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Photopolarimetric investigations of the anchoring energy strength for a nematic liquid crystal on polyaniline boundary surfaces

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We report a photopolarimetric study concerning with the influence of the boundary surfaces and the surface charge buildup on the anchoring energy in nematic liquid crystalline electo-optical cells. By employing a field-on approach combined with a high precision photopolarimetric polarization method we simultaneously measure the Stokes parameters of the transmitted light. By using a standard Saturation Voltage Method (SVM) we implicitly determine the anchoring energy values for two different sets of samples, having soft and hard rubbing boundary constraints. The polyaniline coated substrates play a key role in weakening the anchoring energy during a bias-controlled injection process and allows obtaining important physical information on the investigated systems.

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1. Introduction

Liquid crystalline (LC) materials, surface alignment mechanisms and special confinement conditions have been extensively studied in the past decade primarily due to their great importance to the liquid crystal display industry and other application fields [1-5]. Novel materials (polymers, oxides, etc) and alignment techniques [6-12] have been developed and exploited to characterize and better understand the phenomenon of orientation (and anchoring) of liquid crystals by the surface boundaries.

Most of the research in the field was done by using nematic liquid crystals (NLC), which have the simplest known liquid-crystalline structure - the elongated rod-like molecules orient on average parallel to each other. The macroscopic behavior of NLCs is described by the unit vector field n(r) which is called the director. n(r) represents the local average orientation of the long molecular axes [13]. The surface alignment of the director is determined by the competition between surface, bulk interactions and possible external stimuli (mechanical, electrical, magnetical). These interactions have been the subject of intensive analysis with surface anchoring being one of the highlights of theoretical and experimental investigations [14-17]. The structure of the liquid crystalline phase in close proximity to an interface is different from that in the bulk, and this behavior changes the boundary conditions and influences the director distribution in the bulk region. The nematic phase is especially sensitive to external agents, in particular, to surface forces.

The alignment of liquid crystals (LCs) on solid substrates involves a broad variety of interfacial phenomena, such as surface ordering, surface transitions, surface wetting, etc., which are still not completely understood. From the technological point of view, it is essential to have a reliable procedure that allows a fine control and yields high-quality alignment of LCs used in electro-optic devices.

The anchoring energy parameter is a key factor for a LC electro-optical device because it affects not only the LC alignment/orientation but also the electro-optical properties such as threshold voltage and response time. Different experimental techniques have been developed for measuring the anchoring energy. Generally, they can be classified in two major groups depending on whether the measurements were accomplished in a field-free condition or not. Examples of the field-off methods are wedge-cells technique [18] and light-scattering method [19]. In the field-on approaches, both electric-field [20,21] and magnetic-field [22] techniques could be considered. The field-on methods consist in measuring the LC dielectric or diamagnetic Freedericksz transition effects. Typically, a strong enough electric field is more easily accessible and convenient than a magnetic field. For very strong fields even the LC molecules situated in the surface regions can be reoriented - the surface anchoring energy represents the work needed to realign the nematic liquid crystal surface region towards the bulk director orientation.

In this paper we present an experimental analysis of the influence of the boundary surfaces and the surface charge buildup on the anchoring energy in nematic liquid crystalline electro-optical cells. By cold plasma polymerization technique we obtain an interesting material (polyaniline) that we utilize as an alignment layer for liquid crystals. Employing a field-on approach combined with a high precision polarization optical technique (photopolarimetry) we study the near-surface behavior of a liquid crystalline material and we determine the anchoring energy values for various imposed boundary conditions.

2. Materials and Methods

Understanding the interfacial properties of nematic liquid crystals is a challenge for many researchers in the field of soft matter physics and it is also relevant for controlling and improving the features of the optical devices based on these materials. The physical behavior of LCs is mainly characterized by the boundary properties and in particular the surface energy plays a major role in both surface liquid crystal physics and technical applications. Surface energy emerges from the reduced symmetry in the vicinity of a boundary and from the direct interaction between the nematic liquid crystal and the substrate.

The standard and most widely used method for achieving a well determined LC alignment (planar or homeotropic) is by employing treated boundary substrates, usually a rubbed polymer [14, 23].

