

Structure, Wettability, and Frictional Properties of Phenyl-Terminated Self-Assembled Monolayers on Gold

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Alkanethiols possessing terminal phenyl groups ($C_6H_5(CH_2)_nSH$, $n = 12-15$) were adsorbed onto the surface of gold to afford phenyl-terminated self-assembled monolayers (SAMs). The SAMs were characterized by optical ellipsometry, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), atomic force microscopy (AFM), and contact angle goniometry. The films generated from the phenyl-terminated alkanethiols exhibited greater thicknesses but similar crystallinities and well-ordered lattice structures when compared to analogous SAMs generated by the adsorption of normal alkanethiols onto gold. Advancing contact angle measurements using water as the test liquid supported the presence of interfacial phenyl moieties. Furthermore, contact angle measurements using the test liquids methylene iodide (MI), dimethyl formamide (DMF), and nitrobenzene (NB) revealed an odd–even effect as a function of the number of methylene units underneath the terminal phenyl groups. The tribological properties of the phenyl-terminated films were characterized by AFM and compared to those of films derived from normal alkanethiols and other materials presenting aromatic hydrocarbon moieties at the interface (i.e., graphite and C_{60}). The phenyl-terminated SAMs exhibited a substantially higher frictional response than graphite, a slightly higher frictional response than normal alkanethiol SAMs, but a much lower frictional response than C_{60} -terminated SAMs.

Introduction

Self-assembled monolayers (SAMs) have been widely adopted as model thin-film systems in molecular-level investigations of interfacial properties such as wetting, adhesion, and friction.^{1,2} SAM technology can be used to prepare well-defined ultrathin organic films on a variety of solid substrates. In addition, the structure and chemical functionality of SAMs can be controlled using organic synthesis, thus allowing one to systematically explore the relationships between structure/chemical functionality and the interfacial properties of organic thin films.

SAMs generated from aromatic thiols^{3–16} have attracted significant attention because of their (i) high anisotropy

and strong intermolecular interactions, (ii) delocalized electron distribution and high conductivity, and (iii) ease of synthetic modification.³ Previous studies of phenyl-terminated SAMs, however, have been restricted to studies of those generated from simple molecules, such as benzenethiol (C_6H_5SH), benzyl mercaptan ($C_6H_5-CH_2-SH$),^{4–8} and their derivatives.^{9–16} These studies demonstrated that phenyl-terminated SAMs exhibit well-defined packing similar to that of SAMs generated from normal alkanethiols. A ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ overlayer structure has been observed for SAMs on gold derived from benzyl mercaptan.^{4–8} A herringbone packing of the terminal phenyl groups appears to be the thermodynamically favored structure for these adsorbed aromatic thiols.^{6,7} Lattice structures different from those of *n*-alkanethiol SAMs have also been observed for SAMs terminated with derivatized phenyl groups.^{9–15} To date, little effort has targeted the characterization of the interfacial properties (e.g., wetting, adhesion, and friction) of phenyl-terminated SAMs.

Several previous studies have shown an odd–even chain length dependence of the interfacial properties of methyl-terminated (i.e., normal alkanethiol) SAMs on gold.^{17–20} Indeed, SAMs having an all trans-extended methylene backbone structure possess distinct orientations of the terminal group depending on whether the number of backbone methylene units is odd or even.^{17–20} By analogy

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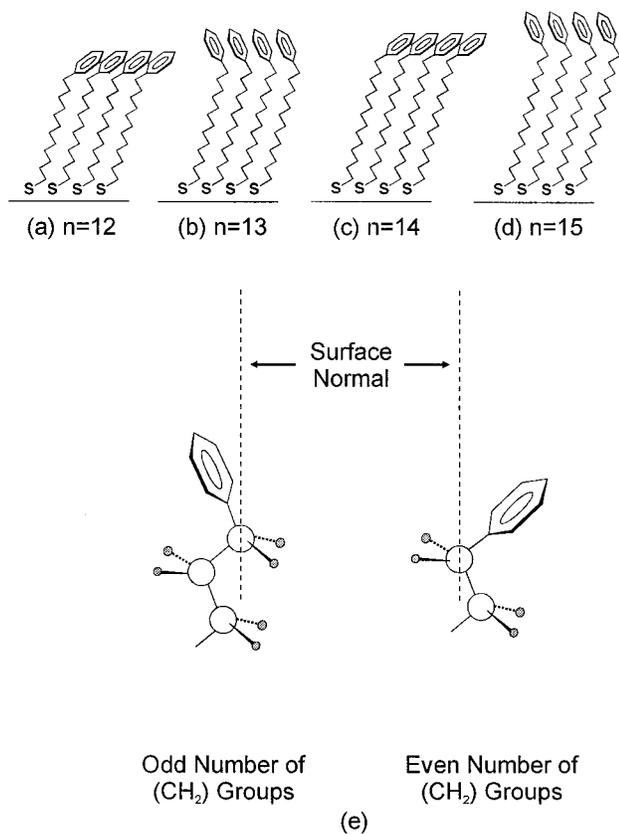


Figure 1. Depiction of phenyl-terminated SAMs derived from the following adsorbates: (a) 12-phenyldodecanethiol, (b) 13-phenyltridecanethiol, (c) 14-phenyltetradecanethiol, (d) 15-phenylpentadecanethiol. The lower graphic (e) illustrates the anticipated average tilt angles of the terminal phenyl group as a function of an odd number of CH₂ groups (left) and an even number of CH₂ groups (right).

