1. Introduction

Bottle-brushes are macromolecules consisting of a flexible backbone with densely grafted side chains.1–4 In the case of polymer backbone being longer than the length of the side chains, a bottle-brush molecule has a cylindrical shape with side chains pointing in the radial direction outward from the chain backbone. (See Figure 1.) The experimental1–10 theoretical,11–13 and computational14–23 studies have shown that the structure of these macromolecules is the main reason for their unique response to the external stimuli (temperature, pH, light, and solvent). This has potential for applications of bottle-brush macromolecules for molecular engineering, for design of novel materials with programmable properties, and for utilization as model systems in biomedical research.1,2 In particular, the cylindrical bottle-brush macromolecules have structure similar to agarcan molecules24,25 that are composed of polysaccharide chains tethered to a protein backbone. These agarcan molecules play an important role in controlling the lubricating properties of cartilage.26,27 The unique...
In this Article, we use molecular dynamics simulations to study the effect of the electrostatic interactions and structure of bottle-brush macromolecules on the properties of brush layer. By changing the brush grafting density and the side chain degree of polymerization of the bottle-brush macromolecules, we establish what effects these parameters have on counterion distribution inside and outside the brush layer, conformations of individual bottle-brush molecules, and layer thickness.

2. Simulation Details

We performed molecular dynamics simulations of grafted layers of the charged bottle-brushes with explicit counterions. Polyelectrolyte bottle-brush macromolecules were modeled by chains of charged Lennard-Jones (LJ) particles (beads) with diameter \( \sigma \). The bottle-brush macromolecules consisted of a main chain with the degree of polymerization \( N = 97 \) and side chains with the degree of polymerization \( m \). (See Figure 1.) We performed simulations of the bottle-brush macromolecules with the side chain degree of polymerizations \( m = 9, 15, \) and 21. There was a total 31 side chains per each bottle-brush macromolecule that corresponds to every third monomer of the main chain to have a side chain attached to it. Only side chains were charged to every third monomer carrying a negative electrical charge, \(-e\). The number \( N_B \) of the bottle-brush macromolecules was grafted to a substrate. The substrate was modeled by a periodic hexagonal packed lattice of beads composed of 80 \( \times \) 70 beads with diameter \( \sigma \). The grafting density of the substrate, \( \rho_g \), was varied between 2.06 \( \times \) 10\(^{-4}\) \( a^{-2} \) and 8.04 \( \times \) 10\(^{-3}\) \( a^{-2} \) by changing the number of grafted chains \( N_B \) per simulation box from 1 to 39. The grafting points were randomly distributed over the substrate surface. A similar nonselective surface was located at the opposite side of the simulation box to prevent counterions from escaping and, hence, maintaining 2-D periodicity in the lateral (\( x \) and \( y \)) directions. The system dimensions in the \( x \) and \( y \) directions. The system dimensions in the \( z \) direction were equal to 150.0 \( \sigma \). The height of the simulation box \( L_z \) was equal to 150.0 \( \sigma \) for all simulations. The system configuration is shown in Figure 1, and the system parameters are listed in Table 1.

All particles in the system interacted through truncated-shifted Lennard-Jones (LJ) potential

\[
U_{\text{LJ}}(r) = \begin{cases} 
4\varepsilon_{\text{LJ}} \left( \frac{\sigma}{r} \right)^{12} - \frac{2\varepsilon_{\text{LJ}}}{\sigma} \left( \frac{\sigma}{r} \right)^{6} & \text{if } r \leq r_{\text{cut}}, \\
\frac{\varepsilon_{\text{LJ}}}{r} & \text{if } r > r_{\text{cut}}.
\end{cases}
\]

Table 1. System Parameters

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<th>( m )</th>
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\(^{*} \) \( N_B \), number of brush molecules per simulation box; \( N_{\text{part}} \), number of particles in a system including substrates; \( N_e \), number of counterions.
Article

