



## Structure and lubrication of solvent-free dendron brushes



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### ABSTRACT

Using analytical and numerical self-consistent field (SCF) methods we analyze equilibrium structure of dry (solvent-free) brush of branched polymers in wide range of chain grafting densities. A detailed analysis is performed for starlike polymers end-tethered to planar surface by terminal monomer of one of their branches. At moderate grafting densities ensuring Gaussian elasticity of tethered stars the brush structure is described by strong stretching SS-SCF theory employing parabolic molecular potential. At high grafting densities an approximate analytical AA-SCF theory is used to describe stratification of dry brush. Analytical predictions are supplemented by results of numerical Scheutjens-Fleer SF-SCF model. Interpenetration between dry brushes is analyzed as a function of grafting density and degree of branching of tethered chains. Comparison of interpenetration and friction between dry brushes with varied chain architectures pointed at optimal lubrication by macrocycles tethered to the surface by branching point. It is demonstrated that shear stress in sliding brushes of starlike macromolecules sharply decreases at high grafting densities corresponding to almost full stretching of the longest elastic path in the polymers.

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### 1. Introduction

A conventional way to modify interactions between particles is to tether polymer chains onto their surfaces [1]. Both normal and shear forces are mediated by the tethered macromolecules. In recent years a lot of the theoretical and experimental research was devoted to study interactions between tethered polymer monolayers (see, e.g., reviews [2–6]).

It was demonstrated that brushlike layers of linear macromolecules combine a significant resistance to external pressures with a relatively low friction providing thereby low values of the friction coefficient [2,7,8].

Various physical/chemical mechanisms contribute to the lubricating properties of solvated brushes. For example, the extreme lubrication of surfaces bearing polyzwitterionic polymers is linked to the strong hydration of its phosphorylcholine-like monomers. In this case, the low friction between strongly compressed brushes is believed to be due to the lubricating action of bound but labile

water molecules around their hydrated monomers [9]. In the case of weakly-to-moderately compressed polyelectrolyte or neutral brushes, the disjoining force is attributed either to the osmotic pressure of mobile counterions or to an increase of the van der Waals interaction between monomers in the gap between surfaces, while their shear force is governed by the rubbing of monomers in the interpenetration zone of the brushes. Although the width of the interpenetration zone increases with decreasing distance between the surfaces and eventually coincides with the interplate distance, the excluded volume interactions between monomers in neutral brushes as well as the osmotic pressure of counterions in polyelectrolyte brushes remain dominant over the shear force upon brush compression, preserving thereby lower values of the friction coefficient [10]. The asymmetry of apposing brush-decorated surfaces (e.g., neutral brush against charged counterpart) extends the range of options even more to regulate the interactions and interpenetration of compressed brushes [11].

It has been demonstrated that interactions between polymer-decorated surfaces can be also tuned by changing architecture of the tethered chains. Extensive MD simulations of normal and shear forces have been performed for brushes of neutral and charged comblike macromolecules [12,13]. These studies established the

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length scales that control the deformation of the comblike macromolecules, and predicted lower friction coefficients for the charged brushes compared to neutral ones under similar conditions. Recent MD simulations [14] demonstrated lower values of the normal pressure and shear stress for brushes of cyclized polymers (rings) compared to linear chain brushes with the same polymer mass per unit area and distance between plates. The adsorbed layers of diblock copolymer with linear anchoring block and comblike brush-forming block demonstrated a high loading capacity combined with a low friction force, proving thereby to be good lubricants [15]. In our previous studies [16–18] we theoretically investigated brushes of branched treelike macromolecules (dendrons with variable number of generations) under good and theta solvent conditions, and examined how a compression of apposing brushes affects the disjoining pressure and the mutual interpenetration of the brushes. By using analytical and numerical SCF approaches, we have shown that the branching of tethered macromolecules decreases both the disjoining pressure and interpenetration of dendron brushes compared to brushes of linear chains with the same polymer mass per unit area and distance between surfaces. The former observation pointed at possible inferior stabilizing properties of the dendron brushes, while the latter indicated that branching of brush-forming macromolecules might enhance the lubrication of the dendron-decorated surfaces.

In this study we consider dry (solvent-free) brushes of polymers that have branched architectures. Self-assembled dry brushlike layers of tethered chains are found in melts of block copolymers in the strong segregation limit [19,20]. They are also formed by adsorption of the polymeric surfactants from melts [21–24] and found in composite materials of microsegregated block-copolymers and nanoparticles [25]. When brushes contact each other, they interpenetrate by delegating peripheral sections of the tethered polymer into apposing counterpart. The width of interpenetration zone is governed by the molecular weight of the chains and their grafting density [26,27]. It has been demonstrated recently [18] that interpenetration of apposing brushes could be also mediated by architecture of the tethered macromolecules. Because friction between sliding brushes is associated with rubbing of monomers in the interpenetration zone, it is fundamentally important to understand how the width and structural organization of this zone depend on the architecture of the tethered macromolecules.

