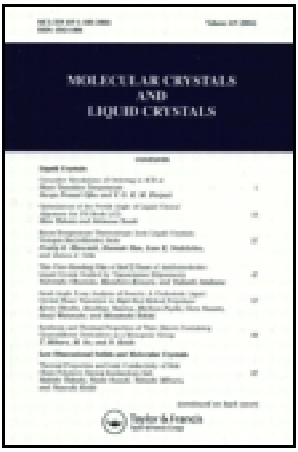

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In-Situ Microscopic Observation of Photomechanical Response in Monolayers of Azobenzene Derivatives on Water Surface

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IN-SITU MICROSCOPIC OBSERVATION OF PHOTOMECHANICAL RESPONSE IN MONOLAYERS OF AZOBENZENE DERIVATIVES ON WATER SURFACE

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Abstract Brewster angle microscopic (BAM)study was successfully achieved for a photosensitive monolayer composed of a poly(vinyl alcohol) derivative bearing an azobenzene (Az) side chain. BAM observation revealed clear differences in the morphological and rheological properties between the *trans*- and *cis*- isomerized monolayers. The morphological changes accompanied by the UV light induced expansion of this monolayer was successfully observed. An as-spread domain structured inhomogeneous monolayer was converted to a highly homogeneous one after a photochromic cycle.

INTRODUCTION

Photochromic polymer systems frequently show a macro-size photomechanical effect.[1] Observations of photochromic responses both in three dimensional materials such as films and solvent-swollen gels and in two dimensional monomolecular films (monolayers) on a water surface have been subjects of extensive investigation. Photomechanical effects in monolayers of photochromic polymers at the air-water interface have attracted a considerable interest due to their characteristic behavior taking place in a two dimensional state in which the photochromic units are arrayed or aligned.[2-11] In such systems, more detailed information on the photomechanical response is anticipated to be obtained. According to existing data, however, studies of photoresponsive polymeric monolayers have been limited to macroscopic observations such as surface pressures and film area changes. To obtain a better insight in the film deformation, an *in-situ* microscopic investigation at the air-water interface is highly required. Visualization of monolayers can be achieved either by fluorescence microscopy[12,13] or Brewster angle microscopy (BAM).[14,15] These techniques are powerful tools to obtain knowledge on morphology and rheological property of monolayers. BAM method detects reflection of light at the interface, and seems more profitable for the observation of photosensitive monolayers because it avoids use of a fluorescence probe which may influence the photochemical processes.

We reported a large area changes in a poly(vinyl alcohol) derivative bearing an azobenzene side chain which is designated as 6Az10-PVA (Chart 1).[7-9] With this material, ca. 3-fold macroscopic area expansion and contraction are observed upon alternate UV (365 nm) and visible (436 nm) illumination, respectively (Figure 1).[7-9] The photoirradiation induces polarity changes of the Az unit; the dipole moment changes from 0.5 to 3.1 D as the Az unit is isomerized from the *trans* to *cis* form.[16] It is assumed that the reversible on/off contact of the Az unit with the water surface leads to the photoinduced deformation of the monolayer (Figure 2).[7,9] This paper presents our preliminary results on the BAM observation of this photoresponsive 6Az10-PVA monolayer. Interesting dynamic nature of Az containing monolayers comprised of low-molecular-mass materials have recently been observed by BAM.[17,18]

