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Chain-length and tacticity effects on the conformational behavior of MMA-oligomer thin films on an Au (1 1 1) substrate

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ABSTRACT

Chain-length and tacticity effects on the conformational behavior, including density distributions and conformations, of MMA-oligomer thin films deposited on an Au (1 1 1) substrate at room temperature were investigated using molecular dynamics (MD) simulations. Three kinds of MMA-oligomer thin film with the oligomers containing m repeat units with m = 5, 10, and 20, respectively, were selected to examine the chain-length effects. Three types of MMA-oligomer thin film (made of isotactic, syndiotactic, and atactic PMMA isomers, respectively) were utilized to inspect the tacticity effects. For ease of investigation, the thin film was divided into three regions (the contact, the bulk, and the surface regions) according to the through-thickness distribution of density of the thin film. For short-chain thin films (with m = 5 and 10), the density distribution had a remarkable peak in the contact region of the thin film. The density peak, however, was not evident for the long-chain thin film (with m = 20). Regarding tacticity, the isotactic thin films had a prominent peak density in the contact region as compared with the syndiotactic and atactic thin films. Moreover, the MMA oligomers were found to exhibit a flattened conformation parallel to the Au substrate in the contact region and a slightly flattened conformation in the surface region for both the short-chain and the long-chain thin films. The flattened conformation remained in the bulk region of the long-chain thin film. However, it was not present in the bulk region of the short-chain thin film, which had a randomly orientated conformation–a characteristic similar to bulk MMA. It was also observed that the tacticity of the MMA-oligomer thin films did not have obvious effects on the conformations of the thin films for both the short-chain and the long-chain cases.

1. Introduction

A polymer thin film on a solid substrate has quite different behavior from that in its bulk phase due to the presence of an interface between the polymer thin film and the solid substrate. This may yield various important applications in engineering, especially in manufacturing of electronic nanodevices. Nanoimprinting [1], nanolithography [2], and ultrahigh storage devices [3] are some typical examples. Consequently, investigation into the structural and dynamic properties of polymer thin films on solid substrates has attracted considerable interest in recent years. Several experimental [4–6] and numerical [7–9] studies have been conducted.

Among various polymer thin films, the poly(methyl methacrylate) (PMMA) thin film is widely used in engineering because it exhibits a glassy state at room temperature. A lot of research, including experimental and numerical studies, has been carried out on the properties of PMMA thin films on solid substrates. Van der Lee et al. [10] used X-ray reflectometry to investigate through-thickness density profiles in PMMA thin films spin-cast on silicon wafers. In their work, an increase in the density in the vicinity of the solid silicon surface was observed regardless of the thickness and tacticity of the PMMA thin film. The authors later applied ellipsometry to measure the thickness-dependent glass-transition temperatures of PMMA thin films in a confined geometry [11] and on a silicon substrate [12].

Conformations of PMMA thin film on a solid substrate are another interesting issue for researchers. Grohens et al. [13] investigated the influence of tacticity on chain flattening of PMMA thin films spin-cast on aluminum mirror surfaces with the aid of reflectance infra-red spectrometry. Their results showed that isotactic PMMA thin films might adsorb on the aluminum surface in a more flattened fashion than the syndiotactic and atactic PMMA thin films. In a recent study, Zhang et al. [14] employed reflection–absorption infra-red and surface-enhanced Raman scattering spectroscopy to examine the orientation of the bulk and the interface of

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an atactic PMMA thin film dip-coated onto a silver-particle deposited substrate. They observed that the chain axis of the bulk atactic PMMA tended to orient slightly parallel to the silver substrate, but the chain axis of the polymer at the interface had a configuration that was clearly parallel to the substrate.

Experimental methods may obtain various structural properties of a PMMA thin film on a solid substrate and have been used with success in several studies. The methods, however, cannot provide thorough conformations of PMMA thin films at an atomic level. Molecular dynamics (MD) simulation is a powerful numerical method to overcome the limitation of experimental methods. It can reveal detailed interfacial behavior, at an atomic level, of a polymer thin film on a solid substrate. Nevertheless, compared to experimental studies, not many numerical studies have been conducted on the behavior of PMMA thin films on solid substrates. The extensively computational effort required for MD simulations is the main reason. In a recent study, Lu and Tung [15] utilized the MD simulation technique to examine the tacticity effect on the free volume morphology of PMMA membranes. In their work, it was noticed that the syndiotactic PMMA membrane has less flexibility in the backbone and has a longer end-to-end distance than that of the isotactic PMMA membrane. Prathab et al. [16] also used MD simulations to explore PMMA-polymer and PMMA-metal oxide interactions. The adsorption behavior of MMA oligomers with several metal oxides (Al_2O_3, Fe_2O_3, SiO_2, and TiO_2) was investigated in their work.

In our previous research [17], MD simulations were carried out for the analysis of temperature effects on the structure and properties of MMA thin films on an Au (1 1 1) substrate. The research revealed that the MMA molecules have a higher density near the interface and the density decreases as the temperature increases. In addition, MMA molecules near the interface were found to orient themselves parallel to the Au surface. The orientation of the MMA molecules did not significantly vary with increasing temperature.

