

**The existence of structure progressions and wetting transitions in intermediately disordered monolayer alkyl chain assemblies**

David L. Allara, Atul N. Parikh, and Elizabeth Judge

Citation: *The Journal of Chemical Physics* **100**, 1761 (1994); doi: 10.1063/1.466604

View online: <http://dx.doi.org/10.1063/1.466604>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/100/2?ver=pdfcov>

Published by the [AIP Publishing](#)

---

**Articles you may be interested in**

[Effects of the alkyl chain length in phosphonic acid self-assembled monolayer gate dielectrics on the performance and stability of low-voltage organic thin-film transistors](#)

*Appl. Phys. Lett.* **95**, 203301 (2009); 10.1063/1.3259816

[Electronic properties of self-assembled alkyl monolayers on Ge surfaces](#)

*Appl. Phys. Lett.* **92**, 223306 (2008); 10.1063/1.2939221

[Statistical representation of intrinsic electronic tunneling characteristics through alkyl self-assembled monolayers in nanowell device structures](#)

*J. Vac. Sci. Technol. B* **26**, 904 (2008); 10.1116/1.2905237

[Stripes of partially fluorinated alkyl chains: Dipolar Langmuir monolayers](#)

*J. Chem. Phys.* **122**, 094717 (2005); 10.1063/1.1858852

[Simulation of a monolayer of alkyl thiol chains](#)

*J. Chem. Phys.* **91**, 4994 (1989); 10.1063/1.457621

---



# The existence of structure progressions and wetting transitions in intermediately disordered monolayer alkyl chain assemblies

David L. Allara,<sup>a)</sup> Atul N. Parikh, and Elizabeth Judge

*The Departments of Materials Science and Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802*

Partial monolayers of uniform length alkyl chains  $[\text{CH}_3(\text{CH}_2)_n-; n=10-21]$  bonded at constant coverage onto a disordered lattice of silanol groups on amorphous  $\text{SiO}_2$ , exhibit a distinct change in surface wetting behavior for  $14 < n < 17$  which correlates closely with a significant shift in the average conformational ordering of the chains. These data provide definitive evidence for the existence of a family of surface-constrained, intermediately ordered phases of discrete length, flexible chains and imply that broad classes of these families exist.

Molecular level control over the structural order and defect composition of supported monolayers of molecular films has been an object of much recent interest<sup>1-3</sup> both because of important fundamental scientific issues related to surface constrained phases and the relevance to applications ranging from biological processes<sup>4</sup> to micro/nanoscale fabrication.<sup>5</sup> The major experimental focus has been to prepare films with the highest possible values of relevant translational and orientational order parameters. Dominant examples are self-assembly of monolayers of alkanethiolates on Au(111)<sup>2,3,6</sup> and the forced assembly of surfactants on inert substrates (e.g., amorphous  $\text{SiO}_2$ ) by Langmuir-Blodgett (LB) transfer.<sup>2,7</sup> The molecules in alkanethiolate/Au(111) monolayers are strongly pinned<sup>8</sup> at specific Au lattice sites to form a hexagonal  $\sqrt{3} \times \sqrt{3}$ ,  $R30^\circ$  overlayer<sup>9,10</sup> with a 0.51 nm spacing<sup>3,10</sup> which leads to tilted structures<sup>11</sup> while in contrast, the substrate lattice in LB films is usually approximated by an isotropic potential field (featureless surface) and the intermolecular interactions drive the structure to approach hexagonal closest packing (0.45 nm) of nearly vertically aligned chains.<sup>7</sup> Most films, however, are not ideal and the actual conditions of preparation and substrate character can impart disordering which can occur specifically in the arrangement of adsorbate pinning sites in the substrate plane (e.g., missing molecules and substrate lattice imperfections), molecular alignments, and individual chain conformational sequences. Since important film properties such as wetting and transport clearly depend directly on film organization, it is critical to characterize this disorder. However, because these types of disordering are strongly coupled, the film structures can be quite complex and their characterization difficult. We have chosen to study these effects systematically by the deliberate introduction of controlled disorder in the adsorbate pinning lattice. Since molecular alignments and conformational sequences for short alkyl chains relax on a very fast time scale, the preparation of monolayers with fixed pinning geometry provides convenient probes of the degree of coupling which exists between the frozen, in-plane pinning lattice correlations<sup>12</sup> and dynamic, equilibrium out-of-plane chain configurations. Although no theoretical studies appear to have been done, recent molecular dynamics simulations have investigated the propagation of an ordered pinning lattice into the

