

Nano-rubbing of a liquid crystal alignment layer by an atomic force microscope: a detailed characterization

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Abstract

Locally rubbing the surface of a polymer using the stylus of an atomic force microscope (AFM nano-rubbing) has recently found extensive applications in prototyping novel micro- and nano-structured liquid crystal (LC) electro-optic devices. We report here on the detailed characteristics of the AFM nano-rubbed polyimide in terms of the friction force and the LC alignment capability. A unidirectionally rubbed polyimide by the contact mode AFM showed anisotropic friction, along and against the rubbing direction, even at a rubbing load as small as 1 nN and yielded a finite pretilt angle reflecting the asymmetry. Rubbing at high loads generated conspicuous scratches on the polyimide surface; when annealed at temperatures well below the glass transition or soaked into an organic solvent, however, these scratches quickly relaxed and completely disappeared while maintaining the capability of aligning LCs. When the load was small, the LC alignment also disappeared altogether. These experimental observations suggest that although the top thin layer might be sufficient to initially orient LCs, persistent surface alignment entails deeper cultivation of anisotropic structures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Realizing uniform alignment of liquid crystals (LCs) between glass substrates is an important process in manufacturing LC displays and devices [1]. Several techniques are known for this purpose such as rubbing, photo-alignment and oblique evaporation. Although the rubbing technique is the most conventional and industrially wide spread among them, the mechanistic details of the rubbing process are still largely obscure. One might generally imagine that the aligned LC layer grows epitaxially from the surface of the alignment layer endowed with an anisotropic property [1–3], yet it is only recently that structural aspects of the rubbed alignment layer, in favour of the simple picture, have become experimentally

available [4–8]. The crudity of the conventional rubbing method could be a source of technical problems in future LC applications, requiring even more precise control of the direction of alignment and the surface anchoring strength.

Using the stylus of an atomic force microscope (AFM), one can locally conduct the rubbing process in any small region down to the nanometre scale. The structural anisotropy induced by the AFM nano-rubbing (ANR) technique was demonstrated to be sufficiently strong to induce good LC orientation even at a moderate load force [9–12], and the ANR was recently successfully applied to fabricating novel electro-optical LC devices requiring nano- and micro-scopically textured surface alignment such as the highly efficient switchable diffraction grating and the surface-induced bistable

nematic devices [13–16]. Despite its obvious drawbacks such as limited size and long processing time, the ANR technique enables, by its nature, us to precisely control the direction and strength of rubbing, which is hardly possible in the conventional rubbing process. It is thus expected to be useful in exploring the underlying mechanism of the rubbing process as well. It has indeed been shown that the azimuthal anchoring strength grows systematically with the increase in scanning density and load force [15]. The purpose of this paper is to describe in more detail the characteristics of the ANR on polyimide alignment layers in terms of the topographical and frictional changes in relation to the LC alignment capability. We demonstrate, in particular, that the unidirectional rubbing can generate finite tilt angles of the LC alignment in a systematic manner reflecting the degree of asymmetry induced by the ANR.

2. Experiment

Substrates were glass slides spin-coated with a layer of polyimide (SE150, Nissan Chemical). This polyimide is a main-chain type polymer, which is known to yield industrial-quality planar alignment of LCs on rubbing. Spin coating of the precursor polyamic acids was carried out at the rotation speed of 2500 rpm for 20 s. The coated substrate was then baked at 180 °C for 1–2 h to completely imidize the precursor film to the final thickness of several hundred nanometres. There was no clear indication of baking-time dependence in all the experiments reported here.

Nano-rubbing was carried out by a commercial AFM (SPI-500, SEIKO Instruments) in the contact mode under various load force using a standard cantilever (Si-AF01, SEIKO Instruments). For experimenting with small scanning densities, fresh cantilevers were always employed to ensure reliability. However, a prolonged use was inevitable for high-density and/or large-area rubbing scans. The fresh tip had a 10 nm radius of curvature at the apex³, which became two times more blunt after continuous use as a result of accumulation of the polymer debris. As a consequence, a new tip generated more distinctive scratches compared to a used one for a given force. However, the LC alignment quality remained indistinguishable within the present experimental resolution.

