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Photomechanical Effect in Monolayers of Azobenzene Side Chain Polymers

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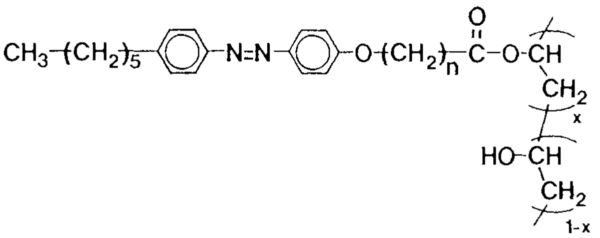
Expansion ⇄ shrinkage behaviors of photoresponsive monolayers at the air/water interface are investigated using azobenzene side chain polymers. Influence of the spacer length implies that the photomechanical effect in the present systems is attributed to the reversible on/off contact of the azobenzene side unit with the water surface.

The studies of induced mechanical effects in photochromic monolayers has been an area of great interest.1–5) Monolayers at the air/water interface provide intriguing systems for observing photomechanical effects because the interpretation of the phenomena is simplified in two dimensional and oriented molecular films compared to that of bulk materials.6–8) Monolayer systems have been explored by detecting changes in either the surface pressure1,2,4) or in the film area.3,5) For azobenzene (Az) monolayers, contraction/expansion of the interfacial monolayers has been previously reported by Blair et al.3) with polymers containing Az units in the backbone. For such backbone type polymers, photoisomerization of Az essentially induces a contraction of the film upon UV irradiation as the consequence of shrinkage in the macromolecular dimensions on the surface. In this letter we report the other type of monolayer transformation using *side chain* Az polymers having poly(vinyl alcohol) (PVA) as the backbone. With the latter polymers, film expansion occurs upon UV irradiation. A mechanism for this photoresponse is proposed.



6Azn-PVA

n=1 6Az1-PVA (x=0.29)
n=5 6Az5-PVA (x=0.42)
n=10 6Az10-PVA (x=0.24)

Chart 1.

The Az polymers employed in this work (6Azn–PVA, degree of polymerization = ca. 500) are indicated in Chart 1. The preparation of these materials and previous monolayer experiments are described elsewhere.9–11) A chloroform solution (1×10^{-3} mol dm^{-3}) of 6Azn–PVA was spread onto doubly distilled water in a Lauda MGW film balance held at 21 ± 1 °C under dimmed red light. For the photoresponse experiments, UV (365 nm) and visible (436 nm) light was alternately illuminated onto the spread monolayers. A 500 W high pressure Hg lamp equipped with appropriate Corning glass filters was used as a light

