Phase Transitions in a Methyl-Terminated Monolayer Self-Assembled on Au{111}

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Molecular dynamics simulations have been performed to study the behavior of $CH_3(CH_2)_{12}S$ chain molecules self-assembled on a Au{111} surface. The temperature dependence of the packing of the chains to form the monolayer has been investigated. The self-assembled monolayer is found to undergo at least two phase transitions. The first transition is a change in tilt direction from nearest neighbor to next-nearest neighbor below room temperature. At temperatures higher than room temperature, there is a transition from the next-nearest neighbor tilt to an orientationally disordered state. The Au−S interface region exhibits characteristics similar to those of two-dimensional melting prior to completion of the second phase transition.

Introduction

Methyl-terminated thiols self-assembled on Au{111} are a prototypical model for studying self-assembled monolayers (SAMs), since they exhibit promise in a variety of technological applications, such as corrosion, wetting, optical devices, and biosensors,[1−4] and can be easily prepared. They form spontaneously within a few hours when a solution containing methyl-terminated thiol chains is chemisorbed onto Au{111}.[5] In order to acquire the ability to control and predict the behavior of these systems under a variety of conditions, it is essential to understand their structural and dynamical properties. In this study, we have investigated the structure of $CH_3(CH_2)_{12}S$ chains adsorbed on a Au{111} surface as a function of temperature. We use a molecular dynamics (MD) approach that incorporates several features of a real system and is not limited by many of the assumptions and simplifications made in previous MD simulations involving these systems.

Given the widespread interest in SAMs, it is not surprising that several different experimental techniques, including IR spectroscopy,[6] X-ray,[7] and He diffraction,[8] have been used to gain insight into the structural characteristics of SAMs. The commonly used techniques for structure determination, using either X-ray or electron diffraction, however, are too penetrative to isolate the structure of the top CH_3 surface from that of the CH_2 bulk. Therefore, Chidsey *et al.* used low-energy He atom diffraction to probe the structure of the monolayer surface.[8] They found that at low temperature (<100 K), diffraction peaks are obtained, indicating the presence of ordered domains on the surface. Above 100 K, however, the He diffraction peaks disappear, indicating the disappearance of these ordered surface domains. The authors predict that this is due to thermal motion at the surface of the monolayer. This finding is consistent with experiments by Nuzzo *et al.*, who used IR spectroscopy[6] to confirm that the chains actually undergo a bulk phase transformation below 300 K from one ordered phase to another ordered phase, with the transformation temperature being chain-length dependent. In addition, they found that at 300 K there was a concentration of gauche conformations at the surface of the SAMs, even though the bulk of the SAMs remained crystalline.

The fact that the SAMs are crystalline even at 300K implies that at higher temperatures another phase transformation involving the disordering (or melting) of the entire chain could take place. This second phase transformation has been documented in several recent studies. For example, Fenter and Eisenberger[7] performed a grazing-incidence X-ray diffraction study on SAMs by varying n, the number of carbon atoms within each chain, and *T*, the temperature. They characterized different phases on the basis of the tilt direction and two-dimensional periodicity and constructed a global (*n*, *T*) phase diagram. They found phase transitions as a function of both chain length and temperature. In particular, they found that for longer chain lengths the SAMs adopted a configuration closer to the next-nearest neighbor (NNN) than the nearest neighbor (NN) configuration, while the shorter chains did not. Also, the chains underwent a melting transition as the temperature was increased above 343 K, with both the solid and liquid phases coexisting at intermediate temperatures of 323−343 K. Such order−disorder transformations have also been found by Badia *et al.*,[9] who used an electrochemical technique to study phase transitions in SAMs in solution. They, too, found a chain-length dependence of the melting temperature, the values of which ranged between 313 and 338 K. The existence of this transformation was further confirmed by Bensebaa *et al.*,[10] who used a reflection−absorbance IR spectroscopic technique at grazing incidence to study the thermal stability of SAMs. They found that the chains gradually untilt up to about 350 K, followed by an irreversible transition to a liquid-like phase characterized by a large number of gauche defects.

