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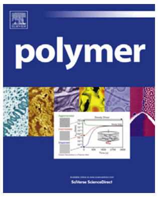

Starlike polymer brushes in Θ-solvent

Chan-Fei Su [a], Wei Cui [a], Holger Merlitz [a, b, *], Chen-Xu Wu [a, **], Jens-Uwe Sommer [b]

[a] *Department of Physics and ITPA, Xiamen University, Xiamen 361005, People's Republic of China*
[b] *Leibniz-Institut für Polymerforschung Dresden, 01069 Dresden, Germany*

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ABSTRACT

The properties of starlike polymer brushes in Θ-solvent are investigated using molecular dynamics simulations, scaling- and mean-field theory. Deviations of layer thickness and monomer density from predictions of scaling theory are analyzed and explained. Contrary to common believes, we conclude that the Alexander-deGennes scaling theory is not valid for starlike polymer brushes in Θ-solvent, unless the grafting density is extremely low. A comparison with structural and dynamical properties of starlike polymer brushes in good solvent is carried out. Previous studies in good solvent reported about the dual-population structure of these branched polymer brushes, with coexisting phases of stretched and retracted molecules; the same separation emerges in Θ-solvent, though at higher grafting densities. Molecular tension and population fractions are shown to be solvent-dependent, and a reduced dynamical flip-rate between the two populations is observed for the case of the Θ-brush.

1. Introduction

Densely grafted polymer layers, commonly known as polymer brushes, have been studied and received ample attention in recent years because of their important applications in technical coatings, biomaterials or colloid stabilization. As the properties of brushes made of linear chains have been thoroughly studied in the past several years, recently more and more attention is being paid on more complex architectures, e.g. randomly or regularly branched polymers. These systems are interesting for a couple of reasons: Since they are offering an enhanced number of end groups which could be functionalized, they are regarded good candidates for stimuli-responsive surface layers [1–5]. They are further expected to offer improved anti-inflammatory and anti-fouling properties, i.e. barriers against a penetration by bacteria or proteins [6,7]. If grafted onto colloids, they lead to a higher stability against coagulation with a thinner polymeric layer than a decoration of linear chains [8]. Most importantly, branched polymer brushes are known to play vital roles in biological materials such as airway epithelia [9], are serving as anti-viral barriers [10] or highly efficient drug-delivery systems [11].

On the theoretical side, Alexander and deGennes [12,13] were the first to propose the blob-based scaling approach to polymer brushes. Later on Semenov, Skvortsov, and Milner used self-consistent field (SCF) theory to study linear polymer brushes based on the strong stretching assumption [14–16]. Scaling properties of star and comb- brushes were analyzed by Zhulina and Birshtein [17,18], followed by a more advanced scaling theory of dendritic brushes given by Kroeger et al. [19]. Among the most important consequences of these studies was the proof that Alexander-deGennes scaling theory remains valid for starlike polymer brushes in good solvent, the simplest type of dendrimer polymer brushes, as shown in recent studies by Polotsky et al. [20,21] using numerical SCF theory, and by Merlitz et al. using molecular-dynamics (MD) and semi-analytical mean-field theory [22]. In particular, MD simulations have verified the validity of scaling theory at low- and moderate grafting densities, though with certain deviations at high grafting densities [23].

The properties of brushes not only depend on molecular architecture but also on solvent quality. Most of the previous investigations have focused on polymer brushes in good solvent, with far less works addressing brushes in Θ – or poor solvent. Recent examples can be found in terms of the three-dimensional SCF results on linear brushes in Θ-solvent achieved by Suo and Yan [24], and Flory-type mean-field calculations presented in Ref. [25]. A scaling- and SCF-theoretical modeling of planar and spherical polymer brushes in both good and Θ-solvent has been presented by Rud et al. [8] and Borisov et al. [26]. It is worth noting that here, just

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[*] Corresponding author. Leibniz-Institut für Polymerforschung Dresden, 01069 Dresden, Germany.
[**] Corresponding author.
E-mail addresses: merlitz@gmx.de (H. Merlitz), cxwu@xmu.edu.cn (C.-X. Wu).

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as in previous publications, the universal validity of the Alexander-deGennes scaling theory has been suggested. This fact is questioned in the present paper, in which we compare scaling predictions resulting from the Alexander-deGennes theory with mean-field predictions for brushes in Θ-solvent, the latter including higher-order virial terms. Only in leading order approximation, both approaches lead to identical scaling predictions, while the higher virials alter the scaling behavior of the brushes at common grafting densities. These deviations are clearly verified in the MD-simulations presented here.

Further on, a comparison between structural properties of brushes in Θ-solvent and in good solvent is carried out. It is found that in both cases, a segregation of chain conformations into two distinct populations or phases, called “up” and “down”, depending on their degree of stretching, occurs. However, in Θ-solvent, this segregation takes place at considerably higher grafting densities. Static properties like layer-thickness, concentration and chain tension of simulated brushes are compared with scaling- and mean-field theory. Further on, the dynamical motions of molecules, which are flipping between their up- and down states, are investigated and compared with previous results obtained in good solvent.

The rest of the paper is organized as follows: In Section 2, the numerical models and simulation tools are introduced. Scaling/mean-field theory of layer-thickness and concentration are discussed in Section 3.1, followed by the analysis of the dual-population structure in Section 3.2, and the dynamics of individual chains in Section 3.3. Section 4 summarized the findings.

