Homeotropic-planar anchoring transition induced by \textit{trans-cis} isomerization in ultrathin polyimide Langmuir–Blodgett films

A. V. Zakharov\textsuperscript{a)}

\textit{Laboratorium voor Akoestiek en Thermische Fysica, Department Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium}

Mitsumasa Iwamoto\textsuperscript{b)}

\textit{Department of Physical Electronics, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo, 152-8552, Japan}

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The influence of the charge separation during the \textit{trans-cis} conformational change between the surface azobenzene 6Az5PV A monolayer on polyimide Langmuir–Blodgett film on the surface charge density is investigated, using the Maxwell displacement current technique. It is theoretically shown, in the framework of the molecular model, which takes into account interactions between the surface polarization (in the quadrupole approximation) and surface electric field, that the experimentally observed changes of the surface charge density in $\sim 3 \times 10^{-4} \text{C/m}^2$, caused by the charge separation in $\sim 2 \text{pC}$, taking place during the conformational change, may lead to changing of the surface alignment of liquid crystalline molecules, such as 4-n-pentyl-4’-cyanobiphenyl (5CB), having contact with that solid substrate. © 2003 American Institute of Physics.

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The problem of \textit{trans-cis} photoisomerization in mono- and multilayer systems remains one of the fundamental problems in Langmuir monolayers physics.\textsuperscript{1–3} Some organic materials such as azobenzene which also may exhibit the liquid crystalline properties (azobenzene exhibits a nematic liquid crystal (NLC) phase in the temperature range $\sim 300–341$ K), undergo a \textit{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 \textit{trans-cis} isomerization due to the vertical component of dipole moment of surface azobenzene monolayer. Recently, the Maxwell displacement current (MDC) method\textsuperscript{4,5} has been usefully suggested to observe the changing of the surface charge density during the \textit{trans-cis} conformational transition between the surface azobenzene monolayer on poliyimide-Langmuir–Blodgett (PI-LB) film.\textsuperscript{6} The MDC signals allow us to determine the changing of the surface charge density in azobenzene monolayer, sandwiched between suspended electrode and substrate (metal, water, etc.) (see Fig. 1). Specifically, it has been observed that the monolayer of the PI-LB film, which in the initial state exhibits the \textit{trans} conformation, with the transmittance of a He–Ne laser beam (632 nm in the wavelength) undergoes the \textit{trans-cis} isomerization.\textsuperscript{7} By putting, for instance, the PI-LB film in contact with the liquid crystal (LC) phase, 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 between the surface azobenzene monolayer on PI-LB film and LC phase. In order to examine the magnitude of the changing surface charge density $\Delta\sigma$, we consider data for changing of the charge $\Delta Q$, provided by the MDC measurement of the poly (vinyl alcohol) with azobenzene units in the side chains (6Az5PV A), sandwiched between suspended electrode and substrate.\textsuperscript{5} The our MDC measurement has shown that the $\Delta Q$ can be estimated, for the 6Az5PV A Langmuir monolayer during the \textit{trans-cis} conformational change, to be $\sim 2 \text{pC}$. Briefly, in the measurement, transient short-circuited current generated across 6Az5PV A monolayer on the water surface was recorded during the ultraviolet (or visible light) irradiation, using suspended electrode placed parallel to the water surface.\textsuperscript{4} The gap distance $L$ between suspended electrode and water surface is $\sim 1 \text{mm}$, the length $l$ of the 6Az5PV A molecule is $\sim 2 \text{nm}$, and the electrode working area $S$ is $\sim 40 \times 10^{-4} \text{m}^2$. These data allow us, using a simple relationship, $\Delta\sigma = QL/(SI)$, to estimate $\Delta\sigma$ to be $\sim 2.5 \times 10^{-4} \text{C/m}^2$. A similar result for $\Delta\sigma$ ($\sim 10^{-3}–10^{-4} \text{C/m}^2$), during the \textit{trans-cis} isomerization, has been obtained also for 6Az5PV A LB monolayer deposited on transparent indium-tin oxide electrode.\textsuperscript{7} Furthermore it has been revealed that as deposited PI-LB films were charged on various metals (Au, Ag, Sn, Cr, and Al), due to the displacement of excess charges from metals to films.\textsuperscript{8}

