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Energetic and conformational aspects of dendrimer overcharging by linear polyelectrolytes

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Extensive Brownian dynamics simulations of conformational changes accompanying the overcharging of a dendrimer by an oppositely charged long linear polyelectrolyte (LPE) have been carried out. The simulated results have been compared with the predictions of the Nguen and Shklovskii correlation theory [Physica A **293**, 324 (2001)] for impenetrable charged spherical macroion. Dendrimer overcharging is caused by the spatial correlations between the "excess" of the LPE charges adsorbed onto its surface. The simulated LPE-length dependence of the corresponding "correlation" energy is in agreement with the theoretical predictions. Maximum of the LPE adsorption occurs at some critical LPE length N_{ch}^{c}, and the first order phase transition from completely coiled conformation to the conformation with released tails takes place. The phase transition is accompanied by the drastic increase in the relative fluctuations of the polyelectrolyte size. Upon increasing the linear-chain length above N_{ch}^{c}, the one-long-tail conformation becomes energetically preferable; the exchange time between the long-tail conformation and the short-tail conformation is very large.

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I. INTRODUCTION

The physics of adsorption of linear polyelectrolytes (LPE) on oppositely charged surfaces is both remarkable and puzzling. The reason is that the total amount of adsorbed charge may exceed that of a bare surface, implying that the overall surface-polyelectrolyte complex is not neutral but has a net charge opposite to that of the bare surface. This overcharging effect can, in fact, be so strong as to reverse completely the bare surface charge, making possible the formation of complex structures of adsorbed layers of alternating charge. The sequential adsorption of very large number of layers of oppositely charged polyelectrolytes has been achieved in experiment; this phenomenon is of significant technological importance and found applications in, e.g., food technology, gene delivery, and antigraffiti coatings [1–5]. One of the most important applications of this phenomenon is gene delivery: it is known that usually the cell surface is charged negatively, and the complex of charged carriers (dendrimers for example) with an oppositely charged drug or DNA has to be charged positively in order to reach the cell.

The overcharging effect has been intensively studied theoretically [6–14], experimentally [15–17], and by computer simulation [13,14,18–23]. A fundamental understanding of charge reversal in the polyelectrolyte adsorption is still lacking, although the consensus view is that it must be due to the correlation effects typical in systems containing highly charged particles [6–8]. These are not adequately described by mean-field theories, and difficult to study even by the renormalization group treatments on account of the long-ranged and nonlinear character of ionic interactions [8]. It is not surprising, then, that the intensity of research in the field of polyelectrolyte theory and simulations does not seem to have reached its pinnacle yet, in fact, quite to the contrary.

The overcharging effect is strongly influenced by solvent quality [14], excluded volume interactions [13], radius of macroion [19], and flexibility of LPE [18]. The degree of the overcharging may be measured, for example, by the electrophoretic mobility [16] and light-scattering methods [17]. Yager *et al.* [15] have shown that the negatively charged DNA molecule forms a complex winding around a positively charged liposome and, after enzymatic cutting of the DNA, the resulting nucleosome has a net negative charge.

The correlation theory accounting the interrelations between small excesses of the opposite charge onto the macroion surface is usually used to describe the overcharging of an impenetrable macroion [6–8]. This correlation theory [6–8] predicts that the overcharging of a macroion becomes preferable due to the regular location (similar to Wigner crystal) of the "exceeds" of the opposite charges on the macroion surface. Both theory [7,8] and Monte Carlo simulations [8,20,23] maintain the following features of the overcharging of an impenetrable sphere (colloidal particle) by LPE with constant charge density. At any LPE length $N_{\mathrm{ch}} \geqslant N_n$, where N_n is the value that is necessary for the electric neutralization of the macroion, the overcharging effect of the impenetrable colloidal particle by an oppositely charged linear polyelectrolyte takes place. Upon increasing its length, LPE is completely adsorbed onto a sphere until its length reaches the critical value N_{ch}^{c}. At $N_{\mathrm{ch}}=N_{\mathrm{ch}}^{c}$ the first-order phase transition takes place, and the amount of the adsorbed LPE monomers decreases dramatically. At the same time the amount of the nonadsorbed LPE part increases, and the long LPE tails release. This phase transition corresponds to the change of the LPE coiled conformation to the "coiled with tails" conforma-

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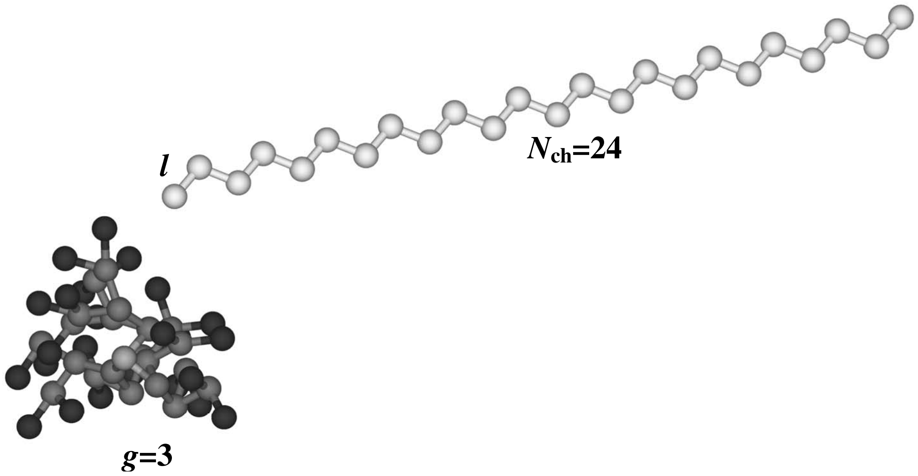

FIG. 1. The freely joint bead-rod model employed in this study. Shown is the initial (nonequilibrium) configuration of a $g=3$ charged dendrimer with a $N_{ch}=24$ oppositely charged LPE. All LPE beads are colored in white, the core of the dendrimer is colored in light gray, the terminal beads of the dendrimer are all black, and the remaining dendrimer beads are colored in gray.

tion. Upon further increasing the LPE length the length of these tails also increases, but the fraction of the adsorbed LPE part remains constant achieving the saturation.

