

ARTICLE

Collapse of 4-Arm Stars Polyelectrolyte Brushes Under An Electric Field in the Presence of Trivalent Salt Coions

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(Dated: Received on April 29, 2020; Accepted on July 3, 2020)

Langevin dynamics (LD) simulations were conducted to study the collapse of grafted partially charged 4-arm star chains onto the oppositely charged grafting electrode in the presence of trivalent salt coions. Simulation results revealed that the average charge fraction of the grafted star chains and the salt concentration play critical roles in the competitive adsorption of charged monomers and trivalent salt coions onto the oppositely charged electrode. For grafted star chains with relatively high charge fraction, charged monomers are the dominant species collapsing on the oppositely charged electrode with the emergence of charge reversal on the grafting electrode. At a low charge fraction such that the total amount of charges on a grafted star molecule is comparable to that of a trivalent salt coion, trivalent salt coions absorb more strongly onto the electrode than grafted stars even at very low salt concentration. It was found that at relatively low charge fraction of star chains, the addition of trivalent salt coions does not lead to charge overcompensation of the surface charges on the grafting electrode. The stretching of star brushes under an electric field in the presence of trivalent salt coions was also briefly investigated.

Key words: Polymer brush, Charged polymer, Electric field, Adsorption, Molecular dynamics, Electrostatics, Multivalent ion

I. INTRODUCTION

Polyelectrolyte (PE) brushes made of charged polymer chains densely end-grafted onto solid substrates can modify and improve surface properties and have great potential as smart sensors and actuators for a wide range of technological applications [1–15]. Due to the long-range Coulomb interaction, PE brushes can respond to a much wider external stimuli, such as salt concentration and valence, solution pH, external electric fields than their neutral counterparts.

Up to now, most of the theoretical and computational studies of PE brushes involved only neutral grafting surfaces. However, in many realistic systems, the grafting substrates can be charged. For instance, solid substrates made of silica become charged when immersed in water due to the ionization of the surface functional groups and a thin layer of charges forms on the outer surface of the solid substrate. When polyelectrolyte chains are grafted onto metal electrodes to fabricate sensors and actuators in the configuration of a planar capacitor, the opposite surface charges on the grafting electrode and the second electrode generate an electric field across the two electrodes, leading to the stretch-

ing and collapsing of the grafted polyelectrolyte chains [16, 17]. Therefore, the adsorption or collapse of PE brushes onto oppositely charged grafting substrates is an important and interesting problem which warrants theoretical and computational studies.

Zhulina and Borisov theoretically investigated the adsorption of polyelectrolyte brushes into an oppositely charged layer immersed in a salt-free aqueous solution [18]. The parabolic electric potential inside the brush derived from the analytical self-consistent field theory in the strong stretching limit was employed in the theoretical study [19]. In the region above the brush surface, Poisson-Boltzmann equation was solved analytically to afford the electric potential profile. For the case of the thickness of the oppositely charged sub-layer smaller than that of the brush layer, it was found that a fraction of polyions are adsorbed into the sub-layer to neutralize the opposite and immobilized charges. Thus, the uncollapsed polymer chains form a polymer brush with a re-normalized grafting density. The above theoretical predictions were confirmed by a recent molecular dynamics simulation study in the regime of small Bjerrum length [20]. Later on, Zhulina and coworkers extended their study to the case involving added monovalent salt ions using three complementary approaches, *i.e.*, scaling, analytical self-consistent field, and numerical self-consistent field [21]. It was revealed that the ratio of the surface charge density of immobilized char-

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ges in the sub-layer to that of polyions and the ionic strength of the solution significantly affect the conformations of the grafted polyelectrolyte chains. It was shown that the brush height can vary non-monotonically with the ionic strength of the solution for relatively high ratio of the surface charge density to that of polyions. With the initial increase of the salt concentration, the repulsive interaction between polyions themselves is screened, leading to the contraction of the brush. However, at high salt concentration, the attractive interaction between polyions and the fixed charges in the sub-layer is strongly screened, resulting in the increase of the brush height with increasing salt concentration. In the above studies, the immobilized surface charges are almost exactly neutralized by the adsorbed polyions. Nevertheless, in our recent molecular dynamics simulations of the response of charged star brushes to external electric fields, it was demonstrated that the adsorbed monomer charges onto the oppositely charged grafting electrode can overcompensate the surface charge for charge star brushes with long enough arm length and high enough charge fraction [22, 23].

