Macromolecules

Conformational Behavior of a Single Polyelectrolyte Chain with Bulky Counterions

A. A. Gavrilov,* A. V. Chertovich, and E. Yu. Kramarenko

Physics Department, Lomonosov Moscow State University, Moscow 119991, Russia

S Supporting Information

ABSTRACT: We report a dissipative dynamic simulation study of a polyelectrolyte chain conformational behavior with small and bulky counterions. The size of the small counterions was equal to the size of a monomer unit, while the bulky counterions were modeled as big spherical particles with twice the radius of a monomer unit. Two cases of the charge location within the bulky counterions were studied: (i) in the center (symmetrical case) or (ii) on the counterion surface (asymmetrical case). The strength of electrostatic interactions, λ , as well as the fraction of charged beads on the polymer



chain, f, was varied. At high charge fractions the chains with both small counterions and symmetrical bulky counterions collapsed at large λ . In contrast, the chain with asymmetrical bulky counterions did not collapse at all; instead, it adopted swollen conformations with counterions strongly attached to the chain backbone. At low charge fractions and high λ the multiplet structures observed in the systems with small and symmetrical bulky counterions were completely different: bulky counterions favored formation of significantly larger multiplets (mainly ionic rings). On the contrary, almost no multiplets were found for the case of asymmetrical bulky counterions. This distinction in behavior was explained by possible steric restrictions, entropic effects and differences in dipole–dipole interactions. Finally, it was shown that the mobility of small counterions in ionic aggregates formed at high λ depends significantly on the charge fraction and chain rigidity. It was found that at high f ion pairs are unstable within the polyelectrolyte globule and counterions can freely migrate within the globule volume. At low f, the counterion mobility is realized through "hopping" between ion pairs.

I. INTRODUCTION

Ion-containing systems have been attracting unquenchable interest during decades. Being mainly water-soluble, they find numerous applications in various fields, in particular, in medicine, food, cosmetic, agricultural industries. Furthermore, biological macromolecules such as DNA, RNA, and proteins carry charges and their functioning cannot be understood without taking into account the contributions from electrostatics. In spite of extensive research, ion-containing systems have not yet gained a similar level of understanding as their neutral counterparts, many fundamental aspects of their behavior still remain unclear. This is largely due to the presence of long-range electrostatic interactions introducing new length scales and competing with short-range volume interactions of electrically neutral monomer units.

Usually, in polar media such as water ionizable groups on polymer can dissociate, and, as a result, the polymer chains become charged while mobile counterions are released into solution (polyelectrolyte regime). Many peculiar properties of polyelectrolytes are governed by the presence of low-molecularweight counterions, in particular, their osmotic pressure is responsible for high swelling degrees of polyelectrolyte gels while an interplay between the Coulomb interactions and translational entropy of counterions results in microphase separation in poor-solvent polyelectrolyte solutions. One of the problems in the field of polyelectrolytes arises from possible nonlinear effects caused by counterions trapping by highly charged macromolecular objects giving rise to their nonhomogeneous distribution and affecting conformational transitions in polymer chains. In particular, for highly charged rodlike polyelectrolytes the concept of Manning condensation is well-known.^{1,2} According to this concept above a certain ionization degree, counterions become condensed in the vicinity of polymer chain partially neutralizing its charge. This threshold is defined by interplay between electrostatic attraction of counterions to the polyion and their translational entropy loss due to the confinement. It has been shown that for flexible polyelectrolytes the counterion condensation deviates from the Manning mechanism.³⁻¹⁴ Counterion distribution itself affects considerably the chain conformation which is far from the rod-like, furthermore increasing electrostatic interactions induces ion pair formation between counterions and ions on polymer chains. Ion pairing is enhanced in nonpolar media where a strong dipole-dipole attraction between ion pairs on polymer chains can result in a complicated multiplet structure formation (ionomer regime).

Received: November 3, 2015 Revised: January 11, 2016

Switching between polyelectrolyte and ionomer regimes in a single polyelectrolyte chain taking place upon increase of the Coulomb interaction strength has been observed in computer simulations,^{3–11} starting from the pioneering work of Winkler et al.,7 and has been studied theoretically under different conditions in refs 12-14. Similar transition from the polyelectrolyte chain swelling to strong collapse accompanied by counterion trapping and multiplet formation upon increase of ionization degree has been experimentally observed for dilute poly(acrylic acid) and poly(methacrylic acid) solutions in methanol being less polar than water as early as in the middle of the 1980s of the last century.¹⁵⁻¹⁷ Formation of ionomer-like collapsed conformations was also demonstrated for polyelectrolyte gels both theoretically and experimentally.^{18-22'} The formation of the collapsed state was also studied for complexes formed by two oppositely charged flexible polyelectrolytes by means of molecular dynamics simulations.