To understand the overcharging phenomenon for penetrable objects which can be used as nanocontainers is a much more difficult task. Several publications related to the study of the complexes formed by such macroions and LPEs appeared recently [22–26]. In general, the main features of the impenetrable-macroion overcharging are also observed for the penetrable charged dendrimers [27]. At the same time, unlike a hard sphere, dendrimer is fairy flexible, does not possess a clearly defined surface, and allows penetration of the LPE inside. This, in turn, results in a fact that even the criterion of the LPE adsorption onto the penetrable macroion is not easy to define. The "local" criterion for calculation of the total amount N_{ads} of the adsorbed LPE monomers has been suggested earlier [27], and will be used in the present study as well. The LPE bead r_i with a characteristic bead diameter σ is considered to be adsorbed onto a dendrimer if there exists another dendrimer bead r_j such that $|r_i - r_j| < r_c$, where r_c is some parameter chosen to be equal to $r_c = 2.5\sigma$. As will be shown later in Secs. III and IV the amount N_{ads} of the adsorbed LPE monomers exceeds the quantity which is necessary for the dendrimer electroneutralization. The value of N_{ads} depends nonmonotonically on the LPE length N_{ch} (see Fig. 2, where N_{ads} is shown together with the total number of LPE monomers in tails N_{tails} and in loops N_{loops} see also further discussions in Sec. IV). The maximum in the amount of the adsorbed LPE is observed well above the point of electroneutrality: at $N_{ch}^c = 45 \pm 5$ for the complexes formed by a dendrimer of $g=3$ generations (with $N_n = 24$ charged terminal beads) and $N_{ch}^c = 80 \pm 10$ for the complexes formed by a dendrimer of $g=4$ generations (with $N_n = 48$ charged terminal beads). However, the locations of the maxima are eroded and shifted to higher values as compared to the theoretical predictions [7] for impenetrable spheres.

The influence of the overcharging phenomenon on structural properties of the complexed parts and the nature of the accompanying phase transition is not clear yet. It has been shown by the authors earlier [27] that due to the overcharging the LPE conformational properties are changed drastically. At the same time the structure of the "complexed" dendrimer remains almost unchanged as compared to the single, loose object. The correlation theory predicts the presence of one long LPE-tail for the complexes formed by sufficiently long linear polyelectrolytes [7]. At the same time Monte-Carlo simulations of Welch and Muthukumar [28] show the release of two LPE tails with a "random walk" of a dendrimer along LPE.

In the present paper we try to shed light on the nature of the phase transition, conformational and some dynamic changes accompanying the dendrimer overcharging by the LPE of different length using Brownian dynamics (BD) simulations. The remainder of the paper is organized as follows. In Sec. II the model and the simulation algorithm are described. In Sec. III the energetic aspects of the dendrimer overcharging by linear polyelectrolytes are discussed. The LPE configurations in the complexes with oppositely charged dendrimers are studied in Sec. IV. Section V deals with the relative motion of a dendrimer along sufficiently long LPE. Finally, some conclusions are summarized in Sec. VI.

II. MODEL AND SIMULATION ALGORITHM

A. Model of a complex

We consider a bead-rod freely joint model of a dendrimer [29–31] and of an oppositely charged LPE, Fig. 1. The dendrimer is represented by beads (centers of viscous friction) connected by the rigid bonds of length l. No valence- and torsion-angle potentials are taken into consideration. Dendrimers with a three-functional core and three-functional groups are simulated. The $g=0$ dendrimer consists of four beads including the core. Only dendrimers with rigid one-bond spacers have been simulated, i.e., every bead of a dendrimer is branched. The total number N of beads in a generation-g dendrimer is calculated as

$$N = 3(2^{g+1} - 1) + 1. \tag{1}$$

In the present simulations the case has been considered where all N_n terminal beads of a dendrimer are charged with the same charge $+e$. Such a situation is realized, for example, for PAMAM and other dendrimers in water solutions at neutral pH [32,33]. The oppositely charged LPE is represented as a system of N_{ch} beads connected by the rigid bonds of the same length l.

The interaction potentials of the present study are described below and have been approved in our previous publications [27,31,34,35]. All the nonbonded beads in a dendrimer-LPE complex interact via the modified Lennard-Jones potential in which the attractive term is omitted

$$\widetilde{U}_{\text{LJ}}(r_{ij}) = 4\varepsilon_{\text{LJ}}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{\text{cut}}}\right)^{12}\right], \quad r < r_{\text{cut}},$$

$$\widetilde{U}_{\text{LJ}}(r_{ij}) = 0, \quad r \geqslant r_{\text{cut}}, \tag{2}$$

where r_{ij} is the distance between ith and jth beads, ε_{LJ} and σ are the characteristic energy and length parameters, and r_{cut} is the cutoff distance, $r_{\text{cut}}=2.5\sigma$. This potential corresponds to the case of the athermal solvent. The values $\sigma=0.8l$ and $\varepsilon_{\text{LJ}}=0.3k_bT$ have been taken from our previous studies [31,34].

Each bead of the LPE is charged with the charge $-e$, and the total charge of LPE is equal to $-eN_{\text{ch}}$. The jth charged bead interacts with all other charged beads via the Debye-Hückel potential (electrostatic screened Coulomb potential)

$$\frac{U_j^C}{k_bT} = \lambda_B \sum_i \frac{\exp(-kr_{ij})}{r_{ij}}, \tag{3}$$

where r_{ij} is the distance between the charged beads i and j, λ_B is the Bjerrum length describing the strength of the Coulomb interactions in a medium with dielectric constant $\tilde{\varepsilon}$

$$\lambda_B = \frac{e^2}{4\pi\tilde{\varepsilon}k_bT}. \tag{4}$$

The value of λ_B in water at room temperature is 7.14 Å and is close to the segment length for a usual flexible polymer. Therefore, we put $\lambda_B=l$ without much practical loss of generality. The inverse Debye length k in Eq. (3) describes the screening of the electrostatic interactions due to the presence of counterions and salt in the realistic solution

$$k^2 = 4\pi\lambda_B \sum_i z_i^2 c_i. \tag{5}$$

Here c_i is the concentration of the ith ion and z_i is its valence.

