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Anchoring properties of a nematic liquid crystal on anisotropic hydroxypropylcellulose films

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Thin solid films of hydroxypropylcellulose ($\sim 15\text{--}30\ \mu\text{m}$) prepared from liquid crystalline and isotropic aqueous solutions are used as liquid crystal alignment layers. Using the standard nematic liquid crystal 5CB we measured the interface properties of these solid films as a function of the polymer concentration in the aqueous precursor solution, expressed in terms of zenithal and azimuthal anchoring orientations and extrapolation lengths. The hydroxypropylcellulose thin films are found to induce a planar orientation of 5CB independently of the polymer concentration, with the alignment along the polymer backbone. The zenithal anchoring strength is found to be strong and essentially independent of the temperature far from the nematic–isotropic transition, with an extrapolation length $\xi_\theta \approx 50\ \text{nm}$. The zenithal anchoring becomes weaker near the nematic–isotropic transition, as expected. The azimuthal anchoring strength is found to be intermediately weak and strongly dependent on the polymer concentration, with an extrapolation length varying from $\xi_\phi \approx 250\ \text{nm}$ to $\xi_\phi \approx 500\ \text{nm}$. These films are particularly interesting since their surface topography and morphology may be tuned by varying a few parameters in the film preparation process, such as the polymer concentration in the aqueous solution.

1. Introduction

Polymeric liquid crystalline solutions submitted to shear can show unstable banded textures [1, 2], that may be locked within the polymer surface by evaporating the solvent [3]. In particular, hydroxypropylcellulose (HPC) thin films prepared in specific conditions exhibit different types of bands with tunable properties, depending on the shear rate and the polymer concentration of the precursor solution [4].

Previous studies showed that HPC films obtained from cholesteric solutions induce homogeneous alignment of liquid crystals (LCs) [5, 6]. It was also found that the homogeneous surface alignment is independent of the microscopic anisotropic grooves that may develop on the film surface [6]. The coating flow seems to induce high orientation of HPC molecules near the film surface, leading to LC alignment, even for films prepared from isotropic solutions.

In particular, atomic force microscopy (AFM) studies showed the existence of two types of band, with roughly perpendicular directions and with typical periods of

$\sim 2\text{--}5\ \mu\text{m}$ (intermediate bands) and $\sim 0.3\text{--}2\ \mu\text{m}$ (small bands) [4]. HPC films are particularly interesting as liquid crystal alignment layers [5], due to the presence of competing anchoring mechanisms [7], namely: (i) the van der Waals (VDW) interactions [8] between the HPC backbone, aligned along the shear direction, and the liquid crystal molecules; (ii) the surface topography anchoring contribution, generally described by the Berreman model [9].

The use of cellulose layers for electro-optical applications was introduced in 1982 [10]. Later in 1996 a different approach was proposed, specifically an optical cell produced by a rugose cellulose derivative film obtained from an isotropic solution was enclosed by two nematic liquid crystal layers and the set placed between two transparent conducting substrates [11]. These cells were found to achieve high transmissions with moderate switching voltages [12]. Cells prepared with a ferroelectric liquid crystal using cellulose derivative films as alignment layers were also reported [13]. In order to optimize and understand the electro-optical properties presented by these kinds of cells an important consideration is the study of the anchoring properties of the LC on the solid cellulose films.

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In the present work we measured the interfacial properties of HPC films with the nematic liquid crystal 4-cyano-4'-*n*-pentylbiphenyl (5CB), in terms of the zenithal (out of plane) and azimuthal (in plane) anchoring orientations and anchoring strengths.

2. Experimental

2.1. Alignment layers preparation

Different solutions of HPC (Aldrich 100 000 molecular weight) in water (30, 50, 60 and 65 wt %) were prepared at room temperature, followed by centrifugation to remove air bubbles. In this paper we use the abbreviation 50HPC (or 30HPC, 60HPC, 65HPC) for the films prepared from aqueous solutions of corresponding strength. Solid films were cast and sheared simultaneously on top of ITO (indium tin oxide) coated glass, using a calibrated casting knife with controlled shear rate of $5 \times 10^{-3} \text{ m s}^{-1}$. The films were dried at room temperature, and their thickness measured using a digital micrometer, with typical values varying between 15 and 30 μm . Depending on the preparation conditions the HPC films show three types of band, characterized by their orientation with respect to the shear direction, period and amplitude, with values summarized in table 1.

