

Measurement of the Azimuthal Anchoring Energy of Liquid Crystals in Contact with Oligo(ethylene glycol)-Terminated Self-Assembled Monolayers Supported on Obliquely Deposited Gold Films

Brian H. Clare, Orlando Guzmán, Juan J. de Pablo, and Nicholas L. Abbott*

Department of Chemical and Biological Engineering, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received December 29, 2005. In Final Form: March 8, 2006

We report measurements of the orientations and azimuthal anchoring energies of the nematic liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) on polycrystalline gold films that are deposited from a vapor at an oblique angle of incidence and subsequently decorated with organized monolayers of oligomers of ethylene glycol. Whereas the gold films covered with monolayers presenting tetra(ethylene glycol) (EG4) lead to orientations of 5CB that are perpendicular to the plane of incidence of the gold, monolayers presenting tri(ethylene glycol) (EG3) direct 5CB to orient parallel to the plane of incidence of the gold during deposition of the gold film. We also measure the azimuthal anchoring energy of the 5CB to be smaller on the surfaces presenting EG3 ($3.2 \pm 0.8 \mu\text{J}/\text{m}^2$) as compared to EG4 ($5.5 \pm 0.9 \mu\text{J}/\text{m}^2$). These measurements, when combined with other results presented in this paper, are consistent with a physical model in which the orientation and anchoring energies of LCs on these surfaces are influenced by both (i) short-range interactions of 5CB with organized oligomers of ethylene glycol at these surfaces and (ii) long-range interactions of 5CB with the nanometer-scale topography of the obliquely deposited films. For surfaces presenting EG3, these short- and long-range interactions oppose each other, leading to small net values of anchoring energies that we predict are dependent on the level of order in the EG3 SAM. These measurements provide insights into the balance of interactions that control the orientational response of LCs to biological species (proteins, viruses, cells) on these surfaces.

Introduction

Nematic liquid crystals (LCs) are materials that can exhibit orientational order over distances that are much greater (micrometer) than the sizes of their molecular components (nanometer).¹ Near the surface of a structured solid, a LC will typically assume a preferred average orientation due to interactions with the solid.^{2,3} The orientation of the director of the LC near such an interface, in the absence of an additional external field, is defined as the easy axis, η_0 . A variety of approaches have been investigated to prepare structured solid surfaces that lead to changes in the orientation of η_0 , including the mechanical shearing of polymers and the use of microfabricated surfaces with micrometer- and nanometer-scale topography.^{2,3} An equally important aspect of the phenomenon of the anchoring of LCs at surfaces is the energy of interaction between the substrate and LC. The energy of interaction leading to a particular azimuthal orientation can be characterized by the so-called azimuthal anchoring energy, defined as

$$\tau = W_{az} \sin 2\varphi/2 \quad (1)$$

where τ is the magnitude of torque applied to the LC at the surface (surface anchoring torque) that leads to a departure of the azimuthal orientation of the director of the LC from the easy axis by an angle of φ . Knowledge of W_{az} permits prediction of the responses of LCs to external perturbations (e.g., electrical or magnetic fields) and also provides fundamental insights into the nature of the interactions between the LCs and surfaces that define the preferred orientations of LCs. In this paper, we report

measurements of the azimuthal anchoring energy of the nematic LC 4-cyano-4'-pentylbiphenyl (5CB) with structured interfaces that present oligomers of ethylene glycol.

A number of past studies have reported measurements of the azimuthal anchoring energy of mechanically sheared, polymeric surfaces.^{4–7} It is now understood that mechanical shearing of polymeric surfaces simultaneously introduces two elements of surface structure that can influence the anchoring energy of a LC: (1) micro- and nanogrooves (topography)⁸ and (2) preferred alignments of the polymer chains in the near-surface region of the substrate.^{9,10} Several groups have isolated the contributions that surface topography can make to azimuthal anchoring energies by studying LCs in contact with substrates having feature sizes that can be systematically controlled (e.g. surface gratings^{11,12} or periodic microrelief structures prepared by the deformation of hard coatings supported on soft polymeric substrates¹³). Distortion of the director of the LC over the topography of the surface can create an “elastic contribution” to the anchoring energy.⁸ In addition, the influence of the molecular-level organization of substrate molecules on azimuthal anchoring energies of LCs have been studied independently of topography

(4) Sato, Y.; Sato, K.; Uchida, T. *Jpn. J. Appl. Phys.* 2 **1992**, 31, L579.

(5) Lee, E. S.; Vetter, P.; Miyashita, T.; Uchida, T. *Jpn. J. Appl. Phys.* 2 **1993**, 32, L1339.

(6) Ban, B. S.; Kim, Y. B. *J. Phys. Chem. B* **1999**, 103, 3869.

(7) Oka, S.; Mitsumoto, T.; Kimura, M.; Akahane, T. *Phys. Rev. E* **2004**, 69, 061711.

(8) Berreman, D. W. *Phys. Rev. Lett.* **1972**, 28, 1683.

(9) Toney, M. F.; Russell, T. P.; Logan, J. A.; Kikuchi, H.; Sands, J. M.; Kumar, S. K. *Nature* **1995**, 374, 709.

