

Transitions in the orientational order of liquid crystals induced by periodic patterned substrates

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The orientational order of liquid crystals (LCs) induced by periodic patterned substrates has been investigated with cells coated by azopolymer films that could be photoaligned in a controlled way. Two regimes were observed depending on the period of the patterns: (i) above $3.0\ \mu\text{m}$ the LC follows the direction imposed by the patterned substrate since the energy stored in the surface potential minimizes the elastic energy of the LC medium. (ii) For periods smaller than $1.0\ \mu\text{m}$ a homogeneous in-plane state was induced and the LC did not follow the orientation imposed by the surface. This in-plane transition could be explained qualitatively by a theoretical model based on the competition between the Frank-Oseen elastic energy and the phenomenological surface potential. The results also suggest an out-of-plane transition for the LC director as the period was reduced. These results agree with data in the literature for patterned substrates with completely distinct architectures. This indicates that for a particular LC sample the overall behavior depends basically on the texture period instead of the texture architecture. The textures were characterized with a scanning near-field optical microscope (SNOM), which allowed simultaneous morphological and optical images in the submicrometer range.

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I. INTRODUCTION

The development of experimental techniques to control liquid crystal (LC) alignment in the submicrometer scale has become of special interest in many technological areas, such as photonics and optoelectronics. Nanorubbing of polymers with an atomic force microscope (AFM) tip provides local alignment [1], which may produce surface patterns with neighboring orthogonal square domains and surface bistability [2]. For example, the reduction in periodicity of the texture to less than $0.8\ \mu\text{m}$ induced a uniform configuration of the LC director with a large pretilt of approximately 40° [2]. This transition was theoretically investigated using a model based on the competition between the Frank-Oseen elastic energy and the phenomenological surface potential, which exhibited good agreement with the experiment [3]. Polymers bearing azogroups (azopolymers) have also been used to induce LC alignment, by exploiting the photoalignment of azogroups with linearly polarized light. Owing to a series of *trans-cis-trans* photoisomerization cycles, the azodyes tend to align perpendicularly to the polarization direction, thus creating a film anisotropy that is ultimately responsible for the orientation of the LC molecules. The magnitude of such interaction (the anchoring energy) depends on the concentration of the chromophores in the film and on the irradiation time [4]. A further use for LC alignment is with surface relief gratings (SRGs) photoinscribed on azopolymers, where the LC molecules tend to align along the grooves of the SRGs due to minimization of the elastic distortions close to the surface [5,6]. Such photoinduced methods are considered “clean,” i.e., there is no mechanical contact with the surface during preparation. In addition, they are reversible and the anchoring energy can be easily controlled.

In an earlier work, the preferred LC configuration for the director induced by flat periodic patterned substrates with different aligning directions was theoretically obtained. We

observed that in the limit of large periods, this configuration depended on the aligning directions of the individual stripes and the ratio of the elastic constants K_1/K_3 [7]. This model also predicts an orientational in-plane transition to a homogeneous state as the period of the pattern is reduced. Here the in-plane transitions for the configuration described in Ref. [7] are experimentally and theoretically investigated, considering the system initially in state II ($\alpha \approx \pm 60^\circ$) and reducing the period. The patterns have been recorded on polymers containing azogroups covalently attached to the main chain, by illuminating the film with a periodic pattern of constructive and destructive interference fringes. This resulted in alternating patterns with different orientation directions in the microsize domain. We changed the period of the patterns down to the submicrometer range for a fixed irradiation time. Such substrates were optically and morphologically characterized with a scanning near-field optical microscope (SNOM).

