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Rubbing-induced charge domains observed by electrostatic force microscopy: effect on liquid crystal alignment

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The rubbing of polymer-coated substrates is one of the most frequently used techniques for liquid crystal alignment. However, the aligning mechanisms are not completely understood. The influence of friction charges induced by the rubbing process has been taken into account in theoretical publications. In this work we investigate the rubbing-induced charge domains of three polymers (PMMA, PI and PVA) with the electrostatic force microscopy technique, which allows the simultaneous determination of the surface topography and electrostatic potential. We observed a large intensity of the potential for the PMMA substrate, whereas no charge domains were observed for PVA. In addition, we followed the time evolution of the surface charge domains, and surprisingly after five days the charges were still present with a small reduction of intesity. Using polarizing optical microscopy we studied the influence of the charge domains on the LC aligning properties.

1. Introduction

The use of liquid crystals (LCs) in technological applications requires these materials to be confined between specially treated substrates. A good performance of these devices is generally achieved by a controlled uniform alignment of the LC molecules at the boundary surfaces that propagates into the bulk [1]. A large number of methods have been proposed for obtaining such surface alignment, but no consensus has been reached with regard to the mechanism involved in the molecular orientation on the treated surfaces [2, 3]. Nevertheless, it is commonly accepted that the molecular orientation of nematic liquid crystals may depend mainly on two distinct factors: (i) physicochemical interactions such as hydrogen bonding, van der Waals interactions, or dipole–dipole interactions between the liquid crystal molecules and the substrate [4, 5]; and (ii) the elastic interactions due to the surface geometrical shape [6]. The former interactions may be dominant in the case of polymer aligning surfaces that give rise to parallel, perpendicular or tilted alignment. The elastic interactions are merely involved when microgrooves are created in the aligning surface. In most cases, both types of interaction may be simultaneously present at the surface; the LC alignment then results from an alignment competition between these surface attractors [7].

Due to its simplicity, rubbing of polymeric-coated substrates is one of the most common method applied to obtain LC alignment. Many workers have studied a large number of polymers as well as the material used to perform the rubbing process; the aligning properties are discussed and experimentally determined [1, 8–10]. Theoretical work has suggested that friction charges created by the rubbing process may contribute to the nematic molecular alignment [11]. The authors considered the coupling of the LC molecular dipole and the electric field generated by static electric charges, dependent on the surface topography. Experimentally, absortion of negative charge was observed on rubbed polyimide layers by electric force microscopy (EFM) [12]. Recently, other authors investigated theoretically the effect of absorbed ions at the surface and the resulting electrical potential (due to ionic impurities of the medium) to the anchoring properties of a LC sample [13, 14]. In both cases, the

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electric field resulting from the surface charge density seems to destabilize the LC alignment in the bulk, depending on the LC dielectric anisotropy sign, and contributes also to the effective anchoring energy.

In this work, we used the EFM technique to investigate the presence of surface charge domains induced by the rubbing process on different polymeric substrates: poly(methyl methacrylate) (PMMA), polyimide (PI) and polyvinyl alcohol (PVA), well known polymers for LC aligning surfaces. We studied the influence of the number of rubbings on the topography of the surface, on the surface electrostatic potential (generated by the static induced charge domains) and on the final orientation induced in the LC medium.

2. Experimental

2.1. *Electrostatic force microscopy*

Atomic force microscopy (AFM) is a technique used to image the surface topography of samples. EFM is a modified non-contact AFM. A d.c. voltage ($V_{\mathrm{d.c.}}$) and an a.c. voltage ($V_{\mathrm{a.c.}}$ at a frequency f) are applied between the conductive tip and the sample. During the scanning, the lock-in amplifier selects from the photodiode signal the part that vibrates at the fundamental frequency f. The signal is sent inside the microscope and processed, so that it is possible to visualize simultaneously the topographical signal and the signal related to the electrostatic force at frequency f.

The EFM measurements were performed by a Nanoscope IIIa (Digital Instruments) in taping mode, at 1.0 Hz scanning rate and 256 × 256 lines (see figure 1). We used tips made of silicon, and covered with platinum-iridium (Pt-Ir) from Nanosensors.

