

Conformational Behavior of Single Circular Semiflexible Polyelectrolyte in the Presence of Multivalent Counterions

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Electronic Supplementary Information

Abstract Langevin dynamics simulations are employed to explore the effects of chain stiffness and electrostatic interaction (EI) on the conformational behavior of a circular semiflexible polyelectrolyte (CSPE) in presence of trivalent counterions. We investigate the effect of bending energy b and the dimensionless Bjerrum length A on the conformational behavior of the CSPE with a fixed chain length. The competition among the EIs, chain stiffness and entropy of the system leads to rich conformations for the CSPE. As the b is less than or equal to 50, The shape of the CSPE changes from a oblate ring to a rod at small A , then to a toroid at intermediate A , and finally to a globule at very large A . However, the globular conformation is not observed for large b . In addition, we find that the number of torus ring increases with A increase, while decreases with b increase. This study should be helpful in gaining insight into the conformational behaviour of charged biopolymer.

Keywords Langevin dynamics simulation; Circular semiflexible polyelectrolyte; Trivalent counterions; Electrostatic interaction

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INTRODUCTION

Charged polymers are ubiquitous in nature. The understanding of charged polymers has long been drawing great attention because it is believed to be the key knowledge to the fundamentals of biology.^[1–5] They also have constituted an important research field^[6–11] for several years due to their large involvement in essential industrial (bio, pharma, food, fragrances, and flavors), e.g., for use as rheology modifiers in food or as chemical sensors in diagnostics.^[12,13] In addition, charged polymers are fundamental in biological systems—important biological macromolecules such as nucleic acids, proteins, and polysaccharides are polyelectrolytes (PE). Being intrinsically different from neutral polymers, each charged polymer carries multiple charges along its backbone, which generates long-range electrostatic interaction. The long-range electrostatic interaction between charges gives the PE interesting and unique properties compared to the neutral analogues. At the meantime, this also makes charged polymers among the least understood macromolecules. Furthermore, the polyelectrolyte backbone is always accompanied by numerous mobile counterions. Due to the

interplay of short-range excluded volume and long-range electrostatic interaction, and the presence of the counterions, PE solutions display a rich variety of intriguing phenomena. The peculiar phenomena of like-charged attractions in biological and soft materials that causes the condensation of highly charged deoxyribonucleic acid (DNA),^[14–19] the aggregation of viruses,^[20,21] and the network formation in actin filaments^[22] is observed. These attractions are often mediated by multivalent ions like the aggregation of M13 viruses by divalent diamine ions,^[21] the condensation of DNA,^[23,24] or the folding of ribonucleic acid^[25] by Mg^{2+} . This important topic has been attracting intensive efforts for decades, and much new understanding has been achieved, however, there are still lots of mysteries to be solved.^[26]

Many biologically relevant polymers such as DNA, actin, and microtubules have charged, rigid, or semiflexible backbone structures. The study of PE stiffness has been an active field of research in the past 30 years. It is arguably one of the most controversial domains of polymer physics. The understanding of the PEs' conformations in varying ionic environments is critical, and many properties depend on their stiffness. Therefore, it is necessary to explore the effect of chain stiffness on the properties of the PE. Responses of PEs to change in ionic environment and chain stiffness have been extensively studied in polymer sciences.^[1,27–30] Their prediction under given conditions is still a challenging problem.

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Therefore, responses of PEs to given conditions are still a rewarding subject for theoretical and simulation studies.

Furthermore, on the basis of the polymer architecture, polymer can be divided into linear and nonlinear (including branched and cyclic) types of polyelectrolytes. The dynamics of PEs with different architectures other than linear counterparts is very important because PEs play unique roles in nature and also exhibit special properties in many aspects. Biology is replete with natural circular polymers bearing charge, such as cyclic deoxyribonucleic acid and circular PEs, which were discovered in virus and bacterial, etc. In comparison with linear polymers, the circular architecture imposes a stronger constraint on the polymer's shape.^[31,32] This constraint leads to a smaller size for a circular polymer than its linear counterpart at the same degree of polymerization, making the monomers distribute more tightly around the center of mass.^[33] Thus, the shape of a circular PE should be more sensitive to electrostatic interaction (EI) than its linear counterpart.^[34,35] The combination of charge and cyclic topology is crucial for properties such as self-replication, biological recognition and activities. As such, circular PEs are emerging topics attracting growing interest from both the chemistry and materials perspectives. In addition, the behavior of circular PE in presence of counterions is of fundamental importance for its relevance to certain biological processes. To understand the effects of topological constraints on chain conformation, it is desirable to obtain a picture of any circular polyelectrolyte. In this context, this work deals with semiflexible PE having the circular architecture in presence of multivalent counterions.

In the study, we simulate the shape transition of single circular semiflexible PE in presence of multivalent counterions using Langevin dynamics simulations. The effects of electrostatic interaction strengths and PE's stiffness on the conformation of PE are investigated. The paper is organized as follows: Section 2 provides the details of the simulation model and corresponding simulation method. Section 3 describes the results of our numerical simulations, and provides the discussion of the results. Brief conclusions are provided in the final section.

MODEL AND SIMULATION METHOD

Our system consists of single circular semiflexible polyelectrolyte (CSPE) modeled by a positively charged bead-spring chain and spherical counterions. The CSPE chain is composed of $N=180$ monomers with mass m and electric charge q_m each. Each counterion carrying a charge $q_c = -Zq_m$ is taken into account explicitly with the same mass and size as the chain monomer, where $Z=3$ is the valency of the counterions. Thus, two types of particles are present in the system under study.

Four types of interaction are involved in the simulations. The first one is excluded-volume interaction, which is applied for all the particles, including monomers and counterions. It is described by the Lennard-Jones (LJ) potential,^[36]

$$U_{\text{LJ}}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (1)$$

where r_{ij} is the distance between particles i and j , σ is the inter-particle distance at which the potential is zero. Both ϵ and σ (in

reduced units) are set to $\epsilon=1.0$ and $\sigma=1.0$ for all pairs of particles. The LJ potential is chosen to be zero beyond a cutoff distance $r_c=\sigma$, such that the excluded volume interaction between all pairs is purely repulsive.^[36,37] The detailed discussion about $r_c=\sigma$ can be found in the electronic supplementary information (ESI).

The second one is the bond connectivity interaction. Adjacent monomers along the CSPE chain are connected by harmonic springs,^[36]

$$U_{\text{bond}}(r_{ij}) = \frac{1}{2}k(r_{ij} - r_0)^2 \quad (2)$$

where k is the spring constant and r_0 is the equilibrium bond length. We set $r_0=1.12$ and $k=500.0$.