II. THEORETICAL MODEL

Consider a nematic LC sample of thickness d bounded at both sides at $z=0$ and $z=d$ by two identical, aligned patterned substrates, as depicted in Fig. 1. Due to this special

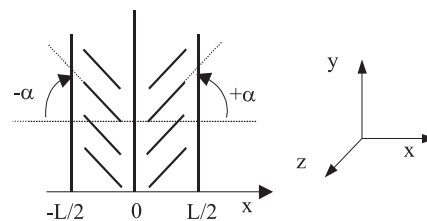


FIG. 1. Schematic representation of the pattern periodic micro-textured substrate used in this work.

substrate structure, the angle between the LC director \mathbf{n} and the x axis can be either $\varphi=0$ or $\pi/2$, in the boundary of the domains, i.e., at $x=nL/2$ ($n=0, \pm 1, \pm 2, \dots$). In Ref. [7] we calculated the preferred φ_0 value and the $\varphi(x)$ profile with the Frank-Oseen continuum elastic theory, with the profile being given by

$$\left[\frac{d\varphi(x)}{dx} \right]^2 = \frac{\left(\frac{W}{d} \right) \sin^2[\varphi(x) - \alpha] - C}{K_1 \sin^2[\varphi(x)] + K_3 \cos^2[\varphi(x)]}, \quad (1)$$

where α is the angle between the easy axis and the x axis, and C is an integration constant, written as

$$C = \left(\frac{W}{d} \right) \sin^2[\varphi_{nL/4}(x) - \alpha], \quad (2)$$

where $\varphi_{nL/4}$ is the angle of the LC director at $x=nL/4$. In the limit of large L , $\varphi_{nL/4} \rightarrow \alpha$ and, consequently, $C \rightarrow 0$. For a general L , $\varphi_{nL/4}$ can be determined from Eq. (1) with the initial condition of either $\varphi=0$ or $\pi/2$ and by noting that

$$\left[\frac{d\varphi(x)}{dx} \right]_{x=nL/2+L/4} = 0. \quad (3)$$

The stable configuration of $\varphi(x)$ is the one that minimizes the energy per unit area given by

$$\begin{aligned} \frac{F}{ld} = 4 \int_0^{L/4} \frac{1}{2} \left\{ K_1 \sin^2[\varphi(x)] \left[\frac{d\varphi(x)}{dx} \right]^2 + K_3 \cos^2[\varphi(x)] \right. \\ \left. \times \left[\frac{d\varphi(x)}{dx} \right]^2 + \left(\frac{W}{d} \right) \sin^2[\varphi(x) - \alpha] \right\} dx, \end{aligned} \quad (4)$$

where l is a length due to the integration in y , and d is the sample thickness, resulting from the integration in z . Integration from zero to $L/4$, instead of over the whole period (from $-L/2$ to $L/2$), can be performed if L is very large, or when $K_1=K_3$.

In this work, the pattern period L of the substrate was systematically varied in order to investigate the LC configuration. In particular, we simulate the special case where the angle between the easy axis and the x axis is $\alpha = \pm 60^\circ$. Let us, first, define a mean angle φ_M as

$$\varphi_M = \frac{\int_0^{L/4} \varphi(x) dx}{\left(\frac{L}{4} \right)} = 4 \frac{\int_0^{L/4} \varphi(x) dx}{L}. \quad (5)$$

The model considers a flat substrate, with a planar configuration of the director. The assumption of a flat substrate may not hold experimentally, and then the LC molecules may suffer elastic distortions along the out-of-plane direction, resulting in a nonzero initial pretilt at the patterned surface. However, this effect is not important for deformations that are much smaller than the period of the patterns, as we shall indicate as being the case in the experiments performed in this paper. Furthermore, this approximation enabled us to solve the equations analytically.

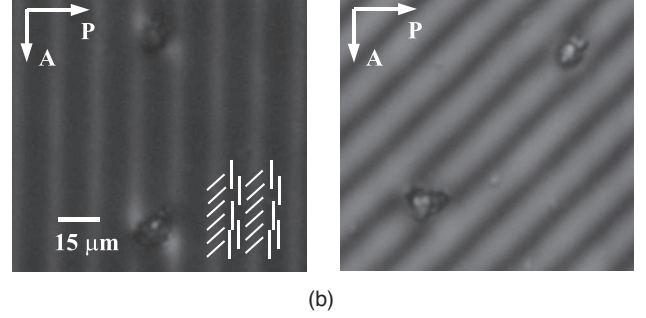
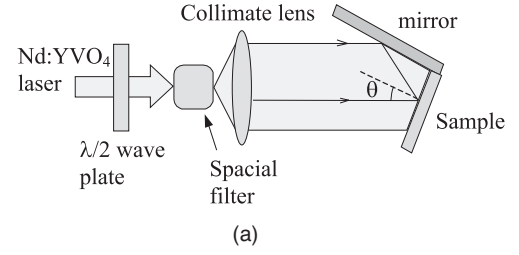


