Molecular Dynamics Investigation into the Effect of Temperature on the Structure and Properties of Methyl Methacrylate Thin Films on a Au(111) Surface

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Received March 6, 2007. In Final Form: May 6, 2007

An atomistic modeling approach is performed to investigate the effect of temperature on the structural properties of the MMA (methyl methacrylate) thin film and a Au(111) surface. The density profile and orientation of the MMA molecule in the thin film have been analyzed. We found that there is a significant effect on the density profile and orientation of the MMA molecule in the region near the interface between the thin film and the Au substrate. As the temperature increases, the density clearly decreases in this region; in addition, the orientation of the MMA molecule also changes. Next, we calculated and examined the relationships between the stress, surface tension, and free energy and the density profile. Finally, we analyzed the influence of temperature on the interaction strength between the MMA molecules and between the MMA molecules and the Au(111) surface. We found that the influence of the interaction strength is more significant between MMA molecules than between MMA molecules and the Au(111) surface.

Introduction

The structure and dynamic behavior of polymer molecules in a thin film on a solid substrate have attracted considerable interest in recent years.1–4 This interest arises primarily because such molecules exhibit different material properties than those in the bulk and have the potential for application in such diverse fields as nanoimprinting,5 nanolithography,5,6 nanoelectronic devices, bulk and have the potential for application in such diverse fields as thermal conductivity,7 and dielectric relaxation.17 However, it is difficult to observe the structural arrangement of the polymer molecules at the interface between the thin film and the substrate at the atomic level using direct experimental methods. Accordingly, experimental approaches fail to provide an adequate understanding of the influence of the interface on the structural properties of the thin film. However, the interface effect becomes increasingly important when the thickness of the film is less than several nanometers because the thickness of the interface then accounts for a considerable portion of the total film thickness. Molecular dynamics (MD) simulations overcome the limitations of traditional empirical approaches and enable detailed observations of the interfacial behavior between a thin polymer film and a solid substrate on the atomic scale.21–24 Xia et al.23 conducted MD simulations on polymer thin films to investigate the effects of temperature on the structural properties of the thin film. However, the influence of the interaction strength is more significant between MMA molecules than between MMA molecules and the Au(111) surface.

Thin films, $T_g$ is relatively insensitive to the film thickness but is significantly influenced by the substrate material. For example, Van Melick et al.12 showed that the value of $T_g$ was reduced when the PMMA film was deposited on a Au(111) surface, but increased when the film was grown on a silicon substrate with a native oxide layer. In recent studies, various experimental approaches have been employed to observe the structure and dynamic properties of polymer thin films on solid surfaces, including thermal probe measurements,13,14 ellipsometry,10 positron annihilation lifetime spectroscopy,15 X-ray reflectivity,16 and dielectric relaxation.17–20 However, it is difficult to observe the structural arrangement of the polymer molecules at the interface between the thin film and the substrate at the atomic level using direct experimental methods. Accordingly, experimental approaches fail to provide an adequate understanding of the influence of the interface on the structural properties of the thin film. However, the interface effect becomes increasingly important when the thickness of the film is less than several nanometers because the thickness of the interface then accounts for a considerable portion of the total film thickness. Molecular dynamics (MD) simulations overcome the limitations of traditional empirical approaches and enable detailed observations of the interfacial behavior between a thin polymer film and a solid substrate on the atomic scale.21–24 Xia et al.23 conducted MD simulations on polymer thin films to investigate the effects of temperature on the structural properties of the thin film. However, the influence of the interaction strength is more significant between MMA molecules than between MMA molecules and the Au(111) surface.

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Simulations to investigate the variation in the density profile of \( \alpha \)-hexadecane films with different thicknesses on Au(111) surfaces. The results showed that the density profile had oscillatory behavior in the region of the thin film near the interface but gradually became smooth at a greater distance from the substrate. Daoulas\(^{22}\) explored the volumetric, structural, and conformational aspects of PE melt/graphite and PE melt/vacuum interfaces, respectively. The corresponding density profiles indicate that the PE thin film had at least three adsorption layers near the substrate. The chain conformations were mainly flattened in the first adsorption layer, but the polymer molecules gradually tended toward their bulk characteristics at greater distances from the solid surface. Additionally, sudden changes in the dihedral angle distribution of molecules were observed between one absorption layer and the next. The topic of liquids adsorbed on solid surfaces has been widely researched using simulation approaches.\(^{25} - ^{31}\) For example, Xin et al.\(^{27}\) studied the spreading of polymer droplets of functional and non-functional PFPE (perfluoropolyether) on solid surfaces using coarse-grained MD simulations. The results reveal that the non-functional PFPE films form caplike structures on the substrate, and the functional PFPE film will give rise to a hat structure in the spreading process. Grest et al.\(^{28}\) conducted MD simulations to examine the spreading of liquid polymer droplets of varying chain lengths on chemically patterned surfaces. The numerical results showed that the spreading behavior was governed by the pattern width, the length of the polymer chain, and the interaction strength of the lyophilic strips.

