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The Influence of Depositing Velocity on Polyamic Acid Salt Langmuir–Blodgett Alignment Films for Nematic Liquid Crystal

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The characterization of Langmuir–Blodgett (LB) orientation films in terms of the optical retardation as a function of the LB depositing velocity has been studied, and the surface anchoring strength of the LB films for a nematic liquid crystal has been estimated. The optical retardation decreases as the LB depositing velocity increases. In contrast, the anchoring strength increases as the LB depositing velocity increases. The macroscopic anchoring strength may not have a positive correlation with the optical retardation which reflects the microscopic orientational order. Furthermore, we succeeded in generating the high pretilt angle by only using the LB method. The pretilt angle gradually decreases with increasing the depositing velocity.

Keywords: Langmuir–Blodgett films, polyamic acid salt, nematic liquid crystal, depositing velocity, optical retardation, anchoring strength.

1 INTRODUCTION

The alignment of liquid crystals on the qualified surfaces has been eagerly examined by many researchers from both the fundamental and practical points of view. Concerning the industrial technique for Liquid Crystal Displays (LCDs), the alignment surface of LCD characterizes its capability. In practice, most of the LCD panels were made by using the rubbing alignment technique[1] nowadays. However, the rubbing process generates a lot of dust particles and static electricity which sometimes causes the break-down of LCD pixels or attached semiconductor devices. In this context, various alignment methods, without using the rubbing process, have been sought and proposed. Particularly, the alignment using the Langmuir–Blodgett (LB) film is one of the most possible methods,[2] and which has some merits such as the ultra-thin

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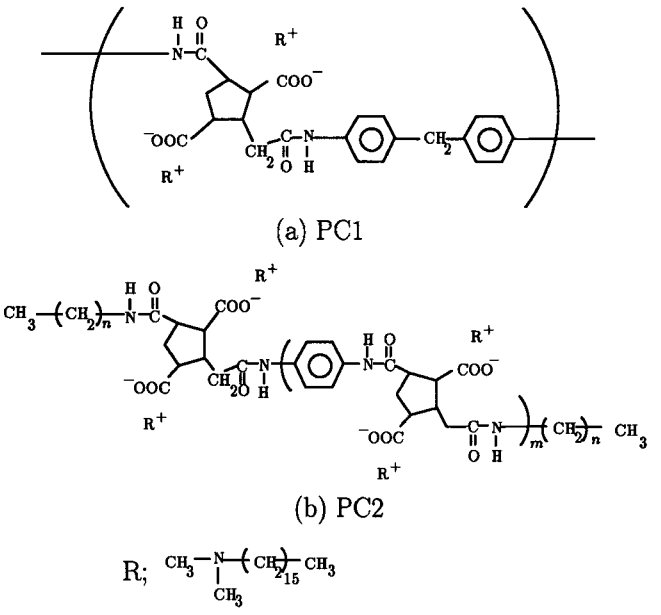
and controllable film thickness. Ikeno *et al.*[3] demonstrated an excellent optical performance on the surface-stabilized ferroelectric liquid crystal (SSFLC) device using polyimide (PI) LB alignment films, where the experimental result was interpreted that the thin film thickness contributes to neutralize the depolarization electric field which deteriorates the optical memory capability.[4] Recently, the surface alignment nature of the nematic liquid crystal (NLC) using PI-LB alignment films was measured in terms of the anchoring strength[5] and optical retardation of LB films.[6] In these papers, the values of the ordinary PI-LB films were simply compared with one of the rubbed PI-LB films, and there was few detailed discussions in regard to the influence of LB preparative conditions such as the depositing velocity.

In general, the anisotropic molecular arrangement of PI film induced by the fluidal motion of Langmuir film during the vertical dipping depositing[7] seems to affect the LC orientational order near the surface of LB film.[8] Hence the LB preparative conditions such as the subphase, surface pressure, depositing velocity etc. are important issues to control the induced surface alignment of PI films. The present investigation was carried out with the aims to know how the depositing velocity affects the induced surface anisotropy in terms of orientational texture, anchoring strength of NLC molecule and optical retardation of LB films. Furthermore, we succeeded in the generation of high pretilt angle by controlling LB preparative conditions without any extra techniques or chemical modifications of LB material. The relationship between the magnitude of pretilt angle and the depositing velocity was also studied.