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Carrillo and Dobrynin

where \( r_{ij} \) is the distance between \( i \)th and \( j \)th beads and \( \sigma \) is the bead diameter chosen to be the same regardless of the bead type. The cutoff distance, \( r_{cut} = 2.5\sigma \), was chosen for polymer–polymer interactions, and \( r_{cut} = 2.1\sigma \) was chosen for all other pairwise interactions. The interaction parameter \( e_{ij} \) was equal to \( k_B T \) for polymer–counterion, counterion–counterion, polymer–substrate, and counterion–substrate interactions, where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The value of the Lennard-Jones interaction parameter for the polymer–polymer pair was set to 0.3 \( k_B T \); which is close to a \( \theta \) solvent condition for the polymer. By selecting the strength of the polymer–polymer interactions close to the \( \theta \) point, we minimized the effect of the short-range interactions on the bottle-brush properties.

The connectivity of monomers to bottle-brush macromolecules was maintained by the finite extension nonlinear elastic (FENE) potential

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

with the spring constant \( k_{\text{spring}} = 30k_B T/\sigma^2 \), where \( R_{\text{max}} = 1.5\sigma \) is the maximum bond length. The repulsive part of the bond potential was represented by the truncated-shifted LJ potentials with \( e_{ij} = k_B T \) and \( r_{cut} = 2.1\sigma \).

Interaction between any two charged particles with charge valences \( q_i \) and \( q_j \) and separated by a distance \( r_{ij} \) was given by the Coulomb potential

\[
U_{\text{Coulomb}}(r_{ij}) = k_B T \frac{l_B q_i q_j}{r_{ij}}
\]

where \( l_B = e^2/\epsilon k_B T \) is the Bjerrum length, defined as the length scale on which the Coulomb interaction between two elementary charges, \( e \), in a dielectric medium with the dielectric constant, \( \epsilon \), is equal to the thermal energy, \( k_B T \). In our simulations, the value of the Bjerrum length, \( l_B \), was equal to \( 1\sigma \).

The particle–particle particle–mesh (PPPM) method implemented in LAMMPS with the sixth-order charge interpolation scheme and estimated accuracy of \( 10^{-5} \) was used for calculations of the electrostatic interactions between all charges in the system. The 2D periodic images of the system were periodically replicated along the \( z \) direction with distance \( L_z = 3L_z \) between their boundaries. This reduced the problem of calculation of the electrostatic interactions in a 2D periodic system to those in a 3D system.

Simulations were carried out in a constant number of particles, volume, and temperature ensemble (NVT) with periodic boundary conditions. The constant temperature was maintained by coupling the system to a Langevin thermostat. In this case, the equation of motion of the \( i \)th particle is

\[
m \frac{dv_i(t)}{dt} = \bar{F}(i) - \xi \bar{v}_i(t) + F_R^B(i)
\]

where \( \bar{v}(i) \) is the bead velocity and \( \bar{F}(i) \) is the net deterministic force acting on the \( i \)th bead of mass \( m \). \( F_R^B(i) \) is the stochastic force with zero average value \( \langle F_R^B(i) \rangle = 0 \) and \( \delta \)-functional correlations \( \langle F_R^B(i)F_R^B(j) \rangle = 6\sigma g_{ij} T \delta(t - t') \). The friction coefficient \( \xi \) was set to \( \xi = m/\tau_{LJ} \), where \( \tau_{LJ} \) is the standard LJ time \( \tau_{LJ} = \sigma^2/\epsilon k_B T \). The velocity–Verlet algorithm with a time step of \( \Delta t = 0.01\tau_{LJ} \) was used for integration of the equations of motion (eq 4).

Simulations were performed using the following procedure. At the beginning of each simulation run: the main and side chains of the bottle-brush macromolecules were in fully extended conformation with the main chains pointing along the \( z \) direction and side chains were randomly oriented in the \( x-y \) plane. Neutralizing monovalent counterions were uniformly distributed over the volume of the simulation box. The system was pre-equilibrated for \( 2 \times 10^6 \) MD steps. This was followed by the production run lasting \( 10^6 \) MD steps. During the production run, we averaged the brush thickness, bottle-brush gyration tensor, and counterion and monomer distribution functions.

