Properties of Star-Branched Polymer Brushes†

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A simple model of a polymer brush was constructed. The star polymers with three arms were terminally attached with one arm (the stem) to an impenetrable surface with the other two arms (branches) free. The excluded volume effect was included into the model as the only interaction. Therefore, the system was studied in good solvent conditions. The simulations were carried out by means of the dynamic Monte Carlo method using the local changes of chain conformations to sample efficiently the conformational space. The influence of both the number of chains (the grafting density) and the length of chains on the static properties of the polymer brush was studied. The internal and local structure of a formed polymer layer was determined. It was shown that the size of the stems increased rapidly with the increase of the grafting density, while the size of the branches diminished. The changes of the spatial orientations of the stems and the branches for different grafting densities were shown and discussed.

INTRODUCTION

Polymer systems consisting of grafted chains, i.e., macromolecules terminally attached to a surface called polymer brushes, attracted attention because of their practical importance, such as lubrication, colloidal stabilization, and wetting properties.[1] Experimental techniques were recently developed to synthesize such brushes by adsorbing chain ends to the surface or by growing chains in situ from grafted initiators.[2] Such systems are also interesting from the theoretical point of view because the understanding of the details of the structure and factors that have impact on it should help in predicting important properties of polymer brushes on a macroscopic scale (viscoelastic properties, phase transitions, ordering).

The simulation studies of polymer brushes were started by Murat and Grest.[3] They carried out Molecular Dynamic simulations and confirmed results of the analytical theory of Milner, Witten, and Cates[4] concerning the monomer distribution and the size of the brush. Polymer brushes were also studied by means of the Monte Carlo simulation. Milik built a simple model of tetrahedral chains grafted on the surface.[5] Local ordering and the dynamic properties of this system were studied in this work. It was shown that a short-time dynamic behavior (relaxation) was very similar to that of the polymer melts, while the long-time dynamics (diffusion) featured the hindered collective motion for moderate times. Lai and Binder studied models of polymer brushes using the bond-fluctuation model by means of the Monte Carlo method.[6] Some further studies concerning the comparison between the theory and simulation results were done by Pepin and Whitmore.[7] Sotta at al. simulated grafted linear chains confined in a tube.[8] They found and described the scaling behavior of such chains, the distribution of polymer segments, and the free energy of the system. Monte Carlo simulations of a single grafted linear chain were recently performed by Han et al.[9] They showed that single grafted chains were always considerably larger than free chains because of the repulsion of the surface. The same conclusion concerned the shape of the grafted chains. Recently Binder presented the progress in simulation studies of polymer brushes showing that they were valuable tools for testing analytical theories and interpreting experimental results.[10]

Star-branched polymers were recently a subject of extensive experimental and theoretical studies. Recent excellent review articles can give insight into the state of art in synthesizing and simulating star-branched polymers.[11,12] A general scaling theory of star-branched polymers at a surface was formulated by Ohno and Binder.[13] Carignano and Szleifer calculated the properties of some off-lattice nonuniform star-branched chains (individual arms had different lengths).[14] They found out that the properties of the brush depended strongly on the chain internal architecture. The mean-field theory concerning grafted star-branched polymers was presented by Mayes at al.[15] Their results concerned grafted star-branched polymers, mostly the dependencies of the grafting density and the number of arms on density profiles. Unfortunately, the lack of the proper experiments did not allow for making the comparison with real systems and to verify the model.

