Photomechanical Response of Azobenzene Containing Monolayers on Water Surface

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Monolayers of amphiphilic poly(vinyl alcohol)s and related low-molecular-mass compounds containing photochromic azobenzene (Az) were spread on a water surface. Their photomechanical responses induced by photoirradiation of UV (365 nm) and visible (436 nm) light were investigated. Illumination by UV light induced area expansion of Az monolayers up to ca. three times in magnitude, which strongly depended on the material, monitoring surface pressure, and subphase conditions. The expanded film of these molecular films reverted to the original area upon illumination with visible light. Use of a polymeric material was found to be advantageous to attain sufficient mechanical strength for full reproducibility and faster response. At a fixed area, reversible surface pressure changes were observed upon alternate UV and visible light illumination, and at 10—15 $\mathrm{mN\,m^{-1}}$ with the 6Az10-PVA monolayer the changes could be visualized plainly by watching motions of camphor grains. In the case of an Az amphiphile having the dissociative carboxylic acid head group, the photoresponsiveness was altered by pH changes and addition of $\mathrm{Cd^{2+}}$ ion in the subphase. Variations in the magnitude and response time of the photoinduced deformation were related to the packing state of Az monolayers evaluated by UV-visible absorption spectroscopy at the air–water interface.

Polymeric gels have been occupying the central position in the research field of stimuli-responsive materials.¹⁾ These soft materials are quite promising for the future industries such as artificial actuators, highly selective membrane for separation, drug delivery systems, and medical utilities.¹⁾ Light stimulated mechanical responses have been successfully attained by use of photochromic molecules.²⁾ Among many types of photoresponsive materials, monolayer systems at the air- water interface seem to us fascinating for observation of mechanical responses. In the oriented molecular films macroscopic deformations of materials can be directly explained in terms of summation of individual molecular processes; such an explanation is extremely difficult in three-dimensional randomly oriented bulk or gel systems. Therefore, studies of monolayer systems should provide important data for essential understanding of the mechanism of stimuli-responsiveness at the molecular levels.

Two typical photochromic units: spirobenzopyran and azobenzene (Az), have been utilized for observation of the photoresponsive monolayers. Both low molecular mass amphiphiles³⁻⁵⁾ and polymeric materials⁶⁻¹⁵⁾ have been used, the polymer systems have been attracting more attention in recent years. Rondelez's group⁶⁻⁸⁾ dealt with monolayers from copolymers of methyl methacrylate bearing a spiropyran unit, while Blair et al.⁹⁾ reported photoresponsive poly(methyl methacrylate) monolayers containing photochromic molecules as additives. For these spiropyran containing monolayers, UV light illumination generates the photomerocyanine form, and commonly causes film expansion due to increased attractive interaction of this unit with the water surface. Az containing monolayers have also been explored with large varieties of materials, and have been found to behave in more complicated manners depending on the molecular structures. Blair et al.¹⁰,¹¹⁾ reported earlier the photomechanical effects in Az polyamids. For these materials, UV illumination induced contraction of monolayers, and in particular cases, a slow expansion process follows as the result of a secondary relaxation. Bio-related polypeptides bearing Az unit in the side residue were also explored.¹²⁻¹⁴⁾ Malcolm and Pieroni¹²⁾ found UV-light induced contraction of a monolayer of an Az-containing poly(L-lysine) derivative. Poly(L-glutamate) derivatives having Az side chain were investigated by Menzel.¹³⁾ Their monolayers, in contrast, exhibited photoinduced expansion. Higuchi et al.¹⁴⁾ reported quite recently the photoresponsive behavior of monolayers of a poly(L-glutamate) derivative in which an Az unit bridges two helical rods.

We have been studying the photomechanical behavior of poly(vinyl alcohol)s having an Az side chain. Our previous

