Average Structures of a Single Knotted Ring Polymer

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Two types of average structures of a single knotted ring polymer are studied by Brownian dynamics simulations. For a ring polymer with \( N \) segments, its structure is represented by a \( 3N \)-dimensional conformation vector consisting of the Cartesian coordinates of the segment positions relative to the center of mass of the ring polymer. The average structure is given by the average conformation vector, which is self-consistently defined as the average of the conformation vectors obtained from a simulation each of which is rotated to minimize its distance from the average conformation vector. From each conformation vector sampled in a simulation, \( 2N \) conformation vectors are generated by changing the numbering of the segments. Among the \( 2N \) conformation vectors, the one closest to the average conformation vector is used for one type of the average structure. The other type of the averages structure uses all the conformation vectors generated from those sampled in a simulation. In the case of the former average structure, the knotted part of the average structure is delocalized for small \( N \) and becomes localized as \( N \) is increased. In the case of the latter average structure, the average structure changes from a double loop structure for small \( N \) to a single loop structure for large \( N \), which indicates the localization-delocalization transition of the knotted part.

KEYWORDS: knot, ring polymer, single polymer, average structure, Brownian dynamics simulations, knot localization

1. Introduction

One of the important problems of the polymer physics is the effect of the topological constraints on polymer systems. In the case of systems of linear polymers, the topological constraints caused by the entanglement of the polymers vary temporally and the time-averaged properties of the constraints have been studied.\(^1,2\) In contrast, in the case of a single ring polymer, the topological constraints caused by its entanglement with itself, which is called a knot, are determined by the type of the knot and do not change with time. Therefore, a single ring polymer system can be considered as an ideal system for the study of topological effects and its investigation is expected to provide a basis for further understanding of the topological effects on polymer systems. The interest in single knotted ring polymers has been growing in recent years.\(^3-14\) A crucial but unresolved problem in a single knotted ring polymer is how topological effects of the knot depend on the polymer length. There have been studies predicting that the topological effects vanish and properties of the knotted ring polymer become the

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same as those of the unknotted ring polymer for infinitely long chains.\textsuperscript{3–7} This prediction can be understood from the argument that the knotted part of a ring polymer becomes localized to a part of the polymer as the polymer length increases and that the rest of the polymer behave like an unknotted ring polymer.\textsuperscript{7–14} The localization of the knotted part has been studied by measuring the chain length $l$ of the knotted part through simulations.\textsuperscript{8–12} It has been found that the equilibrium average $\langle l \rangle$ of $l$ behaves as $\langle l \rangle \propto N^t$ with $t \simeq 0.75$ for a single knotted ring polymer of $N$ segments in good solvent.\textsuperscript{8,9} The fact that $0 < t < 1$ indicates the localization of knotted part. It has been discussed and shown to be consistent with the simulation data that the behavior of $\langle l \rangle$ appears in the $N$-dependence of the mean square radius of gyration as a leading correction to its scaling behavior. In contrast, a behavior $\langle l \rangle \propto N$, which corresponds to the knot delocalization, has been found for a single knotted ring polymer in poor solvent. Similar results has been obtained for single ring polymers in two dimensions\textsuperscript{12–14} and linear polymers.\textsuperscript{10} Recently, the present authors studied the relaxation rate spectrum of single ring homopolymers in good solvent.\textsuperscript{7} Because a ring homopolymer has the translational symmetry along the polymer, its relaxation rates are classified by a wave number $q$. In ref. 7, the relaxation rate $\lambda_q$ for a wave number $q$ is estimated from the time $t$ dependence of the correlation function $C_q(t) = N^{-1} \sum_i \sum_j (1/3) \langle (r_i(t) - r_c(t)) \cdot (r_j(0) - r_c(0)) \rangle \exp \left[ -i2\pi q(i - j)/N \right]$ on the basis of the relaxation mode analysis,\textsuperscript{15–17} where $r_i(t)$ denotes the position of the $i$th segment of a ring polymer with $N$ segments at time $t$ and $r_c(t) = \frac{1}{N} \sum_{i=1}^{N} r_i(t)$ is the position of the center of mass of the polymer. It is found for single ring polymers with the trefoil knot that the slowest relaxation rate for each $N$ is given by $\lambda_q$ with $q = 2$ for small values of $N$ and that with $q = 1$ for large values of $N$. This transition is considered to correspond to the change of the structure of the ring polymer caused by the localization of the knotted part. In the studies mentioned above, however, the structures of single knotted ring polymers in three dimensions are not observed directly.