to the structures of normal methyl-terminated SAMs, we assume that phenyl-terminated SAMs having an odd number of methylene units will possess terminal phenyl groups with the C1–C4 ring axis oriented slightly ($\sim 30^\circ$) from the surface normal; in contrast, phenyl-terminated SAMs having an even number of methylene units will possess terminal phenyl groups with the C1–C4 ring axis tilted more substantially ($\sim 60^\circ$) from the surface normal as illustrated in Figure 1. Because phenyl groups and methyl groups represent ubiquitous hydrocarbon moieties with distinct chemical and physical properties,²¹ a systematic investigation of the interfacial properties of a sequential series of phenyl-terminated SAMs provides an excellent opportunity to explore the chemical origin(s) of odd–even interfacial effects. Moreover, given that Porter and co-workers documented an “odd–even” effect in their examination of the frictional properties of methyl-terminated SAMs on gold,²⁰ studies of the frictional properties of the phenyl-terminated SAMs permit a unique opportunity to examine the tribological properties of these interfaces relative to those of other aromatic interfaces (e.g., graphite and C₆₀-terminated SAMs)²² in order to evaluate the role(s) of aromatic hydrocarbons in boundary layer lubrication.^{23,24}

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In the present work, we prepare a series of phenyl-terminated alkanethiols having long methylene chains connecting the phenyl group to the thiol moiety (C₆H₅-(CH₂)_n-SH, where $n = 12–15$), and generate SAMs on gold as shown in Figure 1. We use this system to investigate the influence of terminal aromatic moieties on the structure, wettability, and friction of hydrocarbon thin films. In studies using atomic force microscopy (AFM), we measure and compare the lattice structures of the phenyl-terminated SAMs to those of analogous methyl-terminated SAMs. Also with AFM, we measure the frictional properties of the phenyl-terminated SAMs and compare them to those of other aromatic hydrocarbon interfaces, namely, those of graphite and C₆₀-terminated SAMs.

2. Experimental Section

Figure 1 illustrates the structure of the four phenyl-terminated SAMs studied in this work, which were derived from the following four phenyl-terminated alkanethiols: 12-phenyldodecanethiol ($n = 12$, Ph(CH₂)₁₂SH), 13-phenyltridecanethiol ($n = 13$, Ph(CH₂)₁₃SH), 14-phenyltetradecanethiol ($n = 14$, Ph(CH₂)₁₄SH), and 15-phenylpentadecanethiol ($n = 15$, Ph(CH₂)₁₅SH). All chemicals used in the syntheses of these adsorbates were purchased from commercial suppliers and were of the highest purity available (excluding reagent-grade solvents). Schemes outlining the syntheses and the corresponding experimental details are provided as Supporting Information. Complete analytical data for all phenyl-terminated alkanethiols are provided below.

12-Phenyldodecanethiol (Ph(CH₂)₁₂SH). ¹H NMR (300 MHz, CDCl₃): δ 7.15–7.30 (m, 5 H), 2.61 (t, $J = 7.5$ Hz, 2 H), 2.51 (q, $J = 7.2$ Hz, 2 H), 1.56–1.67 (m, 4 H), 1.20–1.40 (m, 16 H). ¹³C NMR (75.5 MHz, CDCl₃): δ 142.84, 128.31 (2 C), 128.14 (2 C), 125.47, 35.94, 34.01, 31.47, 29.57, 29.53 (2 C), 29.47 (2 C), 29.30, 29.04, 28.34, 24.59. Anal. Calcd for C₁₈H₃₀S: C, 77.63; H, 10.86. Found: C, 78.00; H, 10.98.

13-Phenyltridecanethiol (Ph(CH₂)₁₃SH). ¹H NMR (300 MHz, CDCl₃): δ 7.14–7.30 (m, 5 H), 2.59 (t, $J = 7.8$ Hz, 2 H), 2.51 (q, $J = 7.5$ Hz, 2 H), 1.54–1.64 (m, 4 H), 1.20–1.40 (m, 18 H). ¹³C NMR (75.5 MHz, CDCl₃): δ 142.93, 128.37 (2 C), 128.18 (2 C), 125.51, 35.98, 34.04, 31.51, 29.61 (2 C), 29.56 (2 C), 29.50 (2 C), 29.33, 29.07, 28.37, 24.65. Anal. Calcd for C₁₉H₃₂S: C, 78.01; H, 11.03. Found: C, 78.17; H, 11.25.

14-Phenyltetradecanethiol (Ph(CH₂)₁₄SH). ¹H NMR (300 MHz, CDCl₃): δ 7.13–7.25 (m, 5 H), 2.56 (t, $J = 7.8$ Hz, 2 H), 2.48 (q, $J = 7.2$ Hz, 2 H), 1.52–1.62 (m, 4 H), 1.22–1.31 (m, 20 H). ¹³C NMR (75.5 MHz, CDCl₃): δ 142.94, 128.39 (2 C), 128.21 (2 C), 125.53, 36.01, 34.08, 31.56, 29.66 (3 C), 29.61 (2 C), 29.54 (2 C), 29.37, 29.10, 28.41, 24.68. Anal. Calcd for C₂₀H₃₄S: C, 78.36; H, 11.18. Found: C, 77.99; H, 11.40.