The modern state of the art in description of the electrostatic interactions in the polyelectrolyte complexes, including charged dendrimers [36], corresponds to the explicit account of counterions in solutions. Explicit counterions affect significantly the structural and dynamical properties of a polyelectrolyte. However, in a solution with a low salt concentration screened Debye-Hückel approximation does not necessarily lead to the wrong evaluation of the electrostatic energy, especially when the Debye screening length $r_D=1/k$ exceeds the size of the macroion. Such a value of r_D takes, in fact, all actual electrostatic interactions. In the present study the sufficiently large value of $r_D=8.96\ l$ has been chosen which corresponds to 2.2 mM aqueous salt concentration at 25 °C [37]. This value of r_D was also used by the authors previously for the simulations of single charged dendrimers [31,34], their complexes with long LPE [27] and complexes of LPE with hyperbranched polymers [38,39]. Additionally, in polyelectrolyte complexes formed by a charged macroion and an oppositely charged LPE, counterions should be replaced by the LPE charges due to the entropic reasons [40]. This fact was confirmed recently by the molecular-dynamics simulations of complexes formed by the charged dendrimer and short linear chains, with explicit counterions and explicit solvent [41]. Such a replacement of the counterions by the linear-polyelectrolyte charged monomers would be even more probable for much longer chains considered in the present study. Thus, counterions condensation should be very small for the simulated systems and counterions have not been taken into account explicitly. As a first approximation we consider here nonelectroneutral systems, when the total LPE charge is larger than the dendrimer charge.

In the simulated systems the overcharging always exists, i.e., some uncompensated charge always presents inside the complex. This "extra" charge may lead to the presence of some LPE chain counterions inside the complex and, consequently, to the slightly larger screening of the electrostatic interactions inside. This effect would be similar to the increase of a salt concentration in the solution. However, as was shown by many authors [7,9,19,42] the additional presence of salt may only increase the degree of overcharging and the discussed overcharging effects should be more pronounced. Contrast to the case of the long LPE chains, neglecting the explicit counterions for the complexes formed by charged dendrimers and oppositely charged short LPE chains becomes impossible because of the significant counterion condensation. Such complexes in explicit solvent with explicit counterions are simulated in our recent publication [41]. Therefore, in the present study we use appropriate coarse-grained models with Debye-Hückel approximation. This helps to decrease significantly the CPU time of the production runs and forestall more expensive detailed models. The simulations have been performed for complexes with $g=3$ ($N=46$, $N_n=24$) and $g=4$ ($N=94$, $N_n=48$) dendrimers in which the total LPE charge is equal to or exceeds that of an individual dendrimer, i.e., for $60 \geqslant N_{\text{ch}} \geqslant 24$ (in complexes with $g=3$ dendrimers) and for $90 \geqslant N_{\text{ch}} \geqslant 48$ (in complexes with $g=4$ dendrimers).

B. Simulation algorithm

In the present study the hydrodynamically impenetrable model has been chosen for the simulated complexes, and hydrodynamic interactions (HI) between different beads have been taken into account explicitly. All beads are characterized by the friction coefficient ζ. The finite-difference numerical scheme implemented here is based on the Ermak-McCammon equation [29–31] and was also used in simulations of a single charged dendrimer in the preceding

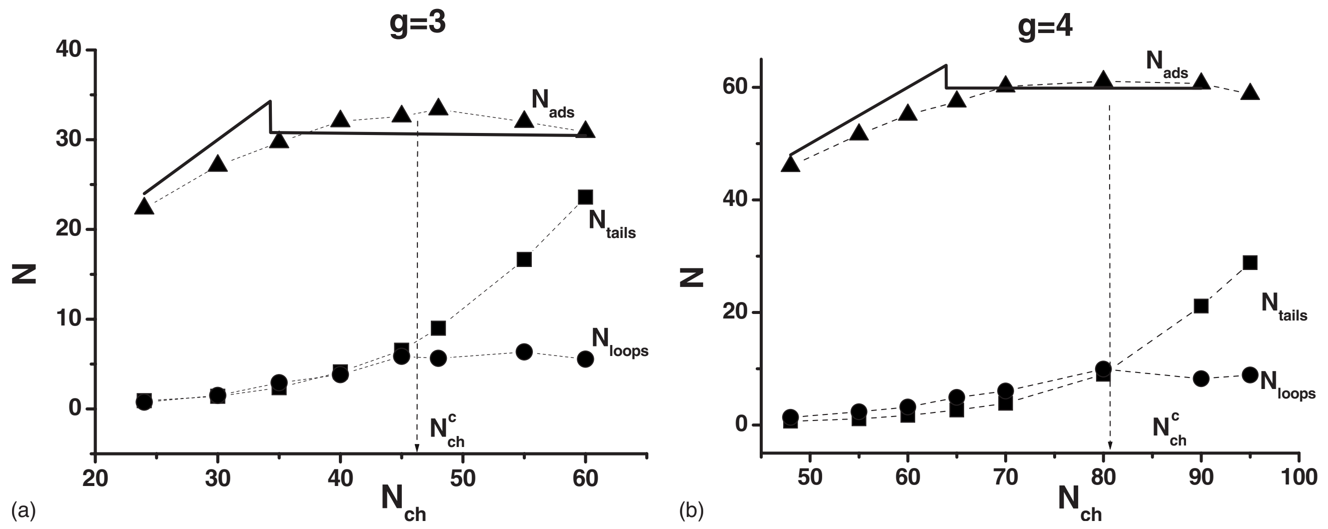

FIG. 2. The average values of $N_{\rm ads}$, $N_{\rm loops}$, and $N_{\rm tails}$ for complexes formed by (a) $g=3$ and (b) $g=4$ dendrimers, as functions of the LPE length. Solid lines in both panels correspond to the predictions of the correlation theory [7] for a rigid impenetrable sphere with the same charge as for the simulated dendrimer and radius $R_D=\sqrt{\frac{5}{3}R_g^2}$, where R_g^2 is the dendrimer average squared gyration radius. Dotted lines are done as guides to the eye.

publication [31]. HI are taken into account with the help of the Rotne-Prager-Yamakawa tensor; all other details can be found elsewhere [27,31,34,35]. The total force $\vec{F}_j^0$ acting on a bead j in the system is given by

$$\vec{F}_j^0 = -\sum_{k=1}^{N} \mu_k \left(\frac{\partial \nu_k}{\partial \vec{r}_j}\right)_{r^0} - \partial \tilde{U}_{\rm LJ}/\partial \vec{r}_j^{\,0} - \partial U_j^C/\partial \vec{r}_j^{\,0}, \tag{6}$$

where $\nu_k=\frac{1}{2}(\vec{r}_{k+1}-\vec{r}_k)^2-l^2=0$ is the equation for the kth rigid constraint, μ_k is the corresponding Lagrange multiplier, and $\vec{r}_j^{\,0}$ is the position vector for the jth bead before a time step Δt. The SHAKE algorithm [43] with the relative tolerance of 2×10^{-6} is used to maintain a fixed bond length. In the present simulations dimensionless quantities are used in which the bond length l, the thermal energy k_bT, and the translational friction coefficient $\zeta=6\pi\eta_0 a$ (a is the hydrodynamic radius of a bead) were used as units. It follows that time is expressed in units $\frac{\zeta l^2}{k_bT}$, the diffusion coefficient in units $\frac{k_bT}{6\pi\eta_0 a}$, and the force in units $\frac{k_bT}{l}$. The dimensionless integration step was chosen as $\Delta t=10^{-4}$ in order to have the maximum displacement of a bead less than 10% of the bond length.