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These experimental studies give evidence that SAMs undergo two phase transformations, one at low temperatures between two ordered phases and one at higher temperatures between an ordered and a disordered phase. To detect this second phase transformation using molecular dynamics simulations, it is felt not only that the model system should specifically include the substrate Au atoms but also that the interface atoms should be allowed to move as the temperature is increased. Hautman and Klein[11] have also performed MD simulations to study the properties of alkanethiols on Au{111} and have shown that the tilt angle of the chains with respect to the surface normal gradually decreases with increasing temperature. Their system, however, consisted of a flat, rigid substrate with the sulfur atoms effectively constrained in the $(\sqrt{3}\times\sqrt{3})$R30° positions. This approach constrains some degrees of freedom that may be important for the structural changes required to attain the most stable configuration. For example, the packing of chains within a monolayer can change as the headgroups are allowed to move over the surface, because that allows the chains to change their relative orientations—an effect that might be otherwise unachievable when using rigid headgroups. Also, the presence of a moving interface makes it possible to study the packing characteristics of the monolayers not only with respect to the chains but also with respect to the interface. Allowing both the headgroups and the interface to move makes this study on temperature-related structural changes uniquely different from those attempted before using MD simulations and provides greater insight into the possible activity at the interface. Both the transitions that have been reported by experimental studies have been reproduced and are described below, after a brief description of the simulation method.

Simulation Model

The molecular dynamics (MD) method consists of following the motion of all the individual atoms constituting a system by integrating Newton's equations of motion. This method allows one to follow the temporal evolution of the system being studied and is thus ideal for obtaining a microscopic picture of the phenomena involved. The system studied comprises a self-assembled monolayer formed from 90 $CH_3(CH_2)_{12}S$ chain molecules adsorbed onto a Au{111} substrate in a $(\sqrt{3}\times\sqrt{3})$R30° overlayer. The Au substrate slab is eight-layers thick, consisting of 270 atoms each. The top three Au layers are allowed to move according to Newton's equations of motion. The bottom-most layer of the slab is kept rigid to hold the crystal in place. The remaining four intermediate layers are treated as a heat-bath using the generalized Langevin equations (GLE)[12] so the whole system could be maintained at a desired temperature. The GLE method allows one to control the temperatures using the metal atoms several angstroms away from the molecules of interest, thus not directly altering the trajectories of the organic film as happens with the velocity-rescaling approach. The CH_x units comprising the chains are treated within the united-atom limit, and the potentials used to describe the inter- and intrachain forces are given by Hautman and Klein,[13] where we used the smallest of the S−S interactions in Table 2 of this reference. The bonds connecting the CH_x units are kept at a fixed length using the RATTLE algorithm.[14] We developed the potentials used to describe the interface and the substrate−chain interactions. For the Au−S interactions, we use a Morse potential fit to parameters obtained from quantum mechanical calculations by Sellers,[15] and for the Au−CH_x interactions, we use a 12−6 Lennard-Jones potential. The Au atoms are described by the many-body MD/MC corrected effective medium potentials developed by De Pristo *et al.*[16−18] The details of all the potentials used and their specific values can be found in ref 19.

There are numerous other molecular dynamics or Monte Carlo calculations similar to those performed by Klein and presented here.[20−27] The main difference in these calculations is the use of explicit Au atoms.

The simulations are initiated by placing the monolayer chains in an all-trans configuration at the $(\sqrt{3}\times\sqrt{3})$R30° sites on the Au{111} surface. The system is then allowed to equilibrate for 100 ps (time step = 3 fs) after it has attained the required temperature. Averages of the various structural features of interest, such as the angle of chain tilt with respect to the surface normal, the direction of the tilts both with respect to the surface and with respect to the neighboring chains, and the distribution of gauche defects within the monolayer, are collected over the next 75 ps, and movies are made to understand the temporal evolution of the system. These averages and time-elapse movies are examined for information on changes in the structure and dynamical behavior of the monolayers.

Results and Discussion

We discuss two phase transitions, a low-temperature nearest neighbor (NN) → next-nearest neighbor (NNN) transition and a high-temperature melting transition in a self-assembled monolayer formed from $CH_3(CH_2)_{12}S$ chains assembled on a Au{111} surface. To demonstrate the occurrence of these phase transitions, we use the azimuthal tilt direction as the property that most clearly exhibits the changes. We define the relative azimuthal angle as the angle that the projection of the axis of a given chain makes with the nearest neighbor direction. Hence, peaks centered at 0° and 60° signify a nearest neighbor tilt and those centered at 30° point to the fact that the chains prefer a next-nearest neighbor tilt. Figure 1 gives the relative azimuthal angle distribution of all such nearest-neighboring pairs, averaged over all the 90 chains comprising the monolayer and over the entire 75 ps duration of the run, as a function of temperature. The peak widths and the background are deceptively large, and this problem is inherent in this method of calculation. The absolute azimuthal distributions are much sharper with much smaller backgrounds. To test the robustness of our observations, we have performed temperature scans for chains with different lengths. We find the two transitions described below in all the chain lengths examined, although the specific transition temperatures depend on the chain length.