(10) Stohr, J.; Samant, M. G.; Luning, J.; Callegari, A. C.; Chaudhari, P.; Doyle, J. P.; Lacey, J. A.; Lien, S. A.; Purushothaman, S.; Speidell, J. L. *Science* **2001**, 292, 2299.

(11) Newsome, C. J.; O'Neill, M.; Farley, R. J.; Bryan-Brown, G. P. *Appl. Phys. Lett.* **1998**, 72, 2078.

(12) Wood, E. L.; Bradberry, G. W.; Cann, P. S.; Sambles, J. R. *J. Appl. Phys.* **1997**, 82, 2483.

(13) Belyaev, V.; Misnik, V.; Trofimov, S.; Volynsky, A.; Kononov, V.; Muravski, A. *Appl. Phys. Lett.* **2005**, 86, 011904.

* To whom correspondence should be addressed. Phone: (608) 265-5278. Fax: (608) 262-5434. E-mail: abbot@engr.wisc.edu.

(1) de Gennes, P. G. *The Physics of Liquid Crystals*, 1st ed.; Oxford University Press: London, 1974.

(2) Cognard, J. *Mol. Cryst. Liq. Cryst. Suppl.* **1982**, 78, 1.

(3) Jerome, B. *Rep. Prog. Phys.* **1991**, 54, 391.

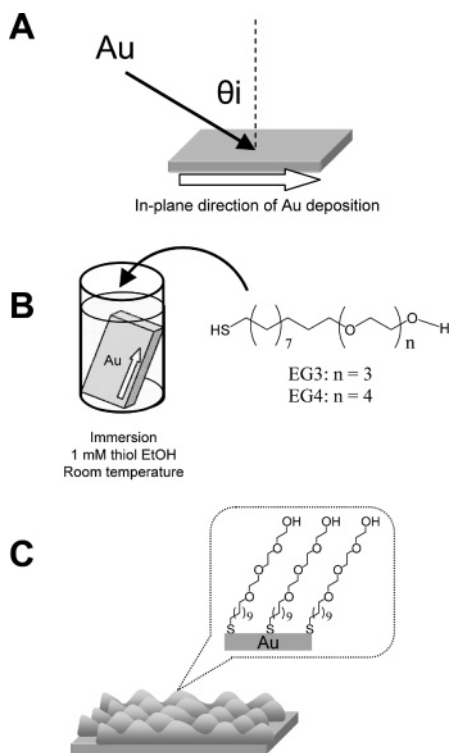


Figure 1. Preparation of self-assembled monolayers supported on obliquely deposited gold films. (A) Vapor deposition of gold at the oblique angle of incidence, θ_i . (B) Immersion of gold films into ethanolic solutions of EG3 or EG4. (C) Schematic illustration of surfaces with nanometer-scale topography that support SAMs.

via the exposure of photoactive polymeric layers to linearly polarized light.^{14–17} Intermolecular forces, such as van der Waals interactions, define the anchoring energies of LCs on these surfaces. In this paper, we report a methodology that permits measurement of the azimuthal anchoring energy of LCs on self-assembled monolayers (SAMs) of ω -functionalized alkanethiols supported on gold films prepared by the vapor deposition of gold at oblique angles of incidence (θ_i , measured from the surface normal), as shown in Figure 1A,B. This experimental system permits manipulation of the nanometer-scale topography of the surface¹⁸ and the in-plane ordering of organosulfur species that present a wide range of chemical functional groups to the LC (Figure 1C).¹⁹ The in-plane ordering of molecules on obliquely deposited gold films is guided by the crystallographic texturing of the underlying gold film (caused by oblique deposition).^{19,20} The choice of the terminal group of the SAMs also allows one to tune the nature of the molecular-level interaction between substrate and the LC, such as hydrogen-bonding,²¹ van der Waals,²² or electrical double layer interactions.²³

The study we report in this paper is broadly motivated by recent demonstrations that the orientations of LCs can serve to

amplify changes in surface structure brought about by the binding of biological species (e.g., proteins,^{18,24–26} viruses,²⁷ and cells²⁸) to interfaces. Oligo(ethylene glycol)-terminated SAMs (EGX SAMs) on gold films have formed the basis of some of these approaches,^{29,30} as they are known to resist (or partially resist) the nonspecific adsorption of proteins.^{31–36} The study reported here sought to develop a deeper understanding of the behavior of LCs in contact with EGX SAMs, as the molecular-level organization of SAMs and morphology of the supporting gold film are known to influence the sensitivity with which LCs report the presence of bound analytes.^{18,26} We also note that the study reported in this paper, in which the orientation of LCs depends on the organization of EGX SAMs, is broadly relevant to understanding protein adsorption on these interfaces, as the tendency of EGX SAMs to resist protein adsorption has been proposed to depend on the extent of order present in the monolayer.^{37–40} Finally, we comment that the methodology described below may also provide approaches to quantitation of LC-based assays for molecular and biomolecular interactions.

