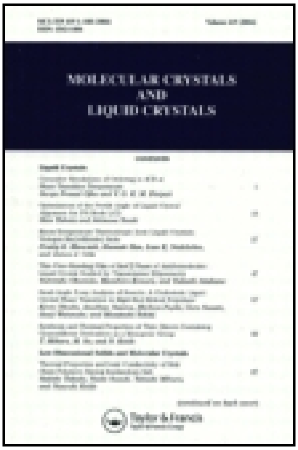

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Spontaneous Orientational Ordering of Liquid Crystal Layer During Evaporation onto Silica

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The ordering process of nematic liquid crystal (LC) during evaporation onto silica substrate was investigated. The optical second-harmonic generation and polarized absorption measurements were employed to determine the orientational order parameters S_1 and S_2. A sudden increase of S_1 was observed during the first layer deposition while S_2 gradually increased. Interestingly, S_1 was nearly constant after the completion of the first layer deposition, while S_2 was similar to that in the first layer deposition. The results suggest that spontaneous orientational ordering process is induced during the first monolayer formation.

Keywords: interface; liquid crystal; spontaneous ordering

1. INTRODUCTION

It is well-known that director distribution in a liquid crystal (LC) cell is dependent on substrate surface treatment [1]. Up to now, a variety of alignment methods have been proposed for the LC device fabrication. Along these, many techniques have been developed to characterize orientational orders of LCs at the interface [2]. Among them are optical absorption and second-harmonic generation (SHG) measurements [3–5]. From theoretical side, orientational order parameters (OPs) [6]

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defined as $S_n = \langle P_n(\cos\theta) \rangle$ are used, where P_n is the nth Legendre polynomial, θ is tilt angle of molecular long axis, and $\langle\ \rangle$ is the thermodynamic average. Optical second harmonic generation (SHG), Maxwell displacement current [7], surface potential measurements [8], etc., are employed to determine S_1. On the other hand, wall-induced birefringence [9], polarized absorption (PA) [10,11], Brewster angle reflectometry [12] measurements are used to determine S_2.

The liquid crystalline properties are specified using $S_2 \neq 0$. Nevertheless, symmetry breaking at the interface induces polar orientational ordering ($S_1 \neq 0$). Thus order parameter S_1 also gives insightful information on LCs at the interface. Keeping these in mind, we have been examining the ordering process of LCs at the interface using both S_1 and S_2. Spontaneous ordering of LCs is induced during the evaporation of LC molecules, due to the interaction between the evaporated molecules. In the present study, we probe spontaneous orientational ordering of LC layer during the evaporation of 5CBs by means of SHG (S_1) and absorption (S_2) measurements.

2. EXPERIMENT

2.1. Material and Evaporation Technique

4-pentyl-4′-cyanobiphenyl (5CB) was used in the experiment. The molecular structure is depicted in Figure 1. 5CBs exhibit nematic phase at a temperature between 24 and 35°C. The cyano-group has a permanent dipole (5D) which can cause polar ordering at the interface [13]. The transition dipole moment ascribed to the HOMO-LUMO excitation is parallel to the molecular long axis, and gives a strong absorption peak at a wavelength of $\lambda = 280\,\text{nm}$.

Synthetic silica substrate was used here. The substrate was chemically treated as follows: washed with detergent; cleaned in an ultrasonic-wave cleaning bath with distilled water, aceton, ethyl-alcohol, distilled water; dried at 80°C for $\geq$ 12 h; cleaned in a UV/ozone cleaning apparatus to remove organic residuals. After these treatments, we started the experiment immediately.