We have also performed simulations of neutral bottle-brush layers consisting of the bottle-brush macromolecules with the degree of polymerization of the side chains \( m = 21 \) in the same range as the brush grafting densities. The parameters for bond potential and Lennard-Jones interaction potentials were the same as those in the case of the charged bottle-brush macromolecules. The total duration of the simulation runs for these systems was \( 4 \times 10^6 \) MD steps, and the last \( 10^6 \) MD steps were used for the data analysis.

3. Simulation Results

3.1. Layer Structure. We begin discussion of our simulation results by describing the dependence of the bottle-brush layer structure on the brush grafting density. In Figure 2a, we plot the layer thickness as a function of the bottle-brush grafting density. The average layer thickness \( \langle H \rangle \) was obtained from the brush density profile \( \rho(z) \) along the normal to the surface direction \( z \)

\[
\langle H \rangle = 2 \int_0^{L_z} \frac{dp(z)}{dz} dz / \int_0^{L_z} \rho(z) dz
\]

The average layer thickness first decreases with increasing the brush grafting density, \( \rho_g \); then, it saturates. For bottle-brushes with longer side chains, this decrease in the layer thickness is less pronounced. This behavior is qualitatively different from the one observed for the brush layer made of linear polyelectrolyte chains for which the thickness of the brush layer usually increases with the brush grafting density.36–38 Note that increase in the brush layer thickness with increasing the brush grafting density was also observed for charged bottle-brush macromolecules with rigid side chains.39 The decrease and saturation of the layer thickness is due to high linear charge density that is achieved in the bottle-brush by grafting charged side chains to the polymer backbone. Therefore, the bottle-brush macromolecules are strongly stretched because of electrostatic repulsion between charged side chains. It is important to point out that the decrease in the brush layer thickness can be explained by counterion condensation within the brush layer with increasing the brush grafting density. (See the discussion below.) The layer thickness increases with increasing length of the side chains. This increase in the brush layer thickness is due to the orientation of the side chains located close to the top of the grafted bottle-brush macromolecules along the brush backbone. (See the discussion below.)

To illustrate the difference in behavior of charged and neutral bottle-brush layers, in Figure 2b, we show dependence of the average layer thickness of the charged and neutral bottle-brush layers consisting of the bottle-brush macromolecules with the

degree of polymerization of the side chains \( m = 21 \). As one can see, the electrostatic interactions between charges lead to much stronger elongation of the charged bottle-brush macromolecules in comparison with elongation of the neutral bottle-brushes induced by the short-range (Lennard-Jones) interactions. The backbones of the polyelectrolyte brushes are strongly stretched and have rod-like conformations, whereas the backbones of the neutral bottle-brushes have coil-like conformations. (See the insets in Figure 2b.) The end-to-end vector of the polyelectrolyte brush backbone shows much stronger alignment with the \( z \)-axis in comparison with that for the end-to-end vector of the neutral bottle-brushes. The strong orientation of the backbone of the charged bottle-brushes is due to long-range interbrush electrostatic repulsion. The thickness of the neutral brush layer starts to increase with increasing brush grafting density when the bottle-brush macromolecules begin to overlap. The increase in the layer thickness is due to interbrush short-range repulsion. The thickness of the charged bottle-brush macromolecules stays almost constant throughout the entire interval of the studied brush grafting densities.

The side chains of the charged bottle-brush macromolecules show larger separation than those of the neutral bottle-brush. The side chains of the charged bottle-brush macromolecules show larger separation than those of the neutral bottle-brush. (See the insets in Figure 2b.) This is due to strong electrostatic repulsion between the side chains. The electrostatic repulsion between side chains of the charged bottle-brush also leads to their orientation with respect to the brush backbone. In Figure 3, we show variation along the \( z \)-direction of the average value of the cosine of the angle between the end-to-end vector of the brush backbone and that of the side chains. It follows from this plot that in the middle of the bottle-brush the side chains are oriented perpendicular to the bottle-brush backbone. This chain orientation minimizes the electrostatic repulsion between chains. However, for the side chains located close to the top and bottom of the bottle-brush macromolecules, the side chains are aligned along the bottle-brush backbone. At the top of the bottle-brush, the side chains show a stronger orientational correlation with the brush backbone than chains at the bottom of the bottle-brush. This is due to the different origin of the side-chain orientation. At the top of the bottle-brush, the side-chain orientation is due to electrostatic repulsion of the side chains located on the top portion of the bottle-brush from the chains located underneath of them. However, at the bottom of the bottle-brush, the side-chain orientation is caused by the short-range repulsion between side chains and substrate.