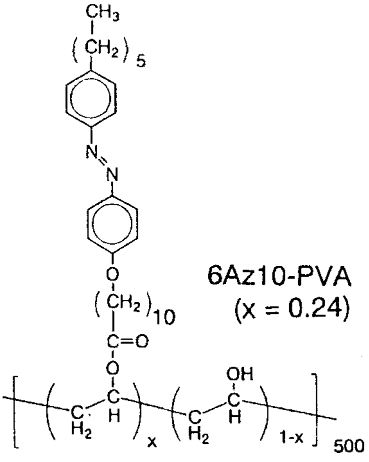

CHART 1

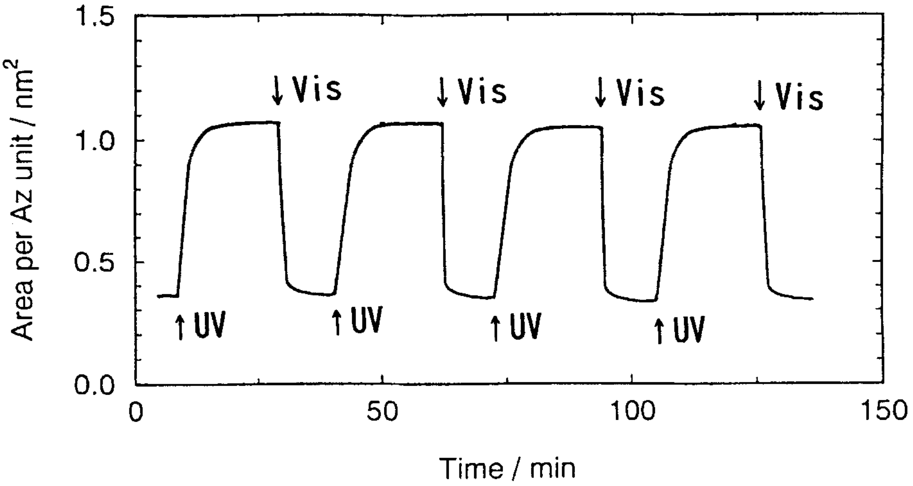

FIGURE 1 Area changes of 6Az10-PVA monolayer upon alternative UV and visible light illumination.

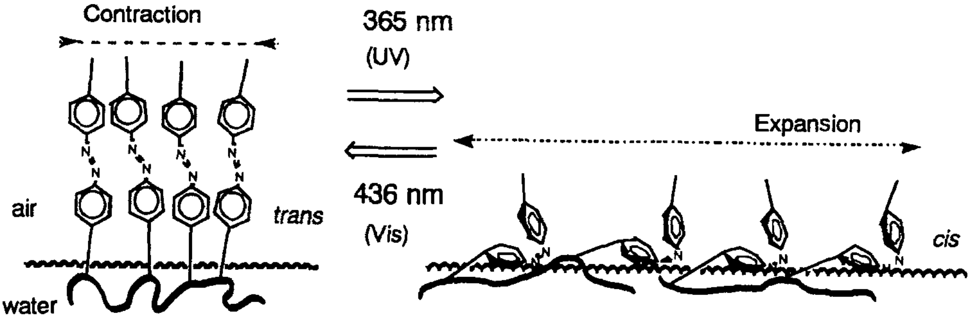

FIGURE 2 Schematic illustration of photoinduced film deformation of 6Az10-PVA.

EXPERIMENTAL

The synthesis of 6Az10-PVA was described previously.[19]

6Az10-PVA monolayer was spread on pure water (Milli-Q SP grade) filled in a Lauda FW-1 film balance at 20±0.5 ℃ from a chloroform solution (1×10^{-3} mol dm^{-3}). BAM observation was carried out with a home-built apparatus. The incoming He-Ne laser light of 30 mW was p-polarized by a Glan-Thompson polarizer at an angle of incidence of 53.1° with respect to the surface normal (Figure 3). The reflected images were taken and recorded with a Panasonic video camera connected to a TV monitor and a Hitachi video printer. UV (365 nm) and visible (436 nm) light irradiation onto the water surface was performed with a 150 W mercury-xenon lamp (San-ei UVF-202S) guided with a quartz optical fiber. Optical glass filters were equipped at the terminus of the fiber for wavelength selection.

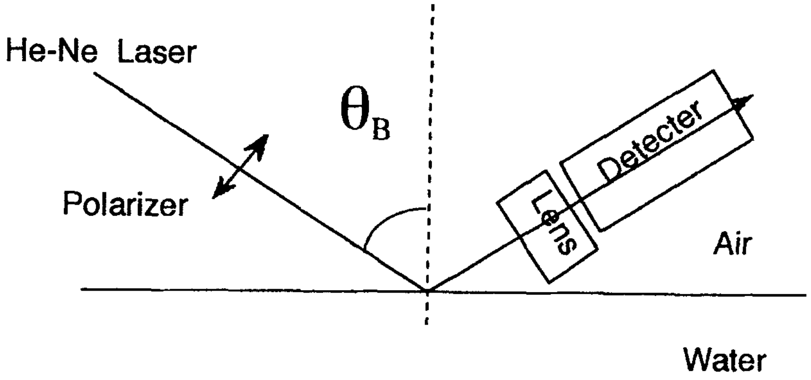

FIGURE 3 Brewster angle Microscope

RESULTS AND DISCUSSION

BAM images on the Compression Process

To obtain an insight of intrinsic properties of the 6Az10-PVA monolayer, BAM images were taken in correlation with the surface pressure-area curve. BAM images of *trans*-6Az10-PVA and *cis*-6Az10-PVA (*cis* isomer content of ca. 90 %) observed at given pressures are displayed in Figures 4 and 5, respectively.