The third one is a harmonic angle potential, which characterizes the chain stiffness^[36]

$$U = b(1 + \cos\theta) \quad (3)$$

where θ is the angle between two consecutive bonds, and b is the bending energy. b can be considered as a penalty for successive bonds deviating from a straight arrangement, i.e., the chain rigidity can be adjusted by varying b . In addition, b is in the units of $k_B T$.

The fourth one is the electrostatic interaction (EI), which is applied for all the particles, including monomers and counterions.^[36] It can be given by

$$U(r_{ij}) = \frac{q_i q_j}{4\pi \epsilon_0 \epsilon_r r_{ij}} \quad (4)$$

where q_i and q_j are the charges of the i^{th} and the j^{th} particles, which can take the value q_m or q_c , based on whether it is a monomer or counterion and ϵ_r is the effective dielectric constant of the medium ($\epsilon_r=1$). The relative strength of electrostatic interactions is defined by the dimensionless Bjerrum length, A :^[36]

$$A = \frac{l_B}{r_0} \quad (5)$$

where l_B is the Bjerrum length between two monomer charges, q_m , the length scale below which EIs dominate thermal energy,^[36] and is defined as

$$l_B = \frac{q_m^2}{4\pi \epsilon_0 \epsilon_r k_B T} \quad (6)$$

where k_B is the Boltzmann constant, T is the temperature. We set $k_B=1$ and $\epsilon_r=1$. The strength of electrostatic interactions in the system can be scaled via A .

The simulations are carried out using LAMMPS package.^[38] A Langevin thermostat^[39] is used to maintain a constant temperature ($T=1.0$) of the system, the friction coefficient was chosen to be constant $\zeta = m/\tau$ where $\tau = \sqrt{m\sigma^2/\epsilon}$ is the time unit of the system, and all particles have the same reduced mass $m=1$. The standard Ewald summation with estimated accuracy of 10^{-4} is used for the calculation of long-rang EIs. The time step for integrating equations of motion is chosen as 0.001. One CSPE chain and $N/Z=60$ counterions are placed in a cubic periodic box of box length $L=100 \sigma$. The number of counterions is chosen so that the system is overall charge neutral. The system relaxes with 10^7 timesteps to reach equilibration. Then the equilibration systems are further simulated for 10^7 timesteps to sample and data are saved every 10^4 timesteps, resulting in 1000 regularly time-spaced snapshots, and ten independent runs are performed.

RESULTS AND DISCUSSION

Equilibrium Phases of the Circular Semiflexible Polyelectrolyte

The snapshots of the circular semiflexible polyelectrolyte (CSPE) and trivalent counterions at the end of 10^7 steps are shown in Fig. 1(a) for different dimensionless Bjerrum lengths A and fixed bending energy $b=60$. It can be observed that the CSPE exists in three different phases. The CSPE assumes oblate ring at $A=0$. The counterions are dispersed in the whole space, and only a few are in the neighborhood of the CSPE. As A increases to $A=1.5$, the CSPE collapses a bit but still assumes oblate ring. Many counterions adsorb onto the CSPE. When A increases further, the shape of the CSPE becomes rod-like at $A=3$ and 5. When A is large than or equal to 5.5, the CSPE folds into toroid. The size of toroid decreases with A increase in the torus region, and the number of torus rings N_{ring} increases. In addition, more and more counterions adsorb onto CSPE. The similar phase transitions occur for circular semiflexible polyelectrolyte chains in presence of monovalent counterions. Some discussions are added in ESI. The physical rationale for the phase transition is the competition between the total bending energy and the total electrostatic interactions, which are controlled by the parameters b and A , respectively. Fig. 1(b) shows a schematic of

the competition between the expansion conformation and the collapse one. For example, the polyelectrolyte suddenly transits from circular structure to rod-like structure with the increase of A from 1.5 to 3 because the increase of total electrostatic interaction can bear the increase of bending energy, which leads to the formation of a rod-like structure. If A increases further from 5 to 5.5, the larger electrostatic interactions can offset the stronger bending energy, and the transition from rod to toroid occurs.

In order to analyze the conformation of a chain, one needs a method that would let us know the monomer contact distribution. This can be achieved by generating so-called contact maps, which are essentially a representation of 3D connectivity in a two-dimensional map. We regarded a monomer i and a monomer j in contact when they are found within the radius of 2.5.^[40] Fig. 2(a) shows the contact maps of the corresponding representations of the circular semiflexible polyelectrolyte's conformation of Fig. 1. A series of straight lines present in the contact maps. The next quantity that has been calculated to characterize conformations of the chain is the average cosine $\langle \cos \theta_{ij} \rangle$ between the backbone bond vector $\vec{u}_i$ and $\vec{u}_j$ as a function of the distance along the chain backbone $|i-j|$. Fig. 2(b) shows the $\langle \cos \theta_{ij} \rangle$ of the corresponding snapshots of Fig. 1. If the slope of straight line is positive in con-

