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Monolayer alignment on azobenzene surfaces during UV light irradiation: Analysis of optical polarized absorption measurement results and theoretical treatment

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The influence of the charge separation during the *trans-cis* conformational change on the surface of *azobenzene* 6Az10PVA monolayer on the polar liquid-crystal monolayer film, such as 4-*n*-pentyl-4′-cyanobiphenyl(5CB), is investigated. The effective anchoring energy (in the Rapini-Papolar form) is phenomenologically described in the framework of the molecular model, which takes into account the interaction between the surface polarization and surface electric field, for number of conformational states of the boundary surface. It is shown, using the experimental data for the voltage across the 6*Az*10PVA+5CB film, provided by the surface-potential technique, that the charge separation during the conformational changing, caused by the UV irradiation, may lead to changing of the surface alignment of liquid-crystalline molecules. The influence of the photoisomerization process on the orientational order parameter $S_2(t)$ using the optical polarized absorption measurement is also investigated. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2141956]

One of the most attractive methods for controlling the surface anchoring is the photoalignment technique which uses light-induced anisotropy in mono-(multi) layer(s) Langmuir films on the photosensitive substrates. The problem of *trans-cis* photoisomerization in mono- and multilayer systems remains one of the fundamental problem in Langmuir monolayer physics.[1–3] Some organic materials such as *azobenzene*, which may exhibit the liquid-crystalline properties [azobenzene exhibits a nematic liquid-crystal (LC) phase in the temperature range ~300−341 K], undergo a *trans-cis* isomerization during a laser beam transmittance. The photoisomerization process, however, may result in changes of the surface charge density caused by the charge separation, taking place during the *trans-cis* isomerization due to the vertical component of dipole moment of surface azobenzene monolayer. Recently, the Maxwell-displacement-current (MDC) and surface-potential measurements have been usefully suggested to observe the changing of the surface charge density during the *trans-cis* conformational transition between the surface *azobenzene* monolayer and LC film.[4] The surface-potential signal allows us to determine the changing of the surface charge density in *azobenzene* monolayer deposited on the metal electrodes (see Fig. 1).

Specifically, it has been observed that the monolayer of 6Az5PVA, which in the initial state exhibits the *trans* conformation, with the transmittance of a He–Ne laser beam (632 nm in wavelength) undergoes the *trans-cis* isomerization.[5] By putting, for instance, the 6Az10PVA monolayer in contact with the polar LC monolayer film, such as 4-*n*-pentyl-4′-cyanobiphenyl(5CB), one can expect the changing, during the laser beam transmittance, of the surface alignment of the LC molecules. Such orientational transition, in turn, can be induced by changing of the surface charge density caused by the charge separation, taking place during the conformational change on the surface *azobenzene* monolayer. In order to examine the magnitude of the changing surface charge density $\Delta\sigma=\sigma_{trans}-\sigma_{cis}$, we consider the data for changing of the voltage $V(z)$ across both the 6Az10PVA and 6Az10PVA+5CB films on the metal electrodes. Using the potential which is built up across these films, the spatial charge density ρ can be written in the following form:[6]

$$\rho=\frac{\sigma}{L}=\frac{\epsilon_w\epsilon_0}{L}\frac{dV(z)}{dz}, \tag{1}$$

where L is the film thickness, $\rho=\sigma/L$ is the spatial charge density, $L\sim l_{5\text{CB}}+l_{\text{Az}}$ or $L\sim l_{\text{Az}}$ is the film thickness both for the 6Az10PVA+5CB and 6Az10PVA films on the metal electrodes, ϵ_0 is the dielectric permittivity of free space, and z is the distance away from a metal electrodes. In the following we use the experimental data for the dielectric constant of 6Az10PVA $\epsilon_w\sim 3.0$,[7] and the values of the lengths of the 5CB and 6Az10PVA molecules to be equal to $l_{5\text{CB}}\sim 2.0$ nm and $l_{\text{Az}}\sim 4.5$ nm, respectively. The sequences of the surface potential values V and the conformational states changes both in azobenzene 6Az10PVA+5CB [upper lines both in Figs. 2(a) and 2(b)] and azobenzene 6Az10PVA

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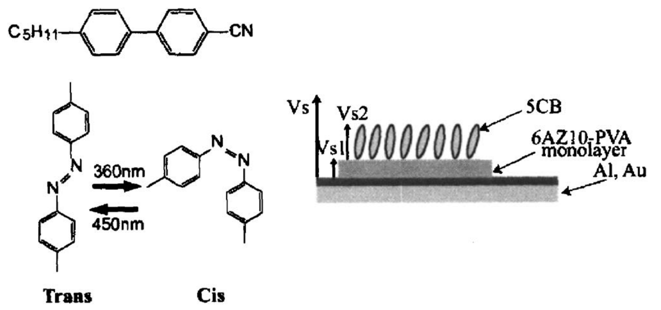

FIG. 1. Sample structure for the surface-potential measurements of the surface voltage across the 6 Az 10 PVA+5CB film on Al electrodes.

