Computer Simulations of Bottle Brushes: From Melts to Soft Networks

Zhen Cao, ‡ Jan-Michael Y. Carrillo, § Sergei S. Sheiko, † and Andrey V. Dobrynin*†

†Polymer Program and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-3136, United States
‡Center for Nanophase Materials Sciences and §Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
¶Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3220, United States

ABSTRACT: Using a combination of molecular dynamics simulations and analytical calculations, we study dense bottle-brush systems in a melt and network state. Analysis of our simulation results shows that bottle-brush macromolecules in melt behave as ideal chains with effective Kuhn length \( b_K \). Simulations show that the bottle-brush-induced bending rigidity is due to an entropy decrease caused by redistribution of the side chains upon backbone bending. The Kuhn length of the bottle brushes increases with increasing the side-chain degree of polymerization \( n_c \) as \( b_K \propto n_c^{0.46} \). This model of bottle-brush macromolecules is extended to describe mechanical properties of bottle-brush networks in linear and nonlinear deformation regimes. In the linear deformation regime, the network shear modulus scales with the degree of polymerization of the side chains as \( G_0 \propto (n_c + 1)^{-1} \) as long as the ratio of the Kuhn length, \( b_K \), to the size of the fully extended bottle-brush backbone between cross-links, \( R_{\text{max}} \), is smaller than unity, \( b_K/R_{\text{max}} \ll 1 \). Bottle-brush networks with \( b_K/R_{\text{max}} \ll 1 \) demonstrate behavior similar to that of networks of semiflexible chains with \( G_0 \propto n_c^{-0.5} \). In the nonlinear network deformation regime, the deformation-dependent shear modulus is a universal function of the first strain invariant \( I_1 \) and bottle-brush backbone deformation ratio \( \beta \) describing stretching ability of the bottle-brush backbone between cross-links.

INTRODUCTION

Elasticity of polymeric networks originates from deformation of the individual polymer strands making up the network.\(^1\)\(^,\)\(^2\) Under applied external stress these strands extend reducing the number of available conformations and therefore decreasing the total entropy of the system. The network shear modulus \( G \) is proportional to product of number density of polymeric strands \( \rho_{ch} \) and thermal energy \( k_B T \) (where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature). In dry (solvent-free) networks, the strands number density \( \rho_{ch} \) is inversely proportional to the number-average degree of polymerization, \( N_e \) of network strands, resulting in \( G \propto N_e^{-1} \). This suggests that polymeric networks could be made softer by decreasing cross-linking density, i.e., increasing \( N_e \). However, this scaling relation holds until the degree of polymerization of strands between cross-links, \( N_e \), is below the degree of polymerization between entanglements of overlapping strands, \( N_c \). For longer network strands, \( N_e > N_c \), these entanglements are locked by cross-linking reaction and thus restrict configurational space accessible to polymeric strands. As such, the entanglements play a role of topological cross-links that control elastic properties of the networks as modulus saturates at \( G \propto 1/N_c \). For dry polymeric networks, this imposes a lower limit on the network shear modulus to be on the order of 0.1 MPa independent of the chemical degree of polymerization \( N_c \).

These topological constraints (chain entanglements) pose challenges in making supersons networks with shear modulus below 1000 Pa that could be good candidates for synthetic substitutes of biological tissues.\(^4\)\(^,\)\(^5\)\(^,\)\(^6\) Note that these values of the shear modulus could be achieved in polymeric gels, but this requires for gel to be swollen in a solvent which may leak upon gel deformation and dry upon storage. There are several approaches that allow overcoming this restriction. In the first approach networks are prepared by cross-linking polymer chains in a semidilute solution followed by the solvent evaporation.\(^7\)\(^,\)\(^8\) This results in remarkably stretchable elastomers with the ultimate strain over 3000%.\(^9\) The second group of approaches utilizes synthetic modifications of polymer chains to increase effective entanglement molecular weight through chain branching in combs, stars, dendrimers, and bottle brushes.\(^9\)\(^–\)\(^19\) This may be considered as effective dilution of a polymer network by binding solvent molecules to macromolecules. Bottle-brush systems (see Figure 1) are the most promising example of the modification of the macromolecular structures achieving the entanglement shear modulus \( G_c \), to be on the order of 100 Pa with increasing the degree of polymerization of the side chains.\(^17\) In this paper, we use a
combination of molecular dynamics simulations and theoretical calculations to study elasticity of networks made by cross-linking bottle-brush macromolecules and show how to relate these properties to structure of bottle brushes in a melt.

**RESULTS AND DISCUSSION**

To study properties of the bottle-brush networks, we have performed coarse-grained molecular dynamics simulations of cross-linked bottle-brush macromolecules. In our simulations polymer chains making up bottle-brush macromolecules were modeled by Lennard-Jones particles (beads) with diameter \( \sigma \) connected by the FENE bonds (see Figure 1). For all studied systems the number of monomers (beads) in the bottle-brush backbone was equal to \( N = 100 \) with every monomer of the backbone having a side chain attached to it. The number of monomers in the side chains, \( n_{sc} \), was varied between 0 (linear chains) and 20. The networks were prepared by randomly cross-linking melt of bottle-brush chains at monomer concentration 0.8\( \sigma \). Simulation details are described in Simulation Methods section.