A *trans*-6Az10-PVA monolayer at 0 mN m^{-1} exhibited an iceberg-like domain structure having solid boundaries (Figure 4, A). When a large domain was damaged mechanically with a needle tip, cracking of the domain was observed. This indicates that *trans*-6Az10-PVA monolayer is rigid and solid-like. At a surface pressure of 2 - 3 mN m^{-1}, the domains started to fuse one another (B) and formed a homogeneous monolayer until the collapse pressure (C). When the monolayer was compressed beyond the collapse point below 0.2 nm^2 per Az unit area, bright stripes of ca. 0.1 mm widths appeared (D), clearly indicating a collapse of the rigid monolayer. The direction of the stripes was orthogonal to the compression direction. Similar BAM observation of stripes in a collapsed state was reported by Hirano and Fukuda[20] for monolayers composed of polyamic acid tertiary amine salts.

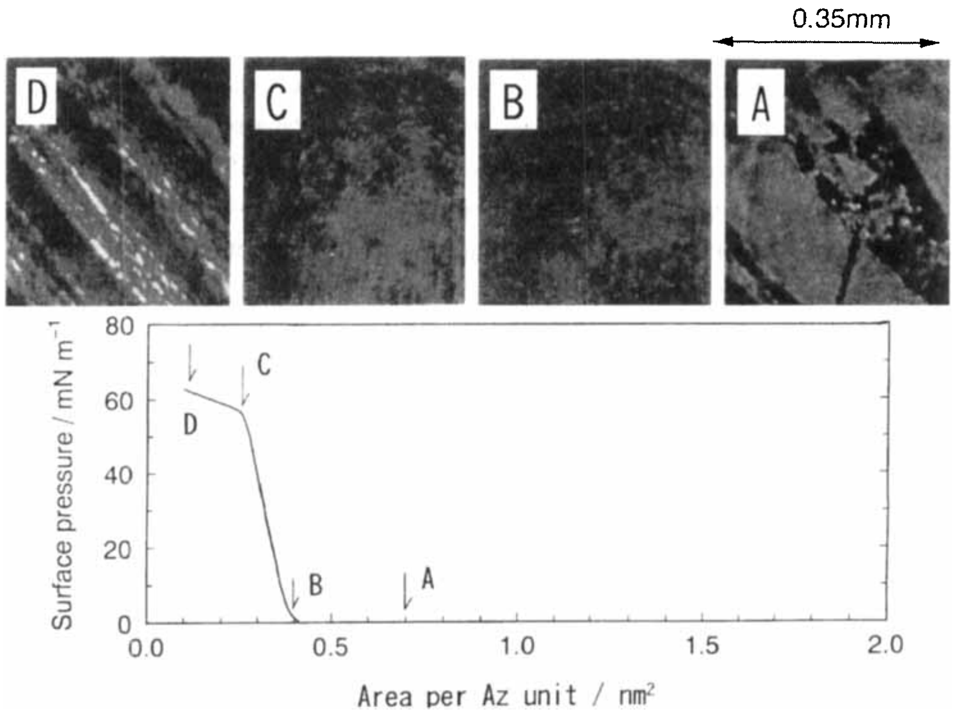

FIGURE 4 Surface pressure-area curves of a *trans*-6Az10-PVA monolayer at 20 ℃, and BAM images taken at given areas indicated by arrows A - D.

A *cis*-6Az10-PVA monolayer was highly homogeneous in all area regions (Figure 5). The reflected light at an expanded state (A) was very weak and the *cis* film was difficult to be distinguished from the water surface. This should be attributed to reduced film thickness and lowered density. Lu and Nakahara[21] observed a melting process of long chain fatty acid monolayers by BAM, and according to their data, the light reflectivity of the melted fatty acid monolayers was also largely reduced. On the process of compression, the reflected light became stronger in almost proportional to the area decrease (A - D). Interestingly, even after the film collapse below 0.3 nm^2, the film maintained homogeneous morphology with an enhanced light reflection (D). The above facts imply that the *cis*-6Az10-PVA monolayer is fluid and highly amorphous.

