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Alignment layers with variable anchoring strengths from Polyvinyl Alcohol

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In the study of polyvinyl alcohol (PVA) alignment layers for liquid crystal devices, we found that the anchoring strength can be greatly varied by changing the alignment film thickness. Both the polar and azimuthal anchoring strengths increased with increasing film thickness; however, they had different film thickness dependences. It was also noticed that the quartic term in the expansion of the Rapini-Papoular anchoring energy was important for describing the polar anchoring. In the experiment, solid PVA was dissolved in a thinner and spin-coated on glass substrates to create alignment layers. The substrates were assembled to make electrically-controlled birefringence liquid crystal cells. The polar anchoring strength of the alignment layer was measured using the high field method and the azimuthal anchoring strength using the twist angle method.

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I. INTRODUCTION

The interaction between the liquid crystal (LC) molecules and a solid substrate presents a fundamental problem for researchers. The boundary breaks the symmetry of the LC phase, yielding fascinating phenomena, such as the anchoring behavior at the substrates, where the molecules follow the alignment imposed by the surfaces. To describe this behavior, Rapini and Papoular proposed an energy form that is widely used. Nonetheless, this energy depends on a phenomenological parameter \( W \) called anchoring strength, and no information about the interaction is given. The interaction between the substrate and the LC molecules has been intensively studied by taking the van-der Walls and short-range interactions to describe the anchoring behavior, but a complete understanding is yet to come.

Most LC devices need alignment layers which predetermine the orientation of the LC. The anchoring strength and the “easy” direction of the alignment layers are of great importance for practical applications. Alignment layers are usually made from polymers, such as polyimide and polyvinyl alcohol, which are dissolved in solvents and spin coated on solid substrates and rubbed. Strong anchoring enables fast relaxation from field-driven states while weak anchoring makes possible high contrast ratios under low driving voltages. Many studies developed methods such as varying rubbing pressure and rubbing number to change the anchoring strength, and in manufacturing processes the desired anchoring can be tailored to fit the application.

In this paper, we report a study of alignment layers from polyvinyl alcohol (PVA) with various thicknesses. The relation between alignment layer thickness and anchoring strength has been rarely investigated by either experimental or theoretical work. In Ref. 15 the authors found evidence that the increase of PVA alignment layer thickness (up to 10 nm) led to an increase of azimuthal anchoring strength in ferroelectric cells. In our work, we assembled electrically controlled birefringence (ECB) cells filled with nematic/chiral nematic LC. We were intent on finding the effect of alignment layer thickness in both in-plane (azimuthal) and out-of-plane (polar) anchoring strength. The range of uniform thickness was achieved within 14–120 nm. We demonstrated that both polar and azimuthal anchoring strengths can be varied significantly by changing the alignment layer thickness. We also showed that the quartic term in the polar anchoring energy is important.

II. EXPERIMENTS AND RESULTS

A. Cell preparation

The polyvinyl alcohol used in the experiment was provided by MFLEX UK Ltd.: PVA MS-88 (15% dissolved in aqueous solution). We diluted the original PVA solution by adding de-ionized water. The weight concentrations of PVA in the final solutions used in spin-coating were 4.3%, 3.8%, 3.0%, 2.3%, 1.5%, and 1.0%. The solutions were spin-coated on 3.5 \( \times \) 3.5 in. \( \times \) 0.5 in. indium tin oxide (ITO) patterned glass substrates at a speed of 1500 rpm for 30 s. The substrates with the PVA coating were pre-baked at 90 \( ^\circ \) C for 1 min, and then oven baked at 120 \( ^\circ \) C for about 1.5 h. Afterward, the alignment layers were rubbed with a cloth under fixed pressure and direction. Two substrates with the same alignment layer were anti-parallel assembled with UV glue to make one panel of a cell. The cell gap was controlled by 5 \( \mu \)m spacers. The large cell was then cut into 20 single cells in a programed fashion. This process ensured that all the single cells had the same alignment layer and rubbing direction. The cell gap of each single cell was measured to be between 4.85 and 4.95 \( \mu \)m. Liquid crystal was then filled into the cells in a vacuum chamber.