Chemical and electrochemical polymerizations are common methods used to obtain polymer thin films on different types of substrates. However, the technique of plasma polymerization is increasingly being used as an alternative for obtaining polymer substrates [24]. Polymer thin films obtained by cold discharge plasma polymerization are in many ways different from those obtained by conventional methods; the properties of these films can be tailored according to requirements by varying the deposition parameters such as pressure, applied voltage, monomer flow rate and time of polymerization. Pinhole free, chemically inert, thermally stable and of uniform thickness polymer thin films can be deposited by employing plasma polymerization technique [25].

By using a DC plasma glow discharge reactor presenting special electrode geometries for conferring uniform depositions we obtained several polyaniline (PANI) thin films deposited onto conductive ITO (Indium Tin Oxide) glass substrates. This experimental procedure is well described in a previous paper [3]. The film thickness depends on the intensity and time of plasma reaction but mainly on the vapor pressure of the aniline monomer. The thickness of the PANI films was determined by AFM (Atomic Force Microscopy) and ellipsometric techniques to be in the region of 20-30 nm. Furthermore, after performing AFM topographical investigations we concluded that the films were highly homogeneous and did not present variations in thickness or morphological irregularities (Fig. 1).

The thin polymer substrates were then rubbed by means of a standard rubbing machine such that we obtained two sets of samples (with Soft and Hard rubbing).

The experimental LC cells were constructed by capillary filling with pentylcyanobiphenyl (5CB) nematic liquid crystal the space enclosed between two conducting surfaces coated with PANI. The positive anisotropy liquid crystal was sandwiched between the two plates and homogeneously oriented in a direction parallel to the boundary layers (planar alignment). The desired thickness for the LC was ensured by using appropriate Mylar spacers (in our case 19 μm) while the active surface area of the electrodes was around 4 cm^2. The characteristic parameters for 5CB nematic liquid crystal were provided by Merck company and are the following : elastic constants (K_{11}= 6.4, K_{22}=3, K_{33}=10 values in dyn x 10^{-7}); dielectric permitivities ($\varepsilon_\perp$ = 6.7 , ε_{II} = 19.7); dielectric anisotropy ($\Delta\varepsilon$ = 13) with ε_0 = 8.85 x 10^{-12} F/m.

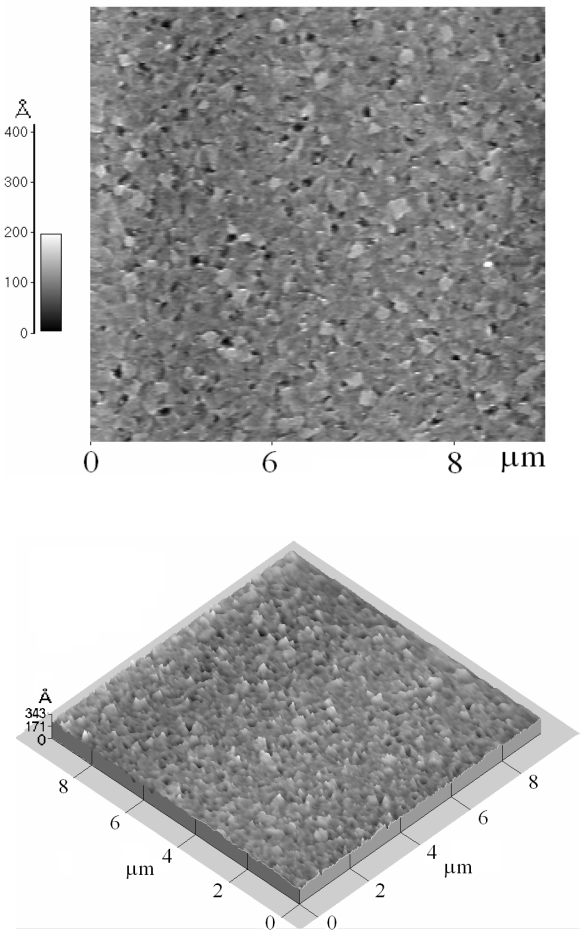

Fig. 1. Typical AFM topographical scans of the PANI layer surface. A square scan of 10 x 10 μm is reported. (a) Top view (b) Isometric view.