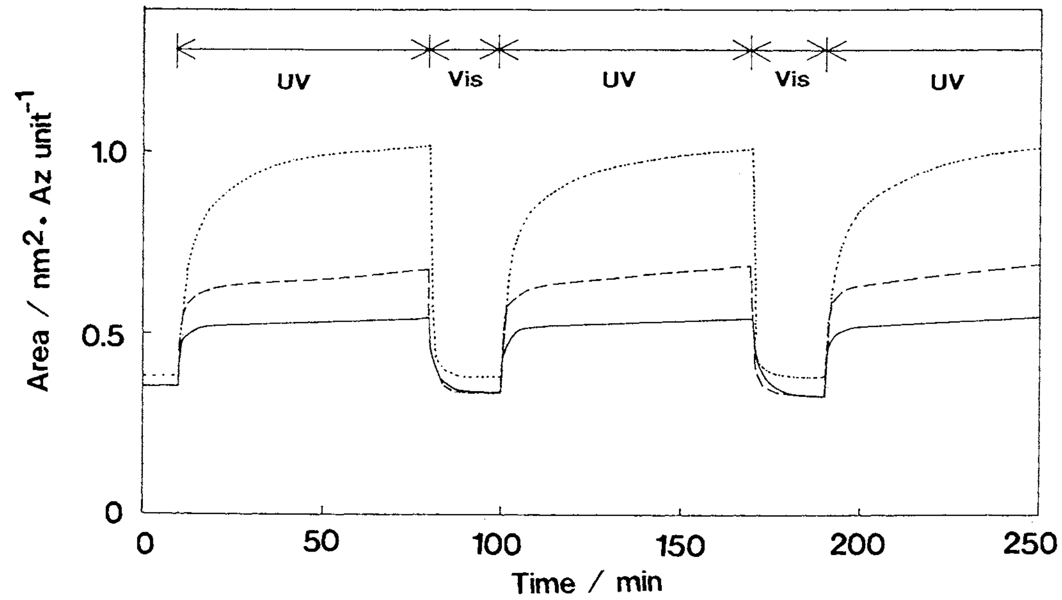


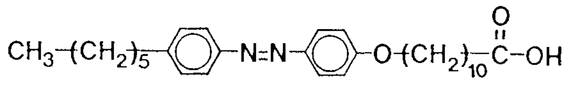
Fig. 1. Area changes of monolayers on the water surface upon alternate exposure to UV (365 nm) and visible (436 nm) radiation for 6Az1–PVA (solid line), 6Az5–PVA (dashed line), and 6AZ10–PVA (dotted line) at 21 °C. The ordinate is normalized as to indicate the area per Az unit.

source. The Hg lamp was placed at a distance of 20 – 30 cm from the air/water interface and a grazing angle was set as ca. 20° with respect to the water surface. In this geometry, the entire monolayer film was exposed to light from the lamp.

After the 6Azn–PVA monolayer (trans–form) was spread on the water surface, the moving film barrier of the trough was adjusted so as to monitor the film area at a constant surface pressure of 2 – 3 mN m^{-1}. Figure 1 shows the area changes of 6Azn–PVA monolayers on the water subphase upon alternate exposure of UV and visible radiation. Light induced area changes of the monolayer films were observed for all three polymer systems. In the figure, the ordinate indicates the area per Az unit. The film expanded when irradiated with UV light and shrunk with visible light, and the area changes were completely reversible. Both the expansion and contraction behaviors were monophasic, which is not always applicable for the Az backbone polyamides of Blair et al.[3] At the photostationary state on UV illumination, the film area increased by a factor of 1.5, 1.9, and 2.7 of the initial (trans) state, for 6Az1–PVA, 6Az5–PVA and 6Az10–PVA, respectively.

For obtaining the reversible photoinduced area changes, use of polymeric materials was essential. A monomer analog, 6Az10COOH, did not sufficiently sustain the pressure from the moving bar when illuminated with UV light, thus the reversibility was poor.

The thermal artifacts from the Hg lamp and non–irradiative relaxation of the excited chromophore can be ruled out. The temperature of the water subphase was carefully monitored



6Az10COOH

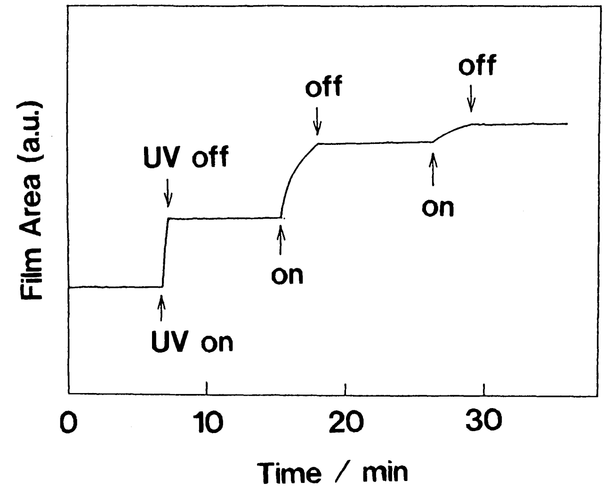


Fig. 2. Monitored area changes of 6Az10-PVA on the water surface upon interrupted UV exposure.

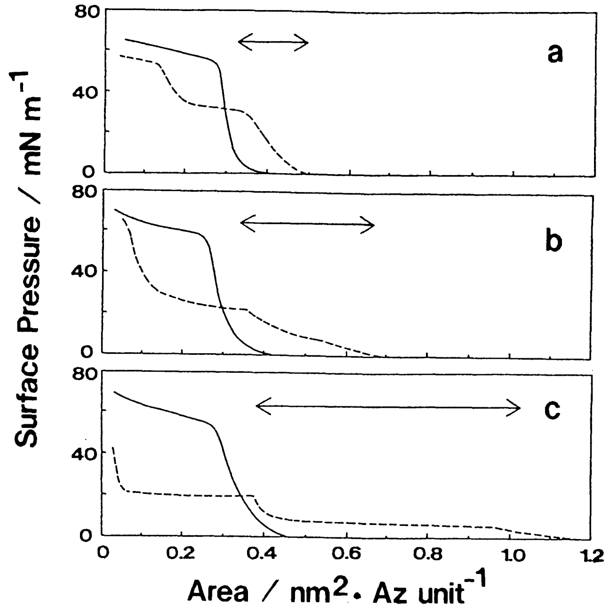


Fig. 3. Surface pressure–area isotherms per Az unit for 6Az1–PVA (a), 6Az5–PVA (b), and 6Az10–PVA (c) at 21 °C, redrawn from Ref. 10 (Fig. 2). Monolayers are spread in the trans (solid line) and cis (dashed line) forms.

