Systematic Control of the Packing Density of Self-Assembled Monolayers Using Bidentate and Tridentate Chelating Alkanethiols

Joon-Seo Park, Andy Nguyen Vo, David Barriet, Young-Seek Shon,‡ and T. Randall Lee*†

Department of Chemistry, University of Houston, 4800 Calhoun Road, Houston, Texas 77204-5003

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The structural and interfacial properties of self-assembled monolayers (SAMs) on gold derived from the adsorption of a series of 1,1,1-tris(mercaptopropyl)alkanes (i.e., CH₃(CH₂)ₙC[CH₂SH]₃, where \( m = 9, 11, 13, 15 \)) were investigated. The new SAMs, which possess uniformly low densities of alkyl chains, were characterized by ellipsometry, contact angle goniometry, and polarization modulation infrared reflection absorption spectroscopy. Additional analysis of the SAMs by X-ray photoelectron spectroscopy permitted a direct calculation of the packing densities of the SAMs on gold. The results as a whole, when compared to those obtained on SAMs generated from normal alkanethiols (CH₃(CH₂)ₙSH), 2-alkylpropane-1,3-dithiols (CH₃(CH₂)ₙCH[CH₂SH]₂), and 2-alkyl-2-methylpropane-1,3-dithiols (CH₃(CH₂)ₙC(CH₃)[CH₂SH]₂) having analogous chain lengths, demonstrate that the 1,1,1-tris(mercaptopropyl)alkanes afford SAMs with alkyl chains having the lowest packing density and least conformational order.

Introduction

Self-assembled monolayers (SAMs) have been widely investigated for the past two decades due to their potential use in a number of technologies, including those involving adhesion, wetting, corrosion prevention, and lubrication. Furthermore, the applications of SAMs have been expanding into emerging areas, such as nanoelectronics and biosensors. The widespread interest in and use of SAMs can be attributed in part to their densely packed and highly ordered structures. In particular, the macroscopic surface properties of semicrystalline SAMs are dictated by their microscopic structure and composition. Thus, the interfacial properties of densely packed and highly ordered SAMs are predictable and readily controlled through the use of specific chain lengths and tailgroups.

Loosely packed and thus conformationally disordered SAMs have received relatively little attention from interfacial scientists. Our research group, however, believes that the conformational flexibility of alkyl chains in loosely packed SAMs offers distinct characteristics that can lead to unique technological applications. For example, SAMs having a low density of alkyl chains can be used to control thrombus formation on the surface of biomedical devices. Because thrombus formation through protein adsorption on surfaces is a critical obstacle in the development of biocompatible devices, much research has been carried out to prepare surfaces that are resistant to protein adsorption. One strategy for controlling protein adsorption is to deposit or grow a protective layer of protein, such as human serum albumin (HSA), on surfaces to prevent the adsorption of other blood proteins. Foster and co-workers investigated the effect of the packing density of SAMs on HSA adsorption. These researchers observed that HSA bound more tenaciously to loosely packed SAMs than to densely packed SAMs due to the penetration of HSA into the loosely packed SAMs. Another application of loosely packed SAMs involves reversibly switching surfaces, which were reported by Langer and co-workers. Prior to Langer's work, attempts to control the in situ structure of densely packed SAMs had been unsuccessful due to relatively strong van der Waals interactions between chains, especially when long chain alkanethiols were employed. In contrast, the flexibility of alkyl chains in loosely packed SAMs, arising from void space between the chains, led to reversible changes in interfacial properties in response to an electrical potential.

Although loosely packed SAMs are beginning to find intrinsic technological applications, the quantitative control of packing density remains a challenge to this field of research. Excluding our approach involving chelating adsorbates (vide infra), at least four methodologies have been employed to prepare loosely packed SAMs. Low packing densities of alkyl chains have been achieved via the coadsorption of two or more adsorbates having different chain lengths. This method provides a useful tool to

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* To whom correspondence should be addressed. E-mail: trlee@uh.edu

† Current address: Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101.

control the surface composition by adjusting the ratio of mixed adsorbates. The coadsorption, however, can lead to phase segregation (‘islanding’) if the adsorbates are quite different in their chemical functionalities and/or structures.\textsuperscript{14,16} In the case of mixed normal alkanethiol SAMs, phase segregation at room temperature has been observed when the chain length difference is larger than four carbon atoms.\textsuperscript{10} In addition, the composition and thus the packing density of adsorbates having long alkyl chains cannot be easily predicted from the composition of mixed alkanethiol solutions; for example, depending on the experimental conditions, the preferential adsorption of one adsorbate is typically observed.\textsuperscript{14}

An alternative strategy for preparing loosely packed SAMs is based on the use of unsymmetrical disulfides.\textsuperscript{17–19} A critical drawback of this method is that the surface composition and/or packing density cannot be controlled systematically. Furthermore, this strategy can potentially lead to phase segregation and/or preferential loss of one of the components because dialkyl disulfides are known to dissociate upon adsorption.\textsuperscript{20} Although unsymmetrical sulfides can be used to avoid the problems related to dissociation, one study has reported that SAMs generated from sulfides are markedly less stable than those generated from alkanethiols.\textsuperscript{21}

An intriguing approach for preparing loosely packed SAMs was recently reported.\textsuperscript{11} The self-assembly of a 16-mercaptohexadecanoic acid (MHA) derivative possessing a bulky endgroup (2-chlorophenylphenylmethyl group) followed by cleavage of the endgroup was used to generate a low density MHA SAM. Although this method appears to offer control over the packing density of the resulting SAMs by varying the steric bulk of endgroups of the adsorbates, the authors have yet to demonstrate this capability. Moreover, current adsorbates are restricted to alkanethiols possessing acid-labile endgroups, leading exclusively to hydrophilic surfaces exposing carboxylate moieties. This limitation might prevent the general use of this strategy in the preparation of loosely packed SAMs. The low packing density near sulfur headgroups also might lead to unstable monolayers due to diminished chain–chain interactions.

A fourth strategy for preparing loosely packed SAMs employs a relatively short equilibration time of substrates in adsorbate solutions. The immersion of silicon wafers into a hexadecyltrichlorosilane solution for 30 s was used to generate relatively loosely packed SAMs, while immersion for 5 h led to densely packed monolayers.\textsuperscript{22} Given, however, that the generally accepted two-step adsorption mechanism involves the formation of islands at the initial stage of SAM formation (the fast regime),\textsuperscript{23} this strategy probably affords inhomogeneous surfaces in the loosely packed regime.

