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Molecular dynamics study of the effects of chain properties on the order formation dynamics of self-assembled monolayers of long-chain molecules

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The order formation dynamics of self-assembled monolayers (SAM) of long-chain molecules were studied using coarse-grained molecular dynamics simulations. The primary kinetic processes of surface order formation from solution are adsorption to the surface and surface diffusion. For long-chain molecules, the degrees of freedom of the chain structure and motion add various complexities to the order formation dynamics. Specifically, the strength of the chain interaction, the chain flexibility and the chain length play a significant role, and this work focused on the effects of these chain properties on the order formation dynamics. The adsorption dynamics of SAM molecules can be explained by the same theoretical framework as the polymer brush. On the other hand, the evolution of highly ordered structure is specific to SAM systems. Simulation results revealed that the development of oriented domains can be grouped into three types, isolated island growth, packing growth, and growth suppression, which depend on temperature and chain flexibility. In packing growth, oriented domains are formed gradually due to the decrease in free volume as the surface density becomes high, while the tilt of the adsorbed chain molecules does not become upright gradually as a whole. Rather, inside the oriented domains, the adsorbed chains adopt "standing" states with tilt angles almost equal to the final values, which contributes to the gradual increase in the total tilt order. The effect of chain length was also studied. In the case of semirigid chain molecules, longer-chain systems showed slightly slower growth in adsorption but faster growth in oriented domains. These simulation results reveal how chain properties influence the dynamics of oriented structure formation on surfaces.

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I. INTRODUCTION

A self-assembled monolayer (SAM) is obtained by the adsorption and arrangement of molecules on a flat surface. The molecules which form such ordered monolayer structures have many variations in structure, from small to long-chain molecules [1]. There have been many experimental studies on the dynamics of self assembly processes [2–8]. It has been shown that the ordering processes of chainlike molecules such as alkanethiol systems consist of two steps of differing speeds, in which adsorption processes are ascribed to the fast step, and chain ordering processes are ascribed to the slow step. However, compared to experiments concerning SAM static structure properties, the dynamics have been less well explored, and there remain many unresolved questions concerning the details of the ordering dynamics. In order to obtain a highly ordered monolayer structure, it is important to understand the fundamental mechanism of structure formation on the substrate. These are complicated ordering processes, in which various factors such as adsorption to the substrate and surface diffusion of the molecules are concerned. In addition, for monolayers of long-chain molecules, the interactions between chain molecules and chain flexibility may play a large role in ordering. These are the distinct differences between the order formation dynamics of small molecular systems and those of chain molecules. For long-chain systems, the molecules have large internal degrees of freedom due to the extended connectivity. It would be interesting to elucidate how these properties affect ordering dynamics through chain orientation or hindrances by other chain molecules. An understanding of these effects would be useful in designing chain molecules and the preparatory conditions for the production of a highly oriented monolayer film.

For studies of the physical properties of monolayer formation, simulation is a useful tool since the various detailed microscopic behaviors of the chain molecules can be obtained simultaneously during a single simulation run. There have been many simulation studies on self-assembled monolayers, but most of them have discussed various equilibrium properties, such as orientation structure, once the molecules were completely, or at least partially, adsorbed on the surface. These include the static properties of self-assembled monolayers of various kinds of molecules [9–19], the coarse-grained approach [17], the mixture system [18], and tribology [19]. As a result, there has been considerable knowledge obtained concerning the structure and physical properties of the self-assembled monolayer. However, the kinetic aspects, including the order formation processes from solution, have been seldom studied by molecular simulation before now.

It would be important to consider the relationship between the order formation processes of SAMs and those of polymer brushes. The polymer brushes are surface grafted polymers. Their structures have some kind of similarity to those of SAMs. The dynamics of the polymer brush formation has been studied by kinetic Monte Carlo simulations [20–24]. These studies revealed the adsorption processes of polymers and the changes of chain conformation on the surface. Since the adsorption processes of polymer chains are single chain problems especially at the initial period, the adsorption processes of SAM molecules might be explained by those of polymer brushes. However, SAMs have dense packed aligned structures, in which high orders in the alignment and the chain orientation are essential properties. Hence, in the case of SAMs, the surface diffusion and the attractive interaction between chain molecules would become important factors. In addition, the chain bending rigidity is an additional factor that must be taken into consideration, since it plays an important role in the development of the orientation orders. These factors have not been included in the past simulation studies of the polymer brush formation, in which the excluded volume effect of the chain molecules has been the dominant interaction for the chain molecules. Thus, it would be interesting to find out how these additional new factors affect the order formation dynamics, especially for the orientation orders.

For studying the slow dynamics of SAM formation processes, molecular simulation by the atomistic model, often used for precise reproduction of real systems, is not applicable due to computational resource limitations. On the other hand, coarse-grained models have been useful for the elucidation of structure formation dynamics in polymer systems, and they are suitable tools for understanding the basic physics of structure formation dynamics involving slow relaxation processes and large systems [17–19,25–28]. Thus, such models would be helpful in elucidating such universal features as the role of chain connectivity on the ordering dynamics. SAMs have some structure formation features in common with polymer systems in that they are the order formation processes of chain molecules. Hence, in this study, the order formation dynamics of SAMs of long-chain molecules were considered by means of coarse-grained molecular simulations, specifically focusing on the effects of chain interactions, chain flexibility, and chain length.

II. MODEL

The difficulties in simulating structure formation dynamics as opposed to static properties come from the extremely slow dynamics and the large number of solvent molecules which may be included in the solutions. In order to overcome these obstacles, a coarse-grained model was used, along with a higher initial concentration of chain molecules, and suitable interactions to avoid aggregation in the initial states.

In coarse-grained molecular dynamics simulations, chain molecules are represented by a beads-springs model in which bending rigidity is included. The merit of the coarse-grained model is the fast ordering dynamics. Since the dynamic ordering processes of soft materials are generally slow, it is important to omit unnecessary potential barriers which could significantly slow the chain dynamics. In addition, the smaller effective friction between segments in the coarse-grained models would accelerate the order formation dynamics [29–31]. Although some detail might be lost in coarse-grained dynamics, these models are effective in understanding the basic physics and universal features of complicated ordering dynamics. Since the time scale of overall order formation is sufficiently long, we suppose that these effects would not alter the basic mechanism of order formation.

In this study, chain segment connectivity is introduced by the harmonic potential as given by $U(b)=\frac{1}{2}K_c(b-b_0)^2$. Here, b_0 is the equilibrium bond length and K_c is the force constant. The chain rigidity is given by $U(\theta)=\frac{1}{2}K_b(\cos\theta-\cos\theta_0)^2$, in which θ is the angle formed by two adjacent bonds and K_b is the force constant.