Theoretical studies on the rheology of dense polymer brushes focused mostly on linear unentangled chain brushes [2,28–32]. It has been generally accepted that shear stress in sliding brushes of flexible unentangled chains exhibits two regimes with linear and sublinear dependences on the sliding velocity. A more complex behavior has been observed in the nonlinear regime of friction between brushes of comblike polymers [12,13]. In the linear friction regime the width of the interpenetration zone, and the end-point distribution of the tethered chains remain almost unaffected by the shear rate and retain their equilibrium values. The target is to know how the architecture and grafting density of the branched macromolecules affect the shear stress in sliding brush-decorated surfaces compared to their linear counterparts. Here a comprehensive analysis is performed for brushes formed by starlike polymers that are end-tethered to a surface by one of its branches. We aim to examine the dependence of the friction force on the chain grafting density including the regime of moderately dense grafting that ensures the Gaussian elasticity of the tethered stars, and the regime of dense grafting wherein the starlike polymers undergo vertical segregation. As in our previous studies [16–18] we check and complement the analytical predictions with the results of the numerical SF-SCF model.

The remainder of the paper is organized as follows. In section 2 we apply the analytical SS-SCF and the numerical SF-SCF models to

study two contacting dry brushes in the Gaussian elasticity regime. We investigate here the dependence of brush-brush interpenetration length on the system parameters. In section 3 we analyze the structure of dry brushes of symmetric starlike polymers at high grafting densities by using an approximate analytical (AA-SCF) model to examine the effect of brush stratification on the interpenetration length. In section 4 we formulate an expression for the shear stress between sliding brushes of starlike polymers in the linear regime of friction, and vary the architecture of the tethered dendrons to optimize lubrication of brush-decorated surfaces. Finally, in section 5 we formulate the conclusions.

## 2. Dry brush of starlike macromolecules

### 2.1. Model and SS-SCF formalism

We consider a dry (solvent-free) brush composed of flexible starlike homopolymers that are end-tethered by the terminal monomers of one of their branches (stem with  $n_0$  monomer units of size  $a$  each) to a planar surface. Each starlike molecule has  $q$  free arms (branches) with  $n$  monomer units each, and the total number of monomer units in the macromolecule and its longest elastic path are  $N = n_0 + nq$  and  $n_0 + n$ , respectively (see Fig. 1a). The chains are tethered to a planar surface with grafting area  $s$  per molecule corresponding to dimensionless grafting density  $\sigma = a^2/s$ . The net thickness of the dendron brush

$$H = aN\sigma \quad (1)$$

and the volume fraction of monomer units  $\phi = Na\sigma/H$  are independent of the chain architecture. The chains are assumed to be stretched normally to the surface with respect to the unperturbed size of the longest path, yet exhibiting Gaussian (linear) elasticity. Two identical dry brushes of starlike polymers (dendrons of the first generation) in contact with each other are depicted in Fig. 1e.

The analytical strong stretching self-consistent field (SS-SCF) approach to polymer brushes was first developed for linear chains [20,33,34] and later extended to branched polymers [35–37]. The analytical SS-SCF model presumes linear elasticity of the stretched chains on all length scales and operates with the chain trajectories  $z(m)$  that specify the most probable height  $z$  of the monomer unit with ranking number  $m$ . In the framework of the strong stretching (SS) approximation monomers in the brush are subjected to the self-consistent field potential

$$\frac{U(z)}{k_B T} = \frac{3}{2a^2} k^2 (H^2 - z^2) \quad (2)$$

where  $z$  is the distance from the grafting surface, and  $k$  is the

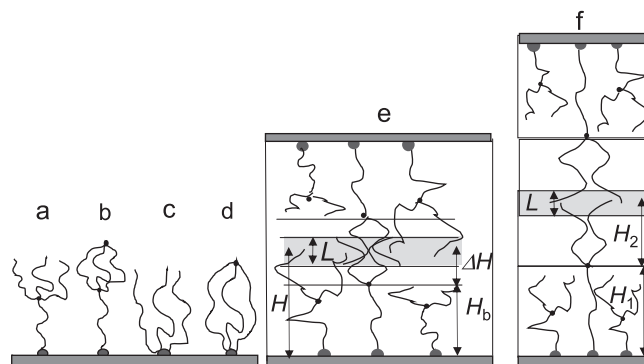


Fig. 1. Schematics of macromolecular architectures (a,b,c,d) and interacting brushes (e,f).

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