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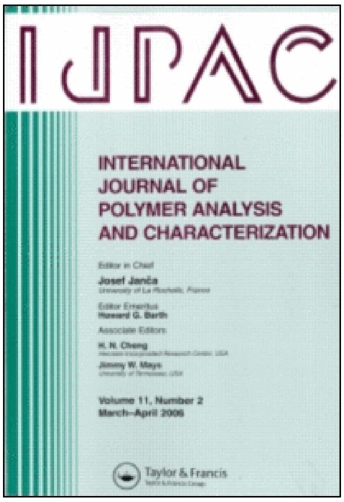

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Properties of Heteropolymer Linear Brushes

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Abstract: We studied a simplified model of a polymer brush. It consisted of linear chains, which were restricted to a simple cubic lattice. Chain macromolecules consisted of a sequence of two different kinds of segments were 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 number of chains was varied from low to high grafting density. The model system was studied at different solvent qualities from good to poor solvent. The properties of this model system were studied by means of Monte Carlo simulation. The sampling Metropolis-type algorithm was based on local changes of chain's conformations. The structure of the brush film was analyzed and the roughness of the surface was determined. The distribution of both types of segments was given for different grafting densities.

Keywords: Adsorbed linear polymer; Monte Carlo simulation; Polymer brush; Polymer film

INTRODUCTION

Recently, experimental and theoretical efforts have been made to determine the structure and to understand the properties of heteropolymer and polypeptide chains in solution and at interfaces. The interfaces of such polymer systems are even of greater interest because of the importance of their industrial and biomedical applications, such as lubrication, adhesion, and stabilization of colloids.[1]

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Experimental techniques of synthesizing and studying polymer brushes were recently reviewed.[2] Computer simulations of polymer brushes consisting of grafted linear chains were also extensively studied theoretically.[3] A series of theoretical articles concerning grafted block copolymers were published recently by the group of A. C. Balazs. They performed Monte Carlo simulations of brushes with attractive ends, i.e., diblock copolymers showing the possibility of forming clusters as well as the morphology of diblock polymer brushes.[4] They also studied triblock brushes using the scaling analysis, and self-consistent field (SCF) theory presented also the morphology of the brush surface.[5] Stadler and Schmid[6] carried out simulation of the off-lattice model of amphiphilic chains on surfaces, finding surprisingly many ordered phases of the formed monolayer. Drefahl et al.[7] studied properties of amphiphilic monolayer chains on nanorough surfaces by means of the Monte Carlo method. They showed the influence of the surface roughness on the structure of the formed layer. Romiszowski and Sikorski[8] developed lattice models of grafted polypeptides and they found by means of the Monte Carlo simulations that the structure of the brush is mainly determined by the sequence of amino acid residues.

In this article, we present simulation results of the system of linear heteropolymer brushes grafted on a flat surface. We describe the model of the brush and the simulation by the Monte Carlo method. The results show the influence of grafting density on the structure of the film.

MODEL AND SIMULATION ALGORITHM

The polymer brush was formed of linear chains that were terminally attached (grafted) onto an impenetrable surface. In our simulations, we

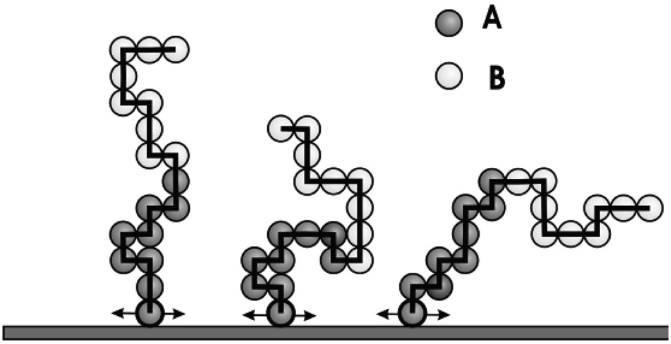

Figure 1. Schematic representation of the multichain polymer brush formed by tethered linear chains. The polymer segments of *A* and *B* type are depicted by the darker and lighter circles respectively.

