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Adsorption of Homopolymer Chains on a Strip-Patterned Surface: A Monte Carlo Study

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Abstract In this study we investigated the process of chemisorption of polymers on solid surfaces. The formation of a strongly adsorbed polymer film was studied by Monte Carlo simulations. The adsorbing planar surface was patterned with strip-like repulsive sites. The polymer chains were represented by a sequence of schematically constructed objects (united atoms) and we considered star-branched macromolecules with $f = 3$ arms of equal length. The chains were studied at good solvent conditions and thus the excluded volume was the only potential of interaction between the polymers. A Metropolis-like sampling algorithm was employed in order to calculate the properties of the adsorbed chains. The influence of the chain length, the system density and the type of the pattern on the adsorbing surface on size of chains and the structure of the polymer film were determined and discussed. We found that the roughness of the polymer film surface depends non-monotonics on the number of polymer beads in the system. The shape of this surface reflects the pattern imposed on the substrate.

Keywords Adsorption · Branched polymers · Monte Carlo method · Patterned surfaces

1 Introduction

The adsorption of polymer chains on solid surfaces has many practical applications like colloidal stabilization, lubrication, catalysis etc. [1]. The structure of adsorbed polymer chains is usually described in the terms of their size and shape as well as by the structures formed (trains, loops and tails). In the case of strong surface–polymer interaction the adsorption is almost irreversible. In the case of weak adsorption the influence of the chain length plays an important role, since the desorption of short chains is more probable than the long ones due to the number of possible surface–polymer contacts. The answer concerning the question of number and mean length of trains, loops and tails was given in a mean-field theory of Scheutjens and Fleer [2, 3]. Experimental works were not able to study the detailed structure of the adsorbed chains, i.e. to determine their size, shape, density profiles, number of trains, loops and tails as well as their distribution. The influence of the pattern formed on the adsorbing surface on the structure of adsorbed chains is interesting from the theoretical point of view [4] and was recently studied experimentally [5, 6]. Homo- and heteropolymer system on patterned surfaces was also studied by means of computer simulations [7–11].

In our previous works we studied the influence of the chains' internal architecture on the size of single chains and their structure [12, 13]. Similar models and simulation algorithms were also used previously for studies of star-branched chains in solutions and in the adsorbing slit [14, 15]. It was shown that the size of adsorbed chains scaled like for three-dimensional chains (exponent 1.2) and two-dimensional chains (exponent 1.5) for the case of weak and strong adsorption, respectively. The transition from a weakly to a strongly adsorbed chain was found to take place at the same temperatures for all chains' architectures under consideration: linear, star and ring chains. The differences in the distribution of polymer beads near the surfaces, the degree of adsorption and the dynamic properties were also shown.

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In this work we present and discuss the results of Monte Carlo simulations concerning the simple model of a solution of branched polymers near a patterned surface. The star-branched chains were used in this study because they were very appreciative objects of studies as the simplest model of branched chains and they could be studied experimentally [16]. The adsorption of star polymers on homogenous surface was studied theoretically by scaling analysis [17]. The simulation algorithm used was based in our previous studies [15, 18]. The main goal of this work was to determine the structure of the adsorbed polymer film and to check the influence of the patterns of the adsorbing surfaces on the structure of the adsorbed polymer film.

2 The Model and the Method

In order to simplify the design and speed up simulations all atomic details were suppressed and the model chains were represented as the sequences of united atoms. The homopolymer chains were studied only. The macromolecules were represented by a discrete model and were embedded to a simple cubic lattice. Each chain consisted of $f = 3$ arms of equal length n beads emanating from the branching point. Therefore, each chain was assembled of $N = f \times n + 1$ beads and there were m chains of the same length in the system—see Fig. 1. To avoid chains overlapping (good solvent conditions) the excluded volume was employed and the double occupancy of one lattice point was forbidden [18].