2.2. *Substrate preparation*

The substrates were glass plates coated with ITO, a transparent conductive material needed to give electrical contact between the microscope tip and substrate. Before any specific surface treatment the plates were carefully cleaned and dried.

The PMMA ($[-CH_2C(CH_3)(CO_2CH_3)-]_n$) and PVA ($[-CH_2CH(OH)-]_n$) were obtained from Aldrich; the polyimide Pyralin PI2555(PI) was obtained from HD Microsystems, it is a commercial product and the precise structure is not available. The polymers were dissolved at 2 wt % concentration in suitable solvents obtained from Aldrich: chloroform for the PMMA and PVA; 1-methyl-2-pyrrolidone (NMP) for the PI. All products were used without further purification. The PMMA and PVA, solutions were sonicated at 30°C for 20 min; the PI solution was filtered through a P4 ceramic filter. The final solutions were drawn by spin coating (3000 rpm) on the glass plates and baked at 80°C for one hour. The film thickness obtained was about 200–300 nm.

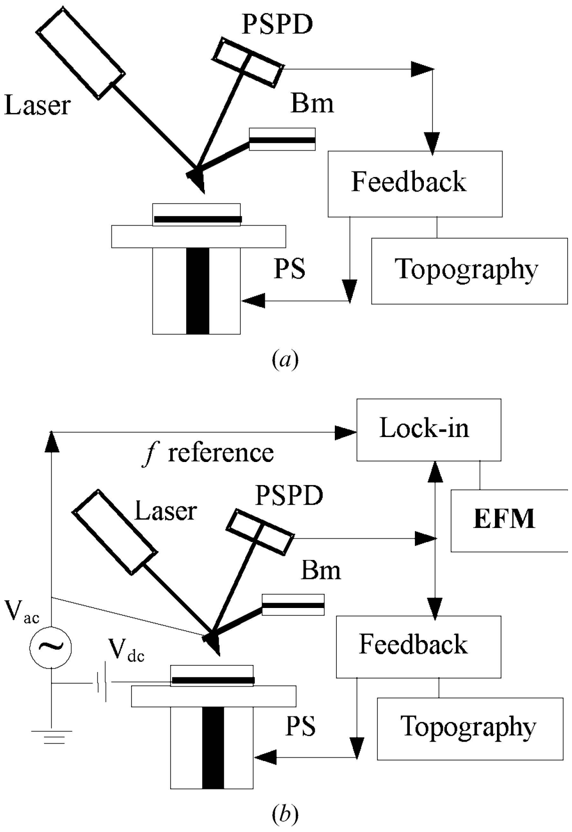


Figure 1. Schematic representation of (*a*) AFM, (*b*) EFM. Bm = bimorph, PSPD = position sensitive photodiode, PS = piezoelectric scanner.

The rubbing process was performed manually with a soft velvet cloth, just before the EFM measurements. We controlled the pressure and the number of times the process was performed. Each polymer was rubbed with different pieces of velvet to avoid contamination of the surfaces.

3. Results

As presented above, the EFM technique allows the determination of the surface topography and the electrostatic potential simultaneously. Therefore, in all the following figures, it is possible to observe the topography image on the lefthand side and the corresponding electrostatic potential on the right. The z scale for the topographic image is related to the height, given in nanometers (nm), whereas, for the electrostatic image, z is given in Volts (V) and corresponds to the surface electrostatic potential.

Initially, we measured the PMMA surface without rubbing and, as expected, neither topographic deformation nor electrostatic charge domains were observed, see figure 2(*a*). In the sequence, the sample was removed from the microscope, rubbed once and placed again in