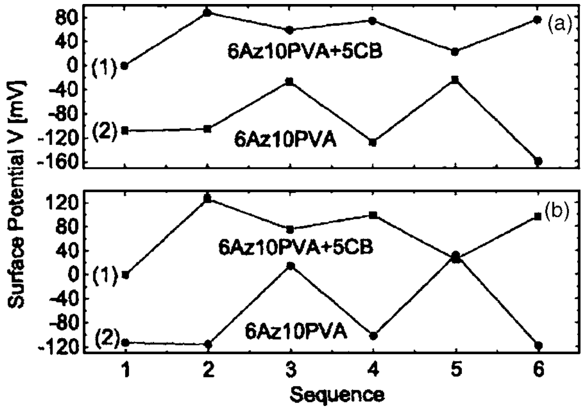

FIG. 2. The relationship between the surface potential V and the conformational state both the 6 Az 10 PVA+5CB [lines (1) and (3)] and 6Az10PVA [lines (2) and (4)] films on metal electrodes, during the *trans-cis* and *cis-trans* conformational transitions in the 6Az10PVA monolayer caused by UV illumination, at $T=298$ K. (a) 6Az10PVA is in *trans* form at sequence 1, 3, and 5, and in *cis* form at sequence 2, 4, and 6, respectively. (b) The same as (a), but for another sequence of the *cis-trans* conformational changes. 6Az10PVA is in *cis* form at sequence 1, 3, and 5, and *trans* form at sequence 2, 4, and 6, respectively.

[lower lines both in Figs. 2(a) and 2(b)] films, caused by the charge separation, taking place during *trans-cis* and *cis-trans* isomerizations are measured using the surface-potential signals and shown in Figs. 2(a) (case 1) and 2(b) (case 2), respectively.

The values of the surface charge densities σ and the voltages V across both 6Az10PVA+5CB and 6Az10PVA films were measured by the surface-potential technique, and these data are collected in Table I.

The isomerization involves a decrease of the distance between the pair carbon atoms in azobenzene from about 0.9 nm in the *trans* form to 0.55 nm in the *cis* form. The *trans* planar isomer, which has a rod-shaped configuration, is transformed to the bent-shaped *cis* conformations in which the $-\mathrm{N}\equiv\mathrm{N}-$ group is in a plane perpendicular to the *phenylene* groups. Likewise, *trans-azobenzene* has very small dipole moment (0–0.5 D), while the dipole moment of the *cis* compound is 3.0–3.5 D.[8] This large conformational change induced by isomerization is reversible. In case 1, it was observed that the initial state of surface azobenzene monolayer, which exhibits the *trans* conformation with the molecular area $A\sim 0.4\ \mathrm{nm}^2$, with the transmittance of a He–Ne laser beam undergoes the *trans-cis, cis-trans, trans-cis*, and *cis-trans* sequences of the isomerizations, at the different values of the voltages V across both 6Az10PVA+5CB and 6Az10PVA films. In case 2, the initial state of surface azobenzene monolayer exhibits the *cis* conformation ($A\sim 1.2\ \mathrm{nm}^2$), and with the transmittance of the laser beam undergoes the inverse, to case 1, sequence of the photoisomerization changes.

It should be pointed out that the voltage V across the 5CB film on 6Az10PVA monolayer, caused by UV illumination, generates a positive charge density range in the interval of $1.66\times10^{-3}\ \mathrm{C/m}^2 \leqslant \sigma \leqslant 11.25\times10^{-3}\ \mathrm{C/m}^2$, whereas the voltage V across the 6Az10PVA film on Al electrode generates a negative charge density range in the interval of $-7.74\times10^{-3}\ \mathrm{C/m}^2 \leqslant \sigma \leqslant -0.77\times10^{-3}\ \mathrm{C/m}^2$, respectively. The surface charge density in $\sigma\sim10^{-3}\ \mathrm{C/m}^2$ corresponds to a surface ion concentration $n_{\mathrm{surf}}=\sigma/e=6.25\times10^{+15}\ \mathrm{m}^{-2}$, which is in agreement with the experimental data $n_{\mathrm{surf}}\approx10^{15}-10^{16}\ \mathrm{m}^{-2}$.[9] Here e is the proton charge.