The evaporation box illustrated in Figure 1 was used in the experiment. 5CBs were evaporated at 85°C. A piece of a filter paper containing 5CBs was used as an evaporation source. The heater was set at a distance of about 2 cm from the light spot for the optical measurement (see top view in Fig. 1). A cylindrical plate was installed as a wind breaker. Another heater was placed at a position of about 5 cm above the silica plate, for regulation of substrate temperature. The substrate temperature was monitored using a thermocouple contacted with

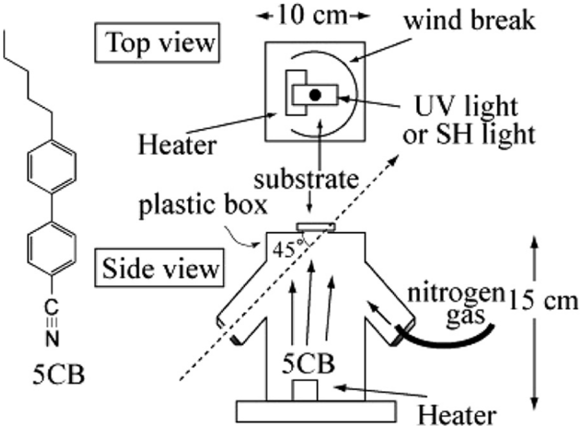

FIGURE 1 Evaporation box.

surface of silica placed inside the box. The surface temperature was kept at 30°C during measurements. The room temperature was 20 ± 2°C. The flow rate of nitrogen was 2 $\mathrm{dm}^3\,\mathrm{min}^{-1}$. It takes 120 sec to heat 5CBs up to 85°C.

2.2. Optical Measurements of S_1 and S_2

The SHG measurement was employed for determining S_1. The optical setup was illustrated in Figure 2(a). S_1 was determined as follows: The SH light intensity generated from a polar ordered layer with $\mathrm{C}_{\infty\mathrm{v}}$-symmetry was described as [14],

$$I(2\omega) \propto n_s^2 |A(\delta,\ \gamma)S_1 + B(\delta,\ \gamma)S_3|^2 I(\omega)^2 \tag{1}$$

where n_s is the molecular number per unit area, $I(2\omega)$ and $I(\omega)$ are the light intensities of the SH and fundamental lights. $A(\delta, \gamma)$ and $B(\delta, \gamma)$ are the coefficients, and they are expressed using the Fresnel's coefficients, incidence angle of the fundamental light, and the polarizing angles of the fundamental (δ) and the SH (γ) lights. The p-polarized fundamental light was irradiated onto the evaporated 5CB, and the p-polarized SH light was detected (pp-condition). In our experimental condition, Eq. (1) was rewritten as $I(2\omega) \propto |6S_1 - S_3|^2 I(\omega)^2$. Assuming 5CBs lie parallel to the substrate surface, S_1 is obtained from the square root of the SH light intensity with $\langle\cos\theta\rangle \gg \langle\cos^3\theta\rangle$. Pulsed laser light at the wavelength $\lambda = 532\,\mathrm{nm}$ from the second-harmonic light of Nd:YAG laser was used as a fundamental light (repeating

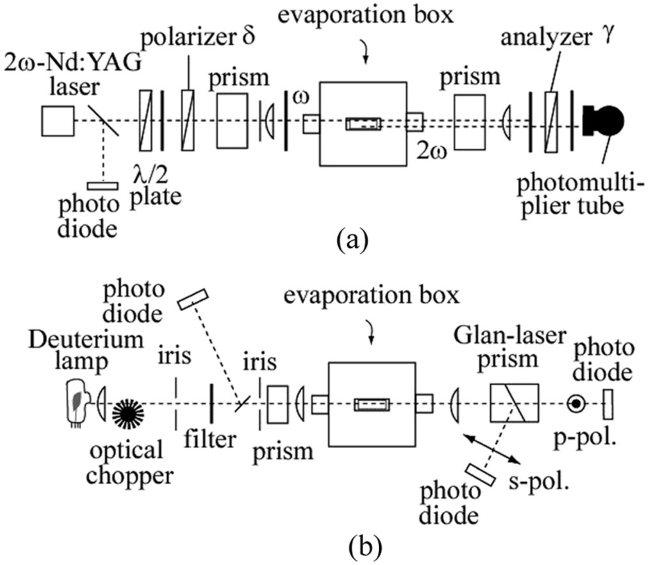

FIGURE 2 The optical setup for (a) second-harmonic generation measurement, and (b) polarized absorption measurement.

