

Phase behavior of aqueous polyacrylic acid solutions using atomistic molecular dynamics simulations of model oligomers



Ratna S. Katiyar, Prateek K. Jha*

Department of Chemical Engineering, IIT Roorkee, Uttarakhand, 247667, India

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ABSTRACT

We have performed fully atomistic molecular dynamics simulations of aqueous solutions of a weak, pH-responsive polyelectrolyte, polyacrylic acid (PAA). Model oligomers of PAA of different tacticities, molecular weights, degrees of deprotonation, and deprotonation patterns are simulated with water molecules. Deprotonation of PAA chains that occurs with an increase in pH results in an increase in Coulomb repulsion between chain segments on one hand, and a non-monotonic change in the hydrogen bonding between chain segments on the other hand. Consequently, at the single chain level, PAA chains are stretched at higher pH values, where the amount of stretching varies with chain tacticity. For the multiple chains case, PAA forms aggregates at higher concentrations, which are relatively denser and contain lesser water (solid-like) at lower pH than compared to higher pH (liquid-like). Such phase transitions of PAA aggregates with pH has possible implications in the design of pH-responsive polyelectrolytes for applications in drug delivery.

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1. Introduction

According to the IUPAC definition, polyelectrolyte is a “polymer composed of macromolecules in which a substantial portion of the constitutional units contains ionic or ionisable groups, or both” [1]. Depending on the strength of the ionisable group, they can be classified as strong or weak. Strong polyelectrolytes contain strong acidic/basic groups (e.g. sulfonate, hydroxyl, etc.) that remain ionized at all practical pH conditions. On the other hand, weak polyelectrolytes contain weak acidic/basic groups (e.g., carboxyl, amide, etc.) that undergo a transition from a neutral state to a charged state with change in pH. This transition from neutral to charged state occurs due to deprotonation of acidic groups with an increase in pH or protonation of basic groups with a decrease in pH. In general, polyelectrolytes have better aqueous solubility than neutral polymers. Moreover, they exhibit interesting self-assembly behavior driven by electrostatic forces [2,3]. For example, oppositely charged polyelectrolytes self-assemble to form polyelectrolyte complexes, which can either be solid-like (precipitate) or a liquid/gel-like (coacervate) depending on the pH and ionic strength (salt concentration) of the medium [4–8]. Similar self-

assembly behavior can also be observed in systems containing identical polyelectrolytes, by either varying the degree of ionization by changing pH [9,10] or screening the Coulomb repulsion between the chains by increasing salt concentration [11,12]. Such self-assembly behavior of polyelectrolytes finds use in a range of applications; some recent areas of applications include fuel cell technology [13,14], drug delivery [15–17], tissue engineering [18,19], and optoelectronic devices [20].

Physical properties of polyelectrolytes are fundamentally interesting and have intrigued scientists working in the area of biology and soft matter from last several decades [2,21,22]. At the single chain level (dilute concentrations), polyelectrolyte chains are stretched and have high persistence length due to Coulomb repulsion between chain segments. For charge densities beyond a threshold value or for the case of multivalent salts, counterions condense on the polyelectrolyte backbone (Manning condensation [23]), resulting in chain collapse. Concentrated solutions of polyelectrolytes possess strong ion-ion correlations resulting in the formation of strongly segregated structures. These behaviors have been captured in field-theoretical studies [24,25] and coarse-grained simulations [26,27], which however have mainly focused on strong polyelectrolytes. Such studies of pH-responsive, weak polyelectrolytes are relatively few [28,29]. Although the field-theoretical and coarse-grained simulation approaches succeed in achieving a qualitative understanding of polyelectrolyte behavior,

* Corresponding author.

E-mail address: pkjchfch@iitr.ac.in (P.K. Jha).

they do not adequately account for the chemical details of polyelectrolytes and thus do not provide a molecular-level insight of the underlying physics. In particular, physical interactions that vary strongly with the polymer chemistry (e.g., hydrogen-bonding) are only captured at a rudimentary level and often requires a priori knowledge about the magnitudes of such interactions. Atomistic simulations, on the other hand, include the necessary chemical details and thus capture such interactions in a predictive manner, that is, without a priori knowledge about these interactions. Despite this obvious advantage, studies of polyelectrolyte systems using atomistic simulations are relatively scarce, mainly because of the computational expense of these simulations. While atomistic simulations of realistic large molecular weight polymers remains impossible, simulations of reasonably long oligomers that mimic the behavior of real polymers are only now becoming feasible [30–33]. Atomistic simulations of long oligomers coupled with systematic coarse-graining approaches [34–36] now provide a pathway to study polyelectrolyte systems at atomic resolution, and is being actively pursued.

