

Orientations of Liquid Crystals in Contact with Surfaces that Present Continuous Gradients of Chemical Functionality

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We report the formation of continuous spatial gradients in the density of grafted semifluorinated chains on silicon oxide surfaces by vapor-phase diffusion of semifluorinated silanes. We quantify the orientations of the nematic liquid crystal (LC) 4-cyano-4'-pentybiphenyl on these surfaces as a function of local surface composition obtained by using NEXAFS. These measurements demonstrate that it is possible to obtain the full range of tilt angles of a LC on these surfaces. We also use the data provided by these gradient surfaces to test hypotheses regarding the nature of the interaction between the LC and surfaces that give rise to the range of tilted orientations of the LC. We conclude that the orientations of the LC are not determined solely by the density of grafted semifluorinated chains or by the density of residual hydroxyl groups presented at these surfaces following reactions with the silanes. Instead, our results raise the possibility that the tilt angles of the semifluorinated chains on these surfaces (which are a function of the density of the grafted chains) may influence the orientation of the LC. These results, when combined, demonstrate the potential utility of gradient surfaces for screening surface chemistries that achieve desired orientations of LCs as well as for rapidly assembling experimental data sets that can be used to test propositions regarding mechanisms of anchoring LCs at surfaces.

Introduction

A central element of most liquid crystal (LC)-based optical devices is a surface that serves to template the average orientation of a LC over a macroscopic length.¹ Surfaces that provide control over the out-of-plane tilt of a LC (θ_t , depicted in Figure 1a) over a wide range of possible angles have been prepared by the controlled illumination of photoactive groups contained within polymeric thin films.^{2,3} However, in the context of substrates that support monolayer coverages of molecular species (e.g., Langmuir–Blodgett films,^{4,5} adsorbed monolayers of amphiphiles,⁶ chemisorbed thiols on gold,⁷ organosilanes on oxide surfaces^{8,9}), the orientations of LCs are commonly observed to be homeotropic ($\theta_t = 0^\circ$) or planar ($\theta_t = 90^\circ$)^{6,7,9} with only limited control over intermediate tilt angles.^{4,5,8} Similar effects are

observed when photoactive groups are incorporated into monolayers.^{10,11} The study reported in this paper sought to establish a methodology that would permit identification of chemically functionalized interfaces that can template a range of desired orientations of LCs. The approach we report is based on the creation of surfaces with continuous gradients in chemical functionality.

The study reported in this paper is founded on the observation that the orientations of LCs at interfaces can be manipulated in useful ways by using interfaces that possess submonolayer coverages of molecular species, such as solid substrates that are patterned with nanometer-sized patches of chemical functionality^{12,13} or aqueous-liquid crystal interfaces that are decorated with submonolayer coverages of surfactants.¹⁴ Here, we report the orientations of LCs in contact with well-characterized substrates that present continuous spatial gradients (prepared by controlled-vapor transport^{15–17}) in the density of two organosilane molecules,

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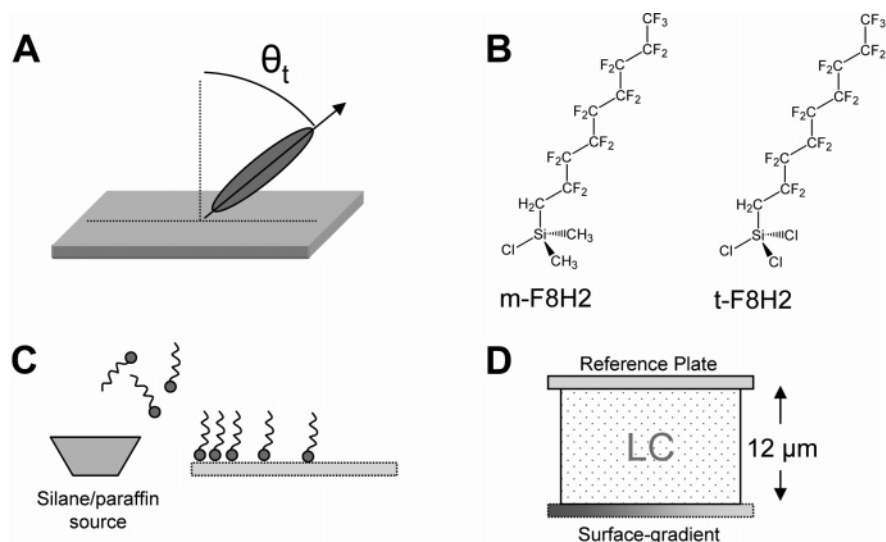