pulse rate: 10 Hz). With irradiation of the laser light onto a polar ordered 5CBs, strong SH light is generated due to the resonant-enhanced mechanism in the SHG process because the wavelength of SH light $532/2 = 266$ nm corresponds to the shoulder of the absorption peak ($\lambda = 280$ nm). The average power and the spot diameter of the fundamental light were 2 mW and <1 mm, respectively.

The PA was measured for determining S_2. Figure 2(b) shows the optical setup. Through an optical filter, ultraviolet light ($\lambda = 280 \pm 13$ nm) was irradiated onto the substrate. The spot diameter and the power of the irradiated light were 3 mm and 50 nW, respectively. *s*-and *p*-polarized lights were separated using polarizing prism. The light intensities were monitored, and the absorbance for the linearly polarized lights was recorded. The OP S_2 is given as [11]

$$S_2 = 2(A_p - A_s)/(2A_p + A_s) \tag{2}$$

assuming $C_{\infty v}$-symmetry. Here, A_s and A_p are the absorbance for *s*- and *p*-polarized lights, respectively. The surface molecular density n_s was determined using A_s and A_p as

$$n_s = \sigma^{-1}(A_s + 2A_p)/3 \tag{3}$$

where σ is the absorption cross section. Note that the molecular density is determined using the Lambert-Beer's law for optical absorption of isotropic material. Using Eq. (3), the molecular density for evaporated 5CBs is calculated. As a reference, silica substrate coated with 5CB LB monolayer was used. Here well-packed monolayer was transferred on the silica plate at a surface pressure of 4 mN/m and molecular area 35 Å^2. The absorbance of the reference 5CB monolayer was $A_s = 0.012$ and $A_p = 0.007$ ($A_s + 2A_p = 0.026$), and $\sigma = 0.91$ Å^2 was estimated using Eq. (3).

3. RESULTS AND DISCUSSION

Figure 3 shows the results of the SHG and PA measurements. Regions n ($n = 1,2,3$, and 4) corresponds to nth 5CB monolayer depositing process. Here n is determined by optical absorption $n = (A_s + 2A_p)/0.026$. In the region 1, an arrow indicates that a sudden increase of the SH intensity was observed during the first layer deposition. Accordingly, the absorbance A_s and A_p increased with a change. These results suggested that S_1 and S_2 increased accompanying the abrupt orientational change. For the second layer deposition, the SH intensity was saturated, while the absorbance changed in a manner as in the first layer deposition. S_2 started increasing in the region 2 at the deposition time indicated by an arrow in Figure 3(e). For further deposition, the SH intensity was saturated, and the absorbance change was similar as in the first and second layer deposition. In the following, we confine our discussion to regions 1 and 2. Firstly, the abrupt change observed during the first layer deposition indicated that spontaneous ordering was induced in the layer. Secondly, $S_2 < 0$ suggested that molecular long axis aligned nearly parallel to the surface, i.e., $0.96 < \theta < \pi/2$ assuming that molecules point in the same direction. The orientational order before (region 1a) and after ordering (region 1b) is illustrated in Figure 4 where 5CB is depicted as a rod with an arrow. The arrow represents the permanent dipole of the cyano-group.