Some initial computer simulation studies of the simple model of polymer brushes formed from the regular star-branched polymers were recently published.[16] In this work, we studied long-time dynamic properties of star polymers grafted onto an impenetrable surface. It was shown that in the limit of a very long time the behavior of such a brush is Rouse-like, and the scaling behavior was intermediate for a single polymer chain and for a polymer melt.[17] It was also shown that the dependence of the self-diffusion coefficient on the grafting density for moderately low densities (for grafting densities below 0.3) was different than that for a brush formed by linear chains. The decrease of the chain's mobility with the increase of the grafting density was much

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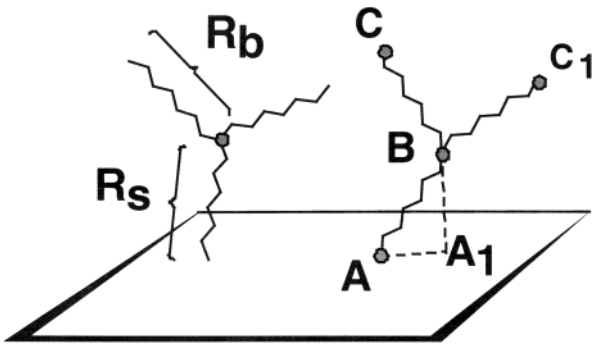

Figure 1. Schematic representation of the multichain system of the grafted star-branched chains. The arrow shows the resulting possible lateral motion of the entire chain.

faster than in polymer melts and different comparing with brushes formed by linear chains.

In this paper we studied a simple model of a polymer brush formed by chains grafted onto an impenetrable surface. To study the influence of branching we simulated star-branched polymers that consisted of three branches (linear chains) of equal lengths. The influence of the number of grafted chains on the properties of the entire polymer brush was also studied. Hence, the system studied can be treated as a crude model of a polymer layer near an interface, a micelle, or a polymer membrane. The algorithm used to calculate properties of such a system was developed based on the classical Monte Carlo algorithms designed to study the properties of star-branched polymers.[18,19]

THE MODEL AND THE ALGORITHM

The model polymer brush under consideration was formed from star-branched polymers which were grafted to the flat surface (hereafter we use the term "grafted" for the case of tethered chains, which are not firmly anchored and can move along the surface). Each star-branched macromolecule was built of identical structural elements (polymer segments).[18,19] The topology of branched chains was the simplest possible: each chain consisted of 3 arms (branches) of an equal length. The positions of polymer segments were restricted to a simple cubic lattice, i.e., to the vectors of the type [±1, 0, 0], [0, ±1, 0], [0, 0, ±1]. The excluded volume was the only potential of interaction introduced into the model. The excluded volume was realized by the forbidding of double occupancy of lattice points being polymer segments and the forbidding of crossing the surface by these segments. All polymer−polymer, polymer−solvent, and polymer-surface contacts were assumed to be exactly the same, and therefore the model was athermal. The model grafted chains were located in the Monte Carlo box with the edge $L = 20$, and the periodic boundary conditions were imposed in x and y directions only. At $z = 0$ an impenetrable wall was put up, and the chains were attached to that wall with one end of an arm. The number of chains was varied between $n = 1$ and 80. The grafting density can be defined as $\sigma = n/L^2$, and hence the grafting density was varied from 0.0025 up to 0.2. The larger densities were not studied within the framework of this model because they were hardly sampled by the simulation algorithm.[17] The scheme of the star-branched polymer system under consideration is shown in Figure 1. In this figure one can notice some star polymers fragments

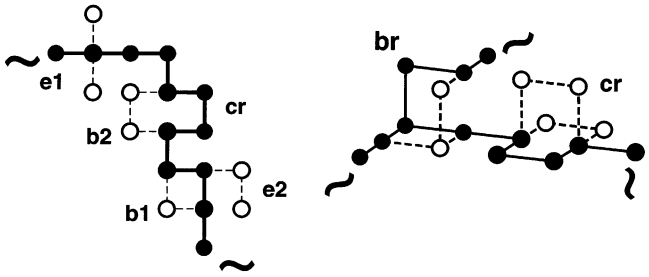

Figure 2. Set of local micromodifications used in the simulation algorithm: two-bond motion (denoted as *b*1), three-bond motion (*b*2), three-bond crankshaft motion (*cr*), one-bond end reorientation (*e*1), two-bond end reorientation (*e*2), and branching point collective motions (*br*).

which properties were studied in this work. The arm that was grafted we called a "stem", while the remaining arms were called "branches".