The adsorbing surface was assumed to be parallel to the XY plane of the size $L \times L$. The periodic boundary conditions were imposed in x and y directions [18]. The surface was impenetrable for polymer beads and was heterogeneous. The entire plane of the substrate was designed as follows: the pattern consisted of parallel stripes which were one after the other attractive (‘valleys’) or repulsive (‘hills’) for polymer beads. The stripes were parallel to the y axis. The width of the ‘hills’ was assumed to be 1 lattice unit, while the width of “valleys” $d_v = 5$ and 10 lattice units. In order to realize the process of chain adsorption we applied the following simple polymer bead—surface potential:

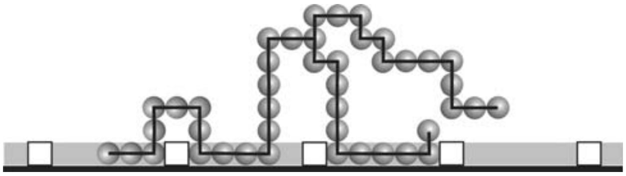

Fig. 1 The scheme of a polymer system consisted of star-branched chains adsorbed on the strip-patterned surface. Light fragments of the *substrate* denote the repulsive areas, *gray ones* stay for the attractive parts

$$V(x, z = 1) = \begin{cases} \varepsilon & \text{for} \quad (x, d_v) = 0 \\ -\varepsilon & \text{for} \quad (x, d_v) \neq 0 \end{cases} \tag{1}$$

The strength of the potential was chosen to be $\varepsilon = 1$, in kT units, assuming $k = 1$. This selection was based on our previous findings because it corresponded to the strong adsorption regime [12].

All simulations were carried out employing the Monte Carlo method. A Metropolis-like algorithm with local changes of chain’s conformation was used. There were allowed the following micro modifications of chain’s conformation: two-bond motion, three-bond motion, three-bond crankshaft motion, end reorientations, branching point collective motion [18]. All the local moves were carried out during the simulation run for randomly selected chain fragments. As the attractive and repulsive interactions between the surface and polymer beads were defined, the transition into a new conformation was accepted according to the Metropolis scheme, i.e. the conformations were sampled with the probability which is proportional to the their Boltzmann factors.

The protocol of the simulation was the following. The starting configuration of the model system was built in a process of simultaneous growth and equilibration of chains [14]. An initial configuration of m chains each of length N underwent a series of micro modifications in the order of 10^8 Monte Carlo steps. This procedure was repeated many times (at least 20 times) starting from quite different conformations.

3 Results and Discussion

The simulations were carried out for star-branched chains consisting of $N = 49$, 100, 199, 400, 799 and 1,201 beads. The number of chains in the system was set to $m = 1$, 5, 10, 20, 40 and 80 and, therefore, the total number of polymer beads in the system was approached the value up to 7 times larger than the number of points on the adsorbing surface L^2. The size of the Monte Carlo box L was varied from 50 to 200 depending on the length of the chain. The polymer density (substrate coverage) per substrate site was, therefore, defined as $\phi = Nm/L^2$.

The size of the chains is usually expressed by means of the mean-squared radius of gyration $<S^2>$. In our simulations the substrate was patterned along the y axis, thus, we will characterize the dimensions of the chains in terms of two components of $<S^2>$, namely $<S_x^2>$ (perpendicular to repulsive strips) and $<S_y^2>$ (parallel to repulsive strips). The third component perpendicular to the substrate $<S_z^2>$ was rather small because of the strong adsorption regime and thus, its behavior was not considered in this study. Figures 2a and b present the components $<S_x^2>$ and $<S_y^2>$ as a function of the substrate coverage ϕ for different number of chains in a system. The plots are shown in a log–log coordinate system enabling one to determine the scaling behavior of chains' size (One should notice that the scaling exponents are the same regardless of the usage of coveage φ and the chain length N.). The size of the chain in the x direction scales as $<S_x^2>$–N^{γ}. The scaling exponent for one chain system was found $\gamma = 1.35$, while for the systems containing greater number of chains the scaling exponents were $\gamma \approx 1$ (the standard errors were below 3%). This means that one chain system exhibits scaling which is between three-dimensional chains (1.2) and 2-dimensional chain (3/2). The insertion of more chains causes that the scaling exponent approaches the value that is characteristic for dense polymer melts. The behavior of polymer size along the direction parallel to y axis is different. The size of the system consisting of one chain scales with the exponent $\gamma = 1.57$. This means that this scaling exponent is located beyond that for two-dimensional chains (3/2) in the direction of that for a stiff rod (2). The scaling behavior for the systems with $m = 5$ chains and more is different. For the systems with $m = 5$ and 10 chains one can distinguish two regimes. The first one corresponds to relatively short chains $N \leq 199$ and the scaling was found 1.35. The second regime was found for longer chains and the scaling exponents was 0.3. For $m = 10$ chains the scaling exponents were 1.35–0.56, respectively. In the first regime chains are small and their mutual interaction is rather limited. Longer chains have contacts between themselves because of their size and thus, they behave like a dense melt. For the higher number of chains, we found one scaling regime only: for $m = 15$ exponent was 0.70 while for $m = 20$ it was 0.74. The main conclusion is that the presence of the repulsive patterns on the adsorbing surface causes significant changes in the scaling of adsorbed polymer chains' size: the scaling exponents are larger for the component along the repulsive strips.

