Liquid Crystal Alignment on Solid Substrates

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Abstract

The mechanism responsible for liquid crystal (LC) alignment on solid substrates treated with mechanical rubbing or polarized UV is not understood. The results of x-ray reflectivity study of LC alignment on a large number of different alignment layers show that the anisotropy in the surface roughness of the substrate completely determines the LC alignment. The anchoring energy depends on the degree of roughness anisotropy and chemical interactions between the substrate and LC molecules.

1. Introduction

A number of systems prepared by different processes have been known to align liquid crystals. These include 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 LC [5], and other grooved surfaces [6]. Berreman [7] suggested that long-range anisotropic elastic effects of liquid crystals at grooved surfaces are responsible for LC alignment. However, this was not fully supported by interpretations of LC alignment based on measurements of surface morphology on a macroscopic (~ μm) length scale [8]. We show, through x-ray reflectivity experiments, complemented by Atomic Force Microscopy, that substrate morphology at nano- and sub-μm scales is of greatest importance in determining LC alignment.

In general terms, the LC alignment is expected to depend on: (i) the chemical [8,9] interactions between the substrate [10] and the LC, and (ii) LC's anisotropic elastic properties and substrate's topography [7]. It has been difficult to separate the contribution and importance that each of the two factors plays [11]. The results of our comprehensive high-resolution x–ray reflectivity [12] (HRXR) of a large number of alignment layers prepared by different methods prove that *the vertical roughness anisotropy of the substrate's surface fully determines the direction of LC alignment and controls its anchoring energy*. Chemical interactions between the alignment layer and LC coupled with the roughness anisotropy are expected to control the magnitude of polar and azimuthal anchoring energies.

In this study, we used commercially available poly-vinyl-alcohol (PVA), glass, photopolymerizable polymer (LPP) [13], PI (SE610, Nissan Chemical Co.), and polystyrene (PS). The polymers are spin coated and heat-treated per standard prescriptions. Mechanically buffed PI and PS films align LCs parallel and perpendicular to the rubbing direction, respectively. The aligning surfaces used in our study can be divided in to two groups: (i) homogeneous alignment parallel to rubbing: PI, PVA, and bare glass, and (ii) alignment perpendicular to the treatment direction: LPP and PS films.

2. X-ray reflectivity

The inset in Fig. 1 schematically shows the x-ray reflectivity experiment. A beam of incident monochromatic x rays with wavevector $\mathbf{k}_i$ is made incident on the substrate at a small angle. The real part of the index of refraction for x rays in all materials is smaller than unity and the corresponding critical angle, below which 100% of the incident beam is reflectied, is in the range of 0.25 to 0.8° for most materials. The reflected beam with wavevector $\mathbf{k}_f$ contains information about the surface structure and *root mean square* roughness, σ, in the vertical direction.

The (Fresnel) reflected intensity by an *ideally* smooth surface should drop [12] as $\sim 1/|q|^4$ beyond the critical angle. The roughness of *real* surfaces is traditionally modeled using a Gaussian distribution of surface points resulting in a reduction of the reflectivity by a Debye-Waller-like [12] factor, $\exp(-q^2\sigma^2)$. In the case of a uniform film on a substrate, Kiessig fringes are generated by the interference between the x rays partially reflected from the air-film and film-substrate interfaces. The fringe amplitude diminishes with increasing σ averaged over the coherence area of the x-ray beam. Experimental details of the HRXR experiment are described in ref. 12.

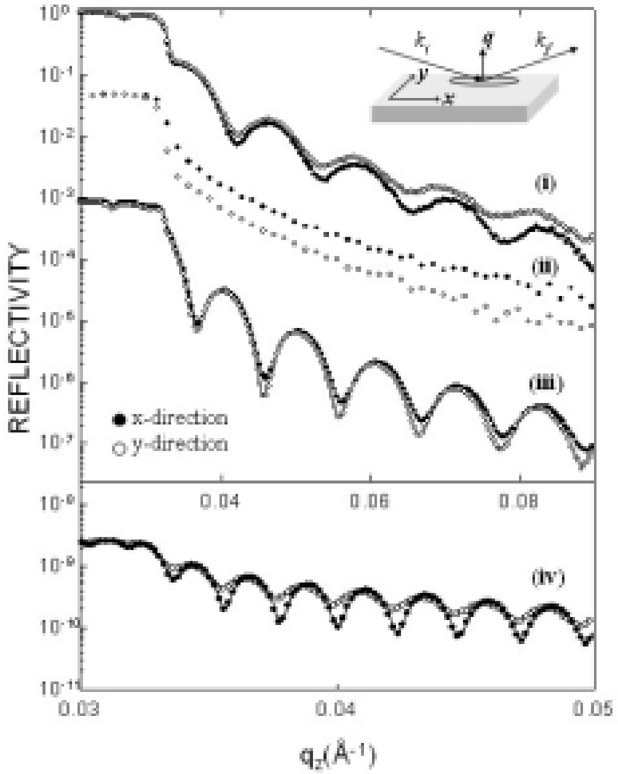

Fig. 1: HRXR profiles for *x*- (●) and *y*-directions (○), both in the scattering plane (inset), for (i) ~530 Å rubbed PVA, (ii) rubbed glass, (iii) ~610 Å LPUV exposed LPP, and (iv) 2900 Å rubbed PI films. The curves (ii), and (iii) are shifted down by 1.5 decades each; (iv) has been shifted down and the horizontal scale has been expanded for clarity.