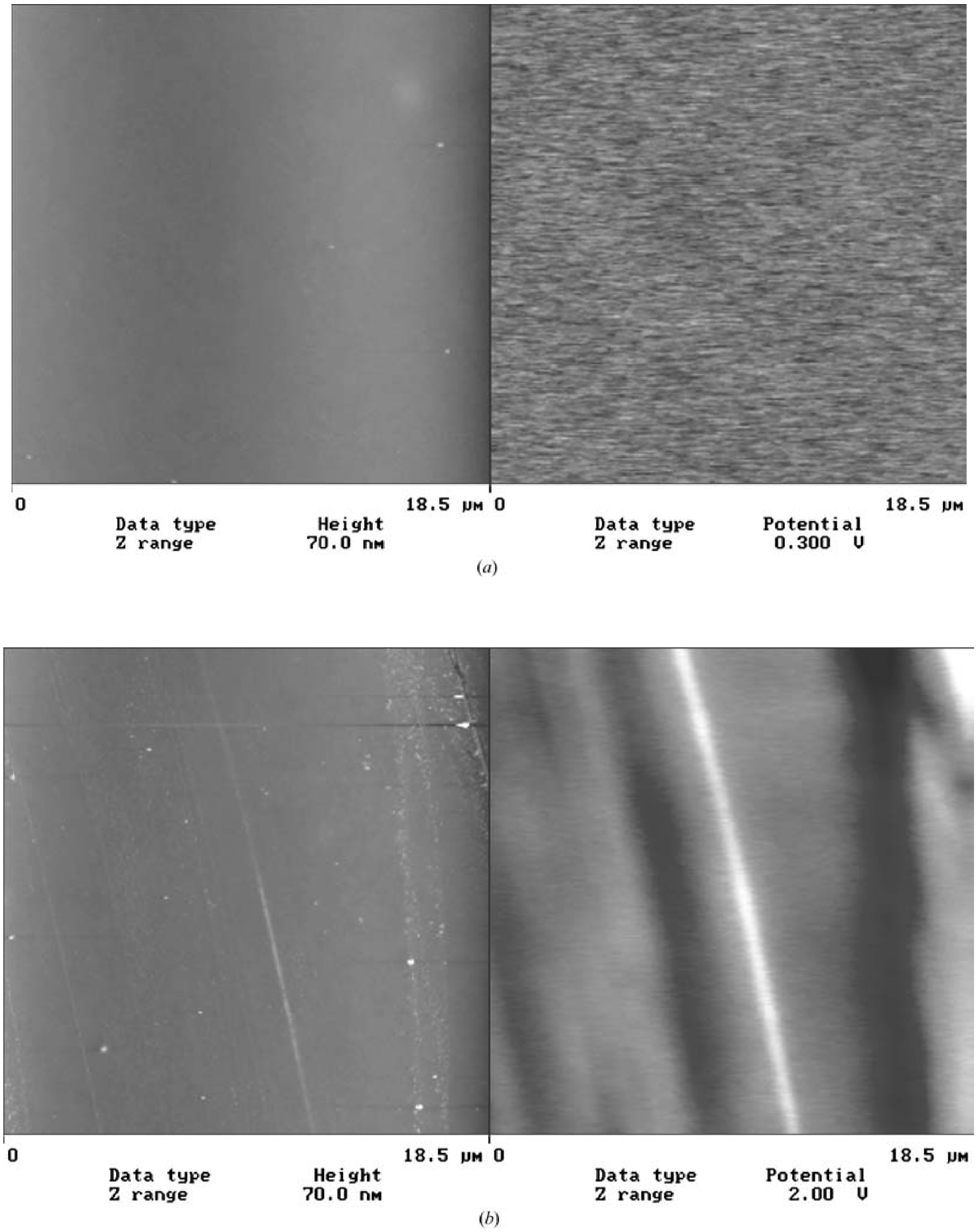