2 EXPERIMENTAL

2.1 Polyamic Acid Salt Langmuir–Blodgett Films

The first description of the PI-LB film was given by Kakimoto *et al.*[9] In the present investigation, the precursors used were two types of modified polyamic acid salt, which are shown in Figure 1, and two types of solution were prepared. PA1 is a solution containing PC(1) (Figure 1(a)) 1 mmol/*l* in the mixed solvent [N-methyl-pyrrolidon/Toluene = 8/2], which has a capability of homogeneous aligning. PA2 is a mixture containing PC(1) (Figure 1(a)) 0.9 mmol/*l* and PC(2) (Figure 1(b)) 0.1 mmol/*l* in the prescribed solvent, which has a capability of homeotropic aligning. The trough used was the conventional type of Langmuir trough. Monolayers of the PAs were prepared upon purified water at a subphase temperature of about 20°C. Typical compression π-A isotherm diagrams of precursors used were shown in Figure 2. These two diagrams exhibited similar behavior. Ikeno *et al.* also used the precursor PA1, and they controlled the surface pressure at 25 mN/m which is the region of steep inclining part in the π-A diagram and corresponds to the monolayer solid film formation.[2,3] Thus we also kept the surface pressure at 25 mN/m before depositing. 5 layers of Y-type films were deposited onto an ITO (Indium Tin Oxide) coated glass plates, the size of glass plate was $20 \times 15\,mm^2$. In order to investigate the effect of depositing velocity on the NLC alignment, the depositing velocity was ranged from 7.5 mm/min to 20 mm/min. When the depositing velocity was high value like 20 mm/min, it may be difficult to maintain the surface pressure at 25 mN/m. The surface pressure-loss[7] may also occur because of the high viscosity of polyamic acid. However, it seems that the deviation of the surface



(a) PC1

(b) PC2

R; $CH_3-\underset{CH_3}{\overset{|}{N}}-(CH_2)_{15}-CH_3$

FIGURE 1 Molecular structures of the polyamic acid salt.

pressure is small because the glass substrate is sufficiently small. After depositing onto the glass plate, the PA-LB layers were dried in the air.

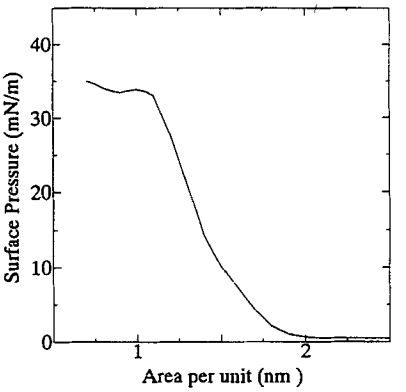
2.2 Sample Preparation and Measurement

For proper estimation, two kinds of sample glass plate were prepared. One is the conventional type of glass plate (1.1 mm thickness) with ITO for preparation of the NLC cell, and the other is a thin glass plate (110 μm in thickness) for accurate measurement of the retardation of LB films. The former glass plate cannot be used to measure the fairly small quantity of retardation because of the high retardation of the glass plate itself.

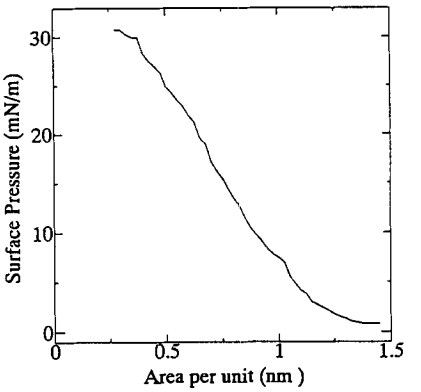
The measurement of the retardation is useful for estimating the orientational degree of LB films. Recently, Kuniyasu *et al.*[10] developed a new system for measuring the retardation. In the present study, our system was improved which has an accuracy of about 0.01 degree. The light source used is an He–Ne laser (10 mW) and the spot area is about 1.5 mm^2.

The structure of the sample NLC cell was the ordinary homogeneous type consisting of two glass plates whose inner surfaces were covered with PA-LB films and the depositing direction is antiparallel. The cell gap d was about 10 μm, and the area of the ITO electrode is 100 mm^2. The NLC used was 4-cyano-4'-*n*-pentylbiphenyl (5CB). In order to measure the pretilt angles, the crystal rotation method[11] was used.

