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Bistable nematic azimuthal alignment induced by anchoring competition

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We present a novel method to obtain bistable azimuthal anchoring conditions for nematic liquid crystals. The fine control of the anchoring strengths of two independent planar surface anchoring attractors, perpendicular to each other, induces controlled surface transitions that give bistability. The independent anchoring sources are obtained by means of a composite surface made with a film of photopolymer on an anisotropic SiO layer. A phenomenological model, based on anchoring competition between the two orienting layers, is developed to describe the surface bistability. © *1998 American Institute of Physics.* [S0021-8979(98)03613-5]

I. INTRODUCTION

The alignment of nematic liquid crystals (NLCs) on solid substrates has been investigated widely due to its importance for electro-optical applications. Various treatments are used to get a uniform NLC surface orientation.[1,2] For instance, it is well known that a preferential surface orientation exists when a NLC is in contact with a thermal polymerized film submitted to a rubbing treatment. In this case the NLC surface director generally lies along the rubbing direction, but there are also polymers which give a perpendicular orientation with respect to this direction.[3] The Berreman model,[4] which is based on an elastic approach, is usually applied to explain this behavior, but there is more evidence of its inadequacy.

A recent alternative treatment is the linear photopolymerization (LPP) of photosensitive polymers by means of polarized ultraviolet (UV) light. Compared to the rubbing technique, this is a ''noncontact'' method for the polymer surface, which is not submitted to any mechanical stress. Experimental observations show that the NLC easy axis usually lies in the direction perpendicular to the linear polarization of the incident UV light.[5] This kind of alignment on polymers is explained in terms of the chemical change of the polymer structure induced by LPP.[5]

One of the most interesting anchoring condition for NLC was obtained a few years ago by coating a glass or indium–tin–oxide (ITO) substrate with a film of SiO. In this case, with suitable deposition conditions, two equivalent tilted easy directions can be obtained on the surface.[6,7] This kind of bistable surface alignment for NLC makes possible development of novel electro-optical cells with interesting characteristics for applications: threshold effects with electrical response in the microsecond range and infinite multiplexing capability.[8] Recently, experimental evidence of anchoring bistability has been also obtained on Langmuir–Blodgett films by means of double exposure to polarized UV light.[9]

In this article, we present a new technique which allows us to obtain a new kind of planar bistable NLC anchoring. The basic idea is to use surface anchoring competition conditions[10] between two superposed aligning films. The lower anisotropic film is a SiO coating layer, which gives a unidirectional planar NLC orientation. The upper film is a linearly photopolymerized thin layer inducing a NLC orientation perpendicular to that given by SiO. We show that there is a critical range for the photopolymer layer thickness, which gives rise to NLC planar bistable anchoring. The effect of the UV polymer exposure time on the azimuthal anchoring direction of the nematic is also studied.

II. THEORETICAL MODEL

Let us consider the system shown in Fig. 1: the x axis coincides with the planar orientation P induced by the SiO coating, and the y axis identifies the planar NLC orientation L given by the LPP process. The z axis is directed toward the bulk of the nematic material. φ defines the actual azimuthal anchoring direction.

In a first approximation, the orienting effect of the SiO film is due mainly to the elastic energy associated with the topography of the SiO.[11,12] According to the Berreman model, the anchoring energy strength is given by $w_{\mathrm{SiO}}=kA^2q^3$, where $q=2\pi/\lambda$ is the grooves' wave vector, k is the NLC elastic constant, and A is the grooves' amplitude.[4]

The orienting effect of the polymer can be connected to an anisotropic van der Waals interaction. For a given stable configuration of the polymer layer, the anchoring energy strength can be expressed simply in the form $w_{\mathrm{Pol}}=R$, where R is a constant.