The computer simulations of this model were carried out by using the Monte Carlo method. In the sampling algorithm we used the following set of local changes of chains' conformations in order to sample efficiently the conformational space:[18] (i) two-bond motion, (ii) three-bond motion, (iii) three-bond crankshaft motion, (iv) one- and two-bond end reorientations, and (v) branching point collective motions.

All these local motions are presented in Figure 2. The arm's end grafted onto the surface was allowed to move with the local micromodification (iv). To prevent the detachment of the chain from the surface this motion was limited to $z \leq 2$. Therefore, the grafted ends were able to move along (slide) the surface, and the lateral motion of the entire chain was enabled.

To obtain correct properties of the system we carried out several simulation runs for every system studied. Usually there were about 20 independent runs starting from different initial configurations. Each run lasted 1 order of magnitude longer that the longest relaxation time of a single chain. Initial configurations were prepared in the way that resembled that of polymer melts.[17,20] At the beginning n short chains (each consisting of 4 segments) were randomly attached to the surface with one end. Than all chains underwent a process of growing and equilibration simultaneously until the proper number of segments in one branch was reached. From that moment the two branches of the polymer chain were constructed in the same way. After reaching the requested total number of segments N the simulation of the system was started. To check the algorithm some simulations started from chains extended toward z axis. No difference in properties of the system were found even when starting from those unusual configurations, which suggested that our algorithm was proper to study the moderately dense polymer brushes.

RESULTS AND DISCUSSION

We studied star-branched polymers consisting of $N = 49$, 100, 199, 400, and 799 segments. It implied that in a single arm there were 17, 34, 67, 134, and 267 segments, respectively. It was previously shown that these lengths of star-branched polymers cover the wide entanglement regime at least in a regular melt without any confinement. Chains with $N = 49$ segments were too short to produce entanglements in dense melts and brushes, and while in chains with $N = 799$ segments some entanglements should appear (the

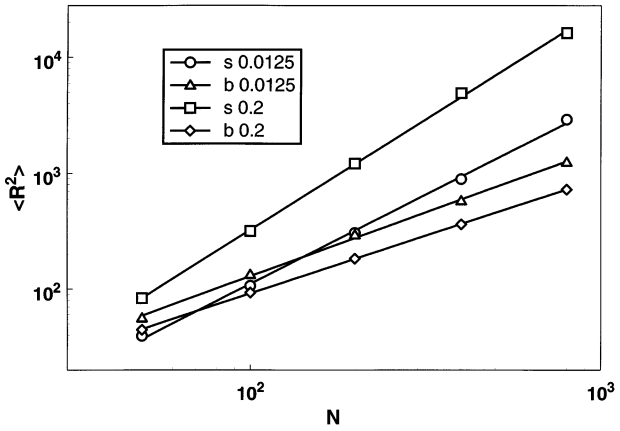

Figure 3. The mean-square center-to-end distance of a stem $\langle R_s^2 \rangle$ and of a branch $\langle R_b^2 \rangle$ versus the chain length N. The grafting densities are shown in the inset.

entanglement length $n_e = 164$ was found for the cubic lattice model of melt containing star-branched polymers).[20]

The parameters determining the size and the structure of the brush were the mean values obtained from the simulation trajectories and averaged over 10^7-10^8 points. To investigate the influence of grafting density on the structure of the brush we made the analysis of the trajectories. The star-branched polymer attached to the surface can be characterized by the location of its branching point, the position of the ends of the branches, and the angle of the vector connecting the attachment and the branching point as well as the angle of the vector connecting the ends of the branches (with respect to the surface).