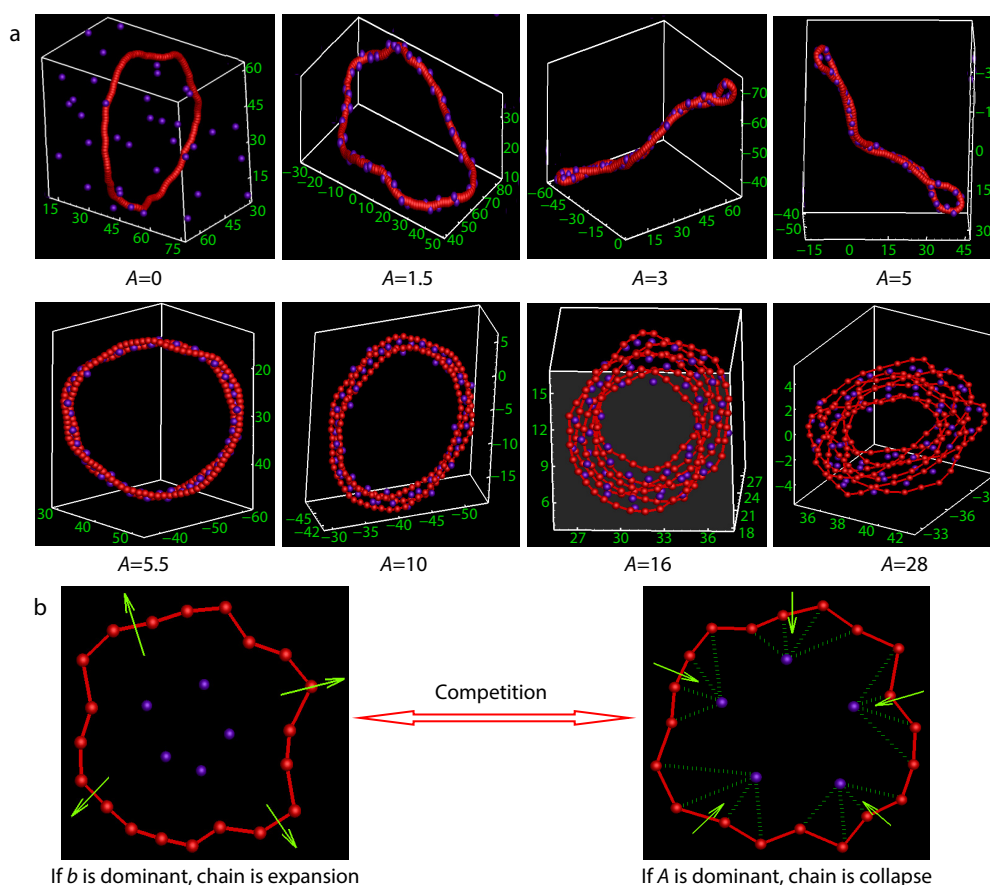


Fig. 1 (a) The snapshots of circular semiflexible polyelectrolyte and counterions for different the dimensionless Bjerrum length A and fixed bending energy $b=60$. The circular semiflexible polyelectrolyte and counterions are colored in red and blue, respectively. (b) A schematic of the competition between the expansion conformation and the collapse one for semiflexible polyelectrolyte chain in the presence of counterions. The dotted lines represent the electrostatic attraction between monomers and counterions. For clarity, we do not label all.

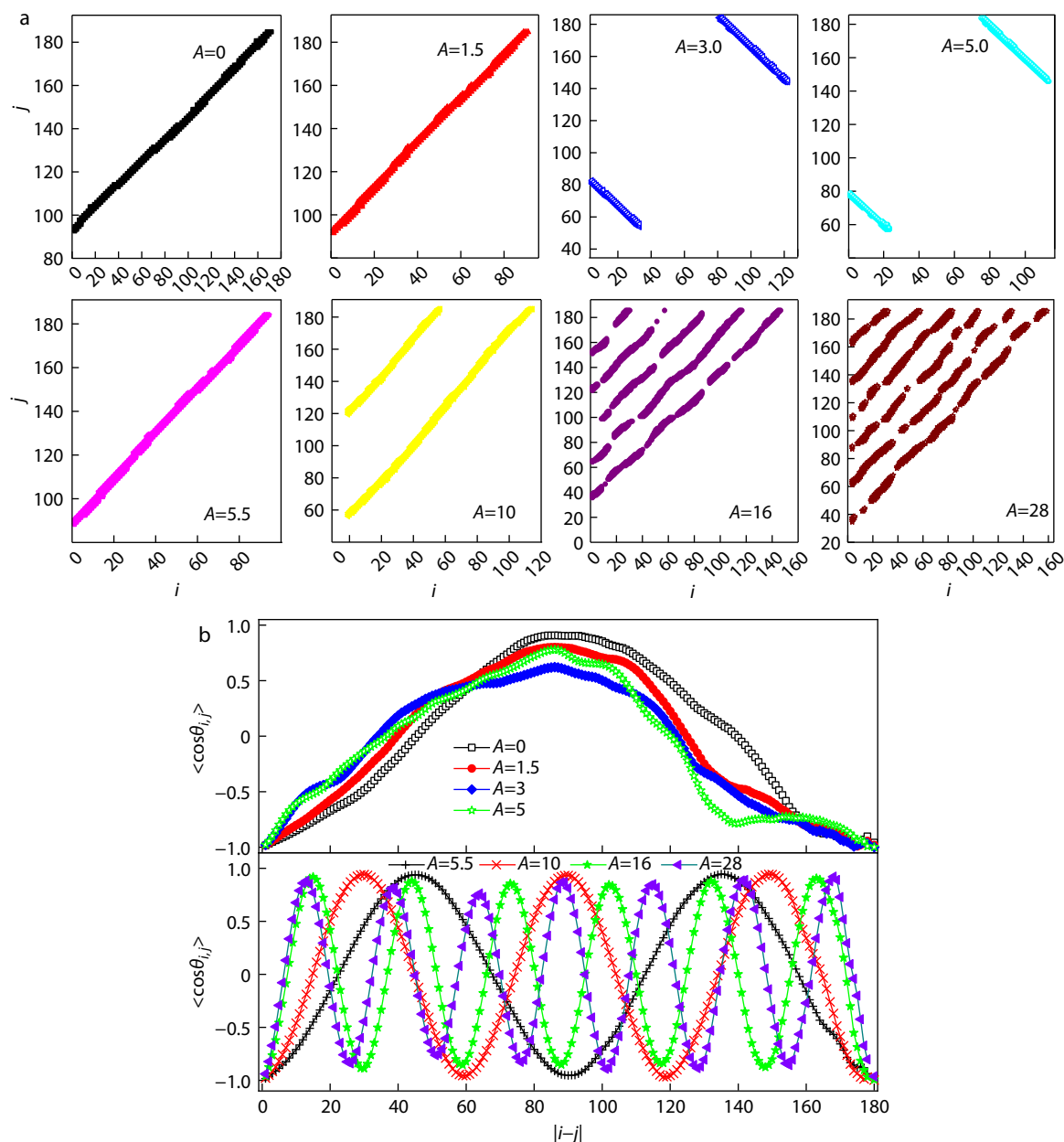


Fig. 2 (a) Corresponding representations of the circular semiflexible polyelectrolyte's conformation of Fig. 1 in the contact map space, (b) the average cosine between bonds versus the distance along the polyelectrolyte of the corresponding snapshots of Fig. 1.

tact maps and the $\langle \cos \theta_{ij} \rangle$ does not present periodicity, the shape of CSPE is ring. If the slope is negative and the $\langle \cos \theta_{ij} \rangle$ does not present periodicity, the shape of CSPE is rod. If the slope is positive and the is of periodicity, the CSPE assumes toroid. It can be observed that all maxima of are located at a characteristic distance from each other. Each maximum appears when the chain makes another turnover. Therefore, the number of period of $\langle \cos \theta_{ij} \rangle$ is equal to the number of torus rings N_{ring} . The number of straight lines is one less than N_{ring} . The combination of the contact map and $\langle \cos \theta_{ij} \rangle$ can be used to distinguish the three different phases of the CSPE.

