# Sequence Dependence of Conformations of Polyampholytes

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*Received August 17, 1995*
*Revised Manuscript Received December 11, 1995*

Polyampholytes are polymers which bear both positive and negative charges along their backbone. The conformations of these polymers[1−6] are strongly influenced by their overall composition and their environment. The conformation is determined by the interplay of electrostatic interactions and elastic effects due to chain entropy. Polyampholytes collapse when the chain is electrically neutral and adopt extended conformations when there is a net charge on the chain. This interesting conformational behavior has led to applications in biosensors and in amphoteric buffers for electrophoresis; they are also used as viscosity stabilizers. Polyampholytes can also serve as a simple model[7−14] for understanding the complex behavior of random copolymers such as proteins. An attempt has been made here to study the conformations of polyampholytes with different sequences.

We have studied 20 different randomly charged neutral copolymers of length 50 using Monte Carlo simulations. In the simulation the chains are represented as freely jointed chains consisting of $N$ monomers connected by freely rotating bonds of Kuhn length $l$. Each segment is ascribed a hard-core diameter $a$ in order to account for excluded volume interactions. A fraction, $f_+$, of the monomers are assigned a unit positive charge, while a fraction, $f_-$, of the monomers are assigned a unit negative charge. The monomers interact through an excluded volume interaction due to hard-core repulsion

$$V_1(r_{ij}) = \begin{cases} 0, & \mathrm{r}_{ij} > a \\ \infty, & \mathrm{r}_{ij} \le a \end{cases} \tag{1}$$

and a screened Coulomb interaction

$$V_2(r_{ij}) = \frac{\alpha q_i q_j}{\beta} \frac{\mathrm{e}^{-\kappa r_{ij}}}{r_{ij}} \tag{2}$$

where $r_{ij}$ is the separation between the $i$th and $j$th segments and $q_i = +1, -1$, or 0 if the $i$th segment is positively charged, negatively charged, or neutral, respectively. α is the Bjerrum length at the reference temperature $T_0$,

$$\alpha = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_{\mathrm{B}} T_0} \tag{3}$$

where $e$ is the electronic charge, $\epsilon_0$ is the permittivity of vacuum, $\epsilon_r$ is the dimensionless dielectric constant of the medium bearing the macromolecule, and $k_{\mathrm{B}}$ is the Boltzmann constant. $\beta$ of eq 2 is the ratio of the absolute temperature $T$ to the reference temperature $T_0$. $\kappa$ is the inverse Debye length, determining the range of the Coulombic interaction. $\kappa^2$ is determined by the concentrations of various ions in the system, both the counterions and the ions arising from the presence of any added salt,

$$\kappa^2 = \frac{4\pi\alpha}{\beta}\sum_i c_i z_i^{\,2} \tag{4}$$

where $c_i$ and $z_i$ are the concentration and valence, respectively, of the $i$th ion.

The range of the excluded volume interaction is chosen such that bonds do not intersect during rotation; $a = \sqrt{3}l/2$. Also $f_+ = 0.1 = f_-$. The Bjerrum length at the reference temperature, α, and the inverse screening length, $\kappa$, have been taken to be 1.0 and 0.1, respectively. The chains are allowed to evolve by the kink-jump algorithm. In this algorithm a monomer chosen at random is rotated through a random angle about the axis defined by the two adjacent monomers; if an end monomer is chosen, it is moved to a new position by rotation through two randomly chosen angles. This new conformation is accepted according to the Metropolis sampling rules.[15] The attempted move is counted even if the new trial configuration is not accepted. $N$ such elementary moves constitute one Monte Carlo (MC) time step. Simulations have been carried out at several different temperatures, $\beta$, starting from $\beta = 5.0$ and then successively reducing the temperature at each stage. At each stage, the chain is equilibrated for $5 \times 10^4$ MC steps and then sampled at unit intervals for $10^5$ MC steps. Five independent simulations have been carried out for each sequence of charges along the chain.

Results for six representative sequences from among the twenty sequences studied are discussed here. These sequences were created by independently assigning each monomer on a chain a unit positive or negative charge with probability $f_+$ and $f_-$, respectively, and ensuring that the resulting sequence was neutral. The sequences obtained were random and are shown in Figure 1; we refer to these sequences as *S*62189, *S*47977, *S*72959, *S*90371, *S*67049, and *S*82307, respectively.

