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Anomalous anchoring effect of nanopolyimide Langmuir-Blodgett films in a twisted nematic liquid-crystal cell

Akihiko Sugimura,[1] Keiji Matsumoto,[1] Ou-Yang Zhong-can,[2] and Mitsumasa Iwamoto[3]
[1]*Department of Information Systems Engineering, Osaka Sangyo University, 3-1-1 Nakagaito, Daito, Osaka 574, Japan*
[2]*Institute of Theoretical Physics, Academia Sinica, P.O. Box 2735 Beijing 100080, China*
[3]*Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan*

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In a recent paper [Phys. Rev. E **52**, 681 (1995)] we showed that in the absence of an external field, the twisted structure of substrates with weak anchoring can induce a deviation of the director at the surfaces from the easy axis and that the anchoring energy can be evaluated by measuring this deviation. To test the prediction, the anchoring energy for nematic 4-pentyl-4′-cyanobiphenyl and polyimide Langmuir-Blodgett (LB) substrates with thicknesses in a range less than 10 nm has been measured. The anchoring energy is found to increase and saturate with the number of LB layers. This result, unlike that expected for the isotropic van der Waals interaction, reveals the anomalous anisotropic interfacial tension between a liquid-crystal slab and polyimide LB films with nanometer thickness. The generalized nonretarded van der Waals energy for the chain-chain interaction is proposed to explain the experimental result. [S1063-651X(96)06511-7]

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The director of nematic liquid crystals (NLCs) can be oriented on solid boundaries. This orientation is phenomenologically described by the Rapini-Papoular (RP) [1] anchoring energy per unit area, which describes the anisotropic interaction between the nematic director and the substrate

$$g_s = -\frac{A}{2}(\vec{n}\cdot\vec{e})^2, \tag{1}$$

where $\vec{n}$ is the NLC director at the surface, $\vec{e}$ is the ''easy'' direction as denoted by de Gennes [2], and A is the anchoring strength or anchoring energy coefficient, which reflects the ability of the director to deviate from the easy direction. Although there are reports of the measurement of anchoring energies [3], there is a large discrepancy in the values between authors even when they have used the same method for the same substrates (values differing by more than one or two orders of magnitude are often reported in literature) [4]. In recent years two approaches have been proposed to investigate this disagreement. One is based on the preliminary choice of a ''Gibbs dividing surface'' between the nematic liquid crystal and the substrates, which depends on the measurement methods used [5]. The other is to generalize the RP model by introducing the effect of the surface order parameter [6]. Both macroscopic approaches result in a thickness dependence of the anchoring energy at the interfaces. However, these two models do not make the mechanism of the anchoring clear from a microscopic viewpoint.

So far, knowledge of the thickness dependence of an anchoring energy is limited, although a number of experimental studies have provided some information. By depositing Langmuir-Blodgett (LB) films on a mica surface, Blinov *et al.* [7] found that the orientation of the director is maintained until the thickness of the LB films reaches a critical value of a few hundred angstroms. This critical value depends on both the nematogenic material and the polarity of the LB film. On crystalline substrates Jérôme and Pieranski [8] have shown that the thickness of NLCs interacting with a mica sheet is of the order of 14 Å. The experimental results reported also show a decrease in the anchoring energy with the thickness of the substrates; however, this is not the case for all experiments. A strange result is also found by using the method of optical second-harmonic generation [9]; for all the substrates studied the mesogenic molecules of octylcyanobiphenyl (8CB) in the first monolayer make an angle of about 70° with the substrate normal and then planar alignment in the bulk is obtained. The mechanism of director orientation responsible for the variation with the thickness of a very thin substrate is thus not clear [4]. Therefore, the anchoring behavior for aligned nematic films on a substrate is of considerable interest.

In this paper we report experimental results for the dependence of the unified anchoring energy between 4-pentyl-4′-cyanobiphenyl (5CB) and polyimide (PI) LB films on the thickness. These results show a different phenomenon, namely, that the anchoring energy increases and saturates with increasing film thickness. This effect, which is unlike the common isotropic van der Waals attractive interaction, reveals the speciality of the anisotropic surface tension in a nanometer scaling. The generalized nonretarded van der Waals model for the chain-chain molecular interaction [10] is proposed as a possible mechanism to explain the anomalous effect.