When the polymer is deposited over the SiO layer, A becomes smaller and smaller as the thickness of the polymer film increases, as shown in Fig. 2. We expect that a competition of the two orienting effects exists when the two an-

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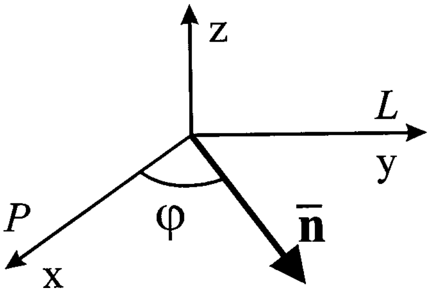

FIG. 1. Geometry of the analyzed problem. The nematic director **n** lies on the plane $x-y$ of our reference frame, making an azimuthal angle φ with the x axis. P and L are anchoring attractors corresponding, respectively, to the SiO film and the photopolymerized layer.

choring strengths w_{SiO} and w_{Pol} are of the same order of magnitude, i.e., for

$$kA_{\mathrm{eff}}^2 q^3 = R, \tag{2.1}$$

where A_{eff}^2 is the effective amplitude of the surface grooves, taking into account that the polymer film partially fills the holes of the starting SiO structure. In practice, Eq. (2.1) defines a critical thickness l_c, of the photopolymer film for which the aligning competition exists.

Since it has been demonstrated that the NLC anchoring strength on a photopolymer film can be controlled by UV exposure dosage,[13] we can, in principle, use the UV exposure time to control the NLC azimuthal orientation. Let us imagine that:

(1) the NLC director $\bar{n}$ is parallel everywhere to the $x-y$ plane,

(2) the bulk follows the surface orientation, i.e., one can neglect the elastic energy coming from NLC deformations.

For a layer of polymer close to the critical thickness defined by Eq. (2.1), the total energy contains the following term

$$f_{\mathrm{SiO}} = \tfrac{1}{2} w_{\mathrm{SiO}} \sin^2 \varphi \tag{2.2}$$

due to nematic-SiO layer interactions and

$$f_{\mathrm{Pol}} = -\tfrac{1}{2} w_{\mathrm{Pol}} \sin^2 \varphi + \tfrac{1}{4} b \sin^4 \varphi \tag{2.3}$$

due to nematic–photopolymer interactions. Here, φ is the azimuthal angle defined in Fig. 1. In Eqs. (2.2) and (2.3), $w_{\mathrm{SiO}}>0$ means that the NLC easy orientation given by the f_{SiO} term is parallel to the x axis and $w_{\mathrm{Pol}}>0$ that the f_{Pol} term tries to orient the NLC molecules parallel to the y axis. The term $\frac{1}{4}b \sin^4 \varphi$ is connected with the effect of a stochastic contribution to the surface energy coming from the random distribution of molecules in the orienting film.[14]

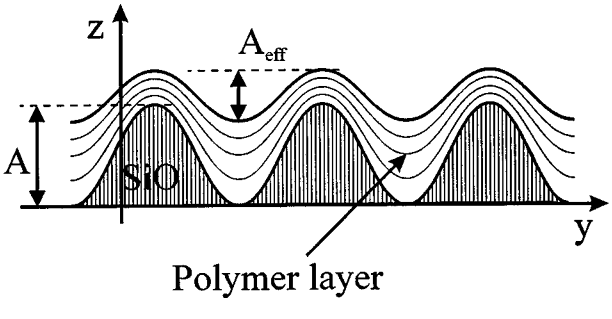

FIG. 2. Outline of the composite surface used for our experiments. An anisotropic SiO layer is covered by a photopolymer layer. The polymeric material fills the holes in the SiO structure reducing their depth from A to A_{eff}.

The total free energy per unit area of the considered system is then given by

$$f = f_{\mathrm{SiO}} + f_{\mathrm{Pol}} = -\frac{a}{2}\sin^2 \varphi + \frac{b}{4}\sin^4 \varphi, \tag{2.4}$$

where $a = w_{\mathrm{Pol}} - w_{\mathrm{SiO}}$.