structures of monolayers of discrete-length alkyl chain molecules.<sup>13</sup> Here we report results on the extremely important limiting case of a pinning lattice of translationally uncorrelated, strong-binding sites. Specifically, we show that a self-consistent series of intermediately disordered self-assembled monolayers can be prepared using alkyl  $[\text{CH}_3(\text{CH}_2)_n-; n=10-21]$  chains, of discrete but variable length, chemically bonded, at a constant  $\sim 50\%$  coverage, to the randomly placed silanol groups of an amorphous  $\text{SiO}_2$  surface on an oxidized silicon substrate. We further present the observation of a unique transition in wetting behavior, driven by change in the molecular chain length between two differently disordered structures: (1) a low- $n$  regime structure, consisting of folded chains and (2) a high- $n$  regime structure, consisting of partially aligned and extended chains. This transition can be considered to be the small molecule or short chain analog of a mushroom-brush transition, a phenomenon of recent intense theoretical and experimental study.<sup>14</sup> To our knowledge, the present study is the first systematic experimental investigation of disordered monolayers and the results point to important new aspects of structures in self-assembled monolayers.

The films were prepared by reacting oxidized silicon wafers with neat  $n$ -alkanols for 20 hours at  $140.0^\circ\text{C} \pm 0.5^\circ\text{C}$  under Ar. The silicon substrates were precleaned in peroxysulfuric acid solution (4:1 v/v mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  at  $\sim 90^\circ\text{C}$ ) for approximately 20–25 minutes, washed in deionized water, and blown dry with nitrogen. Final cleaning was done by uv-ozone treatment. After reaction with the alcohols, the wafers were removed and solvent rinsed to constant ellipsometry readings. Neither additional solvent immersion, thermal cycling (up to  $120^\circ\text{C}$ ) nor variation of the temperature of the solution during sample removal affected the analysis results, implying that equilibrium film structures result. Analyses were carried out using ellipsometry, forward recoil scattering (FRS), transmission infrared spectroscopy (TIRS), and liquid-drop, contact angle wetting measurements.<sup>15</sup> Film coverages were determined from averages of null-ellipsometry measurements of film thicknesses for multiple ( $> 10$ ) preparations at each chain length and FRS measurements of the total H atom surface density based on three series of samples. The TIRS and wetting results are

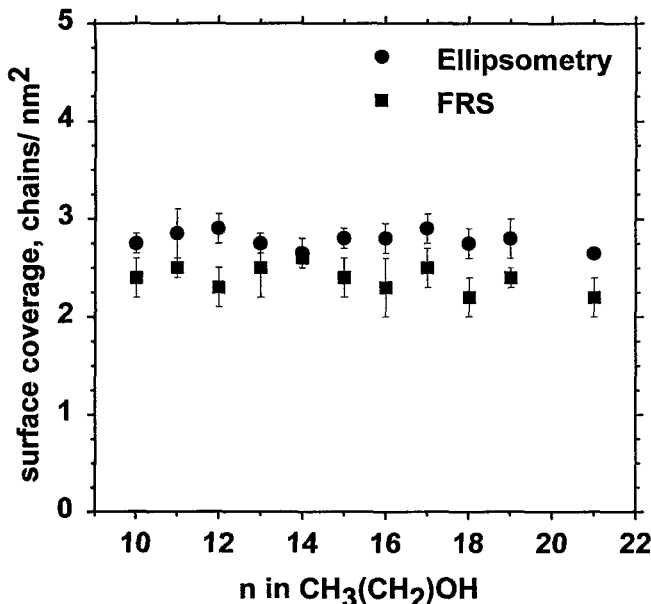


FIG. 1. Surface coverage of  $\text{CH}_3(\text{CH}_2)_n\text{O}-$  films on  $\text{SiO}_2/\text{Si}$  substrates as a function of  $n$ . Coverages are determined from ellipsometric and forward recoil scattering measurements (for details, see text).

presented as averages of measurements based on the same multiple sets of samples used for ellipsometry measurements.

