

Surface Patterns of a Tetrahedral Polyelectrolyte Brush Induced by Grafting Density and Charge Fraction

Hong-Ge Tan*, Gang Xia, Li-Xiang Liu, Xiao-Hui Niu, and Qing-Hai Hao

College of Science, Civil Aviation University of China, Tianjin 300300, China

Abstract A tetrahedral polyelectrolyte brush in the presence of trivalent counterions is researched under the condition of good solution by means of molecular dynamics simulations. Grafting density and charge fraction are varied to generate a series of surface patterns. Lateral microphase separation happens and various interesting pinned patches appear at appropriate charge fraction and grafting density. Through a careful analysis on the brush thickness, the pair correlation functions, the distributions of net charge, and the four states of trivalent counterions in the brush, we find that the ordered surface patterns and special properties are induced by the pure electrostatic correlation effect of trivalent ions even in the good solvent. Furthermore, the dependences of electrostatic correlation on the charge fraction of tethered chains are evaluated for fixed grafting density. Also, our results can serve as a guide for precise control over the stimuli-responsive materials rational and self-assembly of nanoparticles.

Keywords Surface patterns; Tetrahedral polyelectrolyte brush; Molecular dynamics simulation; Electrostatic correlation

Citation: Tan, H. G.; Xia, G.; Liu, L. X.; Niu, X. H.; Hao, Q. H. Surface patterns of a tetrahedral polyelectrolyte brush induced by grafting density and charge fraction. *Chinese J. Polym. Sci.* 2020, 38, 394–402.

INTRODUCTION

Polyelectrolyte (PE) brushes are thin films of PE chains with chain-end tethered to substrates in different geometries.^[1,2] The stimuli-responsive characteristic induced by the intrinsic behaviors of individual PE chains as well as the emergent collective physical-chemical properties in the brush has triggered a significant growth of interest in a diverse range of applications, such as colloidal stabilization,^[3] advanced drug delivery,^[4] biological lubrication,^[5] and smart materials.^[6] These versatile applications are closely related to the surface morphologies of PE brushes, which can be tuned by a series of surrounding environmental parameters, for example, the grafting density, the charged fraction of PE chains, the salt concentration and valence, the geometric shape of grafted substrates, and so on.^[7–19]

There are a lot of studies concentrated on the surface morphologies of planar PE brushes.^[7–17] By means of scaling theory and self-consistent field calculation (SCF), Zhulina *et al.*^[7] firstly reported that morphologies of the planar PE brushes with monovalent counterions in poor solvents can evolve from the pinned micelle structure to a laterally uniform layer with increasing degree of ionization. Rich surface patterns of planar PE brushes with monovalent counterions were found in different bulk pH and quality of the solvent by Tagliazucchi *et al.*^[8,9] using molecular theory, such as micelles, stripes,

holes, and micelles coexisting with isolated chains. Based on the theoretical model, Brettmann *et al.*^[10] analyzed an analogous collapse of planar PE brushes induced by multivalent ions in poor solvent, providing an explanation based on energy balance for the formation of pinned micelles and cylindrical bundles.

On experiment, using X-ray reflectivity and grazing incidence diffraction, Günther *et al.*^[11] firstly investigated the bundle formation within planar PE brushes with monovalent counterions in the poor solvent and found that the bundle would shrink with the increase of grafting density and counterion concentration. Yamada *et al.*^[12] demonstrated the morphology variation of planar lipophilic PE brushes induced by immersing in various organic solvents. A series of fiber-like structures were indentified by atomic force microscopy (AFM) images in the solvents with different dielectric constants. Based on AFM apparatus, Bracha *et al.*^[13] reported the formation of dendritic and nanowire domains of planar DNA brushes induced by the trivalent cation spermidine. By means of AFM and surface forces apparatus (SFA) measurements, the lateral inhomogeneous aggregated structures of the planar PE brushes induced by multivalent ions were observed by Yu and coworkers.^[14]

Employing MD simulations, Dobrynin *et al.*^[15] examined the effects of solvent quality and electrostatic interaction strength on the accessible structures of planar PE brushes with monovalent counterions in salt-free solutions. Vertical bundles of chains, maze-like structures, and homogenous polymeric layers were formed as a result of the fine interplay

* Corresponding author, E-mail: thg@iccas.ac.cn

Received July 23, 2019; Accepted September 2, 2019; Published online November 8, 2019

between electrostatic repulsion and short range monomer-monomer interactions. He *et al.*^[16] presented the morphological changes of salt-free planar PE brushes with monovalent counterions induced by lowered temperature (solvent quality) using MD simulations. Homogenous brush, vertical bundles of chains, and collapsed brush were reported. Jackson *et al.*^[17] revealed that the non-uniform aggregation structures of planar PE brushes can be induced by both solvophobic solvents and multivalent ion bridging, which exhibited a distinct mechanism.

There have also been some attempts focused on the surface patterns of spherical PE brushes up to now. Combining molecular dynamics simulations and scaling analysis, Dobrynin and coworkers also observed the formations of lateral morphologies of the spherical PE brushes with monovalent counterions induced by the electrostatic strength under poor solvent conditions, such as a star-like conformation, pinned cylindrical micelles, a micelle-like conformation, and collapsed brush.^[18] Samokhina *et al.*^[19] experimentally studied the complex between an anionic spherical PE brush and the cationic surfactant in salt-free solutions. It was demonstrated that the surface layer of the brush exhibited a partially collapsed structure, namely, a dilute phase of some chains diffusing into the aqueous phase and a dense proximal layer formed directly on the core.

On the other hand, non-spherical nanoparticle decorated by polymers has attracted research interest recently.^[20–25] On experiment, Choueiri *et al.*^[22] developed a new strategy for surface patterning of polymer brush grafted on the nanoparticles with different geometries. It was observed that the segregation of a neutral polymer brush into different surface pinned patches was triggered by changing the geometric shape of nanoparticles and varying the solvent from tetrahydrofuran to water. Kravchenko *et al.*^[23] proposed computer simulations of the self-assembly of polymers grafted non-spherical nanoparticles in poor solvents. They pointed out that non-spherical vesicles resembling a monocrystal can be stable in dilute solution.

