Conformational transitions of a weak polyampholyte

Arun Kumar Narayanan Nair, Sahin Uyaver, and Shuyu Sun

Citation: *The Journal of Chemical Physics* **141**, 134905 (2014); doi: 10.1063/1.4897161View online: <http://dx.doi.org/10.1063/1.4897161>View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/141/13?ver=pdfcov>Published by the [AIP Publishing](#)

Articles you may be interested in[A statistical theory of cosolvent-induced coil-globule transitions in dilute polymer solution](#)J. Chem. Phys. **141**, 014902 (2014); 10.1063/1.4884958[Conformational transitions of weak polyacids grafted to nanoparticles](#)J. Chem. Phys. **137**, 144704 (2012); 10.1063/1.4757284[First-order conformation transition of single poly\(2-vinylpyridine\) molecules in aqueous solutions](#)J. Chem. Phys. **126**, 091104 (2007); 10.1063/1.2711804[Stoichiometric polyelectrolyte complexes as comb copolymers](#)J. Chem. Phys. **122**, 084902 (2005); 10.1063/1.1849160[Configurational properties of a single semiflexible polyelectrolyte](#)J. Chem. Phys. **115**, 4367 (2001); 10.1063/1.1386924

Conformational transitions of a weak polyampholyte

Arun Kumar Narayanan Nair,^{1,a)} Sahin Uyaver,² and Shuyu Sun¹

¹Computational Transport Phenomena Laboratory, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia

²Istanbul Commerce University, Faculty of Applied Sciences, Istanbul, Turkey

(Received 1 August 2014; accepted 23 September 2014; published online 6 October 2014)

Using grand canonical Monte Carlo simulations of a flexible polyelectrolyte where the charges are in contact with a reservoir of constant chemical potential given by the solution pH, we study the behavior of weak polyelectrolytes in poor and good solvent conditions for polymer backbone. We address the titration behavior and conformational properties of a flexible diblock polyampholyte chain formed of two oppositely charged weak polyelectrolyte blocks, each containing equal number of identical monomers. The change of solution pH induces charge asymmetry in a diblock polyampholyte. For diblock polyampholyte chains in poor solvents, we demonstrate that a discontinuous transition between extended (tadpole) and collapsed (globular) conformational states is attainable by varying the solution pH. The double-minima structure in the probability distribution of the free energy provides direct evidence for the first-order like nature of this transition. At the isoelectric point electrostatically driven coil-globule transition of diblock polyampholytes in good solvents is found to consist of different regimes identified with increasing electrostatic interaction strength. At pH values above or below the isoelectric point diblock chains are found to have polyelectrolyte-like behavior due to repulsion between uncompensated charges along the chain. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4897161>]

I. INTRODUCTION

Charged polymers are macromolecules that contain ionizable groups that dissolve in polar solvents, leaving charged monomers on polymer backbone and releasing counterions into solution.¹ Charged polymers can be classified into polyelectrolytes with a single sign of charged monomers and polyampholytes with both positive and negative charges on the same chain.^{2–4} Many charged polymers found in nature, including proteins, are in fact polyampholytes. In recent years, polyelectrolytes and polyampholytes have received considerable interest especially because of their importance in biology, materials science, and soft matter research.^{5,6} Depending on the different dissociation behavior one can distinguish between weak and strong polyelectrolytes, a classification widely used in the chemistry community,¹ or between annealed and quenched polyelectrolytes, the common classification of the same polymers used in the physics community.⁷

Weak or annealed polyelectrolytes, for example, poly(acrylic acid), dissociate in a limited pH range only. Because of dissociation and recombination of ion pairs, the charges can effectively move along the chain. The imposed quantity is the chemical potential of the charges, which is equal to the pH of the solution except for a trivial additive constant. Therefore, by tuning the pH of the solution, the total charge of the polymer can be monitored. In the absence of electrostatic interactions (ideal case), and according to the solution pH, the fraction of charged monomers in a polymer

is

$$f = \begin{cases} \frac{1}{1+10^{\text{pK}_0^{\text{A}}-\text{pH}}}; & \text{(acid)} \\ \frac{1}{1+10^{\text{pH}-\text{pK}_0^{\text{B}}}}; & \text{(base)}, \end{cases} \quad (1)$$

where pK_0^{A} and pK_0^{B} are the intrinsic pK_a of acid and base, respectively. Generally, the intrinsic pK_a of the charged polymer will be replaced by an apparent one in Eq. (1) because of electrostatic interaction between charges. The difference between the apparent and intrinsic dissociation constants, e.g., of an acid is obtained as^{8–11}

$$\Delta\text{pK} = \text{pH} - \text{pK}_0^{\text{A}} - \log(f/(1-f)). \quad (2)$$

The ΔpK is related to the electrostatic contribution to the chemical potential defined by

$$\mu_{\text{el}} = (1/N)(\partial F_{\text{el}}/\partial f), \quad (3)$$

where $F_{\text{el}}(f)$ represents the electrostatic free energy of the chain via

$$\Delta\text{pK} \approx \mu_{\text{el}}/(k_{\text{B}}T \ln 10). \quad (4)$$

Note that at finite screening, the self-energy of a released proton gives an additional contribution to ΔpK in Eq. (4).¹² The specific properties of weak polyelectrolytes have attracted considerable interest in experimental,^{11,13} theoretical,^{7,10,14,15} and simulation studies.^{8,9,16–21} On the other hand, strong or quenched polyelectrolytes, for example, poly(sodium styrene sulfonate), where the distribution of charges along the backbone is solely imposed by polymer synthesis dissociate completely in the total pH range accessible by experiment. The rich behavior of strong polyelectrolytes is qualitatively different from that of uncharged polymers.^{4,22–25}

^{a)} Author to whom correspondence should be addressed. Electronic mail: arun.narayanannair@kaust.edu.sa

The behavior of polyelectrolytes in solutions strongly depends on the solvent quality for polymer backbone. Many polymers are based on a hydrophobic hydrocarbon backbone, and the solubility of polyelectrolytes in water is often only given by charged side groups. To minimize the interfacial area with the solvent an uncharged hydrophobic polymer immersed in water forms a globule.²⁶ After adding charges to the polymer the globule loses its spherical shape²⁷ and can form pearl necklaces.^{28–31} Molecular dynamics simulations of partially charged polyelectrolytes with explicit counterions in poor solvent conditions have shown that polyelectrolyte chains at dilute polymer concentrations adopt necklace-like conformation only in the narrow range of the interaction parameters.³⁰ A similar trend in Monte Carlo (MC) simulations of titration of hydrophobic polyelectrolytes have been observed where depending on the solvent quality for polymer backbone and pH – pK₀ value, a polyelectrolyte chain could be in five different conformational states: coil, globule, pearl necklace, sausage-like conformation, and fully stretched chain.⁸

Raphael and Joanny have analyzed the behaviour of weakly charged quenched polyelectrolytes in a salt-free poor solvent using Khokhlov blob model.^{7,27} The crucial point is that the electrostatic contribution to the chemical potential has a nonmonotonic variation with the degree of ionization.⁷ For $\tau > N^{-1/2}$, where the solvent quality is measured by the dimensionless distance from the Θ -point, $\tau = 1 - T/\Theta$ and N is the number of monomers, the chain size and the chemical potential can thus be calculated to be

$$\frac{R_g}{b} \approx \begin{cases} (N/\tau)^{1/3}; & f < (\tau/(Nu))^{1/2} \\ N(u f^2)^{2/3}/\tau; & (\tau/(Nu))^{1/2} < f < (\tau^3/u)^{1/2} \\ N(u f^2)^{1/3}; & f > (\tau^3/u)^{1/2} \end{cases} \quad (5)$$

and

$$\frac{\mu_{el}}{k_B T} \approx \begin{cases} f u (\tau N^2)^{1/3}; & f < (\tau/(Nu))^{1/2} \\ (u/f)^{1/3} \tau; & (\tau/(Nu))^{1/2} < f < (\tau^3/u)^{1/2} \\ (f u^2)^{1/3}; & f > (\tau^3/u)^{1/2}, \end{cases} \quad (6)$$

respectively. In the above equations, the dimensionless parameter $u = \lambda_B/b$, where b is the bond length and $\lambda_B = e^2/4\pi\epsilon_0\epsilon k_B T$ is the Bjerrum length that determines the strength of the Coulomb interaction.

