

Monte Carlo simulation for the adsorption of symmetric triblock copolymers

II. Adsorption layer information

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Abstract

By using Monte Carlo simulation, adsorption of both end-adsorbed and middle-adsorbed symmetric triblock copolymers from a non-selective solvent on an impenetrable surface has been studied. Influences of the adsorption energy, the bulk concentration, the chain composition and the chain length on the adsorption behavior including the surface coverage, the adsorption amount and the layer thickness are presented. It is shown that the total surface coverage for both end-adsorbed and middle-adsorbed copolymers increases monotonically as the bulk concentration increases. The higher the adsorption energy and the more the attractive segments, the higher the total surface coverage is exhibited. Surface coverage θ decreases with increasing the length of the non-attractive segments, but the product of θ and the proportion of the non-attractive segments in a triblock copolymer chain is nearly independent of the chain length. The adsorption amount increases almost monotonically with the bulk concentration. The logarithm of the adsorption amount is a linear function of the reciprocal of the reduced temperature. When the adsorption energy is large, the adsorption amount exhibits a maximum as the composition of the attractive segment increases. The adsorption isotherms of copolymers with different length of the non-attractive segments can be mapped onto a single curve under certain energy indicating that copolymers with different chain length have the same adsorption amount. The adsorption layer thickness for the end-adsorbed copolymers decreases as the energy and the number of adsorbing segments increases. The longer non-attractive segments, the larger adsorbed layer thickness is found. The tails mainly govern the adsorption layer thickness.

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1. Introduction

Amphiphilic polymers are often adsorbed selectively on surfaces, with, e.g., the polar moieties are strongly adsorbed while the non-polar parts are effectively repelled from the surface. Generally, the adsorption behavior of triblock copolymers is naturally richer than

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that of diblock copolymers. Many of the recent studies, experimental [1–3], theoretical [4–7] and Monte Carlo simulations [7–10] on triblock chains have focused on the adsorption behavior.

In the first paper of this series, the density profiles, the mean size of the tails, the loops and the trains, as well as the size distributions of these adsorption configurations were depicted in detail by Monte Carlo simulations. In the second paper of this series, we will further provide simulation results including the surface coverage, the adsorption amount and the adsorption layer thickness for both end-adsorbed and middle-adsorbed symmetric triblock copolymers at a solid–liquid surface.

The whole paper is organized as follows: First, we give a brief description about the method to calculate the adsorbed layer information. Then, in the third section, the adsorption layer information including the surface coverage, the adsorption amount and the adsorption layer thickness for symmetric triblock copolymer are depicted in detail by using Monte Carlo simulation data. Finally, we present conclusions in the fourth section.

2. Calculation method

The type of molecular motion and the simulation algorithm was described in detail in our previous papers [11–13].

The adsorption amount Γ is defined as the average number of segments of the adsorbed chains per surface lattice site,

$$\Gamma = (N_a \times r) / (L_X \times L_Y) \quad (1)$$

where N_a is the number of the adsorbed chains with a chain length r on a surface, $L_X \times L_Y$ is the surface area or the total number of lattice sites on a surface.

The surface coverage θ is defined as the segment density or concentration at layer $Z = 1$ or $Z = L_Z$, i.e., $\theta = \phi_1$ or $\theta = \phi_{L_Z}$, θ_A and θ_B are the corresponding segment densities of the segments A and B, respectively. Various methods can be all used to calculate the adsorption layer thickness. We adopt the root-mean-square layer thickness employed by Scheutjens and Fleer [14] in this work.

$$\sigma^2 = \sum_{i=1}^L i^2 \phi_i / \sum_{i=1}^L \phi_i \quad (2)$$

where i is the consecutive number of layers, ϕ_i is the segment concentration in layer i . In the similar way, we can define the root-mean-square thickness due to the loops σ_{loop} and that due to the tails σ_{tail}

$$\sigma_{\text{loop}}^2 = \sum_{i=1}^L i^2 \phi_{i,\text{loop}} / \sum_{i=1}^L \phi_{i,\text{loop}} \quad (3)$$

$$\sigma_{\text{tail}}^2 = \sum_{i=1}^L i^2 \phi_{i,\text{tail}} / \sum_{i=1}^L \phi_{i,\text{tail}} \quad (4)$$

where $\phi_{i,\text{loop}}$ and $\phi_{i,\text{tail}}$ are the segment concentrations in layer i belong to loops and tails, respectively.

3. Results and discussion

Three categories of results including the surface coverage, the adsorption isotherms and the adsorption amount as well as the adsorption layer thickness, respectively, are presented. The influence factors are the adsorption energy, the chain composition, the bulk concentration and the chain length, the latter is adjusted by altering the number of non-adsorbing segments.

3.1. The surface coverage

Fig. 1 gives the surface coverage in different bulk concentration for $A_9B_6A_9$, where (A) for the end-adsorbed copolymers, (B) for the middle-adsorbed copolymers. The bulk concentration ϕ_b can be determined by averaging

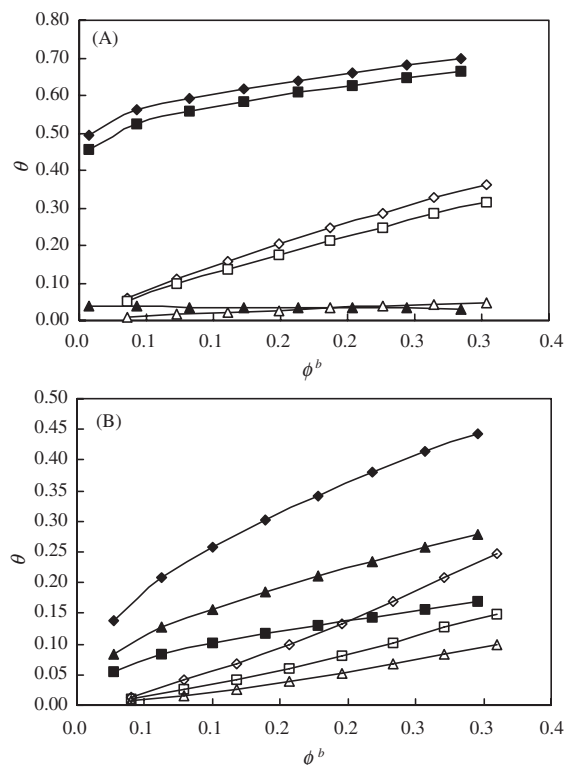


Fig. 1. Influence of bulk concentration on surface coverage for $A_9B_6A_9$. (A) $\tilde{e}_{Ba} = 0$, $\tilde{e}_{Aa} = 0.4$ (open symbols), $\tilde{e}_{Aa} = 1.2$ (filled symbols); (B) $\tilde{e}_{Ba} = 0$, $\tilde{e}_{Ba} = 0.4$ (open symbols), $\tilde{e}_{Ba} = 1.2$ (filled symbols); diamond: θ ; square: θ_A ; triangle: θ_B .

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