

Modeling the Interface Region of Command Surface 1. Structural Evaluations of Azobenzene/Liquid Crystal Hybrid Langmuir Monolayers

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Langmuir films composed of mixtures of an amphiphilic polymer containing azobenzene (Az) side chain (6Az n -PVA, n being the spacer length) and a nematic liquid crystal (LC) molecule, 4'-pentyl-4-cyanobiphenyl (5CB), were prepared at the air–water interface in an attempt to construct the interface model of the command surface system which performs the photoswitching of LC alignment. Surface pressure–area isotherms, visualization by Brewster angle microscopy (BAM) and atomic force microscopy (AFM), and UV–visible absorption spectroscopy revealed that the two components are homogeneously mixed at a molecular level without lateral phase separation under proper conditions concerning the way of mixing, the mixing ratio, and the spacer length of the side chain. Upon homogeneous co-spread mixing, both the Az side chain of 6Az n -PVA and the LC molecule were oriented highly perpendicular to the water surface, which was unavailable with the individual component. This orientational induction can be ascribed to a mutual insertion of the two rod-shaped components attained in a cooperative fashion. The above structural features of the hybrid monolayer fulfill important criteria in modeling the interface region of the photoswitchable LC alignment layer. Effects of changes in mixing ratio and the spacer length (n) on the film structure are also described.

1. Introduction

Alignment of liquid crystal (LC) molecules crucially depends on the nature of the substrate surface.^{1–3} The assembling nature of LC molecules within a correlation distance involves strong molecular cooperativity, which leads to a great amplification of orientational information possessed by the surface. This assembling cooperativity allows photocontrols of the LC alignment by molecular layers or polymer films containing various kinds of photoreactive units such as azoaromatics,^{4–10} cinnamate,^{11–15} coumarin,^{16,17} and others.^{18–20} Elucidation of the molecular mechanism of photoalignment is of great importance from the standpoints of both fundamental LC research and display technologies.^{21,22}

Reversible alignment switching of LC molecules can be performed by a photochromic monolayer which is termed as a command surface or command layer.^{4–8} The most typical and promising chromophore for the reversible orientational switching is azobenzene (Az). Since the mechanistic responsive properties of the bulk LC phase can be understood by the intrinsic physical constants (e.g., viscosity, elasticity, etc.) of the LC,²³ a precise and essential understanding of the command surface system requires information on the dynamic molecular processes occurring in the contact region of the Az command layer with LC molecules.

In the vicinity of the interface, a collective host (command layer)—guest (LC molecule) recognition should be essential. The rod-shaped Az derivative arrayed in the two dimensions recognizes the rodlike LC molecules.⁷ UV–visible and infrared spectroscopies are promising tools for the elucidation of the intermolecular dynamics. However, once an LC cell with a thickness of micrometers is fabricated, spectroscopic signals

from the surface molecules are completely hidden by those from the majority of the bulk LC molecules. Optical analysis in the reflection mode provides information on the dynamics of LC molecules near the surface,^{24–26} but this method collects signals in the range of a few hundred nanometers, and does not provide knowledge on the surface region at the molecular level. To overcome this problem, we started an investigation to study a two-dimensional model system which mimics the molecular contact region.²⁷

We anticipated that the model hybrid architecture of a molecular array composed of Az and LC molecule can be processed by the Langmuir–Blodgett (LB) method (Figure 1). In the series of this approach, poly(vinyl alcohol) derivatives having the Az side chain (6Az n -PVA)^{28,29} and 4'-pentyl-4-cyanobiphenyl (5CB) were used as the Az and LC components, respectively (Figure 2). 5CB was chosen here for the two reasons. First the cyano group in the LC molecule works as the hydrophilic head for the monolayer formation at the air–water interface.^{30,31} Second, for structural and dynamic measurements, the cyanobiphenyl chromophore and the cyano group can be utilized as a good reporter part in the UV–visible absorption and IR spectroscopy, respectively, as will be indicated in the subsequent paper.³²

For the appropriate mimics of the command surface interface, the hybrid LB film should implement the following criteria: (i) Fulfillment of the molecular mixing in the film without lateral phase separation, (ii) achievement of cooperative interactions between the two components, and (iii) realization of molecular orientational changes in the hybrid film in a *reversible* fashion. Among these concerns, this paper mainly deals with (i) and (ii)—namely, the structural features of hybrid layers of the Az component and LC molecule on the water surface. Structural justification of the Langmuir monolayer at the air–water interface before transfer onto a solid substrate is the first step

