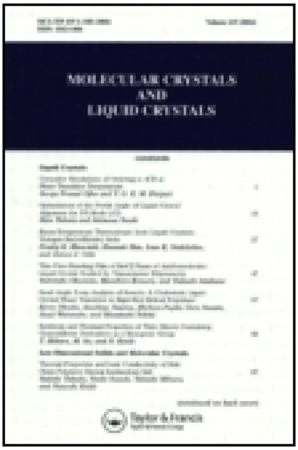

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# PHOTOINDUCED MOLECULAR MOTION OF THE AZOBENZENE MONOLAYER INVESTIGATED BY MAXWELL DISPLACEMENT CURRENT TECHNIQUE

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# PHOTOINDUCED MOLECULAR MOTION OF THE AZOBENZENE MONOLAYER INVESTIGATED BY MAXWELL DISPLACEMENT CURRENT TECHNIQUE

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*Photoinduced molecular motion of the azobenzene command surface polymer was investigated by means of the Maxwell displacement current (MDC) technique. Two kinds of command surface polymer, 6AZn-PVA and 6AZn-CBm-PVA, were investigated in order to study the microscopic interaction between photochromic molecules and liquid crystal (LC) molecules. The MDC measurements were carried out during monolayer compression and ultra-violet photoirradiation. For photoirradiation measurements, the direction of current flowing closed circuit was reversed for these two kinds of polymers and this indicates that the orientational motion of LC molecules was successfully detected by the MDC measurement.*

*Keywords*: azobenzene; command surface; Langmuir monolayer; Maxwell displacement current

## INTRODUCTION

Langmuir-Blodgett (LB) films of azobenzene derivative have called much attention to photofunctional applications such as optical memory. It is well known that azobenzene molecules change their conformation from *trans*-form to *cis*-form by ultra-violet (UV) photoirradiation. In particular, alignment switching of nematic liquid crystals (LC) between the homeotropic and planar phase can be controlled by this *trans-cis* photoisomerization of the surface [1,2,3]. With this background, they are called "command surface". Using such photofunctional molecules, the optical transmittance and the capacitance of the LC cells can be controlled without the aid of

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applying the external electric field. However, the detail of these mechanisms is still unclear. So far, to clarify the LC driving mechanism, photo-induced structural change of the surface has been investigated by means of FT-IR, AFM, X-ray diffraction technique, and others.

It is important to obtain some knowledge about the molecular motion of the azobenzene for practical applications. For a decade, we have been developing a novel detection system named Maxwell-displacement current (MDC) technique that can directly probe the molecular motion [4,5,6]. Using the MDC measurement, dipole moment of the molecules located between two parallel placed electrodes can be determined. We have used this method in order to detect the generation of displacement current across monolayer containing azobenzene groups due to the *trans-cis* photoisomerization of the azo-group. Usually, the command surface alignment layer is composed of thin film of polymer with photoactive azobenzene side chains. In this paper, photo-induced conformational change of the surface molecule is investigated by MDC technique. It will be helpful to discuss the mechanism of driving bulk LC layer using command surface.

## EXPERIMENT

The materials used are poly(vinyl-alcohol) (PVA) derivatives attaching azobenzene and cyano-biphenyl (CB) side chains, abbreviated as 6AZn-PVA and 6AZn-CBm-PVA, respectively. The chemical structure for 6AZn-CBm-PVA is shown in Figure 1. Including the CB side chain in the PVA, we can study the effect of the packing density of the side chain to

