Properties of Grafted Amphiphilic Chains. A Computer Simulation Study[†]

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The model of a heteropolymer film formed by polypeptide chains was used for theoretical considerations. The linear chains consisting of amino acid residues were approximated by alpha carbon chains. Each chain was constructed on a very flexible [310] lattice. The inter- and intramolecular interactions consisted of the long-range contact potential between residues. The chains were built of hydrophilic and hydrophobic residues. Chains were terminally attached to an impenetrable surface with lateral motions possible. The Monte Carlo simulations of this model were carried out by using the Metropolis algorithm. The influence of the grafting density, the sequence of the amino acid residues, and the temperature on the static properties of the formed layer were studied and discussed. It was shown that homopolymer chains collapsed at higher temperature than the heteropolymers. The size of the polymers forming brush was smaller for homopolymers than for heteropolymers. The structure of the resulting polymer film and of its external surface was determined. The block copolymers formed well defined hydrophobic and hydrophilic layers, while for the amphiphilic case the composition of the brush layers changed continuously at high temperature. It was observed that the latter effect vanished at the collapsed amphiphilic copolymer.

INTRODUCTION

An experimental and theoretical effort was recently done in order to determine the structure and to understand the properties of heteropolymer and polypeptide chains in the solution and at interfaces. The interfaces of such polymer systems are even of greater interest. This is caused by the importance of industrial and biomedical applications, such as lubrication, adhesion, and stabilization of colloids.[1,2]

The enormous progress in experiments on the polymer brushes was done during the last 20 years. Experimental techniques of synthesizing and studying systems consisting of grafted polymer chains (the so-called polymer brushes) were recently reviewed.[3] Computer simulations of the polymer brushes consisting of grafted linear chains were also extensively studied theoretically.[4] The model systems containing amphiphilic chains on a surface can also be treated as a Langmuir monolayer.[2] A series of theoretical papers concerning grafted block copolymers were published not long ago by the group of A. C. Balazs. Using the Monte Carlo they simulated method brushes with attractive ends, i.e., diblock copolymers showing the possibility of forming clusters.[5] The morphology of the diblock polymer brushes was also studied by this group.[6] Balazs at al. also studied the triblock brushes using the scaling analysis, and the SCF theory also presented the morphology of the brush surface.[7] Recently, Schmid at al. carried out simulations of an off-lattice model of the amphiphilic chains on the surface finding suprisingly many ordered phases of the formed monolayer.[8] Drefahl et al. studied properties of the amphiphilic mono-layers chains on nanorough surfaces by the Monte Carlo method.[9] They showed the influence of the surface roughness on the structure of the formed layer.

Various models of heteropolymer and polypeptide chains were studied by computer simulations.[10,11] It was shown that such simplified models were very useful and that they could provide additional insight into the behavior of real biomolecules. Kolinski and Madziar developed a simple lattice model of a heteropolypeptide.[12] In this model authors studied the influence of the amino acid residues sequence in the chain on its secondary structures (α-helices and β-strands). They showed that the number of secondary structures in the chain at low temperatures was rather limited and only slightly higher than in an athermal system and still lower than in globular proteins. Romiszowski and Sikorski extended this model by introducing a local potential that preferred certain conformations (helical states).[13] They showed that the mean conformational properties of a model chain at low temperatures are determined mainly by the local potential rather than by the bead sequence. The further extension of this model enabled one to determine the thermodynamic properties of the model system.[14] It became possible after combining the classical Metropolis-type simulation method with the Histogram Method. In this method the distribution of the total energy of the system is collected during a simulation run. Basing on the entropy definition one can easily determine the entropy (and other thermodynamic functions) as a function of energy. The full thermodynamic description of the coil-to-globule transition can be achieved, i.e., free energy, the height, and the shape of energetic barriers are determined. Also the transition temperature can be determined with much greater accuracy. In this study we investigated the free single unconfined chains (nontethered to the surface). The main purpose of the study was the investigation of the formation of secondary structures in simple models of polypeptides. The extension of the previous single chain model is the present study concerning the multichain system with some geometrical confinement. In the present paper our main goal was to determine the role