Figure 1 shows the film coverages calculated from ellipsometry and FRS measurements to be constant with  $n$ . An average value from the two sets of measurements is  $2.65 \pm 0.25$  chains  $\text{nm}^{-2}$  which corresponds to a

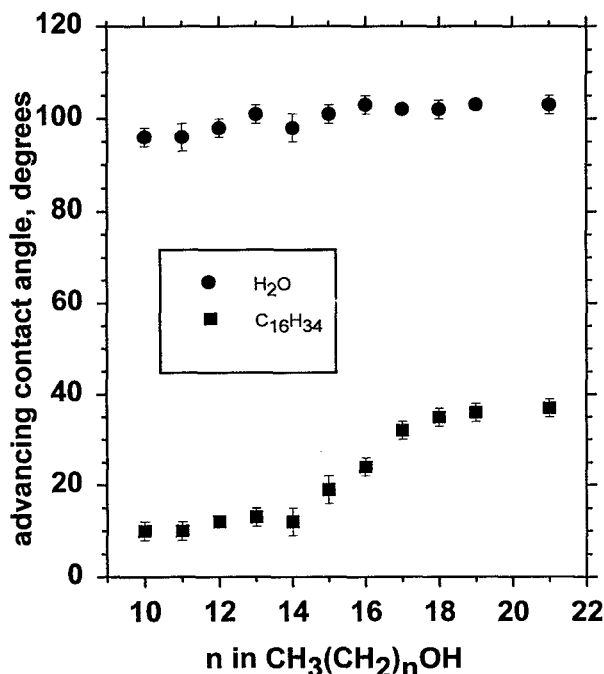


FIG. 2. Water and hexadecane advancing contact angles of  $\text{CH}_3(\text{CH}_2)_n\text{O}-$  films on  $\text{SiO}_2/\text{Si}$  as a function of  $n$ . The dashed lines are the guides to the eye.

$53\% \pm 5\%$  yield calculated on the basis that 100% equals 5.0 per  $\text{nm}^2$ , the maximum Si-OH site density,<sup>16</sup> and a 49% coverage on the basis of a maximum of 5.4 chains  $\text{nm}^{-2}$  for a perfect monolayer (crystalline polyethylene density).

The central property of importance in this series of films is the wetting behavior. Figure 2 shows that the water values are virtually chain-length independent. In order to relate this behavior to film structure, we consider a very simple model<sup>17</sup> of two phases exposed at the wetted surface with a resulting surface tension equal to the sum of the surface tensions of each of the exposed components weighted by their surface areas. It follows that

$$\cos \theta_L = x_1 \cos \theta_{L1} + (1 - x_1) \cos \theta_{L2},$$

where  $\theta_L$  is the contact angle for a probe liquid L on the mixed surface,  $\theta_{L1}$  and  $\theta_{L2}$  are the contact angles of L on the pure component surfaces, and  $x_1$  is the fractional coverage of component 1. Using known values<sup>18</sup> of  $\theta_L$  for the pure component surfaces  $-(\text{CH}_2)_n-$ ,  $-\text{CH}_3$ , and hydrated  $\text{SiO}_2$ , calculations show that the surface exposure of the  $\text{SiO}_2$  substrate must be less than several percent, even for the thinnest films.

