Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Orientation effects of PTFE nanolayers upon the nematic 5CB

Y. Marinov[a]; S. D'Elia[b]; L. Todorova[a]; A. G. Petrov[a]; C. Versace[b]; N. Scaramuzza[b]
[a] Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia 1784, Bulgaria [b] LICRYL-INFM and Center of Excellence CEMIF.CAL, Department of Physics, University of Calabria, Via P. Bucci, Italy

To cite this Article Marinov, Y. , D'Elia, S. , Todorova, L. , Petrov, A. G. , Versace, C. and Scaramuzza, N.(2006) 'Orientation effects of PTFE nanolayers upon the nematic 5CB', Liquid Crystals, 33: 10, 1219 — 1225

To link to this Article: DOI: 10.1080/02678290601010923

URL: http://dx.doi.org/10.1080/02678290601010923

Liquid Crystals, Vol. 33, No. 10, October 2006, 1219–1225

Orientation effects of PTFE nanolayers upon the nematic 5CB

Y. MARINOV†, S. D'ELIA‡, L. TODOROVA†, A.G. PETROV†, C. VERSACE‡ and N. SCARAMUZZA*‡
†Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia 1784, Bulgaria
‡LICRYL-INFM and Center of Excellence CEMIF.CAL, Department of Physics, University of Calabria, Via P. Bucci, Cubo 33B, I-87036 Rende (CS), Italy

(*Received 12 December 2005; in final form 7 August 2006; accepted 15 August 2006*)

Planar nematic layers of 5CB oriented by 'sliding on' nanolayers of PTFE were studied by electro-optic methods. Deposited layers were characterized by AFM and spectroscopic ellipsometry. It was found that at 100°C presumably single PTFE chains (4 nm thickness) are deposited. By ellipsometry measurements *c.* 0.1° pretilt angle of the nematic layer was determined. In planar nematic layers low frequency flexoelectric splay oscillations were excited. An overall 1/*f* shape of the oscillation spectrum was found in the range 1 to 1000 Hz, giving no evidence of a surface viscosity effect in this range.

1. Introduction

Producing highly oriented liquid crystal films is important in many electro-optical applications such as displays, temperature sensors optical processing, etc. A wide variety of techniques has been developed to promote LC orientation. One common technique makes use of rubbed oriented layers of different kinds of organic materials. Treated surfaces affect the orientation phenomena of the LC–solid interface, in a process known as anchoring. The anchoring properties are not easy to predict since they involve a wide variety of physical properties ranging from intermolecular and surface energies to flexoelectricity and adsorption–desorption processes. Recently a new highly versatile method for orienting liquid crystals was demonstrated [1]. It consists in mechanical deposition of a thin crystal-like film of poly(tetrafluoroethylene) (PTFE) on a smooth glass substrate. In fact PTFE induces homogeneous alignment of the liquid crystals. This method is innovative with respect to the enabling of a new generation of fast switchable surface driven displays, nanodevice elements and nanoassembly for molecular electronics.

PTFE layers are also interesting candidates for testing the flexoelectricity of nematics. Flexoelectric effects provide linear coupling between an electric field and the nematic director orientation. Due to the flexoelectricity (representing a LC analogue of piezoelectricity) [2], an applied field not only orients the nematic director along the field direction but also causes a slight fan-like distortion, called splay, of the director field. The most important aspect of this effect is that positive and negative voltages cause opposite splays, thus producing a first harmonic electro-optic response. Flexoelectric deformations depend strongly on the boundary conditions. Our recently developed flexoelectric spectroscopy [3] provides a fine tool for analysing the orientational surface viscosity, thus revealing important dynamical aspects of the interaction between a nematic liquid crystal and a solid surface.

The purpose of the present work is to present some new results on liquid crystal orientation alignment promoted by nanostructured PTFE films, as studied by AFM, polarizing videomicroscopy and elipsometry. In addition, the flexoelectric spectra of a planar nematic 5CB liquid crystal film, oriented by an ultrathin PTFE layer, were recorded by the method of flexoelectric spectroscopy. In the frequency domain below 1000 Hz the flexoelectric measurements provide evidence that surface viscosity for planar anchoring is lower than for homeotropic anchoring.