attached the chains to a surface placed at the plane $z = 0$. Hence, along the z-axis the chains were restricted in motion and thus the periodic boundary conditions were imposed in x and y directions only. The Monte Carlo box was 20×20 lattice units in directions parallel to the surface. Each model chain was built of so-called statistical segments of two kinds, which we denoted as A and B. We simulated the chains with $N/2$ of A-type segments attached to the surface and the next $N/2$ segments of B-type on the top part of the chain. The idea of the model is represented in Figure 1. Model polymers were built in a simple cubic lattice, i.e., the positions of polymer segments were restricted to vectors of the type $[\pm 1, 0, 0]$. The potential of interactions between a pair of segments was defined as:

$$V_{ij} = \begin{cases} \infty & \text{for } d < l \\ \varepsilon & \text{for } d = l \\ 0 & \text{for } d > l \end{cases} \tag{1}$$

where d is the distance between a pair residues, and l is the length of a lattice unit. We assumed the following scheme of interactions: the AA interactions were set as $\varepsilon_{\mathrm{AA}} = -1$ kT, while the A-B and B-B interactions were set as $\varepsilon_{AB} = \varepsilon_{BB} = 0$. This choice enabled us to study the effect of the solvent quality on the properties of the brushes. According to the above given potential definition, one can treat the $AAAAA\ldots BBBBBB$ chain as consisting of two parts: the grafted 'lower' part, which is sensitive to the quality of the solvent, and the 'upper' part, which is permanently immersed in the good solvent.

The polymer brush was then simulated by the Monte Carlo method in order to obtain the mean properties of the system. The algorithm used was based on the local changes of chain conformations. We used a set of such conformation micromodifications that was set for linear chain models on a simple cubic lattice: 2-bond move, 3-bond move, 3-bond crankshaft move, 1-bond and 2-bond end reorientations.[9] During the simulation, the grafted end of the arm remained at the surface although it could slide along it. One attempt of every micromodification per one polymer segment defined a time unit. The acceptance of each micromodification was possible if the following three circumstances were present: (1) chain connectivity was maintained, (2) excluded volume effect was satisfied, (3) the Metropolis sampling algorithm enabled the change of the conformation with the probability $\mathrm{P}_{\mathrm{old}\rightarrow\mathrm{new}} = \min[1, \exp(-\Delta E/kT)]$, where ΔE is the difference between the energy of the attempted 'new' conformation and the 'old' conformation that could be replaced by a 'new' one.

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

RESULTS AND DISCUSSION

The simulations were performed for the total number of beads in one chain $N = 100$. The brush was studied at good solvent conditions (an athermal system) as well as for bad solvent conditions (below the theta point). The latter conditions were realized at the temperatures $T^* = 2.5$ and 2.0. We defined the polymer grafting density σ as the ratio of number of grafted chains M to the total number of lattice point on the surface K: $\sigma = M/K$, where $K = 400$. We simulated the system not only at different solvent qualities but also for varying grafting densities from $\sigma = 0.0075$ to $\sigma = 0.25$. During the simulations the data were recorded for further analysis-usually we used 3000 snapshots of the system with the time interval 1000 time units. All the data presented here are the averages over the total simulation trajectory.

The properties of the brush can be described by the analysis of the film formed by the chains. One can analyze both the internal structure of a film as well as the surface of the film, which consisted of the uppermost beads of the system, as the z-coordinate is considered. Such surface has its shape, which depends on the properties of the brush itself. The surface is not smooth when it represents the uppermost elements of the chains (i.e., the set of the largest values of the z-components of the chain's coordinates). During the simulation run the conformations of all chains are modified, which causes the surface to change its shape too. In order to characterize the property of the 'mean' surface we calculated the roughness of such surfaces (for each snapshot separately and then the results were averaged over the whole trajectory)–this parameter was defined as the mean deviation from the mean z-coordinate: $R_a = \langle |z - \langle z \rangle| \rangle$. In our calculations of R_a we took into account all $x \times y$ (here $20 \times 20 = 400$) points on the grafting surface. Thus, the points of the grafting surface that were not covered by the polymer chains also contributed to the value of the roughness parameter. Figure 2 presents the plot of R_a calculated from the whole trajectories as a function of the grafting density σ. One can observe that at low densities the roughness of the surface increases with increasing grafting density. The maxima are observed at densities close to $\sigma = 0.025$ (10 grafted chains). Further increase of the