The detailed dependence of the two smaller bands on the processing conditions are described, using AFM, elsewhere [14, 4]. We note here that the larger bands were not previously observed by AFM, since they lie outside its standard observation range.

2.2. Zenithal and azimuthal anchoring orientations

Sample cells were prepared using two identical HPC films deposited on top of ITO-treated glass (with surface resistance $Rq \approx 20 \Omega/\text{sq}$). The use of symmetrical cells minimizes the contribution of distortions produced from non-symmetries of the liquid crystal alignment layers. Uniform cells were prepared with anti-parallel alignment. The use of anti-parallel aligned cells is necessary in order to eliminate distortions, in this way

Table 1. Periodic features of thin HPC films sheared from liquid crystalline solutions. L is the average period, H is the average peak-to-valley height, α is the average angle with respect to the shear direction. The exact values of periodicities 2 and 3 depend on the shear rate and polymer concentration of the precursor solution [4].

Periodicity	$L/\mu\text{m}$	H/nm	α/deg
1	~ 100	~ 3000	~ 0
2	2–5	70–100	~ 90
3	0.3–2	2–9	$\sim 8\text{--}30$

obtaining a uniform orientation of the liquid crystal [15]. The cells were assembled using mylar film spacers (thickness $\sim 20 \mu\text{m}$) and the thickness uniformity controlled by observing interference fringes from standard fluorescent light. Pressure was applied to obtain uniform thickness, and epoxy glue used to fix the cell thickness permanently. Using a standard optical interference method [11], the cell thickness was measured before the liquid crystal filling.

The cells were then filled with 5CB at 15 K above the nematic–isotropic transition temperature, in order to minimize any memory effects of the filling process, and cooled slowly (0.1 K min^{-1}) close to the transition. Measurements were performed under an optical microscope between crossed polarizers.

The azimuthal anchoring orientation was determined using a Berek compensator with a rotating crystal that produces an optical path difference δ_c between the two polarization directions. Placing the compensator at $\pm 45^\circ$ from the direction of the minimum in light transmission we have the addition position ($\delta_{\text{total}} = \delta_{\text{lc}} + \delta_c$) and the subtraction position ($\delta_{\text{total}} = \delta_{\text{lc}} - \delta_c$); thus it is possible to know the azimuthal direction of the liquid crystal molecules.

Using the same sample cells, we determined the zenithal anchoring angle (or pre-tilt) using the prism method [16], by measuring the total optical path difference δ_{total} in both normal and oblique incidence of light.

2.3. Zenithal anchoring strength

The zenithal anchoring strength, expressed in terms of zenithal extrapolation length, was determined by measuring the optical path difference δ_{total} as a function of the applied voltage V , using a local measurement previously reported [10]. The measurement of $\delta_{\text{lc}}(V_{\text{app}})$ enables the numerical determination of the liquid crystal average orientation along the cell and thus the zenithal extrapolation length ξ_θ . Applying the method for a range of voltages it is possible to use a stability criterion [10] (i.e. the anchoring strength is a property of the interface independent of the applied voltage, minimizing the dependence of external parameters, namely, the elastic and dielectric anisotropies of the liquid crystal).

We note that in this particular case where the alignment layer thickness is larger than the liquid crystal layer thickness, the voltage applied on the liquid crystal, V_{lc} is no longer the applied voltage V_{app} , but depends on the liquid crystal and HPC capacitances [17]. The HPC capacitance C_{hpc} is determined knowing that the charge is constant and by measuring the total capacitance at zero voltage and the applied voltage for