FIG. 2. (a) Experimental setup for the texture inscription; (b) optical image of a texture with $15 \mu\text{m}$ period. The lines indicate the alignment direction of the azogroups at the individual stripes.

III. EXPERIMENTAL DETAILS

The azopolymer PS119, purchased from Aldrich and used as received, was dissolved at 0.2 wt % in water and cast on the substrates. LC cells were prepared using glass plates. For SNOM measurements the substrates were polished silicon wafers to increase the light reflectivity by the surface. The process responsible for the pattern formation is the well-known photoalignment of the azogroups induced by linearly polarized light, which is reversible and governed by *trans-cis-trans* photoisomerization cycles [8]. We used a Nd:YVO₄ laser of $\lambda=532$ nm passing through a spatial filter and collimated by a lens. The light intensity measured at the sample position was 160 mW/cm^2 . The pattern inscriptions were performed in two steps: (i) the film was first homogeneously photoaligned at a given direction (perpendicularly to the light polarization direction), with normal incidence on the polymer surface; (ii) this film was then irradiated again with the interferometric setup described in Fig. 2(a) using a different light polarization direction. Using the latter procedure, a new orientation direction is induced in the illuminated regions, i.e., at the constructive interference fringes, whereas the first photoalignment direction remains unchanged at the dark regions given by the destructive interference fringes. The incidence of interference fringes can also produce SRGs [9,10].

The period of the fringes corresponds to the period of the texture (L) and can be easily controlled, according to the equation $L=2\pi/k=\lambda/2 \sin\theta$, where θ is given by the sample holder position. For $\lambda=532$ nm it is possible to obtain a period ranging from 0.5 to $15 \mu\text{m}$. The irradiation time was 60 and 30 s, in the first and second steps, respectively, in order to keep the same irradiation at the illuminated regions, because in the second step (on the constructive fringes) the light intensity is doubled. It is important to emphasize that

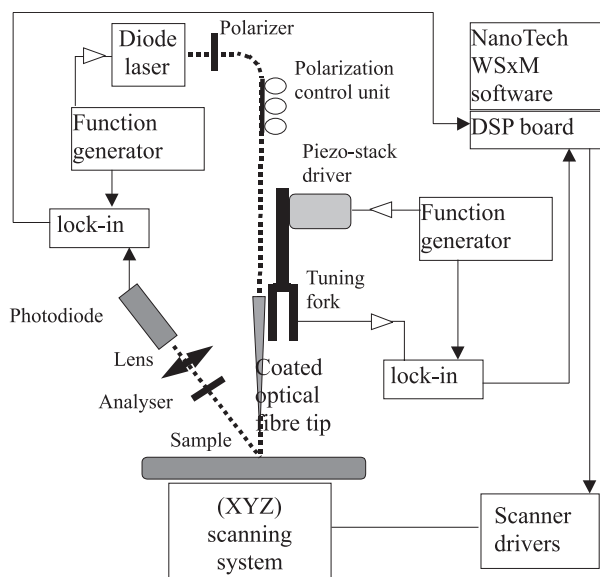
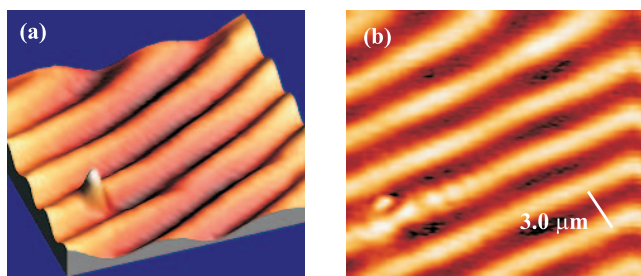
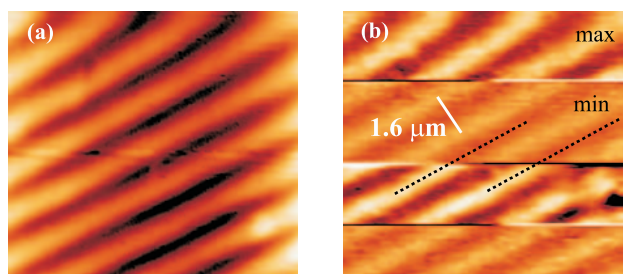