**Properties of Bottle-Brush Melt.** We begin our discussion by presenting results of molecular dynamics simulations of melts of bottle-brush macromolecules. The purpose of this initial study is to understand factors controlling bending rigidity and, hence, the Kuhn length, \( b \), of individual bottle-brush macromolecules in a melt. This will allow mapping bottle-brush macromolecules into the discrete chain model with internal bending rigidity \(^{21} \) that was recently applied to describe nonlinear elasticity of polymeric and biological networks and gels.\(^{22,23} \)

![Figure 1. Bottle-brush macromolecule with N monomers belonging to bottle-brush backbone colored in blue and side chains consisting of \( n_{sc} \) monomers shown in green (left). Snapshot of the bottle-brush network with three individual bottle-brush macromolecules highlighted (right).](Image)

The Kuhn length of a bottle-brush macromolecule is obtained from bond–bond correlation function. This function describes decay of the orientational memory along the bottle-brush backbone between two unit bond vectors \( \vec{n}_i \) and \( \vec{n}_{i+l} \), pointing along the backbone bonds and separated by \( l \)-bonds as shown in the inset of Figure 2. This function is defined as

\[
G(l) = \frac{1}{N_b - l} \sum_{i=1}^{N_b-l} \langle \vec{n}_i \cdot \vec{n}_{i+l} \rangle \tag{1}
\]

where \( N_b = N - 1 \) is the number of bonds in the bottle-brush backbone and the brackets \( \langle \cdot \rangle \) denote averaging over backbone configurations. Figure 2 shows dependence of the backbone bond–bond correlation function on the side chain degree of polymerization, \( n_{sc} \). As follows from this figure, bottle brushes become stiffer with increasing the degree of polymerization of the side chains. Furthermore, one can identify two different regimes in the bond–bond correlation functions in Figure 2. All curves first show a fast drop of the orientational memory followed by a much slower memory decay with increasing number of bonds between unit bond vectors. This form of the bond–bond correlation function resembles that observed in polyelectrolytes, where electrostatic interactions between charged groups induce chain bending rigidity.\(^{24-26} \)

For polyelectrolytes, the existence of two regimes with fast and slow decay of the orientational memory is a manifestation of two different mechanisms of chain deformation. At short length scales, the bonds’ orientational memory is due to local chain tension, while at the longer length scales, it is determined by chain’s bending rigidity induced by long-range electrostatic interactions. Thus, we can argue that steric interactions between side chains in the bottle-brush macromolecules play a role similar to electrostatic interactions in polyelectrolyte systems, i.e., increasing bending rigidity of bottle-brush macromolecules. To test this hypothesis, we fit data sets shown in Figure 2 by empirical bond–bond correlation function in the following form:\(^{24} \)

\[
G(l) = (1 - \alpha) \exp\left(-\frac{||l||}{\lambda_1}\right) + \alpha \exp\left(-\frac{||l||}{\lambda_2}\right) \tag{2}
\]

where \( \alpha, \lambda_1, \) and \( \lambda_2 \) are fitting parameters. Indeed, one can see a very good fit of the simulation data by sum of two exponential functions. It is important to point out that our approach to describe bottle-brush bending properties is different from a single-exponential fit used in refs 27–31 at short length scales. By utilizing a single-exponential function to fit simulation data at short length scales, one neglects local stretching of the backbone induced by interactions between the neighboring side chains and its contribution to the bottle-brush Kuhn length. Note that at the longer length scales, however, the bond–bond correlation function begins to deviate from the double-exponential form given by eq 2 and in accordance with ref 29 should follow power law decay. Unfortunately, for studied backbone degree of polymerization, we have not been able clearly identify this regime.

We can further verify the validity of the correlation function given by eq 2 to describe bottle-brush backbone bending
rigidity by comparing the analytically calculated mean-square end-to-end distance of a backbone section with $s$-bonds

$$\langle R^2_n(s) \rangle = \frac{1}{N_b s} \sum_{i=1}^{N-1} \langle (\vec{r}_i - \vec{r}_{i+1})^2 \rangle$$

(3)

using for bond–bond correlation function expression eq 2 and those obtained from simulations. In eq 3, $\vec{r}_i$ is the radius vector of the $i$th monomer on the bottle-brush backbone. For bond–bond correlation function given by eq 2, the mean-square end-to-end distance of the section of the chain can be written as follows

$$\langle R^2_n(s) \rangle = b^2[(1 - \alpha)g(\lambda_1, s) + ag(\lambda_2, s)]$$