The chain molecules consist of two parts, head segment groups and tail segment groups, in which the interaction potential is different. For the pairwise interactions, both the Lennard-Jones (LJ)-type attractive interaction and the soft-core repulsive interaction were used. The LJ-type attractive interaction potential is given by $U(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]$, which applies to the interactions between: tail segments and tail segments of chain molecule pairs; tail segments of chain molecules and solvent pairs; the solvent and solvent pairs; and head segments and head segments of chain molecule pairs. Nearest-neighbor and second-nearest-neighbor segments along the same chain molecule were excluded in the pairwise calculations. The strength of the attractive potential ε was 1.0, and the cutoff distance was 3σ. The soft-core repulsive interaction is given by $U(r)=4\varepsilon_r[(\sigma/r)^{12}-(\sigma/r)^6]+\varepsilon_r$, and the cutoff distance was $2^{1/6}\sigma$. This repulsive potential was used for the interaction between the head segments and tail segments of chain molecules pairs, and the solvent and head segments of chain molecule pairs. The strength of the repulsive potential ε_{r} was 1.0.

The model parameters and simulation results are expressed in dimensionless reduced units, where the segment diameter σ, the energy parameter ε of the LJ interaction potential, and the segment mass are all 1.0. The equilibrium bond length b_0 was 0.4, the elastic constant K_c of the bond springs was 9000, and the equilibrium angle θ_0 was 0. The bending force constant K_b was 2000 for the semiflexible chain molecules, and 4000 for the semirigid chain molecules. Detailed properties of this coarse-grained model polymer were reported in Ref. [28]. The chain length N was 20, 30, or 40. The number of head segments, N_h, and tail segments, N_t, were $N_h=3$ and $N_t=17$ for the $N=20$ chain, $N_h=4$ and $N_t=26$ for the $N=30$ chain, and $N_h=5$ and $N_t=35$ for the $N=40$ chain. The number of polymers in the system was 320. The number of solvent molecules in the system was 23 200 for the $N=20$ systems, 20 000 for the $N=30$ systems, and 16 800 for the $N=40$ systems. The number of solvent molecules was determined so that the total number of chain and solvent segments in the entire simulation box was constant. The initial size of the simulation box was 19.98 along the x axis, 20.507 482 along the y axis, and 90.0 along the z axis.

At the bottom of the simulation cells, four layers of (111) surface substrate were prepared. The positions of surface atoms belonging to the bottom layer were fixed, and the surface atoms belonging to the other three layers were connected by harmonic potentials with a force constant of 20 000. The mass of a surface atom was 10, and the diameter of surface metal atoms was 0.74. There were strong attractive forces between the edge segments of the chain head and the surface. This attractive potential is given by $U(r)=D[1-e^{-a(r-r_e)}]^2-D$, where here $D=100$, $a=5.0$, and $r_{\mathrm{e}}=0.75$. The cutoff distance of the interaction was 3.0. Although this study focused on universal properties and not specific materials, the interaction usually corresponds to S-Au bonding in alkanethiol-gold systems, and thus, the strength of interaction was chosen to be near the same range

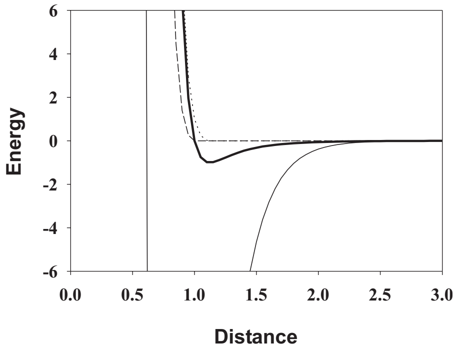


FIG. 1. The interaction potentials used in the simulation. The length and energy scales are shown in dimensionless reduced units. The bold, solid, dashed, and dotted lines indicate the Lenard Jones, surface-polymer head, repulsive wall, and soft-core interactions, respectively.

as follows. There have been large varieties in the calculated values of adsorption energy between alkanethiol and gold surface, but they are in the range of $2.4–3.9\times10^{-19}$ J [32–34]. Although the unit of the reduced energy scale in the coarse-grained model is often an adjustable parameter, it might be roughly in the range of $0.8–1.7\times10^{-21}$ J. Since the number of the nearest-neighbor atoms at hollow sites is three, we have estimated the strength of potential D as 100. For interactions between the surface atoms and the solvent or chain molecules, an LJ-type attractive interaction was applied for the head segments of chain molecules and surface pairs, and a soft-core repulsive interaction was applied for both the solvents and surface pairs as well as the tail segments of chain molecules and surface pairs. In order to confine the solvent and the chain molecules to the simulation box, a repulsive wall at the top of simulation box was also prepared. The potential is given by $U(r)=4\varepsilon[\frac{1}{5}(\frac{\sigma}{r})^{10}-\frac{1}{2}(\frac{\sigma}{r})^{4}+0.3]$, in which the cutoff distance of the interaction is 1.0. Periodic boundary conditions were applied in the horizontal directions (along the x and y axes). The profiles of the potentials used in this study are summarized in Fig. 1.

The initial states were prepared by thermally equilibrating using an NVT ensemble with the condition that the chain head-surface attractive interaction was disabled and replaced by a soft core repulsive potential in order to avoid adsorption in the equilibrium runs. Then, the chain edge-surface attractive interaction was suddenly introduced, which corresponds to immersing the metal surface into the solution. In the simulations, the mass of the thermostat was 30 000. The equations of motion were integrated using a fourth-order predictor-corrector method with a time step of 0.001. Since the ordering processes are affected by random noise and fluctuations, it may not be sufficient to discuss the evolution curves of only one sample. Therefore, four simulation runs were carried out from different initial states and the average properties of all simulation runs were examined.

In order to compare and discuss the ordering behaviors in these systems, the surface coverage, oriented domain ratio, and order parameters of the adsorbed molecules were calculated. The surface coverage was calculated by the ratio of adsorbed chain molecules to the maximum possible adsorption number for the area given. The maximum possible adsorption number was determined by the lattice structure of the surface metal, and the ratio of the diameter of the chain head to that of a surface atom. In these simulations, it corresponded to one-third of the number of the first layer of surface atoms. The oriented domain ratio was calculated as the ratio of the segment number belonging to ordered domains over the ideal segment number (in which the surface is completely covered by the oriented chain molecules). Here, an ordered domain was defined as a group of segments whose bond vectors were within a distance of 1.5 of each other and whose orientation difference was less than 10°. Groups of less than 50 segments were not included among the ordered domains. The order parameters of the molecular orientation are given by $\langle 3\cos^2\theta-1\rangle/2$, where θ is the angle formed by two bond vectors of the main chain. Using these calculation methods, the orientation order parameters can be classified into three types. The global order was obtained by averaging over all bond pairs in the entire set of adsorbed molecules, except for bond pairs within the same molecule. The interlocal order was calculated only for pairs of adjacent bonds in different adsorbed molecules. (In this simulation, two bonds were regarded as adjacent when the distance between them was less than 1.5.) The intralocal order was calculated for pairs of adjacent bonds within the same adsorbed molecule.