The first problem we addressed was a change of a polymer's dimensions with the increase of the chain length and the grafting density. In Figure 3, we presented a log−log plot of the dependence of the mean-squared center-to-end distances in a single chain on the number of segments N. Apparently as the properties of grafted arms and free arms are different we calculated this parameter separately for the stem and both branches (see Figure 1). The mean-squared center-to-end distance of the stem we denoted as $\langle R_s^2 \rangle$, while this parameter concerning the branches we denoted as $\langle R_b^2 \rangle$. One can observe that all parameters describing the mean dimensions of star-branched polymers scaled N^γ which was characteristic for the polymer chain in various conditions. One can also notice that the scaling of the stems differed significantly from that of the branches. The scaling exponents for the stems were 1.54 ± 0.03 (at low grafting density $\sigma = 0.0125$) and 1.91 ± 0.03 (at higher grafting density $\sigma = 0.2$), while for the branches they are 1.10 ± 0.02 and 1.00 ± 0.01, respectively. The main conclusion was that the stems became much more extended with the increase of the chain length. The size of the branches changed in a way very similar to that in a regular polymer melt.[17,20] The stretching of a stem with the grafting density was apparently caused by the fact that the stems had difficulties with penetrating other parts of the chain and themselves.

The results concerning the arms' size can be compared with those carried recently by Han at al.[9] They found that the scaling behavior of a single linear grafted chain was the same as that for a free (i.e., nongrafted) linear chain. However, they observed that the dimension of the grafted chain was continuously larger than that of a free chain:

Table 1. Size of Stems and Branches for Different Grafting Densities and Chain Lengths Compared with the Dimensions of a Free Chain

N	σ	$\langle R_{free}^2 \rangle^a$	$\langle R_s^2 \rangle$	$\langle R_b^2 \rangle$	$\langle R_s^2 \rangle / \langle R_{free}^2 \rangle$	$\langle R_b^2 \rangle / \langle R_{free}^2 \rangle$
49		33.09				
	0.0125		39.31	55.95	1.19	1.69
	0.2		82.81	44.36	2.50	1.34
100		78.69				
	0.0125		105.9	132.3	1.35	1.57
	0.2		315.1	92.7	4.00	1.18
199		181.5				
	0.0125		304.2	292.1	1.68	1.61
	0.2		1213	182.0	6.68	1.00
400		406.9				
	0.0125		888.0	576.0	2.18	1.42
	0.2		4900	361.0	12.0	0.89
799		936.0				
	0.0125		2916	1246	3.12	1.33
	0.2		16100	723.6	17.2	0.77

[a] Values taken from ref 18.

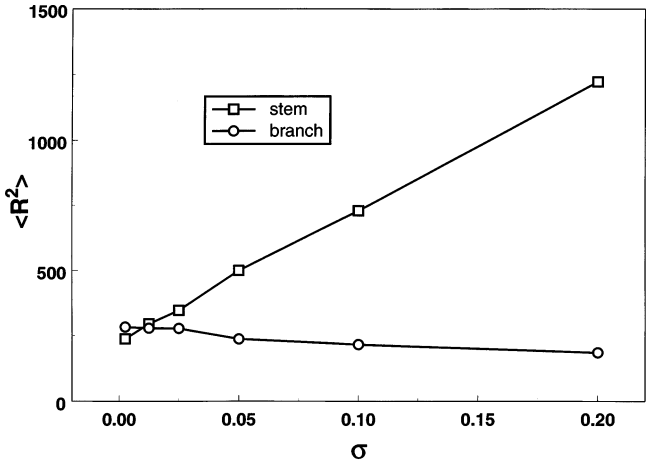

Figure 4. The mean-square center-to-end distance of a stem $\langle R_s^2 \rangle$ and of a branch $\langle R_b^2 \rangle$ versus the grafting density σ. The case of the chain consisted of $N = 199$ beads.

$\langle R^2 \rangle_{grafted} / \langle R^2 \rangle_{free} = 1.32$. This extension of a grafted chain was explained by the repulsion of the surface. We calculated these ratios for the stems and the branches separately and put them into Table 1. One can observe that this ratio strongly depended on the grafting density and chain length. The ratios comparable with that of Han at al. were found for short chains and low densities only.