The development of a general method for preparing well-defined loosely packed SAMs is one of our major research objects. In previous work,\textsuperscript{24} our group has prepared loosely packed SAMs via the adsorption of the chelating 2-monoalkyloxypropane-1,3-dithiols (CnC2, Figure 1). The resulting liquidlike organic films exhibited substantially enhanced wettabilities and frictional properties when compared to densely packed analogues prepared from normal alkanethiols (Cn).\textsuperscript{25–27} Furthermore, the chelating alkanedithiols provided enhanced stabilities to the resulting SAMs due to the chelate effect and the energetically disfavored formation of cyclic disulfide and/or multimeolecular desorption products.\textsuperscript{26} We also have demonstrated that unsymmetrical chelating alkanedithiols can be used to prepare homogeneously mixed SAMs at the molecular level.\textsuperscript{27} In further efforts to control the packing density, we prepared a series of 2-alkyl-2-methylpropane-1,3-dithiols (CnC3) that possess all methyl groups near the quaternary carbon center.\textsuperscript{28} Due to the steric bulk of the methyl group, the SAMs derived from CnC3 exhibited even lower packing densities than those derived from CnC2.

In this report, we describe a new series of loosely packed SAMs generated from the tridentate chelating alkanethiols, 1,1,1-tris(mercaptomethyl)alkanes (t-Cn, Figures 1 and 2). We anticipated that the SAMs derived from t-Cn would exhibit a lower packing density of alkyl chains than those derived from the bidentate analogues due to the low alkyl-to-sulfur ratio of t-Cn (1:3) relative to those of CnC2 and CnC3 (1:2). We also anticipated that the t-Cn adsorbates would generate thermodynamically more stable SAMs than the bidentate chelating alkanethiols because of an enhanced chelate effect. Furthermore, we
expected that the t-C\textit{n} adsorbates would provide homogeneously distributed alkyl chains across the surface as reported for the dithiol systems. Consequently, the tridentate chelating alkanethiols (t-C\textit{n}) can be used in conjunction with the CnC2 and CnC3 adsorbates to control the packing density of alkyl chains on surfaces in a systematic fashion.

This paper describes the synthesis of 1,1,1-tris(mercaptomethyl)alkanes (t-C\textit{n}) and their use in the preparation of loosely packed SAMs on gold. The SAMs were characterized by ellipsometry, contact angle goniometry, polarization modulation infrared reflection–absorption spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS). The data were compared with those obtained from SAMs generated via the adsorption of normal alkanethiols (C\textit{n}), 2-monoalkylpyrrole-1,3-dithiols (CnC2), and 2-alkyl-2-methylpyrrole-1,3-dithiols (CnC3) to demonstrate their relative packing densities and interfacial structure and properties.

**Experimental Section**

**Materials and Methods.** Gold shot (99.99%) was obtained from Americana Precious Metals, and test-grade polished single-crystal silicon(111) wafers were purchased from NESTEC. Aqueous formaldehyde (36.5–38.0%), potassium hydroxide (KOH), triethylamine (Et3N), sodium bicarbonate (NaHCO3), methylene chloride (CH2Cl2), hexanes, anhydrous diethyl ether, and tetrahydrofuran (THF) were purchased from EM Sciences; THF was distilled over calcium hydride and then dried over and stored under argon. Lithium aluminum hydride (LAH) and magnesium sulfate (MgSO4) were obtained from Alfa Aesar and Fisher Scientific Co., respectively. Pyridinium chlorochromate was prepared using a route reported by Corey and Suguirs. Methanesulfonyl chloride and potassium thioacetate (KSAc) were purchased from Acros, and absolute ethanol was purchased from Aaper Alcohol and Chemical Co. and used as received. Column chromatography was performed using Natkal International silica gel, 60–200 mesh. Thin-layer chromatography (TLC) was performed using 200-μm-thick silica gel plates purchased from Sorbent Technologies. An iodine chamber was used to analyze the eluted TLC plates because most compounds were not visible under UV light (254 nm). 1H and 13C nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 spectrometer operating at 300 and 75 MHz for 1H and 13C nuclei, respectively. The spectra were obtained in choloroform-\textit{d}, purchased from Cambridge Isotope Laboratories, and chemical shifts were referenced relative to the residual proton or carbon signal of the deuterated solvent (δ 7.26 for 1H and δ 77.00 for 13C spectra).

**Synthesis of Chelating Alkanethiol Adsorbates.** The 1,1,1-tris(mercaptomethyl)alkanes (t-C\textit{n}) were prepared using the strategy outlined in Scheme 1. The starting aldehyde 1 for the Tollens condensation was synthesized by oxidation of the corresponding alcohol by pyridinium chlorochromate. To prepare the key intermediate, 1,1,1-tris(hydroxymethyl)alkane 2, we employed a Tollens condensation, which proceeds via two steps: aldol condensation of formaldehyde with an aldehyde followed by a Canizzaro reduction. After purification of the crude 2 by triturating in diethyl ether, treatment of the resulting white powder with methanesulfonyl chloride and triethylamine readily afforded the 1,1,1-tris(methanesulfonyloxymethyl)alkane 3.

As an illustrative example, we provide below detailed procedures for the synthesis of 1,1,1-tris(mercaptomethyl)heptadecane (t-C18). We also provide complete analytical data for all other t-C\textit{n} adsorbates, including 1H and 13C NMR spectra (see Supporting Information). Please note that the products often contained trace amounts of the corresponding disulfides, and the reaction conditions were not optimized to improve the overall yield. Also, previous reports have described the synthesis and characterization of the 2-monoalkylpyrrole-1,3-dithiol (CnC2) and the 2-alkyl-2-methylpyrrole-1,3-dithiol (CnC3) adsorbates.