The snapshots of the system at the end of 10^7 steps are shown in Fig. 3 for different b and fixed $A=5.5$. It can be observed that the CSPE exists in three different phases. The

CSPE collapses into a compact globule at $b=0$. As b increases to $b=10$, the shape of the CSPE becomes swollen globule. The CSPE condenses into toroid in the range of $b=20$ – 60 . The size of toroid increases with b increase in the torus region, and N_{ring} decreases. The CSPE folds into rod at $b=80$ and 100 .

Fig. 4 shows the contact maps and $\langle \cos \theta_{ij} \rangle$ of the CSPE of the corresponding snapshots of Fig. 3. The contact map is totally disordered at $b=0$, and the $\langle \cos \theta_{ij} \rangle$ fluctuates around 0.0. At $b=10$, the contact map presents a bit of order, and the $\langle \cos \theta_{ij} \rangle$ presents aperiodic oscillation. At $b=20, 30, 40$ and 60 , the contact map presents a series of parallel straight lines whose slopes are positive, and the $\langle \cos \theta_{ij} \rangle$ oscillates periodically. The number of period is in agreement with the N_{ring} and the number of straight lines is one less than the N_{ring} . One can

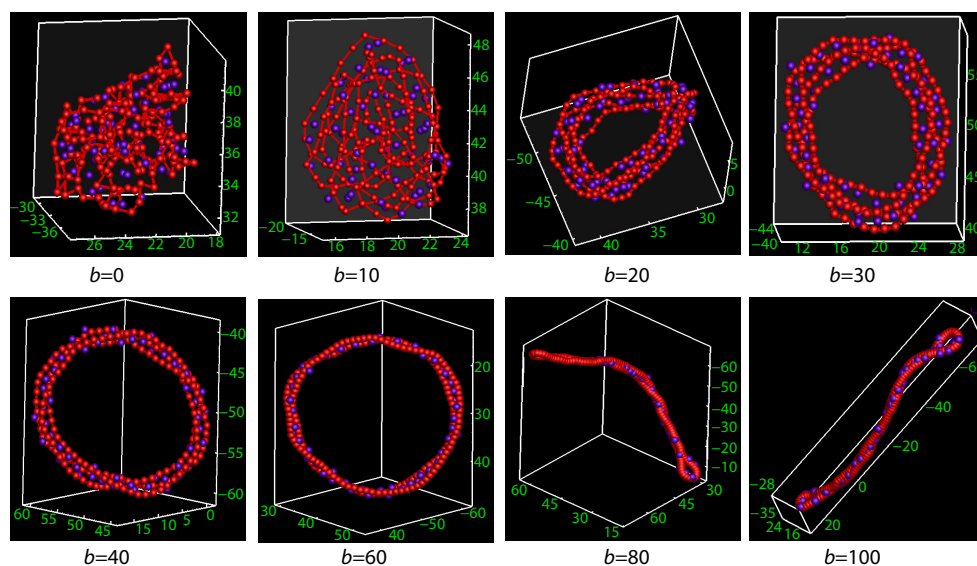


Fig. 3 The snapshots of circular polyelectrolyte and counterions for different bending energy b and fixed dimensionless Bjerrum length $A=5.5$. The circular polyelectrolyte and counterions are colored in red and blue, respectively.

see that the distance between the adjacent maxima increases with b increase in the range of $b=20\sim60$ in Fig. 4(b). Since the CSPE length is fixed, the N_{ring} of toroid decreases with b increase in the range of $b=20\sim60$. The slopes of straight lines are negative in the contact map, and the $\langle \cos\theta_{ij} \rangle$ is not of periodicity at $b=80$ and 100. It is further verified that the combination of the contact map and $\langle \cos\theta_{ij} \rangle$ can be used to distinguish the different phases of the CSPE.

Statistical Properties of the Circular Semiflexible Polyelectrolyte

To a visual examination of the conformational structure, we calculate radial density distributions $P(r_m)$ of monomers relative to the center of mass of the CSPE, i.e., the mean local volume fraction of monomers in the spherical layer of a width dr at a distance r_m from the center of mass of the CSPE.^[41] The obtained distributions for different b are shown in Fig. 5. The counterions have a natural direction along the CSPE, hence it is also instructive to analyze the charge distribution with respect to the CSPE backbone. To better understand the folding mechanism of the CSPE, the radial density distributions $P(r_c)$ of counterions relative to the center of mass of CSPE (r_c is the distance from the center of mass of the CSPE) are shown in Fig. 6.

Fig. 5 allow us to detect the different conformation of the CSPE easily. The density profile is the Gaussian distribution with a left short tail for $A=1.5$ and 2.5, and there are no monomers nearby the center of mass of the CSPE. The position of Gaussian distribution shifts to the left a bit with A increase from $A=1.5$ to 2.5. It indicates that the size of CSPE decreases a bit, due to the effective attraction mechanism caused by the counterions which adsorb onto the CSPE. Fig. 6 shows the radial density distribution of counterions shifts to the left a little with A increase from $A=1.5$ to 2.5. It indicates that the number of counterions adsorbing onto the CSPE increases with A increase. The intrachain electrostatic repulsion begins to be mitigated by electrostatic attraction between monomers and counterions. The CSPE begins to collapse with A increase. That is why the peak of $P(r_m)$ shifts to the left with

A increase from $A=1.5$ to 2.5. The bending energy dominates over their entropy and attractive EI, therefore, the shape of the CSPE is oblate ring at $A=1.5$ and 2.5. As A increases, radial density distribution of monomers becomes plateau at $A=3$ and 5, and the plateau height is about 40.0. It indicates that the CSPE folds into rod. The $P(r_c)$ shows that more counterions distribute around the center of mass of CSPE with A increase from $A=3$ to 5. The attraction between the beads and counterions begins to contribute significantly. However, the electrostatic attraction is not large enough to drive the CSPE bend, therefore, the CSPE forms rod. At $A\geq 5.5$, the distributions of $P(r_m)$ become qualitatively different. It indicates that all chain monomers are concentrated in a layer at a distance from the center of mass of the CSPE. These kinds of radial distributions are typical for toroidal conformation. The position of the density maximum shifts to the left with A increase. It indicates that the size of the toroid decreases with A increase. The distributions of $P(r_c)$ shows that the most counterions are concentrated in a layer at a distance from the center of mass of the CSPE, and other counterions are far away from the toroid. The counterions and the monomers are almost distributed in the same region. It indicates that more and more counterions adsorb onto the CSPE with A increase. This leads to intrachain attraction, working against the intrachain swelling. That is why the size of toroid decreases with A increase from $A=5.5$ to 28.

