Photomechanical Response in Monolayered Polymer Films on Mica at High Humidity

Takahiro Seki,* Keisuke Tanaka, and Kunihiro Ichimura

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Received May 7, 1997
Revised Manuscript Received August 8, 1997

Stimuli-induced mechanical responses in polymeric materials and their understandings now constitute a major subject area in polymer science due to their potential applicability to new industrial uses such as biomedical and soft-mechanical devices.[1] For fabrication of photoresponsive materials, a wide variety of photochromic polymers have been investigated.[2,3] Photoinduced conformational changes of photochromic polymers cause macrosize changes in dry films,[2] viscosity changes or sol−gel transitions in solutions,[3] and deformation of cross-linked solvent-swollen gels.[3]

Reduction of dimensionality in materials can exclude phenomenological complexities, and in this context, several groups have attempted to observe mechanical responses in monolayered photochromic polymers floating on a water surface.[4−10] In monolayers, the aligned constitution of photochromic units at the interface allows efficient macroscopic deformations. We have demonstrated that the monolayer of a poly(vinyl alcohol) derivative having an azobenzene (Az) side group (6Az10-PVA, Chart 1) exhibits a large (ca. 3-fold) and reversible photoinduced expansion and contraction upon alternate UV and visible light illumination.[8−10] Supposedly, the photoinduced change in the dipole moment of the Az unit[11] leads to an active motion of the side group, which then results in macroscopic in-plane area changes. Most recently, an *in-situ* Brewster angle microscopic (BAM) study was undertaken and the very dynamic characters of 6Az10-PVA monolayers on the water surface at a submillimeter scale was elucidated.[10]

In this communication, we wish to present the highly mobile nature of transferred monolayers of 6Az10-PVA on a mica surface under high-humidity conditions as proven by atomic force microscopy (AFM). Depending on the lateral packing density, these monolayers showed photodriven large and characteristic two- and three-dimensional (2D and 3D) morphological changes at a submicrometer scale. To our knowledge, this work presents the first visualization of the photomechanical response of a monolayered photochromic polymer taking place on a *solid surface*.[12]

The synthesis of 6Az10-PVA (degree of polymerization = ca. 500, $M_w = 1.0 \times 10^5$, $M_w/M_n = 1.7$) was described previously.[13] Transfer of a 6Az10-PVA monolayer onto mica was performed by the Langmuir−Blodgett (LB) method. A chloroform solution containing 6Az10-PVA (1.0×10^{-3} unit mol dm^{-3}) was preirradiated with 365 nm light and then spread onto the water surface using a Lauda FW1 film balance at 20 ± 0.5 °C. Approximately 90% of the Az units were transformed to the *cis*-isomer. Since the *cis*-isomerized 6Az10-PVA monolayer is highly expanded and fluid,[10] the packing density of the Az side group can be largely controlled by the deposition conditions.[13] Single-layered LB films were prepared by vertical lifting at two pressures, 13 and 2 mN m^{-1}, onto a freshly cleaved mica surface. These conditions rendered molecular films having average areas per Az unit of ca. 0.4 (film A) and 1.2 nm^2 (film B), respectively. The average packing densities are ca. 1.6- (film A) and 4.8-fold (film B) lower than that of the closest packing of a 6Az10COOH monolayer (0.25 nm^2).[14] The LB monolayers were stored in a highly humid vessel containing wet cotton at room temperature (relative humidity, ca. 100%) in the dark for 4 days. This dark adaptation allowed a complete thermal conversion from the *cis* to *trans* form of the Az unit. UV light irradiation (365 nm, 4.5 mW cm^{-2}) onto these LB films was then performed in the same vessel. AFM measurements were achieved with a SPA300/SPI3700 system (Seiko Instruments Inc.) in the dynamic force (tapping) mode using a rectangular-shaped Si_3N_4 cantilever at a scan speed of 2.00−4.00 Hz. All images were recorded under ambient air conditions (ca. 20 °C, relative humidity of 30−40%).

