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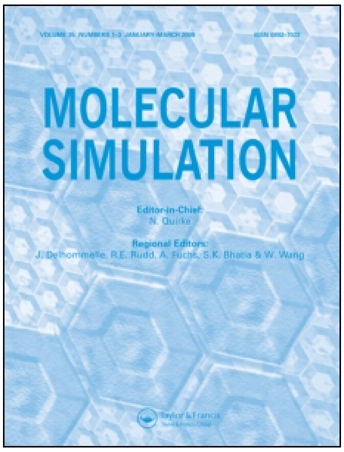

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Adsorption Behavior of Polydisperse Polymeric Systems

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Adsorption Behavior of Polydisperse Polymeric Systems

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Adsorption behavior of polydisperse polymers at interfaces is studied by the Monte Carlo simulation method based on a lattice model. Effects of temperature and adsorption energies on the polymer density profile, cluster distributions and adsorption layer thickness are evaluated in two different polydisperse systems. It is found that adsorption properties are greatly different in these two systems. In normal distribution polydisperse systems, polymers are more sensitive to the excluded volume effects while in average distribution polymers are more inclined to adsorb on adsorbing interfaces. As higher temperature and lower attraction constrain the polymer adsorption, more clusters are found under these conditions. When temperature approaches the critical temperature of monodisperse systems, stable and large clusters exist in these two polydisperse systems. These results suggest that micro phase transition may exist in polydisperse systems. Polydisperse systems take little change of phase transition temperatures but altered the clusters morphology to some extent. The adsorption layer thickness changes are more sensitive to both temperature and polymer–interface interactions in average distribution systems when the whole polymer concentration increases slightly. This work also suggests significant differences between the polydisperse and the monodisperse systems in adsorption behavior. Therefore, quantitative system errors may exist when the monodisperse system models are used in simulation to evaluate polymer adsorption properties.

Keywords: Polydisperse polymer; Polymer adsorption; Monte Carlo simulation; Molecular dynamics simulation

INTRODUCTION

Polymer adsorption at interfaces has attracted continuous interests for both theoretical and practical importance. Many effective computational simulation methods like Monte Carlo (MC), molecular dynamics (MD) simulations were developed [1–10]. Detailed information like the density profile [11], conformation information [12], phase transition point [13] and many other important properties can be well evaluated with these methods. But most models used monodisperse polymeric system and uniform interface with unrealistic simplifications.

During the past few years, attention has been made to more realistic models, and several different models were introduced. Wang *et al.* [8,14] and Jiang *et al.* [15] introduced different models with polydisperse polymers containing binary and quaternary mixtures of monodisperse polymers into simulation. Apparent conformation differences were found for different polymers. But this was just an approximation, in contrast with some definite distributions of polymers existing in nature. It is difficult to introduce polydisperse polymeric system in simulation and theory. Finite polymer differences still could not model the real distributions of polymers and polydisperse models should be introduced.

In this paper, polymers with normal and average distributions are introduced into physical adsorption models. The adsorption properties, especially the total density profile, cluster distributions, and adsorption layer thickness are evaluated in detail.

SIMULATION METHODS

Simulations were performed in a canonical ensemble. Linear chain molecules of different sizes are modeled by self-avoiding walks on a cubic lattice with height (L_Z), length (L_X) and width (L_Y), typically being 64(sites) × 64(sites) × 64(sites). Periodic boundary conditions are applied in x, y directions. Either one solvent molecule or one polymer segment occupies one lattice site. The interactions between

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solvents are ignored. So solvent sites should be considered as holes. There are two parallel planes $z = 0$ and $z = L_Z + 1$ that polymer cannot penetrate. The $z = 0$ surface is the adsorbing interface with attractive energies to polymer segments. The $z = L_Z + 1$ surface is the non-adsorbing interface with no interaction to polymer segments at all.

The random variable $\xi' = \xi \times b + \bar{N}_B$, which follows the normal distribution N ($\bar{N}_B$, b) [16], is generated. Here,

$$\xi = \sum_{i=1}^{12} r_i - 6 \tag{1}$$

$\bar{N}_B$ is the average chain length of polymers, b is the variance and r_i is a random number between 0 and 1.

We use $N_B \in [A, C]$ to denote an average distribution system. It implies that the chain lengths of polymers are located in the region $[A, C]$. It is possible to have a polymer with random integral chain length in this region.

Simulation begins by introducing polymers into the simulation box with the modified Rosenbluth–Rosenbluth [17] growing method. After that four different motions are carried out for relaxation. They are Verdier–Stockmayer motion [18] (0.5) including end-rotation, L-flip, crankshaft motions and slithering snake motion [19] (0.5). Values in round brackets are the corresponding selection probabilities. After about 1×10^8 moves, the systems are in equilibrium and the statistic data of the subsequent 4×10^7 steps give the final results.