The degree of deprotonation of polyelectrolytes at a given pH can be obtained using the Henderson-Hasselbalch equation [37], that is, in the case of polyacids,

$$f = \frac{1}{1 + 10^{pKa-pH}} \quad (1)$$

Here, f is the fraction of deprotonated groups (degree of deprotonation) and pKa is the negative logarithm (base 10) of the acid dissociation constant, K_a . There are two major issues in the use of this equation for polyelectrolytes. First, the pKa values of polyelectrolyte solutions are a function of the polyelectrolyte molecular weight and salt concentration [5] and are generally not available. Second, the Henderson-Hasselbalch equation can only provide the average fraction of charged groups and provide no information on the actual positions of these charged groups on the polyelectrolyte chain, which further keep changing due to dynamic nature of protonation-deprotonation equilibrium. This is demonstrated in Fig. 1, where the two PAA chains have the same deprotonation fraction but different deprotonation patterns. COO^- groups are closer to each other in Fig. 1b compared to Fig. 1a, which results in relatively larger intra-chain electrostatic repulsion. Therefore, the structure and properties of these two PAA chain conformations, both of which can be obtained at the same pH, may be strikingly different. Further, the Henderson-Hasselbalch equation provide no clue about which of these conformations would be more likely. It ignores the fact that the deprotonation free energy of a $COOH$ group is generally expected to be larger if a COO^- group is present on the neighbouring monomer(s), since the deprotonation would lead to high electrostatic repulsion. Thus, we need to resort to molecular simulations that provide detailed insights into the effect of pH on the polyelectrolyte behavior. Yet another advantage of molecular

simulations is their predictive nature; simulations can be performed to study behavior of novel molecules that have not been synthesized to access their potential for a given application [33]. This can save experimental effort and expense, while screening molecules for different applications.

Two distinct approaches can be used in the atomistic simulations of weak polyelectrolytes. First is the conventional molecular dynamics (MD) simulations performed in the canonical (NVT) ensemble or isothermal-isobaric (NPT) ensemble simulations of polyelectrolytes, performed for different degrees of deprotonation and deprotonation patterns [38,39], which include the pH-induced changes in the average deprotonation but do not account for the dynamic nature of protonation-deprotonation equilibrium. Second is the constant-pH molecular dynamics approaches [40,41] that have originally been developed for proteins and can be extended for simulations of weak polyelectrolytes as done in a recent study [9]. Constant-pH simulations also accounts for the dynamic protonation-deprotonation processes and therefore can predict the pKa values and the titration curve of polyelectrolytes. However, there are several issues in the practical implementation of these methods. For instance, the use of an artificial barrier potential, a reference “chemically similar” compound, incorporation of explicit titratable water, and presence of multiple titration sites on a molecule remains problematic from a fundamental standpoint and computationally difficult [40]. More importantly, such methods should be adequately able to sample 2^M possible deprotonation patterns for a polyelectrolyte chain containing M ionisable groups, which results in a very large number of possible conformations in a solution of polyelectrolytes. We therefore adopt the first approach and vary both the degree of deprotonation and deprotonation patterns to understand the effect of these on the phase behavior. We expect that the main conclusions of our study will be the same for constant-pH simulations, provided they are able to adequately sample all possible conformations. However, the effects of dynamic changes in the deprotonation patterns are not captured in our study.

In this paper, we discuss atomistic MD simulations of aqueous solutions of PAA oligomers (chains) of different tacticities, concentrations, degrees of deprotonation, and deprotonation patterns. Simulation protocol and methods employed in the analysis of simulation data are discussed in the next section. This is followed by the Results and Discussion section, which include a detailed discussion of the effects of various parameters (tacticity, PAA concentration, degree of deprotonation, deprotonation patterns) on the single-chain characteristics and the solution phase behavior. We conclude with the main outcomes of this study and an outlook for future studies.

2. Methods

Simulations are performed in the GROMACS 4.6.7 simulation

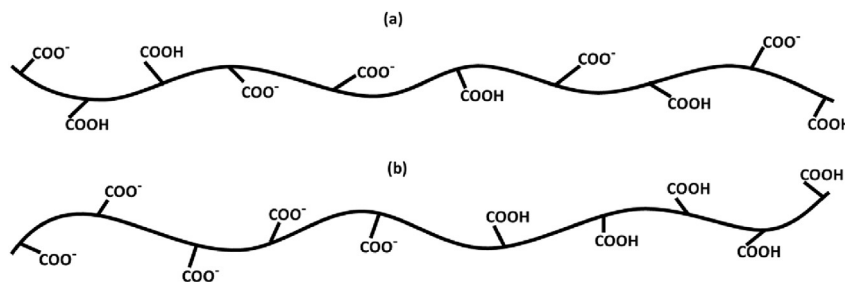


Fig. 1. PAA chains with same fraction of deprotonation, but different deprotonation patterns.

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