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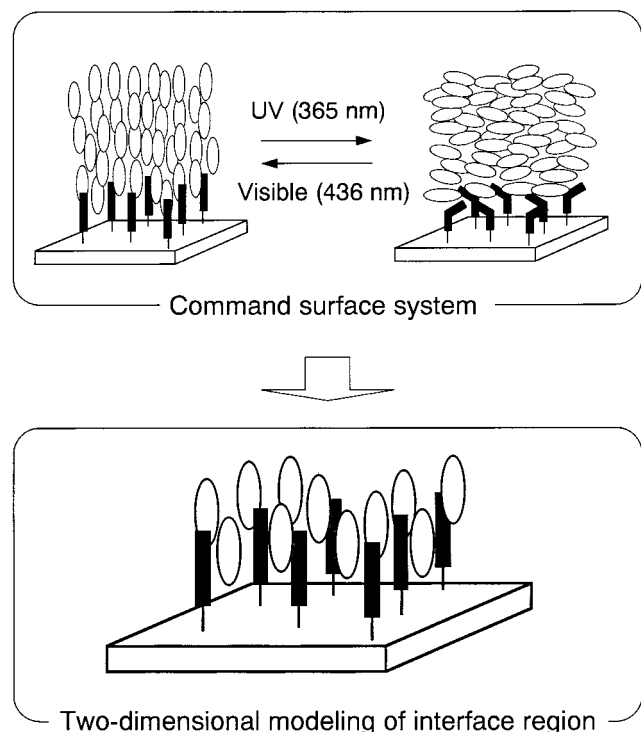


Figure 1. Schematic illustration of the modeling concept of this work.

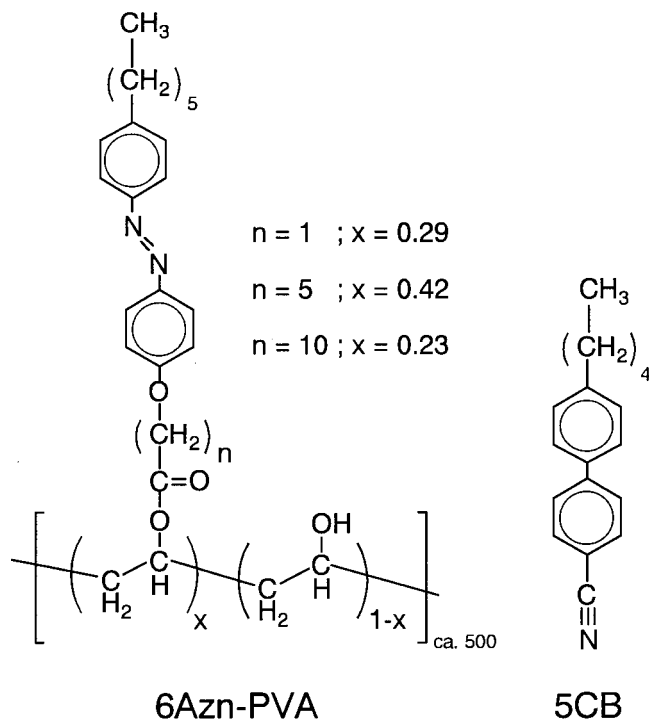


Figure 2. Molecular structure of materials.

of the series of this study. In the succeeding paper,³² preparation of LB films of these mixtures onto a solid substrate and photoresponse behavior of these model LB films by spectroscopic methods for justification of the criterion (iii) are presented in detail.

2. Experimental Section

Materials. The synthesis and characterization of the polymeric Az amphiphile 6Az10-PVA were described in the previous papers.^{7,28,29} 5CB was purchased from Merck and was used

without further purification. Ultrapure water used for LB experiments was of Millipore grade ($18 \text{ M}\Omega \text{ cm}^{-1}$). Chloroform for monolayer preparation was of spectroscopic grade (Uvasol, Cica-Merck).

Methods. The spreading behavior of monolayers at the air–water interface was evaluated on pure water filled in a Lauda FW-1 film balance at $20 \pm 0.5^\circ\text{C}$. 6Az10-PVA and 5CB were separately dissolved in chloroform at a concentration of $1 \times 10^{-3} \text{ mol dm}^{-3}$. Mixed solutions were prepared from these mother solutions at target mixing ratios. After evaporation of the solvent, the monolayer was compressed at a speed of $20 \text{ cm}^2 \text{ min}^{-1}$, and the surface pressure was monitored.

The single layer deposition of the monolayer was undertaken in the upstroke direction onto a freshly cleaved mica for the atomic force microscopic (AFM) observation. For deposition of monolayers, the spreading solution was preirradiated with 436 nm light to a photoequilibrated state (ca. 70% trans-isomer content). This procedure was required for successful and reproducible deposition. The transfer ratio was essentially unity (1.0 ± 0.1).

Morphologies of monolayers at the air–water interface were observed with a Brewster angle microscope (BAM) (NL-LB/EMM633; Nippon Laser Electronics). *p*-Polarized light from a 10 mW He–Ne laser (633 nm) was reflected off the air–water interface at the Brewster angle (53.1° for the air–water interface). The reflected beam passed through an analyzer fixed near 0° to the incident polarization was directed into an interference-free CCD camera (Hamamatsu Photonics). The obtained images were recorded by a Sony video-printer.