In stark contrast to the  $\text{H}_2\text{O}$  behavior, the hexadecane contact angle behavior shown in Fig. 2 clearly forms two well-defined regimes separated by a transition regime between  $n=13-17$ . In the latter,  $\theta_{\text{HD}}$  shows a steady steep increase with increasing chain length. Applying the above wetting model, the calculations show that the near-surface structure below the transition regime is composed of a high fraction (90%–96%) of methylene units and/or unoccupied substrate silanol sites, both of which are wet by hexadecane ( $\theta_{\text{HD}} \sim 0^\circ$ ). The high  $\theta_{\text{water}}$  value (Fig. 2), however, limits the fraction of exposed  $\text{SiO}_2$  to  $\leq 5\%$  so the wetted surface of the film therefore must contain 90%–96% methylene character, according to our simple model. This character requires the majority of methyl end groups to be screened from the wetting liquid and thus to be buried  $>5$  Å into the film interior.<sup>19</sup> Since the fully extended length of the chains in this low- $n$  regime is  $\sim 15-20$  Å, the average folding of the chains in the surface phase is severe. A similar analysis of the high- $n$  regime, in contrast, indicates that as much as 65%–70% of the surface is of  $\text{CH}_3$  character. This class of structures requires an increase in chain orientational ordering which, in turn, implies increase in chain extension. In order to offset the resulting loss in configurational entropy, the assembly will be driven to maximize attractive chain-chain interactions, which at the  $\sim 50\%$  coverage would result in a structure between the limiting cases of a collectively tilted phase with some long range correlation or localized regions of bunches or tufts of extended chains with correlation lengths of the order of the chain lengths. Since the folded-extended structural transition is driven by an increase in chain length, one can view chain length as an influence to remove the effects of surface pinning on the structure of the chain termini.<sup>20</sup> A cartoon-type of representation which captures the essential features of chain folding and extension in the two structural phases is given in Fig. 3. This transition can also be considered as

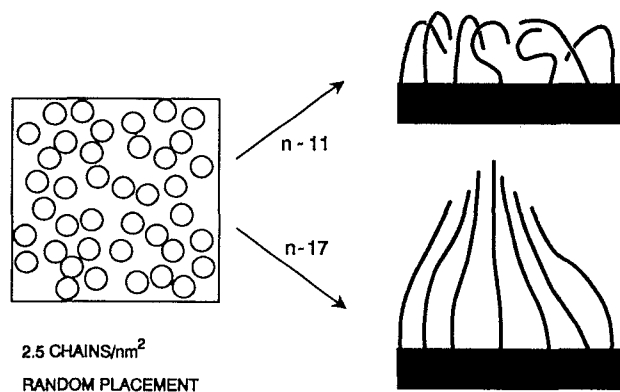


FIG. 3. A cartoon representation of limiting structures of  $n$ -alkoxy films selected to have values of  $n$  on either side of the transition region as discussed in the text. The chains are represented by a one-dimensional array of solid lines attached to points placed randomly at a coverage of  $\sim 2.5 \text{ nm}^{-2}$ . The circles approximate the diameter of an all-*trans* chain. Line curvature represents qualitative departure from a fully extended all-*trans* structure.

a short-chain analog of the mushroom to brush transition associated with polymer chains.<sup>21</sup>

Definitive support for the increase in chain extensions throughout the transition regime is given by the TIRS measurements. It has been established that the frequencies of the C-H symmetric ( $d^+$ ) and antisymmetric ( $d^-$ ) stretching modes in alkyl chains shift to lower values with a lowering of *gauche* defect content.<sup>22</sup> Figure 4 shows the drop in observed peak frequencies with increasing chain length. We note the approach to frequencies typically reported for highly organized, high coverage self-assembled monolayers. For example, compare our lowest values in the range 2919–2920  $\text{cm}^{-1}$  for some preparations of the  $\text{C}_{22}$  alkoxy assembly in this work, to 2917–2918  $\text{cm}^{-1}$  typ-

ically observed for an ordered  $\text{C}_{22}$  alkane thiolate monolayer self-assembled on Au(111) surfaces<sup>11</sup> and finally to  $\sim 2926\text{--}2928 \text{ cm}^{-1}$ , values associated with complete conformational disorder (liquid phase).<sup>22</sup> It has been estimated that the value of  $2917 \text{ cm}^{-1}$  associated with the alkane thiolates on Au corresponds well with a low defect picture,  $\sim 1\%\text{--}4\%$  *gauche* defects at room temperature in a direct comparison<sup>3</sup> with independent molecular dynamics results.<sup>23</sup> These correlations establish that the alkoxy films in the high- $n$  limit approach quite good conformational order in spite of their *inherent translational disorder* and *very low coverage*. A further comparison can be made to alkylsiloxane films on  $\text{SiO}_2$ , the latter typically prepared by self-assembly from octadecyltrichlorosilane (OTS) solutions.<sup>2,24–26</sup> Typical reported values for densely-packed (close to 100% theoretical coverage) OTS films are  $\sim 2917\text{--}2919 \text{ cm}^{-1}$ ,<sup>2,27</sup> again close to the lowest values for the disordered alkoxy assemblies. Both comparisons above demonstrate the weak correlations of translational ordering and coverage with  $d^+$  and  $d^-$  frequencies.