The surface pressure $\pi-A$ isothermal diagram, both for *trans* and *cis* conformations of 6Az10PVA monolayer, is shown in Fig. 3.

To produce the *trans* form, the monolayer of 6Az10PVA was spread in the absence of light and the *cis* form was produced by irradiating the spread layer with ultraviolet radiation. The two molecular configurations produce qualitatively different isotherms. In the case of the *trans* conformational state of 6Az10PVA monolayer, the surface pressure shows a steep increase at a molecular area $A\sim0.4\ \mathrm{nm}^2$ (solid line), and saturates at $\pi(trans)\sim 43\ \mathrm{mN/m}$, whereas the *cis* conformational state occurred at $A\sim1.2\ \mathrm{nm}^2$ (dashed line), and saturates at $\pi(cis)\sim33\ \mathrm{mN/m}$, respectively. So, the surface area per molecule is markedly higher for the *cis* configuration, which reflects the more efficient packing possible with the *trans* state. The existence of higher collapse pressure for the *trans* isomer compared to the *cis* isomer suggests that intermolecular interactions are stronger in *trans* monolayer. In order to elucidate the role of the charge separation during the *trans-cis* or *cis-trans* conformational changes on the surface azobenzene monolayer, sandwiched between liquid-crystal film and Al substrate, we use the molecular model which takes into account the interactions between the surface polarization and surface electric field. The interaction of the LC film with the solid surface leads to changing of the molecular orientation in the film. Our two-dimensional (2D) LC monolayer system is composed of axially symmetric molecules, the hydrophilic heads of which are uniformly distributed on the azobenzene surface and the hydrophobic tails are directed away from the interface. It allows us to consider the model of axially symmetric molecular rods, the hydrophilic heads of which are uniformly distributed on the surface and the hydrophobic tails are directed away from the water surface and tilted at the average equilibrium angle $\theta_{\mathrm{eq}}(A)$ with respect to the unit vector $\hat{\mathbf{k}}$ directed perpendicular to the interface. The unit vector $\hat{\mathbf{i}}$ is directed to be parallel to the interface with the distance x, whereas z is the distance away from the air-azobenzene interface (see Fig. 1). We use the molecular model which takes into account the interaction between the surface polarization (SP) and the surface electric field originating from surface charges density σ. In the simplest case that electric field can be written in the form

TABLE I. The values of the surface charge density σ and the voltage V across both 6 Az 10 PVA+5CB and 6Az10PVA films on Al electrode, during the *trans-cis* and *cis-trans* conformational transitions in the 6Az10PVA monolayer caused by UV illumination, at $T=298$ K.

	trans	*cis*	*trans*	*cis*
6 Az 10 PVA+5CB monolayer (*trans* form)				
$\sigma(\times 10^{-3}\ \mathrm{C/m^2})$	9.75	4.94	6.0	1.66
V(mV)	87.5	58.0	70.5	19.5
6Az10PVA monolayer (*trans* form)				
$\sigma(\times 10^{-3}\ \mathrm{C/m^2})$	−6.3	−1.49	−7.74	−1.09
V(mV)	−106	−25	−131	−18.5
	trans	*cis*	*trans*	*cis*
6 Az 10 PVA+5CB monolayer (*cis* form)				
$\sigma(\times 10^{-3}\ \mathrm{C/m^2})$	11.25	6.37	7.48	2.15
V(mV)	131.5	75	88	31
6Az10PVA monolayer (*cis* form)				
$\sigma(\times 10^{-3}\ \mathrm{C/m^2})$	−6.7	−0.77	−5.9	−1.49
V(mV)	−113	−13	−100	25