The second parameter that could have had an impact on the properties of our brush was the number of chains (the grafting density). Figure 4 presents the changes of $\langle R_s^2 \rangle$ and $\langle R_b^2 \rangle$ parameters with the grafting density σ. The presented case concerned the star-branched polymer with $N = 199$ segments. For both low and moderate σ one can observe the linear (at least for larger σ) changes of $\langle R_s^2 \rangle$ and $\langle R_b^2 \rangle$. However, for low densities the slope of the curve was different than for a large number of chains—this phenomenon will be investigated in the forthcoming study. For higher densities one can observe evident differences in the dependence of $\langle R_s^2 \rangle$ and $\langle R_b^2 \rangle$ on the grafting density: the mean size of a stem strongly increased, while the dimensions of the branches slowly decreased. The behavior of the branches

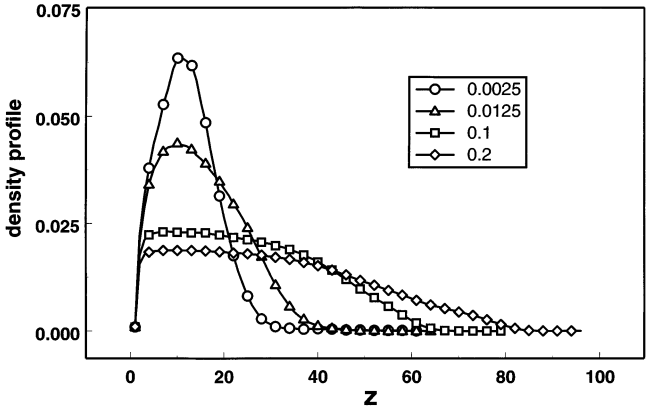

Figure 5. The density profiles for the chain consisted of $N = 199$ beads. The grafting densities are shown in the inset.

was obvious in view of the fact that the excluded volume effect forced the stems to expand and to take the vertical positions (see below the discussion about the orientation of the stems and the branches), while the branches had to interpenetrate themselves. The stems had to have difficulties with penetrating other chains. A stem did not have mobile ends to penetrate other chains; it had to bend to get into other coiled fragments of other chains. The stem was apparently less mobile, and on the other end (the branching point) it had two branches to drag with. Analytical theories of star-branched polymer brushes also predicted that the stems were stretched even for moderate grafting densities.[14,15]

The morphology of the polymer brush consisting of star-branched polymers was an interesting problem, since the layer formed by the grafted molecules could be divided into two components: one formed by the stems, another one formed by the branches. The number of segments belonging to the branches was $2nN/3$, since the number of segments in the stems was $nN/3$. This implied that the concentration of the segments in the branch layer was different from that in the stem layer. As the grafting density increased, the branch layer reaches the high-density regime well before the stem layer did. In Figure, 5 we plotted the fraction of lattice sites occupied by the grafted polymers for the different grafting density σ as a function of the distance from the surface z (density profiles). For comparison we also plotted the results for a single chain which corresponded to the grafting density $\sigma = 0.025$. This exemplary plot concerned the chain length $N = 199$. One can notice that for a single chain the distribution was almost Gaussian. As the concentration increased one can observe that the distribution curves became flatter with a long tail at increasing distances from the surface. This means that the systems filled the space uniformly forming a thick layer, at which the concentration of beads was almost constant. Similar density profiles were found in the analytical theories of Carignano and Szleifer[14] for a brush formed from nonuniform star polymers and of Mayes and al.[15]

In Figure 6 we plotted the density profiles of polymer beads as well as the distribution of the beads that belong to the stems and the branches, respectively. The figures were made for the case of the chain with $N = 199$ beads for the grafting density $\sigma = 0.0125$ and 0.2 (parts a and b, respectively, of Figure 6). For low grafting density one can observe the asymmetric Gaussian distribution of beads along the z axis. The maximum for the stems was close to the small