Given that the above researches generally focus on neutral polymers other than charged polymers, it is interesting to imagine that nanoparticles with different shapes tethered with PE chains can subject to different external stimuli, and their assemblies can exhibit new collective properties. By now, DNA brushes have been attached to tetrahedral and various other shapes on experiments in the work of Mirkin and Schatz.^[24,25] The simulations of PE-grafted nanocolloids with non-spherical shapes are still far from being fully carried out, especially in good solvents and multivalent ion conditions. In this work, we carry out MD simulations to explore the surface patterns of tetrahedron PE brushes with trivalent counterions under good solvents. Our focus is on elucidating the effects of grafting density and charged fraction of the PE backbone on the structuring of tetrahedral PE brush under the condition of electrostatic correlation, which can provide important insights into the understanding of responsive behavior of the PE-grafted non-spherical nanocolloid to the environmental conditions. A series of surface patterns can be identified through a careful analysis on the snapshots of brush morphologies, brush thickness, the net charge distribu-

tion, the pair correlation functions, as well as the four states of the trivalent counterions.

SIMULATION MODEL AND METHOD

The simulations are performed by means of a well-tested coarse-grained model,^[15,16,18] which is implemented in the software LAMMPS.^[26] In our model, the tetrahedral PE brush is modeled as M flexible chains grafted on the triangular lattices for each surface of a neutral tetrahedral colloid. Each PE chain consists of $N = 60$ monomers and a certain percentage of the monomers are charged and distributed uniformly along the polymer backbone. Every charged monomer carries one unit negative charge $-e$. The trivalent counterions are inserted randomly into the system to guarantee the whole neutrality of charges. All beads are considered as spherical particles with a diameter σ regardless of the bead type. The tetrahedral surface of the colloid is constructed by a certain number of overlapping particles, which is used to prevent the monomers as well as ions from penetrating into the interior of the colloid. The tetrahedral colloid is located at the center of the cubic simulation box with a side length of $L = 160\sigma$ and periodic boundaries, which is large enough to avoid interactions between the brush and its periodic image.^[18,27,28] The number of the tethered chains is selected as $M = 20$, which is fixed in our simulations. The charge fraction f is changed by varying the percentage of charged monomers. The grafting density σ_g is tuned by varying the edge length of tetrahedral colloid L_c , namely, $\sigma_g = M/(3^{1/2}L_c^2)$, which is illustrated in Table 1.

Table 1 The length of tetrahedral colloid and corresponding grafting density.

L_c	24	21	18	15	12	9	6	5
σ_g	0.020	0.026	0.036	0.051	0.080	0.143	0.321	0.461

The excluded volume interaction between any two beads is described by a truncated-shifted Lennard-Jones (LJ) potential,

$$U_{\text{LJ}}(r_{ij}) = \begin{cases} 4\epsilon_{\text{LJ}} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \left(\frac{\sigma}{r_c} \right)^{12} + \left(\frac{\sigma}{r_c} \right)^6, & r \leq r_c \\ 0, & r > r_c \end{cases} \quad (1)$$

where r_{ij} denotes the distance between any two beads, ϵ_{LJ} is the strength of pairwise interaction, and r_c is the cutoff distance. The cutoff distance for monomer-monomer interactions is selected as $r_c = 2.5\sigma$, while $r_c = 2^{1/6}\sigma$ applies to all otherwise interactions. ϵ_{LJ} equals $0.1k_{\text{B}}T$ (k_{B} is Boltzmann constant and T is the desired temperature) for monomer-monomer interactions and $1.0k_{\text{B}}T$ for all otherwise interactions in implicit solvent.^[29,30] Those choices represent a good solvent for the polymer backbone.^[18,31]

The adjacent monomers along the chain are connected via a finite extensible nonlinear elastic (FENE) potential,^[32,33]

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

where $k_{\text{spring}} = 30k_{\text{B}}T/\sigma$ and $R_{\text{max}} = 1.5\sigma$ are the spring constant and the maximum bond length, respectively. This attractive potential combined with the excluded volume interaction can prevent the bonds from crossing each other.

The electrostatic interaction between charged particles is described by the Coulomb potential,

$$U_{\text{Coul}}(r_{ij}) = k_B T \frac{\lambda_B q_i q_j}{r_{ij}} \quad (3)$$

where q_i and q_j are the valences of particles i and j . The Bjerrum length $\lambda_B = e^2/(\epsilon k_B T)$ is set as 3.0σ ,^[34,35] where ϵ is the dielectric constant of solvent. The Coulombic interactions are calculated by the particle-particle/particle-mesh (PPPM) algorithm with estimated accuracy of 10^{-3} .^[36] All physical quantities are dimensionless based on the three basic units (length σ , mass m , and energy $k_B T$).

The temperature is controlled by a Langevin thermostat based on fluctuation-dissipation theorem.^[26] The equation of motion of the particles can be expressed as

$$m \frac{d^2 \mathbf{r}_i(t)}{dt^2} = -\nabla U_i - \xi \frac{d\mathbf{r}_i(t)}{dt} + \mathbf{F}_i^R(t) \quad (4)$$

where $m = 1.0$ is the mass of the bead irrespective of the bead type. U denotes the total potential energy of the system, namely, $U = U_L + U_{\text{bond}} + U_{\text{Coul}}$. ξ is the friction coefficient. $\mathbf{F}_i^R(t)$ is the random force with zero average value and with the correlation function of $\langle \mathbf{F}_i^R(t) \cdot \mathbf{F}_j^R(t') \rangle = 6m\xi k_B T \delta_{ij} \delta(t - t')$. This correlation function is used to couple the system to the heat bath. The value of friction coefficient is set as $\xi = 0.143m/\tau$, where τ is the standard LJ-time unit.

Simulations are performed using the following procedure. Initially, the grafted chains are in the fully extended conformation. The trivalent counterions are randomly inserted into the simulation box. Disorder tethered chains as the initial configuration are produced by employing a soft potential before the equilibrated run. Then, the soft potential is changed to the full LJ potential and the system is equilibrated for 2.0×10^6 MD steps with the full LJ potential until the time evolution of thermodynamic quantities (temperature, energy and pressure) and radius of gyration reach a stable state regime. After the equilibrated run, another production run is performed for 2.0×10^6 MD steps. During the production run, one configuration is sampled every 2.0×10^3 time steps and 1001 configurations are collected for analyzing the properties of the tetrahedral PE brush in our programs. The integration time step $\Delta t = 0.005\tau$ is used.

RESULTS AND DISCUSSION

A series of interesting phase structures of the tetrahedral PE brush have been discovered, as displayed in Fig. 1. Along the column and row, charge fraction f and grafting density σ_g are varied, representing the complex competing between electrostatic effect and excluded volume effect for the phase behavior.