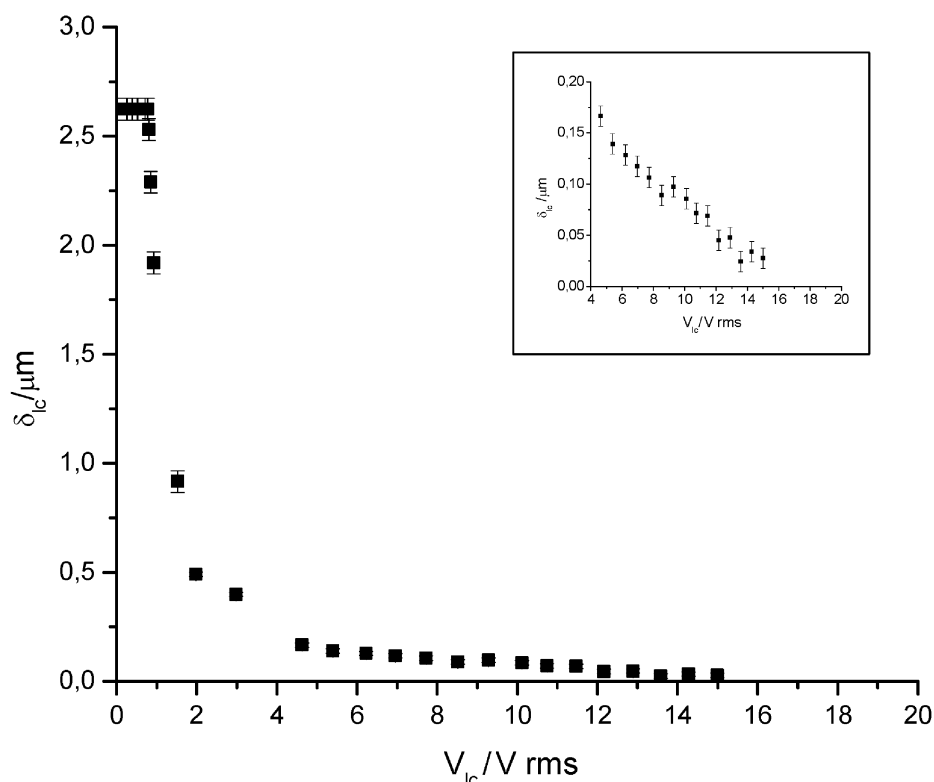


Figure 1. Optical path difference as a function of the applied voltage in a symmetric and uniform cell. The measurements are performed using the compound 5CB at 7 K below the nematic–isotropic transition temperature and 65HPC films. The Fréedericksz transition is clearly visible, confirming the planar anchoring of the interface. The raw data are used for the determination of the zenithal extrapolation length, disregarding the values to weak voltages.

the Fréedericksz transition. The liquid crystal capacitance is first estimated by considering all molecules aligned with the electric field, and finally C_{lc} is determined in the iteration loop of the measuring method of [10].

$$V_{lc} = V_{\text{appl}} \frac{C_{\text{hpc}}}{C_{\text{hpc}} + 2C_{lc}}. \quad (1)$$

2.4. Azimuthal anchoring strength

For the azimuthal anchoring strength measurements, we prepared wedge-shaped sample cells, with the HPC films placed at the upper and lower cell plates in an orthogonal configuration (90° twist). Cells were filled with 5CB at ~ 15 K above the nematic–isotropic transition temperature, and then cooled slowly (0.1 K min^{-1}) through the transition. All measurements of the azimuthal anchoring strength were performed ~ 1 h after the liquid crystal filling, observing by optical microscopy the light transmission through the twisted liquid crystal cell.

For regions with a large thickness, in the waveguide regime, the liquid crystal will follow the 90° twist. Decreasing the cell thickness, the liquid crystal director will deviate from its easy axis at both surfaces. The surface deviation angle φ is directly related to the azimuthal anchoring strength.

The light transmission is an oscillating function of different parameters, namely the light wavelength and the cell thickness. This oscillating behaviour is usually an obstacle for accurate measurements, but in our case we explore an interesting averaging effect when using white light [17]. For sufficiently thick cells ($d > 4 \mu\text{m}$), the white light transmission minimum is equivalent to the waveguide regime. We may then measure the surface deviation angle φ simply by determining the angle of the polarizer that corresponds to the minimum of white light transmission [13].