2. Materials And Methods

PTFE (Teflon™) nanolayers were deposited on clean glass plates by the method of rubbing a preheated glass by a piece of Teflon [1]. A scheme of the deposition set-up is shown in figure 1. This frictional transfer method consists of using smooth microscope glass slides as hot substrates; PTFE film is then deposited by sliding a solid PTFE bar against the preheated substrate surface at 100°C and a constant pressure of 130 N cm^{-2}, and at a sliding rate of 0.2 cm s^{-1}. Using this technique, the

---

*Corresponding author. Email: scaramuzza@fis.unical.it

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290601010923

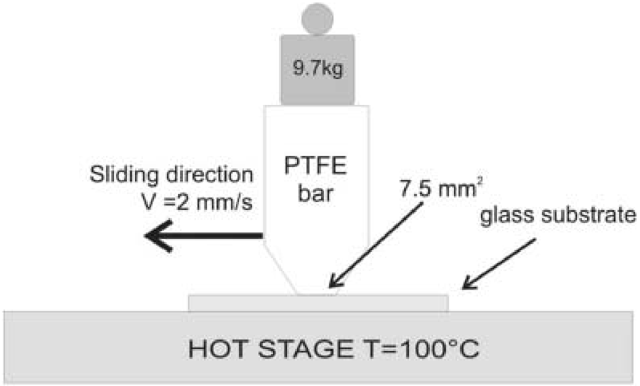


Figure 1. Set-up of the 'sliding on' method for the coating of substrates by thin PTFE films.

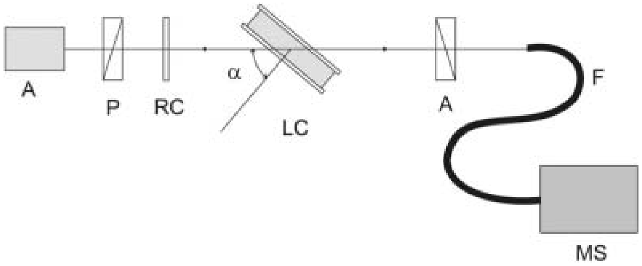


Figure 2. Ellipsometer set-up: A=xenon lamp; P=polarizer; RC=rotating compensator; LC=planar liquid crystal cell; A=analyser; F=multimode optical fibre; MS=multichannel spectrometer.

chain axes of the PTFE macromolecules are forced to orient in the sliding direction.

Deposited layers were characterized by AFM (PERCEPTION, Assing) in the no contact mode. The layers were further characterized by spectroscopic ellipsometry. Spectra of the ellipsometry angles Ψ and Δ for deposited layers were acquired by a J.A Woollam M2000 F rotating compensator ellipsometer in the 0.3–1 μm range. Ellipsometric spectra (SE) were modelled by an optical model based on the Bruggman effective medium approximation (BEMA): This procedure models the sample by layer stacks; each layer can be completely described by its thickness and its complex dielectric function, which are determined by a fitting routine (Levenberg–Marquardt).

Cells with PTFE layers over ITO layers were assembled with the glass plates facing their PTFE-coated sides in an antiparallel configuration and separated by 5 μm Mylar spacers. The cells were filled with the LC 5CB (Merck, T_c=35°C) by capillarity in the isotropic phase and then slowly cooled to room temperature. In this way uniform planar alignment of the LC imposed by PTFE-treated surfaces was achieved.

The pretilt angle of the nematic director was measured ellipsometrically in transmitted mode (see figure 2). These measurements were performed by rotating the LC cell with respect to the direction of incidence of the ellipsometer light beam. Firstly, the planar LC cell was carefully aligned to have the nematic director on the incidence plane, then the optical phase retardation,

$$\Delta = \frac{2\pi}{\lambda}(n_{\text{eff}} - n_o)d \tag{1}$$

was measured as function of the angle of incidence α of the ellipsometer light beam. In equation (1), λ is the wavelength of the light beam, d is the thickness of the cell, and n_o and n_{eff} are respectively the ordinary refractive index and the effective refractive index experienced by the extraordinary ray propagating trough the cell:

$$n_{\text{eff}}(\theta) = \left(\frac{n_0 n_e}{n_0^2 \sin^2\theta + n_e^2 \cos^2\theta}\right)^{\frac{1}{2}}. \tag{2}$$

The value of Δ which corresponds to the maximum optical path $(n_{\text{eff}} - n_o)d$ is measured when the incident beam is exactly at 90° with respect to the optical axes of the sample measured. If the pretilt angle is zero this condition should be reached at normal incidence (α=0°), otherwise the director pretilt angle is given directly by the angle α_m which correspond to the extreme, either maximum or minimum, of Δ.

