Azimuthal anchoring transition of nematic liquid crystals on self-assembled monolayers formed from odd and even alkanethiols

Vinay K. Gupta and Nicholas L. Abbott
Department of Chemical Engineering and Materials Science, University of California, Davis, California 95616
(Received 26 June 1996)

A first order orientational transition, characterized by a 90° azimuthal rotation of the surface easy direction, is reported for nematic liquid crystals (NLCs) anchored on self-assembled monolayers (SAMs). The SAMs are formed from alkanethiols [$CH_3(CH_2)_{n-1}SH$; $5 \leqslant n \leqslant 16$] on obliquely deposited films of gold. The anchoring of the NLC is uniform and planar; the azimuthal orientation of the nematic director is, however, perpendicular to the direction of deposition of gold on SAMs formed from alkanethiols with odd chain lengths (n = odd) and is parallel to the direction of deposition of gold on SAMs formed from alkanethiols with even (n = even) chain lengths. [S1063-651X(96)50411-3]

PACS number(s): 42.70.Df, 61.30.Gd, 64.70.Md, 82.65.−i

Solid surfaces are known to orient or anchor liquid crystals (LCs) along a preferred ''surface easy'' direction $\mathbf{n}_0$ [1,2]. Subsequent anchoring transitions to different directions $\mathbf{n}_j$ can be induced by changes in thermodynamic (e.g., temperature, strain, and chemical potential) or structural (e.g., surface roughness and substrate thickness) parameters of the LC-substrate system [1–3]. These transitions are described, in general, by changes in one or more contributions (e.g., elastic, flexoelectric, and ordoelectric) to the overall free energy of the system [4–6]. In this paper, we report a discontinuous azimuthal anchoring transition for nematic LCs (NLCs) anchored parallel to the surface of self-assembled monolayers (SAMs) formed from alkanethiols on obliquely deposited gold. The transition is characterized by a 90° rotation of the nematic director parallel to the surface of the SAM, and results from odd-even progression in the number of methylenes in the alkyl chains that form the SAMs. Such an azimuthal transition resulting from odd-even effects has not, to our knowledge, been reported previously [7].

Self-assembled monolayers provide the capability to design and control the structure of organic surfaces and have made possible, in recent years, advances in understanding of the surface phenomena such as wetting, adhesion, and adsorption [8]. The structures of SAMs formed by chemisorption of n-alkanethiols [$CH_3(CH_2)_{n-1}SH$] on gold have been intensively studied using scanning tunneling microscopy (STM), diffraction (using x rays, electrons, and helium atoms), and infrared spectroscopy [8,9]. At saturation coverage, alkanethiols on Au(111) form a commensurate $\sqrt{3}\times\sqrt{3}R30°$ lattice on which a $c(4\times2)$ superlattice is superimposed [9]. Because the structures of these SAMs are now known in some detail, recent studies [10,11] of anchoring of LCs on surfaces have used SAMs formed from alkanethiols on gold as an alternative to the common physical methods of coating surfactants or polymers on surfaces followed by treatments such as rubbing. For NLCs anchored on mixed SAMs formed from long and short alkanethiols on gold, a polar anchoring transition from planar alignment (parallel to the surface) to homeotropic alignment (perpendicular to the surface) as a function of the composition of the mixed SAM has been reported [10].

In this paper we report the anchoring of LCs by single-component SAMs formed from $CH_3(CH_2)_{n-1}SH$ ($5 \leqslant n \leqslant 16$) on thin (≈100 Å thickness), semitransparent films of gold prepared by oblique deposition. The gold was deposited from a fixed direction and with a 50° angle of incidence (relative to the normal of the surface). The bulk anchoring behavior of the nematic liquid crystal 4-cyano-4′-pentylbiphenyl (5CB) was studied by sandwiching the NLC between the surfaces of two films of gold supporting SAMs formed form alkanethiols and by observing the optical textures with a polarizing microscope. The tilt angle of the nematic director was measured by using the crystal tilt method [12]. Detailed descriptions of the experimental procedures have been reported elsewhere [11].