In this work, the reduced value of interaction energy ε_P/kT° between polymer segments is set to 1. The reduced value of attraction energy between adsorbing interface and polymer segment is denoted as $\varepsilon^* = \varepsilon_i/kT^\circ$. The reduced temperature T^* equals T/T°. Polymer segment density ϕ_Z is described by the following equation

$$\phi_Z = N_Z/(N_C \times \bar{N}_B) \tag{2}$$

where T° is the temperature of referenced state, k is Boltzmann constant, ε_P is the interaction energy between polymer segments of different molecules, and ε_i is the interaction energy between adsorbing interface and polymer segments. N_C is the number of polymer chains and N_Z is the total number of polymer segments at the zth layer of lattice box.

RESULTS AND DISCUSSION

Total Density Profiles in Different Polydisperse Systems

Effects of Temperature

The density profiles of polymers at different temperatures are shown in Fig. 1. A few differences are found in polymer density profiles in these two distribution systems. In normal distribution systems, the excluded volume effects are much stronger near the non-adsorbing interface, which gives a larger change in the density profile near the non-adsorbing interface. The polymer segment density near adsorbing interface is much higher in average distribution systems than that in normal distribution systems. Polymer segment density near the interface changes greatly with temperature. Because the whole polymer concentration for different systems is unified, there is little difference in the polymer density profiles in solution. But the polymer segment density near the adsorbing interface will decrease when temperature rises as high temperature constrains free vibration of polymer segments near the interface. When the whole polymer concentration decreases, polymer segments with more proportion are inclined to adsorb on the adsorbing interface. The density profiles near the critical temperature 2.1 of monodisperse systems [13,20] are also shown as dashed lines in Fig. 1. Apparent oscillations are found in density profiles, which suggest existence of clusters in these systems. We can also observe this in the later discussion of cluster distributions.

Effect of Polymer–Interface Interactions

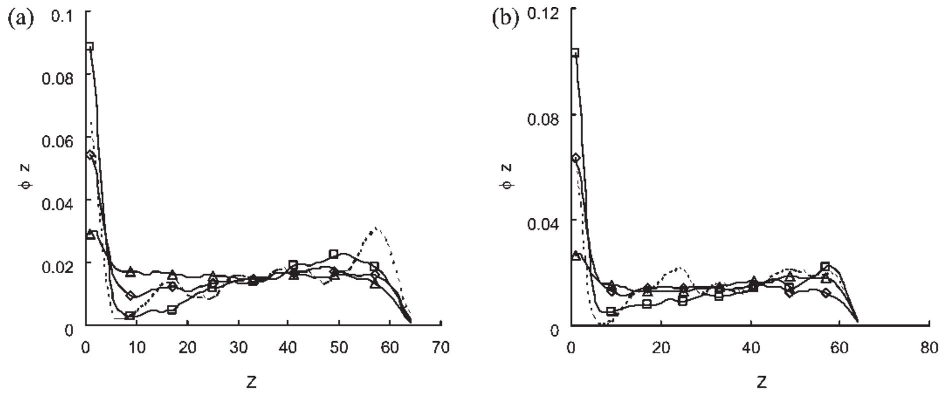
The density of polymer segment near the interface increases sharply when polymer–interface interactions go up, as in Fig. 2. In contrast with earlier studies [7,11], the density profile changes with temperature and interface attractions with nearly the same trend as monodisperse systems. But, as mentioned above, the polymer segment density differs in these two polydisperse systems. Quantitative differences exist between monodisperse systems and polydisperse systems.

Cluster Distributions in Different Polydisperse Systems

Effect of Temperature

A cluster is defined as a group of polymers, each of which has at least s segments neighboring another polymer in the same group in a polymer solution. In this work, we assigned s as 1. The cluster size is the number of polymers in the group. Figure 3 gives the results of cluster distribution at different temperatures.

In Fig. 3, the x-axis represents how many polymer molecules are in a cluster, and y-axis represents the number of this kind of cluster. There is a similarity between the two different polydisperse systems. Free single molecules take a dominant role under all conditions. The larger the clusters of one kind,



Solid line: $\varepsilon^*=1.5, T^*=$ □ -3.1; ◇ -4.1; △ -5.1;