In this work, by performing Langevin dynamics simulations, we studied the competitive adsorption of grafted partially charged 4-arm stars and trivalent salt coions onto the oppositely charged grafting electrode. This study was motivated by the fascinating conformational properties of PE star brushes which are drastically different from those of PE brushes made of linear chains. PE brushes made of branched polyelectrolyte chains, *e.g.* dendrons, stars, emerge as a new class of PE brushes with potential technological applications and have attracted much attention [24–33]. Furthermore, due to the fact that previous theoretical and numerical studies of the adsorption of PE brushes onto the oppositely charged grafting substrates were limited to salt-free and monovalent salt scenarios, it is interesting to study how trivalent coions influence the collapse of partially charged polymer brushes under an external electric field and examine the competitive adsorption of charged monomers and trivalent coions onto the oppositely charged grafting electrode. It is extremely challenging to analytically study the correlation effect of multivalent ions and the phenomenon of charge overcompensation. Simulation techniques such as Langevin dynamics are well suited to tackling the current problem. For completeness, the stretching of charged star brushes under an electric field in the presence of trivalent coions was briefly studied.

II. MODEL AND METHOD

Our simulation system is an ensemble of $M=8\times 8$ flexible 4-arm stars with one end monomer of each star uniformly anchored on a periodically replicated square lattice with dimensions $L_x\times L_y$ (xy plane) at $z=0$. A second planar wall is situated at $z=L_z$. The graft-

ing density of the brush is given by $\sigma_g=M/(L_xL_y)$. The 4-arm star chains were generated by a coarse-grained bead-spring model. Neutral and negatively charged monomers, negatively charged trivalent salt ions as well as the monovalent counterions released by charged monomers, and trivalent salt ions were modeled as spherical Lennard-Jones (LJ) beads (σ, ε) with equal mass m and diameter σ . The two neighboring monomers in the same arm are connected by a spring with the finitely extensible nonlinear elastic bond potential. For 4-arm stars, each arm consists of $N_{ms}=45$ monomer units, leading to a molecular weight of 180 (in unit of m) and a longest path length $L_{lp}=90$ (in unit of σ). The charge fraction of 4-arm stars f was varied with $f\in\{1, 1/3, 1/5, 1/7, 1/9, 1/15, 1/45\}$ in the simulations. The charged monomers are uniformly distributed along the arms of star chains separated by equal number of neutral monomers. For example, if $f=1/5$, then every fifth monomer in each arm of a star macromolecule carries a negative charge (in unit of elementary electronic charge). Each negatively charged monomer in 4-arm stars and each trivalent salt ion release one or three monovalent counterions into the aqueous solution between the two walls to maintain an overall charge neutrality of the brush system. As an implicit solvent model, water was treated as a uniform dielectric background ($\varepsilon_r\approx 78$ at the room temperature) in LD simulations. An electric field \vec{E} was applied in the positive z direction which exerts an electric force $eq\vec{E}$ on a charged particle to cause the collapse of the brushes onto the grafting electrode (e stands for an elementary charge, $q=\pm 1$ for monovalent ion species, $q=-3$ for trivalent salt coions, $q=-1$ for charged monomers). Conversely, an electric field \vec{E} applied in the negative z direction causes the stretching of the grafted 4-arm stars away from the grafting electrode. The long-range Coulomb interaction was calculated using the smooth particle mesh Ewald method (SPME) with an approximate root mean square (rms) force error of 10^{-3} [34, 35]. The methodological detail can be found in the supplementary materials.