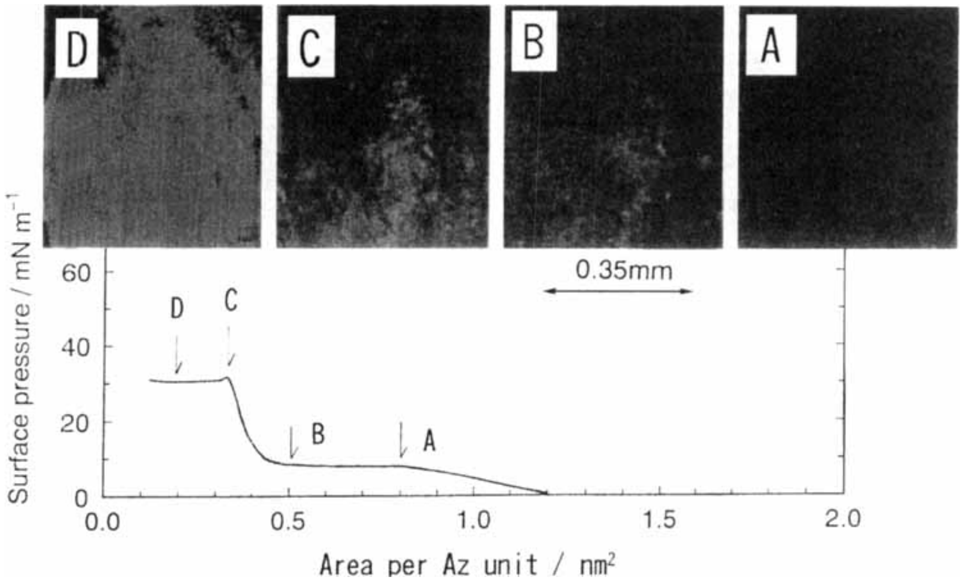

FIGURE 5 Surface pressure-area curves of *cis*-6Az10-PVA (*cis*-isomer content of ca. 90 %, lower) monolayer at 20 ℃, and BAM images taken at given areas indicated by arrows A - D.

Direct Observation of UV Light-Induced Film Deformation

Figure 6 shows the direct observation of UV light induced morphological changes of the 6Az10-PVA monolayer. The *trans*-6Az10-PVA monolayer was locally irradiated with UV light (3 mW cm^{-2}) around the microscope field, and the BAM images were taken before (a) and after UV irradiation (b - d). UV light irradiation was achieved at 0 mN m^{-1} so that changes of domain contours could be readily monitored. Upon UV light irradiation, clear contours of iceberg-like domains of the domains of the *trans* monolayer (a) immediately became obscure (b) and the canal-like water surface between domains became narrower (c). Finally a homogeneous image which was characteristics of the *cis*-monolayer was obtained (d). This presents the first real time direct observation of morphological changes in a photoresponsive monolayer.

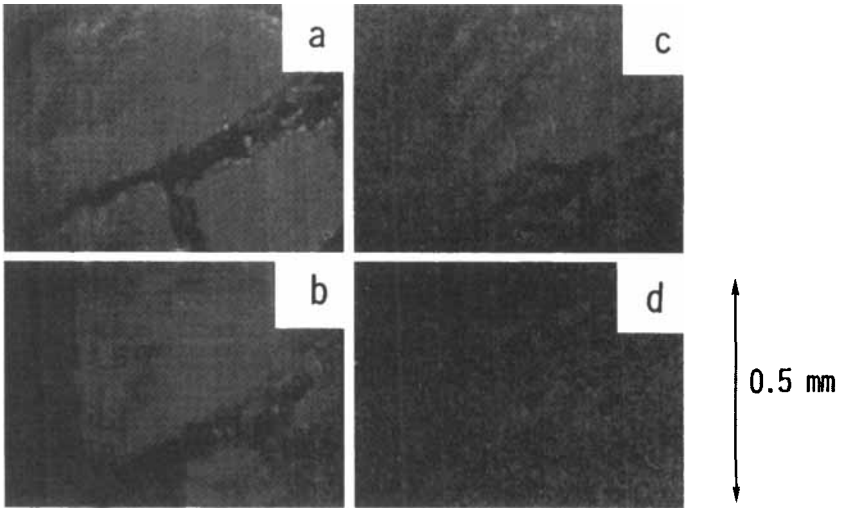

FIGURE 6 *In-situ* observation of photoinduced morphological changes of 6Az10-PVA monolayer induced by locally irradiated UV light (3 mW cm^{-2}). Images were taken before (a), and after irradiation for 1 s (b), 2 s (c) and 3 s (d).