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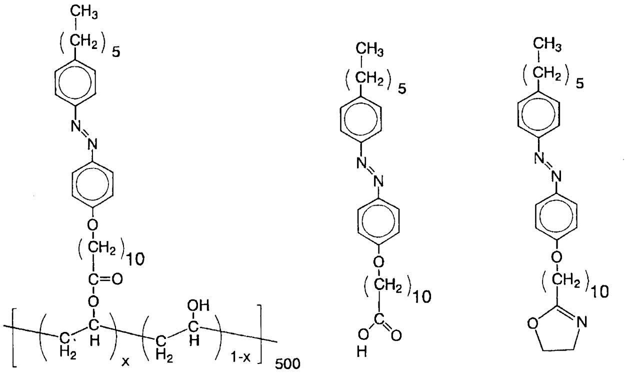
report[15] showed that these monolayers exhibit a large expansion upon UV light illumination. A typical material, 6Az10-PVA, is indicated in Chart 1. This film deformation behavior can not be understood by the shape change of the Az unit, but is explained by motions of reversible contact/detachment of Az unit with the water surface. This behavior is attributed to the polarity change of this unit accompanied by the *cis/trans* photoisomerization (Fig. 1). The *trans* to *cis* photoisomerization of Az chromophore is known to induce a large polarity change from a dipole moment of the Az unit in the *trans* form of 0.5 D to 3.1 D in the *cis* form.[16] The model mentioned above is justified by good agreement with molecular areas obtained by surface pressure–area curves with anticipated dimension of molecules for the series materials with varied spacer lengths.[15] For the polymer having the methylene spacer of ten carbons between the hydrophilic part and the Az unit, the UV light induced expansion causes an approximately three times increase in area when the monolayer area is monitored at 2—3 mN m^{-1}. To our knowledge this is the largest photochemical area change in monolayers hitherto reported.



6Az10-PVA (x = 0.24) 6Az10COOH 6Az10-Oxa

Chart 1.

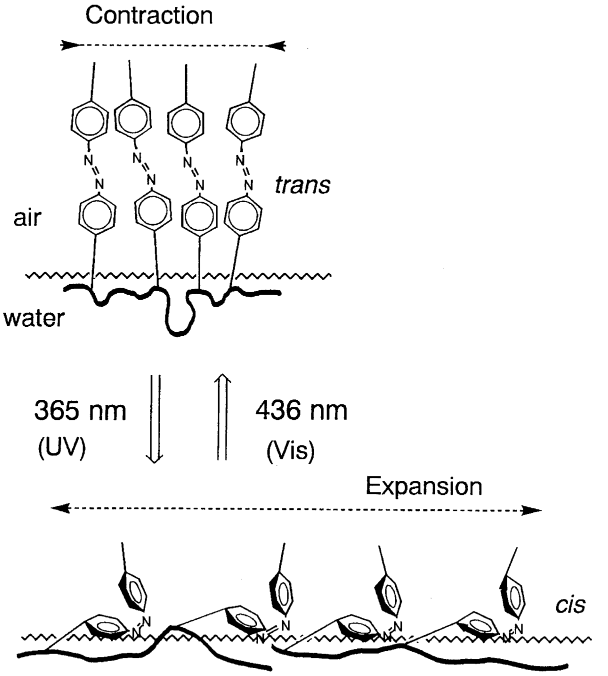


Fig. 1. Schematic illustration of UV and visible light induced deformation of a polymeric Az monolayer at the air–water interface. In the process of *trans* to *cis* photoisomerization upon UV light illumination, the Az unit increases its polarity and experience attraction from the water surface. This movement induces film expansion of the monolayer. Upon visible light illumination the reverse process takes place, resulting in photocontraction.

On the basis of the above observations, this paper describes our extension of this work to related Az monolayers including polymeric and low-molecular-mass amphiphiles.[17] The Az materials have the common structure except for the variations in the hydrophilic head part, which are denoted as 6Az10-PVA, 6Az10COOH, and 6Az10-Oxa (Chart 1). In this paper, we will show some important roles of the head part in the photomechanical behavior. Differences in the photoinduced expansion process observed in various Az monolayers are shown to depend on the Az packing state evaluated by UV-visible absorption spectroscopy.

Experimental

Preparation of 6Az10-PVA and 6Az10COOH was described previously.[18] The material with the oxazoline head 6Az10-Oxa was synthesized in our laboratory; the procedure will be reported elsewhere.

Observation of photomechanical effects in Az monolayers were performed on a Langmuir trough of a Lauda FW-1 film balance at 21 °C equipped in a dark room. The photochemically induced area expansion and contraction were observed as follows. The Az derivative in the *trans* form dissolved in chloroform (1×10^{-3} mol dm^{-3}) was spread on a given water subphase. After the solvent had evaporated, the monolayer was compressed and unless stated otherwise, the surface pressure was maintained at 2 mN m^{-1}. UV (365 nm) or visible (436 nm) light from a 150 W high pressure mercury lamp passed through appropriate Corning optical grass filters was used to irradiate the top of the water surface. The light beam was spread to allow irradiation of the entire film area at all times in the most expanded state of monolayers. The terminus of the optical fiber was set 25 cm above the water surface. The exposure energy of UV irradiation around the center was ca. 2 mW cm^{-2}.