UV–visible absorption spectra of monolayers at the air–water interface were taken on a spectrometric system composed of a multichannel photodiode array detector system (MCPD-2000, Ohtsuka Electronics) assembled with a D_2 – I_2 lamp (Ohtsuka Electronics) and a processing computer. In this system, the probing beam was reflected by a mirror at the bottom of the trough passing through the monolayer twice, and was led to the detector. UV–visible absorption spectra of solution samples were obtained using a Hewlett-Packard 8452A diode array type spectrometer.

The AFM image was taken by a Seiko Instruments SPA300 module combined with a SPI3700 probe station in the noncontact mode (dynamic force mode). Commercially available Si cantilevers with a force constant of 16.0 N m^{-1} were used. All procedures were carried out in dimmed red light.

3. Results and Discussion

3.1. 6Az10-PVA/5CB Monolayer of Equimolar Mixing.

3.1.1. Surface Pressure–Area Isotherms. We started with examinations on the monolayers consisting of an equimolar mixture of 6Az10-PVA and 5CB. The mixing was done in two ways: (i) spreading from two chloroform solutions of each component onto the water surface (separate spreading), and (ii) spreading from a premixed solution (co-spreading). In the former method, the 6Az10-PVA solution was spread first, and then 5CB solution was successively poured onto the water surface.

Figure 3 shows the surface pressure–area (π – A) isotherms of pure 5CB (a), pure 6Az10-PVA (b), the 1:1 mixtures prepared by co-spreading (c), and separate spreading (d). Pure 5CB gave a monolayer isotherm with a pressure lift-up area at 0.42 nm^2 , and an inflection corresponding to the monolayer collapse at 0.33 nm^2 and 5 mN m^{-1} (a). The mixed monolayer of the separate spreading method provided a π – A isotherm which could be regarded as the sum of the isotherms of pure 5CB and 6Az10-PVA monolayers (d), exhibiting an initial collapse at

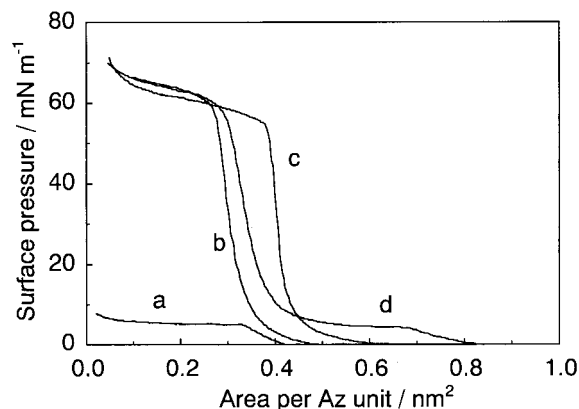


Figure 3. Surface pressure–area isotherms of pure 5CB (a), pure 6Az10-PVA (b), co-spread 6Az10-PVA/5CB (1:1 molar mixture) (c), and separately spread 6Az10-PVA/5CB (1:1 molar mixture) (d) on pure water at 20 °C.

low pressure (ca. 5 mN m⁻¹), a plateau at this pressure, and a final collapse at a high pressure (ca. 60 mN m⁻¹). The collapses at the low and high pressures correspond to the contributions of 5CB and 6Az10-PVA monolayers, respectively. The shape of the isotherm of the co-spread mixture (c), on the other hand, was essentially different from that of the separate spreading. The features of the curve resembled that of pure 6Az10-PVA monolayer but showed some modifications characterized by an expansion in the limiting area and a lower compressibility at the steepest uprise region. The limiting areas of 6Az10-PVA and the co-spread monolayers were 0.33 and 0.42 nm², respectively. This increment of the occupying area (0.09 nm²) is considerably smaller than that expected for the contribution of pure 5CB molecule (ca. 0.33 nm², see curve a). This shows that 5CB is squeezed out partly toward the air side of the monolayer or the co-spread monolayer is composed of a molecular mixture of 6Az10-PVA and 5CB. In any case, the behavior of the co-spread film eliminates the possibility of lateral phase separation.

3.1.2. Brewster Angle Microscopy. BAM is a promising method for direct morphological visualizations of molecular films at the air–water interface.^{33,34} The BAM observation was achieved on the compression process with simultaneous monitoring of surface pressure. Figure 4 displays BAM images of the co-spread (a), separately spread (b) films of 6Az10-PVA/5CB at 10 mN m⁻¹, and pure 5CB at 6 mN m⁻¹ film (c).

