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Design of PAMAM-COO Dendron-Grafted Surfaces to Promote Pb(II) Ion Adsorption

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ABSTRACT

An expanding area of green technology is in the wastewater treatment for heavy metal ions. As the adsorption of cations to solid surfaces has been proven to be successful, recent research has demonstrated enhanced adsorption profiles by dendron brushes grafted onto a solid support. *Via* the molecular dynamics technique, we examine the adsorption of Pb(II) ions onto polyamidoamine (PAMAM) with carboxylate terminal groups through a coarse-grained implicit solvent model. We identify dendron generations and grafting densities, or surface coverage levels, which demonstrate optimal adsorption of Pb(II) ions. Our results can be potentially be used to design functionalized surfaces for metal ion adsorption in application entailing environmental remediation or protective surface coating.

KEYWORDS: polyamidoamine dendrons, dendron brushes, metal ion removal, chelation, molecular dynamics

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INTRODUCTION

Hyperbranched polymers and dendrimers are increasingly being used in applications for environmental remediation, nanoparticle synthesis, and nanomedicine. [1,2,3] For example, environmental remediation in mining, electroplating or refining industries frequently require highly effective approaches to remove heavy metal ions from waste streams. [4] This need gives rise to a continuous push for developing alternate technologies which are more efficient than existing precipitation, ion exchange, reverse osmosis, and nanofiltration methods. [4] Among the various techniques, approaches harnessing adsorption are popular for their simplicity and low cost. [5] Adsorbents with large surface areas are able to reach high efficiencies in removing the chemicals of interest. [5] Silica gel is one such adsorbent where its effectiveness is dependent on functional groups covalently bonded to the surface. [6,7,8,9] Starburst polyamidoamine (PAMAM) dendrimers have demonstrated binding affinities for metal ions. [1,10] By tethering dendrimers to the solid support, promising novel adsorbents can possess the mechanical and thermal stability of the support, and the strong affinity and high loading capacities of dendrimers. [6,8,11,9] Dendrimers such as PAMAM are frequently studied due to its versatility in the variety of terminal groups, including carboxylic acids. [12] One of the main mechanisms of adsorption is the coordination of metal cations *via* electrostatic binding. Studies have proposed charge transfer mechanisms where the amine groups of PAMAM serve as chemisorption sites for metal ions as shown in experiments on the chelation of Pb and Fe ions. [1,6]

Several numerical techniques have been adopted to investigate the behavior of dendrimer-based systems. [13] Studies using the Monte-Carlo technique have examined dendritic polyelectrolytes, with charged terminal groups, to observe the conformation of the shells and cores due to a range of salt concentrations. [14] Other investigations have used coarse-grained molecular dynamics to investigate charged PAMAM dendrimers in salt-free solutions. [15] Efforts have also been focused towards understanding the behavior of starburst dendrimers in solutions *via* the use of models resolving the interactions at different scales. [16] Atomistic molecular dynamics show niacin interaction with PAMAM starburst dendrimers for aqueous solubility. [17] In addition, Brownian dynamics and self-consistent field theoretical approaches have queried the dynamics and morphological properties of charge neutral dendritic brushes grafted on flat and curved surfaces. [18,19,20,21]

We are interested in studying the adsorption of Pb(II) ions by PAMAM-COO dendrons grafted onto a solid surface *via* the use of implicit solvent coarse-grained molecular dynamics simulations. We investigate the role of dendron generations G1.5 to G5.5 and the grafting density, or the surface coverage levels, on the Pb(II) ion adsorption efficiency of the dendron brushes. Our results can be potentially used to design functionalized surface for metal ion adsorption in applications entailing environmental remediation or protective surface coatings.