**Scheme 1**

![Scheme 1](attachment:image1.png)

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dried over MgSO₄, and filtered. After the solvent was removed by rotary evaporation, the crude product was placed in THF (20 mL), and LAH (1.50 g, 39.5 mmol) was added slowly at room temperature. The reaction mixture was refluxed for 4 h under an atmosphere of argon and then quenched by slow addition of ethanol (25 mL). The mixture was acidified by careful addition of 1 M HCl solution (150 mL) and then extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with dilute HCl solution (2 × 100 mL) and brine (1 × 100 mL). The organic phase was dried over MgSO₄ and filtered. After removal of the volatiles by rotary evaporation, the crude product was purified by column chromatography on silica gel (hexanes/diethyl ether, 1/0)

The instrumenta-adsorbates, an adsorption/equilibration time of 48 h was used to gold substrates were immersed in solutions containing the primary (longer) chain (see Figure 1).

Preparation and Characterization of SAMs. Detailed procedures for the preparation of gold-coated silicon wafers and SAM formation have been provided in previous reports. The gold substrates were immersed in solutions containing the specified adsorbates at 1 mM concentrations. For all chelating adsorbates, an adsorption/equilibration time of 48 h was used to generate SAMs having maximum coverages. The instrumenta-adsorbates, the potential for incomplete binding to the 3-fold hollow sites on Au(111) surfaces. Recent work by grazing incidence X-ray diffraction suggests, however, that the sulfur atoms in gold must be considered. As mentioned above, we anticipated that the trithiols (t-C₃) would form more loosely packed SAMs on gold than normal alkane-thiols (Cₙ) and dithiols (CₙC₂ and CₙC₃) due to their low alkyl-to-sulfur ratio (1:3). Furthermore, we anticipated that the enhanced chelating effect of t-Cₙ adsorbates would lead to more stable monolayers than the CₙC₂ and CₙC₃ SAMs as well as the Cₙ SAMs. To realize these expectations, it is essential that all three sulfur atoms of a t-Cₙ adsorbate bind to the surface of gold. We, therefore, sought to characterize the chemical state of the sulfur atoms in SAMs generated from t-Cₙ on gold before further experimentation.

Figure 3. XPS spectra of the S₂p region for SAMs derived from 1,1,1-tris(mercaptomethyl)tridecane (t-C₁₃) in the indicated solvents.

Results and Discussion

Throughout this article, we compare the SAMs generated from t-Cₙ to those generated from Cₙ, CₙC₂, and CₙC₃ that possess the same number of carbon atoms from the sulfur headgroup to the terminal methyl group in the primary (longer) chain (see Figure 1).

Effect of Solvent on the Formation of t-Cₙ SAMs. Early studies by electron diffraction and low energy helium diffraction showed that the sulfur–sulfur spacing on the surfaces of SAMs generated from normal alkane-thiols (Cₙ) is approximately 5 Å, with the sulfur atoms binding to the 3-fold hollow sites on Au(111) surfaces. Molecular modeling of the 1,1,1-tris(mercaptomethyl)pentadecane adsorbate (t-C₁₅) indicated, however, that the average distance between sulfur atoms in a single t-C₁₅ adsorbate is approximately 3.5 Å in a conformation in which the three sulfur atoms point in the same direction (e.g., toward a surface). Given the structural constraints of the t-Cₙ adsorbates, the potential for incomplete binding

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(35) Recent work by grazing incidence X-ray diffraction suggests, however, that the sulfur headgroups dimerize in the form of surface-bound disulfides: Fenter, P.; Eberhardt, A.; Eisenberger, P. Science 1994, 262, 1266.
(36) Molecular modeling was performed using AM1 semiempirical calculations with PC Spartan Plus, Wave function, Irvine, CA.
to its relatively low price, its availability in high purity, and its low toxicity. In addition, ethanol has a low tendency to be incorporated into SAMs.\textsuperscript{40} Based on these considerations and the fact that ethanol is known to form robust and fully bound $Cn$, $CnC2$, and $CnC3$ SAMs on gold,\textsuperscript{28} we chose to employ ethanol as the solvent in initial probes of the formation of $t$-$Cn$ SAMs. The gold substrates were immersed in 1 mM ethanolic solutions of $t$-$C16$ and allowed to equilibrate for 48 h. The slides were exhaustively rinsed with toluene and ethanol and then dried under a vigorous stream of ultrapure nitrogen before examination by XPS. Unfortunately, the XPS spectra of the resulting $t$-$C16$ SAMs reproducibly exhibited an $S_{2p}$ peak at 164 eV, indicating incomplete binding of the adsorbate on gold. Apparently for these structurally strained adsorbates, solvation of the thiols through hydrogen bonding with ethanol disrupts the complete binding of the sulfur atoms.

We then explored the use of a nonpolar aprotic solvent, isooctane, for the formation of $t$-$Cn$ SAMs. However, XPS spectra of SAMs prepared similarly in isooctane also exhibited an $S_{2p}$ peak at 164 eV, albeit with a markedly weaker intensity (see Figure 3). Although we cannot fully rationalize the incomplete binding of the adsorbates, we reasoned that polar solvents might be required for complete binding of all three thiolates of $t$-$Cn$ if the mechanism of adsorption involves at least partial charge separation.\textsuperscript{41} We therefore explored the use of polar aprotic solvents, such as dimethylformamide (DMF) and THF. Analysis by XPS of $t$-$Cn$ SAMs prepared in DMF still exhibited an $S_{2p}$ peak at 164 eV, but the relative intensity of the peak (164 eV peak/162 eV peak) was smaller than those observed for the SAMs prepared in ethanol and isooctane. In contrast, the use of THF led to little or no peak at 164 eV, indicating that all (or nearly all) of the sulfur atoms in the $t$-$Cn$ SAMs are bound when prepared in THF. Consequently, we used THF as the solvent to prepare all $t$-$Cn$ SAMs for further characterization and evaluation. For the reasons outlined above, ethanol was used for all other adsorbates.

**Ellipsometric Thickness.** Ellipsometry is normally employed as one of the principle tools for the characterization of SAMs. From the ellipsometric thickness, the quality of a well-known SAM, such as that generated from a normal alkanethiol, can be evaluated, and the degree of coverage for a unique SAM can be estimated. For all of the organic monolayers prepared in this study, we assumed a value of 1.45 for the refractive index. Given, however, that the refractive index values might be substantially influenced by the surface coverage and/or chain length, the measured ellipsometric thicknesses should be always supported by other analytical data before drawing conclusions. Nevertheless, ellipsometry provides a convenient and powerful tool for preliminary evaluation of the relative degree of coverage of SAMs.