From the discussions above, it is clear that MD simulation provides a powerful tool for investigating the interfacial behavior of polymer thin films on solid substrates at the atomic level. Accordingly, the present study adopts the MD simulation approach to investigate the molecular adsorption mechanisms of MMA (methyl methacrylate) thin films on a Au FCC (111) surface at different temperatures. The density and free-energy profiles are calculated to analyze the overall molecular arrangement of MMA thin films. Then, the normal stresses, tangential stresses, and surface tension in the MMA film and the interaction strength between the individual MMA molecules and between the MMA molecules and the Au(111) surface are systematically examined. The orientation factor is used to estimate the structural characteristics of MMA molecules in the thin film. Finally, we discuss and summarize the important findings.

### Simulation Model

In the present research, the ENCAD potential\(^{32}\) is employed to model the atomic interaction between the MMA molecules and the intra-interaction of an MMA molecule. In this model, the potential force field (FF) is expressed as the bond stretching, the bond angle, the torsional-angle energy, the van der Waals energy, and the Columbic energy, respectively. Accordingly, the total potential, \( U \), is given by

\[
U = \sum_{\text{bonds}} K_b (b_i - b_0)^2 + \sum_{\text{bond angles}} K_b (\theta_i - \theta_0)^2 + \sum_{\text{torsion angles}} K_t \{ 1 - \cos[n (q_i - q_0)] \} + U_{\text{nb}}
\]

where \( K_b \), \( K_b \), and \( K_t \) are force constants representing the bond stretching, bond bending, and rotational barrier of the \( i \)th bond, respectively, and \( b_i \), \( \theta_i \), \( q_i \), \( b_0 \), \( \theta_0 \), and \( q_0 \) are the \( i \)th bond length, the \( \theta \)th bending angle, the \( q \)th torsional angle, respectively.

\( U_{\text{nb}} \) is given by

\[
U_{\text{nb}} = \sum_{\text{pairs}} \left[ A_{\text{c}} e^{r_{ij} / r_{ij0}} - 2 e^{r_{ij} / r_{ij1}^6} - S_{\text{vdw}} (r_{ij}) \right]
\]

where \( A_{\text{c}} \) is the Coulomb potential parameter.

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where $\xi$ is an effective hopping integral, $r_0$ is the distance between atoms $i$ and $j$, and $r_{ij}$ is the first-neighbor distance. Parameters $A$, $p$, $q$, and $\xi$ are determined by incorporating the experimental data related to the cohesive energy, the lattice parameter, the bulk modulus, and the shear elastic constants $C_{44}$ and $C'_{12} = \frac{1}{2}C_{44} - C_{12}$, respectively. The values of the tight-binding potential model employed in the present simulations are taken from Cleri et al.35

The interaction between the Au substrate and the adsorbed MMA molecules is described using the Dreiding force field, which has the following exponential $-6$ form

$$E_g = D\left[\frac{6}{r_{ij} - 6} \exp\left(1 - \frac{r_{ij}}{\rho}\right) - \left(\frac{z}{r_{ij} - 6}\right)^6\right]$$

where $D$ is the energy barrier, $r$ is the distance between the gold atom and the atom in the MMA molecule in an energy-minimum state, $r_{ij}$ is the distance between the gold atom and the atom in the MMA molecule, and $z$ is a dimensionless constant whose value is dependent on the curvature or stiffness of the inner repulsive wall. The values of the $D$, $r$, and $z$ parameters are taken from Jang et al.36 as shown in Table 1. These parameters were fitted from the quantum mechanical geometry and binding energy.