Morphological Changes on the Cyclic Process

Morphologies of 6Az10-PVA monolayer were then observed on a cycle process (UV →visible) under irradiation of the whole film area at 2 - 3 mN m^{-1} (Figure 7). Most of the experiments on the photomechanical response have been made under these conditions.[7-9] In the present experiment, the film area was simultaneously monitored, and a 3-fold film deformation was actually observed. The initial *trans*-6Az10-PVA monolayer consisting of irregularly shaped domains (a) became homogeneous after UV light irradiation (b) as stated above. The following contraction process on visible light irradiation resulted in a highly homogeneous monolayer (c). The reverted monolayer was cracked by a mechanical damage (d), exhibiting the rheological character of *trans*-6Az10-PVA film. Difference in the film homogeneity between the as-spread (a) and photochemically reverted (c) *trans* monolayer is worth mentioning. Long chain fatty acid monolayers in the as-spread monolayer is worth mentioning. Long chain fatty acid monolayers in the as-spread state mostly show heterogeneous domained morphology, but they can be converted to more homogeneous films by annealing.[22,23] In the present system, a homogeneous film was isothermally obtained by the irradiation process instead of heating. The microscopic observation studied here explains our remaining question on the macroscopic area change behavior that the monolayer area of 6Az10-PVA was thoroughly reverted to the original one after an irradiation cycle.[7] This is not fully understood only from a viewpoint of the *trans* unit content since the as-spread monolayer contains 100 % *trans* units whereas the light reverted state should contain ca. 10 % of *cis* isomers. The initial monolayer thus involves unoccupied water surface among the rigid domains, and after irradiation, the involvement of ca. 10% *cis*-isomers seems to be compensated for the loss of water surface.

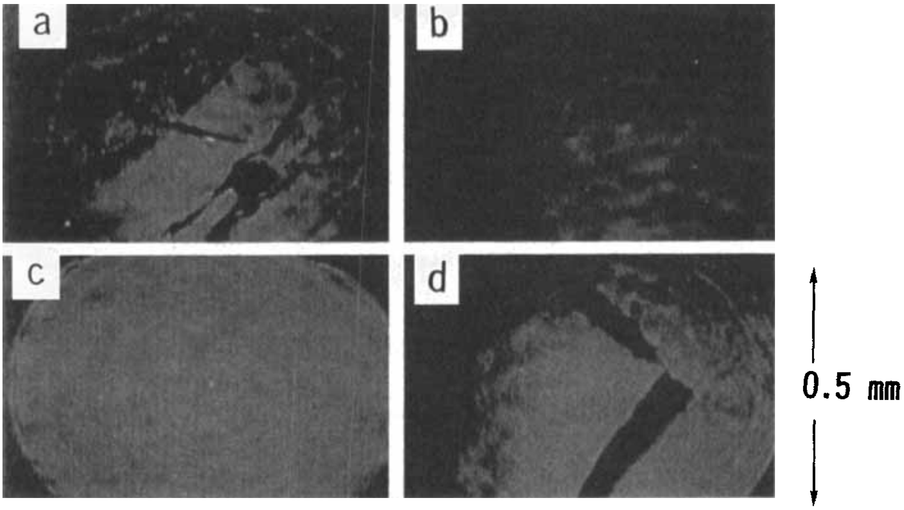

FIGURE 7 Morphological changes of 6Az10-PVA monolayer at 3 mN m^{-1} on the cyclic irradiation process. Photographs present images taken for *trans*-6Az10-PVA monolayer before irradiation (a), after UV light irradiation (0.2 mW cm^{-2} for 3h) (b), and after successive irradiation of visible light (0.7 mW cm^{-2} for 3h) (c). The photochemically reverted *trans*-monolayer (c) was mechanically cracked by a needle tip (d) to confirm the rigidity of the *trans*-monolayer.

In conclusion, morphological features of photoresponsive monolayer were successfully observed by BAM. As indicated here, direct microscopic observation of monolayers provides a new insight in the photomechanical response of photochromic monolayers.

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