Computer Simulation of Multiblock-Copolymers in Presence of Colloidal Particles

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SUMMARY: The results of Monte Carlo computer simulation of systems containing AB-copolymer chains and colloidal particles are presented. The regular multiblock copolymers were studied, and the strong dependence of the shape of formed structures on the block length in the primary structure of copolymer chain was obtained. For system with long blocks of monomeric units the microphase separation and well-defined microstructures were observed. The colloidal particles and the attracting monomeric units of copolymer chains form the "pumice-stone"-like structure. In this structure colloidal particles look like bubbles in massive aggregate of attracting monomeric units. On the contrary, for short blocks no microstructures were formed, and polymer chains formed a well distributed spatial structure like a web.

Introduction

Synthetic and natural polymers are often used as stabilizers of colloidal systems (sols, dispersions, micellar solutions, etc.). The property of polymers to affect strongly the aggregation and kinetic stability of colloidal particles has found a wide use in food industry and in pharmacology.

In the systems of polymer chains and colloidal particles different microstructures are formed that can be studied experimentally by high precision methods (in particular, by small-angle neutron scattering). For example, Cabane and Duplessix [1, 2)] have shown that in semidilute solution long enough macromolecules can join up to 300 ionic surfactants micelles forming structure like a "necklace".

The formation of aggregates of polymer chains and colloidal particles has been also studied theoretically. The scaling mean field results were obtained by Klimov and Khokhlov [3)]. As

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they have shown in their work, when particles are fixed in space the polymer chain takes a strongly elongated conformation. In contrast to this, when adsorption occurs on moving particles the chain takes a conformation similar to a typical conformation of a free chain in solution.

In the works [4, 5] the detailed theoretical study of interaction of colloidal particles with macromolecules in solutions was carried out using the integral RISM equation technique. It was shown that upon increasing the concentration of polymers the tendency to aggregation of colloidal particles normally increases. The diagram of states for polymer/colloid system was constructed, i.e. the regions of stabilization and flocculation of colloidal particles by polymer chains were determined.

Along with theoretical and experimental studies of polymer-containing colloidal systems the lattice Monte Carlo computer simulations of polymers in solution of colloidal particles has been performed recently [6-9] for some particular choices of interactions parameters. Namely, the formation of complexes of polymers and colloidal particles has been discussed for the case of non-selective adsorption of homopolymer chains [6-8] (i.e., when all monomeric units of a polymer chain can adsorb on colloidal particles) and for the case of selective adsorption of telechelic chains [9] (i.e., when only monomeric units at both ends of a polymer chain can adsorb on colloidal particles). In this paper we present our results on continuum Monte Carlo computer simulation of systems containing AB-copolymer chains with multiblock primary structure and colloidal particles.

The adsorption of polymers on colloidal particles essentially differs from adsorption of polymers on flat surface [10,11]. This is connected with the small size of colloidal particle (its size can be of order or even much less than the gyration radius of polymer chain) which leads to strong deformation of polymer chains adsorbing on the particle and hence to large energies of excluded volume. The second difference from adsorption on flat surface is that the surface of colloidal particle is very small, therefore the concept of adsorption capacity of colloidal particle should be considered. On the other hand, when system contains many colloidal particles their total surface is sufficiently large to adsorb all monomeric units. All these facts lead to formation of different structures that consist of polymer chains and colloidal particles: it is possible that one colloidal particle is a matrix for adsorption of several polymer chains, another possibility is that one polymer is adsorbed on several colloidal particles. The type of

these structures depend on different parameters such as temperature, potentials of adsorption etc. In this paper we consider the dependence of type of formed structures on primary structure of AB-copolymer in the case of selective adsorption of monomeric units. We study the influence of the block length of copolymer chain on the complex formation.

Model and method of computation

The computer simulation was performed in continuum space by using Monte Carlo method. The cubic cell with periodic boundary conditions was used [12,13]. In spite of larger computational time the continuum model occurs to be more suitable for this task because of small size of colloidal particle and the possibility of blocking of motion of polymer chains in concentrated systems.