15-Phenylpentadecanethiol (Ph(CH₂)₁₅SH). ¹H NMR (300 MHz, CDCl₃): δ 7.13–7.23 (m, 5 H), 2.56 (t, $J = 7.5$ Hz, 2 H), 2.48 (q, $J = 7.2$ Hz, 2 H), 1.52–1.61 (m, 4 H), 1.22–1.39 (m, 22 H). ¹³C NMR (75.5 MHz, CDCl₃): δ 142.94, 128.40 (2 C), 128.22 (2 C), 125.55, 36.03, 34.10, 31.58, 29.70 (4 C), 29.64 (2 C), 29.57 (2 C), 29.13, 29.16, 28.43, 24.69. Anal. Calcd for C₂₁H₃₆S: C, 78.68; H, 11.32. Found: C, 78.98; H, 11.47.

Self-assembled monolayers were generated by the spontaneous adsorption of the phenyl-terminated thiols (~ 1 mM in ethanol, 24 h) onto gold substrates. Ellipso-

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metry, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and wettability studies were performed on SAMs grown on polycrystalline gold substrates thermally evaporated onto silicon wafers.²⁵ Topography and frictional studies were performed on crystalline Au(111) substrates prepared by annealing a gold wire in H₂/O₂ flame. The details of the preparation of the latter gold substrates have been provided in a previous publication.²⁶

Ellipsometry was used to measure the thicknesses of the SAMs. Data were collected using a Rudolf Research Auto EL III model equipped with a He-Ne laser (632.8 nm at an incident angle of 70°). A refractive index of 1.45 was assumed for all films. A ramé-hart model 100 contact angle goniometer was used to measure the wettabilities of these films. Spectroscopic PM-IRRAS data were obtained using a Nicolet MAGNA-IR 860 Fourier transform spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instruments PEM-90 photoelastic modulator operating at 37 kHz. The polarized light was reflected from the sample at an incident angle of 80°. The spectra were generated from 256 scans at a spectral resolution of 4 cm⁻¹.

The surface structure and frictional properties of the SAMs were characterized with an AFM based upon conventional beam-deflection methods and employing a single tube piezo scanner (0.5 in. o.d. × 1.0 in. length).²⁶ In this approach, light from a laser diode is focused on the backside of a V-shaped cantilever (Digital Instrumentation, CA), having a sharp silicon nitride tip underneath. In all cases, the sample was scanned relative to a fixed tip-cantilever position. Deflections of the cantilever generated from interaction of the probe tip and the sample surface were detected by a four-quadrant position-sensitive detector. This technique allows simultaneous and independent recording of both normal and lateral deflections of the cantilever. Positioning of the samples, data collection, and data processing were controlled by RHK AFM 100 and RHK STM 100 electronics and software.

3. Results and Discussion

3.1. Characterization of the Films. We first measured the thicknesses of the phenyl-terminated SAMs by ellipsometry. Figure 2 illustrates the change in thickness as the length of the methylene chain is increased. For comparison, the ellipsometric thicknesses of methyl-terminated normal alkanethiol SAMs having the same number of methylene groups are also plotted (see also Table 1). The data show that the ellipsometric thicknesses of both types of films increase as the length of the methylene chain increases, but that the phenyl-terminated SAMs show higher thicknesses (by ~3 Å on average) than the methyl-terminated SAMs for a given number of methylene units.²⁷ A relatively smaller thickness difference between the two types of SAMs was reproducibly observed for the *n* = 12 SAMs; this minor deviation probably arises because of weaker interchain van der Waals stabilization and thus less conformational order in these films. The observation of higher thicknesses of phenyl-terminated SAMs relative to those of methyl-terminated SAMs were anticipated given that phenyl

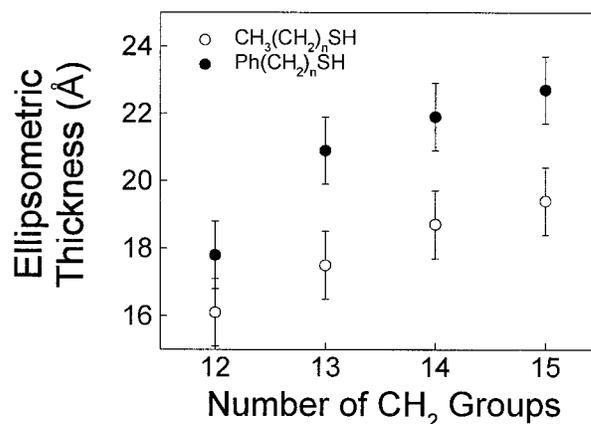


Figure 2. Ellipsometric thicknesses of phenyl-terminated SAMs (●) and the corresponding methyl-terminated SAMs (○) as a function of the number of methylene units.

Table 1. Ellipsometric Thicknesses and Advancing Contact Angles of Water (H₂O), Methylene Iodide (MI), Nitrobenzene (NB), and Dimethyl Formamide (DMF)^a

	thickness	θ_a H ₂ O	θ_a HD	θ_a MI	θ_a NB	θ_a DMF
Ph12SH	17.8 Å	90.3°	< 10°	44.8°	38.1°	38.6°
Ph13SH	20.9 Å	92.3°	< 10°	48.5°	41.6°	42.4°
Ph14SH	21.9 Å	92.5°	< 10°	44.9°	39.1°	39.6°
Ph15SH	22.7 Å	92.7°	< 10°	49.2°	41.9°	42.5°
CH ₃ 12SH	16.1 Å	112.7°	45.7°	68.7°	67.3°	70.9°
CH ₃ 13SH	17.5 Å	113.5°	48.7°	73.2°	69.4°	74.0°
CH ₃ 14SH	18.7 Å	112.5°	46.0°	70.2°	67.0°	71.0°
CH ₃ 15SH	19.4 Å	112.8°	48.5°	72.9°	70.1°	73.9°
graphite	N/A	86°	-	-	-	-
C ₆₀ N11S ₂	21.8 Å	87°	-	-	-	-