B. Alignment layer thickness measurement

The PVA alignment layer thickness was measured by atomic force microscopy (AFM). Each alignment layer sample was cut through and scratched by a surgical blade. Thereby a sample was created with one side of the polymer...
shaved off and the other side left on the substrate. Some AFM pictures illustrating this measurement are shown in Fig. 1. The measured thicknesses are plotted as a function of PVA concentration in Fig. 2, from which we can conclude that the alignment layer thickness decreased more than linearly with decreasing PVA concentration in the aqueous solution. This is due to the fact that when the PVA concentration was reduced, the viscosity of the solution was also decreased, and therefore a thinner layer of solution was dispensed on the substrate during spinning, combining with the result from the solvent’s evaporation. The AFM pictures also show the grooves produced by the rubbing. The depth of the grooves is larger on the thicker PVA films.

C. Polar anchoring strength measurement

In the ECB cell, the nematic liquid crystal molecules are aligned homogeneously in the absence of applied voltage because of the PVA alignment layers on the inner surfaces of the cell with almost zero pretilt angle. The easy direction of the alignment layers has $0^\circ$ polar angle and $0^\circ$ azimuthal angle. When an external field is applied, the liquid crystal will be
tilted away from the easy direction. The surface anchoring energy produced by the deviation of the liquid crystal from the easy direction is given by the Rapini-Papoular Equation\textsuperscript{1,18}

\[
F_s = \frac{1}{2} W_{p1} \sin^2 \theta_o + \frac{1}{4} W_{p2} \sin^4 \theta_o + \frac{1}{2} W_{o1} \sin^2 \phi_o + \frac{1}{4} W_{o2} \sin^4 \phi_o,
\]

(1)

where \(\theta_o\) and \(\phi_o\) are the polar and azimuthal angles of the liquid crystal director at the surface; \(W_{p1}\) and \(W_{p2}\) are the polar anchoring strengths; \(W_{o1}\) and \(W_{o2}\) are the azimuthal anchoring strengths. When \(\theta_o\) and \(\phi_o\) are small, only the quadratic terms of Eq. (1) are needed. When a voltage is applied across the cell, the generated electric field tends to tilt the liquid crystal (\(\Delta \theta > 0\)) toward its own direction normal to the cell plane while the alignment layers tend to keep the liquid crystal in the cell plane.\textsuperscript{2} The polar angle at the surface is determined by the balance between the electric and surface forces. Due to the boundary condition imposed by the alignment layer, the liquid crystal \(\vec{n}\) in bulk is not uniform as shown in Fig. 3(a). The bulk free energy of the liquid crystal per unit area is given by\textsuperscript{2,4}

\[
F_e = \int_0^h \left( \frac{1}{2} K_{11}(\nabla \cdot \vec{n})^2 + \frac{1}{2} K_{22} (\vec{n} \cdot \nabla \times \vec{n})^2 + \frac{1}{2} K_{33} (\nabla \times \vec{n})^2 - \frac{1}{2} \Delta \varepsilon_0 (\vec{E} \cdot \vec{n})^2 \right) dz,
\]

(2)

where \(h\) is the cell thickness and \(\vec{E}\) is the electric field. In the reorientation of the liquid crystal, only the polar angle of the liquid crystal director changes, and thus the azimuthal angle remains at \(0^\circ\) and need not be considered. The liquid crystal director is described by \(\vec{n} = \cos \theta \hat{x} + \sin \theta \hat{z}\). Under a given electric field, the polar angle of the liquid crystal director at the surfaces of the alignment layers and in the bulk of the cell is determined by minimizing the total free energy given by

\[
F = \int_0^h \left[ \frac{1}{2} (K_{11} \sin^2 \theta + K_{33} \cos^2 \theta) \left( \frac{\partial \theta}{\partial z} \right)^2 - \frac{1}{2} \Delta \varepsilon_0 \sin^2 \theta \right] dz + \frac{1}{2} W_{p1} \sin^2 \theta_o + \frac{1}{4} W_{p2} \sin^4 \theta_o + \frac{1}{2} W_{o1} \sin^2 \phi_o + \frac{1}{4} W_{o2} \sin^4 \phi_o,
\]

(3)

because the top and bottom alignment layers are the same, \(\theta_{o1} = \theta_{o2}\).

In the optical measurement, the liquid crystal director plane makes an angle of 45° with respect to the crossed polarizer and analyzer. When an incident light with wavelength \(\lambda\) propagates through the liquid crystal cell, the transmittance is given by

\[
T = \sin^2 \left( \frac{\pi}{\lambda} \int_0^h \left[ \frac{n_o n_e}{\sqrt{n_o^2 \cos^2 \theta + n_e^2 \sin^2 \theta}} - n_o \right] \right) dz,
\]

(4)

where \(n_o\) and \(n_e\) are the ordinary and extraordinary refractive indices of the liquid crystal, respectively.