For an annealed polyelectrolyte in a poor solvent, a first-order conformational transition from a globule to an extended state of the chain predicted by theory⁷ was confirmed by simulations.^{18–20} This phenomenon explains the anomalous titration curves and the sharp increase in the viscosity observed in experiments.^{11,32} Note, however, that if the system is close to the Θ point the discontinuous phase transition is suppressed and intermediate structures, such as pearl necklaces, can be stable.^{7,19}

However, if the polyelectrolyte is in reasonably good or Θ solvents, the electrostatic chemical potential is a smooth monotonic increasing function of charge fraction.^{7,16,21} For a given pH, average charge fraction is well defined and the properties of the chains are very similar to that of quenched

polyelectrolytes except a non-homogeneous charge distribution close to chain ends.^{14,17} The chain size and the ΔpK can thus be calculated, for example, in a Θ solvent to be^{14,16,24}

$$\frac{R_g}{b} \approx N(\ln N)^{1/3} (u f^2)^{1/3} \quad (7)$$

and

$$\Delta pK \approx (\ln N)^{2/3} (f u^2)^{1/3}, \quad (8)$$

respectively. Polyelectrolytes are more strongly stretched in the middle than at the ends,^{14,24} which yields a weak logarithmic correction in Eqs. (7) and (8).

If one type of charge is in large excess, properties of polyampholytes are similar to those of polyelectrolytes.³ If the polyampholytes are nearly charge-balanced, polymer properties depend noticeably on the charge distribution along the chain backbone. The opposite charges can, e.g., be distributed randomly along the chain, or similar charges can be arranged into blocks. One principal advantage of polyampholytes is that their association and stabilization behavior can be easily regulated by adjusting solution pH. This leads to many potential applications⁵ and considerable interest in experimental,^{33–40} theoretical,^{2,28,41–45} and simulation^{46–56} studies of polyampholytes. The conductivity, viscosity, as well as coil size of random polyampholytes have a minimum at the isoelectric conditions where there are equal numbers of positive and negative charges on the polymer backbone.³ Random polyampholytes collapse into globules due to the attractive interactions between the opposite charges along the chain and have a strong tendency to precipitate in the vicinity of the isoelectric point. The present understanding of, in particular, random polyampholytes in solution and their interaction with polyelectrolytes and surfaces has recently been reviewed.³ The localization of like charges within a block causes stronger electrostatic attraction between oppositely charged sections. Thus, at the isoelectric point, diblock polyampholytes have a stronger tendency to precipitate compared to random polyampholytes.^{33,34} At pH values above or below the isoelectric point, block polyampholytes possess a net charge and can associate into soluble micelles.^{33,35} Recently, computer simulations of a single diblock polyampholyte^{48–50} and theoretical studies of diblock polyampholytes in solutions^{43,44} have been performed. Grand canonical Monte Carlo simulations have also been performed to study the phase diagram of diblock polyampholyte solutions.⁵¹ A charge-symmetric diblock polyampholyte chain with equally charged positive and negative blocks collapses into a globule, while a charge-asymmetric block polyampholyte has a tadpole shape with a globular head and a polyelectrolyte tail.⁴⁴ The association of block polyampholytes is driven by the charge density fluctuation-induced attractive interactions between oppositely charged blocks.^{43,44} The conformational properties of symmetric flexible diblock polyampholytes with fixed charge distributions along the polymer backbone have been investigated by using scaling theory and molecular dynamics simulations.^{44,48} The physical picture of weakly associated globules is a dense packing of electrostatic blobs where each blob is predominantly surrounded by oppositely charged blobs. The size of

the symmetric diblock polyampholyte globule can thus be calculated to be^{43,44,48}

$$\frac{R_g}{R_{g0}} \approx [\lambda_B(fN)^2/R_{g0}]^{(1-3\nu)/[3(2-\nu)]}, \quad (9)$$

where $R_{g0} \approx N^\nu b$ is chain size in the absence of electrostatic interactions, and the value of the scaling exponent ν is 0.5 in a Θ -solvent and 0.588 in a good solvent. In addition, systems composed of diblock polyampholytes grafted onto uncharged spherical particles^{54,55} and flat surfaces⁵⁶ were investigated by computer simulations. Monte Carlo simulations^{54,55} revealed that the brush structure of anchored diblock polyampholytes strongly depends on charges of the blocks and the chain flexibility. Molecular dynamics simulations showed a linear dependence of the average brush thickness of flexible, semi-flexible, and rodlike diblock polyampholytes on the grafting density regardless of different flexibility of anchored chains.⁵⁶

Despite recent interest,^{33–40,45,52,53} understanding of block polyampholytes carrying weak acids or bases still constitutes a challenging area for both fundamental and applied studies. Using Monte Carlo simulations in the grand canonical ensemble Ulrich *et al.* systematically studied polyampholytes carrying weak acids or bases by considering titration curves.⁵² Simulations with screened Coulomb potentials for different primary structures such as statistical (diblock, octablock, and alternating) and random polyampholytes obtained various chain conformations such as extended, globular, and pearl-necklace conformations.⁵² The complexation behavior of a weak polyampholyte with a positively charged nanoparticle was also investigated.⁵³ It was found that nanoparticle charge inversion is an important ingredient for the formation of multilayer structures at the nanoparticle surface.

The aim of our paper is to present a systematic investigation on the conformational properties of weak polyampholytes in order to understand the underlying physical mechanism of their coil-to-globule transition. We extend the earlier investigation^{52,53} on the conformational properties of diblock polyampholytes in good solvents to include the important case of varying solvent conditions. We have performed extensive grand canonical Monte Carlo simulations in order to study the influence of solution pH on ionization and conformational properties of a flexible diblock polyampholyte chain formed of two oppositely charged weak polyelectrolytes each containing equal number of identical monomers, in both good (hydrophilic) and poor (hydrophobic) solvent conditions. These are compared to the titration behavior of homopolymers, and differences in their behavior are discussed in the context of polyelectrolyte theory. We demonstrate that a first order transition between collapsed and extended chains of a diblock polyampholyte can be obtained by varying the solution pH. We expect that our model could help design experiments with a better understanding of the interplay between electrostatic and hydrophobic/hydrophilic interactions in polyampholytes. Polyampholytes are also of interest as they provide simple but useful models to investigate the protein-folding.⁵⁰ The outline of the paper is as follows: In Sec. II, we describe the model of diblock polyampholytes and the details of our Monte Carlo simulations. The

simulation results are presented in Sec. III and a brief summary as well as our conclusions can be found in Sec. IV.