The size of the side chains decreases with increasing brush grafting density. (See Figure 4.) For this plot, we used only the side chains located in the middle of the bottle-brush covering 1/3 of the bottle-brush layer thickness. This allowed us to eliminate the end effects in obtaining the size of the side chains. The solid line in this Figure describes the average distance between grafted bottle-brush backbones

\[
R_n \approx (\pi \rho_g)^{-1/2}
\]

The data points on this line represent the average value of the distance between grafting points obtained by averaging the actual distances between neighboring grafting points of the bottle-brush.
backbones. Therefore, for most of the brush grafting densities used in our simulations, the bottle-brush molecules do not overlap because the distance between bottle-brush chains is larger than the size of the side chains. This corresponds to the so-called “mushroom regime”.37 It is interesting to point out the similarity between contraction of the side chains with increasing bottle-brush grafting density and contraction of the polyelectrolyte chains in dilute polyelectrolyte solutions.40–42 In both cases, the contraction is caused by accumulation of the counterions within the volume occupied by macromolecules, which reduces the intrachain electrostatic repulsion resulting in chain contraction.

A more detailed discussion of the effect of the counterions on the structure of the bottle-brush is given below in Section 3.2. Note that only bottle-brush macromolecules with the longest side chains crossover to the overlap bottle-brush regime. It is interesting to point out that neutral bottle-brushes crossover to the overlap brush regime at lower brush grafting densities than polyelectrolyte bottle-brushes. This is due to the larger size of the neutral bottle-brushes in the $xy$ plane. (See insets in Figure 2b.)

Further analysis of data shown in Figure 4 indicates that the data sets obtained for bottle-brushes with different degrees of polymerization of the side chains are shifted with respect to each other. To illustrate universality in the deformation of the side chains of the bottle-brush macromolecules in Figure 5, we plotted the dependence of the reduced side chain size $\langle R_m^2 \rangle^{1/2} / mb$ (where $b = 0.97 \sigma$ is the average bond length of the side chains) on the reduced value of the brush grafting density. The data points corresponding to bottle-brush macromolecules with the degree of polymerization of the side chains $m = 15$ and 21 show a reasonably good overlap. The data obtained for the bottle-brush with the shortest side chains $m = 9$ demonstrate weaker dependence on the reduced brush grafting density. The difference between two data sets can be explained by a finite size effect, which is stronger for shorter side chains.

3.2. Counterion Distribution. A counterion distribution plays an important role in determining a structure of a brush layer. There are different length scales that are involved in a counterion distribution process. First, the counterion localization occurs within a brush layer. With increasing the brush grafting density, the Gouy–Chapman length, $\lambda_{GC} = (2\pi \rho_e f m N_m)^{-1}$, determining a length scale within which half of the brush counterions is localized, becomes on the order of the brush thickness. This corresponds to a crossover to the so-called “osmotic brush” regime when the stretching of the bottle-brush backbone is caused by a translational entropy of localized within brush counterions.37 For bottle-brush systems, this occurs at very low brush grafting densities because of the large value of the net charge $efmN_m$ on each bottle-brush macromolecule in comparison with that for the brush made of the linear chains. In addition

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to counterion localization within a brush layer, we have counterion localization within the volume occupied by the bottle-brush macromolecule. Localization of the counterions within bottle-brush volume reduces the effective linear charge density along bottle-brushes to the critical Manning—Oosawa value.\(^{41,43}\) Because of the internal structure of the bottle-brush macromolecules, the counterions can be localized in the vicinity of the side chains and prevent an increase in the linear charge density of the side chains above the critical value. Note that this process can also be described in the framework of the Manning—Oosawa counterion condensation (localization) model. Below we will illustrate this multiscale picture of counterion distribution within a brush.