The purpose of the present paper is to confirm the localization of the knotted part of a single knotted ring polymer by directly observing its average structure in three dimensions through simulations. The structure of a ring polymer with $N$ segments is represented by a $3N$-dimensional conformation vector consisting of the Cartesian coordinates of the segment positions relative to the center of mass of the ring polymer. The average structure is given by the average conformation vector, which is self-consistently defined as the average of the conformation vectors obtained from a simulation each of which is rotated to minimize its distance from the average conformation vector.\textsuperscript{18} The average structure has been frequently used in simulation studies of biopolymers. Especially, static properties of fluctuations from the average structure have been studied by the principal component analysis method.\textsuperscript{19–21} Recently, the dynamic properties, such as the relaxation modes and rates, are also studied by the relaxation mode analysis method.\textsuperscript{22} In the case of the studies of biopolymers, polymers
studied are usually heteropolymers. In contrast, a ring polymer studied in the present paper is a homopolymer and has the translational symmetry along the polymer chain. In the present paper, by utilizing the translational symmetry, we propose an extension of the definition of the average structure and examine how the localization of the knotted part appears in the new and conventional types of the average structures.

The present paper is organized as follows. In §2, a model used in the present study and the two types of the average structures of single homopolymers are explained. The results of the simulations are presented in §3. Summary and discussion are given in the last section.

2. Model and Average Structures

In order to study a single knotted ring polymer in good solvent, Brownian dynamics simulations of a bead-spring model are performed. The dynamics of a single ring polymer with \( N \) segments is described by the Langevin equation

\[
\frac{d\mathbf{r}_i(t)}{dt} = -\frac{1}{\zeta} \frac{dV}{d\mathbf{r}_i} + \mathbf{w}_i(t),
\]

(1)

Here, \( \mathbf{r}_i(t) \) is a three-dimensional column vector consisting of the Cartesian coordinates of the position of the \( i \)th segment at time \( t \) and \( \zeta \) is the friction constant. The random force \( \mathbf{w}_i \) acting on the \( i \)th segment is a Gaussian white stochastic process satisfying \( \langle w_{i,\alpha}(t) \rangle = 0 \) and \( \langle w_{i,\alpha}(t) w_{j,\beta}(t') \rangle = (2k_BT/\zeta) \delta_{i,j} \delta_{\alpha,\beta} \delta(t-t') \), where \( w_{i,\alpha}, k_B \) and \( T \) denote the \( \alpha \)-component of \( \mathbf{w}_i \), the Boltzmann constant and the temperature of the system, respectively. The potential \( V(\{\mathbf{r}_i\}) = V(r_1, \ldots, r_N) \) represents the interaction between the segments. In the present paper, we use the potential given by

\[
V(\{\mathbf{r}_j\}) = \sum_{i=2}^{N} \sum_{j=1}^{i-1} V_R(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^{N} V_A(|\mathbf{r}_{i+1} - \mathbf{r}_i|),
\]

(2)

where \( \mathbf{r}_{N+1} = \mathbf{r}_1 \) in the last summation of the right-hand side because the \( N \)th segment is connected to the first segment. Here, \( V_R \) is given by the repulsive part of the Lennard-Jones potential

\[
V_R(r) = \begin{cases} 
4e \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right) & \text{for } r \leq 2^{\frac{3}{4}} \sigma, \\
0 & \text{for } r > 2^{\frac{3}{4}} \sigma,
\end{cases}
\]