As shown, the morphological evolutions induced by the electrostatic correlation effect originated from the increasing charge fractions at given grafting density are observed along the columns. In the low grafting density range $\sigma_g \leq 0.036$, phase transition induced by the charge fraction that results in pattern formation is observed from top to bottom along the column. The surface morphology starts with a micelle-like conformation at a small charged fraction of $f = 0.1$, transforms to collapsed chains at larger fraction of $f = 0.5$, and demonstrates pinned patches when $f = 1.0$. This is the manifestation of the strong electrostatic correlation existing in an electrostatic system with trivalent counterions. Namely, an effective attractive interaction between charged monomers is mediated by the trivalent ions under a large f , which results in the formation of pinned patches morphologies even in good solvent conditions. It is found that the number of pinned patches decreases with increasing grafting density, which displays the similar variation to patch number of the uncharged polymer tethered on a nanosphere surface in the poor solvent condition by experiment.^[22] In addition, pinned patches tend to stay near the places of high curvatures (edges or vertexes) at $\sigma_g = 0.020, 0.026$, and 0.036 for $f = 1$. Compared to a spherical colloid, the non-uniform curvature of a tetrahedral colloid breaks translational symmetries of the system along the surfaces and results in the non-uniform distribution of free volumes. Due to more free volumes near the places of high curvatures, trivalent counterions are more accumulated there in order to maximize their translational entropy. This accumulation then leads to the fact that pinned patches of PE brush tend to be formed near the places of high curvatures.

In the regime of $0.051 \leq \sigma_g \leq 0.143$, the increasing grafting density promotes the trivalent counterions to play a bridging role among the monomers with the same charge fraction. Thus, for $f = 1.0$, sufficient bridging counterions make all the

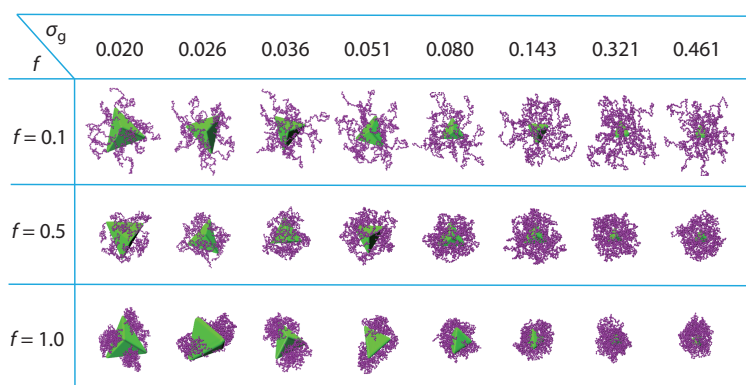


Fig. 1 Snapshots of the tetrahedral PE brush in parameter spaces of grafting density σ_g and charge fraction f . For clarity, only monomers (the purple bead) and grafted colloid (the green tetrahedral surface) are shown.

PE chains aggregate together and only a part of the colloid surface is exposed. This type of asymmetric cluster is a transitional structure when the electrostatic correlation of trivalent ions and the excluded volume interactions are comparable. Such asymmetric clusters were also observed experimentally by Lane *et al.*^[37] for alkanethiol-coated Au spherical nanoparticles in dilute solutions of water. However, for $f = 0.1$ and 0.5 , the number of bridging counterions is not sufficient and no obvious lateral phase separation happens with the increase of grafting density. In the regime of $\sigma_g > 0.143$, a uniform PE layer is observed regardless of the charge fraction, but this brush layer adopts a tight conformation with the increase of charge fraction.

We further examine the global structure of PE chains using the tetrahedral PE brush thickness H , which can be characterized by

$$H = \frac{2 \int_0^{+\infty} r \cdot \sqrt{3(L_c + 2\sqrt{6}r)^2} \rho_m(r) dr}{\int_0^{+\infty} \sqrt{3(L_c + 2\sqrt{6}r)^2} \rho_m(r) dr} \quad (5)$$

where, $\rho_m(r)$ is the local density of polymer monomers along the direction perpendicular to the grafting surface and r is the vertical distance between the location and the grafted surface of the tetrahedron. The entire integral region is divided into many tetrahedral bins with the thickness of $dr = 0.2$ and $\sqrt{3}(2\sqrt{6}r + L_c)^2$ represents the surface area of a tetrahedral bin to calculate the brush thickness.

The variations of brush thickness with respect to the grafting density at different charged fractions are plotted in Fig. 2. With charge fraction increasing, the relationship between brush thickness and grafting density is changed. For $f = 0.1$, the monotonic dependence of brush thickness on the grafting density is clearly demonstrated, which indicates that the excluded volume interaction is dominant for $f = 0.1$. For $f = 0.5$ and 1.0 , the nonmonotonic dependence is clearly demonstrated in this plot. Specifically, the brush thickness experiences a decrease firstly and then a rise with the increase of grafting density.

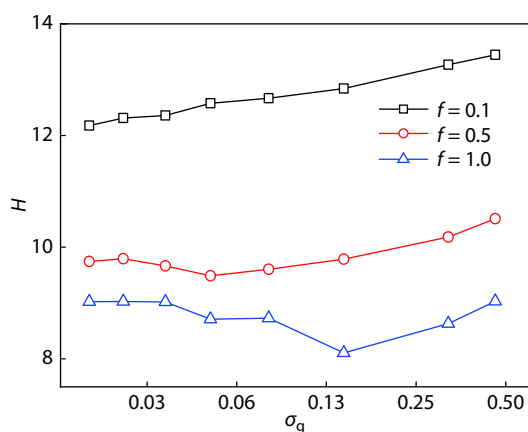


Fig. 2 The thickness of tetrahedral PE brushes versus different grafting densities at different charge fractions.

The decreasing trend of the brush thickness is attributed to electrostatic attraction between monomers coming from the charge correlation. Comparing $f = 1.0$ with $f = 0.5$, the brush

collapses seriously for $f = 1.0$ but slightly for $f = 0.5$. Furthermore, the critical grafting density corresponding to the collapsed-to-stretched transformation of the brush is larger for $f = 1.0$ than for $f = 0.5$. It indicates that the effect of electrostatic correlation is stronger and wider for $f = 1.0$ than for $f = 0.5$. Specifically, for $f = 1.0$, more condensed counterions play the role of inter-chain bridging leading to an aggregation of the PE chains. This will be further clarified by investigating the state of counterions in the following. The lateral heterogeneous structures formed by chain aggregation cause more chains to bend to the grafting surface. The relatively low grafting density ensures that the tetrahedral grafting surface can accommodate lateral bending chains, which leads to serious collapse of the brush. Such deep collapse of the brush results in larger collapse-swell critical grafting density for $f = 1.0$.