The UV-visible absorption measurement of floating monolayers was carried out using an Ohtsuka Electronics MCPD-1000 (28c) system equipped with a 150 W xenon lamp quartz optical fiber. A beam reflected by a mirror at the bottom of the trough passed through the Az monolayer and was led to a multichannel photodiode array detector of MCPD-1000. The sampling time was 100 ms, and 25 spectra were integrated.

Results and Discussion

1. Spreading Behavior of Az Monolayers. Figure 2 represents the surface pressure-are a (π–A) curves of Az monolayers upon continuous compression at 50 cm^2 min^{-1} at 21 °C. Monolayers were spread from the *trans* (solid line) and UV-irradiated (dotted line) chloroform solutions. For the UV irradiated solution, the *cis* content was ca. 90% at the photostationary state. For simplicity, it is denoted as *cis*-

Az monolayers. *Cis*-Az monolayers in the low surface pressure region were commonly expanded by factors of above three. The limiting area of the *trans* monolayer evaluated as extrapolation from the steepest region increased in the order of 6Az10COOH (0.25 nm^2), 6Az10-Oxa (0.33 nm^2), and 6Az10-PVA (0.37 nm^2). These area variations reflect the differences in the lateral packing state influenced by the hydrophilic head group. The monolayer of *trans*-6Az10COOH is most densely packed, probably with a contribution of hydrogen bonding between the COOH head groups. *Trans*-6Az10-PVA monolayer occupied a larger area, which should be due to lateral steric requirement of the PVA backbone. For *trans*-6Az10-Oxa, the packing state of monolayer seem to be disordered from lack of hydrophilicity of the Oxa head group, which can result in an expansion. This may be justified by the lower collapse pressure observed compared to the other *trans* monolayers.

Cis-monolayers of the three materials, on the other hand, showed almost the same π–A features with some deviations in the surface pressure of the plateau regions ranging 0.8—0.4 nm^2 and below ca. 0.35 nm^2.

2. Photoinduced Deformation of Az Monolayers. Figure 3 indicates photoinduced area changes of 6Az10COOH (a), 6Az10-Oxa (b), and 6Az10-PVA (c). Although the light irradiation was performed to cover the whole area of the monolayer, the light intensity was not homogeneous within the entire area. The light intensity was the highest around the center part just under the optical fiber, and decreased radially at positions away from it. Due to this inhomogeneous irradiation and limitation in the speed of the mechanical servo system (50 cm^2 min^{-1}), quantitative analysis of the time profile in Fig. 3 is of limited meaning.

For the low-molecular-mass materials, 6Az10COOH and 6Az10-Oxa, the expansion process on UV illumination decreased by ca. 10% each cycle. Thus these monolayers were partially damaged during the photoinduced deformation processes. The film damage probably involves partial collapse of the monolayer state. Collapse of the monolayers is most likely to occur near the edge of the moving barrier where the largest distortion of monolayers is observed for the uniaxial compression in rectangular shaped troughs.[19] In fact, Brewster angle microscope observation of 6Az10COOH monolayer revealed that strips showing the collapsed monolayer exist near the edge of moving barrier.[20] On the contrary, the area expansion of 6Az10-PVA monolayer was exactly reproduced to the previous levels upon repetition. We consider that the polymer backbone, in this manner, mechanically reinforces the monolayer and prevents film damage.

Figure 4 compares the response behavior of 6Az10COOH

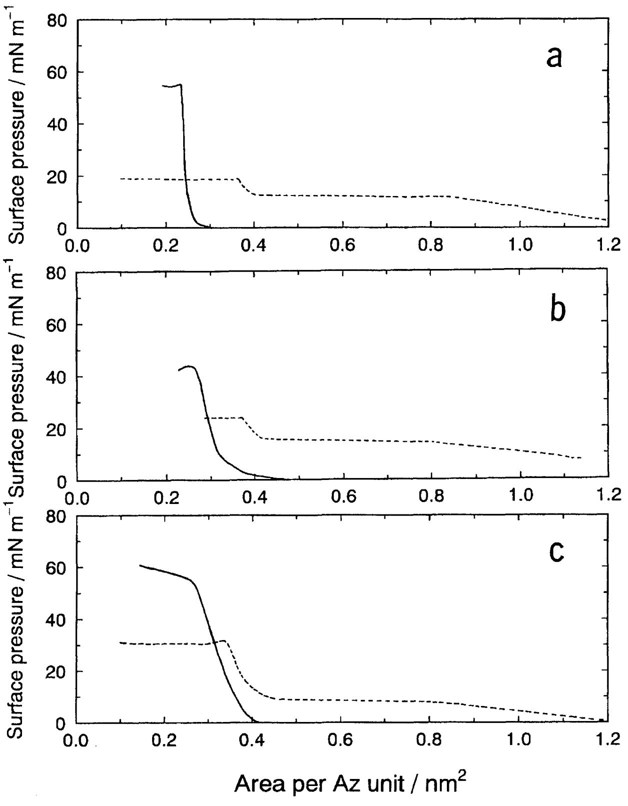


Fig. 2. Surface pressure-area curves, 6Az10COOH (a), 6Az10-Oxa (b), and 6Az10-PVA (c) on pure water at 21 °C. Solid and dotted lines indicate monolayers in the *trans* and *cis* (ca. 90% contents) form, respectively.