Up to now, most of the theoretical and computer simulation studies in this area were limited to small size counterions. In computer simulations the counterion size usually coincides with the size of monomer units while in theoretical considerations point-like charges are considered. However, recently, in a combined experimental and theoretical research²⁴ it has been shown that counterion size is of crucial role for polyelectrolyte gel swelling in low polar solvents where a competition between polyelectrolyte and ionomer-type conformations exists. Experimental research was focused on poly(methacrylic acid) and poly(acrylic acid) gels in methanol neutralized with different bases providing sodium, cesium, and tetramethyl-, tetraethyl-, or tetrabutylammonium counterions. In this ionic row, the size of counterions increases considerably from sodium to tetrabutylammonium ions. It has been found theoretically and demonstrated experimentally that, depending on the counterion size, three different regimes of the gel conformational behavior occur. For small counterions (Na⁺, Cs⁺), the gel swelling at low ionization degrees is succeeded by its collapse due to ion association with the formation of ion pairs and multiplets. This type of behavior corresponds to that found previously for gels^{18–22} as well as for dilute polyelectrolyte solutions.^{7,15–17,20} On the contrary, in the case of bulky tetrabutylammonium counterions, the gel was shown to swell upon ionization, demonstrating purely polyelectrolyte behavior. Finally, a new type of behavior was observed and theoretically described for the gels with counterions of intermediate sizes (tetramethyl- and tetraethylammonium). In this case, the gel ionization causes first swelling and then collapse and finally reswelling of the gel at higher ionization degrees. This distinction in gel behavior with counterions of different types has been explained by decreasing tendency for ion pair and multiplet formation with growing counterion dimensions. The effect of the counterion size on the gel collapse behavior was also demonstrated theoretically in ref 25.

With regard to these new results, a further thorough study of the polyelectolyte-ionomer transitions in polyelectrolytes, especially of multiplet structures formed in the ionomer regime depending on the nature and size of counterions, is needed. In this paper, we dwell on these problems. We study the effect of the counterion size considering conformational behavior of a single polyelectrolyte chain in a dilute solution by computer simulation. The method of dissipative particle dynamics with explicit treatment of electrostatic interactions is applied. This method allows us to model a rather long polymer chain and to study the polyelectrolyte chain collapse in the presence of solvent molecules. Besides, we analyze in detail the ion pair and multiplet structure depending on the size of counterions as well as the position of the charge in the case of bulky counterions. In the next section the model and the simulation method are described. Then the results of the simulation together with discussion are presented. Conclusions are formulated in the last section.

II. SIMULATION TECHNIQUE

In our simulations, we used dissipative particle dynamics (DPD) method explicitly accounting for electrostatic interactions. DPD is a version of the coarse-grained molecular dynamics adapted to polymers and mapped onto the classical lattice Flory–Huggins theory.^{26–29} It is a well-known method which has been used to simulate properties of a wide range of polymeric systems, such as single chains in solutions,³⁰ polymer melts³¹ and networks.^{32–34} In short, macromolecules are represented in terms of the bead-and-spring model (each coarse-grained bead usually represents a group of atoms), with beads interacting by a bond stretching force (only for connected beads) F_{ij}^b a conservative force (repulsion) F_{ij}^c a dissipative force (friction) F_{ij}^d and a random force (heat generator) F_{ij}^r . The total force is given by

$$F_{i} = \sum_{i \neq j} (F_{ij}^{b} + F_{ij}^{c} + F_{ij}^{d} + F_{ij}^{r})$$
(1)

The soft core repulsion force between i- and jth beads is equal to

$$F_{ij}^{c} = \begin{cases} a(1 - r_{ij}/R_{c})r_{ij}/r_{ij}, r_{ij} \leq R_{c} \\ 0, r_{ij} > R_{c} \end{cases}$$
(2)

where r_{ij} is the vector between *i*th and *j*th bead, *a* is the repulsion parameter, and R_c is the cutoff distance, which represents the size of each bead in real units. R_c is basically a free parameter depending on the volume of real atoms each bead represents.²⁹