(3)

and represents the excluded volume interaction between all the segments. The potential \( V_A \), which is called a finitely extensible nonlinear elastic (FENE) potential, is given by

\[
V_A(r) = \begin{cases} 
-\frac{1}{2} kR_0^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] & \text{for } r < R_0, \\
\infty & \text{for } r \geq R_0,
\end{cases}
\]

(4)

and represents the attractive interaction between neighboring segments along the ring polymer. The same model is used for simulations of a single linear polymer with \( N \) segments, where the upper limit of the last summation of the right-hand side of eq. (2) is \( N-1 \).
In the following, the average structures are explained for a linear or ring homopolymer with \( N \) segments. The average structures are estimated by using conformations of the polymer sampled in simulations. In a simulation, \( M \) conformations are sampled at interval of time \( \Delta T \) after an initial equilibration time \( T_i \). Let \( \mathbf{R}_i(m) \) denote the position of the \( i \)th segment relative to the center of mass of the polymer in the \( m \)th sample:

\[
\mathbf{R}_i(m) = \mathbf{r}_i(t_m) - \mathbf{r}_c(t_m),
\]

and \( t_m = T_i + (m - 1) \Delta T \), where \( m = 1, \ldots, M \). A structure of the polymer in the \( m \)th sample is represented by a \( 3N \)-dimensional conformation vector \( \mathbf{C}(m) = [\mathbf{R}_1(m), \mathbf{R}_2(m), \ldots, \mathbf{R}_N(m)] \). From each \( \mathbf{C}(m) \), \( K \) conformations, \( \tilde{\mathbf{C}}(m,k) \) with \( k = 1, \ldots, K \), each of which has the same statistical weight as \( \mathbf{C}(m) \), can be generated by changing the numbering of the segments, which is possible for homopolymers. Here, \( K = 2 \) for linear homopolymers and \( K = 2N \) for ring homopolymers. In both cases, \( \tilde{\mathbf{C}}(m,k) \) is given by

\[
\tilde{\mathbf{C}}(m,k) = [\mathbf{R}_{n(1,k)}(m), \mathbf{R}_{n(2,k)}(m), \ldots, \mathbf{R}_{n(N,k)}(m)],
\]

where \( n(i,k) = (1 - 2r)i_j + r(N + 1) \) with \( i_j = ((i + j - 1) \mod N) + 1, j = \lfloor (k-1)/2 \rfloor \), and \( r = (k - 1) \mod 2 = k - 1 - 2j \). Note that \( i_j \) represents the integer between 1 and \( N \) which is equal to \( i + j \) modulo \( N \). For odd or even values of \( k \), \( n(i,k) \) is equal to \( i_j \) or \( N - i_j + 1 \), respectively.

From the set of conformation vectors \( \{\tilde{\mathbf{C}}(m,k); m = 1, \ldots, M \text{ and } k = 1, \ldots, K\} \), the average conformation vector \( \mathbf{C}^{av} = [\mathbf{R}_1^{av}, \mathbf{R}_2^{av}, \ldots, \mathbf{R}_N^{av}] \), which gives one of the two types of the average structures, is calculated as follows. Here, the superscript \( av \) denotes either \( av0 \) or \( av1 \) representing the type-0 or type-1 average structure explained in the following, respectively. For each conformation vector \( \tilde{\mathbf{C}}(m,k) \), a three-dimensional rotation \( \mathcal{R}_{m,k} \) which minimizes the square distance \( d^2(m,k) \) between the conformation vector \( \mathcal{R}_{m,k} \left( \tilde{\mathbf{C}}(m,k) \right) \) obtained by the rotation of \( \tilde{\mathbf{C}}(m,k) \) and the average conformation vector \( \mathbf{C}^{av} \) is determined. The rotation \( \mathcal{R}_{m,k} \left( \tilde{\mathbf{C}}(m,k) \right) \)

