DYNAMIC PROPERTIES OF STAR-BRANCHED POLYMER BRUSHES *

Andrzej Sikorski and Piotr Romiszowski

Department of Chemistry, University of Warsaw
Pasteura 1, 02-093 Warszawa, Poland

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We studied a simplified model of a polymer brush. It consisted of star-branched chains, which were restricted to a simple cubic lattice. Each star-branched macromolecule consisted of three linear arms of equal length emanating from a common origin (the branching point). The chains were grafted to an impenetrable surface, *i.e.* they were terminally attached to the surface with one arm. The number of chains was varied from low to high grafting density. The model system was studied at good solvent conditions because the excluded volume effect was the only potential of interaction included in the model. The properties of this model system were studied by means of Monte Carlo simulation. The sampling algorithm was based on local changes of chain conformations. The dynamic properties of the polymer brush were studied and correlated with its structure. The differences in relaxation times of particular star arms were shown. The short-time mobility of polymer layers was analyzed. The lateral self-diffusion of chains was also studied and discussed.

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1. Introduction

Star-branched polymers are interesting objects from the theoretical point of view because they are the simplest non-linear polymers. These simple branched chains were subjects of extensive experimental and theoretical studies [1–3]. The polymer chains tethered to the surface with one end form brush structure, which has many interesting properties. Carignano and Szleifer studied off-lattice non-uniform star-branched chains [4]. According to their results the properties of the brush depended strongly on the chain's internal architecture. Mayes *et al.* studied star-branched chains

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using a mean-field theory [5] investigating the influence of the grafting density and the number of arms on density profiles. Polymer brushes formed by many star-branched grafted chains were also studied and some preliminary results were already published [6–8]. In this series of papers we showed the differences between the structure of the brush formed by linear and star-branched polymers. It was shown that the grafting density has the major impact on the properties of the polymer layer formed by the brush.

In this paper we present the dynamic properties of polymer brushes represented by a reduced model. The structure and the properties of brushes composed of linear chains were already determined by Binder [9]. Therefore, we built a model of a brush with star-branched chains consisting of $f = 3$ arms. Polymer chains were embedded to a simple cubic lattice. The model chains were studied at good solvent conditions (exclude volume effect only). The algorithm we used was based on a Verdier–Stockmayer type local chain motions [6].

2. Model and simulation algorithm

The polymer brush was formed of chains that were terminally attached (grafted) onto an impenetrable surface. A model chain was built of so-called statistical segments. Each macromolecule consisted of $f = 3$ chains (arms) emanating from the common origin (the branching point) and each arm was of the same length (the uniform star). Model star-branched polymers were built in a simple cubic lattice, *i.e.* the positions of polymer segments were restricted to vectors of the type $[\pm 1, 0, 0]$.

Interactions between polymer segments and solvent molecules were assumed to be the same. Therefore, the system can be treated as athermal and no long-distance attractive interactions were introduced. The double occupancy of lattice sites by polymer segments was forbidden what means that the excluded volume was introduced to the model. This model of interaction mimics good solvent conditions. The system under consideration consists of M chains attached to an impenetrable planar surface with the end of one arm what is shown in figure 1. During the simulation the grafted end remains at the surface but it can slide along it. The polymer brush formed by grafted star-branched chains was put into the Monte Carlo box. The grafted surface was placed at the plane $z = 0$. Hence, along the z-axis the chains were restricted in motion and the periodic boundary conditions were imposed in x and y directions only.

The model brush was then simulated by the Monte Carlo method in order to calculate its dynamical properties. The Monte Carlo simulation algorithm we developed was based on the classical asymmetric Metropolis scheme, where all chains underwent a series of random local changes of con-

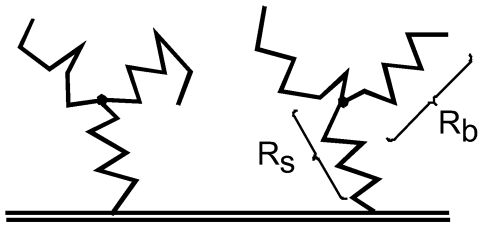

Fig. 1. The schematic representation of the multichain polymer brush formed by tethered star-branched chains.

formations. The program code was developed in our laboratory. In our algorithm we used a set of such conformation micromodifications which was proposed for star-branched chains models: 1-bead move, 2-bead move, 2-bead crankshaft move, 1-bead and 2-bead end reorientations, and the branching point collective motion [6]. One attempt of every micromodification per one polymer segment is defined as a time unit. A new conformation of a chain was accepted provided that the chain connectivity and the excluded volume (including the points forming the grafting surface) were maintained. 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: at the beginning M points were selected at random on the grafting surface. Then, self-avoiding walks started to grow from these points until chain lengths reached n segments (the length of an arm). From that point two self-avoiding chains (arms) started to grow. During the chains propagation the system was equilibrated, *i.e.* it underwent a series of local micromodifications.