It is known that the alkyl chains in SAMs generated from normal alkanethiols ($Cn$) are fully trans extended and tilted 30° from the surface normal, maintaining a stabilizing interchain van der Waals distance of 4.2 Å.\textsuperscript{1} We assume, however, that the alkyl chains in loosely packed SAMs are more tilted from the surface normal due to their diminished interchain van der Waals attraction and the void space between chains. As a result, loosely packed SAMs can be expected to exhibit lower ellipsometric thicknesses than their densely packed analogues. Further, due to their enhanced interchain spacing, the alkyl chains in loosely packed SAMs are expected to possess a substantial number of gauche defects. For loosely packed SAMs, therefore, we will use the “average” tilt angle to describe the chain tilt angle because a single tilt angle cannot represent the actual state of all of the alkyl chains (see Figure 2). Figure 4 shows the ellipsometric thicknesses of the SAMs generated from all of the adsorbates examined in this study. The thicknesses of the SAMs generated from $t$-$Cn$ are $\sim 8$, 3, and 1 Å lower than those of the corresponding SAMs generated from $Cn$, $CnC2$, and $CnC3$, respectively. As noted above, a lower ellipsometric thickness suggests a lower packing density of alkyl chains and thus a higher average tilt angle. From the measured ellipsometric thickness, the relative packing densities of the SAMs can be estimated as follows: $Cn > CnC2 > CnC3 > t$-$Cn$. The relative packing densities of the SAMs estimated from ellipsometric thicknesses are identical to those expected on the basis of the structures of the adsorbates. Given, however, the alkyl-to-sulfur ratio of the adsorbates (1:1 for $Cn$, 1:2 for $CnC2$ and $CnC3$, and 1:3 for $t$-$Cn$), the small difference in the ellipsometric thicknesses between the $CnC3$ and $t$-$Cn$ SAMs is somewhat surprising. One possible explanation for such a small difference is that the structurally more constrained sulfur moieties in $t$-$Cn$ might allow a more densely packed monolayer with regard to the sulfur headgroups. This assumption, however, requires a more quantitative analysis of the packing density of the SAMs because the refractive index for $t$-$Cn$ SAMs might be markedly different from those for $CnC2$ and $CnC3$ SAMs as well as that for $Cn$ SAMs.

The average tilt angle of the alkyl chains can be estimated from the slopes shown in Figure 4. The slope in a plot of ellipsometric thickness versus the number of carbon atoms corresponds to the film thickness per ethylene unit for each adsorbate. Bain and co-workers have reported a theoretical slope of 1.27 Å/CH$_2$ unit for $Cn$ SAMs using known bond angles and bond lengths and assuming fully trans extended monolayers tilted 30° from the surface normal.\textsuperscript{46,47} Given that all of the adsorbates used in this research are saturated hydrocarbons and thus should have the same bond angles and bond lengths, a lower slope should represent a highly tilted monolayer and/or increased gauche defects. In Figure 4, the slope for

\begin{figure}[h]
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\caption{Ellipsometric thicknesses of SAMs derived from $Cn$ (squares), $CnC2$ (circles), $CnC3$ (diamonds), and $t$-$Cn$ (pentagons).}
\end{figure}

\begin{table}[h]
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\begin{tabular}{|c|c|c|c|c|}
\hline
Adsorbate & $\langle$Tilt$\rangle$ (deg) & $\langle$Slope$\rangle$ (Å/CH$_2$) & $\langle$Density$\rangle$ (chains/Å$^2$) \\
\hline
$Cn$ & 110.5 & 1.27 & 1.81 \\
$CnC2$ & 110.5 & 1.27 & 1.81 \\
$CnC3$ & 110.5 & 1.27 & 1.81 \\
t-$Cn$ & 110.5 & 1.27 & 1.81 \\
\hline
\end{tabular}
\caption{Ellipsometric thicknesses of SAMs derived from $Cn$ (squares), $CnC2$ (circles), $CnC3$ (diamonds), and $t$-$Cn$ (pentagons).}
\end{table}

The following values were used to calculate the theoretical slope: $C-C = 1.545$ Å, $\angle$CCC = 110.5°, $C-S = 1.81$ Å, $C-H = 1.1$ Å, and contribution from S = 1.5 Å.
The distance between them is the smallest, 40 loosely packed the van der Waals forces between the contacting liquid might interact through van der Waals interactions between the surface and the contacting liquid, and thus enhances the wettability. 25, 28

It is known that interfacial methylene groups are more wettable than interfacial methyl groups. 14, 25, 40, 43

We have rationalized this phenomenon using an atomic contact model. 25, 28 Densely packed and well-ordered SAMs derived from Cn expose predominantly methyl groups at the surface, where the methyl—methyl spacing is ~5 Å. 25, 34

In contrast, loosely packed SAMs expose a substantial fraction of methylene groups at the surface, and thus the surface consists of both methyl and methylene groups. Given that the C—C bond length in saturated alkyl chains is 1.54 Å, which is significantly shorter than the methyl—methyl spacing in densely packed SAMs (~5 Å), loosely packed SAMs expose a greater number of atomic contacts per unit area than do densely packed analogues. The higher density of atomic contacts enhances the van der Waals interactions between the surface and the contacting liquid, and thus enhances the wettability. 25, 28

Examination of Figure 5a reveals lower contact angles of hexadecane on the t-Cn surfaces than on the CnC2 and CnC3 surfaces as well as the densely packed Cn surfaces. According to the atomic contact model described above, the SAMs derived from t-Cn apparently expose a higher fraction of methylene groups at the surface than those derived from CnC2 and CnC3 as well as Cn. From the observed wettabilities, therefore, the relative packing densities of the SAMs can be estimated in the following order: Cn >> CnC2 > CnC3 > t-Cn.

