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Properties of Star-Branched Polymer Chains Near a Surface

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Summary: We considered two model systems of star-branched polymers near an impenetrable surface. The model chains were constructed on a simple cubic lattice. Each star polymer consisted of $f = 3$ arms of equal length and the total number of segments was up to 799. The excluded volume effect was included into these models only and therefore the system was studied at good solvent conditions. In the first model system polymer chain was terminally attached with one arm to the surface. The grafted arm could slide along the surface. In the second system the star-branched chain was adsorbed on the surface and the strength of adsorption was varied. The simulations were performed using the dynamic Monte Carlo method with local changes of chain conformations. The lateral diffusion and internal mobility of star-branched chains were studied as a function of strength of adsorption and the chain length. It was shown that the behavior of grafted and weakly adsorbed chains was similar to that of a free three-dimensional polymer, while the strongly adsorbed chains behave as a two-dimensional system.

Keywords: adsorption; lattice models; Monte Carlo simulation; polymer brushes; star polymers

Introduction

Polymer systems near a surface were a subject of numerous studies because of their practical importance like lubrication, colloidal stabilization etc.[1-2] Polymer near surfaces were usually grafted or adsorbed. The tethering (end grafting) and adsorption of polymers on a solid surface is very interesting from the theoretical point of view because the presence of a surface distorts the properties of a chain when compared with a free chain in solution. Monte Carlo simulations of

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single grafted linear chain were recently performed by Han et al.[3] They showed that single grafted chains were always considerably larger than free chains because of the repulsion of the surface; their shape was also less spherical when compared to the latter. Star-branched polymers were recently a subject of extensive experimental and theoretical studies [4-5] but few works were devoted to the case where a surface is present. A general scaling theory of star-branched polymers at a surface was formulated by Ohno and Binder.[6] Off-lattice non-uniform star-branched chains (grafted in the branching point) were studied by Carignano and Szleifer.[7] They found that the properties of the brush depended strongly on the chain internal architecture. Mayes at al. built a mean-field theory concerning grafted star-branched chains studying the grafting density and the number of arms on density profiles.[8] Simple models of adsorbed star-branched chains with 3 arms were recently studied by means of the Monte Carlo method.[9-11] The detailed analysis of a size, shape, structure and dynamic properties was done there. Polymer brushes formed by many star-branched grafted chains were also recently studied.[12] It was shown that their static and dynamic properties depended strongly on the grafting density. The behavior of the grafted arms was quite different from that of the free arms. In this paper we compare properties of a single star-branched chain grafted onto an impenetrable surface and the same chain adsorbed on such a surface. The size and the structure of both kinds of star-branched polymers near the surface as well as the dynamic properties were analyzed here.

The Models and the Simulation method

Each star-branched macromolecule was constructed of identical structural units (segments) and consisted of $f = 3$ chain arms of equal length. The positions of polymer segments were restricted to a simple cubic lattice.[13-14] The excluded volume was introduced into the model by forbidding the double occupancy of lattice points. Here we will explain the difference between the two cases of a brush: grafted and adsorbed polymers. The difference between both cases is that the grafted polymers are attached to the surface with one end of a chain. The changing of the position of the grafting point (a monomer which is located at the end of the chain) was realized by allowing it to jump to the nearest lattice site, provided that the geometry of the chain was conserved. The position of the last segment was limited to $z = 0$ or 1. The absorbed chains are "attached" to the surface by interaction of some polymer monomers with the surface – the points of attachment are not necessarily constant and both their number and the position can change in time. The model system of grafted chains was athermal because all long-range interactions were assumed to be exactly the same. The same was assumed for adsorbed chains although a contact potential between polymer segments and the surface ε was introduced. The chain was put into the Monte Carlo box with edge $L = 100$ with the periodic boundary conditions imposed in x and y directions. At $z = 0$ an impenetrable wall was built. The so-called grafted chains were attached to that wall with one end of an arm while adsorbed chains had at least one contact with the surface.[9] The properties of model adsorbed and grafted chains were studied by means of the Monte Carlo simulation method. In the simulation algorithm the following set of local changes of conformations of chains was used: two-bond motion, three-bond motion, three-bond crankshaft motion, one- and two-bond end reorientations and branching point collective motions.[13] The lateral motion of grafted and adsorbed chains was enabled. For each set of parameters 25 independent simulation runs starting from different initial configurations were carried out in order to collect good statistics for all important parts of the conformational space.

