Monte Carlo Simulations of Self-Assembling Copolymer Brushes

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Summary: We studied a simplified model of a polymer brush formed by linear chains, which were restricted to vertices of a simple cubic lattice. The macromolecules consisted of a sequence of two different kinds of united atoms arranged in a specific sequence. The chains were grafted to an impenetrable surface, *i.e.* they were terminally attached to the surface with one end. The model system was studied at different solvent quality from good to poor solvent. The properties of this model system were determined by means of Monte Carlo simulation using a Metropolis-like sampling algorithm based on local changes of chain's conformations. The size and the structure of the brush were determined.

Keywords: coil-to-globule transition; diblock copolymers; lattice models; Monte Carlo method; polymer brushes

Introduction

Many experimental and theoretical efforts were done in order to determine the structure and predict the properties of heteropolymers in solutions and at interfaces. The interfaces of such macromolecular systems are even of the greater interest because of the importance of its industrial and biomedical applications, such as lubrication, adhesion and stabilization of colloids etc.[1] The brushes can be synthesized and studied using experimental techniques.[2] Computer simulations of polymer brushes consisted of grafted linear chains were also extensively performed.[3] A series of theoretical papers concerning grafted block copolymers was published by the group of A.C. Balazs. The Monte Carlo simulations of brushes with attractive ends, *i.e.* showing the possibility of forming clusters as well as the morphology of diblock polymer brushes were done.[4] The triblock polymer brushes were also studied using the scaling analysis and *SCF* theory.[5] Schmid *et al.* performed simulations of off-lattice model of amphiphilic chains on surface and found many ordered phases of the formed monolayer.[6] Drefahl *et al.* simulated amphiphilic monolayers chains formed on nanorough surfaces and determined the influence of the surface roughness on the structure of the layer.[7] Romiszowski and Sikorski developed lattice models of grafted polypeptides and showed the influenced of the amino acid sequence on the brush structure.[8] In this paper we present the results concerning the system of heteropolymer brushes built of linear chains grafted upon a surface. The results show the influence of the solvent quality (temperature) on the structure of the formed film.

Model and Simulation Algorithm

The polymer brush was built of n linear chains of equal length N that were terminally attached onto a surface. Each chain consisted of two kinds of beads (united atoms) denoted as A and B. The chains had $N/2$ of A-type segments (called a stem) attached to the surface and $N/2$ segments of B-type on the end part of the chain (called a branch). The brush is schematically shown in Figure 1.

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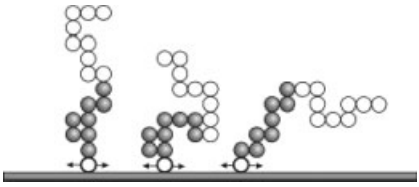

Figure 1.
The schematic representation of the multichain polymer brush formed by grafted linear chains. The polymer blocks consisted of *A* and *B* beads are depicted by the darker and lighter lines respectively.

Model macromolecules were embedded to a simple cubic lattice. The model system was put into a Monte Carlo box 20×20 lattice units in directions parallel to the surface (xy plane) with periodic boundary conditions imposed in x and y directions only. The potential of interactions between a pair of polymer beads was defined as follows:

$$V_{ij} = \begin{cases} \infty & for \quad r_{ij} < l \\ \varepsilon & for \quad r_{ij} = l \\ 0 & for \quad r_{ij} > l \end{cases} \qquad (1)$$

where r_{ij} is a distance between a pair of residues, $l = 1$ is a length of a lattice unit. The following scheme of interactions was assumed: the *AA* and *AB* interactions were set as $\varepsilon_{AA} = \varepsilon_{AB} = 0$, while the *BB* interactions were set as $\varepsilon_{BB} = -1kT$, where T is the temperature and $k = 1$ is the Boltzmann's constant. One can treat the *AAAAA*.... *BBBBBB* chain as consisting of two parts: the grafted 'lower' part, which is immersed in good solvent and the 'upper' part, which is solvent sensitive.

The model brush was then studied by the Monte Carlo method with the algorithm based on the local chain moves: 2-bond move, 3-bond move, 3-bond crankshaft move, 1-bond and 2-bonds end reorientations.[9] During the simulation the grafted end of the chain remained at the surface although it could slide along it. The acceptance of each move was possible due to chain connectivity, the excluded volume effect and the Metropolis criterion (the change of the conformation took place with the probability $P_{old \Rightarrow new} = min[1, exp(-\Delta E/k_B T)]$, where ΔE is the difference between the energy of the 'new' conformation and the 'old' conformation).

Each Monte Carlo simulation run consisted of 10^6–10^7 steps and were performed 20–25 times starting from quite different conformations in order to obtain the proper sampling of the conformational space. The initial configuration of a brush was prepared in the following way: n points were selected at random on the grafting surface. Then, self-avoiding walks started from these points until chain lengths reached the proper value N. During the propagation of chains the system was equilibrated, *i.e.* it underwent a series of local micromodifications.

Results and Discussion

The simulations were carried out for the brush consisted of $n = 50$ chains, what corresponded to the grafting density $\sigma = 0.125$. The length of chains in the brush was changed between $N = 50$ and $N = 800$ beads. The brush was studied in a wide ranger of the temperature: from good solvent conditions ($T = 10$) to bad solvent conditions well below the theta point ($T = 1$).

