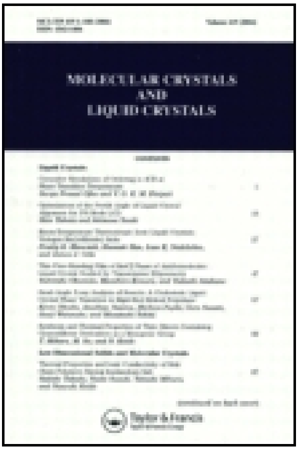

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Anchoring Transition Dominated by Surface Memory Effect

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Anchoring Transition Dominated by Surface Memory Effect

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We study a first order transition of the anchoring direction imposed by PVA coating of SiO layer. Contrary to the model of anchoring competition, no vanishing of the anchoring strength was observed close to the transition. We explain this behaviour by memory effects.

Keywords: anchoring; anchoring transition; memory effect; nematic

INTRODUCTION

The molecular anchoring of nematic liquid crystals on a solid substrate can be defined by the anchoring strength and the easy axis orientation (described by the polar angle θ_o and the azimuthal one ϕ_o). The anchoring is characterised by the function $g(\theta_s,\phi_s)$, the anisotropic component of the superficial energy of interaction between the substrate and the liquid crystal. Here θ_s and ϕ_s are the angles describing the surface orientation of the nematic. Usually, the two contributions to the anchoring energy, polar and azimuthal, can be studied separately. In the Rapini-Papoular approximation[1] we assume :

$$g(\theta_s,\phi_s) = \frac{w_p}{2}\sin^2(\theta_s - \theta_o) + \frac{w_a}{2}\sin^2(\phi_s - \phi_o) \qquad (1)$$

where w_p and w_a are the polar and azimuthal anchoring energy coefficients.

Both the bulk anisotropy of the substrate (e.g. in the case of stretched polymer) and the anisotropy of the surface microtopography (e.g. rubbed glass plate) can contribute to the anchoring energy. To separate these contributions one can coat the substrate with a layer of a variable thickness, e.g. obliquely evaporated SiO covered by thin PVA layer[2].

Recently, an anchoring transition depending on the PVA film thickness has been reported[3] for this kind of system. A 25Å SiO layer is evaporated at 75° incidence angle, giving planar (zero pretilt) alignment of the nematic 5CB, perpendicular to the evaporation plane. A PVA layer, spin coated over the SiO, does not change the nematic orientation up to a film thickness of about 100Å. For larger thickness an anchoring transition is observed, with 90° azimuthal rotation of the easy axis on the plane of the substrate. This behaviour is similar to the well known anchoring transition on bare SiO when the thickness δ of the SiO layer is increased at constant evaporation angle : for small δ the orientation of the nematic is planar and perpendicular to the evaporation plane, for large δ it becomes tilted and parallel to the evaporation plane, and between these regimes one observes two symmetrical bistable states[4]. By analogy, one can expect that in the PVA over SiO case too the bistable states are possible and potentially interesting for applications.

Here we study this anchoring transition and the azimuthal anchoring strength variation across it. We show experimentally that the bistable states are never realised and the 90° azimuthal rotation transition is of first order. The anchoring extrapolation length varies continuously across the transition, without the divergence expected by the originally proposed anchoring screening model[5]. We explain our observations by the anchoring memory phenomena as opposed to the simple elastic anchoring.

EXPERIMENTAL RESULTS

The SiO layer was obliquely evaporated on the glass substrates in the same conditions as in the original experiment of the Cosenza group[3] (δ=25Å, incidence angle 75°). The PVA coating was realised by the dipping method already described by S.Frunza et al.[2]. The SiO deposited plates were withdrawn vertically at a constant speed of 0.05 mm/s from an aqueous PVA solution and then dried 2 hours at 110°C. We modify the polymer thickness by changing the concentration of dipping solution. For the concentration, an upper limit of c=2.5 wt.% was imposed by the solubility of our product. We have not been able to measure directly the PVA thickness, but we expect it to be proportional to the concentration. Comparing our observations with the reported data[3] we expect a PVA layer thickness of about 100Å for a concentration of c=1.0 wt.%, corresponding to the anchoring transition. To induce a more isotropic behaviour of the PVA layer, we used a material having a small degree of polymerisation (300 monomers). We observed that the substrate properties do not depend on the relative orientation of the SiO evaporation plane and the withdrawing direction.

