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Alignment of Liquid Crystal Confined in Polydimethylsiloxane Channels

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The alignment of liquid crystal confined in polydimethylsiloxane channels with a rectangular cross-section is studied. The aspect ratio (depth to the width) of the channel is shown to be a critical parameter. In a channel of aspect ratio less than a critical value the liquid crystal adopts a homeotropic alignment, whereas in a channel with aspect ratio greater than the critical value, the molecules align parallel to the substrate.

Keywords liquid crystal alignment; micro-replica; polymer walls; polydimethylsiloxane confinement

1. Introduction

Effective control of the orientation of liquid crystal (LC) molecules is a prerequisite for the operation and performance of LC devices. In calamitic LCs, which comprise rod-like molecules, the orientation state is adequately described by the director $\mathbf{n}(\mathbf{r})$, the vector that describes the local average orientation of the molecular long-axes at position $\mathbf{r}$[1]. In their general form, LC devices are typically constructed with a thin layer of a liquid crystalline continuum sandwiched between two bounding surfaces of solid matter. The interactions at the LC-solid interface determine the conformation that leads to the establishment of a molecular alignment in the LC. In the nematic phase, the constituent rod-like molecules tend to align along a locally preferred direction, i.e. the easy direction [1]. There are two principal classes of alignment, each of which represents an extreme of molecular orientation: homeotropic alignment, in which the molecules align to form a unique director field $\mathbf{n}$ in the entire cell with $\mathbf{n}$ oriented normal to the bounding surfaces; and planar alignment, in which $\mathbf{n}$ is confined to a specific direction with in the plane parallel to the bounding surfaces. In most conventional LC devices, the LC is aligned in a uniform manner across the entire cell. In such devices, the lateral dimension (say of the order of cm to 10s of cm) of the LC layer is much greater than its thickness (usually on the order of one to several microns).Therefore, the effect of the sidewalls of the LC cell on the configuration of the director can be omitted, and the way that the LC molecules align is determined by the nature and the anchoring strength of the bounding surfaces. Most conventional LC displays operate in monostable mode in which the device can support two optical states, only one

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of which is stable without an applied field. It thus requires continuous electrical power to maintain the information in the display. There has been growing interest in creating bi-stable and multi-stable orientations in a nematic LC cell [2-6] in response to the demand for LC devices that have the ability to retain a static image in the absence of electrical power [4,7-9] in situations where the display does not require to be constantly changed or updated.

For the different states to remain stable with no applied field, effective energy barriers must be built up to prevent the LC from spontaneously transitioning between states. One way to build up proper energy barriers is to create lateral confinement by the provision of a structured surface morphology on one or both of the bounding surfaces thus separating the otherwise continuous LC layer into square wells [4,10,11] or into parallel channels [12,13]. A key parameter of the LC under confinement is its director field which is established as a result of the interactions within the confinement. Thereupon, the behaviour of nematic LC in confined geometries becomes a research topic of great interest for both basic scientific and technological reasons. Depending on the competition between the bulk elastic energy and the surface free energy, nematics in a confinement can exhibit a variety of nontrivial structures, which may contain the crucial codes of this phase. On the other hand, comprehensive knowledge of the effect of the geometries of the confinement structures on the profile of the director field is advantageous in device design as it allows prediction of optimal operation and determine the nature of the devices.

Recently, we studied the macroscopic alignment of a nematic LC confined in polydimethylsiloxane (PDMS) micro-channels with a rectangular cross-section. In this case, the interactions of the side-walls imposed on the LC become very strong when the distance between the walls is comparable to the LC layer thickness, i.e. the distance between the bounding surfaces, of the cell, and can no longer be ignored. PDMS is a polymeric organosilicon compound. In thin-film form, PDMS, with a very low surface free energy, is capable of supporting vertical anchoring of the rod-like LC molecules [14]. When the surfaces are uniform and all physicochemically similar, the configuration of the director field of the LC encased in the PDMS channel is largely determined by the geometry of the channel. We demonstrate that with modification of the geometry of the PDMS channels the LC alignment can be switched from one alignment type to the other.

