Studies on the Adsorption of Asymmetrical Triblock Copolymers by Scheutjens-Fleer Theory and Monte Carlo Simulation

PENG, Chang-Jun(彭昌军)　　　LI, Jian-Kang(李健康)　　　LIU, Hong-Lai*(刘洪来)
HU, Ying(胡英)

Department of Chemistry, The State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

The adsorption of asymmetrical triblock copolymers from a non-selective solvent on solid surface has been studied by using Scheutjens-Fleer mean-field theory and Monte Carlo simulation method on lattice model. The main aim of this paper is to provide detailed computer simulation data, taking $A_{8-k}B_{20}A_k$ as a key example, to study the influence of the structure of copolymer on adsorption behavior and make a comparison between MC and SF results. The simulated results show that the size distribution of various configurations and density-profile are dependent on molecular structure and adsorption energy. The molecular structure will lead to diversity of adsorption behavior. This discrepancy between different structures would be enlarged for the surface coverage and adsorption amount with increasing of the adsorption energy. The surface coverage and the adsorption amount as well as the bound fraction will become larger as symmetry of the molecular structure becomes gradually worse. The adsorption layer becomes thicker with increasing of symmetry of the molecule when adsorption energy is smaller but it becomes thinner when adsorption energy is higher. It is shown that SF theory can reproduce the adsorption behavior of asymmetrical triblock copolymers. However, systematic discrepancy between the theory and simulation still exists. The approximations inherited in the mean-filed theory such as random mixing and the allowance of direct back folding may be responsible for those deviations.

Keywords　　triblock copolymer, surface adsorption, Scheutjens-Fleer theory, Monte Carlo simulation

Introduction

During the past decades, the behavior of polymers near a surface has been one of main research topics in colloid science and polymer physics because of its great practical value. For example, it can be used to stabilize or destabilize colloidal particles, to improve or inhibit the deposition of particles on macroscopic surfaces. These studies can all adopt the experimental techniques and theoretical analysis as well as computer simulation method to corroborate each other.

In recent years, many studies have gradually focused on the adsorption properties of triblock copolymers. The adsorption behavior of triblock copolymer at interface has been studied in the literature by experimental[1-5] and theoretical[6-9] as well as Monte Carlo (MC) method.[10-13] Among theoretical treatments, Scheutjens-Fleer (SF) theory taken from random mixing approximation (RMA)[14,15] has attracted more attention because it can clearly distinguish different configurations such as train, loop and tail. However, the validity and reliability of theoretical model must be tested against experimental or MC results. Several examples for performing this test with MC results have been reported in the literature. Smith *et al.*[16] ever examined the conformations of

chains in polymer melts confined between surfaces by the lattice Monte Carlo simulation and compared their results with that from SF theory. Wang *et al.*[17] made a comparison between Monte Carlo simulation and SF theory but limited to homopolymers. They found that SF theory could reproduce major features of conformations, but quantitative differences between theory and simulation still existed. The effect of excluding direct chain back-folding from the mean-field theory has been performed by Simon[18] through the comparison with corresponding MC simulation. Although notable progresses have appeared for the study of adsorption of polymers at interface, the adsorption behavior by MC simulation and a comparison with SF theory for asymmetrical triblock copolymer at solid-liquid surface is rarely found in literature.

The core of this paper is to provide detailed computer simulation datum for asymmetrical triblock copolymer to study the influence of the structure of copolymer on the adsorption behavior and make a comparison between MC and SF results. Adsorption information including segment density profiles, adsorption amount, adsorption layer thickness, bound fraction, surface coverage, and size distributions of train, loop and

tail configurations, will be presented.

MC simulation method and SF theory

MC simulation method

Asymmetrical triblock copolymer molecules are modeled as self-avoiding linear chains and composed of m segments of A and n segments of B arranged as $A_{m-k}B_nA_k$ ($k=0, 1, \cdots, m/2$), segment A is assigned as the adsorbing segment and segment B is the non-adsorbing segment. The molecular structure can be distinguished by arranging the number of adsorbing segments in two ends. $A_kB_{20}A_{8-k}$ is an emphasis examined in this paper for saving content. Simulations are performed in a box of size $L_X \times L_Y \times L_Z = 50 \times 50 \times 50$ with periodical boundary conditions applied in both X and Y directions on a simple cubic lattice model. Impenetrable hard surfaces are located at layers $Z=0$ and $Z=L_Z+1$. Each segment of copolymer chain occupies one site. Those empty sites are considered to be occupied by a solvent molecule S. Adsorption energies be-

tween the surface and segments A are reduced by $-k_B T$ (k_B is Boltzmann constant) and designated by ε_{Aa}^*, while $\varepsilon_{Ba}^* = 0$. No energetic distinction between copolymer-copolymer and copolymer-solvent contacts is considered. The simulation algorithm and the calculations of adsorption information were described in detail previously[19,20].