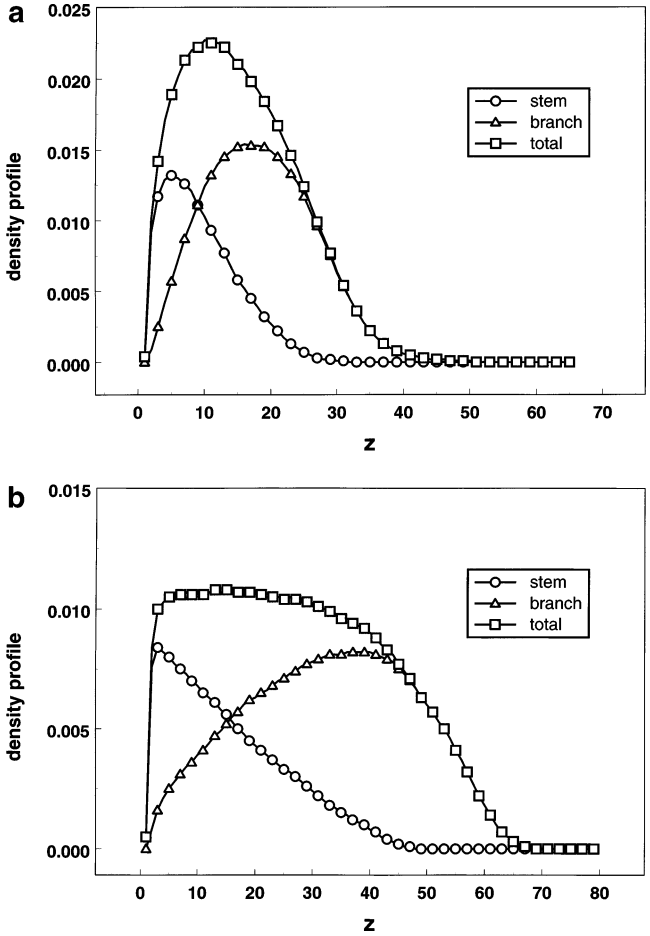

Figure 6. Polymer segments density profiles along the z-axis: all beads, beads belonging to the stems, and beads belonging to the branches. The case of the grafting density 0.0025 (a) and 0.2 (b).

values of z since the maximum density of the branches was located at some distance apart from the plane. It means that the branches formed a separate layer. For the case of a medium-dense system the total distribution of beads was dramatically different from the previous case—the distribution almost did not exhibit a maximum reaching a plateau spanning from the surface to the whole thickness of the layer. The distribution of beads belonging to the stems decreased rapidly along with z, while the distribution of beads belonging to the branches was close to a symmetrical one with the pronounced maximum. The comparison of these two cases showed us that when the grafting density increased the total distribution of the beads as well as the stems became less Gaussian. However, the distribution of the branches remained Gaussian.

To investigate the morphology of the brush layer more completely we studied the orientation of both important parts of the chains, i.e., of the stems and the branches. Therefore, we calculated the angles α_s formed by the vectors connecting the grafting point and the branching point with respect to the xy plane. This angle corresponded to the angle formed by the lines AB and AA_1 in the Figure 1. These angles indicated the position of the star-branched molecule, whether it was more or less perpendicular to the surface. One can expect that, as the grafting concentration increases, the stems will take the position perpendicular to the plane—the high grafting density enforced the structure which consisted of stretched stems. Figure 7 presents the distribution of angles

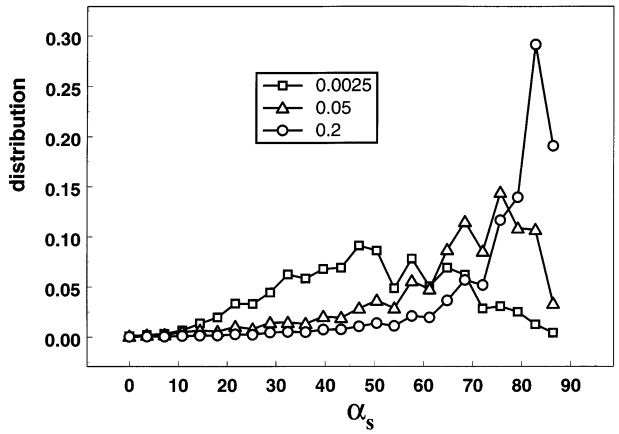

Figure 7. The distribution of angles α_s indicated the slope of the stems (see text and Figure 1 for details).