2. Brush model and simulation

Since the details of the simulation model have been described by the authors in previous publications [27], a short summary suffices here. The polymers were modeled using a coarse-grained bead-spring model without explicit twist or bending potential, i.e. the bonds were freely rotating and freely jointed within the limits set by excluded volume interactions with nearby monomers. The beads represent spherical monomers which interact among themselves via a shifted Lennard–Jones (LJ) potential given by

$$U_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{b}{r}\right)^{12} + \left(\frac{b}{r}\right)^{6} - \left(\frac{b}{r_{\mathrm{c}}}\right)^{12} - \left(\frac{b}{r_{\mathrm{c}}}\right)^{6}\right], \tag{1}$$

where ε defines the strength of interaction, b stands for the bead diameter, and r_{c} is the cutoff distance. It is easy to verify that this potential has a minimum at $r_{\mathrm{min}} = 2^{1/6}b$ with the depth $U_{\mathrm{LJ}}(r_{\mathrm{min}}) = -\varepsilon$. If a cutoff $r_{\mathrm{c}} = 2^{1/6}b$ at the potential minimum is implemented, then the attractive range of the potential is eliminated and thus polymers in athermal (good) solvent can be simulated. Otherwise, either the ε-parameter (the interaction strength) or the temperature can be varied to simulate different (implicit) solvent qualities.

The Θ-point has to be determined through simulations of long linear polymers in dilute solution, in which their end-to-end distance (or alternately their radius of gyration) scales as ~$N^{1/2}$, N being the degree of polymerization. In the current model, this condition is satisfied at the effective temperature $T^{*} = T/\varepsilon = 3.0 \pm 0.1$ [25], while the Boltzmann factor k_{B} is set to unity. For this paper, $\varepsilon = 0.25$ and $T = 0.75$ were used to simulate brushes at the Θ-point, while the cut-off length was $r_{\mathrm{c}} = 2.5b$. Systems in athermal solvent were simulated at a temperature $T = 1.2$.

The connectivity between monomers was enforced through a finite extensible nonlinear elastic (FENE) potential [28], defined as

$$U_{\mathrm{FENE}}(r) = -0.5KR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] + 4\varepsilon\left[\left(\frac{b}{r}\right)^{12} - \left(\frac{b}{r}\right)^{6}\right] + \varepsilon, \tag{2}$$

where the first term is attractive and extending to a maximum bond length of $R_0 = 1.5b$, whereas the second term, a Lennard–Jones potential, contributes a short-range repulsion, which is cut off at $2^{1/6}b$, the minimum of the LJ potential (a double count of pair interactions of neighboring monomers was excluded by the simulation algorithm). The coefficient K is set to be $K = 22.5/k_{\mathrm{B}}T$, which was well tested in earlier studies [29]. For uncharged and relaxed polymers, this parameter set leads to an average bond length of $r_{\mathrm{av}} = 0.97b$.

The substrate forms a planar wall, defining the $x - y$-plane at $z = 0$, where monomers are prohibited to penetrate through a 9-3 type LJ wall potential

$$U_{\mathrm{WALL}}(r) = \varepsilon\left[\frac{2}{15}\left(\frac{b}{r}\right)^{9} - \left(\frac{b}{r}\right)^{3}\right], \tag{3}$$

including a cutoff at the minimum to deliver a purely repulsive short-range potential.

The simulations were carried out using the open source LAMMPS molecular dynamics package [30]. The equation of motion of any nongrafted monomer in the implicit solvent (neglecting any hydrodynamic interaction) is given by the Langevin equation:

$$m\frac{\mathrm{d}^2\mathbf{r}_i}{\mathrm{d}t^2} + \zeta\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} = -\frac{\partial U}{\partial \mathbf{r}_i} + \mathbf{F}_i, \tag{4}$$

where $\mathbf{r}_i$ is the position of the i' th monomer, U is the total conservative potential energy acting on the i' th monomer, m is mass for one monomer, and $\mathbf{F}_i$ is a random external force without drift and a second moment proportional to the temperature and the friction constant ζ. In this work, the bead size defines the unit-length $b = 1$ (also referred to as LJ-unit length), and the monomer mass the unit-mass $m = 1$. Energies and forces are presented in units of $k_{\mathrm{B}}T$ and $k_{\mathrm{B}}T/b$, respectively. Times are in units of the LJ-time $\tau_{\mathrm{LJ}} = \sqrt{\varepsilon/(mb^2)}$; note that there is a potential source of confusion here: The ε-parameter did not equal unity in case of systems at Θ-temperature. Yet, we consistently refer to the unit-LJ-time $\tau = 1$, in which $\varepsilon = m = b = 1$. The simulation time-step was set to $\Delta t = 0.0025$ of these time units, and the friction coefficient to $\zeta = 1$ (in units of the inverse LJ-time). The applied friction leads to an overdamped motion on length scales of the bead size and hence to a Brownian motion under the approximation of an immobile solvent, i.e., approximate Rouse dynamics [31].

Star polymers were made of 4 arms, with one single arm grafted onto a flat and impenetrable substrate, to form 10 × 10 arrays in a checkerboard pattern. The grafting density σ of the brush is then defined as the number of grafted monomers per unit-area. As long as the layer is in its brush-regime, i.e. the layer thickness is significantly exceeding the average grafting distance, the grafting pattern has no influence on the properties of the brush. This is so because the correlation length of the polymers is limited to length-scales of the order of the grafting distance, and the brush is losing any memory on the mode of grafting over these distances. The ”spacer length” (here: number of monomers of each arm) amounted to $N_{\mathrm{s}} = 50$, sufficiently long to guaranty an overlap even at low grafting densities and therefore allowing for a wide range of densities for the scaling analysis (note that the grafting density of the brush is defined as the number of grafted monomers per unit-area). To enable the analysis at even lower grafting densities, we

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