Scheutjens-Fleer theory

In this work, we simply extend the original SF theory. Related details can be found in corresponding literatures.[14,15] The physical model of the SF theory is the same in simulation. For a given layer in cubic lattice, the fraction of the nearest neighbor sites of a certain position within the same layer is $\lambda_0 = 4/6$, and that in each adjoining layer is $\lambda_1 = 1/6$. For a copolymer solution adsorbed on a wall, the canonical partition function can be established in which the Flory-Huggins type interactions are assumed. The probability of finding a segment A and a segment B in layer i relative to that in bulk solution, *i.e.*, p_i^A and p_i^B, can be derived[14]

$$p_i^A = \frac{\phi_i^0}{\phi_*^0}\exp\left\{\chi_{AS}\delta_{1,i} + \chi_{A0}\left[(<\phi_i^A> - \phi_*^A) - (<\phi_i^0> - \phi_*^0)\right] + (\chi_{B0} - \chi_{AB})\left[<\phi_i^B> - \phi_*^B\right]\right\} \tag{1a}$$

$$p_i^B = \frac{\phi_i^0}{\phi_*^0}\exp\left\{\chi_{BS}\delta_{1,i} + \chi_{B0}\left[(<\phi_i^B> - \phi_*^B) - (<\phi_i^0> - \phi_*^0)\right] + (\chi_{A0} - \chi_{AB})\left[<\phi_i^A> - \phi_*^A\right]\right\} \tag{1b}$$

where ϕ is the volume fraction, χ is the Flory-Huggins interaction parameter (corresponding to ε^* in MC simulation), A, B, 0 and S stand for segment A, segment B, solvent and surface, respectively, * means bulk phase, and δ is a Kronecker function.

Through the "bridging" role of $p(s,i;r)$ (the probability that the sth segment of any chain of r segments finds itself in layer i), the segment volume fractions can be evaluated from free segment probability. Thus, for a given system the segment density profiles and the corresponding segment probabilities are determined self-consistently. Other properties can then be determined.[20]

The probability $p(s,i;r)$ has a simple relationship with the segment concentration after selecting the bulk solution as the reference state

$$\phi_i^k = \sum_{s=1}^{r}\phi_i^k(s) = \frac{\phi^*}{r}\sum_{s=1}^{r}p(s,i;r)\delta_{x(s),k} \quad (k=A, B) \tag{2}$$

To solve $p(s,i;r)$, it must first establish the relation between $p(s,i;r)$ and $p(i,r)$, and the latter is the probability of end segment of any chain of r segments in layer i.

$$p(s,i;r) = p(i,s)p_{inv}(i,r-s+1)/p_i \tag{3}$$

where $p_{inv}(i,r-s+1)$ is also the end segment probability like $p(i,s)$, but counts from the different side of the chain. The matrix procedure introduced by DiMarzio and Rubin[21] can establish the relation between the free segment probability and the end segment probability by the

recursion formula

$$p(i,r) = p_i[\lambda_1 p(i-1,r-1) + \lambda_0 p(i,r-1) + \lambda_1 p(i+1,r-1)] \tag{4}$$

Note that the above derivation involves an implicit approximation: the copolymer is modeled as a first-order Markov chain. The probability distribution of the end segment is only a function of the position of the previous segment, namely, the direct chain back-folding is not prohibited here.