II. SIMULATION MODEL AND METHOD

The polymer is represented by the standard bead-spring chain model.^{22,30,31} For a diblock polyampholyte, each N-mer consists of two blocks, namely, A and B. The A block is considered to be an acid (each monomer carries zero charge in the protonated state and one negative unit of charge in the deprotonated state) and the B block represents a base (each monomer carries zero charge in the deprotonated state and one positive unit of charge in the protonated state). In the present paper, we focus on the case with the same number of monomers ($N/2$) in each block. All monomers interact via a truncated-shifted Lennard-Jones (LJ) potential

$$U_{\text{LJ}}(r) = \begin{cases} 4\epsilon_{\text{LJ}} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{R_C}\right)^{12} + \left(\frac{\sigma}{R_C}\right)^6 \right]; & r \leq R_C \\ 0; & r > R_C, \end{cases} \quad (10)$$

where r is the distance between the centers of two monomers, and R_C is the cutoff radius. The parameter ϵ_{LJ} controls the strength of the short-range interactions, and the LJ diameter σ is used to set the length scale. We present the results for both poor and athermal (good) solvent conditions. For the good solvent condition, the cutoff R_C is taken to be $2^{1/6}\sigma$, thus presenting a purely repulsive potential U_{LJ} . The interaction parameter of this potential is chosen to be $\epsilon_{\text{LJ}} = k_B T$, where k_B is the Boltzmann constant and T is the absolute temperature. For the poor solvent, a larger cutoff $R_C = 2.5\sigma$ is utilized in order to include the attractive interaction between the monomers, and a value of $\epsilon_{\text{LJ}} = 1.5k_B T$ is used for the LJ parameter, which is far below the Θ point corresponding to $\epsilon_{\text{LJ}}^\Theta \approx 0.34k_B T$ for the uncharged system.³¹

The connectivity of the bonded monomers is maintained by the finite extensible nonlinear elastic (FENE) potential

$$U_{\text{FENE}}(r) = -\frac{1}{2} k_{\text{FENE}} R_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right), \quad (11)$$

where the spring constant $k_{\text{FENE}} = 7k_B T/\sigma^2$ and the maximum bond length $R_0 = 2\sigma$ at which the elastic energy of the bond becomes infinite.^{30,31} The solvent is modeled as a continuous dielectric medium with dielectric constant ϵ . The charged monomers are thus interacting with each other via the unscreened Coulomb potential

$$U_{\text{Coul}}(r_{ij}) = k_B T \frac{\lambda_B q_i q_j}{r_{ij}}, \quad (12)$$

where r_{ij} is the distance between the centers of i and j particles, and q_i is the charge valence of the i th particle, equal to -1 ($+1$) for the monovalent negative (positive) charges and 0 for the neutral monomers. The Bjerrum length $\lambda_B = e^2/(\epsilon k_B T)$, where e is the elementary charge, determines the strength of the electrostatic interactions.

Equilibrium properties are studied by using standard Metropolis MC simulation. To equilibrate both long and short

length scales, we combine two different configurational MC moves: (i) local and (ii) pivot. During local moves a random displacement is given to a randomly chosen monomer. In a pivot move, the randomly chosen connected chain on either side of a randomly picked monomer is randomly rotated around that monomer. The annealed polyelectrolyte or polyampholyte is simulated in a grand canonical ensemble where the chain is in contact with a reservoir of charges of fixed chemical potential imposed by the solution pH via^{12,52,53}

$$\frac{\mu}{k_B T} = \begin{cases} -\ln 10 (\text{pH} - \text{pK}_0^A); & (\text{acid}) \\ \ln 10 (\text{pH} - \text{pK}_0^B); & (\text{base}). \end{cases} \quad (13)$$

Exactly speaking the ensemble is a semi-grand canonical one where the total number of particles (monomers) is fixed but the number of particles which carry a charge is fluctuating. In addition to the configurational MC moves introduced above the algorithm is completed with a charge move by which the charge state of a randomly chosen monomer is switched. The energy change of a complete MC move reads

$$\Delta E = \Delta E_c \pm \mu, \quad (14)$$

where ΔE_c is the change in configurational energy

$$\Delta E_c = \Delta U_{LJ} + \Delta U_{\text{FENE}} + \Delta U_{\text{Coul}}. \quad (15)$$

The $\pm$ sign in Eq. (14) was changed depending on whether a protonation or deprotonation was attempted.

We also employed a conservative early-rejection scheme⁵⁷ for accelerating MC simulations of uncharged polymers. The conservative early-rejection MC scheme satisfies the detailed balance and uses exactly the same standard Metropolis criterion to check whether a move is accepted or rejected. We prefer the conservative early-rejection scheme over the conventional Metropolis because the latter computes all the interactions before checking the acceptance/rejection condition, while the former checks the condition at every step of the loop assuming that the unevaluated interactions contributes with the minimum energy possible, $U_{\min}$. The interactions at the new position are separated into two terms. The first term collects the evaluated interactions up to say the k th particle, and the second accounts for the unevaluated interactions for the rest of the particles (i.e., the $N - k$ particles). Thus, a move is rejected if and only if the following inequality is true:

$$\sum_{j=1, j \neq i}^k U_{ij}^n + U_{\min}(N - k) > \sum_{j=1, j \neq i}^N U_{ij}^o - k_B T \ln(R), \quad (16)$$

where R is a uniformly generated random number in the interval $[0,1]$, U_{ij}^n accounts for the energy associated with the displaced particle i at the new position due to the interaction with the other j particles, while U_{ij}^o is the energy associated with it at the old position. In reality, of course, not all the remaining particles are at this exact distance corresponding to the minimum energy ($U_{\min}$) away from the translated particle. However, if at any stage along the loop, the relation in Eq. (16) was true, with this minimum energy associated with

the remaining $N - k$ particles, then this move is guaranteed to be rejected regardless if the calculations proceeded or not.

To ensure that the simulations generate equilibrium data we start from both straight and random initial conformations and require that after appropriate relaxation they yield identical averaged quantities. For local MC moves, random displacements are chosen uniformly from the intervals $-0.5\sigma \leq \Delta x, \Delta y, \Delta z \leq 0.5\sigma$. A 1:1:200 combination of the local, charge and pivot MC moves, respectively, was found to be the most efficient choice. Details on the general simulation route as well as on statistical error analysis can be found in Ref. 19. Each diblock polyampholyte is equilibrated for a period of $3 \times 10^6 - 5 \times 10^6$ Monte Carlo steps per monomer (MCM), and the physical properties of the chain are obtained by averaging over the production run of $6 \times 10^6 - 7 \times 10^6$ MCM after the equilibration. The simulation results presented below are obtained by averaging the production data over six trajectories which started from different initial conformations. Finally, the relative error of the root mean square end-to-end distance was found to be less than 5% and the fraction of charges are reproducible within less than 2% independently of the conformation of the charged polymer.