NN → NNN Transition. The chains prefer to tilt toward their nearest-neighboring chains at low temperatures, as shown in Figure 1. At 40 K there is no intensity at 30°, which would indicate that none of the chains tilt toward their next-nearest neighbors. As the temperature is increased above 40 K, the NN peaks become wider and flatter. Upon heating to 275 K, the relative azimuthal distribution shows that the NNN orientation clearly dominates. This change from NN to NNN orientations has been experimentally observed in tilted hexatic phases.

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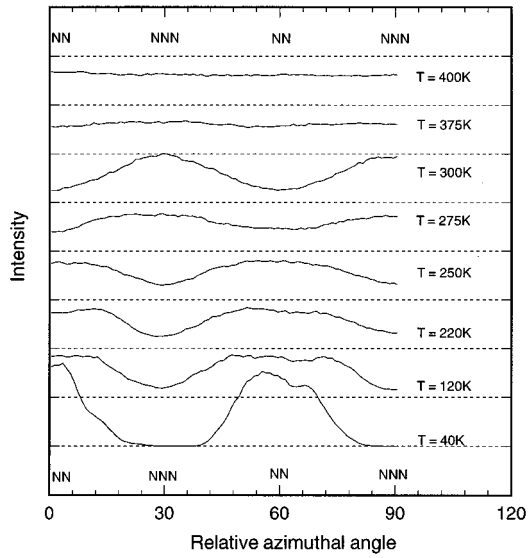

Figure 1. Distribution of the relative azimuthal angle between the chains and their nearest-neighboring chains as a function of temperature. Peaks at 0° and 60° correspond to a nearest neighbor tilt, and the peaks at 30° correspond to a next-nearest neighbor tilt. The baselines for each curve are shifted and are shown as dashed lines.

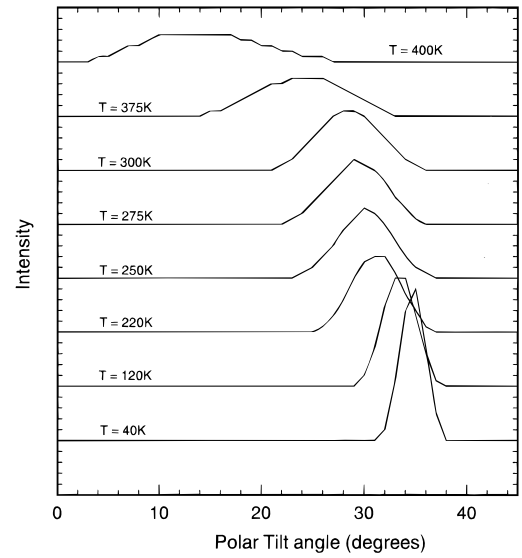

Figure 2. Distribution of polar tilt angles between the chain axis and the surface normal with respect to temperature.

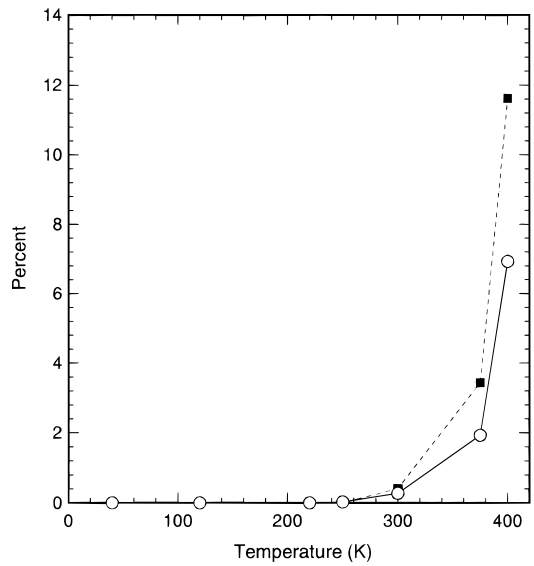

Figure 3. Percent gauche fraction and defects as a function of temperature. The dashed line is the percent gauche content. The solid line is the percent defects, where defects are nonsixfold coordinated S atoms. The points are averages over several steps.