Chart 1

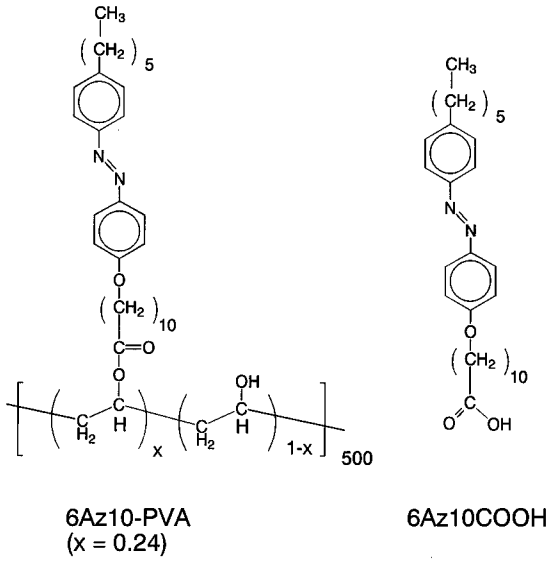

Figure 1 shows topographical AFM images of film B (a lower coverage density film).[15] After dark adaptation for 4 days, the film exhibited network-shaped morphologies (a), which can be ascribed to a contraction of the film during the process of the *cis* to *trans* thermal isomerization.[16] The darker regions in the AFM image should indicate the bare mica surface, judging from the flatness within 0.2 nm. After UV light irradiation for 7 h, the network-shaped films exhibited marked swelling, nearly maintaining the film thickness (b). Typical widths of the network before and after UV light irradiation were ca. 100 nm (a) and above 200 nm (b), respectively. The height profiles indicate that the photoinduced expansion was accompanied by a slight decrease in the film thickness from 2.4 ± 0.2 to 2.1 ± 0.2 nm (13% reduction). The swollen morphology virtually reverted to the original one after another dark adaptation in the highly humid vessel for 4 days (c). In this manner, the morphological change was a reversible process. The film thicknesses observed here correspond to approximately 70% of the length of extended 6Az10-PVA side chain (3.4 nm, estimation from the CPK model). The reduction of film thickness from the ideal molecular length may be explained by disordering and tilting of the side chain. It is thus reasonable to assume

* To whom correspondence should be addressed. Phone and fax: +81-45-924-5247. E-mail: tseki@res.titech.ac.jp.

