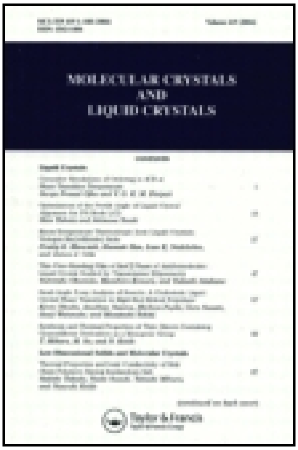

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Morphological Observation of Photoisomerizable Monolayers of Azobenzene Derivatives on Water Surface

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To cite this article: Takahiro Seki, Hidehiko Sekizawa, Kazuaki Kudo, Yuko Hayashi & Kunihiro Ichimura (1997): Morphological Observation of Photoisomerizable Monolayers of Azobenzene Derivatives on Water Surface, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 47-50

To link to this article: http://dx.doi.org/10.1080/10587259708032245

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 47–50
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MORPHOLOGICAL OBSERVATION OF PHOTOISOMERIZABLE MONOLAYERS OF AZOBENZENE DERIVATIVES ON WATER SURFACE

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Abstract Brewster angle microscopic (BAM) study was successfully achieved for photoresponsive monolayers composed of poly(vinyl alcohol) derivatives bearing an azobenzene (Az) side chain. BAM observation revealed clear differences in the morphological and rheological properties between the *trans*- and *cis*-isomerized monolayers. The deformation process was also monitored under UV irradiation, which correspondingly visualized the magnitude of expansion stemmed from the difference in the methylene spacer length of the amphiphilic Az polymer.

INTRODUCTION

Photochromic polymer systems frequently show a macro-size photomechanical effect.[1] Photomechanical effects in monolayers of photochromic polymers at the air-water interface have attracted a considerable interest due to their characteristic behavior taking place in a two dimensional state in which the photochromic units are arrayed or aligned.[2] In such systems, more detailed information on the photomechanical response is anticipated to be obtained. According to existing data, however, studies of photoresponsive polymeric monolayers have been limited to macroscopic observations such as surface pressures and film area changes. To obtain a better insight in the film deformation, an *in-situ* microscopic investigation at the air-water interface is highly desired.

We reported on a large area changes in a poly(vinyl alcohol) derivative bearing an azobenzene side chain which is designated as 6Azn-PVA (Chart 1).[2-4] With these materials, macroscopic area expansion and contraction are observed upon alternate UV (365 nm) and visible (436 nm) illumination, respectively. The magnitude of UV-light induced expansion is the function of spacer length. 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 *cis* form.[5] 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 (Figure 1).[2-4] This paper presents our results on the *in-situ* BAM observation of 6Azn-PVA monolayers, in particular focusing on the influence of the spacer length (n).

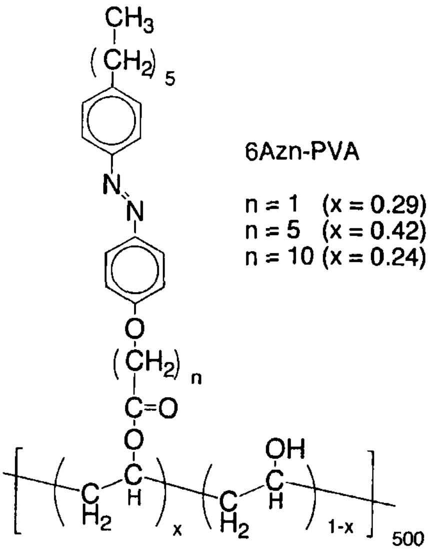

CHART 1

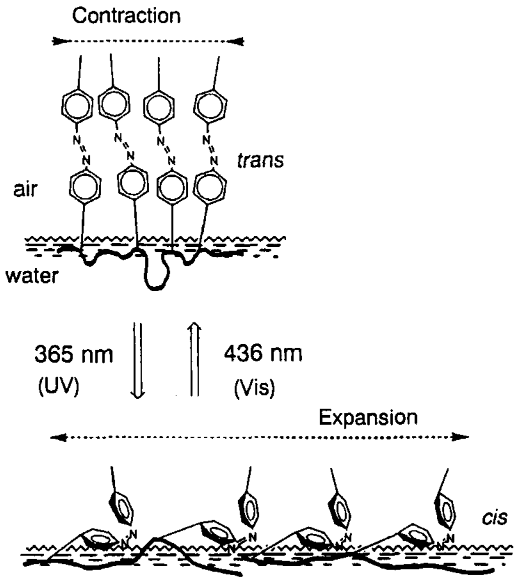

FIGURE 1 Schematic illustration of photoinduced deformation of 6Azn-PVA monolayers.

EXPERIMENTAL

The synthesis of 6Azn-PVA was described previously.[6]

6Azn-PVA monolayer was spread on pure water (Milli-Q SP grade) filled in a Lauda FW-1 film balance at 20±0.5 ℃ from a chloroform solution (1 x 10^{-3} mol dm^{-3}). BAM observation was carried out with a home-built apparatus or a commercially available one (Nippon Laser Electronics, EMM-633). The reflected images were taken and recorded with a CCD camera (Hamamatsu Photonics, C-5948) or a Panasonic video camera connected to a TV monitor and a Hitachi video printer. UV (365 nm) and visible (436 nm) light irradiation onto the water surface was performed with a 150 W mercury-xenon lamp (San-ei UVF-202S) guided with a quartz optical fiber. Optical glass filters were equipped at the terminus of the fiber for wavelength selection.