The co-spread monolayer at 0 mN m⁻¹ showed domain structure having low contrast with the water surface. As the surface pressure rose, the domains started to fuse each other and formed a highly homogeneous monodomain monolayer without phase separation as shown in (a), which was retained until the film collapse (55 mN m⁻¹). In the case of the separately spread monolayer, in contrast, a clear lateral phase separation indicating two discernible parts was observed at 10 mN m⁻¹. One of them was highly homogeneous with solid boundaries, and the other exhibited a number of bright circular dots having a diameter of approximately 10 μm (b). Very similar dot structure was observed for the pure 5CB in the plateau region (c), showing that the separately spread monolayer (b) is the constitution of the two components of pure solid 6Az10-PVA monolayer³⁵ and pure fluid 5CB film. The bright dots should correspond to multilayered parts formed in the course of the monolayer collapse.^{31,36–38} The UV–visible absorption spectra taken at different positions of measurement did not coincide with each other (data not shown), which also shows the heterogeneous and phase-separated structure of the separately

spread film. In this way, mixing the two components in the solution before spreading was found to be essential for obtaining the homogeneous molecular film.

3.1.3. UV–Visible Absorption Spectroscopy. UV–visible absorption spectra were taken for the floating monolayers on the water surface in the transmission mode. Figure 5 shows the UV–visible absorption spectra of pure 6Az10-PVA, pure 5CB, and the equimolar mixture of the film (co-spreading) on the water surface (a) obtained at a common area of 0.6 nm² per molecule. Spectra of chloroform solutions were shown in Figure 5b. The absorption maximum of the π – π^* band (long axis) of the pure 6Az10-PVA monolayer and 5CB were observed at 322 and 280 nm, respectively. As obviously indicated in Figure 5a, the absorptivity of these bands of the mixed film (solid line) was markedly reduced from those of pure 6Az10-PVA (dotted line) and 5CB (dashed line) monolayers. This unequivocally indicates that the long axis of both the Az side chain and 5CB molecule was oriented highly perpendicular to the water surface. In solutions, the spectrum of the mixture was, as anticipated, exactly the sum of the two spectra of pure 6Az10-PVA and 5CB (b).

The above orienting behavior at the air–water interface should 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 mixed film shifted to a longer wavelength (ca. 350 nm), which shows dissociation of H-type aggregation which is formed in the pure 6Az10-PVA monolayer. The striking reduction in absorption of the long axis transition of both the Az unit and 5CB and the spectral shift of the Az unit both provide strong evidence for the attainment of complete mixing at a molecular level. Hence the mixed film can be termed a hybrid film.

3.1.4. Atomic Force Microscopy. The BAM observation provides the morphological features at a resolution of a few micrometers. The homogeneity of the mixed film was further evaluated by AFM. The co-spread mixed film of 6Az10-PVA/5CB compressed to 10 mN m⁻¹ was transferred onto a freshly cleaved mica surface in the upstroke direction of the vertical lifting. The AFM image of this film is shown in Figure 6.

As indicated, the lateral phase separation was not recognized also from the AFM image. The surface roughness of this film was within 1 nm, which is smaller than the molecular length of the both components. Furthermore, the skeletonized film after removal of 5CB molecules essentially gave the same flat surface (data not shown here).³⁹ These facts further support the formation of the molecular hybrid.

In summary, on the film structure at the air–water interface, the data of π –A isotherms, BAM, UV–visible absorption spectroscopy, and AFM all support the interpretation that the co-spreading of the equimolar mixture of 6Az10-PVA and 5CB onto the water surface provides homogeneously mixed film without a trace of lateral phase separation. Thus, the structure of the mixed film fulfills first criterion on the molecular mixing for the model of the contacting region of the command surface systems. Furthermore, UV–visible spectroscopic data indicate that both components are aligned perpendicular to the surface through molecular cooperativity. The second criterion of the modeling is also properly satisfied.

3.2. Variations of the Mixing Ratio. Investigation of the co-spread films at other mixing ratios was further carried out. Figure 7 shows π –A isotherms of monolayers consisting of a mixture of 6Az10-PVA and 5CB at various molar ratios ($r = [5CB]/[Az \text{ unit}]$). The inset of the figure depicts the pressure lift-off areas (open circles) and limiting areas estimated from