If two beads (i and j) are connected by a bond, there is also a simple spring force acting on them

$$F_{ij}^{b} = -K(r_{ij} - l)\frac{r_{ij}}{r_{ij}}$$
(3)

where *K* is the bond stiffness and *l* is the equilibrium bond length. We do not give here a more detailed description of the standard DPD (without electrostatic interactions); it can be found elsewhere.²⁹

A method to introduce long-range electrostatic interactions into DPD was proposed by Groot.^{3S} The main idea was to use smeared charges instead of point-like ones in order to avoid infinitely large force at zero interbead distance (it becomes possible due to the soft nature of the repulsive potential). Following ref 35 in this work, we used the linear charge distribution to simulate smeared charges:

$$\kappa(r) = \frac{3}{\pi R_e^3} (1 - r/R_e), \quad r < R_e$$
(4)

where R_e is the smearing radius; it was chosen to be equal to $1.6R_e$.

The strength of electrostatic interactions can be characterized by the dimensionless electrostatic coupling constant:

$$\Gamma_0 = \frac{e^2}{4\pi k T \varepsilon_0 \epsilon R_c} \tag{5}$$

where ε_0 is the dielectric constant of vacuum and ε is the dielectric constant of the solution. Γ_0 describes the relative strength of the electrostatic interaction between two point-like unit charges separated by the distance R_c to the thermal energy kT_i i.e., it is just the ratio of the Bjerrum length l_b to R_c .

In what follows, we use reduced (dimensionless) units with R_c being the length unit, kT being the energy unit, and e being the charge unit.

It should be noted that for the case of smeared charges, the electrostatic energy is not simply inversely proportional to the distance between charges r, but has a different functional form at $r < 2R_e$ and a finite value at $r = 0^{35}$ in contrast to the electrostatic energy between two point-like charges. However, to estimate the relative electrostatic contribution we will use the standard expression for the Bjerrum length (applicable for point-like charges) $l_b = \frac{e^2}{4\pi k T e_0 e}$ because we are interested in the region of strong electrostatic interactions where this expression is valid. Please note that even for rather weak electrostatic interactions the used expression would give a good estimation of l_b because at $R_e = 1.6$ the interaction energy between two smeared charges starts to differ significantly (2-fold difference) from the energy between two point-like charges of the same

The electrostatic field was calculated by solving the Poisson equation numerically on a lattice,^{35,36} the meshsize was chosen to be equal to 0.8.

III. MODEL

magnitude at only $r \approx 0.5$.

We studied the behavior of a polyelectrolyte chain consisting of N = 256 beads in a dilute solution. The solvent was modeled explicitly. Namely, a single chain was placed in a box of size 48^3 (the number density was equal to 3, so the box contained ~330 000 beads).

The polymer chain contained fN charged beads with charge magnitude in the reduced units -q uniformly distributed along the chain (we will call f "charge fraction"). In the simulations, the value of f was varied from zero (neutral chain) to unity (fully charged chain), the. Interaction between the charges was described by the parameter $\lambda = q\sqrt{\Gamma_0}$, which we will call "electrostatic strength"; it can be understood as a parameter that "rescales" the electrostatic energy between two charges at a given distance compared to the case when $l_b = R_c$. Increase in λ can be interpreted by either increasing the total bead charge, or decreasing the dielectric constant of the medium, or decreasing the temperature.

In order to maintain the system electroneutrality, fN counterions were added to the solution. The absolute value of the counterion charge was equal to that of a charged polymer bead but had an opposite sign. Three different types of counterions (see Figure 1) were studied: small counterions and two kinds of bulky counterions. The size of the small counterion was equal to the size of a charged chain bead, while the bulky counterions were much larger and consisted of 19 beads. For bulky counterions the position of the charged bead was varied: the charge was either located on the central bead or on one of the peripheral beads (Figure 1).

All the remaining beads in the box were solvent beads. We studied the case of a good (athermal) solvent; the solvent and



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Figure 1. Three types of counterions used in simulations: small (1bead) counterion (left); bulky (19-bead) symmetrical (middle); bulky asymmetrical (right). Red beads are charged with charge q_i and all others (green) are neutral.

monomer beads were equivalent in terms of volume interactions.

The parameter *a* of the soft repulsive force (see eq 2) between all beads was equal to 100, which means that the Flory–Huggins $\chi = 0$ for all pairs of species. Such a high value was chosen in order to prevent too strong overlapping of oppositely charged beads forming an ion pair at high electrostatic strengths. Modeling polymer chain bonds we used the bond stiffness K = 20 and equilibrium bond length l = 0.8 eq 3, while for the bonds connecting beads of the bulky counterions we used K = 150 and l = 0.7 in order to make them shape-persistent.