Past studies have shown that contact angles of hexadecane measured on SAMs supported on films of gold deposited uniformly (with no preferred direction of deposition) increase with length of the alkanethiols [13]. Our measurements of contact angles on SAMs formed from $CH_3(CH_2)_{n-1}SH$ on obliquely deposited gold were consistent with these past studies, including the odd-even modulation in the contact angles [Fig. 1(a)]. Past studies have used the antisymmetric (r_a^-) and symmetric (r^+) methyl stretches to characterize differences in the orientation of the methyl groups [inset of Fig. 1(b)] of SAMs formed form odd and even (e.g., $n=16$ and 17) alkanethiols [14]. We observed the ratios of intensities of the antisymmetric and symmetric methyl stretches in the IR absorption spectra for SAMs formed from $CH_3(CH_2)_{14}SH$ ($\approx 3.6 \pm 0.3$) and $CH_3(CH_2)_{15}SH$ ($\approx 1.2 \pm 0.3$) to be the same on obliquely deposited gold and gold deposited uniformly [Fig. 1(b)].

Self-assembled monolayers formed from n-alkanethiols ($5 \leqslant n \leqslant 16$) on obliquely deposited gold caused azimuthally uniform, planar anchoring of 5CB; the azimuthal orientation of the nematic director changed, however, with the alkanethiol [15]. In particular, the alignment of the director on SAMs formed from even alkanethiols (e.g., $n=6$, 8, 10, 14, 16) was orthogonal to the alignment on SAMs formed form odd alkanethiols (e.g., $n=5$, 7, 9, 11, 13, 15). Figure 2(a) shows an optical cell assembled with surfaces supporting SAMs formed from alkanethiols that differed by a single methylene group [i.e., $CH_3(CH_2)_{10}SH$ and $CH_3(CH_2)_{11}SH$]

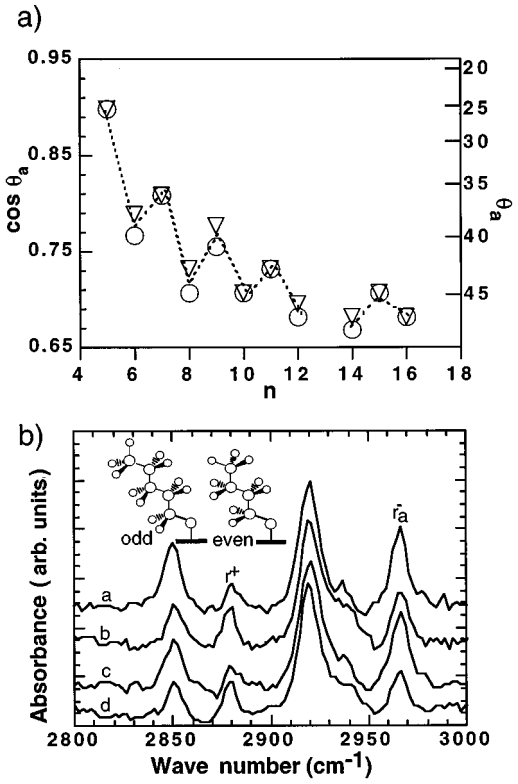

FIG. 1. (a) Contact angles (degrees) measured after advancing drops of hexadecane across SAMs formed from *n*-alkanethiols on obliquely (▽) and uniformly (○) deposited films of gold. The hysteresis in the contact angles was less than 5°. (b) Reflection-absorption IR spectra of SAMs formed from $CH_3(CH_2)_{14}SH$ (curve *a*) and $CH_3(CH_2)_{15}SH$ (curve *b*) on uniformly deposited films of gold and $CH_3(CH_2)_{14}SH$ (curve *c*) and $CH_3(CH_2)_{15}SH$ (curve *d*) on obliquely deposited films of gold. The IR light was incident at a 84° grazing angle. The inset is a schematic illustration of the methyl orientation of SAMs formed from odd and even chain lengths. r_a^- is the peak corresponding to the in-plane, antisymmetric stretch for CH_3. r^+ is the peak corresponding to the symmetric stretch for CH_3.