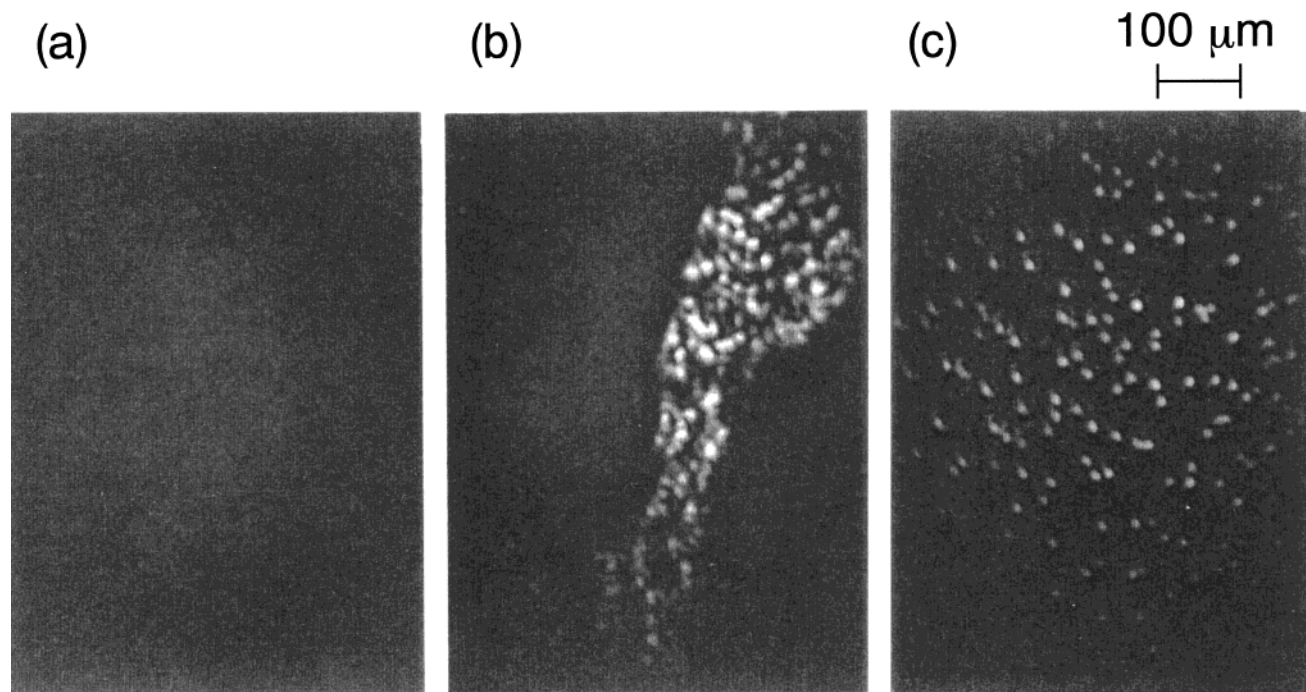


Figure 4. BAM images of the co-spread (a), separately spread (b) films of the equimolar mixture of 6Az10-PVA and 5CB taken at 10 mN m^{-1} , and pure 5CB film at 6 mN m^{-1} (c).

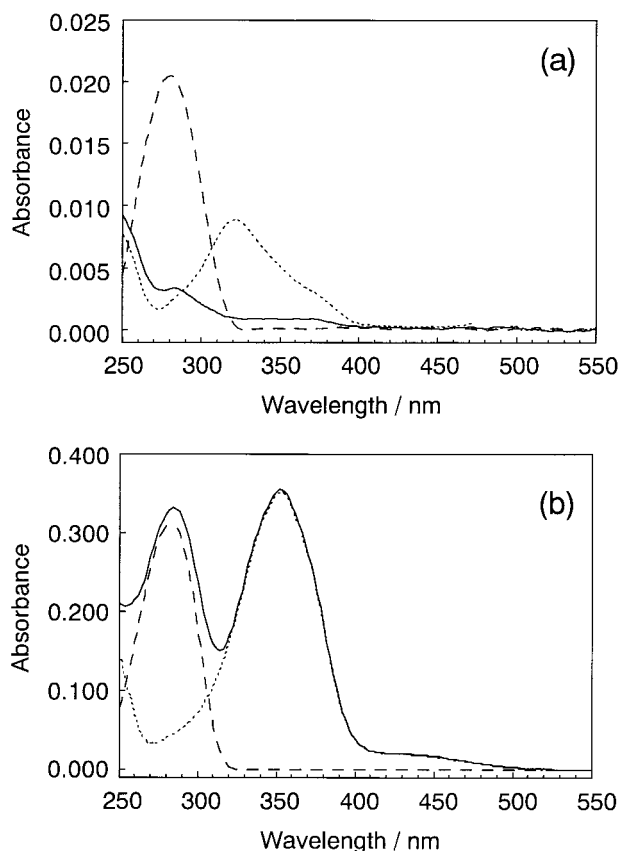


Figure 5. UV-visible absorption spectra of the monolayers at the air-water interface taken at an occupying area of 0.6 nm^2 per Az unit (a) and identical materials in chloroform [$1.2 \times 10^{-5} \text{ mol dm}^{-3}$] (b). In both figures, dotted, dashed, and solid lines indicate the spectra of 6Az10-PVA, 5CB, and 6Az10-PVA/5CB (1:1) mixture, respectively.

the extrapolation of the steepest region to the zero pressure (closed circles) as a function of r . The π - A isotherms at $r = 1$ and 2 were quite similar to that of pure 6Az10-PVA monolayer. Their limiting areas showed a minor expansion that differed

from that of 6Az10-PVA by 0.09 and 0.17 nm^2 , respectively. The increment of the occupying area was significantly smaller than that anticipated from the pure 5CB monolayer (ca. 0.33 nm^2 , see section 3.1.1).