This paper reports use of the so-called elastic torque-balance method to measure W_{az} for nematic 5CB in contact with three substrates that were prepared with different nanometer-scale topographies and SAMs.^{12,41,42} Briefly, two identically treated substrates are used to confine the LC and are arranged such that the easy axes η_0 are oriented orthogonally (Figure 2A). The surfaces are spaced apart in a wedge-shaped geometry, such that the thickness of the film of LC varies across the sample (Figure 2B). For sufficiently thin LC films, the bulk elastic torque of the twisted LC competes with the surface anchoring torque, resulting in an equilibrium orientation of the director at η_d (Figure 2C), where the behavior of the twisted LC is governed by the following expression (see ref 42 for derivation)

$$W_{az} = \frac{2K_{22}\Psi}{d \sin 2\varphi} \quad (2)$$

where K_{22} is the twist elastic constant for the LC, d is the thickness of the film of LC, φ is the angle with which the equilibrium position of the director deviates from the easy axis, and Ψ is the angular twist of the director in the LC. φ and Ψ are measured using an optical method that we have adapted from Fonseca and Galerne,⁴² where we employ the use of patterned SAMs to

(14) Li, X. T.; Pei, D. H.; Kobayashi, S.; Iimura, Y. *Jpn. J. Appl. Phys.* **2** **1997**, *36*, L432.

(15) Hasegawa, M. *Jpn. J. Appl. Phys.* **2** **2002**, *41*, L1167.

(16) Thieghi, L. T.; Barberi, R.; Bonvent, J. J.; Oliveira, E. A.; Giacometti, J. A.; Balogh, D. T. *Phys. Rev. E* **2003**, *67*, 041701.

(17) Mitsumoto, T.; Oka, S.; Kimura, M.; Akahane, T. *Jpn. J. Appl. Phys.* **2005**, *44*, 4062.

(18) Skaife, J. J.; Brake, J. M.; Abbott, N. L. *Langmuir* **2001**, *17*, 5448.

(19) Follonier, S.; Miller, W. J. W.; Abbott, N. L.; Knoesen, A. *Langmuir* **2003**, *19*, 10501.

(20) Everitt, D. L.; Miller, W. J. W.; Abbott, N. L.; Zhu, X. D. *Phys. Rev. B* **2000**, *62*, R4833.

(21) Luk, Y.-Y.; Yang, K.-L.; Cadwell, K.; Abbott, N. L. *Surf. Sci.* **2004**, *570*, 43.

(22) Gupta, V. K.; Abbott, N. L. *Phys. Rev. E* **1996**, *54*, R4540.

(23) Shah, R. R.; Abbott, N. L. *J. Phys. Chem. B* **2001**, *105*, 4936.

(24) Gupta, V. K.; Skaife, J. J.; Dubrovsky, T. B.; Abbott, N. L. *Science* **1998**, *279*, 2077.

(25) Skaife, J. J.; Abbott, N. L. *Langmuir* **2000**, *16*, 3529.

(26) Skaife, J. J.; Abbott, N. L. *Langmuir* **2001**, *17*, 5595.

(27) Tercero Espinoza, L. A.; Schumann, K. R.; Luk, Y.-Y.; Israel, B. A.; Abbott, N. L. *Langmuir* **2004**, *20*, 2375.

(28) Fang, J.; Ma, W.; Selinger, J. V.; Shashidar, R. *Langmuir* **2003**, *19*, 2865.

(29) Clare, B. H.; Abbott, N. L. *Langmuir* **2005**, *21*, 6451.

(30) Luk, Y.-Y.; Tingey, M. L.; Hall, D. J.; Israel, B. A.; Murphy, C. J.; Bertics, P. J.; Abbott, N. L. *Langmuir* **2003**, *19*, 1671.

(31) Prime, K. L.; Whitesides, G. M. *Science* **1991**, *252*, 1164.

(32) Pale-Grosmange, C.; Simon, E. S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 12.

(33) Sigal, G. B.; Bamdad, C.; Barberis, A.; Strominger, J.; Whitesides, G. M. *Anal. Chem.* **1996**, *68*, 490.

(34) Lahiri, J.; Isaacs, L.; Grzybowski, B.; Carbeck, J. D.; Whitesides, G. M. *Langmuir* **1999**, *15*, 7186.

(35) Houseman, B. T.; Huh, J. H.; Kron, S. J.; Mrksich, M. *Nature Biotechnology* **2002**, *20*, 270.

(36) Houseman, B. T.; Gawalt, E. S.; Mrksich, M. *Langmuir* **2003**, *19*, 1522.

(37) Schwendel, D.; Dahint, R.; Herrwerth, S.; Schloersholz, M.; Eck, W.; Grunze, M. *Langmuir* **2001**, *17*, 5717.

(38) Harder, P.; Grunze, M.; Dahint, R.; Whitesides, G. M.; Laibinis, P. E. *J. Phys. Chem. B* **1998**, *102*, 426.

(39) Herrwerth, S.; Eck, W.; Reinhardt, S.; Grunze, M. *J. Am. Chem. Soc.* **2003**, *125*, 9359.

(40) Vanderah, D. J.; Valincius, G.; Meuse, C. W. *Langmuir* **2002**, *18*, 4674.

(41) Polossat, E.; Dozov, I. *Mol. Cryst. Liq. Cryst.* **1996**, *282*, 223.

(42) Fonseca, J. G.; Galerne, Y. *Appl. Phys. Lett.* **2001**, *79*, 2910.