III. SIMULATION RESULTS

We have investigated weak polyelectrolytes (homopolymers) consisting of $N = 128$, and 256 monomers. For the case of the diblock polyampholytes formed of two weak polyelectrolyte blocks, the number of monomers is taken to be $N = 64, 128$, and 256. Because of the fact that counterions are not treated explicitly in our model, the value of the Bjerrum length has to be chosen as $\lambda_B \lesssim \sigma$ to avoid problems with counterion condensation.³⁰ Therefore, our simulation results need to be compared with experiments where counterion condensation plays an insignificant role. In our simulations, we have set the Bjerrum length to the value $\lambda_B = \sigma$ unless otherwise stated. The Bjerrum length of bulk water is about 7.14 Å at room temperature, which sets the length scale for our simulation, i.e., $\sigma \approx 7.14$ Å. In our simulation, the average bond length is given by $b \approx \sigma$, leading to $b \approx 7.14$ Å and the dimensionless Manning ratio is $f\lambda_B/b \lesssim 1$, below the Manning condensation limit for a fully stretched chain.³⁰ The values of pK_0^A and pK_0^B are set to 5.5 and 7.5, respectively. The current choice, for example, is comparable to the apparent pK_a values cited in the experimental study of weak poly(methacrylic acid)/poly[2-(dimethylamino)ethyl methacrylate] diblock polyampholyte brush.³⁶ Note that our model could be extended to consider several types of monomers with specific intrinsic pK_a values so as to mimic the behavior of biopolymers^{52,53} such as proteins. In the previous simulation studies of diblock polyampholytes,⁵² pK_0^A and pK_0^B were arbitrarily set to 2.17 and 9.53, respectively. As we show below, our simulation results are in quite good agreement with earlier simulations.⁵² In the following, conformational changes of polyelectrolytes and diblock polyampholytes with the pH (or with the corresponding average charge fraction) are analyzed in detail in both poor and good solvent conditions for polymer backbone.

A. Titration curves

Titration curves are defined as the variation of average charge fraction f as a function of the solution pH and have been proven to be a valuable approach in the understanding of the acid-base properties of weak polyelectrolytes.^{8–10} The overall shape of the titration curve depends on the nature of the charged polymer that is titrated. Fig. 1 presents the simulation results of the titration curves for a diblock polyampholyte in the absence of electrostatic interactions between the monomers ($\lambda_B = 0$), where a perfect agreement with the theoretical prediction, Eq. (1) is obtained. The change of the solution pH induces charge asymmetry in weak polyampholytes. As shown in Fig. 1, at the isoelectric point, pH = 6.5, both the average charge fraction of the A block, f_A , and the average charge fraction of the B block, f_B , are equal. The charge fractions f_A and f_B as a function of solution pH are symmetric with regards to the pH value corresponding to the isoelectric point. Fig. 1 also serves as a test of the charge moves (see Eqs. (13) and (14)) used in the simulations of weak polyampholytes. Note that the simulation results in Fig. 1 are independent of polymer models or solvents used.

The electrostatic interactions between charges along the chain are expected to influence the titration curves of diblock polyampholytes.⁵² We present in Fig. 2 simulation results as solid symbols for average charge fraction of the B block f_B of the diblock polyampholyte as a function of the solution pH in (a) poor and (b) good solvent conditions for polymer backbone. The strength of electrostatic interactions $\lambda_B = \sigma$. The results of corresponding A blocks are not shown in Fig. 2 because titration curves of A and B blocks are symmetric with respect to the isoelectric point (pH = 6.5). As compared to ideal case represented by solid lines in Fig. 2, electrostatic interactions strongly influence the acid-base properties of flexible diblock polyampholytes in both poor and good solvents by promoting the coexistence domain of both negative and positive charges.

FIG. 1. Simulation results of average charge fractions of individual blocks f_A (circles) and f_B (squares) of a diblock polyampholyte chain, as a function of solution pH at vanishing electrostatic interactions between the monomers ($\lambda_B = 0$). The values of pK_0^A and pK_0^B are 5.5 and 7.5, respectively. Theoretical predictions of acid (dashed line) and base (solid line) are obtained using Eq. (1). The isoelectric point is at pH = 6.5.

FIG. 2. Titration curves of the diblock polyampholytes (solid symbols). Shown is average charge fraction of the B block f_B of the diblock polyampholyte as a function of solution pH: (a) poor, and (b) good solvent conditions for polymer backbone. The Bjerrum length $\lambda_B = \sigma$, $pK_0^A = 5.5$, and $pK_0^B = 7.5$. The ideal titration curves (solid lines) in (a) and (b) are the same as in Fig. 1. For a comparison, titration curves (open symbols) obtained using separate simulations of weak polyelectrolytes (homopolymers) having an intrinsic pK_a of 7.5, and the Bjerrum length $\lambda_B = \sigma$ are also presented for corresponding solvent conditions.

Ulrich *et al.*⁹ recently studied the complexation behavior of a weak polyelectrolyte with an oppositely charged nanoparticle, where it was shown that the presence of one oppositely charged nanoparticle significantly modifies the acid-base properties of the weak polyelectrolyte. For comparison purposes, titration curves obtained using separate simulations of corresponding weak polyelectrolytes (homopolymers) in poor and good solvents are shown as open symbols in Figures 2(a) and 2(b), respectively. A similar situation is obtained where the presence of an oppositely charged weak polyelectrolyte block significantly modifies the acid (base) property of a weak polyelectrolyte by promoting the formation of negatively (positively) charged monomers over the whole pH range in poor as well as good solvents. A notable observation, however, is a discontinuous transition of the average charge fraction as a function of pH for polyampholytes in poor solvents. The discontinuous transition^{7,18–20} of the average charge fraction is observed at pH ≈ 4 in the monoblock

case. Due to interactions between opposite charges, discontinuous transitions of diblock polyampholytes occur at relatively higher pH values ($\text{pH} \approx 12$). Below we provide more quantitative analysis and discussions about the results in Fig. 2 separately for each case. Note that, in order to compare theory and simulation, the pH value was converted to the corresponding ΔpK using Eq. (2).

B. Weak polyelectrolytes

In this section, we discuss simulation results by considering weak polyelectrolytes (homopolymers) in poor and good solvent conditions for polymer backbone. Previous studies have observed qualitative agreement between simulations^{18–20} and theoretical prediction⁷ that electrostatic chemical potential or ΔpK has a nonmonotonic variation with average charge fraction f in poor solvents. Here we show that our simulation results follow the scaling predictions⁷ by Raphael and Joanny not only on a qualitative but also on a semiquantitative level. In order to directly test theoretical predictions,⁷ Eqs. (5) and (6), in Fig. 3 we plot as symbols the simulation results of root-mean-square radius of gyration R_g , which is defined as

$$R_g = \left\langle \frac{1}{2N^2} \sum_{i,j=1}^N (\mathbf{r}_i - \mathbf{r}_j)^2 \right\rangle^{1/2}, \quad (17)$$

and ΔpK (Eq. (2)) of weak polyelectrolytes as a function of average degree of charging in poor solvent conditions. In order to collapse the data of different degree of polymerizations at high charge fractions, root-mean-square radius of gyration and ΔpK are rescaled according to Eqs. (7) and (8), respectively. The reason for fitting the simulation data obtained in poor solvent condition with the theoretical predictions (Eqs. (7) and (8)) derived for the ideal solvent case is justified by the fact that at high charge fractions the chain in a poor solvent behaves like rod of ideal blobs.⁷ The effect of the first-order transition is approximately marked by transition regimes with ΔpK decreasing as a function of average charge fraction in the plots. The insets of Fig. 3 show log-log plot of the data in the main figures which provide a more direct comparison of the simulation data with the theoretical predictions obtained for the poor solvent condition (Eqs. (5) and (6)). However, for the purpose of clarity, only the data for the degree of polymerization $N = 256$ are given in the insets. Overall, the simulation results are in good agreement with theoretical predictions.⁷ Note that deviation from the scaling predictions (see, e.g., insets of Figures 3(a) and 3(b) depicting power laws $4/3$ and $-1/3$, respectively) occur due to first-order transition.⁷