\[
\mathcal{R}_{m,k} \left( \tilde{\mathbf{C}}(m,k) \right) = \mathcal{R}_{m,k} \left( \mathbf{R}_{n(1,k)}(m) \right), \mathcal{R}_{m,k} \left( \mathbf{R}_{n(2,k)}(m) \right), \ldots, \mathcal{R}_{m,k} \left( \mathbf{R}_{n(N,k)}(m) \right)
\]

and

\[
d^2(m,k) = \left( \mathcal{R}_{m,k} \left( \tilde{\mathbf{C}}(m,k) \right) - \mathbf{C}^{av} \right)^2 = \sum_{i=1}^{N} \left( \mathcal{R}_{m,k} \left( \mathbf{R}_{n(i,k)}(m) \right) - \mathbf{R}_i^{av} \right)^2.
\]

Thus, the rotation \( \mathcal{R}_{m,k} \) fits the conformation \( \tilde{\mathbf{C}}(m,k) \) to the average conformation \( \mathbf{C}^{av} \).

In the case of the conventional average structure, which has been used for heteropolymers, the \( i \)th segment of a sampled structure is fitted to the \( i \)th segment of the average structure. We call this type of average structure the type-0 average structure (type-0 AS). Because the numbering of the segments is crucial, the conformation vectors \( \tilde{\mathbf{C}}(m,k), k = 1, \ldots, K \) are considered to represent different structures, although they are obtained from \( \mathbf{C}(m) \) by only changing the numbering of the segments. The average conformation vector \( \mathbf{C}^{av0} \) for the type-0 AS is then given by

\[
\mathbf{C}^{av0} = \frac{1}{MK} \sum_{m=1}^{M} \sum_{k=1}^{K} \mathcal{R}_{m,k} \left( \mathbf{C}(m,k) \right).
\]
In the following, we propose a new type of an average structure for homopolymers, which we call the type-1 average structure (type-1 AS). Because all the segments of a homopolymer are equivalent, the conformation vectors \( C(m, k) \), \( k = 1, \ldots, K \) are considered to represent the same structure as \( C(m) \), although they have different numbering of the segments. Therefore the best fit of a sampled conformation \( C(m) \) to the average conformation is given by the rotation \( R_{m, k_{\text{min}}(m)} \), where \( k_{\text{min}}(m) \) is the value of \( k \) which gives the smallest value of \( d^2(m, k) \) with \( m \) fixed. Thus, the average conformation vector \( C_{\text{av}} \) for the type-1 AS is given by

\[
C_{\text{av}} = \frac{1}{M} \sum_{m=1}^{M} R_{m, k_{\text{min}}(m)} \left( \tilde{C}(m, k_{\text{min}}(m)) \right).
\]  

Because the definition of the rotation \( R_{m, k} \) contains \( C_{\text{av}} \), eqs. (7) and (8) should be solved self-consistently. In practice, \( C_{\text{av}} \) is calculated iteratively. By using the \( n \)th candidate for the average conformation vector \( C_{\text{av}} \) calculated from the \( n \)th iteration, which may be chosen as one of \( \tilde{C}(m, k) \) for the first iteration (\( n = 0 \)), all the rotations \( R_{m, k} \) are determined. Then, the right-hand side of eq. (7) or (8) is calculated and the result is used as the next candidate \( C_{\text{av}} \). The calculation is iterated for \( n = 0, 1, 2, \ldots \) until the distance between \( C_{\text{av}} \) and \( C_{\text{av}}^{n+1} \) becomes sufficiently small and the self-consistency of eq. (7) or (8) is achieved.

3. Results

Brownian dynamics simulations of the model described in the previous section are performed for a single linear polymer and single ring polymers with the trivial knot and the trefoil knot. The following parameters are used: \( T = 1, k_B T/\epsilon = 1, k\sigma^2/\epsilon = 30 \) and \( R_0/\sigma = 1.5 \). The Euler algorithm with a time step \( \Delta t = 10^{-4} \zeta \sigma^2/\epsilon \) is employed for a numerical integration of the equation of motion (1). Hereafter, we set \( \sigma = 1, \zeta = 1 \) and \( \epsilon = 1 \).