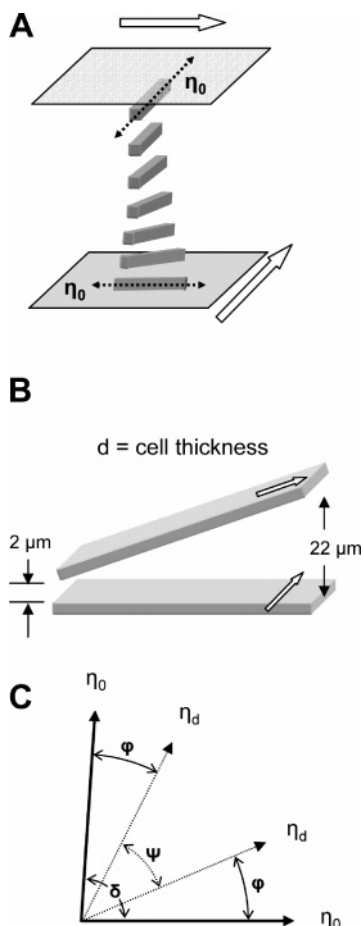


Figure 2. Geometry of LC cell for measurement of azimuthal anchoring energy. (A) Confining surfaces are oriented orthogonally so as to induce a twist distortion in the LC. (B) Wedge-cell construction for control of spacing between surfaces. (C) Diagram depicting the equilibrium position of the director and easy axis near each interface.

determine the angle formed between η_0 of the top surface and η_0 of the bottom surface (abbreviated as δ).

Materials and Methods

Materials. All materials were used as received, unless otherwise noted. Fisher's Finest glass slides were obtained from Fisher Scientific (Pittsburgh, PA). Gold (99.999% purity) was obtained from International Advanced Materials (Spring Valley, NY). Titanium (99.99% purity) was obtained from PureTech (Brewster, NY). Liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) was obtained from EM Industries (New York, NY), sold under the trademark name Licristal (K15). Oligo(ethylene glycol)-terminated thiols were synthesized using previously published methods.³² Ethanol (200 proof) was obtained from Aaper Alcohol (Shelbyville, KY) and purged at least 1 h with argon gas prior to use. Poly(dimethylsiloxane) (PDMS) elastomeric stamps were prepared using Sylgard 184 silicone elastomer kit obtained from Dow Corning (Midland, MI).

Preparation of Gold Substrates. Glass slides were first cleaned using a piranha solution as outlined in a prior publication.⁴³ The slides were then positioned within the chamber of an electron beam evaporator such that the incident angle of the flux of metal onto the substrate (depicted in Figure 1A) could be controlled. The incident angles were measured manually using a digital level, with an accuracy of $\pm 2^\circ$. All metal films were deposited at chamber pressures $< 1 \times 10^{-6}$ Torr and at deposition rates of $< 0.2 \text{ \AA/s}$. First, a thin film of titanium (total thickness of $42\text{--}60 \text{ \AA}$) was deposited onto the glass substrate to serve as an adhesion layer. Next, semitransparent films

of gold (total thickness $105\text{--}140 \text{ \AA}$) were deposited onto the substrate. These substrates will be referred to as "obliquely deposited gold films". All gold substrates were used within 1 h of removal from the evaporator chamber.

Formation of Patterned Self-Assembled Monolayers (SAMs).

We prepared patterned SAMs to determine the angle formed between η_0 of the top surface and η_0 of the bottom surface (abbreviated as δ). First, a PDMS elastomeric stamp $2\text{--}3 \text{ mm}$ in width and $2\text{--}3 \text{ mm}$ in height was cast from an aluminum master. The stamp was inked with a 1 mM ethanolic solution of either pentadecanethiol or hexadecanethiol and then gently dried using a stream of nitrogen gas. The stamp was placed in contact with the obliquely deposited gold film for $5\text{--}10 \text{ s}$. Next, 1 mM solutions of oligo(ethylene glycol)-terminated thiols were prepared using argon-purged ethanol. These solutions were stored under an argon atmosphere to prevent oxidation of the sulfhydryl functionality. The gold substrates were next immersed into the thiol solutions for 18 h, rinsed with copious amounts of water and ethanol, and then gently dried under a stream of nitrogen gas prior to placing them in contact with 5CB.

Preparation of Optical Cell Having Wedge-Shaped Geometry.

Two identically treated substrates of interest were placed face-to-face, such that the in-plane direction of deposition of gold for the bottom surface was rotated approximately 90° relative to the in-plane direction of gold deposition of the top surface (shown in Figure 2A). The surfaces were separated by a $22 \mu\text{m}$ spacer (Mylar film) at one end and were not separated by a spacer at the other end, to create a wedge-shaped cell (shown in Figure 2B). The optical cell and 5CB were both warmed to approximately $40\text{--}45^\circ \text{C}$ (above the clearing point for 5CB). 5CB was then drawn into the optical cell by capillary action and slowly cooled to room temperature. Measurements of the optical properties of the LC films were performed 30 min after cooling the samples to room temperature (22°C), as both temperature⁴⁴ and age of the sample (surface gliding)⁴² have been reported to influence the measured anchoring strength on some surfaces.