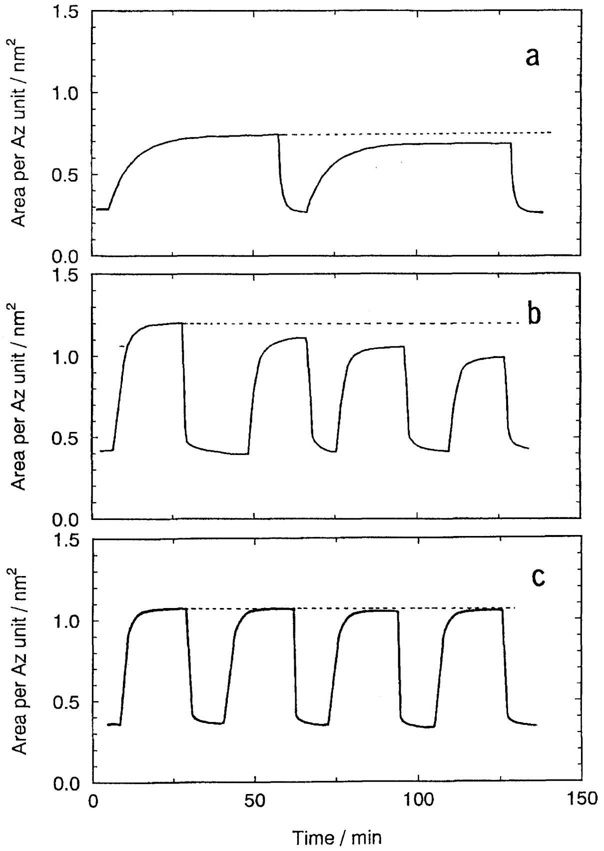


Fig. 3. Time profiles of photoinduced deformation of 6Az10COOH (a), 6Az10-Oxa (b), and 6Az10-PVA (c) at 21 °C. The exposure energy of the illumination was ca. 2 mW cm^{-2} at both 365 (UV) nm and 436 (visible) nm lines. The surface pressure was maintained at 2 mN m^{-1}.

at pH 7 and 6Az10-PVA monolayers. In this figure, the areas in the *trans* and *cis* forms are normalized at the smallest and largest area levels. When the response time is defined as the time required for the 90% deformation of the total change (T_{90}), the 6Az100-PVA monolayer expanded ca. five times faster than the 6Az10COOH monolayer. UV-visible spectroscopic measurements implied that the discrepancy in the expansion rate is due to the difference in the rate of the *trans* to *cis* photochemical process. It therefore appears that the packing state influences the rate of the *trans* to *cis* photoisomerization and accordingly the response time in the expansion process. The monolayer of 6Az10-Oxa expanded at a rate comparable to that of 6Az10-PVA. A resemblance in the 6Az10-Oxa and 6Az10-PVA monolayers can be also found in the spreading behavior in the *trans* form; the limiting area of these two monolayers was larger than that of 6Az10COOH (see Fig. 2).

The polymer backbone thus plays a favorable role in the photomechanical behavior from the viewpoints of both mechanical strength and efficient response.

The photoinduced film deformation behavior of 6Az10-PVA monolayer was observed at different monitoring surface pressures: 2, 5, and 10 mN m^{-1} (Fig. 5). The magnitude of area expansion decreased as the monitoring surface pressure increased. Factors of the film expansion at 2, 5, and 10 mN m^{-1} were 3.1, 2.8, and 1.3, respectively. The film expansion is highly suppressed at 10 mN m^{-1}. Contact of *cis* Az unit with the water surface at this high pressure region seems to be highly difficult. These situations can be predicted from the static knowledge of π–A curves shown in Fig. 2c.

Response time T_{90} increased as the surface pressure increased. T_{90} values were 4, 8, and 10 min, for surface pressures of 2, 5, and 10 mN m^{-1}, respectively. At 5 mN m^{-1} the expansion occurred in a biphasic way. At this pressure, a fast component corresponding to the expansion at 2 mN m^{-1} was followed by a slow process, and the area expansion was not fully saturated within 30 min. In contrast, the film expansion at 2 mN m^{-1} was completed within 10 min (see also Fig. 4). The slower relaxation at higher pressures seem to be a consequence of motional restrictions in a more compressed environment.