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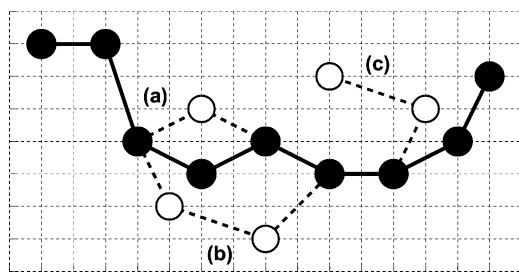[†] Dedicated to Dr. George W. A. Milne, a former long-term Editor-in-Chief of *JCICS*.

Figure 1. An example of a model chain on a (310) lattice with local changes of the chain's conformation use in the simulation algorithm: one-residue motion (a), two-residue motion (b), and two-residues end reorientations (c).

of the composition of the polymer brush on the process of a coil-to-globule thermal collapse. Also the morphology of the brush and the structure of its surface were analyzed.

The amphiphilic copolymer brushes were also investigated experimentally using nanotechnological techniques. The helical-like superstructures were built of the diblock amphiphilic polymers and grafted on golden plate.[15] Properties of the mixed polymer brushes exposed to different solvents were also theoretically studied using self-consistent field calculations, and the results were compared with an experimental study.[16]

This paper was arranged in the following way. In the section *The Model and the Simulation Method* we described the assumptions of the model and the Monte Carlo simulation method. In the section *Results and Discussion*, we discussed the obtained simulation results and compared them with other theoretical predictions. In the last section, *Conclusions*, the major and essential conclusions were presented as well as some perspectives of further development of our model.

THE MODEL AND THE SIMULATION METHOD

It was assumed that the model chains were built of structural elements that could be treated as amino acid residues or polymer segments.[12,13] The representation of a chain was highly reduced: the entire amino acid residue was represented by a united atom located at the alpha carbon position. The location of residues and its spatial orientation were restricted to a vertex of a quasi-crystalline lattice. We used a very flexible lattice [310], where the coordination number $z = 90$. The examples of the chain's conformation on this lattice are shown in Figure 1. Chains can be represented with the accuracy of $0.6-0.7$ Å with respect to real polypeptides when the lattice unit was equal to 1.22 Å. Each model chain consisted of N segments and was attached terminally to an impenetrable surface. The surface was placed at $z = 0$, and the system was put into the Monte Carlo box with an edge of $L = 100$. The periodic boundary conditions were imposed along x- and y-axes in order to make the constant density of the system.

A pair of amino acid residues interacted with a simple contact potential V_{ij} which could be described as

$$V_{ij} = \begin{cases} \epsilon_{\text{rep}} \text{ for } < r_1 \\ \epsilon_a \text{ for } r_1 \leq r_{ij} \leq r_2 \\ 0 \text{ for } r_{ij} > r_2 \end{cases} \tag{1}$$

where r_{ij} is the distance between a pair of residues ith and jth. The nearest neighbors along the chain contour did not

interact, i.e., eq 1 was valid for $|i - j| \geq 2$. The above equation indicated that the repulsion ϵ_{rep} appeared when the distance r_{ij} was below a certain r_1 and an attractive part of the potential was in action for distances located between r_1 and r_2. Based on the experience arising from our previous studies of similar models, we chose $r_1 = 3^{1/2}$ and $r_2 = 5$ (both distances were given in lattice units). The repulsive potential ϵ_{rep} was set to $5k_BT$, with $k_B = 1$.