2. Experimental

PDMS thin layers comprising microtrenches were produced using a micro-replica molding technique. The polymer precursor used for the replica was Sylgard 184 (Dow Corning Corp.), which is a two-component silione elastomer that is supplied in two separate parts, the base resin and the curing agent. A mixture was made by mixing one weight-part of curing agent into 10 weight-parts of base resin, and left in a vacuum chamber at a pressure of 20 Pa for 1 hr to remove trapped air bubbles.

The master molds were produced using standard photolithographic fabrication procedures. A negative photoresist resin SU8-GM1060 (GersteltechSarl) was spun onto anoptical-flat glass slide of 15 $\times$ 15 mm^2, and then soft-baked at 60 $^\circ$C for about 15 min to remove the solvent by evaporation. The baked photoresist layer was masked, exposed to ultraviolet (UV) light of wavelength 365 nm, and then developed. The portion of photoresist that was exposed to the UV irradiation became insoluble to the photoresist developer, and remained on the substrate, whereas the unexposed portion of the photoresist was dissolved by the developer, and washed away. The pattern of the photoresist remained on

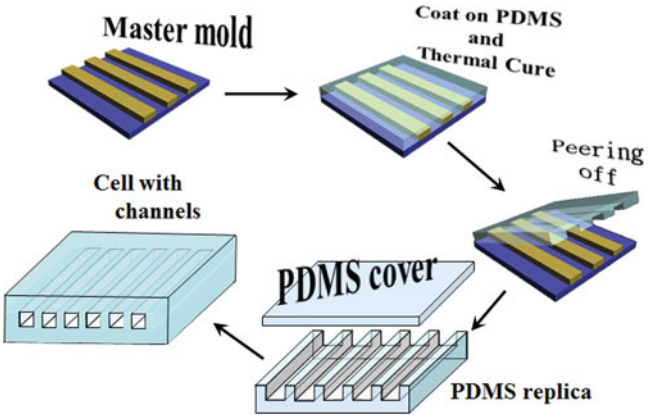

Figure 1. Schematic illustrating the main steps involved in the procedure for producing PDMS micro-channels using a micro-replica molding technique.

the substrate was determined by the mask pattern. In the present study, masks comprising parallel UV-transparent stripes with purposefully selected pitches and 50% duty cycle were used. Therefore, a master comprising parallel grooves was made. As the unexposed part of the photoresist layer is completely washed away, the depth of the grooves is equal to the thickness of the photoresist layer, and controlled by the speed of the spin-coater.

The procedure of the micro-replica molding process is shown schematically in Fig. 1. The PDMS precursor was spin-cast into the mold, and was thermally cured at 130 °C for 1 hr. After thermal curing, the PDMS thin film was peered from the mold. As a result of the replica-molding process, the surface pattern of the master is transferred onto the PDMS replica. A cell, which consists of micro-channels with a rectangular cross section (c.f. Fig. 1), was constructed by covering the PDMS film bearing the micro-grooves with a piece of PDMS. The nematic liquid crystal E49 (Merck) was flowed into the micro-trenches by capillary action at 110 °C, above the isotropic-nematic transition temperature of 100 °C. After filling, the device was cooled at a rate 0.3 °C/min to room temperature. The molecular alignment of the LC in the sample cells was examined using a polarizing optical microscope (POM) (ZEISS, Axioskop40).

3. Results and discussions

The geometry of the channel used in the investigations is shown in Fig. 2. The long axis of the PDMS channels runs in the z-direction, the x-direction is parallel to the substrate. A nematic LC layer of thickness d, measured in the y-direction, was confined in the channel of width w. In this geometry, the PDMS surfaces that are parallel to zx-plane are defined as bounding surfaces of the channels, whereas the surfaces that parallel to the yz-plane are referred to as the walls of the channels.

Figure 3 shows optical images of the LC confined in PDMS channels of width $w = 10\ \mu$m and depth $d = 2.0$ mm. Viewed under a polarising microscope, the sample appears black (Fig. 3a). The black appearance did not change when the sample was rotated in the POM (Fig. 3b). These optical characteristics indicate that a homeotropic alignment has been attained.