The time step for integration was equal to 0.01, and the length of productive trajectory (during which the averaging was performed) was 10 mln integration steps.

Three parameters were varied in the simulations: the electrostatic strength λ from 0 to 10; the charge fraction f from 0.06 (weakly charged chain) to 1 (strongly charged chain); and, finally, the counterion type.

IV. RESULTS AND DISCUSSION

A. Chain Size Depending on the Electrostatic Strength. Let us first analyze the conformational behavior of fully charged polyelectrolyte chains when every bead carries a charge (f = 1). The radius of gyration of the polyelectrolyte chain swollen with different types of counterions vs the electrostatic strength in the solution is plotted in Figure 2.

When the electrostatic strength is relatively low ($\lambda < 1$) all the systems behave quite similarly: the polymer chain swells upon increasing λ ; the counterions move freely throughout the



Figure 2. Dependences of squared radius of gyration on the electrostatic strength for the three studied types of counterions and f = 1. The cyan line reflects the size of an uncharged chain and it is drawn as a guide to the eye.

system (see Supporting Information, Figure S1) and the chain size does not depend on the counterion type (within the averaging error). The polyelectrolyte swelling due to electrostatic repulsion between uncompensated charges on the chain has been studied in a number of previous works;^{7,12,37–39} therefore we do not discuss it here in detail. At approximately $\lambda = 1$ the condensation of counterions on polymer chain sets in and the chain size starts to depend on the counterion type: the chain with small counterions adopts more compact conformations than the one with bulky counterions. At $\lambda > 3$, the chains with small counterions and bulky symmetrical counterions induced attraction, this behavior is also in agreement with the previous investigations.^{7,12,13,37,40,41} The formation of a somewhat larger globule in case of bulky symmetrical counterions are obviously due to the large counterion volume.

Completely different situation occurs when the counterion charge is located on the surface. Indeed, as can be observed in Figure 2 the chain with bulky asymmetrical counterions does not collapse at all, its gyration radius is much larger than that for a neutral chain. Apparently, the chain in this case adopts conformations of a chain in a good solvent (see Supporting Information, Figure S2), with the only difference from an uncharged chain being an increased effective size of a monomer unit due to the presence of condensed large counterions. Since the formation of the dense globular state is usually attributed to the correlation-induced attraction, one can conclude that contribution of this attraction to the free energy is too low to compete with excluded volume interactions and entropic contribution. Indeed, steric restrictions imposed by the uncharged part of the counterions prevent energetically profitable packing due to the highly asymmetrical shape of the counterion. At $\lambda = 2$, one can see a maximum in R_{σ}^{2} probably due to the same reason: at that λ a significant part of the counterions are not condensed (about 50% for the bulky asymmetrical counterions); the residual chain charge forces the chain to unwrap, and the volume of the condensed counterions increases the effective segment size, while the correlation effects cannot create a significant force which could lead to the chain compaction (unlike the case of bulky symmetrical counterions). The chain size decreases upon increasing λ because of the chain neutralization. A similar effect was observed in ref 39, where ionic surfactants with different tail lengths were used as counterions.

It is should be also noted that we do not see any qualitative difference in behavior between the two "symmetrical" counterions (small and bulky symmetrical), even despite the difference in size. Typical conformations for the three studied cases at $\lambda = 10$ are depicted in Figure 3. One can mention that all counterions are trapped by the chain. A significant difference between two globular states and a coil conformation is clearly seen.

B. Chain Size Depending on the Charge Fraction. Let us now study the conformational behavior of a polyion at fixed $\lambda = 10$ but with the fraction of charged beads on polymer chain being varied. One should note that at such a high λ the number of free counterions is close to zero. The dependences of the gyration radius for the chain with different types of counterions on the charge fraction are presented in Figure 4.

The behavior of the system with small counterions at $\lambda = 10$ is rather simple—the chain starts to shrink abruptly at the lowest studied charge fraction f = 0.06, reaching its minimum at f = 0.25. Further growth of f results in a minor increase in the



Figure 3. Typical chain conformations at $\lambda = 10$ for the three studied types of counterions: small (left), bulky symmetrical counterion (middle), and bulky asymmetrical counterion (right).