The actual movement of the cantilever in the standard contact mode of the AFM consists of repeated cycles of a complete line scan (forward and backward along the same path) followed by translation to the end of the next line under the constant load. For the pretilt angle generation that requires asymmetrical rubbing, however, we modified the movement of cantilever into a unidirectional scanning so that the cantilever is loaded only for the forward scan, but is retracted from the surface during the backward motion.

The load force for the present ANR was limited below ~30 nN in order to avoid disruption of the tip geometry as much as possible. Note that this load range is considerably low in comparison with those adopted by previous workers [9–12, 15], who used hard (probably highly crystalline) polyimides such as LX-1400 (Hitachi Chemical). For these stiff polyimides, the effects of ANR can barely appear in this low and moderate

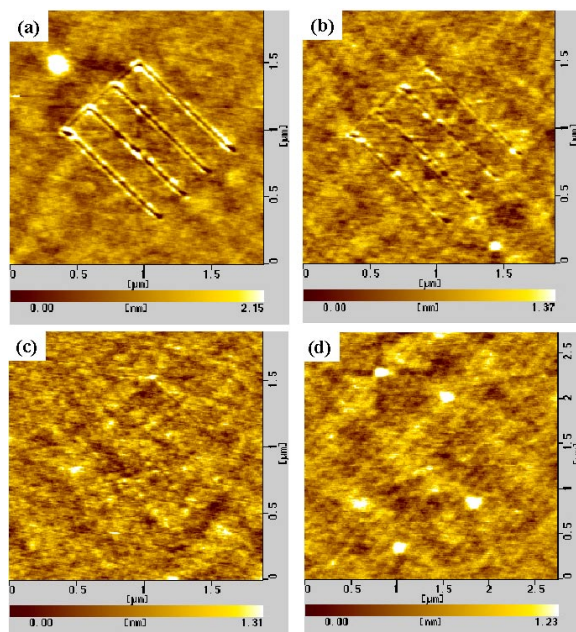


Figure 1. Topography images of the ANR processed polyimide surface under different load forces. The load forces are (a) 23 nN, (b) 16 nN, (c) 9 nN and (d) 2 nN. The scanning speed was $2 \mu\text{m s}^{-1}$.

force range, thereby making it extremely difficult to undertake detailed characterization of ANR processes without substantial deterioration of tips. For this reason, we chose the soft-type polyimide as described above. Although relatively soft, the polyimide is still a highly durable polymer whose glass transition temperature has been confirmed to be at least above 200 °C according to our differential scanning calorimetry and rheological experiments. For topographic and friction imaging, the load force was maintained below 1 nN to minimize destruction of processed surfaces; no appreciable changes in topographical images were in fact observed even after repeated measurement at room temperature.

The LC textures were observed by optical polarizing microscopy, and the pretilt angle was measured at room temperature by the crystal rotation method. The LC was 4-n-pentyl-4'-cyanobiphenyl (5CB), which is a room-temperature nematic LC with the nematic-isotropic transition point at 35.3 °C.

3. Atomic force microscopy

Scratches, which are ubiquitous on conventionally rubbed polyimide surfaces, were also generated in a far more controlled manner by the ANR at relatively high load forces as shown in figure 1. Parallel long lines are the scratches caused by ANR, and those along the side of the rubbed area are due to the translation of the tip to the starting position of the next line. In figure 1(a) obtained for the load force of 23 nN, scratches are clear and their typical depth and width were 1 and 50 nm, respectively. As the load is reduced down below 10 nN, however, the ANR left no more than a faint shadow of scanning (figures 1(c) and (d)), though these surfaces exhibit a fairly good LC alignment as will be described below.

³ Manufacturer's specifications.

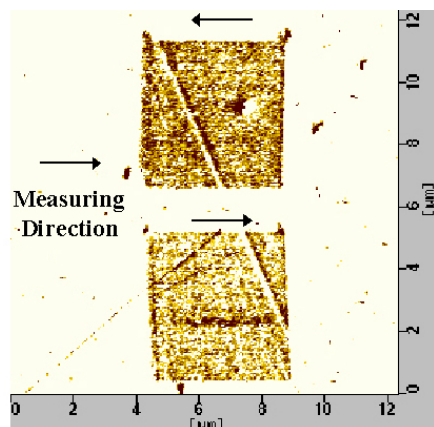


Figure 2. Friction image of the polyimide surface, which contains two areas with opposite scanning directions to each other. The two squares were scanned before friction measuring. Because of the imaging direction, the darker area has larger friction than the brighter one. The image was amplified to put emphasis on the distinction of signals. The arrows indicate scanning and imaging directions, respectively. The scanning density was $150 \text{ line}/\mu\text{m}$. The force was 3 nN . The speed was $30 \mu\text{m s}^{-1}$. The imaging force was less than 1 nN .