In the Langevin dynamics simulations, the temperature of the system was kept at $k_BT=1.2\varepsilon$ with ε denoting the amplitude of LJ potential [36], and the friction coefficient $\zeta=1.0m\tau^{-1}$ with $\tau=\sigma(m/\varepsilon)^{1/2}$ [36, 37]. Bjerrum length λ_B was set to 0.71 nm and $\lambda_B=3\sigma$ ($\sigma\approx 0.24$ nm) in the simulations [36, 37]. The LD unit of the external electric field is $\varepsilon/(e\sigma)=k_BT/(1.2e\sigma)\cong 9.0\times 10^7$ V/m. In this work, the electric field strength was set to $|\vec{E}|=1.0$ corresponding to 9.0×10^7 V/m, which is about the maximum allowed magnitude in experiments [38]. In the simulations, the dimensionless grafting density $\sigma_g^*\equiv\sigma_g\sigma^2$ was fixed at 0.008, which is in the low grafting density regime. The dimensionless grafting density at the transition point between the “mushroom” conformation of the grafted chains to the brush regime was found to be about 0.005.

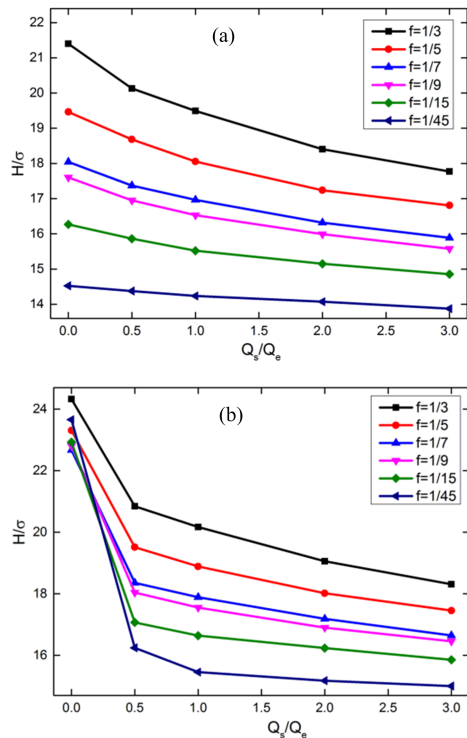


FIG. 1 Brush center of mass heights as a function of the ratio of the total amount of charges of added trivalent salt coions to that of charged monomers at different charge fractions of 4-arm star brushes with $\sigma_g^* = 0.008$ in the absence of external electric fields (a) and under a stretching electric field of $E = -1.0$ (b).

The largest ratio of the surface charge density on the grafting electrode to that of grafted polyions in the simulations is about 0.7 at $E = 1.0$ and $f = 1/45$.

III. RESULTS AND DISCUSSION

A. Stretching of star PE brushes with added trivalent coions in an electric field

The dependence of the center of mass height of star PE brushes on the trivalent salt concentration in the absence of external electric fields is illustrated in FIG. 1(a). As expected, the brush height decreases with increasing salt concentration due to the increasing screening effect of salt ions. However, the effect of salt concentrations on the brush height is rather weak. Compared with the brush height at $Q_s/Q_e = 0$, the brush height is reduced by no more than 20% at $Q_s/Q_e = 3$ (equal numbers of trivalent salt coions and charged monomers). The rather weak screening effect of trivalent salt ions is due to the fact that trivalent salt coions are of the same charge sign as the monomer charges, resulting in most of the trivalent salt ions being expelled from the interior of the brush layer.

Under a strongly stretching electric field, the effect of

the added trivalent salt is shown in FIG. 1(b). Under the condition that no salt is added to the brush system, the star PE brushes are stretched to almost the same height for grafted star chains with different charge fractions. So the star PE brushes with the lowest charge fraction, *i.e.*, $f = 1/45$, are stretched to the highest degree due to the lowest degree of electrostatic screening of the external electric field by the lowest monomer and counterion charge densities. The brush height decreases considerably with the initial addition of trivalent salt, *i.e.*, $Q_s/Q_e = 0.5$, and levels off with the further addition of trivalent salt.