When grafting density reaches a threshold, the peripheral space of the grafted colloid is fully occupied by the monomers, which promotes the domination effect of excluded volume interaction. A swell of the brush with increasing grafting density is observed.

Collapse-swell process of brush height for tetrahedral brush with grafting density has not been reported for the spherical brush, as far as we know. Only the case that brush height increases with grafting density at larger grafting density was once reported for spherical brush.^[28] The collapse-swell process of tetrahedral PE brush at $f = 1.0$ may provide guidelines for designing controlled release devices.

Besides, increasing the charge fraction f leads to chain collapse due to the enhanced electrostatic interaction (Fig. 2). Such collapse is similar to that occurring in the systems with monovalent counterions by reducing the temperature or increasing the chain length.^[38,39] In a PE system with only electrostatic interaction, reducing the temperature of the system or increasing the chain length results in enhanced electrostatic interaction. When the electrostatic interaction is strong enough, chain collapse will also occur even in the monovalent system. It is worth noting that trivalent systems have special bridging effects, which not only leads to collapse but also to lateral microphase separation of PE brushes.

To characterize the local structuring of tetrahedral PE brush, we calculate the pair correlation functions (PCF). The monomer-monomers PCFs $g_{mm}(r)$ with different charge fractions are plotted in the left panels of Fig. 3. For clarity, only four different grafting densities are discussed, which correspond to four different surface morphologies in the third row of Fig. 1.

The first peak of $g_{mm}(r)$ locates around $r = 1.0$, which is the manifestation of the intra-chain neighbor correlations, and the second peak locating around $r = 2$ corresponds to an inter-chain structural order, which becomes more pronounced with increasing grafting density for a fixed charge fraction due to the decreased distance between monomers with the increase of grafting density. Furthermore, the magnitude of peaks, especially the secondary one, becomes stronger with the increase of charge fraction. This can be ascribed to the long-range order induced by the electrostatic correlation of the increasing trivalent counterions.

The monomer-counterion PCFs $g_{mc}(r)$ under a variety of

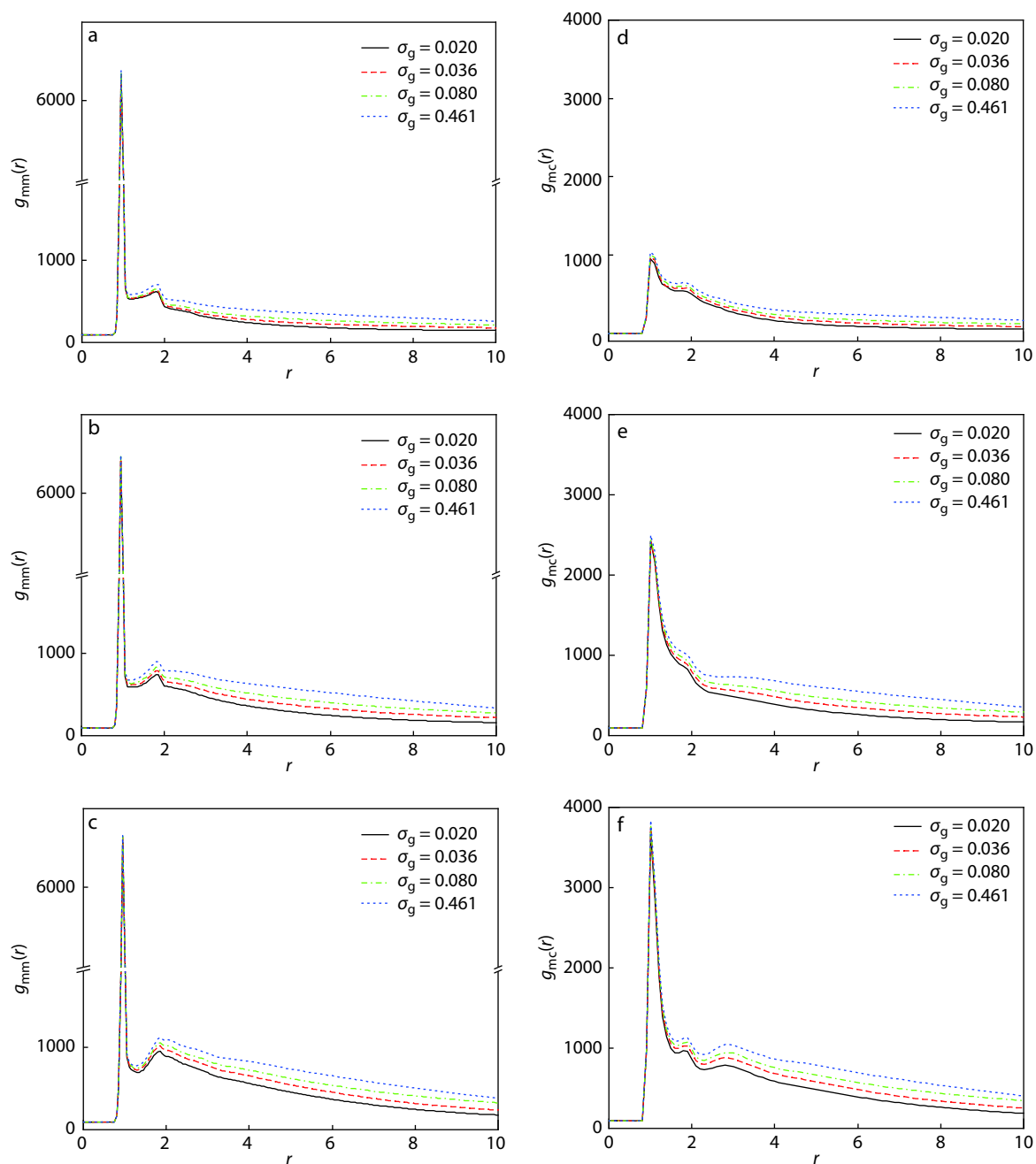


Fig. 3 Monomer-monomer pair correlation functions (left panels) and monomer-counterion pair correlation functions (right panels) for different charge fractions: (a, d) $f = 0.1$, (b, e) $f = 0.5$, (c, f) $f = 1.0$.

charge fractions are presented in the right panels of Fig. 3. It is expected that the correlations between monomers and trivalent counterions are weak in the case of $f = 0.1$ (see Fig. 3d), which indicates that isolated counterions account for the largest proportion. Thus, the translational entropy of counterions is very large, which makes phase separation difficult for PE brush (see Fig. 1). With increasing charge fraction, the primary peak and the sub-peaks become more pronounced as demonstrated in Figs. 3(e) and 3(f). For the largest charge fraction $f = 1.0$, both the nearest neighbor correlation and the long-range correlation are obvious due to the strong

electrostatic attraction in the presence of trivalent ions. Loss of translational entropy of counterions drives the brush into phase separation (see Fig. 1).