$\mathbf{E}=E_0\hat{\mathbf{k}}=\sigma/\epsilon_0\bar{\epsilon}\hat{\mathbf{k}}$, where $\bar{\epsilon}=(\epsilon_\parallel+2\epsilon_\perp)/3$ is the average dielectric permittivity, and $\epsilon_\parallel$ and $\epsilon_\perp$ are the dielectric constants parallel and perpendicular to the director $\hat{\mathbf{n}}$, respectively. The electric field $\mathbf{E}$ has, therefore, an orienting effect on the LC monolayer, and the related dielectric energy per unit area can be written in the form

$$f_{\mathrm{el}}=\int_0^d F_{\mathrm{el}}(z)dz=-\frac{1}{2}\epsilon_0\epsilon_a\int_0^d(\mathbf{E}\cdot\hat{\mathbf{n}})^2dz$$

$$=-\frac{1}{2}w_{\mathrm{el}}\cos^2(\theta_s-\theta_0), \tag{2}$$

where $w_{\mathrm{el}}=\epsilon_0\epsilon_a\int_0^dE^2(z)dz=\sigma^2\epsilon_a d/\bar{\epsilon}^2\epsilon_0, d$ is the monolayer thickness, $\theta_s=\theta_{\mathrm{eq}}=\cos^{-1}(\hat{\mathbf{n}}\cdot\hat{\mathbf{k}})$ is the angle between the surface director and the substrate normal, $\theta_0=\cos^{-1}(\hat{\mathbf{n}}_0\cdot\hat{\mathbf{k}})$ is the polar angle of the easy axis $\hat{\mathbf{n}}_0$, and $\epsilon_a=\epsilon_\parallel-\epsilon_\perp$ is the dielectric anisotropy of the LC monolayer. The additional contribution to the effective anchoring energy should be accounted for by adding the term $-\int_0^d\mathbf{P}_s\cdot\mathbf{E}dz$, where $\mathbf{P}_s=n_s\Delta(A)\hat{\mathbf{n}}=n_s\Delta(A)(\sin\theta_s\hat{\mathbf{i}}+\cos\theta_s\hat{\mathbf{k}})$, n_s is the film surface density given by $n_s=1/Ad$, $\Delta(A)=\mu_z\cos\theta_s+4\pi\epsilon_0\alpha E_k$ is the total magnitude of the depolarized dipole moment of the 5CB molecules on the azobenzene surface, μ_z is the z component of the molecular dipole moment corresponding to the tail of the 5CB molecule on the azobenzene surface, α is the electronic polaralizability, and E_k is the depolarizing field.[10] The depolarizing field due to a single-point dipole of moment μ in the plane $z=0$ is given by[11] $\mathbf{E}_k^s=-\mu/(4\pi\epsilon_0a^3)\hat{\mathbf{k}}$, where a is the distance between the nearest neighbors. Summing for the infinite array, the total field $\mathbf{E}_k=\Sigma_{i=-\infty}^{+\infty}\mathbf{E}_k^i$ is given by[11]

$$\mathbf{E}_k=-\frac{\mu}{4\pi\epsilon_0a^3}\sum_{u=-\infty}^{+\infty}\sum_{v=-\infty}^{+\infty}\sqrt{1/(u^2+v^2-uv)^3}\hat{\mathbf{k}}$$

$$=-\frac{11.0342\mu}{4\pi\epsilon_0a^3}\hat{\mathbf{k}}. \tag{3}$$

Here the double summation has been evaluated by Topping[12] as 11.0342. Hence, the following expression for the $\Delta(A)$ is obtained,[4] $\Delta(A)=\mu_z\mathcal{F}(A)\cos\theta_s$. Here $\mathcal{F}(A)=1-(10.27\alpha/A^{3/2})[1+(\epsilon_w-1/\epsilon_w+1)]$, μ_z is the z component of the molecular dipole moment corresponding to the tail of the 5CB molecule on the azobenzene surface, ϵ_w is the dielectric constant of 6Az10PVA, $a=(2A/\sqrt{3})^{1/2}$, A is the molecular area in Å^2, and α is the electronic polarization given by[9] $|4\pi\epsilon_0|$(Å^3). By putting the easy axis $\hat{\mathbf{n}}_0$ normal to the substrate ($\theta_0=0$), and by integrating over the z component of the $-\mathbf{P}_s\cdot\hat{\mathbf{k}}E_0$, one has $-\int_0^d\mathbf{P}_s\cdot\mathbf{E}dz=-(\sigma\Delta(A)/\bar{\epsilon}\epsilon_0A)\cos^2\theta_s$. So, the total energy per unit area, playing the role of the effective anchoring energy, is given by