Finally, cells with PTFE layers only and no ITO layer were assembled with the glass plates facing their PTFE-coated sides in an antiparallel configuration and separated by copper foils of 75 μm thickness serving as electrodes; the electrode distance was 2 mm. Cells were filled with 5CB in the same manner as before, they were then placed between crossed polarizers. An electric field parallel to the cell plates directed at 45° with respect to the crossed polarizers was applied to the nematic cell by means of the copper spacers. The optical appearance of the layers was imaged using a CCD colour camera TCM 112 (GDS Elettronica) and recorded on a computer.

The frequency dependence of the transmitted light modulation was obtained by means of a flexoelectric spectrometer [3, 4] in the range 1–1000 Hz. We measured the first harmonic of the intensity of flexoelectrically modulated light transmitted through the planar nematic layer, following a slow frequency sweep provided by a computer-interfaced lock-in amplifier (SR830).

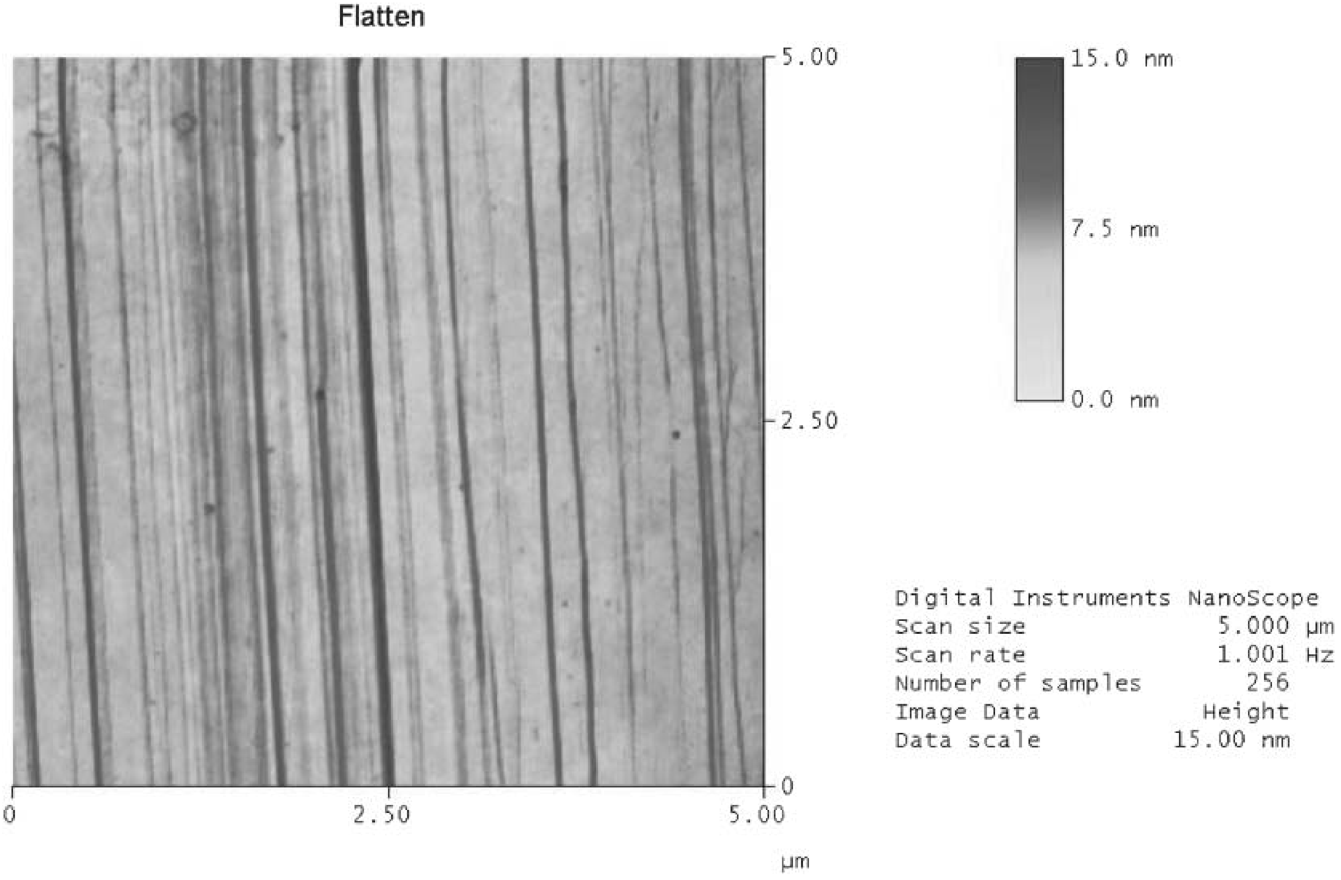
Theoretically, the problem for the description of these oscillations was solved earlier [4]. Basically, the amplitude of the 1st harmonic of modulated light decreases with frequency as $I(\omega)\propto\omega^{-1}$, due to the frequency decrease of the penetration depth of the director oscillations induced by surface flexoelectric torques. This frequency decrease is related to the bulk dissipation of orientational energy governed by the bulk viscosity γ_1. However, when the surface dissipation of orientational energy governed by the surface viscosity κ becomes comparable to the bulk dissipation, a cross-over to a steeper frequency decrease, $I(\omega)\propto\omega^{-3/2}$ takes place [3]. This is expected above a cross-over frequency [4]:

