

Original

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Orientational Ordering Process of Liquid Crystalline Molecules Evaporated on Azobenzene Monolayer: Optical Polarized Absorption Measurements and Adsorption Kinetics

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The orientational order of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) molecules deposited on silica substrates coated with *trans*-form azobenzene monolayer was examined during deposition, *in-situ*, using optical polarized absorption measurements. It was revealed that the orientational order change was induced by monolayer formation, due to the change of adsorption kinetics

Key Words : orientational order parameter, 5CB, optical polarized absorption measurements, anchoring

1 Introduction

Anchoring phenomena is of great importance in liquid crystal (LC) science and the control of anchoring phenomena is one of the most important technologies in liquid crystal display (LCD) fabrication [1]. This phenomenon can be phenomenologically treated using easy axis and anchoring strength in its mathematical expression. Easy axis is defined to express the orientational restriction imposed on surface LC molecules by a substrate, whereas anchoring strength is defined to express the strength by the restriction imposed on surface LC molecules by the substrate.

In order to use anchoring phenomena purposefully for the alignment of LCs on the substrates, rubbing process is widely employed, where geometrical surface roughness and intermolecular interaction are considered as main contributing factors, especially for so-called in-plane anchoring [2-4]. For the polar anchoring, e.g. anchoring in the direction normal to the substrate surface, the details are still not clear though phenomenological expression such as Friedel-Creagh-Kmetz (FCK) rule is conventionally used [5,6]. In the present study, for a profound understanding of the anchoring phenomena along surface normal direction, we focused on the orientational order of evaporated liquid crystalline molecules at interface. To describe the orientational order of LC molecules at the interface, an apparent orientational order parameters defined as $S_n = \langle P_n(\cos \theta) \rangle$ (P_n ; n -th Legendre polynomial, $0 < \theta < \pi$; tilt angle from substrate normal, $\langle \dots \rangle$; thermodynamic average) [7] are introduced. Using the set of orientational order parameters S_1 , S_2 and S_3 , the orientational order of molecules at interface is well specified as shown in Figure 1. In our previous work [8], we determined the orientational order parameters, S_n ($n=1, 2, 3$), of a polar LC molecule, 4-*n*-pentyl-4'-cyanobiphenyl (5CB), on

trans-/*cis*-form azobenzene-coated silica substrate by *in-situ* observation during 5CB deposition using both optical SHG measurements and optical polarized absorption measurements. The experimental results revealed that the orientational order of 5CB molecules changed as 5CB surface density increased during deposition. It was also found that the orientational order depended on the conformation of azobenzene group. However, the details were not clear. In this paper, focusing on the second orientational order parameter, S_2 , determined by the optical polarized absorption measurements, we argue that the formation of a "5CB monolayer", ruled by the adsorption kinetics, is a main origin of the above mentioned orientational order change.

2 Experimental

5CB was purchased from Merck and used as received without further purification. This molecule has a rod-like shape and modeled using an arrow. This molecule has a transition dipole which is attributed to the transition from the highest occupied

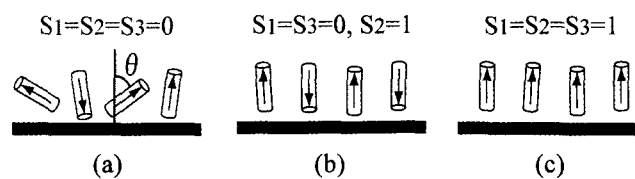


Figure 1: Relationship between the orientational order of rod-like polar molecules like an arrow at the interface and the orientational parameter, S_n ($n=1,2,3$).

(a) Molecules are randomly oriented, (b) molecular long axes are oriented along the substrate surface normal direction, (c) molecules are oriented in the same direction.

molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and its direction is along the molecular-long axis. For azobenzene monolayer, we used 6Az10PVA molecule, i.e., polyvinylalcohol with azobenzene side chains. Synthesized silica substrates were used and they were cleaned as follows: initially, the substrates were roughly cleaned with detergent. Then, they were cleaned with distilled water, acetone, ethanol and distilled water using ultrasonic cleaner successively. Subsequently, substrates were dried in a box kept at 80°C. After that, substrates were cleaned using UV/ozone cleaner (Nippon Laser & Electronics Lab. NL-UV253S) to remove residual organic solvents. On the silica substrate, we deposited *cis*-form azobenzene monolayer by Langmuir-Blodgett technique at a pressure of 8 mN/m. At this surface pressure, surface area per azobenzene side chain is 35 Å² which is roughly equal to the cross section of the side chain. Therefore, the side chain is assumed well packed in the resulting film. After that, azobenzene coated substrate was irradiated by LED (emission peak wavelength: 470 ± 10 nm, intensity: 1 mW/cm²) for 30 minutes and the conformation of azobenzene side chain was changed due to photoisomerization from *cis*-form to *trans*-form. 5CB molecules were deposited by evaporation method in the air (temperature; 27-28 °C, relative humidity; 40 ± 10%). 5CB drop put on the heater was kept at 90°C and molecules gradually evaporated from the heater and they were deposited on the substrate surface covered with *trans*-form azobenzene monolayer.