At higher molar ratios ($r = 3$ and 6), a plateau region emerged at low pressures before appearance of the steep uprise in the π - A isotherm, which is in analogy with the behavior of the separately spread equimolar 6Az10-PVA/5CB monolayer (Figure 3, curve d). In this range the increase in r caused the expansion of the plateau region whereas the limiting area stayed constant at ca. 0.60 nm^2 . These features can be well seized from the inset of the figure. The first lift-off area increased in a parallel fashion to the limiting area in the range of $r = 0$ –2, and it showed large deviations at r exceeding 3.

The BAM images taken on the compression process also showed clear differences in the morphologies of the films between the lower ($r = 1$ and 2) and higher ($r = 3$ and 6) molar ratios. The morphology of the high molar ratio film in the plateau region was characterized as the coexistence of homogeneous parts and patched ones where many bright circular domains were present as shown in Figure 4b. The films at smaller r gave a highly homogeneous BAM image below the collapse pressure similarly to Figure 4a. These results imply that the 6Az10-PVA monolayer can accommodate two 5CB molecules per Az side chain unit without phase separation, and that, above this ratio, the lateral phase separation starts to occur.

3.3. Variations of the Spacer Length. In the photochemical alignment controls of nematic LC molecules by 6Az n -PVA, the length of the spacer (n) which connects the Az unit and PVA backbone influences the response behavior to a large extent.⁷ In this context, mixed films for 6Az n -PVA having the shorter spacer ($n = 1$ and 5) seemed worthwhile to work with. π - A isotherms of co-spread monolayers of 6Az5-PVA and 6Az1-PVA with 5CB at various molar ratios ($r = [\text{5CB}]/[\text{Az unit}]$) are shown in Figures 8a and 8b, respectively. The inset depicts the pressure lift-off areas (open circles) and the limiting areas (closed circles) as a function of r .