For estimating the anchoring energy, we used the high field method[12] employing the retardation measurement system and capacitance meter. Under the high electric



(a)PA1



(b)PA2

FIGURE 2 Typical compression π-A isotherm diagrams. We controlled the surface pressure at 25 mN/m which is the region of steep inclining part in the π-A diagram and corresponds to the monolayer solid film formation.

field ($V > 6V_{th}$), the anchoring strength A can be determined from the following relationship:

$$\frac{R}{R_0} = \frac{I_0}{CV} - \frac{2(K_1 \cos^2\theta + K_3 \sin^2\theta)}{dA}, \tag{1}$$

where R and R_0 are the optical retardation with and without the applied electric field, θ is the pretilt angle, C and V are the cell capacitance and applied voltage, and I_0 is a constant which depends on the NLC substance parameters. K_1 and K_3 are the elastic

constant for the splay and bend deformation of NLC. The pretilt angle and anchoring strength were measured at the temperature $T = T_{NI} - 10.0$ (°C), where T_{NI} is the clearing point (35.3°C).

3 RESULTS AND DISCUSSION

Figure 3 shows the microphotographs of NLC textures for the PA1-LB sample under the crossed polarizer, where the LB depositing velocities are 7.5 mm/min (Figure 3(a)) and 20 mm/min (Figure 3(b)), respectively. Clear differences between Figure 3(a) and Figure 3(b) can be observed in the texture. The former microphotograph (Figure 3(a)) reveals the multidomain formation, and the extinction angles for each domains are different (as indicated by the arrows in the Figure 3(a)). However, the latter sample (Figure 3(b)) reveals the almost complete monodomain texture. This result indicates that the NLC alignment depends on the LB depositing velocity. In regard to the

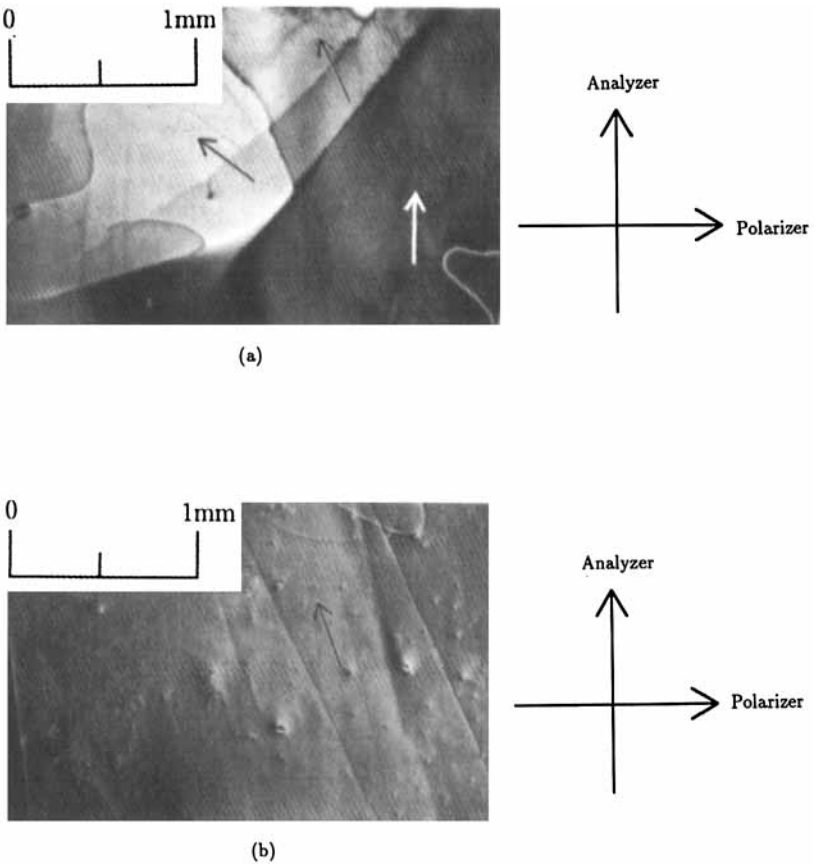


FIGURE 3 Polarizing microphotographs of NLC textures for PA1-LB sample. The LB depositing velocities were 7.5 mm/min (Figure 3(a)) and 20 mm/min (Figure 3(b)), respectively. See Color Plate VI.