Another interesting observation from Figure 5a is that the liquid is held at a sufficiently large distance from the surface for all chain lengths examined; hence, the van der Waals interactions in the loosely packed SAMs (CnC2, CnC3, and t-Cn) are largely independent of chain length. In contrast, the contact angles of hexadecane on the loosely packed SAMs (CnC2, CnC3, and t-Cn) progressively increase as a function of chain length. This chain length dependence can be rationalized on the basis of the following two hypotheses. First, for loosely packed SAMs, the degree of conformational order might increase with increasing chain length, 35, 36 exposing a lesser fraction of methylene groups at the surface. Therefore, loosely packed SAMs having shorter alkyl chains exhibit enhanced wettabilities compared to those having longer alkyl chains. Second, the contacting liquid might interact through van der Waals forces with the underlying gold substrate due to the low film thicknesses of the loosely packed SAMs. 40 Because the van der Waals forces between the contacting liquid and the underlying gold substrate are greatest when the distance between them is the smallest, 40 loosely packed SAMs having shorter alkyl chains would be expected to be more wettable than those having longer alkyl chains.

Figure 5. Advancing contact angles of (a) hexadecane, (b) decalin, and (c) water on SAMs derived from Cn (squares), CnC2 (circles), CnC3 (diamonds), and t-Cn (pentagons). The SAM derived from t-C12 was completely wet by hexadecane (θa < 10°).

Of these two hypotheses, the former is unsupported by the ellipsometric thickness measurements (and the IR data presented in a subsequent section). Specifically, the ellipsometric thicknesses for the loosely packed SAMs (CnC2, CnC3, t-Cn) increase linearly as a function of chain length. This linear dependence suggests that the degree of conformational order of the loosely packed SAMs (CnC2, CnC3, t-Cn) is roughly the same for all chain lengths examined in this research. The relatively invariant wettability of the Cn series probably arises from the fact that the liquid is held at a sufficiently large distance from the surface for all chain lengths examined; hence, the van der Waals forces are small and largely inconsequential. 40

Given these considerations, we propose that the chain

Cn is 1.3 Å/CH3, which is in good agreement with the theoretical slope as well as that reported previously by our group. 25 In contrast, the slopes for CnC2, CnC3, and t-Cn are 1.1, 0.81, and 0.81 Å/CH2, respectively. The data suggest that the average tilt angle of alkyl chains in the t-Cn SAMs is substantially higher than that of the Cn SAMs as well as those of the CnC2 SAMs. The slope, however, for the t-Cn is identical to that for the CnC3 SAMs, suggesting similar average chain tilts for these two adsorbates.

Wettability. As an apolar aprotic contacting liquid, hexadecane has been widely employed to characterize hydrocarbon surfaces. 15, 25 In particular, our group has demonstrated that hexadecane is a powerful tool for exploring the nanoscale conformation of loosely packed SAMs. 25, 26, 28 It is known that interfacial methylene groups are more wettable than interfacial methyl groups. 14, 25, 40, 43

We have rationalized this phenomenon using an atomic contact model. 25, 28 Densely packed and well-ordered SAMs derived from Cn expose predominantly methyl groups at the surface, where the methyl—methyl spacing is ~5 Å. 25, 34

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Another interesting observation from Figure 5a is the dependence of the wettability on the chain length of the adsorbates in the loosely packed SAMs. For example, the contact angles of the densely packed SAMs derived from Cn are largely independent of chain length. In contrast, the contact angles of hexadecane on the loosely packed SAMs (CnC2, CnC3, and t-Cn) progressively increase as a function of chain length. This chain length dependence can be rationalized on the basis of the following two hypotheses. First, for loosely packed SAMs, the degree of conformational order might increase with increasing chain length, 35, 36 exposing a lesser fraction of methylene groups at the surface. Therefore, loosely packed SAMs having shorter alkyl chains exhibit enhanced wettabilities compared to those having longer alkyl chains. Second, the contacting liquid might interact through van der Waals forces with the underlying gold substrate due to the low film thicknesses of the loosely packed SAMs. 40 Because the van der Waals forces between the contacting liquid and the underlying gold substrate are greatest when the distance between them is the smallest, 40 loosely packed SAMs having shorter alkyl chains would be expected to be more wettable than those having longer alkyl chains.
Table 1. Contact Angle Hysteresis (°) of Hexadecane, Decalin, and Water on SAMs Derived from the Indicated Adsorbatesa

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<th>hexadecane</th>
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<tr>
<td>Cn</td>
<td>6</td>
<td>6</td>
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<td>CnC2</td>
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<tr>
<td>t-Cn</td>
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a We report values from at least three independent experiments, and values were reproducible within ± 1° of those reported. Entries marked by (–) could not be measured because advancing and/or receding contact angles are less than 10°, which we define as fully wettable.

length dependence of the wettability of loosely packed SAMs arises from changes in the strength of the van der Waals interaction between the contacting liquid and the underlying gold substrate.

As shown in Figure 5a, the SAM derived from t-C12 was completely wettable by hexadecane (θw < 10°). In addition, Table 1 shows that the contact angle hysteresis values (Δθ = θa – θr) of hexadecane on the loosely packed bidentate SAMs (CnC2 and CnC3; ~10°) are measurably larger than those of the densely packed analogues (Cn; 6°). Furthermore, the contact angle hysteresis of hexadecane on the SAMs derived from t-Cn could not be determined because the receding angles on those SAMs were too low to be measured reliably.

It is known that the contact angle hysteresis is influenced by the heterogeneity of surfaces and by certain interactions between the surface and the liquid, such as the reorganization of surface molecules and the adsorption of contacting liquids.45 Given that one of the major merits of our system is the formation of homogeneously distributed components, the increased hysteresis of hexadecane on the loosely packed SAMs is surprising, given the large differences in the alkyl chain tilt angles of hexadecane and those of short-chain alkanes.48 Consequently, the normal alkanethiol SAMs on GaAs(100) exhibit a lower contact angle of hexadecane (41°) than the analogous SAMs on gold (~60°). The lower contact angle on GaAs can be rationalized on the basis of the partial wetting of underlying methylene units arising from the higher chain tilt. The comparison thus illustrates that the wettability and ellipsometric thickness cannot provide an unequivocal measure of the degree of conformational order in organic thin films.