(4)

where $b$ is the bond length and function

$$g(\lambda, s) = \frac{1 + e^{-1/\lambda} - 2e^{-1/\lambda} + 1 - e^{-s/\lambda}}{(1 - e^{-1/\lambda})^2}$$

(5)

Note that the calculations are similar to those used for calculation of the mean-square value of the end-to-end distance of a chain with a fixed bond angle as discussed elsewhere. The data points in Figure 3a show our simulation data while the lines correspond to eq 4. This figure suggests that short backbone segments with $s < 10$ are not fully stretched since the scaling dependence of $\langle R^2_n(s) \rangle$ on $s$ is weaker than quadratic. In addition, the stretching of the backbone at small length scales is independent of the degree of polymerization of the side chains and is controlled by local packing and interactions between monomers in the vicinity of grafting points. Note that for large backbone sections with the number of bonds $s$ in a backbone segment approaching $N_b$, the mean-square end-to-end distance $\langle R^2_n(s) \rangle$ demonstrates linear scaling dependence. This is expected for an ideal chain with an effective Kuhn length, $b_k$. The $b_k$ of the bottle-brush macromolecules can be obtained from eq 4 in the limit when both $s/\lambda_1$ and $s/\lambda_2$ are larger than unity

$$b_k = \left. \frac{\langle R^2_n(s) \rangle}{sb} \right|_{s>1} \approx b((1 - \alpha)h(\lambda_1) + ah(\lambda_2))$$

(6)

where we introduced function $h(\lambda)$

$$h(\lambda) = \frac{1 + e^{-1/\lambda}}{1 - e^{-1/\lambda}}$$

(7)

Figure 3b confirms that bottle-brush macromolecules at large length scales behave as ideal chains with Kuhn length $b_k$ and bond length $b$. All our data sets in the range of large $s$ can be collapsed into one universal curve by normalizing $\langle R^2_n(s) \rangle$ by the product $b_kb$. Figure 4 shows how the bottle-brush Kuhn length $b_k$ on the side chain degree of polymerization $n_w$ for bottle-brush macromolecules with two different values of the FENE potential spring constants: $k_{spring} = 30k_BT/\sigma^2$ (filled squares) and $k_{spring} = 500k_BT/\sigma^2$ (open circles). Different spring constants of the FENE potential. As expected, the scaling dependence does not depend on the potential strength, while the stronger spring constant results in larger Kuhn length. This is ascribed to a shorter bond length $b$, resulting in stronger crowding of monomers close to the grafting points of the side chains to the bottle-brush backbone, which in turn stiffens the bottle brush. Note that both data sets show scaling exponent close to 0.5. The error estimate for scaling exponent was obtained by using jackknife method. The data for the bottle-brush Kuhn length can also be presented as a function of the bottle-brush diameter, which provides information about the aspect ratio of the Kuhn segment. In Figure 5a, we plot dependence of the bottle-brush diameter $D$ defined as

$$D^2 = 4\langle R^2_n \rangle = 4 \frac{s}{n_w} \sum_{i<j} \langle (\vec{r}_i - \vec{r}_j)^2 \rangle$$

(8)
on the degree of polymerization of the side chains, $n_{sc}$. Both data sets exhibit nearly the same scaling dependence $D \propto n_{sc}^{0.54}$, which indicates that in average the side chain conformations are close to that of an ideal chain. Figure 5b shows that the Kuhn length of the bottle brush is only slightly longer than diameter $D$, suggesting that bottle-brush macromolecules in a melt state can be presented as random walk of effective monomers of size equal to bottle-brush diameter similar to the case of single bottle-brush macromolecules.$^{31}$

The slight extension of the side chains with respect to the ideal chain dimensions is ascribed to the crowded environment in the vicinity of the backbone, which leads to nonuniform stretching of the side chains. As shown in Figure 6, the elongation of the side chains is stronger close to the grafting point. For each monomer on the backbone, we have defined the backbone bending plane by combining backbone bonds in groups of three for each monomer as shown in Figure 7. This procedure defines a set of unit vectors $\{\vec{n}_i^1, \vec{n}_i^2\}$ pointing along radius vectors $\vec{n}_i^1$ and $\vec{n}_i^2$. In order to minimize the end effects, we have excluded three side chains at each end of the backbone. Each pair of the vectors $\vec{n}_i^1$ and $\vec{n}_i^2$ determines the backbone bending plane, and their cross-product, $\vec{n}_i^3 = \vec{n}_i^1 \times \vec{n}_i^2$, defines the direction normal to this plane. The unit vector pointing in the direction of the local backbone bending is defined as $\vec{n}_i^4 = (\vec{n}_i^1 - \vec{n}_i^2)/|\vec{n}_i^1 - \vec{n}_i^2|$. To complete the local system of coordinates, we introduce a unit vector pointing along the $y$-axis $\vec{n}_i^5 = \vec{n}_i^1 \times \vec{n}_i^2 \times \vec{n}_i^3$.

