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Dynamics of Grafted Star-Branched Polymers.
A Monte Carlo Study

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Summary: Monte Carlo simulations of simple models of star-branched polymers were carried out. The model chains were confined to simple cubic lattice and consisted of f = 3 branches of equal length and the total number of polymer segments as well as the density of grafted chains on the surface were varied. The chains have had one arm end attached to an impenetrable plate. The simulations were performed by employing the set of local micromodifications of the chain conformations. The model chains were athermal, i.e. good solvent conditions were modeled, the excluded volume effect was present at the model. The density of grafted chains on the surface was varied from a single chain up to 0.3. The static and dynamic properties of the system were studied. The influence of polymer concentration as well as the polymer length on static and dynamic properties of the system studied was shown. The relation between the structure and short-time dynamics (relaxation times) was discussed.

Model and simulation algorithm

The model star-branched chains consisting of f = 3 arms were confined to a simple cubic lattice, i.e. polymer segments were represented by vectors of the type [±1, 0, 0], [0, ±1, 0], [0, 0, ±1]. The total number of polymer beads N was varied between 49 and 799. The excluded volume was introduced into the model, forbidding the double occupancy of lattice sites by polymer segments. There was no energetic distinction between polymer-polymer and polymer-solvent contacts (an athermal model). The model chains were put into the Monte Carlo box with periodic boundary conditions only in two directions. In the third direction there was a hard wall, to which the chains were grafted with one end of an arm. The grafted end can move freely along the surface and therefore a system resembling a micelle or a membrane was formed (Figure1).

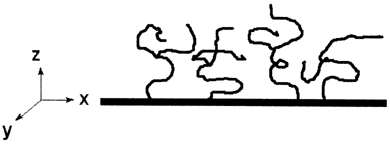

Figure1. Schematic representation of the model system.

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The simulation algorithm was based on local reorientations of chains' conformations. The set of these micromodifications consisted of the following moves: (a) two-bond motion, (b) three-bond motion, (c) three-bond crankshaft motion, (d) end reorientations (linear and star-branched chains only), (e) branching point collective motion (star-branched chains only). The above set of local motions defines the time unit.[1, 2]

Results and discussion

The displacement of chains was studied by the autocorrelation functions. Figure 2 presents center-of-mass autocorrelation function split for *z*- and *xy*-contributions. One can observe that after a short initial period *z* component reaches plateau (as no long-distance motion along *z*-axis is possible) while *xy* component scales for longer times with time as t^1. That suggests the Rouse-like behavior of the grafted chains what was previously found for linear chains.[3]

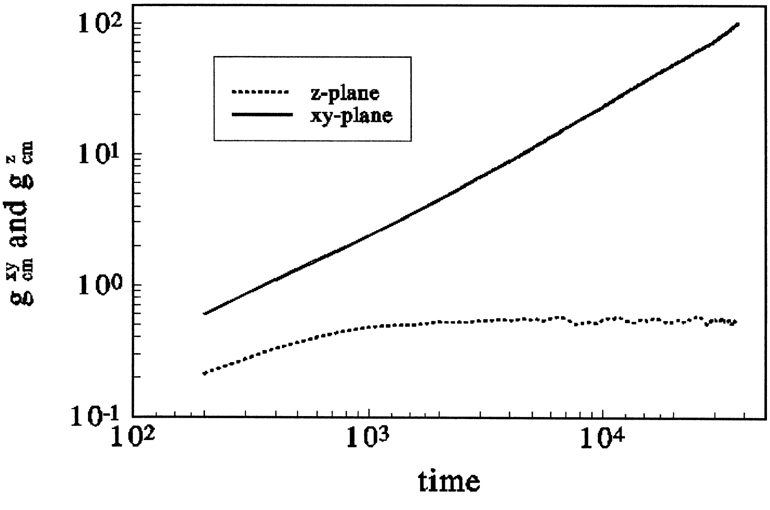

Figure 2. The center-of-mass and single-bead autocorrelation functions for $N = 199$.