Figure 1. Schematic illustrations of: (a) the out-of-plane tilt (θ_t) of a LC as measured from the normal surface; (b) structures of the semifluorinated organosilanes used in this study; (c) schematic illustration of controlled-vapor transport used to prepare surface gradients; and (d) illustration of an optical cell used to study the tilt of the LC on the gradient surface.

m-F8H2 and t-F8H2 (Figure 1b), grafted onto oxide substrates. By using these gradient surfaces, we demonstrate that it is possible to control θ_t of the nematic LC 4-cyano-4'-penylbiphenyl (5CB) over all possible angles (from 0 to 90°). In addition, by using these gradient surfaces, we rapidly obtain data sets that provide knowledge of the orientation of the LC as a function of the composition of the surface, thus allowing hypotheses regarding the mechanisms of interaction between the LC and chemically functionalized interface to be tested.

Methods

Preparation of Surface Gradients. The methods used to prepare surface gradients of organosilanes supported on silicon oxide substrates have been described in detail in prior publications.^{16,17} In brief, silicon surfaces were exposed to UV/ozone for 30 min in order to generate a high density of surface silanol (hydroxyl) groups. These samples were placed lengthwise away from a paraffin/organosilane composite source (5:1 w/w) at a fixed distance (Figure 1c). Control over the diffusion times allowed for the preparation of gradients with different profiles along the x -axis of the substrate.

Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS). NEXAFS involves the resonant X-ray excitation of a K or L shell electron to an unaccompanied low-lying molecular orbital of σ or π symmetry, σ^* and π^* , respectively.¹⁸ A measurement of the intensity of NEXAFS spectral features enables the identification of chemical bonds and determination of their relative population density (and average orientation) within the sample. We mounted samples on a computer-controlled goniometer and translated the sample in one (or more) direction(s) while collecting partial electron yield (PEY) NEXAFS data at various fixed incident X-ray energies; this produced two-dimensional NEXAFS images in space and energy with submillimeter spatial resolution and submonolayer sensitivity.^{16,17} All measurements reported here were corrected by subtracting the PEY NEXAFS signal recorded on bare silicon oxide substrates from the raw measurements.

Preparation of *n*-Octyltrichlorosilane-Treated Glass (OTS-glass). Glass slides (Fishers Finest, Pittsburgh, PA) were piranha-

cleaned, as previously outlined in a prior publication.¹⁹ These slides were then immersed for 30 min in a solution of 0.324 mL of *n*-octyltrichlorosilane in 140 mL of anhydrous *n*-heptane. The slides were rinsed 2×5 min in dichloromethane and then gently dried under a stream of nitrogen.

Assembly of Optical Cell. Each surface gradient was placed face-to-face with an OTS-treated glass surface, separated by 12 μm thick Mylar spacers (Figure 1d). The surfaces were held together using bulldog clips. 4-Cyano-4'-pentylbiphenyl (5CB, EM Industries, NY) was heated to its isotropic phase and introduced into the optical cell by capillary action. The samples were cooled to room temperature and viewed under a polarizing microscope in reflectance mode.

Image Capture. Images were captured by mounting a digital camera onto a BX-60 Olympus polarizing microscope. To ensure consistency between images, we used fixed settings on the microscope light source (lamp intensity set at half maximum and aperture also set at half maximum) and the digital camera (f-stop 2.8, shutter speed 1/650).

Determination of the Tilt Angle of the LC (θ_t). The optical method used to quantify the tilt of the LC was based on procedures described by Brake and co-workers.²⁰ In brief, interference colors of films of LCs of known thickness (12 μm in the experiments reported in this paper) were recorded using polarized light microscopy under white light illumination to estimate the effective birefringence (Δn_{eff}) of the LC in contact with the region of the surface of interest.^{21,22} We note here that when using reflectance mode polarized light microscopy, the path length of the light is twice the film thickness (24 μm).²¹ By determining the effective birefringence of the LC as a function of position (0.5 mm steps) along the x -axis of the substrate, we used the method of Brake to determine the tilt of the liquid crystal across the gradient surface. Additional details of the method are described below, along with the presentation of the results.