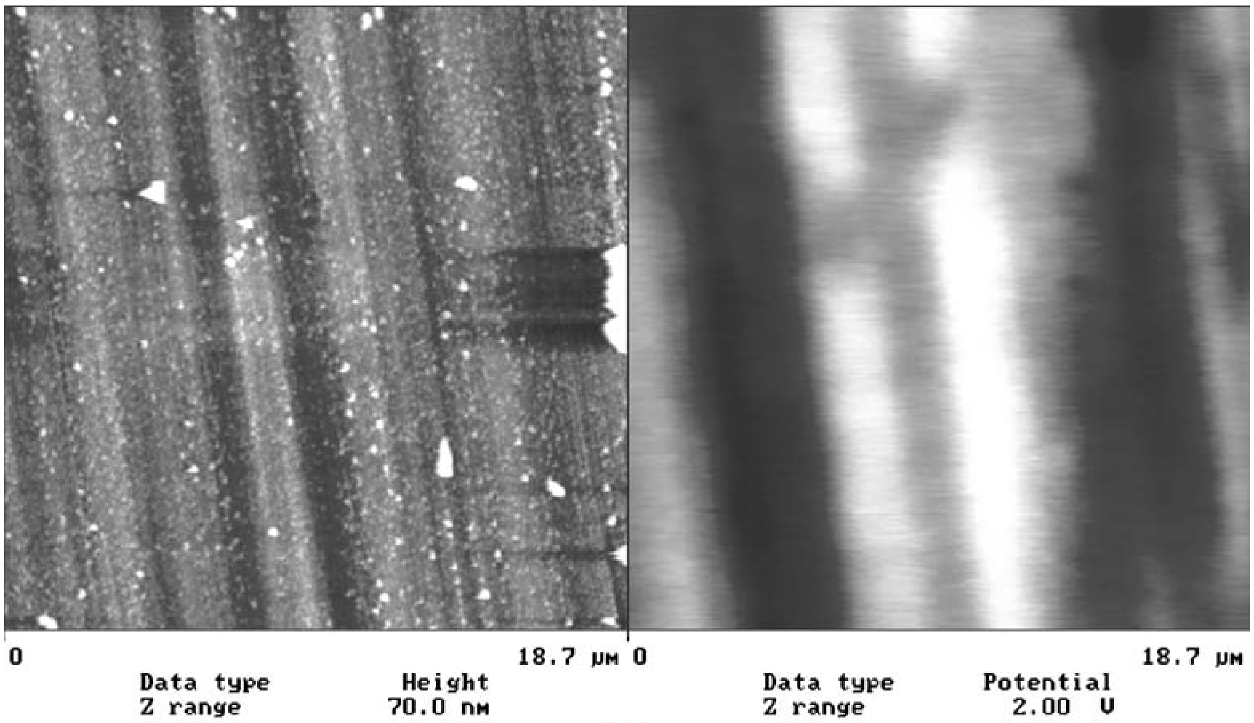