In order to elucidate the role of the charge separation during the homeotropic-planar anchoring transition, caused by the conformational \textit{trans-cis} changing, we use the molecular model which takes into account the interaction between the surface polarization (in the quadrupole approximation) and the surface electric field, caused by the charge...
angles of \( \mathbf{n} \) are used now, for a small deviation of the surface director from \( \mathbf{n} \), enologically anchoring may be described by a surface potential or anchoring free energy, which depends on the surface director \( \mathbf{n}_0 \). In the vicinity of a solid surface there is a well-defined direction called the easy axis \( \mathbf{n}_0 \), which minimizes the anisotropic part of the surface energy. Although many contradictory expressions of the surface anchoring energy are used now, for a small deviation of the surface director \( \mathbf{n}_s \) from \( \mathbf{n}_0 \), the surface energy may be written in the form \( f_0 = -\frac{w_0}{2} \cos^2 (\theta_s - \theta_0) \),

\[
f_0 = -\frac{w_0}{2} (\mathbf{n}_s \cdot \mathbf{n}_0)^2 = -\frac{w_0}{2} \cos^2 (\theta_s - \theta_0),
\]

where \( w_0 \) is an anchoring strength, \( \theta_s \) and \( \theta_0 \) are the polar angles of \( \mathbf{n}_s \) and \( \mathbf{n}_0 \), (Fig. 2), respectively. It should be pointed out that the anchoring strength energy \( w_0 \) determines the ability of the director to deviate from the easy direction, which in a number of cases, for instance a twisted LC sample, must include a nonlinear combination of the azimuthal \( \varphi \) and polar \( \theta \) angles. In most cases, the mechanism which is responsible for the surface orientation of the LC based on long-range electric forces originates from surface charge density \( \sigma \), so the resulting anchoring energy strength \( w_0 \) is expected to be a quasilocal. After making contact with the LC phase [in our case the 4-n-pentyl-4’-cyanobiphenyl (5CB)], the surface electric field \( E_0 \), originating from surface charges density \( \sigma \), will penetrate the bulk on the order of the Debye screening length \( \lambda_D = \left( \frac{\epsilon_i k_B T}{2 e^2 n_{eq}} \right)^{1/2} \),

\[
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\]

where \( \epsilon \) is the proton charge, \( k_B \) is the Boltzmann constant, \( \epsilon_i \) is the absolute dielectric permittivity of free space, \( \epsilon = \epsilon_0 (\epsilon_i \cos^2 \varphi + \epsilon_\parallel \sin^2 \varphi) \) (a case of the bulk screening), and \( n_{eq} \) is the bulk ion concentration. The distance dependence of the surface electric field with bulk screening is given by

\[
E(z) = E(z) \mathbf{k} = E_0 \exp \left( -\frac{z}{\lambda_D} \right) \mathbf{k},
\]

where \( \mathbf{k} \) is the unit vector directed away and perpendicular to the substrate, \( E_0 = \sigma / \epsilon_\parallel \epsilon \) is the surface electric field of the charged plane, \( \epsilon = (\epsilon_i + 2 \epsilon_\parallel) / 3 \) is the average dielectric permittivity, \( \epsilon_i \) and \( \epsilon_\parallel \) are the dielectric constants parallel and perpendicular to the director \( \mathbf{n} \), respectively. The electric field given by Eq. (3) has, therefore, an orienting effect on the LC, and the related dielectric energy per unit area has been shown to be

\[
f_{\text{el}} = \int_0^\infty F_0(z) dz = -\frac{1}{2} w_{\text{el}} \cos^2 (\theta_s - \theta_0),
\]