III. RESULTS AND DISCUSSION

A. Growth curves of the surface coverage and oriented domain formation

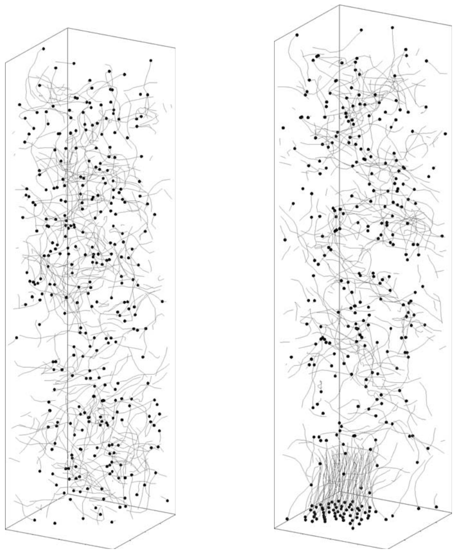
Structure formation of the oriented layer of chain molecules from solution is largely affected by the chain rigidity, intermolecular interactions and temperature. In Fig. 2, examples of the monolayer formation processes of semirigid (K_b=4000) chain molecules with a chain length of N=30 at low temperature (T=12) are shown. Under these conditions, as shown in Fig. 2(b) for t=1000, molecules that were adsorbed on the surface form the oriented domains initially. The layer formation ratio and the orientation order parameters under these conditions are plotted against time in Fig. 3. The adsorption rate, the gradient of the surface coverage curve, takes its maximum value at time=0, and decreases gradually thereafter. There are many theories on the adsorption dynamics of molecules on the surface. One is the Langmuir kinetics given by

$$\frac{d\sigma}{dt}=k_a c(1-\sigma)-k_d\sigma \tag{1}$$

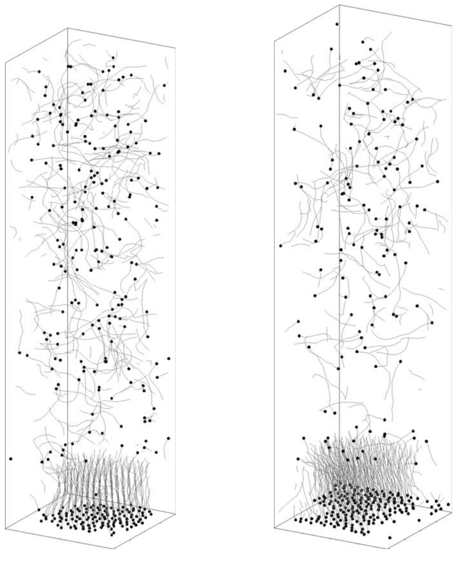
in which σ is the surface coverage ratio, k_a is an adsorption rate constant, k_d is a dissociation rate constant and c is the concentration of chain molecules. The solution to Eq. (1) is given by the exponential function

$$\sigma(t)=\frac{k_a c}{k_a c+k_d}\{1-\exp[-(k_a c+k_d)t]\}. \tag{2}$$

As shown in Fig. 4(a), the simulation result is not expressed by the single exponential behavior of Eq. (2). Even if we consider the effect of concentration change of chain mol-



(a) t=0 (b) t=1000



(c) t=4000 (d) t=10000

FIG. 2. Representations of the order formation processes of semirigid chain molecules on a surface at low temperature ($T=12$) over time. Time is shown in dimensionless reduced units.

ecules described by $c(t)=c_0[1-0.9\sigma(t)]$ in our simulation conditions, the solution given by Eq. (3) does not agree with the simulation results.

$$\sigma(t)=\frac{(A+B)[1-\exp(t/\tau)]}{1-\dfrac{A+B}{A-B}\exp(t/\tau)} \tag{3}$$

in which c_0 is the initial concentration and

$$A=[(19/18)+(5k_d/9k_ac_0)],$$

$$B=\{[(19/18)+(5k_d/9k_ac_0)]^2-10/9\}^{1/2},$$

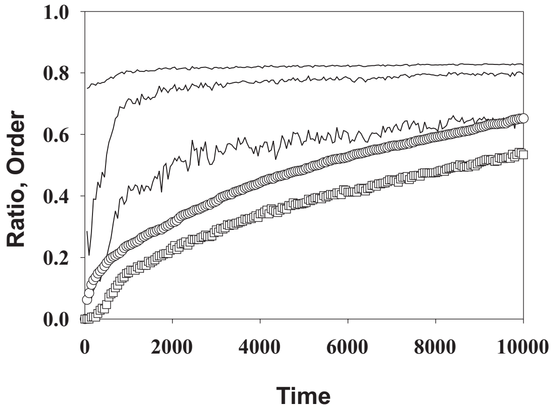


FIG. 3. Growth of various ordering properties during the order formation process. The circles and squares indicate surface coverage and oriented domain ratio, respectively. The lines indicate the orientation order parameters. The upper, middle, and lower lines indicate the intralocal, interlocal, and global order parameters, respectively.

$$1/\tau=1.8Bk_ac_0. \tag{4}$$

Another theory is the diffusion limited adsorption. When the adsorption is governed by the diffusion of molecules in solutions, the adsorption kinetics in the initial period can be expressed by the power function [21–23,35,36]

$$\sigma(t)\sim At^{1/2} \tag{5}$$

In this case, the simulation results were described by

$$\sigma(t)=At^{\nu} \tag{6}$$

in which $A=0.012$ and $\nu=0.43$. Although the exponent ν was slightly smaller than the theoretical value of 0.5, the function gives better fitting as shown in Fig. 4(b). Hence, these results indicate that the adsorption kinetics of the SAM molecules could be explained by the same theoretical framework as the polymer brush.