Optical Determination of d , δ , Ψ and φ . The measurement of the anchoring energy required determination of the parameters d , δ , Ψ , and φ , as defined in eq 2 and the associated text. Here we briefly outline the methodology and refer the reader to the Supporting Information for a detailed description. First, we determined the thickness of the LC, d , by measuring interference colors generated upon illumination of the liquid crystals with white light. Second, the value of δ , which characterizes the relative orientation of the easy axis of the liquid crystal at the top and bottom surfaces of the cell, was determined optically. As described in the Supporting Information, our approach takes advantage of the use of microcontact printing to create "reference regions" on the surfaces for determination of δ . Using these regions, the sample was aligned on a polarized light microscope with the easy axis on the bottom surface of the cell in an orientation that was parallel to the plane of polarization of the incident light. The analyzer was then rotated to determine the easy axis of the liquid crystal at the top surface (corresponds to a minimum in intensity of light transmitted through the analyzer). Measurements were taken using a polarized light microscope (BX 60, Olympus) equipped with an $X\text{--}Y$ translating stage and fitted with a digital camera for image capture. A similar protocol permitted determination of Ψ and φ for each value of d on regions of the surface presenting the EG3 or EG4 SAMs.⁴² We refer the reader to the Supporting Information for detailed procedures. Inspection of eq 2 reveals that a plot of $2\Psi/\sin 2\varphi$ as a function of d should be linear with a slope corresponding to W_{az}/K_{22} .

Results

We prepared three types of surfaces (surfaces I–III) for measurements of azimuthal anchoring energies. These surfaces were prepared by oblique deposition of thin films of gold and

(43) Skaife, J. J.; Abbott, N. L. *Chem. Mater.* **1999**, *11*, 612.

(44) Iimura, Y.; Kobayashi, N.; Kobayashi, S. *Jpn. J. Appl. Phys.* **1995**, *34*, 1935.

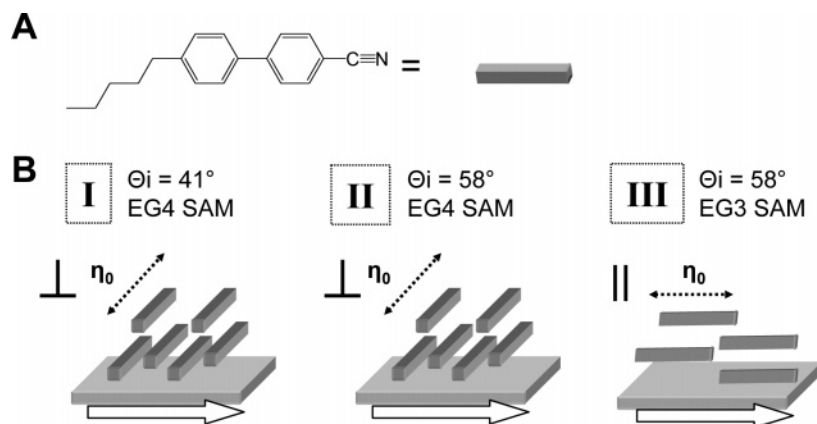


Figure 3. Three interfaces for which the azimuthal anchoring energy is determined. (A) Molecular structure of 4-cyano-4'-pentylbiphenyl (5CB). (B) Schematic illustration of surfaces I–III. Surfaces I and II differ in deposition angle θ_i . Surfaces II and III differ in the molecular structure of thiol used to form the SAM. The large arrow indicates the direction of deposition of the gold. The orientation of the easy axis of 5CB on each surface is also depicted.

the self-assembly of oligo(ethylene glycol)-terminated monolayers. Surfaces I and II (see Figure 3) differ in the angle at which the gold was deposited onto the titanium-primed surface of the glass microscope slide. Surface I was deposited at an angle of incidence of 41° (measured from the surface normal), whereas surface II was deposited at an angle of incidence of 58° . As discussed in more detail below, manipulation of the angle of deposition of the gold leads to changes in the nanometer-scale morphology of gold films.⁴³ On surfaces I and II, SAMs were formed using EG4, and the easy axis η_0 was determined to be within the plane of the surface (planar anchoring) and perpendicular to the plane of incidence of the gold during deposition of the gold (Figure 3B; see Supporting Information for details of methods used to determine the orientation of the LCs). A third type of surface (surface III) was prepared by using gold films deposited at angles of incidence of 58° and SAMs formed from EG3. Comparison of the azimuthal anchoring energies on surfaces II and III thus permits assessment of the influence of changes in the molecular level structure of these SAMs (EG4 versus EG3) on the orientation and anchoring energy of the liquid crystal. On surface III, we determined that the easy axis of the LC was *parallel* to the plane of incidence of the gold during deposition of the gold film (see Figure 3B).