where \( w_{\text{el}} = \epsilon_0 \epsilon_i \int_0^\infty E(z) dz \), \( \theta = \cos^{-1} (\mathbf{n} \cdot \mathbf{k}) \) is the angle between the surface director and the substrate normal, and \( \epsilon_i = \epsilon_\parallel - \epsilon_\perp \) is the dielectric anisotropy of the NLC. Moreover, when the mirror symmetry is broken at the substrate, the surface polarization \( \mathbf{P}_s \) may arise to be perpendicular to the surface. The microscopic reason for this polarization might be preferential asymmetric attachment of dipolar molecules to the surface, ion adsorption, or spatial dependence of the nematic OP \( \mathbf{P}_2(z) \) (the so-called ordo-electric polarization). In the quadrupolar approximation, the surface (ordo-electric) polarization (SP) of LCs takes the form

\[
\mathbf{P}_s = \frac{3}{2} e^* \nabla \mathbf{P}_2(z) \cdot \left( \mathbf{n} - \frac{1}{3} \mathbf{1} \right),
\]

where \( e^* \) is the quadrupolar coefficient of a nematic. The SP arises in a thin surface layer \( \lambda_s \sim 10–100 \text{ nm} \) for any (planar, homeotropic, or oblique) alignment of a liquid crystal. Although the difference in direction of the \( \mathbf{P}_s \) vector for homeotropic and planar alignments follows, of course, from the dipolar nature of the surface layers, it can also be explained in the framework of the ordo-electric polarization model [Eq. (5)]. By putting the director normal to the substrate and on
the $xz$ plane to give $n = (\sin \theta, 0, \cos \theta)$, and by integrating over the $z$ component of the $P_s$ vector, $P_s k$, one has\(^\text{13}\) \[ P_s^z = \frac{1}{2} e^*(\cos^2 \theta - 1) \Delta P_2, \]
where $\Delta P_2 = P_{2b} - P_2(0)$, $P_{2b}$ and $P_2(0)$ are the bulk and surface OPs, respectively. For the homeotropic alignment ($\theta = 0$), $\langle P_s^z \rangle_h = e^* \Delta P_2$, whereas for the planar one ($\theta = \pi/2$), $\langle P_s^z \rangle_p = -\frac{1}{2} e^* \Delta P_2$. Since the quadrupolar coefficient $e^*$ and the flexoelectric coefficients $e_1$ and $e_3$ related to the splay and bend distortions of the NLC\(^\text{17}\) are connected by a simple relationship\(^\text{18}\)
\[
e^* = \frac{e_1 + e_3}{3 P_s},
\]
the following expressions for the $z$ component of $P_s$ vector are obtained: \(\langle P_s^z \rangle_h = e_+ \Delta P_2/3 P_s(z)\), and \(\langle P_s^z \rangle_p = -e_+ \Delta P_2/3 P_s(z)\), respectively. Here $e_+ = e_1 + e_3$. Now the SP takes the form\(^\text{19}\) $P_s = A k_1 \cdot (n n - \mathbf{I} - \mathbf{k}) + (\cos^2 \theta - 1) k_1$, where
\[
A = \frac{e_+}{2} \frac{d \ln P_s(z)}{dz},
\]
$k_1$ is a unit vector which defines the direction of the $z$-component SP vector, and $i$ is a unit vector perpendicular to $k$. The coefficients $\xi = 1$ when $k_1$ is parallel to $k$ and $\xi = -1$ when $k_1$ is antiparallel to $k$. In the simplest case of the electric field $E(z) = E(z) k$, the SP energy per unit area can be obtained by integrating the linear term $F_{pol}(z) = -P_s \cdot E(z)$, to give
\[
f_{pol} = \int_0^\infty F_{pol}(z) dz = \int_0^\infty -e_+ E_0 J(\lambda_D) \xi \cos^2(\theta - \theta_0) + \text{const},
\]
where
\[
J(\lambda_D) = \int_0^\infty d \ln P_s(z) \frac{dz}{dz} \exp(-z/\lambda_D) dz.
\]
In Eq. (6), the flexoelectric coefficient $e_+(z)$ in the vicinity of the surface has been assumed to change weakly in comparison with the spatial variations of the OP $P_2(z)$, and the constant term is not important in our analysis, since it is independent of the nematic orientation. One can suppose, in addition to the existing functional dependence for the effective anchoring energy $f_{eff}$, an extra one contribution, due to the elastic energy $f_{elast}$, which can be written in the form\(^\text{19}\)
\[
f_{elast} = \frac{\lambda_{ex}}{2} \left[K_1 (\nabla \cdot n)^2 + K_2 (\nabla \nabla \cdot n)^2 + K_3 (\nabla \nabla \nabla \cdot n)^2\right],
\]
where $K_i (i = 1, 2, 3)$ are the Frank elastic coefficients, for splay, twist, and bend distortions, respectively, which gives an extrapolation length $\lambda_{ex} \sim 0.5–1.0 \mu$m, comparable, for instance, to the range of the electric forces, originating from the surface charge density $\sigma$. So, in an addition to the $f_{el}$ and $f_{pol}$ contributions, $f_{elast} = \int_0^\infty F_{elast}(z) dz$ contribution is delocalized over a bulk layer of thickness an extrapolation length $\lambda_{ex}$ close to a substrate. Taking into account that for plane geometry $n = (\sin \theta, 0, \cos \theta)$, $F_{elast}(z) = -\frac{1}{2} (K_3 - K_1) \times (\partial \theta(z)/\partial z)^2 \cos^2(\theta - \theta_0) + \frac{1}{2} K_1 (\partial \theta(z)/\partial z)^2$, and $\theta(z)$, related to elastic energy per unit area, expanded up to the second order in $\cos(\theta - \theta_0)$, can be expressed as