The response of the probability density distribution of the branching points (the central monomers of star chains from which the arms emanate) to the added trivalent salt is shown in FIG. 2. A sharp peak located at $z \in (30 - 40\sigma)$ emerges in the probability distribution of the branching points under a strongly stretching electric field at $Q_s/Q_e = 0$, indicating a fraction of grafted star chains are strongly stretched. The peak shifts to lower height as the charge fraction of grafted star chains decreases. However, with the initial addition of trivalent salt, *i.e.*, $Q_s/Q_e = 0.5$, the sharp peak corresponding to the fraction of strongly stretched star chains disappears. This explains the initial sharp decrease of the brush height when Q_s/Q_e is increased from 0 to 0.5 as shown in FIG. 1(b). Under a stretching electric field, some positive monovalent counterions released from both the star chains and the trivalent salt are attracted towards the negatively charged grafting electrode, and some trivalent salt coions are enriched in the immediate vicinity of the second positively charged electrode. As expected, charge overcompensation near the second electrode emerges due to the adsorption of the trivalent salt coions, and some monovalent counterions also accumulate near the second electrode to maintain overall charge neutrality at the second grafting electrode.

B. Collapse of star PE brushes with the added trivalent coions in an electric field

1. Center of mass heights of the brushes, persistent lengths and distributions of trivalent salt coions

The effect of added trivalent salt coions on the center of mass height of 4-arm star polyelectrolyte brushes under a collapsing electric field was examined in the simulations. As shown in FIG. 3, the brush height depends on the amount of added trivalent salt coions in a non-trivial manner. At relatively high charge fractions, the brush height decreases monotonically with increasing salt concentration. But the brush height becomes nearly insensitive to added salt coions at $f = 1/15$. More interestingly, at the lowest charge fraction of $f = 1/45$ (one charge per arm and a total of 4 charges per grafted chain), the brush height initially increases with increas-

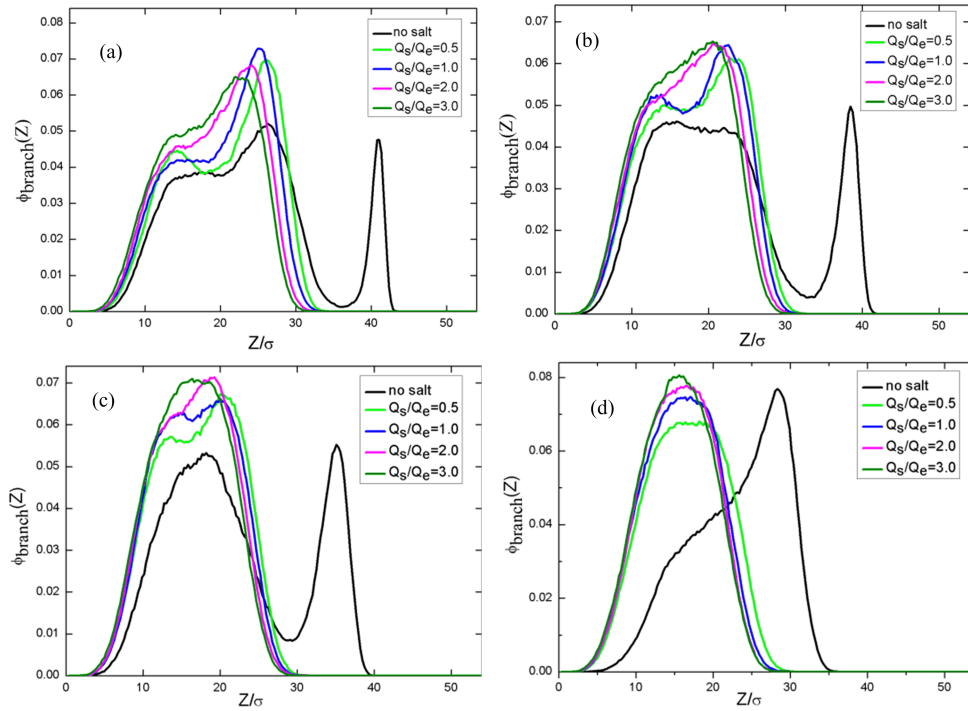


FIG. 2 Normalized probability distributions of the branching points of star PE brushes with different average charge fractions at different concentrations of trivalent salt ions under a stretching electric field of $E=-1.0$. The charge fractions are (a) $1/3$, (b) $1/7$, (c) $1/15$, and (d) $1/45$ respectively.