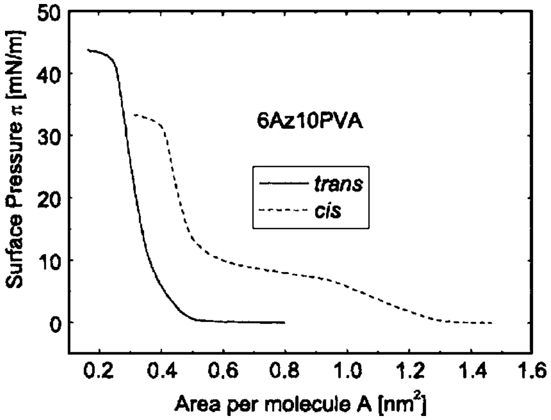

FIG. 3. $\pi-A$ isotherm of the 6Az10PVA monolayer during the lateral compression, for two *trans* (solid line) and *cis* (dashed line) conformational states of azobenzene monolayer.

$$f_{\mathrm{eff}}=-\frac{1}{2}w_{\mathrm{eff}}\cos^2\theta_s=-\frac{1}{2}(\alpha_1\sigma^2+\alpha_2\sigma)\cos^2\theta_s, \tag{4}$$

where $w_{\mathrm{eff}}=\alpha_1\sigma^2+\alpha_2\sigma$ is the effective anchoring energy strength in the Rapini-Popular form,[13] $\alpha_1=(\epsilon_ad)/(\bar{\epsilon}^2\epsilon_0)$, $\alpha_2=(2\Delta(A))/(\bar{\epsilon}\epsilon_0A)$, and σ is the surface charge density corresponding to the *trans* or *cis* conformational state.

It is important to stress here that the coefficient α_1 is the constant, and has dimension in meters, whereas coefficient $\alpha_2=\alpha_2(A)$ is the function of the molecular area A, and has dimension in D/m^2. In order to elucidate the role of the charge separation during the conformational *trans-cis* or *cis-trans* changing on the surface azobenzene monolayer or in azobenzene+5CB monolayer film, caused by the ultraviolet (or visible light) irradiation, one needs the data $\epsilon_\parallel$, $\epsilon_\perp$, A, μ, and σ. In the following, we use the calculated $\epsilon_\parallel=18$, $\epsilon_\perp=8$, $\bar{\epsilon}=11.3$, and $\epsilon_a=10$ from molecular-dynamics simulation of 5CB at $T=300$ K,[14] using the conventional potential-energy function composed of intra- and intermolecular contributions. Taking into account that the electronic polarizability of a C-H bond is $\sim 0.65\times 4\pi\epsilon_0$ (Å^3),[9] the upper bonds for α can be taken as $\sim 1.95\times 4\pi\epsilon_0$ (Å^3).[11] Figure 4 shows the dependence of $w_{\mathrm{eff}}(\sigma)$ on the surface charge density σ, both for *trans* ($A\sim 0.4$ nm^2) and *cis* ($A\sim 1.2$ nm^2) conformational states in 6Az10PVA+5CB monolayer film. In the framework of the SP mechanism, such changing of the anchoring energy can be explained by changing of the surface charge density, for instance, from σ_{trans} to σ_{sic} (see Fig. 4), taking place during UV irradiation.

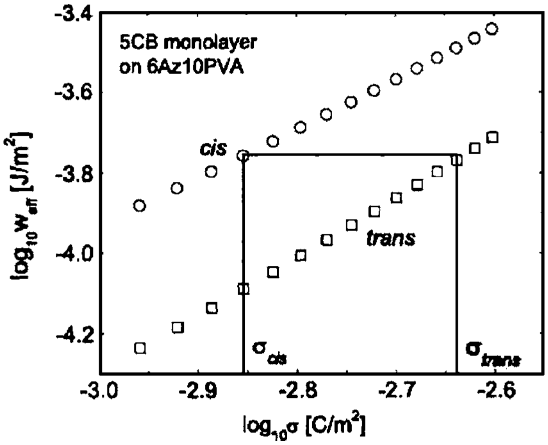

FIG. 4. The surface charge density σ dependences of $w_{\mathrm{eff}}(\sigma)$ calculated using Eq. (4) at $T=300$ K for *cis* (circles) and *trans* (squares) conformational states, respectively.