Results and discussion

### Total density profiles and the surface coverage

Figure 1 shows the total segment density profiles Φ_Z of triblock copolymer $A_{8-k}B_{20}A_k$ obtained from Monte Carlo simulation (scattered data points) and the corresponding SF theory (solid curve) with chain concentration of system $\Phi_C = 0.0024$ and $\varepsilon_{Aa}^* = 1.0$. The simulated results show that the segment density in the beginning would become smaller gradually as k varies from zero to 8. This tendency is kept until at $Z=7$. Once Z is greater than 8, the position of the density profiles will be reversal. It means that the total segments decrease near interface but increase apart from surface as molecular symmetry increases. The figure also shows that SF theory can reproduce the major features of the total segment density profiles as compared to the simulation results. Generally, the SF theory calculations are in quite good agreement with MC data near the place in the bulk solution about 8 layers away from the surface. However,

deviations of theoretical predictions from the simulation results become more obvious for the region near the surface.
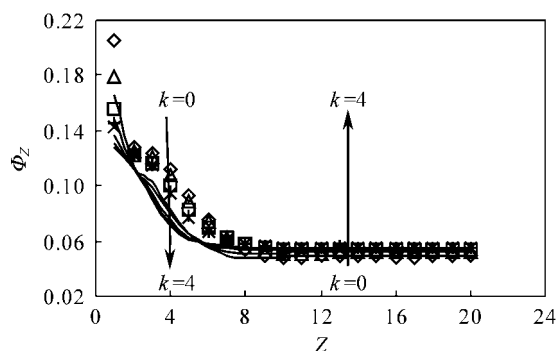
Figure 1 The total segment-density profiles for $A_{8-k}B_{20}A_k$ when $\varepsilon_{\mathrm{A}a}^{*} = 1.0$ and $\Phi_C = 0.0024$. $k=0$ (diamond), 1 (triangle), 2 (square), 3 (plus), 4 (cross), MC results. Line: corresponding SF results.

Figure 2 shows a comparison of the total surface coverage θ obtained from MC simulation and SF theory for $A_{8-k}B_{20}A_k$ with $\varepsilon_{\mathrm{A}a}^{*} = 0.5$ (A) or $\varepsilon_{\mathrm{A}a}^{*} = 1.0$ (B) under different bulk concentration ϕ_b, where, the surface coverage θ is defined as the segment density or concen-
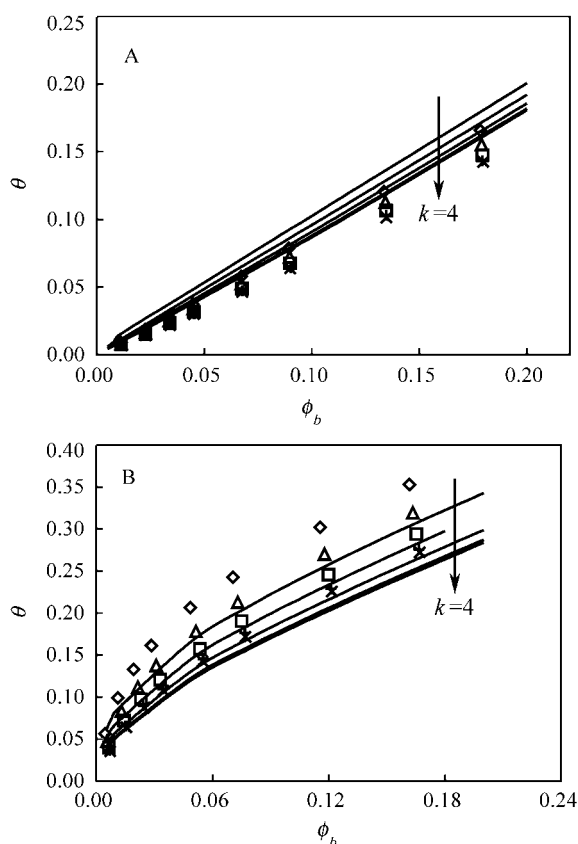
Figure 2 The surface coverage as a function of the bulk concentration for $A_{8-k}B_{20}A_k$ when $\varepsilon_{\mathrm{A}a}^{*} = 0.5$ (A) and $\varepsilon_{\mathrm{A}a}^{*} = 1.0$ (B). $k=0$ (diamond), 1 (triangle), 2 (square), 3 (plus), 4 (cross): MC results. Line: corresponding SF results.

tration at layer $Z=1$ or $Z=L_Z$.

When the adsorption energy is smaller, says $\varepsilon_{\mathrm{A}a}^{*} = 0.5$, SF theory overestimates the segment density in the first adsorption layer, *i.e.* the surface coverage θ. However, when the adsorption energy is relatively large, for example $\varepsilon_{\mathrm{A}a}^{*} = 1.0$, the calculation exhibits a totally different trend, which underestimates the segment density in the adsorption layer as compared to the simulation result. It is guessed without difficulty that the mean-field calculation agrees with the simulation a little well if the adsorption energy is moderate. On the other hand, the molecular structure leads to a difference of the surface coverage. This discrepancy would be enhanced with increasing of the adsorption energy and is proved by both MC simulations and SF calculations.