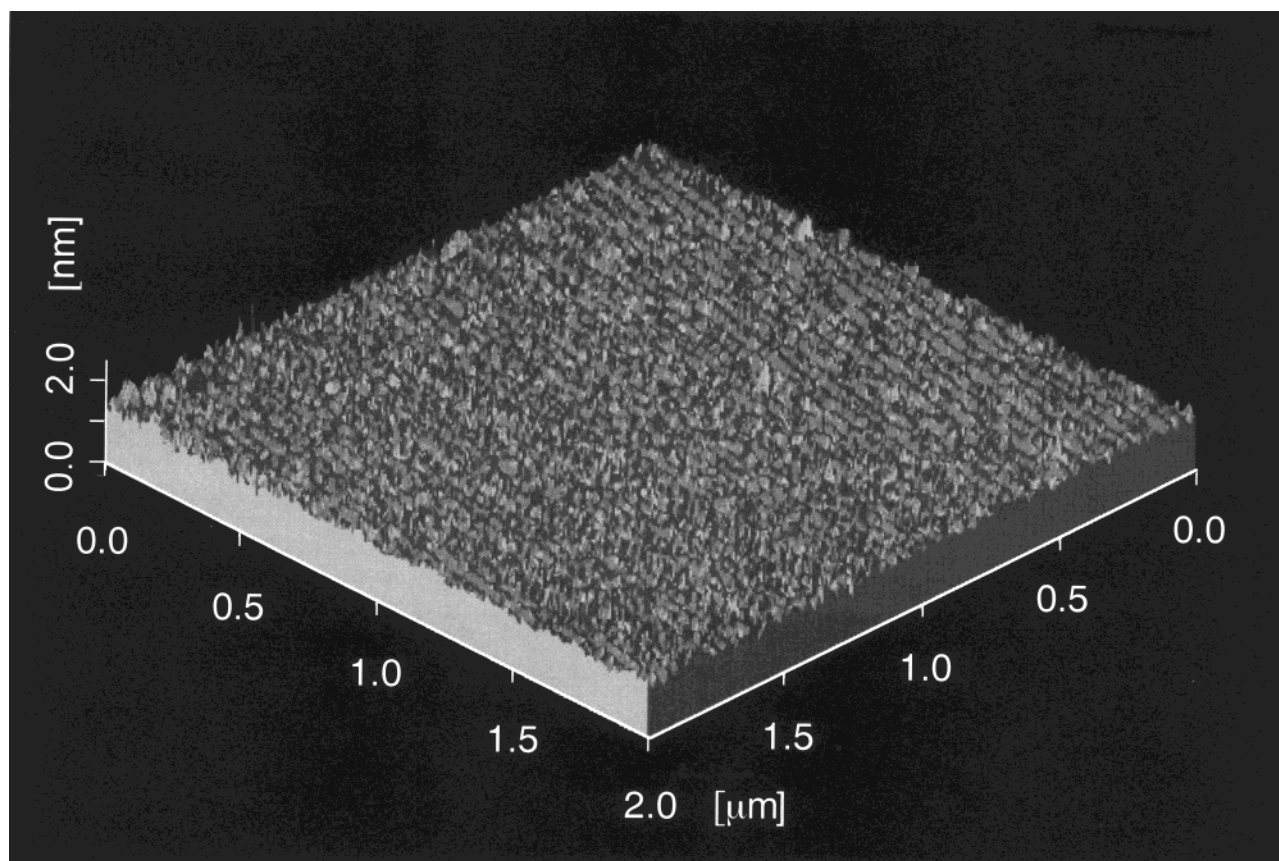


Figure 6. AFM topography ($2 \times 2 \mu\text{m}^2$) of co-spread 6Az10-PVA/5CB (1:1) film on mica taken in the dynamic force mode.

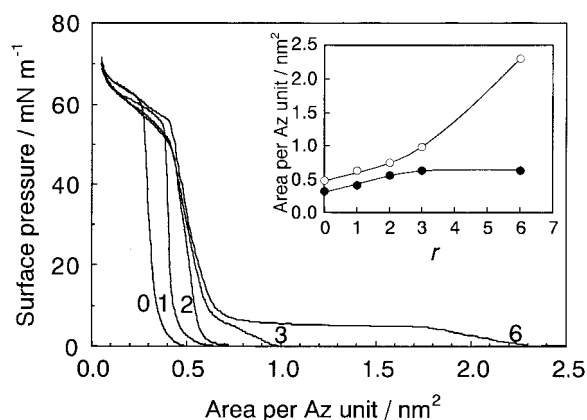


Figure 7. Surface pressure–area isotherms of monolayers consisting of a mixture of 6Az10-PVA and 5CB at $r = 0, 1, 2, 3$, and 6 (noted in the figure) at 20°C . The inset depicts the pressure lift-off area (open circles) and limiting area (closed circles) as a function of r .

Similar to the 6Az10-PVA system below $r = 2$, π -A isotherms of the equimolar mixture between 6Az n -PVA ($n = 1$ and 5) were commonly characterized by a slight expansion in the limiting area without appreciable expansion due to the molecular hybridization with 5CB. In the case of $n = 1$ for the equimolar mixing, an inflecting point at 30 mN m^{-1} in the π -A isotherm (b, $r = 1$) was observed. BAM gave an image showing bright dots which started to appear from this inflecting point. The 6Az1-PVA/5CB monolayer is thus mechanically brittle against lateral compression.

In both cases for $n = 1$ and 5 , a plateau originating from the pure 5CB layer was observed at $r = 2$ and 3 in the low-pressure region (ca. 7 mN m^{-1}), indicative of lateral phase separation. These results indicate that the 6Az5-PVA and 6Az1-PVA

monolayers can accommodate one 5CB molecule per Az side chain unit without phase separation, and that above this ratio lateral phase separation occurs. Consequently, the molecular mixing is fulfilled up to the equimolar ratio for 6Az1-PVA and 6Az5-PVA systems, and one additional 5CB molecule (two in total) can be accepted by the 6Az10-PVA monolayer (see section 3.2). The reason for the capacity to accommodate two 5CB molecules for 6Az10-PVA is as follows. One 5CB molecule per Az side chain can be commonly positioned on the air side (tail part) of Az unit. The molecular length of 5CB (1.8 nm) is similar to that of C_{10} methylene spacer (1.7 nm). Therefore it would be possible to adapt one additional 5CB molecule in a space formed between Az unit and the backbone polymer only for 6Az10-PVA. The cavity for insertion of a 5CB molecule may be made up by the difference in cross sectional area between the Az unit (0.25 nm^2)⁴⁰ and alkyl chain (0.20 nm^2).⁴¹

To obtain information on the orientation and packing state of the chromophores in the mixed film, UV–visible absorption spectra were measured on the water surface. Figure 9 indicates absorption spectra of the 6Az n -PVA/5CB monolayers prepared at $r = 1$. Here the film area was fixed at 0.60 nm^2 per Az unit for all cases.