Fig. 7 shows that $P(r_m)$ assumes Gaussian distribution for $b=0$ and 10, and the density profile shifts to the right with b increase from $b=0$ to 10, at $A=5.5$. The distribution range is narrow but the distribution width increases with b increase. It indicates that the CSPE forms globule, and the shape of the CSPE changes from compact globule to swollen globule with b increase from $b=0$ to 10. Except the long tail, the density profile of counterions is almost the same with that of monomers at $b=0$ and 10, as shown in Fig. 8. It indicates that only several counterions are far away from the CSPE at $b=0$ and 10. The collapse of the CSPE is due to counterion-

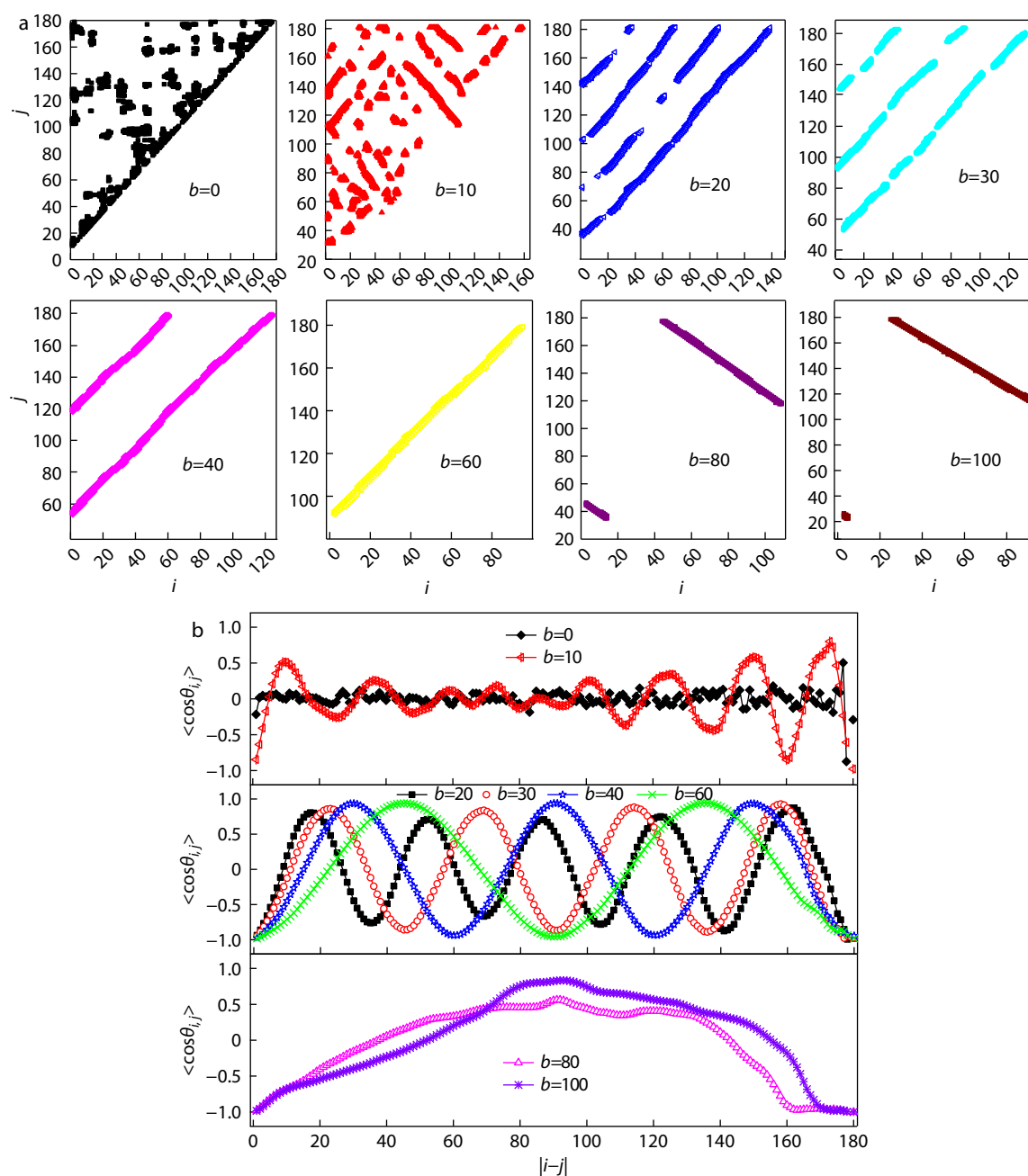


Fig. 4 (a) Corresponding representations of the circular polyelectrolyte's conformation of Fig. 3 in the contact map space, (b) the average cosine between bonds versus the distance along the polyelectrolyte of the corresponding snapshots of Fig. 3.

bridging, *i.e.*, due to the presence of multivalent counterions that connect two distant monomers. At $A=5.5$, the EIs is medium, while the chain is flexible at $b=0$ and 10. The attractive EI plays the dominant role. The density profiles in Figs. 7 and 8 indicate that the CSPE of $b=20, 30, 40$ or 60 folds into toroid at $A=5.5$, and the CSPE of $b=80$ or 100 forms rod. The conformational state of a CSPE is determined by the subtle competition among the electrostatic interactions, entropy and chain stiffness.

To discuss the shape of the CSPEs further, another two characteristic quantities are introduced to characterize its shape. The mean radius of gyration $\langle R_g^2 \rangle^{1/2}$ scaled by its equi-

librium value is calculated to analyze the conformation of the CSPE with different b and A , as shown in Fig. 9(a). The value of the $\langle R_g^2 \rangle^{1/2}$ can be used as a reasonable dividing boundary among the different conformations. To know the conformation of the CSPE in detail, its average shape factor $\langle \sigma \rangle$ is studied, as shown in Fig. 9(b). The $\langle \sigma \rangle$ is calculated by the method reported.^[42,43] It varies between 0 (sphere) and 1 (rod).