METHODOLOGY

The particle dynamics can be resolved by using classical molecular dynamics (MD) simulations. [22,23,24] The equation of motion for each bead i is given by $\mathbf{F_i} = m_i\mathbf{a_i}$ where $\mathbf{F}_i$ is the force acting on bead i, m_i is the mass and $\mathbf{a}_i$ is the acceleration of the bead i. The force can be expressed as the gradient of the potential energy U by the relations $\mathbf{F}_i = -\nabla_i U$ with $U = U_{pair} + U_{bond} + U_{angle}$, where U_{pair}, U_{bond} and U_{angle} are the potential energies from all its pair, bond and angle interactions, respectively. The dynamics of each bead i can be determined by the following equations $-\nabla_i U = m_i \mathbf{a}_i = m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2} = m_i \frac{\partial \mathbf{v}_i}{\partial t}$ and $\mathbf{v}_i = \dot{\mathbf{r}}_i$, where $\mathbf{r}_i$ and $\mathbf{v}_i$ are the position and

velocity vectors of bead i. The equations of motion will be integrated using the Velocity Verlet method [23,24] which has greater stability, time reversibility and preserves the symplectic form in the phase space compared to the Euler method. [23,24] The MD simulations will sample the canonical ensemble and will be run using the open source parallelized MD program called LAMMPS. [25]

In this study, the dual prerequisites for the resolution of the multiscale dynamics and the frequent sampling of independent system configurations will be addressed through the adoption of coarse-grained representations of the components in the system. A coarse-grained representation of a chemical entity models a group of atoms as a single bead at a larger scale by reducing the internal degrees of freedom. The concept of coarse-graining stems from renormalization group theory [26] where a methodical process of smoothening out the degrees of freedom is used to attain a larger scale at which the coarse-grained interactions operate. [27] The coarse-grained potentials for the non-bonded pairs, bonds, and angles are determined by the MARTINI force field. Lee and Larson utilized the MARTINI coarse-graining method to model acetylated and un-acetylated PAMAM starburst dendrimers forming pores in lipid bilayers. [28] The MARTINI coarse-graining scheme involves grouping approximately four heavy atoms into one bead and assigning it a classification based on its charge, polarity, and ability to form hydrogen bonds. [29] MARTINI coarse-graining is limited to fluids [30], and so this study maintains a generic solid as silica and focuses on the dynamics of the dendrons. For PAMAM, the amine and amide groups are considered nonpolar (N). In addition, the amides are capable of being both donors and acceptors of hydrogen bonds (Nda). [28] The carboxylate terminal groups labeled as charged species (Qda) based on an environment where the pH is greater than the pK_a of the carboxylic acid group. PAMAM is overall neutral at high pH, with the terminal groups becoming protonated at lower pH [31]. As the pH decreases, the tertiary amines of PAMAM become protonated as well; this has been modeled by Lee and Larson through the extension of their previous MARTINI coarse-grained model [31]. Fig. 1 illustrates this categorization for a G0.5 PAMAM-COO. Also, the hydrated ions are also considered charged species (Qda) with the implicit screening approximated by a reduced charge of ±0.7e, for the monovalent ions and carboxylates. [29] The hydrated ions are capable of being donors and acceptors of hydrogen bonds due to the water shell. [29] The Pb(II) ion has been experimentally determined to have stable hydration with six to eight water molecules. [32] Studies have shown that ion adsorption is affected by pH and ion solvation [33,34]. Our assumptions on keeping these factors constant are based on inducing adsorption through electrostatics. The relative masses in the system are coarse-grained, and this method of coarse-graining results in a uniform bead diameter of $\sigma = 0.47$ nm, for all bead types. [29]

The interaction between coarse-grained beads, according to the MARTINI force fields, is captured by non-bonded pair potential energies as shown in Table 1. [28,29] The functional form of the non-bonded pair interactions which capture the hydrophobic effect or steric repulsion are modeled by the shifted truncated 12-6 Lennard-Jones (LJ) potential given by [23]

$$E_{LJ} = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \qquad r < r_c \qquad (2)$$

where the potential cutoff distance r_c is set at 2.5σ for all bead pairs except those pairs examining the interaction between non-surface and surface beads. The 12-6 LJ potential cutoff for repulsive interactions with beads encompassing the surface is set at $2^{1/6}\sigma$, as represented by the Weeks-Chandler-Andersen (WCA) potential. [35]

