci., 103, 178, (1985).

(6) B. Tieke, Adv. Polym. Sci., 71, 79 (1985).

(7) B. Tieke, G. Wegner, D. Naegele, and H. Ringsdorf, Angew. Chem., Int. Ed. Engl., 15, 764, (1976).

(8) R. F. Fischetti, M. Filipkowski, A. F. Garito, J. K. Blasie, Phys. Rev. B., 37, 4714 (1988).

(9) T. Seki, M. Sakuragi, Y. Kawanishi, Y. Suzuki, T. Tamaki, R. Fukuda, and K. Ichimura, Langmuir, 9, 211 (1993).