\[
f_{elast} = -\frac{1}{2} (K_3 - K_1) \int_0^\infty \left(\frac{\partial \theta(z)}{\partial z}\right)^2 dz + \text{const},
\]
Here we took into account the contributions to the effective anchoring energy in the Rapini–Popoular form.\(^\text{10}\) The total energy per unit area, playing the role of the effective anchoring energy, now is given by
\[
f_{eff} = f_0 + f_{el} + f_{pol} + f_{elast},
\]
and the effective anchoring energy strength $w_{eff}$ can be expressed in
\[
w_{eff} = -\frac{1}{2} w_{eff} \cos^2(\theta - \theta_0)
\]
\[
= -\frac{1}{2} (w_0 + w_{el} + w_{pol} + w_{elast}) \cos^2(\theta - \theta_0),
\]
where
\[
K_3 - K_1 \lambda_{ex} \left(\frac{\partial \theta(z)}{\partial z}\right)^2 + w_0 = \lambda_{ex},
\]
and
\[
\theta(z) = \theta(0) \left(\frac{\Delta \theta}{\theta(0)} \frac{z}{\lambda_{ex}} + 1\right), \quad \lambda_{ex} = \lambda_{bulk}, \quad \theta(z) > \lambda_{ex}.
\]
Then both $J(\lambda_D)$ and $w_{elast}$ take the simple forms
\[
J(\lambda_D) = (\lambda_D/\lambda_{ex}) (\Delta P_2/\bar{P}_2(0)) \times (\Delta \theta)^2, \quad \Delta \theta = \theta_{bulk} - \theta(0), \quad \theta_{bulk} \quad \text{and} \quad \theta(0) \quad \text{are the bulk and surface polar angles, of vectors $n_{bulk}$ and $n_s$, respectively.}
\]
In order to examine the effect of the charge separation in $\sim 2$ pC, during the trans-cis 6Az5PVA conformational change, which leads to changing of the negative magnitude of the surface charge density in $\sim 3 \times 10^{-4}$ C/m$^2$, the above-mentioned model, for description of the effective anchoring energy, both for homotropic and planar alignments, is considered. Taking into account that $\sigma = e n_{surf}$, where $n_{surf}$ is the surface charge density, the $n_{surf}$ can be estimated as $1.9 \times 10^{15}$ m$^{-2}$, which agrees with experimental values $\sim 10^{15} - 10^{16}$ m$^{-2}$.\(^\text{14}\) The orientational order of LCs is traditionally quantified in terms of OPs $P_{2L}$ ($L = 1, 2, 3$). Recently the bulk orientational distribution function (ODF) $f(\cos \theta)$ and
Oćz P2L have been calculated in the framework of molecular dynamics (MD) simulations, with realistic atom–atom interactions. At temperature 300 K and density 10^3 kg m^{-3}, the order parameter was found to be P2 = 0.51. Now using the ODF \( f(\cos \theta) \), one can calculate the average polar angle \( \bar{\theta}_{\text{bulk}} \) for the bulk director n orientation, as \( \bar{\theta}_{\text{bulk}} = \int_0^{\pi} f(\cos \theta) \sin \theta d\theta \), where \( \theta_i \) is the polar angle of the ith molecule. We found that angle to be 0.577 (33.05°) (at the same thermodynamics condition). In the following we use the experimental data^{21} \( (\epsilon_\parallel = -13.5 \text{ pC m}^{-1}, \text{ at } T = 298 \text{ K}) \), the calculated \( \epsilon_\parallel = 18, \epsilon_\perp = 8, \epsilon_\perp = 11.3, \) and \( \epsilon_\parallel = 10^{32} \) as well as the calculated \( K_1 = 9.5 \text{ pN} \) and \( K_2 = 13.8 \text{ pN} \), using the molecular dynamics simulation of 5CB,^{20} at the same temperature. The magnitude of the Debye length depends solely on the properties of the LC and not on any property of the surface. In the case of homeotropic alignment of 5CB on the PI-LB film, with a monolayer thickness \( (\sim 0.4 \text{ nm}) \), the surface polarization \( \mathbf{P}_s \) is directed from a substrate to a liquid crystal along the vector \( \mathbf{K} \), because the coefficient \( \xi = 1, \) and \( \lambda_D = 0.58 \mu \text{m} \). Moreover, \( \theta^*_s = 0 \), i.e., \( P_{2}(0) = 1 \) at the surface, and one has \( \Delta P_{2} = -0.5 \). The bulk angle \( \theta_{\text{bulk}} = 0.577, \theta(0) = 0, \) and \( \Delta \theta = 0.577 \). In the case of planar alignment of 5CB molecules on the PI-LB film, \( \xi = 1, \) and the SP vector \( \mathbf{P}_s \) is directed from a substrate to the bulk of a LC, \( \theta^*_s = \pi/2, \) i.e., \( P_{2}(0) = -0.5 \) at the surface, \( \Delta P_{2} = 1.1, \) and \( (\Delta \theta)^2 = 0.98 \). Figure 3 shows the dependence of \( w_{\text{eff}}(\sigma) \) on the surface charge density \( \sigma \), calculated using Eq. (11) with \( J(\lambda_D) \), both for homeotropic and planar alignments, as well as their difference \( \Delta = \ln w_{\text{eff}}^b - \ln w_{\text{eff}}^p \), for \( w_0 = 10^{-3} \text{ J/m}^2 \). Such value of the \( w_0 \) is in agreement with the experimental data for 5CB LC obtained using both the optical interference and capacity methods.^{23}

