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What Alings Liquid Crystals on Solid Substances? The Role of Surface Roughness Anisotropy

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The mechanism responsible for liquid crystal (LC) alignment on mechanically buffed or UV exposed polymer films is poorly understood. A comprehensive study of LC alignment on variously prepared substrates unequivocally shows that the anisotropy in the surface roughness of the substrate completely determines the direction of LC alignment. In all the cases studied, including those where an anchoring transition occurs with temperature, the LC director (re)aligns in the directions of low roughness.

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It has been known for a long time that rubbed [1] polymer films, Langmuir-Blodgett (LB) films [2], vacuum deposited dielectric layers [3], polymer films [4] exposed to linearly polarized ultraviolet (LPUV) light, photoaligned liquid crystal (LC) [5], and other methods which produce a grooved surface [6] induce alignment of LCs. Berreman [7] suggested that long-range anisotropic elastic effects induced by grooved surfaces are responsible for LC alignment. It was later reported that the surface structures produced upon rubbing a polymer layer may not be responsible for LC alignment [8]. However, these interpretations were based on measurements of surface morphology on a macroscopic (≈μm) length scale and did not address the influence of morphology at a more appropriate microscopic scale. We show here that substrate morphology at sub-μm scales is of great importance in determining LC alignment.

The LC alignment is believed to be influenced by (i) the chemical [8,9] interactions between the alignment layer [10] and the LC, and (ii) the interplay between LC anisotropic elastic properties and the substrate’s topography [7]. The specific role that each of these factors plays has been difficult to separate [11] and quantify. The results of our comprehensive high-resolution x-ray reflectivity [12] (HRXR) and atomic force microscopy (AFM) study [using Nanoscope III (Digital Instruments) in the contact mode] of a large number of alignment layers prepared by different processes establish that the anisotropy in the root mean square (rms) vertical roughness of the substrate’s surface fully determines the direction of LC alignment. Chemical interactions between the alignment layer and LC, on the other hand, are expected to determine the polar and azimuthal anchoring energies.

In this study, we used films or surfaces of commercially available polyvinyl alcohol (PVA), bare glass, linearly photopolymerizable polymer (LPP) [13], polyimide (PI) (SE610, Nissan Chemical Co.), and polystyrene (PS). Different polymers are spin coated and thermally cured per standard prescriptions. Rubbed PI and PS films are selected because they align LCs parallel and perpendicular to the rubbing direction, respectively. The PI, PVA, and PS layers are rubbed by a velvet cloth, bare glass with a scotchguard pad (3M), and LPP films are exposed to LPUV. They can be divided into two groups: (i) the PI, PVA, and bare glass align LCs parallel to the rubbing direction, and (ii) the LPP and PS films align LCs perpendicular to the UV’s polarization and the rubbing direction, respectively. Additionally, we studied a system [14] [PVA alignment layer reacted with trifluoroacetic anhydride (TFAA) in the gas phase to substitute the polar -OH group by -OCOCF3] in which the direction of alignment changes with temperature.

For a (hypothetical) smooth surface the Fresnel reflectivity should drop [12] as ~1/|q|2 beyond the critical angle. The roughness of real surfaces is traditionally modeled using a Gaussian distribution of surface points resulting in attenuation of the reflectivity by a Debye-Waller-like [12] factor exp(−q2σ2), σ being the rms roughness. In the case of a film on a substrate, Kiessig fringes are generated by the interference between the x rays partially reflected from the air-film and from film-substrate interfaces. The amplitude of fringes diminishes with increasing surface roughness averaged over the coherence area of the x-ray beam. Experimental details of the HRXR experiment are described in Ref. [12].