Results and Discussion

The single star-branched chain consisted of $N = 49$, 100, 199, 400 and 799 segments was studied. The arm of a star polymer that was tethered to the surface was called 'a stem' while the remaining arms were called 'branches'. This distinction between these chain fragments of the star was important as their properties differed what will be shown and discussed below. In the adsorbed chain all three arms were equivalent, *i.e.* each arm could interact with the surface. The two cases of adsorption were studied: 'weak' adsorption with $\varepsilon = -0.3$ and 'strong' adsorption with $\varepsilon = -0.6$.

In Figure 1 we presented the dependence of the mean-squared radius of gyration $< S^2 >$ on the chain length N under consideration for adsorbed and grafted chains. What is interesting here is that there are almost no differences between the size of a grafted chain and a weakly adsorbed ($\varepsilon = -0.3$) chain. The $< S^2 >$ parameters scale for grafted chains as $N^{1.243\pm0.015}$ while for weakly adsorbed chains it scales as $N^{1.970\pm0.007}$. But the differences existed in the internal structure of both kinds of chains. Stems scaled as $N^{1.277\pm0.029}$ while branches as $N^{1.184\pm0.005}$. The case of the strongly adsorbed chain with $\varepsilon = -0.6$ shows that one deals with almost two-dimensional chain – it scales as $N^{1.491\pm0.031}$ (the theoretical predictions for 2-dimensional chains are $N^{3/2}$).

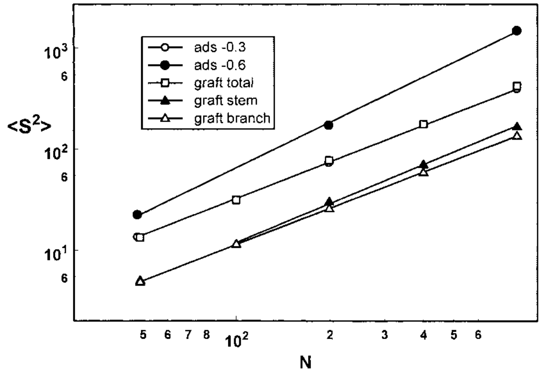

Fig.1 The mean-square radius of gyration $< S^2 >$ as a function of the chain length N. The radius of gyration for stems and for branches of grafted chains were also given.

The instantaneous shape of a polymer chain can be described in terms of the asphericity factor, i.e. by the following equation $\delta^* = <\Sigma (L_i - L_j)^2> / 2<S^4>$, where L_i were the principal components of the gyration tensor.[5] In Figure 2 we present the variations of this parameter with the chain length. The asphericity factor of all chains increases generally with the chain length with the exception of strongly adsorbed chains where this parameter is rather fluctuating without significant changes. The factor δ^* is close to 0.45 for the longest chains for both models what corresponds to the higher asphericity when compared with free star-branched chains where δ^* = 0.34.[9-10]

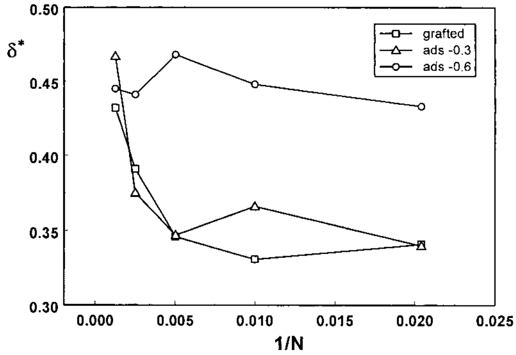

Fig.2 The asphericity factor δ^* as a function of chain length N.

Further insight into the structure of both kinds of chains near the surface can be obtained from the analysis of polymer segment density profiles. In Figure 3, we present density profiles for grafted and adsorbed chains of the total length $N = 199$. For a grafted chain the distribution of segments is very similar to that of a weakly adsorbed chain in case of an adsorbed chain the maximum is shifted toward the surface compared with the grafted case. The case of a strongly adsorbed chain is dramatically different – its density profile confirms that it forms a quasi two-dimensional structure.

