

# Light-Driven Dot Films Consisting of Single Polymer Chain

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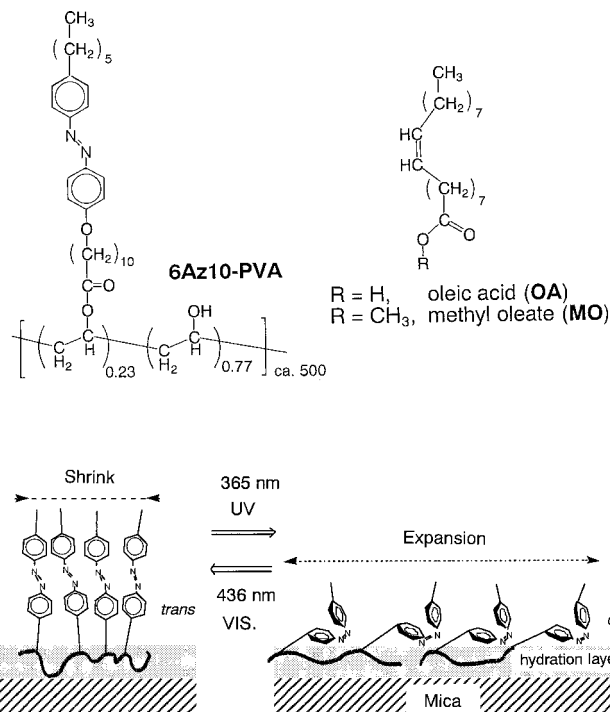
Reversible deformation of materials may provide new opportunities for creation of artificial muscles and smart actuating systems. Despite many efforts, no attempt has been made to observe the response of polymers at a single polymer chain level. Here, we describe a successful method for isolation of a photoresponsive polymer in a monolayer state via so-called skeletonization. Atomic force microscopic observation clearly revealed a large and reversible light-driven morphological response of dot-shaped nano-films on mica most probably consisting of one polymer chain. The dot films observed here can be regarded as the smallest polymer material in response to stimuli.

## Introduction

Photochromic molecules change their geometry and polarity by illumination, and are regarded as the light-switchable molecular machines.<sup>1,2</sup> When they are attached to a polymer chain, the photoisomerization triggers conformational changes of the main and side chains, resulting in induction of secondary macro-size effects such as viscosity changes and induction of sol–gel transition in the solvated systems, and changes in surface wettability, glass transition temperature, and shape changes in a bulk state.<sup>1,2</sup> For observations of precise response behavior of photochromic polymers, reduction of the material's dimension (3D → 2D → 0D) is highly desired.

Microscopic observations of the monolayer consisting of a poly(vinyl alcohol) having an azobenzene (Az) unit in the side chain (6Az10-PVA, Figure 1) in the 2D state has been the subject of our current investigation.<sup>3–6</sup> A monolayer of this polymer on a water surface shows large and reversible expansion and contraction upon alternative irradiation of 365 nm (UV) and 436 nm (visible) light, respectively.<sup>3,4</sup> Surface pressure–area ( $\pi$ –A) isotherm,<sup>3</sup> surface potential,<sup>4</sup> Brewster angle microscopy (BAM),<sup>4</sup> UV–visible spectroscopy,<sup>4</sup> and X-ray reflectometry<sup>5</sup> all support the model for the light-driven motility as follows. The UV light illumination causes the *trans* (rodlike shape)-to-*cis* (bent shape) isomerization of the Az unit in the side chain. The *cis*-Az isomer has a higher affinity to water due to increased polarity of this unit,<sup>7</sup> leading to the film expansion with a reduction of film thickness (Figure 1). In addition, our recent study indicated that the photoinduced morphological changes occurs also on the solid surface of mica in a humidified atmosphere.<sup>6</sup> The hydration of mica should play an important role in providing the high mobility of the monolayer.<sup>8</sup> Matsumoto et al.<sup>9</sup> also observed related light-induced morphological inductions in a polyion complex type azobenzene-containing LB films on mica.

Segregation to the pseudo 0D state to the level of the single polymer involvement may be achieved by high dilution of solution<sup>10,11</sup> or monolayer.<sup>12</sup> For 6Az10-PVA monolayer, however, the lipophilic long side chain strongly prohibit the isolation



**Figure 1.** Molecular structure of materials (6Az10-PVA) and stuffing amphiphiles (OA and MO) for skeletonization, and the supposed motility scheme of a 6Az10-PVA monolayer on a hydrated mica surface.