$$v^* = K_{11}\gamma_1/\pi\kappa^2. \tag{3}$$

3. Results and discussion

Deposited PTFE layers were first characterized by AFM. It was found that elevated temperature produces deposited structures of a substantial thickness, while at 100°C presumably single PTFE chains (4 nm thickness) are deposited. In the last case well oriented planar layers with some pretilt of nematic PCB are produced. Figure 3 shows an AFM image, with a 5 × 5 µm field of view, of a highly oriented PTFE film deposited onto a glass surface. The film thickness variation was estimated using an indicator bar, shown on the right of the figure. The PTFE film appears to have typicale row-like structure with PTFE macromolecules oriented in the sliding direction. The mean value of the film height distribution was calculated along the line perpendicular to the polymer layer grooves (figure 3). The average film thickness was determined to be about 4 nm. The adjacent spacing measured between ridges ranging from 0.01 to 0.1 µm and ridges as high as 15 nm above the average film thickness were occasionally observed.

As mentioned above, ellipsometric spectra were modelled by an optical model based on the Bruggman effective medium approximation (BEMA). This procedure models the sample by layer stack, where each layer



```
Digital Instruments NanoScope
Scan size              5.000 µm
Scan rate              1.001 Hz
Number of samples        256
Image Data             Height
Data scale           15.00 nm
```

Figure 3. AFM image of a highly oriented PTFE film deposited on glass substrate with a 5 × 5 µm field of view. The unidirectional film grooves are oriented in the vertical direction of the image.

is completely described by its thickness and its complex dielectric function, determined by a fitting routine (Levenberg–Marquardt).

3.1. *ITO model*

At first we obtained a reliable model of the ITO–glass substrates. We obtained values of the refractive index and extinction coefficient (which represents the damping of an EM wave inside the material) of the float glass from the manufacturer (Balzers) and retained these values in the modelling procedure. The ITO films were modelled by the superposition of two layers (see figure 4), each of them described by a combination of N Lorenz oscillators by the relation:

$$\varepsilon(E)=\varepsilon_{\infty}+\sum_{k=1}^{N}\frac{A_k}{E_k^2-E^2-\mathrm{i}\Gamma_i E} \tag{4}$$

where E is the energy of the incident photons, ε_{∞} is the real part of the dielectric function when $E\longrightarrow\infty$, A_k is the strength expressed in eV^2, Γ_k is the broadening in eV and E_k is the central energy of the k-th oscillator. Finally the estimated values of the optical constant spectra were refined by fitting every single wavelength. Figure 5 demonstrates the variable angle ellipsometric spectra of the ITO coated glass substrates. In Figures 6 (*a*) and 6 (*b*) we show the dispersion curves of the optical constants obtained.

3.2. *PTFE model*

In figure 7 we represent the BEMA model of the PTFE-coated substrates. The film was modelled as a Cauchy layer according to:

$$n(\lambda)\cong A+\frac{B}{\lambda^2}+\frac{C}{\lambda^4}. \tag{5}$$

Figure 8 demonstrates the variable angle ellipsometric spectra of the ITO and PTFE-coated glass substrates. In Figure 9 we show the dispersion curves of the optical constants n and k for the deposited PTFE layer.