An important task in measuring the anchoring strength *A* is related to introducing a standard measurement method in field-on conditions. It could be an appropriate route for this purpose to consider the saturation transition, in which the molecular director becomes totally homeotropic, that is, the entire nematic including the boundary layers is oriented along an applied electric field direction at the saturation voltage. This approach was theoretically predicted by several scientists [26,27] while introducing the saturation transition in which with decreasing surface-anchoring strength the saturation transition voltage decreases and then reaches zero at a critical strength. The existence of the saturation transition for a NLC phase with a strong anchoring boundary condition was previously observed experimentally [20]. As proposed in the unified surface anchoring model [28] the saturation transition is highly associated to an externally applied voltage and is supposed to appear at non-zero voltages for all types of dielectric NLCs without imposing any restrictions on the surface anchoring energy.

The study for determining the anchoring strength of the nematic liquid crystal at the PANI boundary substrates was performed by applying an appropriate electric field to the LC samples and then recording the temporal evolution in the polarization state of the transmitted light by means of a Four Detectors Polarimeter (FDP). The light passing through a liquid crystal sample is usually elliptically polarized. The change with respect to the initial incident polarization state is associated to the birefringence of the LC medium. The effective birefringence rely on the LC molecules orientation and could reach zero value in the case of a completely homeotropic configuration (that can be attained in our situation by applying a strong electric field to the sample).

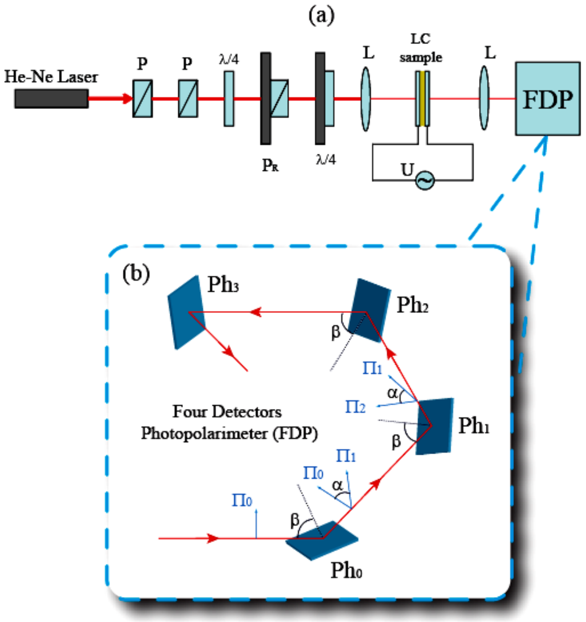

Fig. 2. Schematic of the experimental set-up used for the photopolarimetric measurements. (a) Optical line consisting in a He-Ne Laser, polarizers (P), quarter wave plates (λ/4) and lenses (L) used for controlling the input polarization state of the incident beam. (b) The Four Detectors Photopolarimeter (FDP) system (Ph$_i$ are the four silicon photodiodes).

A He-Ne laser beam (632.8 nm) was focused to arrive at normal incidence and linearly polarized at 45° with respect to the original alignment direction of the molecules on our nematic sample.

The transmitted light emerging from the sample was then analyzed and the polarization characteristics recorded by a four detectors photopolarimeter (FDP) system, while a varying AC electric field (starting from 0V up to V_{max} with a 5V step, and 1Kz frequency) was applied to the cell (Fig.2).

The FDP is formed by four analyzers together with the corresponding electronics for the signal detection, amplification and A/D conversion [29, 30]. The analysis of the polarization state for the incoming beam is obtained by means of the reflection on the surfaces of four silicon photodiodes positioned at appropriate incidence angles (β) and orientation of the incidence plane (α). For our experimental set-up, β and α were fixed at 65° and 45°, respectively. The electrical signal from the photodiodes was processed using a fast 12 bit card and the results stored on a computer. The system then determined with an accuracy of 0.3% the components of the Stokes vectors for the light transmitted through our LC sample.