Using the optical method described by Fonseca and Galerne,⁴² we next measured (1) φ (deviation of director η_d from the easy axis η_0) and (2) Ψ (twist angle of the liquid crystal) for each set of substrates depicted in Figure 3B as a function of thickness of the film of LC. For clarity in our discussion here, we describe the measurements of φ as a function of cell thickness for the specific case of the EG4 SAM formed on the gold films deposited at an angle of incidence of $\theta_i = 58^\circ$, as shown in Figure 4. Inspection of Figure 4 reveals that as the thickness of the LC film (d) decreases, the equilibrium position of the director deviates by a larger angle from the easy axis. This behavior is consistent with the anticipated balance of torques acting on the LC, as the bulk elastic torque (which causes the deviation of the director away from the easy axis) is inversely proportional to d . When using very thick films of LC ($d \geq 50 \mu\text{m}$), we measured the deviation angle φ to approach zero (data not shown). Error bars in the y -direction reflect uncertainty in the measurement of the two angles used to determine φ ($\pm 0.5^\circ$), and error bars in the x -direction reflect uncertainty in thickness measurements. The interpretation of the optical properties of the twisted LC that we use to determine φ (and Ψ) is only valid for films of LC of sufficient thickness, in the Mauguin waveguide regime.⁴²

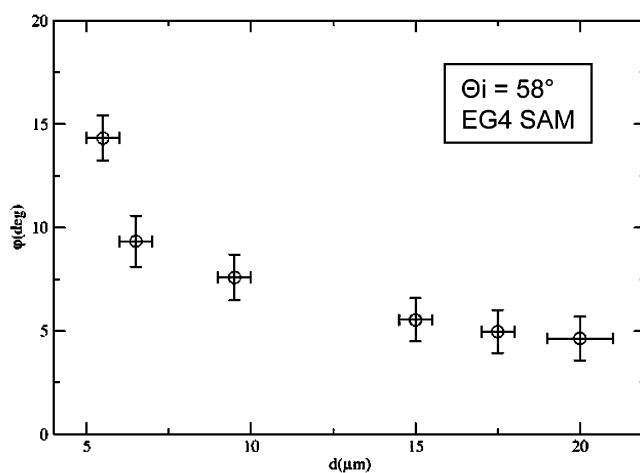


Figure 4. Deviation of director from easy axis on surface II, reported as a function of LC film thickness.

To estimate W_{az} , we first fit our data according to the torque balance eq 1.^{12,41,42} For each set of substrate conditions (surfaces I–III), we plot (Ψ/d) vs $(\sin 2\varphi)/2$, as shown in Figure 5A. The error bars in the x - and y -direction for each data point reflect uncertainties in our measurements of thickness (d) and of the angles used to calculate Ψ and φ . For some points, the y -axis error bar is small enough that it fits within the data point. According to the torque-balance model, a linear fit of these data will have a slope equal to the ratio W_{az}/K_{22} . We note that the data point (filled) corresponding to the smallest thickness of the cell deviates substantially from the linear fit. We believe this systematic deviation from linearity reflects a departure from the Mauguin waveguide regime. Our linear fits of each data set were subjected to a χ^2 test, and each fit was acceptable with a significance level of 95%. We calculated the azimuthal anchoring energy W_{az} for each set of substrate conditions, summarized in Figure 5B, using a value for K_{22} at 22°C of $4.22 \pm 0.52 \text{ pN}$.⁴⁵ We note here that we assume that the surfaces do not cause local changes in the twist elastic constant of the liquid crystal, as discussed in a previous publication.⁴³ Inspection of Figure 5B reveals that the anchoring energies are in the $\mu\text{J}/\text{m}^2$ range and that both the morphology of the gold (surfaces I and II) and the structure of the SAM (surfaces II versus III) impact the value of the anchoring energies. The influence of these parameters is discussed in more detail below.

(45) Toyooka, T.; Chen, G.-P.; Takezoe, H.; Fukuda, A. *Jpn. J. Appl. Phys.* **1987**, *26*, 1959.

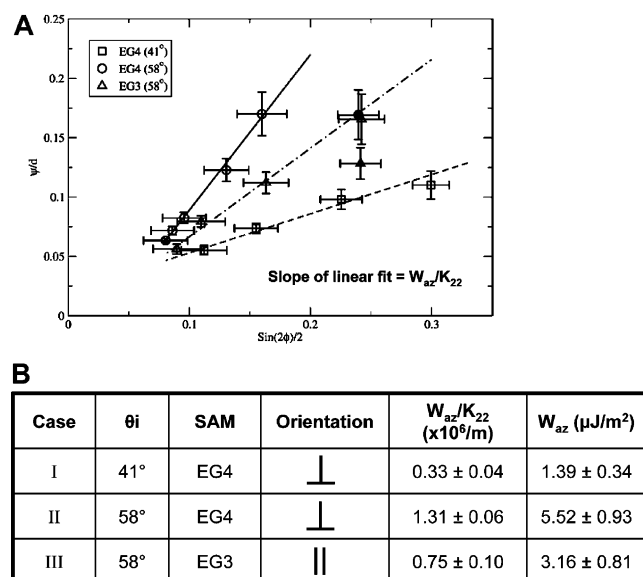


Figure 5. Optical measurements used to determine the azimuthal anchoring energy for surfaces I–III. (A) Fit of experimental data obtained using surfaces I–III to the torque-balance model (eq 2). (B) Summary of azimuthal anchoring energies determined for surfaces I–III.