3. Results and discussion

3.1. Zenithal and Azimuthal Anchoring Orientations

The nematic liquid crystal is found to be aligned along the shear direction, independently of the polymer

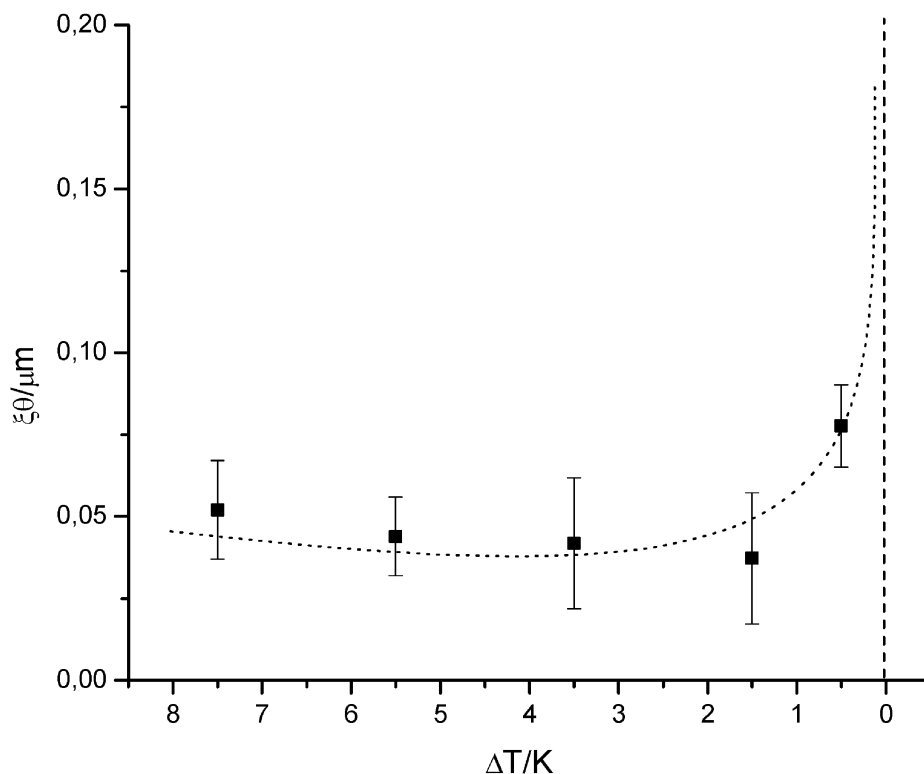


Figure 2. Zenithal extrapolation length as a function of the temperature. Results refer to the interface of 5CB with 65HPC films. Far from the nematic–isotropic transition, the anchoring is found to be essentially independent of the temperature, and rather strong, with an extrapolation length similar to that measured for the 5CB–Teflon interface.

concentration (30HPC, 50HPC, 60HPC, 65HPC). These findings are in agreement with the results published by Mori *et al.* [6], where this behaviour was explained by the flow-induced orientation of HPC chains at the film surface due to the long relaxation time of orientation.

This is a first indication that the azimuthal anchoring is dominated by the VDW interactions between the HPC backbone and the liquid crystal molecules. Due to the shear rate, the chiral liquid crystalline polymer becomes nematic and so the HPC backbone is aligned along the shear direction after the solvent evaporation [18].

3.2. Zenithal anchoring strength

Figure 1 shows the electro-optic measurements at 7 K below the nematic–isotropic transition ($\Delta T = 7 \text{ K}$) and for the 65HPC film. The Fréedericksz transition is clearly visible by the sharp decrease of the optical path difference δ , when increasing the applied voltage ($V_{\text{th}} = 0.9 \text{ V}$). The zenithal extrapolation length is measured using only the experimental data above 6 V, discarding the values close to the Fréedericksz

transition, where the sample is critically sensitive to small perturbations [10].

Figure 2 shows the zenithal extrapolation length as a function of the cell temperature, for the 65HPC film. The anchoring is found to be strong, with an extrapolation length $\xi_\theta \approx 50 \pm 20 \text{ nm}$, similar to the zenithal anchoring strength measured for the Teflon–5CB interface [10]. Far from the nematic–isotropic transition, the anchoring is found to be almost independent of the cell temperature. Close to the transition, the anchoring strength is found to be weaker, in agreement with a general trend already reported [19, 20].