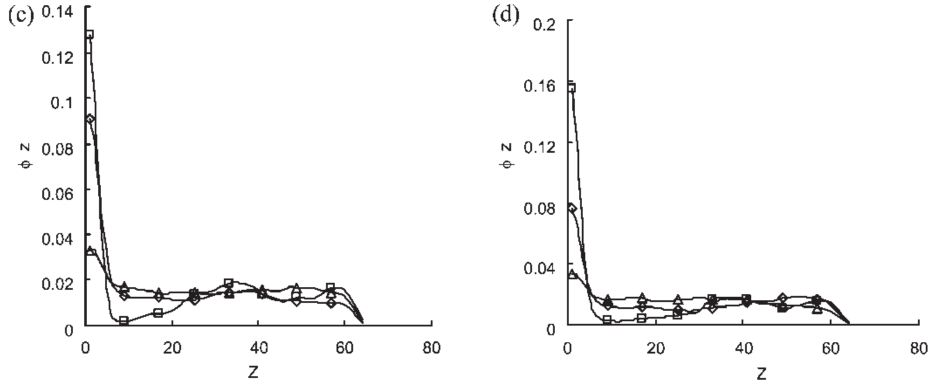
Dashed line: $\varepsilon^*=1.5$,T=2.1

Normal distribution N (64,2), $N_C = 200$

Solid line: $\varepsilon^*=1.5, T^*=$ □-3.1; ◇-4.1; △-5.1;

Dashed line: $\varepsilon^*=1.5$,T=2.1

Average distribution $N \in [54,73]$, $N_C = 200$

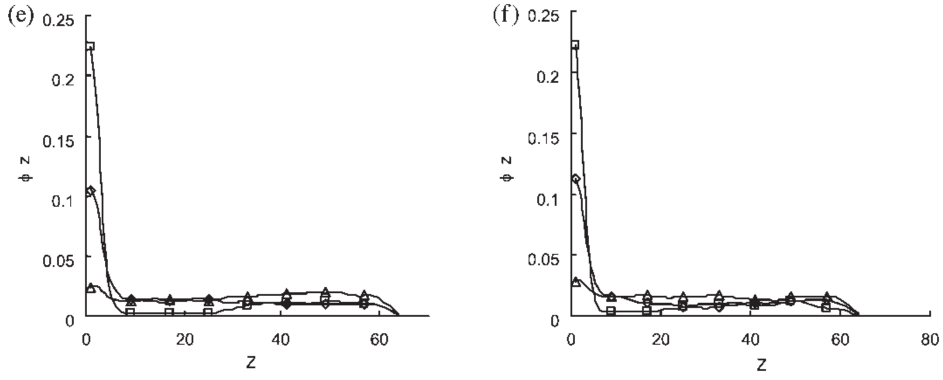


$\varepsilon^*=1.5, T^*$: □-3.1; ◇-4.1; △-5.1;

Normal distribution N (64,2),$N_C = 100$

$\varepsilon^*=1.5, T^*$: □-3.1; ◇-4.1; △-5.1;

Average distribution $N \in [54,73]$, $N_C = 100$



$\varepsilon^*=1.5, T^*$: □-3.1; ◇-4.1; △-5.1;

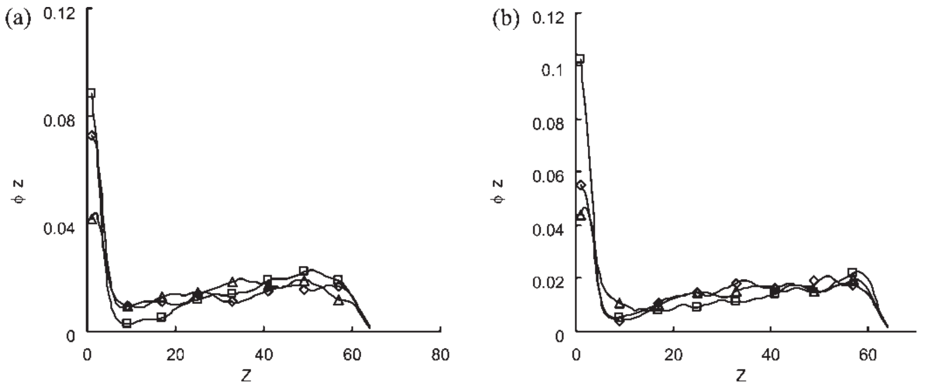
Normal distribution N (64, 2), $N_C = 40$

$\varepsilon^*=1.5, T^*$: □-3.1; ◇-4.1; △-5.1;

Average distribution $N \in [54,73]$, $N_C = 40$

FIGURE 1 Effect of temperature on density profile in different polydisperse systems.

the fewer their quantities. When the total polymer concentration is slightly high (in dilute polymer solution), the size distribution of clusters changes little with temperature. But as the total polymer concentration decreases, the number of clusters at a given size increases rapidly with temperature. The reason is that at higher temperatures the vibration of polymer segments accelerates. This is not helpful to the polymer adsorption. It is found that there are more small clusters in normal distribution systems. In the "Effects of temperature" section, apparent oscillations in polymer segment density are found near the critical temperature

