



Topological catenation induced swelling of ring polymers revealed by molecular dynamics simulation

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ABSTRACT

Equilibrium conformational properties of a ring polymer (named by 'inner ring') simultaneously concatenated with a varying number of outer rings in a 'flower'-shaped polymer catenane are explored by molecular dynamics simulations. Two different cases have been considered. In Case I, the excluded volume interactions between the outer rings are absent in a polymer catenane, while they are present in Case II. Results demonstrate that, compared to an isolated ring polymer, size and shape properties of the same, inner ring in a polymer catenane can be greatly modified by the catenation topology in both Cases. It is concluded that the topological catenation can induce a swelling of the inner ring in a catenane compared to the same ring in isolation. Importantly, scaling relationships between the swelling degree, f_{sw} , of the inner ring and number of the outer rings, n , have been established in both Case I and Case II, $f_{sw} = an^\alpha$, where the prefactor a and scaling exponent α are all predominantly dependent on molecular-weight ratio of the inner to outer rings in catenane. Besides, swelling of inner ring in a catenane of Case II is more pronounced than the same inner ring in a catenane of Case I. The mean asphericity of the inner ring is slightly increased due to the catenation topology, while its mean prolateness is remarkably modified by the catenation topology. The inner ring in a catenane becomes more oblate, compared to the same ring in isolation, with increasing either number or molecular weight of the outer rings in the catenane. Profiles of the mean prolateness changes of the inner ring from those of the same isolated ring with respect to number of the outer rings are also mainly controlled by the molecular-weight ratio of the inner to outer rings.

1. Introduction

Topological constraint is an important concept in polymer physics, and plays a crucial role in many conformational properties of polymers [1–3], which essentially are molecular origins of all the physical properties and functions of polymers [4]. Notably, the topological constraint in polymer systems is an emergent phenomenon resulting merely from connectivity of a polymer chain, which implies two polymer strands cannot cross each other. This uncrossability of polymer chains leads to a 'one-dimensional' motion, or reptation, of polymers in dense systems (e.g. a concentrated solution or melt) of long linear chains [1–3]. The polymer dynamics under the (interchain) topological constraints in linear polymers acts as physical origin of their fruitful dynamic and rheological properties [5,6].

Topological constraints can also influence static conformations of polymer chains, e.g., in ring polymer systems. For ring polymers, uncrossability of polymer strands makes the topological state of a chain fixed, which thus reduces the conformational space accessible by the

polymer. Therefore, even the conformational statics of ring polymers can be significantly affected by the (intrachain) topological constraint. For example, in a single trivial-knot ring, keeping the topology fixed generates repulsive interactions between different parts of the chain, or effectively topological excluded volume of the segments in the chain, even though there is no explicit excluded volume interactions [7,8]. Computer simulation results [9–11] revealed that the topological constraint in a single trivial-knot ring swells the chain, e.g., its mean-squared radius of gyration, $\langle R_g^2 \rangle$, scales with the chain length, N , in a similar way as a linear polymer in a good solvent, $\langle R_g^2 \rangle \sim N^{2\nu}$ with $\nu \approx 0.6$.

Further topological constraints can be introduced into a ring polymer when it is concatenated with other rings [12,13]. Very interestingly, concatenated ring biopolymers, such as DNA catenanes [14,15] and protein catenanes [16–24], have been found in nature. For example, concatenated DNA structures were first discovered to exist inside living cells in 1960s. Afterwards, several natural protein catenanes

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have been identified sequentially since 2000. Furthermore, it is found that surprisingly naturally occurring catenated DNAs exist not only as linear catenanes but also as branched or even network catenanes [25–27], in which some circular DNAs are interlocked with more than one other DNAs through the *Hopf link*. Polymer catenanes of varying architectures (e.g. linear, branched, network) of both naturally occurring [28–34] and synthetic ring molecules [12] have been already successfully prepared in lab via modern synthetic techniques.