The simulation system consists of an MMA thin film with 378 molecules deposited on a Au(111) substrate with a thickness of 20 Å and comprising 6 separate Au layers. The simulation box has dimensions of $L_x = 54.95$ Å and $L_y = 49.03$ Å, and periodic boundary conditions are imposed in both the $x$ and $y$ directions. A virtual repulsive wall is introduced at an initial height of 81 Å above the substrate. The objective of this wall is to confine the MMA molecules above the Au surface. Adopting a similar approach to that employed by Jang et al.,36 the following four-step procedure was performed to obtain the equilibrium structure of the MMA molecules on the Au(111) surface: (1) The MMA molecules were positioned on the Au(111) surface with an initial density of 0.35 g/cm$^3$ and were then gradually compressed to a density of 0.94 g/cm$^3$ (consistent with the experimental value) by moving the repulsive wall toward the substrate. (2) The system was annealed from 500 K to room temperature at a cooling rate of 3 K/ps. The system was annealed at this target temperature for 40 ps. In the simulations, the velocities of the atoms were randomly assigned according to the Maxwell distribution, and the velocity-rescaling thermostat37,38 was employed to maintain a uniform temperature. The time integration of the Newtonian equations of motion was performed using the Verlet algorithm to obtain the new velocities and positions of each atom.37,38

Figure 1 presents a schematic illustration of the relaxed MMA film on the Au(111) substrate. As shown, the substrate was modeled as six separate layers, with five layers providing a thermal control function and the lower layer used to fix the simulation system. The objective of the current MD simulations was to investigate the structural properties, stress, and energy distribution of the MMA thin film at various temperatures in the range of 200 to 300 K. In the investigations, data collection and analysis were performed on the final 100 ps.

### Results and Discussions

Figure 2 shows the distributions of the density and the free energy or, equivalently, the potential of mean force (PMF) of the MMA molecules along the $z$ direction of the thin film at temperatures of 200, 245, and 300 K. The density distribution is computed by counting the number of molecules in a slab of thickness 0.6 Å positioned parallel to the Au(111) surface at various heights above the substrate. Meanwhile, the value of the local free energy is derived as

$$G(z) = -k_B T \ln \left( \frac{\sigma(z)}{\sigma_{\text{bulk}}} \right)$$

where $k_B$, $T$, $\sigma(z)$, and $\sigma_{\text{bulk}}$ are the Boltzmann constant, the system temperature, the local density at height $z$, and the bulk number density, respectively. The density distributions at 200, 245, and 300 K are shown in the upper panel of Figure 2. It can be observed that the density profile at each temperature has a prominent peak at the interface of the MMA layer and the Au(111) surface. However, the density decreases significantly within a short distance of the interface before increasing once again. Thereafter, the density fluctuates about an approximately constant

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The density distribution in the perpendicular direction can be divided into four different regions, namely, the contact region (I), the transition region (II), the bulk region (III), and the surface region (IV). In the contact region, the value of PMF is negative, which results in a higher density and also indicates that the Au(111) surface and the MMA molecules have an attractive interaction. In the bulk region, the PMF profiles have an average value of zero and fluctuate only mildly. The density in the corresponding region of the film also has an approximately constant value. The bulk region and the contact region are separated by a transition region, within which the high density of the contact region decreases to the low density of the bulk region. The interaction between the substrate and the MMA molecules has a significant effect on the structure of the MMA thin film only in the contact region. Consequently, the compact packing of the MMA molecules in the contact region that is due to the interaction of the Au(111) surface prevents other MMA molecules with a density as high as that in the bulk region from existing stably in the transition region. Therefore, the density in the transition region is lower than that in the bulk region, and the PMF profiles have positive values. The density in the transition region is lower than that in the bulk region, and the PMF profiles have positive values.

**Figure 2.** Variation of density and free energy across an MMA thin film at different temperatures. Vertical dashed lines indicate boundaries between four distinct regions of a thin film: contact (I), transition (II), bulk (III), and surface (IV). The horizontal dashed line indicates the experimental value of bulk MMA density at 300 K.

**Figure 3.** Variation of average mass density of MMA molecules with temperature in contact, transition, and bulk regions. The horizontal dashed line indicates the experimental value of bulk MMA density at 300 K.

**Figure 4a,b** present the variation of the normal stress and the tangential stress in the z direction, respectively, at various system temperatures. The two stress tensors are calculated in accordance with Kirkwood–Buff theory,

\[
P_N(z) = \rho(z)k_B T - \frac{1}{V_{slab}} \sum_{i,j} \frac{z_{ij}^2}{r_{ij}} \frac{da(r_{ij})}{dr_{ij}}
\]

\[
P_T(z) = \rho(z)k_B T - \frac{1}{V_{slab}} \sum_{i,j} \left( x_{ij}^2 + y_{ij}^2 \right) \frac{da(r_{ij})}{dr_{ij}}
\]