The initial configuration of a dendrimer is built [29–31] using a procedure similar to that proposed by Murat and Grest [44]. The core bead is put into the center of the coordinate system. Onto the core bead, along the X, Y, and Z axes, three monomers are attached, which constitute the generation $g=0$ dendrimer. The next generation is built adding two monomers to each of the free ends of the $g=0$ dendrimer. The distance between a newly added bead and all the previous beads is constrained to be larger than some distance $r_{\rm min}=0.8\sigma$. Obviously, as g increases, it becomes increasingly difficult to fulfill the constraint of no overlap of beads. If a bead cannot be inserted after a set of 1000 trials, the whole dendrimer is discarded, and the process is started again with a new random-number seed.

To create the initial configuration of LPE the maximum values of coordinates of all dendrimer beads $x_{\rm max}$, $y_{\rm max}$, $z_{\rm max}$, have been calculated. The first bead of LPE has the coordinates $x_{\rm max}+1$, $y_{\rm max}$, $z_{\rm max}$. Then LPE has been initially created in a planar extended configuration with fixed valence angles $\Theta=90°$, Fig. 1. The initial configuration of each complex has been equilibrated for 6–11 runs of 2×10^6 steps each, then seven production runs of 2×10^6 time steps each are performed. During each run the instantaneous values R_g^2 of the squared radius of gyration are calculated and averaged, both for a complex as a whole, an individual LPE, and a dendrimer in a complex

$$\langle R_g^2\rangle = \frac{1}{N+1}\sum_{n=0}^{N}\langle(\vec{r}_n-\vec{r}_C)^2\rangle, \tag{7}$$

where $\vec{r}_C$ is the radius-vector of the corresponding center of mass (for a complex as a whole, LPE, or a dendrimer), $\vec{r}_n$ is the radius vector of nth bead, and brackets denote the averaging over time.

During the equilibration the mean-squared radius of gyration of a dendrimer remains almost unchanged, and the length of the whole equilibration procedure is completely determined by the relaxation of the LPE radius of gyration. It takes about 5×10^5 BD steps to equilibrate the complex of a $g=4$ dendrimer and $N_{\rm ch}=48$ LPE chain.

III. ELECTROSTATIC INTERACTIONS BETWEEN DENDRIMER AND LPE

As was shown in our previous study [27] the overcharging of a charged dendrimer by a long LPE takes place [see dependence $N_{\rm ads}(N_{\rm ch})$ in Fig. 2] in a qualitative agreement with a correlation theory for a hard sphere [7]. In the Nguen and

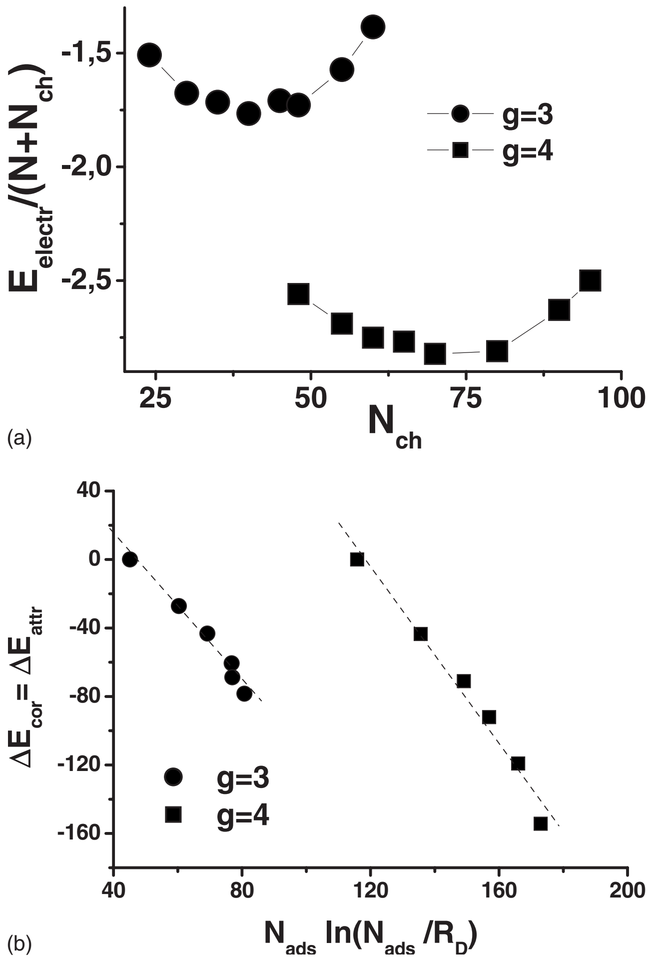

FIG. 3. (a) The LPE-length dependence of the electrostatic energy E_{electr} normalized to the total number $N+N_{\text{ch}}$ of beads for complexes formed by $g=3$ and $g=4$ dendrimers. (b) The simulated dependence of the correlation energy $\Delta E_{\text{cor}}=E_{\text{cor}}-E_{\text{cor}}^{\text{neutr}}=\Delta E_{\text{attr}}$ on the total amount of adsorbed monomers. Dotted lines are linear fits following the predictions of the correlation theory [7].