Since topological constraints play a key role in conformational properties of polymers, it is expected that many unique conformational properties of the catenated ring polymers can emerge due to presence of topological interactions. This may give rise to promising applications of polymer catenanes as functional materials, nanomachines etc. in a future nanotechnology era, which physically are attributed to unconventional conformational properties of their underlying building-blocks, e.g., catenated (macro)cycles. However, the conformational properties of catenated ring polymers have been less studied both theoretically [35,36] and experimentally, and thus influence of topological catenation on the conformations of rings being concatenated with others still remains incompletely understood. Only recently, Bohn et al. [36] studied the conformational properties of ring polymers catenated with a second ring of the same molecular weight using Monte Carlo simulations. Their simulation results conclude that the mean-squared radius of gyration of a ring topologically interlocked to a second ring can be enlarged by about 10% (in the case of infinitely long rings) compared to that of isolated ring of the same molecular weight, while the absolute degree of enlargement of the mean-squared radius of gyration increases with decreasing molecular weight of the catenated ring. Concerning influence of topological catenation on shape properties of rings, it is concluded through their simulation study that the topological interaction makes the catenated ring polymers more aspherical and more oblate. We note that in their study [36] the polymer catenanes are the simplest kind, where the valence of catenated ring (or the number of rings that a given ring is topologically interlocked to) is one, and the molecular weights of two concatenated rings are equal.

In this work, using molecular dynamics (MD) simulations, we investigate static conformational properties of a ring polymer (called ‘inner ring’) being simultaneously topologically interlocked to a varying number of other rings (called ‘outer rings’) of different molecular weights as depicted in Fig. 1. Our aim is to reveal influence of topological catenation on changes of size and shape properties of the inner ring in a catenane. The paper is organized as following. In Section 2, we present the computational model and simulation details. Simulation results are given in Section 3, which is followed by discussion (Section 4) and conclusions (Section 5).

2. Model and simulation

Each of the catenanes under study is composed of one ‘inner’ ring (colored by red in Fig. 1) and n ‘outer’ rings (colored by blue in Fig. 1) being topologically interlocked to the former in a way depicted in Fig. 1. Each inner ring and outer ring constitute m_i and m_o particles, respectively. In this work, we tune the molecular parameters, n , m_i and m_o , to investigate how the conformational properties (size and shape properties) of the inner ring are changed from those of its corresponding isolated ring polymer.

We employ Kremer–Grest model, [37] a widely-used *minimal* model for polymers with topological constraints, to simulate the catenane systems considered in this work. Specifically, each ring polymer in a catenane is composed of a number of particles, each of which interacts with its two bonded particles along the chain backbone by a finite extensible nonlinear elastic potential (FENE),

$$U_{\text{FENE}}(r) = \begin{cases} -0.5kR_0^2 \ln [1 - (r/R_0)^2], & r \leq R_0 \\ \infty, & r > R_0. \end{cases} \quad (1)$$

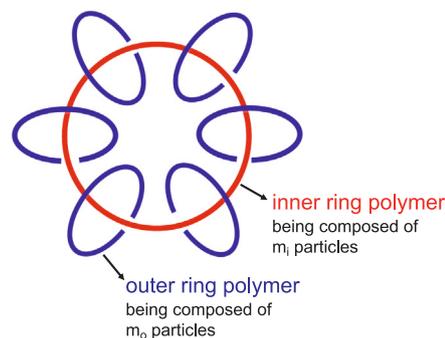


Fig. 1. Schematic demonstration of polymer catenane under study in this work. In this example, the inner ring polymer (red circle) is simultaneously topologically interlocked with $n = 6$ outer ring polymers (blue circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In addition, in this model, all particles interact with each other by a purely repulsive Lennard-Jones excluded volume interaction,

$$U_{\text{LJ}}(r) = \begin{cases} 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon, & r \leq r_c \\ 0, & r > r_c. \end{cases} \quad (2)$$

Here, $k = 30\epsilon/\sigma^2$, $R_0 = 1.5\sigma$, and $r_c = 2^{1/6}\sigma$. The temperature and time unit of the model are $T = \epsilon/k_B$ and $\tau = \sigma\sqrt{m/\epsilon}$, respectively, where k_B is the Boltzmann constant and m is the mass of each particle in the catenane. We run MD simulation of the Kremer–Grest model in canonical ensemble using Langevin thermostat to maintain the temperature ($T = 1.0$), with a time step and friction coefficient of 0.01τ and $1.0\tau^{-1}$, respectively. The velocity Verlet method was used to numerically integrate Newton’s equations of motion, and the simulations were performed within a cubic simulation box with periodic boundary conditions in all dimensions, with each edge dimension much larger than twice of gyration radius of polymer catenane. The initial conformation of the catenane is set-up manually, while chain topology is preserved all the time during the simulation because of uncrossability of polymer strands within the Kremer–Grest model. Equilibration of the chain conformation is achieved once mean-squared radius of gyration of the polymer reaches a converged value. After equilibration, we run MD simulation for $1 \times 10^6\tau$ for the production.