The morphology of the polymer film can be described by the distribution of polymer beads along the plane perpendicular to the repulsive strips. Density profiles are presented in Fig. 3 and the example shows the case of $N = 199$ and $m = 10$. The profile was calculated as the mean number of polymer beads located at given x and z coordinates—that means that the number of beads was counted over all y coordinates and the results were normalized by the size of the system along the y axis and averaged over all simulation runs. The plot shows that the highest density of polymer beads is located between the repulsive stripes ('hills') and the distribution along the x-axis is repeatable for the whole surface of the substrate. Most of the beads are located in the first layer over the substrate.

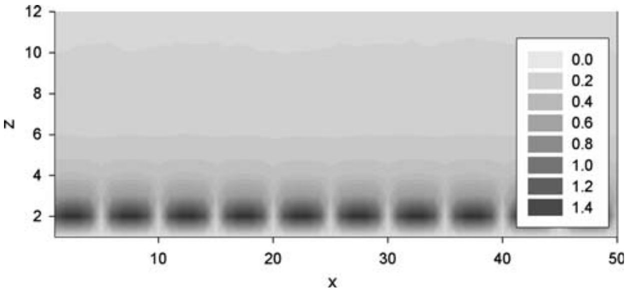

Fig. 3 Polymer beads density profiles along the xz plane. The case of $d_v = 5$, $m = 10$, $N = 199$

The properties of the surface of a polymer film (the most outer beads from the substrate for a given (x, y) coordinates) can be described in the terms of roughness which characterizes the surface of the system. This parameter is defined as:

$$R_a = \frac{1}{L^2}\sum_{i=1}^{L^2} |Z_i - \langle Z\rangle| \qquad (2)$$

where z_i is the coordinate of the ith point of the surface along z-axis and $\langle Z\rangle$ is the mean value of z_i. Figure 4 presents the values of the roughness parameter R_a obtained for the variety of chain lengths and the various number of chains. One can notice that all points form a common dependence which can be approximated by a master curve. Three different regimes can be distinguished in this curve:

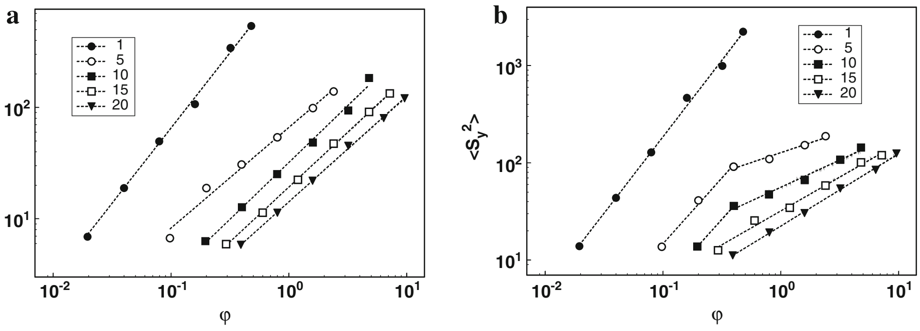

Fig. 2 The mean-squared radius of gyration components $<S_x^2>$ (**a**) and $<S_y^2>$ (**b**) as a function of the polymer coverage ϕ. The case of $d_v = 10$, the number of chains is given in the *inset*

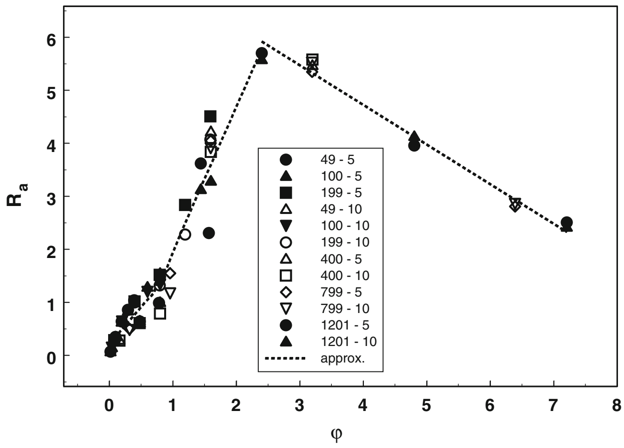

Fig. 4 The roughness of the polymer surface R_a as a function of the polymer coverage. The chain lengths and a type of the repulsive pattern are shown in the *inset*