In a NLC display device rubbed polymer films are widely used to obtain uniform director alignment. There are two kinds of anchoring mechanism proposed to explain this alignment. The first is that rubbing induces the orientation of the polymer chains in the direction of rubbing and the interaction between the polymer and the liquid crystal forces the director to lie parallel to the polymer chains. The second is that the grooves created by rubbing cause the director to orient in the direction of the grooves to reduce the Oseen-Frank deformation energy [2]. In view of these different mechanisms proposed, the rubbed polymer is not an ideal substrate to investigate the effect of the film thickness on the anchoring energy. Instead we use a LB technique to produce

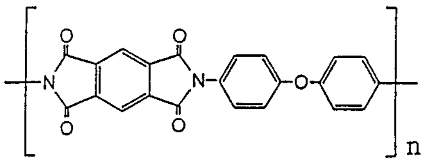

FIG. 1. Chemical structure of the polyimide used in our experiment.

a uniform PI surface on a transparent glass electrode (In_2O_3). This was achieved by using the process described in Ref. [11]. The chemical structure of the polymer constituting the PI-LB film is shown in Fig. 1. In the deposition process the shear strain causes the polymer chains in each layer to align in the same direction, which is just the easy axis. The thickness of the PI-LB multilayers is also well controlled by the number of times the glass support is pulled through the surface of the LB trough, i.e., the number of the layers. The thickness of a monolayer is found to be 0.4 nm [11]. In our experiment, five PI-LB films were used whose thickness were $d=1\times0.4$, 5×0.4, 9×0.4, 15×0.4, and 21×0.4 nm. In other words, our experiment was carried out under the condition of well-controlled ultrathin film with a thickness less than 10 nm.

The most challenging task in measuring the anchoring strength A is how to introduce a deviation of the director $\vec{n}$ from the easy direction $\vec{e}$ by a pure surface effect in the absence of an external magnetic or electric field and then how to estimate A from the deviation observed in the experiment. Recently, on the basis of a general RP expression for the anchoring energy Eq. (1), we have reported a theoretical study of the director deformation of a twisted chiral nematic sample with weak anchoring boundaries [12]. We consider a nematic slab sandwiched between the two planes located at $X_3=0$ and l, as illustrated schematically in Fig. 2. The easy directions at the top and bottom substrate surfaces are denoted by the unit vectors $\vec{e}^{\,+}$ and $\vec{e}^{\,-}$, respectively. Assuming that the easy directions at the top and bottom substrate surfaces are in a plane orthogonal to X_3, the following rigorous relationship between the anchoring strength A and the pretwisted-angle ϕ was derived [see Eq. (38) in Ref. [12]]

$$\phi_t - 2\phi = \frac{Al}{k_{22}} \sin\phi \, \cos\phi, \tag{2}$$

where ϕ_t is the twist angle, k_{22} is the twist elastic constant of the NLC, and ϕ is the deviation angle of $\vec{n}$ at the surfaces from $\vec{e}$ in zero field. In our experiment the condition of $\phi_t=90°$ for pure 5CB was used. The thickness l of the NLC slab was 22.1 μm for each sample with $d=2.0$, 3.6, and 6.0 nm being the thickness of the PI-LB substrates. For other samples with $d=0.4$ and 8.4 nm, $l=24.6$ and 22.0 μm, respectively. The values of l were measured and confirmed by both the optical interference and capacity methods with a measurement error of $\pm1\%$. Under these conditions Eq. (2) gives a rigorous relationship between ϕ and A, and so A can be completely determined by measuring ϕ.

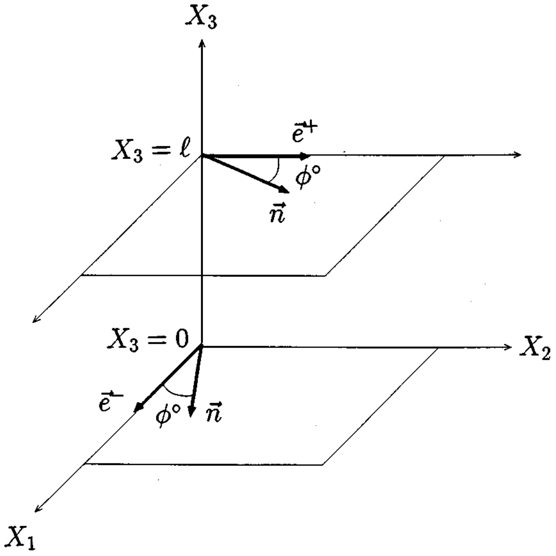

FIG. 2. Geometry of the twisted chiral nematic slab sandwiched between the two planes $X_3=0$ and l. The easy directions and the director at the top and bottom substrate surfaces are denoted by the unit vectors $\vec{e}^{\,+}$ and $\vec{e}^{\,-}$, and $\vec{n}$, respectively.