Because of the popularity of hexadecane wetting as a measure of film organization, it is instructive to compare our data with other reported data for highly organized films. There is a close approach of the alkoxy film contact angles ( $36^\circ \pm 2^\circ$ ) in the high- $n$  regime to those of typical values for alkane thiolate/Au<sup>2,3,11</sup> ( $44^\circ\text{--}48^\circ$ ) and OTS films<sup>2,23,26,27</sup> ( $43^\circ\text{--}48^\circ$ ). While a value of  $36^\circ$  would normally be interpreted in terms of a “disordered” or low coverage self-assembled monolayer, it should be realized that in the above cases the surface chain densities are  $\sim 2.6$ ,  $4.6$ , and  $5.4 \text{ nm}^{-2}$  for the alkoxy, thiol/Au,<sup>3,11</sup> and OTS<sup>28</sup> films, respectively, and further, the  $2.65 \text{ nm}^{-2}$  film is translationally disordered. It is obvious then that an  $\sim 10^\circ$  drop in contact angle values can occur over a large range of intermediate surface densities ( $2.6 \text{ nm}^{-2}$  and higher) with the broadest range of translational ordering. Thus, given typical errors and lab-to-lab variations of  $\sim \pm 2^\circ$ , the ability of contact angles to predict structural detail appears tenuous. Our data by themselves also show that calamitous effects in wetting ( $\sim 30^\circ$  range) can occur by less than twofold changes in chain length at a constant surface coverage.

In summary, to our knowledge, the above results represents the first systematic experimental definition of an important class of surface-constrained, intermediate ordering flexible chain structures, manifested specifically by the discovery of a *family* of phases in which the common parameter is the constant, translationally disordered pinning array of  $2.65 \text{ sites nm}^{-2}$ . The members of this family are related by out-of-plane conformational and orientational order driven by variations in chain length. It is obvious that other families of structures must also exist in which each family is similarly defined by a different symmetry and spacing of the pinning lattice and within each family, a wide, nearly continuous spectrum of density distribution correlations is manifested as a function of the molecular chain length. All possible cases would lie between the extreme limits of an assembly of all-*trans* chains pinned on a lattice commensurate with a close-packed array of vertical

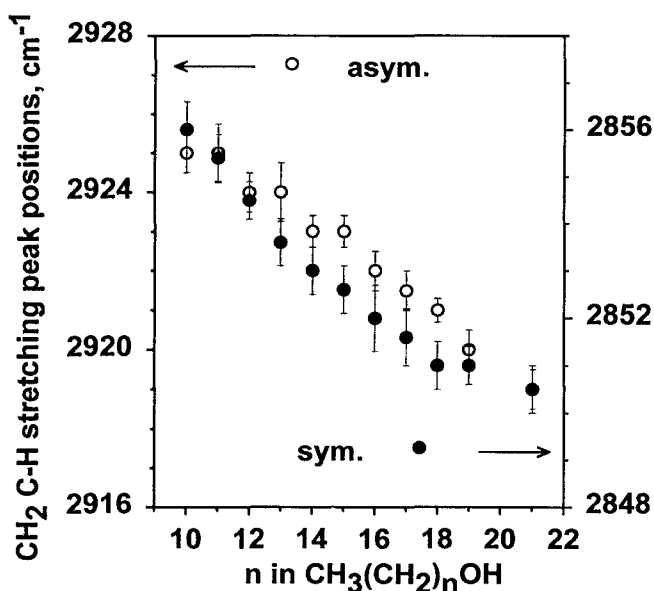


FIG. 4. Infrared peak frequency positions of the symmetric and antisymmetric C-H stretching mode absorptions for the  $\text{CH}_2$  units of  $\text{CH}_3(\text{CH}_2)_n\text{O-}$  films on  $\text{SiO}_2/\text{Si}$  substrates as a function of  $n$ .