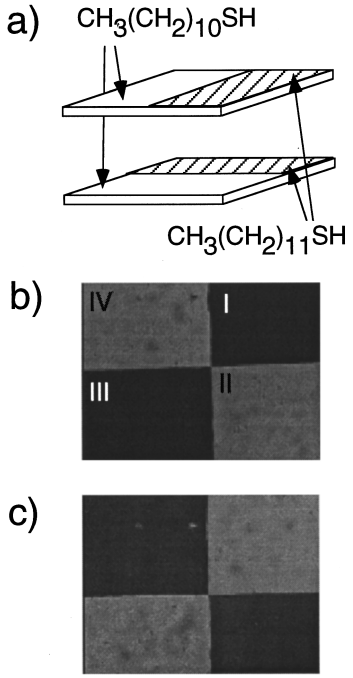

FIG. 2. (a) Schematic illustration of an optical cell with surfaces that support SAMs formed from odd and even alkanethiols. The textures were observed by transmission of light through the cell between (b) crossed polarizers and (c) parallel polarizers. The horizontal dimension of the image is 550 μm.

[17]. In such an optical cell, 5CB was sandwiched between two SAMs formed from either $CH_3(CH_2)_{11}SH$ (region I) or $CH_3(CH_2)_{10}SH$ (region III) or a combination of the two (regions II and IV). When viewed through crossed polarizers, regions I and III, in which the liquid crystal was anchored by symmetric surfaces [top and bottom SAMs both $CH_3(CH_2)_{11}SH$ or both $CH_3(CH_2)_{10}SH$], are dark due to extinction of the transmitted light [Fig. 2(b)]. The bulk orientation of the LC was, therefore uniform and along a single direction. In contrast, regions II and IV, in which 5CB was sandwiched between unlike-SAMs [top SAM formed from $CH_3(CH_2)_{10}SH$ and bottom formed from $CH_3(CH_2)_{11}SH$, or vice versa], were uniformly bright under crossed polarizers, suggesting that the bulk orientation of the nematic liquid crystal twisted the polarization of light as it was transmitted through the cell. Observation under parallel polarizers (i.e., with the analyzer rotated by 90°) showed that regions I and III turned bright while regions II and IV turned dark [Fig. 2(c)]. This result indicates that the twist in regions II and IV was nearly 90°. The 90° twist of the nematic director of 5CB was observed on all odd-even combinations of SAMs formed from $CH_3(CH_2)_{n-1}SH$ ($5<n<16$) on obliquely deposited gold [18].

Because the director of nematic 5CB is parallel to the axis with high refractive index (slow axis), orientation of the director relative to the direction of deposition of gold was inferred from the orientation of the slow axis of the nematic phase (determined by shift in retardation colors [19]). In region I, where 5CB was sandwiched between SAMs formed from $CH_3(CH_2)_{11}SH$, the shift of color indicated that the optical axis of 5CB (the slow axis) was parallel to the deposition direction of gold. In region III, where 5CB was sandwiched between SAMs formed from $CH_3(CH_2)_{10}SH$, the optical axis of 5CB was orthogonal to the direction of deposition of gold. The anchoring of another nematic liquid crystal, *p*-methoxybenzylidene-*p*-*n*-butyl-aniline was found to be similar to the anchoring reported here for 5CB.

Past studies of anchoring of NLCs on obliquely deposited inorganic oxides or metals (''bare'') have reported the anchoring to depend on the angle of incidence (θ_i measured from the surface normal) during deposition of the metal or oxide [16,20]. For example, on silicon oxide (SiO) deposited with $\theta_i \approx 60°$, the nematic director is planar and perpendicular to the deposition direction of SiO; for $\theta_i \approx 83°$, the director is tilted away from the surface and parallel to the direction of deposition of SiO [20]. Goodman *et al.*[20] report the formation of columnar aggregates in films of SiO deposited obliquely (due to self-shadowing effects) and propose the topography of the SiO films to be the primary factor that determines the anchoring of the LCs on these surfaces. A Berreman–de Gennes-type model [1,21] was used to describe the influence of the surface roughness in terms of an elastic energy. For $\theta_i \approx 60°$, the surface is believed to be

statistically ''grooved'' and alignment parallel to the deposition direction (perpendicular to the grooves) gives rise to a large excess of elastic energy (due to distortion of the nematic director field) when compared to alignment perpendicular to the deposition direction [20,21]. For $\theta_i \approx 83°$, the grooves are not well formed and a tilted anchoring of the LC parallel to the direction of deposition is produced [20]. A second, more recent, model describes anchoring of LCs on surfaces such as thin (~0–200 Å), obliquely deposited SiO with roughness (or surface disorder) on scales of a few molecular lengths (~50–100 Å) [5]. The model considers these surface irregularities to lower the nematic surface order parameter from the bulk value and thereby cause order-electric contributions to the free energy of the LC-substrate system. The transition from planar anchoring perpendicular to the deposition direction to tilted anchoring parallel to the deposition direction has been attributed to the order-electric polarization (the tilted director minimizes the electrostatic self-energy [5]).