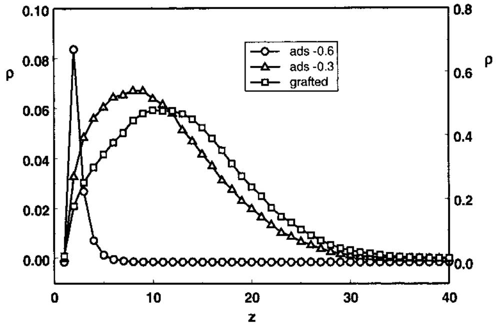

Fig.3 The density profiles for the chains consisting of $N = 199$ segments.

The short-time dynamic behavior of grafted and adsorbed chains can be studied in terms of the longest relaxation times. These relaxation times can be extracted from center-to-end vector autocorrelation function. Figure 4 shows the plots of the longest relaxation times τ_R as a function of a total chain length N. For the chain length under consideration the relaxation times of weakly adsorbed chains and of branches of grafted chains are similar and both scale as $N^{2.19}$. In grafted chains the stems relax much slower than the branches and their relaxation times scale as $N^{1.82}$. Quite a different scaling behavior was observed in the case of strongly adsorbed chains where the scaling exponent was 2.86. For free star-branched chain $\tau_R \sim N^{2.30}$.[13] The scaling behavior of adsorbed chains is close to the Rouse model in three dimensions (for weakly adsorbed chain) and in two dimensions (for strong adsorption case).

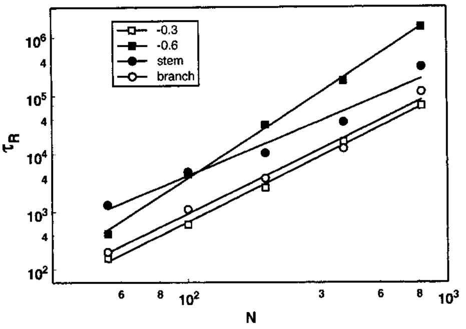

Fig.4 The relaxation times of arms of a adsorbed chains, of stems and of branches as a function of the chain length *N*.

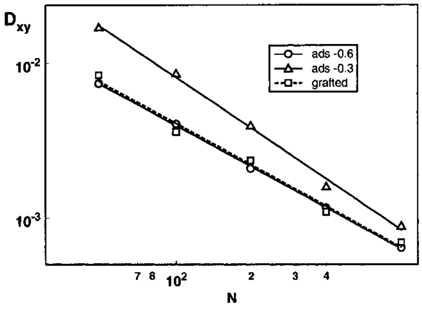

Fig.5 The self-diffusion coefficient D_{xy} as a function of the chain length *N*.

A long-time dynamic behavior is usually described by the self-diffusion coefficient. In order to determine the latter first we calculated the center-of-mass autocorrelation function from which we extracted the value of the self-diffusion coefficient *D* using the Einstein's relation. For our models we studied the chain motion along *xy* direction only as the motion along the *z*-axis was limited. [11-12]. Figure 5 presents the self-diffuison coefficient D_{xy} as a function of the chain length. The plots for grafted and strongly adsorbed chains are practically identical and the scaling was found $N^{-0.90}$. The weakly adsorbed chains show greater mobility than the latter and the scaling exponent was found $\gamma = -1.08$. The identity of self-diffusion coefficient D_{xy} for the grafted and strongly adsorbed cases show that besides the different structure of the polymer layer (see Fig.3). The scaling exponents are very close to that of the free chain case where $D \sim N^{-1}$ [13]

Conclusions

In this paper we studied the properties of star-branched chains near an impenetrable surface. The model star polymers were limited to a simple cubic lattice and to good solvent conditions. The weakly adsorbed as well as the grafted chain were three-dimensional and distorted only when compared with a free chain. The strongly adsorbed chain had quite different size and could be considered as two-dimensional structures. It was shown that although the size and the structure of grafted and weakly adsorbed chain were almost the same their long-time dynamic behavior were different: the mobility of the weakly grafted chain was significantly larger. On the other hand the mobility of the strongly adsorbed chain was almost the same as that of a grafted chain.

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