formation of the multidomain structure for the monolayer on the Langmuir trough, it has been mentioned that the molecules on the water tend to form a crystalline structural domain.[13,14] When the multidomains on the water subphase were compressed by the barrier, the resulting Langmuir monolayer film might end up with many domains and distinct boundaries. In the case of highly viscous film as PA, such multidomain structures were consequently transferred as it was to the substrate surface when the vertical depositing velocity was relatively small. Thus, although the polymer strands of PA were aligned toward the inherent directions originating from each domain formation, there was no macroscopic and coherent alignment throughout the monolayer. This is the reason why the extinction angle of NLC cell gave various directions as shown in Figure 3(a). On the other hand, the LB depositing velocity may give an macroscopic orientational effect similar to the rubbing treatment. It seems that the surface polymers are stretched along the substrate depositing direction, and the stretched polymers were well aligned parallel to the depositing direction, where the degree of surface order may depend on the LB depositing velocity. As Nakayama *et al.*[7] mentioned before, the surface pressure during the depositing process may be decreased unsuitably when the depositing velocity is fairly high. However it seems that such surface pressure-loss does not affect the macroscopic orientational effect.[8] Accordingly, the high-depositing velocity contributes to align the orientational surface polymers and NLC were aligned fairly uniformly as a monodomain orientation.

It is most important for estimating the microscopic orientational order to measure the induced surface retardation. Figure 4 shows the dependence of the optical retardation on the depositing velocity, where the LB material used was PA1. It is noteworthy that the optical retardation decreased with increasing the LB depositing velocity. Concerning the PI rubbing alignment films, in general, the optical retardation increases with increasing the rubbing strength by which the surface order was influenced. If the

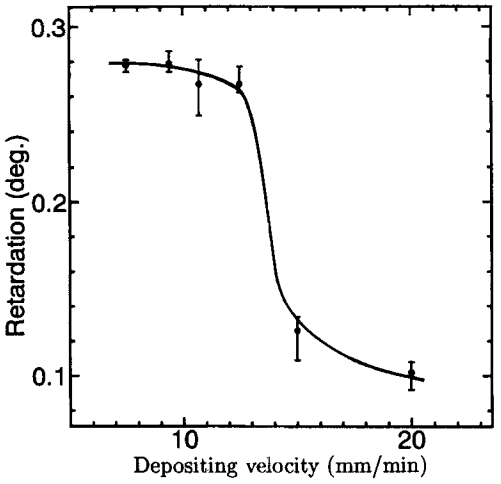


FIGURE 4 The dependence of the optical retardation on the depositing velocity, where the LB material used was PA1.

LB depositing velocity gives some microscopic orientational effect, the optical retardation should increase with increasing the LB depositing velocity. For a low depositing velocity region, the molecules on the water tend to form a multidomain, and the domain can be transferred onto the substrates. The measured area (laser spot) for optical retardation which is comparable to the domain size is so narrow that the area may be regarded as microscopic. Hence the measured value of the optical retardation indicates the degree of the microscopic orientational surface order. Therefore, the optical retardation is the inherent value of PA-LB multidomains where the orientational direction was distributed variously as shown in Figure 3(a). Furthermore, the fairly higher value of the optical retardation seems to come from the crystalline structural domain of PA LB, therefore the microscopic orientational order may be higher in each multidomain. On the other hand, as we mentioned, the fast-depositing velocity gives an optional anisotropic stretching effect which contributes to align the orientational surface polymers macroscopically. The external stretching force seems to break the inherent (microscopic) domain of the PA polymers, then reorients the polymers macroscopically parallel to the depositing direction. Therefore the measured value of retardation is not corresponding to the inherent value of the PA-LB domains.

It may be natural to expect that the surface anchoring strength has a positive correlation with the optical retardation. Figure 5 shows the dependence of the NLC surface anchoring strength on the depositing velocity, where the LB material used is PA1. The anchoring strength tends to increase with increasing the depositing velocity. From this result, the tendency of anchoring strength seems to contradict that of the optical retardation which corresponds to the microscopic alignment. The reason for the apparent contradiction is considered as follows. Concerning the measurement of the anchoring strength, the measured values should be understood as macroscopic values, because the high-field method needs to measure the capacitance which was

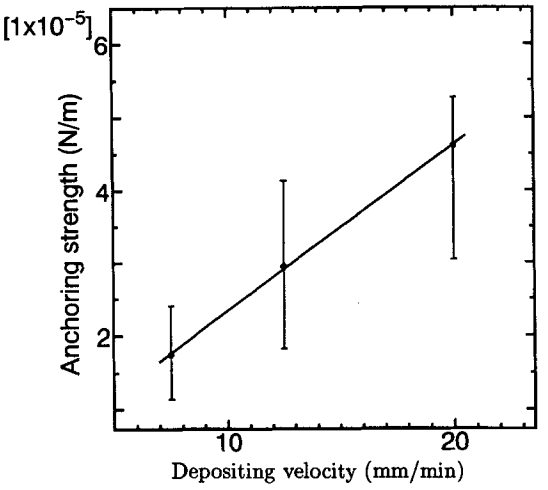


FIGURE 5 The dependence of the NLC surface anchoring strength on the depositing velocity, where the LB material used was PA1.