A type of a residue can be distinguished by its attractive part of the interaction with other residues. It was assumed that the model chains were constructed of two kinds of species (residues, segments): hydrophobic (denoted as H) and hydrophilic (denoted as P). The attractive part of the potential ϵ_a took the following values: $\epsilon_{HH} = -2k_BT$, $\epsilon_{PP} = -1k_BT$, $\epsilon_{HP} = 0$ for a pair of hydrophobic residues, a pair of hydrophilic residues, and a pair of hydrophobic−hydrophilic residues, respectively. The selection of this set of interactions was made in order to make the results comparable with those of other similar models. One has to comment that the above interaction can be actually called "strongly hydrophobic" (H) and "weakly hydrophobic" (P).[14] It was shown that this choice was a better conception for polypeptide models than the concept of pure hydrophobic potential.[10]

The Monte Carlo method was used to estimate the properties of the system of model chains. The conformation of each chain was modified using a set of local changes involving from one to two polymer beads. These micro-modifications were a one-residue motion, a two-residue motion, and two-residue end reorientations. The examples of these motions are shown in Figure 1. The attempts of these conformational changes were selected at random along the chain contour. The set of micromodifications used allowed the chain's end grafted to the impenetrable plane to slide along the surface. A new conformation of a chain was accepted with a probability $P_{i \rightarrow j}$ proportional to its Boltzmann's factor. This can be realized by the following formula

$$P_{i \rightarrow j} = \exp\left(\frac{E_j - E_i}{k_B T}\right) \tag{2}$$

where E_j is the energy of a new conformation, and E_i is the energy of an old conformation. The temperature T used in our simulations was simply a parameter that scaled the force field.

The protocol for the simulation was the following. A set of n very short self-avoiding walk chains ($N = 4$) was attached to the plane at random points. Then, the chain started to grow gradually; after the attempt of growing, all chains underwent a series of micromodifications. Therefore, the system was equilibrated in every step of growing. The process of growing of the chain was performed until all grafted chains reached the required length N. The brush prepared in such a way was then annealed. The temperature of the multichain system was gradually lowered in order to investigate the changes of the structure and dynamic properties along with cooling of the system. For the lowest temperatures under consideration the algorithm was much less efficient. Therefore, we introduced some heating and cooling sequences during each annealing run (the "thermalization" procedure) in order to help the system to escape from local energy minima. Simulation runs were performed
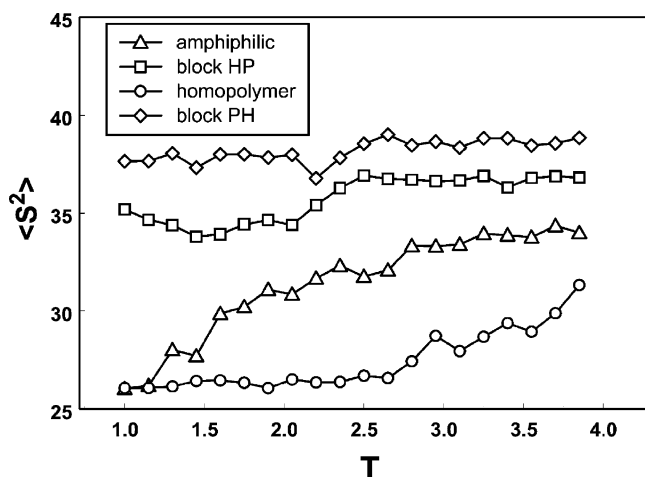
Figure 2. The mean-square radius of gyration $\langle S^2 \rangle$ as the function of the temperature T. The case of the chain with $N = 10$ and the grafting density $\sigma = 0.5$.

several times (usually 20) starting from quite different initial conformations of chains.