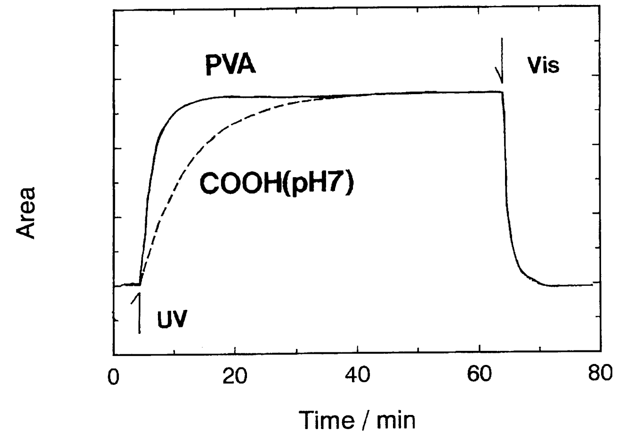


Fig. 4. Comparison of time profiles of photoinduced area changes of 6Az10-PVA (denoted as PVA) and 6Az10COOH (denoted as COOH (pH 7)) monolayers. The areas of *trans* and *cis* monolayers are normalized. The light intensity is the same as indicated in Fig. 3. The surface pressure was maintained at 2 mN m^{-1}.

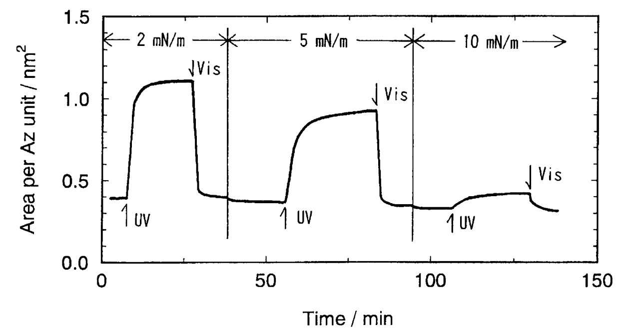


Fig. 5. Photoinduced expansion and contraction behavior of 6Az10-PVA monolayer at surface pressures of 2, 5, and 10 mN m^{-1}.

3. Visualization of Photoinduced Surface Pressure Changes. The deformation of Az monolayers was observed as changes in the surface pressure when the film area was fixed. In this work, motion of camphor grains at the air-water interface,[21] which is often called "camphor dance," were monitored as an attempt to visualize the surface pressure changes. Grains of camphor were placed on UV-irradiated 6Az10-PVA monolayer. This monolayer was gradually compressed until the surface pressure reached to 15 mN m^{-1}, and then the film area was fixed. This surface pressure corresponds to the area of ca. 0.4 nm^2. Under this condition, the camphor grains were almost at a standstill. Upon visible light irradiation, the surface pressure was reduced in a minute to 10—11 mN m^{-1}, and the camphor grains started to move accordingly. Subsequent UV irradiation induced the increase in the surface pressure, and the camphor stopped moving again. This light-triggered switching of the "camphor dance" could be repeated several times (Fig. 6).

This switching can be interpreted as the consequence of competition of the surface pressure between camphor monolayer and photo-tunable 6Az10-PVA monolayer. Changes in the surface viscosity may be the other factor that influences the motion of camphor on the water surface, but according to the recent work of Nakata et al.,[22] the primary importance of the surface pressure is implied in understanding the camphor motion. When the surface pressure in the system is above that of the camphor monolayer, which corresponds to the UV-irradiated 6Az10-PVA monolayer, camphor grains stop moving. Upon visible light illumination, the surface pressure is released below that of the camphor monolayer, and they start to move. A precise evaluation of the surface pressure of pure camphor monolayer is difficult due to its sublimative nature. Nevertheless, an approximate estimation could be made as follows. An excessive amount of camphor grains was placed on pure water; the surface pressure rose to ca. 8 mN m^{-1} and the camphor moved violently at this stage. When the water surface was subsequently compressed by the