^a Values of thickness have error bars of ± 1 Å, and contact angles have error bars of $\pm 1^\circ$ of the reported average value.

groups are larger than methyl groups.⁶ Absolute values of film thickness obtained from the ellipsometric measurements should, however, be interpreted with some degree of caution in light of uncertainties in the refractive indexes of the films.^{6,10}

We further characterized the structures of the phenyl-terminated SAMs through PM-IRRAS measurements. The differential reflectivity spectra are shown in Figure 3a. In these spectra, the symmetric methylene stretch ($\nu_s^{\text{CH}_2}$) appears at 2850 cm⁻¹, the antisymmetric methylene stretch ($\nu_a^{\text{CH}_2}$) appears at 2919 cm⁻¹, and the C-H stretches associated with the terminal phenyl groups appear above 3000 cm⁻¹.^{6,11,28} Previous studies have shown that the position of the $\nu_a^{\text{CH}_2}$ band is sensitive to the degree of conformational order (or crystallinity) of organic thin films.²⁹⁻³³ We find that, despite the incorporation of the bulky, planar phenyl groups into the terminal portion of the films, the $\nu_a^{\text{CH}_2}$ bands appear at the identical position of those of well-ordered normal alkanethiol SAMs having the same chain lengths.²⁹⁻³³

(27) We note that the use of 1.50 as the refractive index of the phenyl-terminated SAMs instead of 1.45 ($n_D^{20} = 1.5$ for benzene, whereas $n_D^{20} = 1.43$ for cyclohexane, *The Merck Index*, 10th ed.) in the ellipsometric thickness measurements gave rise to higher thickness values. Thus, the assumption of 1.45 as the refractive index for these films (vide supra) represents a conservative choice with regard to comparison with normal alkanethiol SAMs. As a consequence, the observed higher thicknesses for the phenyl-terminated SAMs cannot be accounted for by the uncertainty in the values of refractive index employed in these analyses.

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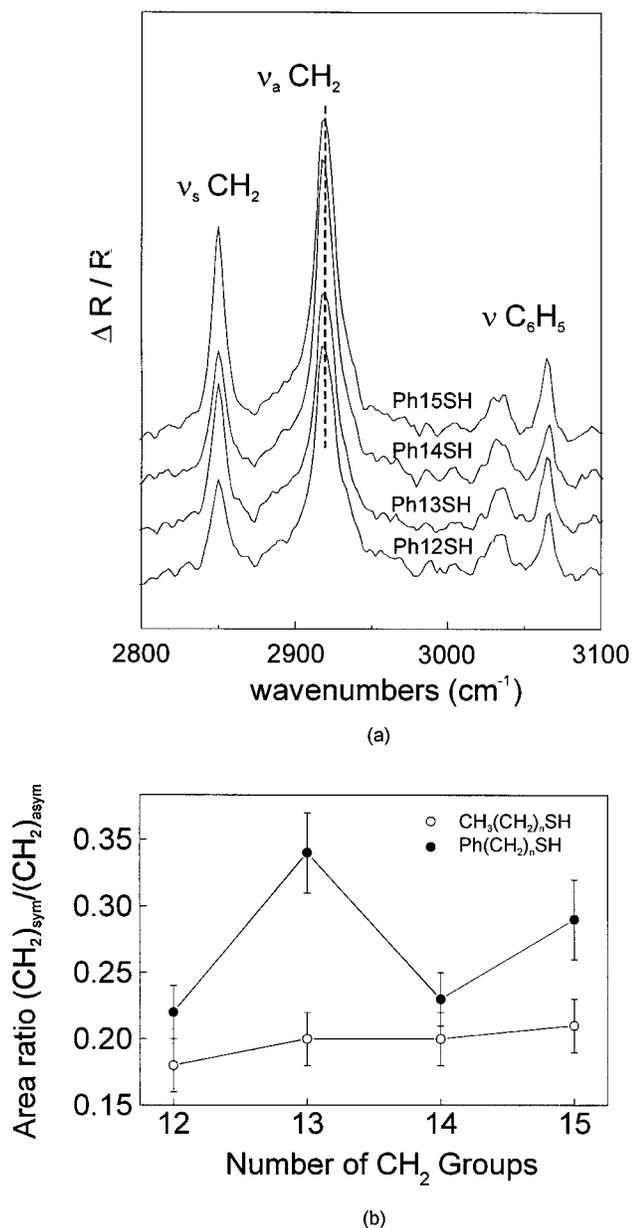


Figure 3. PM-IRRAS spectra of the phenyl-terminated SAMs: (a) 2800–3100 cm⁻¹ region exhibiting an alternating intensity ratio of the symmetric and antisymmetric methylene stretches. (b) Area ratio between the symmetric and antisymmetric methylene stretches vs the number of methylene units in phenyl-terminated SAMs (●) and methyl-terminated SAMs (○).