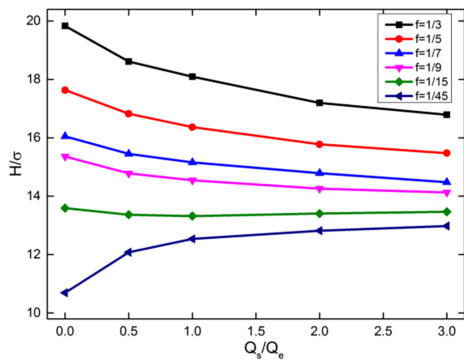


FIG. 3 Brush center of mass heights as a function of the ratio of the amount of charges of added salt ions to that of charged monomers at different charge fractions of 4-arm star brushes with $\sigma_g^*=0.008$ under a collapsing electric field.

ing salt concentration and eventually levels off at high salt concentration. The reason for the abnormal behavior of the brush height at $f=1/45$ is that with increasing salt concentration, the trivalent salt ions become more competitive for adsorbing onto the oppositely charged grafting electrode than the monomer charges on grafted star chains each of which carries only 4 elementary charges. Thus, some adsorbed monomer charges are replaced by trivalent salt ions, leading to the initial increase of the brush height with the addition of trivalent salt. As shown in FIG. 4, some trivalent salt

ions are expelled from the brush region and enriched in the region between the top surface of the brush layer and the second electrode for relatively high charge fractions of star brushes.

The effects of the charge fraction of the grafted 4-arm star chains and the salt concentration on the persistent lengths of the stems and free branches were investigated. The persistent length l_p of either the free branches or the stems was calculated using the following equation:

$$\langle \cos \theta_{ij} \rangle = e^{-|j-i|\sigma/l_p} \quad (1)$$

where θ_{ij} is the angle between the j th and i th monomers in one free branch or a stem and σ is the monomer bead diameter. As shown in FIG. 5, the persistent length of the stems is about twice to 4 times as large as the monomer size σ . The persistent length of the free branches is much larger than that of the stems (the grafted arms), indicating that the free branches are much more extended than the stems. It can also be seen from FIG. 5 that the persistent lengths of both the stems and the free branches increase with increasing charge fraction of the grafted star chains. The addition of trivalent salt leads to the decrease of the persistent lengths, especially for the persistent length of the free branches at relatively high charge fractions. FIG. 5 further shows that the electric field has a very weak effect on the persistent lengths of both the free branches and the stems.

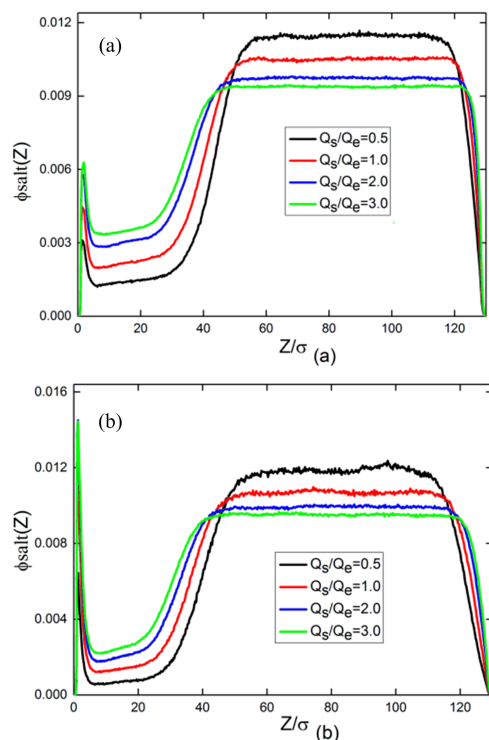


FIG. 4 Normalized probability distributions of trivalent salt coions at different salt concentrations in a collapsing electric field ($E=+1.0$). The charge fractions of star brushes are for (a) $1/3$ and (b) $1/5$, respectively.