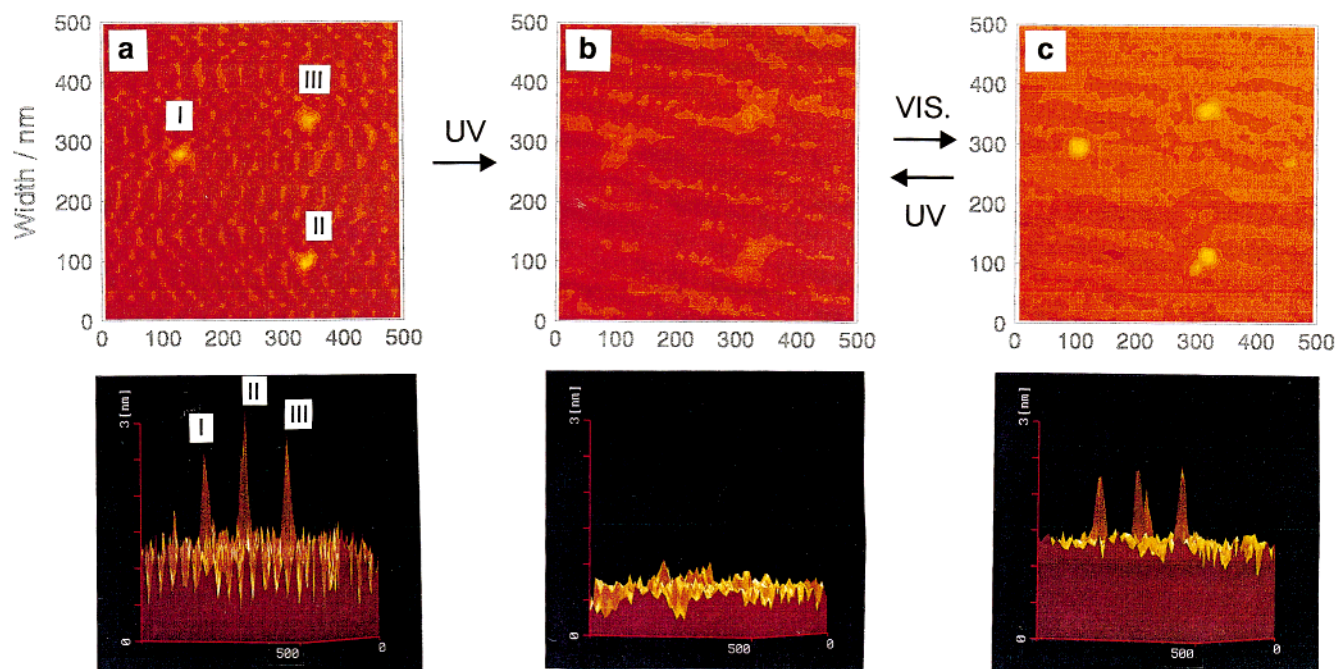
to single chains.<sup>4</sup> In the present study, we adopted the process of so-called skeletonization of the LB monolayer to achieve the pseudo 0D (dot) state. Skeletonization<sup>13–15</sup> involves selective removal of one component out of the two from an LB film, which was first achieved by K. Blodgett.<sup>13</sup>

## Experimental Section

**Materials.** Synthesis of 6Az10-PVA ( $M_w = 1.0 \times 10^5$ ,  $M_w/M_n = 1.7$ ) was described previously.<sup>16</sup> Methyl oleate (MO) and oleic acid (OA) were obtained from Sigma and Aldrich, respectively, and used as received.

**Sample Preparation.** A freshly cleaved mica (clear and lightly stained grade) of  $20 \times 10$  mm<sup>2</sup> size was first immersed

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**Figure 2.** Photoinduced morphological changes of dot-shaped nano-films of 6Az10-PVA obtained by skeletonization with MO ( $R = 9$ ) as observed by noncontact mode AFM [top (upper) and side (lower) views]. The images were taken before illumination (a), after 365 nm light (b), and after successive 436 nm light illumination (c), at humidity above 80%. The light dose was  $600 \text{ mJ cm}^{-2}$  for both processes. The darker parts correspond to the bare mica surface. The dot films are termed I, II, and III for identification (see text). Light-driven morphological changes between (b) and (c) were repeatable. Changes in the height and noise levels of the base plane (mica surface) are the artifacts of measurements.

into pure water (Milli-Q grade,  $18 \text{ M}\Omega \text{ cm}^{-1}$ ) filled on a Lauda FW2 film balance. The monolayer of *cis*-6Az10-PVA and the mixture with OA or MO was spread from a chloroform solution ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) on pure water. The monolayer was transferred onto the mica by upward vertical lifting. These mica plates were attached onto a glass slide with an adhesion tape for AFM measurements. All procedures were carried out in dimmed red light at  $20 \pm 1^\circ \text{C}$ .