The experimental setup used to measure ϕ is shown schematically in Fig. 3; Po and An are the polarizer and the analyzer, respectively, PD and PC are the photodetector and personal computer, respectively and BS is a Babinet-Soleil compensator. The output of a He-Ne laser (Spectra Physics Co., model-117A, output stability within $\pm0.1\%$) was linearly polarized by means of a polarizer (Polaroid HN-38). The laser beam was passed through the thermostated LC cell with its axis at angle of 45° with respect to the polarization direction of the beam. The resulting elliptically polarized light passes through a Babinet-Soleil (BS) compensator (Siguma Koki Co., Auto Babinet Soleil Stage B-83). Its optical retardation is adjusted by means of an electrical stepped motor (its precision in the optical retardation for $\lambda=633$ nm is 1.66×10^{-5} μm/step) to compensate for the optical phase difference due to the birefringence of the LC slab, which depends on ϕ_t, ϕ, l, and the refractive indices of the NLC. By this precise compensation the light transmitted through the analyzer having a crossed relationship with the polarized direction of a polarizer has a minimum beam intensity. Typical values of R measured at a constant temperature of 298 K are shown in Fig. 4 for the samples with the thickness of the PI-LB being $d=0.4$, 2.0, 3.6, 6.0, and 8.4 nm and with the thickness of the LC slab being $l=24.6$, 22.1, 22.1, 22.1, and 22.0 μm, respectively.

In order to obtain the relationship between the optical retardation of the LC slab and ϕ we calculate the optical transmission for all the optical passes in our experimental setup including the polarizer, LC cell, BS compensator, and analyzer. The 4×4 matrix method described by Berreman [13] is used, which has universal applicability. It can be used to compute the beam intensity and phase difference of the transmitted light for a light beam with normal incidence. By this method the intensity of light passing through the optical setup is calculated for each value of ϕ as a function of the optical retardation of the BS compensator, whose variation is in the region of 0–0.633 μm, with a separation of 4.52×10^{-4} μm. Calculations are performed for ϕ in the range 0.2°–22.4° in steps of 0.2°. From these calculations, the optical retardation showing a minimum transmitted intensity of light, that is, to compensate the phase difference of the LC cell, is obtained for each ϕ. In our calculation we use the following parameters: the birefringence of the BS com-

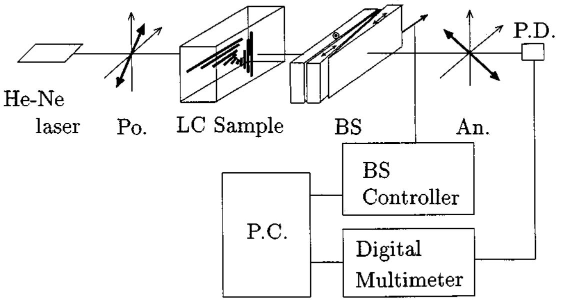

FIG. 3. Experimental setup used to measure the optical retardation of a LC cell. Po and An are the polarizer and the analyzer, respectively. BS is a Babinet-Soleil compensator whose phase difference is adjusted precisely by a computer controlled steper motor. PD and PC are the photodetector and personal computer, respectively.