In our study, we distinguish catenated ring polymers in two different cases. In the first case (Case I), a given ring polymer is topologically interlocked with a varying number of other rings (outer rings), between which excluded volume interactions are *absent*. Looking into such systems enables us to uncover the *direct* effect of topological catenation on modifying conformations of the target ring polymers. Then, excluded volume interactions between the outer rings are switched on in the second case (Case II), in order to identify possibly *combinational* effect of the topological catenation (between the inner and outer rings) and excluded volume interactions (between the outer rings) on the static conformations of the inner rings. We consider a series of catenanes which are distinguished from each other by both molecular weight of the inner ring, m_i , and molecular-weight ratio of the inner to the outer rings, m_i/m_o . In this work, we look into systems where $80 \leq m_i \leq 480$ and m_i/m_o ranges from 1 to 20.

To quantify the relatively dimensional changes of the inner ring with respect to an isolated ring of the same molecular weight, we define a swelling degree for the former ring, $f_{\text{sw}}(n)$, as

$$f_{\text{sw}}(n) = \frac{\langle R_g^2(n) \rangle}{\langle R_{g,0}^2 \rangle} - 1, \quad (3)$$

in which $\langle R_g^2(n) \rangle$ denotes the mean-squared radius of gyration of the inner ring catenated with n outer rings, and $\langle R_{g,0}^2 \rangle$ represents the

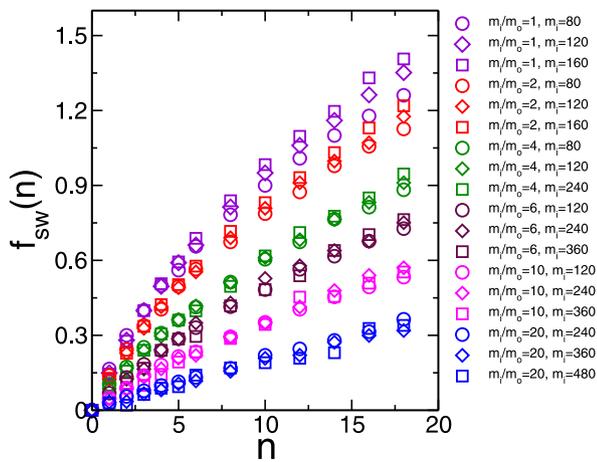


Fig. 2. Swelling degree of the inner ring, $f_{sw}(n)$, as a function of number of the outer rings, n , in a catenane of Case I, where excluded volume interactions between the outer rings are switched off.

mean-squared radius of gyration of isolated ring of the same molecular weight. Clearly, $f_{sw} = 0$ if there is no dimensional changes of the catenated ring compared to the isolated one, while $f_{sw} > 0$ ($f_{sw} < 0$) indicates the former one swells (shrinks) with respect to the latter ring polymer.

The shape properties of rings [38–41] are quantified by two *independent* quantities, the asphericity, A , and the prolateness, P , which are defined as

$$A = \frac{(\lambda_1 - \lambda_2)^2 + (\lambda_1 - \lambda_3)^2 + (\lambda_2 - \lambda_3)^2}{2(\lambda_1 + \lambda_2 + \lambda_3)^2}, \quad (4)$$

$$P = \frac{(2\lambda_1 - \lambda_2 - \lambda_3)(2\lambda_2 - \lambda_1 - \lambda_3)(2\lambda_3 - \lambda_1 - \lambda_2)}{2(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - \lambda_1\lambda_2 - \lambda_1\lambda_3 - \lambda_2\lambda_3)^{2/3}}. \quad (5)$$