Shklovskii [7] correlation theory the charge inversion effect has an energetic origin and is connected to the interactions between excesses of charges adsorbed onto a surface of the impenetrable macroion. Such energetic correlations for the simulated penetrable dendrimers have been studied first. In the present BD simulations the driving force for a complex formation is the Coulomb attractions between the oppositely-charged dendrimer and LPE beads. The average total electrostatic energy E_{electr}

$$E_{\text{electr}} = -\lambda_B \sum_{i,j} \frac{e^{-r_{ij}/r_d}}{r_{ij}} \tag{8}$$

for all simulated complexes has been calculated, Fig. 3. Clearly the chain-length dependence of the electrostatic energy E_{electr} is nonmonotonic, and has a minimum at some LPE length above the value N_n for the corresponding dendrimers. Nguen and Shklovskii [7] have calculated the dependence of the correlation energy E_{cor} on the amount of the adsorbed charge as

$$E_{\text{cor}} \sim L_1 \ln(L_1/R), \tag{9}$$

where L_1 is the length of the adsorbed part of LPE (in the present study $L_1=N_{\text{ads}}$) and R is the radius of the macroion. As shown by us previously [31], both neutral and charged dendrimers have almost spherical shape with radius R_D which can be easily estimated as $R_D=\sqrt{\frac{5}{3}R_g^2}$, where R_g^2 is the mean-squared radius of gyration of a dendrimer. To check the theoretical prediction, Eq. (9), the difference $\Delta E_{\text{cor}} = E_{\text{cor}}-E_{\text{cor}}^{\text{neutr}} = E_{\text{attr}}(N_{\text{ch}})-E_{\text{attr}}(N_n) \equiv \Delta E_{\text{attr}}$ of the attractive electrostatic energy between an "overcharged" complex and an electroneutral complex (i.e., the complex with the shortest simulated LPE of the length N_n) has been calculated. Attractive electrostatic energy E_{attr} was calculated as

$$E_{\text{attr}} = -\lambda_B \sum_{\substack{i=1,N_n \\ j=1,N_{\text{ch}}}} \frac{e^{-r_{ij}/r_d}}{r_{ij}}.$$

The simulation results for complexes with LPE in the length interval $N_{\text{ch}}^c \geqslant N_{\text{ch}} \geqslant N_n$ (i.e., below the point of maximum adsorption) are plotted in Fig. 3(b) as functions of $N_{\text{ads}} \ln(N_{\text{ads}}/R_D)$; after the tail release the part responsible for the interaction with the tail in total attractive energy will be present, this part cannot be separated from the total attractive energy because the tail is not stable. The linear dependence is clearly observed, with the same slope for all simulated complexes.

As will be shown later the minimum in the chain-length dependence of the electrostatic energy E_{electr}, Fig. 3(a), corresponds to the maximum of the LPE adsorption. It means that the nonmonotonic LPE-length dependence of the amount of the adsorbed monomers does have an energetic origin. Thus, we conclude here that the overcharging of a dendrimer by a linear polyelectrolyte has an energetic nature and takes place due to the correlations between small "excesses" of LPE charge on a dendrimer surface, in agreement with the theoretical predictions for impenetrable sphere [7]. The corresponding contribution to the free energy F_{cor} due to the presence of the correlation effects is

$$F_{\text{cor}} \sim N_{\text{ads}} \ln\left(N_{\text{ads}}/\sqrt{\frac{5}{3}R_g^2}\right). \tag{10}$$

IV. LPE CONFORMATION IN A COMPLEX: PHASE TRANSITION FROM COILED TO THE TAIL-RELEASED CONFORMATION

In Ref. [38]. the influence of the topological structure of branched macroion on the peculiarities of the overcharging has been investigated. We demonstrated that in the complexes formed by the hyperbranched polymer with preferable branching close to the core (i.e., the macroion with a compact core) the dependence of $N_{\text{ads}}(N_{\text{ch}})$ has clear nonmonotonic behavior. A possible first-order phase transition is not accompanied by the change of the shape anisotropy due to this compact structure. Contrast to this case in complexes formed by the hyperbranched polymers with preferable branching close to the periphery (i.e., the macroion with a less compact interior), maximum of the chain adsorption and tail release is accompanied by the monotonic behavior of $N_{\mathrm{ads}}(N_{\mathrm{ch}})$, exhibiting clear saturation behavior due to the change of the shape anisotropy. In Ref. [38]. such a behavior was explained by rather easy change of the macroion shape due to the less compact interior. Having these results in mind we suggest that the monotonic behavior of $N_{\mathrm{ads}}(N_{\mathrm{ch}})$ should be accompanied by the change of the shape anisotropy, which is not the case for a perfect dendrimer.

As shown by the authors earlier [27] the conformation of a charged dendrimer in complexes with an oppositely charged LPE is similar to that for a single neutral dendrimer. In order to understand better the conformations of the same complexes after overcharging the average amount N_{tails} of LPE beads in tails, loops (N_{loops}, loop is a part of LPE between neighboring adsorbed sites) and trains (N_{ads}, i.e., the total amount of the adsorbed charges) has been calculated, Fig. 2. The amount N_{ads} of the adsorbed charges has been calculated using "local" criterion of adsorption [27]. It is clearly seen that at some value $N_{\mathrm{ch}}=N_{\mathrm{ch}}^{c}$ the maximum of the overcharging effect (i.e., the maximum in the amount N_{ads} of the adsorbed charges) is observed.

For all simulated complexes the total amount $N_{\mathrm{tails}}=N_1+N_2$ of LPE beads in both tails and the number N_{loops} of beads in all loops increase initially with the increase of the LPE length due to the repulsive electrostatic interactions. The dependences $N_{\mathrm{loops}}(N_{\mathrm{ch}})$ and $N_{\mathrm{tails}}(N_{\mathrm{ch}})$ are very similar to each other until $N_{\mathrm{ch}}=N_{\mathrm{ch}}^{c}$, Fig. 2, because only the very small fraction of LPE beads is present in both loops and tails; almost all LPE beads are adsorbed onto a dendrimer. For longer LPE with $N_{\mathrm{ch}}\geqslant N_{\mathrm{ch}}^{c}$ these two dependences are very different: contrast to tails the fraction of the LPE beads in loops does not change anymore and saturates.