Figure 4. Dependences of squared radius of gyration on the charge fraction for the three studied types of counterions at $\lambda = 10$.

chain size (from $R_g^2 = 11.6$ to 13.7) due to increasing number of counterions. The chain with bulky symmetrical counterions behaves similarly: one can see collapse upon introducing charges (f = 0.06), the minimum size at f = 0.125 and then a slight size increase upon growing f. For the case of bulky asymmetrical counterions the situation is drastically different: increasing f from 0 to 0.33 results only in a slight chain compaction, while the further growth of f leads to a significant increase in the chain size.

The comparison of the chain sizes at f = 0.06 reveals an interesting feature: the chain with bulky symmetrical counterions adopts a more compact conformation compared to the chain with small counterions. In order to understand the underlying reason for this effect, we analyzed typical chain conformations at f = 0.06; they are depicted in Figure 5.

One can see that for the system with small counterions all charges form ions pairs; some fraction of these ion pairs join into multiplets. Two types of multiplets can be observed: quadrupoles (a pair of dipoles forming a square) and dipole chains. Usually from three to five multiplets of these types are observed in the simulations.

In the case of bulky symmetrical counterions significantly different conformations are realized: all the ion pairs form multiplets, and in the majority of the observed chain conformations the most part of the ion pairs form a ring-like structure consisting of 8-16 ion pairs. Such ring-like multiplets have been previously observed in ref 42 for the case of diblock polyampholyte chains. The ion pairs that do not form the biggest multiplet usually create smaller multiplets in the form of smaller rings.

Analysis of the chain conformations with bulky asymmetrical counterions shows that the formation of multiplets is indeed hindered—one can only find 0-2 quadrupoles and no more complex multiplets (so the fraction of ion pairs participating in



Figure 5. Typical chain conformations at f = 0.06 for small counterions (top left), bulky symmetrical counterions (top right) and bulky asymmetrical counterions (bottom). Each chain contains 16 charged beads. Negatively charged chain beads are depicted as blue balls, and positively charged counterion beads are depicted as red balls. The neutral beads forming the "corona" of the bulky counterions are depicted as semitransparent green balls for the sake of visual clarity.

multiplets is rather low). This agrees well with the trend observed in Figure 4: weak dipole association is enough to reduce the chain size to some extent, but it is not enough to overcome the chain unfolding due to the increasing effective size of monomer units.

In order to analyze the multiplet formation more quantitatively, we calculated the distributions of the following quantities: (1) the distance between a charged chain bead and the closest counterion charged bead; (2) the distance between a charged chain bead and next to the closest counterion charged bead; (3) the distance between a charged chain bead and the closest another charged chain bead (Figure 6).

The first distribution (ion-closest counterion, black lines) shows the dipole size and the amount of condensed counterions. As expected, the dipole size for the case of bulky symmetrical counterion is approximately two times larger compared to the other systems. Indeed, in this case two charged beads cannot come closer to each other due to the presence of the neutral shell of the counterion. One can also see that all the charged chain beads are always paired with a counterion, as there are no events when the distance to the closest counterion is larger than 1.5 (1.65 for the case of bulky symmetrical counterions).

The second distribution (ion-next to the closet counterion, red lines) basically shows the fraction of charged chain beads forming a multiplet. In agreement with the visual analysis, we obtain that for the case of bulky symmetrical counterions charged chain beads are in a multiplet almost in 100% of conformations used for averaging: the peak is almost as high as



Figure 6. Distributions of the distances between charged beads. The curves were averaged over 1000 chain consecutive conformations separated by 10 000 integration steps; the bin size for data collection was equal to 0.05.

that for the closest counterions (black curve) and the tail of the distribution is negligible. The distribution for the system with small counterions also demonstrates a pronounced peak; however, there is a significant tail indicating the presence of separated ion pairs. On the contrary, for the system with bulky asymmetrical counterions there is a very wide tail and almost no peak on the distribution; i.e., while single multiplets are still present, the majority of ion pairs are separated. It is obviously the steric restrictions caused by the neutral part of the counterions that make formation of multiplets unfavorable.

The third distribution (blue line) gives us some information about the type of multiplets present in the system. One can see that for bulky symmetrical counterions the distribution has only one peak located at the distance approximately equal to the doubled dipole length. This indicates the formation of chainlike multiplets (forming rings in our case). The distribution for small counterions has the same peak as well as a peak located at approximately $\sqrt{2}$ dipole length, which is obviously characteristic for quadrupoles and similar multipoles of higher orders (hexapoles, octapoles etc.). It is interesting that there is no evidence of the quadrupole formation for the system with bulky symmetrical counterions.