Size distributions of various adsorption configurations

Figure 3 shows both the SF and MC simulation results on the size distributions of trains, loops and tails for $A_2B_{20}A_6$ when $\varepsilon_{\mathrm{A}a}^{*} = 1.0$ and $\Phi_C = 0.0024$. Larger deviation between the theory and the simulation has been found for the train configuration. When $\varepsilon_{\mathrm{A}a}^{*}$ is small, the size distribution of trains by the simulation has a peak at $L=2$, where L is the size of configuration. The number of trains with one segment is much lower than that by the theoretical calculation, because in the simulation the one-segment train configuration can only occur in the two ends of absorbed polymer chains. However, the corresponding peak by the theory is at $L=1$. Because of the allowance of direct chain back-fold, the size distributions of trains in the theoretical calculation always show a maximum at $L=1$ under different $\varepsilon_{\mathrm{A}a}^{*}$. With increasing $\varepsilon_{\mathrm{A}a}^{*}$, the size distribution of trains by the simulation has another peak at $L=6$, which is just the length of long attractive block. It implies that the long adsorbing block favors to be whole adsorbed onto surface when the adsorption energy is higher. The position of second peak could be reproduced by SF theory, but the predicted value is much lower than that in the simulated results except for $L=1$.

The results of MC simulation show that the size distribution of loops always has a peak at $L=2$, which im-
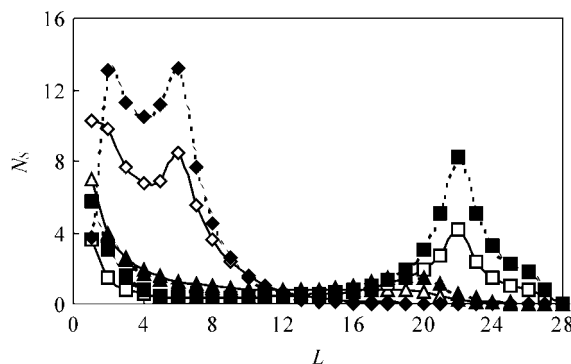
Figure 3 The distributions of trains (diamond), loops (triangle) and tails (square) for $A_2B_{20}A_6$ when $\varepsilon_{\mathrm{A}a}^{*} = 1.0$ and $\Phi_C = 0.0024$. Dashed line: MC results; solid line: corresponding SF results.

plies that the smallest loop of 2 segments is the most likely configuration in adsorption layers. The number of loops monotonically decreases firstly and then increases with the increase of the size L, finally shows the second peak at $L=20$, which is just the length of middle block. However, in the theoretical results, the size distribution of loops has a peak at $L=1$ instead of 2. This is due to the allowance of direct chain back-folding which makes the loop with single segment length possible. However, direct chain back-folding is not allowed in MC. The number of different size obtained from SF theory is lower than that from MC simulations. The theory does not reproduce the second peak of loop configuration at $L=20$, either.

The size distribution of tail obtained from SF theory shows qualitative agreement with the result of MC simulation. The size distribution profile is bimodal. The first peak appears at $L=1$, which comes from the contribution of segment A, while the other peak appears at $L=22$, which is just the sum of the length of a middle and a shorter block. The theoretical prediction coincides with the simulation result well, but only peak intensity is smaller than that of MC simulations. The underestimation of the number of long tails implies that the adsorption layer predicted by the theory is more compressed than that in simulation.

The effect of adsorption energy on the size distribution of tails configuration is very interesting. Under different energy, distribution is totally changed for a given structure. Figure 4 shows size distributions of tails for $A_8B_{20}A_{8-k}$ by MC simulations. The figures show that the size distribution of tails is more than one peak. The first peak all appears at $L=1$. The location of the other peaks depends on the molecular structure. When $k=0$, it is at $L=20$, indicating that entire non-adsorbing block extends to the bulk phase. For copolymer of $k\neq0$, it should shows another two peaks: one is at $L=20+k$, the other at $L=20+(8-k)$, indicating that one of the two A blocks is fully adsorbed leaving the block B and the other block A as a tail. It can be observed easily from the figures that the curve of distribution would give two turning points at $L=20+k$ and $L=20+(8-k)$, if $k\neq4$, when energy is relatively small. However, for a system with a higher energy, the curve only exhibits one turning point at $L=\text{mix}[20+k, 20+(8-k)]$. It implies that the shorter adsorbing block has almost the same chance to meet surface compared to the longer one when energy is small, but the longer absorbing block has a higher chance to adsorb onto surface than the shorter one when energy is higher.