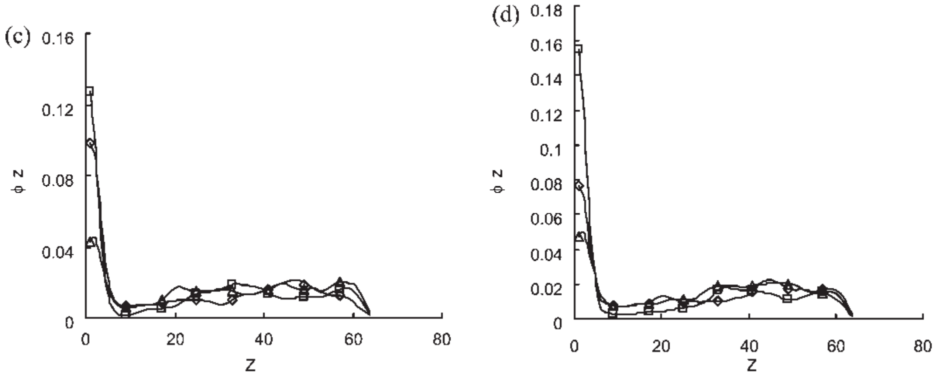


$T^* = 3.1$, ε^*: □-1.5; ◇-1.2; △-1.0

Normal distribution N [64, 2], $N_C = 200$

$T^* = 3.1$, ε^*: □-1.5; ◇-1.2; △-1.0

Average distribution $N \in [54,73]$, $N_C = 200$

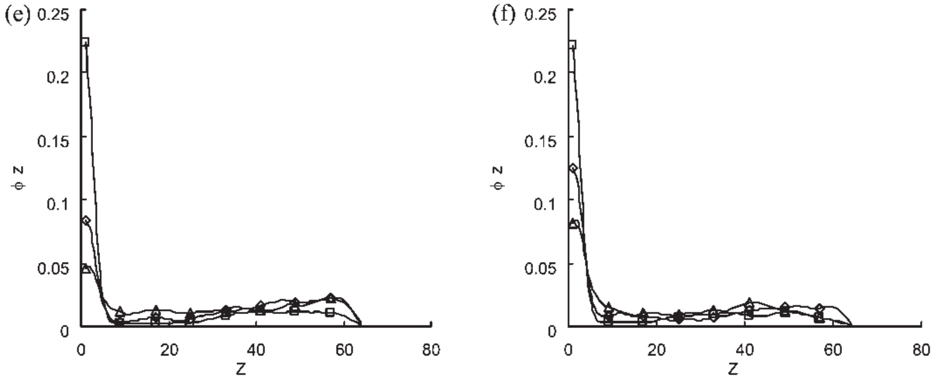


$T^* = 3.1$, ε^*: □-1.5; ◇-1.2; △-1.0

Normal distribution N [64, 2], $N_C = 100$

$T^* = 3.1$, ε^*: □-1.5; ◇-1.2; △-1.0

Average distribution $N \in [54,73]$, $N_C = 100$



$T^* = 3.1$, ε^*: □-1.5; ◇-1.2; △-1.0

Normal distribution N [64, 2], $N_C = 40$

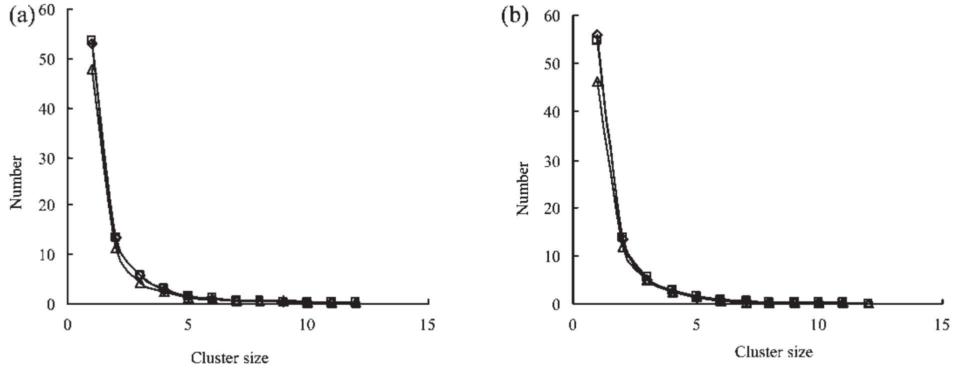
$T^* = 3.1$, ε^*: □-1.5; ◇-1.2; △-1.0

Average distribution $N \in [54,73]$, $N_C = 40$

FIGURE 2 Effect of polymer–interface interaction in different polydisperse systems.

of monodisperse system. The distribution of clusters in solution at this temperature of 2.1 are evaluated in Fig. 4.