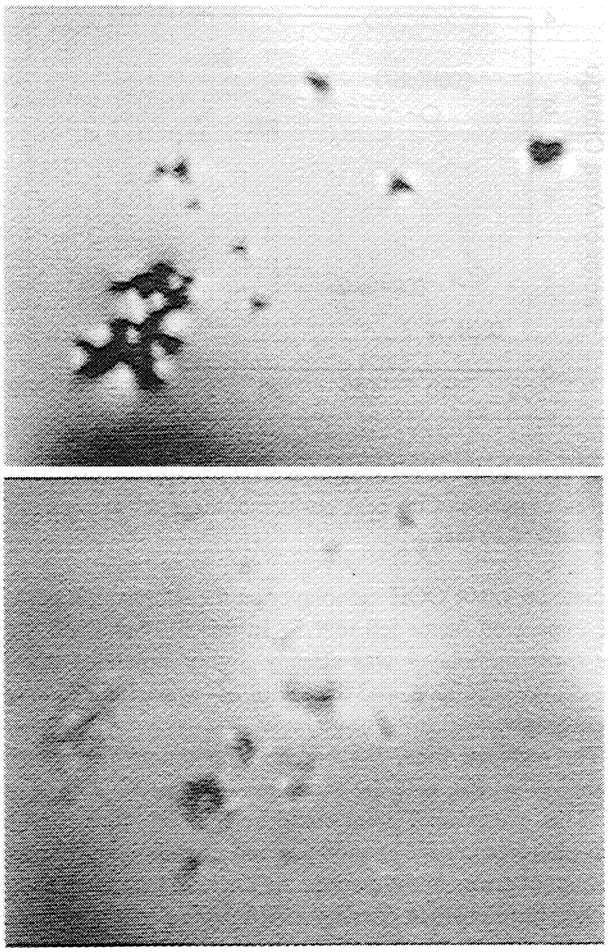


Fig. 6. Photochemical regulation of "camphor dance". Camphor grains were placed on a 6Az10-PVA monolayer. Photocontrols of the motion of camphor grains are feasible upon UV (upper, stop moving) and visible (lower, start moving) light irradiation. Motion of camphor grains was recorded on a video tape and photographs were taken from the video monitor with 0.5 s exposure time.

moving barrier at the rate of 50 cm^2 min^{-1}, and the surface pressure reached to ca. 10 $mN\,m^{-1}$. The motion of the camphor grains became obviously slower upon compression, and this pressure can be roughly regarded as a apparent surface pressure of camphor. Consequently, the photo-tunable surface pressure between 15 and 10 $mN\,m^{-1}$ of 6Az10-PVA monolayer can switch the motion of the floating camphor.

4. Chemical Modifications of Photomechanical Responses. It was anticipated that changes in the ionization state of the carboxylic acid head of 6Az10COOH would modify the photomechanical behavior of this monolayer. Figure 7 presents the photoresponse behavior of 6Az10COOH monolayers spread on the water subphase of various conditions.

On an acidic subphase at pH 2, the photochemical expansion was severely suppressed (dashed line in Fig. 7a). The first UV irradiation induced a 1.3-fold expansion, but repetition of the cycle seriously impeded the film expansion. It is known that long chain carboxylic acids in the monolayer at the air–water interface are partially charged at neutral pH.[23] Full protonation at acidic pH diminishes lateral charge repulsion of the partial anionic charge and is expected to promote lateral hydrogen bonding to a larger extent. It seems that, at the first cycle, the UV light induced a small expansion (loosening) of the monolayer which promoted protonation of the carboxylic acid group to higher extents. This may induce a closer packing of the Az monolayer after the first cycle. Even at pH 7, the presence of a divalent cation such as Cd^{2+} also suppressed the film expansion (Fig. 7b). In this case, this effect was observed from the first cycle. The UV-visible absorption spectra were measured for these monolayers. Very little photoisomerization proceeded in these densely packed monolayers.

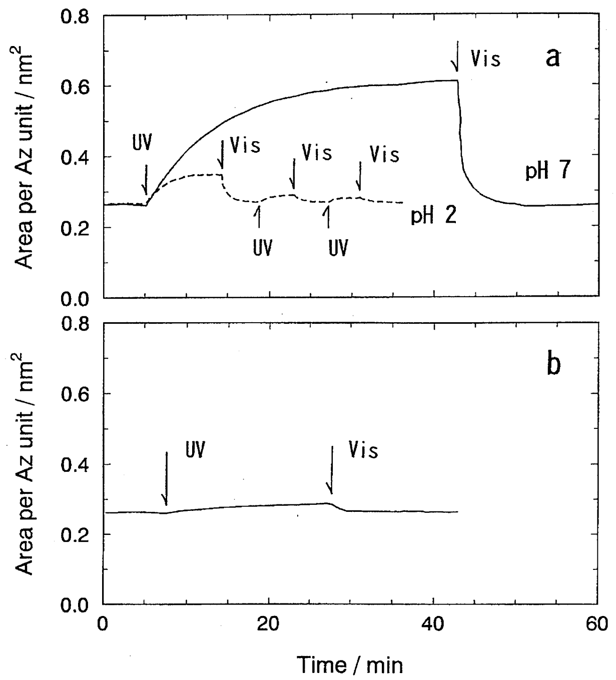


Fig. 7. Chemical switching in the photomechanical behavior of 6Az10COOH monolayer. Film expansion was suppressed at pH 2 (a) and addition of Cd^{2+} ion (b) in the subphase.

