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Computer Simulations of Grafted Amphiphilic Polymer Chains

*Andrzej Sikorski, Piotr Romiszowski**

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warszawa, Poland
E-mail: prom@chem.uw.edu.pl

Summary: We designed a simple model of a polymer layer formed by many chains. Each chain was built on a flexible [310] lattice. All chains were terminally attached to an impenetrable surface and the lateral motion of the entire chain was enabled. The force field used consisted of the contact potential regarding attractive interaction as well as the excluded volume effect. between polymer segments with short-range repulsion. It was assumed that the chains were built of hydrophilic and hydrophobic segments. The Monte Carlo simulations of this model were carried out using the Metropolis algorithm. The influence of both the grafting density and the temperature on static properties of the system were studied and discussed. The size, shape and structure of the polymer film formed near the surface were determined. The low temperature structures formed by the brush were described.

Keywords: amphiphiles; lattice models; Monte Carlo simulations; polymer brushes; polypeptides

Introduction

Experimental and theoretical efforts were recently made in order to determine the structure and to understand the properties of heteropolymer and polypeptide chains in solution and at interfaces because of their importance for industrial and biomedical applications.[1] One of these systems are polymer brushes consisting of polymer chains grafted onto a surface.[2] Less attention was paid to brushes formed from heteropolymer chains. A series of theoretical papers concerning simulations of grafted block copolymer brushes by means of the Monte Carlo method were published recently by the group of Balazs.[3-5] They showed that diblock copolymers with attractive ends can form clusters. The morphology of diblock polymer brushes was also studied. Balazs at al. also investigated triblock brushes using scaling analysis and SCF theory. Recently Schmid at al. carried out simulation of an off-lattice model of amphiphilic chains on surface finding many ordered phases of the formed monolayers.[6]

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Some computer simulations of simple lattice models of macromolecules were recently carried out for these systems.[7-10] In these works it was shown that such simplified models were very useful because they could provide the insight into the important aspects of behavior of real biomolecules. The influence of amino acid residues sequence in the chain on the formation of secondary structures (α-helices and β-strands) was also studied and discussed. This model was extended by Romiszowski and Sikorski who introduced a local preference of certain helical conformations.[8] The thermodynamical characteristics of the coil-to-globule transition were also found by combining the classical Metropolis-type simulation method with the Histogram Method.[9]

The Lattice Model and the Monte Carlo Algorithm

The detailed description of the model and the algorithm was presented elsewhere[7-8] and therefore only an outline is given here. The model chains that represented polymers were constructed of statistical segments of equal length and size. The locations of polymer segments were restricted to the [310] lattice with the coordination number $z = 90$. A square well potential with repulsive interaction $\varepsilon_{rep} = 5kT$ for distances smaller than $3^{1/2}$ (lattice units), attractive interaction in the range $[3^{1/2}, 5]$ and zero for still larger distances was used. The chains were built of two kinds of segments, which we called hydrophilic (H) and hydrophobic (P). We have chosen the following set of the attractive part of the potential for each pair of segments: $\varepsilon_{HH} = -2kT$, $\varepsilon_{PP} = -1kT$, $\varepsilon_{HP} = 0$. Figure 1 presents the scheme of model brush.

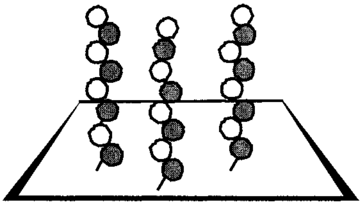

Fig.1 A scheme of an amphiphilic polymer brush. Dark and white circles denote hydrophobic and hydrophilic residues respectively.