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The non-bonded pair interactions arising due to electrostatic interactions between the Pb(II) ions and the carboxylate terminal groups can be modeled by the screened Coulombic potential to account for the screening by the counterions, and is given by

$$E_{SC} = \frac{q_i q_j}{4\pi\varepsilon_r r}\exp(-\kappa r) \qquad (3)$$

where ε_r is the relative permittivity and κ is the inverse Debye length. Since the solvent is considered to be aqueous, it is assumed that the electrostatic interactions between the ions can be explained by the Debye-Huckel theory. [36]

The bead-spring representation of the PAMAM-COO dendron is modeled by linking two consecutive monomers along a chain *via* a finite extensible nonlinear elastic (FENE) bond. [37] The FENE bond potential provides an attractive force to ensure that the bond length does not exceed 1.5σ. This constrains the equilibrium bond length to equal bead diameter σ. The FENE bond potential's functional form is

$$E_{FENE} = -0.5KR_0^2 \ln\left(1 - \left(\frac{r}{R_0}\right)^2\right) \qquad (4)$$

where R_0 is the maximum bond length and K is a prefactor.

The bond torsions of the coarse-grained dendrons can be modeled *via* three-body or angle potentials. We have adopted a cosine squared angle potential [28] which is described by the following functional form

$$E_{cos2} = K(\cos(\theta) - \cos(\theta_0))^2 \qquad (5)$$

where θ_0 is the equilibrium angle and K is a prefactor.

To develop the model for a PAMAM-COO dendron, we compare our measurements of the mean square R_g of a free starburst PAMAM dendrimer with reported experimental [38] and simulation research.[28] The radius of gyration is calculated using the following equation

$$R_g^2 = \frac{1}{N}\langle\sum_{i=1}^{N}|\boldsymbol{r}_i - \boldsymbol{R}_{cm}|^2\rangle \qquad (6)$$

where N is the number of monomers, r_i is the position of monomer i and R_{cm} is the dendrimer's center of mass. The three-body angle potentials are tuned to compensate for the excluded volume from the implicit water. The hydrodynamic radius of an acetylated G5 PAMAM dendrimer starburst has been experimentally determined to be 2.35 nm by size-exclusion chromatography. [38] Atomistic molecular dynamics has found G4 PAMAM dendrimers to have a radius of gyration given by 2.104 ± .041 nm [17] which is in agreement with analogous experimental measurements given by 2.14 ± .08 nm. [39] Maiti *et al.* hypothesized that the discrepancy between experimental and simulation measurements of the radius of gyration is attributed to solvent conditions, with the dendrimer branches or number of generations moderating the protonation of terminal amines and therefore, the swelling. [40] Coarse-grained simulations by Lee and Larson achieved a radius of gyration given by 1.99 ± 0.01 nm at 310 K for the same dendrimer with explicit solvent. [28] By adjusting the angle potential to K = 600 kJ mol^{-1} $radian^{-1}$, we achieve a radius of gyration corresponding to 2.03 ± 0.02 nm at 310 K with the same coarse-grained dendrimer in implicit water.

To construct a system of dendrons tethered to a surface, we build the surface by repeating unit cells composed of hexagonally close packed surface beads in a monolayer (as shown in Fig. 2). The surface beads are equally spaced from one another and serve as locations for tethering the dendrons. A grafted dendron is said to isolated if it is outside the interaction range from neighboring grafted dendrons. In contrast, the grafted dendrons form brushes if the

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grafting density enables the dendrons to be within interaction range from one another. The box boundaries are periodic in the x and y dimensions and non-periodic in the z dimension. The upper z boundary is a fixed WCA wall such that ε = 3.4 kJ/mol, σ = 0.47 nm, and r_{cut} = 0.528 nm. The lower z boundary consists of PAMAM-COO dendrons tethered at amorphous silica sites distributed uniformly on the surface. Each amorphous silica bead represents four atoms following the MARTINI coarse-graining scheme. [29] The x and y dimensions of the simulation box are approximately 47 nm by 47 nm with the z dimension ranging from 9.64 nm to 113.37 nm. In this study, we have maintained the concentration of the Pb(II) ion at 0.1 M. The charge neutrality in the system is preserved by compensating for the valency of the Pb(II) ion by counter charges on the dendron terminal groups. Hence, the variation in the number of generations and dendron grafting densities results in different number of Pb(II) ions for each system. Thus, the height of the simulation box changes with dendron generation and grafting densities to maintain charge neutrality and the desired Pb(II) ion concentration. A Langevin thermostat is implemented to keep the temperature at 310 K and to mimic the Brownian dynamics of implicit water molecules. [41] We adopt a microcanonical (NVE) ensemble to ensure that the system maintains a constant number of beads, volume, and energy. [24] The timescale for the system is determined by dimensional scaling such that $\tau = (\varepsilon/(m\sigma^2))^{0.5}$ = 1.08 ps. [24] Each system is equilibrated for at least 100 ns and is sampled every 1 ns for a duration of 100 ns. All the results have been obtained by averaging over particle trajectories from four simulations which have identical initial conditions but different random seeds. Illustrations of the surfaces and dendrons are drawn using the Visual Molecular Dynamics (VMD) software package. [42]