FIG. 3. Scheme of the SNOM.

this irradiation time is much lower than the time required for saturation of the photoalignment process, which is approximately 120 min. for this polymer. We chose a short irradiation time to avoid formation of SRGs with large amplitudes.

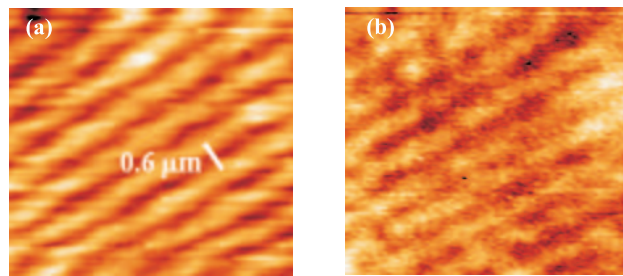
Figure 2(b) shows an optical image of a patterned substrate with $L=15\ \mu\text{m}$, collected with a digital camera coupled to a polarized microscope. By rotating 45° one can identify the orientation of the chromophores, as represented schematically in the figure. We infer that the difference in orientation for the azogroups along two neighboring stripes is 45° . This pattern was used in the SNOM measurements because it represents the maximum optical contrast between two neighboring stripes. SNOM operates in the noncontact mode at a fixed distance of 20 nm from the surface, where the tip comprises a tapered optical fiber with 200 nm diameter at the end. The light of a diode laser ($\lambda=670\ \text{nm}$) is transmitted through the fiber, which illuminates the surface in the near field and is detected by a photodiode in the far field after interaction, giving the optical image of the surface with a resolution of approximately $\lambda/5$. The topographic image is obtained in the shear force mode, with contrast originating from changes in the mechanical vibrations of the tip fixed on a tuning fork oscillating near the resonance frequency [11]. Therefore during the scanning, it is possible to

FIG. 4. (Color online) Images obtained simultaneously with the SNOM for a period of $3.0\ \mu\text{m}$; (a) topography and (b) optical image.FIG. 5. (Color online) Images obtained simultaneously with the SNOM for a period of $1.6\ \mu\text{m}$; (a) topography and (b) optical images. The polarization of light was changed during the measurement between maximum (max) and minimum (min) of transmitted light to the photodetector.

obtain simultaneously the optical and morphological images in the submicrometer range. The SNOM scheme is presented in Fig. 3, where the polarization control unit allows for manipulation of the direction of the light polarization impinging on the film. The polarization can be controlled by monitoring the intensity of the light captured by the photodiode coupled to an analyzer, in such a way that a maximum means that the incident polarization direction is parallel to the analyzer. In the experiments with LC, performed at room temperature, we used the 4-cyano-4'-n-pentylbiphenyl (5CB, Merck).

IV. RESULTS AND DISCUSSIONS

SNOM images of the textured films are presented in Figs. 4–6, for periods of 3.0 , 1.6 , and $0.6\ \mu\text{m}$, respectively, with those on the left representing topography and those on the right corresponding to the optical image of the substrate. Figure 4(a) shows the periodic deformations in the surface topography, with a period of $3.0\ \mu\text{m}$ and amplitude of $10.0\ \text{nm}$. A perfect correlation in terms of the period is observed in the optical image of Fig. 4(b). However, one may wonder whether the patterns in the optical image were caused by distinct directions of alignment of the azogroups in the stripes or by interference due to the light traveling different thicknesses in the film. To check this point, we scanned a patterned surface, by imposing variations in the incident light polarization during the scanning process, which are identified by maximum (max) and minimum (min) of the captured light. If the correlation resulted from the

