Spatial and Orientational Control of Liquid Crystal Alignment Using a Surface Localized Polymer Layer

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Spatial and orientational control of liquid crystal alignment using a surface localized polymer layer

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We present an alignment method for the surface contacting liquid crystal (LC) director. This method allows complete control of the polar pretilt angle as a function of position in a liquid crystal device, and has the potential of controlling the azimuthal orientation of LC. Important considerations of this method are to form a thin layer of reactive monomers at the LC cell interior surface, and to control the deleterious effects of flow due to polymerization induced concentration gradients. To achieve these, the voltage and frequency of the applied electric field and the UV intensity during the polymerization process are significant. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4773010]

Applications of liquid crystals (LCs) to modern electro-optical devices such as diffraction gratings, optical phase plates, lenses, displays systems for 3D imaging, optical systems for vision correction, and aberration compensation devices require spatial control of the LC surface director alignment. Uniform alignment of LC director is generally achieved by rubbing a polyimide coated surface that is in contact with LC. Beyond that, a variety of techniques, such as micro-rubbing technique, fabrication of nano-structures, as well as the usage of chemically modified polyimides, have been used for spatial manipulation of the polar pretilt angles. Further, both the LC azimuthal angle and polar pretilt angle can be controlled by the photoalignment techniques. However, most of these methods cannot form an alignment layer that provides spatially variable pretilts within a full range of polar angles. Spatially varying pretilts can be achieved by stacked alignment layer, which consists of nano-domains of planar and homeotropic alignment materials. However, the usage of a non-homogeneous alignment layer can potentially induce undesirable light scattering.

Adjustable pretilt angles can be achieved by stabilizing the LC director with a polymer network that is formed via polymerization of photo-reactive monomers (RMs), which has been utilized for the improvement of optical performance of LC displays and for the fabrication of LC lenses. However, the introduction of a polymer network into the bulk of the LC cells results in light scattering. In order to minimize scattering and for a better control of the pretilt angle, a rigid polymer network confined to a thin layer with the thickness less than the wavelength of visible light should be localized in the vicinity of the LC layer boundary. While an intrinsic tendency of forming the polymer layer preferentially on the surface has been shown, in a separate work, we showed the beneficial effect of electric field on forming a surface localized polymer alignment (SLPA) layer. However, the physics related to achieving a spatially varying LC pretilt angle via the SLPA layer have not been focused on. The objective of this paper is to consider the physics of the SLPA method to achieve a spatially controllable LC alignment.

The method starts with a planar cell filled with a mixture of LC and RMs. The initial alignment is determined by rubbed polyimide layers that generate a planar alignment (Figure 1(a)). When a high voltage is applied to the cell, the resultant equilibrium director distribution is determined by the balance of volume and surface torques resulting in a splay director configuration in the vicinity of the cell substrates and more vertical alignment of the LC director in the bulk. The thickness of the transition layer of the LC director is given by the electric coherence length

\[
\xi = \sqrt{\frac{K}{\varepsilon_0 \Delta \varepsilon E^2}},
\]

where \(K\) is the elastic constant in the one-constant approximation, \(\Delta \varepsilon\) is the dielectric anisotropy of LC, and \(E\) is the electric field strength. If a polymer network is formed only at the surface of the LC layer, the distorted director field can be “frozen” in place, and the director in the polymerized areas will not relax after removing the external electric field. An electric field is applied before the polymerization process (Figure 1(b)) to form a monomer-rich layer. In a separate work, we examined the mechanism behind the LC-RMs mixture separation and showed that the application of the low-frequency external electric field facilitates the ion-assisted drift of RMs to the electrodes due to high ion association of the RMs’ ester groups. The subsequent UV light-induced polymerization of RMs leads to the formation of a rigid polymer network that holds the director at the high polar angles (Figure 1(c)). After polymerization is complete, the polymerized layer provides an alignment layer for the LC molecules in the bulk. The average director angle is then determined by the molecular inclination angle at the boundary of the polymerized layer, making the director configuration equivalent to a planar cell with a high polar angle. If only a small area of the cell is irradiated, the polar angle can be set locally, allowing for the...
formation of spatially varied pretilts (Figure 1(d)). Therefore, this method can be considered for achieving spatially variable LC alignment.

The resultant pretilt angle ($\varphi$) is determined by the director profile at the LC boundary (which is a function of the applied voltage at the time of polymerization), and by the thickness of the polymer layer (which depends on the RM concentration and polymerization conditions). The director tilt angle in the presence of the electric field can be estimated from the electric coherence length ($\xi$)

$$\beta(z) = \beta_0 e^{-z/\xi},$$

where $\beta$ is measured with respect to the cell normal, and $z$ is the distance from the cell surface. If the anchoring is strong, $\beta_0 \approx 90^\circ - \varphi$. With above equations, we calculated $\beta(z)$ for various applied voltages for the LC with $\Delta e = 17.3$; $K = 25.7 \times 10^{-12}$ N corresponding to the fluid used in our experiments (Figure 2).