PMIRRAS. The C–H stretching region of surface infrared spectra can be used to evaluate the orientation and conformational order of organic thin films.23,24,29,50 In particular, the frequency and bandwidth of the methylene antisymmetric and symmetric bands (νs(CH2) and νas(CH2)) are known to be strongly influenced by the conformational order of hydrocarbons, including organic monolayers.44,51–53 For example, crystalline polyethylene exhibits a νas(CH2) band at 2920 cm⁻¹ and a νs(CH2) band at 2850 cm⁻¹, while liquid polyethylene shows these bands at 2928 and 2856 cm⁻¹, respectively.51 The same trend has been reported for normal alkanethiols: the νas(CH2) and νs(CH2) peaks of crystalline n-docosanethiol appear at 2918 and 2851 cm⁻¹, while those of liquid state n-octanethiol appear at 2924 and 2855 cm⁻¹.44

Figure 6 and Table 2 show the positions of the νas(CH2) and νs(CH2) bands for the SAMs generated from Cn, CnC2, CnC3, and t-Cn. Assignment of the C–H stretching bands is based on literature precedents.28,29,50 The νas(CH2) and νs(CH2) bands for the Cn SAMs appear at 2919 and 2851 cm⁻¹, respectively, indicating the crystalline-like conformational order of the alkyl chains. The loosely packed SAMs (CnC2, CnC3, and t-Cn) exhibited only small differences in νas(CH2), and νs(CH2) band positions. The νas(CH2) bands for the CnC2, CnC3, and t-Cn SAMs appeared at 2924, 2925, and 2926 cm⁻¹, respectively. The observation of such small differences in the νas(CH2) band positions for the loosely packed SAMs is surprising, given the large differences in the contact angles of hexadecane shown in Figure 5a: Δ ~ 12° for the CnC2 and CnC3 SAMs and Δ ~ 6° for the CnC3 and t-Cn SAMs. As noted previously,26 the νas(CH2) band position is relatively insensitive to small differences in nonpolar species because the liquids are highly self-associated through hydrogen bonding.23,47 Nevertheless, water also exhibited a distinguishable decreasing trend in wettability with increasing chain length on the loosely packed SAMs (Figure 5c). As a whole, the observed wettabilities are in good agreement with the ellipsometric thicknesses, a fact which further confirms that the alkyl chain density and the conformational order of the SAMs decrease in the following order: Cn > CnC2 > CnC3 > t-Cn. We note, however, that loosely packed SAMs possessing well ordered and highly tilted alkyl chains can also exhibit significantly enhanced wettabilities and diminished ellipsometric thicknesses. For example, the alkyl chains in the SAMs derived from normal alkanethiols on GaAs(100) are highly ordered and tilted away from the surface normal by 57°, while the corresponding SAMs on gold possess a chain tilt angle of 30°.48

Figure 6. C–H stretching region of the PM-IRRAS spectra of SAMs derived from octadecanethiol (C18), 2-hexadecylpropane-1,3-dithiol (C18C2), 2-hexadecyl-2-methylpropane-1,3-dithiol (C18C3), and 1,1,1-tris[mercaptopropyl]heptadecane (t-C18).

Table 2. Band Positions of the Methylene Antisymmetric Stretch ($v_{as}^{CH2}$) and the Methylene Symmetric Stretch ($v_{s}^{CH2}$) for SAMs Generated from the Indicated Adsorbates

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>C12</th>
<th>C14</th>
<th>C16</th>
<th>C18</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Methylene Antisymmetric Stretch ($v_{as}^{CH2}$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cn</td>
<td>2921.0</td>
<td>2919.0</td>
<td>2919.0</td>
<td>2918.5</td>
</tr>
<tr>
<td>CnC2</td>
<td>2924.1</td>
<td>2924.0</td>
<td>2924.1</td>
<td>2924.2</td>
</tr>
<tr>
<td>CnC3</td>
<td>2925.2</td>
<td>2925.1</td>
<td>2925.2</td>
<td>2925.4</td>
</tr>
<tr>
<td>t-Cn</td>
<td>2925.8</td>
<td>2926.0</td>
<td>2925.9</td>
<td>2926.0</td>
</tr>
<tr>
<td><strong>Methylene Symmetric Stretch ($v_{s}^{CH2}$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cn</td>
<td>2851.2</td>
<td>2850.7</td>
<td>2850.8</td>
<td>2850.7</td>
</tr>
<tr>
<td>CnC2</td>
<td>2855.2</td>
<td>2854.2</td>
<td>2853.9</td>
<td>2854.0</td>
</tr>
<tr>
<td>CnC3</td>
<td>2855.3</td>
<td>2854.7</td>
<td>2854.7</td>
<td>2855.4</td>
</tr>
<tr>
<td>t-Cn</td>
<td>2855.8</td>
<td>2855.6</td>
<td>2855.2</td>
<td>2855.0</td>
</tr>
</tbody>
</table>

The $v_{as}^{CH2}$ and $v_{s}^{CH2}$ band positions were obtained from at least three independent experiments and were reproducible within ±1 cm$^{-1}$ of those reported.

In the degree of conformational order of liquidlike SAMs. Despite this limitation, the observed positions of the $v_{as}^{CH2}$ bands suggest that the conformational order of the SAMs decreases in the following order: Cn > CnC2 > CnC3 > t-Cn. This conclusion is consistent with the observed $v_{as}^{CH2}$ band positions, which appeared at 2854, 2855, and 2855 cm$^{-1}$ for the CnC2, CnC3, and t-Cn SAMs, respectively, indicating a liquidlike conformational order for all three types of SAMs.

It is difficult to evaluate the position of the methyl symmetric band ($v_{s}^{CH3}$) because the intensity of the peak decreases markedly with decreasing conformational order (Figure 6). Instead of the peak position, the relative intensity of the $v_{s}^{CH3}$ band can provide qualitative information regarding the degree of conformational order. According to the schematic model of the normal alkanethiol SAMs (Cn), the $v_{s}^{CH3}$ transition dipole is oriented nearly parallel to the surface normal (especially in the even-numbered SAMs), leading to a strong absorption for the mode. In loosely packed SAMs, however, the presence of gauche defects might be expected to randomize the orientation of methyl groups and thus diminish the intensity of the $v_{as}^{CH2}$ bands.52,53 Indeed, Figure 6 shows that the loosely packed SAMs (CnC2, CnC3, and t-Cn) exhibited substantially diminished $v_{as}^{CH2}$ peak intensities compared to the densely packed analogues (Cn).