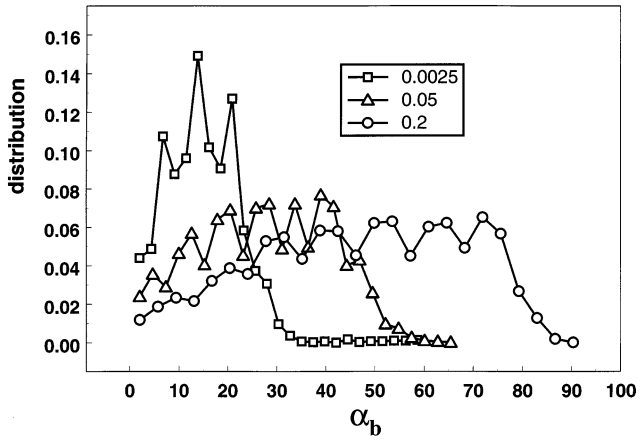

Figure 8. The distribution of angles α_b indicated the slope of two branches (see text and Figure 1 for details).

α_s. One can notice that for the low grafting density $\sigma = 0.0125$ the distribution was very wide, and all the positions of the stems were possible. As the grafting density σ increases, the distribution became more asymmetric and for $\sigma = 0.2$ most of the stems were almost perpendicular to the surface. This effect should be more pronounced in a brush formed by star-branched polymers when compared to that formed by linear ones. One can argue that the only difference between these brushes was the presence of an additional branch (a linear chain can be treated as a stem plus one branch). This additional branch introduced more polymer beads into the middle and upper layers of the brush.

The similar investigation was made for the orientation of the branches. The angle of the vector linking the ends of the branches α_b (C and C_1 in Figure 1) with respect to the *xy* plane was studied. The distribution of these angles was presented in Figure 8. For the case of low densities the angles α_b were mostly in the range 10−30 deg, which means that the branches were not so far from the horizontal position. As the grafting density increased, the distribution became flat with a certain asymmetry toward the higher values of α_b. This means that some branches took vertical positions (one branch of a molecule pointing up while the second one points down) which diminished the high concentration effect in the middle layer of the brush. The orientation of the branches was also studied by Carignano and Szleifer.[14] They suggested that one branch was stretched toward the solvent, while the second branch pointed toward the grafting surface. This conclusion was not contradictory to our findings; however, the problem needs more study.

In this paper, we presented the Monte Carlo simulations of a cubic lattice model of a polymer brush. The polymers forming the brush were star-branched and tethered to the flat surface by an end of one arm. It was shown that there were significant differences between the size of a grafted arm called the stem and the two remaining arms called the branches. The increase of the grafting density forced the stems to stretch-out, while the mean dimensions of the branches remained almost unchanged (slightly diminished). The distribution of polymer segments showed a wide region where the density was almost constant which was expected for the star-branched brushes. The analysis of the angles formed by some of the elements of the chains (stems and branches) showed that the orientation of the chains depended strongly on the grafting density. At low concentration the branches were free to extend parallel to the surface, while as the concentration of the polymer increased the density of the branches (twice of that for the stems!) enforces a more vertical position of the branches.

In the next step of the research we will study the changes in the structure of the brush for low densities (1−5 chains only) where an interesting behavior was found which is underway. The properties of brushes composed of miktoarm star-branched polymers, where different properties of the polymer layers near the surface should be magnified by their chemical components, are also in preparation.