In that case, $w_{\mathrm{eff}}^{trans}=w_{\mathrm{eff}}^{cis}$, and one deals with changing of the surface charge density from $\sigma_{trans}=2.15\times10^{-3}$ C/m^2 to $\sigma_{cis}=1.66\times10^{-3}$ C/m^2, respectively. Such changing of the surface charge density in $\Delta\sigma=\sigma_{trans}-\sigma_{cis}\sim4.9\times10^{-4}$ C/m^2 can be caused by the charge separation taking place during the conformational change on the surface azobenzene 6Az10PVA+5CB monolayer. In order to examine the magnitude of the changing surface charge density $\Delta\sigma$, one should be considered data for changing of the voltage V across the 6Az10PVA+5CB film on metal electrodes. The surface charge density $\sigma_{trans}\sim2.15\times10^{-3}$ C/m^2 (see Fig. 4), corresponding to the *trans* conformational state of the surface azobenzene monolayer, may realized at $V\sim31$ mV [see Fig. 2 (upper curve, $N=5$)], whereas the surface change $\sigma_{cis}\sim1.66\times10^{-3}$ C/m^2, corresponding to the *cis* conformational state of the surface azobenzene monolayer, may realized at $V\sim19.5$ mV [see Fig. 2 (upper curve, $N=5$)], respectively. So, our analysis shows that the conformational changes *trans-cis*, during the photoisomerization in azobenzene monolayer, caused by the UV (or visible light) irradiation may lead to changing of the surface alignment of liquid-crystalline molecules, such as 5CB, having contact with that solid substrate.

In the wide region of the molecular area, the MDC signals allows us to determine the dipole moment $\Delta(A)$ of the *cyanobiphenyl* molecules at the air-solid interface. It has been found from MDC measurement of 5CB molecules at the air-water interface[15] that with decreasing of the molecular area the z component of the molecular dipole moment μ_z corresponding to the tail of the 5CB molecule on the water surface increases from zero, at the molecular area of $0.6\ \mathrm{nm}^2\leqslant A\leqslant1.2\ \mathrm{nm}^2$, up to 0.5 D per molecule, at the molecular area of $0.2\ \mathrm{nm}^2\leqslant A<0.6\ \mathrm{nm}^2$. Physically, this means that the initial dipole moment of the 5CB molecule ($\delta\sim5D$) is the fully compensated, due to interaction with the water molecules, at the molecular area of $0.6\ \mathrm{nm}^2\leqslant A\leqslant1.2\ \mathrm{nm}^2$, and that compensation is decrease up to 0.5 D per molecule, with increasing of the molecular area. When the same tendency is true for the case of 5CB+azobenzene system, the value of the total molecular dipole moment $\Delta_z(A_{trans})$ corresponding to the z component of the 5CB molecule on the azobenzene monolayer in the *trans* conformational state is different from the value of $\Delta_z(A_{cis})$ corresponding to *cis* conformational state. So, by using of equation

$$\Delta=\mu_z\mathcal{F}(A)\cos\theta_s,$$

one can calculate the tilt angle $\theta_s=\cos^{-1}[\Delta(A)/\mu_z\mathcal{F}(A)]$, which is composed of director with respect to the air-solid interface. At the molecular area $A_{trans}\sim0.4$ nm^2, the z component of the total dipole moment $\Delta_z(A_{trans})$, greater than $\Delta_z(A_{cis})$, at the molecular area $A_{cis}\sim1.2$ nm^2. It means that the director $\hat{\mathbf{n}}_s$ in the 5CB film both on *trans* and *cis* conformational states of 6Az10PVA monolayer aligns to be tilted to the interface, and that tilting is higher in the case of *cis* conformational state $[\theta_s(A_{cis})>\theta_s(A_{trans})]$ than in the case of *trans* conformational state of 6Az10PVA monolayer.

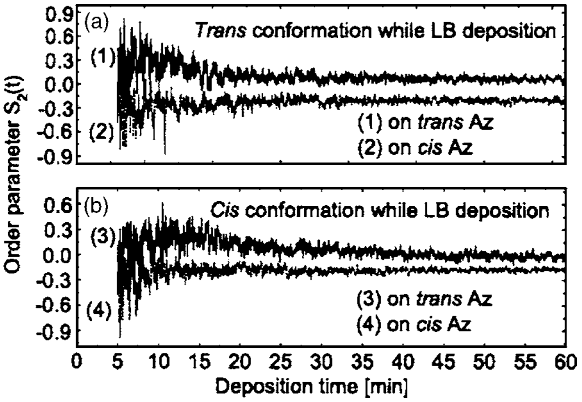

FIG. 5. *In situ* observation of the second orientational order parameter $S_2(t)$ during 5CB deposition onto the *trans* (a) and *cis* (b) conformation azobenze monolayers. The solid lines represent that azobenzene was in *trans* form (curves 1 and 3) when Langmuir-Blodgett (LB) deposition was done and the dashed lines represent that azobenzene was in *cis* form (curves 2 and 4) when LB deposition was done. Surface pressure of 6Az10PVA was kept at 5 mN/m during deposition.