The STM images (5000 Å) of ''bare,'' obliquely deposited films of gold presented in our recent report (see [11]) show a pebbly texture formed by grains with dimensions ≈300 Å and a rms roughness of ≈5 Å [22,23]. For order-electric polarization to play a governing role in the azimuthal anchoring of NLCs on SAMs, the polarization would have to differ for odd and even SAMs and the anchoring transition would be accompanied by a change in the tilt of the director. The tilt angle of 5CB was measured to be $0.1° \pm 0.1°$ on the surface of bare obliquely deposited gold as well as on SAMs formed from $CH_3(CH_2)_{14}SH$ and $CH_3(CH_2)_{15}SH$. Because we see no change in the tilt of the nematic director on odd and even SAMs, we conclude that order-electric effects (and changes in polar anchoring energy) do not cause the azimuthal anchoring transition of the NLCs on odd and even SAMs.

A recent theoretical analysis by Barbero and Durand [6] predicts that flexoelectric polarization (deformation-induced polarization) in NLCs can stabilize alignment of a NLC parallel to the direction of deposition on obliquely deposited substrates under certain conditions. The authors model electrostatic and elastic contributions to the free energy of the LC substrate on a statistically rough surface (with wavelength λ) formed by coating a conducting material with a dielectric layer of thickness h and static dielectric constant ϵ. When $\epsilon \coth(2\pi h/\lambda)$ is greater than a critical value (ϵ_c), the nematic director is predicted to align parallel to the grooves, whereas for $\epsilon \coth(2\pi h/\lambda) < \epsilon_c$, a 90° azimuthal reorientation of the director causes the director to align perpendicular to the grooves.

If flexoelectric polarization is the cause of the azimuthal anchoring transition reported here, a modulation in $\epsilon \coth(2\pi h/\lambda)$ about ϵ_c is required for odd and even SAMs. Because differences between the chain-end order of odd and even alkyl chains [24] are known to cause changes in macroscopic properties such as transition temperatures, Kerr constants, and orientational relaxation times [25], the dielectric properties of SAMs in contact with LCs could, plausibly, change with the orientation of methyl groups of SAMs with odd and even chain lengths [inset of Fig. 1(b)] [26]. The role of the orientation of the methyl group in the azimuthal anchoring transition is supported by preliminary results of anchoring of 5CB on SAMs formed form $CH_3(CH_2)_{n-1}SH$ on obliquely deposited silver: the methyl orientation does not change with odd-even progression for SAMs formed on silver [27]. No odd-even effect in the nematic director orientation is observed for NLCs anchored on SAMs formed form $CH_3(CH_2)_{n-1}SH$ on silver. The goal of ongoing studies is to test the hypothesis of odd-even modulation in the dielectric properties of SAMs formed from alkanethiols on obliquely deposited gold.

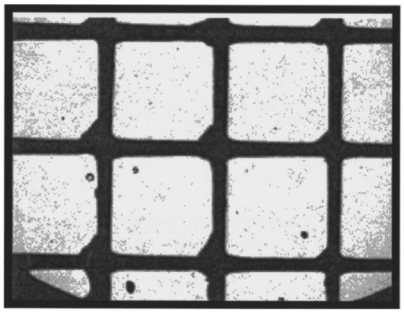

FIG. 3. Optical texture formed by LC within a cell with surfaces that supported mesoscale, patterned SAMs formed from alkanethiols on obliquely deposited gold. The top surface of the cell was patterned with $CH_3(CH_2)_{15}SH$ and $CH_3(CH_2)_{10}SH$ by using microcontact printing [17]. A TEM grid was used as a master for making the stamp and $CH_3(CH_2)_{15}SH$ was used as the ''ink.'' The stamped film of gold was then immersed in a solution of $CH_3(CH_2)_{10}SH$. A second film of gold that supported a SAM formed from $CH_3(CH_2)_{10}SH$ was used as the bottom surface. The NLC sandwiched between $CH_3(CH_2)_{10}SH$ and $CH_3(CH_2)_{15}SH$ twisted the polarization of light transmitted through the cell. The texture shown here is for the cell under cross polarizers. The vertical dimension of the image is 860 μm.