Once the FDP is calibrated, any polarization state of the incoming light can be measured in terms of the Stokes vector S. The simultaneous measurement of the four Stokes parameters (S_0, S_1, S_2, S_3) of the transmitted light provides detailed information on the ellipticity (e), azimuthal angle of the major axis (Θ) of the polarization ellipse and the degree of polarization (p). The Stokes parameters can be defined as follows:

$$S_0 = I \tag{1}$$

$$S_1 = I_p \cos 2\varphi \cos 2\chi \tag{2}$$

$$S_2 = I_p \sin 2\varphi \cos 2\chi \tag{3}$$

$$S_3 = I_p \sin 2\chi \tag{4}$$

where I_p, 2φ and 2χ are the spherical coordinates of the polarization state in the three-dimensional space of the last three Stokes parameters. I is the total intensity of the beam, and p is the degree of polarization. These relations are valid for totally polarized light and the system does not produce depolarization of the transmitted light (no decorrelation is present in the components of the electric field of the probe beam). It follows [31] that

$$p = \frac{\left(S_1^2 + S_2^2 + S_3^2\right)^{\frac{1}{2}}}{S_0} \tag{5}$$

$$\Theta = \frac{1}{2} arctg\left(\frac{S_2}{S_1}\right) \tag{6}$$

$$e = tg\left\{\frac{1}{2}\arcsin\left[\frac{S_3}{\left(S_1^2+S_2^2+S_3^2\right)^{\frac{1}{2}}}\right]\right\} \tag{7}$$

When applying the AC electric field on the sample (from 0 to V_{max}) the ellipticity decreases from an initial value, which depends on the cell thickness and the birefringence of the sample, until it drops to a minimum value, when all the molecules are aligned almost homeotropically (normal to the substrates). In this way we can determine the surface anchoring energy (A) by using a saturation transition method called saturation voltage method (SVM), in which A is not separated into polar and azimuthal components. The anchoring strength, A, depends on the saturation voltage, V_S, in the following manner [32]:

$$A = \frac{V_s K_{22}\sqrt{\varepsilon_0 \Delta\varepsilon K_{33}}}{l K_{11}} \tanh\left(\frac{V_s}{2}\sqrt{\frac{\varepsilon_0 \Delta\varepsilon}{K_{33}}}\right) \tag{8}$$

where K_{11}, K_{22} and K_{33} are Frank's elastic constants for the NLC, ε_0 is the dielectric constant, $\Delta\varepsilon$ is the dielectric anisotropy of the liquid crystal and l is the thickness of the sample. The surface anchoring energy, A, can be completely estimated, without any additional numerical calculation, if the saturation voltage (V_S) is known.

3. Results and discussions

For determining the saturation voltage, V_S, we analyzed the dependence of the ellipticity (e) of the transmitted light on the applied voltage amplitude. The saturation voltage cannot be obtained directly from the applied field as this would be excessively high and would damage the LC sample. Figure 3 shows the behavior dependence of ellipticity (e) on the inverse of the applied voltage in the high electric field regime measured by means of the FDP at room temperature (approx. 300 K), in which it is obvious the theoretically predicted linear behavior [26,27].

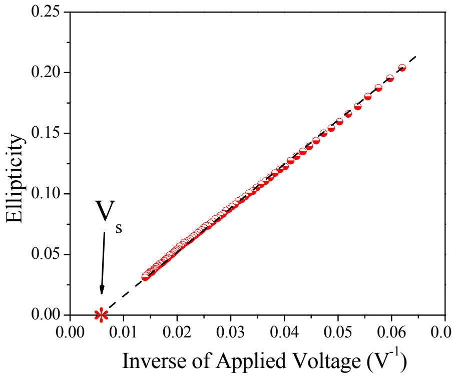

Fig. 3. The ellipticity e of the transmitted light in function of the inverse of the applied voltage for high field regime. With increasing applied voltage the ellipticity value decreases linearly as theoretically predicted, until it drops to zero at the saturation voltage, V_S (*) – this value can be obtained by linearly fitting the experimental data (by SVM method).