averaged over the whole electrode area, where the area was fairly large, such as 100 mm^2. In particular, in the case of a multidomain cell, even though the characterization between the domains is different, it is difficult to recognize the difference of capacitance. Furthermore, the domain wall in the texture may prevent with the reorientation under the electric field and the variation of capacitance is apparently lower. From the Eq. (1), the diminution of the capacitance variation has a bad influence upon the measurement of the anchoring strength. That is, it is not possible to measure the anchoring strength accurately for the multidomain cell. Thus the high-field method is suited for the uniform alignment sample, but may not be suited for the multidomain samples. In contrast to the measurement of capacitance, the measurement of optical retardation corresponding to the microscopic alignment was that of a very small spot area, such as 1 mm^2, because of using the laser light. We think that it is better to estimate the anchoring strength for the multidomain sample based on only using the optical retardation, because the high-field method needs both the macroscopic (capacitance) and microscopic (retardation) values. The novel measurement method based on the optical retardation is now in progress. It is expected that the anchoring strength estimated by this new method has a positive correlation with the optical retardation of the LB film.

Figure 6 shows the dependence of the pretilt angle on the depositing velocity, where the LB material used is PA2. The high pretilt angle was generated without using the additional treatment such as the rubbing process. The pretilt angle gradually decreased with increasing the depositing velocity. The experimental results are interpreted as follows. The LB material used here, which has the long-alkyl amine, has a capability for generating the high pretilt angle. As Kobayashi mentioned before,[15] the steric interaction between the NLC molecule and long-alkyl branches seems to be the origin of generating the high pretilt angle. When the surface polymers were stretched toward the

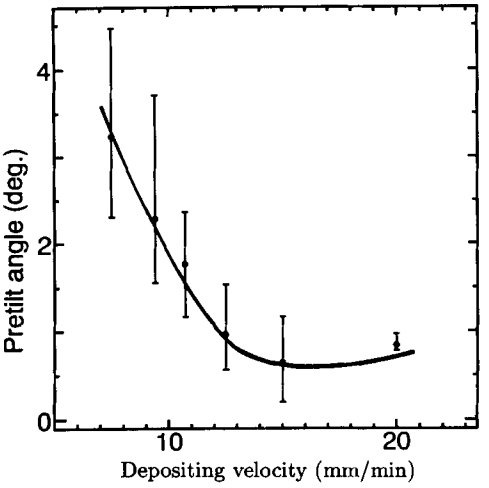


FIGURE 6 The dependence of the pretilt angle on the depositing velocity, where the LB material used was PA2.

substrate depositing direction, the stretched polymers were well aligned parallel to the depositing direction. For the fast depositing velocity region, the surface polymers were highly ordered and the polymer chains of PAs were reoriented horizontally parallel to the substrate, consequently the pretilt angle tends to be lower. Therefore the pretilt angle depends on the surface order which was influenced by the LB depositing velocity.

4 CONCLUSIONS

The research on the characterization of the LB orientation in terms of the optical retardation as a function of depositing velocity was carried out. We have firstly pointed out that the optical retardation decreases as the LB depositing velocity increases, because the microscopic PA polymer alignment was reoriented by the LB deposition artificially. For the low-depositing velocity region, the PA-LB multidomain structure was formed onto the substrate which came from the crystalline texture on the Langmuir trough. As the depositing velocity was higher, the PA polymers were reoriented toward the depositing direction macroscopically.

The surface anchoring strength of the LB films for a nematic liquid crystal cell has been estimated. In contrast to the result of the retardation measurement which reflects the microscopic orientational order, the macroscopic anchoring strength increases as the LB depositing velocity increases. However, the result of anchoring strength for the multidomain sample may not be correct, and the anchoring strength estimated by the novel method may have a positive correlation with the optical retardation.

Furthermore, we succeeded in generating the high pretilt angle by only using the LB films. It was recognized that the pretilt angle decreases with increasing the depositing velocity.

The method for estimating the anchoring strength based only on the optical retardation is now in progress and will be presented in the near future.

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