**Measurements.** Light irradiation was performed with a 150 W Hg–Xe lamp (San-ei UV Supercure-203S) equipped with an optical fiber which favors irradiation to a target part. The 356 nm (UV) and 436 nm (visible) lines from the lamp were selected with the combination of Toshiba optical filters, UV-35/UV-D36A and Y-44/V-42, respectively. The irradiation was performed at a high humidity ( $\text{RH} > 80\%$ ).

AFM observations were conducted in noncontact dynamic force mode (tapping mode) with a Seiko Instruments SPA300/SPI3700 system in ambient atmosphere ( $\text{RH} < 35\%$ ). A micro-cantilever of SI-DF20 (20 mm scanner, a rectangular-shaped Si cantilever was used (spring constant, 11 N/m). The scanning speed was 2.0–4.1 Hz.

A transmission electron microscopic (TEM) image of a carbon replica of 6Az10-PVA was taken with a Zeiss CEM-902.

## Results and Discussion

6Az10-PVA in the *cis* form was spread with OA or MO onto pure water at  $20^\circ \text{C}$  (mixing ratio,  $R = [\text{OA or MO}]/[\text{Az unit}]$ , of 3 or 9). All these materials gave highly expanded liquid monolayers. The 1:1 molar mixture of the polymer and AO or MO provided a  $\pi$ -A isotherm with a shape different from the sum of those obtained for the individual ones, showing that the polymer has a high compatibility with OA or MO. A single layer of the mixed monolayer was deposited onto freshly cleaved mica by vertical lifting at a low surface pressure of  $1 \text{ mN m}^{-1}$  with a transfer ratio of  $1.0 \pm 0.1$ . The oily stuffing amphiphile

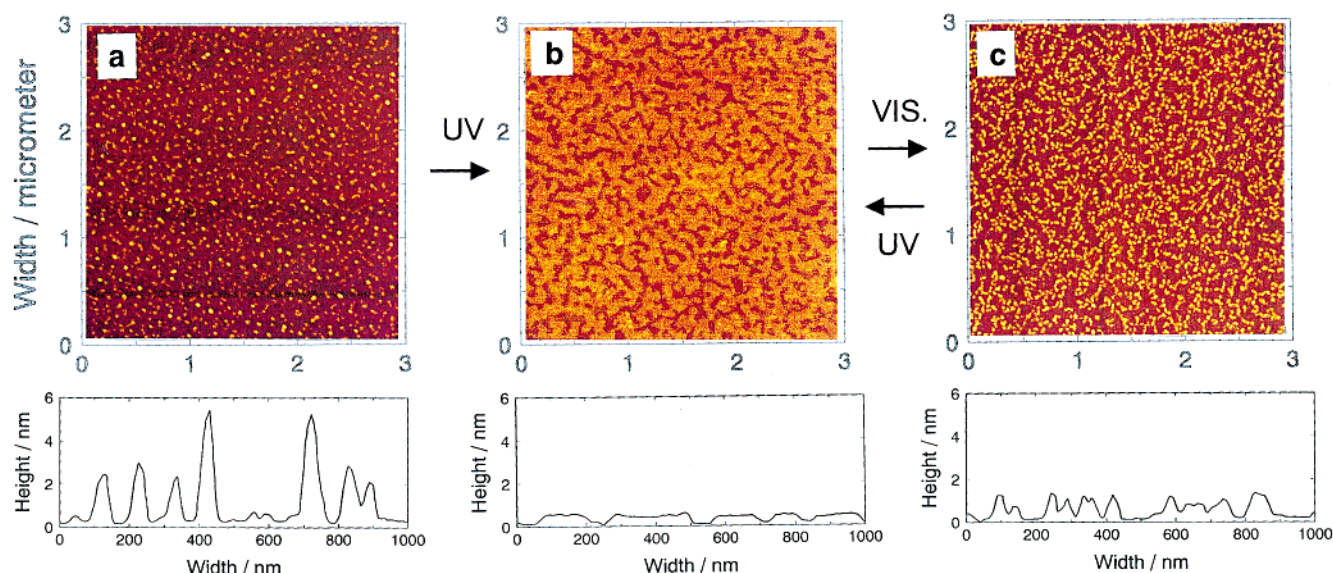
component (OA or MO) was then removed by immersing into methanol for 1 min or evaporation at  $120^\circ \text{C}$  for 2 h. The resulting film was then stored in a humidified atmosphere (relative humidity exceeding 95%) for a week, which allowed the complete thermal reversion to the *trans* form of Az accompanied by the film contraction.<sup>6</sup>