aligned chains (no degrees of freedom) and on a lattice of isolated chains with all spacings greater than the fully extended length of the chains (preventing intermolecular interaction). Recent simulations<sup>29</sup> of constrained alkyl-chain phases on a square lattice have produced structural characteristics similar to those we report. While the current study has dealt with strong binding pinning interactions (covalent bonds), the introduction of surface mobility and site interchange are important dynamic aspects since they provide a mechanism for interconversion of structures. In this regard, all of the surface-constrained structures can be considered simply as quenched forms of translationally mobile structures such as Langmuir films.

We acknowledge S. K. Kumar and D. R. Nelson for valuable discussions and Z. Wang for conducting the FRS measurements. Financial support from the National Science Foundation (DMR-90-1270 for D.L.A. and A.N.P.; REU support for E.J.) and the Monsanto Chemical Company is acknowledged.

<sup>a</sup>To whom correspondence should be addressed. Electronic address: dla3@psuvm.bitnet

<sup>1</sup>J. D. Swalen *et al.*, *Langmuir* **3**, 932 (1987).

<sup>2</sup>A. Ulman, *Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly* (Academic, San Diego, 1991).

<sup>3</sup>L. H. Dubois and R. G. Nuzzo, *Annu. Rev. Phys. Chem.* **43**, 437 (1992).

<sup>4</sup>H. Ringsdorf, B. Schlarb, and J. Venzmer, *Angew. Chem. Int. Ed. Engl.* **27**, 114 (1988); K. L. Prime and G. M. Whitesides, *Science* **252**, 1164 (1991); D. A. Stenger *et al.*, *J. Am. Chem. Soc.* **114**, 8345 (1992).

<sup>5</sup>N. L. Abbott, J. P. Folkers, and G. M. Whitesides, *Science* **257**, 1380 (1992); R. C. Tiberio *et al.*, *Appl. Phys. Lett.* **62**, 476 (1993).

<sup>6</sup>R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.* **105**, 4481 (1983); C. D. Bain and G. M. Whitesides, *Angew. Chem. Int. Ed. Engl.* **101**, 522 (1989); G. M. Whitesides and P. E. Laibinis, *Langmuir* **6**, 87 (1990).

<sup>7</sup>S. Garoff *et al.*, *J. Phys. (Paris)* **47**, 701 (1986); L. Bourdieu, P. Silberzan, and D. Chatenay, *Phys. Rev. Lett.* **67**, 2029 (1991); J. Garnaes, D. K. Schwartz, R. Vishwanathan, and J. A. N. Zasadzinski, *Science* **257**, 508 (1992).

<sup>8</sup>R. G. Nuzzo, B. R. Zegarski, and L. H. Dubois, *J. Am. Chem. Soc.* **109**, 733 (1987); H. Sellers, A. Ulman, Y. Shnidman, and J. E. Eilers, *ibid.* **115**, 9389 (1993).

<sup>9</sup>L. Strong and G. M. Whitesides, *Langmuir* **4**, 546 (1988); C. E. D. Chidsey, G.-Y. Liu, P. A. Rowntree, and G. Scoles, *J. Chem. Phys.* **91**, 4421 (1991); C. A. Widrig, C. A. Alves, and M. D. Porter, *J. Am. Chem. Soc.* **113**, 2805 (1991).

<sup>10</sup>P. Fenter, P. Eisenberger, and K. S. Liang, *Phys. Rev. Lett.* **70**, 2447 (1993).

<sup>11</sup>P. E. Laibinis *et al.*, *J. Am. Chem. Soc.* **113**, 7152 (1991).

<sup>12</sup>D. R. Nelson, in *Phase Transition and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8, Chap. 1.

<sup>13</sup>N. Collazo and S. A. Rice, *Langmuir* **7**, 3144 (1991).

<sup>14</sup>S. T. Milner, *Science* **251**, 905 (1991).