The determination of the anisotropy in a film’s morphology by HRXR is made possible by inherent unequal x-ray coherence lengths of ~5000 Å and ~60 Å in directions longitudinal and transverse to the direction of incidence, respectively. Specular reflectivity scans are conducted in two different orientations of the sample obtained by 90° rotations about the scattering vector, q (see the inset in Fig. 1) which is perpendicular to the substrate. The y direction is defined to be the direction of treatment (rubbing or the direction of UV’s polarization), and the x direction is orthogonal to it. If the surface is anisotropically rough, then the reflectivities measured with x and y directions in the scattering plane are different. Off-specular scans, conducted at an offset of 0.02° from the specular condition, are subtracted from the specular scans.
and the resultant reflectivity analyzed to obtain \( \sigma \). The difference, \( \Delta \sigma \), between the \( \sigma \)’s obtained for the \( x \) and \( y \) directions provides a quantitative measure of the surface roughness anisotropy.

Prior to the treatment, reflectivity scans in the \( x \) and \( y \) orientations for PI, PVA, bare glass, and LPP are identical, showing that they are initially isotropic. HRXR profiles for the two orientations of rubbed PI, PVA, bare glass, and LPPUV exposed LPP films are shown in Fig. 1. Kiessig fringes are clearly seen for all except bare glass. After the treatment, fringes remain brighter in the \( x \) direction for rubbed PVA and PI, but in the \( y \) direction for LPP. For bare glass, the reflectivity in the \( y \) direction diminishes at a faster rate than in the \( x \) direction because of the increased roughness anisotropy.

The mechanism which gives rise to the changes in the roughness is, of course, different for each film and depends on the treatment method: the polymer chains in PI and PVA may undergo reorientation upon rubbing [8,10], LPUV exposure causes photopolymerization in LPP film [13], and rubbing should cause simple linear scratches [5] on bare glass. Whatever the mechanisms may be, different treatments induce roughness anisotropy on substrates’ surface. Alignment of LC along the direction of lower roughness, as expected from Berreman’s calculation, is found to be a universal feature of all alignment films irrespective of how they are prepared.

Contrary to the intuitive expectation that a rubbed polymer film should always align LC parallel to the rubbing direction, PS films align [8] LCs perpendicular to the rubbing direction. Figure 2(a) shows the dependence of \( x \)-ray reflectivity for such a film on the number of times, \( n \), the film is rubbed. Initially, reflectivities in the \( x \) and \( y \) orientations yield essentially the same roughness of \( \sim 7 \pm 1 \) Å. Upon rubbing, the amplitude of Kiessig fringes begins to diminish dramatically in the \( x \) direction and remains relatively large in the \( y \) direction. The difference grows with \( n \). Results show that the roughness is dramatically increased in the \( x \) direction. For \( n = 6 \), the roughness increases to \( 21 \pm 1 \) Å in the \( x \) and \( 11.5 \pm 1 \) Å in the \( y \) direction. The LC aligns along the smoother \( y \) direction, i.e., perpendicularly to rubbing.

To further verify this surprising relationship between LC alignment and the surface roughness anisotropy, real space morphologies of rubbed PI and PS surfaces are acquired with the AFM in air at room temperature using a pyramidal shaped \( \text{Si}_3\text{N}_4 \) tip integrated into a rectangular cantilever with a spring constant of 0.58 N/m. The surface morphol-
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FIG. 5. Optical micrographs of (a) homeotropic TFAA cell, at 25 °C, which undergoes an anchoring transition to (b) homogeneous alignment at 87 °C. The white specs in (a) are defects. (c) Reflectivities indicate increasing roughness anisotropy (inset) with temperature above 75 °C for a ~2500 Å thick TFAA film.

In conclusion, the anisotropy in surface morphology of a substrate on a submicron length scale appears to play the defining role in determining the direction of LC alignment and the increase in anchoring energy with Δσ (or degree of rubbing). However, overall strength of the anchoring energy is expected to primarily depend on chemical interactions between the LC and the alignment layer. This is analogous to the necessary (but not sufficient) requirement that the shape of molecules be anisotropic for the formation of a LC phase. Just as the physical properties of a LC such as viscosity, birefringence, transitions temperatures, and transition enthalpies depend on intermolecular interactions, the anchoring energy of a LC depends on the interfacial roughness anisotropy and interactions between the LC and the interface.

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