RESULTS AND DISCUSSION

In this paper we studied the systems of chains that were built of four different sequences of amino acid residues. At first we chose a regular homopolymer (the sequence *HHHHHHHH*...) for our studies in order to check if our model exhibited the proper features and also to have the state of reference for studying amphiphilic sequences. The next sequences under consideration were a regular amphiphilic heteropolymer (the sequence *HPHPHPHP*...) and two block copolymers: with a hydrophobic part attached to the surface (the sequence ...*HHHHHPPPPPP*...) and the reversed sequence with hydrophilic block attached the surface (the sequence ...*PPPPPHHHHHH*...). The number of chains was varied between $n = 1$ and $n = 30$ which implied that the grafting density was changed between $\sigma = 0.0225$ and $\sigma = 0.675$. The grafting density was calculated as $\sigma = nMr_1^2/L^2$, where $r_1 = 3$ was a radius of single chain unit. The chain length was varied between $N = 10$ to $N = 160$ residues. This diapason of the grafting density and the chain length was caused by the computational abilities: the algorithm became inefficient for densities above 0.7 especially for longer chains. Each simulation run started from the temperature $T = 4$, and the final temperature was set to $T = 1$. This range of temperatures was chosen based on our previous investigations of single polypeptide chains where the annealing process started there from random coil conformations, while at the lowest temperatures a dense packed globule was formed.[13]

The static properties of a film formed by grafted chains can be studied by observing the mean-square radius of gyration $\langle S^2 \rangle$

$$\langle S^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{cm})^2 \qquad (3)$$

where $\mathbf{r}_i$ is a coordinate of an ith residue and $\mathbf{r}_{cm}$ is a coordinate of the center-of-mass. In Figure 2 we present the plots of mean radii of gyration for different chain sequences. The points were calculated during the annealing process at
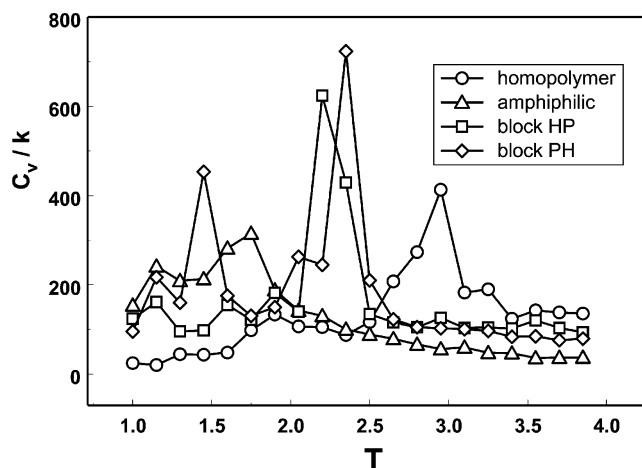

Figure 3. The heat capacity C_v/k_B as the function of the temperature T. The case of chain with $N = 10$ and the grafting density $\sigma = 0.5$.

intervals of $\Delta T = 0.15$. The sizes of heteropolymers were larger than for the homopolymer analogue. One can also observe the gradual decrease of the dimensions of the molecule—the greatest changes of the radius of gyration were visible for an amphiphilic heteropolymer, the least for the block copolymer. This means that the amphiphilic chain collapsed to a compact dense globule, in contrast to both block heteropolymer cases (*HP* and *PH*), which produced a less compact structure. The size of the two block copolymer brushes are similar in the entire range of the temperature studied, while the *PH* block brush is slightly larger than that composed of the *PH* block brush.

The heat capacity of the system studied can be calculated as the dispersion of its mean energy:

$$C_v/k = \frac{\langle E^2 \rangle - \langle E \rangle^2}{(k_B T)^2} \qquad (4)$$

Figure 3 presented the plot of heat capacity C_v/k_B as the function of temperature of the system T. Each curve represents a different sequence of the heteropolymer (see the legend). The grafting density for each case was $\sigma = 0.5$, and each chain consisted of 10 segments. One can observe that there were peaks on the curves denoting the coil-to-globule transition. However, the temperature of this transition was different for each sequence pattern. The homopolymer collapsed at a much higher temperature ($T = 3.0$) than the heteropolymers ($T = 2.3$ for *PH* block brush, $T = 2.20$ for *HP* block brush, and $T = 1.75$ for amphiphilic brush), respectively. The most pronounced transition was observed in both cases of the block heteropolymer (*HP* and *PH*)—in this case the coil-to-globule transition was possible only by breaking the symmetry of the molecule what was accompanied by the dramatic rearrangements of the conformation of the molecule. The least pronounced transition was observed for the case of an amphiphilic chain—the folding process in this case did not require any fundamental changes of the conformation of the macromolecule.