The vapor stream of 5CBs consists of the isotropic system of molecules, i.e., $S_1 = S_2 = 0$. However, in region 1a, at the beginning of the deposition, $S_1 \neq 0$ and $S_2 = -0.4$. This result suggested that the isotropic 5CB molecules were reoriented as soon as they touched with the substrate. Then, in region 1b, orientational ordering resulted in the increase of S_1 and S_2. This is reasonably explained by assuming that intermolecular interaction between 5CBs dominates when 5CBs are densely packed. The increase of S_1 and S_2 indicates the polar-head of 5CB, i.e., cyano-group, pointing towards the surface, and molecular long axis rotating towards normal to the surface. That is, spontaneous

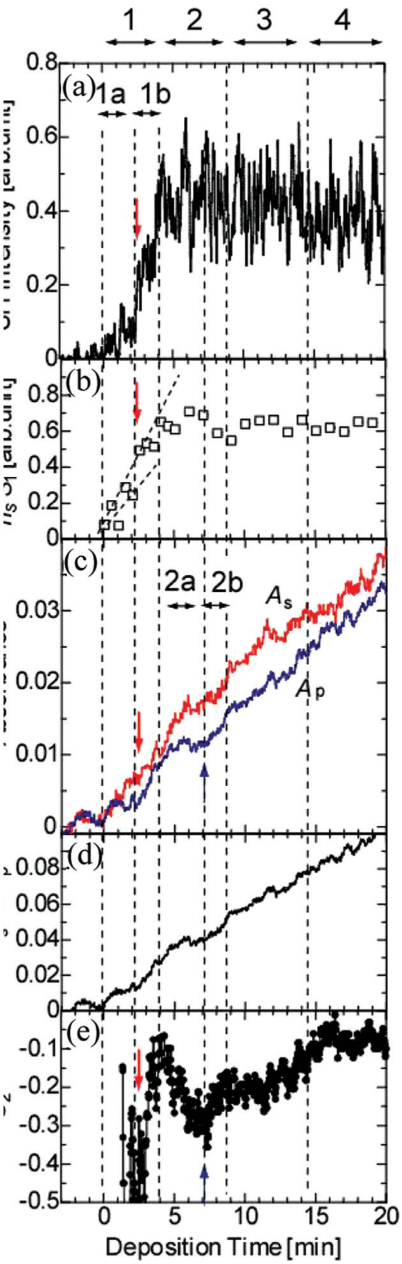

FIGURE 3 Orientational ordering process during evaporation of LC. 1, 2, 3, 4 on the top of the figures represent regions where *n*th ($N = 1,2,3,\ 4.$) layer is deposited. (a) SH light intensity, (b) square root of the SH intensity, proportional to S_1. (c) absorbance for *s*- and *p*-polarized lights, (d) absorbance $A_s + 2A_p$, (e) S_2.

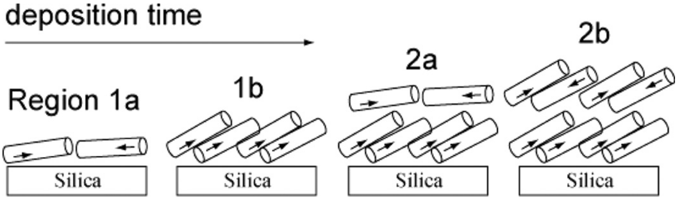

FIGURE 4 Orientational ordering process suggested by the in-situ SHG and PA measurements during evaporation.

polarization was induced in the first layer. The electrostatic energy caused by spontaneous polarization prohibits 5CBs from standing up ($\theta = 0$) on the surface. The sudden change of S_1 suggests a very fast reorientation of the polar-head, though the reorientation of molecular long axis is slow. We explain these results in terms of relaxation process as follows: firstly, the reordering of polar-group reflects the orientational polarization, where relaxation time τ_p is given by Debye relaxation time of the LC director. For bulk 5CB, it was found relaxation time of $\tau_p = 24\,\text{ns}$ [15]. In contrast, reorientation of molecular long axis reflects the director reorientation. The relaxation time of director rotation is $\tau_d > 1$ ms. In Figure 3, the change of S_2 happens during several ten seconds, i.e., much slower than 1 ms, but qualitatively accounts for the slowly reordering process of S_2. The response time of S_2 at the interface is ruled by the surface anchoring energy [16], but this is out of scope in the present study. The slow S_2 relaxation suggests that the first monolayer exhibits liquid crystalline nature, i.e., slow orientational relaxation of the nematic director. This is consistent with the immediately reorientation of 5CBs at the beginning of deposition, where 5CBs are gaseous.