The fraction of the LPE beads in tails increases further with increase of the LPE length beyond $N_{\mathrm{ch}}=N_{\mathrm{ch}}^{c}$. Most probably the entropic effects are responsible for that. Namely, for a sufficiently long linear polyelectrolyte unadsorbed LPE charges need to have as many different conformations as possible. A fraction of LPE beads in each tail has only one "frozen" end, such a conformation is much more preferable as compared to the loop with its both ends almost completely "frozen" due to the strong adsorption. Additionally, the presence of several short loops instead of one very long loop should be more preferable. In Fig. 4 the average number of loops and the average length of each loop have been shown. In all simulated complexes the average number of loops increases with the increase of LPE length up to $N_{\mathrm{ch}}=N_{\mathrm{ch}}^{c}$. Upon further increase of the LPE length this number starts to fluctuate around some average value. Furthermore, the average length of each loop is 2–3 beads, and is the same for both $g=3$ and $g=4$ dendrimers. The presence of these very short loops could be directly related to the presence of the excesses of the absorbed charges which, following the correlation theory [7], create some regular structure and give additional "correlation" contribution F_{cor} to the free energy.

To investigate the nature of the phase transition from coiled to tail-released LPE conformation, the tail-length distribution function $f_{\mathrm{tails}}(N_{\mathrm{tails}})$ has been calculated. Each value of this distribution function corresponds to the fraction of LPE in all tails of the total length N_{tails}, Fig. 5. For rather short LPE ($N_{\mathrm{ch}}\leqslant 35$ and $N_{\mathrm{ch}}\leqslant 60$ for complexes formed by $g=3$ and $g=4$ dendrimers, correspondingly) tails are not preferable energetically, and the distribution function f_{tails} has obviously a single maximum at $N_{\mathrm{tails}}=0$. With further increase of LPE length the second maximum appears which corresponds to the existence of LPE conformations with tails. At $N_{\mathrm{ch}}=N_{\mathrm{ch}}^{c}$ both maxima have approximately the same value, and both LPE conformations—with and without tails—have the same probability. At $N_{\mathrm{ch}}>N_{\mathrm{ch}}^{c}$ the first maximum disappears and the conformation of LPE without tails becomes impossible. Such behavior of the distribution function is very typical for the first-order phase transition, which has been predicted theoretically for the complexes formed by the impenetrable macroions [7]. In Ref. [7] this phase transition was characterized by the clear change of the conformation of LPE, from the completely coiled conformation to the conformation with a long tail (or tails) and a coiled adsorbed part. Similar features have been observed in the present simulations for the complexes formed by the penetrable dendrimers.

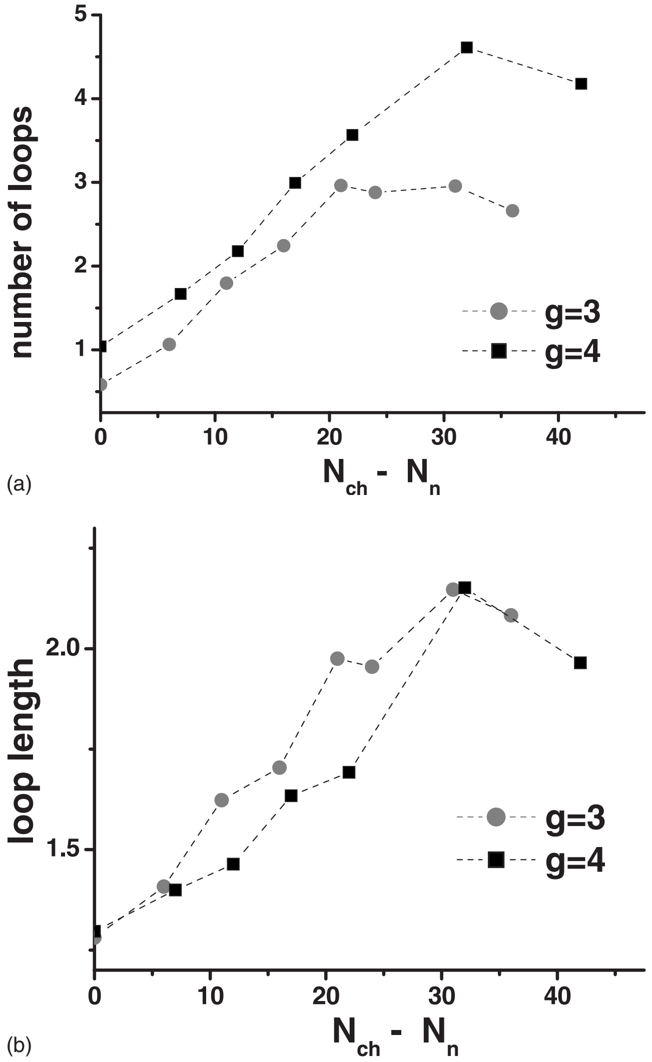

FIG. 4. (a) The average number of loops and (b) the average length of loops in complexes formed by $g=3$ and $g=4$ dendrimers. Dotted lines are done as guides to the eye.

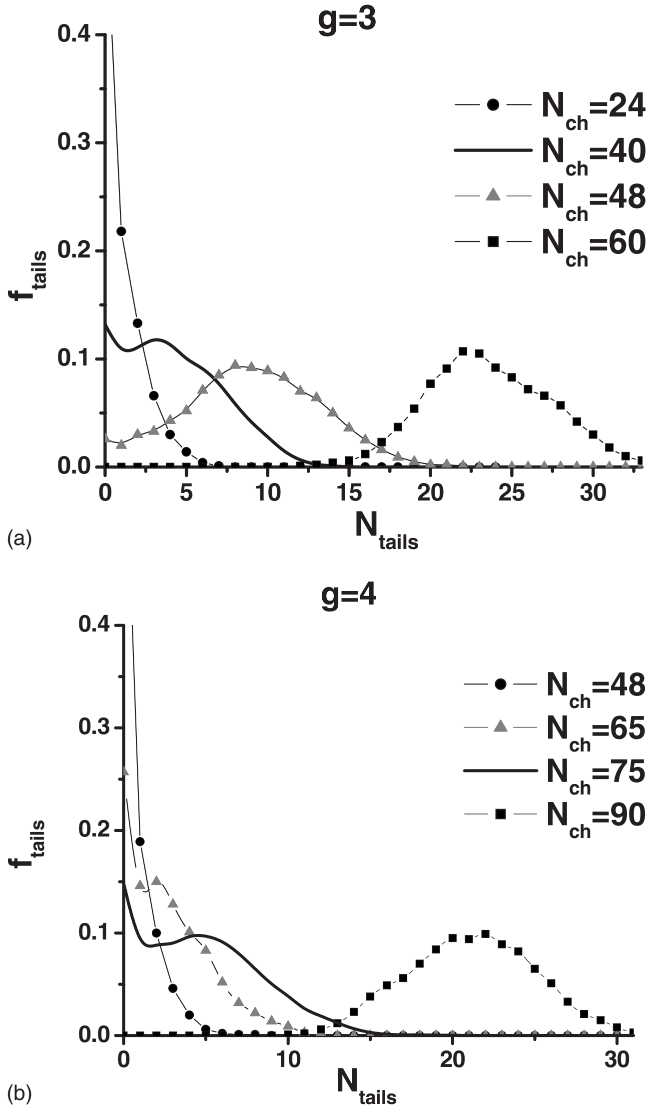

FIG. 5. The tail-length distribution function for complexes formed by (a) $g=3$ and (b) $g=4$ dendrimers. The LPE conformation with a long tail is preferable for longer LPE.