The actual azimuthal orientation of the nematic surface director can be obtained by minimizing the expression (2.4). The condition $df/d\varphi = 0$ implies

$$-\frac{a}{2}\sin(2\varphi) + \frac{b}{2}\sin^2 \varphi \sin(2\varphi) = 0 \tag{2.5}$$

and gives three possible solutions:

$$\varphi = 0; \quad \varphi = \frac{\pi}{2},$$

and

$$\sin^2 \varphi = \frac{a}{b}. \tag{2.6}$$

For $a<0$, the equilibrium state corresponds to $\varphi=0$ and the nematic follows the orientation imposed by the SiO layer. For $a>b$, the stable state is $\varphi=\pi/2$ and the surface nematic orientation is determined by the photopolymer layer. For $0<a<b$, the sample presents an intermediate azimuthal orientation between the P and L planar surface attractors. The condition $a=0$, which corresponds to

$$w_{\mathrm{Pol}} = w_{\mathrm{SiO}} \tag{2.7}$$

defines the critical state when the orienting anchoring competition begins to take place.

To analyze the effect of the exposure time t of linearly polarized UV light on the azimuthal angle of the nematic easy axis, let us consider the simplest phenomenological expression for w_{Pol}:

$$w_{\mathrm{Pol}} = R(1 - e^{-t/\tau}), \tag{2.8}$$

where R characterizes the highest energy strength of the polymer film after a long enough irradiation time and τ is connected with the dynamics of orientation of the chemical bonds.[5,13]

From Eqs. (2.7) and (2.8), we expect that the orientation effect is characterized by a critical time t_c given by

$$R(1 - e^{-t_c/\tau}) = w_{\mathrm{SiO}}. \tag{2.9}$$

For $t<t_c$, the SiO layer orienting effect dominates and the nematic easy axis lies along the P direction. For $t>t_c$, the nematic easy axis presents an azimuthal orientation different from zero.

When $a>b$, the energy terms obey the following relation:

$$R(1 - e^{-t/\tau}) - w_{\mathrm{SiO}} > b, \tag{2.10}$$

which defines a second critical time t_c^*. For $t>t_c^*$, the orienting effect of the photopolymer layer dominates and the surface director lies along the L direction.

For $t_c<t<t_c^*$, from the third solution in Eqs. (2.6), one obtains

$$\sin^2 \varphi(t)=\frac{R(1-e^{-t/\tau})-w_{\mathrm{SiO}}}{b} \tag{2.11}$$

In a first approximation, one can consider $b\propto w_{\mathrm{Pol}}$,[14] i.e., $b=C(1-e^{-t/\tau})$, where C is a suitable constant. Hence, taking into account Eqs. (2.9) and (2.11), one obtains for the nematic azimuth

$$\sin^2 \varphi(t)=\frac{R}{C}\left(1-\frac{1-e^{-t_c/\tau}}{1-e^{-t/\tau}}\right). \tag{2.12}$$

This last result, in practice, means that if the thickness of the polymer layer is the critical one defined by condition (2.1), all possible surface azimuthal orientations φ in the range $(0,\pi/2)$ can be, in principle, obtained by using only the UV exposure time t as control parameter.

As reported by Schadt *et al.*[5] and Chen *et al.*,[13] during the LPP process the azimuthal anisotropy of the photopolymeric layer grows for short UV exposure time (a few minutes) and decreases when the UV exposure time is longer. As we investigate the best conditions for the nematic bistable anchoring, our model does not take into account the reduced azimuthal anisotropy for the photopolymer for very long UV exposure time.

III. EXPERIMENTAL RESULTS AND DISCUSSION

We made some experimental investigations into the aligning competition of two orienting layers, by considering the effect of a photopolymer film on an anisotropic SiO substrate. For our experimental observations, we used the nematic material 4′-*n*-pentyl-4 cyanobiphenyl (5CB). Nematic samples were realized in the standard sandwich geometry[8] and they were observed by means of a polarizing microscope (Axioscope by Zeiss). The first plate of a typical nematic cell was treated with dimethyloctadecyl-3-(trimethoxysilyl)-propylammonium-cloride (DMOAP) to obtain a standard homeotropic alignment. The second one is the surface that we want to investigated and it was treated with a freshly coated SiO layer, covered by a photopolymer film.