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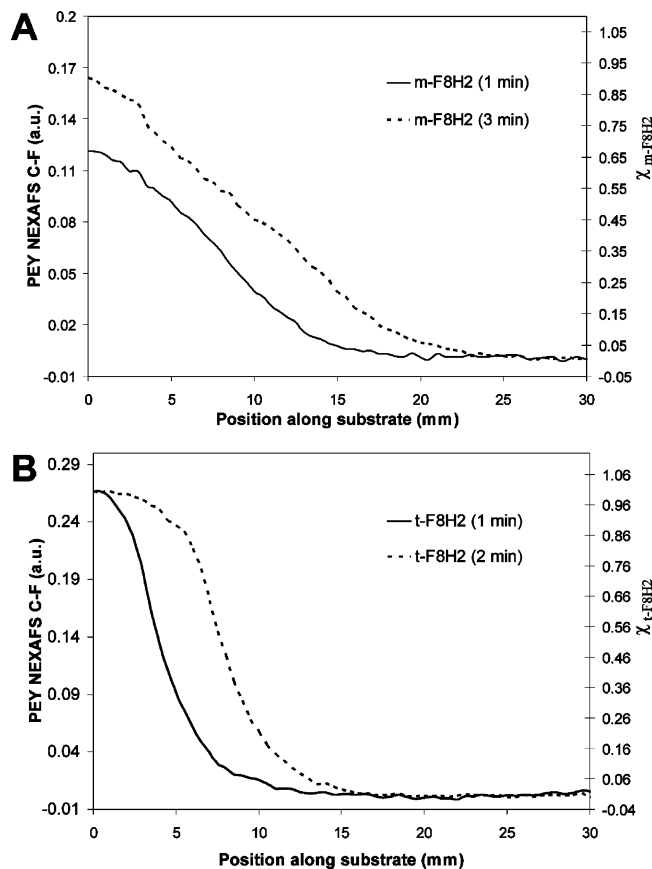


Figure 2. PEY NEXAFS (C–F $1s \rightarrow \sigma^*$ transition) recorded as a function of position along each sample for surface gradients prepared from (a) m-F8H2 and (b) t-F8H2.

Results

Preparation and Characterization of Gradients in Chemical Functionality. Surface gradients were prepared by exposing bare, flat silicon oxide substrates to the diffusion-controlled vapor^{15–17} of two semifluorinated organosilanes: m-F8H2 (for 1 and 3 min) and t-F8H2 (for 1 and 2 min). Each sample was then characterized by NEXAFS, recording the carbon K-edge partial electron yield (PEY) intensity corresponding to the $1s \rightarrow s^*$ transition of a C–F bond as a function of position along the substrate.^{16,17,23} When recorded at a so-called magic angle, PEY NEXAFS is insensitive to the orientation of bonds at the surface.¹⁸ Therefore, the signal intensity is proportional to the number of C–F bonds present at the interface and can be used to indicate the number density of grafted organosilanes at a given position along the sample (see Methods). PEY NEXAFS measurements for surface gradients prepared from m-F8H2 and t-F8H2 are shown in panels a and b of Figure 2, respectively.

The PEY NEXAFS intensities of saturated monolayers of m-F8H2 and t-F8H2 supported on silicon oxide substrates have been reported previously to be 0.183 and 0.266 au, respectively.^{23,24} Therefore, we also report our measurements in terms of the fraction of monolayer coverage (χ) on the secondary y-axis of Figure 2. Our findings are consistent with past studies of gradient surfaces prepared by controlled-

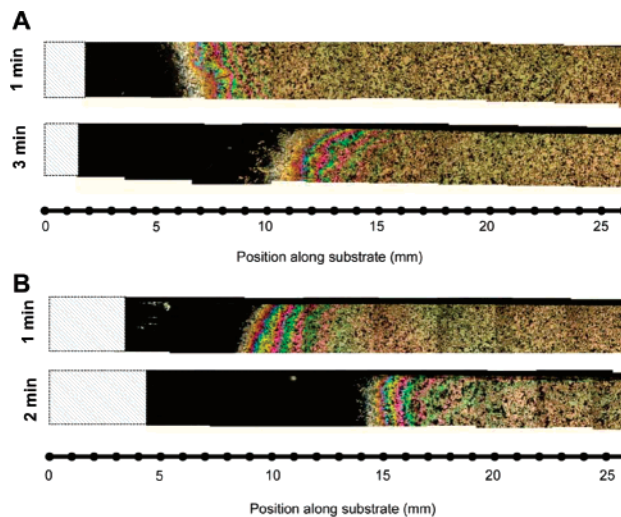


Figure 3. Optical appearances of LC (when viewed using reflectance-mode polarized light microscopy) in contact with surface gradients prepared from (a) m-F8H2 and (b) t-F8H2.