Figures 8a–c show projections on the $x$–$y$ plane of the orientational distribution functions of the unit vectors pointing along the end-to-end vectors of the side chains and side chain sections (see Figure 7). These figures clearly illustrate redistribution of the side chains between concave and convex regions of the bottle-brush backbone upon its bending. The redistribution is especially evident for shorter side chains (Figure 8a). For longer side chains this redistribution is less pronounced as shown in Figure 8b. However, in this case, the correlation between orientation of the side chain sections and the bending direction can be clearly seen for section of the side chains close to the bottle-brush backbone. Furthermore, redistribution of the side chains from the concave bottle-brush bending region decreases extension of the side chains as shown in Figures 8d–f. It is important to point out, however, that stretching of the chains in the concave bottle-brush bending region is relatively weak and is below 5% of the ideal size of the side chain except for sections of the side chains close to the bottle-brush backbone (see Figure 8f).
We will assume that the side chain redistribution is a driving force behind bottle-brush bending rigidity and will use this mechanism to derive the effective bending constant of a bottle-brush. In our approach we will map bottle-brush macromolecule into a chain with bending rigidity. According to this chain model, the Kuhn length $b_K$ of the bottle-brush macromolecules with diameter $D$ and bending constant $K_B$ is equal to\(^\text{31}\)

$$b_K \approx D \left(1 + \coth(K_B) - K_B^{-1}\right) / \left(1 - \coth(K_B) - K_B^{-1}\right)$$  \hspace{1cm} (9)

In our calculations of the bottlebrush bending constant $K_B$, we will bend a cylinder with diameter $D$ occupied by bottle brush into a toroidal sector with radius of curvature $R$ (Figure 9). Consider deformation of the section of the cylinder with length $D$ equal to the diameter into a toroidal sector with angle $\theta$ and having volume

$$\delta V(\theta) \approx \frac{\pi}{4} \theta RD^2 \approx \frac{\pi}{4} D^3$$  \hspace{1cm} (10)

In order to maintain monomer density within the toroidal sector constant, the side chains should redistribute between upper and bottom parts of the sector. The number of the side chains in the upper, $m_u(\theta)$, and bottom, $m_b(\theta)$, parts of the toroidal sector is proportional to their volumes

$$m_u(\theta) \approx m_u \left(\frac{1}{2} + \frac{D}{3\pi R}\right) \quad \text{and} \quad m_b(\theta) \approx m_u \left(\frac{1}{2} - \frac{D}{3\pi R}\right)$$  \hspace{1cm} (11)

where $m_u$ is the number of the side chains within deformed volume $\delta V(\theta)$. Redistribution of the side chains due to cylinder bending results in change of the bottle-brush configurational free energy. This can be estimated as a change of the free energy due to partitioning of side chains into two groups with number of side chains in each group to be $m_u(\theta)$ and $m_b(\theta)$. For small bending angles $\theta$ this free energy change is

$$\frac{\Delta F_{\text{Reduced}}(\theta)}{k_B T} \approx \frac{2}{9\pi} m_u \theta^2$$  \hspace{1cm} (12)

The effective bending constant of the bottlebrush chain $K_B$ is estimated by mapping deformation of the bottle brush on that of a chain with internal bending rigidity $K_F$ and bond length $D$. For such chain the bending energy per bond due to bending on small-angle $\theta$ is equal to $K_F \theta^2/2$. Comparing this expression with eq 12, we obtain for bending constant of a bottle brush

$$K_B \approx \frac{4}{9\pi^2} m_d \approx \frac{4D}{9\pi^2}$$  \hspace{1cm} (13)

where we assume that the bottle-brush backbone is almost fully stretched such that $m_d \approx D/b$. Analysis of eqs 13 and 9 and data shown in Figure S5a indicates that for our systems $(D/b < 5)$, $K_B < 1$ and $b_K \approx D$, which is in agreement with the scaling coefficient $0.87 \pm 0.04$ in Figure S5b. The weaker than linear dependence results from the ratio $0.46/0.54 = 0.85$ of the corresponding scaling exponents for $b_k$ and $D$ on degree of polymerization of the side chains $n_w$ shown in Figures 4 and 5a, respectively.

Note that our conclusion about flexible nature of the bottlebrush macromolecules is in agreement with experimental,\(^{34-37}\) simulation,\(^{27-30,38}\) theoretical,\(^{39}\) and self-consistent field calculation\(^{40}\) results. Furthermore, for sufficiently long side chains, $n_w > 100$, our model recovers a quadratic dependence of the Kuhn length on the bottlebrush diameter, $b_K \propto D^2/b$. For such long side the bottle-brush macromolecules are expected to behave as worm-like chains.\(^{40-42}\)

**Bottle-Brush Networks.** In this section, we will discuss mechanical properties of bottle-brush networks obtained by random cross-linking of bottle-brush melts as described in Simulation Methods section. After cross-linking each bottle-brush molecule in a system with $k_{\text{spring}} = 30k_B T/\sigma^2$ has four cross-links, while systems with $k_{\text{spring}} = 500k_B T/\sigma^2$ have five cross-links per molecule randomly distributed along the bottle-brush backbone. The corresponding cross-linking densities are displayed in Table 1.