Diffusion coefficients of star-branched polymers were determined from the autocorrelation function g_{cm} basing on the Einstein formula.[2,4] Figure 3 presents a typical plot of the dependence of the self-diffusion coefficient along the *xy*-plane D_{xy} on the total length of the chain N. The diffusion coefficient scales as N^{γ} where the scaling exponent γ is between -1 and -1.5 what is characteristics for polymer melts at moderate densities. The dependence of D_{xy} on the grafting density φ is shown in Figure 4. The diffusion coefficient decreases along with the rise of the grafting density. This decay is much faster than in the case of polymer solutions.[2,4] The behavior of the diffusion coefficient is different from the case of linear chains where $D_{xy}/D_{xy}^{o} \sim 1 - c^{2}$ where D_{xy}^{o} is a diffusion coefficient at infinite dilution.[5]

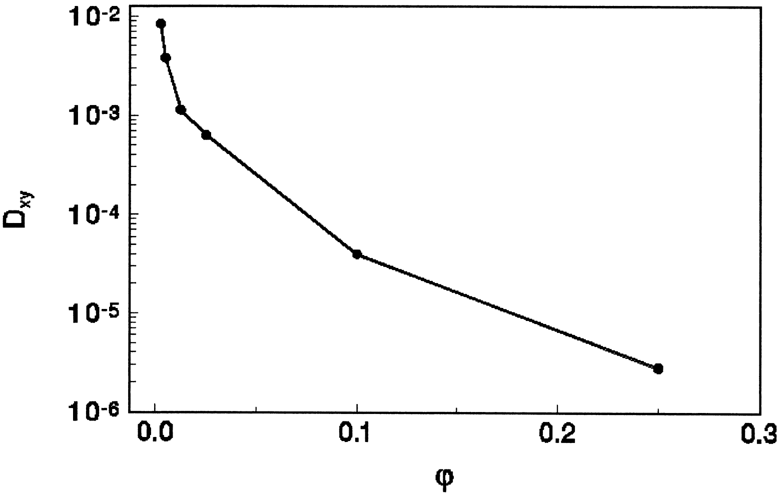

Figure 3. Diffusion coefficient D_{xy} as a function of the grafting density φ for $N = 199$.

As one can notice, the most dramatic change of the diffusion coefficient takes place at the small grafting densities; the decrease of D_{xy} is one order of magnitude. Apparently this strong dependence is caused by the presence of branched structure of chains.

As shown in Figure 4, the distribution of polymer segments, even in a case of a small grafting density (0.05), qualitatively changes its shape as compared with the single chain case. Closer examination of the density that the presence of even small number of grafted chains introduces a specific order of the grafted layer, namely the grafted arms are positioned vertically to the plane; also the non-grafted arms exhibit similar, but less pronounced ordering effect.

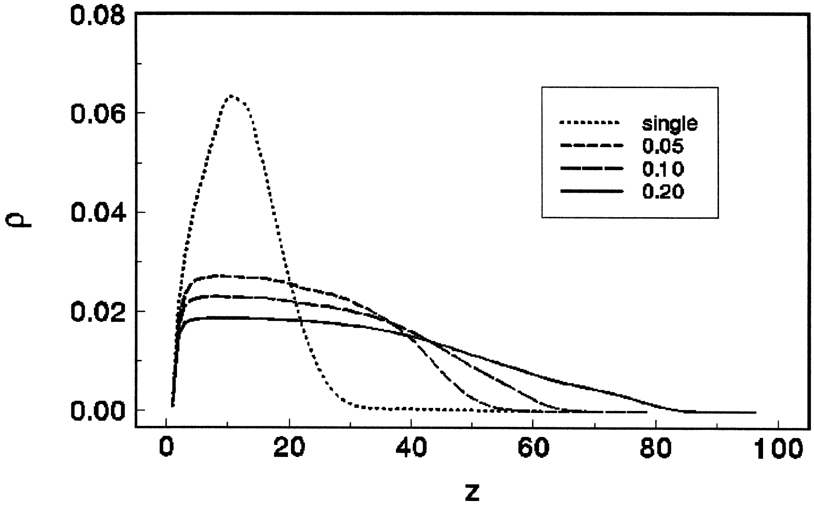

Figure 4. Distribution of polymer segments along the z-axis for $N = 199$.

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