Here, $\lambda_1 \geq \lambda_2 \geq \lambda_3$ denote the three eigenvalues of radius of gyration tensor of a ring conformation, which give squared lengths of the principal axes of gyration. The asphericity measures the degree of deviation of a polymer conformation from a fully spherical one, and it is bounded between $0 \leq A \leq 1$. For $A = 0$, the polymer conformation is completely spherical, i.e., $\lambda_1 = \lambda_2 = \lambda_3$, and $A = 1$ is for a fully extended, rodlike polymer conformation. The prolateness is used to specify the nature of shape anisotropy, i.e., whether the shape is prolate or oblate. It is bounded between $-1 \leq P \leq 1$, and $P = -1$ is for a fully oblate shape ($\lambda_1 = \lambda_2 > \lambda_3$), such as a disk, while $P = 1$ for a prolate object ($\lambda_1 > \lambda_2 = \lambda_3$). When $\lambda_2 < (\lambda_1 + \lambda_3)/2$, then $P > 0$, i.e., polymer shape is prolate. And when $\lambda_2 > (\lambda_1 + \lambda_3)/2$, $P < 0$, i.e., polymer shape is oblate. As the asphericity and the prolateness are two independent quantities, there may exist two polymer conformations, whose asphericity values are the same but nature of asphericity differs.

3. Results

First, we study effect of the catenation topology on conformational properties (e.g. size and shape) of the inner rings in polymer catenanes of Case I, where excluded volume interactions between the outer rings are absent. Aim is to reveal topological catenation induced changes of size and shape properties of the inner rings in catenanes compared to their counterparts in isolation. Fig. 2 shows simulation results about the swelling degree (defined in Eq. (3)) of the inner ring, $f_{sw}(n)$, as a function of number of the outer rings being interlocked to the former, n , for a series of polymer catenanes of Case I. Detailed findings are summarized in the following. (i) For all catenanes under study in this work, we have $f_{sw}(n) > 0$, indicating that the inner ring in catenane becomes swollen compared to the same isolated ring. (ii) Swelling of the inner ring gets more pronounced either when it is concatenated

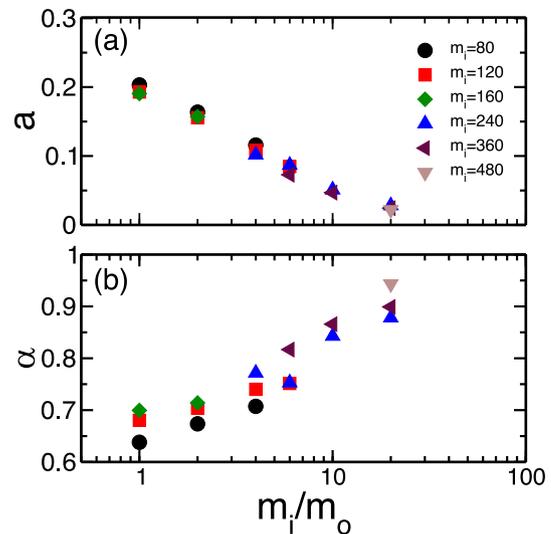


Fig. 3. Dependence of the fitting parameters a and α in Eq. (6) on the molecular-weight ratio of the inner to outer rings in the polymer catenane of Case I, m_i/m_o .

with more outer rings (i.e., larger n) or with increasing molecular weight of the outer rings (i.e., smaller m_i/m_o). (iii) It turns out that the swelling degree, $f_{sw}(n)$, shown in Fig. 2 can be well described by equation

$$f_{sw}(n) = an^\alpha, \quad (6)$$

with a and α being fitting parameters. In Fig. 3, shown are values of a and α obtained by fitting simulation data in Fig. 2 to Eq. (6). It is concluded that both a and α are predominantly controlled by m_i/m_o , while dependence of a and α on m_i is small. In details, the scaling exponent α increases with increasing m_i/m_o , while a decreases as m_i/m_o increases. However, more theoretical endeavors are required for us to achieve a deep understanding of these findings.

Recently, Bohn et al. [36] reported conformational properties of ring polymer in catenanes characterized by $m_i/m_o = 1$ and $n = 1$. Unfortunately, it is a lattice Monte Carlo model that was employed in their work, making a direct quantitative comparison of their computational results with our findings inaccessible. In their work, it is concluded that the swelling degree, $f_{sw}(n)$, of the inner ring decreases as molecular weight of the inner ring increases. For instance, the extrapolation value of $f_{sw}(n)$ in the limit of large chain lengths is 0.105(2), and it decreases to about 0.14 for the shortest ring polymer being studied in Ref [36]. Consistently, in this work we find that $f_{sw}(n)$ for catenanes of $m_i/m_o = 1$ and $n = 1$ is also inversely proportional to molecular weight of the inner ring, i.e., $f_{sw}(n) \approx 0.17, 0.15, 0.14$ for $m_i = 80, 120, 160$, respectively.