Easy axis orientation

We started our study with an observation of the spontaneous orientation of the nematic 5CB on the substrates as a function of the PVA film thickness. The orientation is strongly influenced by the perturbations during the cell filling. For example, introducing the nematic in the cell at ambient temperature often resulted in irregular flow alignment patterns masking the spontaneous orientation. Filling in the isotropic phase and slowly cooling down resolved this problem but revealed a strong interaction between the substrate under study and the anchoring conditions on the second plate (counterplate), used to prepare our sandwich cells. For strong planar or tilted anchoring on the counterplate (SiO evaporation) we observed «imprinting» of the counterplate alignment on the PVA during the cooling down of the sample. This parasitic effect, due to the bulk nematic elasticity, decreases with increasing cell thickness d, but remains quite strong even for thick cells (d≅50 μm).

To observe only the unperturbed spontaneous anchoring direction, we used a counterplate coated with a silane (DMOAP) to give an homeotropic alignment. The thickness of the cell was imposed by 12 μm Mylar spacers. No azimuthal torque is transmitted to the substrate under study in this case. Throughout the cell the director azimuth is constant, defined by the spontaneous easy axis on the substrate. The hybrid geometry of the cell allows the measurement of both the azimuthal and the zenithal orientation of the easy axis, respectively by rotation of the sample under a compensator equipped polarising microscope and by the relative birefringence of the twin hybrid domains[6].

Despite the different method used for the PVA deposition, the anchoring transition was observed, for concentration between 0.9 and 1.1%, confirming the main observations of the Cosenza group. For c<0.9 wt.%, the substrate keeps the anchoring direction perpendicular to the SiO evaporation plane. For c>1.1 wt.%, the easy axis lies in the SiO evaporation plane. No pretilt angle was detected. For intermediary concentrations (0.9%-1.1%) the nematic is oriented at random along one of the two possible directions. Sometimes, the two anchoring directions form large domains on the same plate. The choice between them is sensitive to the filling direction of the cell.

Once the cell is filled, the anchoring direction is memorized and does not change after repetitive heating of the nematic to the isotropic state.

We never observed in our cells bistable states. Sometimes we observe domains with easy axis rotated at a few degrees from the main directions of orientation, but the irregularity and the lack of symmetry of these domains show that they are not spontaneous, but induced by the filling perturbations. Moreover, we never observed domains with a large (~45°) deviation from the two main states. We conclude then, that the observed anchoring transition is of first order, with discontinuous jump between the 0° and 90° states and without intermediate bistable orientations.

This first order behaviour of the transition can be understood in the frames of the model[7] of anchoring competition between the SiO and the PVA layers. This model supposes the anchoring energy as a superposition of two individual contributions, favoring two orthogonal orientations. Choosing the SiO evaporation plane as a reference, we denote by $\phi_{01} = 0$ and $\phi_{02} = 90°$ the two directions. The anchoring energy is :

$$g(\phi_s) = \frac{w_1}{2}\sin^2(\phi_s - \phi_{01}) + \frac{w_2}{2}\sin^2(\phi_s - \phi_{02}) \approx g_0 + \frac{w_a}{2}\sin^2\phi_s \tag{2}$$

where $w_a = w_1 - w_2$ is the effective azimuthal anchoring energy. Here w_1 and w_2 are due to the interaction of the nematic with the SiO film and the PVA layer. These two coefficients depend on the polymer thickness : w_2 increases and w_1 decreases as the PVA concentration increases. The transition occurs when the two energies become equal. This model predicts for the transition an abrupt 90° jump of the anchoring direction, accompanied by a vanishing of the anchoring strength. To check this we measured the azimuthal anchoring strength in and around the transition domain.