Figure 2. EFM images for the PMMA film: (*a*) without rubbing; (*b*) rubbed once; (*c*) rubbed ten times. On the left is topography and on the right electrostatic potential.



(*c*)

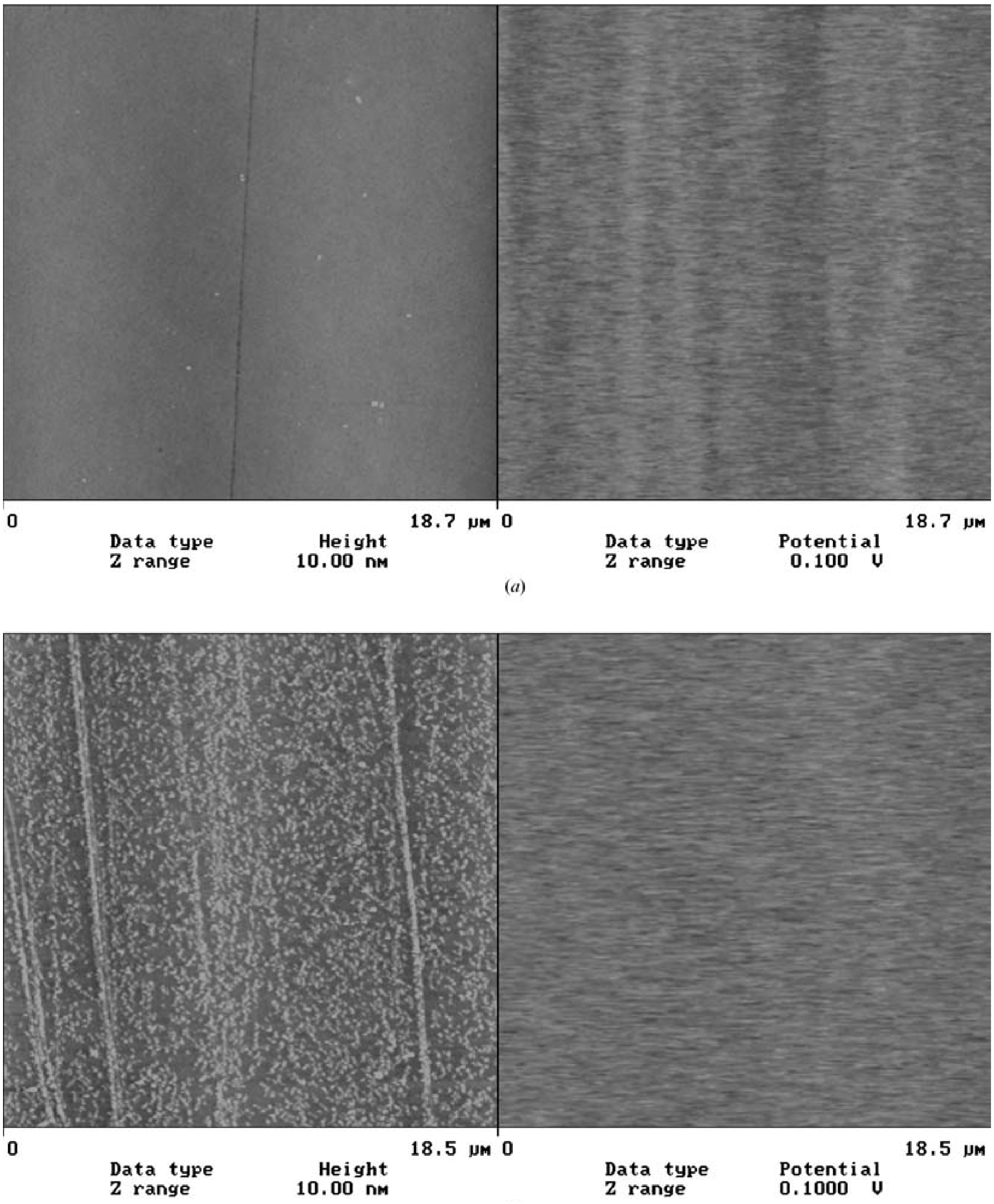
Figure 2. (*Continued.*)

the microscope to investigate the presence of charges and surface deformations. The result is presented in figure 2(*b*), where it is possible to see small variations in the surface topography and charge domains oriented along the rubbing direction, given by the changes in the electrostatic potential. Following the same procedure as before, we observed that on increasing the number of rubbings the surface deformations and electrostatic potential also increased. The image after ten times rubbing is presented in figure 2(*c*), where both, the topography and the electrostatic potential present large variations. It is important to note that in figures 2(*b*) and 2(*c*) the *z* scales are constant (70 nm for the topography and 2.0 V for the surface potential). For this sample (ten times rubbed) we followed the temporal evolution to observe if such charge domains remain constant or disappear in time. Surprisingly, after five days we observed almost the same features, with only a very small reduction of the potential.

The same measurements were performed for the PI and PVA surfaces; the results are presented in figures 3(*a*) and 3(*b*), respectively, after ten times rubbing. Compared with figure 2(*c*) (PMMA rubbed ten times), the surface topography is less rough, although the *z* scale was reduced from 70 to 10 nm. This indicates that the PMMA surface is softer than the others. However, the most important information is related to the charge domains; it can be clearly seen that PI presents a lower surface potential ($z = 0.1$ V), and in the case of PVA no charge domains were observed.

The aligning properties of such substrates for LC orientation were investigated by preparing cells with the substrate surfaces parallel to each other, using 20 μm thick Mylar spacers. The liquid crystal (5CB) was introduced by capillary action at room temperature, i.e. with the sample in the nematic phase. With a polarizing optical microscope we observed that the LC bulk alignment induced by PVA and PI is more homogeneous than that induced by PMMA.