Calculations demonstrate that the director tilt angle varies in a wide range 5°–90° as a function of distance from the cell surface. In our alignment method, the polymer layer formed on the surface is constrained within a wavelength of light to minimize light scattering. By considering Figure 2, we can estimate the surface pretilt angle which will be locked in on the top of the polymerized layer at a particular applied voltage and layer thickness. For example, if a 200 nm layer of monomer is polymerized during the application of 100 V, the expected pretilt angle is approximately 80°. Thus, by varying the applied voltage during the UV curing step, one can vary the resultant pretilt in the finished cells.

The proposed method has two advantages: (1) The SLPA method not only allows a fully controllable pretilt angle but also allows different pretilt angles to be set in different areas by choosing the UV illumination zone. (2) It is a simple, low cost approach which does not require complicate micro-rubbing technique, special electrode structure, or modified polyimide layer. However, expected issues with polymerization induced flow need to be considered.

In this work, we used the BL006 nematic mixture ($\Delta n = 0.286, \Delta e = 17.3$), which contains 1.2% of RM-257 (both by EM Industries) and 0.12 wt. % of Irgacure 651 photoinitiator (by Aldrich). Glass plates with an indium-tin oxide conducting layer were spin-coated with PI-2555 (by HD Microsystems, provides a planar alignment $\varphi = 2^\circ$), baked at 275°C for one hour, and rubbed with a velvet cloth. LC cells were assembled with anti-parallel rub directions with the cell gap of 22 μm. In order to set the polar angle over a small and isolated area, we irradiated a LC cell with a collimated UV light source through a mask with slits. The mask was fabricated via a photolithographic process to obtain sharp slit edges.

The molecular pretilt angle in the cured cells was estimated from the optical retardation of the cell, assuming the uniform director tilt angle was in the bulk. Observing the phase retardation difference ($\Delta \delta$) between the cured area ($\delta_c$) and non-cured area ($\delta_{non}$), we calculate the LC pretilt angle ($\varphi$) in the cured area with the correlation between pretilt angles and phase retardation ($\delta$). The phase retardation of a LC cell measured in terms of the path length difference is:

$$\delta = \Delta n d,$$

where $d$ is cell thickness, $\Delta n$, a function of the LC pretilt angle ($\varphi$), is the effective birefringence of the LC

$$\Delta n = \frac{n_0 n_e}{\sqrt{n_0^2 \sin^2 \varphi + n_e^2 \cos^2 \varphi}} - n_0.$$

Here, $n_e, n_o$ are the extraordinary and ordinary refractive indexes of the LC material. For BL006, $n_o = 1.816$ and $n_o = 1.530$. For the non-cured area, $\varphi$ is about 2°; but for the cured area, the pretilt angle is controllable. When $\varphi = 90^\circ$, $\Delta n = 0$; $\delta_c = 0$, the phase retardation difference ($\Delta \delta = \delta_{non} - \delta_{cured}$) reaches the maximum value.

Previously, we found that the application of a voltage before the UV (pre-cure voltage) helps localize monomers. In this work, it is important to know about the memory time of the pre-cure voltage effect. Cells were pre-cured at 100 V
60 Hz for 20 min. The electric field was then turned off, and the cell was allowed to relax for several minutes. After a waiting period, the cell was irradiated through the mask under UV light (3.5 mW/cm²) for 20 min while the 100 V 6 kHz AC field was applied across the cell. For waiting times of 0, 5, 10, and 60 min, the resulting pretilt were 64°, 64°, 55°, and 49°. A cell not subjected to the pre-cure voltage application has a pretilt angle at 49°. By correlating the waiting time to the resultant pretilt angle, we found that the characteristic time of dissipation of the RM-rich layer (memory time) is about 5 min.

The larger the voltage applied at the time during the formation of the polymer network (cure voltage), the higher is the expected resulting pretilt. To quantitatively support this, we measured the pretilt angle as a function of the duration of the polymerization step for a set of voltages (Figure 3). Cells in Figure 3 were pre-cured at 100 V 60 Hz AC for 20 min, and cured with UV light (3.5 mW/cm²) in the 6 kHz external field.

To demonstrate frequency dependence of the applied voltage on obtained pretilt angles, we pre-cured samples as in the previous experiment, and then cured them at 80 V 200 Hz and 80 V 6 kHz (Figure 4). A low-frequency AC field is more efficient in concentrating monomers in the vicinity of the LC boundary, due to the transit time of the ion-monomer group.

The RM motion resulting from the concentration gradient, if present during curing, can lock-in problematic non-uniformities in the alignment. Therefore, the polymerization rate and resulting diffusion rate of RMs are the key issues to make the cured texture uniform. To verify this, we compared cells cured at low and high UV light intensity (Figure 5). Microphotographs of the cured cells show that polymerization with the low-intensity light source (3.5 mW/cm²) results in a uniform alignment layer, whereas curing at the higher intensity (28 mW/cm²) produces azimuthal non-uniformities. Polarized light microscope with a color filter (λ = 543 nm) was used to show the uniformity of the isolated cured area. The dark diagonal lines are lines where Δδ = Nλ (N is an integer), and show the gradient in Δδ.