The tip size and the shape of the scratches in figure 1 do not fit with each other. For the given depth of the scratch, the width is much larger than the tip diameter. The diameter of the tip at the point 1 nm away from the apex is only around 10 nm , given the 10 nm radius of curvature of the tip. It then follows that the tip must have penetrated deeper into the bulk than apparently seen in the topographic image. The pyramidal shape of the tip, having the maximum of 60° cone angle (see footnote 3) requires that the depth of penetration at the time of scratch formation should be about 30 nm to yield the width of 50 nm . The deep scratches thus formed initially might have relaxed to the observed shape rather quickly due to the softness of the polyimide.

When the scanning density was as high as $100 \text{ line}/\mu\text{m}$ (10 nm line separation), it became virtually impossible to distinguish individual scratch lines irrespective of the load force. This is a natural consequence of the larger width of scratches than the scanning interval. The ANR processed area, however, was still recognizable over the rest in terms of a slight increase in overall height, or more clearly of an increase in friction (lateral force). Regardless of the load force, the friction was found to steadily increase relative to the non-scanned area. We measured, in particular, the anisotropy of friction on the ANR processed area relative to the rubbed direction at the high-density scanning. For unidirectional ANR, the friction antiparallel to the rubbed direction was found to be appreciably lower than that along the rubbing direction (figure 2). Similar anisotropic friction has been observed for Langmuir–Blodgett monolayers of tilted lipid molecules deposited on solid surfaces [17, 18]. An intuitively appealing explanation for this anisotropic friction is that the tilted molecules allow smoother passage of an AFM tip along the tilt direction than against it, just as the situation we experience in combing hair. According to the recent sum frequency generation (SFG) studies of rubbed polyimide by Oh-*et al* [7], indeed, the main-chain of polyimide tends to

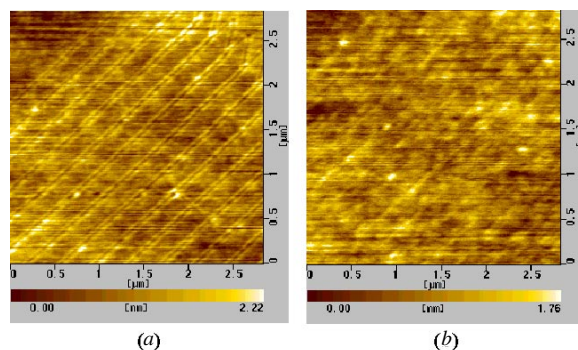


Figure 3. Changes of the topography image with the thermal ageing. (a) After scanning at 20°C , (b) after ageing at 60°C for 10 min . The measurement was at 20°C . The scanning force was 30 nN . The imaging force was less than 1 nN .

attain a finite tilt out of the plane of the substrate when subjected to unidirectional rubbing. It, therefore, seems reasonable to suspect that the similar tilting of main chain took place, giving rise to the anisotropic friction.

In order to study the structural relaxation of the ANR processed polymer substrate, the processed samples were soaked in an isopropyl alcohol supersonic bath for 15 min at room temperature. The scratches made by the ANR disappeared altogether for all the ANR conditions. The temperature stability of the scratches was also examined as shown in figure 3. The processed substrates were heated up to the target temperature and maintained for 10 min , and were cooled to room temperature for AFM imaging. This cycle was started at room temperature with successively increasing the target temperature. The relaxation of scratches was found to become appreciable even at a temperature of 60°C , and was enhanced at higher temperatures. The friction image also began to fade away at 70°C . In view of the intrinsically high glass transition temperature of the polyimide used (at least 200°C), the observed relaxation temperature is surprisingly low, and should have a significant impact on the surface alignment of LCs. One probable explanation is that, the glass transition may be easier to occur at surfaces where the entanglement of polymer chains are less significant than in the bulk [19].