Also, to obtain more information on electrostatic interaction, the distributions of net charge around the charge monomers along the radial direction are presented in Fig. 4. For clarity, only four different grafting densities are focused on. As we can see, the effect of grafting density on the distributions of net charge is negligible for fixed charge fraction. On the other hand, different charge fractions produce different net charge distributions.

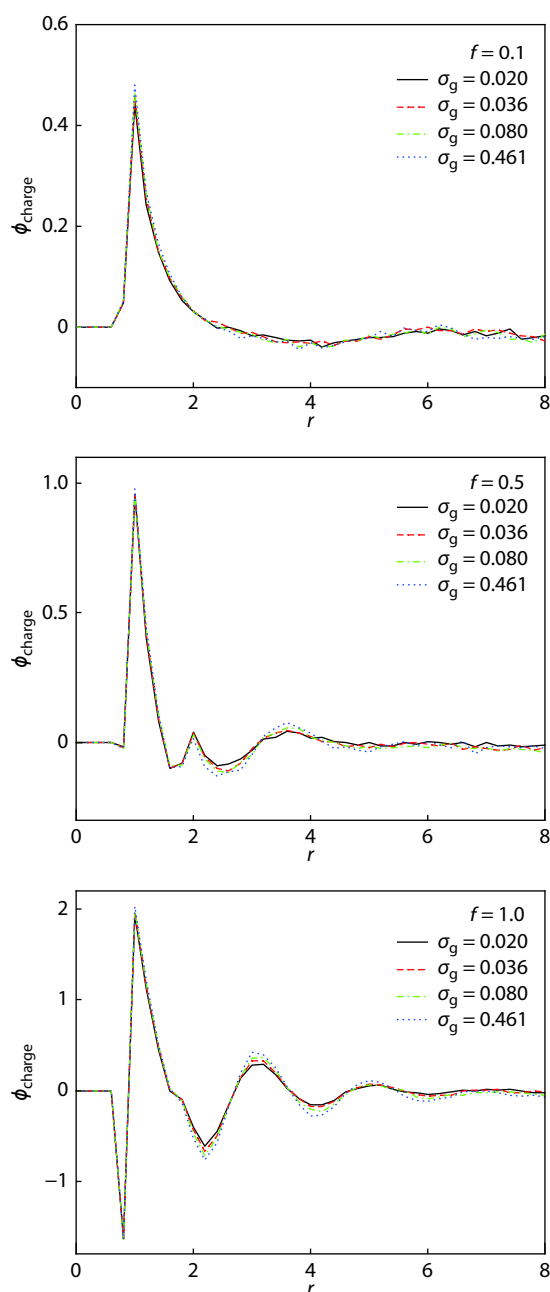


Fig. 4 The distributions of net charge around the charge monomers along the radial direction for different charge fractions.

Firstly, there is a prominent peak near $r = 1.0$ for all charge fractions due to the electrostatic attractions between negative polymer monomers and positive trivalent counterions. With charge fraction increasing, this peak becomes pronounced, indicating more counterions gather onto the charge polyions because the electrostatic attractions predominate over the translational entropy of counterions in this region. For $f = 1.0$, a negative peak near $r = 0.8$ appears, which is attributed to the covalent bonding between negative charges. Due to the mutual effect of covalent bonding and electrostatic attractions, positively and negatively charged regions appear alternately in the range of $1 < r < 6$. Similarly,

the appearance of the negative peak near $r = 1.6$ is attributed to the covalent bonding between negative charges at $f = 0.5$. Because every two monomers along the chain carry a negative unit charge $-e$, the profile shows an oscillatory behavior in the range of $1 < r < 4$ at $f = 0.5$. By comparison, it is found that increasing the charge fraction leads to a deviation from local electrical-neutrality. All profiles subsequently decrease to zero, indicating the overall electrical-neutrality of the systems.

Since the structures of tetrahedral PE brush are mainly determined by the electrostatic effect of trivalent ions, we further study the states of the trivalent counterions by classifying them into four states, that is, isolated, nearest neighbor condensation, intra-chain bridging, and inter-chain bridging counterions. This has been demonstrated schematically in Fig. 5.

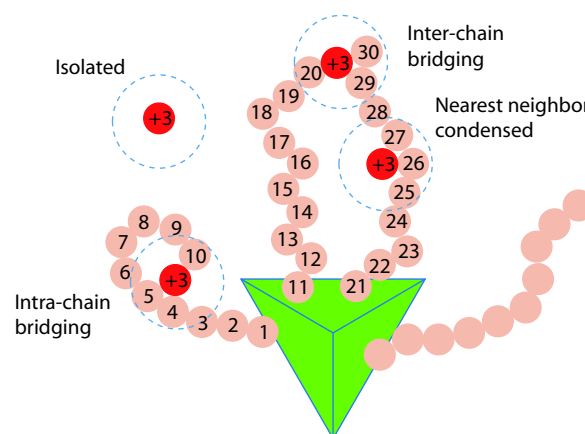


Fig. 5 Schematic for classifying trivalent counterions into four states, namely, the isolated, the nearest neighbor condensed, the intra-chain bridging, and the inter-chain bridging states. Green tetrahedron indicates the tethered colloid, red beads represent the trivalent counterions, and pink beads correspond to the PE monomers.

The number fractions of trivalent counterions that are in the corresponding state are quantified in terms of a topological parameter α . The definition of α can be obtained from Ref. [14]. $\alpha = 0$, $0 < \alpha \leq 0.816$, $0.816 < \alpha \leq 5.0$, and $\alpha > 5.0$ correspond to isolated, nearest neighbor condensed, intra-chain bridging, and inter-chain bridging counterions, respectively.[14] The fractions of trivalent counterions are plotted against the grafting density in Fig. 6.