The $v_{as}^{CH3}$ bands consist of in-plane and out-of-plane modes, and the relative intensities of these modes vary with the degree of conformational order.54 Furthermore, the $v_{as}^{CH2}$ peak position is known to be insensitive to the conformational order of the alkyl chains in SAMs.44 For example, normal alkanethiol SAMs (Cn, n = 3–21) exhibit $v_{as}^{CH3}$ in-plane modes at 2965–2966 cm$^{-1}$ regardless of the degree of conformational order.44 Likewise, for all of the SAMs examined in this research, the $v_{as}^{CH3}$ in-plane modes are observed at 2965–2966 cm$^{-1}$. The $v_{as}^{CH3}$ out-of-plane mode has been reported to appear at 2956 and 2957 cm$^{-1}$ for crystalline n-dodecanethiol and liquid n-octanethiol, respectively. As shown in Figure 6, however, it is impossible to track the precise position of the $v_{as}^{CH3}$ out-of-plane mode. Instead, we suggest that the relative intensity of the $v_{as}^{CH3}$ in-plane and out-of-plane modes (i.e., $v_{as}^{CH3}$ in-plane/$v_{as}^{CH3}$ out-of-plane) can provide qualitative insight regarding the conformational order of the SAMs. In most surface infrared spectra, the methyl antisymmetric out-of-plane modes are masked by the in-plane modes due to the orientation of the former mode with respect to the surface.44 In loosely packed SAMs, however, the random orientation of the methyl groups leads to a substantial number of the $v_{as}^{CH3}$ out-of-plane modes oriented along the surface normal. In Figure 6, the C18 SAM exhibits what appears to be a predominant $v_{as}^{CH3}$ in-plane mode at 2965 cm$^{-1}$, while the corresponding loosely packed SAMs (C18C2, C18C3, and t-C18) exhibit both in-plane and out-of-plane modes at 2966 and 2958 cm$^{-1}$, respectively.

As a whole, the PM-IRRAS spectra support the relative packing densities of the SAMs inferred from the ellipsometry and contact angle measurements. Furthermore, the PM-IRRAS data offer a direct evaluation of the conformational order of the SAMs. The peak position and bandwidth of C–H stretches are, however, relatively insensitive to small changes in conformational order for highly disordered, liquidlike SAMs.28

**Packing Density.** In XPS, the binding energy ($E_b$) of an electron in an atom is a function of the type of atom and its environment.37 Thus, bond formation between atoms can be evaluated by monitoring the binding energy shift because bonding can change the electron distribution of the atom of interest. Another factor that influences binding energy is the electrical conductivity of the sample.37 For normal alkanethiol SAMs (Cn), it has been reported that the binding energy of the C–H photoelectron shifts to a lower value when the alkyl chain length decreases.17,40 Assuming that the nature of gold–thiolate bonds is unaffected by changing the length of alkyl chains,

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Table 3. XPS Binding Energies (eV), Integrated Photoelectron Intensities (counts), Relative Chain Densities, and S2p/Au4f Peak Intensity Ratios of SAMs Derived from the Indicated Adsorbates*

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>C1s (eV)</th>
<th>S2p (eV)</th>
<th>Au4f (counts)</th>
<th>C1s (counts)</th>
<th>S2p (counts)</th>
<th>chain density from Au4f (%)</th>
<th>chain density from C1s (%)</th>
<th>S2p/Au4f</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16</td>
<td>285.0</td>
<td>162.0</td>
<td>93500</td>
<td>11035</td>
<td>597</td>
<td>100</td>
<td>100</td>
<td>0.0064</td>
</tr>
<tr>
<td>C16C2</td>
<td>284.8</td>
<td>162.0</td>
<td>110435</td>
<td>7783</td>
<td>814</td>
<td>66</td>
<td>66</td>
<td>0.0074</td>
</tr>
<tr>
<td>C16C3</td>
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<td>162.1</td>
<td>113920</td>
<td>7207</td>
<td>864</td>
<td>56</td>
<td>56</td>
<td>0.0076</td>
</tr>
<tr>
<td>t-C16</td>
<td>284.6</td>
<td>162.0</td>
<td>116571</td>
<td>6697</td>
<td>984</td>
<td>51</td>
<td>51</td>
<td>0.0084</td>
</tr>
<tr>
<td>C18</td>
<td>285.1</td>
<td>162.0</td>
<td>86359</td>
<td>11759</td>
<td>549</td>
<td>100</td>
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<td>801</td>
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<td>65</td>
<td>0.0077</td>
</tr>
<tr>
<td>C18C3</td>
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<td>848</td>
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</tr>
<tr>
<td>t-C18</td>
<td>284.7</td>
<td>162.0</td>
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<td>951</td>
<td>51</td>
<td>51</td>
<td>0.0085</td>
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</tbody>
</table>

*We report average values of three independent measurements. The binding energies were referenced to Au4f 7/2 at 84.0 eV. Although the absolute peak areas varied from sample to sample, the calculated chain densities from Au4f were always within ±2%, and those from C1s were within ±3% of those reported.

Analyzing the Au4f peak intensities, we inferred that the Au4f peak is attenuated by overlying adsorbates, and thus the intensity of the peak is reversely proportional to the amount and/or thickness of the adsorbed overlayer. Consequently, the packing densities of alkyl chains in loosely packed SAMs relative to that in densely packed Cn SAMs can be obtained by comparing their attenuated Au4f peak intensities, because the packing density and thickness of Cn SAMs are precisely known. Analysis of the composition of SAMs in a quantitative manner requires knowledge of the absolute value of the attenuation length (λ). First, we monitored the attenuation of the Au4f peak in a series of normal alkanethiol SAMs (C10, C12, C14, C16, and C18). The attenuated Au4f signal is described by eq 1:

\[
\ln \text{Au}_n = -n d / (\lambda \sin \theta) + \text{constant}
\]

where Au_n is the intensity of the Au4f signal attenuated by an n carbon monolayer, d is the thickness of the SAM per methylene unit, λ is the attenuation length, and θ is the takeoff angle. The contribution of sulfur to the attenuation of the gold signal must also be considered and was assumed to be equivalent to attenuation by 1.5 carbon atoms. A least-squares analysis of the attenuated gold signals obtained from the series of Cn SAMs yielded an attenuation length of 41 Å, which is in good agreement with previously reported values. Next, we measured the attenuated gold signals of the loosely packed SAMs and then derived an “effective” number of carbon atoms per adsorbate from the signals using the calibration curve constructed from the Cn SAMs. Finally, a direct comparison of the “effective” number of carbon atoms per adsorbate with the actual stoichiometric number of carbon atoms per adsorbate in the loosely packed SAMs gave the alkyl chain density of the SAMs relative to that of the densely packed Cn SAMs. As shown in Table 3, the CnC2, CnC3, and t-Cn SAMs were found to possess 65, 57, and 51%, respectively, of alkyl chain density relative to the corresponding Cn SAMs (normalized to 100% packing density).

