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Morphological changes in monolayer of a photosensitive polymer observed by Brewster angle microscopy

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Brewster angle microscopic (BAM) observation was undertaken for a photosensitive monolayer composed of a poly(vinyl alcohol) derivative bearing an azobenzene (Az) side chain. BAM images revealed clear differences in the morphological and rheological properties between the *trans* and u.v.-light isomerized *cis* monolayers. Real time observation of the u.v. light induced expansion of this monolayer was successfully achieved. An as-spread domain structured monolayer was converted to a highly homogeneous one after a *trans*→*cis*→*trans* photochemical cycle. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: photochromic monolayer; Brewster angle microscopy; azobenzene)

Introduction

Photomechanical effects in monolayers of photochromic polymers at the air–water interface have attracted a considerable interest due to their characteristic response taking place in a two-dimensional state[1–11]. According to existing data, however, studies of photoresponsive polymeric monolayers have been limited to macroscopic observations such as surface pressures and film area changes. For a better understanding of these phenomena, an *in situ* microscopic investigation at the air–water interface is required. Visualization of monolayers can be achieved 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. The 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 large area changes in a poly(vinyl alcohol) derivative bearing an azobenzene side chain which is designated as 6Az10-PVA[7–9]. With this material, *ca.* three-fold area expansion and contraction are observed upon alternative u.v. (365 nm) and visible (436 nm) illumination, respectively[7]. 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 the *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[7]. This communication describes our preliminary results on the BAM observation of this photoresponsive 6Az10 – PVA monolayer[17,18].

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°C from a chloroform solution (1×10^{-3} mol dm^{-3}). BAM observation was carried out with a home made 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. The reflected images were taken and recorded with a Panasonic video camera connected to a TV monitor and a Hitachi video printer. U.v. (365 nm) and visible (436 nm) light irradiation onto the water surface was performed with a 150 W mercury–xenon lamp (San-ei u.v.F-202S) guided with a quartz optical fibre. Optical glass filters were equipped at the terminus of the fibre for wavelength selection.

Results and discussion

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 *Figure 1*.

A *trans*-6Az10-PVA monolayer at 0 mN m^{-1} exhibited an iceberg-like domain structure having solid boundaries (*Figure 1A*). When a large domain was damaged mechanically with a needle tip, cracking of the domain was observed. This indicates the *trans*-6Az10-PVA monolayer is rigid and solid-like. At a surface pressure of 2–3 mN m^{-1}, the domains started to fuse to 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.

A *cis*-6Az10-PVA monolayer was highly homogeneous in all area regions (*Figure 1*, lower). The reflected light at

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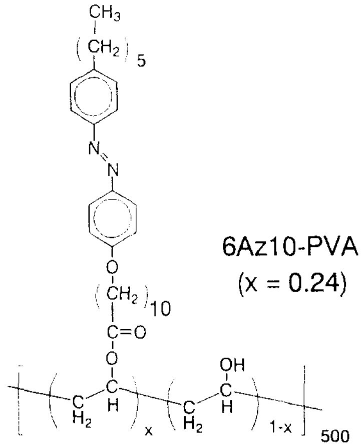

an expanded state (E) was very weak and the *cis* film was difficult to distinguish from the water surface. This should be attributed to reduced film thickness and lowered density. Lu and Nakahara[21] observed a melting process of long chain fatty acid monolayers by BAM and, according to their data,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

Figure 2 shows the direct observation of u.v. light induced morphological changes of the 6Az10-PVA monolayer. The *trans*-6Az10-PVA monolayer was locally irradiated with u.v. light (3 mW cm^{-2}) around the microscope field, and the BAM images were taken before (a) and after u.v. irradiation (b–d). U.v. light irradiation was achieved at 0 mN m^{-1} so that changes of domain contours could be readily monitored. Upon u.v. light irradiation, clear contours of iceberg-like 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 characteristic of the *cis*-monolayer was