Yan *et al.* [13,20] gave the model phase transition points of homopolymer adsorption at interfaces. But few theoretical works reported the phase transition phenomenon of polydisperse polymers. In this work, it is found that when temperature approaches 2.1 (the critical temperature at polymer concentration 0.05 and $\varepsilon^* = 1.5$ in monodisperse polymeric systems [13,20]), there are stable and larger clusters that exist in polydisperse systems. In average distribution systems, the large cluster size is much bigger than that in normal distribution systems. Polydisperse systems led to few changes of phase transition temperatures but altered the morphology of clusters to some extent. Sometimes

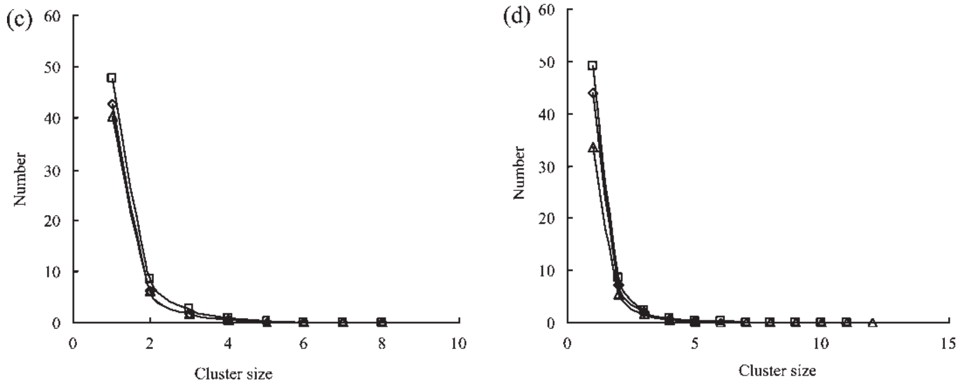


Solid line: $\varepsilon^* = 1.5$, $T^* =$ □-5.1; ◇-4.1; △-3.1

Normal distribution N [64, 2], $N_C = 200$

$\varepsilon^* = 1.5$, T^*: □-5.1; ◇-4.1; △-3.1

Average distribution $N \in [54,73]$, $N_C = 200$

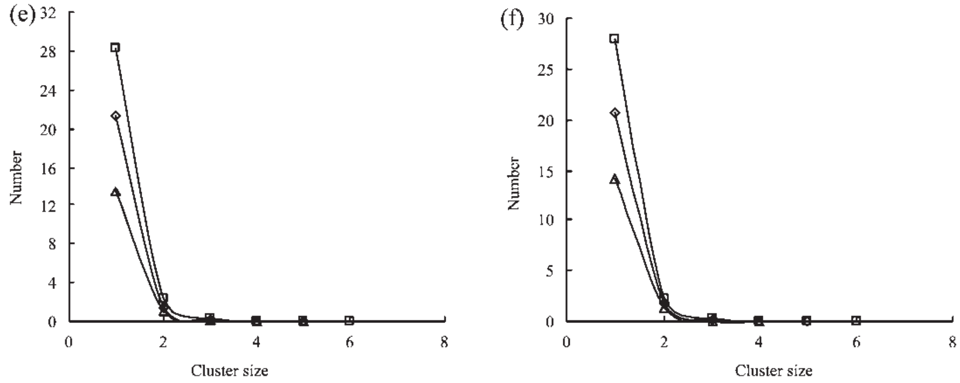


$\varepsilon^* = 1.5$, T^*: □-5.1; ◇-4.1; △-3.1

Normal distribution N [64, 2], $N_C = 100$

$\varepsilon^* = 1.5$, T^*: □-5.1; ◇-4.1; △-3.1

Average distribution $N \in [54,73]$, $N_C = 100$



$\varepsilon^* = 1.5$, T^*: □-5.1; ◇-4.1; △-3.1

Normal distribution N [64, 2], $N_C = 40$

$\varepsilon^* = 1.5$, T^*: □-5.1; ◇-4.1; △-3.1

Average distribution $N \in [54,73]$, $N_C = 40$

FIGURE 3 Effect of temperature on clusters in solution.

this difference in morphology can cause distinct properties in different polydisperse polymeric systems.

Effects of Polymer–Interface Interactions on Cluster Distributions

When the total polymer concentration is slightly high (in dilute polymer solution), only a few differences with the polymer–interface interaction are found in cluster distribution, as in Fig. 5. As the total polymer concentration decreases, the number of clusters at a given size decreases rapidly with the polymer–interface interaction because there are more polymer segments adsorbed on the adsorbing interfaces.