S0024-9297(97)00639-6 CCC: $14.00

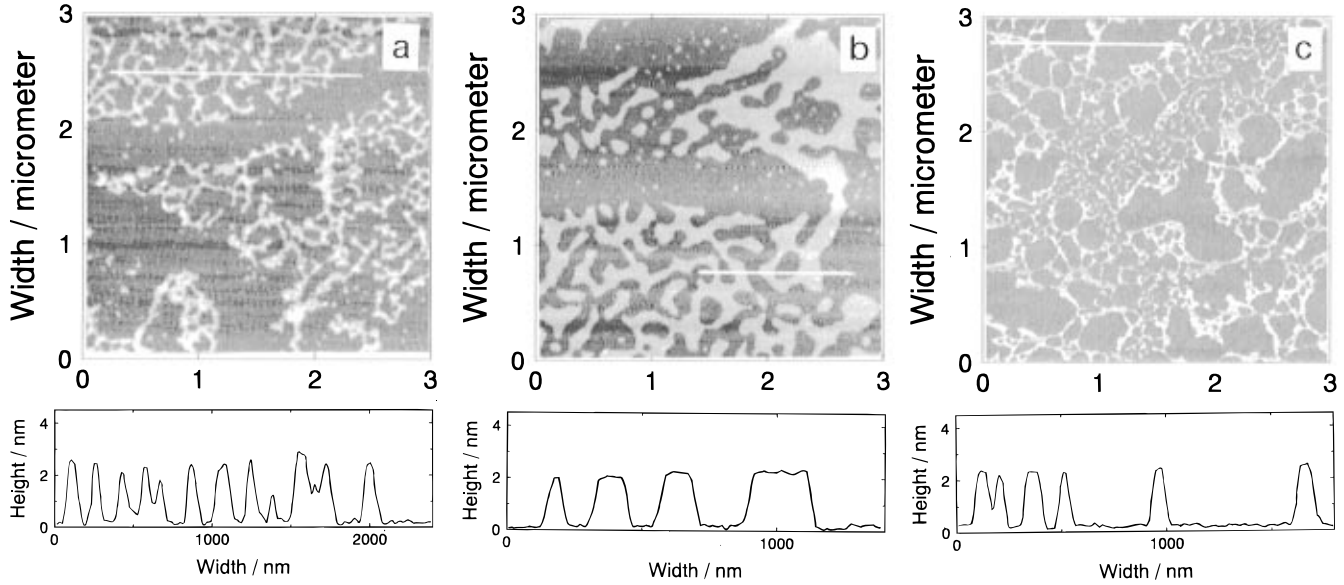

Figure 1. Topographical AFM images of the 6Az10-PVA monolayer on mica (film B, a low-coverage film) before (a) and after (b) UV light irradiation (at 365 nm, 4.5 mW cm^{-2} for 7 h) followed by the dark adaptation at room temperature for 4 days (c). The film was transferred giving an area per Az unit of 1.2 nm^2. The sample was kept at a relative humidity of ca. 100% during all processes. The lower part indicates the cross sectional height profiles for the solid line shown in the AFM image.

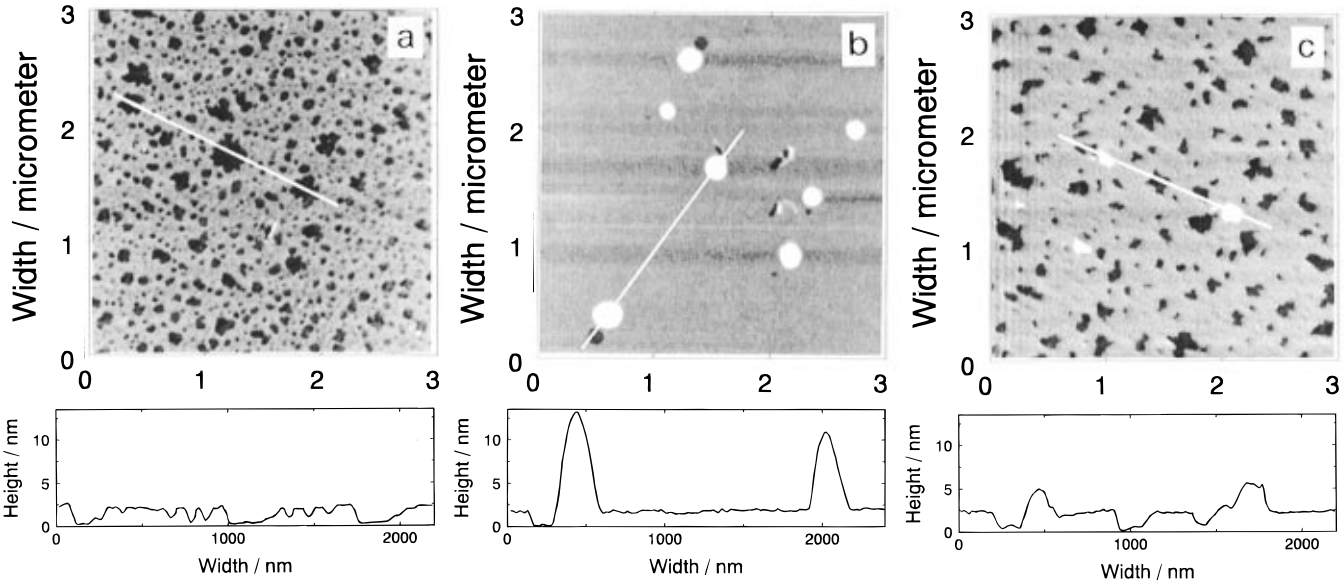

Figure 2. Topographical AFM images of the 6Az10-PVA monolayer on mica (film A, a high-coverage film) before (a) and after (b) UV light irradiation, followed by the dark adaptation (c). The experimental conditions are the same as for Figure 1 except for the lateral film density. The average area per Az unit was 0.4 nm^2.

that film B exhibits a 2D expansion and contraction maintaining the monolayer state.