Anchoring energy

To measure the azimuthal anchoring energy, a simple method was used[8], based on the symmetry properties of a $\pi/2$ twisted cell. A small curvature glass lens, treated to induce planar anchoring, is used as counterplate. The lens surface is polyimide treated to assure strong anchoring. The substrates under study were first assembled with homeotropic counterplate to observe their spontaneous alignment without azimuthal torque. Then the counterplate was replaced by the lens, with 90° twist between the easy axes of the two surfaces. The lens is in contact with the substrate in the centre of the cell, allowing the measurement of the azimuthal surface director deviation $\delta\phi = \phi_S - \phi_O$ as a function of the cell thickness d. At decreasing thickness $\delta\phi$

increases, due to the increasing bulk elastic torque applied to the surface. When the cell thickness decreases to the azimuthal anchoring extrapolation length $l_e = k_{22}/w_a$, the surface torque can no more equilibrate the large bulk torque and the anchoring is broken[9]: the director now is everywhere along the lens easy axis and $\delta\phi$ becomes exactly 90°. The typical experimentally observed dependence is presented in Fig. 1.

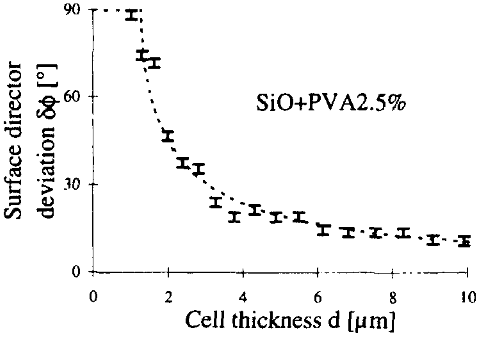

FIGURE 1 Thickness dependence of the azimuthal surface director deviation. The dashed line is the best fit with Rapini -Papoular form of the anchoring energy giving $l_e = 1.3\mu m$.

We can also find the form of the anchoring energy function. The surface director deviation is related to the torque

$$\Gamma_b = \frac{k_{22}}{d}\left(\frac{\pi}{2} - \delta\phi\right) \qquad (3)$$

applied on the surface from the bulk. The typical dependence $\Gamma_b(\delta\phi)$ is presented on Fig. 2, along with the best fit with the Rapini-Papoular model :

$$\Gamma_b = \frac{w_a}{2}\sin(2\cdot\delta\phi) \qquad (4)$$

The azimuthal anchoring energy was studied as a function of the PVA concentration c in the dipping solution in the range 0.2<c<2.5 wt.%, corresponding to thickness of the PVA films from ~20 Å up to 250 Å, on both sides of the anchoring transition region. In all the cases we found a good agreement, like in Fig. 2, with the sinusoidal Rapini-Papoular form of the anchoring torque.

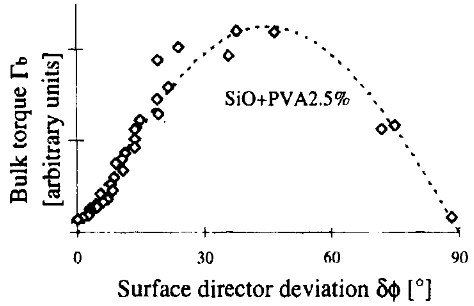

FIGURE 2 Dependence of the bulk torque on the surface director deviation. The dashed line is a Rapini-Papoular fit with l_e = 1.3μm.

In Fig. 3 we present our results for the extrapolation length l_e. It increases monotonously with increasing PVA film thickness. At low concentration $l_e \cong 0.2$ μm, comparable with the bare SiO value. At high concentration the extrapolation length increases and becomes comparable to the value of few micrometers observed for thick PVA film deposited on flat glass substrate[10].