4. Liquid crystal alignment property

Figure 4(a) shows the polarizing optical micrograph of the resultant LC alignment. A layer of LC was put on the ANR processed polyimide with a free upper boundary where the LC molecules are self-aligned perpendicular to the free surface. The thickness of the LC layer was not strictly controlled, but was limited within the depth of focus of the microscope. The quality of LC alignment was found almost invariable with diverse scanning conditions. In particular, even at the load force as low as the usual imaging level (1 nN or less), the capability of the scanned area to give uniform LC alignment is clearly seen. Though all the ANR patterns were of the same size, regions rubbed at lower load forces seem to have smaller effective size due to the elastic frustrations with the surrounding LC alignment.

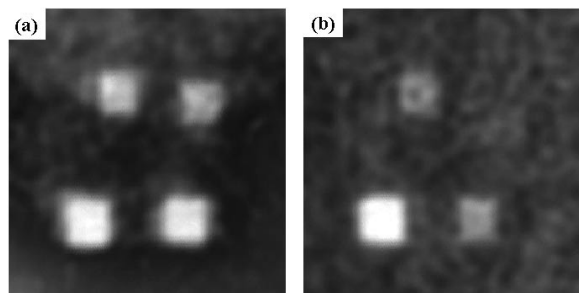


Figure 4. LC texture changes for scanning conditions and washing. (a) shows the textures before washing and (b) after washing. The conditions of the scanning are (23 nN, 6 line/ μm), (23 nN, 1 line/ μm), (1 nN, 1 line/ μm) and (1 nN, 6 line/ μm) for load force and line density from left bottom in counter-clockwise. Every pattern has size of 10 $\mu\text{m} \times 10 \mu\text{m}$. The optical image was got with maximum contrast between scanned area and non-scanned area under crossed polarizers.

The ANR processed substrate was soaked in the supersonic bath containing isopropyl alcohol for 10 min at room temperature. The LC was then put on that substrate to observe texture. Unlike the case of scratches, domains rubbed at relative high load forces retained their ability to align LC as shown in figure 4(b). The quality of LC alignment, however, varied following the ANR condition. The texture on 23 nN and 6 line/ μm was practically the same before and after washing. But in the case of 1 nN and 1 line/ μm scanning, the alignment disappeared completely.

Finally, we have explored the possibility of pretilt angle generation by conducting unidirectional ANR. Initially, we confirmed that the pretilt angle is zero, i.e. the LC molecules lying flat on the substrate, when the bi-directional scanning was carried out on the same line. The unidirectional scanning was executed at a constant force and speed for the size of 150 $\mu\text{m} \times 150 \mu\text{m}$; this rather large size was chosen to allow a reliable optical measurement of the resultant pretilt angle. Using the unidirectionally nanorubbed substrates, we fabricated a sandwich-type homogeneous cell with the thickness of about 50 μm . The cell was then injected with the LC in the isotropic phase along the perpendicular direction to the alignment direction. The pretilt angle was measured at room temperature by the crystal rotation method.

Figure 5 shows the pretilt angle as a function of the scanned line density. Despite considerable scatter of data, the pretilt angle seemed, on average, to occur up to 2.5° with the scanning density and saturate in the high-density regime. The direction of tilting was along the scanning direction, which is the same behaviour as that in the case of conventional rubbing. This, however, is not in accordance with the previous result [12]. Though a non-zero pretilt angle was generated up to 2.5° in this experiment, this polyimide is known to yield a pretilt angle as large as 5 degrees for the conventional rubbing⁴. This discrepancy might be due to the different nature of the ANR and the conventional rubbing that the former is an essentially localized process at the tip apex whose shearing effect on the polyimide rapidly decays through the film thickness. The conventional rubbing, on the other hand, consists in uniform shearing of the film surface

⁴ Manufacturer's specifications.

