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Molecular Hybrids of Azobenzene Polymer and Liquid Crystal Molecule. A New Approach for Understanding the Command Surface System

Takashi Ubukata, Takahiro Seki*, Kunihiro Ichimura

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

SUMMARY: Langmuir-Blodgett (LB) films consisting of the hybrid of a polymer having the azobenzene (Az) side chain and 4'-pentyl-4-cyanobiphenyl (5CB) are prepared. Microscopic observations and spectroscopic data both indicate that the Az side chain and 5CB are homogeneously mixed at a molecular level without phase separation in the layer. This provides a satisfactory model of the command surface system. Time course accumulation of spectroscopic data for multilayered hybrid films reveals the cooperative nature of the photo-motivated molecular motions.

Introduction

Monolayers of azobenzene (Az) derivatives on a solid substrate is able to induce reversible alignment changes of liquid crystal molecules of micrometers thickness (corresponding to the 10^4 order in the numbers of molecules). Thus this photochromic layers can be called command surfaces.[1,2] Understandings of this phenomenon require detailed knowledge on the molecular motions at the molecular interface, however, it is absolutely difficult to obtain selectively the information on the interfacial region by spectroscopic methods with ordinary liquid crystal cells. We constituted, in this context, to make a model of the

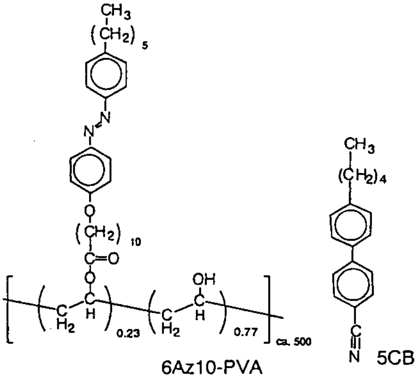

Fig. 1: Molecular structure

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surface region by Langmuir-Blodgett (LB) method.$^{3)}$ Quite recently we reported that the concurrent spreading of Az containing polymer (6Az10-PVA) and 4'-pentyl-4-cyanobiphenyl (5CB) on a water surface provides highly homogeneous hybrid film in which the molecular mixing of the two components are perhaps fulfilled. The deposited film of this hybrid monolayer can be used as a suitable model of the interface region of the command surface, which allows spectroscopic monitoring of light driven processes both for the Az moiety and 5CB molecule. We report herein the structural justification for the molecular homogeneity of the films and observation of the time profiles of the orientational change of molecules upon continuous irradiation.

Experimental

Materials. Synthesis of 6Az10-PVA was described previously.$^{2)}$ 5CB was obtained from MERCK and used without further purification. Water used for LB experiments was of Milipore grade (18 MΩ cm^{-1}).

Instrumentation. Evaluation of spreading behavior of monolayers and its deposition onto a CaF_2 plate were achieved on a Lauda FW-1 film balance at 20 °C. The morphologies of the monolayer was observed by Brewster angle microscopy (BAM) using an NLE EMM633 (Nippon Laser Electronics). UV-visible absorption spectra at the air water interface was taken with a MCPD2000 (Ohtsuka Electronics) system combined with a D_2-I_2 lamp as the light source. Atomic force microscopic (AFM) observation was performed using a SPA300/SPI3700 system (Seiko Instruments) in the dynamic force (non contact) mode. UV visible absorption spectra of deposited LB multilayers were obtained using a Hewlett Packard HP 8452A diode array type spectrophotometer. All measurements were performed in subdued red light.

Results and Discussion

Morphology of the hybrid film. The spreading behavior of pure 6Az10-PVA, pure 5CB, and the 1:1 molar mixture of the two materials were shown in the previous report.$^{3)}$ The spreading from a mixed solution (co-spreading) and a separate pure solutions (separate spreading) gave completely different shapes in the surface pressure-area (π-A) isotherm. The former mixing procedure gave an entirely different curve, indicative of attainment of the molecular mixing. The latter, in contrast, provided an isotherm corresponding to the sum of those for the two pure materials, which can be explained by the phase separation.

BAM observation justified the interpretation deduced from the ι-A isotherm data (Fig. 2). The co-spread hybrid film exhibited a highly homogeneous BAM image (a), whereas the morphology of the separate-spread film was constituted of co-existence of homogeneous area regions corresponding to 6Az10-PVA and patched 5CB regions (b). The existence of patches in the 5CB regions indicate that multilayering of this molecule to form lens-like structure which is characteristic in films of a cyanobiphenyl type liquid crystal molecule.[4,5]