In summary, we report that SAMs formed from alkanethiols that differ by a single methylene—the result of which is a difference in the orientation of the methyl group presented at the surface of the SAMs—can cause a 90° rotation in the macroscopic azimuthal anchoring of a LC. An azimuthal transition of 90° caused by odd-even effects within the anchoring surface has not, to the authors' knowledge, been reported before. The odd-even effect we report, when combined with methods for forming macroscopic and microscopic patterned SAMs, provides a simple route to induce 90° twist in nematic LCs and can, we believe, form the basis of methods for obtaining bistable anchoring. Figure 3 shows an example: the odd-even effect was used to cause twisted and untwisted nematic fields in specific regions of a SAM prepared by microcontact printing [17]. Application of an external electric field normal to the cell surfaces erases the pattern and, upon removal of field, the pattern reforms. Potential applications of micropatterning and the electro-optic behavior extend to diffractive optical phase gratings and light valves for separation of orthogonal polarizations [28].

This research was supported, in part, by NSF Grants Nos. CTS-9410147 and DMR-9400354). The authors would like to thank William Miller for helpful discussions.

[1] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[2] B. Jerome, Rep. Prog. Phys. **54**, 391 (1991); A. A Sonin, *The Surface Physics of Liquid Crystals* (Gordon and Breach, New York, 1995).

[3] P. Pieranski and B. Jerome, Mol. Cryst. Liq. Cryst. **199**, 167 (1991).

[4] G. Barbero, I. Dozov, J. F. Palierne, and G. Durand, Phys. Rev. Lett. **56**, 2056 (1986); G. Barbero and G. Durand, J. Phys. (France) II **1**, 651 (1991); A. L. Alexe-Ionescu, Nuovo Cimento D **15**, 1489 (1993); M. Petrov, A. Braslau, A. M. Levelut, and G. Durand, J. Phys. (France) II **2**, 1159 (1992).

[5] M. Monkade, M. Boix, and G. Durand, Europhys. Lett. **5**, 697 (1988).

[6] G. Barbero and G. Durand, J. Appl. Phys. **68**, 5549 (1990).

[7] Past reports of odd-even effects in LC systems include (a) alkyl chains of mesogens, changes in macroscopic properties such as isotropic-nematic phase transition temperatures (T_{ni}) [see R. Yamamoto, S. Isihara, S. Hayakawa and K. Morimoto, Phys. Lett. **60A**, 414 (1977)], and (b) alkyl chains of a polyimide surface (rubbed); changes of a few degrees in the tilt angles of nematic LCs anchored on the polyimide films [see H. Yokokura, M. Oh-E, K. Kondo, and S. Oh-Hara, Mol. Cryst. Liq. Cryst. **225**, 253 (1993); D. Johannsmann, H. Zhou, P. Sonderkaer, H. Wieranga, B. O. Myrvold, and Y. R. Shen, Phys. Rev. E **48**, 1889 (1993)].

[8] A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir Blodgett to Self-Assembly* (Academic, Boston, 1991); L. H. Dubois and R. G. Nuzzo, Annu. Rev. Phys. Chem. **43**, 437 (1992); G. M. Whitesides and P. E. Laibinis, Langmuir **6**, 87 (1990), and references cited therein.

[9] P. Fenter, A. Eberhardt, and P. Eisenberger, Science **266**, 1216 (1994); N. Camillone III, C. E. D. Chidsey, G.-Y. Liu, and G. Scoles, J. Chem. Phys. **98**, 4233 (1993); G. E. Poirier and E. D. Pylant, Science **272**, 1145 (1996), and references cited therein. In these references STM and diffraction techniques have been used primarily for the characterization of SAMs formed from $CH_3(CH_2)_{n-1}SH$ with an odd number of methylenes.