In order to calculate the average structures, conformations of a single polymer with \( N \) segments are taken from a simulation every \( \Delta T = 10^{-2} \tau(N) \). For single linear polymers, the time \( \tau(N) \) is chosen as \( \tau(N) = A_L N^{x_L} \), which corresponds to the behavior of the longest relaxation time of single polymers.\(^\text{1,2,16,17}\) For single ring polymers, \( \tau(N) \) is chosen as \( \tau(N) = A_R N^{x_R} \), which corresponds to the behavior of the longest relaxation time for the wave number \( q = 1 \) of single ring polymers with the trivial knot.\(^\text{7}\) The parameters are chosen as \( A_L = 21.05, x_L = 2.22, A_R = 22.96 \) and \( x_R = 2.095 \). The values for linear polymers are estimated from the relaxation mode analysis of the time-displaced correlation matrix \( \langle (\mathbf{r}_1(t) - \mathbf{r}_c(t)) \cdot (\mathbf{r}_j(0) - \mathbf{r}_c(0)) \rangle \) calculated through simulations. The values for ring polymers are taken from the previous study.\(^\text{7}\) The equilibration time \( T_1 \) is chosen as \( T_1 \simeq 10 \tau(N) \). The number of sampled conformations \( M \) is given by \( M = 10^5 \) for \( N = 30, 40, 60 \) and \( 80 \), \( M = 2 \times 10^5 \) for \( N = 110 \) and \( 120 \), \( M = 1.5 \times 10^5 \) for \( N = 160 \) and \( M = 5 \times 10^4 \) for \( N = 240 \), respectively.

Figure 1 shows the average structures for a single linear polymer with \( N = 40 \) segments. In this and the following figures, the bonds connecting adjacent segments of a polymer are
represented by cylinders and the center of mass of the polymer is shown as a sphere. The axes of the Cartesian coordinates are chosen to be the principal axes of the moment of inertia tensor and the length scale is chosen to normalize the contour length of each average structure. In the figures, only the directions of the axes are indicated. The origin of the Cartesian coordinates is chosen to be the center of mass of each average structure in the following descriptions. The type-0 AS shown in Fig. 1(a) has a parabolic shape in the x-y plane, which has C$_2$ symmetry about the y axis. This result agrees with that of the previous study of the average structure of single linear polymers. The C$_2$ symmetry is induced by the symmetry of a single linear homopolymer that the $i$th and $(N - i + 1)$th segments are equivalent, because the numbering of the segments is conserved in the type-0 AS. On the other hand, the type-1 AS shown in Fig. 1(b) does not have the symmetry, although it has a similar shape in the x-y plane. Each sampled conformation $C(m)$ does not have the C$_2$ symmetry, that is, there is no rotation which changes $C(m) = \tilde{C}(m,1)$ into $\tilde{C}(m,2)$. This asymmetry in the sampled conformations is conserved in the type-1 AS, because it neglects the numbering of the segments. The reason why the type-1 AS is in the x-y plane is as follows. Let $M$ denote a reflection operation with respect to a plane containing the origin, which is the center of mass of conformations in the present case. For a rotation operation $R$, we define another rotation operation as $R' = MRM$. Then, $(R(\tilde{C}(m,k)) - C^{av*})^2 = (\tilde{M}(R(\tilde{C}(m,k))) - M(C^{av*}))^2$ holds. Therefore, if $R_{m,k_{\text{min}}(m)}$ gives the smallest square distance calculated from $C(m)$ and $C^{av1}$, $R'_{m,k_{\text{min}}(m)}$ gives the smallest square distance calculated from $M(C(m))$ and $M(C^{av1})$. By considering the mirror image of eq. (8), we have

$$\mathcal{M}(C^{av1}) = \frac{1}{M} \sum_{m=1}^{M} \mathcal{M}(R_{m,k_{\text{min}}(m)}(\tilde{C}(m,k_{\text{min}}(m))))$$

$$= \frac{1}{M} \sum_{m=1}^{M} R'_{m,k_{\text{min}}(m)}(M(\tilde{C}(m,k_{\text{min}}(m)))).$$ (9)