In addition, double-minima structures^{18,58} in probability distributions of free energy $E = E_c + \mu N_c$,¹² where N_c is the number of charged monomers, demonstrated that conformational transitions in our model indeed are of first order nature (see Fig. 4). The conformation of the weakly charged chain is globule,⁷ and this is found in one of the two minima of the free energy profile. At high charge fractions, the chain is elongated to, e.g., rod-like conformation of ideal blobs⁷ which could be found in the second minimum of the free energy profile. Since the two minima of the free energy profile have the

FIG. 3. Simulation results: (a) reduced root-mean-square radii of gyration and (b) reduced ΔpK as a function of average degree of charging for a weak polyelectrolyte (homopolymer) under poor solvent conditions. The Bjerrum length $\lambda_B = \sigma$. Lines are fits to guide the eye. The solid lines in (a) and (b) are given by equations $R_g = 0.14f^{2/3}N(\ln N)^{1/3}\sigma$ and $\Delta\text{pK} = 1.47f^{4/3}(\ln N)^{2/3}$, respectively, while the dashed lines are given by equations $R_g = 0.53N^{1/3}\sigma$ and $\Delta\text{pK} = 0.68fN^{2/3}$, respectively. Insets show log-log plot of the data in the main figures for the degree of polymerization $N = 256$. Solid lines in insets (a) and (b) are power law predictions of the scaling theory Eqs. (5) and (6) with $\Delta\text{pK} \approx \mu_{el}/k_B T$, respectively.

globule and extended character, respectively, the first-order-like transition we found in the poor solvent belongs to the globule-extended chain transition. Yamaguchi *et al.* showed that chain conformations near the transition state consists of one blob and one or two strings.²⁰ We obtained similar tadpole (one blob and one string) shaped conformations in the plateau region of the titration curves, where the pH remains almost constant, that closely resemble the first-order transition state²⁰ with relatively weakly charged globular head, while charges accumulate along the string. A detailed analysis of the conformational properties of chains demonstrating this transition as well as numerical evidence supporting the charge accumulation along the string of the tadpole can be found in previous simulation studies.^{18–20}

However, if the polyelectrolyte is in good solvents, the electrostatic chemical potential is a smooth monotonic increasing function of charge fraction.^{7,16,21} The

FIG. 4. Simulations results of the energy distribution function, $P(E)$, at pH = 3.7 demonstrating the first-order transition of a weak polyelectrolyte (homopolymer) in poor solvent conditions. Each arrow points to snapshot of an equilibrium conformation with the corresponding free energy. The neutral and charged monomers are colored red and blue, respectively. The Bjerrum length $\lambda_B = \sigma$ and the degree of polymerization $N = 256$.

conformational properties of a polyelectrolyte can be analyzed using the concept of electrostatic blobs.^{26,27} On length scales smaller than the electrostatic blob size, ξ_e , the chain statistics are almost unperturbed by the electrostatic interactions. Therefore, ξ_e and the corresponding number of monomers g_e in it are determined by the balance between the electrostatic and thermal parts of the free energy

$$\lambda_B k_B T (f g_e)^2 / \xi_e \approx k_B T, \quad (18)$$

where ξ_e follows the scaling law of a neutral chain:

$$\xi_e \approx g_e^\nu b, \quad (19)$$

and the value of the scaling exponent ν is about 0.588 in good solvents. Following Eqs. (18) and (19), the size of the electrostatic blob is

$$\xi_e \approx b(\lambda_B f^2 / b)^{-\nu/(2-\nu)}, \quad (20)$$

and the number of monomers inside the electrostatic blob is found to be

$$g_e \approx (\lambda_B f^2 / b)^{-1/(2-\nu)}. \quad (21)$$

On length scales larger than ξ_e , electrostatic interactions dominate and the blobs repel each other to form a fully extended chain of size

$$R_g \approx (N/g_e)\xi_e \approx N b(\lambda_B f^2 / b)^{(1-\nu)/(2-\nu)}. \quad (22)$$

The energy of a polyelectrolyte in the elongated conformation is on the order of the thermal energy $k_B T$ per electrostatic blob

$$F_{\text{polyel}} / k_B T \approx (N/g_e) \approx N(\lambda_B f^2 / b)^{1/(2-\nu)}. \quad (23)$$

From the definition of the electrostatic chemical potential (see Eqs. (3) and (4)), finally we obtain

$$\Delta pK \approx (1/N)(\partial F_{\text{polyel}} / \partial f) \approx (\lambda_B / b)^{1/(2-\nu)} f^{\nu/(2-\nu)}. \quad (24)$$

Logarithmic correction in the scaling formulation has been previously applied in the case of Θ solvent (Eqs. (7) and

FIG. 5. Simulation results of root-mean-square radii of gyration and ΔpK represented as circles in main figure and inset, respectively, as a function of average charge fraction for weak polyelectrolytes (homopolymers) in good solvent conditions. The Bjerrum length $\lambda_B = \sigma$. The lines are given by the equations $R_g = 32.64 f^{0.584} \sigma$ (solid line) and $\Delta pK = 4.10 f^{0.416}$ (dashed line).

(8)).^{14,16,24} The derivation of logarithmic correction in good solvent case is non-trivial and it is out of scope in this paper. However, the logarithmic correction is observed to modify mainly the scaling dependence of ΔpK or R_g on degree of polymerization N and not on average charge fraction f .¹⁶ To verify the predictions derived above, in Fig. 5 we plot root-mean-square radius of gyration and ΔpK as a function of average charge fraction for weak polyelectrolytes in good solvent conditions. The simulation results indicate that the conformational transitions are correctly predicted by Eqs. (22) and (24).

C. Diblock polyampholytes in poor solvents

In this section, we analyze simulation results by considering the case of diblock polyampholytes formed of ionizable groups of weak acids and weak bases in poor solvent conditions for polymer backbone. Simulations have been done sufficiently deep in the poor-solvent region, i.e., the corresponding neutral block is collapsing into a globular state. The simulation results of root-mean-square radii of gyration of an individual block of the diblock polyampholyte as a function of average charge fraction of the same block follow the scaling law for a neutral globule, $R_g \approx N^{1/3} \sigma$ (Eq. (5)) except for high charge fractions ($f_A = f_B \approx 1$). At high charge fractions, the individual block size of the diblock polyampholyte increases from $R_g \approx N^{1/3} \sigma$ to the single chain value $R_g \approx N(u)^{1/3} \sigma$ (Eq. (5)). As discussed above, in the case of a homopolymer under poor solvent conditions there is a cross over in the scaling law of chain size from $R_g \approx N^{1/3} \sigma$ at low charge fractions to $R_g \approx N(u f^2)^{2/3} \sigma$ for the intermediate charge fractions (Eq. (5)). However, due to interaction between opposite charges, a similar cross over of scaling law is absent in the corresponding case of the diblock polyampholytes. There is also negligible effect of the discontinuous transition on the scaling law of size of an individual block as a function of average charge fraction of the same block in the poor solvent

FIG. 6. The energy distribution function, $P(E)$, for the diblock polyampholyte with degree of polymerization $N = 256$ in poor solvent conditions at $\text{pH} = 11.65$ (dashed line) and $\text{pH} = 11.67$ (solid line). The Bjerrum length $\lambda_B = \sigma$, $\text{p}K_0^A = 5.5$, and $\text{p}K_0^B = 7.5$.

condition. The individual chain size still follows the scaling law of $R_g \approx N^{1/3}\sigma$ at intermediate charge fractions or in the discontinuous transition regime ($\text{pH} \approx 12$). In the vicinity of the isoelectric point, $\text{pH} = 6.5$, the diblock polyampholytes display globular conformations. In fact, in the whole pH range, the diblock polyampholyte chains exhibit either a globular conformation or a tadpole⁴⁴ conformation for the systems studied.