Stress–strain curves for uniaxially deformed networks are shown in Figure 10. The stress $\sigma_{xx}$ generated in the network upon uniaxial deformation was obtained from the pressure tensor $P_{ij}$ as follows:

\[ \sigma_{xx} = g_{11} P_{xx} + g_{22} P_{yy} + g_{33} P_{zz} + 2 \left( g_{13} P_{xz} + g_{23} P_{yz} \right) \]
Table 1. Parameters of Bottle-Brush Networks

<table>
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<th>nsc</th>
<th>K</th>
<th>G [kT/σ²]</th>
<th>G₀ [kT/σ₀²]</th>
<th>βfit</th>
<th>βcrit</th>
<th>bK/Rmax</th>
<th>bK/b</th>
<th>ρσσ²</th>
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<td>0.30</td>
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<td>2.30 × 10⁻²</td>
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</tbody>
</table>

nsc = number of monomers in side chains, K = bending constant of the bottlebrush obtained from eq 17; G = network shear modulus obtained from fitting σₙ₀(λ) curves in Figure 10 by using eq 15; G₀ = network shear modulus at small deformations, λ → 1 (see eq 19); βfit = value of the parameter β obtained from fitting σₙ₀(λ) curves in Figure 10 by using eq 15; βcrit = value of the parameter β obtained from simulations; ρσσ² = cross-linking density of bottle-brush networks; Rmax = bN_b = end-to-end distance of the fully extended bottle-brush backbone strand between cross-links; bK = Kuhn length of bottle brush shown in Figure 4.

Figure 10. Dependence of the network stress σₙ₀ on the deformation (extension) ratio λ for bottle-brush networks obtained by cross-linking bottle-brush macromolecules with different side chain degree of polymerization, nsc, and two different values of the FENE potential spring constants: (a) kₛpring = 30kT/σ² and (b) kₛpring = 500kT/σ².

σₙ₀ ≈ 3/2 Pₓ – 1/2 ∑ Pᵢ (14)

These data show that the bottle-brush networks are softer than the networks of linear chains. A transition to the nonlinear network deformation regime occurs earlier for bottle brushes than for the networks of linear chains. A transition to the nonlinear deformation regime occurs earlier for bottle brushes than for the networks of linear chains. A transition to the nonlinear network deformation regime occurs earlier for bottle brushes than for the networks of linear chains.

The lines in Figures 10a,b correspond to the best fit to the nonlinear network deformation model for which the true (physical) stress generated in the uniaxially deformed network is equal to 23

σₙ₀(λ) = G/3(λ² – λ⁻¹)

× (3 + 2bK/b √ K² + (1 – βλ₁(λ))² – 2bK/b √ K² + 1) (15)

where I₁(λ) = λ² + 2/λ is the first strain invariant of the deformation matrix for uniaxially deformed network with λ₁ = λ; λ₂ = λe = 1/√k. The shear modulus of the network consisting of bottle-brush backbone strands can be written as

G ≈ kₙ₀T βRmax² N_b bK/Rmax ≈ kₙ₀T βRmax² N_b bK (16)

where β is the number density of backbone monomers that support the stress in the network, N_b is the number of backbone monomers between cross-links, and β = (Rmax²)/Rₙ₀ is the ratio of the mean-square distance between cross-links in the undeformed network, (Rₙ₀), and the square of the end-to-end distance of the fully extended bottle-brush backbone strand, Rmax = bN_b. Parameter β determines maximum possible extension of a backbone strand without bond deformation and varies between 0 and 1. Note that for flexible linear chains this parameter approaches zero while for fully extended backbone in densely grafted bottlebrushes with long side chains it is close to one. The value of the effective backbone bending constant K was obtained from bottlebrush Kuhn length, bK, using the equation

bK = b₁ + coth(K) – K⁻¹

1 – coth(K) + K⁻¹ (17)