vapor deposition of organosilanes onto oxide substrates^{16,23} and can be summarized as follows: (1) For each sample, there is a continuous gradient in the density of grafted organosilanes as a function of position along the substrate. (2) The density of grafted species at a fixed position can be changed by tuning the time for which the oxide substrates were exposed to the organosilane vapor. Interestingly, the qualitative natures of the profiles of surface gradients formed from m-F8H2 are different than those formed from t-F8H2. This observation will form the basis of a separate publication. Below, we focus on the results of studies aimed at characterizing the orientations of LCs in contact with surfaces possessing density gradients of m-F8H2 and t-F8H2.

Orientations of LC in Contact with Surfaces Presenting Gradients in Chemical Functionality. The orientations of LCs are known to be sensitive to the composition and molecular structure of interfaces.^{1,9} We sought to characterize the orientations of the LC 4-cyano-4'-pentylbiphenyl (5CB) in contact with the above-described surfaces presenting gradients in the densities of organosilanes. We determined the orientations of the LC in contact with the gradient surfaces by preparing optical cells in which a gradient surface was placed face-to-face with an *n*-octyltrichlorosilane (OTS)-treated glass slide (see Methods). The two surfaces were separated by 12 μm spacers and held together using clips, as depicted in Figure 1d. The OTS-treated glass slide was used as the second surface in the optical cell because 5CB is known to assume a homeotropic orientation at that surface. 5CB was warmed to its clearing point and then introduced into the optical cell by capillary action. The optical appearances of the LCs within these optical cells were recorded using reflectance-mode polarized light microscopy.

As the size of each sample (5 mm \times 35 mm) exceeded the field of view of our microscope when using a 4 \times objective, we constructed composite images using several separate photographs (Figure 3). Inspection of Figure 3 reveals that the optical appearance of 5CB in contact with each gradient surface changes as a function of the position along the sample. In each image in Figure 3, 5CB in contact with the leftmost region of the gradient surface (possessing

the highest grafting densities of the organosilane as determined by NEXAFS) is black. As discussed below, these black regions correspond to areas of the gradient surface on which the LC has assumed a homeotropic (perpendicular) orientation. As one moves along the gradient surfaces to the right (toward lower densities of grafted organosilane), the LC exhibits bands of interference colors that extend over distances of millimeters across each gradient surface. At the rightmost end of each sample shown in Figure 3, the 5CB has a grainy optical appearance and constant color. The grains correspond to domains of liquid crystal that possess different azimuthal orientations (as discussed below, within these domains, the orientation of the LC is parallel to the surface).

The bands of interference colors seen in Figure 3 are caused by changes in the birefringence of the LC on the gradient surface.²¹ Because the thickness of the film of the LC is constant across the optical cell, the gradient in birefringence is caused by a gradient in the orientation of the LC across the surface. Because the orientation of the LC is fixed at the OTS-treated surface, we conclude that the orientation of the LC must be changing at the surface that possesses the gradient in chemical functionality.

As described in Methods, we have quantified the orientation of the LC at various positions across the gradient surface.²⁰ When a film of LC is confined by the boundary conditions shown in Figure 4a, the tilt of the LC changes linearly as a function of position across the film of the LC (i.e., $\theta(z)$) to minimize the elastic distortion energy in the LC.²⁵ This permits the establishment of a relationship between the effective birefringence of the LC and the tilt of the LC at the bottom surface (θ_t in Figure 4a)²⁰

$$\Delta n_{\text{eff}} \approx \frac{1}{d} \int_0^d \left(\frac{n_{\perp} n_{\parallel}}{\sqrt{n_{\perp}^2 \sin^2 \left(\frac{z}{d} \theta_t \right) + n_{\parallel}^2 \cos^2 \left(\frac{z}{d} \theta_t \right)}} - n_{\perp} \right) dz \quad (1)$$