The relative intensities of the $\nu_s\text{CH}_2$ and $\nu_a\text{CH}_2$ bands provide additional insight into the structures of the phenyl-terminated films. Two previous studies have discussed in detail the vibrational features of thiol-based monolayers containing aromatic groups. Chang and co-workers¹⁰ investigated SAMs generated from aromatic-derivatized thiols possessing phenyl moieties near the sulfur atoms, 4'-alkoxybiphenyl-4-methanethiol (4'-CH₃(CH₂)_mOC₆H₄C₆H₄-4-CH₂SH), (6-alkoxynaphth-2-yl)methanethiol (6-CH₃(CH₂)_mOC₁₀H₆-2-CH₂SH), and 4'-alkoxybiphenyl-4-thiol (4'-CH₃(CH₂)_mOC₆H₄C₆H₄-4-SH) ($m = 15, 16$) on both gold and silver substrates. Tamada and co-workers³⁴ studied

the infrared-reflection absorption spectra (IRRAS) of hexyl azobenzenethiol (C₆H₁₃(C₆H₄)N₂(C₆H₄)O(CH₂)₁₂SH) SAMs on Au(111). In both studies, the large aromatic moieties were observed to influence the structures of the hydrocarbon portions of the films. Specifically, the aromatic-derivatized SAMs exhibited distinctively higher symmetric to antisymmetric methylene stretch intensity ratios when compared to those of normal alkanethiol SAMs. This higher intensity ratio was interpreted to reflect a smaller twist of the alkyl chains,^{10,34} which is defined as the angle between the CCC backbone plane and the plane perpendicular to the surface containing the chain axis.³⁵

As shown in Figure 3 for the phenyl-terminated SAMs, the ratio of the symmetric and antisymmetric methylene C–H stretch intensities varies systematically as a function of the number of methylene groups.³⁶ In contrast, this variation is not observed for SAMs generated from normal alkanethiols (unfilled symbols, Figure 3b). Upon the basis of the studies cited above, we propose that this spectral variation arises from a systematic change in the twist angle of the backbone chain, although a change in chain tilt angle cannot be entirely ruled out. Assuming that our proposal is valid, the IR results can be interpreted to indicate that the SAMs with an even number of methylene units exhibit a greater chain twist than the SAMs with an odd number of methylene units. As shown in Figure 1e, the terminal phenyl groups of even-numbered films are expected to be more tilted on average from the surface normal than those of odd-numbered films. Consequently, the different chain twists suggested by the IR data might arise from different degrees of terminal phenyl group interactions (e.g., π stacking and/or steric repulsion) in odd- vs even-numbered films. We examined the vibrational data collected by PM-IRRAS in the C–C stretching region (1350–2000 cm⁻¹) in an attempt to further characterize the SAM structures through an analysis of the aromatic ring-breathing modes near 1490 cm⁻¹.^{6,11} However, the intensity of these modes was below the detection limit of our instrument, which prevented further analysis.

We characterized the topographies of the film surfaces by atomic force microscopy. Over large areas ($\geq 0.5 \times 0.5 \mu\text{m}$), all of the film surfaces were smooth and featureless, except for the well-defined steps and terraces arising from the underlying gold substrates. Images collected over small areas ($\sim 75 \times 75 \text{ \AA}$), however, revealed the structure of SAMs through periodic fluctuation of the lateral force.³⁷ A representative lattice image is shown in Figure 4a in which the spacing of the hexagonal lattice structure is $4.9 \pm 0.2 \text{ \AA}$, which is indistinguishable from that of normal alkanethiols on Au(111).²⁶ These observations are consistent with previous scanning probe microscopy⁶ and theoretical⁷ studies of SAMs generated from benzylmercaptan (C₆H₅CH₂SH) and [1,1':4',1''-terphenyl]-4-methanethiol (*p*-C₆H₅(C₆H₄)₂CH₂SH).⁸ The most plausible and widely accepted packing structure for aromatic groups incorporated into SAMs exhibiting a hexagonal lattice is the herringbone structure.^{4,7,10} On the basis of these established models and the $4.9 \pm 0.2 \text{ \AA}$ periodicity observed here by AFM, we believe that the long chain phenyl-terminated SAMs exist with their terminal groups packed in a herringbone fashion. A simple illustration of this model is shown in Figure 4b. Although the vibrational data described above and the wettability described below are consistent with a systematically varying "odd-even"

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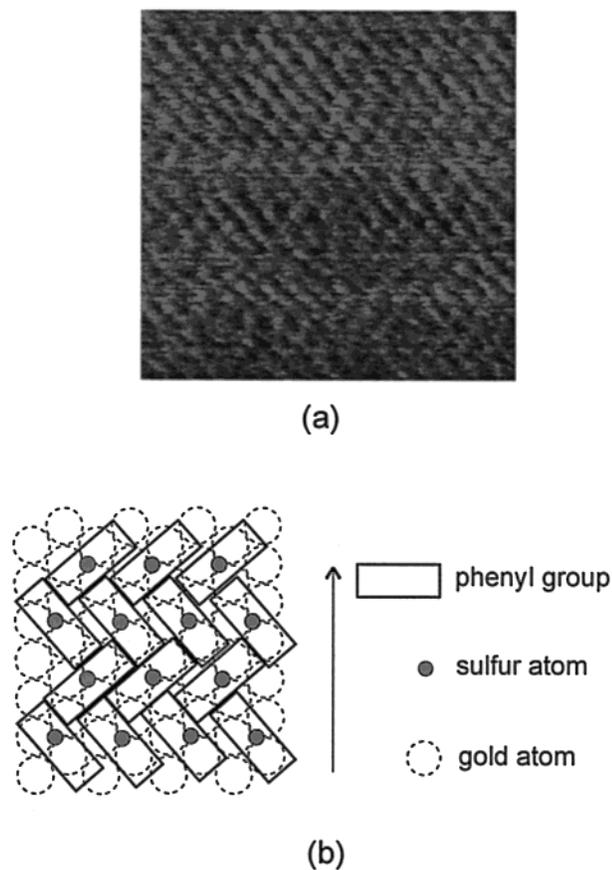


Figure 4. (a) Lattice resolution images ($75 \times 75 \text{ \AA}$, unprocessed) obtained by AFM for SAMs derived from 15-phenylpentadecanethiol ($\text{Ph}(\text{CH}_2)_{15}\text{SH}$). (b) Simple schematic showing the herringbone structure of phenyl-terminated SAMs on gold (top view).

orientation of the terminal phenyl groups with chain length, we would not anticipate (because of the convoluted stick-slip motion of the tip and the potential mechanical deformation of the films under the measurement conditions), nor have we observed any detectable odd-even effects in the film structures measured by AFM.