The inset of Fig. 9(a) shows that $\langle R_g^2 \rangle^{1/2}$ of $b=0$ decreases with A increase. The $\langle R_g^2 \rangle^{1/2}$ curves of $b>0$ are totally different from that of $b=0$, as shown in the main plot of Fig. 9(a). It can be observed that the $\langle R_g^2 \rangle^{1/2}$ of $b>0$ have several plateaus with A increase. Shifting from one plateau to another plateau in-

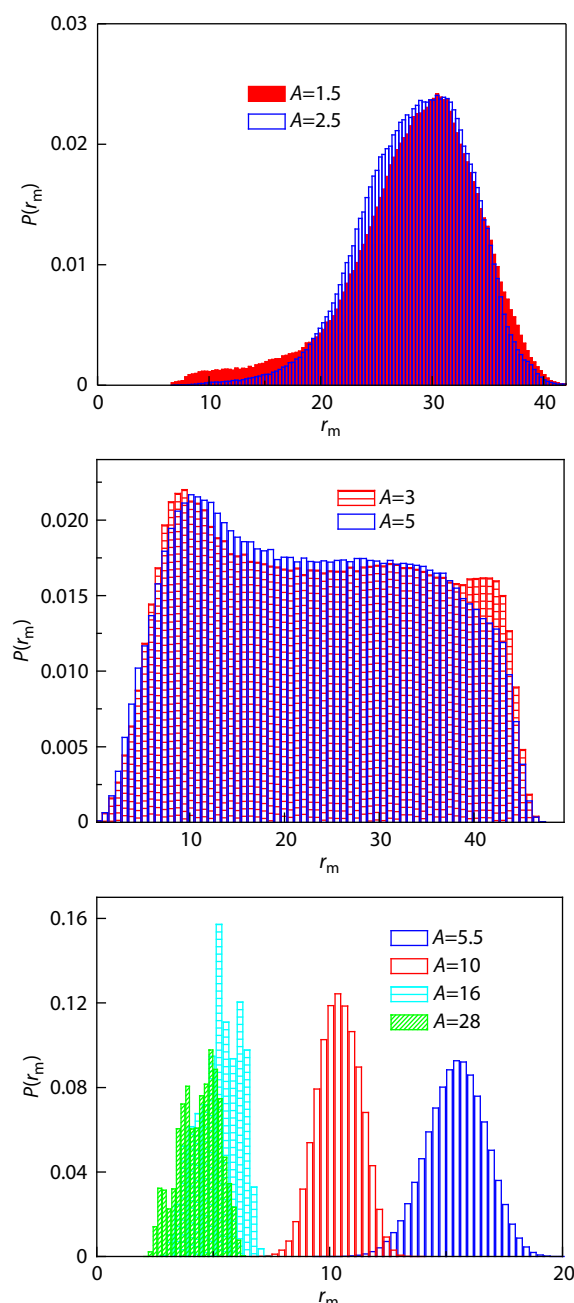


Fig. 5 The number density of monomers $P(r_m)$ as a function of the distance r_m from the center of mass of circular semiflexible polyelectrolyte for different dimensionless Bjerrum length A at $b=60$.

indicates the occurrences of the chain conformation change. The first plateau appears at small A . The contribution of attractive EI to the free energy is too small to compete with bending energy and entropic contribution. The CSPE forms oblate ring, and the transition points of $\langle R_g^2 \rangle^{1/2}$ and $\langle \sigma \rangle$ are totally in agreement, as shown in Figs. 9(a) and 9(b). The more rigid the chain is, the more difficult the chain deforms. That is why the plateau becomes broader and broader with b increase. The $\langle R_g^2 \rangle^{1/2}$ abruptly shifts to the second plateau with A increase. The feature is the characteristic of conformational transitions. When the $\langle R_g^2 \rangle^{1/2}$ shifts from the first plateau to

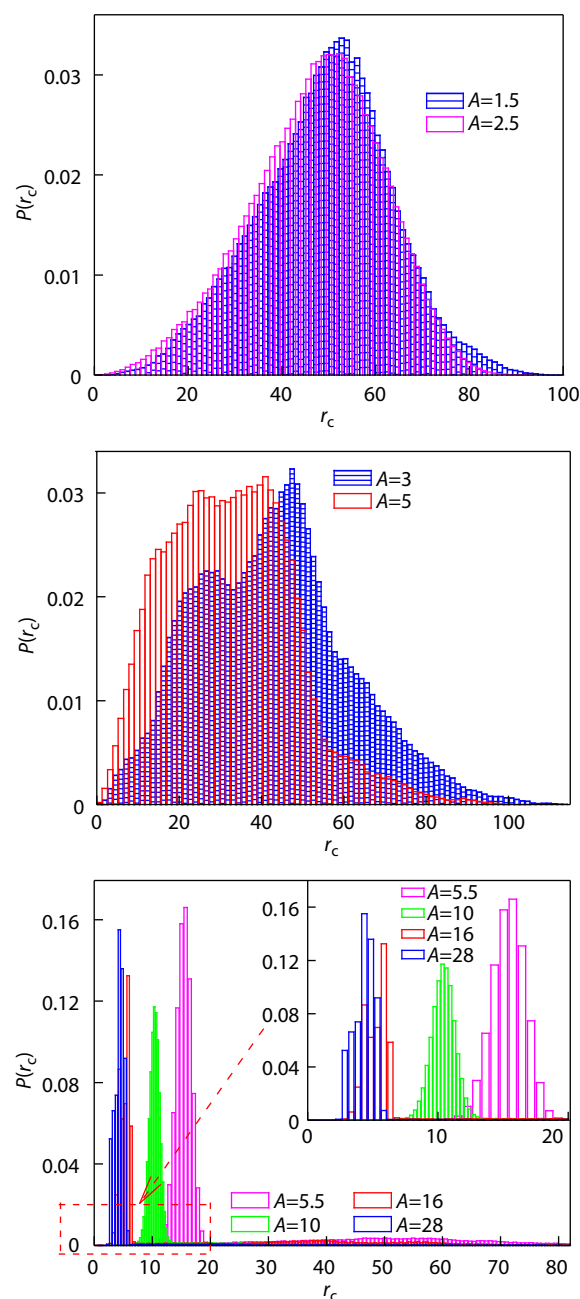


Fig. 6 The number density of counterions $P(r_c)$ as a function of the distance r_c from the center of mass of circular semiflexible PE for different dimensionless Bjerrum length A at $b=60$.

the second plateau, the declining amplitude is small. The contribution of electrostatic attraction to the free energy becomes large but attractive EI does not take the dominant role. The conformation results from the competition between the bending energy and attractive EI. The shape of the CSPE is rod, as shown in Fig. 9(b). As the $\langle R_g^2 \rangle^{1/2}$ increases further, it abruptly shifts to third plateau for $b=40, 60, 80$ and 100 , and the height of plateau is the same. In addition, the declining amplitude is very large. It indicates that the CSPE experiences drastic phase transition. The CSPE folds into toroid with $N_{\text{ring}}=2$. As the $\langle R_g^2 \rangle^{1/2}$ shifts to new plateau, the size of toroid