The saturation voltages (V_S) have been determined for each set of experimental data, by extrapolating the linear state of polarization of the transmitted light (for e = 0). For studying the effects of the PANI boundary layers in our system and the possible presence and influence of charge buildup at the interfaces on the anchoring energy value, the measurements were repeatedly performed with a DC bias voltage V_0 (in the range 0 - 10 V), that was superimposed to the already applied AC voltage. V_0 was unchanged during the sweeping of the alternating electric field (from 0 to V_{max}), giving rise to a controlled charge-injection process during the induced molecular reorientation of the LC sample. In this case the value for the anchoring energy (A) can be calculated using equation (8), where V_S is obtained by using the standard SVM extrapolation method, but the effective voltage (V_{eff}) in the ellipticity vs. inverse applied effective voltage is now given by:

$$V_{eff} = \sqrt{V_{AC}^2 + V_0^2} \tag{9}.$$

The results that were obtained for the Soft and Hard rubbing of the PANI substrates are presented in the Figure 4 and 5, respectively.

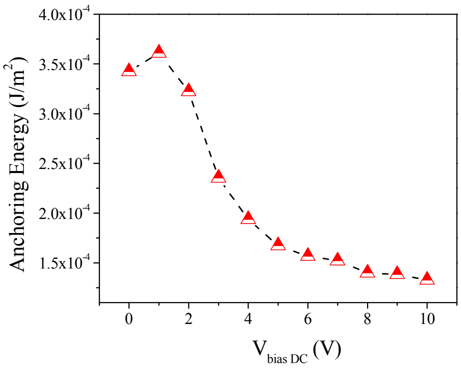

Fig. 4. Anchoring energy dependence on the applied bias voltage in the case of the Soft rubbed LC sample. The maximum value for the anchoring energy is around 3.6 x 10^{-4} J/m^2.

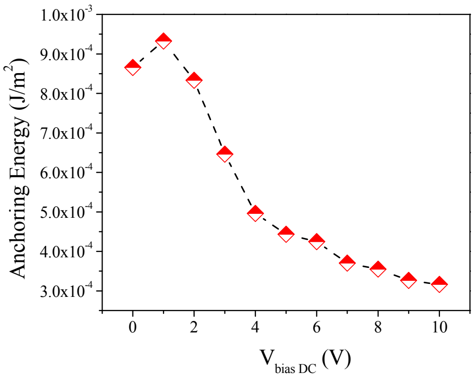

Fig. 5. Anchoring energy dependence on the applied bias voltage in the case of the Hard rubbed LC sample. The maximum value obtained for the anchoring energy is about 9.3 x 10^{-4} J/m^2.

By analyzing the figures one observes that the variation of the surface anchoring energy vs. the superimposed bias DC voltage has a certain trend. This dependence is very interesting and gives the possibility of controlling the surface anchoring energy properties by applying an external factor (i.e. DC bias voltage).

For low bias values we can notice a small increase in the anchoring energy, but upon application of a higher bias DC voltage the surface anchoring energy starts to decrease towards saturation values in the case of Soft (1.3×10^{-4} J/m^2) and Hard (3.1×10^{-4} J/m^2) rubbing. An explanation for this behavior can be given by taking into account the role played by the surface charge concentration from the PANI surface-liquid crystal interface [3]. The superimposed bias DC voltage is responsible of the surface charge buildup at the PANI-NLC interface. This particular phenomenon was previously observed in electro-optical cells having PANI boundary layers [2,3] and in samples with LC-oxide interfaces [29,30] where this charge accumulation generating an additional internal field was explained by the formation of a Debye double layer structure.

4. Conclusions

In the manuscript is presented a study concerning with the influence of the polyaniline boundary surfaces on the anchoring energy in nematic liquid crystal electro-optical cells. This analysis was accomplished by performing photopolarimetric investigations on cells having symmetric boundary layers of PANI (obtained via cold discharge plasma polymerization technique).

From the ellipticity vs inverse of the applied voltage behavior, by using a standard Saturation Voltage Method (SVM), we determined the saturation voltage and implicitly the anchoring energy values for two different sets of samples (having Soft and Hard rubbing boundary constraints). As expected, the highest value for the anchoring energy is obtained in the case of the hard rubbed PANI surfaces (approx 9×10^{-4} J/m^2).

Other observations emphasize the exciting behavior of the anchoring energy during the DC bias controlled charge buildup process, which reveals a limited inhibition in the switching mechanism. These results are very interesting from the technological point of view allowing for manufacturing sensitive NLC devices capable of changing in real-time the inner anchoring energy properties of the system. In addition, the obtained results are in good agreement with previous experiments and theoretical models present in the scientific literature involving similar materials and imposed boundary constraints.

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