throughout the irradiation experiments with a platinum resistance thermometer, and no significant temperature increase was detected. In addition, when the irradiation was stopped at midpoints of saturation, then re-illuminated, the film response followed exactly these procedures without an appreciable time delay (Fig. 2). This indicates that the area changes are uniquely a function of the cis/trans ratio of the Az unit in the monolayer.

Figure 3 indicates the surface pressure–area isotherms (π–A curves) per Az unit of 6Azn–PVA, redrawn from Fig. 2 of Ref. 10. The 6Azn–PVA was spread in the trans-form (solid lines) and in the pre-isomerized cis-form (90 % of the total Az units) (dashed lines). The photoresponse in Fig. 1 is in agreement with the π–A isotherms in that the area of the photostationary states of Fig. 1 coincides with the area position at 2 – 3 mN m^{-1} in the π–A curves of Fig. 3. The variable region over which the monolayer area varies is exhibited by the horizontal bars in the figure.

From the shape of the π–A isotherms, the following can be deduced: In the trans form, π–A curves of the three polymers are nearly identical regardless of the spacer length (the limiting area per Az ranges 0.31 – 0.38 nm^2), implying that the Az chromophore remains in the air phase without substantial interaction with the water subphase. On the other hand, the profound spacer effect for the cis monolayers may be understood by assuming direct contact of the chromophore with the water surface due to increased polarity of the cis form. Macroscopically this event is observed by an increased wettability for water of Az containing materials.$^{12)}$ If both the PVA backbone and the cis-Az unit contact with the water surface, the dimension of the connecting spacer should critically influence the occupying area. This interpretation is consistent with rough area estimation of occupying areas of planarly laid alkyloxybenzenes on the basis of the Van der Waals radii and monolayer data of Az derivatives.$^{13)}$ With assumptions that (i) one methylene unit occupies ca. 0.067 nm^2 and (ii) the half area of 4,4'-bis-substituted azobenzene (0.37 nm^2)$^{13)}$ nearly corresponds to that of phenyl moiety, methoxyenzene (model compound for cis-6Az1-PVA), pentyloxybenzene (for cis-6Az5-PVA), and decyloxybenzene (for cis-6Az10-PVA) should occupy area of approximately 0.50, 0.77, and 1.10 nm^2, respectively. The observed area data per cis-Az unit in the low pressure region in π-A curves of Fig. 3 are comparable to these values.

In conclusion, the direction of film transformation depends on whether the Az unit is introduced into the backbone or into the side chains. Therefore, different mechanisms on the photoinduced effect must be considered in each case. For the backbone polymers, the shape change, namely, bending of the Az unit induces film contraction on UV irradiation.3) For side chain polymers, by contrast, the increased polarity of the cis-Az unit initiates a film expansion. Figure 4 displays a cartoon representation of photoinduced dynamic response that is proposed to take place in 6Azn-PVA monolayers. In this model, contact = detachment of the Az chromophore with the water surface induces the macroscopic expansion = shrinkage of the monolayer films, and the magnitude of film transformation is controlled by the molecular structure, i.e., the spacer length of the side chain.

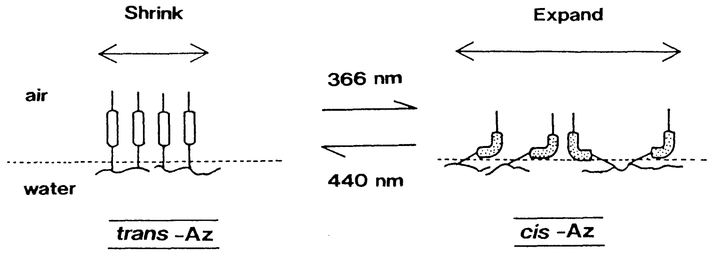


Fig. 4. Proposed mechanism of photoinduced reversible film expansion ⇄ contraction in monolayers of side chain type Az polymers.

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