The SiO film was coated, under vacuum, on a clean ITO–glass plate with the technique described in Refs. 1 and 6. The SiO deposition rate was fixed at about 5 Å's by using a quartz balance perpendicular to the deposition beam and the deposition time was about 20 s. The angle between the normal to the substrate and the SiO deposition beam was fixed at 75°. The anisotropy of the SiO film can be revealed by the well defined uniform planar alignment of the NLC, perpendicular to the SiO deposition beam.[6] A preliminary morphological analysis[11] made by means of an atomic force microscope (Autoprobe by Park Scientific) shows that this kind of SiO film presents a surface roughness in the order of a few tens of angstroms, which should be compatible with the required uniformity of the polymer layer.

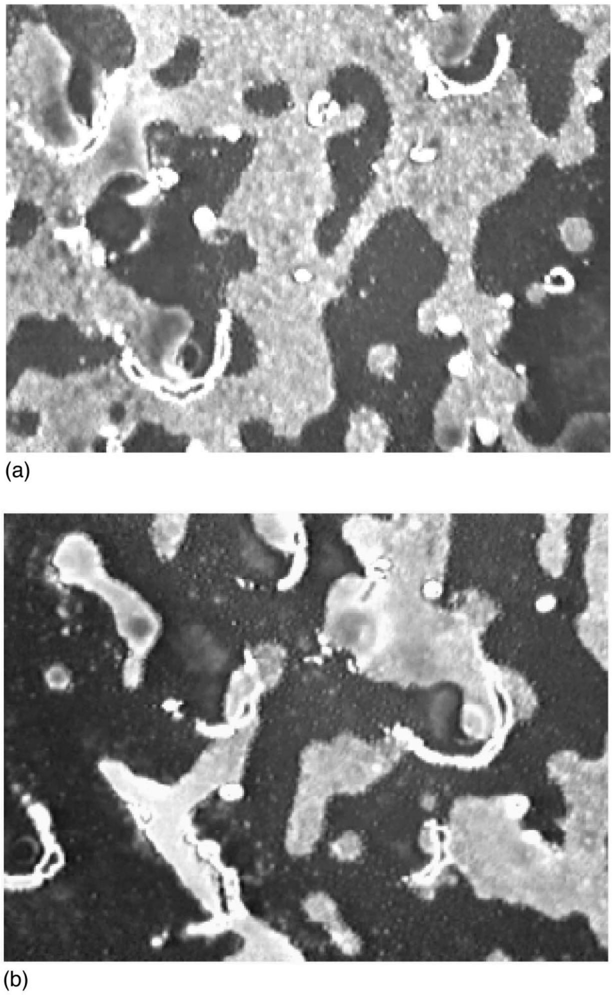

FIG. 3. A bistable cell is observed between crossed polarizers. (a) The optical axis of the right region is aligned along one of the two polarizers. (b) The sample is rotated to obtain the light extintion condition for the left region.

The photopolymer used in this work is poly vinyl 4-methoxy-cinnamate, (PVMC) by ROLIC. The polymeric material was deposed by using the spin-coating technique and then treated with a standard thermal process at 120 °C for 1 h at a pressure of about 10^{-3} mbar. The linear photopolymerization of the PVMC film was achieved by exposition to the wide spectrum UV light of three 15 W HNS-OFR fluorescent lamps by Osram. Samples were placed at a distance of about 10 cm from the lamps. The incident light was linearly polarized by means of a UV dichroic polarizer Oriel 27320.