Another interesting feature is that for the chain with small counterions not all the ion pairs participate in multiplets even though formation of multiplets should be energetically more favorable than for the system with bulky symmetrical counterions simply because the charges in the former system can come closer to each other. However, the formation of a ring-like multiplet for the latter system does not involve such big losses on the excluded volume interactions and of the entropy from the loop (an uncharged chain section) formation because the large counterions form large spacers between two consecutive chain charges in such a ring, which allows the loops not to overlap. For the system with small counterions a ringlike multiplet would be too small, leading to loop overlapping. In other words, while multiplets of higher order are more favorable from the point of view of the electrostatic energy, the system with small counterions has to form small multiplets for not to lose in the entropy and excluded volume interactions.

Thus, one can conclude that the size and asymmetry of counterions play a dramatic role in the system properties.

C. Mobility of Counterions. It has been mentioned in refs 41 and 43 that the condensed counterions do not form longliving ion pairs with the charged chain groups, but can rather move freely along the chain. In order to test if this is true, we calculated the mean square displacement (MSD) of the small counterions relatively to the positions of the chain charged beads closest to the counterions at the initial moment of time (Figure 7). In other words, the curves in Figure 7 show how far



Figure 7. Dependences of mean square displacement of counterions in respect to the positions of the chain charged beads which were closest to them in the initial moment of time for different λ and *f*. The green curve if calculated for a rod-like chain, the other systems correspond to those studied in the previous sections. The cyan line reflects the diffusion of solvent particles and is given for comparison. The magenta thin line shows the asymptotic dependence for normal (Brownian) diffusion.

the counterion diffuses from the ion on the chain with which it forms an ion pair at time = 0. It is obvious that while the solvent particles show normal diffusion at large times as it was expected, the motion of the counterions is subdiffusive in all the cases (the exponent of the dependences of MSD on time is less than 1).

For comparison we have studied counterion mobility in case of a very rigid chain at $\lambda = 10$ for f = 1 (green curve in Figure 7) and f = 0.06 (not presented). The parameter of the bond angle potential was chosen in such a way that the chain did not collapse but rather remained in an almost unbent rod conformation. For f = 0.06 the counterions do not diffuse at all; i.e., they form very stable ion pairs with the charged chain beads. However, if the chain is flexible, one can see from Figure 7 that there is some counterion diffusion. As we know from Figure 6, at $\lambda = 10$, there are no free counterions; it means that the only possible way of diffusion is hopping, when a counterion changes its closest-neighbor ion upon breakup of a multiplet and then diffuses with the new ion away from the initial one.

The MSD curve for the rigid chain at f = 1 also demonstrates a nonzero slope. Since no multiplets can be formed in this system, we can conclude that the counterions move along the chain and no stable ion pairs are formed.

The globular state (f = 1, $\lambda = 10$, and $\lambda = 5$) shows a very rapid counterion diffusion, while at large times the counterion displacements are restricted by the globule volume. At small times, the diffusion rate is comparable to that of the solvent beads (cyan line). It indicates that the globular state indeed resembles a metal where all the electrons are shared.

One should note that the curves in Figure 7 do not show the "true" mean square displacement of the counterions, but rather describe the mobility of the counterions inside the chain volume and demonstrate that ion pairs are unstable. Figure S2 shows the total MSD for the three cases presented in Figure 7 at $\lambda = 10$; in general, the same subdiffusive motion can be observed.

We can conclude that at high charge fractions stable ion pairs are present neither in the globular state nor in the rod-like chain.

V. CONCLUSIONS

In this work, we used dissipative dynamics (DPD) simulations with explicit treatment of electrostatic interactions and solvent molecules to study the conformational behavior of a single polyelectrolyte chain in a good solvent under increasing strength of electrostatic interactions, λ , and at different charge fractions, *f*. The main focus was on the effect of the counterion size and charge location within the bulky counterion on the polyelectrolyte collapse and ionic structures formed at high λ . Three types of counterions were modeled, namely, small counterions whose size was equal to the size of a polymer chain unit and bulky counterions with different positions of the charged bead (symmetrical counterions with the charged bead located in the center of a big spherical particle and asymmetrical counterions with the charged bead located on the surface of a big spherical particle).

The obtained results for the case of a strongly charged chain with small counterions are in agreement with the previous investigations.^{7,12,13,37,40,41} In particular, at weak electrostatic strengths chain ionization first leads to the chain swelling due to Coulomb repulsion between the charged beads; when the counterion electrostatic energy becomes comparable to their thermal energy, counterion condensation takes place, leading to the chain compaction and ultimately resulting in the formation of a dense globule due to the charge correlation effects. In the case of bulky symmetrical counterion the chain behavior was qualitatively similar. The only difference was the formation of a larger globule due to additional excluded volume of bulky

counterions. A drastically different chain behavior was realized for the system with bulky asymmetrical counterion. Namely, no globular state was observed, even at high λ the chain remained in a completely unwrapped state. A possible reason could be the steric restrictions preventing energetically profitable packing due to the highly asymmetrical shape of the counterions.