This equation means that if the type-1 AS calculated from $M$ samples $C(m)$, $m = 1, \ldots, M$ is given by $C^{av1}$ then that calculated from $M$ samples $M(C(m))$, $m = 1, \ldots, M$ is given by $M(C^{av1})$. For a sampled conformation $C(m)$, its mirror image $M(C(m))$ has the same statistical weight as $C(m)$ in the ensemble of conformations, because a single linear polymer has no chirality. In other words, the ensemble of conformations $M(C(m))$ is the same as that of conformations $C(m)$. Therefore, the average conformation $C^{av1}$ and its mirror image $M(C^{av1})$ represent the same conformation, that is, there exists a rotation $R$ which satisfies $C^{av1} = R(M(C^{av1}))$. It should be a conformation in a plane or a three-dimensional conformation with a plane of reflection symmetry.

Figure 2 shows the average structures of a single ring polymer with the trivial knot for the case of $N = 40$. The type-0 AS shown in Fig. 2(a) forms a regular polygon of $N = 40$
Fig. 1. The type-0 AS (a) and the type-1 AS (b) of a single linear polymer with $N = 40$. In each figure, the cylinders and the sphere represent the bonds connecting adjacent segments and the center of mass of the polymer, respectively.
Fig. 2. The type-0 AS (a) and the type-1 AS (b) of a single ring polymer with the trivial knot for \( N = 40 \). The meaning of the cylinders and the spheres is the same as in Fig. 1.

between the position vectors projected onto the \( x-y \) plane of the first and the \( i \)th segments:

\[
\cos \theta_i = \frac{R_{av0}^{i,x} R_{av0}^{i,x} + R_{av0}^{i,y} R_{av0}^{i,y}}{\sqrt{R_{av0}^{i,x}^2 + R_{av0}^{i,y}^2} \sqrt{R_{av0}^{i,x}^2 + R_{av0}^{i,y}^2}}
\]

\[
\sin \theta_i = \frac{R_{av0}^{i,x} R_{av0}^{i,y} - R_{av0}^{i,y} R_{av0}^{i,x}}{\sqrt{R_{av0}^{i,x}^2 + R_{av0}^{i,y}^2} \sqrt{R_{av0}^{i,x}^2 + R_{av0}^{i,y}^2}}
\]

Here, \( R_{av0}^{i,\alpha} \) denotes the \( \alpha \)-component of the position vector \( R_{av0}^{i} \) of the \( i \)th segment relative to the center of mass in the type-0 AS. Figure 4 shows a plot of \( \theta_i/2\pi \) versus \( (i - 1)/N \). It is clearly seen that the type-0 AS forms a double loop for \( N \leq 110 \) and a single loop for \( N \geq 120 \). In other words, the type-0 AS forms a regular polygon of \( N/2 \) sides for \( N \leq 110 \), where \( N \) is even, and a regular polygon of \( N \) sides for \( N \geq 120 \). Note that in the case of the double loop structure with even \( N \), the symmetry operations corresponding to the 2\( N \) ways of changing the numbering of the segments become those of \( D_{N/2} \), because \( R_{av0}^{i} = R_{av0}^{n(i,N/2)} \) for \( i = 1, \cdots, N/2 \). The region of the double loop structure and that of the single loop structure must be separated by a transition segment number \( N_{av0} \) between 110 and 120. This transition is considered to correspond to the localization-delocalization transition of the knotted part, because if the knotted part of a conformation \( \mathcal{R}_{m,k} \left( \hat{C}(m,k) \right) \) is delocalized, its projection onto the plane of the type-0 AS encompasses the center of mass while the projection of the knotted part does not encompass the center of mass if the knotted part is localized. Note that the form of the type-0 AS of the ring polymer with the trefoil knot for \( N \geq 120 \), which is a regular polygon of \( N \) sides, is the same as that with the trivial knot.