The first-order phase transition is also characterized by the increase of the size fluctuations. The relative fluctuations $\Delta\langle R_g^2\rangle_{\rm chain}$ of the mean-squared radius of gyration R_g^2 for LPE

$$\Delta\langle R_g^2\rangle_{\rm chain}=\frac{\langle R_g^4\rangle_{\rm chain}-\langle R_g^2\rangle_{\rm chain}^{\;2}}{\langle R_g^2\rangle_{\rm chain}^{\;2}} \qquad (11)$$

have been calculated, Fig. 6. In Eq. (11) averaging is made over all simulated trajectories for each complex. The increase of these fluctuations upon approaching the critical length $N_{\rm ch}^c$ (i.e., when maximum of adsorption takes place) is clearly recognized in Fig. 6.

V. MOTIONS OF A DENDRIMER RELATIVE TO LPE

Welch and Muthukumar [28] were the first who simulated the coarse-grained model of a dendrimer-LPE complex by Monte Carlo simulation. They obtained snapshots of the complex which suggest possible "random" walk of a dendrimer along the long LPE. The similar snapshots have been produced in the present study, and three possible conformations of a complex—with one long LPE tail on either side of a dendrimer, or with two LPE tails of approximately the same length—are identified. Can the motion of a dendrimer along LPE be considered as a random walk or not? To answer this question the dynamics of the complexation is analyzed below more quantitatively.

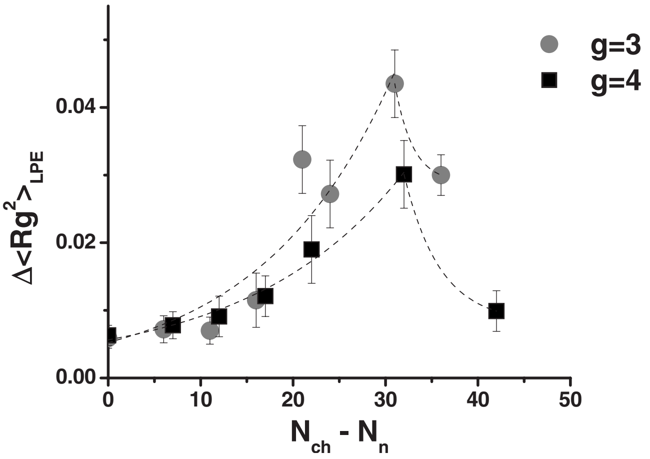

FIG. 6. The relative fluctuations of the LPE size $\Delta\langle R_g^2\rangle_{\rm chain}$ for complexes formed by $g=3$ and $g=4$ dendrimers. Dashed lines are drawn as guides to the eye.

A. Relaxation of the unit vector between LPE center of mass and dendrimer center of mass

In order to understand better the mutual motion of the complex components the autocorrelation function $C_{\rm DC}(t)$ for the unit vector $\vec{e}_{\rm DC}$ connecting the centers-of-mass of the dendrimer and LPE chain has been calculated,

$$C_{\rm DC}(t)=\langle\vec{e}_{\rm DC}(0)\vec{e}_{\rm DC}(t)\rangle. \qquad (12)$$

The time $\tau_{\rm DC}$ at which $C_{\rm DC}(t)$ decays in e times has been taken as a measure for the $\vec{e}_{\rm DC}$ relaxation and is shown in Fig. 7 as a function of $N_{\rm ch}-N_n$. A two-stage relaxation dynamics is clearly observed. For all simulated complexes the value of the relaxation time $\tau_{\rm DC}$ remains constant till $N_{\rm ch}=N_{\rm ch}^c$, Fig. 7. However, for tail-released conformations at $N_{\rm ch}>N_{\rm ch}^c$ the relaxation times increase significantly with the increase of the LPE length.

Rather fast initial relaxation of $C_{\rm DC}(t)$ at $N_{\rm ch}\leqslant N_{\rm ch}^c$ may be explained by the very fast small displacements of the LPE center-of-mass relative to the center-of-mass of the dendrimer. Initially, adsorbed LPE part adopts coiled conformation, similar to the shell of a nut [35], and both centers-of-mass for LPE and a dendrimer are very close to each other. Then even very small (and fast) fluctuations of the dendrimer, or the LPE shape or size, may lead to the significant relative displacements of their centers-of-mass.

After the tail release the dendrimer can move along the released LPE tail. Thus, the relatively slow fluctuations of $C_{\rm DC}(t)$ at $N_{\rm ch}>N_{\rm ch}^c$ after the long tail release may be ex-

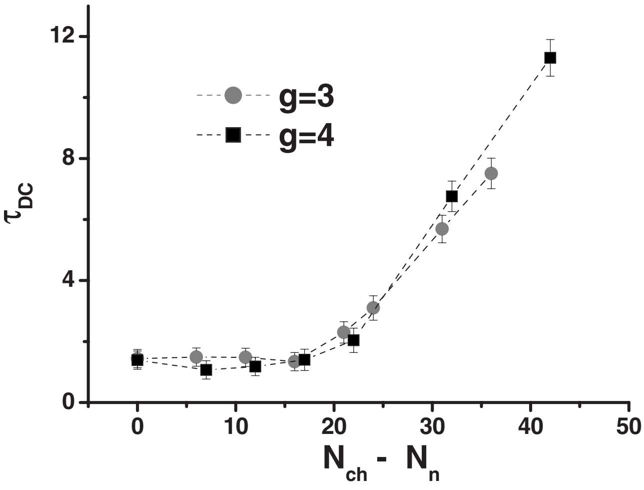

FIG. 7. The relaxation time τ_{DC} for complexes formed by $g=3$ and $g=4$ dendrimers. Dotted lines are drawn as guides to the eye.

plained by the increase of the distance between the corresponding centers-of-mass. In this case changes in the dendrimer or LPE shape and size does not necessarily lead to the significant rotation of the unit vector connecting their centers-of-mass. It means that after the tail release the fluctuations of $C_{DC}(t)$ can be slowed down drastically.