Considering the PMMA surface, which presented the largest electrostatic surface potential, we investigated the possibility of changing the charge domains orientation by rubbing a previously rubbed surface in another direction. The results indicated that the initial orientation of the charge domains induced by the first rubbing direction cannot be erased. The charge domains oriented along the second rubbing direction depend on the number of times the rubbing process was applied, but in all situations it was possible to see both directions, as shown in figure 4 where a PMMA surface was rubbed once in one direction and then once in another ($\approx 45^\circ$ to the first one), keeping the rubbing pressure constant. The topographic image also shows grooves due to the rubbing process in both directions.



(*a*)

(*b*)

Figure 3. EFM images: (*a*) PI, (*b*) PVA; both rubbed ten times.

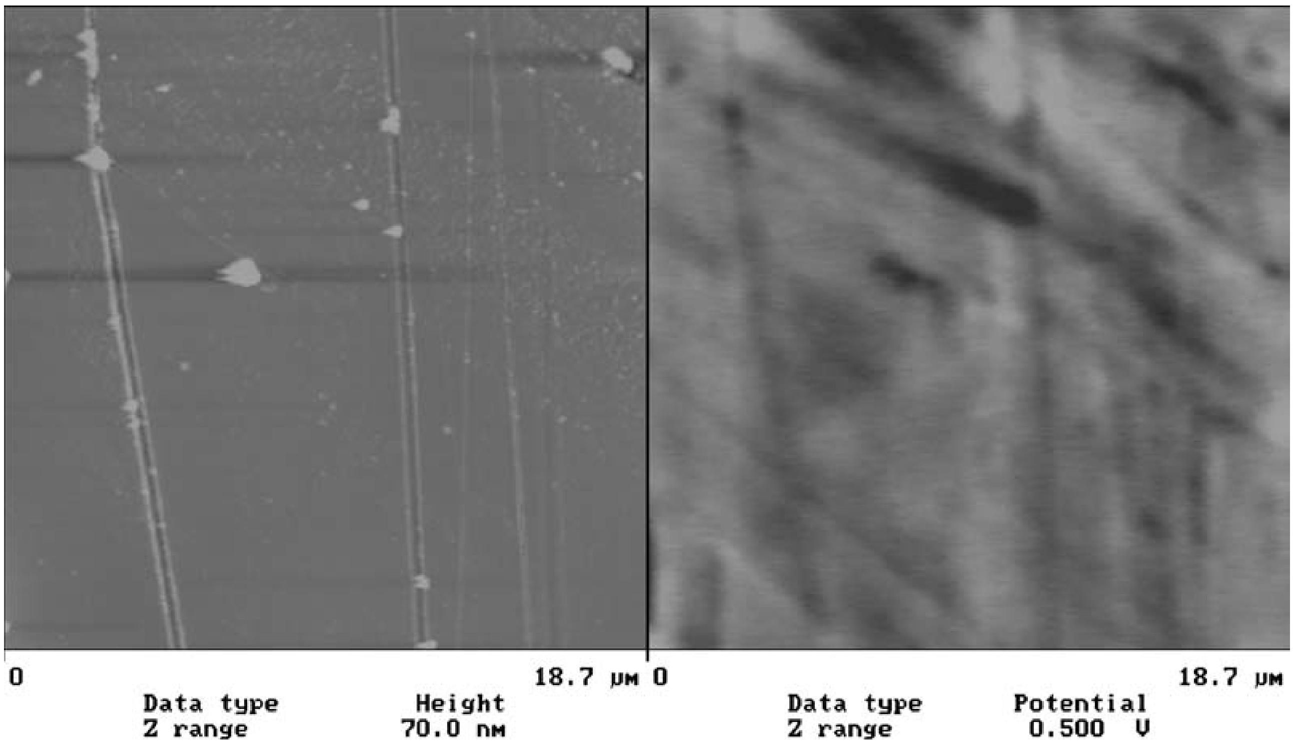


Figure 4. EFM image for PMMA rubbed once in one direction and then once again ≈45° relative to the first rubbing direction.