Noncontact mode AFM images were taken for perfectly isolated dot-shaped monolayered films after removal of MO from a mixture of  $R = 9$ . Here, three dot films are completely separated in the  $500 \times 500 \text{ nm}^2$  field. The dot films had 50–60 nm (uncorrected for the cantilever shape) in diameter and 1.5–2.0 nm in height (a). UV light illumination induced an expansion of the nano-film (see the top view) accompanying a considerable decrease in film thickness (see the side view) (b). The area showed a ca. 4-fold expansion with a reduction of the thickness to the level of 0.5 nm. Such behavior is reasonably understood by the assumed deformation model shown in Figure 1, and is in good agreement with the BAM data obtained on the water surface.<sup>4</sup> Visible light illumination almost reverted the initial dot shape (c).

Dots I and III shown in Figure 2 shrank to a single spot again after visible light illumination; in contrast, dot II was divided into two (c). It can be postulated from the consideration mentioned below that dots I and III consisted of one polymer chain, and that the single dot II in the initial state involved two polymer chains. In this way, the photoirradiation cycle causes further isolation of the chains into the smallest level. It seems probable that, on the shrinking process, the intrachain assembling force surpasses the interchain aggregation. Once the films were isolated to the smallest level, the morphology and the size of dot were quite reproducible through many cycles ( $b \rightleftharpoons c$ ).

The skeletonization from a 6Az10-PVA/OA mixture ( $R = 3$ ) with immersing into methanol provided a more crowded ensemble (Figure 3). In the initial state, the dot films were larger and irregular sized (see the height profile in (a)). After one





**Figure 3.** Photoinduced morphological changes between dots and continuous sheets of 6Az10-PVA obtained by skeletonization with OA ( $R = 3$ ) as observed by noncontact mode AFM. Illumination procedures were basically the same as those indicated in Figure 2. Light-driven morphological changes were repeated between (b) and (c). The darker parts correspond to the bare mica surface.

photocycle via expansion (b) in a humidified atmosphere, the dots were separated into equally sized smaller ones with the monolayer thickness upon subsequent visible light illumination (c). Again, the features and size in photoinduced changes were highly reproducible in many cycles ( $b \rightleftharpoons c$ ). For this crowded ensemble, the expanded films come in contact with each other to form continuous films (b), nevertheless, the dot films were precisely reproduced without fusion after shrinkage (c).

From the morphological features, we infer that the final dot films consist of one polymer chain. First, the diameter of the dots are even-sized, irrespective of the isolation procedures, namely skeletonization or photoassisted segregation. Second, the smallest dot films retained the features in size and shape after many repeated photocycles. Such size stability is most likely explained by assuming the involvement of one polymer chain. Third, the volume of the dot corresponds to that expected for a single polymer as stated just below.

The height information obtained by AFM is accurate, in contrast, the quantitative estimations of lateral direction are problematic, which are highly distorted by the tip geometry and operation artifacts. In this respect, TEM observation was carried out, which supplies precise complimentary data in the in-plane direction.<sup>15</sup> Since we obtained a TEM image of a carbon replica of a spongy-shaped 6Az10-PVA monolayer<sup>6</sup> with a lateral Az density of  $0.4 \text{ nm}^2 \text{ Az}^{-1}$ , we compared the defect size of the monolayer observed by TEM and AFM for the tip correction. The radius deviation stemming from the AFM tip geometry was estimated to be 13 nm (tip radius of curvature = 10–15 nm, according to the manufacturer). The mean size of the dot in Figure 3 was 24 nm in radius and 1.2 nm in height. By subtracting the tip influence from this value, one obtains 11 nm as the corrected mean radius. With an assumption of a flat cylindrical geometry for the dot film, one obtains a figure of  $4.6 \times 10^2 \text{ nm}^3$  as the observed volume ( $V_{\text{obs}}$ ). On the other hand, one polymer particle of 6Az10-PVA ( $M_w = 1.0 \times 10^5$ ) would occupy a volume of  $1.7 \times 10^2 \text{ nm}^3$  ( $V_{\text{ideal}}$ ) from a simple calculation using a tentative film density of  $1.0 \text{ g cm}^{-3}$ . Thus,  $V_{\text{obs}}$  and  $V_{\text{ideal}}$  are in the same order of magnitude. We suppose that this coincidence is satisfactory taking into account the undeterminable quantities concerning the film density and film geometry.

Significance in visualization of this polymer would not be limited to light-driven systems. Since the participation of water (hydration) is essential in the film motility, the driving principle observed here should provide many implications in other stimuli-responsive 2D Langmuir films and 3D hydrogel systems.

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