To find the critical thickness of the photopolymer layer, we varied the photopolymer concentration in a solution with *n*-methyl pyrrolidone (NMP). The solution was spun at a fixed spin-coating rate (3000 rpm) and the effective thickness was checked with the ellipsometry technique.[15] From our experimental observations, the result was that for a PVMC concentration of 0.2%, the NLC always follows the alignment direction imposed by the SiO substrate, whereas for a PVMC concentration of 0.3%, the NLC aligns along the direction given by the LPP treated photopolymer layer. Under our experimental conditions, the critical thickness l_c

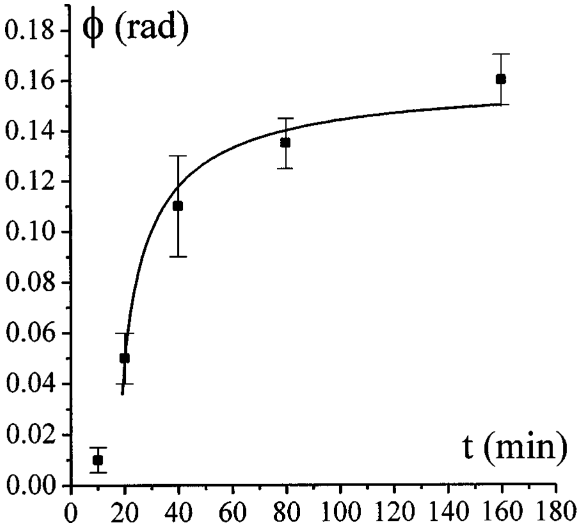

FIG. 4. Experimental values of the azimuthal anchoring direction φ vs the exposure time t. A fit, made by means of theoretical curve reported in Eq. (2.12).

was found to be about 30 Å, corresponding to a PVMC concentration of 0.25%. Note that there is also a screening thickness[10] $l_s > l_c$, above which, if the photopolymer is not treated with UV light, a planar degenerated NLC orientation results and, on the contrary, after the LPP treatment, the NLC always follows the alignment imposed by the polymer layer. l_s and l_c depend on the polymeric material and on the roughness of the anisotropic SiO layer: a systematic experimental investigation is in progress.

When the photopolymer layer thickness is l_c, i.e., anchoring competition exists, and one observes that the azimuthal surface orientation φ of the NLC changes, depending on UV exposure time. Moreover, two distinct and equivalent orientation directions, symmetric with respect to the y axis, are obtained. This experimental result is not surprising, because the symmetry of the investigated surface ($P \perp L$) allows both left and right rotations of the surface director during the transition from P towards L. This means that, for each director φ, there is also a twin director $\pi - \varphi$ and the final anchoring is bistable. Two pictures of a bistable plate are shown in Figs. 3(a) and 3(b).

The experimental results of the dependence of the twist angle φ of the bistable anchoring on the exposure time t are reported in Fig. 4 and a fit was done by using the simple exponential relaxation given by Eq. (2.12). The observed φ values start from the alignment along P (x axis) but, under our experimental conditions, seem to saturate at $\varphi_S \approx 0.175$ rad$=10°$. The agreement of the theoretical curve with the experimental data is reasonably good. In particular the critical time t_c, estimated to be on the order of 18.6 min, compares well with the measured value. The quite large value of t_c indicates that the photopolymer orientation under LPP is a slow phenomenon, at least in the case of very thin layer thickness on a starting anisotropic substrate. This anchoring is really bistable because, if such a sample is heated at a temperature to about 10 °C above the nematic melting point and it stay in its isotropic phase for a few minutes, when it is cooled down to the nematic phase the local surface director can change from one possible alignment direction to the other.

Preliminary observations have been made for the case in which P and L are not perpendicular: we always observe a change of the starting orientation from P towards L, but now only one surface director exists and the surface bistability is lost, indicating that the symmetry of the anchoring attractors is fundamental for obtaining surface nematic bistability.

IV. CONCLUSIONS

We may stress that a new kind of bistable NLC alignment has been obtained by using the surface anchoring competition between two aligning films. A simple model of the total energy of the system NLC-photopolymer-SiO coated layer has been done by means of an elastic term coming from the topography of the SiO layer and of an anisotropic van der Waals-like term connected with the photopolymer–nematic interaction. When the photopolymer thickness is in a range that allows the anchoring competition between alignments induced by SiO and by photopolymer, the nematic surface azimuthal angle depends on the UV exposure time. Bistable anchoring is achieved when the alignment directions imposed by SiO and photopolymer are perpendicular to each other. The experimental results can be described quantitatively by the theoretical model presented.

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