The relative chain density can also be derived from the C1s peak intensities. In this approach, we constructed a calibration curve using the C1s peak intensities and the actual stoichiometric number of carbon atoms per adsorbate. In this case, sulfur cannot influence the C1s peak intensity because all of the carbon atoms lie above the sulfur atoms. This approach afforded the same trend obtained from the attenuated gold signals (Table 3). As

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a whole, quantitative analyses by XPS demonstrated that the packing densities decrease in the order Cn \(\gg\) CnC2 \(\gg\) CnC3 > t-Cn. The results provide strong evidence that the low film thicknesses, enhanced wettabilities, and decreased degree of conformational order of loosely packed SAMs arise from the loose packing of the alkyl chains. Furthermore, the results suggest that the alkyl chain density in hydrocarbon SAMs can be precisely varied between 50% and 65% by selecting an appropriate chelating adsorbate.

The XPS data in Table 3 can also be used to estimate the relative density of thiolutates on the surface, although the low signal-to-noise ratio of the S_{2p} region hinders precise integration of the peaks. According to the XPS spectra in Figure 3 and previous work, we infer that all of the thiolutates in the SAMs examined in this paper are completely bound (vide supra). Therefore, the surface density of the thiolutates can be estimated from the ratio of the sulfur-to-gold signal intensities (S_{2p}/Au{4f}). As shown in Table 3, the densities of thiolutates in loosely packed SAMs generated from the bidentate adsorbates (CnC2 and CnC3) are indistinguishable from each other and \(\sim 20\%\) greater than those in normal alkanethiol SAMs (Cn). In contrast, the surface densities of thiolutates in the SAMs derived from the tridentate adsorbates (t-Cn) are even higher (\(\sim 30\%\) greater than the Cn SAMs).

Despite these data, we are presently unable to provide accurate structural information for the SAMs on gold. Given, however, the increased sulfur densities in loosely packed SAMs, we can safely assume that the average sulfur-sulfur spacing is substantially longer than that of densely packed Cn SAMs (5 Å). Thus, some of the thiolute groups must occupy sites other than the 3-fold hollows on Au(111).

**Preliminary Evaluation of the Thermal Stability of SAMs Generated from t-Cn.** Recently, we reported an enhanced thermal stability for SAMs generated from the bidentate chelating adsorbates (CnC2) when compared to SAMs generated from normal alkanethiols (Cn). The enhanced stability of the CnC2 SAMs was rationalized on the basis of the chelate effect and the ring strain generated in the formation of intramolecular cyclic disulfide desorption products. Given this background, we anticipated that the tridentate chelating adsorbates (t-Cn) would form monolayers on gold that were even more stable than the analogous bidentate chelating adsorbates (CnC2 and CnC3). To test this hypothesis, we examined SAM desorption in decalin at elevated temperatures using a previously established protocol. Decalin was chosen due to its high boiling point (189–191 °C) and its ability to minimize possible intercalation into the decomposed SAMs. The preformed SAMs were immersed in decalin at temperatures ranging from 70 to 110 °C. Upon removal from the decalin solution at selected intervals of time, the SAMs were rinsed thoroughly with ethanol and blown dry with a stream of ultrapure nitrogen. The fraction of SAM remaining on the surface was then measured by ellipsometry. These preliminary trials showed the relative stabilities of the SAMs are as follows: t-Cn \(>\) CnC2 \(>\) CnC3 \(>\) Cn. For example, an experiment conducted at 110 °C showed that after 3 min, \(\sim 33\%\) of the SAM derived from t-C18 and \(\sim 20\%\) of the SAMs derived from C18C2 and C18C3 remained on the surface, while the SAM derived from C18 decomposed almost completely after only 1 min. These preliminary results suggest that SAMs derived from the tridentate adsorbates (t-Cn) are more thermally stable than those derived from the bidentate adsorbates (CnC2 and CnC3), which are themselves more stable than those derived from normal alkanethiols (Cn).

**Conclusions.** A series of new tridentate chelating adsorbates were synthesized and used to prepare loosely packed SAMs on gold. Characterization of the SAMs revealed that the tridentate t-Cn adsorbates generate uniform monolayer films having low densities of alkyl chains. The data were compared with those obtained on SAMs generated from bidentate chelating alkanedithiols and normal alkanethiols. The comparison showed that the t-Cn SAMs possess lower packing densities of alkyl chains than the Cn, CnC2, and CnC3 SAMs. Correspondingly, the SAMs derived from t-Cn are the least conformationally ordered and most tilted from the surface normal on average. The trends in packing density and conformational order of the SAMs were observed to decrease as follows: Cn \(>\) CnC2 \(>\) CnC3 \(>\) t-Cn. Furthermore, a preliminary evaluation of thermal stability revealed that the t-Cn SAMs are more stable than those derived from Cn, CnC2, and CnC3, apparently due to an enhanced chelate effect. As a whole, the results demonstrate that the packing density, conformational order, and thermal stability of SAMs on gold can be precisely controlled by tailoring the structures of chelating alkanethiol adsorbates.

**Acknowledgment.** The Robert A. Welch Foundation (Grant No. E-1320), the National Science Foundation (NIRT Award ECS-0404308), and the Texas Advanced Research Program (003652-0307-2001) provided generous support for this research.

**Supporting Information Available:** 1H and 13C NMR spectra of 1,1,1-tris(mercaptomethyl)alkanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(61) This method of estimation assumes that the attenuation length of S_{2p} photoelectrons is the same as that of Au{4f} photoelectrons in hydrocarbon SAMs. An alternative method in which the absolute S_{2p} photoelectron intensities are compared directly is less reliable because the S_{2p} intensities are attenuated by different overlayers for each of the different samples.