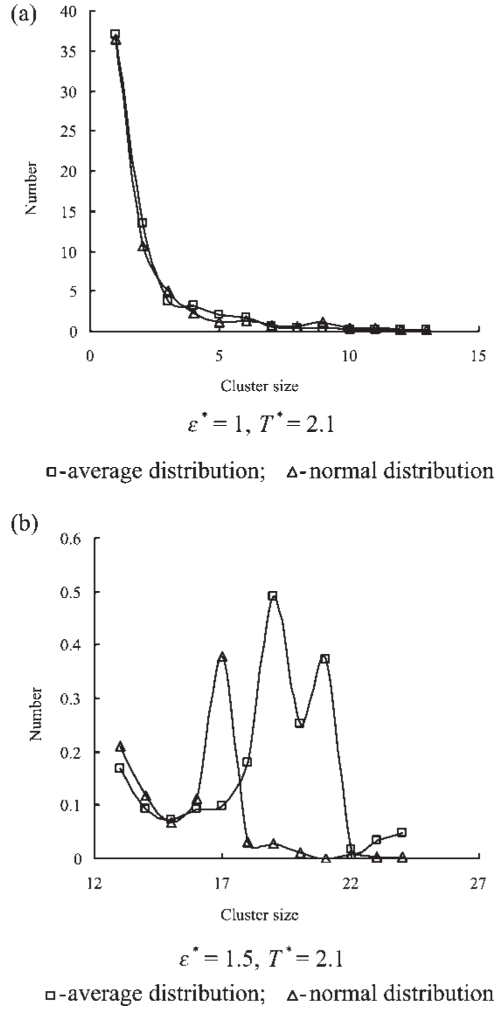


FIGURE 4 Cluster distribution near critical temperature of monodisperse systems.

Adsorption Layer Thickness

As the adsorbed polymers lies in those aggregates at the adsorbing interfaces, the adsorption layer thickness U can be easily obtained. We define projection percentage as $\psi(U) = N_U/(64 \times 64)$, where N_U is the number of projecting sites on the adsorbing interface of a certain specific layer thickness.

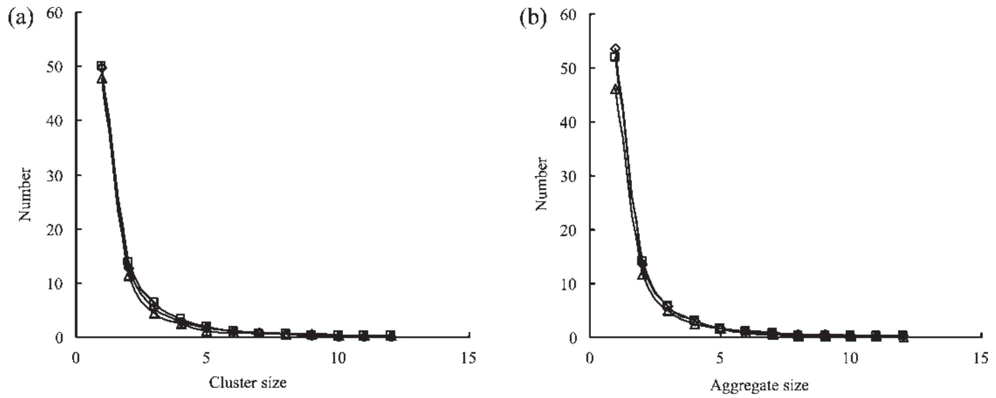
It is found that the projection percentage is at maximum values when adsorption layer thickness equals the length of two polymer segments, as in Fig. 6. The projection percentages of the little adsorption layer thickness decrease with temperature but opposite tendencies are found for large adsorption layer thickness. The reason is that at high temperature, the increased vibration of polymer segments and polymers prefer to form stand-up tails or loops conformations [15]. Figure 6 also shows the opposite effects of different polydisperse systems on adsorption layer thickness at different temperatures. When the total polymer concentration is slightly high ($N_c = 200$ or 100) the adsorption layer thickness changes more sensitively with temperature in average distribution systems. When temperature is lower, the density of little adsorption layer thickness is much bigger in average distribution systems. But the density of little adsorption layer thickness is much bigger in normal distribution systems when temperature is high. When the total polymer concentration decreases ($N_c = 40$), there are nearly no differences between these two polydisperse systems. Many factors like temperature, polymer–interface interactions and spatial constriction may affect the adsorption layer thickness. But when the total polymer concentration is low enough, the spatial constriction can be omitted for much lower coverage of polymer segments at adsorbing interfaces. In this work, we shall find that when N_c equals 40 the coverage of polymer segments on adsorbing interfaces is less than 0.10 even at lower temperatures. Therefore, there are nearly no spatial constrictions. This is the reason that tends to appear differently in Fig. 6(c). This work also indicates that most differences between polydisperse systems are related to the space constriction of polymer segments.

Apparently, the attraction energies of adsorbing interface will benefit the adsorption of polymers and compress the adsorbing layer. Figure 7 shows that the projection percentage of little adsorption layer thickness will increase with polymer–interface interactions and the projection percentage of large adsorption layer thickness moves in the opposite way.

CONCLUSIONS

(1) Tendencies in adsorption behaviors in polydisperse systems are consistent with those in monodisperse ones. But quantitative difference may still exist between these two systems. Polymer segment density near adsorbing interface will decrease with rising temperature or decreasing polymer–interface interactions. When the total polymer concentration increases slightly, only a little change in cluster distribution with temperature or polymer–interface interactions is found. Once the total polymer concentration is low enough, the number of small clusters will increase rapidly with rising temperature or decreasing polymer–interface interactions.