Figure 5 shows the type-1 ASs of single ring polymers with the trefoil knot for \( N = 30, 40, 60, 80, 110, 120, 160 \) and 240. In the case of the trefoil knot, the type-1 ASs do not have reflection symmetry. This is because a ring polymer with the trefoil knot has chirality and therefore the mirror image of a sampled conformation \( C(m) \) is topologically different.
from $C(m)$ and does not appear in the ensemble of conformations to which $C(m)$ belongs. Moreover, the knot type of the type-1 AS is identical with that of the original structure for each $N$. It is clearly seen that the knotted part is delocalized for small values of $N$ and is localized for large values of $N$. The crossover segment number $N_{av1}^x \simeq 120$ from the delocalized state, where the center of mass is inside of the knotted part, to the localized state, where the center of mass is outside of the knotted part, is consistent with the transition segment number $N_{av0}^t$ of the type-0 AS.

4. Summary and Discussion

In the present paper, the two types of average structures are calculated for a single linear polymer and single ring polymers by Brownian dynamics simulations. The average conformation vector, which specifies the average structure, is self-consistently defined by eqs. (7) and (8): It is the average of the sampled conformation vectors each of which is rotated to minimize its distance from the average conformation vector. From a conformation vector $C(m)$ of single homopolymers, $K$ conformation vectors $\tilde{C}(m, k)$ with $k = 1, \ldots, K$ are generated by changing the numbering of the segments, where $K = 2$ for linear homopolymers and $K = 2N$ for ring homopolymers with $N$ segments. In the calculation of the type-0 average structure, which has been used for heteropolymers, the position of the $i$th segment of a sampled conformation is fitted to that of the $i$th segment of the average conformation. Therefore, in the case of homopolymers, the above-mentioned $K$ conformation vectors represent different structures and are used with the same statistical weight in the calculation as shown in eq. (7). Thus, the type-0 AS should be invariant under the $K$ ways of changing the numbering of the segments. For a single linear polymer, the type-0 AS has a parabolic shape in the $x$-$y$ plane with the $C_2$ symmetry about the $y$ axis, where the two symmetry operations of the group $C_2$ correspond to the two ways of changing the numbering. In the case of a single ring polymer of $N$ segments with the trivial knot, the type-0 AS is given by a regular polygon of $N$ sides with the $D_N$ symmetry, where the $2N$ symmetry operations of the group $D_N$ correspond to the $2N$ ways of changing the numbering.

In the calculation of the type-1 average structure, which is proposed in the present paper, differences in the numbering of the segments are neglected and all the $K$ conformation vectors represent the same structure. Therefore, among the $K$ conformation vectors, the only one conformation $\tilde{C}(m, k_{min}(m))$, which becomes the closest to the average conformation vector by the rotation $R_{m,k_{min}}(m)$, is used in the calculation of the type-1 AS as shown in eq. (8). Thus, deviations from the symmetric form of the type-0 AS in the sampled conformations are conserved in the type-1 AS. The type-1 AS of a single linear polymer has a distorted parabolic form without the $C_2$ symmetry in the $x$-$y$ plane. For a ring polymer of $N$ segments with the trivial knot, the type-1 AS forms a distorted polygon of $N$ sides without the $D_N$ symmetry in the $x$-$y$ plane. It is shown that the mirror image of the average structure calculated from
conformations of a polymer gives the average structure calculated from the mirror images of the conformations. In the ensemble of conformations of a linear polymer or a ring polymer with the trivial knot, which has no chirality, a conformation and its mirror image have the same statistical weight and the ensemble of the mirror images of the original conformations is the same as the original ensemble. Therefore the average structure and its mirror image represent the same structure. Thus, the average structure is given by a conformation in a plane or a three-dimensional conformation with a plane of reflection symmetry. All the average structures of a single linear polymer and single ring polymers with the trivial knot are planar and consistent with the above consideration.