RESULTS AND DISCUSSION

Our goal is to understand the mechanisms which promote the adsorption of Pb(II) ions onto PAMAM-COO dendrons and the factors which control the adsorption process, such as the dendron architecture and surface coverage. We vary the dendron architecture through the generation, and explore generations G1.5, G2.5, G3.5, G4.5 and G5.5 (as shown in Fig. 2). The surface coverage is determined by the ratio of the total projected area of the dendron to the area of the support. We investigate isolated dendrons G1.5 to G5.5 as well as dendritic brushes at surface coverage levels that are at, below, and above full coverage. To define what encompasses under-coverage, full coverage, and over-coverage; we project the area of an isolated tethered dendron, as calculated from radius of gyration (R_g), onto the x-y plane. We then extrapolate the grafting density required to achieve a theoretical surface coverage. Therefore, the grafting density is dependent on the number of generations of the dendron. To calculate the theoretical surface coverage for a given number of dendrons N_d and box dimensions (L_x and L_y), we define coverage as

$$coverage = \frac{N_d \pi R_g^2}{L_x L_y} \qquad (1)$$

where a surface coverage value of about one is considered as full coverage. The radius of gyration is calculated for isolated dendrons of a given generations. After calculating the tether density corresponding to a given coverage level, we graft the dendrons at regular spatial intervals onto the surface. Supplementary Information (SI) Figure SI1 shows the grafting points and spatial configurations of the G3.5 grafted dendrons for different theoretical surface coverage levels. Fig. 3 illustrates an observable swelling of the dendron when the adsorbent changes from an isolated dendron to a dendron brush. Comparison between the radius of gyration of the isolated dendron and the dendritic brushes, along with the corresponding theoretically predicted

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and simulated surface coverages can provide insight into the collective behavior of the multiple dendrons.

Our measurements of the radius of gyration and simulated surface coverage are summarized in Fig. 4. We observe a significant deviation between the radius of gyration for an isolated dendron and the corresponding values for dendrons organized in brushes. The radius of gyration of the dendron brushes will be determined by the interactions between the branches and the charged terminal groups in addition to the generation and the grafting density. The radius of gyration of the brushes is found to be greater for all generations and surface coverages, with the exception of G5.5 at the over coverage level. We surmise that the favorable van der Waals interactions between the branches of neighboring dendrons lead to their extension along lateral directions accompanied by an increase in their height with generations. The electrostatic repulsion between the charged terminal groups of the dendrons becomes increasingly predominant with dendron generations, and causes the individual dendrons to reduce their lateral extension. The interplay between volume exclusion and electrostatic interactions causes the radius of gyration corresponding to a dendron generation to decrease with surface coverage. Measurements of the simulated surface coverage are found to be in agreement with trends in the radius of gyration of the dendron brushes. The unfavorable electrostatic interactions between the terminal groups are sufficiently strong to cause the neighboring dendrons to laterally move away from one another, while further extending out into the vertical direction. Figure SI2 demonstrates the lateral dimensions and the height of an isolated dendron and dendron brushes, for different generations and surface coverage levels. The results show an increase in the lateral dimensions of the dendrons with the number of generations. However, the surface coverage level can induce compaction of the dendrons. The extension of the dendrons along the vertical direction increases with the coverage level as the higher generations overcome the favorable enthalpic interactions in the lateral direction. For a given generation, we observe the height of the dendron forest to exceed that corresponding to an isolated dendron. We find the simulated surface coverage to increase from low to intermediate number of generations. At higher generations, the compaction of the individual dendrons leads to a significantly slower growth in the radius of gyration, resulting in a decrease in the surface coverage.