This mapping procedure allows us to describe a bottle brush by its backbone where effect of the side chains on the bottle-brush bending rigidity is absorbed into bending constant K. Note that
this representation is more convenient for comparison of properties of the bottle-brush networks and of those made of semiflexible chains. In our fitting procedure, we considered network shear modulus $G$ and elongation ratio $\beta$ as two fitting parameters. These values are summarized in Table 1. It follows from this table that the shear modulus $G$ of the bottle-brush networks monotonically decreases with increasing the number of monomers in the side chains. This decrease occurs despite the increase of the value of the parameter $\beta$, which characterizes extension of network strands, and ascribed to two concurrent effect: (i) dilution of the network with side chains, $n_{\text{sc}}$, and (ii) stiffness increase of the network strands, $b_K$. Note that the deviation of analytical expression eq 15 from simulation data occurs in the interval of stresses where backbone bonds begin to deform. In this deformation regime, the network shear modulus is determined by the effective spring constant of the individual bonds. Also comparing values of the parameters $\beta$ obtained from fitting of the stress–strain curves and those calculated from simulations, using end-to-end distance and number of monomers in the bottle-brush backbone between cross-links, we observe that difference between corresponding values of the parameter $\beta$ increases with increasing ratio $b_K/R_{\text{max}}$. This indicates that for bottle-brush networks made of more rigid sections of the bottle-brush backbone between cross-links, the network elastic properties are determined by deformation of the shortest sections of the bottle-brush backbone that are closer to their fully extended conformations rather than the most representative ones.

It is useful to present eq 16 for the shear modulus in terms of the parameters describing the chemical structure of a bottlebrush network that include $\rho = \text{total monomer density in a system, } N = \text{number of monomers in the backbone, } n_{\text{sc}} = \text{number of cross-links per backbone, and } n_{\text{sc}} = \text{number of monomers in the side chains. Using these parameters, we can calculate the number of bottlebrushes per unit volume as } \rho/\sqrt{N}$. Each bottle brush in the system has $n_{\text{sc}} - 1$ backbone strands supporting stress in the network, each having in average $N$, backbone monomers. Therefore, the density of the backbone monomers $\bar{\rho}$ that participate in supporting stress is equal to $\bar{\rho} = \rho(n_{\text{sc}} - 1)/N(n_{\text{sc}} + 1)$. Using this expression for $\bar{\rho}$, we can rewrite eq 16 as

$$G \propto k_B T \frac{\rho}{N} \frac{n_{\text{sc}} - 1}{n_{\text{sc}} + 1} b_K \beta R_{\text{max}}$$

(18)

To verify eq 18, Figure 11 shows dependence of the reduced network modulus $G_{\text{eff}} = G/[n_{\text{sc}} + 1]/[n_{\text{sc}} - 1]]/b_{\text{eff}}^{-1}$ on the number of the Kuhn segments per strand $R_{\text{max}}/b_K$. In accordance with eq 18, the reduced shear modulus $G_{\text{eff}}$ increases linear with increasing number of Kuhn segment per bottle-brush strands between cross-links.

In the linear network deformation regime, the value of the first strain invariant $I_1 \approx 3$. For such deformations, the shear modulus $G_0$ at small deformations is defined as follows:

$$G_0 \equiv \frac{\sigma_{\text{ax}}(\lambda)}{\lambda^2 - 1} = \frac{G}{3 + \frac{2b_K}{b} \sqrt{K^2 + (1 - \beta)^2} - \frac{2b_K}{b} \sqrt{K^2 + 1}}$$

(19)

For networks with weakly extended strands ($\beta \approx b_K/R_{\text{max}} \ll 1$), eq 19 reduces to $G_0 \approx G$. The elastic response of these networks is controlled by entropic elasticity of the bottle-brush strands between cross-links. Figure 12a shows scaling dependence of $G_0/(n_{\text{sc}} - 1)$ on the side chain degree of polymerization. This representation allows us to collapse modulus data for systems with different number of cross-links per bottle brush. For short side chains our data can be described by a scaling law $G_0 \propto (n_{\text{sc}} + 1)^{-1}$. However, with increasing degree of polymerization of the side chains the simulation data deviate from the power law $G_0 \propto (n_{\text{sc}} + 1)^{-1}$, demonstrating a weaker dependence of the shear modulus $G_0$ on the degree of polymerization of the side chains. Note that this deviation correlates with a decrease in the number of the Kuhn segments per strand of the backbone between cross-links (see Table 1); i.e., bottlebrush stiffness increases with increasing a number of monomers in the side chains, $n_{\text{sc}}$. To illustrate this, in Figure 12b we show dependence of the ratio $b_K/R_{\text{max}}$ on the parameter $K(1 - \beta)$, which controls crossover to semiflexible network deformation regime (see eq 19 and ref 23). In this range of parameters, the bottle-brush networks behave as networks of semiflexible chains. For such networks (see ref 23 for details) the strands between cross-links are almost fully stretched with $\beta \approx (1 - 2R_{\text{max}}/3b_K)$, and the shear modulus at small deformations, $G_0$, depends on the number of monomer in the side chains as

$$G_0 \approx \frac{2}{3} \frac{G}{(1 - \beta)^2} \approx \frac{3}{2} \frac{k_B T}{N} \frac{n_{\text{sc}} - 1}{n_{\text{sc}} + 1} R_{\text{max}} \propto n_{\text{sc}}^{-0.54}$$

(20)

In simplifying eq 20, we take into account that the Kuhn length of bottle brushes, $b_K$, scales with the degree of polymerization of the side chains as $b_K \propto n_{\text{sc}}^{-0.4}$ (see Figure 4). Our simulation data, however, show slightly weaker dependence $G_0 \propto n_{\text{sc}}^{-0.5}$ than predicted by eq 20.