FIG. 6. (Color online) Images obtained simultaneously with the SNOM for a period of $0.6\ \mu\text{m}$; (a) topography and (b) optical image.

azogroups' orientation, then a given stripe should alternate between dark and bright domains, whereas no changes would be observed if topography governed the optical images. As shown in Fig. 5 for a period of $1.6 \mu\text{m}$, the optical patterns are due to the azogroups' orientation. The measured amplitude of the surface deformations was 5.0 nm , which is negligible compared to the period of the pattern.

Figure 6 was obtained for a period of $0.6 \mu\text{m}$ and in this case the measured amplitude was only 2.5 nm . Although the morphological and optical images are not so clear, the optical effect is still present in the submicrometer range. This observation has important implications, as we shall discuss later on. It is important to note that the amplitudes of the surface deformations are very small compared to the corresponding periods (about 0.4%), which justifies the assumption of a flat substrate in the theoretical model.

The LC alignment was investigated for surface textures as the one presented in Ref. [7], see Fig. 1, where the orientation of the azogroups had periodic angles of $+60^\circ$ and -60° with the x axis (which is perpendicular to the stripes direction). The idea was to check the transition to a homogeneous state along the y axis (90°), by reducing the period, as it is expected theoretically. The patterned substrates with different periodicities in the submicrometer range were used to build LC cells $20 \mu\text{m}$ thick, using glass plates with polyvinyl alcohol (PVA) at the other side. The LC was inserted in the nematic phase by capillarity and the alignment direction (given by the director \mathbf{n}) was determined with an optical polarized microscope. The images were captured with a digital camera coupled to the microscope. In comparing the optical images of the patterned substrate with the LC orientation, the substrate was divided into two regions: one with the pattern itself and another reference region, referred to as background, corresponding to a uniform orientation of the azodye groups performed in the first step of the pattern inscription. For periods above $3.0 \mu\text{m}$ we observed that the LC follows exactly the direction imposed by the patterned substrate, which means that the energy stored in the surface potential minimizes the elastic energy of the LC medium. However, for smaller periods the LC director points to the direction of 90° .

Figure 7 shows a pattern with a period of $0.6 \mu\text{m}$, with a comparison on the right for the uniform orientation imposed by the photoalignment (background). For this period it is not possible to identify the orientation of individual stripes with a conventional microscope. We could only identify the macroscopic alignment of the polymeric film and the alignment induced to the LC molecules. Despite the limitation of the microscopy, significant differences could be observed: the first and the second rows represent the optical image only of the polymeric film (patterned substrate) and the LC cell at the same position, respectively. The columns named B, C, and D represent different relative orientations of the sample, rotated between crossed polarizers. In column B, the patterned region on the left side is positioned with the stripes along the analyzer direction. According to the first row of Fig. 7, when the sample is rotated by 30° to the right, the background becomes dark, indicating that the film is oriented at 60° from the horizontal direction, i.e., along the x axis (see column C). When the sample is rotated by 30° to the left, the

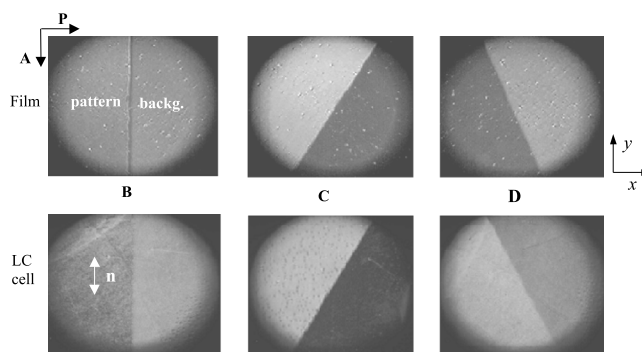


FIG. 7. Optical image at the border of the pattern and the background, for a texture period of $0.6 \mu\text{m}$ with $\alpha = \pm 60^\circ$. The first row is the image of the film and the second row is the image at the same position of a LC cell mounted with the film. The columns B, C, and D represent different relative positions of the sample between the crossed polarizers (A and P).

patterned region becomes dark, i.e., it is oriented at -60° from the x axis (see column D). This observation agrees with the proposed pattern of periodic stripes with angles of $\alpha = \pm 60^\circ$.