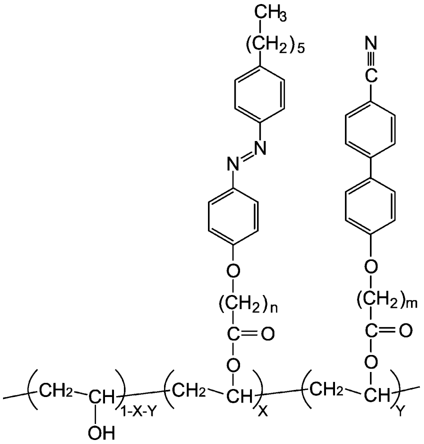

**FIGURE 1** Chemical structure for PVA derivatives, 6AZn-CBm-PVA.

the photo-reactivity and the microscopic interaction between azo and CB molecules. The 6AZn-PVA and 6AZn-CBm-PVA were kindly supplied by Prof. Seki of Nagoya University, and they were used in the experiment without further purification. For Langmuir monolayer preparation, the spreading solution of 6AZn-PVA and 6AZn-CBm-PVA was a 0.2 mmol/l chloroform solution. Using an experimental system schematically shown in Figure 2, we examined the vertical component of dipole moment of these azobenzene monolayers. Electrode 1 is a round-shape ITO-coated electrode with a working area of 45.8 $\text{cm}^2$ and electrode 2 is spiral shaped gold wire. It is placed parallel to the water surface with a spacing of about 1 mm from the water surface. After spreading the solution of 6AZn-PVA and 6AZn-CBm-PVA onto the water surface of the Langmuir-trough made of polytetrafluoroethylene (150 mm × 730 mm in width × length, 10 mm in depth), MDC was measured during the course of monolayer compression and during alternating irradiation with UV and visible lights. Monolayers on the water surface were compressed with aid of two barriers moving at the same speed in opposite direction of 40 mm/min.

Since detailed theoretical considerations of MDC have been described in our previous papers [5,6], we here treat the fundamentals in brief. As shown in Figure 2, when a single monolayer consisting of polar molecules with a dipole moment of $\mu$ is prepared on a water surface, the induced charge $Q$ on electrode 1 is expressed as

$$Q = -\frac{n_s\langle\mu_z\rangle}{d} - C\phi_s, \tag{1}$$

where $n_s$ is the surface density of molecules given by $1/A$ ($A$: molecular area), $d$ is the distance between electrode 1 and the water surface, C is the capacitance between electrode 1 and the water surface, and $\phi_s$ is the surface potential of water of the Langmuir-trough and the suffix $z$ represents the vertical component of the dipole moment. In Eq. (1), $\langle\ \rangle$

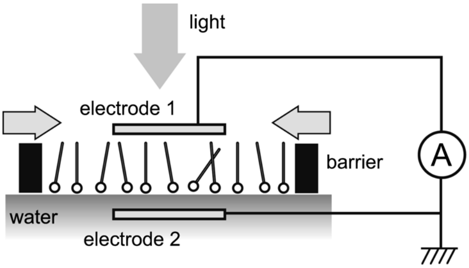

**FIGURE 2** Schematically image of the experimental setup of the MDC measurement.

denotes a thermodynamic average of the distributed components of the molecules.

The MDC is generated across monolayers due to the change of induced charge $Q$ with respect to time. By monolayer compression, MDC is generated and it is expressed as

$$I = \frac{\langle \mu_z \rangle}{d} \frac{d}{dt} n_s + \frac{n_s}{d} \cdot \frac{d}{dt} \langle \mu_z \rangle + C \frac{d}{dt} \phi_s \tag{2}$$

In our experimental system, an air-gap between the water surface and electrode 1 works as a good electrical insulator and it eliminates the flow of leakage current. Thus only the MDC current given by Eq. (2) is allowed to flow. The change of induced charge on electrode 1 can be estimated by integrating the MDC with respect to time. As the dielectric constant of water $\epsilon_w (= 78)$ is so high in comparison with that of air, $\epsilon_a (\approx 1)$, the part of molecule immersed in a water cannot contribute to the MDC. Furthermore, the change of water surface potential is small in comparing with the contribution of the first and second terms of Eq. (2) [5].

## RESULTS AND DISCUSSIONS

Figure 3 shows the results for the MDC measurement of *trans*- and *cis*-6AZ5-PVA Langmuir film on a water surface during monolayer compression. From bottom to top, surface pressure, displacement current and estimated dipole moment are plotted with respect to the area per molecule. As shown in figure, distinctive current spectra were obtained and the results suggest that the side chains gradually stand up with increase of the surface pressure. For *cis*-form, azobenzene side chain bends, whereas the side-chain is straight for *trans*-form azobenzene. This fact suggests that, for *cis*-azobenzene, the surface pressure begins to arise at large area region in comparison with the *trans*-form azobenzene and vertical component of the dipole moment becomes larger than that of *trans*-form azobenzene. This result is consistent with the shape of azobenzene molecules. Also, we can see that the area per molecule that the dipole moment reaches the maximum is coincident with the area that the surface pressure begins to rise up. This implies that the dipole moment does not necessarily orient to the molecular long axis of side chain, and this is also supported by the prediction from the molecular orbital calculations, where oxygen atom attaching to biphenyl contributes markedly even in *trans*-azobenzene to the dipole moment perpendicularly to the side chain.

