Structural transition of charged polymer

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We have performed the canonical molecular dynamics simulations to the di-block polyampholyte in which the Coulomb and the soft core interactions are considered. The di-block polyampholyte has two helical structures which have almost equal potential energy in low temperature region. Controlling the relative strength of two interactions by changing bond length, the stability of these two helical structures is affected from the view point of free energy without any influence on the equality of potential energy.

We have performed the canonical Molecular Dynamics (MD) simulations to di-block polyampholyte (PA), which is one kind of model polymer for proteins. One di-block PA contains N monomers in which $N/2$ monomers on one side of the chain are positively charged and the remaining $N/2$ monomers on another side are negatively charged. The system we have considered contains only one di-block PA in vacuum. The Coulomb interaction and the soft core interaction between monomers are considered to this system.

Thus Hamiltonian of the system is written as

$$\mathcal{H}' = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i'^2}{2m'} + \sum_{i=1}^{N} \sum_{j=i+2}^{N} \left\{ \frac{q_i q_j}{r'_{ij}} + \frac{4r_0\zeta}{e^2} \left(\frac{1}{r'_{ij}} \right)^{12} \right\}, \tag{1}$$

where $q_i = +1$ for $i = 1 \sim \frac{N}{2}$, $q_i = -1$ for $i = \frac{N}{2} + 1 \sim N$ and the primed variables are scaled by changing unit. The unit of length, mass, charge, time and energy are connected monomers' length ($r_0 = r_{ii+1}$), mass of electron (m_e), elementary electric charge (e), $\tau = \frac{e}{\sqrt{m_e r_0^3}}$ and $\frac{e^2}{r_0}$, respectively. During the simulation r_0 is kept to be constant by NIMM [2]. In the potential energy term it is recognized the relative strength of the Coulomb interaction and the soft core interaction can be controlled by r_0. We previously reported the results of MD simulations for this system with $r_0 = 3.4$ au [1] where 1 au is the Bohr radius.

In this paper we performed some MD simulations for two values of r_0, 1.7 au and 6.8 au. In ref. 1) we found two kinds of helical structures, stretched helical structure and spherically helical structure, which have almost same potential energy at temperature $T^* \equiv k_{\mathrm{B}}T/\frac{e^2}{r_0} \sim 0.01$. So we choose one of these helical structures or straight chain structure as initial structure. And in order to see the change of stable structure by r_0 we iteratively perform consecutive processes, raising or lowering T^* and running canonical MD simulation. In $r_0 = 1.7$ au and 3.4 au cases regardless of initial structure the di-block PA finally takes the spherically helical structure at temperature $T^* \sim 0.01$. Besides the previous two kinds of helical structures, another structure which potential energy is same to the previous helical structures appears in $r_0 = 6.8$

au case at $T^* \sim 0.01$. These two kinds of helical structures and the new structure which arrears in $r_0 = 6.8$ au case are distinguished by the average of gyration radius ($\langle R_g \rangle$) and the average of pairing parameter ($\langle R_h \rangle$). $\langle R_g \rangle$ and $\langle R_h \rangle$ are independent to r_0 in this paper because they are scaled, respectively, by each value of di-block PA with straight chain structure. ($\langle R_g \rangle$,$\langle R_h \rangle$)s for the stretched helical structure and the spherically helical structure are almost $(0.18, 0.045)$ and $(0.11, 0.07)$, respectively. And ($\langle R_g \rangle$,$\langle R_h \rangle$) of the new structure appeared in $r_0 = 6.8$ au case is almost $(0.14, 0.05)$. Figure 1 is the probability distribution contour of (R_g, R_h) ($P(R_g, R_h)$) for $r_0 = 6.8$ au case at $T^* \sim 0.027$. It is easily recognized that the new structure appeared in $r_0 = 6.8$ au case lies midway between the stretched helical structure and the spherically helical structure. Although $P(R_g, R_h)$ for $r_0 = 1.7$ au case also has relatively high probability region around $(R_g, R_h) \sim (0.14, 0.05)$, $P(R_g, R_h)$ connecting regions between $(R_g, R_h) \sim (0.11, 0.07)$ and $(R_g, R_h) \sim (0.14, 0.05)$ is very small. Furthermore $P(R_g, R_h)$ around $(R_g, R_h) \sim (0.18, 0.045)$ immediately vanishes by raising temperature in $r_0 = 1.7$ au case. Next we see the probability distribution of bond angle ($P(\theta)$) and torsion angle ($P(\phi)$) at $T^* \sim 0.01$. In $r_0 = 1.7$ au and 6.8 au cases $P(\theta)$ has prominent peaks around $\theta = 80^\circ \sim 100^\circ$ and $\theta \sim 120^\circ$ for three structures. On the other hand $P(\phi)$s for different structure are significantly different as shown in fig. 2. This figure also supposes the new structure appeared in $r_0 = 6.8$ au case lies midway between the two helical structures.

The distance between monomers (r_{ij}) must be extended by the elongation of r_0 because it weakens the attractive force between monomers which is produced by Coulomb interaction. It is considered that the extension of r_{ij} reduces the potential barrier which obstructs the change of ϕ from $\sim 40^\circ$ to $\sim 180^\circ$ and *vice versa*. Consequently it is considered the structure which is close to the stretched helical structure must become more stable from the view point of free energy by the elongation of r_0.

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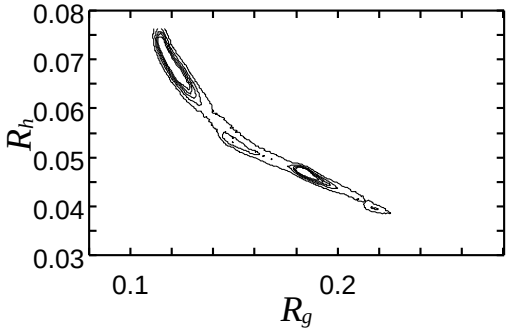

Fig. 1. Probability distribution of R_g and R_h for $r_0 = 6.8$ au at $T^* \sim 0.027$.

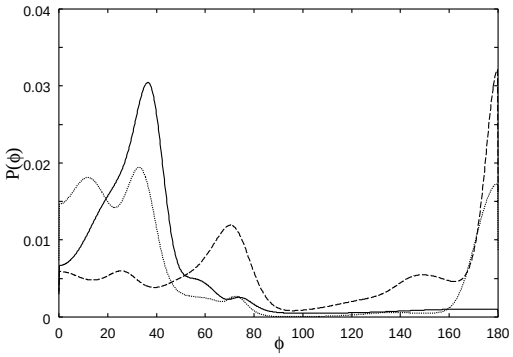

Fig. 2. Probability distribution of torsion angle (ϕ) for $r_0 = 6.8$ au at $T^* \sim 0.01$. The solid line, the dashed line and the dotted line indicate $\langle R_g \rangle \sim$ 0.18, 0.11 and 0.14, respectively.

References

1) H. Shimizu, K. Uehara, K. Yamamoto and Y. Hiwatari, Mol. Sim. **22** (1999), 285.
2) M. Yoneya, H.J.C. Berendsen and K. Hirasawa, Mol. Sim. **13** (1994), 395.