The z-component of the radius of gyration, i.e.

$$\langle S_z^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} (z_i - z_{cm})^2 \qquad (5)$$

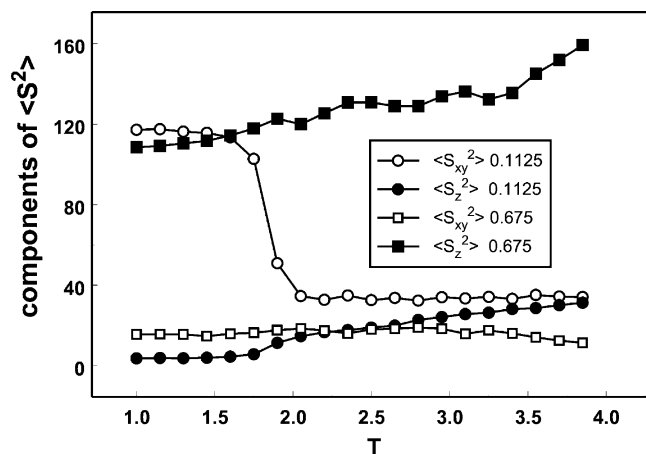was also calculated in order to study the internal structure

Figure 4. The *xy*- and *z*-components of the mean-square radius of gyration $\langle S_{xy}^2 \rangle$ and $\langle S_z^2 \rangle$ versus the temperature *T*. The case of the amphiphilic chain with $N = 20$. Grafting densities are given in the inset.

Figure 5. Mean thickness of the polymer brush $\langle z \rangle$ as the function of the chain length *N*. The case of the amphiphilic chain and the grafting density $\sigma = 0.1125$.

and size of the brush.[17] The similar equation held for the *xy*-component of $\langle S^2 \rangle$.

Figure 4 showed the plots of the components of the radius of gyration $\langle S_{xy}^2 \rangle$ and $\langle S_z^2 \rangle$ for the amphiphilic chains at different grafting densities. The behavior of these components was completely different for both cases. At low-density one can observe the apparent changes at both components at temperature $T = 2$: the *xy* term rapidly increased while the *z*-component decreased. This means that after the transition the collapsed molecule formed a globule which was relatively flat (the ratio of both components $\langle S_{xy}^2 \rangle / \langle S_z^2 \rangle = 32$) which resembled the structure of the weakly adsorbed chains.[18] The case of high grafting density presented different results—the *xy*-component of $\langle S^2 \rangle$ decreased slowly during the annealing process, at the same time the *z*-component stayed almost unchanged. This means that during the collapse of the system the changes of the dimensions of the molecules were considerably less dramatic than those for the low density case. At high grafting density the chains cannot collapse to a globule since the excluded volume effect did not allow for the overlap of the molecules, which would be the only way to form dense globules. Since the overlapping was not possible, the molecules did not have to change the dimensions significantly.

The next interesting results concerned the mean thickness of the polymer film $\langle z \rangle$. This parameter can be calculated as the first moment of the density profile ρ

$$\langle z \rangle = \frac{\sum_{i=1}^{\infty} z_i \rho_i(z)}{\sum_{i=1}^{\infty} \rho_i(z)} \qquad (6)$$