As shown in Fig. 6(a), the trivalent counterions exist in only two states at $f = 0.1$, that is, the isolated and nearest neighbor condensed states. The majority of counterions are in the isolated state for polyions with relatively low linear charge density. The fraction of isolated counterions demonstrates a slight decrease with the increasing grafting density. This is due to the fact that charged monomers can approach each other and lead to a higher local charge density with the increase of grafting density, which promotes more trivalent counterions to condense on the PE chains. Due to the majority of isolated counterions, electrostatic attractions are negligible. The repulsive interactions between polymer monomers due to the excluded volume effect at good solvent conditions are dominant. Thus, microphase separation does not

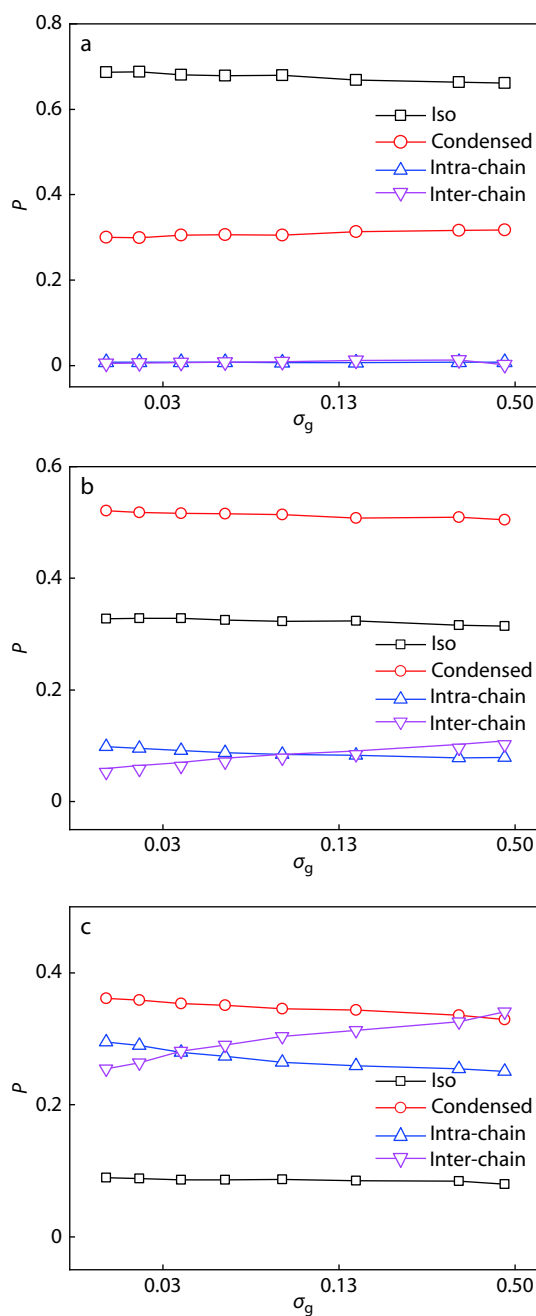


Fig. 6 Fractions of isolated, nearest neighbor condensed, intra-chain bridging, and inter-chain bridging counterions as a function of grafting density: (a) $f = 0.1$, (b) $f = 0.5$, (c) $f = 1.0$.

happen for $f = 0.1$.

For $f = 0.5$ depicted in Fig. 6(b), the nearest neighbor condensed counterions are dominant, which results in the collapse of PE brush. On the other hand, the short inter-chain distance with increasing grafting density puts more counterions into the inter-chain bridging state, which causes the brush thickness to decrease slightly with grafting density in the range of low grafting density. Owing to the low percentage of inter-chain bridging counterions, the chains are not connected to form patches at $f = 0.5$. On further increasing $f = 1.0$, electrostatic attraction is so strong that few isolated

trivalent counterions exist in the system, which leads to sharp collapse of PE brush. More and more trivalent counterions transform into the inter-chain bridging state and induce an effective attraction between polymer segments, manifesting the electrostatic correlation effect and resulting in a lateral heterogeneity of the PE brush and obvious decrease of the brush thickness with grafting density in the low grafting density range.

Due to the importance of the trivalent counterions, we further investigate the fractions of counterions in four states as a function of charge fractions, which are shown in Fig. 7. Both the lowest grafting density $\sigma_g = 0.020$ and the highest grafting density $\sigma_g = 0.461$ are discussed.

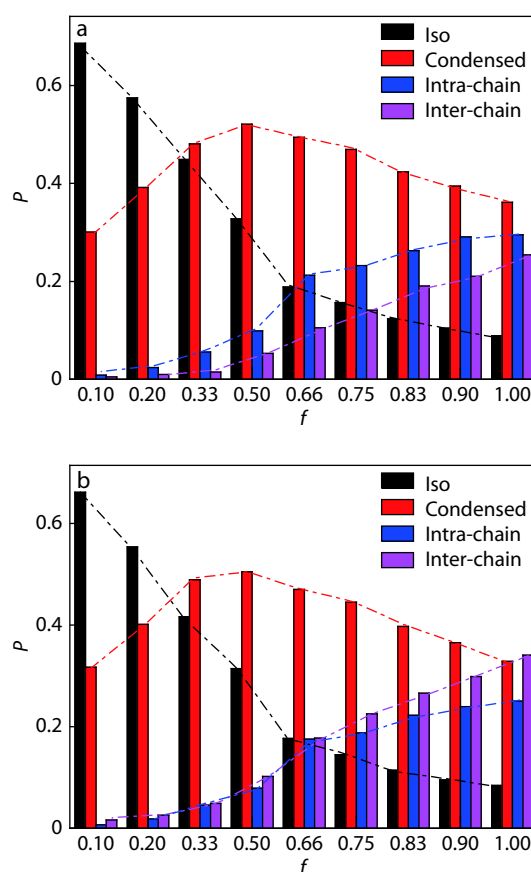


Fig. 7 The fractions of counterions in the isolated, nearest neighbor condensed, intra-chain bridging, and inter-chain bridging states as a function of charge fraction with (a) $\sigma_g = 0.020$ or (b) $\sigma_g = 0.461$. The curves are used to guide the eyes.