In the experiment, the transmission versus voltage curve was measured with high precision with the help of a pair of Glenn-Thompson polarizers. The nematic liquid crystal used was E44 (from Merck). The elastic constants of E44 are \(K_{11} = 15.5 \times 10^{-12} N\), \(K_{22} = 13.0 \times 10^{-12} N\), and \(K_{33} = 28.0 \times 10^{-12} N\). The dielectric anisotropy is \(\Delta \varepsilon = 17\) and birefringence is \(\Delta n = 0.25\) at room temperature. AC voltages of 1 kHz frequency were applied to the liquid crystal cell. An He-Ne laser light with the wavelength of 633 nm was used to illuminate the cells at normal incidence. A photodiode was used to measure the light intensity.

Figure 4 shows the transmittance as a function of applied voltage of the EBC cells with PVA alignment layers of different layer thicknesses. When the applied voltage was 0, the polar angle of the liquid crystal was small and the effective birefringence was large. The optical retardation angle \(2\pi \Delta n_{eg} / \lambda\) was more than \(2\pi\), and the transmittance was low. When the applied voltage was raised above a threshold (1 V), the liquid crystal reoriented and the polar angle increased. The optical retardation decreased and the transmittance increased. When the applied voltage was higher than 5 V, the optical retardation angle became smaller than \(\pi\). When the voltage was increased further, the transmittance decreases monotonically. At low voltages, only the liquid crystal in the bulk reoriented significantly and the transmittance did not depend much on the anchoring. Under high voltages, the liquid crystal on the surface also reoriented and the transmittance depended on the anchoring. This method of measurement of anchoring strength is called the high voltage method.\textsuperscript{3,19–23} For the cells with thinner alignment layers, the transmittance under high voltages was
lower. This was because the thinner alignment layer produced a weaker anchoring strength. The liquid crystal at the surface was tilted more toward the electric field direction.

The anchoring strengths of the alignment layers were obtained by fitting the experimentally measured transmittance-voltage curves of the ECB cells. When only the quadratic term of the Rapini-Papoular Equation was used, the fitting was not good because the polar angle became large (close to 90°) under high voltages. When both terms were used, the theoretically calculated results agreed very well with the experimental ones as shown in Fig. 5. The polar anchoring strengths for the best fitting are shown in Fig. 6. Both the quadratic and quartic anchoring coefficients increased significantly with the alignment layer thickness, with approximately the same trend.

The anchoring strength was on the order of $10^{-4} - 10^{-3} J/m^2$, within which the large end agreed with other reported measurements of PVA with cyanobiphenyl liquid crystal interface prepared under similar conditions.

### D. Azimuthal anchoring strength

In order to measure the azimuthal anchoring, we must use a means to tilt the liquid crystal in the azimuthal direction. The anchoring strength can be calculated from the resistance produced by the alignment layer in the azimuthal direction. Adding a chiral dopant into the liquid crystal can accomplish the task. The chiral dopant causes the liquid crystal to twist through the cell while the alignment layer tries to keep the liquid crystal in the easy direction, against the twisting. The result of the competition between these two factors is that the liquid crystal in the bulk twists less than the intrinsic twist angle produced by the chiral dopant and on the surface the liquid crystal deviates from the easy direction ($\theta = 0, \phi = 0$) as shown in Fig. 3(b). The free energy per unit area of the liquid crystal is given by

$$F = \int_0^\Phi \frac{1}{2} K_{22} \left( \frac{\Phi - \frac{2\pi}{P}}{h} \right)^2 dz + \frac{1}{2} W_a \sin^2 \phi_{a1} + \frac{1}{2} W_a \sin^2 \phi_{a2},$$

where $\Phi$ is the total twist angle from the bottom to the top of the cell. As will be shown later, the twist angle is small in experiment and therefore the quartic term in Eq. (1) is neglected and only the quadratic term is kept in Eq. (5). Because the top and bottom alignment layers are the same, $\phi_{a1} = \phi_{a2} = \phi_a$, the pitch is chosen in such a way that $P > 4h$ in order to avoid an over 90° twist. From Fig. 3(b) it can be seen that $\Phi = \phi_{a1} + \phi_{a2} = 2\phi_a$. Equation (5) becomes