where n_{\perp} and n_{\parallel} are the indices of refraction perpendicular and parallel to the optical axis of 5CB and d is the thickness of the film of the LC. We determined Δn_{eff} by comparing the interference colors shown in Figure 3 against a Michel–Levy chart,^{21,22} and then solved eq 1 to find θ_t for each sample of LC as a function of position when in contact with each surface gradient (panels b and c of Figure 4). Inspection of panels b and c of Figure 4 reveals that the tilt of the LC (θ_t) at the surfaces possessing the gradients in chemical functionality changes continuously across a range of interfacial compositions on each substrate (Figure 4d). Interestingly, the tilts observed on these substrates assume the full range of possible values, varying continuously from 90° (orientation of LC parallel to the surface, as seen on the bare oxide surfaces) to 0° (orientation of LC perpendicular to surface, as seen on the densely packed silane surfaces). These findings are interesting in light of previous reports using plasma-based oxidation of silane monolayers, which describe

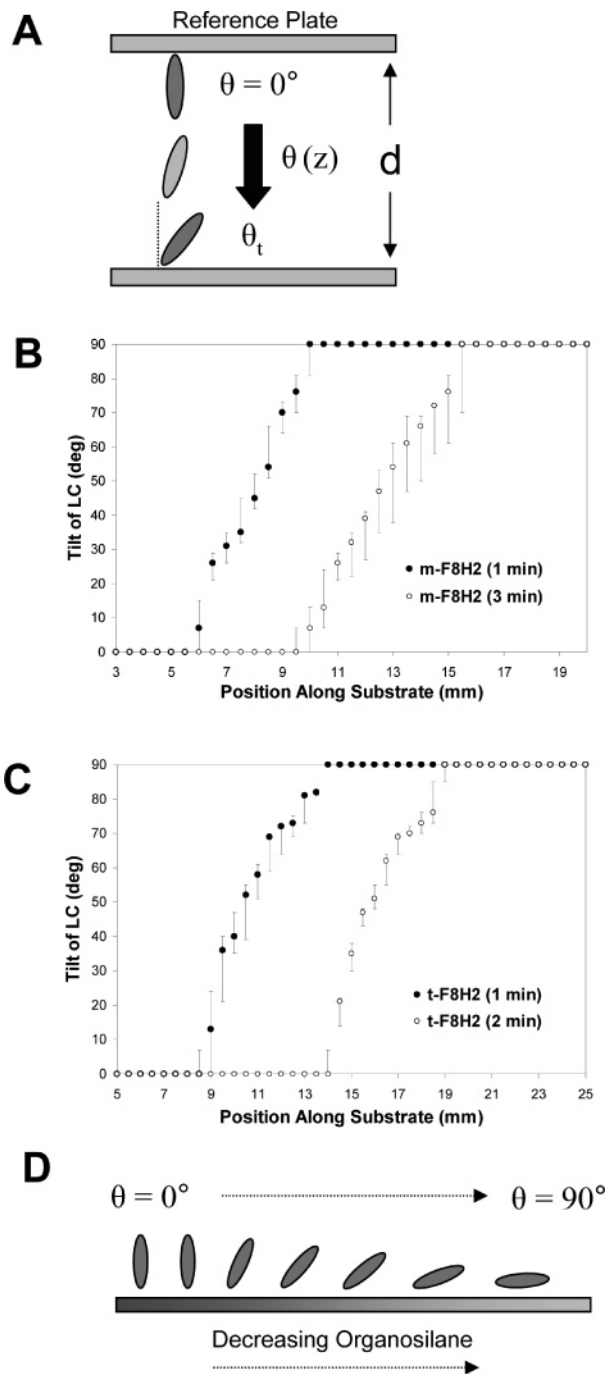


Figure 4. (a) Schematic illustration of the tilt of a LC in an optical cell with perpendicular anchoring of the LC on the top surface, and a tilted orientation of the LC on the bottom surface. (b,c) Tilts of LC across the gradient surfaces, measured using surface gradient formed from m-F8H2 (b) and t-F8H2 (c). (d) Illustration of the tilt of the LC in contact with surface gradients formed from semifluorinated organosilanes.

sharp, discontinuous orientational transitions as a function of the composition of the silane monolayer on the substrate.^{26,27}

Before discussing in more detail the nature of the gradients in interfacial composition and their influence on the orientation of the LC, we note here that the vertical error bars reported in panels b and c of Figure 4 are not caused by

(24) The formation of less-dense monolayers of m-F8H2 can be attributed to steric interactions between the bulky methyl substituents of adjacent species, as described in ref 23.