A “pulse cure” could further improve the resulting uniformity of the alignment layer because it allows the concentration gradient of monomers to relax between UV pulses. With a low frequency AC field (200 Hz) under a low intensity UV light (3.5 mW/cm²), “pulse cure” samples were cured using 25 cure cycles where: the relaxation time per step was 3 s; pre-cure time per step was 2.4 s; cure time per step was 12 s. “Pulse cure” cells show uniform textures and different resultant pretilt angles after curing with different voltages: (a) cured at 80 V, α = 66°; (b) cured at 60 V, α = 45°; and (c) cured at 40 V, α = 19°.

To fabricate a sample with spatially variable pretilts, a cell was pre-cured at 150 V 60 Hz AC for 1 min. The applied voltage (200 Hz) during the cure time was adjusted according to the desired pretilt. To define an area with a particular pretilt, the cell was irradiated through a movable 0.8 mm-wide slit, which allowed the exposure of a narrow strip of

![FIG. 3. Dependency of pretilt angle on the duration of the polymerization step for different voltages applied during polymerization.](image)

![FIG. 4. Dependency of pretilt angles on the duration of the polymerization step for different frequencies when 80 V AC is applied during polymerization.](image)

![FIG. 5. Microphotographs of cells which were pre-cured for 5 min at 100 V 60Hz AC, and cured at 100 V 60 Hz AC through a 0.2 mm slit for 10 min. (a) Cured under 3.5 mW/cm². (b) Cured under 28 mW/cm².](image)
Previously, we showed\textsuperscript{30} that the pretilt angle is set during a different voltage. The cure time per each step was 10 s. UV light was then turned on, and polymerization resumed at the first exposure of the previously unexposed area, and the subsequent exposure at different voltage only strengthens the polymer network. By changing the curing voltage at each step, we created a gradient of the tilt angle across the cell.

Figure 6(a) shows a photograph of the cell, with an observed spatially varying retardation profile. A Michelson interferometer and Interferometric Analysis Software IntelliWave\textsuperscript{TM} are used to check the optical phase difference. Light source wavelength of the laser beam is 543 nm. The optical phase retardation across the 5 mm cured area is changed by 5.70 $\mu$m. The pretilt angles are changed continuously from $2^\circ$ to $90^\circ$ across the cell (Figure 6(b)).

We have shown that LC director pretilt can be controlled within a full range of polar angles by the SLPA layer. The increase of the pretilt angle, with the increase of voltage applied during polymerization and duration of the exposure to UV light, is consistent with the formation of a thin layer of rigid polymer network in the vicinity of LC boundary. Application of the pre-cure voltage increases the resultant pretilt. The correlation between the waiting time (between the pre-cure voltage and cure voltage applications) and the subsequent polymerization is consistent with the time scale of "image sticking"\textsuperscript{24} in LC displays due to the migration of ions, their partial absorption at the LC layer boundary, and subsequent diffusion back in the bulk. These results point toward the ion-assisted transport of monomers toward the cell's electrodes, supporting by experimentally observed increase of the pretilt angles when the pre-curing and curing are performed in the low-frequency AC field.

The flow of monomers in concentration gradients contributes to the polar and azimuthal non-uniformities of the resultant alignment layer. A lower light intensities yield more uniform alignment. This effect is expected, because the diffusion and material flow processes correlate with the polymerization rate.\textsuperscript{39} A high UV light intensity leads to a high polymerization speed,\textsuperscript{41,42} which results in high concentration gradients of RMs. Also consistent with this explanation is the effect of pulsed irradiation, when the pre-polymerization and polymerization steps are alternated. In this case, the local concentration gradients have enough time to dissipate before the onset of turbulence, which improves the uniformity.

With the very low concentration of RMs, we do not expect to see effects of a polymer network in the bulk in terms of scattering, or increased effective viscosity. From the obtained pretilt, we can conclude that the amount of remaining RMs in the bulk is very small. Specifically if all of the 1.2% RMs in the 22 $\mu$m thick cell is polymerized on the surfaces, a polymer layer of about 130 nm is expected. Considering Figure 2, the measured pretilts are consistent with a layer of that approximate thickness. Therefore, the remaining concentration of RMs in the bulk is considered to be too low to form a robust network.

Our method can be modified for controlling the azimuthal direction of the LC easy axis, by using photo-alignment techniques that employs azo-dyes\textsuperscript{19,43,44} or cellulose-cinnamate\textsuperscript{45} alignment layers.

To summarize, we present a surface alignment method which allows a full range of polar angles spatially controllable. The developed technology can be applied to the fabrication of vision correction lenses,\textsuperscript{46} beam steering devices, bistable LC devices, and lenticular lenses for 2D/3D switchable displays.\textsuperscript{8}

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