On the other hand, the order formation kinetics of chain orientation showed different behaviors compared with the adsorption. As shown in Fig. 4(b), the growth dynamics of the oriented domain ratio was not described by the power function. It is well described by the sum of two exponential functions with an induction time given by

$$S(t)=A_{\text{short}}[1-\exp(-t'/\tau_{\text{short}})]+A_{\text{long}}[1-\exp(-t'/\tau_{\text{long}})]. \tag{7}$$

Here, $t'=t-t_0$, which subtracts the induction time $t_0=250$, and $A_{\text{short}}=0.089$, $\tau_{\text{short}}=330$, $A_{\text{long}}=0.55$, and $\tau_{\text{long}}=6300$. The fitting curve using Eq. (7) is shown in Fig. 4(c). The growth of the oriented domain ratio in the initial period is slower than that of the surface coverage, although the growth of the oriented domain ratio in the middle and late periods takes similar behavior to that of the surface coverage. In the initial period before $t=2000$, the intermolecular local orientation order grows rapidly as shown in Fig. 3, which indicates that the orientation of neighboring molecular chains

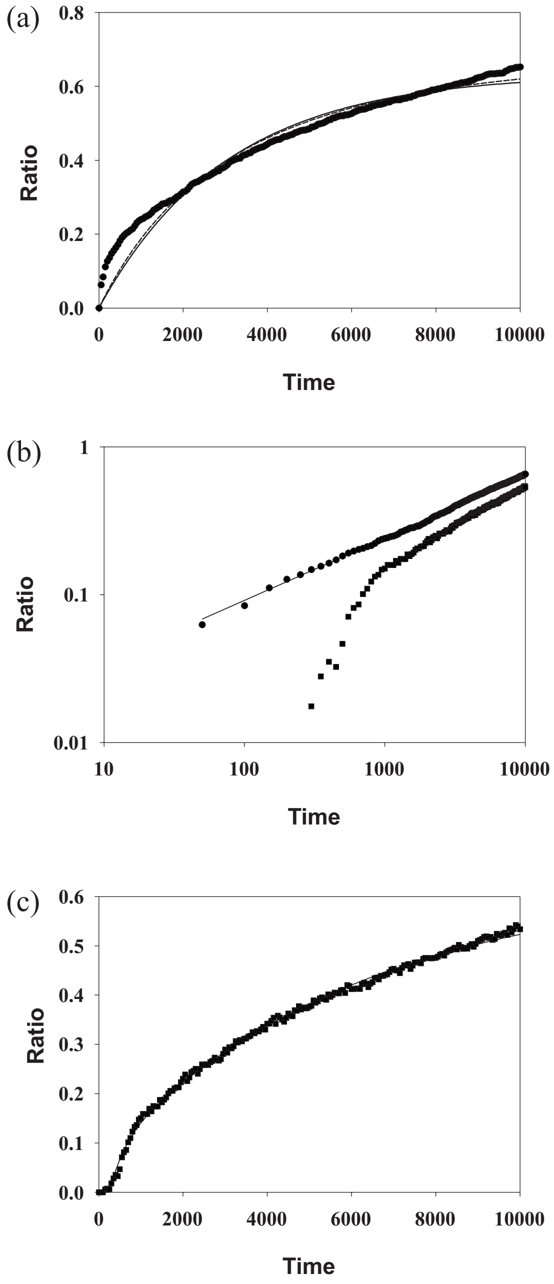
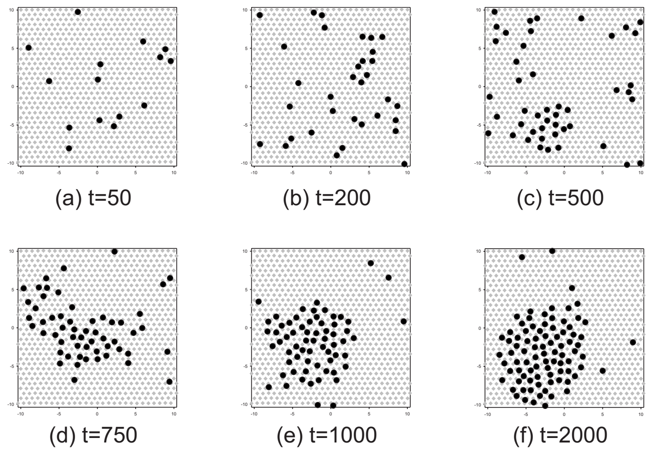


FIG. 4. (a) Fitting of the surface coverage over time. The circles indicate the simulation results. The solid and dashed lines indicate the fitting curves obtained using Eqs. (2) and (3), respectively. (b) Fittings of the surface coverage and oriented domain ratio over time in logarithmic scales. The circles and squares indicate the simulation results of surface coverage and oriented domain ratio, respectively. Best fitting is obtained using Eq. (6) for the surface coverage, which is shown in solid line. (c) Fitting of the oriented domain ratio over time. The squares indicate the simulation results. The solid line indicates fitting curve obtained using Eq. (7), which mostly overlaps the simulation results.


(a) t=50 (b) t=200 (c) t=500

(d) t=750 (e) t=1000 (f) t=2000

FIG. 5. Positions of adsorbed chain heads on the surface during order formation processes. The chain clusters are formed in the initial period.

aligns even in low surface coverage conditions. In this condition, the molecules that are adsorbed on the surface contribute to the formation of the orientation domains efficiently.

The domain formation behavior can be understood in detail by observation of the diffusion or assembly processes of the head position of the adsorbed chain molecules. As shown in Fig. 5, domains are not formed clearly until about $t=200$, when chain adsorption has just begun. After $t=500$, the assembled clusters can be observed due to the surface diffusion of chain molecules. Once large clusters are formed in the system, the molecules that had been adsorbed on the surface are immediately incorporated into them. Thus, the ordering behavior of semirigid chain molecules at low temperature can be grouped into isolated island growth.

Next, the ordering behavior of the semirigid chain molecules at high temperature ($T=15$) is shown in Fig. 6. The surface coverage over time is similar to the previous result at low temperature shown in Fig. 3, and can be described using Eq. (6) with $A=0.014$ and $\nu=0.42$. However, the intermolecular local order and the oriented domain ratio differ greatly over time from those at low temperature. The intermolecular local order grows very slowly for an extended period of time. This behavior is in sharp contrast to the results shown in Fig. 3, since the intermolecular local order at

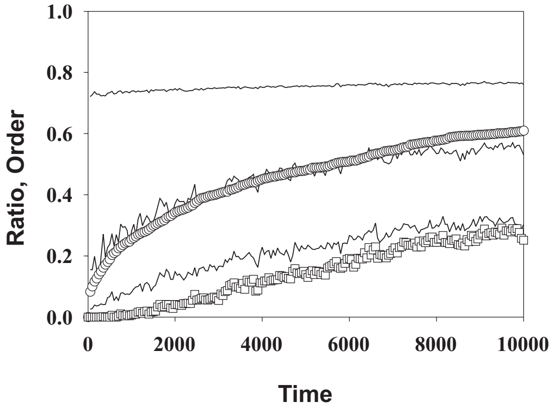
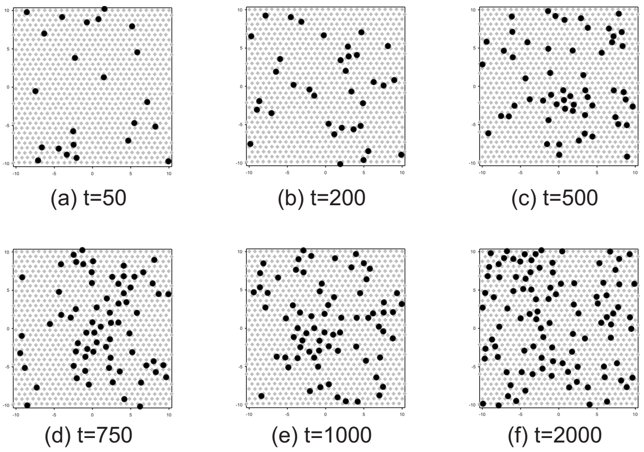


FIG. 6. Growth of various ordering properties during the order formation processes of semirigid chain molecules at high temperature ($T=15$). The circles and squares indicate surface coverage and oriented domain ratio, respectively. The lines indicate the orientation order parameters. The upper, middle, and lower lines indicate the intralocal, interlocal, and global order parameters, respectively.