If we compare the first row with the second row of Fig. 7, which represents the LC alignment at the same position, a different behavior induced by the patterned structure (column D) appears. By rotating the sample 30° to the left, the patterned region did not become dark anymore. In this case, the sample position with lowest intensity of transmitted light was in column B, with the LC director along the y axis (90°). Therefore we conclude that the LC did not follow the orientation imposed by the surface and an orientational transition occurred, which means that the energy of the system is minimized by a homogeneous alignment along the y axis. This position, however, does not represent a complete extinction of light on the patterned region; instead, it indicates that despite an in-plane transition there is also an out-of-plane transition, in which the director adopts a tilted angle, whose value exhibits some dispersion around the y axis.

Further analysis can be performed for a texture with period of $1.0 \mu\text{m}$, as shown in Fig. 8. For the sake of clarity, we present only columns B and D. The minimum in transmitted light for the LC cell (second row) occurs at approximately 10° from the y axis direction, i.e., the director is aligned at 80° . In addition, the transmittance is quite low at this position, suggesting that the director lies in the x - y plane and well aligned along the 80° direction. The same was done for higher periods, with the plot for the final LC alignment direction with respect to the x axis being shown in Fig. 9(a).

Figure 9(b) shows the mean angle φ_M as a function of the pattern period L for $\alpha = \pm 60^\circ$. As a result, a continuous increase of φ_M from 60° towards 90° is expected by decreasing L . This simulation was made using Eqs. (1), (4), and (5), assuming $W = 1.5 \times 10^{-5} \text{ J/m}^2$ that was estimated for PS119 using the hybrid twisted cell method, with a rubbed PVA film at one side of the cell and a homogeneous film of PS119 photoaligned for 60 s at the other side [12]. In a polarized light microscope we observed a texture consistent with a totally twisted angle, indicating that the planar alignment im-

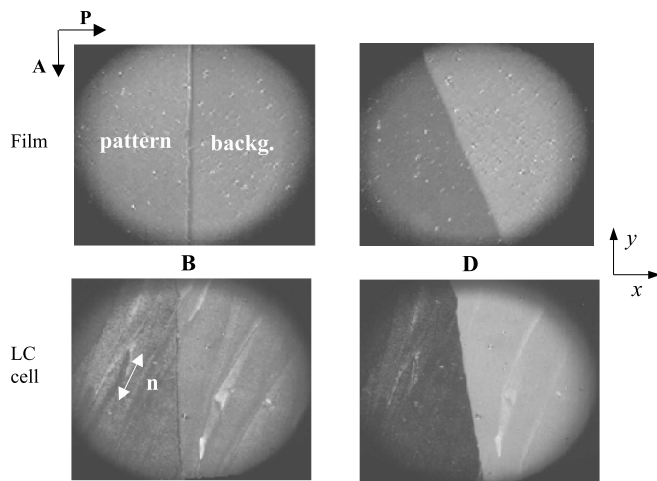


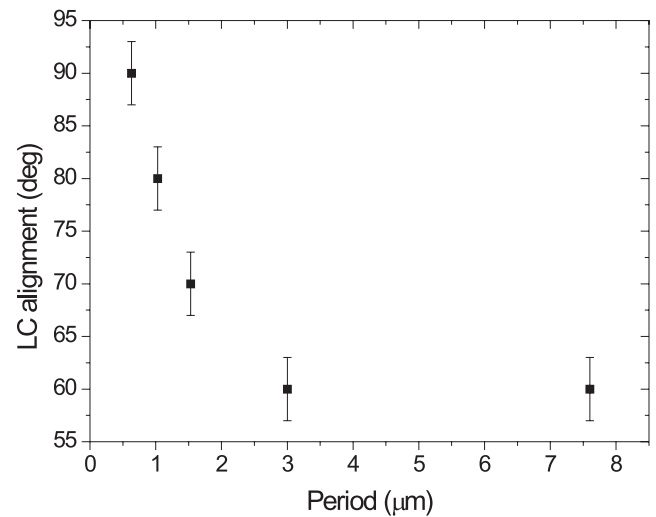
FIG. 8. The same as Fig. 7 for a texture period of $1.0 \mu\text{m}$. Here only the columns B and D are shown.