(2) Adsorption properties are different in two polydisperse polymeric systems. In normal distribution polydisperse systems, polymers are more sensitive to the excluded volume effects while average distribution polymers are more inclined to adsorb on adsorbing interfaces. The adsorption layer thickness is more sensitive to temperature and polymer–interface interactions in average distribution systems when the whole polymer concentration increases

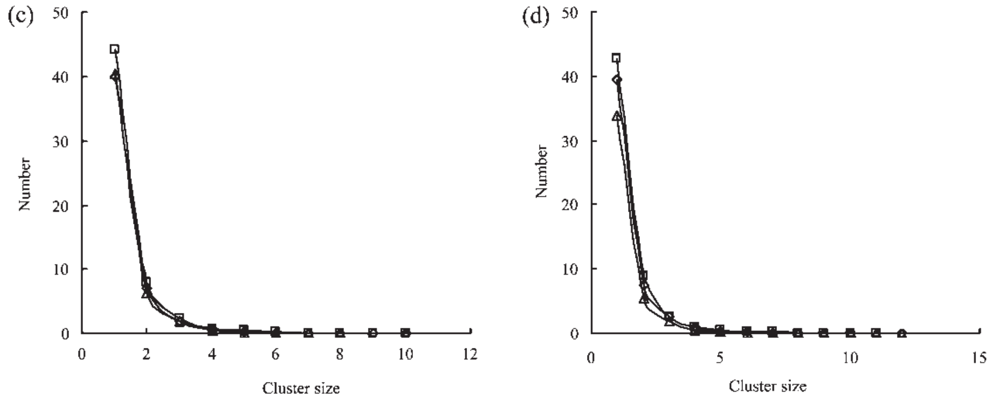


$T^* = 3.1$, ε^*: □-1.0; ◇-1.2; △-1.5

Normal distribution N [64,2], $N_C = 200$

$T^* = 3.1$, ε^*: □-1.0; ◇-1.2; △-1.5

Average distribution $N \in [54,73]$, $N_C = 200$

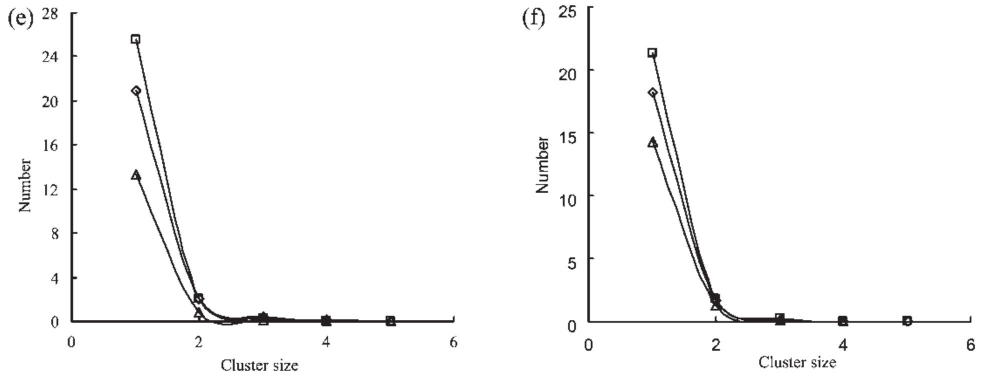


$T^* = 3.1$, ε^*: □-1.0; ◇-1.2; △-1.5

Normal distribution N [64, 2], $N_C = 100$

$T^* = 3.1$, ε^*: □-1.0; ◇-1.2; △-1.5

Average distribution $N \in [54,73]$, $N_C = 100$



$T^* = 3.1$, ε^*: □-1.0; ◇-1.2; △-1.5

Normal distribution N [64, 2], $N_C = 40$

$T^* = 3.1$, ε^*: □-1.0; ◇-1.2; △-1.5

Average distribution $N \in [54,73]$, $N_C = 40$

FIGURE 5 Effect of polymer–interface interaction on clusters in solution.

slightly. It is found that the conformation difference of these two polydisperse polymeric systems is related to spatial constriction of polymer segments to a large extent.

(3) The micro phase transition may exist in polydisperse systems. When temperature approaches the critical points of monodisperse systems, stable and large clusters are found in both polydisperse systems. The size of clusters is bigger in average distributions systems. These also suggest that polydisperse polymeric systems change little in phase transition temperatures but alter the morphology of clusters to some extent compared with monodisperse polymeric systems.