Shape properties of the inner rings in polymer catenanes are represented in Fig. 4. The mean asphericity, $\langle A(n) \rangle$, of the inner ring in a polymer catenane is plotted as a function of number of the outer rings in the catenane, n , in Fig. 4(a). Accordingly, Fig. 4(b) shows deviation of the mean asphericity of the inner ring in a catenane from that of an isolated ring of the same molecular weight, $\Delta A(n) = \langle A(n) \rangle - \langle A(n=0) \rangle$, as a function of number of the outer rings in the catenanes, n . It turns out that topological catenane makes the inner rings more aspherical. In contrast, topological catenation can significantly modify the mean prolateness of the inner rings. Fig. 4(c) shows the mean prolateness, $\langle P(n) \rangle$, of the inner ring in a polymer catenane as a function of number of the outer rings in the catenane. The mean asphericity and prolateness of inner ring in a catenane with $m_i/m_o = 1$ have been reported by Bohn et al. [36]. It is concluded in their work [36] that correspondingly $\langle A(n=1) \rangle \approx 0.26$ and value of $\langle P(n=1) \rangle$ declines from 0.42 to 0.30 as molecular weight of the inner ring decreases. These findings are

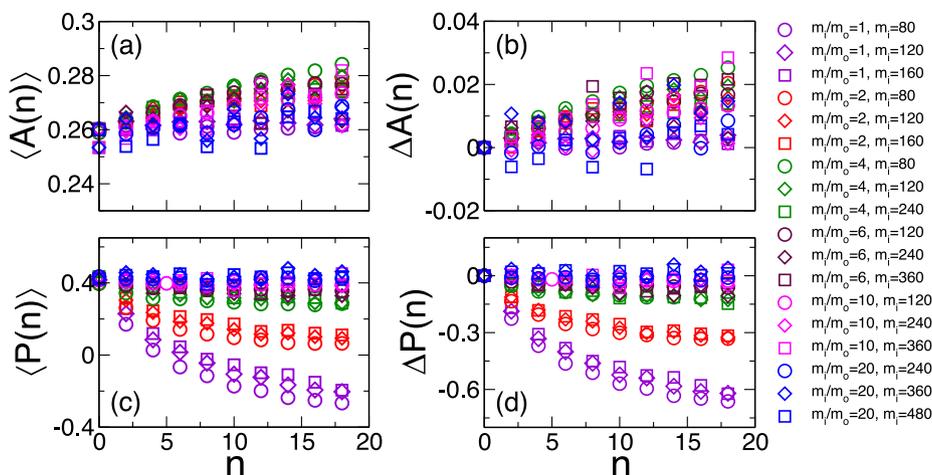


Fig. 4. The mean asphericity (a), $\langle A(n) \rangle$, and the mean prolateness (c), $\langle P(n) \rangle$, of the inner rings in polymer catenanes of Case I as a function of number of the outer rings, n . Note that the case of $n = 0$ is the isolated ring polymer. Changes of values of the mean asphericity, $\Delta A(n) = \langle A(n) \rangle - \langle A(n=0) \rangle$, and the mean prolateness, $\Delta P(n) = \langle P(n) \rangle - \langle P(n=0) \rangle$, of the inner rings in polymer catenanes from those of the same rings in isolation as a function of number of the outer rings in the catenanes of Case I, n , are given in (b) and (d), respectively.