3. Results and discussion

The simulations were performed for polymer brushes formed by star-branched chains for different chain length. Each macromolecule had $n = 17, 34, 67, 134$ and 267 beads in one arm what means that the total number of beads in one chain was $N = 49, 100, 199, 400$ and 799. The number of chains M was varied from 1 to 80, so the grafting density was changed from $\sigma = 0.0025$ to 0.2.

The local (short-time) motion of a chain in a brush can be analyzed by studying the elementary motions of polymer conformation used in the simulation algorithm. Figure 2 presents the accepted fraction of elementary motions as a function of the distance from the grafting surface z. For low grafting density the curves are Gaussian-like what means that the concentration effect is not visible. For the high grafting density one can observe

some interesting effects: the thickness of the layer increases almost twice while the acceptance ratio of the moves decreases roughly twice. Also one can see that the acceptance ratio (except the end moves) is almost constant along the z axis — apparently this means that the polymer chains form a uniform dense brush [9].

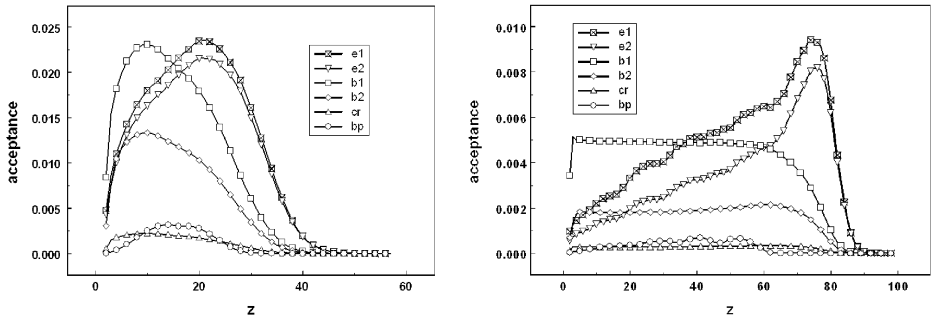

Fig. 2. The fraction of accepted micromodifications *versus* the distance form the surface for the brush containing chains with $N = 199$ beads and for the grafting density $\sigma = 0.0025$ (left) and $\sigma = 0.2$ (right). The types of moves are indicated in insets as follows: e1 — one-bead end move, e2 — two-bead end move, b1 — one-bead move, b2 — two-bead move, cr — crankshaft move and bp — branching point move.

The short-time dynamics of the polymer system can also be expressed by means of the longest relaxation time. In a star-branched polymer the longest relaxation time of the center-to-end vector $\boldsymbol{R}$ is usually studied taking the averages over all arms [6]. However for the case of the polymer brush formed by tethered star polymers the properties of free arms are quite different from those which are connected to the surface [8]. Therefore, we considered branches and stem separately (see figure 1). Both longest relaxation times can be calculated from the center-to-end vectors $\boldsymbol{R}_s$ and $\boldsymbol{R}_b$ autocorrelation functions. One could expect that the longest relaxation times obeyed the relation $C_R \sim \exp(-t/\tau_R)$, where C_R is an autocorrelation function [6]. In figure 3 we present the longest relaxation times of branches τ_b and stem τ_s as a function of the chain length N. One can observe that both longest relaxation times scaled with N and the scaling exponent $\tau_s = 2.75 \pm 0.34$ while $\tau_b = 2.60 \pm 0.16$. These results can be compared with those of free star-branched (non tethered) chains. For the same model of a single free star-branched chain the longest relaxation time of end-to-center vector τ_R (neither branch nor stem can be distinguished here) scaled as $N^{2.20}$. The values of τ_R were smaller than τ_b and τ_s. For a polymer melt containing star-branched chains relaxation times scaled as $N^{2.34}$ at the density 0.5.