We further characterized the phenyl-terminated SAMs by contact angle wettability studies. The results of these measurements using water as the contacting liquid are shown in Figure 5a together with data obtained from an analogous series of normal alkanethiol SAMs (see also Table 1). Values of the advancing contact angles of water on the phenyl-terminated SAMs are consistent with the presence of interfacial phenyl moieties.^{6,28} In contrast to the advancing contact angles of water measured on SAMs formed from the methyl-terminated alkanethiols (113° on average), SAMs formed from the phenyl-terminated alkanethiols exhibited distinctly lower contact angles (92° on average). The fact that the contact angles on the phenyl-terminated SAMs are lower than those on the methyl-terminated SAMs probably reflects the inherent influence of phenyl vs methyl moieties on the interfacial surface free energies given that phenyl groups are more polarizable than methyl groups.²¹ The advancing contact angles of water observed here are nevertheless higher than those observed in previous studies of the wettabilities of phenyl or other SAMs terminated with aromatic groups,^{4,6,12,28,38-40} reflecting the high integrity of the present SAMs and/or

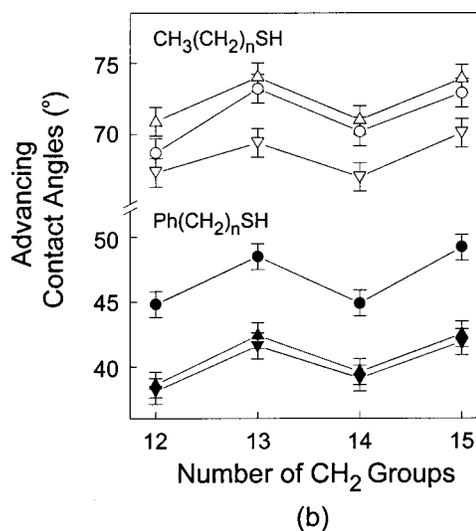
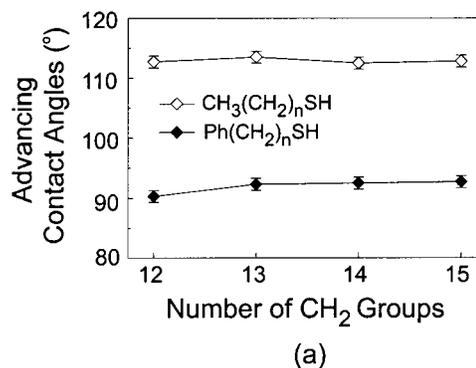


Figure 5. Advancing contact angles measured on the phenyl-terminated SAMs and methyl-terminated SAMs using (a) water (H_2O , \blacklozenge and \diamond), and (b) methylene iodide (MI, \bullet and \circ), nitrobenzene (NB, \blacktriangledown and \triangledown), and dimethyl formamide (DMF, \blacktriangle and \triangle) as the contacting liquids. All filled symbols correspond to phenyl-terminated SAMs and all empty symbols correspond to methyl-terminated SAMs.

the relatively large distance between the phenyl interface and the underlying gold surface.⁴¹

In contact angle measurements using hexadecane (HD) as the test liquid, we observed complete wetting of the surfaces of the phenyl-terminated SAMs ($\theta_a < 10^\circ$; Table 1). Consequently, we chose to further characterize the wettabilities of these films using other contacting liquids having surface tensions higher than that of hexadecane, namely, methylene iodide (MI), *N,N*-dimethyl formamide (DMF), and nitrobenzene (NB). The significance of examining moderately wetting liquids on SAMs lies in the frequent reports of a parity (or odd-even) effect in the contact angle vs chain-length relationship.^{10,18,19,42,43} The results of these measurements are plotted in Figure 5b together with the data obtained from the analogous series of normal alkanethiol SAMs (see also Table 1). In contrast to the contact angles of water, the contact angles of these liquids exhibited a systematic variation among the phenyl-terminated SAMs containing odd and even numbers of methylene groups. Similar variations were also observed for the methyl-terminated SAMs. The odd-even variation

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of contact angles on methyl-terminated SAMs by these liquids has been attributed to a greater exposure of underlying methylene groups for SAMs having an odd number of methylene groups.^{10,18,43,44} In the case of phenyl-terminated SAMs, however, the bulky but well-ordered surface phenyl groups might obscure the underlying methylene groups for both orientations of the terminal groups (Figure 1). Consequently, it is possible that variations in the orientation of the terminal phenyl group itself give rise to the observed chain length variation in the contact angle values.

Collectively, we conclude from all of the data presented above that the SAMs generated from the phenyl-terminated thiols expose phenyl moieties at the interface. The conformational order of the methylene backbones and the packing densities at the surface are indistinguishable from those of SAMs generated from normal alkanethiols. The peak area ratios of the symmetric and antisymmetric methylene stretches in the PM-IRRAS data suggest, however, a systematic structural variation in the twist angles of the backbone alkyl chains as a function of chain length. Furthermore, the contact angle measurements suggest a variation in the orientation of the terminal phenyl groups as a function of chain length.