parted to the LC exhibits strong anchoring properties, comparable to the rubbed PVA [13]. We have tested the possibility of using different values for W (higher and lower than $1.5 \times 10^{-5} \text{ J/m}^2$) and we found that significant effects on the $\varphi_M(L)$ curve are observed only if W changes by one order of magnitude. A comparison between the experimental data and the theoretical simulation of Fig. 9 shows a continuous orientational transition from 60° to 90° due to the reduction of the pattern period. This transition is sharper experimentally, and for lower values of the period, since for periods higher than $3.0 \mu\text{m}$ the LC alignment is along the direction imposed by the texture. Nevertheless, the behavior is qualitatively the same. It should be stressed that approximations had to be done in order to solve analytically the equations in the theoretical model, which can cause the simulated case to depart from the experimental conditions. For example, $K1/K3$ was assumed to be 1.0 in the model, but for the 5CB LC it is 0.7.

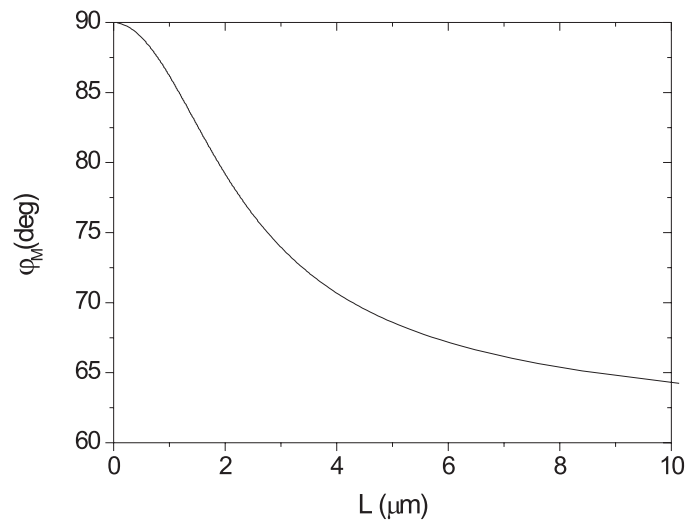
V. CONCLUSIONS

The in-plane orientational transition predicted in the model presented here could be confirmed experimentally, at least qualitatively. The experiments also suggested an out-of-plane transition for patterned substrates with periods below $1.0 \mu\text{m}$. These results agree with those of Kim *et al.* [2], where transitions were observed, in the same range of periodicity, for textures produced with an atomic force microscope tip on polyimide. We conclude that these orientational transitions depend not only on the architecture of the texture, but also on the competition between the distortions imposed to the LC director, periodicity of the textures, and the elastic energy of the LC medium. The advantage of the method presented here is the simplicity for obtaining the textured substrates. In addition, the photoinduced effects are reversible and the use of photopolymers allowed the manipulation of the anchoring energy by controlling the irradiation time and the azo dye concentration [4].

SNOM measurements were proven efficient to characterize the optical and morphological properties of polymeric



(a)



(b)

FIG. 9. (a) Experimental data for the LC alignment as a function of the pattern period; (b) simulated LC director mean angle φ_M as a function of the pattern period L .

substrates in the submicrometer scale. Therefore given that a linearly polarized He: Cd laser of $\lambda=442 \text{ nm}$ could be injected into the fiber, the same equipment can be used to inscribe structures, where the lower dimensions are determined by the optical aperture of the tip. New experiments are underway to investigate the conditions for information inscription using lithographic techniques in the submicrometer scale, which can be used in data storage and specific LC alignment.

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