![Fig. 4. Experimentally measured transmittance-voltage curves of the ECB cells with different alignment layer thicknesses.](image)

![Fig. 5. Transmittance-voltage curves of EBC cells with various alignment layer thicknesses. Blue symbol: experimentally measured. Red line: theoretically calculated.](image)
Because entrance plane and o-mode strength is obtained.

shown in Fig. 7. The analyzer makes the angle fixed in the direction parallel to the rubbing direction as \( / \) to \( o \).

\[ \frac{\phi_o}{\phi_o} \text{ can be found by minimizing the free energy with respect to } \phi_o. 
\] When \( \phi_o \) is small, the equation for the anchoring strength is obtained.

\[ W_a = 2 \left( \frac{\pi}{\phi_o} - \frac{P}{h} \right) K_{22} h. \] (7)

The intrinsic pitch \( P = 1/[(\text{HTP}) \cdot c] \) is calculated from the helical twisting power (HTP) and the concentration \( c \) of the chiral dopant. By measuring the twist angle, the azimuthal anchoring strength can be obtained. This method is called the twist angle method (TAM).\(^{28}\)

In the measurement of the twist angle, the polarizer is fixed in the direction parallel to the rubbing direction as shown in Fig. 7.\(^{29}\) The analyzer makes the angle \( \alpha \) with respect to the orthogonal direction of the polarizer. The electric field of the incident light entering the cell is in the polarizer’s direction. It can be decomposed into two components: e-mode \( E_{in/e} \), parallel to the liquid crystal director \( \vec{n}_{o1} \) at the entrance plane and o-mode \( E_{in/o} \), perpendicular to the liquid crystal director. \( E_{in/e} = E_o \cos \phi_o \) and \( E_{in/o} = E_o \sin \phi_o \).

Because \((n_e - n_o)h/(2\pi/2\phi_o) \gg \lambda \) (Mauguin condition), when the light propagates through the liquid crystal cell, the polarizations of the e- and o-modes follow the twist of the liquid crystal director. Thus they remain parallel and perpendicular to the liquid crystal director, respectively. Their phase changes are, however, different. The e component becomes \( E_{out/e} = E_o \cos \phi_o e^{-i2\pi nh/\lambda} \) and the o component becomes \( E_{out/o} = E_o \sin \phi_o e^{-i2\pi nh/\lambda} \). The sum of their projections along the analyzer is

\[
E_a = E_o \cos \phi_o e^{-i2\pi nh/\lambda} \cos[\pi/2 + \alpha - \phi_o] \\
+ E_o \sin \phi_o e^{-i2\pi nh/\lambda} \cos[\pi/2 + \alpha - (\pi/2 + \phi_o)] \\
= -E_o \cos \phi_o e^{-i2\pi nh/\lambda} \sin(\alpha - \phi_o) \\
+ E_o \sin \phi_o e^{-i2\pi nh/\lambda} \cos(\alpha - \phi_o). \] (8)

The transmittance is given by

\[
T = \frac{I_{out}}{I_{in}} = \frac{E_a \cdot E_o^*}{E_o^2} \\
= \sin^2 \alpha - \sin(2\phi_o) \sin(2\alpha - 2\phi_o) \cos^2(\pi \Delta n h / \lambda). \] (9)

The angle \( \alpha_m \) that gives the minimum transmittance is found by

\[
\frac{\partial T}{\partial \alpha_m} = 2 \sin \alpha_m \cos \alpha_m \\
- \sin(2\phi_o) \cos(2\alpha_m - 2\phi_o) \cos^2(\pi \Delta n h / \lambda) = 0,
\]

which gives

\[
\tan(2\alpha_m) = \frac{\sin(4\phi_o) \cos^2(\pi \Delta n h / \lambda)}{1 - 2 \sin^2(2\phi_o) \cos^2(\pi \Delta n h / \lambda)}. \] (10)

In the experiment, the analyzer is rotated to find the minimum transmittance and thus to determine \( \alpha_m \). \( \phi_o \) is calculated from Eq. (10).