In Figure 10 we show the result of a measurement of the optical dephasing Δ vs. the incidence angle α (glass with ITO). To minimize systematic errors, the measurement was repeated for two different orientation of the cell obtaining the curves (*a*) and (*b*). In the case of curve (*b*) the orientation of the cell was rotated 180° to take $\mathbf{n}$ into $-\mathbf{n}$. The two curves should be symmetric around $\alpha=0°$. In our case the two minima are symmetric around the angle 1.3°; the discrepancy can be attributed mostly to a parallelism error between the glass surfaces of the LC cell. We can thus estimate that the pretilt angle of the molecular director is about 0.1°, i.e. (1.4°–1.2°)/2; this value is consistent with a report of tilt angle measurement of some nematics on Teflon [5]. The typical values reported in [5] there are less then 2° of arc; the authors emphasized the non-polar nature of PTFE, which is sensitive only to London-like interactions.

Figure 4. Bruggman effective medium approximation (BEMA) model of the Balzers ITO-coated glass substrates. The ITO films were modelled by the superposition of two layers, each described by a combination of N Lorenz oscillators.

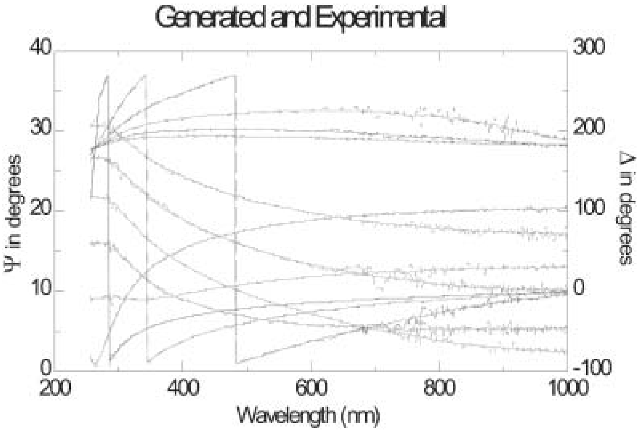


Figure 5. Variable angle ellipsometric spectra of the ITO coated glass substrates. Experimental and simulated ellipsometric angles Δ and Ψ are shown for different incidence angle (50°–75°).

Flexoelectric measurements were performed using nematic cells with reverse pretilt and the application of an in-plane electric field along the director. Flexoelectric oscillations in these pre-splayed cells were then observed under low frequency a.c. field excitation. The existing pretilt, although small, creates a static splay deformation over which the surface torque-induced flexo-oscillations are superimposed. In figure 11 we show the 1st harmonic amplitude vs. frequency spectra of these oscillations for two samples of the nematic 5CB anchored on PTFE nano-layers at room temperature. The shape of the spectra closely follow the theoretical prediction $I(\omega)\propto\omega^{-1}$; this is clear from the fit curve. An overall $1/\omega$ shape of the spectrum was found in the range 1 to 1000 Hz, giving no evidence of a surface viscosity effect in this range. The plot clearly shows that in the frequency domain under consideration we do not approach the viscous properties of the sub-surface nematic layer. In comparison with spectra obtained