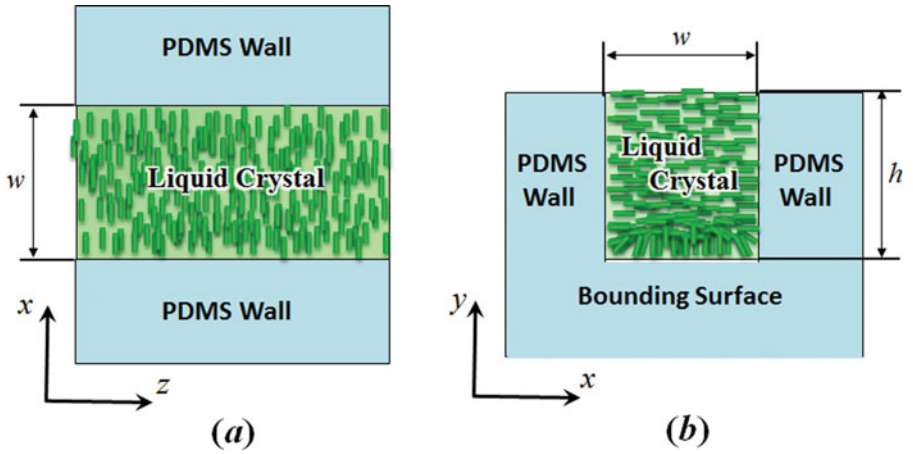

Figure 2. Schematic showing device geometry. (a) Plan view of the structure of the PDSM channel. (b) Side view of the channel with top PDMS cover removed.

Keeping the width fixed, the depth of the channels was increased. As the depth of the channels was increased, the light leakage from the cell became increasingly apparent. The light leakage results from a disturbance in the director field due to more LC molecules, which previously (in the shallow cell) oriented vertically on the bounding surfaces, were driven to orient perpendicular to the walls, i.e. parallel to the bounding surfaces, as the height- and hence area - of the wall increased [15]. Figure 4shows optical images of a sample, in which the depth of the channels (i.e., height of the walls) is 9.3 mm. In the

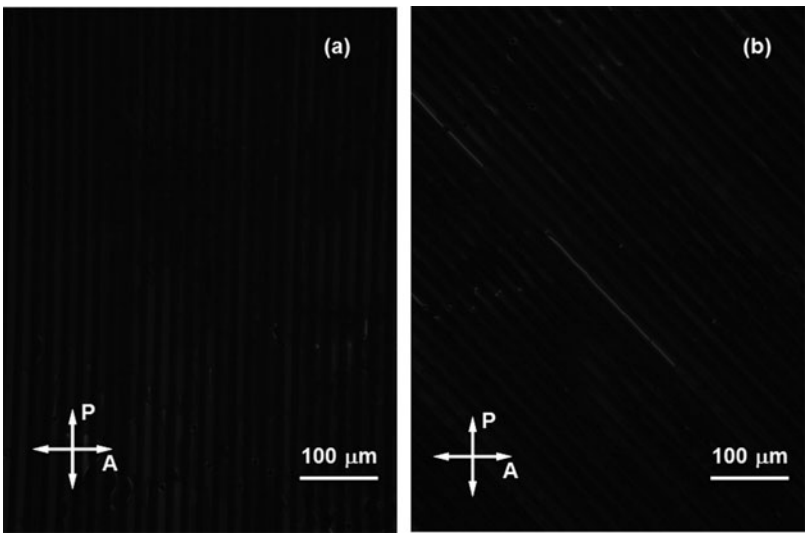

Figure 3. Optical texture of nematic phase E49 confined in PDMS trenches of width $w = 10$ μm and depth $d = 2.0$ mm where the trenches are at azimuthal angles of (a) 0° and (b) 45°, respectively. The cross arrow indicates the optical axes of the polariser (P) and the analyser (A) of the polarising optical microscope.