Discussion

We begin our discussion by comparing the magnitude of the measured azimuthal anchoring energies of nematic 5CB in contact with SAMs supported on obliquely deposited gold films to past measurements of anchoring energies of LCs on obliquely deposited metal oxide films. When compared to obliquely deposited films of SiO (W_{az} for 5CB reported to be $> 10^{-5}$ J/m² at room temperature⁴⁴), the anchoring energies of 5CB in contact with SAMs that are supported on obliquely deposited gold are an order of magnitude smaller. We note that the morphologies of these two surfaces are very different: as discussed in past studies,⁴³ obliquely deposited gold films possess subtle levels of anisotropy in their nanometer-scale roughness (due to the high mobility of the gold on the surface during deposition), whereas obliquely deposited metal oxide films have pronounced, anisotropic surface features. Below we discuss in more detail the influence of (1) the gold film morphology and (2) the molecular-level structure of the SAMs on the anchoring energies measured in our studies.

First, we discuss the influence of the gold film morphology, by comparing anchoring energy measurements obtained for surfaces I and II. Here, an identical SAM (EG4) was formed on two gold films that were prepared at two different angles of deposition ($\theta_i = 41^\circ$ and 58°). We measured the increase in the angle of deposition of the gold to lead to an increase in the anchoring energy of the surface from 1.4 ± 0.3 to 5.5 ± 0.9 $\mu\text{J}/\text{m}^2$. Several past studies have characterized the structure of gold films deposited at oblique angles of incidence by using atomic force microscopy (AFM), X-ray diffraction, and nonlinear optical methods (second harmonic generation).^{19,20,43} These studies reveal that oblique deposition of the gold leads to the introduction of in-plane crystallographic texturing of the polycrystalline film, as well as changes in the sizes and shapes of the gold grains (which is reflected in the nanometer-scale topography of the film measured by AFM).¹⁸ Both the topography of the surface as well as the in-plane crystallographic texturing of the films are expected to influence the orientation and anchoring energies of LCs on these surfaces. By using AFM measurements of the topography and a Berreman-de-Gennes-type model^{8,12} to

describe the contribution to the anchoring energy that arises from elastic distortion of the LC over the topography of the surface, Skaife and co-workers calculated the orientation of the easy axis of the LC as well as the anchoring energy of LC for gold films deposited at angles of incidence of $\theta_i = 15^\circ, 30^\circ, 45^\circ$, and 60° . These calculations led to the prediction that the easy axis defined by the topography is perpendicular to the plane of incidence of the gold and that gold films deposited at larger higher angles of incidence will have larger anchoring energies.⁴³ Our results are qualitatively consistent with these predictions, as we measure the orientation of the LC on these gold films covered with EG4 SAMs to be perpendicular to the plane of incidence of the gold (Figure 3, surfaces I and II) and that an increase in deposition angle from $\theta_i = 41^\circ$ to 58° leads to a 4-fold increase in anchoring energy. Quantitatively, however, Skaife calculated the contribution of topography to the anchoring energy of nematic 5CB in contact with a gold film deposited at $\theta_i = 45^\circ$ to be 14 $\mu\text{J}/\text{m}^2$, whereas we measure the anchoring energy for LC in contact with EG4 supported on a gold film deposited at a similar θ_i (41°) to be an order of magnitude smaller, 1.4 ± 0.3 $\mu\text{J}/\text{m}^2$. Our measurement of anchoring energy for LC in contact with EG4 supported on a gold film prepared from $\theta_i = 58^\circ$ (5.5 ± 0.9 $\mu\text{J}/\text{m}^2$) is also smaller than the contribution of topography predicted by Skaife for $\theta_i = 60^\circ$ (21 $\mu\text{J}/\text{m}^2$). The order of magnitude difference between the experimentally measured anchoring energy and the calculated contribution of topography to the anchoring energy is consistent with prior conclusions that the presence and structure of SAMs formed on these obliquely deposited gold films introduces additional interactions between the LC and surface that can lead to changes in the easy axis^{19,21,22,25,29,43,46–48} and, as we discuss below, also to changes in the azimuthal anchoring energy of LC on these surfaces. We also note below that a past study has demonstrated that a SAM can change the polar (out-of-plane) anchoring energy from that measured on gold substrates without SAMs.⁴⁹

The results described above support the proposition that interactions between the oligo(ethylene glycol)-terminated SAMs and 5CB play an important role in defining the easy axis and anchoring energy of LCs on obliquely deposited gold films. To characterize in more detail the influence of the SAM on the anchoring energy, we performed measurements of the anchoring energies on surfaces II and III, where the angle of deposition (and thus gold morphology) for each film was constant, but two different monolayers (EG3 and EG4) were formed on each substrate. We first note that the orientation of the easy axis of the LC on these surfaces depends on the number of EG repeat units within the oligomer (Figure 3). Because these SAMs were formed on the same gold films, and because the influence of the nanometer-scale topography of these films is to define an easy axis that is perpendicular to the plane of incidence of the gold (as seen for surfaces I and II), these measurements of the orientation of the easy axis confirm that interactions exist between the terminal groups of EGX SAMs and the LCs, and in the case of EG3 SAMs, these interactions override the influence of the topography of the surface to give rise to an alignment of 5CB such that η_0 is oriented parallel to the direction of gold deposition.

We propose that the orientation assumed by the LC on EG3 SAMs is a result of a competition between two types of interactions between the LC and the surface: the deformation of the LC over the nanometer-scale topography of the surface

(46) Gupta, V. K.; Abbott, N. L. *Langmuir* **1996**, *12*, 2587.