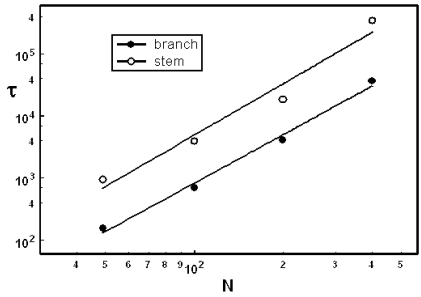

Fig. 3. The longest relaxation times of branches τ_b and of stem τ_s *versus* the chain length N for the grafting density $\sigma = 0.0125$.

The long-scale dynamics of the polymer brush can be described by the self-diffusion coefficient D which can be extracted from the center-of-mass autocorrelation function $g_{\rm cm}$ according to the Einstein formula. In our model the grafted chains can move on the surface, along the xy-plane, while in the third direction the motion was suppressed and this is the reason why we studied the chain long-distance motion along this plane only. Therefore, we calculated two-dimensional diffusion coefficient $D_{xy} = g_{\rm cm}^{xy}/4t$. The diffusion coefficient can be extracted from the xy contribution to the autocorrelation function from the region where this function was linearly time-dependent, *i.e.* when $g_{\rm cm}^{xy} \sim t^1$. This behavior was in general found for displacements larger than $2\langle S^2\rangle$ and we determined the diffusion coefficient in the window $2\langle S^2\rangle < D_{xy} < 10\langle S^2\rangle$. For the mean-square displacements shorter than $2\langle S^2\rangle$ the autocorrelation function $g_{\rm cm}$ does not depend linearly of time (the scaling exponent is less than 1, as in subdiffusion), what indicates that the chain dynamics is somewhat constrained [10].

Figure 4 presents the diffusion coefficient D_{xy} as a function of the total chain length N. One can observe that the diffusion coefficient scales as N^{γ}. The scaling exponent γ was found -0.87 and -0.86 for lower and higher grafting density, respectively. This scaling behavior can be compared with that found for the free star-branched chains where $D \sim N^{-1.10}$ [6]. It seems that despite of the model confinement (chain grafting) the universal scaling laws are preserved, however the scaling exponents as well as the fractal dimensions may be different from those for unrestricted systems.

In figure 5 we present the dependence of the diffusion coefficient on the grafting density σ. The values of D decrease along with the grafting density, especially for small number of grafted chains. One could ask the question what is the mechanism of motion of star-branched chains in a polymer brush. It is believed that linear chains in dense polymer melts move predominately by the reptation mechanism. There is an analog of reptation for

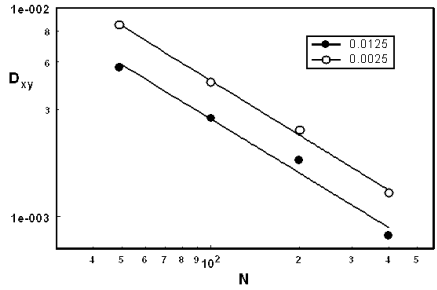

Fig. 4. The self-diffusion coefficient *versus* the chain length for the grafting density $\sigma = 0.0125$.

star-branched polymers called 'the arm retraction mechanism', which can be found in the case of a chain motion in a confined environment and probably in dense melts [2, 3]. The case of grafted chains is interesting because the motion of particular arms of star has to be different: both branches can move using the arm retraction mechanism while the stem can execute only sliding moves along the plane.

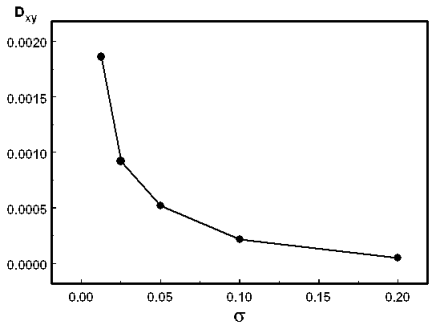

Fig. 5. The self-diffusion coefficient *versus* the grafting density for the chain length $N = 199$.

4. Conclusions

In this work we carried out the computer simulations of the simplified models of polymer brushes composed of star-branched chains. The dynamic properties of the model system were investigated. We found that the behavior of arms which were tethered to the surface differed strongly from that of free branches. The differences in short time dynamics (the longest relaxation times) were one order of magnitude. The local chain dynamics enable

one to conclude about the structure of the brush layer such as the spacial distribution of segments as well as the layer thickness.

The properties of polymer brushes depended also on the grafting densities — increase of the number of chains reduces their mobility significantly. The changes in the diffusion coefficient are especially visible in the low grafting density region. However the scaling exponents remain almost constant at least for grafting densities examined in this study.

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