For a given adsorption system, so called equilibrium state means that with the lowest free energy. The free energy of system is determined by both contribution of energy and entropy. They are two opposite effects on free energy of system. If more segments are adsorbed onto surface, the energy should be decreased. However, the conformation entropy is also decreased because segments are orientated near surface. If the adsorbed energy between segments and the surface is lower, the
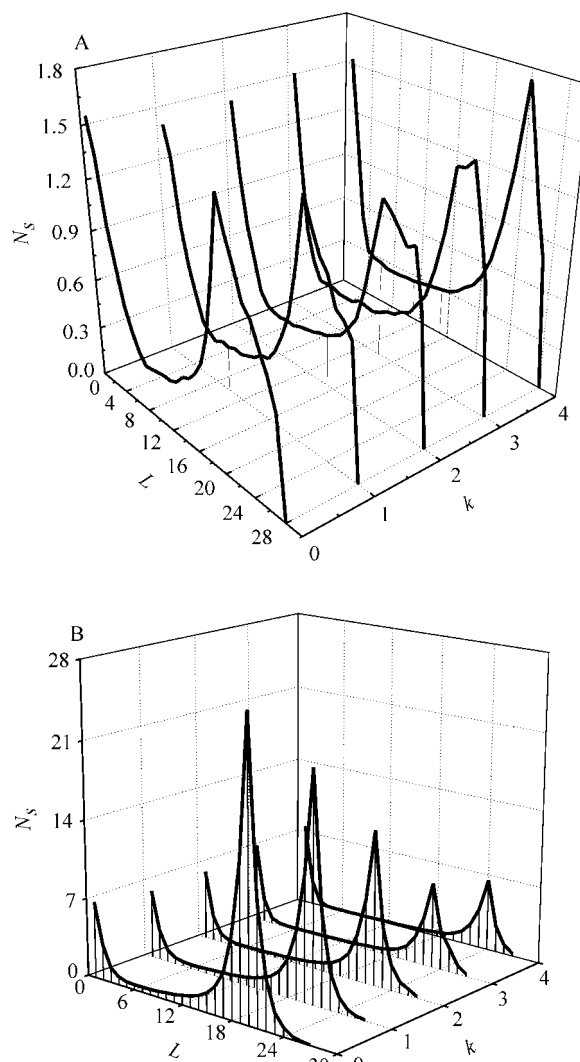

Figure 4 MC simulation of size distributions of tails for $A_8B_{20}A_{8-k}$ when $\Phi_C=0.0024$ and $\varepsilon_{Aa}^*=0.5$ (A) and $\varepsilon_{Aa}^*=1.5$ (B).

depression of the energy due to the adsorption of segments is limited. However, if copolymer chains are dispersed into system, the conformation entropy of system will be then largest and result in the free energy being lowest. Therefore, the contribution of the entropy to free energy is dominating for a system with lower adsorbed energy. Contrarily, the depression of the energy due to the adsorption of segments is dominating for a system with higher adsorbing energy. This is a reason why distribution would give two turning points for a system with lower adsorption energy but only one turning point when adsorption energy is higher. The curves of Figure 4 have been reproduced by SF theory, and only peak intensity is smaller than that of MC simulations.

The adsorption amount

The adsorption amount, Γ, which is the average number of segments of those adsorbed chains per surface lattice site, obtained from MC simulation and SF theory for $A_{8-k}B_{20}A_k$ with adsorption energy $\varepsilon_{Aa}^*=0.5$ and $\varepsilon_{Aa}^*=1.0$ at different bulk concentration is depicted