3.3. Azimuthal anchoring strength

Figure 3 shows the surface deviation angle φ as a function of the cell thickness d , for the 60HPC film at 7.5 K below the nematic–isotropic transition. The dotted line indicates the fit of the experimental data, using the Rapini–Papoular approximation [21]:

$$\xi_\varphi = \frac{d \sin 2\varphi}{\pi - 4\varphi}. \quad (2)$$

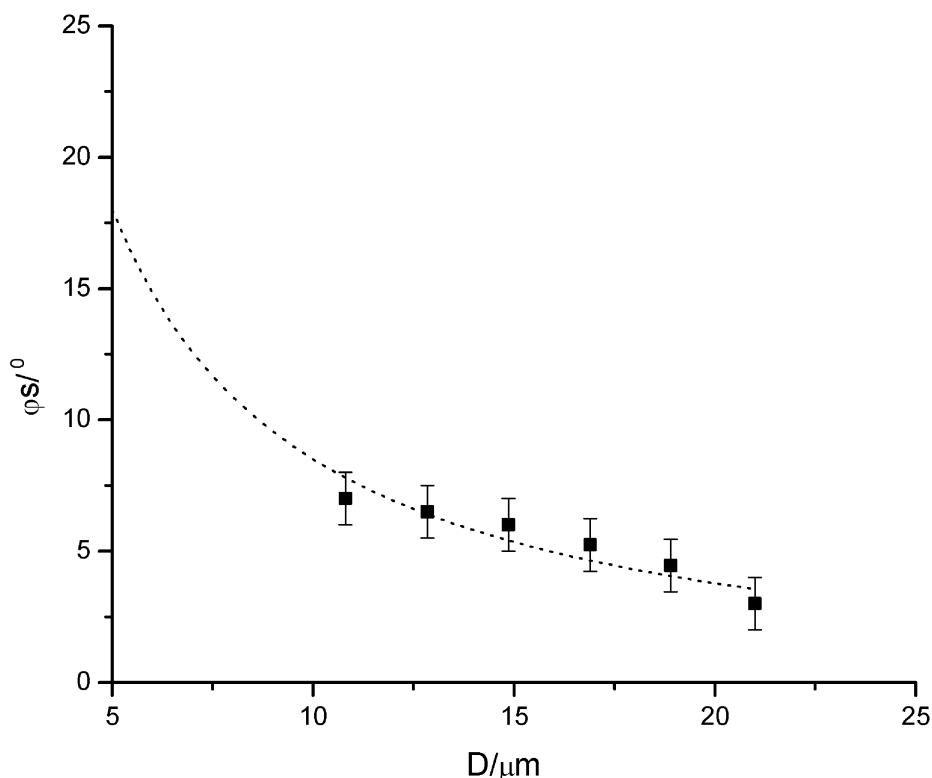


Figure 3. Azimuthal surface deviation angle as a function of the cell thickness, in a twisted wedge cell with 60HPC films. The azimuthal extrapolation length is determined from these results using the Rapini–Papoular approximation (dotted line).

The corresponding azimuthal extrapolation length is found to be $\xi_\phi \sim 0.5 \mu\text{m}$. This result shows an intermediately weak azimuthal anchoring, similar to the one measured for the interface Teflon–5CB (results obtained using the same method and similar temperatures) [23].

Figure 4 shows the measurements of the azimuthal extrapolation length ξ_ϕ as a function of the HPC concentration in the polymer precursor solution. The azimuthal anchoring strength is found to increase with the HPC concentration and this fact is most probably due to the stronger orientational order of the HPC backbone [23].