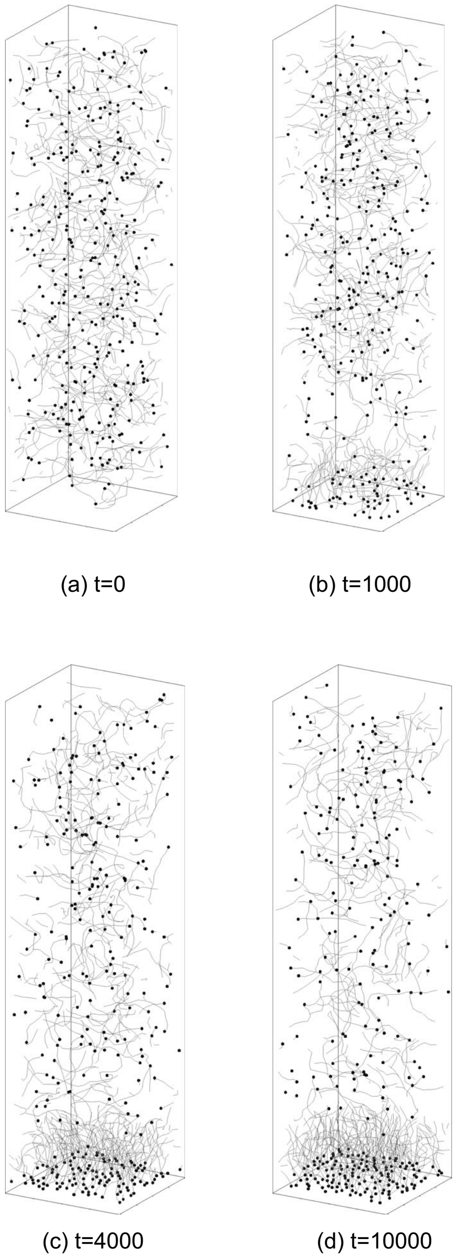

(a) t=50 (b) t=200 (c) t=500

(d) t=750 (e) t=1000 (f) t=2000

FIG. 7. Positions of adsorbed chain heads on the surface during order formation processes. Formation of chain clusters is not remarkable under these conditions.

low temperature grew rapidly before $t=2000$ and showed little change afterward. The oriented domain ratio demonstrates slow linear growth with no initial rapid rise under these conditions. A remarkable difference in the ordering dynamics can be observed in the change of the distribution of the head position of chain molecules over time. As shown in Fig. 7, clusters are not formed on the surface, even at $t=2000$, when the surface coverage exceeds 30%. Even in such a system, chain molecules gradually form a surface monolayer in which the orientation direction of the molecules is aligned, as the surface coverage increases and the chain molecules become more closely packed on the surface. These gradual ordering behaviors are observed at high temperature, and can be grouped into the packing growth.

The rigidity of the chain molecules also influences the order formation dynamics, especially at high temperatures when the packing growth is dominant. Figure 8 shows an example of the structure formation processes of semiflexible ($K_b=2000$) chain molecules at high temperature ($T=15$). A large number of chain molecules are adsorbed on the surface at $t=4000$, but the oriented domains are not yet formed, and the chain molecules take up random orientations on the surface. In this case, the long-chain molecules cover the surface roughly like brush, and these become an obstacle for the adsorption of additional chain molecules on the surface. In Fig. 9(a), order formation over time is shown. The growth of surface adsorption proceeds as usual from the initial periods, but the growth of intermolecular local order and that of the oriented domain ratio has been greatly inhibited. In the case of flexible chain molecules at high temperature, the chain-chain interactions become weak and it is expected that the order formation dynamics comes closer to that of polymer brushes. In Fig. 9(b), the growth curve of adsorption is plotted in logarithmic scales. As shown in this figure, the fitting curve using Eq. (6) is valid until $t=3500$, in which $A=0.0095$ and $\nu=0.45$. When the surface is covered by flexible polymers, the adsorption of chains is governed by the penetration processes of surface brush layers and the rate of adsorption decreases. Hence, the adsorption dynamics changed from the diffusion limited to the penetration limited


(a) t=0 (b) t=1000

(c) t=4000 (d) t=10000

FIG. 8. Representations of the order formation processes of semiflexible chain molecules on a surface at high temperature ($T=15$).

at this time range, which is the feature in common with the polymer brush. The dashed line in the Fig. 9(a) indicates the ideal oriented domain ratio when the chain molecules cover the surface completely. Hence, if the chain molecules on the surface become dense by some means, the oriented domains could approach this level. However, in practice, chain molecules with low orientation order cover the surface, and the development of oriented domains is seldom observed. Since the kinetic pathway to the surface through a brushlike region is limited, an ordered monolayer structure would not be formed under such conditions. In Fig. 10, an example of the development of the head position of adsorbed chain molecules is shown, and although the dispersion is not completely random, a large domain structure is not formed. The

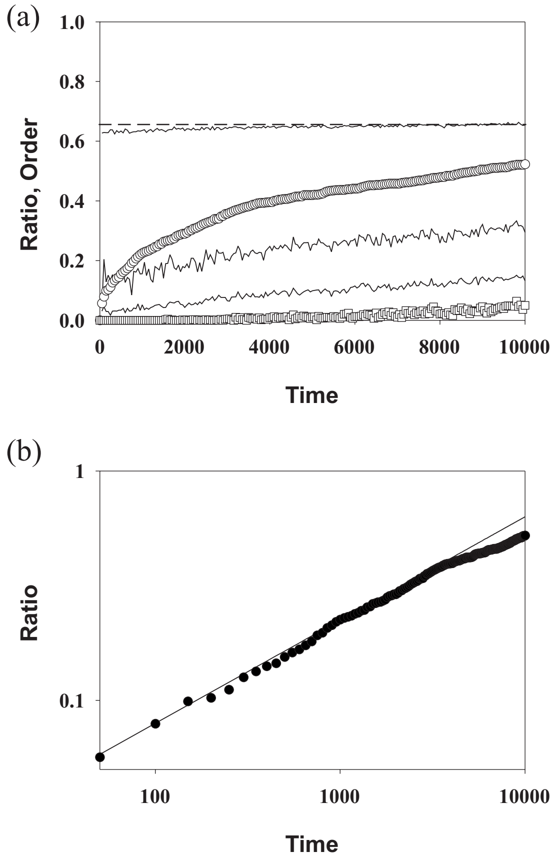


FIG. 9. (a) Growth of various ordering properties during order formation processes. The circles and squares indicate surface coverage and oriented domain ratio, respectively. The lines indicate the orientation order parameters. The upper, middle, and lower lines indicate the intralocal, interlocal, and global order parameters, respectively. (b) Fitting of the surface coverage over time in logarithmic scales. The circles indicate the simulation results. The solid line indicates fitting line obtained using Eq. (6). In the late period, there is a difference between the simulation results and fitting line.