In the nonlinear network deformation regime, we can define the nonlinear network modulus

$$G(\lambda) \equiv \frac{\sigma_{\text{ax}}(\lambda)}{\lambda^2 - 1}$$

(21)

Analysis of the eq 15 for the network stress indicates that it is convenient to plot simulation data using reduced variables $G(\lambda)/G$ as a function of $\beta\lambda/3$. Figure 13 shows representation of our simulation data in these reduced variables. In the wide interval of network deformations our simulation data have
The bending rigidity of the bottle brush is entropic in nature and is due to redistribution of the side chains upon backbone bending (see Figure 8). Analysis of the simulation data indicates that the properties of bottle-brush macromolecules in a melt can be described by representing them as ideal chains with effective Kuhn length \( b_K \).

This representation of the bottle-brush macromolecules can be extended to describe elastic properties of the bottle-brush networks in linear and nonlinear network deformation regime. The bottle-brush network shear modulus monotonically decreases with increasing side chain degree of polymerization (see Table 1). At small network deformations it scales with the degree of polymerization of the side chains, \( G_0 \propto (n_{sc} + 1)^{-1} \), as shown in Figure 12a. The deviation from this scaling behavior takes place when the number of monomers in bottle-brush backbone between cross-links becomes on the order of number of monomers of the backbone within Kuhn length, \( b_K \). These bottle-brush networks demonstrate behavior similar to those of networks of semiflexible chains. Shear modulus of such bottle-brush networks scales with the degree of polymerization of the side chains as \( G_0 \propto n_{sc}^{-0.5} \). Thus, to take a maximum advantage of the effect of the side chains into the shear modulus of the bottlebrush networks, one should choose a cross-linking density in such a way to remain in the regime with \( G_0 \propto (n_{sc} + 1)^{-1} \). In the nonlinear deformation regime the behavior of the bottle-brush networks is controlled by the bottle-brush bending modes (see Figure 13) and can be described in the frameworks of generalized network deformation model\(^{21} \) based on discrete chain model with internal bending rigidity.\(^{21} \)

### SIMULATION METHODS

We have performed molecular dynamics simulations of melt of bottle-brush chains and deformation of bottle-brush networks. Each bottle-brush macromolecule consisted of a main chain backbone with the number of monomer \( N = 100 \) and side chains with the number of monomers \( n_{sc} \) attached to the every monomer of the backbone as shown in Figure 1. In our simulations we have varied the number of monomers in the side chains between 0 and 20 (see Table 2).

Bottle-brush chains were modeled by bead–spring chains made of beads with diameter \( \sigma \). The nonbonded interactions between any two beads were described by the pure repulsive truncated-shifted Lennard-Jones (LJ) potential\(^{20} \).

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**Figure 12.** Dependence of the shear modulus on the side chain degree of polymerization (a) and of the number of Kuhn segments per bottle-brush backbone between cross-links \( R_{max}/b_K \) on the parameter \( K(1 - \beta) \) (b) for bottlebrush networks with two different values of the FENE potential spring constants: \( k_{spring} = 30k_BT/\sigma^2 \) and \( k_{spring} = 500k_BT/\sigma^2 \). Notations are the same as in Figure 10.

**Figure 13.** Dependence of the reduced network shear modulus \( G(I_1)/G \) on the parameter \( \beta I_1/3 \) for bottle-brush networks. The solid line is given by eq 22. Notations are the same as in Figure 10.
After completion of the compression step the system was equilibrated for 10^6 integration steps. Note that the required duration of the simulation runs was established by monitoring relaxation of the autocorrelation function of the bottlebrush backbone (∆R(t)R(t + DT)). To obtain bottle-brush network, the monomers belonging to the bottle-brush backbone were randomly cross-linked. This was done by randomly selecting pairs of monomers that fall within 5σ distance from each other. One cross-link bond was allowed per bottle-brush backbone monomer. The final average number of cross-links per bottle-brush backbone was equal to 5.0 for k_{spring} = 500k_BT/σ^2 and 4.0 for k_{spring} = 30k_BT/σ^2. The other network parameters are summarized in Table 3.