A well pronounced plateau, where the pH remains almost constant, in titration curves has been related to a discontinuous transition between collapsed and stretched states.^{7,15,18} Here we will focus on the plateaus we obtained in the titration curves of diblock polyampholytes in poor solvents (solid symbols in Fig. 2(a)). As suggested for weak polyelectrolytes in poor solvent, a direct way to determine the order of the phase transition is the histogram method of Lee and Kosterlitz.⁵⁸ Thus the double-minima structure in the probability distribution of the free energy, for example, provide direct evidence for the first-order nature of the transition.^{18,20} In Fig. 6, we plot the probability distribution of the corresponding free energy, $E = E_c + \mu(\text{acid})N_- + \mu(\text{base})N_+$,¹² where N_- and N_+ are the number of charged monomers in A and B blocks, respectively. The normalized distribution function $P(E)$ is related to the semi-grand potential via $\mathcal{A}/k_B T = -\ln P(E)$. The free energy distributions of the diblock polyampholytes in poor solvents have the double-minima structures, which clearly indicates that the polymers experience first-order transitions during the pH titrations.

Typical simulation snapshots that illustrate chain structures in the different transition regions at $\text{pH} = 11.65$ are shown in Fig. 7. The equilibrium snapshots are given at $E/(Nk_B T) \approx -4.3$, -4.2 , and -4.1 for Figures 7(a), 7(b), and 7(c), respectively. The probabilities for these different chain conformations to occur at $\text{pH} = 11.65$ are given by the corresponding $P(E)$ values (see Fig. 6). The snapshots suggest that the diblock polyampholyte has a globular or tadpole⁴⁴ shape with a globular head and a polyelectrolyte

FIG. 7. Typical simulation snapshots demonstrating a discontinuous transition of a diblock polyampholyte with degree of polymerization $N = 256$ in a poor solvent at $\text{pH} = 11.65$: (a) globule, (b) conformation that closely resemble the transition state, and (c) tadpole. The neutral, negatively charged and positively charged monomers are colored red, green, and blue, respectively. The Bjerrum length $\lambda_B = \sigma$, $\text{p}K_0^A = 5.5$, and $\text{p}K_0^B = 7.5$.

tail in the transition regions. We conclude, therefore, that the double minima structures obtained in the free energy distributions are the signature of first-order transitions between collapsed (globule) and extended chains (tadpole). Visual inspections of snapshots show that in the vicinity of the transition state (Fig. 7(b)), the head and tail sizes of the tadpole conformations⁴⁴ become approximately equal which has been confirmed by using a cluster-recognition algorithm known from the literature.^{19,30} In addition, there is a significant disbalance between the number of positively and negatively charged monomers within the head of the tadpole near the transition region. The net charges of the globular head and tail in the tadpole conformation, for example, shown in Fig. 7(c) are $\approx -30e$ and $\approx -37e$, respectively.

Note that a neutral nonalternating polyampholyte in a low dielectric solvent undergoes a first-order coil-globule transition as the temperature is varied.⁴¹ At this point, our simulation results have shown that discontinuous transitions of diblock polyampholytes in the degree of charging are closely associated with discontinuous conformational transitions. Polyampholytes can thus be caused to collapse also by varying the charge chemical potential μ , which can be easily done in experiments by changing the pH of the solution. Using the proton bath in the experiments may introduce electrostatic screening (at least, besides explicit counterions or counterion condensation, etc.) for polyions. As a result, weak polyelectrolyte and diblock polyampholyte systems may not be treated as salt-free solutions. Thus the model investigated in this work may require extreme conditions for experimental verification. The effect of varying salt concentration on the first-order transition behavior of weak polyelectrolytes in poor solvent is discussed in Ref. 59.

D. Diblock polyampholytes in good solvents

The striking difference between diblock polyampholytes formed of two oppositely charged weak polyelectrolyte blocks in the poor and good solvent conditions is the

absence of discrete transitions in the latter (see Fig. 2). In order to better understand conformational changes of the diblock polyampholytes with the pH or with the corresponding average charge fraction, simulation results of root-mean-square radii of gyration of B block as a function of average charge fraction f_B in good solvent conditions for polymer backbone are presented as symbols in Fig. 8(a). Our simulation results suggest that the size of an individual block of the diblock polyampholyte has a nonmonotonic variation with average charge fraction of the same block. For $f_B \lesssim 0.4$ and $f_B \approx 1$, B block follows single-chain polyelectrolyte-like behavior (solid line in Fig. 8(a)). The A and B block sizes were found to be approximately equal at the crossover from single-chain polyelectrolyte-like behavior of B block to polyelectrolyte-like behavior due to repulsion between uncompensated charges along the chain ($0.4 \lesssim f_B \lesssim 0.85$). Note that for $N = 256$ case at the isoelectric pH, $f_A = f_B \approx 0.85$. In the interval $0.4 \lesssim f_B \lesssim 0.85$ and with sizes of A (data

FIG. 8. Simulation results in good solvent conditions for root-mean-square radii of gyration (open symbols) of B block of the diblock polyampholyte as a function of: (a) average charge fraction of B block, and (b) difference between average charge fractions of A and B blocks. The Bjerrum length $\lambda_B = \sigma$, $pK_0^A = 5.5$, and $pK_0^B = 7.5$. Each arrow shown in (a) points to snapshot of an equilibrium conformation in the corresponding simulation. Color codes of snapshots are the same as in Fig. 7. The solid lines in (a) and (b) are the same as in Fig. 5, however, the line in (b) is shifted along y-direction (note also the reduced size of B block).

not shown) and B blocks approximately equal, the root-mean-square radius of gyration of B block decreases as a function of average charge fraction of the same block. Inspection of Fig. 2(b) (titration curves of A and B blocks are symmetric with respect to the isoelectric point, pH = 6.5) reveals that in the interval of $0.4 \lesssim f_B \lesssim 0.85$, the charge fraction of A block is approximately constant. Therefore, due to the symmetry of the diblock chain, the same constant charge fraction happens for the B block in the interval of $0.4 \lesssim f_A \lesssim 0.85$. In order to get an insight into the diblock polyampholyte structures at various charge fractions, snapshots of equilibrated conformations are also presented in Fig. 8(a) as a function of average charge fraction of B block. In agreement with previous simulations,⁵² we observe extended as well as globular conformations, and weakly charged block has coiled or extended structures, whereas the strongly charged block has extended conformations.