Optical absorption for *s*- and *p*-polarized light by deposited LC film are described as follows;

$$OD_s = \tilde{\epsilon} N_s \frac{\langle \sin^2 \theta \rangle}{2} \quad (1)$$

$$OD_p = \tilde{\epsilon} N_s \frac{1 + \langle \cos^2 \theta \rangle}{4} \quad (2)$$

assuming deposited LC film is C_{∞v}-symmetry and the incident angle of polarized light is 45°. Here, OD_s and OD_p denote optical density for *s*- and *p*-polarized light, respectively. θ is the tilt angle of molecule from the surface normal direction ($\theta = 0$ when cyano-group of 5CB orients toward substrate along surface normal direction), N_s is molecular surface density, $\tilde{\epsilon}$ is absorption coefficient of 5CB molecule and assumed independent of surface molecular density N_s , and $\langle \dots \rangle$ is thermodynamic average. Using Eqs. (1) and (2), we determined the second orientational order parameter $S_2 = \langle (3 \cos^2 \theta - 1)/2 \rangle$ and N_s , simultaneously, as

$$S_2 = \frac{2(OD_p - OD_s)}{2OD_p + OD_s} \quad (3)$$

$$N_s = \frac{OD}{\tilde{\epsilon}} = \frac{OD_s + 2OD_p}{\tilde{\epsilon}} \quad (4)$$

where OD is optical density for depolarized light (OD = OD_s + 2OD_p). For 5CB film, absorption coefficient was estimated $\tilde{\epsilon} = 9.1 \times 10^{-17} \text{ cm}^2$ by the polarized absorption measurement for 5CB LB monolayer on silica substrate.

Using Eqs. (3) and (4), we performed *in-situ* observation of the second orientational order parameter S_2 , and surface density of 5CB molecules N_s , simultaneously, during 5CB deposition using optical polarized absorption measurements. Optical setup for the polarized absorption measurement is shown in Figure 2.

3 Results and Discussion

Figure 3(a) shows optical density for *s*- and *p*-polarized light OD_s and OD_p, while Figure 3(b) shows S_2 and N_s calculated from OD_s and OD_p. We divided the deposition process into two region indicated as "region 1" and "region 2" as shown in Figure 3(b). In region 1, molecular surface density increases and saturates around 8 min in the manner similar to the Langmuir-type adsorption. Langmuir-type adsorption is valid when the adsorbed molecules interact only with an elementary space on the surface and the interaction between adjacent two adsorbed molecules is negligible. This leads to the saturation of adsorption when single monolayer was formed under thermodynamic equilibrium state. In our case, the saturation in region 1 corresponds to the 5CB monolayer formation by Langmuir-type adsorption. However, probably, the interaction among adsorbed 5CB molecules is not negligible and Langmuir-type adsorption is not necessarily valid. On the other hand, molecular surface density begins to increase again in region 2. With taking into consideration that temperature of substrate is almost the same as the ambient temperature at which 5CB bulk is in nematic LC phase, we may consider that evaporated 5CB molecules are condensed at substrates surface during the deposition.

S_2 is also dependent on 5CB deposition time. Additionally, it was found that the change of S_2 is ruled by the change of adsorption kinetics as discussed above. Figure 3(b) shows that $S_2 \sim 0.5$ in region 1 begins to decrease in region 2. After 20 min deposition, S_2 seems to saturate at around $S_2 = 0$. With the adsorption kinetics discussed above, we may argue S_2 in region 1 is reflecting the property of 5CB monolayer. On the contrary, the change of S_2 reflects the property of bulk in region 2. There are two possible interpretation of the orientational order in region 2 as follows; (1) 5CB bulk-like film is formed on the first monolayer, and (2) transition from 5CB monolayer to 5CB bulk occurred during deposition. In case (1), the orientational order of the first monolayer is unchanged during deposition in region 2. On the other hand, in case (2), orientational order of the first monolayer