During cell assembly, the rubbing directions of the top and bottom alignment layers may not be exactly aligned anti-parallel. In order to assure the anti-parallel rubbing directions, we used the following method. Two large glass plates with rubbed PVA alignment layers were assembled together and then cut into two cells. The two cells thus had the same top and bottom rubbing directions. One of the cells was filled with the nematic liquid crystal to check the relative angle of the top and bottom rubbing directions. The other cell was filled with the chiral nematic liquid crystal for

\[
T = \frac{I_{out}}{I_{in}} = \frac{E_a \cdot E_o^*}{E_o^2} \\
= \sin^2 \alpha - \sin(2\phi_o) \sin(2\alpha - 2\phi_o) \cos^2(\pi \Delta n h / \lambda).
\]
the twist angle measurement. The nematic liquid used was E44 (from Merck). The chiral dopant used was S811 (from Merck), whose helical twisting power in E44 was 10 μm⁻¹.

Figure 8 shows a typical transmittance as a function of the analyzer angle of two twist cells. The chiral dopant concentration was 0.217%, which produced an intrinsic pitch of 46 μm. When the thickness of the alignment was 14 nm, the angle of the analyzer for the minimum transmittance was 5.16°. The optical retardation was $\Delta nh/\lambda = \pi \times 0.25 \times 4.95/0.632 = 1.96\pi$. From Eq. (10), the twist angle was found to be 5.1°. Using this twist angle and Eq. (9), the transmittance versus the analyzer angle was calculated and plotted in Fig. 8, which agreed very well with the experimental result. From Eq. (7), the azimuth anchoring strength was found to be $2.3 \times 10^{-5} \, J/m^2$. When the thickness of the alignment was 120 nm, the azimuthal anchoring was stronger. The angle of the analyzer for the minimum transmittance decreased to 1.33°. The twist angle was found to be 1.3°. Using this twist angle and Eq. (9), the transmittance versus the analyzer angle was calculated and plotted in Fig. 8, which also agreed very well with the experimental result. Similarly, the azimuth anchoring strength was found to be $13.2 \times 10^{-5} \, J/m^2$. When the anchoring was strong, the twist angle was small and the relative experimental error could be large. In order to improve accuracy, the concentration of the chiral dopant was increased to 0.415% to generate larger twist angles. The azimuthal anchoring strengths of the PVA alignment layers with various layer thicknesses are shown in Fig. 9. It was on the order of $10^{-4} \, J/m^2$, which agreed with results reported by other groups.12,30 The azimuthal anchoring strength increased significantly with the alignment layer thickness.

III. DISCUSSION AND CONCLUSION

We demonstrated that both polar and azimuthal anchoring strengths of polyvinyl alcohol alignment layers can be changed by varying the layer thickness. They increased with increasing layer thickness, but their thickness-dependences were different: the azimuthal anchoring strength increased faster in the beginning and then saturated quicker than the polar anchoring strength. The polar anchoring resulted from the anisotropic inter-molecular interaction between the liquid crystal and the polymer.30,31 When both anisotropic directions of the liquid crystal and polymer are in the same direction, the interaction energy is low. When the liquid crystal deviates from the parallel direction the interaction energy increases as described by the surface anchoring energy. Anisotropy of liquid crystal is an intrinsic property, while the anisotropy of the polymer is produced by the mechanical rubbing which causes the polymer chains to align in one direction. Because the inter-molecular interaction is short-range, the increase of the anchoring strength with the alignment layer thickness can be explained in that the polymer chains are aligned better in thicker layers. For the azimuthal anchoring, besides the anisotropic inter-molecular interaction, the microgrooves created by the rubbing also contribute.27,32–38 When the liquid crystal is parallel to the grooves, there is no elastic distortion of the liquid crystal director. When the liquid crystal is not parallel to the grooves, the liquid crystal director varied spatially, resulting in an elastic energy that is counted as a part of the azimuthal anchoring energy. The elastic energy depends on the spatial variation rate and depth of the grooves. When the PVA alignment layer is thicker, not only are the polymer chains more ordered but also the grooves are deeper. Both effects together will make the azimuthal anchoring strength increase faster with the alignment layer thickness in the beginning than the polar anchoring strength.

Control of the surface anchoring strength through the variation of the layer thickness is reliable and repeatable. This method of generating alignment layers with different anchoring strength provides another perspective in basic research and practical applications.

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FIG. 8. Transmittance vs analyzer angle twist angles of two twist cells with PVA alignment layers. Markers: experimental results, solid lines: theoretical fit. PVA alignment layer thickness, ▲: 120 nm, ○: 14 nm.

FIG. 9. The azimuthal anchoring strengths of the PVA alignment layers with various layer thicknesses. The line is a guide for the eyes.