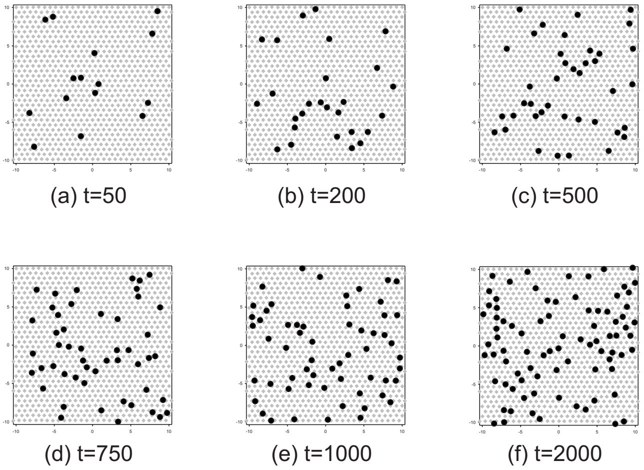

(a) t=50
(b) t=200
(c) t=500
(d) t=750
(e) t=1000
(f) t=2000

FIG. 10. Positions of adsorbed chain heads on a surface during order formation processes. The chain heads are scattered on the surface, and large clusters are not formed.

results of fitting curves for the surface coverage and oriented domain ratio at various simulation conditions are summarized in Table I.

B. Order formation dynamics of chain molecules inside the oriented domains

In order to elucidate the chain alignment dynamics inside the oriented domains, the effect of temperature on the ordering dynamics is considered. In Fig. 11, the surface coverage and oriented domain ratio of semirigid chains is shown at different temperatures. The difference in surface coverage with temperature is not large, but there is a large difference in the growth of the oriented domain ratio, which reflects the differences in the isolated island growth and packing growth. For a more detailed analysis, the change in the tilt angle of the chain molecules with time is plotted in Fig. 12. The cosine of the tilt angle θ is shown, where θ is defined as the angle formed by the bond vector of the chain molecule and the z axis (perpendicular to the surface plane), and two types of cos θ are calculated. One is the average over the bonds of all adsorbed chain molecules, and the other is the average over the bonds which belong to the oriented domains. The former is largely affected by temperature, developing gradually at high temperature. For the latter, only the data after $t=900$ are plotted, since few oriented domains were formed during this initial period, and data fluctuations were large. The average tilt of chain segments belonging to the oriented domains shows a different temperature dependence, varying only slightly over the entire period observed. The mechanism of order formation of semirigid chain molecules at high temperature is shown schematically in Fig. 13. In the packing growth cases, the orientation order gradually proceeds by the packing effect. This is caused by the restriction of the degrees of freedom of chain orientation due to increased chain molecule density on the surface. During structure formation, the increase in the overall tilt angle does not come from a gradual "standing up" of chain molecules as illustrated in Fig. 13(a). Rather, the simulation results support the scheme of Fig. 13(b), in which the oriented part of the chain molecules constitutes an upright structure whose tilt angle is almost identical to the final value, and the chain molecules on the surface are gradually pressed into oriented domains.

Next, the surface coverage and oriented domain ratio of semiflexible chains were evaluated at different temperatures, as shown in Fig. 14. In the initial period before $t=4000$, differences in surface coverage are small. However, there is a large temperature dependence in the oriented domain ratio. At high temperature, hardly any growth is observed. This affects the adsorption behavior of the middle and late periods, during which surface coverage at high temperature slows considerably compared to that at low temperature. Hence, as shown in Fig. 15, unless intermolecular interactions occur to some extent, order formation on the surface will be inhibited from a kinetic point of view, and a highly oriented SAM will not be obtained.

C. Effects of chain length on the order formation dynamics

In the formation of a self-assembled monolayer of chain molecules, the chain length may play two opposing roles in

TABLE I. Fitting results of the surface coverage and oriented domain ratio over time. The parameters of surface coverage were obtained using Eq. (6). The parameters of oriented domain ratio were obtained using Eq. (7). NA means that the fitting is not available for almost linear growth in the simulation range.

Stiffness	Temperature	Surface coverage		Oriented domain ratio			
K_b	T	A	ν	A_{short}	τ_{short}	A_{long}	τ_{long}
4000	12	0.012	0.43	0.089	330	0.55	6300
4000	13	0.013	0.43	0.092	620	0.51	6300
4000	15	0.014	0.42			0.66	16000
2000	12	0.011	0.44	0.009	1170	0.42	5200
2000	13	0.007	0.48			NA	NA
2000	15	0.009	0.45			NA	NA

structure formation. When the chain length is long, domain formation on the surface is expected to be accelerated due to the larger attractive interactions between chain molecules, which might result in an improvement of the orientation order. On the other hand, the long-chain molecules could inhibit further chain adsorption due to brushlike coverage of the surface, which might result in a lower orientation order. Thus, the structure formation dynamics of chain molecules of varying chain lengths ($N=20$, 30, and 40) were examined.

In Fig. 16, the surface coverage vs time and oriented domain ratio vs time curves of semirigid chain molecules of different chain lengths at high temperature ($T=15$) are shown. The growth of the surface coverage becomes slower for longer chain molecules, but the difference is small.

In general, the diffusion coefficient of a polymer chain is given by

$$D_G \sim \frac{k_B T}{\eta b} N^{-\nu}, \tag{8}$$

in which ν is approximately 0.5–0.6 [26]. Therefore, the diffusion of the molecule slows for longer chain molecules. If the adsorption dynamics are determined by molecular diffusion in the solution, the chain length might have a more remarkable effect. In this study, the polymer concentration was high and the difference of the diffusion coefficient does not appear significant. Thus, it is hypothesized that the weak N dependence of the surface coverage might result from other factors, such as relaxation of chain orientation or differences in the effective free surface area.

In contrast to the surface coverage, the growth of the oriented domain ratio shows faster ordering for longer chain molecules. In long-chain molecules, the attractive molecular interaction increases, accelerating the domain formation of adsorbed molecules.