- first, for the coverage ϕ less than 1 (what means, that the number of the polymer beads is less than the number of lattice points on the substrate). As the coverage of the system increases, one observes the increase of the roughness of the system
- for the number of polymer beads in the system larger than L^2 the increase of R_a becomes sharp and rapid along with ϕ. This is caused by the polymer beads which form the structures "one-over-one" and the resulting surface is full of local aggregations of beads and thus, the roughness of the system increases
- the third regime is observed for high values of ϕ, for which the decrease of R_a along the increase of ϕ is observed. This effect is probably controlled by a dense packing of the polymer beads and thus a smoothing of the surface is noticed

The shape of the surface formed by the adsorbed polymer chains can be seen in Fig. 5, which presents an example of the surface for $m = 5$ chains consisting of $N = 199$ beads. One can observe the elevations of the film which are located over the adsorbing 'valleys' while the minima are observed over the repulsive stripes, reflecting the substrate pattern in the shape of the outer surface of the polymer system. For many-chains system the chains are not identical statistically as some of them are almost totally adsorbed while the others have few contacts with the substrate and form the diffuse outer part of the film [19, 20].

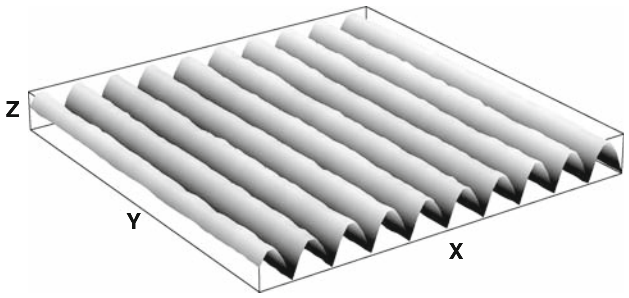

Fig. 5 An example of the surface of the polymer film. The case of $d_v = 5$, $m = 10$, $N = 199$

The properties of the substrate coated by polymer chains can be also described in terms of the fraction of the surface which is not covered by the macromolecules which we present in Fig. 6 as a function of coverage ϕ. The plots show the results for various lengths of chains. The upper plots show the fraction of accessible points located on stripes, whilst the lower points show the fraction of accessible sites in the valleys. One can observe that as value ϕ increases the number of free sites located in the valleys decreases more rapidly than that on the stripes. Further increase of ϕ leads to the situation in which the coverage of the stripes is similar to the coverage of the valleys and its results in total blocking of the sites important from the point of view of catalytic activity of the system.

The results presented above lead to the following conclusions: the dependence of the polymer surface roughness on the number of polymer beads in the system can be presented as a curve which is common for all chain lengths and the number of chains used in the simulations. Its course shows that this curve is not monotonous with a maximum. The analysis of the accessible sites on the substrate shows that the coverage of the adsorbing areas increases rapidly as the number of beads in the system increases, and then the growth of the coverage of these sites is moderate. The coverage of the repulsive stripes is lower in the previous case and exhibits rather a linear increase. The shape of the

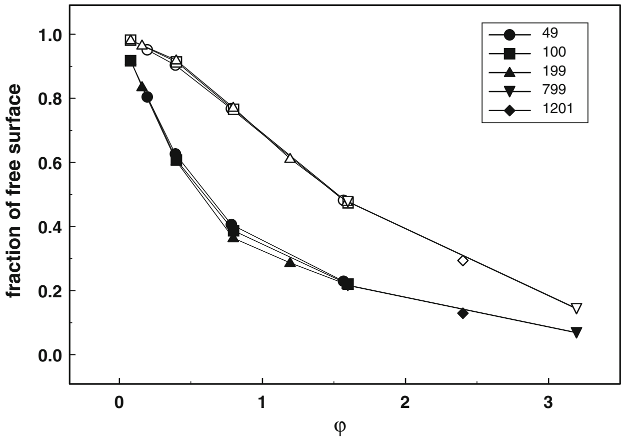

Fig. 6 Fraction of uncovered substrate sites as the function of the polymer coverage ϕ concerning the repulsive strips (*the upper curves*) and the attractive regions (*the lower curves*). The chain lengths are given in the *inset*

outer polymer surface of the film clearly reflects the repulsive pattern of the substrate.

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