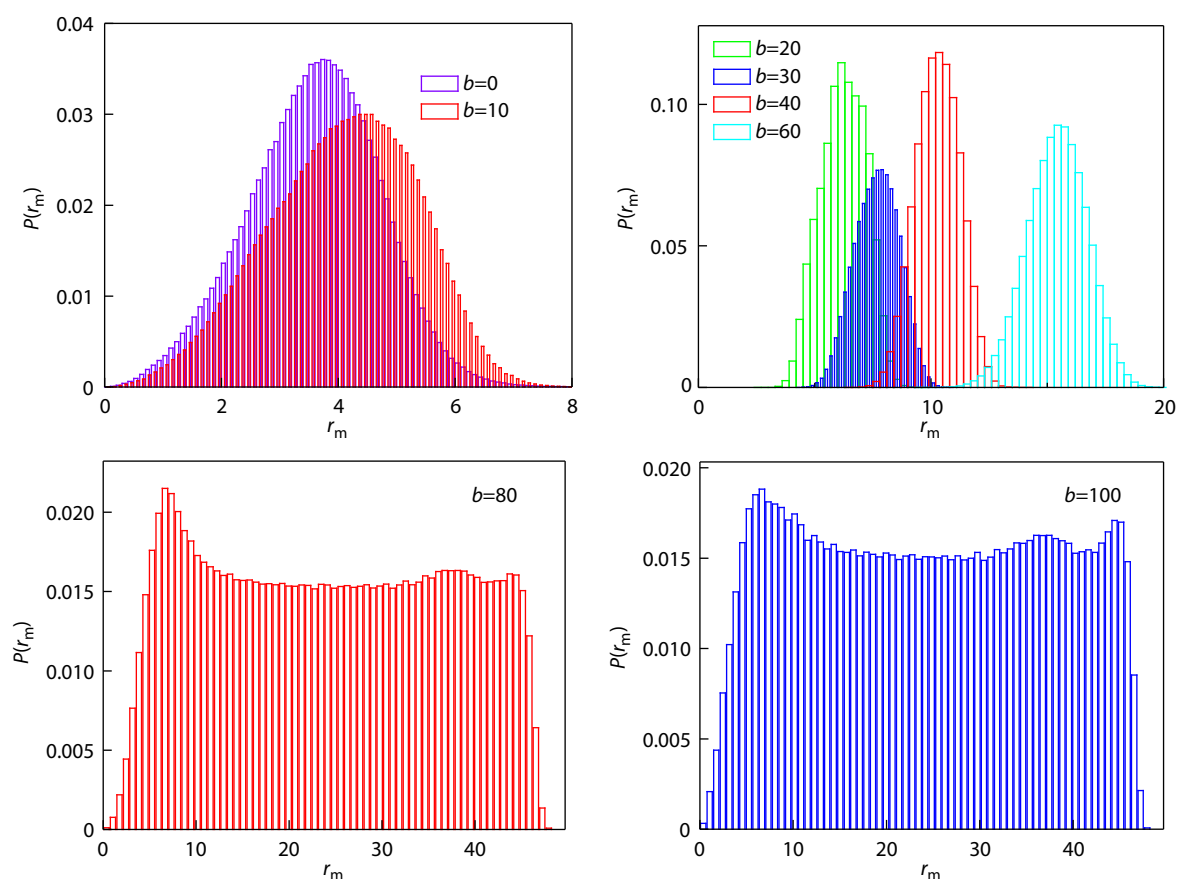


Fig. 7 The number density of monomers $P(r_m)$ as a function of the distance r_m from the center of mass of circular polyelectrolyte for different bending energy b at $A=5.5$.

becomes much smaller and the N_{ring} increases one, except the last plateau of $b=20$ and 40 . The CSPE of $b=20$ and 40 forms globule at $A \geq 16$ and $A \geq 26$, respectively, as shown in Fig. 9(b).

Phase Diagram of the Circular Semiflexible Polyelectrolyte

Summarizing the above results, we have constructed the diagram of states of the CSPE in terms of bending energy b and the dimensionless Bjerrum length A . It is shown in Fig. 10 where the following stable states are distinguished depending on b and A : rod, toroid, globule, oblated ring. We do not distinguish toroid of different N_{ring} . In the torus region, the size of the toroid changes depending on both b and A . The N_{ring} increases with A increase, while it decreases with b increase. To check the stability of these conformation, we start simulations from different initial conformations in each independent run, and ten independent runs are performed at any particular values of b and A .

The shape of circular polyelectrolyte of $b=0$ changes from oblated ring to globule with A increase. As the circular polyelectrolyte is of stiffness, the phase transition of CSPE is different from that of circular flexible polyelectrolyte, as shown in Fig. 10. At $b=10-50$, an increase of A can cause three subsequent transitions, first, the transition from oblate ring into rod at small A , then from rod to toroid at moderate A , finally from toroid to globule at large A . The CSPEs of $b=60-100$ firstly form oblate ring, then fold into rod, finally

condense into toroid with A increase from $A=0.5$ to 28 . The stiffer the CSPE is, the larger both regions of oblate ring and rod are.

Based on the state diagrams shown in Fig. 10, one can conclude that the conformation of the CSPE can be tuned by a fine balance between the electrostatic interactions, chain rigidity as well as entropy. As the attractive EI is weak, the chain rigidity and intrachain electrostatic repulsion are favourable. That is why the CSPE adopts oblate ring at small A . The oblate ring can be considered to consist of two bent rods. The effect of counterion-bridging becomes obvious, and the electrostatic attractions pull together. When A increases, these electrostatic attractions are large enough to drive the CSPE draw close to become large rod. The counterions can induce aggregation of similarly charged rod-like polyelectrolyte chains.^[44] In the rod-like region, the conformation of the CSPE results from the competition between bending energy b and attractive EI. However, any of them does not play dominant role. The linear semiflexible polyelectrolyte chain can fold into rod upon addition of tetravalent salt.^[45] When the A increases further, the electrostatic attraction is large enough to drive the CSPE deform to form two looplike structure. The small one is the nucleus. The nucleation can occur at essentially any point along the chain contour. This nucleus then grows by circumferentially wrapping other monomers until all monomers are in the toroid. In the torus region, the attractive EI is favourable and the effect of intrachain electro-