The above two examples show that modifications of the dissociative head group of the amphiphile change the packing state of Az monolayer, and consequently influence the photoresponsive behavior in crucial manners.

5. The Packing State of Az Monolayers and UV-Induced Expansion Behavior. The preceding sections demonstrated that Az monolayers show a large variety of photomechanical behavior depending on their head group structure and subphase conditions. In an attempt to understand these photoresponsive phenomena in terms of the packing state of the Az monolayers, UV-visible absorption spectra on the water surface were measured. The peak position of the π–π^* band of Az unit is well known to reflect the aggregation state of this chromophore,[24] and thus can be used as the indicator of packing state of the monolayers under investigation. These measurements were consistently carried out at the low surface pressures of 2—3 $mN\,m^{-1}$

which corresponds to optimum conditions for observation of the photomechanical effect.

Figure 8 indicates absorption spectra of the Az monolayers obtained by an optical system drawn schematically on the top of the figure. The monolayers gave absorption maxima of the π–π^* long axis band ($\lambda_{\max}$) ranging from 305 to 352 nm. Since the π–π^* absorption in solution (chloroform) is peaked at 352 nm, hypsochromic spectral shifts in all monolayers expect for 6Az10COOH (pH 12) were observed as the result of side-by-side (H-type) aggregation of the Az unit.[24]

Figures 9 and 10 summarize the factor of the film expansion upon UV light illumination and its response time, T_{90}, respectively, as the function of $\lambda_{\max}$ for the all Az monolayers examined. As seen in these figures, there exist substantial correlations between the packing state and the photoresponse properties.

$\lambda_{\max}$ of the two monolayers, 6Az10COOH at pH 2 and in the presence of Cd^{2+} shifted to the shortest wavelengths below 310 nm, and these monolayers were virtually non-photoresponsive (see Fig. 7). These monolayers are too closely packed for the Az unit to undergo the *trans* to *cis* photoisomerization (see Section 4) as was reported by Nakahara et al.[5] for a similar Az derivative. The 6Az10COOH monolayer at pH 7, 6Az10-PVA and 6Az10-Oxa whose $\lambda_{\max}$ ranged 312—337 nm gave large ca. 3-fold expansion. The fully dissociated 6Az10COOH monolayer on the subphase at pH 12, the expansion factor fell to 1.5. In this fully charged film, the *trans* monolayer was already highly expanded due to the charge repulsion, and the factor of expansion decreased accordingly.

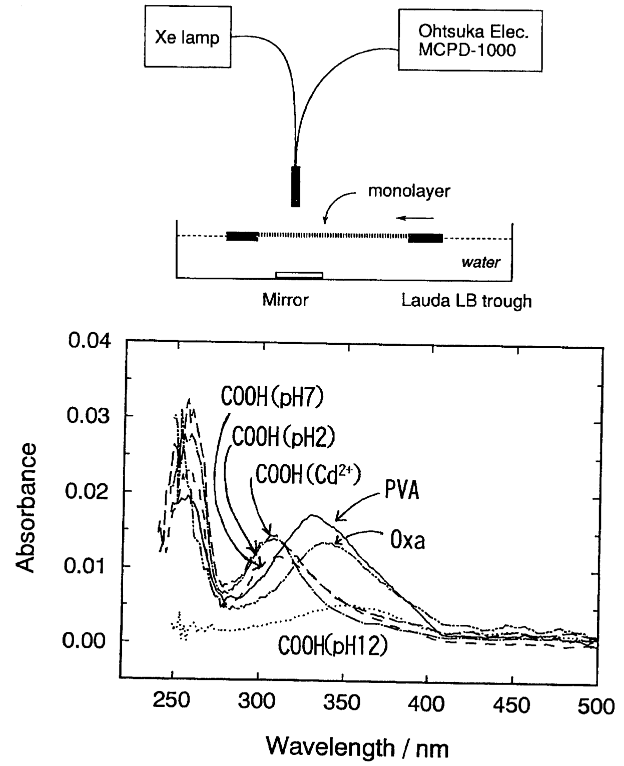


Fig. 8. UV-visible absorption spectra of Az monolayers in the *trans* state on the water surface taken at 2—3 mN m^{-1}. Notations, COOH, Oxa, and PVA represent monolayers of 6Az10COOH, 6Az10-Oxa, and 6Az10-PVA, respectively. The drawing on the top shows a schematic illustration of the spectroscopic measurement system.