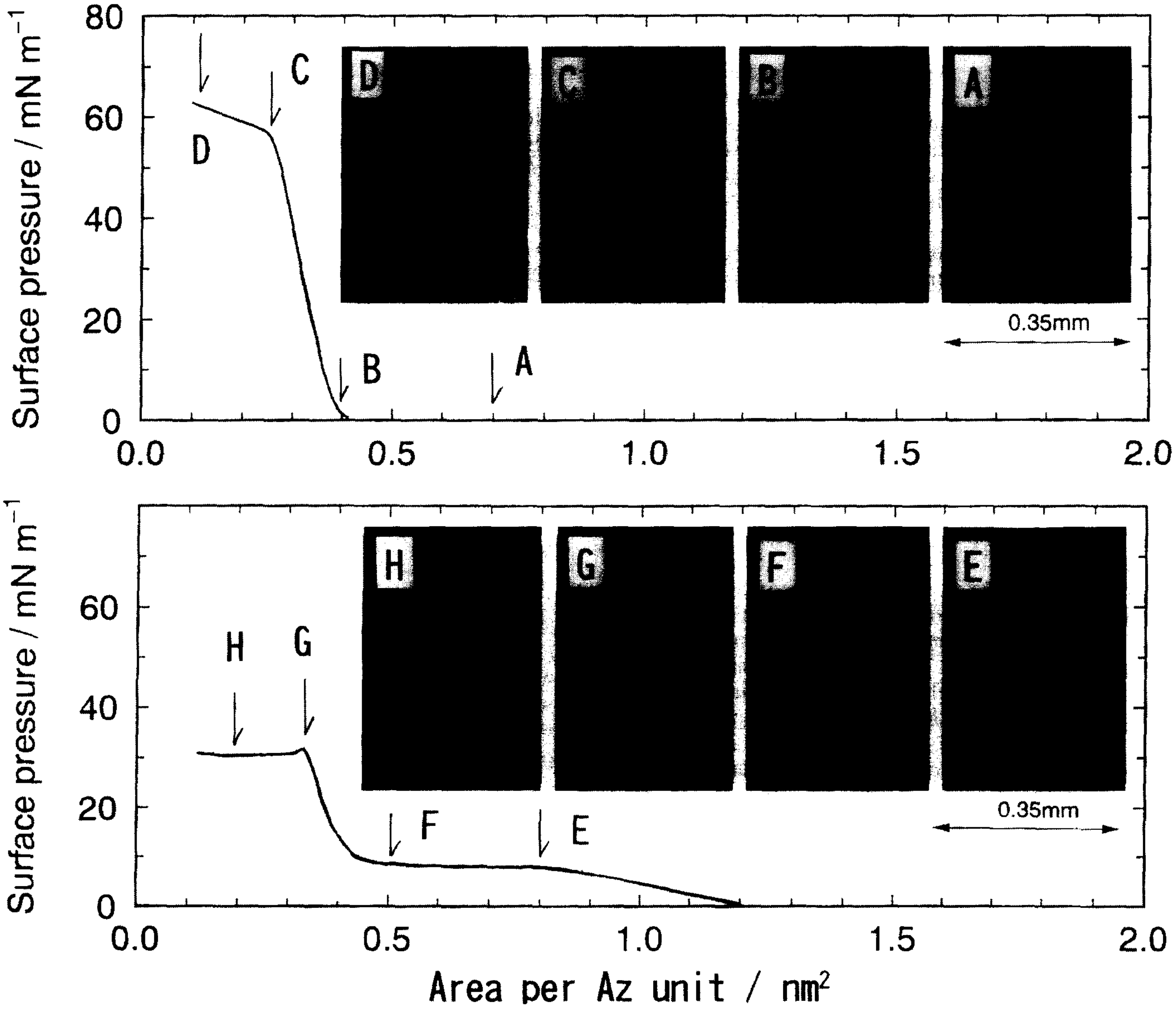

Figure 1 Surface pressure–area curves of *trans*-6Az10-PVA (upper) and *cis*-6Az10-PVA (*cis*-isomer content of *ca.* 90%, lower) monolayers at 20°C, and BAM images taken at given areas indicated by arrows A–H