<sup>15</sup>Thicknesses were determined using a single wavelength (623.8 nm) null-ellipsometer as previously described [D. L. Allara and R. G. Nuzzo, *Langmuir* **1**, 52 (1987)]. The FRS measurements of total proton surface density were carried out at the ion accelerator facility at Cornell University. The use of deuterated alcohols showed adsorbed H<sub>2</sub>O was not an interfering factor. The normal incidence TIRS measurements were done at 2 cm<sup>-1</sup> resolution on a Bomem MB 100 series Fourier transform spectrometer. Fringing effects were minimized both by use of wedged Si(100) wafers (Harrick Scientific). Sessile drop contact angle measurements were conducted in a saturated vapor of the probe liquid at 20 °C ± 0.2 °C and are reported as multiple sample averages with five spots analyzed per sample.

<sup>16</sup>A. A. Kruger, in *Surface and Near Surface Chemistry of Oxide Materials*, edited by J. Novotny and L. C. Dufour (Elsevier, Amsterdam, 1985); L. T. Zhuravlev, *Langmuir* **3**, 316 (1987).

<sup>17</sup>A. B. D. Cassie, *Discuss. Faraday Soc.* **3**, 11 (1948).

<sup>18</sup> $\theta_{\text{hexadecane}}$  and  $\theta_{\text{water}}$  = 46° and 114° for a CH<sub>3</sub> surface and 0° and 103° for CH<sub>2</sub>. [H. W. Fox and W. A. Zisman, *J. Colloid. Sci.* **7**, 428 (1952); S. R. Holmes-Farley *et al.*, *Langmuir* **4**, 921 (1988); Ref. 11]. Hydrated, clean SiO<sub>2</sub> surfaces are fully wet by both liquids.

<sup>19</sup>See, for example, J. Israelachvili, in *Intermolecular and Surface Forces: With Application to Colloidal and Biological Systems* (Academic, London, 1985).

<sup>20</sup>Connections between the chain-length induced structural transitions and 2D systems can be made by invoking recent studies of ordering in 2D vortex lattices on superconductors [C. A. Murray *et al.*, *Phys. Rev. Lett.* **64**, 2312 (1990)] in which magnetic fields have been observed to induce ordering transitions from isotropic phases to hexatic phases by unpinning pair vortices from a disordered defect lattice. One can make an approximate conceptual analogy between the magnetic field as an unpinning force in the vortex field and intermolecular interactions between alkyl chains, which, in the limit of sufficiently flexible and long molecules, should tend to override the pinning lattice disorder in regions towards the termini of the chains (away from the substrate) and thereby force the molecular system into a different structural phase, relatively uncorrelated with the pinning lattice.

<sup>21</sup>We stress, however, that the short chain limit is out of the range of applicability of mean-field polymer theories and associated experiments involving very long chains with polydispersity. These long-chain-limit approaches ignore the local structure of chains and focus purely on long-range scaling behavior of the thermodynamic and structural properties of these polymer assemblies (i.e., the zero wave vector limit alone is considered).

<sup>22</sup>R. A. MacPhail *et al.*, *J. Phys. Chem.* **88**, 334 (1984); R. G. Snyder, H. L. Strauss, and C. A. Elliger, *ibid.* **86**, 5145 (1982).

<sup>23</sup>J. Hautman and M. L. Klein, *J. Chem. Phys.* **91**, 4994 (1989).

<sup>24</sup>R. Maoz and J. Sagiv, *J. Colloid Interface Sci.* **100**, 465 (1984).

<sup>25</sup>A. Ulman, *Adv. Mater.* **2**, 573 (1990).

<sup>26</sup>J. B. Brzoska, N. Shahidzadeh, and F. Rondelez, *Nature* **360**, 719 (1992).

<sup>27</sup>D. L. Angst and G. W. Simmons, *Langmuir* **7**, 2236 (1991), and references cited therein.

<sup>28</sup>A. N. Parikh, D. L. Allara, I. Ben Azouz, and F. Rondelez (to be published).

<sup>29</sup>J. Weinhold and S. K. Kumar, *J. Chem. Phys.* (accepted for publication).