For polymer chain we used the model with fixed bond length [14]. The elementary move for one monomeric unit was its rotation around the axis connecting the left and the right neighbor units along the chain (see fig.1). The "slithering-snake" algorithm was also used for polymer chains to accelerate the equilibration. The colloidal particle was presented by the sphere of radius that was twice the radius of a monomeric unit.

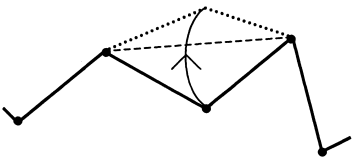

Fig. 1. Model of polymer chain with fixed length of bond

The polymer chain consists of blocks of monomeric units of two different types. The monomeric units of type A (hereafter A-units) are "neutral" and do not interact with each other and with other particles. Monomeric units of type B (B-units) attract to each other and to colloidal particles. The primary structure of the polymer chain, i.e. the sequence of monomeric units A and B along the chain, was the main parameter in the simulation. The other parameters were the strengths of Lennard-Jones potentials for interaction between B-units and between B-units and colloidal particles. The length of polymer chain was equal to 40 monomeric units. The number of colloidal particles was taken to be approximately equal to the number of polymer chains. The total volume fraction of polymer chains and colloidal particles was equal to 0.1.

We have studied 18 different systems. The simulation of each system has taken 40 million of Monte Carlo steps (about 160 hours on Pentium Pro – 200 MHz computer). The systems were

grouped in three series with six systems in each one. In each system the potentials of interaction were fixed and the primary structure of polymer was changed. The primary structures for each system in all series are presented in Table 1. The composition of A and B monomeric units for all polymers was fixed and equal to 1:1. The interaction parameter ε (the strength of the Lennard-Jones potential) for each series are presented in Table 2.

Table 1. Primary structures for polymer chains in each series

# of system in series	Pattern of primary structure
1	BBBBBBBBBBAAAAAAAAAAAAAAAAAAAABBBBBBBBBB
2	AAAAAAAAAABBBBBBBBBBAAAAAAAAAABBBBBBBBBB
3	BBBBBBBAAAAAAAAAABBBBBBAAAAAAAAAABBBBBBB
4	AAAAABBBBBAAAAABBBBBAAAAABBBBBAAAAABBBBB
5	AAAABBBBAAAABBBBAAAABBBBAAAABBBBAAAABBBB
6	AABBAABBAABBAABBAABBAABBAABBAABBAABBAABB

Table 2. Parameter ε for potentials for the systems studied

# of series	ε for interaction between B-units	ε for interactions between B-units and colloidal particles
1	1.0	10.0
2	10.0	10.0
3	10.0	1.0

The following characteristics were studied in computer simulation:

– the mean-squared radius of gyration and the mean-squared distance between the chain ends;

– the mean number and size of aggregates of B-units;

– the mean number of contacts between monomeric units and colloidal particles;

– the pair-correlation function for different types of particles;

– the diffusion coefficients for all types of particles and for center of mass of polymer;

– the acceptance rate.

Results and discussion

The most interesting results were obtained for first series, where the interaction between B-units was weak and the attraction of B-units to colloidal particles was strong. For this series a strong dependence of type of formed structures on primary structure was obtained. In figures 2 and 3 the snapshots of structures for systems #1 and #6 in series #1 are presented where B-

units (small size) and colloidal particles (large size) are colored in more dark color than A-units (small size). As it can be seen from these figures, for system with large blocks of