where the summations went through all *xy* layers containing amino acid residues. Figure 5 presents the mean thickness of the polymer brush formed by the amphiphilic chains as a function of the length of the chain. One can observe that for the high temperature this parameter increased for short and moderate length chains (up to $N = 80$) and then it reached a plateau region. This implied that longer chains rather tried to fill the space than to stay fully stretched. For low
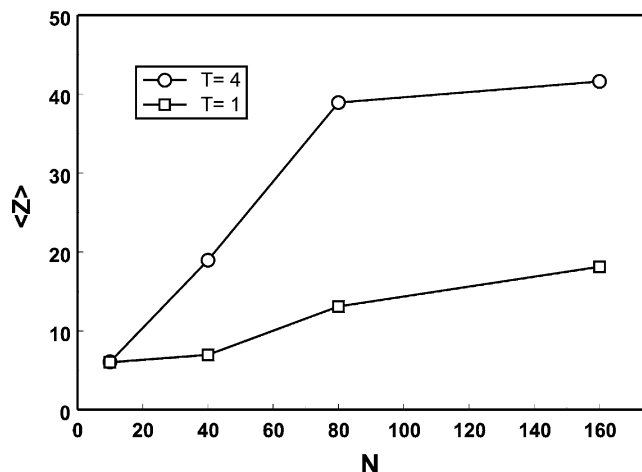
temperatures the brush thickness was almost linear to the chain length in the entire range of the length studied. The thickness was in that case significantly smaller that that for high temperatures.

The structure of the polymer brush formed by our model polymer chains was also studied. In Figure 6a,b, we presented the fraction of hydrophobic residues as a function of the distance from the grafting surface. At high temperatures the distribution of *H* residues dramatically depended on the chain sequence—the amphiphilic chain exhibited a gradual decrease of the contents of *H* as the distance *z* from the grafting plate increased, reaching almost 0 at the surface of the system. A quite different behavior was observed for both block heteropolymer cases (which were almost mirror results): for low values of *z* an interesting behavior was observed—the unexpected content of "opposite" residues was noticed. This means that there was an interpenetration of *H* and *P* fragments of chains. For lower temperatures the fraction of *H* residues in the amphiphilic chain strongly fluctuated with the decreasing tendency, while block copolymers were sharply divided into *H* and *P* layers.

Besides the structure and the thickness of a polymer layer one important question arose: what was the character of the polymer surface and what was the influence of the amino acid sequence on this surface. The typical examples of the surface are shown in snapshots in Figure 7a–c for the multichain system at the high and low temperatures, respectively. Figure 7a presents the snapshots for the case of the amphiphilic chains—the plots of the height of the surface were located on the left side of the figure; the composition of the surface was shown on the right side, respectively. The upper plots were for $T = 4$, and the lower ones were calculated for the collapsed systems ($T = 1$). The height of the surface was presented as follows: the white areas depicted the regions of the surface which were not occupied by the chains (empty sites), other areas were covered by the chains—the darker the color, the higher the surface. Comparing the surfaces for the high and low temperatures (upper and lower plot, respectively) one can notice that the number of unoccupied (white) regions is greater in the collapsed system which was easily predictable. Also the intensity of the dark colors (high regions) was diminished at low temperature. This means that the collapsed chains formed
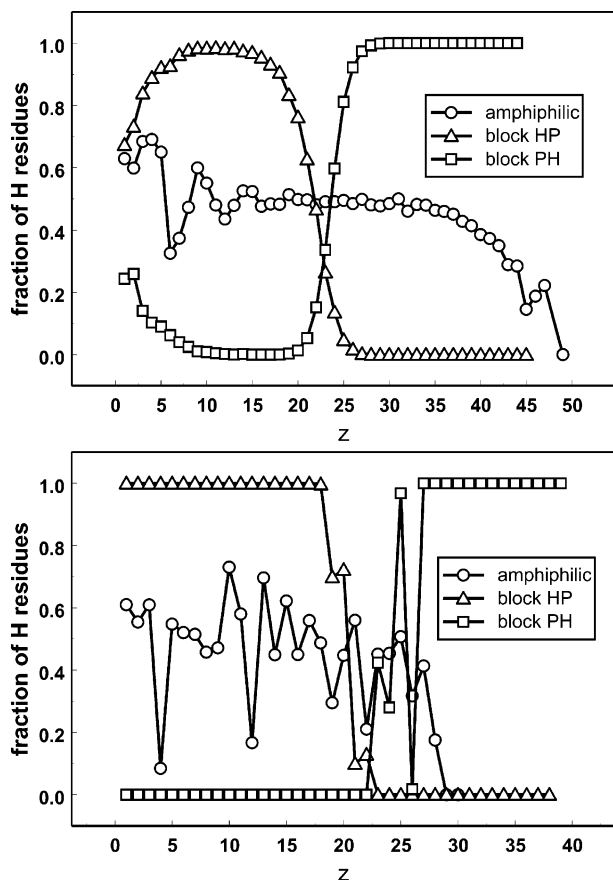
Figure 6. Fraction of hydrophobic residues along z-axis for chains with $N = 20$. The case of the temperature $T = 4$ (a) and $T = 1$ (b).