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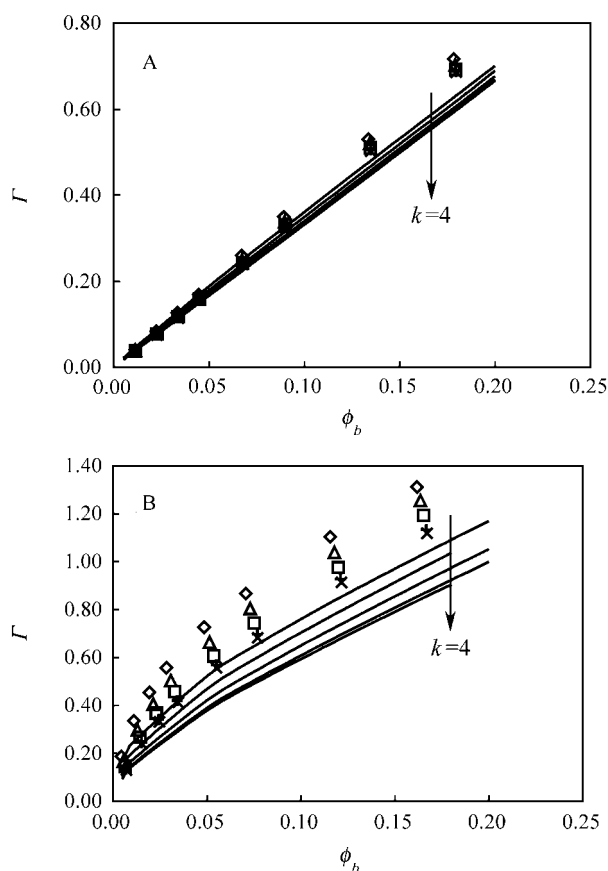
in Figure 5.

Figure 5 The adsorption amount as a function of the bulk concentration for $A_{8-k}B_{20}A_k$ when $\varepsilon^*_{Aa} = 0.5$ (A) and $\varepsilon^*_{Aa} = 1.0$ (B). $k=0$ (diamond), 1 (triangle), 2 (square), 3 (plus), 4 (cross): MC results. Line: corresponding SF results.

The discrepancy of the adsorption amount due to the difference of molecular structure is not large if the adsorption energy is small; however, it would be enhanced with increasing of the adsorption energy. With the increase of bulk concentration, adsorption amount increases, too. However, with different sets of ε^*_{Aa}, the pattern of increase of adsorption amount with the bulk concentration is also different. If the adsorption energy is small and thus the total adsorption energy of copolymer system is small, adsorption is weak and both the theory and MC simulation indicate that the adsorption amount Γ increases almost linearly with the bulk concentration, as shown in Figure 5 (A). Only the adsorption isotherm calculated by SF theory is a little lower than that of simulation. As can be seen from the figures, the shape of adsorption isotherm will change as ε^*_{Aa} changes. The adsorption amount first increases rapidly and then slowly with the increase of ϕ_b. Both the theory and the simulation have the same trend. It was seen again that the theoretical predictions still show a negative deviation in adsorption amount as compared to MC results. The bigger the ε^*_{Aa}, which implies the increase of total adsorption energy, the worse the agreement between SF theory and MC simulation.

It was found that the biggest adsorption amount is achieved by $A_{8-k}B_{20}A_k$ when $k=0$, and the smallest by $A_{8-k}B_{20}A_k$ when $k=4$, indicating that the adsorption amount of diblock is greater than that of triblock at the same bulk concentration. This observation may be inconsistent with the conclusion of some literatures. For example, Haliloglu et al.[13] found by simulation that, at low ϕ_b, the adsorbed amount is greater for $A_{m/2}B_nA_{m/2}$ than for A_mB_n because the surface has a higher chance to meet any one of the two sticky ends belonging to a triblock than only one end of the diblock copolymer chain. However, our results obtained by not only MC but also SF shows clearly that the adsorbed amount is commonly greater for A_8B_{20} than that for $A_4B_{20}A_4$. This is because $A_4B_{20}A_4$ has more chance to form bigger loop configuration when both the two ends are attractive, and loop configuration will counteract more attractive segments approaching surface. In other words, a series of loop configurations can lead to screening effects near the interface, and the adsorbed amount then decreases whether adsorption energy is higher or smaller.

The bound fraction and adsorption layer thickness

The theoretical prediction and MC result for bound fractions P of $A_{8-k}B_{20}A_k$ as a function of bulk concentration are shown in Figure 6 (A) when $\varepsilon^*_{Aa} = 0.5$ and Figure 6 (B) when $\varepsilon^*_{Aa} = 1.0$, respectively, where, the bound fraction P is defined as the average contact proportion of adsorbed chains. It can be seen that qualitative agreement between MC simulations and SF calculations can be found. Both SF theory and MC simulation show that the bound fractions increase when the adsorption energy is smaller but decrease when energy is bigger as bulk concentration increases. Only the bound fractions calculated by SF theory are greater than those of simulation. The more asymmetric the molecular is, the larger the bound fractions will be achieved, which can be reproduced by SF theory.