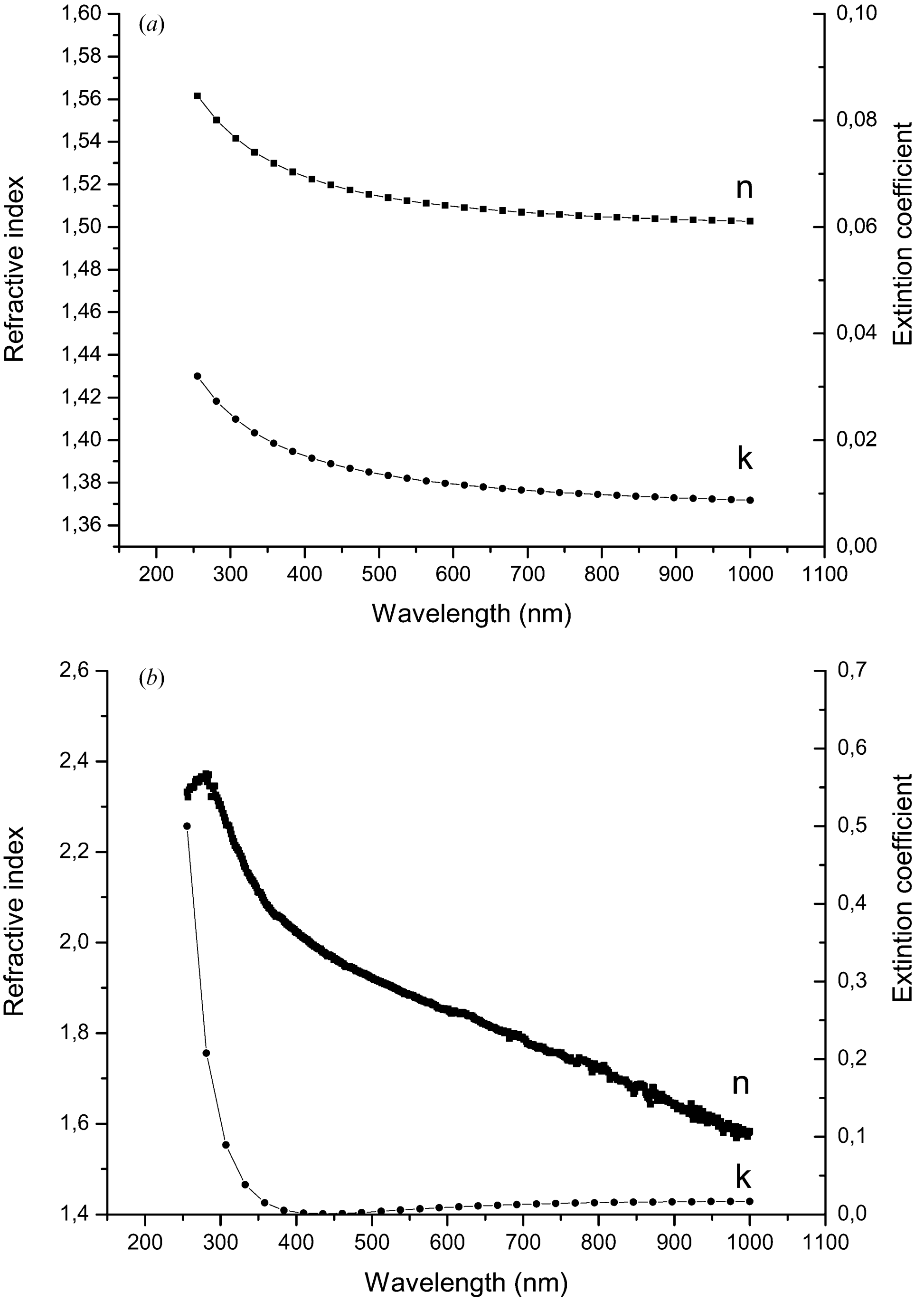


Figure 6. (*a*) Spectra of the optical constants *n* and *k* of the soda lime glass. (*a*) Spectra of the optical constants *n* and *k* of the ITO electrodes.

for homeotropic layers [4] no frequency cross-over was observed with the PTFE orienting layer. This result implies shifting of surface the dissipation of orientational energy to the higher frequency range. The increase in the cross-over frequency, equation (3), indicates a smaller surface viscosity for planar anchoring as compared with homeotropic anchoring [4].

4. Conclusion

We have studied the orientational effects in planar nematic 5CB films oriented by highly nanostructured PTFE monolayers by means of optical polarizing microscopy, ellipsometry, AFM-nanoscopy and flexoelectric spectroscopy. Combining these methods

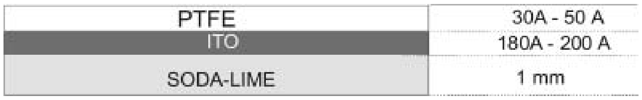


Figure 7. BEMA model of the PTFE coated substrates.