Langmuir films[28] self-assembled on water show that the films have the same two phases with an intermediate coexistence region and that the actual temperatures at which they coexist depend on the density of the film. This is not surprising, since the Langmuir monolayers are similar to SAMs except for the structural details at the interface region. Moreover, the density of thiolate chains assembled on Au{111} is well within the range where the Langmuir films exhibit this phase transition. Because of the differences in the interfacial details, however, we cannot expect that, at any given packing density, the two systems would have the same transition temperatures, since the interaction of the films with the interface changes the energetics of the systems.

Our low-temperature results are in agreement with the simulations using a rigid substrate performed by Hautman and Klein,[11] who found that below a critical temperature the chains prefer to tilt in the NN direction and above that temperature they show no clear preference in tilt direction by continually fluctuating between the NN and the NNN directions. They called this new phase an unlocked rotator. Our simulations indicate, however, that the system makes a transition from a NN tilted phase at lower temperatures to a NNN tilted phase at higher temperatures. This transition temperature was found to increase with an increase in chain length, which is also consistent with previous studies conducted using IR spectroscopy.[6]

We find that the NNN configuration allows more freedom of motion for the methyl and the methylene groups comprising the SAMs. This is best exemplified by examining the polar angle tilt distribution in Figure 2 in conjunction with the relative azimuthal angle distribution in Figure 1. At 40 K, both distributions are relatively narrow, indicating that the motion of the chains covers a limited phase space. As the chains move toward the NNN direction, the peak of the polar angle distribution moves toward the surface normal and broadens. Similar broadening behavior can be observed in the relative azimuthal peaks representing the NNN orientation in Figure 1. Although the NN configuration is the lower-energy (enthalpy) configuration, the entropic contribution becomes significant at higher temperatures favoring a NNN tilt.

Concomitant with the broadening of the peaks in both tilt directions is the appearance of gauche defects in the chains. As shown in Figure 3 below 275 K, where all orientations are NN, the chains have no gauche defects. Even at 300 K when the monolayer is oriented in the NNN direction, the total gauche content is below 0.5%. All these gauche defects appear at the surface of the monolayer, which is consistent with predictions made in order to explain the loss of intensity in the He diffraction peaks above 100 K.[8] As the temperature increases to 375 K, the gauche content rises to 3.4%, and by 400 K it is 11.6%. This change indicates the next phase transition.

Melting Transition. As the temperature of the chains is raised above room temperature to about 400 K, the monolayer shows loss of orientational order, as signified by the following changes. The relative azimuthal angle distribution flattens out (Figure 1), indicating no prefer-

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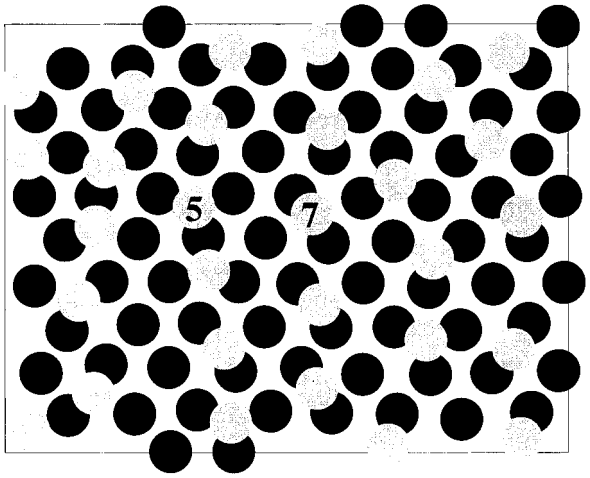

Figure 4. Snapshot of the Au−S interface illustrating a 5−7 pair formed from two neighboring atoms that have deviated from the hexagonal symmetry. The dark circles are the first-layer gold atoms, and the light circles represent the sulfur headgroups.

ence for any given tilt direction. We also observe a sudden increase in the gauche content distribution (Figure 3) with a total gauche content suddenly rising to ∼11.6%, consistent with experimental observations.[10] In contrast to the NNN regime, the gauche defects are not limited to the surface of the monolayer and appear all along the chains. The gauche defects toward the ends of the chains show a tendency to exist independently, whereas the defects in the interior of the chains favor kink, gauche plus kink, or double-kink formations. The distribution of the polar tilt angle with respect to the surface normal broadens to an ill-defined peak at 400 K, and the chains tend to untilt to much lower polar angles, as can be seen in Figure 2. All these changes signify that the monolayer has melted and has undergone an order−disorder transition. In order to test whether the transformation is reversible or not, the system was cooled through the transformation temperature. It was found that some of the gauche defects remained trapped in the system, yielding a higher-energy configuration. It is not possible, however, to run the MD simulations sufficiently long to see if eventually all the gauche defects would anneal out. These results are consistent with all the experimental work quoted earlier which shows that the introduction of these defects on heating is irreversible.