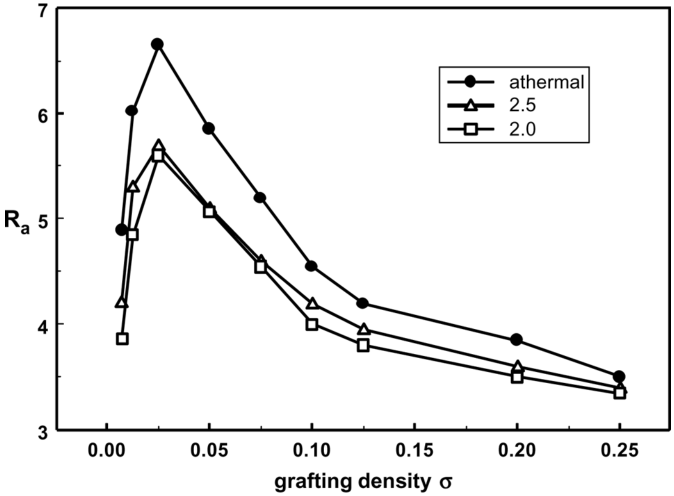

Figure 2. Roughness of the polymer film surface R_a as a function of the grafting density σ. The temperatures are given in the inset.

grafting density gradually reduces the roughness of the surface. The increase of R_a for low grafting densities we explain as the significant contribution of the values of z-coordinate from flat surface to the formula that calculates the roughness. For higher grafting densities this contribution was not significant, however, the crowding of the system leads to the lower values of the roughness. The roughness obtained for an athermal system is greater than that for bad solvent. These results can be illustrated by the snapshots of the polymer film surface taken for two densities $\sigma = 0.05$ and 0.25. The snapshots show the examples of the shape of the surface (Figure 3). The location of the surface along the z-axis shows that for higher density of chains they form film that is much thicker than that obtained for lower density. Also, the roughness of the surface definitely diminishes as the chain density increases. This confirms the results shown in Figure 2.

The structure of the brush is determined by the distribution of the chain segments located at a given distance from the grafting surface, i.e., along the direction perpendicular to the grafting surface. We made this analysis in terms of the *A* and *B* blocks of the chain, taking into account *A* and *B* beads respectively. In Figures 4 and 5, we present the distribution curves of the chain elements located at a given z-coordinate counted from the surface. The set of curves presents the results obtained at $T^* = 2.5$ for varied densities of the system. Figures 4 and 5 present the distributions for the *A* and *B* segments of the chains separately. One can observe that for *A* beads their concentration changes from the

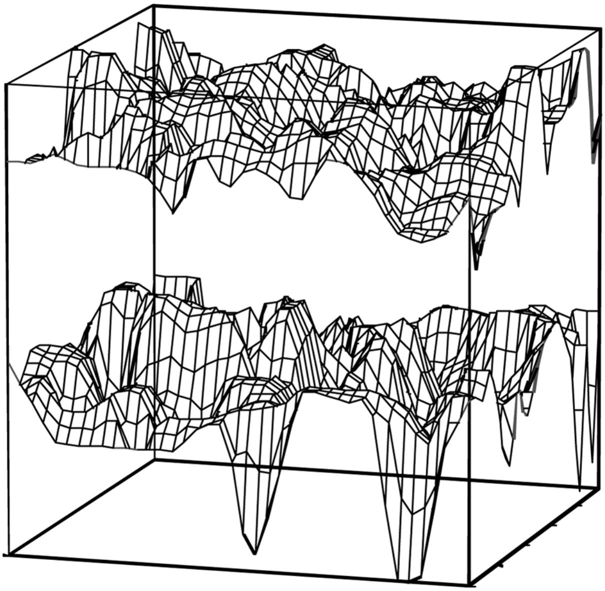

Figure 3. Snapshots of the surfaces obtained for different grafting density $\sigma = 0.05$ (lower surface) and $\sigma = 0.25$ (upper surface).