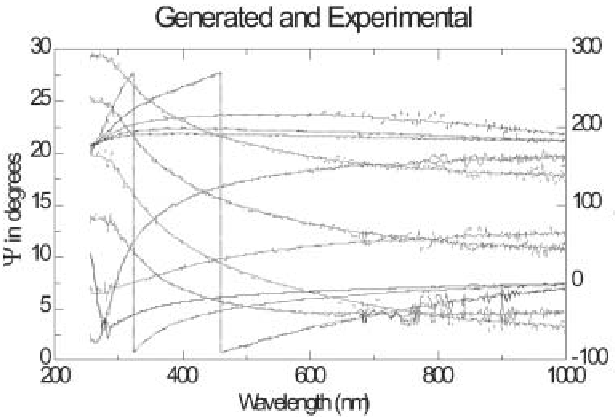


Figure 8. Variable angle ellipsometric spectra of the ITO- and PTFE-coated substrates. Experimental and simulated ellipsometric angles Δ and Ψ are shown for different incidence angles (in the range 50°–75°).

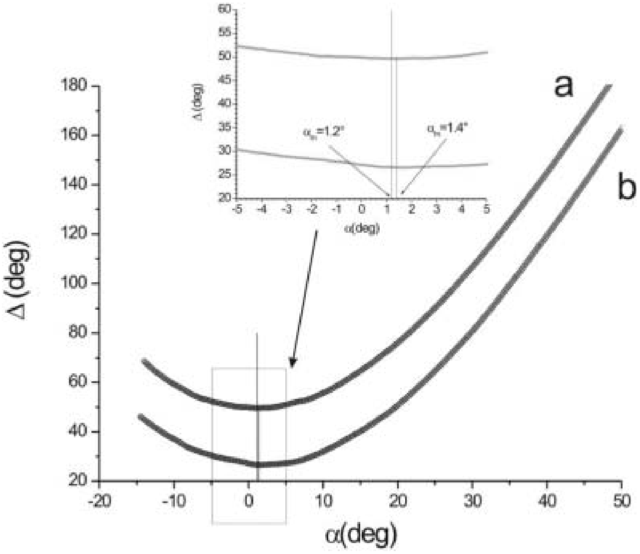


Figure 10. Determination of the NLC pretilt angle α_m; the two curves Δ (α) refer to the orientation $\pm 180°$ of the nematic director lying in the incidence plane. The measured value should be symmetric around $\alpha=0°$, the discrepancy can be attributed mostly to a small divergence angle between the glass surfaces of the LC cell.

provides a tool fully to characterize the orientational effects in a PTFE-oriented 5CB nematic film. The flexoelectric spectroscopy allowed characterization of the dynamic surface structure of the nematic in terms of surface viscosity.

Flexoelectric oscillations generated under planar anchoring provided no evidence of a surface viscosity

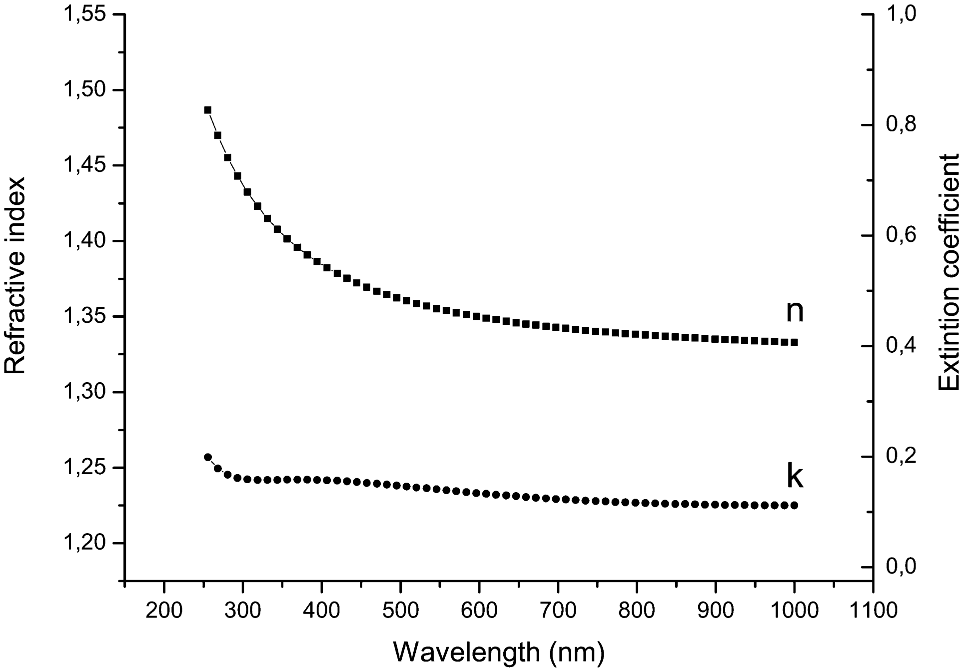


Figure 9. Spectra of the optical constants *n* and *k* of the deposited PTFE.