the dense and therefore thicker surface (the mean thickness of the surface $\langle z \rangle = 11.62$ and $\langle z \rangle = 9.49$ for high and low temperatures, respectively). The structure of the surfaces was presented as follows: the white areas showed the points of the surface which were unoccupied by the chains, the light gray points depicted the points of the surface in which the hydrophobic (H) beads were located, and the dark points showed the hydrophilic beads (P) located at the surface. The number of P residues as well as the number of vacancies increased along with the cooling of the system. The composition of the surface of a block copolymer (Figure 7b) changed significantly after being at the low temperature exposed the P residues. Quite different behavior is observed for the case of the diblock ...*PPPHHH*... polymer. The surface contains mostly H residues; however, their number increased during the cooling of the system. The pattern of the surface ("mountains" and "valleys") shows a kind of regularities, probably caused by a dense packing of the polymer chains. One can also try to find correlations between the elevation of the surface and its composition for the amphiphilic and both diblock sequences of chain. This correlation is especially visible for the case of the reversed (*PH*) block copolymer brush in Figure 7c. The P residues shown in the right part of this figure correspond to the low elevations of the brush surface. It is more difficult to explain how the composition of the surface depended in average on its height, i.e., z-coordinate. The "mountains" visible on the polypeptide surface were predominately covered by hydrophilic residues, while the "valleys" were predominately covered by hydrophobic residues (except in the case of Figure
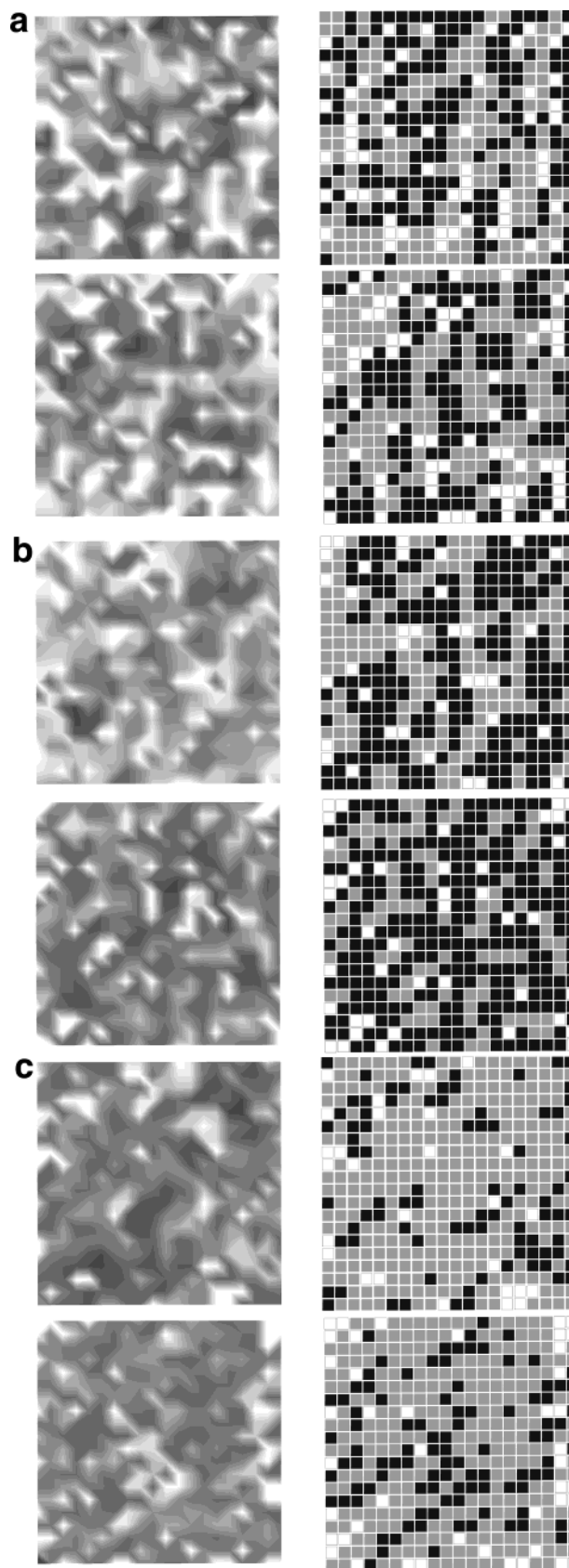