RESULTS AND DISCUSSION

A *trans*-6Azn-PVA monolayer at 0 mN m^{-1} exhibited an iceberg-like domain structure having solid boundaries. In contrast, a *cis*-6Azn-PVA monolayer was highly fluid and homogeneous. This situation resembles that to monolayers of melt long chain fatty acids as reported by Lu and Nakahara[7]. Features of BAM images of *trans*-6Az10-PVA and *cis*-6Az10-PVA (*cis* isomer content of ca. 90 %) monolayers have been described in more detail in connection with the surface pressure-area curves in the previous paper[8].

Figure 2 shows the direct observation of UV light induced morphological changes of the 6Azn-PVA monolayer. These observations were achieved without compression and at areas of 0.6 - 0.7 nm^2 per Az unit. Upon UV light irradiation, clear contours of iceberg-like domains of the *trans* monolayer (left) immediately became obscure and the exposed water surface among domains became narrower (middle). Finally BAM images which exhibit characteristics of the *cis*-Az monolayer were obtained (right).

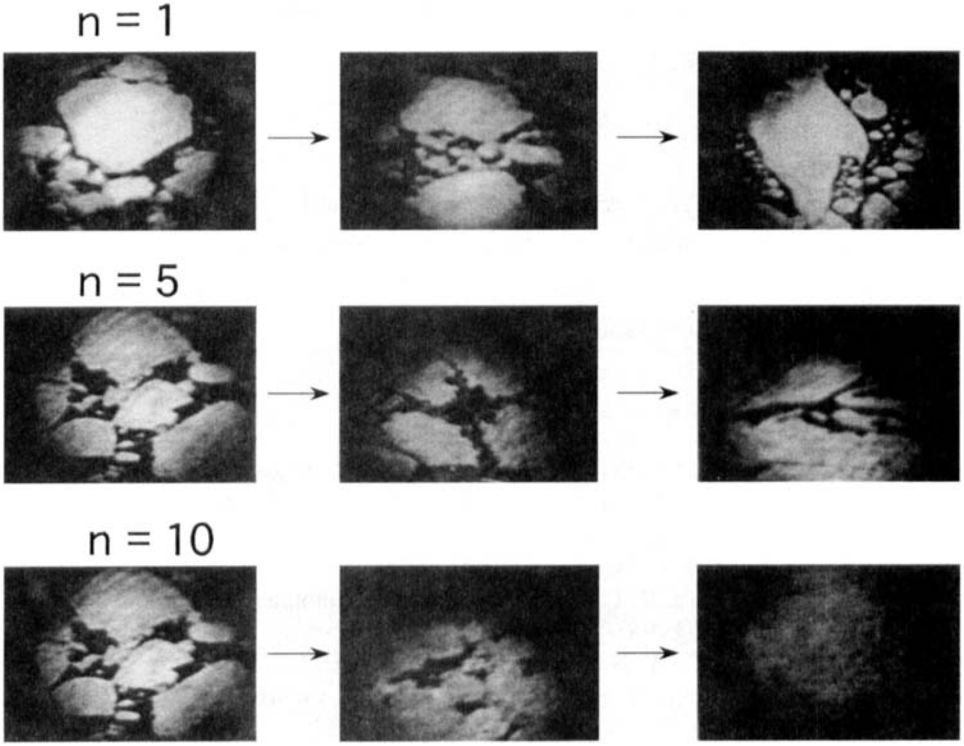

FIGURE 2 Morphological changes of 6Azn-PVA monolayers on water surface upon UV light (365 nm) irradiation at ca. 1 mW cm^{-2}.

The images of the final state were dependent on the spacer length. The resulting area of the exposed water surface should be correlated to the magnitude of film expansion. When the area of 6Azn-PVA was monitored at 2 - 3 mN m^{-1} the magnitude of expansion was ca. 1.5, 2, and 3 times for compounds of n = 1, 5, and 10, respectively. For n = 1, the iceberg-like domains shows the smallest expansion, resulting only in changes of boundary from square-built to round in shape. On the other hand, the most expanding film (n = 10) diminished the exposed water surface, showing a highly homogeneous BAM image. The intermediate image was obtained for n = 5. In these manners, the magnitude of the film expansion was clearly discriminated by direct BAM observation.

As shown here, microscopic *in-situ* observation of 6Azn-PVA film could be correspondingly correlated to the macroscopic area changes. The next step of our approach could be to monitor a single island, which is expected to provide detailed information on the photoresponse behavior. Since islands of the monolayer are highly mobile, they quickly get out of the microscopic field. A monolayer trough equipped with an X-Y stage is in preparation to chase the behavior of a particular island. Work in this regard is now in progress.

ACKNOWLEDGMENT

We thank Drs. H. Yokoyama and Y. Tabe at Electrotechnical Laboratory at Tsukuba for kindly assembling the BAM instrument. This work was partially supported by the Grant-in-Aid for Scientific Research in Priority Areas from Ministry of Education, Science, Sports and Culture, Japan.

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