Our optical polarized absorption measurement, basically based on the linearly polarized absorption measurement,[16,17] using 6Az10PVA azobenzene film deposited in *trans*-form, has shown that the time-dependent order parameter (OP) $S_2(t)=\frac{3}{2}\langle\cos^2\theta_i(t)\rangle-\frac{1}{2}$, [$\theta_i(t)$ is the polar angle between the molecular axis i and the director $\hat{\mathbf{n}}$, and the angular bracket denotes the statistical-mechanical average] during the deposition of 5CB molecules by evaporation onto the film, after changing into *cis*-form azobenzene (lower lines in Fig. 5), results in the final *trans* state, with $\lim_{t\to t_1}S_2(t)\sim-0.2$, whereas the behavior of the $S_2(t)$, during the deposition of 5CB molecules onto the same film, corresponding to the *trans*-form 6Az10PVA azobenzene film (upper lines in Fig. 5), results in the final *cis* state, with $\lim_{t\to t_1}S_2(t)\sim0.1$, respectively, with $t_1\sim60$ min. Experimentally, this means that the orientational order in the monolayer film of 5CB molecules on 6Az10PVA azobenzene monolayer reflects the conformational changes of azobenzene surface layer, and the inequality $\theta_s(A_{cis})>\theta_s(A_{trans})$ is valid over the entire region of the deposition. Indeed, it is expected that in the final stage, the average tilting angle θ_s of 5CB molecules on the *cis*-form film is $\theta_s(cis)\sim63°$, whereas in the case of 5CB molecules on the *trans*-form film that angle is $\theta_s(trans)\sim50.8°$. So, according to our optical polarized measurements, both the *trans* and *cis* molecular configurations of 6Az10PVA produce qualitatively different alignments of the 5CB film on azobenzene substrate, with the average tilting angle $\theta_s(cis) \sim 63°$, corresponding to the *cis* form of the azobenzene film, and $\theta_s(trans) \sim 50.8°$, corresponding to the *trans* form of the azobenzene film, respectively.

The azobenzene in the *trans* phase, which has a rod-shaped configuration, produce a higher degree of orientational order in two-dimensional 5CB monolayer $[S_2(trans) \sim 0.1]$ than the azobenzene in the *cis* phase $[S_2(cis) \sim -0.2]$, with a bent-shaped configuration. This suggests that there are additional molecular interactions between azobenzene molecules in *cis* monolayer and 5CB molecules in LC film compared to the *trans*+5CB system. Actually, our optical polarized absorption measurement using the 6Az10PVA azobenzene film deposited in *cis* form, but changed into *trans* form during the deposition of 5CB molecules by evaporation onto the azobenzene film, was somewhat smaller and results in the final state with $\lim_{t\to t_1} S_2(t) \sim 0$. Taking into account that the *trans*-azobenzene has almost no dipole moment, while the dipole moment of the *cis* compound is high, the dipolar interaction between the hydrophilic head of the 5CB and *cis*-azobenzene molecules decrease the orientational ordering in the LC film.

In this paper we investigate the effect of the charge separation during the *trans-cis* conformational change on the surface of azobenzene 6Az10PVA monolayer on the polar liquid-crystal monolayer film, such as 4-*n*-pentyl-4′-cyanobiphenyl(5CB), both experimentally, using the surface-potential measurements, and theoretically, in the framework of the molecular model, which takes into account interactions between the surface polarization and electric field build up across the LC monolayer film, for number of conformational states of the boundary azobenzene surface. It is shown, using the experimental data for the voltage across the 6Az10PVA+5CB film, provided by the surface-potential technique, that the charge separation during the conformational changing, caused by the UV irradiation, may lead to changing of the surface alignment of liquid-crystalline molecules. We believe that the present study not only shows some useful routes for understanding the nature of the surface charge-density changes due to photoisomerization in Langmuir films, but also for analyzing the surface potential at the metal-organic interface.

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