The adsorption layer thickness σ of $A_{8-k}B_{20}A_k$ versus bulk concentration is depicted in Figure 7 (A) when $\varepsilon^*_{Aa} = 0.5$ and Figure 7 (B) when $\varepsilon^*_{Aa} = 1.0$, respectively. The corresponding SF results are shown in the same figures too. The adsorption layer thickness decreases when $\varepsilon^*_{Aa} = 0.5$ but increases for $\varepsilon^*_{Aa} = 1.0$ with the increase of bulk concentration. The theory predicts nearly the same pattern of change as the simulation does. However, considering the fact that tails play a more important role in determining the thickness of adsorption layer, the adsorption layer predicted by the theory should be thinner than that by simulation due to the underestimation of the number of long tails by the theory. It was found by not only MC but also SF that the adsorption layer thickness will become thicker when the adsorption energy is smaller but thinner when the adsorption energy is larger as the molecule gradually changes symmetry.
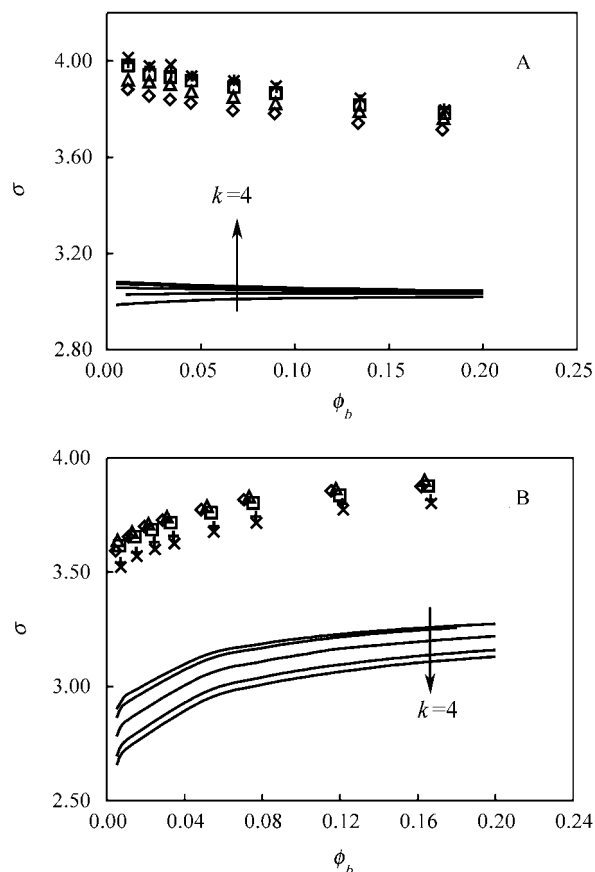
The MC results show that the diversity of fraction and adsorption layer thickness of different molecular
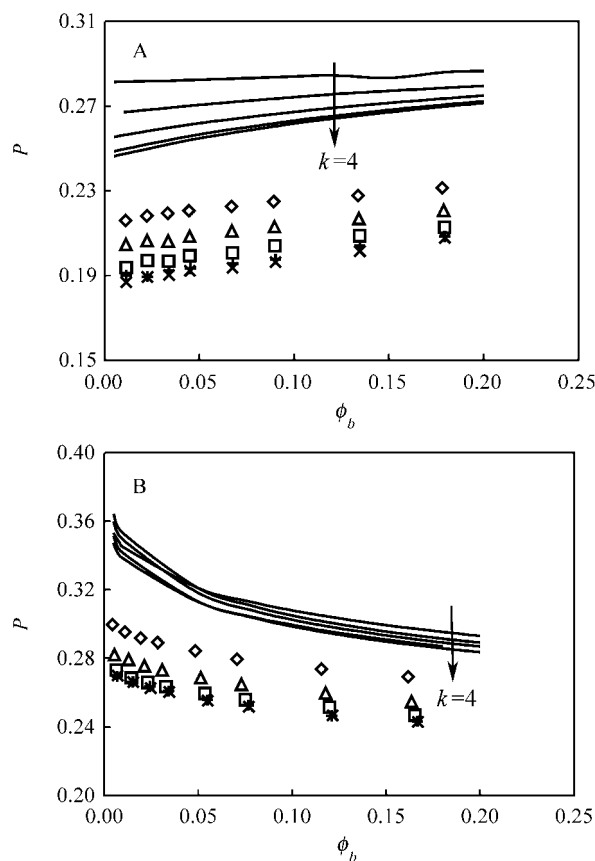
Figure 6 The bound fraction as a function of the bulk concentration for $A_{8-k}B_{20}A_k$ when $\varepsilon^*_{Aa} = 0.5$ (A) and $\varepsilon^*_{Aa} = 1.0$ (B). $k = 0$ (diamond), 1 (triangle), 2 (square), 3 (plus), 4 (cross): MC results. Line: corresponding SF results.