Further, in the following, we discuss the physical reasoning of the increase of S_1. The orientational polarization is expressed as [6,17], $\bar{P} = N\mu S_1 = (2\bar{S}_2 + 1)/3 \times N\mu^2 E/k_B T$ where $\bar{S}_2$ is the second OP along the director, N is the molecular density, μ is the permanent dipole, k_B is the Boltzmann constant, T is the absolute temperature, and E is local electric field. Intermolecular interaction, e.g., image force, makes a contribution to form a local field. Hence, the increase of S_1 is qualitatively explained by the increase of S_2. Based on the above discussion, spontaneous ordering in the first layer deposition is described as follows: spontaneous ordering of molecular long axis is induced when LC–LC interaction becomes a main contributor. After that, S_1 changes because the presence of the nematic order contributes to orientational polarization. Finally, the director reorientates towards the equilibrium orientation, i.e., $S_2 = -0.1$ for 5CB first layer on silica. It is informative here to mention the SHG measurements for 8CB [3–5]. The SH intensity increased continuously during the first layer deposition, where 8CB shows a smectic property, and reordering of LCs is not allowed.

For the second layer deposition, the SH intensity was saturated. Similar behavior was observed for the 8CB deposition [4,5]. This result implies that a layer-by-layer structure was formed at the interface. Assuming that the second layer deposition gives no effect on the orientation of the first layer, the S_2 in region 2 is explained as follows (see Fig. 4): when 5CBs are delivered onto the first layer, 5CB lies paralelly to the surface of substrate with decrease of S_2 (region 2a). On the other hand, as evaporation proceeds, molecular density increases. The intermolecular interaction between 5CBs thus increases. This situation is very similar to the case of the first layer deposition. S_2 increases as 5CBs reorientate their molecular long axis so as to align parallel to each other (region 2b). For the second layer, $S_1 = 0$ and it is reasonable to consider that the molecular long axis points in the surface normal direction. Nevertheless, actually $S_2 < 0$ in our experiment. It is expected that the director of the first layer coincides with the second one, and the values of S_2 at the end of regions 1 and 2 will be identical. The result shows that the maximum value of S_2 in regions 1 and 2 is -0.1 ± 0.1. Note that S_1 and S_2 in experimental result illustrates average orientational order for the whole 5CB layer.

Here it is instructive to note that spontaneous ordering was not observed when the evaporation rate is small. Figure 5 shows the SHG experiment where the 5CB source was evaporated at 60°C. The evaporation rate is about ten times slower than that in the experiment of Figure 3, where there is no sudden increase of the SH light intensity. Nevertheless the maximum intensity of the SH light is the same. Hence the deposition rate does not give effect on S_1 when the first layer deposition is completed whilst it gives effect on the ordering process.

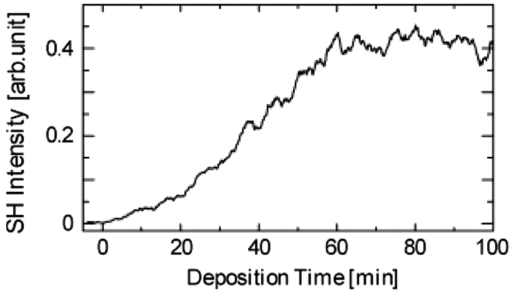

FIGURE 5 The SH light intensity during at 60°C.

4. CONCLUSION

The orientational ordering process of 5CB was investigated using SHG and PA measurements. The orientational order parameters S_1 and S_2 were determined in-situ during evaporation onto silica substrate. It was suggested that spontaneous orientational ordering was induced during the first layer deposition. The ordering was characterized by the increase of S_1 and S_2. In contrast, for the second layer, $S_1 = 0$ while S_2 changes in the same manner as in the first layer deposition.

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