The intrachain electrostatic interactions lead to charge compensation and thus repulsion between uncompensated charges² causes elongation of a polyampholyte chain into an array of effective electrostatic blobs of size $\xi_e \approx \lambda_B (f_A - f_B)^2 g_e^2$ obtained by using Eq. (18) with f replaced by $|f_A - f_B|$, where the number of monomers in a blob is given by $g_e \approx (\xi_e/b)^{1/\nu}$ (Eq. (19)). The simulation results of root-mean-square radii of gyration of B block as a function of $f_A - f_B$ in the interval $0.4 \lesssim f_B \lesssim 0.85$ along with theoretical prediction (Eq. (22) with f replaced by $|f_A - f_B|$) are presented in Fig. 8(b). The agreement is quite satisfactory and therefore following Eq. (23) with f replaced by $|f_A - f_B|$ and by using the definition of the electrostatic chemical potential (Eq. (3)), we thus propose that the electrostatic contribution to the chemical potential of the charges has a monotonic variation with $|f_A - f_B|$ in good solvents if polyelectrolyte-like behavior of the diblock polyampholyte is due to repulsion between uncompensated charges along the chain, i.e., $\mu_{el}/k_B T \approx |f_A - f_B|^{0.416}$. In the vicinity of the isoelectric point, the polymer exhibits the unusual polyampholyte properties. We demonstrate below that the physical properties of diblock polyampholytes at the isoelectric pH and in the weak association regime can be well described by the “scrambled egg” model of electrostatic attraction.⁴⁸

At the isoelectric point, as illustrated in Fig. 9 we obtained quantitative agreement of our simulation results for normalized root-mean-square radii of gyration R_g/R_{g0} of diblock polyampholytes as a function of average interaction parameter $\lambda_B (fN)^2/R_{g0}$ with molecular dynamics simulations performed⁴⁸ for symmetric diblock polyampholytes consisting of two oppositely charged quenched polyelectrolyte blocks. Since the two blocks of the chain each with degree of polymerization $N/2$ are symmetric in average charge fractions at the isoelectric point, their average sizes are expected to be exactly the same at all values of electrostatic interaction strength, λ_B , which is confirmed in our simulations. The electrostatically driven coil-globule transition of the diblock polyampholyte carrying weak acids or bases in good solvents is found to consist of different regimes at the isoelectric point identified with increasing electrostatic interaction strength. In the first folding regime, the size of the whole chain decreases, while the individual block sizes remain approximately

FIG. 9. Normalized root-mean-square radii of gyration of the diblock polyampholyte chains (open symbols) and of the individual blocks (solid symbols) as a function of the average universal interaction parameter under good solvent quality and at the isoelectric point ($\text{pH} = 6.5$). The Bjerrum length is varied from $\lambda_B = 0$ to 4σ . The values of pK_0^A and pK_0^B are 5.5 and 7.5, respectively. The solid line is the power law prediction of the scaling theory Eq. (9) where we used $\nu = 0.588$ to obtain the exponent as -0.18 . Data from Ref. 48 are marked by solid diamonds.

constant. In the second weak association regime, the average sizes of the whole chain and the individual blocks are equal to each other, reflecting the collapse of the chain into a globule.⁴⁸ Here, fluctuation-induced electrostatic attraction between oppositely charged sections of the chain is the driving force for the collapse of the diblock polyampholytes as shown by the agreement between theoretical prediction, Eq. (9), and simulations. We used $\nu = 0.588$ in the power law prediction of the scaling theory Eq. (9) to obtain the exponent as -0.18 . Note that for the simulations at the isoelectric point we performed exactly the same semi-grand canonical MC simulation procedure as described in Sec. II, while the Bjerrum length was varied from $\lambda_B/\sigma = 0$ to 4.

While we have captured the main features of pH-induced transitions with our model, it would be desirable to perform simulations where counterions,²¹ water molecules, and salt ions are considered explicitly. Nevertheless, we emphasize that our goal is to explore qualitatively the interplay between electrostatic and hydrophobic/hydrophilic interactions in our model polyampholyte. It is unlikely that a more refined electrostatic model would change the trends and main conclusions drawn in this paper. We plan to expand the work on diblock polyampholytes to include the effect of explicit counterions on pH-induced transition.

IV. CONCLUSIONS

We performed extensive grand canonical Monte Carlo simulations to investigate the titration behavior and conformational properties of flexible polymers carrying weak acid and weak basic moieties in poor and good solvent conditions for polymer backbone. In particular, we address weak polyelectrolytes (homopolymers) and diblock polyampholyte chains formed of two weak polyelectrolyte blocks namely, A and B,

each containing equal number of identical monomers. The A block is considered to be an acid (each monomer carries zero charge in the protonated state and one negative unit of charge in the deprotonated state) and the B block represents a base (each monomer carries zero charge in the deprotonated state and one positive unit of charge in the protonated state).

In agreement with the theoretical predictions⁷ and earlier simulations,^{18–20} the coil-globule conformational transition, obtained by changing solution pH, of a weak polyelectrolyte (homopolymer) under poor solvent quality has been found to be of first order. In addition, electrostatic contribution to the chemical potential of the charges has a nonmonotonic variation with average charge fraction for a weak polyelectrolyte in poor solvents and follow the scaling predictions⁷ not only on a qualitative,^{18–20} but also on a semiquantitative level. In the good solvent case, chemical potential is a monotonic function of charge fraction which is in good agreement with previous simulations¹⁶ and with our theoretical prediction Eq. (24).

The change of solution pH induces charge asymmetry in a diblock polyampholyte. The analysis of the titration curves clearly demonstrates that the presence of an oppositely charged weak polyelectrolyte block significantly modifies the acid (base) property of a weak polyelectrolyte by promoting the formation of negatively (positively) charged monomers over the whole pH range in poor as well as good solvent conditions. Similar results have also been obtained for simulations of complex formation between a weak polyelectrolyte chain and an oppositely charged nanoparticle.⁹

A charge-asymmetric diblock polyampholyte in poor solvents has a tadpole shape with a globular head and a polyelectrolyte tail in the vicinity of the isoelectric point. For the first time, using computer simulations, the examination of titration curves and probability distributions of the free energy of diblock polyampholyte chains in poor solvents clearly demonstrates that a first order transition between collapsed (globule) and extended chains (tadpole) is obtained by varying the solution pH. The head and tail sizes of the tadpole conformations become approximately equal in the vicinity of the transition point.

A marked difference between diblock polyampholytes formed of two oppositely charged weak polyelectrolyte blocks in the poor and good solvent conditions is the absence of discrete transitions in the latter. In agreement with previous simulations⁵² we observed, for example, globular as well as extended conformations of diblock polyampholytes in good solvents. At pH values above or below the isoelectric point chains show polyelectrolyte-like behavior due to repulsion between uncompensated charges along the chain. At the isoelectric point the polymer exhibits polyampholyte properties and the electrostatically driven coil-globule transition of the diblock polyampholyte in good solvents is found to consist of different regimes identified with increasing electrostatic interaction strength. Our simulation results (see Fig. 9) show quantitative agreement with those obtained by using molecular dynamics simulations performed⁴⁸ for symmetric diblock polyampholytes consisting of two oppositely charged quenched polyelectrolyte blocks. The theoretically predicted^{43,44,48} scaling laws of these conformational properties are in very good agreement with our simulation results.

ACKNOWLEDGMENTS

S.U. and A.K.N. gratefully acknowledge computational facilities provided at the TUBITAK ULAKBIM High Performance Computing Center, Ankara, Turkey.