The most striking feature in Fig. 3 is the absence of singularity of l_e across the anchoring transition. This is in strong disagreement with the model of anchoring competition and, more generally, with any purely elastic and reversible model of the anchoring.

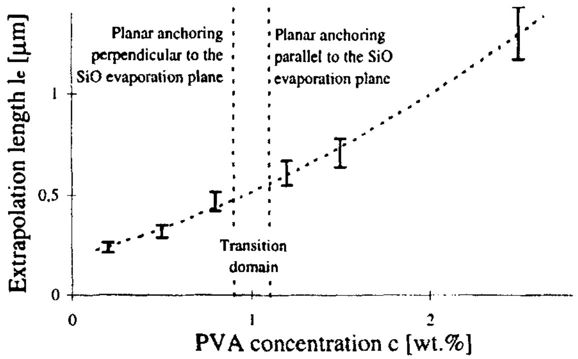

FIGURE 3 Dependence of the extrapolation length l_e on the PVA concentration in the dipping solution.

For the data interpretation we suppose that $\delta\phi$ results from an equilibrium between the bulk and the surface elastic torques. This assumption is partially confirmed experimentally: when the bulk torque is switched off after few minutes of action (e.g. by disassembling the cell), the surface director goes back to the initial easy axis orientation. However, if a strong torque has acted for a long time on the surface, we observe an increasing irreversible contribution to $\delta\phi$, related to easy axis gliding[11]. These observations show that the elastic models are not sufficient to describe the anchoring and one must take into account also the anchoring memory.

DISCUSSION AND CONCLUSION

Our observations confirm the anchoring transition reported earlier[3]. Increasing the thickness of the PVA film, the azimuthal orientation jumps abruptly at 90° from its low-thickness orientation, perpendicular to the SiO evaporation plane. The transition is first order and the director remains in the plane of the substrate, without tilt.

Our observations show that the mechanism of the PVA anchoring transition is different from the bistable transition on bare SiO[4], where the ordoelectric polarisation plays an important role. The ordoelectric effect[12], generated by the roughness induced surface disorder, attracts the director toward a «magic» angle tilted state, azimuthally degenerated. The absence of tilted states on the PVA shows that the ordoelectricity is not important in our case. Probably, the PVA film flattens the surface topography and inhibits the surface disordering.

Let us now try to explain the first order transition on PVA by elastic anchoring competition between different alignment mechanisms. The SiO can induce an orientation of the nematic by anisotropic long range van der Waals interactions, more or less screened by the PVA film. The surface topography also induces an alignment of the nematic by the Berreman[13] elastic mechanism. For bare SiO the surface topography is very complicated[14], with a continuum of surface profile wavevectors, competing between them[15]. The PVA layer smooths the surface undulations, acting as an roughness «filter» with wavelength dependent efficiency. Varying the PVA thickness, one changes the surface anisotropy, favoring one or another anchoring direction.

On the basis of the existing observations it is difficult to understand what is the main competition mechanism responsible for the anchoring transition. However, the anchoring competition alone is not sufficient to explain our data. From Eq. (2) we see that the extrapolation length l_e should diverge at the transition, due to the exact compensation of the two competing terms. This feature is in drastic disagreement with Fig. 3, showing monotonous increase of l_e with the PVA thickness, without singularity. This behaviour seems quite strange, taking into account that on both sides of the transition the anchoring energy is measured around different minima and, in the spirit of the anchoring competition, different alignment mechanisms are responsible for it.