The size of the brush can be characterized in terms of an average size of a single chain The size of the chain can be described by the mean-squared radius of gyration $\langle S^2 \rangle$. In Figure 2 we present the mean size of stems and branches as a function of the chain length N for good ($T = 5$) and bad

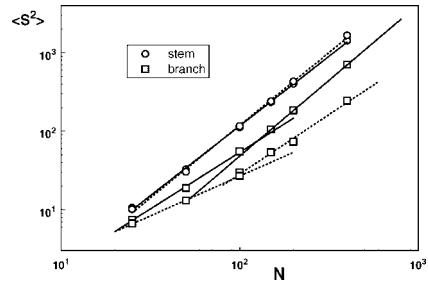

Figure 2.
The size of a polymer as a function of the chain length. The case of $n = 50$ chains. The solid lines denote the $T = 5.0$, the broken lines denote the case $T = 1.25$.

solvent ($T = 1.25$) cases. One can observe that in general the plots are linear for stems only. The scaling for stems' size was as $N^{1.8}$ for both bad and good solvent conditions what was, close to that for rod-like molecules (N^2). In the case of branches one can distinguish two regimes: for relatively short chains the scaling was $N^{1.44}$ (good solvent conditions) and $N^{1.01}$ (bad solvent conditions). Therefore, one can conclude, that scaling exponents for a good solvent are in the regime between the coil ($N^{6/5}$) and the rod-like polymers (N^2). In bad solvent chains scale with a lower exponent than in collapsed globule systems, however, its value is larger than that for a typical dense globule ($N^{2/3}$). For the longer polymers the scaling was as $N^{1.9}$ and $N^{1.6}$ for good and bad solvent conditions respectively, what was closer to the rod-like system. This shows that for the longer chains the formation of the rod-like structures is well pronounced.

The next question concerns the influence of the temperature on the size of the brush as free chains collapse to dense globules during the annealing. Figure 3 presents the changes of the mean-squared radius of gyration of the stems and branches of chains. The decrease of the size of branches is obvious: they decrease during the annealing process for temperature $T < 3$ because of a collapse to dense globules. One can observe that the stems also diminish their size at considerably low temperature ($T < 1.2$). This is caused by the fact that the collapsed

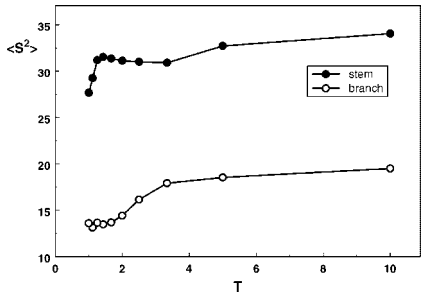

Figure 3.
The size of a chain as a function of the temperature. The case of the chain length $N = 100$ and $n = 50$ chains.

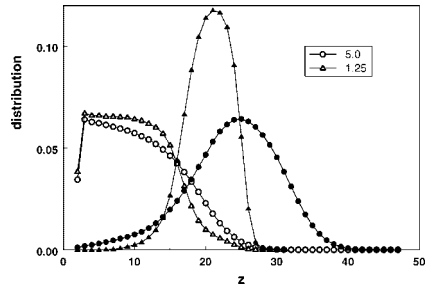

Figure 4.
The distribution of polymer beads in the direction perpendicular to the surface. The case of the chain length $N = 100$ and $n = 50$ chains. The values of T are given in the inset. Open and filled symbols are for stems and branches respectively.

branch reduces considerably the conformational space and the upper part of a stem cannot penetrate the regions more distant from the surface.

The temperature dependence of the brush dimensions can be also investigated by the analysis of the distribution of chain segments for stems and branches at different solvent conditions. Figure 4 presents the distributions of beads for good and bad solvents. One can notice that the curves for

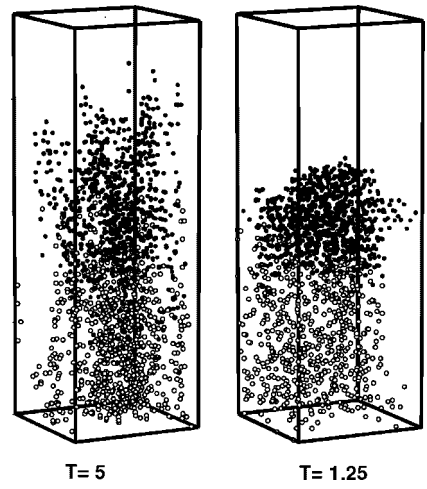

Figure 5.
The snapshot of a chain in the brush for case of the chain length $N = 100$ and $n = 50$ chains at the temperature $T = 5$ (a) and $T = 1.25$ (b). The open symbols denote the beads of stems, black symbols stand for beads of branches.

both cases are different: for a good solvent the distribution plots are more flat, while the case of the bad solvent they are sharper. For $T = 1.25$ case the branches form rather a compact structure, whilst for $T = 5.0$ some beads belonging to branches visit the region $z < 10$, what means that the branches could well interpenetrate the stems.

This effect can be seen in snapshots in Figure 5, when conformations of a single chain are shown at two temperatures. Also the presence of compact (collapsed) branches is visible for the case of the low temperature ($T = 1.25$). Both Figure 4 and 5 also confirm the effect of slim diminishing the dimensions of stems as the temperature of the system decreased, as seen in Figure 3.

Conclusions

In this work we studied and determined the structure of the polymer brush formed of linear heteropolymer chains. The brush consisted of chains restricted to a simple cubic lattice and grafted to an impenetrable surface with one end. Each polymer chain was built of two kinds of blocks: the athermal, attached to the surface called stem and the interacting upper part called branch. The dimensions of chains in the brush scale in two regimes depending on the chain length; the longer chains behave as rods. The differences in scaling exponent are caused by the crowding effect of the upper part of the brush. It was also shown that at low temperature the upper part of the brush (branches) takes form of globular structure which forms a dense layer. The presence of such form caused a slim reduction of the dimensions of the lower part of the brush (stem).

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