Cells of 20 µm thickness were prepared to test the influence of these surface treatments on the LC bulk alignment. To observe the orientation induced by the rubbed PMMA film, a hybrid cell was built where one of the plates of the cell was treated to induce a homeotropic orientation to the LC. It was then possible to identify the alignment direction induced by the surface of interest. In these cells, the PMMA film was submitted to a first cycle of rubbing; six times in the same direction and a second cycle of rubbing making an angle of 45° with respect to the first cycle. The final orientation of the LC is shown in figure 5, as a function of the number of times the rubbing process was applied in the second cycle. We observed that the LC does not always align

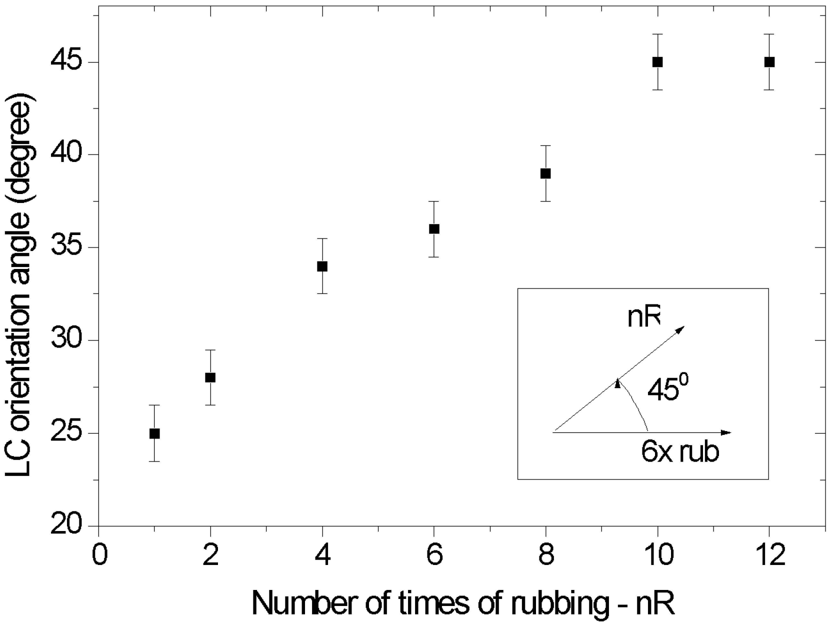


Figure 5. LC alignment direction induced by rubbing of a PMMA substrate in two distinct directions. At 0° it was rubbed six times; the number of times at 45° is given by the horizontal axis.

parallel to the second rubbing direction, even when the number of rubbings is the same as for the first cycle. In fact, the second rubbing cycle is effective only when the number of rubbings is much larger than in the first cycle (ten times).

By superimposing the topographic and EFM images by means of a special software, we could conclude that the charge domains bear no relation to the topography of the film, i.e. the high potential regions (bright domains in the electrostatic potential image), can be found either inside or outside the topographic depressions (grooves). From the electrostatic image it was not possible to say if the charge domains are positive or negative. However, we performed tests with an electronic apparatus, showing that the induced friction charges are positive.

The LC anchoring energies were also investigated for these substrates. PVA and PI are well known to present strong azimuthal anchoring energies ($W_\phi \approx 1.5 \times 10^{-5}$ J m^{-2}), and such polymers are commonly used in technological applications. The PMMA polymer film presents a weak anchoring energy ($W_\phi \leqslant 5 \times 10^{-6}$ J m^{-2}). We used the hybrid twisted cell method [15] to determine the azimuthal anchoring energy for PMMA, by changing the number of times the rubbing process was applied. The results are presented in the table. For comparison, the azimuthal anchoring energy for PVA and PI are also listed in the table; the values were extracted from the literature [16, 17].

4. Discussion and conclusions

It has been shown that EFM is an efficient technique for observing charge domains induced by the rubbing process on polymeric films. In addition, other interesting results were obtained, and some suggestions on aspects related to LC alignment properties can be drawn.

Concerning the polymers under investigation, we observed well defined surface charge domains oriented along the rubbing direction for PMMA, and the electrical potential increases on increasing the number of rubbings; whereas, for PVA no induced charge domains were observed. This can be explained considering the chemical structure of the polymer; the OH groups of the PVA polymeric chains are good charge conductors, therefore the charges formed by the rubbing process can leak out of the surface. Since PMMA contains no OH groups, the charges formed stay attached to the surface for a long time. Actually, after five days the electrostatic potential intensity (for PMMA, ten times rubbed) was almost the same.