The chains were attached to an impenetrable surface (grafting surface) which did not interact with the chains' elements. The surface was a square having an edge length L lattice units. The

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points of attachments were chosen at random. The above model of a polymer brush was studied by means of the Monte Carlo method. The conformation of each chain was randomly modified using the following set of micromodifications: two-segment motions, three-segment motions and two-segment end reorientations. A new probe conformation of a chain was accepted with a probability P_a=min(1,exp$(-(E_{new}-E_{old})/kT)$, where E_{old} and E_{new} are the interaction energies of the previous and new conformations respectively . It was assumed that chains could slide along the grafting surface as follows: the tethered chain end underwent also a two-segment end reorientation (the z coordinate was 0 or 1, what preserved the contact with the surface). An initial configuration of grafted chains was built as follows.[10] A set of n short self-avoiding walk chains each consisting of $N = 4$ residues was attached to the surface at random points (the excluded volume condition was present). The chains started to grow gradually and after every attempt of the built-up procedure conformations of all chains were modified by the simulation algorithm. Thus, the entire system was being equilibrated on each stage of the build-up procedure. This procedure was repeated until all grafted chains reached the required length N. The polymer brush prepared in this way was then annealed. For low temperatures and higher densities the algorithm was much less efficient and thus, we introduced some heating and cooling sequences during each annealing run in order to help the system to escape from local energy minima. Monte Carlo simulation runs were carried out 25-30 times starting from quite different initial configurations of the brush and the averages were calculated.

Results and Discussion

The model chains under consideration were regular amphiphilic heteropolymers, each built of the sequence *HPHPHPHP*... Each chain was of the same length and consisted of $N = 20$ segments (residues). The chains used were relatively short, but in this study we did not try to find out any properties of the system which depend strongly on the chain length, like scalings or coil-to-globule transition temperatures. The simulations were carried out for brushes consisting of n = 5,..,30 chains. One can define a grafting density as $\sigma = r_l^2\, n / L^2$, (a single chain unit had the radius $r_l = 3$).[7, 10] . Therefore the number of grafted chains corresponded to grafting densities from $\sigma = 0.1$ to $\sigma = 0.7$ respectively. In Figure 2 we present the changes of the mean-square radius of gyration $< S^2 >$ with the grafting density σ. One can notice that the error bars are very

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small (below 0.2) for low density but increase for larger values of σ. The existence of the minimum at $T = 1.0$ seems to be significant despite the larger errors.

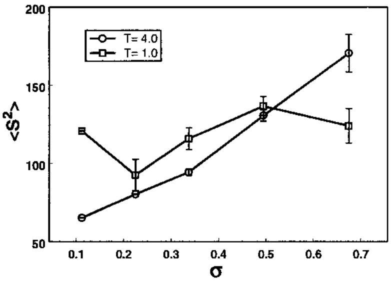

Fig.2 The mean-square radius of gyration $<S^2>$ as the function of the grafting density σ. The temperatures are given in the inset.

One can observe that these changes were quite different for low and high temperatures. At high temperatures the size of chains increases monotonically while at low temperatures the radius of gyration undergoes some changes, however they are not monotonic. Figure 3 showed the changes of the z-component of the radius of gyration $< S_z^2 >$ with the grafting density σ.

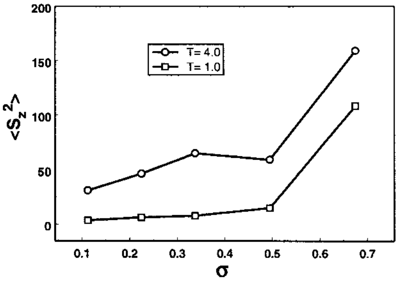

Fig.3 The z-component of the mean-square radius of gyration $<S_z^2>$ as the function of the grafting density σ. The temperatures are given in the inset.

The behavior of $< S_z^2 >$ was qualitatively the same for both temperatures: after a wide plateau a rapid increase of polymer size along the z-axis took place for grafting densities above 0.5, what indicates that the molecules take the position close to the perpendicular (with respect to the

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surface) for high densities ($\sigma > 0.5$). The We also studied the distribution of the amino acid residues along the direction perpendicular to the grafting surface. Figures 4a-b present density profiles ρ as a function of the distance from the surface z. At high temperatures a typical Gaussian-like distribution is observed for the low grafting density. For higher grafting densities the distribution exhibits the plateau covering about 2/3 of the thickness of the layer and then expressing the Gaussian tail. Similar profiles were found by Milchev for homopolymer brushes consisted of linear chains.[11] At low temperatures the thickness of the layer is lower especially for a small density case. The density profiles fluctuate in both cases, what can be caused by the compactness of the collapsed chain structures.