2. Competition of monomer charges and trivalent salt coions for adsorption on oppositely charged grafting electrode

Under a strongly collapsing electric field, the charged monomers and trivalent salt ions with the same charge sign compete with each other for neutralizing the oppositely charged grafting electrode. Generally speaking, a single grafted 4-arm star chain with multiple charged monomers can be viewed as a macro-ion. Depending on the total number of charges on a single grafted chain, such a competition would give rise to interesting conformations of 4-arm star brushes under a collapsing electric field. It was found from simulations that charge overcompensation of the surface charges on the grafting electrode by the collapsed charged monomers and trivalent salt coions takes place if the charge fraction of grafted star chains is high enough. Of course, the collapsed charged species drag some counterions with the same charge sign as the surface charges towards the grafting electrode to maintain an overall charge neutrality near the grafting electrode. In order to quantify the competitive adsorption of charged monomers and trivalent salt coions and the degree of charge overcompensation, the adsorption layer near the grafting electrode was identified first. The normalized probability distributions of charged monomers were employed to demarcate the adsorption layer near the grafting electrode. As shown in FIG. S1 in the supplementary materials,

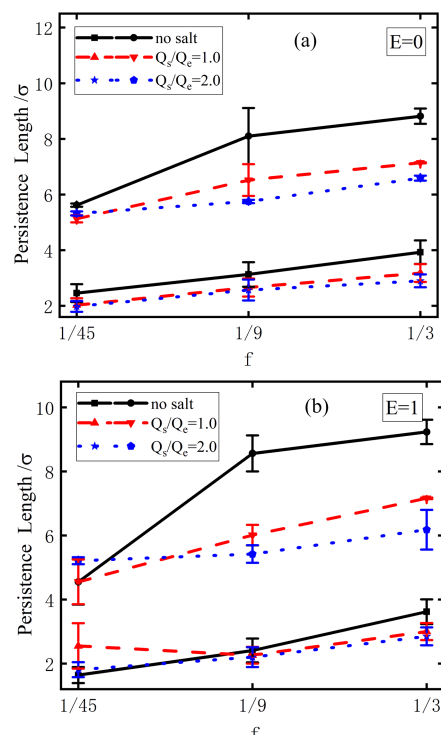


FIG. 5 The persistent lengths of the free branches (the upper three curves) and the stems (the lower three curves) as a function of the charge fraction of grafted star chains at different salt concentrations in the absence of external electric field (a), and under a collapsing electric field $E=+1.0$ (b).

a sharp peak emerges in the probability distribution of charged monomers right near the grafting electrode under a collapsing electric field, which is on top of the corresponding distribution at $E=0$. The region from $z=0$ to the z coordinate of the intersecting point of the above two normalized probability distributions near the grafting electrode was labeled as the adsorption layer. It was found that the thickness of the adsorption layer is about 8σ . The ratio of the total amount of monomer charges to that of trivalent salt coions in the adsorption layer was computed to quantify the competition of these two types of charged species for adsorption on the grafting electrode. This ratio R_q is defined as follows:

$$R_q = \frac{N_m (\beta_m^1 - \beta_m^0)}{N_s (\beta_s^1 - \beta_s^0)} \quad (2)$$

where N_m is the total number of charges on one grafting chain, $N_s=3$; and β_m^1, β_m^0 denote the probability weights of charged monomers in the adsorption layer at $E=1.0, 0$, respectively. Similarly, $\beta_s^1 - \beta_s^0$ denote the probability weights of the trivalent salt coions in the adsorption layer at $E=1.0, 0$, respectively. Furthermore, after plugging in dimensionless quantities, the degree of charge overcompensation Ξ can be calculated from the

following expression:

$$\Xi = \frac{eN_m(\beta_m^1 - \beta_m^0) + eN_s(\beta_s^1 - \beta_s^0)}{s\sigma_e} - 1$$

$$= \frac{4.8\pi\sigma_g^*(\lambda_B/\sigma)[N_m(\beta_m^1 - \beta_m^0) + N_s(\beta_s^1 - \beta_s^0)]}{|E|} - 1 \quad (3)$$

with s denoting the average surface area occupied by one grafted chain ($s=1/\sigma_g$), and σ_e being the surface charge density on the two oppositely charged electrodes ($\sigma_e=\varepsilon_0\varepsilon_r|\vec{E}|$ in SI unit, and ε_0 , ε_r in the expression denote the vacuum permittivity and the dielectric constant of water, respectively). If $\Xi>0$, charge overcompensation takes place near the grafting electrode.