The trends in the radius of gyration as a function of dendron generations and surface coverage levels, along with measurements of the ion coordination, can provide insight into factors which are conducive for promoting the adsorption of Pb(II) ions onto the terminal groups of the dendrons. We define ion coordination to be the moieties coordinating with the Pb(II) ions. We set the inner ion coordination shell to span a radius of 0.705 nm (or, 1.5σ) so as to encompass beads in the immediate vicinity of the Pb(II) ions. Simlarly, the outer ion coordination shell is defined to span 0.705 nm to 1.175 nm (or, 2.5σ), and includes beads which are neighboring but not included in the inner shell of the Pb(II) ion. We observe the number of beads in the inner and outer ion coordination shell of the Pb(II) ion to increase with the number of generations and coverage level, as shown in Fig. 5. However, the ion coordination significantly decreases for the highest coverage level and number of generations due to the compaction of the individual dendrons. A possible explanation of the observation could be the decrease in the lateral dimensions of the dendrons which pushes together the charged terminal groups, resulting in their coordination with fewer Pb(II) ions. This effect should cause the Pb(II) ions to coordinate primarily with other Pb(II) ions. Our calculations of the coordination number of each moiety with the Pb(II) ions supports our hypothesis.

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We determine the distribution of moeities in the inner and outer coordination shells of Pb(II) ions, as shown in Fig. 6. We observe the coordination numbers to increase with the surface coverage level and number of generations, with the exception to G5.5 at the high coverage level. For the G5.5 dendron brushes, the measurements support our hypothesis that the coordination between Pb(II) ions is significantly higher than with the PAMAM-COO components. For the other dendron generations and different coverage levels, our results show the ion coordination distribution of the inner shell of the Pb(II) ion favors the carboxylate moeity. These results stem from the favorable electrostatic interactions between the positively charged Pb(II) ion and the negatively charged carboxylate group. For the outer shell, we observe the number of amine and amide groups coordinating with the Pb(II) ions to be relatively equal to the number of carboxylates due to the sequence in bond connections and the high ratio of amines and amides to carboxylates. With increasing generations, both shells show a decrease in the coordination with the solid surface due to the increasing brush height which serves to impede the ion diffusion. The dependence of the brush height on the dendron generation and the grafting density can be compared with existing theoretical and computational studies [19,20,21] *via* measurements of the scaling exponents.

Scaling exponent measurements for the brush height Z with respect to the dendron molecular weight M and the distance d between the grafting points of the dendrons is shown in Fig. 7, where $s = d^2$. The molecular weight M changes with the generations of the dendrons whereas the spacing between the grafting points varies with the dendron generation. Each data point in Fig. 7 has been averaged over four simulations which have identical initial conditions but different random seeds. The dendron path length N is defined to be the number of bonds between the terminal carboxylate and the grafting point. We calculate the following scaling relations the dendron height: $Z \sim M^{0.4}$ and $Z \sim s$, for a range of surface coverage levels. Similar scaling analyses have been reported for generic dendrons of various architectures in theta, poor and good solvents. [19,20] We surmise the differences in our results from those reported in the literature [19] to arise on the account of the different solvent qualities resulting from the charged terminal groups and Pb(II) ion diffusion within the brush. The poor solvent conditions for the amine and amide groups induce them to interact with each other or collapse onto themselves. The charged carboxylate terminal groups repel each other, causing the dendron branches to move away from one another and extend along the vertical direction. The unfavorable electrostatic interactions between Pb(II) ions or the carboxylate terminal groups pushes the dendrons further apart along the lateral plane and extend along the vertical direction. This hypothesis would support our reported observations of the compaction of the dendrons with increasing generations.

Experimental studies have reported removal efficiencies of over 99% for Cr(III), Pb(II), and Zn(II) ions with G3 and G4 PAMAM grafted to SBA-15 silica in pH 4. [9] The average adsorption percentage of Pb(II) in our low surface coverage simulations show a minimum of 96.3% for G1.5 to 99.7% for G5.5. The only exception being G5.5 at high surface coverage where the abovementioned volume exclusion prevents diffusion and adsorption of Pb(II) ions onto the dendron brush.