Striking results demonstrating significant impact of the counterion nature on the polyelectrolyte chain behavior were obtained at fixed λ varying the fraction of charged beads. In particular, while the chain with either small or bulky symmetrical counterions shrinks upon increasing the charge fraction, the bulky asymmetrical counterions cause drastically different behavior: a slight chain compaction is followed by a significant increase in the chain size.

Detailed analysis of the chain conformations and ionic structures formed with different types of counterions at high λ again demonstrated the important role of counterion size and its asymmetry. It was found that the majority of the ion pairs with bulky asymmetrical counterions are separated and the probability of the multiplet formation is very low. For the system with small counterions the formation of quadrupoles and small ionic chains prevails, although separated ion pairs are also present. Surprisingly, for the bulky symmetrical counterion the ion pairs form a large ring-like multiplet almost in 100% of conformations. A possible reason for this difference in ionic structures could be entropic penalties due to loop formation and additional excluded volume interactions in the course of the multiplet formation; the aforementioned losses are smaller for the case of bulky symmetrical counterions due to a larger size of an ion pair.

Finally, the counterion mobility was studied depending on the chain rigidity and degree of charging. It was shown that for high charge fractions as well as rod-like conformations the counterions migrate along the chain. In the opposite case of low charge fractions and a flexible chain the counterion diffusivity can be attributed to the hopping process when a counterion changes its nearest-neighbor ion through breakup of a multiplet and then diffuses with the new chain ion away from the initial one. The highest diffusivity of counterions was observed within the polyelectrolyte globule formed by highly charged flexible chain. In this case the counterions can diffuse almost freely within the globule volume, this diffusion resembling sheared electron behavior within a metal. Thus, at high charge fractions stable ion pairs are present neither in the globular state nor in a rod-like chain.

Summarizing, we would like to emphasize again that the size and asymmetry of counterions play a dramatic role in the polyelectrolyte system properties. We hope that the findings of this work will encourage further experimental studies of the subject matter. Also, mixing different counterions in the same system can be an interesting tool to control the behavior of the system. We plan to investigate the outcomes of such an approach in our future works.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b02396.

Dependences of the fraction of condensed counterions on the electrostatic strength λ for the three studied types of counterions, dependence of the average squared chain segment end-to-end distance on the segment length for the case of big asymmetrical counterion and $\lambda = 10$, and total mean square displacement of small counterions for different λ and f (PDF)

AUTHOR INFORMATION

Corresponding Author

*(A.A.G.) E-mail: gavrilov@polly.phys.msu.ru.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support of the Russian Foundation for Basic Research (Grants No. 15-53-45014 and 15-03-06221) is gratefully acknowledged. A.V.C. also thanks the Russian Scientific Foundation. The section Chain Size Depending on the Charge Fraction was done within the framework of the Russian Scientific Foundation (Project No 15-13-30007). We thank Moscow State University Supercomputer Center⁴⁴ for providing the computational resources.