The effect of salt concentration on the degree of competition of charged monomers and trivalent salt coions for adsorption on the oppositely charged grafting electrode is shown in FIG. 6. As shown in FIG. 6, the ratio of the total amount of monomer charges to that of trivalent salt coions in the adsorption layer decreases with decreasing charge fraction of the 4-arm star brushes. Moreover, the ratio R_q decreases considerably with increasing salt concentration and eventually levels off at high salt concentration. Thus, with increasing amount of added salt ions, trivalent salt coions become more competitive in neutralizing the oppositely charged grafting electrode. At $Q_s/Q_m=3$ which corresponds to equal numbers of charged monomers and trivalent salt coions in the brush system, the ratio R_q reaches a stable value smaller than 2 for the charge fraction $f\leq 1/7$. Therefore, for 4-arm star brushes with relatively low charge fraction, the trivalent salt ions become as competitive as the charged monomers in adsorbing onto the oppositely charged grafting electrode at high salt concentrations. It is interesting to see from FIG. 6 and its inset that for brushes with the lowest charged fraction of 1/45, the trivalent salt ions are more competitive in adsorbing onto the grafting electrode than the charged monomers, especially at high salt concentrations. Please note that a single grafted 4-arm star chain with a charged fraction of 1/45 carries a total of 4 elementary charges. Therefore, at $f=1/45$, with increasing amount of added trivalent salt coions, some initially adsorbed monomer charges onto the grafting electrode will be released by trivalent salt coions, leading to the initially increase in the brush height as shown in FIG. 3.

FIG. 7 displays the individual contributions of charged monomers and trivalent salt ions to charge compensation of the surface charges on the grafting electrode as a function of the salt concentration. The total amount of charges on adsorbed charged monomers decreases slightly with increasing salt concentration for brushes with high charge fractions. At the highest charge fraction of 1/3, the total amount of adsorbed charged monomers reaches saturation at high salt concentration, whereas more and more trivalent salt ions

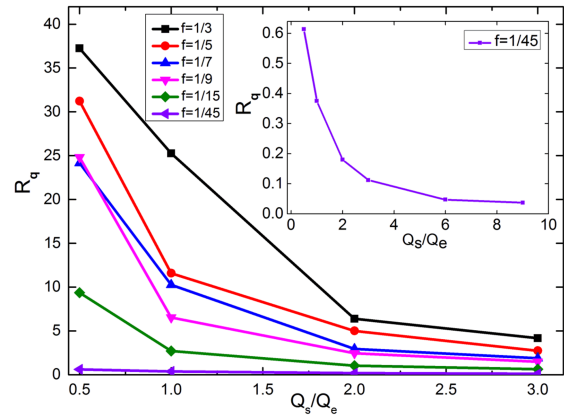


FIG. 6 Ratios of the total amount of charges on charged monomers to that of trivalent salt ions inside the boundary layer as functions of salt concentration at different charge fractions of 4-arm star brushes with $\sigma_g^*=0.008$ under a collapsing electric field ($E=+1.0$).

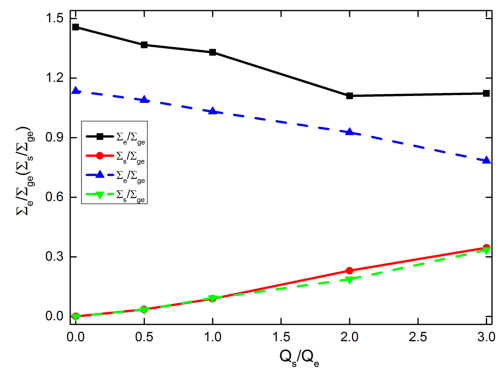


FIG. 7 The ratios of the total amount of charges of adsorbed monomers or trivalent salt ions to that of surface charges on the grafting electrode as a function of salt concentration for 4-arm brushes with different charge fractions at $\sigma_g^*=0.008$. The solid and broken lines correspond to $f=1/3$, $1/5$, respectively. In the figure, Σ_s , Σ_e , Σ_{ge} denote the total amounts of charges of adsorbed trivalent salt ions, charged monomers and the surface charges, respectively.

