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Control of liquid crystal alignment using surface-localized low-density polymer networks and its applications to electro-optical devices

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ABSTRACT

We developed an alignment method for control of the polar pretilt angle at the boundaries of a liquid crystal (LC) layer in a continuous range 2–90° by introducing a low-density polymer network. The network was formed as a result of the electric field-induced segregation of a photo-reactive monomer added in concentrations of 0.5–1% to the LC host and subsequent in-situ UV-light-induced polymerization. LC director was "frozen" within a less than a micron-thick layer in the vicinity of the cell substrates at high average tilt angles anchoring the LC in the bulk similarly to a high-pretilt alignment layer. The resultant pretilt angle was determined by the voltage applied before and during polymerization and the duration of voltage application before UV-light exposure. The desired pretilt angle could be set over a small area of a sample which allowed for the fabrication of LC devices with spatially variable optical retardation. Using this method, we fabricated high-pretilt splay and bend LC cells, optically recorded converging lenses and bi-prisms with electrically controlled optical characteristics, and phase diffraction gratings with resolution better than 50 lines/mm.

1. Introduction

Optimization of liquid crystal-based electro-optical devices requires control of the boundary conditions that define the alignment of the liquid crystal (LC) molecules. This is achieved by introducing an alignment layer that provides anchoring for LC molecules. Many LC display technologies require well-defined in-plane and out-of-plane orientation of the nematic director on the boundary surfaces, and predictable variation of this orientation under electric field during the device operation. Different modes of operation of LC devices (LCDs) require different polar anchoring or pretilt angle α: the twisted nematic mode utilizes a low $\alpha = 1.5–3°$, whereas vertically aligned displays require $\alpha = 85–90°$. Fast LCD modes capable of video-rate switching employ non-bias π-cells with pretilt angles of about 45° [1,2]. Adaptation of LCs for the voltage controlled optical elements with variable optical characteristics require spatially variable optical retardation, which can be achieved by fabricating cells with a spatially varied pretilt angle. Pretilt angles other than for planar and homeotropic alignment are difficult to achieve, and require either the formation of nanostructured surfaces [3,4,7], layering of different types of polyimides [5], fine-tuning of surface hydrophobicity [6], or treating surfaces with ion beams [8,9].

A pioneering method of pretilt control by photopolymerization of the alignment layer was developed by Yu. Reznikov with co-authors [10,11] by cross-linking a polyvinyl cinnamate using linearly polarized UV light in a presence of the oblique magnetic field. Interaction of LC molecules with polymer fragments provided a stable tilted alignment at α about 20°. The development of photo-reactive monomers (RMs) opened a possibility of stabilization of LC alignment by introducing a polymer network that "freezes" the LC director. To form a polymer network, the LC is doped with RM and photoinitiator and then exposed to light that promotes cross-linking of the monomer. When applied to electro-optical devices, the network should allow for molecular reorientation in external fields. If the concentration of the monomer exceeds 1% by weight, the network causes light scattering, which compromises the device's performance. In certain cases, it is desirable to form a network within a thin layer at the LC boundaries. If polymerization occurs at high applied voltages, the resultant boundary layer anchors LC molecules at high polar angles, and the cell has the same optical properties as the one with high-pretilt alignment layers. This method was applied to twisted π-cells resulting in lifting the pretilt angle α to 20° [12], stabilization of the vertically aligned mode at α about 80° [13,14], and to planar cells (with anti-parallel rubbing) increasing α to 50° [15].

Localization of the polymer network near the cell substrates requires separation of the LC-monomer mixture from the bulk and concentration of the cross-linked monomer in the vicinity of the cell substrates. Light-induced polymerization and mixture separation [16] accompanied by motion of the polymer toward the substrates were observed in [13,15,17]. This phenomenon was explained within the frame of the Flory-Huggins theory [18]: a phenomenological approach that describes

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phase separation in polymer melts. In application to LC-polymer mixtures this theory shows that in the process of polymerization long polymer chains become immiscible with LC, and form aggregates. This explains why phase separation occurs predominantly near the cell substrate facing the UV light source.

Other authors studied the motion of polymer particles in liquid crystal in the presence of the electric field [10,19,20]. They observed polymer segregation at the regions where the electric field was weaker, whereas the liquid crystal was pushed to the regions of the stronger field, suggesting the significance of diaphoretic force acting on polarized dielectric particles in electric field gradients. Director distortions were also shown to influence phase separation [21].

As seen from literature, multiple mechanisms can be responsible for mixture separation and motion of the polymer to the LC layer boundaries. We have shown that in application to RM-type monomers (by EM Industries) the ionic association with polar groups drives them to the cell electrodes. In our studies of the mechanisms of mixture separation, we used RM 257 and RM 84 (BAB), both containing multiple polar ester groups that are known to strongly interact with positive ions [22,23]. We observed accumulation of RM 257 at the negative electrode when dc electric field was applied across the cell [24]. AC field application before curing resulted in thinner polymer layers of equal thickness formed at both cell electrodes.