Using the surface parameters of the HPC films (table 1), we may evaluate the topographical contribution to the anchoring strength, using the Berreman model [9]:

$$\xi_{\phi\text{-Berr}} \approx \frac{1}{2\pi^3} A^{-2} L^3 \quad (3)$$

where A and L are the amplitude and period of the bands, respectively. The calculated values for the azimuthal extrapolation length are at least one order of magnitude higher than the experimental results. We may conclude that the contribution of the surface topography to the azimuthal anchoring strength is

negligible. It is then dominated by the anisotropic VDW interactions between the polymer backbone and the 5CB molecules.

4. Conclusion

Hydroxypropylcellulose thin films have been used as liquid crystal alignment layers. The anchoring properties of these films, expressed in terms of the zenithal and azimuthal anchoring strengths and orientations were measured as a function of the polymer concentration of the precursor solution. The zenithal anchoring is found to be planar and rather strong, similar to that measured for the Teflon–5CB interface. The azimuthal anchoring is found to be intermediately weak, and strongly dependent on the polymer concentration of the HPC precursor solution. Using the Berreman model, we evaluated the surface topography contribution to the azimuthal anchoring. We conclude that this contribution is negligible and that the azimuthal anchoring is dominated by anisotropic van der Waals interactions between the HPC backbone and the nematic liquid crystal molecules.

The fine tuning of the surface properties, by varying the preparation process of the solid films prepared from

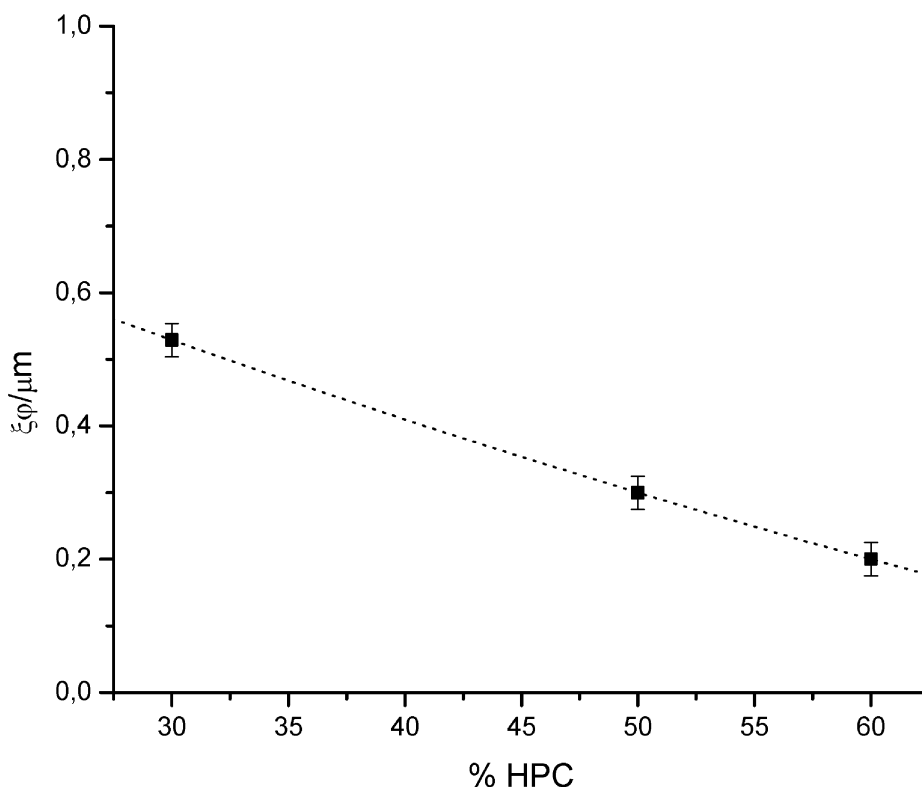


Figure 4. Azimuthal extrapolation length of the interface 5CB–HPC, as a function of the polymer concentration of the precursor solution. The azimuthal anchoring is found to be intermediately weak, and strongly dependent on the polymer concentration (the dotted line is a guide to the eye).

aqueous solutions of HPC, opens new perspectives on tailoring liquid crystal alignment layers. These films are particularly interesting for liquid crystal systems since their surface topography may be tuned by changing the polymer concentration in the starting aqueous solution. In the future, the rational tuning of these anchoring contributions might be exploited for liquid crystal devices.

Acknowledgments

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