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uncertainty in the optical method used to quantify the tilts of the LC but rather are due to changes in interference colors (and Δn_{eff}) that occur in the direction that is orthogonal to the long axis of the sample (indicating that the gradient is not exactly parallel to the long axis of the sample). The two-dimensional nature of the surface gradient thus introduced uncertainty into our assignment of Δn_{eff} (and thus θ_t) for each value of x along the substrate.

Discussion

The main result of the study reported in this paper is that surfaces with continuous gradients in surface chemical functionality serve to template continuous changes in the orientations of liquid crystals across these surfaces. We note here that continuous control over θ_t has also been demonstrated by using discontinuous patterns of organosilanes grafted onto a bare oxide substrate.¹³ The patterned features used in the previous study were separated by small distances (nm) such that the LC assumed an average orientation far from the patterned surface that reflected the influence of two discrete chemical functionalities. In contrast, the work presented in this manuscript uses substrates that present spatially continuous gradients that are sufficiently gradual that the LC ordering is defined locally by the substrate composition. Below, we discuss possible mechanisms by which the local composition of the interface dictates the local orientation of the LC. We note here that our investigation of the mechanism discussed below is facilitated by knowledge of the orientation of the LC as a function of the composition of the surface. This information is rapidly obtained via the use of gradient surfaces.

The discussion below is organized into three parts. Each part of the discussion addresses a possible mechanism of interaction between the LC and the gradient surface. We use knowledge of the orientation of the LC as a function of surface composition to test the possible mechanisms of anchoring. Specifically, we address the correlation between the observed behavior of LC and (1) the local grafting density of the semifluorinated alkyl chains presented across each interface, (2) the number density of hydroxyl groups remaining at each interface following reaction with the silanes, and (3) the average orientation of the grafted semifluorinated alkyl chain presented at each interface.

First, we used the data made available by use of the gradient surfaces to determine if the orientation of the LC was determined by the density of grafted semifluorinated chains on the surface. We note here that m-F8H2 and t-F8H2 (shown in Figure 1b) lead to the presentation of the same semifluorinated alkyl chain, with identical numbers of C–F bonds, to the LC. By using the PEY NEXAFS data in Figure 2, and the measurements of the orientation of the LC in Figure 4, we plot the tilt of the LC as a function of the grafting density of semifluorinated alkyl chains for surfaces prepared from both m-F8H2 and t-F8H2 (Figure 5).

We make three observations using the data shown in Figure 5.

(i) Inspection of the data in Figure 5a for t-F8H2 reveals that surface coverages corresponding to 0.004 ± 0.002 au

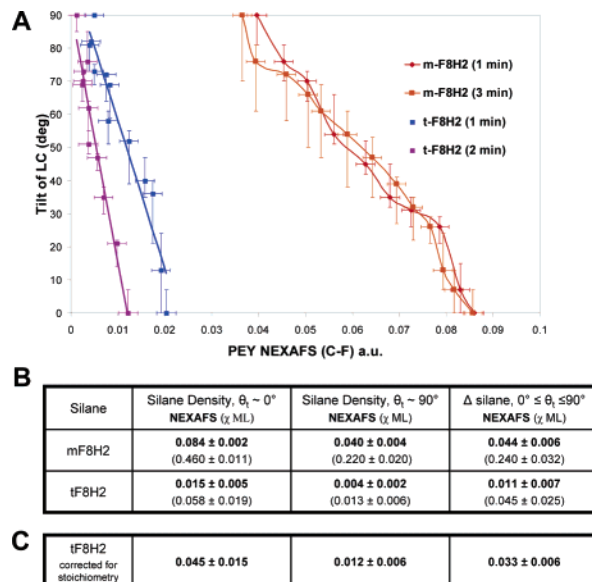


Figure 5. (a) Tilt angles of LC measured across gradient surfaces plotted as a function of the composition of the surfaces. (b) Table showing critical surface concentrations of m-F8H2 and t-F8H2 at which a homeotropic orientation of the LC is observed (column 1), the orientation of the LC is observed to depart from a parallel orientation (column 2), and the range of surface compositions over which tilts in orientation are measured (column 3). (c) Data from row 2 of (b), corrected for the reaction stoichiometry of t-F8H2 with surface hydroxyl groups (see text for details). The quantity in the parentheses indicates the fraction of monolayer coverage.