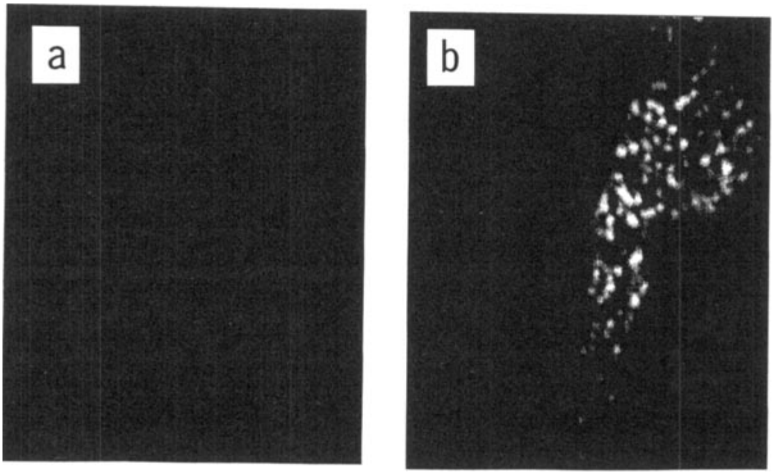

Fig. 2: BAM images of the 6Az10-PVA/5CB (1:1) mixed film on water prepared from co-spreading (a) and separate-spreading (b) procedures.

The 6Az10-PVA/5CB (1:1) hybrid film prepared from the co-spreading was transferred onto a freshly cleaved mica surface, and its topographic AFM image is indicated in Fig. 3. The roughness of the film surface was found to be less than the molecular length (within 1 nm). BAM and (a few μm resolution) AFM (ca. 0.1 μm resolution in this case) observations both indicate the high homogeneity of the film with no indication of phase separation.

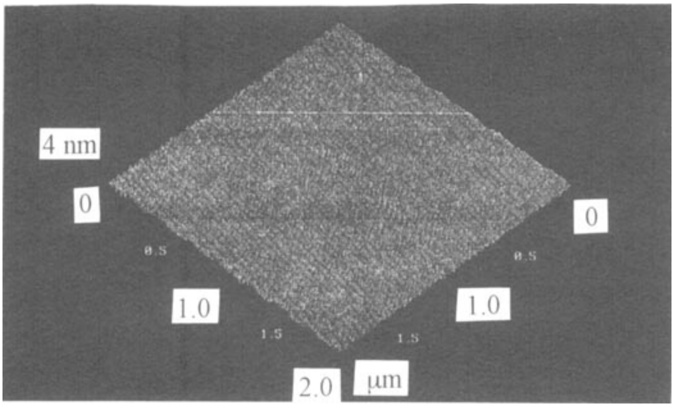

Fig. 3: AFM topography (2 x 2 µm)of the co-spread 6Az10-PVA/AA (1:1) transferred on mica taken in the dynamic force mode.

UV-visible absorption spectra. Figure 4 shows the UV-visible absorption spectra of pure 6Az10-PVA, pure 5CB, and the co-spread (1:1) hybrid film on the water surface. Spectra were taken in the transmission mode. The area of the monolayer was fixed at 0.6 nm^2 per molecules. The absorption maxima of the π–π* band (long axis) of pure 6Az10-PVA monolayer, and that of 5CB were positioned at 320 and 280 nm. As obviously indicated, the absorptivity of these bands for the hybrid film was markedly reduced, indicating that the both molecules were oriented highly perpendicular to the water surface. This behavior can be the consequence of mutual insertion of the two components attained in a cooperative fashion. The peak attributed to the π–π* band of Az in the hybrid film shifted to a longer

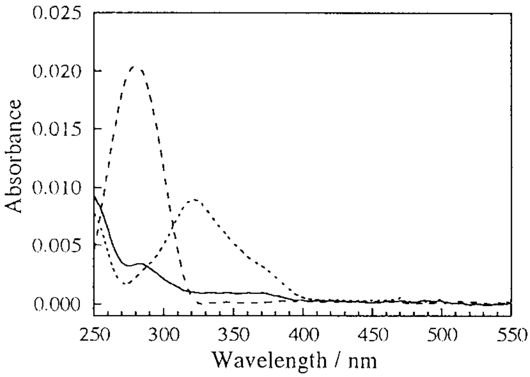

Fig. 4: UV-visible absorption spectra of monolayers of 6Az10-PVA (dotted line), 5CB (dashed), and the hybrid (solid) on a water surface.

wavelength (ca. 350 nm) which shows the destruction of H-type aggregation.

The striking reduction in the absorbance and spectral shift both provide a strong evidence that the two components are mixed at a molecular level. Together with the microscopic observations, we conclude that the two components are molecularly mixed to form a highly oriented monolayer.