(47) Luk, Y.-Y.; Abbott, N. L. *Science* **2003**, *301*, 623.

(48) Shah, R. R.; Abbott, N. L. *J. Am. Chem. Soc.* **1999**, *121*, 11300.

(49) Miller, W. J. W.; Abbott, N. L.; Paul, J. D.; Prentiss, M. G. *Appl. Phys. Lett.* **1996**, *69*, 1852.

and short-range interactions between the oligo(ethylene glycol) groups of the SAMs and the LCs. The latter interactions will depend on the number of EG repeat units in the SAMs as well as the organization of the EG groups (this latter topic is the subject of a separate study that will be reported elsewhere). We note that both van der Waals interactions and hydrogen bonding are possible between 5CB and surfaces presenting EG groups, and our past studies have demonstrated both types of interactions can impact the orientations of LCs on SAMs formed on gold films.^{21,22,46,50} Our proposal that the orientation of the LCs on the EG3 SAMs reflects a balance of two opposing forces is consistent with our measurements of anchoring energies in which we measured the anchoring energy on the EG3 SAM ($3.2 \pm 0.8 \mu\text{J}/\text{m}^2$) to be weaker than the anchoring energy on the EG4 SAM ($5.5 \pm 0.9 \mu\text{J}/\text{m}^2$).

We compare our findings on EG3 and EG4 SAMs, as discussed above, to recent literature describing the anchoring energy of 5CB on mechanically sheared polystyrene (PS) films.⁵¹ Mechanical shearing of PS films induces a topography (scratching) that is parallel to the rubbing direction; however, mechanical shear also induces an alignment of phenyl side groups in the near surface region in an orientation that is perpendicular to the rubbing direction. Similar to the case of EG3 on obliquely deposited gold films, two alignment mechanisms compete and the alignment of the LC is dictated by short-range molecular interactions between the phenyl side groups and molecules in the LC near the interface. Recently, Lee and co-workers measured the azimuthal anchoring of LC in contact with these films and also found much weaker anchoring energies (and lower stability) when compared to rubbed polyimide films (which give rise to alignment in the direction parallel to rubbing).⁵¹ The notion that alignments driven by two opposing forces give rise to weak azimuthal anchoring energy has been demonstrated to provide exquisite control in the gray-scale appearance of twisted LCs,⁵² and in the context of our present studies, this may be useful in the design of very sensitive surfaces on which LCs can be used to amplify the presence of biological species. We propose that, by balancing the opposing contributions to the azimuthal anchoring energies, it may be possible to engineer systems with very weak anchoring that are easily perturbed by small quantities of bound analytes. In experiments that will be published in a future paper, we have recently found that the in-plane ordering of LCs also evolves as

a function of EG3 monolayer formation time, providing further evidence of the central role that the order of the SAMs plays in the orientations of LCs on these surfaces. These results, when combined with the results presented in this paper, suggest that measurements of anchoring energies of LCs (using the methodology reported here) may also provide a convenient means to characterize the ordering of EGX monolayers in investigations, for example, of the adsorption of proteins on these surfaces, a phenomenon that is also proposed to be influenced by the order in EGX SAMs.^{37–40}

Conclusions

This study establishes a methodology that permits measurements of the azimuthal anchoring energy (W_{az}) of liquid crystals in contact with self-assembled monolayers that are supported on obliquely deposited gold films. These measurements of anchoring energies provide insights into the balance of forces that control the orientations of LCs at these structurally well-defined surfaces. By measuring the anchoring energies of nematic 5CB on EG4- and EG3-terminated SAMs supported on gold films deposited at two angles of incidence, we provide evidence that both the nanometer-scale morphology of the supporting gold films and the molecular-level structure of the monolayer influence the magnitude of the anchoring strength. In particular, the orientation of the easy axis of the 5CB as well as the values of the anchoring energies measured on EG3 and EG4 SAMs lead us to conclude that opposing interactions on the surfaces presenting EG3 SAMs cause small anchoring energies ($3.2 \pm 0.8 \mu\text{J}/\text{m}^2$). These results, when combined, provide a basis for understanding past observations in which substrate morphology and molecular structure of SAMs were found to lead to changes in the orientational ordering of LCs on surfaces presenting proteins (reporting protein binding events).^{18,26} The results presented in this paper also suggest a strategy for designing small values of W_{az} , based on control of the molecular-level structure of SAMs on these surfaces and the morphology of the gold.

Acknowledgment. This research was partially supported by the National Science Foundation (DMR 0520527, BES 0330333, CTS-040815) and the National Institutes of Health (R01 CA108467-01).

Supporting Information Available: A detailed description of the experimental methods used to determine the azimuthal anchoring energy of each sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA0535126

(50) Gupta, V. K.; Abbott, N. L. *Science* **1997**, *276*, 1533.

(51) Lee, S. W.; Chae, B.; Kim, H. C.; Lee, B.; Choi, W.; Kim, S. B.; Chang, T.; Ree, M. *Langmuir* **2003**, *19*, 8735.

(52) Yamaguchi, R.; Sato, S. *Appl. Phys. Lett.* **2005**, *86*, 031913.