Table 2. Studied Systems

<table>
<thead>
<tr>
<th>nsc</th>
<th>number of beads</th>
<th>Lx = Ly = Lz [σ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10000</td>
<td>23.0</td>
</tr>
<tr>
<td>2</td>
<td>30000</td>
<td>33.5</td>
</tr>
<tr>
<td>5</td>
<td>60000</td>
<td>42.2</td>
</tr>
<tr>
<td>7</td>
<td>80000</td>
<td>46.4</td>
</tr>
<tr>
<td>10</td>
<td>110000</td>
<td>51.6</td>
</tr>
<tr>
<td>12</td>
<td>130000</td>
<td>54.6</td>
</tr>
<tr>
<td>15</td>
<td>160000</td>
<td>58.5</td>
</tr>
<tr>
<td>20</td>
<td>210000</td>
<td>64.0</td>
</tr>
</tbody>
</table>

U_LJ(rij) = \begin{cases} \frac{4ε}{σ^12} \left(\frac{σ}{rij} \right)^{12} - \frac{2}{rij} \left(\frac{σ}{rij} \right)^{6} + \frac{σ}{rij} \left(\frac{σ}{rij} \right)^{6} & \text{if } rij ≤ rcut \\ 0 & \text{if } rij > rcut \end{cases}

(23)

where r_{ij} is the distance between the i-th and j-th beads and σ is the bead (monomer) diameter. The cutoff distance for the bead–bead interactions was set to rcut = 2^{1/6}σ, and the value of the Lennard-Jones interaction parameter ε_{ij} was equal to 1.5k_BT (where k_B is the Boltzmann constant and T is the absolute temperature). The connectivity of the beads into bottle-brush chains was maintained by the finite extension nonlinear elastic (FENE) potential

U_{FENE}(r) = \frac{1}{2}k_{spring}R_{max}^2 \ln \left(1 - \frac{r^2}{R_{max}^2}\right)

(24)

with the values of the spring constant k_{spring} = 500k_BT/σ^2 and 30k_BT/σ^2 and the maximum bond length R_{max} = 1.5σ. The large value of the spring constant was selected to minimize the effect of the bond stretching at large network deformations. The repulsive part of the bond potential was modeled by the truncated shifted Lennard-Jones (LJ) potential with the value of LJ interaction parameter ε_{LJ} = 1.5k_BT and rcut = 2^{1/6}σ. The average bond length (b^{2})^{1/2} = 0.837σ for k_{spring} = 500k_BT/σ^2 and 0.987σ for k_{spring} = 30k_BT/σ^2.

Simulations were carried out in a constant number of particles and temperature ensemble. The constant temperature was maintained by coupling the system to a Langevin thermostat implemented in LAMMPS. In this case, the equation of motion of the ith bead is

m \ddot{\vec{r}}_i(t) = \vec{F}_i(t) - \xi \vec{v}_i(t) + \vec{F}_\text{LJ}(t)

(25)

where m is the bead mass set to unity for all beads in a system, \vec{v}_i(t) is the bead velocity, and \vec{F}_i(t) is the net deterministic force acting on the ith bead. The stochastic force \vec{F}_\text{LJ}(t) had a zero average value and σ-functional form (\vec{F}_\text{LJ}(t) = \vec{F}_\text{LJ}(t + DT)). The friction coefficient ξ coupling a system to a Langevin thermostat was set to ξ = 0.1m/τ_{LJ}, where τ_{LJ} is the standard LJ time, τ_{LJ} = σ(m/ε_{LJ})^{1/2}. The velocity-Verlet algorithm with a time step DT = 0.005τ_{LJ} was used for integration of the equations of motion. In our simulations we used 3-D periodic boundary conditions. All simulations were performed using LAMMPS.

First we have prepared melt of bottle-brush macromolecules. The system was initialized by placing 100 bottle-brush chains in a simulation box with monomer concentration equal to 0.1σ^3. Then the system was compressed until the monomer density reached 0.8σ^3. The final box dimensions are listed in Table 2.

In order to relax the networks, the cross-link bond potential was initially modeled by a harmonic potential with a spring constant K_b = 10k_BT/σ^2. For the network with k_{spring} = 500k_BT/σ^2, the cross-link spring constant K_b was gradually increased with an increment of ΔK_b = 30k_BT/σ^2 until it has reached 500k_BT/σ^2. For the network with k_{spring} = 30k_BT/σ^2, the cross-link spring constant K_b was increased with an increment of ΔK_b = 10k_BT/σ^2 until it has reached 30k_BT/σ^2. The duration of each step during which the spring constant was incrementally increased was 2 × 10^5 integration steps. After that the potential was replaced by FENE potential with the same parameters as one used to model bonds of the bottle-brush chains. Networks were equilibrated by performing NVT molecular dynamics simulation runs lasting 10^8 integration steps.

In order to obtain stress-strain relation for bottle-brush networks, we have performed sets of simulation runs of uniaxial network deformations. This deformation was achieved by a series of small affine deformation steps \(\{x_0, y_0, z_0\} \rightarrow \{\Delta x_0, y_0, z_0/(\Delta l)^{1/2}\}\) with an increment Δl = 0.025σ. This incremental deformation was achieved by performing simulations of network deformation at constant deformation rate lasting 5 × 10^5 integration steps. After this step the network was equilibrated for 2 × 10^6 integrations steps, which was followed by a production run lasting 3 × 10^6 integration steps.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail avd@ims.uconn.edu (A.V.D.).
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