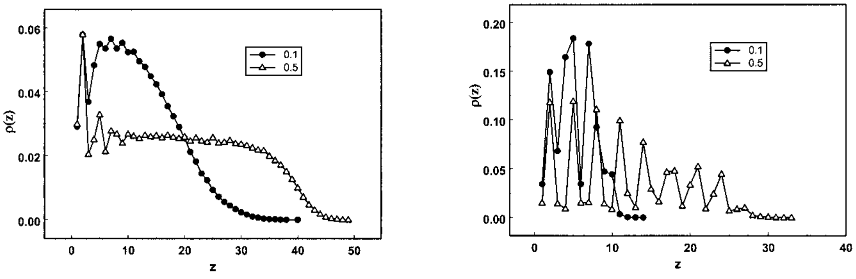

Fig. 4 Density profiles of the amino acid reside at a high temperature $T = 4$ (a) and at a low temperature $T = 1$ (b). The grafting densities are given in the inset.

The properties of the surface of the polymer layer formed were also studied. The surface of the layer under consideration as seen from the bird's eye view was composed of chains' elements, namely P and H residues. There were also observed some xy points on the grafting plane not covered by any residue (called hereafter 'vacancies') – one can easily notice that %H+%P+%vacancies = 100%. Figures 5a-b present the changes of composition of the surface (as defined above) along with the changes of temperature.

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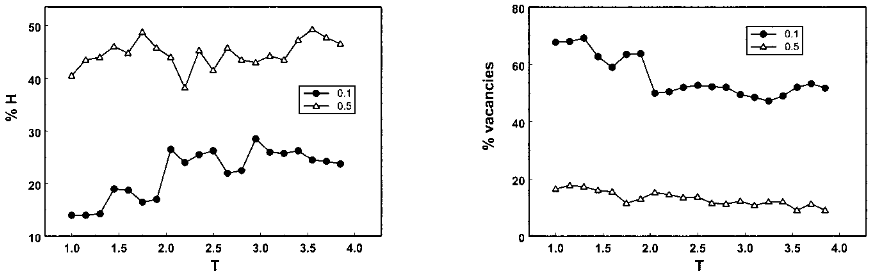

Fig. 5 The percentage of the hydrophobic residues %H located on the polymer film's surface (a) and the percentage of grafting surface points not covered by any residue (b) as a function of the temperature *T*. The values of the grafting densities are given in insets.

For each grafting density the percentage of *H*-residues as well as the percentage of empty sites is plotted. For low grafting density the percentage of *H*-residues changed from ca. 25% at high temperatures to below 15% at low temperatures – the change was well pronounced and took place in the collapse region ($T = 2$). For higher grafting densities the composition of the surface fluctuates between 40 and 50% of the hydrophobic residues with no specific tendency. The number of vacancies for the low-density case stays almost constant for temperature $T > 2$, but increases as the temperature of the system is lowered, especially for the collapsed chain region. It is an effect of aggregation of chains in the collapse region. The number of vacancies for the dense grafting case increases slowly as the temperature decreases, but no specific changes are observed. The above results show that during the collapse of the chains the surface layer becomes more hydrophilic providing that the geometry of the systems enables such a process.[10]

Conclusions

We performed a series of Monte Carlo simulations of a simple lattice model of a heteropolymer brush. In this model short linear amphiphilic chains were terminally attached to a flat impenetrable surface. It was shown that tduring the annealing process of the amphiphilic polymer the properties of the system change along with the decrease of the temperature. We found that the structure of the chains depends on the grafting density – for low grafting densities the system exhibits the well defined phase transition as chains collapse, aggregate and reorient their positions perpendicularly to the surface. On the other hand these processes for the dense system

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happen in a continuous way – whereas the thickness of the layer does not change significantly as well as the position of the molecules changes upright and no evident aggregation is observed.

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