2. Control of the molecular alignment by introducing a polymerized alignment layer localized at the LC boundaries

Before our work, no technique allowed for in-situ manipulation of the pretilt angle. In Refs. [24–27] we presented a new method for fabrication of LC cells with continuously variable pretilt angles in the range of 2–90°. The pretilt angle was controlled locally, within a small area of the cell, which allowed for fabrication of a cell with spatially variable head-on optical retardation R:

$$R=\frac{4\pi}{\lambda}\int_{o}^{d/2}\left(\frac{n_o n_e}{\sqrt{n_e^2\,\sin^2\theta+n_o^2\,\cos^2\theta}}-n_o\right)dz \tag{1}$$

where d is the cell thickness, n_o and n_e are the refractive indices for the ordinary and extraordinary waves, respectively, θ is the angle between the director and substrate, and λ is the wavelength of light. R is a characteristic of the optical performance of LC cells in polarized light. It is related to the optical path for non-polarized light $n_{ave}d$, where

$$n_{ave}=\sqrt{(1/3)n^2+(2/3)n_0^2} \tag{2}$$

and

$$n={}^{n_o n_e}\!\Big/_{\sqrt{n_e^2\,\sin^2\theta+n_o^2\,\cos^2\theta}}. \tag{3}$$

The latter is responsible for the specific optical performance of the optical element: spatial change of $n_{ave}d$ over the area of a prism or lens can cause either the deflection or focusing of a light beam. Using our method we created LC cells with spatially variable α, and therefore spatially variable R. By focusing the curing beam at a small area of the cell we optically recorded the retardation profile which allowed us to fabricate electrically tunable prisms, lenses, and diffraction gratings.

2.1. Materials and cell fabrication

For fabrication of planar cells, prisms, lenses and diffraction gratings we used the MLC 6080 nematic mixture ($n_o=1.508$ and $n_e=1.71$ at $\lambda=589$ nm, dielectric constants $\varepsilon_\parallel=11.1$ and $\varepsilon_\perp=3.9$), which contained 0.5–0.75% of 4,4′-bis-acryloylbiphenil (RM 84, also referred to as BAB; by EM Industries) and about 0.003–0.0075% (by weight) of Irgacure 651 (sensitive to UVA and UV B) photoinitiator by Aldrich. For π-cells we used a mixture of 0.78% BAB in MLC6080. Glass plates with an indium-tin oxide conducting layer were coated with PI2555 (HD Microsystems) which was cured according to manufacturer's instructions. This PI provided a low polar pretilt angle $\alpha=3.5°$ for pure MLC 6080. Planar LC cells and cells for prisms, lenses and diffraction gratings were assembled with anti-parallel rub directions with spacers embedded in the gasket and filled at the isotropic phase temperatures. We worked with a set of planar cells with the thickness ranging from about 19.5 to 20.5 μm, which was high enough to achieve the changes of the optical retardation of multiple λ. π-Cells were assembled with parallel rub directions with 8–8.5 μm spacers embedded in the gasket resulting in cell gaps between 8.2 and 8.7 μm.

The polymer network was formed as a result of the following steps:

Step 1 (a pre-polymerization step): High voltage V_{pre} (60 V for π-cells and 100–120 V for planar cells, square wave AC, 1 kHz) was applied across the cell for $t_{pre}=0.1$–10 s; t_{pre} determined the resultant pretilt angle in the finished cell, and thus was chosen according to the desired α. Movement of RMs to the boundaries of the LC layer and alignment of polymer filaments took place during this step;

Step 2 (a polymerization step): Voltage across the cell was lowered below 100 V to the desired polymerization voltage level V_p, and the cross-linking of the monomer was initiated via the UV light irradiation. The time between V_p was applied and the beginning of irradiation (the settling time) was 0.3–0.5 s to allow for structure relaxation. The duration of the polymerization step t_p was 3–4 s in most cases. In the case when a non-zero voltage is applied during polymerization, both t_{pre} and V_p determine the final α: the higher the polymerization voltage for the same duration of the polymerization step, the higher the final pretilt angle. Polymerization, however, can also take place when no voltage is applied across the cell. In this case, only t_{pre} determines the final pretilt.

In application to planar cells steps 1 and 2 were alternated for a total time of $t_{total}=3$–5 min, until a polymer network was formed. Polymerization of π-cells required $t_{total}=30$–45 min.

Irradiation of the planar cells took place from one or both cell sides. We used two identical fiber optic UV light sources of the same power density $P=1$–50 mW/cm^2 in both the UVA and UVB spectra. Sources were equipped with IR filters to prevent heating of the samples during polymerization.

When a high voltage of 100–120 V is applied across the cell during pre-polymerization, the director tilt angle is very high even in the vicinity of the cell substrates (Fig. 1). In the well-studied guest-host effect [28] elongated molecules added to LC, such as BAB or RM 257, align mostly along the director. The subsequent UV light irradiation promotes cross-linking of the monomer and the formation of polymer chains that also align along the LC director [29]. When the applied voltage is decreased during the polymerization step, the director configuration changes from high to low molecular inclination angles (Fig. 1). This splay configuration is then “frozen” in the polymer network. Alternation of these two steps for many cycles offers better alignment of the polymer chains before each consequent polymerization step, improves alignment of polymer filaments and, consequently, provides for better control of the polar pretilt angle that this layer generates for the molecules in the bulk.

2.2. Measurement of the polar pretilt angle generated by polymerized layers in planar cells

For the measurement of pretilt angles in planar cells we employed two techniques: fitting the transmission versus voltage (T-V) curves [26], and the crystal rotation method [26,30]. The advantage of the first technique is in its applicability to the wide range of pretilts.

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