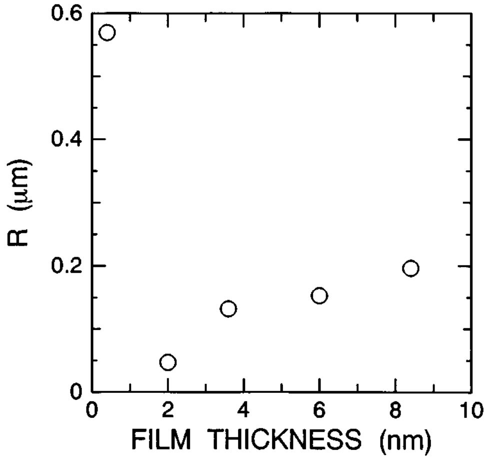

FIG. 4. Typical values of R measured at a constant temperature of 298 K for the samples with the thickness of the PI-LB being $d=0.4$, 2.0, 3.6, 6.0, and 8.4 nm, and with the thickness of the LC slab being $l=24.6$, 22.1, 22.1, 22.1, and 22.0 μm, respectively.

pensator Δn is 9.04×10^{-3}, the thickness of the crystal parallel plate of the BS compensator is 4.24 nm, the crystal wedge angle of the BS compensator is 25.204′, the refractive indices of 5CB for an ordinary and an extraordinary ray are $n_o=1.5296$ and $n_e=1.7072$ at 298 K for $\lambda=633$ nm, respectively, and the refractive index and thickness of the glass substrate are $n=1.515$ and 1.1 mm, respectively. Figure 5 shows an example of the relationship calculated between R and $\phi°$ for the sample with $l=22.1$ μm.

Now we can determine the value of ϕ for each LC cell by comparing the measured value of the optical retardation R with the calculated relationship between ϕ and R from Figs. 4 and 5. Substituting the values of ϕ measured, $k_{22}=3.81\times10^{-12}$ N for 5CB at 298 K, $\phi_t=90°$, and the values of l for each sample into Eq. (2), we obtain the anchoring strength. Open circles of Fig. 6 show the anchoring strength A deduced from the measured values of ϕ and Eq. (2) as a function of a PI-LB film thickness d. In the same figure the solid line gives the theoretical curve based on a simple model, which is described below, and the dashed line is just a guide to the eye for the experimental results. It is clear from Fig. 6 that A increases and saturates with increasing d in the range $d<10$ nm. This result is contrary to the results found by other authors for different substrates [7,8].

Since there is no appropriate theory for the anisotropic interaction of Eq. (1), we propose here a phenomenological model to explain our experimental result. We begin by assuming that the interaction between the polymer substrate and the liquid-crystal molecules is van del Waals like. For two parallel chains with a length L and a separation r, the nonretarded van der Waals interaction energy is written as [10]

$$w=-\eta L/r^5, \tag{3}$$

where η is a physical constant related to the molecular structure. For two nonparallel chains with different lengths, L_P and L_M of the PI and LC molecules, respectively, the energy form of Eq. (3) may be generalized as

$$w=-\eta\sqrt{L_P L_M}(\vec{P}\cdot\vec{M})^2/r^5, \tag{4}$$

where $\vec{P}$ and $\vec{M}$ are unit vectors giving the orientations of the PI and LC molecules, respectively. The term of $(\vec{P}\cdot\vec{M})^2$ can be expressed as $\cos^2\gamma=\frac{1}{3}[2P_2(\cos\gamma)+1]$, where P_2 is the second Legendre polynomial and γ is the angle between $\vec{P}$ and $\vec{M}$. Using the spherical harmonic addition theorem, we can express $P_2(\cos\gamma)$ in a Cartesian frame as

$$P_2(\cos\gamma)=P_2(\cos\theta)P_2(\cos\theta_M)+2\sum_{m=1}^{2}\frac{(2-m)!}{(2+m)!}\times P_2^m(\cos\theta)P_2^m(\cos\theta_M)\cos m(\phi-\phi_M), \tag{5}$$

where (θ,ϕ) are the polar and azimuthal angles of $\vec{P}$ and (θ_M,ϕ_M) are those of $\vec{M}$, and P_2^m are the associated Legendre polynomials. We choose the X_3 direction of the Cartesian frame as the direction of the nematic director $\vec{n}$. Averaging Eq. (5) with respect to the orientation of the LC molecules, we obtain the simple relation

$$\langle P_2(\cos\gamma)\rangle=P_2(\cos\theta)\langle P_2(\cos\theta_M)\rangle=P_2(\cos\theta)S, \tag{6}$$

where S is the second-rank orientational order parameter of the NLC. The second term on the right-hand side of Eq. (5) vanishes because the molecular orientational distribution is independent of ϕ_M in the bulk NLC phase and we assume the same symmetry at the surface. From Eqs. (4) and (6) we obtain

$$\langle w\rangle=-\eta\sqrt{L_P L_M}[2SP_2(\cos\theta)+1]/3r^5, \tag{7}$$

where θ is the angle between $\vec{n}$ and $\vec{P}$. The direction of $\vec{P}$ is simply the easy direction $\vec{e}$. Hence the form of the anisotropic interaction, given in Eq. (1), now is apparent.