(NEXAFS) or 0.013 ± 0.006 of monolayer coverage are sufficient for perturbing the LC away from its planar orientation on the native oxide surface. This result illustrates the sensitivity of the orientations of LCs to the composition of surfaces.

(ii) Inspection of Figure 5 reveals that for a given silane (m-F8H2 or t-F8H2), the data obtained using two different spatial gradients in surface composition collapse to a universal curve when the orientation of the LC is plotted as a function of surface composition rather than position. A summary of the interfacial composition (reported as PEY NEXAFS signal intensity and fraction of monolayer, χ) over which each silane caused a tilted orientation of the LC is presented in Figure 5b. Thus, we conclude that for samples prepared using the same organosilane, θ_t appears to correlate with grafting density.

(iii) Inspection of Figure 5a reveals that the data obtained using both t-F8H2 and m-F8H2 do not collapse onto a universal curve when plotted as a function of the density of semifluorinated chains grafted onto the oxide substrate. From these results, we can conclude that the tilted behavior of LC is, in fact, not determined solely by the grafting density of the semifluorinated chains on these surfaces, because both t-F8H2 and m-F8H2 present the same chains to the LC. This conclusion contrasts with conclusions of prior studies performed on the basis of a single type of silane monolayer.¹³

The second proposition regarding the interactions of the LC and gradient surfaces that we examined considered a possible role for the hydroxyl groups (silanol groups) presented at these surfaces. The hydroxyl groups presented at the surfaces of metal oxide substrates are known to interact (via hydrogen-bonding) with the nitrile functional groups of

5CB.^{28,29} Because the reactions of silanes with these surfaces lead to a decrease in the density of hydroxyl groups, we explore the proposition that the orientations on the LC measured across the gradient surfaces are controlled by the densities of hydroxyl groups remaining after reaction of the silanes with the surfaces.²⁸

Although we do not have a direct measure of the density of hydroxyl groups on these surfaces, we made an estimate by noting that monochlorosilanes (m-F8H2) can only react with one surface-exposed hydroxyl group, whereas trichlorosilanes (t-F8H2) can potentially react with as many as three hydroxyl groups. Although the probability of a reaction stoichiometry of three for t-F8H2 is low, use of this stoichiometry allows us to place a lower bound on the density of hydroxyl groups presented at the surfaces reacted with t-F8H2. To reflect this possible difference in the stoichiometry of the reactions of m-F8H2 and t-F8H2 with the surface hydroxyl groups on the silicon oxide surfaces, we multiplied the NEXAFS signal intensities for t-F8H2 by a factor of 3, as shown in Figure 5c. After this correction (an upper bound), we conclude that the onset of tilting of the LC on the surfaces with t-F8H2 must begin at a higher density of surface hydroxyl groups compared to that of m-F8H2 (by a factor of 2–3). From this analysis, we conclude that the removal of surface-exposed hydroxyl groups (by reaction with organosilanes) cannot provide an account for the observed orientational behavior of the LC on these gradient surfaces.

Third, and finally, we sought to use the data provided by the gradient surfaces to test the proposition that structural features of these surfaces, such as the average orientation of the grafted organosilane species at the interface, may play a role in dictating the orientation of the LC on the surface. Genzer and co-workers,^{23,30} using angle-dependent NEXAFS, have established an empirical relationship (valid for $0 < \chi < 1$) between the average tilt of the semifluorinated alkyl chain (τ , Figure 6a) and the grafting density of both t-F8H2 and m-F8H2

$$\tau_{t\text{-F8H2}} = 54.7 - 7.9(\chi_{t\text{-F8H2}}) - 44.5(\chi_{t\text{-F8H2}})^2 \quad (2)$$

$$\tau_{m\text{-F8H2}} = 54.9 - 5.8(\chi_{m\text{-F8H2}}) - 3.5(\chi_{m\text{-F8H2}})^2 \quad (3)$$

where χ is the fraction of monolayer coverage (panels a and b of Figures 2, secondary vertical axis). In the case of t-F8H2, τ is a strong function of grafting density and can range from 2 to 55°. In contrast, τ for m-F8H2 is not a strong function of grafting density and has a limited range of 45–55°.