Results of the optical response for azobenzene molecules 6AZ10-PVA and 6AZ10-CB10-PVA induced by irradiation of UV light are shown in

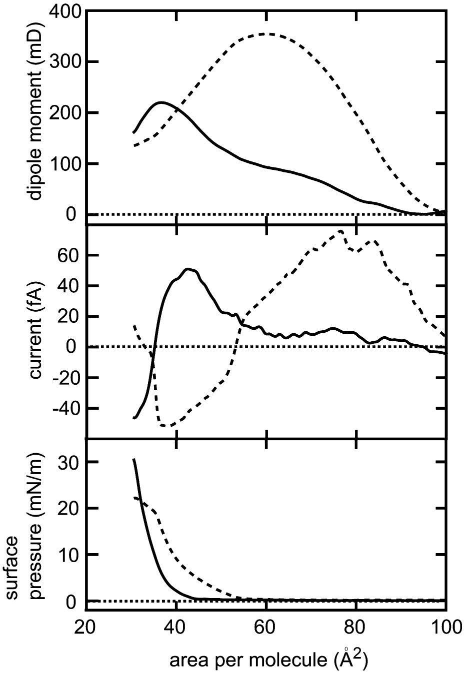

**FIGURE 3** MDC measurements of 6AZ5-PVA Langmuir film on a water surface during monolayer compression. Solid line and broken line represent *trans*-form and *cis*-form of 6AZ5-PVA, respectively.

Figures 4(a) and 4(b), respectively. In these measurements, barrier location was fixed at determined point where the molecular area indicates 50 Å$^2$ and then displacement current was recorded during photoirradiation. Of course, we have confirmed that change of the surface pressure was negligibly small. Distinct peak observed at around 250 seconds and 300 seconds in Figures 4(a) and 4(b), respectively, can be assigned to the molecular motion of the side-chain due to the *trans-cis* isomerization of azobenzene groups. It should be noted here that the sign of the displacement current for 6AZ10-CB10-PVA monolayers is clearly reversed in comparison with 6AZ10-PVA monolayers. These differences contain an important information of microscopic motion of side-chain liquid crystal molecules. We assume that due to compression of the monolayer, each side-chain stand almost normal to the water surface. For that case, the vertical component of the dipole moment of *trans*-form azobenzene directs to upward direction from water surface, whereas that of *cis*-form azobenzene faces downward direction due to the bending azo bond. As a result,

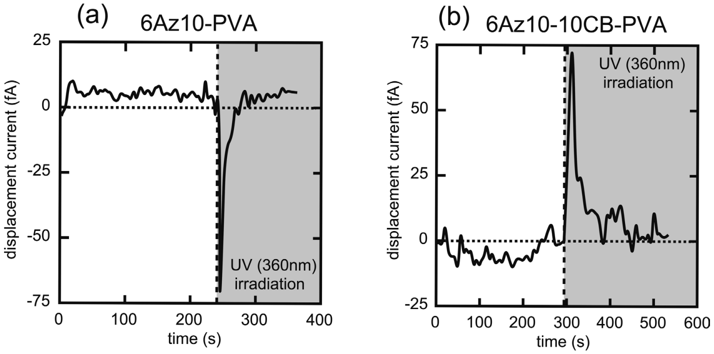

**FIGURE 4** Optical response for photoisomerization of azobenzene molecules (a) 6AZ10-PVA and (b) 6AZ10-CB10-PVA induced by irradiation of UV light.

sign of the current flowing at *trans* → *cis* isomerization of 6AZ10-PVA becomes minus. On the one hand, sign of the current flowing at *trans* → *cis* cis isomerization is plus for 6AZ10-CB10-PVA. This suggests that the liquid crystal side-chain also change the conformation with the photoisomerization of azobenzene side-chain. Cyano group of LC molecule makes a dominant contribution to the MDC. If LC molecule stands almost normal to the water surface, the dipole moment faces a downward direction. Indeed, the result for 6AZ10-CB10-PVA suggests that the LC side-chain change the conformation from homeotropic to planer. Thus we succeeded a detection of the side-chain motion of command surface polymers.

## CONCLUSION

Photoinduced molecular motion of the side-chain of command surface polymer was investigated by means of the Maxwell displacement current (MDC) technique. These molecules change the conformation from *trans* to *cis* by UV light irradiation. According to the UV photoirradiation measurements, direction of the current flowing closed circuit was reversed for 6AZ10-PVA and 6AZ10-CB10-PVA polymers, and this indicates that the motion of LC molecules was successful to detect by the MDC measurements.

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