We will first consider distribution of counterions outside the brush layer. Counterions localized within the bottle-brush layer reduce an effective surface charge density of the brush layer to

\[
\Sigma = (1 - \chi_B) \rho_s \Gamma_{m \sigma} n_{m \sigma}
\]

where \(\chi_B\) is the fraction of localized within bottle-brush counterions, \(\rho_s\) is the fraction of counterions localized within the brush layer. For the remaining counterions outside the brush, their density distribution is given by\(^{44}\)

\[
\rho_c(z) = \frac{1}{2\pi \rho_s h^2} \cos^2 \left( s \left( 1 - \frac{z - H}{h} \right) \right)
\]

where we defined \(h = L_f - H\), and the parameter \(s\) is a solution of the equation \(s \tan(s) = 2\pi \rho_s \Sigma h\). Equation 7 is a solution of the nonlinear Poisson—Boltzmann equation, which couples the distribution of counterions to the electrostatic potential. In Figure 6, we plotted the distribution of the charged monomer and counterion densities as a function of the distance from the substrate surface. The solid line corresponds to eq 7, with the effective surface charge density of the brush layer evaluated at the average height of the brush layer, \(H = 79\sigma\) (shown by an arrow on the plot). The selection of the average brush thickness \(H\) as a dividing plane for the diffusive counterion layer was based on the following arguments. At the distances larger than the average brush thickness \(z > 79\sigma\), the density of the charged monomers becomes smaller than the counterion density (Figure 6), and counterions begin to provide a dominant contribution to the local charge distribution. This choice of the dividing plane results in a very good agreement between theoretical expression for the counterion density distribution and simulation results. It is interesting to point out that inside the brush layer counterions almost completely neutralize charge on the bottle-brush. The excess charge of the bottle-brush layer is located close to the edge of the brush layer where the side chains demonstrate alignment with the brush backbone. This excess charge is compensated by the diffusive layer of counterions outside the brush. Note that neutralization of the bottle-brush bulk charge minimizes the electrostatic energy stored within brush layer.

A qualitatively similar counterion density profile outside the brush layer was also observed in simulations of the polyelectrolyte brushes under good\(^{45}\) and poor\(^{46}\) solvent conditions for the polymer backbone. This supports the idea that the distribution of counterions outside the brush does not depend on the brush structure and is only controlled by the effective surface charge density of the brush layer.

A strong electrostatic attraction between bottle-brush and counterions localized with the brush layer leads to localization of the counterions within the bottle-brush volume. The localization of counterions within the bottle-brush volume is a result of optimization of the counterion translation entropy, electrostatic repulsion between uncompensated charges of the bottle-brush, and elastic free energy of the side chains. Note that the elastic free energy of the bottle-brush backbone does not play a significant role.

\hspace{1cm}

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role in this process because the brush layer thickness remains constant in the wide interval of the brush grafting density. To calculate the fraction of counterions localized within the volume occupied by the bottle-brush macromolecules, we have surrounded each monomer of the brush backbone by a sphere with radius equal to that of the square root of the mean-square average value of the end-to-end distance of the side chains $\langle R_{m}^{2} \rangle^{1/2}$ (Figure 7a) and counted the number of counterions belonging to this volume. It is important to point out that for overlapping bottle-brushes we assigned the counterion to the nearest bottle-brush macromolecule. This prevented double counting of counterions.

Figure 7b shows the dependence of the reduced number charge density of the bottle-brush on the reduced brush grafting density. The fraction of the condensed counterions $x_{B}$ increases with increasing the brush grafting density (inset in Figure 7b), resulting in a decrease in the net charge of the bottle-brush. This is consistent with the reduction in counterion localization penalty as the brush grafting density increases. For the bottle-brush macromolecules with the side chain degree of polymerization $m = 9$, we see a saturation of the reduced linear number charge density at 1.2. For the other side chain degrees of polymerization, even for our lowest grafting densities, the systems are far from the saturation limit. Note that lines corresponding to different degree of polymerizations of the side chains converge with increasing brush grafting density. This could be an indication of the crossover to the regime with universal counterion distribution. Unfortunately, one has to consider bottle-brush macromolecules with longer side chains to eliminate any doubts about the existence of this regime.