B. Tails exchange and "random" walk of a dendrimer

In Fig. 8 the time dependence of the instantaneous length of two tails for complexes formed by a $g=3$ dendrimer with LPE of different length has been shown. Following the correlation theory [7], the LPE conformation with one long tail or with two shorter tails are equally probable for chain length just above the critical, $N_{ch} \geqslant N_{ch}^c$. Upon further increase of the LPE length the conformation with one long tail energetically becomes more preferable. These theoretical results are confirmed also for the present complexes. For short LPE chains ($N_{ch}=55$, just above the critical length) two tails with almost equal length exist during the whole simulation run, and the tail length fluctuates strongly, Fig. 8(a). The stable conformation with one long tail and one very short tail is clearly seen already for $N_{ch}=60$, Fig. 8(b), with very rare exchanges between tails. During the typical BD production run, 1.4×10^7 time steps, only one exchange between long and short tail has been observed. Additional very long simulation for one complex of $g=3$ dendrimer and $N_{ch}=60$ LPE has been carried out. It can be seen, Fig. 8(b), that during 5×10^7 simulation steps the LPE conformation with one long tail is mainly realized. The tails of equal length can coexist for very short time, the exchange between short and long tails occurs only twice. The tails exchange time (which we estimate as about 2.5×10^7 time steps or 2500 dimensionless time units) is several orders of magnitude larger than the characteristic time (8–12 dimensionless time units) for other relaxation processes (rotational diffusion, fluctuations of shape and size of a complex, and orientational mobility of a single dendrimer [34]). Observed dynamic picture—with one stable, long-living tale, very rare tails exchange, and very short periods of the coexistence of two equal tails—suggests that the dendrimer motion along the nonadsorbed LPE tail is not a random walk, in a latter case all possible tail lengths would be equally probable.

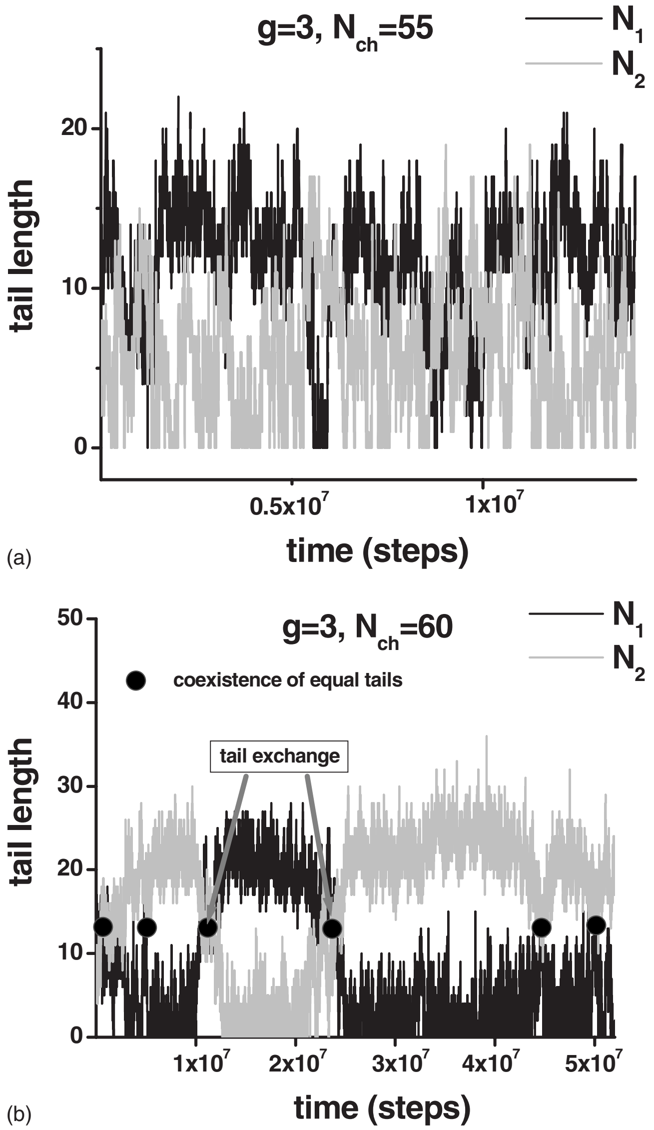

FIG. 8. The time evolution of the LPE tails in complexes formed by a $g=3$ dendrimer and LPE with (a) $N_{ch}=55$ and (b) $N_{ch}=60$. In a latter case much longer simulations have been carried out. N_1 is the first tail length and N_2 is the second tail length.

VI. CONCLUSIONS

The overcharging phenomenon in complexes formed by the dendrimers of different generations with the oppositely charged LPEs has an energetic nature, in agreement with the predictions of the correlation theory for an impenetrable charged sphere [7]. The correlation free energy of the adsorbed LPE is related to the electrostatic attraction between charged LPE and dendrimer monomers. The overcharging and the existence of the excess adsorbed charge are correlated with the presence of very short LPE loops onto the dendrimer surface. The simulation results show no qualitative difference between $g=3$ and $g=4$ dendrimers [see Figs. 4(a), 6, and 7]. The first-order phase transition which accompanies the overcharging phenomenon leads to the nonmonotonic behavior of the amount of adsorption with the increase of LPE length, and to the drastic change in the complexed LPE conformation. Upon increasing the LPE length the conformation of a complex with released tails becomes thermodynamically stable. The nonmonotonic behavior of the amount of adsorption and the corresponding phase transition are accompanied by the pronounced nonmonotonic behavior of the relative fluctuations of LPE size; these fluctuations reach their maximum at the point of maximum adsorption. In complexes with long linear polyelectrolytes the motion of a dendrimer along LPE is a very slow "non-random-walk" process, with very rare exchanges between long and short tails. In spite of the fact that some interesting effects are observed in the present study, nevertheless, it would be rather important to clarify the influence of the salt concentration, Bjerrum length, and pH on the peculiarities of the dendrimer overcharging in the future.

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