[10] R. A. Drawhorn and N. L. Abbott, J. Phys. Chem. **99**, 16 511 (1995).

[11] V. K. Gupta and N. L. Abbott, Langmuir **12**, 2062 (1996).

[12] T. J. Scheffer and J. Nehring, J. Appl. Phys. **48**, 1783 (1977).

[13] C. D. Bain, B. E. Troughton, Y. Tao, J. Evall, G. M. Whitesides, and R. G. Nuzzo, J. Am. Chem. Soc. **111**, 321 (1989); C. D. Bain and G. M. Whitesides, *ibid.* **111**, 7164 (1989).

[14] R. G. Nuzzo, L. H. Dubois, and D. L. Allara, J. Am. Chem. Soc. **112**, 558 (1990).

[15] Nematic 5CB was anchored on ''bare'' gold in a direction perpendicular to the direction of deposition of gold. This is consistent with past reports of anchoring on untreated surfaces of obliquely deposited gold [16].

[16] J. L. Janning, Appl. Phys. Lett. **21**, 173 (1972); W. Urbach, M. Boix, and E. Guyon, *ibid.* **25**, 479 (1974).

[17] The surfaces of the films of gold were patterned with SAMs of different chain lengths by using microcontact printing technique. See A. Kumar, N. L. Abbott, H. A. Biebuyck, and G. M. Whitesides, Acc. Chem. Res. **28**, 219 (1995).

[18] The anchoring of 5CB on SAMs supported on uniformly deposited gold was azimuthally nonuniform (see [11]) and the odd-even phenomenon was, therefore, not observed.

[19] N. H. Hartshorne and A. Stuart, *Crystals and the Polarizing Microscope* (Arnold, New York, 1970).

[20] L. A. Goodman, J. T. Meginn, C. H. Anderson, and F. Digeronimo, IEEE Trans. Electron. Devices **24**, 795 (1977).

[21] D. Berreman, Phys. Rev. Lett. **28**, 1683 (1972).

[22] Similar images have been reported for thin ($\sim$150 Å) films of obliquely deposited SiO. Experimental evidence shows a low surface order for a NLC anchored on these SiO surfaces [see R. Barberi, M. Giocondo, G. V. Sayko, and A. K. Zvedin, J. Phys. Condens. Matter. **6**, A275 (1994)].

[23] No grooves were apparent in images with scales of 5000 Å. Past studies of obliquely deposited films as thin as 100 Å indicate that imaging of statistical grooves is difficult [see J. A. Castellano, Mol. Cryst. Liq. Cryst. **94**, 33 (1983).

[24] S. Marcelja, J. Chem. Phys. **60**, 3599 (1974); J. R. Lalanne, B. Lemaire, J. Rouch, C. Vaucamps, and A. Prouteriere, *ibid.* **73,** 1927 (1980).

[25] F. G. Hanson and Y. R. Shen, Mol. Cryst. Liq. Cryst. **36**, 193 (1976); R. Yamamoto, S. Isihara, S. Hayakawa, and K. Morimoto, Phys. Lett. **69A**, 276 (1978).

[26] Past capacitance measurements ($C^{-1}=h/\epsilon$) of SAMs formed from alkanethiols in aqueous solutions of electrolyte do not show any odd-even modulation [see M. D. Porter, T B. Bright, D. L. Allara, and C. E. D. Chidsey, J. Am. Chem. Soc. **109**, 3559 (1987); M. M. Walczak, C. Chung, S. M. Stole, C. A. Widrig, and M. D. Porter, *ibid.* **113**, 2370 (1991)]. However, the measurements depend on the SAM-solution interface and the type of substrate supporting the SAMs (e.g., gold deposited on mica versus gold deposited on silicon). No measurements of capacitance have been reported for SAMs formed from alkanethiols on obliquely deposited gold in contact with liquid crystalline fluids.

[27] P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y.-T. Tao, A. N. Parikh, and R. G. Nuzzo, J. Am. Chem. Soc. **113**, 7152 (1991).

[28] P. J. Shannon, W. M. Gibbons, and S. T. Sun, Nature (London) **368**, 532 (1994).