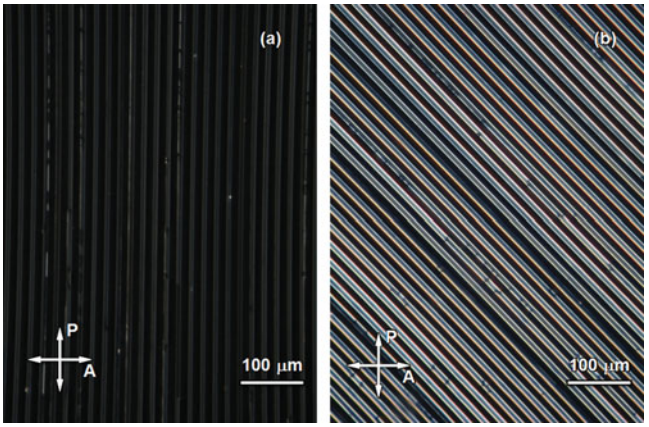

Figure 4. Optical texture of nematic phase E7 confined in PDMS trenches of width $w = 10$ μm and depth $d = 9.3$ mm where the trenches are at azimuthal angles of (a) 0° and (b) 45°, respectively. The cross arrow indicates the optical axes of the polariser (P) and the analyser (A) of the optical polarising microscope.

polarising microscope, one can observe that the appearance of the sample varied from black (Fig. 4a) to white (Fig. 4b) when the sample was rotated. The periodic variation of the light transmission (c.f. Fig. 5a), was resulted from an azimuthal variation in the optical retardation of the LC layers due to the orientational order of the LC molecules LC in the channels, and indicates that macroscopically the LC is in the planar alignment.

With a low energetic state at surface, a PDMS thin film of infinite extent creates a sole easy-direction in the direction of the normal to the surface for the nematic E49. When the LC is in contact with the PDMS, the director of the LC is driven to orient parallel to the easy direction, i.e. the LC is in the homeotropic alignment. A change in the geometry of the PDMS surface will cause changes in the way that the LC molecules orient in the confinement [15].

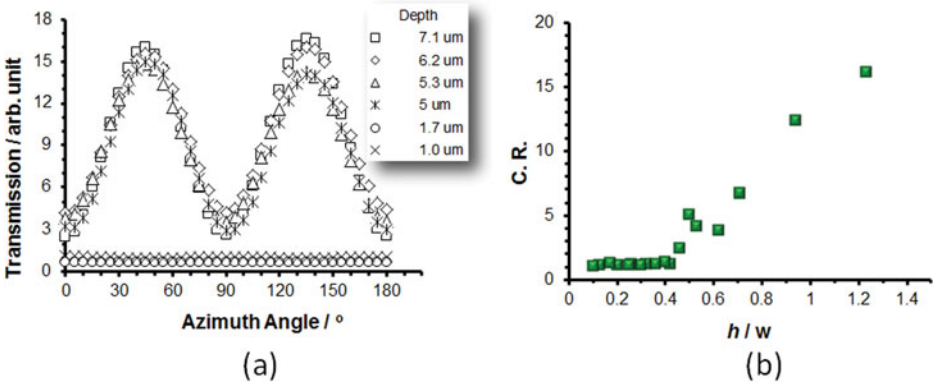

Figure 5. (a) Light transmission as a function of azimuthal angle for the liquid crystal confined channels of width 10 μm at various depths. (b) OCR as a function of aspect ratio for the liquid crystal confined in the PDMS channels.

In the standard angular coordinate system, the director field of the nematic phase can be written as

$$\mathrm{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta), \tag{1}$$

whereθ is the tilt-angle measured from z-axis, and φ is the angleof orientation on the xy-plane measured anti-clockwise from the x-axis. It is a tough job to determine the director profile for a LC confined in a channel since the confinement geometry can usually support a number of stable states. The issue can be simplified if we restricted our attention to consideration of splay and bend distortions. Let the PDMS channels of rectangular cross-section, which confine the LC, extend in z-direction, then $\mathbf{n}(\mathbf{r})$ will lie only in the xy-plane with no tilt in the z-direction, i.e. $\mathbf{n}(\mathbf{r}) \cdot \mathbf{z} = 0$. Therefore the director $\mathbf{n}(\mathbf{r})$ degenerates to a two dimensional field, and can be written, at any position along z-direction, as $\mathbf{n}(x,y) = [\cos\varphi(x,y), \sin\varphi(x,y)]$. Our observations, as described in previous sections, show that an increase in the depth of the channel with a specific width can cause a change in the type of molecular alignment of the LC confined in the channel. The observations suggested that the aspect ratio $\eta = h / w$ of the PDMS channel holds the key to the change of the molecular alignment of the confined LC from one type to the other. The task is then to determine the critical aspect ratio η_c, at which the macroscopic orientation of $\mathbf{n}$ starts to convert from one type, i.e. either the planar or vertical to the bounding surface, to another.