3.2. Frictional Properties of the Films. Having characterized the interfacial structure/composition of the phenyl-terminated SAMs, we measured their frictional properties by AFM and compared them to those of normal alkanethiol SAMs, graphite, and C₆₀-terminated SAMs. As described in the Experimental Section, simultaneous and independent measurement of the normal and lateral forces enabled plots of interfacial friction versus the applied load. The shape and slope of the friction-load plots depend on the interfacial interactions between the silicon nitride AFM tip and the surfaces of the films. The same tip/cantilever assembly was employed for measurements of all surfaces in order to ensure a valid comparison of their frictional properties. A more detailed description of friction-load measurements has been presented elsewhere.²⁶

Figure 6a displays representative friction-load data obtained from the series of phenyl-terminated SAMs for loads up to 30 nN. In these plots, frictional forces were measured as a function of decreasing load; data collected for increasing loads were indistinguishable at positive loads. Negative loads in these plots are indicative of attractive forces. The most negative force is defined as the pull-off force and is the force required to remove the AFM tip from the film surface while sliding. Figure 6b shows the statistical deviations of the frictional responses of the different films, where the frictional force at specific applied loads is plotted against the various lengths of the methylene backbones. The error bars in this plot represent the standard deviation of measurements of friction obtained at different locations across the sample surface. These data show that the frictional responses of this series of phenyl-terminated monolayers decrease with increasing chain length over the range of chain lengths investigated.

Although the trend of decreasing friction with increasing chain length of normal alkanethiol SAMs has been documented, this trend is most apparent for chains containing less than ~10 methylene units.^{45,46} Indeed, the frictional properties of methyl-terminated SAMs having longer chain lengths are largely indistinguishable.^{45,46} In

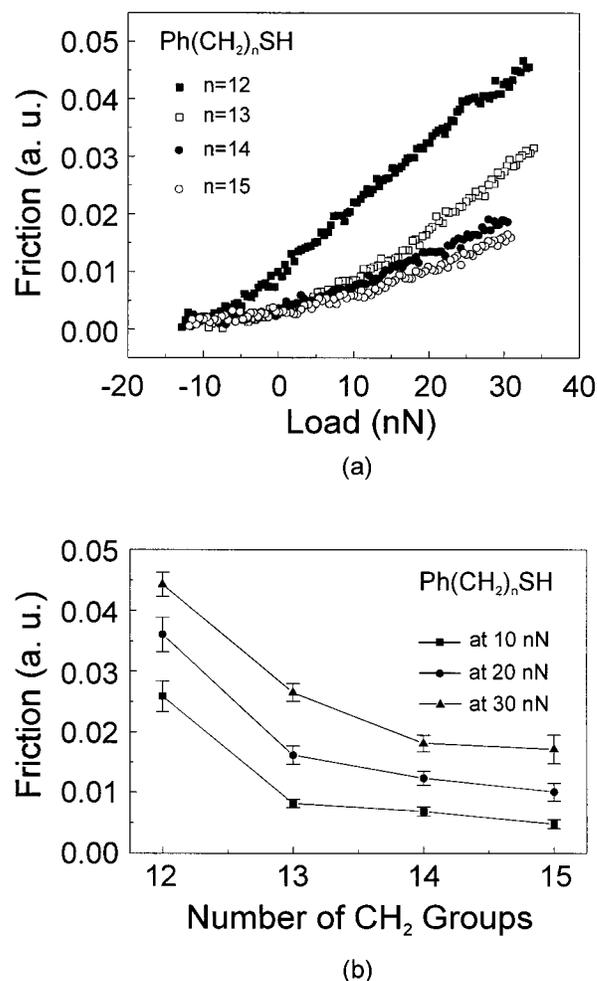


Figure 6. (a) Representative friction-load plots obtained for the phenyl-terminated SAMs under decreasing applied load. (b) Comparison of frictional forces of all four phenyl-terminated SAMs under 10, 20, and 30 nN applied loads.

the present study, the trend of decreasing friction with increasing chain length extends to longer chain lengths and probably arises from the presence of the bulky terminal group and the consequent steric disruption of the film structure.

As noted in the Introduction, Porter and co-workers observed that normal alkanethiol SAMs exhibit an odd-even fluctuation in their frictional properties as a function of chain length (within the range of $n = 12-16$, where n is the number of methylene units).²⁰ Monolayers having an odd number of methylene backbone units (and thus slightly tilted terminal C-C bonds) show lower frictional responses than those having an even number of methylene backbone units (and thus more highly tilted terminal C-C bonds). The authors interpreted this fluctuation in terms of an alternating orientation of surface dipoles, which gave rise to systematically varying surface free energies for SAMs having odd and even length chains. Although we have reproduced these results for methyl-terminated SAMs through independent measurements (data not shown), we find no evidence for an odd-even fluctuation in the frictional properties of the phenyl-terminated SAMs (Figure 6). Although not formally a polar functionality, a terminal phenyl group attached to a hydrocarbon chain will give rise to a dipole that is greater in magnitude than that arising from a corresponding terminal methyl group.²¹ From the data in Figure 6, it is apparent that any such dipole effect is insufficiently strong to influence the frictional properties of the phenyl-terminated SAMs.