We used eqs 2 and 3 to prepare plots of the tilt of LC (θ) as a function of τ , as shown in Figure 6b. Although the average tilt of the semifluorinated chains (τ) ranges from 2 to 55° for t-F8H2 and from 45 to 55° for m-F8H2 across each substrate, inspection of Figure 6b reveals the result that the change in tilt of the LC occurs over a narrow range of τ (from 50 to 54°) for both m-F8H2 and t-F8H2 (Figure 6c). These experimental findings lead to the proposition that the tilted orientation of the semifluorinated alkyl chain may

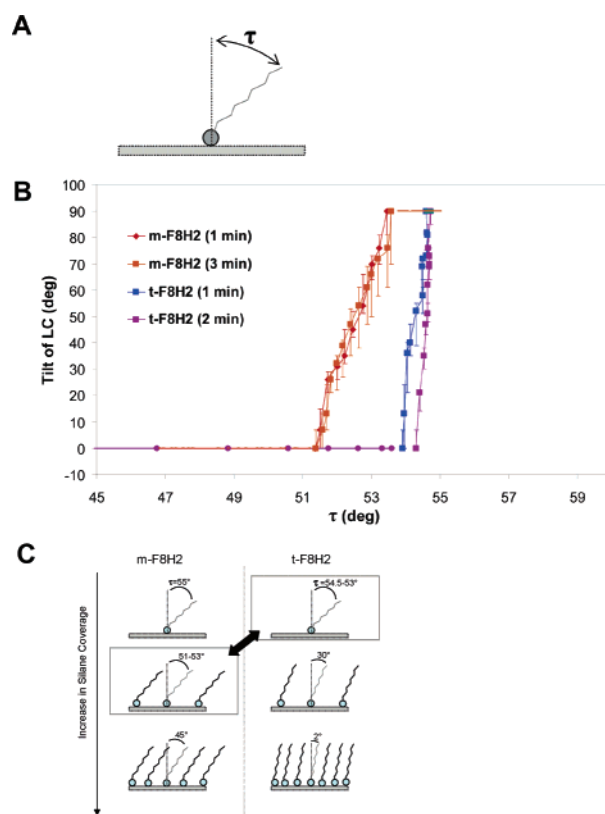


Figure 6. (a) Schematic illustration of the tilt angle of a semifluorinated alkyl chain (τ) as measured from the normal surface. (b) Plot of the tilt of the LC as a function of τ . (c) Schematic illustration summarizing the orientational behavior of LC in contact with submonolayer quantities of organosilane.

influence the orientations of the LCs on surfaces. Although additional studies are required to further test this proposition, the idea finds support in past observations of the orientations of LCs on surface-immobilized azobenzene groups.³¹ In those studies, it was observed that a change in the orientation of the azobenzene group from trans to cis (upon illumination with UV light) gives rise to a new LC orientation. The change in orientation of the LC is interpreted to result from a change in the dipole moment of the azobenzene upon isomerization. We note that semifluorinated alkyl chains, when organized into monolayers at an interface, display dipole moments that are dependent upon the orientation of molecules at the surface.^{32,33} Such oriented dipoles, if present at the surfaces reported here, may influence the orientation of the LC in a manner that depends on the average tilted orientation of the semifluorinated alkyl chains.

Conclusions

The main conclusions of the work reported in this paper are 2-fold. First, we have demonstrated that gradients in chemical functionality presented at surfaces can template continuous spatial gradients in the orientations of the nematic

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LC 4-cyano-4'-pentylbiphenyl on a surface. We observe that a full range of tilt angles of the LC can be realized by continuous control over the density of semifluorinated silanes grafted onto oxidized silicon substrates. Second, we have used the data provided by these gradient surfaces to test hypotheses regarding the nature of the interaction between the LC and surfaces that give rise to the tilted orientations of the LC. We conclude that the orientations of the LC are not determined solely by the density of grafted semifluorinated chains or by the density of residual hydroxyl groups presented at the surfaces following reactions with the silanes. Instead, our results raise the possibility that the tilt angles of the semifluorinated chains on these surfaces may influence

the orientation of the LC. This proposition will be tested further in future studies to be reported elsewhere.

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