where \(P_N(z)\) and \(P_T(z)\) are the normal and tangential components of the stress in a slab in the z direction, \(\rho(z)\) denotes the number density of a slab positioned at point \(z\) on the z axis, \(V_{slab}\) is the slab volume, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature. The contents of the large-angle brackets represent the ensemble average of all of the atoms located in the slab. \(r_{ij}\) is the distance between atoms \(i\) and \(j\). \(x_{ij}\) and \(y_{ij}\) are three components of the vector from atom \(i\) to \(j\), respectively, and \(u(r_{ij})\) is the potential energy of atomic pair \(i\) and \(j\). Kirkwood–Buff theory has been used successfully in previous studies of complicated interfaces mediated by surfactant molecules and general liquid/vapor interfaces. In Figure 4a,b, positive and negative stress values indicate an expansion and a compression of the analyzed volume, respectively. Figure 4a shows that at each of the considered temperatures, the normal stress has a negative value in the contact and surface regions but a positive value before decreasing to zero at the surface of the thin film. According to the PMF profiles shown in the lower panel of Figure 2, the density distribution in the z direction can be divided into four distinct regions, namely, the contact region (I), the transition region (II), the bulk region (III), and the surface region (IV). In the transition region, the value of PMF is negative, which results in a higher density and also indicates that the Au(111) surface and the MMA molecules have an attractive interaction. In the bulk region, the PMF profiles have an average value of zero and fluctuate only mildly. The density in the corresponding region of the film also has an approximately constant value. The bulk region and the contact region are separated by a transition region, within which the high density of the contact region decreases to the low density of the bulk region. The interaction between the substrate and the MMA molecules has a significant effect on the structure of the MMA thin film only in the contact region. Consequently, the compact packing of the MMA molecules in the contact region that is due to the interaction of the Au(111) surface prevents other MMA molecules with a density as high as that in the bulk region from existing stably in the transition region. Therefore, the density in the transition region is lower than that in the bulk region, and the PMF profiles have positive values. The density in the transition region is lower than that in the bulk region, and the PMF profiles have positive values.

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\]

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value in the transition region. Moreover, a tendency that is evident from the simulations shows that the normal stress has a lower negative stress in the contact region and has a lower positive stress in the transition region at higher temperatures. This result is consistent with a previous study\(^{52}\) that shows that a higher temperature causes a lower maximum surface tension. Similarly, the fluctuations in the normal stress profile in the bulk region of the MMA film correspond to the fluctuations in the density profile in the bulk region in Figure 2. In Figure 4b, the tangential stress shows fluctuations, which implies that the MMA molecules in the thin film are relaxed in the tangential direction. Finally, in the bulk region, the tangential stress fluctuates. This result is consistent with the variation in the density profile observed in Figure 2. Figure 5 shows the variation of the surface tension across the thickness of the MMA film at various system temperatures. The surface tension is derived from\(^{36}\)

\[
\gamma = \int_{L_1}^{L_2} dz \left[ P_N(z) - P_T(z) \right] \quad (7)
\]

where \(L_1\) and \(L_2\) indicate the limits of the integration range (i.e., the thickness of the MMA film in the current case). In Figure 5, the positive value of the surface tension obtained for the current MMA thin film on the Au(111) surface indicates that, on average, the value of the normal stress is higher than that of the tangential stress. Also, it can be observed that the contribution of stress to the variations in surface tension is mainly due to normal stress.

Figure 6 shows the average potential energy of the MMA molecules in the contact, transition, and bulk regions of the MMA film at different temperatures. Here, the energy in each region is equal to the ratio of the sum of the potential energy between MMA molecules to the number of MMA molecules in the corresponding region. For a given temperature, the average potential energy in the contact region is consistently higher than that in the other two regions of the film. This result is consistent with the density profiles in Figure 3, which indicate that the MMA molecules are more closely packed in the contact region than in either the transition or bulk region. Consequently, a higher repulsive energy exists between the MMA molecules. The average potential energy in the transition region is higher than that in the bulk region. Figure 3 shows that the transition region has the lowest density of MMA molecules. Hence, each MMA molecule in this region has fewer neighboring molecules and therefore the average potential energy is higher than that of the bulk region. For any given temperature, the average potential energy always has a minimum value in the bulk region. Hence, it can be inferred that the MMA molecules in the bulk region of the film have a more stable arrangement than the MMA molecules in the transition.
region and the contact region. Finally, Figure 6 shows that the average potential energy in each region of the MMA film increases with increasing system temperature.