To calculate the total interaction energy, we have to integrate Eq. (7) over the LB layer as

$$W=\int_a^{a+d}\rho\langle w\rangle dr=-\eta\sqrt{L_P L_M}\,\frac{\rho}{12}[2SP_2(\cos\theta)+1]\times\left[\frac{1}{a^4}-\frac{1}{(a+d)^4}\right], \tag{8}$$

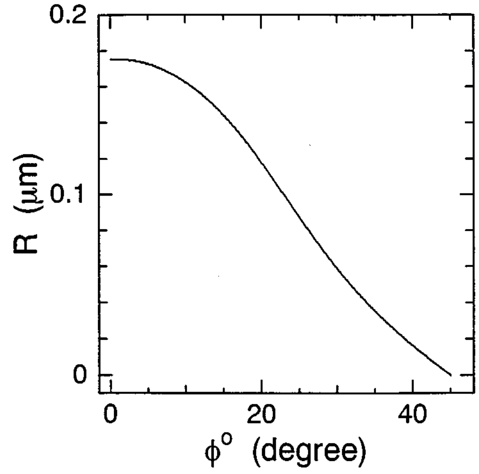

FIG. 5. Calculated relationship between the optical retardation R and the pretwisted angle ϕ for the sample with $l=22.1$ μm.

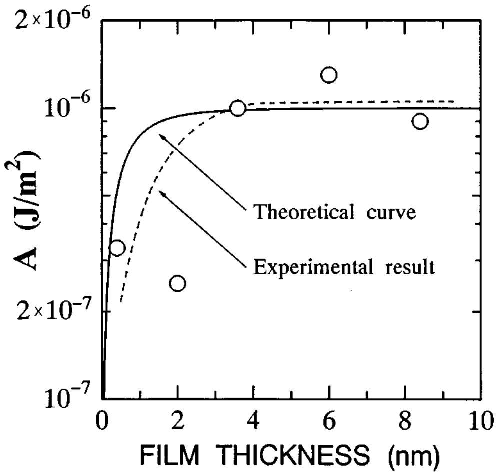

FIG. 6. PI-LB film thickness dependence of the anchoring strength A. Open circles show the anchoring strength A deduced from the measured values of ϕ and Eq. (2) as a function of PI-LB film thickness d. The dashed curve is just a guide to the eye for the experimental results and the solid curve gives the theoretical curve based on a simple model of Eq. (9).

where ρ is the surface density of the polyimide molecules, a is the half-width of the LC molecule, and d has been defined as the thickness of the LB films. From Eqs. (1) and (8) we obtain the expression of the anchoring strength as

$$A=\frac{1}{4}\,\eta\rho\sqrt{L_P L_M}S\left[\frac{1}{a^4}-\frac{1}{(a+d)^4}\right]. \tag{9}$$

The result of the numerical calculation using Eq. (9) is indicated by the solid line in Fig. 6. In our calculation we assumed $a=2$ nm and $(\eta\rho/4)\sqrt{L_P L_M}S=1.6\times10^{-5}$ J m^2. It is clear from Fig. 6 that the anchoring strength A measured increases with increasing d, having a sharp slope within a small range of d, and saturates in the limit of $d\to\infty$. The calculated curve agrees qualitatively with the experimental result in which A increases and saturates with increasing the LB film thickness. Equation (9) can also provide a partial explanation for the large discrepancy between different authors [4] of the measured dependence of A on the thickness of the surface alignment layer. All the parameters in Eq. (9) have simple physical meaning, especially the linear dependence of A on S in the nematic phase, which is theoretically a reasonable result. However, the detailed confirmation of this will require more experimental and theoretical investigations.

To summarize, we have provided a simple method with which to measure the unified anchoring strength. It was shown experimentally for 5CB on substrates with nanometer PI-LB films in a range less than 10 nm that a shear strained PI-LB film forces the director to align in the direction of the monolayer deposition. The experimental result in which the anchoring energy increases and saturates with the number of LB layers on the substrate was explained qualitatively by the generalized chain-chain van der Waals interaction theory.

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