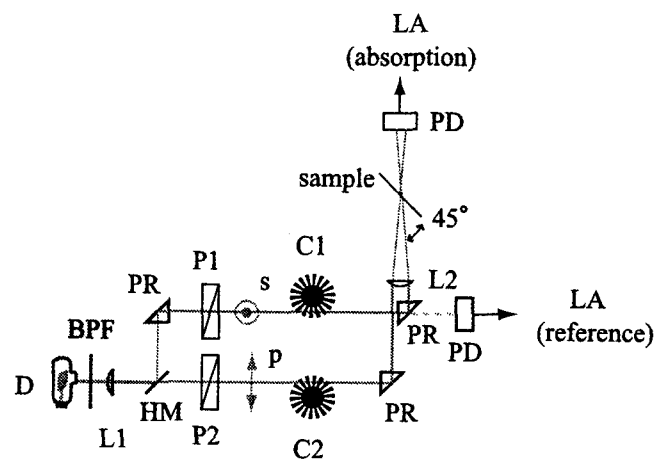


Figure 2: Optical setup for optical polarized absorption measurements. D: Deuterium lamp, BPF: band pass interference filter (280 ± 25 nm), L1: lens (f=40 mm, quartz), L2: lens (f=200 mm, quartz) HM: metal grid-type half mirror, C1: optical chopper (f=4000 Hz), C2: optical chopper (f=400 Hz), PR: prism (quartz), PD: photo diode, LA: lock-in amplifier.

changes. From the previous study using second-harmonic generation (SHG) measurements [8], it was confirmed that the first LC monolayer possesses the polar orientational order while the LC molecules deposited onto the first monolayer does not have such polar orientational order. This result suggests that the case (1) is the most probable process.

It is informative here to discuss experimental results using *cis*-form azobenzene monolayer (not shown), where *cis*-form azobenzene coated silica substrate was prepared in the same way as is the case of *trans*-form azobenzene coated one except for blue light irradiation for photo-isomerization. We could not observe such Langmuir-type adsorption kinetics in the beginning stage of deposition though the deposition rate change was seen around 5 min deposition time. This fact indicates that azobenzene conformation affects the first LC monolayer formation on the surface, though the mechanism is not yet clear.

4 Conclusions

With adsorption kinetics observation from the optical polarized absorption measurements, the orientational order observation during 5CB deposition on *trans*-form azobenzene monolayer was discussed. It was confirmed that adsorption kinetics like Langmuir-type adsorption is observed during 5CB deposition of the first monolayer on the azobenzene. It was found that the second orientational order parameter changes depending on with

or without the formation of 5CB monolayer.

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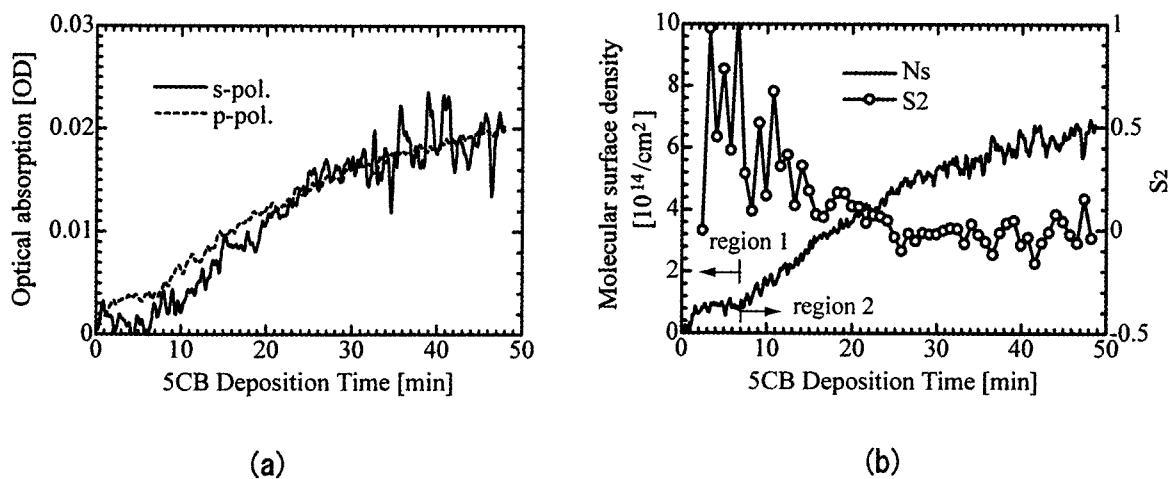


Figure 3: The result from the optical polarized absorption measurements. (a) Optical density for *s*- and *p*-polarized light by deposited 5CB film during deposition. (b) Molecular surface density and the second orientational order parameter S_2 during the deposition calculated from the optical density for polarized light.