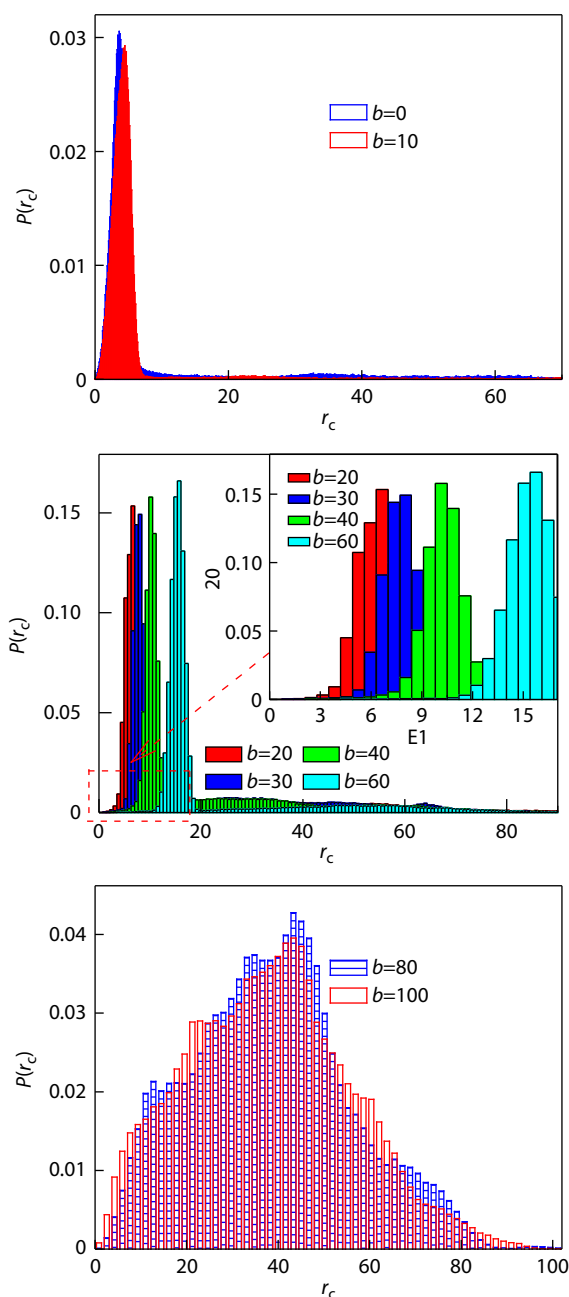


Fig. 8 The number density of counterions $P(r_c)$ as a function of the distance r_c from the center of mass of circular semiflexible PE for different bending energy b at $A=5.5$.

static repulsion weakens, but it does not play the dominant role. Although the attractive EI is large enough to drive the CSPE bend, it is not large enough to drive the CSPE collapse. In the globular region, the attractive EI plays the dominant role. It is large enough to drive the CSPE collapse into globule.

CONCLUSIONS

In summary, we reported on the results of a MD simulation study of the conformational behavior of a circular semiflexible polyelectrolyte (CSPE) in presence of trivalent counterions. The stiffness of circular polyelectrolyte is introduced via a potential

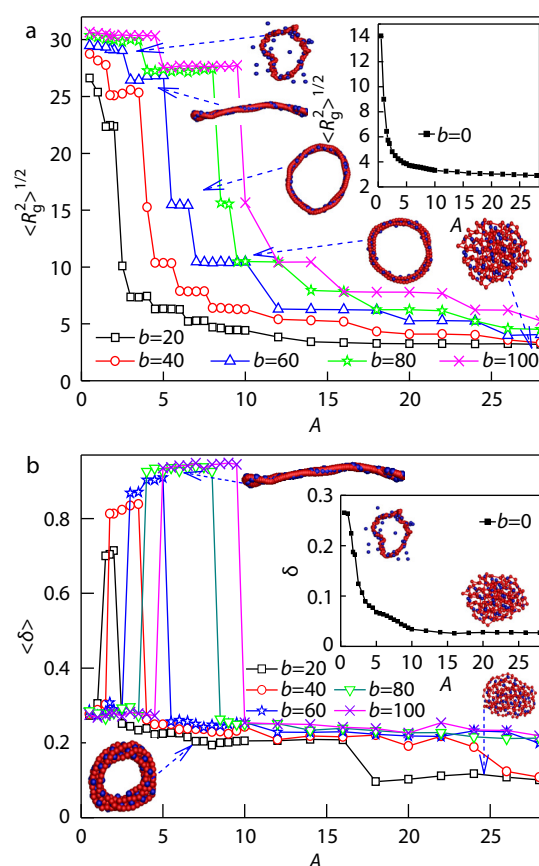


Fig. 9 (a) Mean radius of gyration $\langle R_g^2 \rangle^{1/2}$ as function of the dimensionless Bjerrum length A at different bending energy b ; (b) Shape factor δ as function of A at different bending energy b .

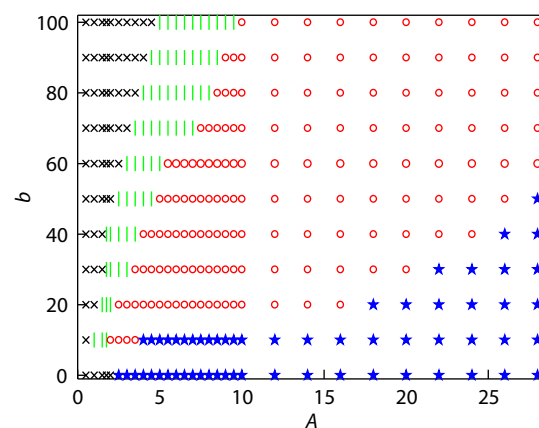


Fig. 10 The circular polyelectrolyte state diagram in the values of the bending energy b and the dimensionless Bjerrum length A . black $\times$ denotes oblated ring, green $|$ denotes rod, red $\circ$ denotes toroid, blue $\star$ denotes globule.

depending on the angle between two adjacent bond vectors with the stiffness parameter b . The effect of electrostatic interaction (EI) and the role of chain stiffness on the CSPE's conformation are discussed in detail.

We consider a wider range of the bending energy b and the dimensionless Bjerrum length A in our simulation to understand the basic physical concepts behind the structural prop-

erties of the CSPE. It can be observed that the CSPE chain morphology crucially depends on b and A . The phase transition of the CSPE is totally different from that of the circular flexible polyelectrolyte. the CSPE of $b=10-50$ transforms from oblate ring to rod with A increase at weak EIs, and then collapses into toroidal structure at intermediate EIs, eventually attains globule at large EI. The shape of the CSPE of $b=60-100$ is toroid at large EIs, and the number of torus ring increases with A increase. The conformation of the CSPE can be tuned by a fine balance between the EIs, chain stiffness as well as entropy of the system. When the attractive EIs and chain stiffness dominate and any of them does not take advantage, the CSPE adopts rod-like conformation. When the attractive EIs takes advantage while it is not large enough to drive the CSPE collapse, the CSPE folds into toroid.

Our research presented here goes further to investigate in detail the microstructure of a CSPE, which gives us a thorough vision of the behavior of polyelectrolytes in presence of counterions. We believe that the results obtained can improve our understanding of the conformational behavior of charged biopolymers.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2842-x>.

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