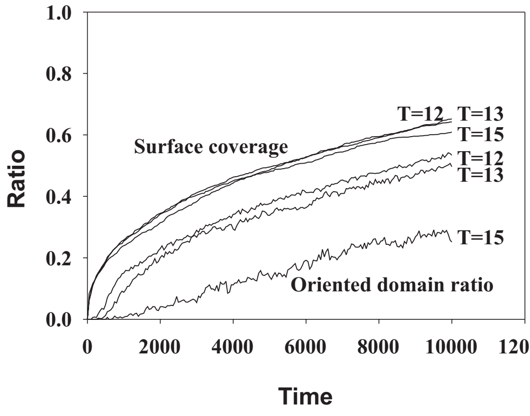


FIG. 11. Temperature dependence of surface coverage and oriented domain ratio over time for semirigid chain molecules.

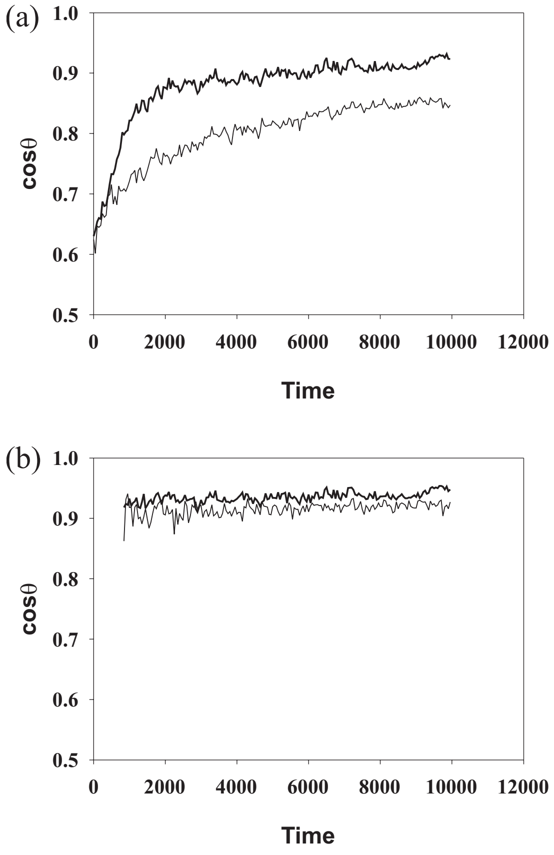


FIG. 12. The cosine of the tilt angle θ of chain molecules. (a) The average for chain molecules adsorbed on the surface. (b) The average for chain segments which belong to an oriented domain. The values at low temperature ($T=13$) are shown in bold lines, and the values at high temperature ($T=15$) are shown in thin lines.

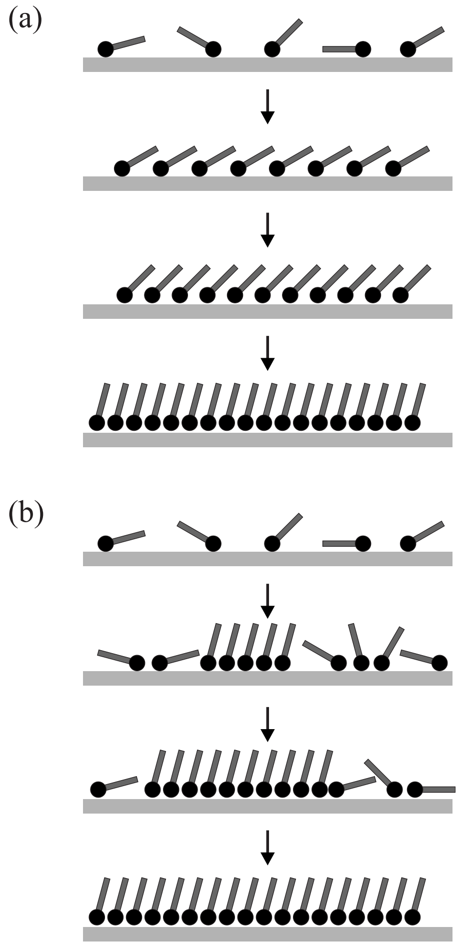


FIG. 13. Schematic picture of the order formation processes of chain molecules. (a) As the surface adsorption increases, the chain molecules are gradually packed. As a result, the chain molecules gradually "stand" on the surface. (b) Oriented domains of chain molecules are formed on the surface. As the surface adsorption increased, the domains become large. Within the oriented domain clusters, the chain molecules stand on the surface. The tilt angle inside the oriented domain is not drastically changed, although the average overall tilt on the surface may gradually increase by merging the chain molecules outside the domains.

There have been several reports concerning the chain length dependence of SAM formation dynamics, but the dynamics are quite complicated, and there remain many unresolved questions. In general, for fast initial kinetics, often ascribed to adsorption processes, the ordering speed is faster for shorter-chain alkyl systems [1,6–8]. On the other hand, for slow kinetics in intermediate periods, often ascribed to chain ordering processes, the ordering speed is faster for longer-chain alkyl systems [1,6]. Thus, the chain length dependence of the structure formation dynamics in these simulation results is consistent with the reported experimental results. However, there remains the possibility that there exists some optimum chain length for SAM formation, especially for flexible chain systems, since the surface adsorption may be inhibited by longer-chain molecules. In this simulation study, longer-chain systems cause association of chain molecules in solution, which results in the failure of efficient SAM formation. Except for these cases, clear inhibition of SAM formation from longer chains due to the behavior of chain molecules on the surface was not observed.

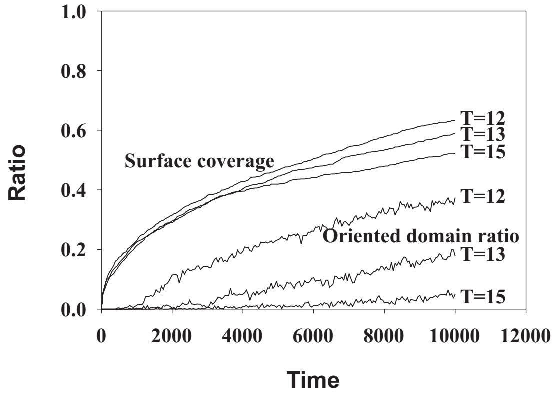


FIG. 14. Temperature dependence of surface coverage and oriented domain ratio over time for semiflexible chain molecules.

However, as shown in Fig. 17, when semiflexible chain molecules are used at high temperature ($T=15$), the growth of the oriented domain ratio is slightly inhibited for longer chains. There is also a large N dependence on the growth of the surface coverage. Since the difference is not significantly large for the duration of this simulation, further simulation for a longer period at more suitable conditions may be required for detailed analysis.