REFERENCES AND NOTES

(1) Eisenriegler, E. *Polymers Near Surfaces*; World Scientific: Singapore, 1993.
(2) Zhao, B.; Brittain, W. J. Polymer brushes: surface-immobilized macromolecules. *Prog. Polym. Sci.* **2000**, *25*, 677−710.
(3) Murat, M.; Grest, G. S. Interactions between grafted polymeric brushes: a molecular-dynamics study. *Phys. Rev. Lett.* **1989**, *63*, 1074−1077.
(4) Milner, S. T.; Witten, T. A.; Cates, M. E. Theory of the grafted polymer brush. *Macromolecules* **1988**, *21*, 2610−2619.
(5) Milik, M.; Kolinski, A.; Skolnick, J. Monte Carlo dynamics of a dense system of chain molecules constrained to lie near an interface. A simplified membrane model. *J. Chem. Phys.* **1990**, *93*, 4440−446.
(6) Lai, P.-Y.; Binder, K. Structure and dynamics of grafted polymer layers: a Monte Carlo simulation. *J. Chem. Phys.* **1991**, *95*, 9288−9299.
(7) Pepin, M. P.; Whitmore, M. D. Mote Carlo and numerical self-consisted field study of end-tethered polymers in good solvent. *J. Chem. Phys.* **1999**, *111*, 10381−10388.
(8) Sotta, P.; Lesne, A.; Victor, J. M. Monte Carlo simulation of a grafted polymer chain confined in a tube. *J. Chem. Phys.* **2000**, *112*, 1565−1573.
(9) Huang, J.; Jiang, W.; Han, S. Dynamic Monte Carlo simulation on the polymer chain with one end grafted on a flat surface. *Macromol. Theory Simul.* **2001**, *10*, 339−342.
(10) Binder, K. Scaling concepts for polymer brushes and their test with computer simulation. *Eur. Phys. J. E* **2002**, *9*, 293−298.
(11) Grest, G. S.; Fetters, L. J.; Huang, J. S.; Richter, D. Star polymers: Experiment, theory, and simulation. *Adv. Chem. Phys.* **1996**, *94*, 67−163.
(12) Freire, J. J. Conformational properties of branched polymers: Theory and simulations. *Adv. Polym. Sci.* **1999**, *143*, 35−112.
(13) Ohno, K.; Binder, K. Scaling theory for radial distributions of star polymers in dilute solution in the bulk and at a surface, and scaling of polymer networks near the adsorption transition. *J. Chem. Phys.* **1991**, *95*, 5444−5458.
(14) Carignano, M. A.; Szleifer, I. Structure and thermodynamics of grafted three-arm branched polymer chains. *Macromolecules* **1994**, *27*, 702−710.
(15) Irvine, D. J.; Mayes, A. M.; Griffifh-Cima, L. Self-consistent field analysis of grafted star polymers. *Macromolecules* **1996**, *29*, 6037−6043.

(16) Sikorski, A.; Romiszowski, P. Dynamics of grafted star-branched polymers. A Monte Carlo study. *Macromol. Symp.* **2002**, *181*, 323−326.
(17) Skolnick, J.; Kolinski, A. Dynamics of dense polymer systems: Computer simulations and analytic theories. *Adv. Chem. Phys.* **1990**, *77*, 223−278.
(18) Sikorski, A. Monte Carlo study of dynamics of star-branched polymers. *Makromol. Chem., Theory Simul.* **1993**, *2*, 309−318.
(19) Sikorski, A.; Romiszowski, P. Motion of star-branched versus linear polymers. A computer simulation study. *J. Chem. Phys.* **1996**, *104*, 8703−8712.
(20) Sikorski, A.; Kolinski, A.; Skolnick, J. Dynamics of star branched polymers in a matrix of linear chains. A Monte Carlo study. *Macromol. Theory Simul.* **1994**, *3*, 715−729.

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