Photoinduced orientational changes. The hybrid film was transferred onto a quartz substrate by the vertical dipping method. Upon illumination, the hybrid film showed a reversible orientational change of both Az unit and 5CB molecules. This was first confirmed by the changes in the UV visible absorption spectroscopy of a single layered hybrid film.[3)] It was newly found here that, also for the built-up multilayers, essentially the same phenomenon takes place as depicted in Fig. 5. This means that the molecular process taking place in the monolayer is multiplied by the deposition number. Therefore, the small changes in the spectroscopic signals of the monolayer (the model of interfacial region) can be amplified, which then allows a time course observation upon continuous illumination in a good accuracy. Enhancement and reversion of the 280 nm band on UV and visible light irradiation,

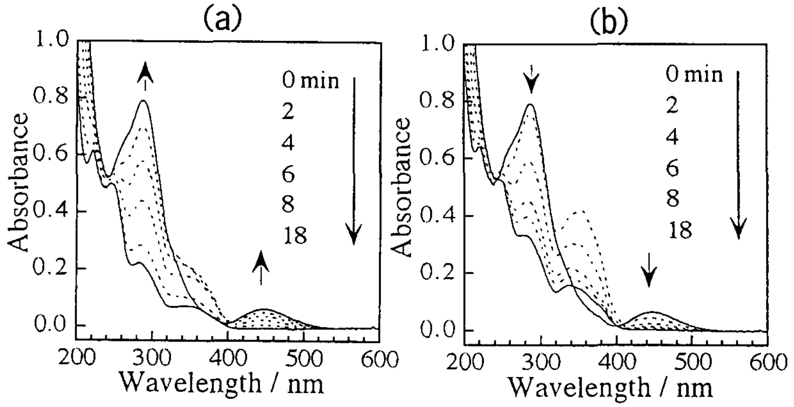

Fig. 5: UV visible absorption spectral changes of a 39-layered hybrid (1:1) LB film on both sides of a CaF_2 substrate deposited at 30 mN m^{-1} upon exposure to UV (365 nm, 0.35 mW cm^{-2}, a) and visible light (436 nm, 0.35 mW cm^{-2}, b).

respectively, indicate that the reversible perpendicular/tilt orientational changes of 5CB molecule are induced by the Az photoisomerization.

Continuous accumulation of spectra on illumination was conducted, and the changes in absorbance at 280 (5CB π–π* long axis), 350 (*trans*-Az π–π* long axis), and 440 nm (n-π* Az) were shown in Fig. 6. It is deduced from these profiles that the perpendicular to tilt orientational change of 5CB occurs concurrently with the *trans* to *cis* isomerization of the Az unit, but the reverse process was found to consist of two steps; an initial retention of the tilt state to ca. 40 % isomerization and a following sudden orientational change to the perpendicular state. This is clearly the consequence of the molecular cooperativity involved in this system.

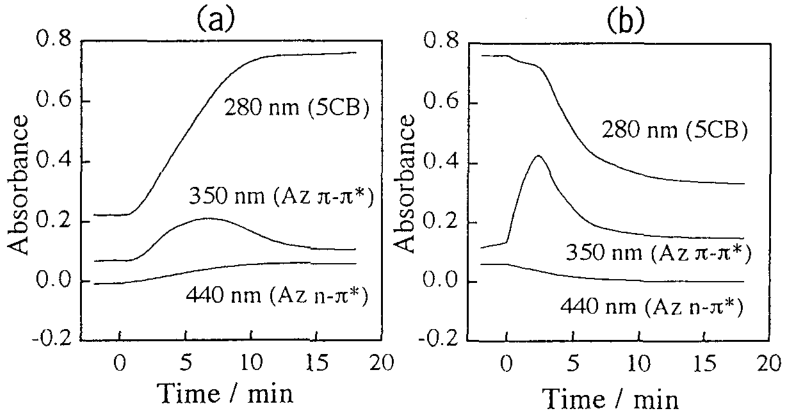

Fig. 6: Time course of the absorbance changes at 280 nm, 350 nm, and 440 nm bands upon exposure to UV (a) and visible (b) light. The sample and irradiation conditions are identical to those shown in Fig. 5.

Conclusion

Modeling of the interfacial region of command surface system was successfully achieved by means of construction of a molecular hybrid by LB method. Multilayers of the hybrid film allowed time course spectroscopic observation of the orientational changes under continuous illumination in a satisfactory accuracy. This approach was found to be quite useful for elucidating the process of local molecular motions and their cooperative behavior at the interface.

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References

1) K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, K. Aoki, *Langmuir* **4**, 1214 (1988)
2) T. Seki, M. Sakuragi, Y. Kawanishi, Y. Suzuki, T. Tamaki, R. Fukuda, K. Ichimura, *Langmuir* **9**, 211, (1993)
3) T. Ubukata, S. Morino, T. Seki, K. Ichimura, *Chem. Lett.* **1998**, 71
4) M. C. Friedenberg, G. G. Fuller, C. W. Frank, C. R. Robertson, *Langmuir* , **10**, 1251 (1994)
5) K. A. Suresh, A. Bhattacharyya, *Langmuir*, **13**, 1377 (1997)