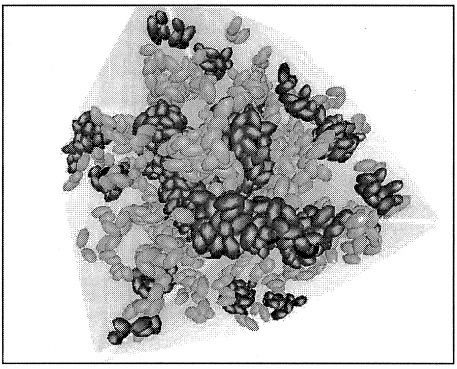

Fig. 2. Snapshot of system #1 in series #1

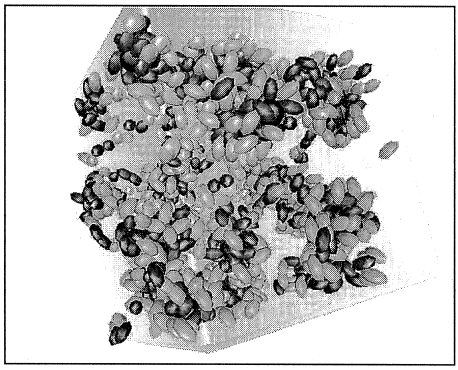

Fig. 3. Snapshot of system #6 in series #1

B-units the microphase separation and well defined microstructures were obtained. On the contrary, for short blocks no microstructures were formed, and polymer chains formed a well distributed spatial structure like a web. In both cases the colloidal particles form the basis of aggregates and are located inside of aggregates of B-units (this is the reason why they are hardly visible). On the other hand, in series #2 and #3 colloids do not participate in formation of aggregates. In series #2 colloidal particles are located on the surface of the aggregates, and in series #3 colloidal particles move independently of B-units.

Based on the results of our simulation we can make the following conclusions. Aggregates of B-units for copolymers with large size of blocks in series #3 are two times smaller than aggregates in series #1. At the same time, with the decrease of the size of blocks this effect is also decreasing and for copolymers with small block size the average size of aggregates of B-units in series #3 is twice as large as that in series #1. This effect is shown in figure 4.

This effect arises as consequence of participation of colloidal particles in formation of aggregates of B-units in series #1. When the block of B-units is large it can cover several colloidal particles, but it does not cover all their surface, and so other block can adsorb on the same colloidal particles. Therefore, many large blocks form a large aggregate. On the contrary, when the block is small it can cover only one colloidal particle, and therefore in one aggregate there can be only one colloidal particle and the aggregates are small but their number increases (see fig. 5). In series #2 and #3 the colloidal particles do not participate in

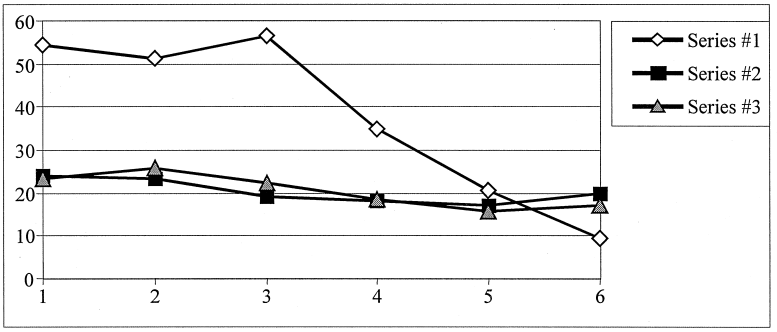

Fig. 4. Dependence of the average size of aggregates of B-units on the size of the blocks (on the x-axis the numbers of systems are shown, with increasing this number the size of blocks decreases).

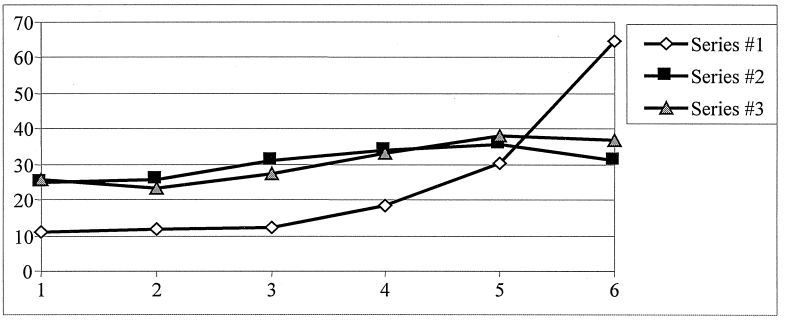

Fig. 5. Dependence of the number of aggregates of B-units on the size of the blocks (on the x-axis the numbers of systems are shown, with increasing this number the size of blocks decreases).

formation of aggregates and hence their size does not depend on the size of blocks so strong. A small decrease of size of aggregates can be explained by the increasing of steric interaction when small blocks form aggregate of the same size as large blocks.