In the classical continuous theory, the total free energy of the LC at the equilibrium state depends on the director profile (i.e. the spatial orientation distribution $\mathbf{n}(\mathbf{r})$ and the spatial gradients $[\nabla\cdot\mathbf{n}(\mathbf{r})]$ of the director) [1]. The critical aspect ratio η_c denotes an energetic state, at which the free energy of the system with the nematic director $\mathbf{n}$ aligned vertical to the substrate is balanced with that of the system with $\mathbf{n}$ orienting perpendicular to the side walls, in the PDMS channel of rectangular cross-section. Crossing that point an energetic template conducive to one of the two particular director profiles will be created, and the crossover of the two types of LC alignment takes place in the channels. Because of the nonlinearity between director profile and the elastic free energy η_c is not necessarily unity. Using conformal mapping techniques and without considering the details of the interactions within the LC-solid interface, Davidson et al. estimated a critical aspect ratio $\eta_c = 0.388$ for surfaces that are capable of planar anchoring of rod-like molecules [16]. We approached the issue by means of experiment. As the director remains in the xy-plane, when light is incident along the normal to the bounding plates (i.e. in the y-direction), the light transmission is a function of only the angle of the director. For a planar aligned LC layer installed between crossed polarizers, the optical transmission can be written as [17]

$$T = \sin^2(2\varphi)\sin^2\delta, \tag{2}$$

whereφ is the azimuthal angle the director makes with either polarizer; $\delta = \pi\,\Delta\mathrm{nd}/\lambda$ is the retardation of the LC; $\Delta n = \mathrm{n_e}–n_o$ is the birefringence of the LC; and λ is the wavelength of the incident light. When the director orients perpendicular to the x-direction, i.e. the LC is in the homeotropic alignment, T becomes zero as the incident light propagates along the director and the birefringence vanishes.

Figure 5a shows light transmission against azimuthal angle the channels made with polarizer for the LC confined in 10 μm widePDMS channels with various aspect ratios. The periodical variation in the transmission indicates that the LC in the channels is in planar alignment. For each sample, we measured light transmission against the azimuthal angle, and defined the optical contrast ration (OCR) as the ratio of the maximum transmission to the minimum transmission of the sample. Figure 5b shows OCR vs aspect ratio for the

LC confined in the 10 μm wide channels with different depths. When the aspect ratio is small, the contrast ratio becomes unity, i.e. there is no obvious difference in the optical transmission (c.f. Fig. 5a), indicating that most LC molecules in the channels, except those in the region very close to the walls, orient perpendicular to the bounding surface. When the aspect ratio is sufficiently large, OCR is greater than unity indicating that the light leakage from the sample becomes significant due to more LC molecules orienting parallel to the bounding surfaces. The transition in the OCR happens when the aspect ratio is equal to 0.4 (c.f. Fig. 5b). Therefore, η_c is determined to have a value of 0.4. When the height of the channel is further increased and η is much greater than η_c, most LC molecules are driven to orient parallel to the bounding surfaces, and as a result the light leakage at the state, in which the channels are aligned parallel to either polarizer, is significantly reduced leading to an increase in the contrast ratio (c.f. Fig. 5b).

4. Conclusion

We have studied the molecular alignment of LC that is confined in a PDMS channel with a rectangular cross-section. In nature, low energetic PDMS thin films generally support the vertical anchoring of the calamitic LCs. A change in the geometrical structure of the surface of the organosilicon polymer thin film leads to a change in the profile of the director field of the LC. In the PDMS confinement, the profile of the director field of the LC is found to be strongly affected by the aspect ratio of the depth to the width of the channel. There is a critical aspect ratio beyond which the macroscopic alignment of the confined LC changes. For the nematic LC E49, the critical aspect ratio of the PDMS channel is approximately 0.4. To obtain vertical alignment of a layer of E49 confined in PDMS channels, the aspect ratio must be less than approximately 0.4, i.e. the width of the channels is greater than the depth of the channels. When the aspect ratio is greater than 0.4, the LC confined in the channels adopts a planar alignment.

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