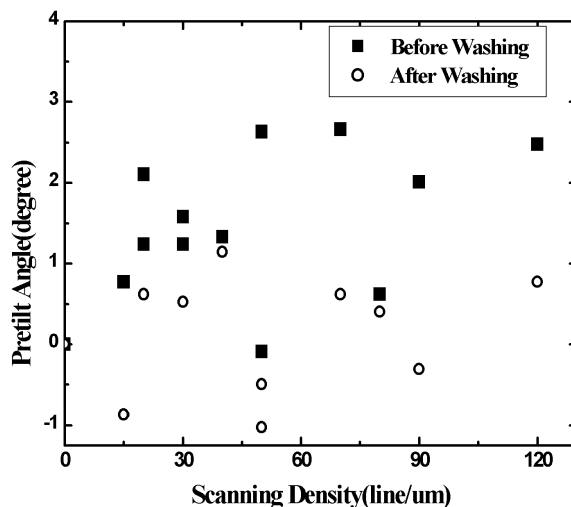


Figure 5. Pretilt angles generated by unidirectional ANR as a function of scanning density. The scanning speed was 500 $\mu\text{m s}^{-1}$ and the load force was 30 nN.

and hence its effect should penetrate through the polyimide layer without decay. In view of the fact that the long-range anisotropic interaction between the LC molecule and the rubbed film is largely responsible for generation of pretilt angle [20], the relatively smaller pretilt angles found for the unidirectional ANR appear quite reasonable. In figure 5 also shown are the changes of pretilt angle after ageing the sample in the isopropyl alcohol bath. As clearly seen, the pretilt angle virtually disappeared after treatment, although the pretilt angle on a conventionally rubbed surface withstands this solvent process. This observation is consistent with the above conjecture that the pretilt angle on the ANR processed surface originates from the superficial region of the alignment film.

In order to further the argument a little more quantitatively, we consider the mechanical effect of the AFM tip on the surface of polyimide. For a given normal load force F_n and the radius of tip-surface contact area R , the pressure that develops at the tip apex is given by the formula $P = 4F_n/\pi R^2$ [11]. If we adopt the yield stress of bulk polyimide, i.e. 1 GPa [21] for the present film, it follows from this equation that $R = 1 \text{ nm}$ at $F_n = 1 \text{ nN}$. Even for a fresh sharp tip with 10 nm radius of curvature, this estimate leads to the penetration depth of the tip apex into the film to be an extremely small value of 0.05 nm. Given the deep scratches we observed, this is an unreasonably tiny value. In view of the unusually high susceptibility of the surface morphology and the alignment characteristics to the heat and solvent treatments, it seems appropriate to consider that the surface region of the polyimide is substantially soft compared to the bulk with much reduced glass transition temperature and yield stress [19].

Finally, it should be of interest to discuss briefly the role played by the scratches in the surface alignment. According to Berreman's groove model [22], the upper bound of the topography contribution to the surface anchoring energy is given by $W_B = \frac{1}{4} K A^2 q^3$, where A is the Fourier amplitude of the surface corrugation at the spatial wavenumber q , and K is the Frank elastic constant of the LC; when the surface shape

involves multiple Fourier components, this expression should be replaced by the summation over the relevant wavenumbers. By assuming a simple sinusoidal surface with $A \approx 1$ nm and $q \approx 2\pi \times 20 \mu\text{m}^{-1}$ as a typical morphology observed here, we obtain $W_B \approx 10^{-3}$ mN m $^{-1}$ with $K = 2 \times 10^{-12}$ N. This anchoring energy value falls in the class of weak anchoring, and is at least three orders of magnitude smaller than the anchoring energy for the alignment on conventionally rubbed substrates [23]. This may be an indicative of the fact that the scratches play a minor, if not totally negligible, role in the surface alignment made by the ANR.

5. Conclusions

We described the basic characteristics of the ANR technique as applied to polyimide alignment layers. Even with a small load force on the order of 1 nN, which does not generate any noticeable scratches, the surface can attain a capability to uniformly align adjacent LCs. This orientational effect is always accompanied by an increased microscale friction, which is asymmetrical with respect to the rubbing direction. This friction anisotropy, presumably originating from the asymmetrical molecular arrangement, is responsible for the non-zero pretilt angle with the unidirectional scanning. Compared to the alignment on the conventionally rubbed surface, the aligning capability endowed by the ANR is relatively more fragile, readily susceptible to relaxation by heat and organic solvent treatments. We argue that the difference may result from the different geometry of the rubbing process, the ANR being more localized thereby altering only the near-surface region.

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