To explain our data we need to consider the anchoring memory, which implies that the anchoring strength is dependent on the history of the sample. Memory effects are known to be important for the nematic alignment, e.g. the memorisation of the flow alignment easy axis, but the studies of these effects remain scarce[16]. Two different mechanisms can be involved in our case, enabling an initially defined easy axis to be memorised and stabilised. One of them is the adsorption of the nematic molecules on the surface[16], creating an oriented and strongly anchored adsorbed layer, keeping the initial alignment and order during the adsorption. Once created, the adsorption layer acts as a new anisotropic substrate with arbitrary strong anchoring, depending on the strong nematic-nematic interactions and evolving slowly in the time by desorption and readsorption. Another possible mechanism is the plastic deformation and orientation of the PVA polymeric chains in the aligning field of the adjacent nematic. In this case too, the initial easy axis direction is memorised due to the anisotropy induced by the nematic in the PVA film. Both these mechanisms can explain our observations, but here we will discuss it in terms of the adsorption model, which is more general and can explain also the currently observed anchoring memory on stiff substrates, like bare glass, ITO or SiO, where the substrate reorientation under the nematic aligning action is impossible.

Let us first consider the initial orientation of our samples, defining the easy axis $\mathbf{n}_e$. While the sample is filled with the mesogen in the isotropic state, the adsorbed layer is almost isotropic because of the vanishing bulk nematic order. At the transition to the nematic phase, the anisotropy of the nematic-substrate interaction becomes much stronger. The surface anisotropy becomes important too, through the Berreman's topographic alignment[13]. At this moment the anchoring competition defines the nematic orientation $\mathbf{n}_s$ close to the surface : the history of the sample is almost «clear» and even small anchoring energies are sufficient to impose $\mathbf{n}_s$. This initial choice of $\mathbf{n}_s$ is defined only by the elastic energy competition.

Once defined, $\vec{n}_s$ induces in its turn the easy axis $\mathbf{n}_e$ on the substrate : the newly adsorbed molecules are oriented along $\mathbf{n}_s$. Progressively the adsorbed layer becomes more and more anisotropic, giving $\mathbf{n}_e$ parallel to $\mathbf{n}_s$

and increasing the anchoring energy. This self-amplification of the anchoring strength continues up to an equilibrium, defined by the desorption and readsorption dynamics. Although the adsorbed layer is very thin, probably less than monomolecular, its order at equilibrium is comparable to the bulk nematic order and the resulting anchoring can be very strong. The anchoring strength is dominated now by the memory.

The equilibrium between the nematic and the adsorbed layer do not depend on the anchoring direction, which explains the monotonous dependence in Fig. 3. Qualitatively, the increase of l_e at higher PVA thickness can be explained by the smoothing of the surface and the resulting decrease of the effective contact area nematic-adsorbed layer. Similar contribution can be expected also by the incomplete covering of the SiO by PVA at low film thickness : we expect the highly porous bare SiO surface to give higher density of the adsorbed layer, compatible with the observed shorter extrapolation lengths for thinner PVA.

All our observations are in good agreement with this memory dominated anchoring. The initial choice of the easy axis was found to be very sensitive even to small perturbations and to be defined easily by weak effects, like the alignment induced by the flow or by the opposite plate, or even to be decided at random in the transition region. Once defined, the easy axis remains stable even under strong applied torque or repetitive nematic to isotropic transitions. The anchoring is relatively strong and does not depend on the initial local perturbations, defining the easy axis direction. We observe also slow gliding of the easy axis when a strong azimuthal torque is applied for a long time (~30 minutes) to the substrate. This can be explained by reorientation of the adsorbed layer, dominated by the slow desorption and readsorption dynamics.

In conclusion, we studied the azimuthal anchoring orientation and strength for PVA coated SiO layers. We confirm the anchoring transition, already reported, and we find it to be of first order, with 90° azimuthal jump of the easy axis and without intermediary bistable states. The measured azimuthal anchoring extrapolation length increases monotonously with the PVA thickness, without divergence at the transition. Our observations show that the anchoring is dominated by the memory, the elastic anchoring competition defining only the initial choice of the easy axis.

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