are adsorbed onto the oppositely charged grafting electrode with increasing salt concentration. It was found that for grafted 4-arm star chains with high charge fractions ($f=1/3$, $1/5$), charge overcompensation takes place near the grafting electrode. As shown in FIG. 8, the degree of charge overcompensation at $f=1/3$ is higher than that at $f=1/5$, and the added salt ions have a weak influence on the degree of charge overcompensation. It can be further seen from FIG. 7 that for brushes with the highest charge fraction ($f=1/3$), the charged monomers alone can overcompensate the opposite surface charges irrespective of the trivalent salt ions. Simulation results revealed that for grafted 4-arm star chains with lower charge fraction ($f<1/5$), regardless of the amount of added salt ions, the phenomenon of charge overcompensation does not emerge and only an

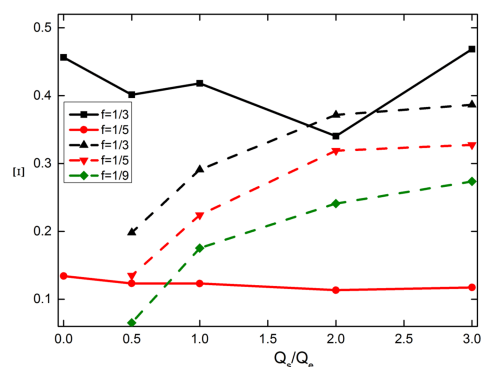


FIG. 8 Degrees of charge overcompensation as a function of salt concentration for brushes with charged monomers (solid lines) and completely neutral monomers (dotted lines). For the dotted lines, the amount of added salt charges is based on the total amount of charges carried by charged monomers at different charge fractions and in these brush systems with added salt ions, the monomers are all neutral.

exact charge neutralization of the grafting electrode by charged monomers and trivalent salt ions takes place. It is well known that multivalent ions charge overcompensate the oppositely charged substrate. As expected, the trivalent salt ions alone charge overcompensate the oppositely charged grafting electrode if the grafted 4-arm star chains are completely neutral (see FIG. 8). The disappearance of charge overcompensation for the case of grafted chains with low charge fractions in the presence of trivalent salt ions is presumably due to the electrostatic repulsion between trivalent salt ions and the somewhat fixed macro-ions which represent the charged monomers in the immediate vicinity of grafted electrode.

IV. CONCLUSION

In this work, we have performed Langevin dynamics simulations to study the competitive adsorption of grafted partially charged 4-arm stars and trivalent salt coions onto the oppositely charged grafting electrode. Simulation results revealed that the average charge fraction of the grafted star chains and the salt concentration play essential roles in the competitive adsorption of grafted 4-arm charged stars and trivalent salt coions onto the oppositely charged grafting electrode. It was found from simulations that the competitive adsorption ability of trivalent salt coions increases with decreasing charge fraction of grafted stars and increasing salt concentration. For the partially charged star brushes with relatively low charge fractions, the trivalent salt coions are nearly as competitive as the charged monomers in neutralizing the grafting electrode when there are equal numbers of added trivalent salt coions and charged monomers in the system. At a low charge fraction such that the total amount of charges on a

grafted star molecule is comparable to that of a trivalent salt ion, trivalent salt ions absorb more strongly onto the oppositely charged grafting electrode than the charged monomers and the addition of trivalent salt ions leads to the desorption of charged monomers and the initial increase of the brush height.

Simulation results showed that at high charge fraction of grafted star chains, the adsorbed charged monomers alone charge overcompensate the surface charges on the grafting electrode. However, it was found that at relatively low charge fraction of star chains, the addition of trivalent salt coions does not lead to charge overcompensation of the surface charges on the grafting electrode and only an exact charge neutralization of the charged grafting electrode by charged monomers and trivalent salt coions takes place. This is presumably due to the electrostatic repulsion between trivalent salt coions and the somewhat fixed macro-ions representing the charged monomers in the immediate vicinity of the grafted electrode.

This work sheds new light on the electrostatic interaction between polyelectrolyte brushes with like charged multi-valent salt ions. It also revealed the critical roles played by the average charge fraction of grafted chains in the competitive adsorption of charged monomers and trivalent salt coions onto the oppositely charged grafting electrode.

Supplementary materials: Methodological details and a schematic diagram displaying the demarcation of the adsorption layer near the grafting electrode are given.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.21774067). C. Tong acknowledges the support from K. C. Wong Magna Fund in Ningbo University.

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