As shown, a monotonic decrease of fraction of the isolated state counterions is induced by increasing the charge fraction irrespective of grafting density, which can be understood from the increasing effective charge density of the polymer backbones. The effective attractive interaction between charged monomers and trivalent counterions dominates over the translational entropy of counterions, which induces more trivalent counterions to condense onto the polyons. It is interesting to observe that the fractions of nearest neighbor condensed counterions increase with the increasing charge fraction firstly, and then decrease. For small

f , increasing charge fraction can only render the counterions condensed onto the polymer backbone. The counterions have not yet begun to play the role of electrostatic correlation, which corresponds to the homogenous micelle-like structure shown in Fig. 1. For $f > 0.5$, the fractions of counterions in the nearest neighbor condensed state begin to decrease due to increasing electrostatic correlation.

Besides, the fractions of intra-chain bridging and inter-chain bridging counterions increase with the charge fraction. For low grafting density $\sigma_g = 0.020$, intra-chain correlations begin to work earlier than inter-chain correlations with the increase of charged fraction. It is because overcoming translational entropy of intra-chain monomers is easier under low grafting density condition. Thus, for low grafting density, the PE brush undergoes a process of collapsing first and then forming lateral heterogeneities of surface morphologies with the increase of charged fraction. For high grafting density of $\sigma_g = 0.461$, inter-chain correlations emerge earlier than inter-chain correlations with the increase of charged fraction due to the short inter-chain distance. Though uniform polymer layers are retained by the strong excluded volume interaction in the high grafting density, the PE brush will collapse with the increase of charged fraction for the increasing electrostatic correlation.

CONCLUSIONS

On the basis of a coarse-grained model, the electrostatic correlation on the surface morphologies of a tetrahedral PE brush in good solvent is studied systematically by means of MD simulations. The tetrahedral PE brush adopts a uniform micelle-like structure and the brush thickness increases monotonously with the grafting density at low charge fraction regardless of grafting density, which is mainly attributed to the hydrophilic effect of the good solvent. Upon increasing the charge fraction to a certain extent, the enhanced electrostatic correlation of multivalent counterions renders the tetrahedral PE brush to separate into inhomogeneous surface patterns, namely, the pinned patch structure is observed in low grafting density range. Pinned patches of PE brush tend to be formed near the places of high curvatures. The number of patches decreases with the increasing grafting density, which is concurrent with the decrease of brush thickness, until a uniform layer of tethered chains is formed when the grafting density exceeds the critical value. For the local structuring, PCFs reveal that the electrostatic-correlation induced order in the presence of trivalent ions becomes more pronounced with the increasing charge fraction, even in the good solvent condition. Moreover, increasing the charge fractions leads to a larger deviation from local electrical-neutrality. Based on the analysis of the fractions of counterions in four states, it is worthwhile to point out that the multivalent counterions can act as a nucleating site to bridge intra- and inter-chain monomers, collectively leading to the special phase behavior. Our systematic analysis in this work can generalize the lateral morphological studies of PE brush, in terms of the responsiveness to the grafting density and charge fraction, to the tetrahedral case. A more complete knowledge about surface structures of PE brush can be constructed, which provides practical guidance for regulating the interfacial properties of nanomaterials and rational material design.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21474005 and 21674005) and the Fundamental Research Funds for the Central Universities (No. 3122018L007) and Quality Course Construction.

REFERENCES

- Rühe, J.; Ballauff, M.; Biesalski, M.; Dziezok, P.; Gröhn, F.; Johannsmann, D.; Houbenov, N.; Hugenberg, N.; Konradi, R.; Minko, S.; Motornov, M.; Netz, R. R.; Schmidt, M.; Seidel, C.; Stamm, M.; Stephan, T.; Usov, D.; Zhang, H. Polyelectrolyte brushes. *Adv. Polym. Sci.* **2004**, *165*, 79–150.
- Hao, Q. H.; Zheng, Z.; Xia, G.; Tan, H. G. Brownian dynamics simulations of rigid polyelectrolyte chains grafting to spherical colloid. *Chinese J. Polym. Sci.* **2018**, *36*, 791–798.
- Jaquet, B.; Wei, D.; Reck, B.; Reinhold, F.; Zhang, X. Y.; Wu, H.; Morbidelli, M. Stabilization of polymer colloid dispersions with pH-sensitive poly-acrylic acid brushes. *Colloid Polym. Sci.* **2013**, *291*, 1659–1667.
- Zhang, X.; Yang, P. P.; Dai, Y. L.; Ma, P. A.; Li, X. J.; Cheng, Z. Y.; Hou, Z. Y.; Kang, X. J.; Li, C. X.; Lin, J. Multifunctional up-converting nanocomposites with smart polymer brushes gated mesopores for cell imaging and thermo/pH dual-responsive drug controlled release. *Adv. Funct. Mater.* **2013**, *23*, 4067–4078.
- Kreer, T. Polymer-brush lubrication: a review of recent theoretical advances. *Soft Matter* **2016**, *12*, 3479–3501.
- ShamsiJazeyi, H.; Miller, C. A.; Wong, M. S.; Tour, J. M.; Verduzco, R. Polymer-coated nanoparticles for enhanced oil recovery. *J. Appl. Polym. Sci.* **2014**, *134*, 40576.
- Zhulina, E.; Singh, C.; Balazs, A. C. Behavior of tethered polyelectrolytes in poor solvents. *J. Chem. Phys.* **1998**, *108*, 1175–1183.
- Tagliazucchi, M.; Cruz, M. O. D. L.; Szeifer, I. Self-organization of grafted polyelectrolyte layers via the coupling of chemical equilibrium and physical interactions. *Proc. Natl. Acad. Sci.* **2010**, *107*, 5300–5305.
- Tagliazucchi, M.; Calvo, E. J.; Szeifer, I. Molecular modeling of responsive polymer films. *AIChE J.* **2010**, *56*, 1952–1959.
- Brettmann, B.; Pincus, P.; Tirrell, M. Lateral structure formation in polyelectrolyte brushes induced by multivalent ions. *Macromolecules* **2017**, *50*, 1225–1235.
- Günther, J. U.; Ahrens, H.; Förster, S.; Helm, C. A. Bundle formation in polyelectrolyte brushes. *Phys. Rev. Lett.* **2008**, *101*, 258303.
- Yamada, T.; Kokado, K.; Higaki, Y.; Takahara, A.; Sada, K. Preparation and morphology variation of lipophilic polyelectrolyte brush functioning in nonpolar solvents. *Chem. Lett.* **2014**, *43*, 1300–1302.
- Bracha, D.; Bar-Ziv, R. H. Dendritic and nanowire assemblies of condensed DNA polymer brushes. *J. Am. Chem. Soc.* **2014**, *136*, 4945–4953.
- Yu, J.; Jackson, N. E.; Xu, X.; Brettmann, B. K.; Ruths, M.; Pablo, J. J. D.; Tirrell, M. Multivalent ions induce lateral structural inhomogeneities in polyelectrolyte brushes. *Sci. Adv.* **2017**, *3*, 1497.
- Carrillo, J. M. Y.; Dobrynin, A. V. Morphologies of planar polyelectrolyte brushes in a poor solvent: molecular dynamics simulations and scaling analysis. *Langmuir* **2009**, *25*, 13158–13168.
- He, G. L.; Merlitz, H.; Sommer, J. U. Molecular dynamics simulations of polyelectrolyte brushes under poor solvent conditions: Origins of bundle formation. *J. Chem. Phys.* **2014**, *140*, 104911.