Counterions localized within bottle-brush volume are preferentially located in the vicinity of the side chains. This reduces the charge on the side chains. To calculate the effective charge of the side chains, we have covered each monomer belonging to a side chain by a sphere with radius $R_{\text{out}} = 2\sigma$ and calculated the fraction $x_{A}$ of counterion located within this volume. In Figure 8, we plotted the dependence of the reduced linear number charge density along the side chains of the bottle-brush on the brush grafting density. (The inset shows the variation of the fraction of the condensed counterions $x_{A}$ with the brush grafting density.) Note that for this plot we used only side chains located within thickness $<\ell_f>/3$ from the brush center of mass. This allowed us to minimize the end effects on the counterion distribution. It follows from Figure 8 that the linear charge density along the side chains does not depend on the side chain degree of polymerization. This has a very simple explanation. The side chains are strongly stretched by the electrostatic repulsion between uncompensated charges such that $(R_{m}^{2})^{1/2} \approx m$ and the effective charge of the side chains is proportional to $(1 - x_{A})(fm)/m$, resulting in the ratio $(1 - x_{A})(fm)/m(R_{m}^{2})^{1/2} \approx (1 - x_{A})^2$ to be independent of the degree of polymerization $m$ of the side chains. The effective linear charge density of the side chains decreases with increasing brush grafting density. This reduction of the side chain charge is consistent with reduction of the configurational entropy penalty for the counterion localization within the bottle-brush volume. The lines begin to spread as systems approach overlapping grafting densities and side chains begin to shrink.

4. Conclusions

We have studied the effect of the side chain degree of polymerization and brush grafting density on conformations of grafted bottle-brush polyelectrolytes. Our molecular dynamics simulations showed that the thickness of the brush layer first decreases with increasing brush grafting density; then, it saturates and remains constant in the wide interval of the brush grafting densities. The saturation of the brush thickness indicates that the stretching of the brush backbone does not change in the wide interval of the brush grafting density. The side chains of the bottle-brush contract with increasing layer grafting density. The contraction of the side chains was explained by the counterion condensation within the bottle-brush volume. This counterion condensation reduces the charge of the bottle-brush, weakening the electrostatic repulsion between and within side chains.

Counterion condensation in the bottle-brush layer is a multiscale process. This reflects different symmetries of the problems. At the distances from the grafting surface larger than the brush layer thickness, a brush layer can be considered as a charge surface with effective surface charge density, the magnitude of which depends on the fraction of the condensed within brush layer counterions. On these length scales, one can use a solution of the one-dimensional nonlinear Poisson–Boltzmann equation to describe counterion distribution outside the brush layer. Inside the brush layer on the length scales larger than the thickness of the bottle-brush molecules, the electrostatic potential and distribution of counterion density have a cylindrical symmetry. On these length scales, the counterion distribution around the bottle-brush molecules can be viewed as counterion condensation on a cylindrical polyion and can be described in the framework of the Manning–Oosawa model of counterion condensation. In this case, the counterion condensation precludes the linear charge number density of the bottle-brush macromolecule to be larger than a critical value. Finally, on the length scales smaller than the bottle-brush thickness, there is a counterion condensation on the side chains. This multiscale counterion condensation is a unique feature of the brushes made from bottle-brush polyelectrolytes.

Flexibility of the side chains plays an important role in determining bottle-brush properties. Comparison of our simulations with simulations of the bottle-brush chains with rigid side chains shows that the thickness of the brush layer made of the bottle-brushes with flexible chains does not depend on the brush grafting density in the wide interval of the brush grafting densities, whereas simulations of the bottle-brushes with rigid side chains demonstrate an increase in the layer thickness with increasing brush grafting density. This qualitatively different behavior can...
be explained by contraction of the side chains with increasing brush grafting density. The rigid side chains lead to stronger brush overlap at lower brush grafting densities resulting in stronger electrostatic repulsion between chains and stretching of the brush backbone. The detailed analysis of the effect of the side chain rigidity as well as orientational correlations between brush backbone and side chains will be the subject of future studies.

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