Table. Azimuthal anchoring energies of the investigated substrates ($\times 10^{-6}$ J m^{-2}).

Polymer	Weak rub.	Strong rub.	1 × rub.	5 × rub.	10 × rub.
PVA and PI	≈5	≈14	—	—	—
PMMA	—	—	1.0	1.3	1.7

The topography of the polymers also indicates a different feature. The surface deformations created by the rubbing process on PMMA are more pronounced with respect to the other polymers, indicating that this surface is softer. From the topographic images, it can also be seen that the rubbing process creates irregularities and defects (dirt) on the polymeric surfaces.

As suggested theoretically [11, 13, 14], the coupling of the electric field generated by the surface density of charges with the nematic medium can affect the bulk orientation of the director by distorting the director profile near the surface. The authors reported that, for a medium with positive dielectric anisotropy (which is the case for 5CB), in a planar configuration of the director, the electrostatic potential seems to destabilize the bulk alignment. In addition, the smaller the anchoring energy of a given substrate, the lower the threshold electrostatic field needed for the instability. According to the authors, the existence of a surface electric field also contributes to the effective anchoring energy; this can be used to justify, from a fundamental point of view, the thickness dependence of the anchoring energy [18].

The considerations described above, seem to fit exactly with our experimental observations. The higher uniformity induced by the PVA substrate to the LC bulk alignment, can be related to the absence of an electrostatic potential. With respect to the azimuthal anchoring energy of such substrates (see the table), it is possible to observe a strong dependence on the rubbing strength for PVA and PI. In this case, the anchoring energy increase is related mostly to the orientation of the polymer chains, with a linear dependence on the rubbing strength [16].

For the PMMA it is reported in the literature [8] that after buffing the polymeric film no birefringence can be detected, indicating that this process is not efficient for inducing alignment of the polymeric chains. For this polymer, the rubbing induces mainly surface deformations, which in principle should contribute negatively to the anchoring energy. From the EFM images we have observed that the rubbing process on PMMA increases the surface electrostatic potential. Therefore, we can argue that the electrostatic potential makes an important contribution to the increase in anchoring energy for PMMA, which is approximately linear with the rubbing strength (see values in the table). However, it is not possible to make a direct correlation between the specific charge patterns observed by the electrostatic potential image and the LC alignment patterns.

The fact that PVA and PI present stronger anchoring energies than PMMA, can be associated with two factors: the molecular interactions between the LC and the chemical structure of the polymers, and the strong influence of the orientation of polymer chains on the LC anchoring energies.

Another interesting point is that by applying a second cycle of rubbing in a different direction relative to the first, topographic grooves as well as oriented charge domains can be seen in both rubbing directions for PMMA. As expected, an intermediate orientation of the LC molecules was observed, which is related to the competition between surface grooves and electrostatic potential created by rubbing in both directions. The LC alignment direction depends on the number of times the rubbing process is applied in the second cycle direction (see figure 5).

In the literature we can find reports of experiments performed with the optical second harmonic generation technique to investigate the induced orientation of rubbed PI films to a monolayer of adsorbed LC molecules. It is reported that the last rubbing direction dominates the LC monolayer, even if the amount of rubbing in the last direction is an order of magnitude less than during the first rubbing cycle [9]. The same behaviour is also observed for PVA films [16]; similar results were also obtained for bulk LC alignment [19]. In this case, the authors suggested that the mechanism responsible for LC orientation is the polymer chains alignment, which cannot be seen by the topographic images. Interestingly, the results of Liang *et al.* [12] indicate that the surface charges on PI also affect the tilt angle of the LC molecules.

To conclude, we observed that the presence of rubbing-induced charge domains depends on the polymeric substrate. The electrostatic potential generated by the charge domains seems to destabilize the LC director orientation in the bulk, but makes a positive contribution to the LC aligning properties when the effect of polymer chain alignment is not observed. In addition, the results indicate that this potential contributes to the effective azimuthal anchoring energy, as expected theoretically.

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