The shape of the absorption spectrum for the monolayer of $n = 5$ virtually coincided with that of $n = 10$, showing that the highly perpendicular orientation of the two components without formation of H-type aggregation of Az unit is attained for 6Az5-PVA. A different type of spectrum was obtained for $n = 1$. The absorbances of the bands assigned to the long axis π - π^* band for Az (330 nm) and cyanobiphenyl (280 nm) were considerably enhanced. The spectral shape of 6Az1-PVA/5CB monolayer indicates that the molecular orientation is less ordered. The existence of the long flexible spacer ($n = 5$ and 10) is seemingly a requisite for the attainment of highly

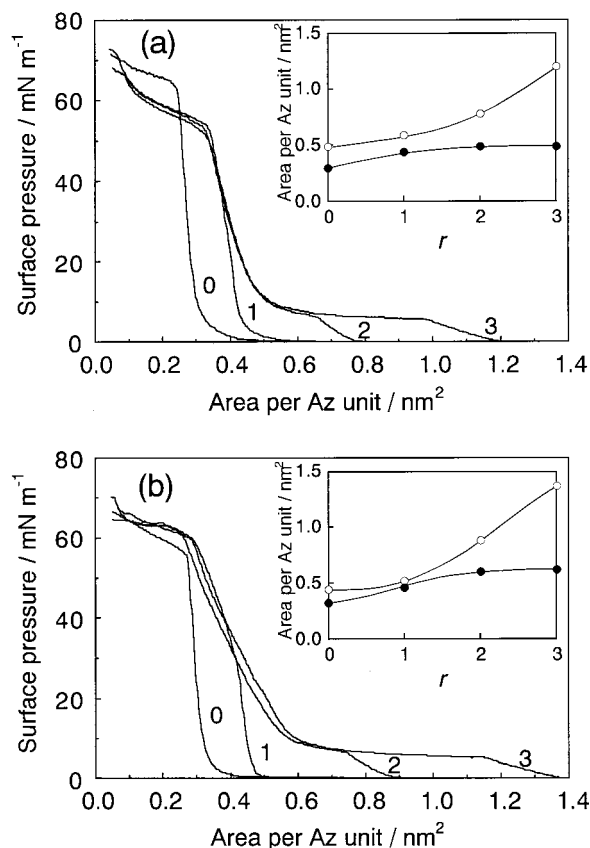


Figure 8. Surface pressure–area isotherms of monolayers consisting of a mixture of 6Az5-PVA (a) or 6Az1-PVA (b) and 5CB at $r = 0, 1, 2$, and 3 (noted in the figure) at 20°C . The inset depicts the pressure lift-off area (open circles) and limiting area (closed circles) as a function of r .

perpendicular molecular orientation. The exceptional result obtained for 6Az1-PVA may be related to the commanding ability of the LC photoalignment. The homeotropic/planar alignment control by the Az photoisomerization can be achieved with monolayers of 6Az10-PVA and 6Az5-PVA, but the 6Az1-PVA monolayer does not have this effect.⁷ The cooperative orienting interaction (interpenetration) should be less favorable in the 6Az1-PVA monolayer whose side chain has minor flexibility to adapt a rodlike molecule.

4. Conclusion

From the structural viewpoints of Langmuir films on the water surface, modeling of the interfacial region of the command surface system was successfully achieved by means of co-spreading of the chloroform solution involving the two components, 6Az n -PVA and 5CB. On the criteria for the appropriate mimicking of the command layer/LC interface (see section 1), the first issue on the complete mixing at a molecular level was justified by π -A isotherms, microscopic observations, and UV–visible spectroscopy. BAM and AFM confirmed that there is no trace of lateral phase separation. AFM showed the highly flat surface of the mixed film. The second criterion on the molecular cooperativity can be drawn from the spectral data. The mixed film gave markedly different transmission spectra, which should be the consequences of the induction of highly perpendicular orientation and dissociation of H-aggregate of the Az unit. These effects are undoubtedly derived through a mutual shape recognition of the rodlike molecules. In the succeeding paper,³² the photoresponse of the transferred hybrid LB film

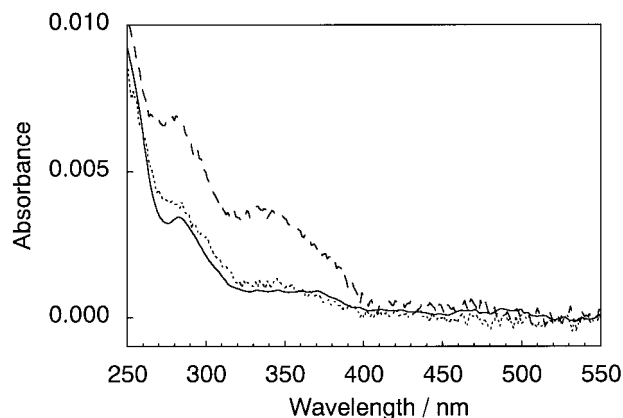


Figure 9. UV–visible absorption spectra of 6Az n -PVA/5CB monolayers of equimolar mixing at the air–water interface at an occupying area of 0.6 nm^2 per Az unit. Dashed, dotted, and solid lines are data for $n = 1, 5$, and 10 , respectively.

will be presented for verification of the final criterion concerning the dynamic cooperative aspects and repeatability.

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