In all series, when decreasing the size of the blocks, the diffusion coefficient of A-units is reduced strongly (see fig. 6). At the same time the diffusion coefficient of B-units varies slightly (see fig. 7). It can be explained by the fact that B-units are frozen in aggregates and practically do not move. A-units can move freely but when the size of the blocks decreases the freedom of its motion becomes more limited due to the connection of B-units along the chain. Due to this fact the diffusion coefficient of the center of mass of polymers is also decreasing but slightly slower. The diffusion coefficients of colloidal particles do not vary in all series when primary structure is changed, but they vary a lot in different series. Thus, for series #1 it is about 6×10^{-7}, for series #2 it equals to 5×10^{-6} and for series #3 it is 2×10^{-2}.

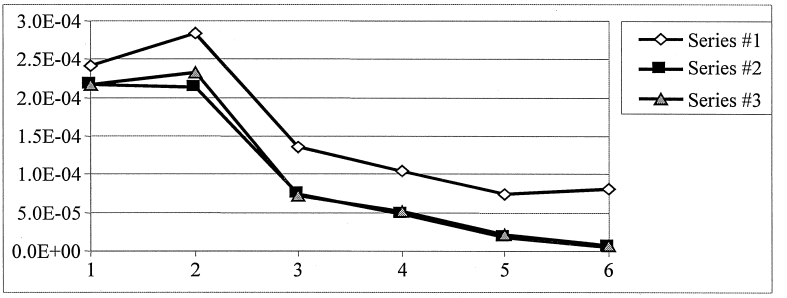

Fig. 6. Dependence of diffusion coefficient of A-units on the size of the blocks (on x-axis the numbers of systems are shown, with increasing this number the size of blocks decreases).

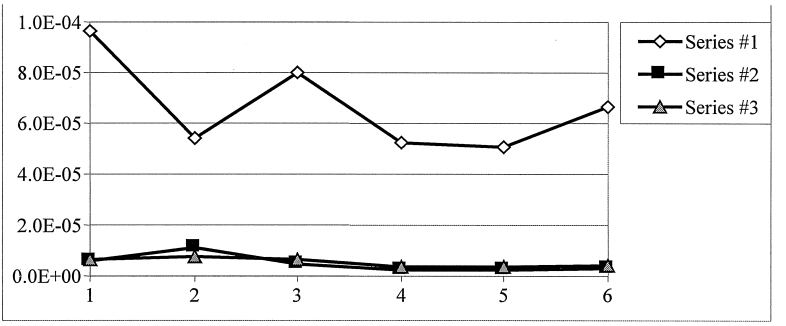

Fig. 7. Dependence of diffusion coefficient of B-units on size of blocks of polymers (on x-axis the numbers of systems are shown, with increasing this number the size of blocks decreases).

The average number of B-units that is in contact with one colloidal particle almost does not depend on the primary structure of polymers (see table 3). At that, when looking at snapshots of systems of series #1, it can be seen that all surface of colloidal particles is covered by B-units. Hence we can calculate adsorption capacity N^* of colloidal particle. In our case $N^* \approx 24$. Theoretical calculations give us $N^* \approx 28$. Small decrease of N^* in the simulation can be explained by driving of adsorbed B-units from colloidal particles by the other monomeric units that are not adsorbed.

Table 3. Average number of B-units that are in contact with one colloidal particle

Series \ System	1	2	3	4	5	6
1	23.34	24.14	23.58	23.82	22.96	21.93
2	6.26	6.17	6.74	8.04	6.72	6.92
3	0.71	0.68	0.58	0.45	0.42	0.22

Conclusions

Using Monte Carlo simulating technique we have studied the formation of aggregates in polymer-containing colloidal solution in case of selective adsorption of AB-copolymers. The considerable dependence of type of formed structures on primary structure of copolymers was obtained in the case of strong adsorption of B-units on colloidal particles. This structures vary from large dense aggregates that consist of many colloidal particles and monomeric units in case of large blocks to well-distributed spatial web with knots consisting of one colloidal particle and several small blocks of B-units. In the case of presence of attraction between B-units the dependence of shape of formed aggregates on primary structure disappear since colloidal particles cease to participate in formation of aggregates. It was also shown that the mobility of polymer chains is essentially reduced when size of blocks decreases.

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