In this paper, we extended our research with the aid of MD simulations to investigate the conformational behavior, including density distributions and conformations, of an MMA-oligomer thin film on an Au (1 1 1) substrate. The influence of the chain-length and tacticity of MMA oligomers on the behavior was examined. This topic, to the best of our knowledge, has not been widely studied. The present research may provide some insight into the chain-length and tacticity effects on conformations of a PMMA thin film on an Au substrate.

2. Simulation model

The MD simulation model used in the present research consists of an MMA-oligomer thin film and an Au substrate on which the MMA oligomers are deposited. Fig. 1 shows a diagram of the present simulation model. There are three different groups of interactions in the simulation model: (1) the intra- and intermolecular interactions of MMA oligomers; (2) the interactions of Au atoms; (3) the interactions between the MMA oligomers and the Au atoms.

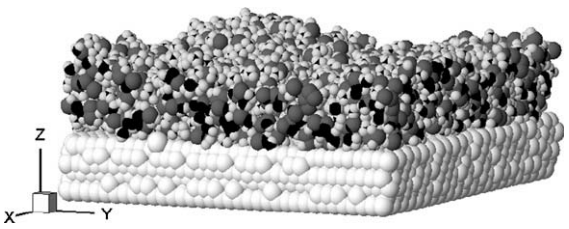

Fig. 1. Diagram of the present simulation model.

In the MD simulations, three different potentials were employed to model the three groups of interactions. First, the energy calculations and dynamics (ENCAD) potential [18,19] was chosen to model the atomic interaction between the intra- and intermolecular interactions of the MMA oligomers. The interaction between the Au atoms of the substrate was described by the tight-binding potential [20,21], whereas the Dreiding force field [22] was used to model the interaction between the MMA oligomers and the Au atoms. The expressions for the three potentials are described below.

2.1. Potential for MMA oligomers

The ENCAD potential was employed to model the atomic interaction between the intra- and intermolecular interactions of the MMA oligomers. In this model, the potential force field (FF) is expressed as the sum of the bond stretching energy U_{bond}, the bond bending energy U_{bend}, the bond torsion energy U_{torsion}, the van der Waals energy U_{vdw}, and the electrostatic energy U_{els}. Accordingly, the total potential, U, is given by:

$$U = U_{\text{bond}} + U_{\text{bend}} + U_{\text{torsion}} + U_{\text{vdw}} + U_{\text{els}} \tag{1}$$

with

$$U_{\text{bond}} = \sum_i K_b^i (b_i - b_0)^2 \tag{2}$$

$$U_{\text{bend}} = \sum_i K_\theta^i (\theta_i - \theta_0)^2 \tag{3}$$

$$U_{\text{torsion}} = \sum_i K_\varphi^i \{1 - \cos[n^i(\varphi_i - \varphi_0^i)]\} \tag{4}$$

$$U_{\text{vdw}} = \sum_{i,j} [A_{sc}\varepsilon^{ij}(r_0^{ij}/r_{ij})^{12} - 2\varepsilon^{ij}(r_0^{ij}/r_{ij})^6 - S_{\text{vdw}}(r_{ij})] \tag{5}$$

$$U_{\text{els}} = 332 \sum_{i,j} [q^i q^j / r_{ij} - S_{\text{els}}(r_{ij})] \tag{6}$$

where K_b^i, K_θ^i, and K_φ^i are force constants representing the bond stretching, bond bending, and torsion barrier of the ith bond, respectively, and b_i, θ_i, φ_i, b_0, θ_0, and φ_0 are the ith bond length, the ith bending angle, the ith torsion angle, the equilibrium bond length, the equilibrium bending angle, and the equilibrium torsion angle, respectively. The bond torsion energy can be represented by a cosine function with a periodicity n^i and an equilibrium torsion angle φ_0. All the summations in the bonded energy terms, Eqs. (2)–(4), are carried out over all corresponding bonds. The van der Waals energy, Eq. (5), is expressed using the Lennard–Jones 6–12 potential, where r_{ij} indicates the atomic distance between atoms i and j in a non-bonded pair and A_{sc} is used to compensate for the interaction lost at small cutoff distances. The values of the energy parameter ε^{ij}, the distance parameter (r_0^{ij}), and the truncation shift function (S_{vdw}) for the van der Waals potential can be found from Levitt et al. [18,19]. The electrostatic energy, Eq. (6), is modeled with the aid of the Coulomb potential, in which q^i and q^j stand for the partial charges of atoms i and j, respectively, of the MAA oligomers within the cutoff distance and the truncation shift function (S_{els}) can be obtained from the references. The summations of the non-bonded terms (U_{vdw} and U_{els}) are carried out over all non-bonded atom pairs i and j closer than the cutoff distance. The potential parameters used in the current study were taken from those of Levitt et al. These parameter values were determined to reproduce energetic, structural, and dynamic properties found from ab initio quantum mechanics calculations, spectroscopic measurements, and crystallographic data [18].

2.2. Potential for Au atoms

The interatomic force between the Au atoms in the substrate was modeled by means of the tight-binding potential. The tight-