The determination of the anisotropy in a film's morphology by HRXR depends on the inherent and unequal x-ray coherence lengths of ~5000Å and ~60Å in directions longitudinal and transverse to the direction of incidence, respectively. Reflectivity scans are conducted in two different orientations of the sample obtained by 90° rotations about the scattering vector, *q*, (inset in Fig. 1) which is perpendicular to the substrate. The *x*-direction is defined to be the direction of *treatment* (rubbing or the polarization direction of UV), and the *y*-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 angle of ~0.02° from the specular condition, are subtracted from the specular scans and the resultant reflectivity analyzed to obtain σ. The difference, $\Delta\sigma$, between the σ's obtained for the *x*- and *y*-directions provides a quantitative measure of the surface roughness anisotropy.

3. Results and Discussion

Initially, before the treatment, reflectivity scans in *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 LPUV 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 larger σ.

Different mechanisms which gives rise to the changes in the roughness are, of course, different for each film and depend on the treatment method: the polymer chains in PI and PVA may reorient upon rubbing [8,10], LPUV exposure causes photo-polymerization 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 the LC along the direction of lower roughness, as expected from Berreman's calculation, is found to be a *universal feature of all alignment films* independently 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. Fig. 2(*a*) shows the dependence of x-ray reflectivity for such a film on the number of times, *n*, the film is rubbed. In the beginning, the reflectivities in the *x*– and *y*–orientations yield essentially the same roughness of ~ 7±1Å. 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±1 Å in the *x*– and 11.5±1 Å in the *y*–direction. The LC aligns along the smoother y-direction, i.e., perpendicularly to rubbing!

It can be generalized that the anisotropy in the surface morphology over the length scale of x-ray beam's coherence length (~5000Å) in particular, determines the direction of alignment. No exceptions to this rule are found in more than 30 alignment layers of different types studied by us which include LB film [12], liquid crystalline polymer films aligned on LPP film, and LPUV exposed poly-vinyl-methoxy-cinamate[12] (PVMC).

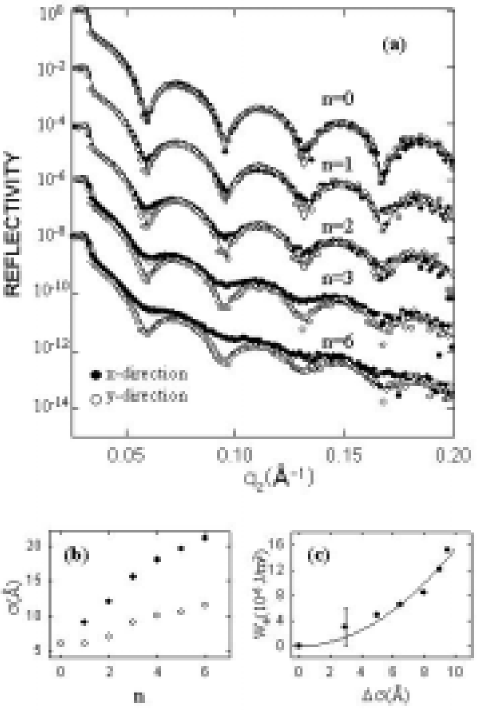

Fig. 2: (a) HRXR profiles for *x*- (●) and *y*-directions (○) of a ~180 Å thick rubbed PS film with increasing number, *n*, of rubbing, the solid lines represent fits. (b) *Rms* roughness σ as a function of *n*, for the two orientations of the substrate. (c) Dependence of anchoring energy W_6 on the roughness anisotropy Δσ.

To ascertain the role of chemical interactions, we measure azimuthal anchoring energy, W_θ, for rubbed PS films and quantitatively examine its dependence on the surface roughness anisotropy. The energy W_θ should encompass the effects of chemical interaction between the LC and the alignment layer as well as the morphological effects. A mixture of the nematic LC 5CB (British Drug House) and chiral dopant (S811) is injected into a wedge cell prepared with rubbed PS substrates and the director inclination angle at the surface is measured under a polarizing microscope and the value of W_θ calculated [14]. W_θ is found to increase [Fig. 2(*c*)] with the roughness anisotropy, Δσ, which in turn depends on the number of rubbings, as shown in Fig. 2(*b*). Now, according to Berreman [7], the surface anchoring energy should increase quadratically with the surface undulation height, or the roughness anisotropy. The solid line fit in Fig. 2(*c*) represents a quadratic dependence of the anchoring energy on the roughness anisotropy. The proportionality constant required to fit the data is expected to depend on the nature and the strength of chemical interactions between the alignment layer and the liquid crystal.

4. Conclusions

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.

5. Acknowledgements

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