The interaction strength between the MMA molecules in the contact region of the thin film and the Au(111) surface can be evaluated using the following formation-energy function

$$E_{\text{formation}} = \frac{E_C}{n}$$

where $n$ is the number of MMA molecules in the contact region and $E_C$ is the interaction energy between the Au atoms and the MMA molecules in the contact region, as calculated by the Dreiding FF. Figure 7 shows the formation energy of the MMA molecules and the corresponding contact surface density at different temperatures. Because the density of the MMA structure in the contact region decreases with increasing temperature (Figure 3), the surface density of the MMA molecules in direct contact with the Au(111) surface also decreases as the system temperature rises. Consequently, as shown in Figure 7, the formation energy increases slightly with increasing temperature. When the system temperature is increased from 200 to 300 K, the average potential energy in the contact region increases by approximately 2.40 eV (Figure 6). However, Figure 7 shows that the formation energy increases by approximately 0.11 eV over the same temperature range. Hence, it can be inferred that the system temperature has a greater effect on the interaction strength between MMA molecules than on the interaction strength between the MMA molecules and the Au(111) surface.

The orientations of the MMA molecules on the Au(111) surface can be investigated by computing the bond orientation factor

$$s(z) = 1.5 \langle \cos^2 \theta \rangle - 0.5$$

where $\theta$ is the angle between the direction of the prescribed bond and the normal direction to the Au(111) surface. The bracketed term expresses the average over the number of prescribed bonds and time steps in the MD simulation. In eq 9, values of $s(z) = -0.5, 0.0,$ and $1.0$ indicate that the prescribed bond is aligned parallel to the substrate surface, randomly oriented, and aligned normal to the substrate surface, respectively.

Figure 8a-c shows the variation of the orientation factor of three prescribed bond directions in the contact, transition, and bulk regions of the MMA film at three different system temperatures. Note that in each part of the Figure the direction of the prescribed bond is indicated by the arrow in the inset. In all three parts, the orientation factor in the contact region is negative, indicating that the prescribed bonds are parallel to the Au(111) surface in most of the MMA molecules. With this result, an MMA molecule has its largest contact area between the MMA molecules and the Au(111) surface and this therefore results in a lower formation energy. Therefore, a more stable adsorption of MMA molecules on the Au(111) surface takes place. However, it is observed that the value of the orientation of MMA molecules...
increases in the contact region as the temperature is increased in each part of the Figure. This finding is consistent with Figure 7, which shows that the formation energy decreases as the temperature increases. The agreement between the two results is reasonable because, as shown in Figure 3, the density in the contact region decreases as the system temperature increases. This results in a reduction in the number of neighboring MMA molecules, and hence the average potential energy falls. However, as shown in Figure 8, the orientation of the MMA molecules with respect to the Au(111) surface does not vary significantly with increasing temperature. Consequently, the formation energy increases only slightly as the system temperature increases. In the transition region, the orientation factor is positive for each of the three prescribed bonds, notably in the direction from a center carbon atom to the side group, as shown in the inset of Figure 8c. The bonds are aligned normal to the Au(111) surface. This result implies that the MMA molecules in the transition region are connected to the molecules in the bulk and contact regions of the thin film via the side groups of the MMA molecules.

Conclusions

We have performed MD simulations to investigate the temperature effect on the structure and properties of an MMA thin film on a Au(111) surface. The density profile of the MMA film suggests that the film comprises four distinct regions, namely, a contact region, a transition region, a bulk region, and a surface region. The numerical results reveal that the MMA molecules have a higher concentration in the contact region, which implies that the MMA structure is in a compressed state. However, as the temperature increases, the number density decreases. Regarding the geometric arrangement of the MMA molecules, the results show that the three prescribed bonds are oriented parallel to the Au(111) substrate surface in the contact region but are normal to the substrate surface in the transition region. Hence, the MMA molecules in the transition region are connected to the molecules in the bulk and contact regions via their side groups. The parallel orientation of the MMA molecules in the contact region increases their contact area with the Au(111) surface. This reduces the formation energy and therefore results in a more stable adsorption of MMA molecules on the Au(111) surface. Finally, the simulations have shown that temperature has a greater influence on the interaction strength between individual MMA molecules than on the interaction strength between the MMA molecules and the Au(111) surface.

Acknowledgment. We gratefully acknowledge financial support provided by the National Science Council of the Republic of China under grant numbers NSC 95-2221-E-110-006, NSC 95-2221-E-110-070, and NSC-095-SAF-I-564-623-TMS.