Thus, the dynamics of SAM formation of long-chain molecules involves complicated ordering processes, in which the internal degrees of freedom due to the long connectivity of chain molecules is coupled with the dynamics of adsorption and surface diffusion. This simulation study systematically reveals the effects of various factors such as flexibility, chain length, and temperature on the order formation dynamics. The microscopic details of the order formation processes,

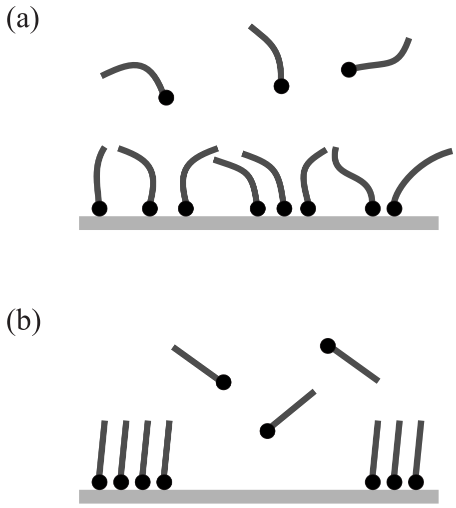


FIG. 15. Effect of chain rigidity on order formation processes on a surface. (a) Flexible chain molecules often randomly cover the surface, which may interfere with further adsorption of chain molecules. (b) For rigid chain molecules, the formation of ordered domains create free surface, which helps the highly ordered monolayers.

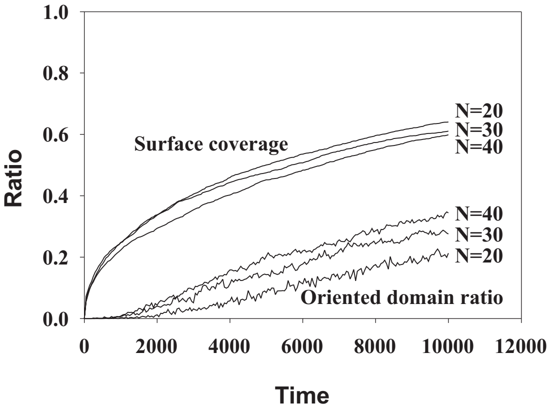


FIG. 16. Comparison of order formation for semirigid chain molecules of different chain lengths.

such as adsorption, domain formation, and orientation order parameters, were observed at once. These are not always easy to obtain in a single experiment, especially in the initial periods when surface coverage is small. In this simulation study, the surface-aligned state at low initial coverage periods was not observed, likely due to the weak chain-surface interaction parameters. It is hypothesized that when the chain-surface interaction assumes some appropriate value, the surface aligned order state might be possible before the formation of an upright, ordered SAM. However, the strong interaction between the middle segments of chain molecules and the surface would make the formation of a SAM extremely slow. The simulation would require further computational resources beyond the scope of the present simulation study. Another interesting point is the comparison of SAM formation in solutions with that in a vacuum. In the case of SAM formation from gaseous phases, the molecule concentration is extremely low in the bulk region. The lack of solvent molecules would reduce the screening effect of chain-chain interactions and the hydrodynamic effect. Since the adsorption process is a single chain problem, we suppose that the adsorption process would not be altered significantly especially in the initial period. On the other hand, the chain orientation and the growth of the oriented domain are driven by chain interactions. It might be expected that the highly ordered structures by the spontaneous domain formation would be easily realized in this condition. Both problems would be interesting to explore in the future. Since the simulation of slow ordering dynamics such as SAM formation requires a coarse-grained model and appropriate simulation conditions to carry out the calculations at present, this simulation study is but a single primitive step toward the full simulation of SAM formation dynamics. The understanding of these microscopic details of SAM formation dynamics will provide us useful hints for exploring the optimum conditions for structure control.

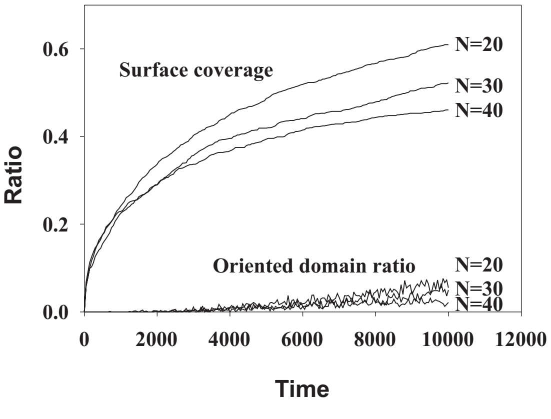


FIG. 17. Comparison of order formation for semiflexible chain molecules of different chain lengths.

IV. CONCLUSION

The ordering dynamics of self-assembled monolayers of long-chain molecules were studied using coarse-grained molecular dynamics simulations. The adsorption dynamics of SAM molecules can be explained by the same theoretical framework as the polymer brush, in which the diffusion limited adsorption and penetration limited adsorption play important roles. On the other hand, the evolution of highly oriented monolayer structure is specific to SAM systems, in which the chain-chain attractive interaction, chain stiffness, and surface diffusion control the order formation dynamics. For semirigid chain molecules at low temperature, the ordering dynamics are characterized by isolated island growth, in which oriented domains are formed spontaneously at the low surface coverage conditions found in the initial periods, and the ordering proceeds by growth of these island domains. In such conditions, a highly ordered monolayer is efficiently obtained. On the other hand, at high temperature, the formation of the oriented domain of chain molecules on the surface is not remarkable in the initial periods. In this case, the ordering dynamics are characterized by packing growth, in which the oriented domains are gradually formed due to the decrease in free volume as the surface density of chain molecules becomes high. During this order formation process, the righting of the average tilt angle of chain molecules that were adsorbed on the surface is quite slow, but the average tilt angles of chain molecules belonging to oriented domains took larger values that did not change significantly from the initial period to the intermediate period. This indicates that in the case of packing growth, the “standing up” of the chain molecules does not proceed gradually as a whole. The growth of the average tilt angle of adsorbed chain molecules is caused by an increase in packed domain areas. For semiflexible chain molecules, the ordering dynamics at low temperatures are similar to those of semirigid chain molecules, while at high temperature, there is different behavior. In this case, the chain molecules randomly cover the surface and the ordering processes are kinetically inhibited even when the oriented monolayer appears as if the surface were covered by these molecules completely. The effect of chain length on the ordering dynamics was also examined, and for semirigid chain molecules, longer chain systems showed slightly slower growth of the surface adsorption, but faster growth of the orientation order. These simulation results generally match the experimental. Therefore, the order formation dynamics of self-assembled monolayers of long-chain molecules have unique features, due to the effects of chain ordering and domain formation of adsorbed molecules on the surface. It has been demonstrated that control of chain flexibility and intermolecular interactions is important for the preparation of highly oriented SAM films.

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