The mean squared radii of gyration $R_{\mathrm{g}}^2$ of the chains are shown in Figure 2 as a function of temperature for these sequences. The results are equilibrium results, as monitored by the acceptance ratio of new configurations, duration of the Monte Carlo time, and the number of independent configurations used in constructing the various averages. The results reported in Figure 2 are free from any kinetic or hysteresis effects. At high temperatures the chains behave as self-avoiding walks and the radii are similar. As the temperature is reduced the radii decrease under the influence of attractive electrostatic interactions. However, there is a significant difference in the radii at any given temperature. This difference arises from differences in the location of charges along the chain even though the overall composition is the same in each case.

The differences in the radii of the six sequences at lower temperatures can be understood in light of the differences in the intrachain energy shown in Figure 3. The intrachain energy arises from the interplay of the polyelectrolyte effect (electrostatic repulsion between like charges) and the polyampholyte effect (electrostatic attraction between unlike charges). The relative importance of the two is determined by the location of charges along the chain. Sequence *S*62189 has a positive intrachain energy at high temperatures and a negative intrachain energy at low temperatures. Sequence *S*82307, on the other hand, has a negative intrachain energy even at high temperatures. This

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**Figure 1.** Six sequences from top to bottom: *S*62189, *S*47977, *S*72959, *S*90371, *S*67049, and *S*82307. Minus and plus circles denote negative and positive charges, respectively. Other circles denote neutral segments.

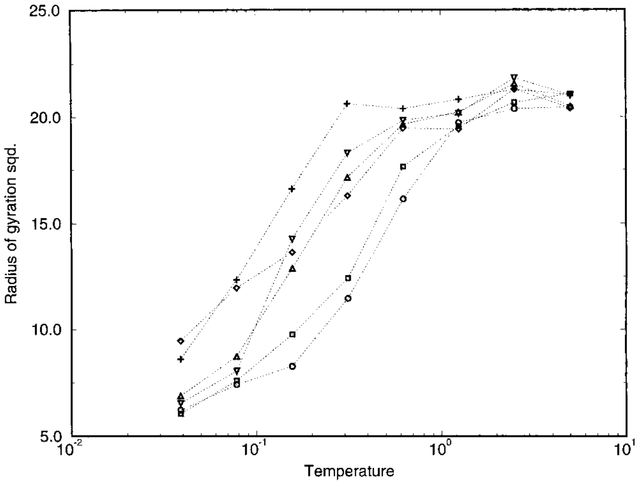

**Figure 2.** Temperature dependence of the mean square radius of gyration for *S*62189 (○), *S*47977 (□), *S*72959 (◇), *S*90371 (△), *S*67049 (▽), and *S*82307 (+).

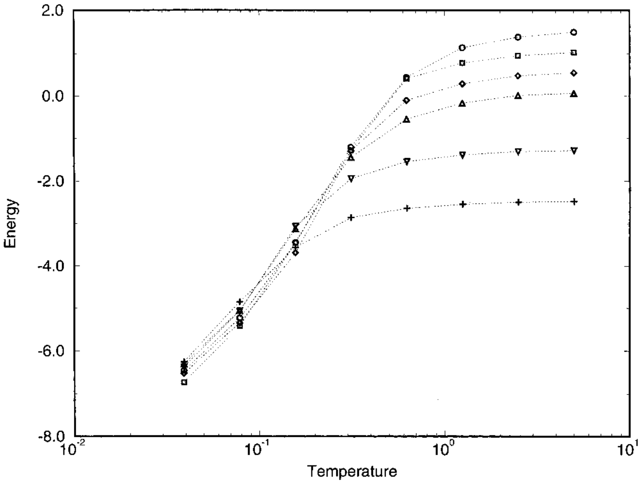

**Figure 3.** Temperature dependence of intrachain energy for different sequences. Symbols denote different sequences as in Figure 2.

leads to a small difference between the intrachain energy at high and low temperatures. This small difference manifests itself in the large radii at low temperatures. This is in accord with the observation that a large energy difference between the high- and low-temperature intrachain energy has the effect of promoting the collapse of a random copolymer.