The mechanism by which the melting transformation takes place was studied in detail by examining the changes in the structure of the interface. Figure 4 shows a snapshot of the SAM/substrate interface at 350 K before it has undergone melting, showing that some of the S atoms have started deviating from the hexagonal symmetry. In particular, the number of nearest neighbor atoms of some of the sulfur atoms increases to seven at the cost of other sulfur atoms whose neighbors are reduced to five. These are the so-called 5−7 dislocation pairs commonly observed in two-dimensional melting transformations.[29] Such pairs could also be observed at 300 K, indicating that their formation occurs well before the monolayer has actually melted. As the temperature approaches the melting temperature, the concentration of these pairs increases and four-coordinate and eight-coordinate atoms along with separate five-coordinate and seven-coordinate atoms begin to appear. The concentration of these nonsixfold coordinated atoms keeps increasing with temperature until the melting transformation is complete, as shown in Figure 3. This mechanism is typical of two-dimensional melting of hexagonal lattices. As the sudden changes in the gauche content and the polar tilt angles take place much closer to the melting temperature, it is possible that these two signatures of melting might actually be a consequence of the formation of these nonsixfold coordinated atoms including the 5−7 dislocation pairs at 300 K. Changes in coordination can create regions in the monolayer where the chains are too crowded and need more room to achieve the same freedom of movement. Untilting of the chains achieves exactly that, as it makes the monolayer less dense. The extra room for chain motion can also facilitate the formation of more gauche defects, and indeed it does. The gradual increase in the 5−7 dislocation pairs and the nonsixfold coordinated atoms is consistent with the suggestion made by Bensebaa *et al.*, that the SAMs undergo a gradual structural transformation with increasing disorder to a liquid-like state.

Hautman and Klein[11] also saw the untilting behavior, but they reported the changes to be gradual whereas we find that the flattening of the polar angle distribution is relatively quite sudden. This difference and the observation of the 5−7 dislocation pairs signifies the importance of the extra degrees of freedom at the interface in the simulation of these films. Also, the fact that Hautman and Klein observe a more gradual increase in the gauche content and untilting behavior, as we do, again points to the fact that the formation of these pairs could be instrumental in these abrupt changes in the behavior of SAMs.

There is always a question of the accuracy of the interaction potentials in the united atom approach. When Hautman and Klein used this method to approximate the units composing the chains, they showed that the chains strongly preferred to tilt toward their nearest-neighbors and that they transformed to an unlocked rotator phase above a critical temperature, where they exhibited no clear preference in the azimuthal tilt directions. In a later paper, Mar and Klein[30] chose to describe the CH_x units using an all-atom method that treated the hydrogen atoms explicitly, and the chains then showed a preference for the NNN direction. On the basis of this, they proposed that an all-atom description was necessary to obtain NNN structures. The simulations presented here exhibit NNN structures even with a united atom description. The NN → NNN transition temperatures, however, are much higher than the values reported in experimental observations for the low-temperature phase transition. Thus, we also believe that the potentials in the united atom method are not sufficiently repulsive but that the problems due to this are not as severe as suggested by Mar and Klein. We think that only the specific values of the phase transition temperatures but not the general features of the transformations are dependent on the united atom approximation. This method provides us with useful qualitative information, and there is basic agreement with several experimental studies conducted for such systems.

Conclusion

Molecular dynamics simulations have been performed on alkyl thiolate chains self-assembled on Au{111} in order to study the temperature dependence of the overlayer structure. Both the low-temperature order−order transformation and the high-temperature order−disorder transformation reported in recent experimental studies have been observed in the simulations. At low temperatures, the chains are found to tilt from a NN orientation

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to a NNN one. A mechanism is proposed for the higher-temperature melting transformation, involving the gradual increase of 5−7 dislocation pairs and of consequent nonsixfold coordinated atoms, analogous to those found in studies of two-dimensional melting, that induces the untilting and the introduction of the large number of gauche defects. The results show that the high-temperature characteristics of the structure can be better understood using a moving interface, as opposed to a rigid one. The existence of the NN → NNN transition implies that we can exercise better control over the structure of self-assembled monolayers. Substituting the methylene or the methyl groups with different functionalities (e.g. CF_2, CF_3) can change the transition temperature and provide the desired orientational behavior at a given temperature.

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