Figure 7. Shape and morphology of surfaces formed by the polymer brush. All plots for case of $N = 20$, $\sigma = 0.5$ (see text for details). Upper row $-$ $T = 4$, lower row $-$ $T = 1$. Left side of the picture presents the elevation of the surface (z increases from white to black). Right side shows the composition of the surface: white squares $-$ vacancies, gray squares $-$ H residues, black squares $-$ P residues. The case of amphiphilic chain (a), diblock copolymer (b), and reversed diblock copolymer (c).

7c). The explanation of this feature can be based on the internal structure of the polymer layer: the number of hydrophobic segments along the *z*-axis shown in Figure 6a,b is in full agreement with the composition of surfaces shown in Figure 7a−c.

CONCLUSIONS

The Monte Carlo simulations were carried out in order to calculate the properties of the lattice model of a heteropolymer (polypeptide) brush. We built a simple lattice model of linear polymer (or polypeptide) chains anchored to a solid surface. The force field used contained the short-distance repulsive part (introducing the excluded volume effect) and the binary contact potential. The model chains were built of two kinds of residues (segments): hydrophobic and hydrophilic.

The location of the transition that took place in the brush was strongly dependent on the chain sequence. The chains consisted of hydrophobic elements only collapsed in the highest temperatures, while the heteropolymer chains collapsed at lower temperatures. The most rapid transition was found for amphiphilic chains. The size of the chain for the heteropolymer was larger than that for homopolymer chains. The fraction of the hydrophobic residues along the direction perpendicular to the grafting surface decreased for all sequences (except for the reversed diblock case) enabling to cover the surface of the brush with hydrophilic residues. The very surface of the polymer brush formed by chains was not flat—its roughness depended on both the sequence and the temperature of the system. Some elements of regularity for the block copolymer case were noticed; however, this would need more studies.

The further studies should reveal in detail the internal structure of the brush, the arrangements and local ordering of the chain fragments, their mobility, and the relaxation phenomena. This work is in progress. The next step would be the full thermodynamical description of the amphiphilic brush. It would be possible by combining the classical Monte Carlo algorithm with the Histogram method.[14] After implementing a local potential that can help with the formation of peptide secondary structures our model can apparently be applied to studying the structures obtained experimentally using nanotechnological techniques, like helical superstructures built of the grafted amphiphilic polymers.[15] Properties of the mixed polymer brushes[16] in different solvents can also be studied using our model.

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