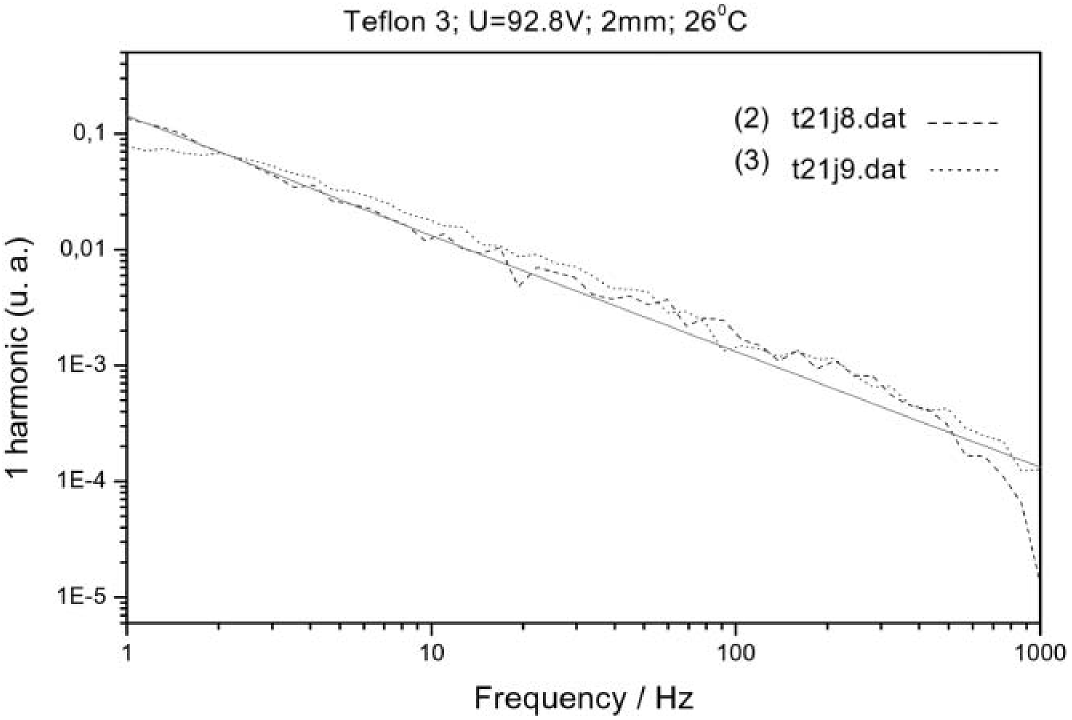


Figure 11. Frequency dependence of the first harmonic of flexo-electrically modulated transmitted light through a planar nematic layer of 5CB for two different samples. Layer thickness is 75 µm, electrode distance is 2 mm; planar orientation by PTFE layers (sliding deposition at 100°C), voltage 90 V_{ac}.

effect in the frequency range 1 to 1000 Hz, suggesting a relatively low value of surface rotational viscosity as compared with the homeotropic case [3, 4]. The experimental results have confirmed the planar orientation of 5CB, and flexoelectric spectra are in agreement with the flexoelectric spectroscopy theory related to the surface viscosity.

Acknowledgements

This study was performed in the framework of a CNR-BAS joint project. The authors are indebted to M. P. De Santo for AFM characterization and to L. M. Blinov and H. Hinov for helpful discussions.

References

[1] J.C. Wittmann, P. Smith. *Nature*, **352**, 414 (1991).
[2] R.B. Meyer. *Phys. Rev. Lett.*, **22**, 918 (1969).
[3] A.G. Petrov, A.Th. Ionescu, C. Versace, N. Scaramuzza. *Liq. Cryst.*, **19**, 169 (1995).
[4] Y. Marinov, N. Shonova, C. Versace, A.G. Petrov. *Mol. Cryst. liq. Cryst.*, **329**, 1145 (1999).
[5] P. Hubert, H. Dreyfus, D. Guillon, Y. Galerne. *J. Phys. II Fr.*, **5**, 1371 (1995).