AFM observations of film A (a higher coverage density film) were performed with the same procedures (Figure 2).[15] The first dark adaptation gave a sponge-shaped film having a thickness of 1.9 ± 0.2 nm (a), similarly due to the contraction after deposition, as observed for film B. The diameters of the defects ranged from a few ten to a few hundred nanometers. After UV light irradiation, the film morphology exhibited a complete change. Most of the defects disappeared, and instead, huge shallow panlike protrusions of 200−300 nm in width and ca. 10 nm in height appeared (b). The protrusions were several times higher than the thickness of the 6Az10-PVA monolayer, and therefore a 3D morphological change took place in this case. We assume at present that the light-driven expansion of the monolayer first fills up the defects, and then an excess lateral film pressure gives rise to structuring of such protrusions. The height profile in Figure 2b also traces a part of the remaining defects. The depth coincided with that of the monolayer thickness, and therefore the flat gray regions that occupy the major part in the image should correspond to the top of the monolayer. This 3D change was again nearly a reversible process; dark adaptation for 4 days almost reversed the film morphologies (c). Most of the protrusions disappeared, and a number of defects were reproduced. The height of the remaining protrusions were substntially decreased to the level of 2−3 nm. Judging from the reversibility, we assume at present a possibility that these 3D protrusions are composed of hollows surfaced by the elastic *cis*-6Az10-PVA monolayer.[10] Structural elucidation of the 3D morphology is a subject of future investigation.

The marked morphological changes stated above were promoted under highly humid conditions. Essentially

no morphological changes were observed in a dry vessel containing silica gels (relative humidity, less than 20%). It can therefore be concluded that formation of an adsorbed water layer on mica plays the critical role in providing the dynamic nature of the 6Az10-PVA film. For this reason, the mechanical behavior of 6Az10-PVA monolayers observed on mica probably has the same origin as that for the monolayers on the water subphase.[8−10] Beaglehole et al.[17] estimated the amount of adsorbed water layer on mica by ellipsometry and found that a water layer of ca. 2 nm thickness exists at a relative humidity near 100%. In dry atmospheres, in contrast, the mobility of the main chain of 6Az10-PVA is frozen, possibly via hydrogen bonding with the mica surface, and large scale motions beyond a nanometer level are restricted. Under ambient air conditions where AFM measurements were made, the 6Az10-PVA monolayers are regarded to be almost at a frozen state. Kumaki et al.[18] successfully obtained AFM images of separated random coiled chains of poly(methyl methacrylate) (PMMA) anchored by folded polystyrene on mica. They pointed out that the extension and isolation of coiled chains of PMMA requires the existence of a thin adsorbed water layer that enhances the chain mobility. The photoresponsive behavior presented here is hence closely related to their observations.

In summary, we have observed large and characteristic photoassisted morphological changes of the monolayered 6Az10-PVA films on a solid mica surface. The mobile properties of the monolayer shown here are discussed on the basis of the final stage of light illumination. Investigation is now in progress to obtain detailed knowledge including the intermediate stages of the dynamic process.

Acknowledgment. We thank S. Morino and H. Sekizawa for helpful discussions. T.S. was greatly inspired by discussions with Dr. J. Kumaki at the Plastic Research Laboratory of Toray Industry Inc. for this research. This work was in part supported by a Grant-in-Aid for Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (No.277/08246217) from The Ministry of Education, Science, Sports, and Culture.

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MA970639W