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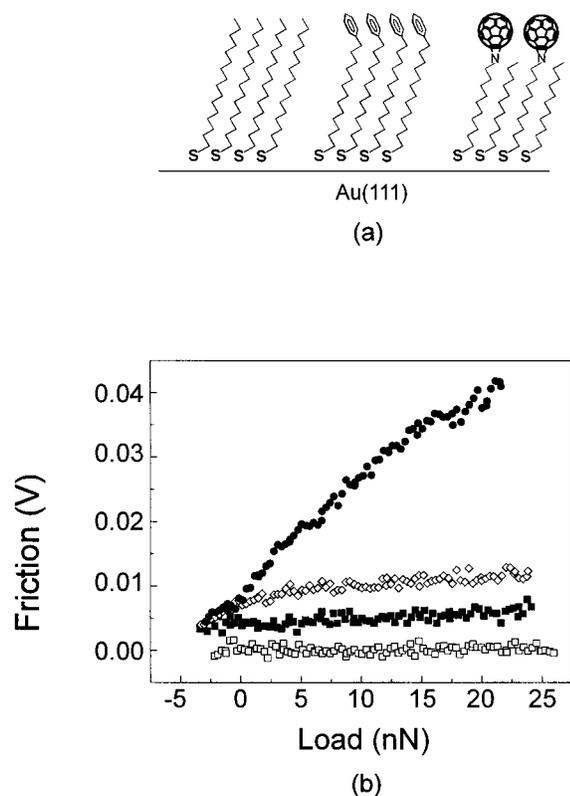


Figure 7. (a) Simple schematic showing the composition of the SAMs. (b) Friction-load plots obtained on graphite (□) and on SAMs derived from CH₃(CH₂)₁₅SH (■), Ph(CH₂)₁₃SH (◇), and C₆₀-N(CH₂)₁₁SS(CH₂)₁₀CH₃ (●).

Moreover, we have proposed in separate studies that the alternating frictional behavior of normal alkanethiol SAMs arises through a mechanism alternative to that proposed by Porter and co-workers.^{44,47,48} Our model accounts for the odd–even effect through the alternating tilt of the terminal C–C bonds of the films as a function of odd vs even chain lengths (see Figure 1). This odd–even alternation affords a corresponding alternation in the degree of exposure of underlying methylene groups, which in turn leads to an odd–even alternation in the degree of van der Waals interactions between the films and the contacting AFM tip. Correspondingly, the enhanced van der Waals interactions between the AFM tip and the films having even numbers of methylene groups gives rise (at least partially)^{44,48} to their enhanced frictional response relative to films having odd numbers of methylene groups. For phenyl-terminated SAMs, however, we believe that the absence of an odd–even frictional response is due to steric blocking of the underlying methylene groups by the large overlying phenyl groups. Other unidentified orientational effects in the vicinity of the phenyl groups, however, might also play a role.

In a separate set of measurements, we compared the frictional properties of the phenyl-terminated SAMs to those of normal alkanethiol SAMs, graphite, and C₆₀-terminated SAMs in order to examine the systematic contribution of aromatic moieties to the tribological properties of model boundary lubricants. As shown in Figure 7a, the chain length of each monolayer was selected to provide the same approximate thickness for all of the films. In

Figure 7b, representative friction-load plots for each of these materials are displayed. As we have previously shown, C₆₀ moieties chemically immobilized on the surfaces of SAMs exhibit significantly higher frictional properties than normal alkanethiols having the same backbone structure.²² In contrast to this observation, the phenyl-terminated SAMs exhibited significantly lower frictional properties than the C₆₀-terminated SAMs, although still slightly higher than the normal alkanethiol SAMs. All SAM films, however, showed higher frictional properties than graphite. These results again indicate that the chemical composition (i.e., hydrocarbon in nature) is not solely responsible for determining the tribological properties of thin-film lubricants.^{22,26,44,47,48} Rather, the local chemical structure and environment of the relevant molecular species also play substantial roles. The moderately low frictional properties observed for the phenyl-terminated SAMs examined here, when coupled with their unique chemical properties, encourages further investigation of these materials in model studies of boundary layer lubrication.⁴⁹

4. Conclusions

In this work, we have synthesized and generated SAMs on gold having long methylene chains and terminal phenyl groups. The structures of the films were characterized by surface IR spectroscopy, AFM, ellipsometry, and wettability measurements. The conformational order of the methylene backbone ($\nu_a\text{CH}_2 = 2919\text{ cm}^{-1}$) and the lattice spacing of the terminal phenyl groups ($4.9 \pm 0.2\text{ \AA}$) were indistinguishable from those of corresponding SAMs generated from normal alkanethiols. The presence of aromatic C–H stretches in the IR spectra, the observed ellipsometric thicknesses, and the distinct wettabilities provided strong support for the model of phenyl-terminated organic thin films. The PM-IRRAS studies suggest an odd–even effect with regard to the twist of the methylene backbones. Similarly, the wettability studies suggest an odd–even effect with regard to the orientation of the terminal phenyl groups. The frictional properties of the films were characterized by AFM, which showed that, in contrast to methyl-terminated SAMs, the phenyl-terminated SAMs failed to exhibit a systematic odd–even variation in the frictional properties. To rationalize this latter observation, we proposed that the relatively large phenyl groups effectively shield access to underlying portions of the film and thus obscure the detection of any odd–even effects. In other tribological studies, the phenyl-terminated SAMs exhibited a much lower frictional response than C₆₀-terminated SAMs, a slightly higher frictional response than normal alkanethiol-terminated SAMs, and a substantially higher frictional response than graphite. From this series of measurements, we concluded that, in addition to chemical composition, the local structural environment of molecular species actively influences their tribological properties.

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Supporting Information Available: Procedures for synthesis of the phenyl-terminated alkanethiols (9 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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