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 \( \sigma_1 \) to \( \sigma_2 \) (see Fig. 3). In that case, \( w_{\text{eff}}^b = w_{\text{eff}}^p \), and one deals with changing of the surface charge density from \( \sigma_1 = 2 \times 10^{-4} \text{ C/m}^2 \) (homeotropic alignment) to \( \sigma_2 = 5 \times 10^{-4} \text{ C/m}^2 \) (planar alignment), respectively. Such changing of the surface charge density in \( \Delta \sigma = \sigma_2 - \sigma_1 \sim 3 \times 10^{-4} \text{ C/m}^2 \) can be caused by the charge separation taking place, during the conformational change, between the surface azobenzene 6AzSPVA monolayer on PI-LB film and LC phase. So, our analysis shows that the changing of the surface charge in \( \sim 2 \text{ pC} \), at the azobenzene monolayer on PI-LB film may lead to changing of the surface alignment of liquid crystalline molecules, such as 5CB, putting in the contact with that substrate. Taking into account that the homeotropic-planar anchoring transition at the interface LC-solid substrate can be easy fixed, for instance, by the electro-optical methods,\(^{24}\) one can suppose that the LC materials, such as cyanobiphenyls, are suitable for indicating the surface charge density changes due to photoisomerization in Langmuir–Blodgett films.

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