REFERENCES

- (1) Manning, G. S. J. Chem. Phys. 1969, 51, 924-933.
- (2) Manning, G. S. Biophys. Chem. 1977, 7, 95-102.
- (3) Stevens, M. J.; Kremer, K. Phys. Rev. Lett. 1993, 71, 2228-2231.
- (4) Stevens, M. J.; Kremer, K. J. Chem. Phys. 1995, 103, 1669-1690.
- (5) Stevens, M. J.; Kremer, K. J. Phys. II 1996, 6, 1607-1613.
- (6) Micka, U.; Holm, C.; Kremer, K. Langmuir 1999, 15, 4033-4044.
- (7) Winkler, R.; Gold, M.; Reineker, P. Phys. Rev. Lett. 1998, 80, 3731-3734.
- (8) Liu, S.; Muthukumar, M. J. Chem. Phys. 2002, 116, 9975-9982.
- (9) Klos, J.; Pakula, T. J. Chem. Phys. 2004, 120, 2496-2501.
- (10) Liu, S.; Ghosh, K.; Muthukumar, M. J. Chem. Phys. 2003, 119, 1813-1823.
- (11) Liao, Q.; Dobrynin, A. V.; Rubinstein, M. *Macromolecules* **2003**, 36, 3399–3410.
- (12) Brilliantov, N. V.; Kuznetsov, D. V.; Klein, R. Phys. Rev. Lett. 1998, 81, 1433–1436.
- (13) Muthukumar, M. J. Chem. Phys. 2004, 120, 9343-9350.
- (14) Kumar, R.; Kundagrami, A.; Muthukumar, M. Macromolecules 2009, 42, 1370–1379.
- (15) Klooster, N. T. M.; Van der Touw, F.; Mandel, M. *Macromolecules* **1984**, *17*, 2070–2078.
- (16) Klooster, N. T. M.; Van der Touw, F.; Mandel, M. *Macromolecules* 1984, 17, 2078–2086.
- (17) Klooster, N. T. M.; Van der Touw, F.; Mandel, M. *Macromolecules* **1984**, *17*, 2087–2093.
- (18) Khokhlov, A. R.; Kramarenko, E. Y. Macromol. Theory Simul. 1994, 3, 45-59.
- (19) Khokhlov, A. R.; Kramarenko, E. Y. *Macromolecules* **1996**, *29*, 681–685.
- (20) Kramarenko, E. Y.; Khokhlov, A. R.; Yoshikawa, K. Macromol. Theory Simul. 2000, 9, 249–256.
- (21) Philippova, O. E.; Sitnikova, N. L.; Demidovich, G. B.; Khokhlov, A. R. *Macromolecules* **1996**, *29*, 4642–4645.
- (22) Starodoubtsev, S. G.; Khokhlov, A. R.; Sokolov, E. L.; Chu, B. *Macromolecules* **1995**, *28*, 3930–3936.
- (23) Winkler, R. New J. Phys. 2004, 6, 11-11.
- (24) Philippova, O. E.; Rumyantsev, A. M.; Kramarenko, E. Y.; Khokhlov, A. R. *Macromolecules* **2013**, *46*, 9359–9367.
- (25) Bodrova, A. S.; Potemkin, I. I. Polym. Sci., Ser. A 2007, 49, 737–744.
- (26) Hoogerbrugge, P. J.; Koelman, J. M. V. A. Europhys. Lett. 1992, 19, 155–160.
- (27) Schlijper, A. G.; Hoogerbrugge, P. J.; Manke, C. W. J. Rheol. 1995, 39, 567–579.

(28) Español, P.; Warren, P. Europhys. Lett. 1995, 30, 191-196.

(29) Groot, R. D.; Warren, P. B. J. Chem. Phys. 1997, 107, 4423-4435.

(30) Guo, J.; Liang, H.; Wang, Z.-G. J. Chem. Phys. 2011, 134, 244904.

(31) Gavrilov, A. A.; Kudryavtsev, Y. V.; Chertovich, A. V. J. Chem. Phys. 2013, 139, 224901.

(32) Raos, G.; Casalegno, M. J. Chem. Phys. 2011, 134, 054902.

(33) Gavrilov, A. A.; Chertovich, A. V.; Khalatur, P. G.; Khokhlov, A. R. *Macromolecules* **2014**, *47*, 5400–5408.

(34) Gavrilov, A. A.; Komarov, P. V.; Khalatur, P. G. *Macromolecules* **2015**, *48*, 206–212.

(35) Groot, R. D. J. Chem. Phys. 2003, 118, 11265.

(36) Beckers, J. V. L.; Lowe, C. P.; De Leeuw, S. W. Mol. Simul. 1998, 20 (20). 369-383.

(37) Cherstvy, A. G. J. Phys. Chem. B 2010, 114, 5241-5249.

(38) Kundu, P.; Dua, A. J. Stat. Mech.: Theory Exp. 2014, 2014, P07023.

(39) Von Ferber, C.; Löwen, H. J. Chem. Phys. 2003, 118, 10774-10779.

(40) Jesudason, C. G.; Lyubartsev, A. P.; Laaksonen, A. Eur. Phys. J. E: Soft Matter Biol. Phys. 2009, 30, 341–350.

(41) Jeon, J.; Dobrynin, A. V. Macromolecules 2007, 40, 7695-7706.

(42) Wang, Z.; Rubinstein, M. Macromolecules 2006, 39, 5897-5912.

(43) Liao, Q.; Dobrynin, A. V.; Rubinstein, M. Macromolecules 2006, 39, 1920–1938.

(44) Lomonosov Moscow State University Supercomputing Center http://hpc.msu.ru.