CONCLUSIONS

In this paper, we investigate the adsorption of Pb(II) ions onto PAMAM-COO dendrons grafted onto a solid surface *via* the use of coarse-grained implicit solvent MD technique. We examine the effect of the dendron generation number and the theoretical coverage level on the spatial organization and ion coordination of the dendron brushes. Our study identifies optimal

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dendron architectures and grafting densities which can maximize the removal of Pb(II) ions from solution.

We report the dendron brush to swell in the lateral directions with corresponding increases in the radius of gyration for smaller number of generations and surface coverage levels. For higher generations and surface coverage levels, the repulsion between the charged terminal groups drives the individual dendrons to move away from one another, reducing the lateral dimensions and extending along the vertical dimensions. The ion coordination measurements for the Pb(II) ions, at low and intermediate generations and surface coverage levels, illustrate the first coordination shell to encompass the carboxylate groups and the second coordination shell to include the amine and amide groups. For a high surface coverage level of the G5.5 dendron brushes, we find a lower adsorption of the Pb(II) ions. A decomposition of the coordination of the Pb(II) cation with different moieties shows a higher count of negative terminal groups residing in the first ion coordination shell. Scaling exponent measurements indicate the electrostatic interactions of the carboxylate and Pb(II) ions to strongly influence dendron brush conformation and dynamics as a function of the dendron generation and grafting density.

Our investigations can be used to design functionalized surfaces which could potentially adsorb other heavy metal ions for applications in environmental remediation and protective coatings. The correlations between the dendron architecture with the measurements of the radius of gyration, surface coverage and the ion coordination distribution can identify how the chemistry of the dendrons and the terminal groups can influence the intra- and inter-dendron interactions and dynamics, and thereby control the cation adsorption efficiency. This approach can also be extended to other linear or hyperbranched polymers where electrostatics is integral in determining the adsorption of metal ions. The coarse-grained models of the dendrons, surface, and metal ions can be applied to other systems, with necessary adjustments in the parameters. Our integrated approach combining modeling with characterization can thus aid in the development of guidelines for the design of grafted surfaces which can be harnessed to remove metal ions from solution.

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FIGURE CAPTIONS

Figure 1. The MARTINI coarse-graining scheme for a G0.5 PAMAM-COO grafted to silicon where each circled group represents a different bead type.

Figure 2. Simulation snapshot of the isolated PAMAM-COO dendron of generation (a) G1.5, (b) G2.5, (c) G4.5 and (d) G5.5. Silica (yellow), amine (green), amide (blue), carboxylate (red), and Pb (brown) groups are depicted.

Figure 3. (a) A G3.5 dendron is compact when isolated from other dendrons. (b) When the grafting density is increased such that the theoretical surface coverage is equal to one, there is an observable expansion. Only one dendron of the brush is drawn. Silica (yellow), amine (green), amide (blue), carboxylate (red), and Pb (brown) groups are depicted.

Figure 4. (a) Radius of gyration measurements for isolated PAMAM-COO dendrimer and PAMAM-COO dendron brushes, for different surface coverage levels and number of generations. (b) Comparison of the theoretical surface coverage with the simulated surface coverage as a function of the number of generations.

Figure 5. Average number of beads from all the moieties in the (a) inner and the (b) outer ion coordination shells of Pb(II).

Figure 6. The distribution of the average ion coordination for the Pb(II) ions in the inner shell for dendrons of generations (a) G1.5, (b) G2.5, (c) G3.5, (d) G4.5 and (e) G5.5, and the outer shell of the dendrons of generations (f) G1.5, (g) G2.5, (h) G3.5, (i) G4.5 and (j) G5.5.

Figure 7. Scaling analysis of brush height Z as a function of the (a) dendron path length N, the (b) the molecular weight M , and the (c) square of the spacing $s=d^2$.

TABLE CAPTIONS

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Table 1: The Lennard-Jones pair potential parameters for the coarse-grained beads of PAMAM-COO dendron.

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