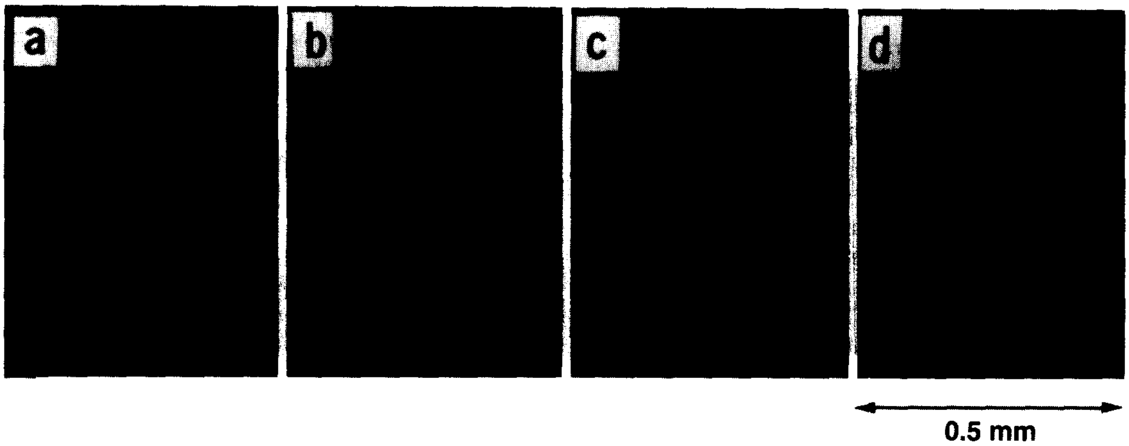

Figure 2 *In situ* observation of photoinduced morphological changes of 6Az10-PVA monolayer induced by locally irradiated u.v. light (3 mW cm^{-2}). Images were taken before (a), and after irradiation for 1 s (b), 2 s (c) and 3 s (d)

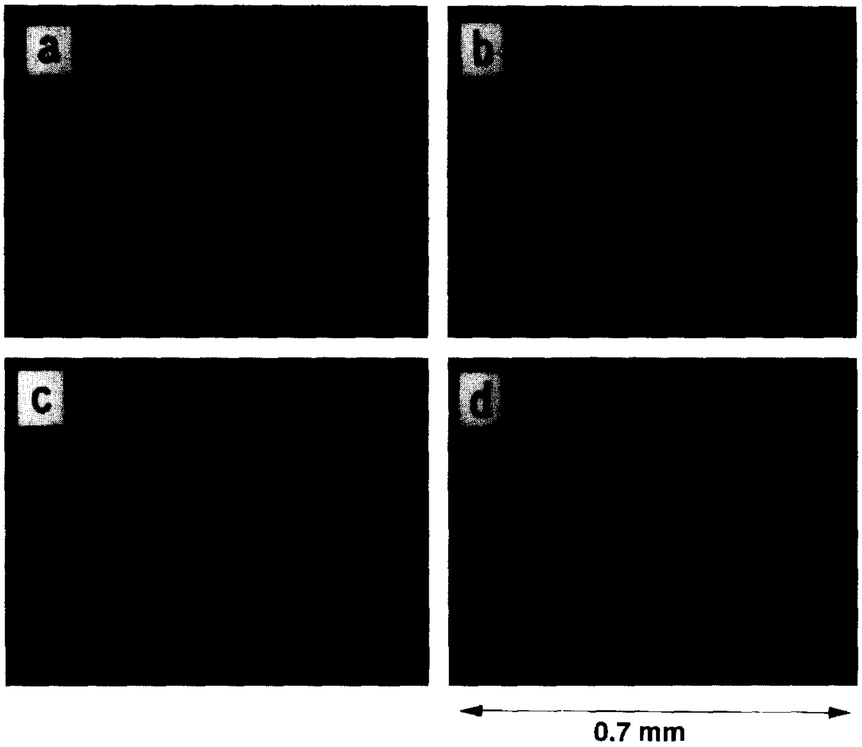

Figure 3 Morphological changes of 6Az10-PVA monolayer at 3 mN m^{-1} on the cyclic irradiation process. Photographs present images taken for *trans*-6Az10-PVA monolayer before irradiation (a), after u.v. light irradiation (0.2 mW cm^{-2} for 3 h) (b), and after successive irradiation of visible light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

obtained (d). This presents the first real time direct observation of morphological changes in a photoresponsive monolayer.

Morphologies of 6Az10-PVA monolayer were then observed on a cycle process (u.v.→visible) under irradiation of the whole film area at 2–3 mN m^{-1} (*Figure 3*). Most of the experiments on the photomechanical response have been made under these conditions[7–9]. In the present experiment, the film area was monitored simultaneously, and a three-fold film deformation was actually observed. The initial *trans*-6Az10-PVA monolayer consisting of irregularly shaped domains (a) became homogeneous after u.v. 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 state mostly show heterogeneous domain 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 behaviour 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.

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

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