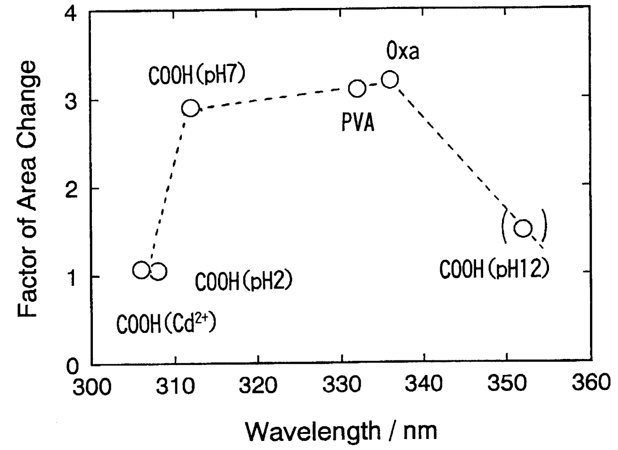


Fig. 9. Factor of area expansion upon UV light illumination as a function of the peak position of the π–π^* absorption band of Az unit.

The response time, T_{90}, had an monotonous relationship with λ (Fig. 10), with the exception of 6Az10COOH of pH 2. This exceptional point could be ignored since it is the non-photoresponsive monolayer and contains considerable amount of errors in estimation. As the rule, the more loosely packed films characterized by a shift of $\lambda_{\max}$ to longer wavelengths led to faster photo-stimulated expansion.

In contrast to the expansion process, the contraction of the Az monolayers upon visible light illumination proceeded at very close rate for all the materials investigated. This is, for example, clearly indicated by the coincidence of the time profiles for the two different Az monolayers upon visible light illumination in Fig. 4. The *cis*-Az monolayers are highly expanded, and probably there exist no individual features arising from the head group among these Az films.

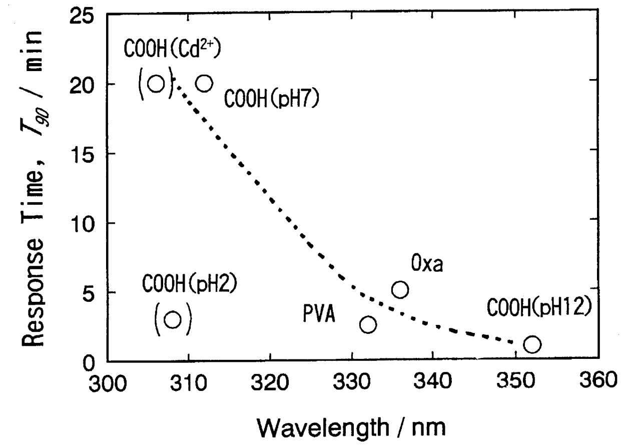


Fig. 10. Response time T_{90} for UV light induced expansion as a function of the peak position of the π–π^* absorption band of Az unit. The light intensity is the same as indicated in Fig. 3.

Thus, the *cis* to *trans* photoisomerizations take place with equal efficiencies. It can be concluded that deviations in the photomechanical response are manifest only in the UV light induced expansion process starting from the *trans* Az monolayers.

Summary

This work was undertaken to clarify the roles of the head group structure, i. e., influences of the polymer linkage and dissociation, and subphase environments in the photomechanical behavior of the floating Az monolayers. Differences in the head group structure affected, to large extents, the mechanical stability, magnitude and time constant of the UV light-induced expansion process. The following results are proposed.

(i) Polymeric amphiphiles have advantageous features in terms of mechanical strength, and promotion of quicker response in photoinduced film expansion.

(ii) Photoinduced changes in the surface pressure can be directly observed by motional changes of camphor grains.

(iii) Chemical modulations in the photomechanical response by the water subphase conditions are feasible when an amphiphile having a dissociative head group is used.

(iv) The behavior of photoinduced expansion is properly correlated with the absorption peak of the π–π^* band of *trans* Az unit which reflects the packing state of the monolayer. For the photoinduced contraction behavior upon visible light illumination, on the contrary, was similar for all the Az monolayers examined.

Investigations on photomechanical response of monolayer so far have been carried out only from macroscopic viewpoints. The next approach should involve an attempt to obtain a precise understanding of photoresponse behavior at the microscopic levels. Since the Az unit is not fluorescent, the microscopic observation by Brewster angle reflection[25,26] is most suited for this purpose. Work in this regard is now in progress.

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