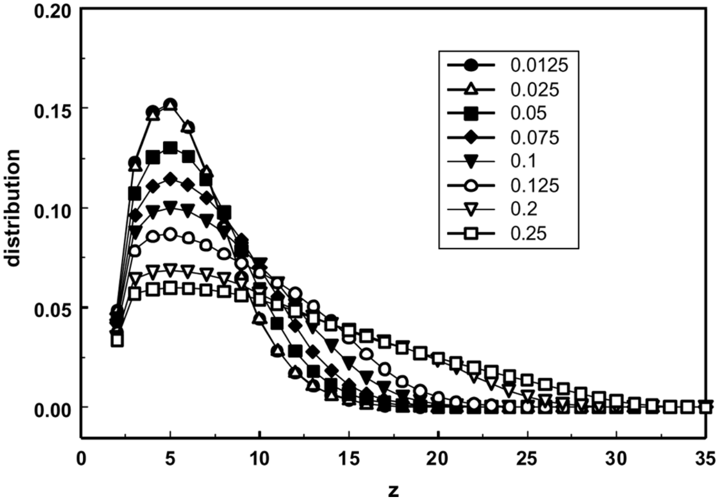

Figure 4. Distribution of A-type segments along the z-axis at the temperature $T = 2.5$. The grafting densities are given in the inset.

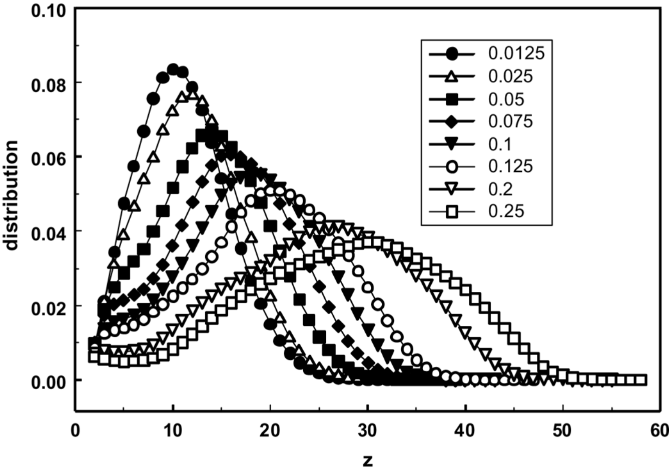

Figure 5. Distribution of B-type segments along the z-axis at the temperature $T = 2.5$. The grafting densities are given in the inset.

asymmetric narrow to broad Gaussian distribution as σ increases. For low densities (up to $\sigma = 0.1$), the A segments of the chain form a layer not thicker than 15 lattice units with the density maximum at $z \approx 5$. As the grafting density increases one can observe the 'tail' on a curve reaching up to $z > 25$ lattice units. This shows that despite attractive A-A interactions, some chains stay upright due to the crowding effect.

The distribution curves of B beads are very close to Gaussian. The increase of grafting density results in broader distribution than for low values of σ. The symmetry of the curves is caused by the absence of B-B interactions that enables chains to behave as a pure statistical system. From the distribution curves, one can easily see that the thickness of the brush layer growths as the number of grafted chains increases. For low grafting densities ($\sigma < 0.15$), the B-type segments are immersed in the lower part of the brush where A-segments prevail. As the number of grafted chains increases one can observe that B-fragments of chains are located mostly in the upper layer of the brush.

CONCLUSIONS

In this work, we determined some properties of a polymer brush formed of linear heteropolymer chains. For this purpose, we designed the idealized model of a system of grafted chains. The model chains were constructed as united atom objects consisting of two kinds of segments and were located in a simple cubic lattice. The Monte Carlo method with

Metropolis sampling was applied in order to study the system. The roughness of the surface of the brush decreased as the grafting density increased, excluding the case when we had a few chains only. The thickness of the brush film also grew with the increase in the grafting density. For grafting densities over 0.15 the segments of A-type remained mostly in the lower layer of the brush, while the B-type segments occupied the upper one.

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