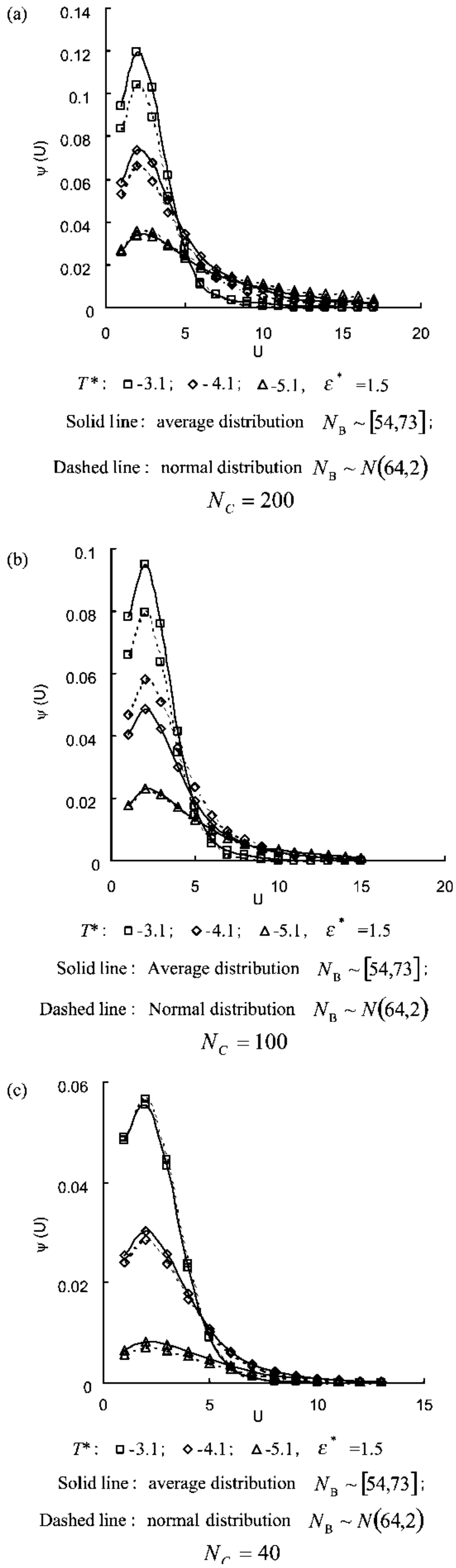


FIGURE 6 Effects of polydisperse systems on adsorption layer thickness at different temperatures.

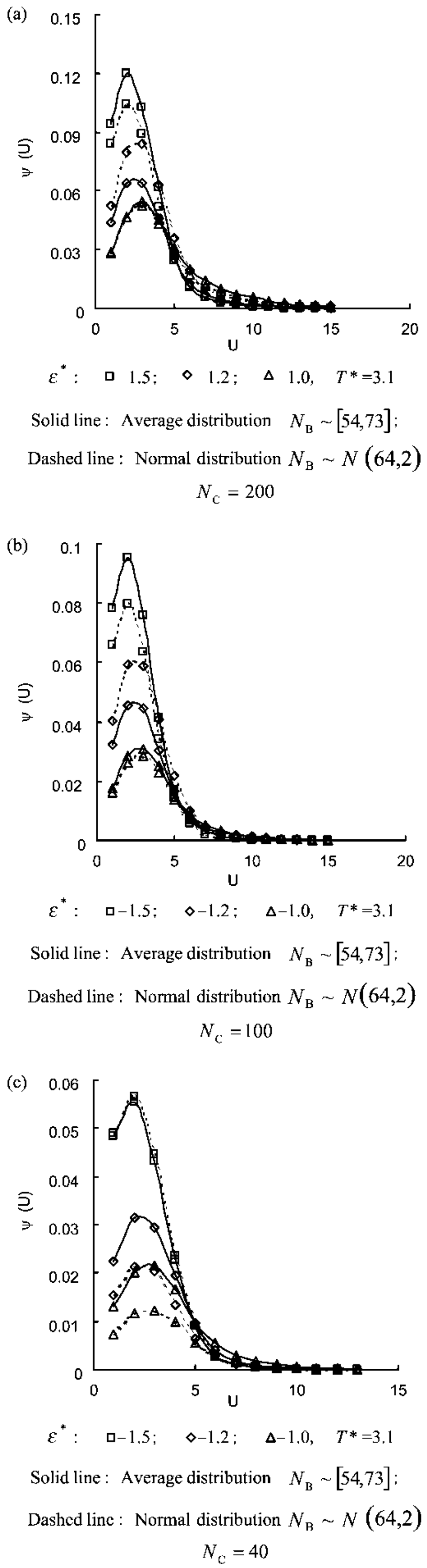


FIGURE 7 Effects of polydisperse systems on adsorption layer thickness at different polymer–interface interaction.

(4) Data from all our results indicate that differences for polymer adsorption properties between monodisperse and polydisperse systems are not negligible. It is essential to introduce polydisperse systems into computer simulation and other investigations.

Acknowledgements

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