Figure 7 The adsorption layer thickness as a function of the bulk concentration for $A_{8-k}B_{20}A_k$ when $\varepsilon^*_{Aa} = 0.5$ (A) and $\varepsilon^*_{Aa} = 1.0$ (B). $k = 0$ (diamond), 1 (triangle), 2 (square), 3 (plus), 4 (cross): MC results; Line: corresponding SF results.

structure is not enlarged as adsorption energy increases. Contrarily, they are lessen a bit. The SF theory can reflect the influence of energy to change tendency of bound fraction but is overestimated. On the other hand, when energy is smaller, differences of layer thickness between different molecules are diminished by mean-filed theory. But they are magnified when energy is higher compared to MC results.

From the above discussion, despite the qualitative agreement except for the size distribution of train and loop configuration, quantitatively, the results predicted for other adsorption behavior by SF theory exhibits a systematic deviation compared with the MC simulation results. Analogical conclusion can be obtained by studying other $A_{m-k}B_nA_k$. As Wang *et al.*[17] discussed, this difference between SF theory and MC simulation can be mainly attributed to the intrinsic random mixing approximation (RMA) in SF theory and the allowance of direct chain back-fold. The former approximation ignores the fact that polymer chains on the surface are localized, namely well separated, instead of delocalized. The latter approximation contradicts the fact that every lattice site can only be occupied by one polymer segment. So the two approximations will inevitably introduce certain errors, as compared to the result of simulation.

The SF theory ignores the difference of segment probability P_i in the same lateral layer parallel to the surface due to RMA. With RMA, the theory takes average of the probabilities in the same lateral layer, so the excluded volume effect inside absorbed chain domain is underestimated. As a result, the excluded volume interaction of the segments within the same chain is also underestimated by the theory, which thus results in an overestimation of the bound fraction, P, as shown in Figure 6. Contrarily, the excluded volume effect between chains outside absorbed chain domain is overestimated due to RMA. Because this excluded volume effect can affect directly chains of the bulk phase adsorbed on the surface, the number of chains adsorbed thus is underestimated by the theory. Namely, the adsorption amount, Γ, is under-predicted as shown in Figure 5. Moreover, extent of underestimation for Γ is higher than that of overestimation for P, the surface coverage, following $\theta = P*\Gamma$, is usually underestimated (see Figure 2 (B)), as compared to the result of simulation.

However, when the adsorption energy is small, or system is in a dilute concentration, the errors due to RAM can be ignored, but the errors are always in existence due to the direct chain back-fold. This allowance of chain back-folding could become a dominating factor

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and would increase the probabilities of chains being adsorbed. The number of chains adsorbed can be then not underestimated and so much as be overestimated slightly by the theory, the surface coverage, following $\theta = P * \Gamma$, is thus usually overestimated, which has been illustrated in Figure 2 (A).

Conclusion

We investigated the surface adsorption behavior of asymmetrical triblock copolymers using a Monte Carlo simulation and made a comparison with the SF theory. The results simulated show that molecular structure has an influence on the size distribution of trains, loops, tails configuration, and total segment-profile. The more asymmetric the molecular is, the larger the surface coverage and the adsorption amount as well as bound fraction will be achieved. In other words, the corresponding smallest value will be given when molecular structure is totally symmetry. The adsorption layer becomes thicker when energy is smaller but thinner when energy is higher with increasing of symmetry of the molecule. The difference of molecular structure and the adsorbing energy would bring up differerent segment density profiles and configuration distributions. The difference of the surface coverage and adsorption amount due to structure would be enlarged with increasing of adsorption energy. Though our study shows that there are some systematic deviations between the SF theory and the MC simulation, we still find that the calculations are in qualitative agreement with Monte Carlo simulation data. The SF theory can reproduce main features of asymmetrical triblock copolymer's adsorption as compared to the simulation. The systematic deviation between the SF theory and Monte Carlo simulation can be primarily attributed to the allowance of the direct chain back-folding and RMA.

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