- ¹H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, C. Seidel, and D. Stscherbina, *Polyelectrolytes: Formation, Characterization and Application* (Hanser Publishers, Munich, 1994).
- ²A. V. Dobrynin and M. Rubinstein, *J. Phys. II* **5**, 677 (1995).
- ³A. V. Dobrynin, R. H. Colby, and M. Rubinstein, *J. Polym. Sci., Part B: Polym. Phys.* **42**, 3513–3538 (2004).
- ⁴A. V. Dobrynin and M. Rubinstein, *Prog. Polym. Sci.* **30**, 1049–1118 (2005).
- ⁵S. E. Kudaibergenov, *Polyampholytes: Synthesis, Characterization, and Applications* (Kluwer Academic, New York, 2002), pp. 186–197.
- ⁶*Polyelectrolytes with Defined Molecular Architecture*, Advances in Polymer Science Vol. 165/166, edited by M. Schmidt (Springer, Heidelberg, 2003).
- ⁷E. Raphael and J.-F. Joanny, *Europhys. Lett.* **13**, 623–628 (1990).
- ⁸S. Ulrich, S. A. Laguerre, and S. Stoll, *J. Chem. Phys.* **122**, 094911 (2005).
- ⁹S. Ulrich, A. Laguerre, and S. Stoll, *Macromolecules* **38**, 8939–8949 (2005).
- ¹⁰J. L. Garces, G. J. M. Koper, and M. Borkovec, *J. Phys. Chem. B* **110**, 10937–10950 (2006).
- ¹¹S. Wang and J. Zhao, *J. Chem. Phys.* **126**, 091104 (2007).
- ¹²Y. Burak and R. R. Netz, *J. Phys. Chem. B* **108**, 4840–4849 (2004).
- ¹³V. Tiratmadja, K. C. Tam, and R. D. Jenkins, *Macromolecules* **30**, 3271–3282 (1997).
- ¹⁴M. Castelnovo, P. Sens, and J.-F. Joanny, *Eur. Phys. J. E* **1**, 115–125 (2000).
- ¹⁵I. Borukhov, D. Andelman, R. Borrega, M. Cloitre, L. Leibler, and H. Orland, *J. Phys. Chem. B* **104**, 11027–11034 (2000).
- ¹⁶M. Ullner, M. B. Jönsson, B. Söderberg, and C. Peterson, *J. Chem. Phys.* **104**, 3048–3057 (1996).
- ¹⁷T. Zito and C. Seidel, *Eur. Phys. J. E* **8**, 339–346 (2002).
- ¹⁸S. Uyaver and C. Seidel, *Europhys. Lett.* **64**, 536–542 (2003).
- ¹⁹S. Uyaver and C. Seidel, *J. Phys. Chem. B* **108**, 18804–18814 (2004).
- ²⁰T. Yamaguchi, T. Kiuchi, T. Matsuoka, and S. Koda, *Bull. Chem. Soc. Jpn.* **78**, 2098–2104 (2005).
- ²¹A. Z. Panagiotopoulos, *J. Phys.: Condens. Matter* **21**, 424113 (2009).
- ²²M. J. Stevens and K. Kremer, *J. Chem. Phys.* **103**, 1669–1690 (1995).
- ²³D. C. Boris and R. H. Colby, *Macromolecules* **31**, 5746 (1998).
- ²⁴Q. Liao, A. V. Dobrynin, and M. Rubinstein, *Macromolecules* **36**, 3386 (2003).
- ²⁵N. A. Kumar and C. Seidel, *Phys. Rev. E* **76**, 020801(R) (2007).
- ²⁶P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1985).
- ²⁷A. R. Khokhlov, *J. Phys. A* **13**, 979–987 (1980).
- ²⁸Y. Kantor, M. Kardar, and H. Li, *Phys. Rev. E* **49**, 1383–1392 (1994).
- ²⁹S. Minko, A. Kiriy, G. Gorodyska, and M. Stamm, *J. Am. Chem. Soc.* **124**, 3218–3219 (2002).
- ³⁰H. J. Limbach and C. Holm, *J. Phys. Chem. B* **107**, 8041–8055 (2003).
- ³¹U. Micka, C. Holm, and K. Kremer, *Langmuir* **15**, 4033–4044 (1999).
- ³²P. Dubin and U. P. Strauss, *J. Phys. Chem.* **77**, 1427–1431 (1973).
- ³³B. Mahltig, J.-F. Gohy, R. Jerome, and M. Stamm, *J. Polym. Sci., Part B: Polym. Phys.* **39**, 709–718 (2001).
- ³⁴C. S. Patrickios, W. R. Hertler, N. L. Abbott, and T. A. Hatton, *Macromolecules* **27**, 930 (1994).
- ³⁵T. Goloub, A. de Keizer, and M. A. C. Stuart, *Macromolecules* **32**, 8441–8446 (1999).
- ³⁶Y. K. Jhon, S. Arifuzzaman, A. E. Ozcam, D. J. Kiserow, and J. Genzer, *Langmuir* **28**, 872–882 (2012).
- ³⁷N. Ayres, C. D. Cyrus, and W. J. Brittain, *Langmuir* **23**, 3744–3749 (2007).
- ³⁸B. Mahltig, N. Cheval, J. Gohy, and A. Fahmi, *J. Polym. Res.* **17**, 579–588 (2010).
- ³⁹H. Lei, M. Wang, Z. Tang, Y. Luan, W. Liu, W. B. Song, and H. Chen, *Langmuir* **30**(2), 501–508 (2014).
- ⁴⁰M. Zhao, G. Zhou, L. Zhang, X. Li, T. Li, and F. Liu, *Soft Matter* **10**, 1110–1120 (2014).
- ⁴¹Y. Levin and M. C. Barbosa, *Europhys. Lett.* **31**, 513 (1995).
- ⁴²R. Everaers, A. Johner, and J.-F. Joanny, *Macromolecules* **30**, 8478 (1997).
- ⁴³M. Castelnovo and J.-F. Joanny, *Macromolecules* **35**, 4531–4538 (2002).
- ⁴⁴N. P. Shusharina, E. B. Zhulina, A. V. Dobrynin, and M. Rubinstein, *Macromolecules* **38**, 8870–8881 (2005).
- ⁴⁵L.-J. Qu, X. Man, C. C. Hant, D. Qiu, and D. Yan, *J. Phys. Chem. B* **116**, 743 (2012).
- ⁴⁶J. Jeon and A. V. Dobrynin, *J. Phys. Chem. B* **110**, 24652 (2006).
- ⁴⁷Z. Posel, Z. Limpouchova, K. Sindelka, M. Lisal, and K. Prochazka, *Macromolecules* **47**(7), 2503–2514 (2014).
- ⁴⁸Z. Wang and M. Rubinstein, *Macromolecules* **39**, 5897–5912 (2006).
- ⁴⁹J. B. Imbert, J. M. Victor, N. Tsunekawa, and Y. Hiwatari, *Phys. Lett. A* **258**, 92 (1999).
- ⁵⁰A. Baumketner, H. Shimizu, M. Isobe, and Y. Hiwatari, *J. Phys.: Condens. Matter* **13**, 10279 (2001).
- ⁵¹D. W. Cheong and A. Z. Panagiotopoulos, *Mol. Phys.* **103**, 3031–3044 (2005).
- ⁵²S. Ulrich, M. Seijo, and S. Stoll, *J. Phys. Chem. B* **111**, 8459–8467 (2007).
- ⁵³S. Ulrich, M. Seijo, F. Carnal, and S. Stoll, *Macromolecules* **44**, 1661–1670 (2011).
- ⁵⁴A. Akinchina and P. Linse, *Langmuir* **23**, 1465–1472 (2007).
- ⁵⁵P. Linse, *J. Chem. Phys.* **126**, 114903-1–114903-13 (2007).
- ⁵⁶M. Baratlo and H. Fazli, *Phys. Rev. E* **81**, 011801 (2010).
- ⁵⁷A. Kadoura, A. Salama, and S. Sun, *Mol. Phys.* (published online).
- ⁵⁸J. Lee and J. M. Kosterlitz, *Phys. Rev. Lett.* **65**, 137 (1990).
- ⁵⁹S. Uyaver and C. Seidel, *Macromolecules* **42**, 1352 (2009).