- 17 Jackson, N. E.; Brettmann, B. K.; Vishwanath, V.; Tirrell, M.; Pablo, J. D. Comparing solvophobic and multivalent induced collapse in polyelectrolyte brushes. *ACS Macro Lett.* **2017**, *6*, 155–160.
- 18 Sandberg, D. J.; Carrillo, J. M. Y.; Dobrynin, A. V. Molecular dynamics simulations of polyelectrolyte brushes: from single chains to bundles of chains. *Langmuir* **2007**, *23*, 12716–12728.
- 19 Samokhina, L.; Schrinner, M.; Ballauff, M. Binding of oppositely charged surfactants to spherical polyelectrolyte brushes: a study by cryogenic transmission electron microscopy. *Langmuir* **2007**, *23*, 3615–3619.
- 20 Chen, Q.; Bae, S. C.; Granick, S. Directed self-assembly of a colloidal kagome lattice. *Nature* **2011**, *469*, 381–384.
- 21 Yang, S. W.; Gao, L. Controlled synthesis and self-assembly of CeO₂ nanocubes. *J. Am. Chem. Soc.* **2006**, *128*, 9330–9331.
- 22 Choueiri, R. M.; Galati, E.; Thérien-Aubin, H.; Klinkova, A.; Larin, E. M.; Querejeta-Fernández, A.; Han, L.; Xin, H. L.; Gang, O.; Zhulina, E. B.; Rubinstein, M.; Kumacheva, E. Surface patterning of nanoparticles with polymer patches. *Nature* **2016**, *538*, 79–83.
- 23 Kravchenko, V. S.; Potemkin, I. I. Self-assembly of rarely polymer-grafted nanoparticles in dilute solutions and on a surface: from non-spherical vesicles to graphene-like sheets. *Polymer* **2018**, *142*, 23–32.
- 24 Ross, M. B.; Ku, J. C.; Vaccarezza, V. M.; Schatz, G. C.; Mirkin, C. A. Nanoscale form dictates mesoscale function in plasmonic DNA-nanoparticle superlattices. *Nat. Nanotechnol.* **2015**, *10*, 453–458.
- 25 Jones, M. R.; Osberg, K. D.; Macfarlane, R. J.; Langille, M. R.; Mirkin, C. A. Templated techniques for the synthesis and assembly of plasmonic nanostructures. *Chem. Rev.* **2011**, *111*, 3736–3827.
- 26 Plimpton, S. Fast parallel algorithms for short-range molecular dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.
- 27 Csajka, F. S.; Seidel, C. Strongly charged polyelectrolyte brushes: A molecular dynamics study. *Macromolecules* **2000**, *33*, 2728–2739.
- 28 Hao, Q. H.; Xia, G.; Tan, H. G.; Chen, E. Q.; Yang, S. Surface morphologies of spherical polyelectrolyte brushes induced by trivalent salt ions. *Phys. Chem. Chem. Phys.* **2018**, *20*, 26542–26551.
- 29 Hoda, N.; Larson, R. G. Explicit- and implicit-solvent molecular dynamics simulations of complex formation between polycations and polyanions. *Macromolecules* **2009**, *42*, 8851–8863.
- 30 Huißmann, S.; Likos, C. N.; Blaak, R. Explicit vs implicit water simulations of charged dendrimers. *Macromolecules* **2012**, *45*, 2562–2569.
- 31 Carrillo, J. M. Y.; Dobrynin, A. V. Polyelectrolytes in salt solutions: Molecular dynamics simulations. *Macromolecules* **2011**, *44*, 5798–5816.
- 32 Grest, G. S.; Kremer, K.; Witten, T. A. Structure of many-arm star polymers: a molecular dynamics simulation. *Macromolecules* **1987**, *20*, 1376.
- 33 Ghelichi, M.; Qazvini, N. T. Self-organization of hydrophobic-capped triblock copolymers with polyelectrolyte midblock: A coarse-grained molecular dynamics simulation study. *Soft Matter* **2016**, *12*, 4611–4620.
- 34 Mei, Y.; Hoffmann, M.; Ballauff, M.; Jusufi, A. Spherical polyelectrolyte brushes in the presence of multivalent counterions: the effect of fluctuations and correlations as determined by molecular dynamics simulations. *Phys. Rev. E* **2008**, *77*, 031805.
- 35 Jusufi, A.; Likos, C. N.; Löwen, H. Counterion-induced entropic interactions in solutions of strongly stretched, osmotic polyelectrolyte stars. *J. Chem. Phys.* **2002**, *116*, 11011–11027.
- 36 Pollock, E. L.; Glosli, J. Comments on P3M, FMM, and the Ewald method for large periodic coulombic systems. *Comput. Phys. Commun.* **1996**, *95*, 93–110.
- 37 Lane, J. M. D.; Grest, G. S. Spontaneous asymmetry of coated spherical nanoparticles in solution and at liquid-vapor interfaces. *Phys. Rev. Lett.* **2010**, *104*, 235501–235504.
- 38 Chi, P.; Li, B. H.; Shi, A. C. Conformation transitions of a polyelectrolyte chain: a replica-exchange Monte-Carlo study. *Phys. Rev. E* **2011**, *84*, 021804.
- 39 Chi, P.; Wang, Z.; Yin, Y. H.; Li, B. H. Finite-length effects on the coil-globule transition of a strongly charged polyelectrolyte chain in a salt-free solvent. *Phys. Rev. E* **2013**, *87*, 042608.