We further illustrate this dependence on the location of charges along the chain for the conformational and energy spectra of two sequences. The distribution $n(R_g^2)$ of the radii at three different temperatures is shown in Figure 4 for sequences *S*62189 and *S*82307. Similarly, the distribution $n(E)$ of intrachain energy $E$ at these three different temperatures is shown in Figure 5. Sequence *S*62189 has a broad distribution of radii at high temperatures and a narrow distribution at low temperatures. Sequence *S*82307, on the other hand, has a broad distribution of radii even at low temperatures. Thus, the location of charges along the chain plays a crucial role in the conformational behavior of the polyampholytes. It is also obvious from Figures 4 and

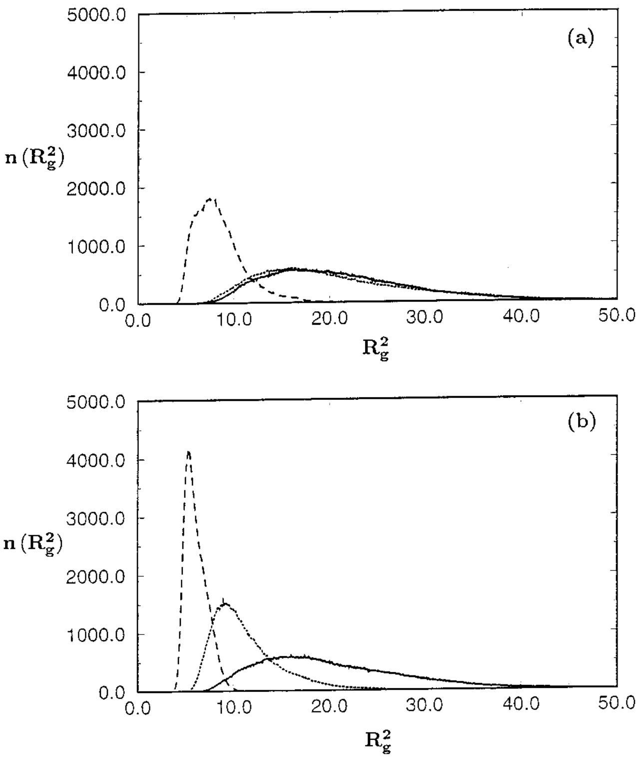

**Figure 4.** Distribution of mean square radius of gyration at three temperatures: $\beta = 0.078\ 125$ (— — —), 0.625 (•••), 2.5 (—); (a) *S*82307; (b) *S*62189.

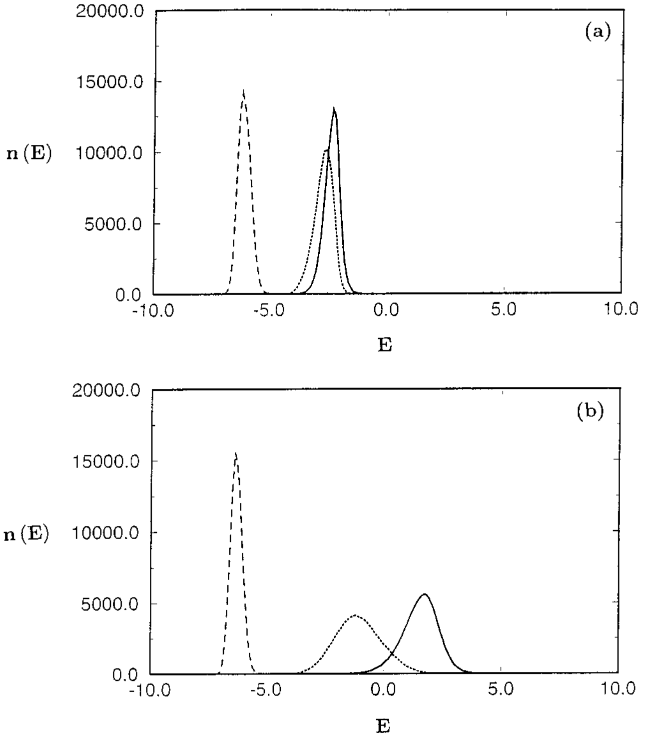

**Figure 5.** Distribution of intrachain energy at three tempertures for two sequences: (a) *S*82307; (b) *S*62189. Symbols as in Figure 4.

5 that knowledge of merely the energy landscape is insufficient to describe the conformational properties of polyampholytes. The entropy associated with the formation of frustrated conformations[14] needs to be accounted for in understanding the conformational properties of heteropolymers with specific sequences.

**Acknowledgment** is made to the NSF for Grant DMR 921146001, the Materials Research Science and Engineering Center at the University of Massachusetts, and the Center for UMass-Industry Research in Polymers.

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MA951204G