The type-0 AS of a single ring polymer of $N$ segments with the trefoil knot forms a double loop on a regular polygon of $N/2$ sides for even $N \leq 110$ and a single loop on a regular polygon of $N$ sides for $N \geq 120$. These structures are invariant under the symmetry operations corresponding to the $2N$ ways of changing the numbering. The transition from the double loop structure to the single loop structure occurs at the transition segment number $N_{t}^{\text{av0}}$ between 110 and 120. This transition is considered to correspond to the localization-delocalization transition of the knotted part. Because a ring polymer with the trefoil knot is chiral, its type-1 AS does not have reflection symmetry and has the same knot type as the sampled conformations. The knotted part of the type-1 AS is expanded along the whole structure for small values of $N$ and localized to a part of the structure for large values of $N$. The crossover from the delocalized state to the localized state occurs around the crossover segment number $N_{x}^{\text{av1}} \approx 120$, which is consistent with the value of $N_{t}^{\text{av0}}$. The transition of the type-0 AS and the crossover of the type-1 AS furnish strong evidence for the localization of the knotted part predicted in the previous study, where the transition segment number is between 120 and 160.\(^{7}\)

It is demonstrated that the analysis of the average structures is useful for studying the localization of the knotted part of single knotted ring polymers. The present paper provides strong evidence for the knot localization by directly observing the average structures in three dimensions. In the case of single ring polymers with the trefoil knot, the transition of the type-0 AS from the double loop structure to the single loop structure is observed as the number of the segments $N$ is increased, which is considered to correspond to the localization-delocalization transition of the knotted part. The trefoil knot is a $(3,2)$-torus knot. Here, a $(p, q)$-torus knot is given by a curve on the surface of a torus which winds $p$ times around the center line of the torus and revolves $q$ times along the center line of the torus.\(^{26}\) In the case of the trefoil knot, the curve revolves twice along the center line of the torus. Therefore, it seems natural that the type-0 AS forms a double loop structure for small $N$ and that the transition to a single loop structure occurs as $N$ is increased. It is expected that the similar transitions occur in the type-0 ASs of single ring polymers with another torus knot, such as $5_1$, $7_1$, or
It is interesting to study how the type-0 ASs of single ring polymers with a nontorus knot depends on $N$. The type-1 ASs of single ring polymers with the trefoil knot have the same knot type as the original conformations and show the knot localization directly. Single ring polymers with the trefoil knot have chirality. Therefore, their type-1 ASs need not to have reflection symmetry. Thus, single knotted ring polymers with chirality have less constraints on the shapes of their type-1 ASs. Because torus knots have chirality, it is expected that the type-1 ASs of single ring polymers with another torus knot show the knot localization in three dimensions. It is interesting to study what kind of structures are formed by the type-1 ASs of single knotted ring polymers without chirality. They must be planar structures or three-dimensional structures with reflection symmetry. The study of the average structures of single ring polymers with the figure eight knot is very important, because the figure eight knot is the next simplest prime knot and a nontorus knot without chirality. The study in this direction is in progress.

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Fig. 3. The type-0 ASs of a single ring polymer with the trefoil knot for $N = 30, 40, 60, 80, 110, 120, 160$ and $240$. The meaning of the cylinders and the spheres is the same as in Fig. 1.
Fig. 4. A plot of $\theta_i/(2\pi)$ versus $(i - 1)/N$ for the type-0 ASs of single ring polymers with the trefoil knot for $N = 60, 110, 120$ and $240$. For clarity, only the data for $(i - 1)/N = n/60$ with $n = 0, 1, \ldots, 59$ are plotted for $N = 120$ and $240$. 
Fig. 5. The type-1 ASs of a single ring polymer with the trefoil knot for \( N = 30, 40, 60, 80, 110, 120, 160 \) and 240. The meaning of the cylinders and the spheres is the same as in Fig. 1.
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