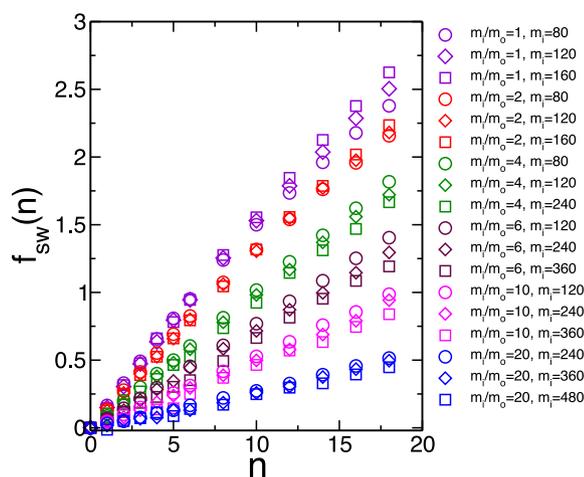


Fig. 5. Swelling degree of the inner ring, $f_{sw}(n)$, as a function of number of the outer rings, n , in a catenane of Case II, where excluded volume interactions between the outer rings are present.

in a good agreement with our simulation results (data not shown in Fig. 4). In Fig. 4(d), changes of the mean prolateness of the inner ring from that of an isolated ring, $\Delta P(n) = \langle P(n) \rangle - \langle P(n=0) \rangle$, are shown. In most of polymer catenanes being studied (except those in which the molecular weight of the outer rings is so small compared to the inner one, i.e., $m_i/m_o \geq 10$), we find that $\Delta P < 0$, suggesting that catenation topology makes the inner rings in catenanes more oblate than those rings in isolation. Furthermore, the oblateness of the inner ring in polymer catenanes becomes more pronounced when the former is concatenated with more outer rings. Interestingly, we find that changes of the mean prolateness of the inner rings are also predominantly determined by molecular-weight ratio of the inner to outer rings. Furthermore, smaller the molecular weight of the outer rings (or larger m_i/m_o), shape of the inner ring tends to be less oblate. One can notice that in those catenanes with $m_i/m_o \geq 10$ the mean prolateness or oblateness of the inner rings becomes approximately unchanged, $\Delta P \approx 0$.

In the following, we investigate how size and shape properties of the inner rings are influenced by the concatenated outer rings, between which excluded volume interactions are present. In Fig. 5, the swelling degree of the inner rings in catenanes, $f_{sw}(n)$, are shown with respect to

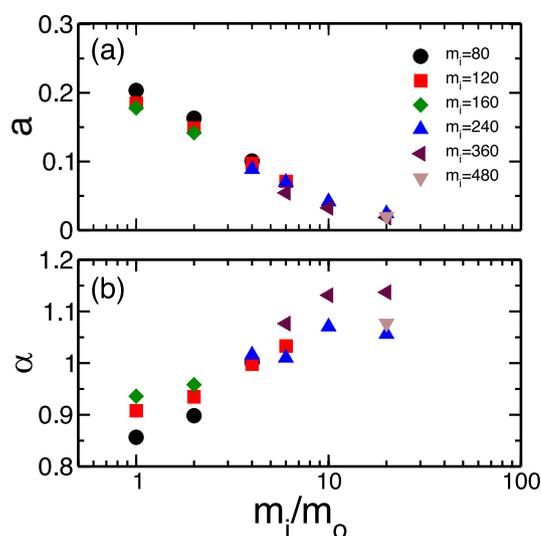


Fig. 6. Dependence of the fitting parameters a and α in Eq. (6) on the molecular-weight ratio of the inner to outer rings in the polymer catenane of Case II, m_i/m_o .

the total number of concatenated outer rings, n . The swelling behavior of the inner rings share many common features as Case I, where there is no excluded volume interactions between the outer rings. For example, the inner ring in a catenane is swollen more and more when it is concatenated with more outer rings or when molecular weight of the outer ring increases. Importantly, one can notice that for the same catenane system the inner ring can swell more significantly in Case II than that of Case I. Furthermore, the swelling degree, f_{sw} , for this case can also be well described by Eq. (6). Detailed values of a and α obtained by fitting simulation data to Eq. (6) in Fig. 5 are shown as a function of m_i/m_o in Fig. 6. One can find, by comparing Figs. 3 and 6, dependence of a on m_i/m_o in Case II is similar as that in Case I, and values of α are larger than those in Case I for the same system in terms of m_i/m_o .

Results about the influence of topological catenation on the mean asphericity and the mean prolateness of the inner rings are shown in Fig. 7. We find that switching on the excluded volume interactions between the outer rings does not affect the qualitative behavior of ΔA and ΔP versus n and the results share common features as those

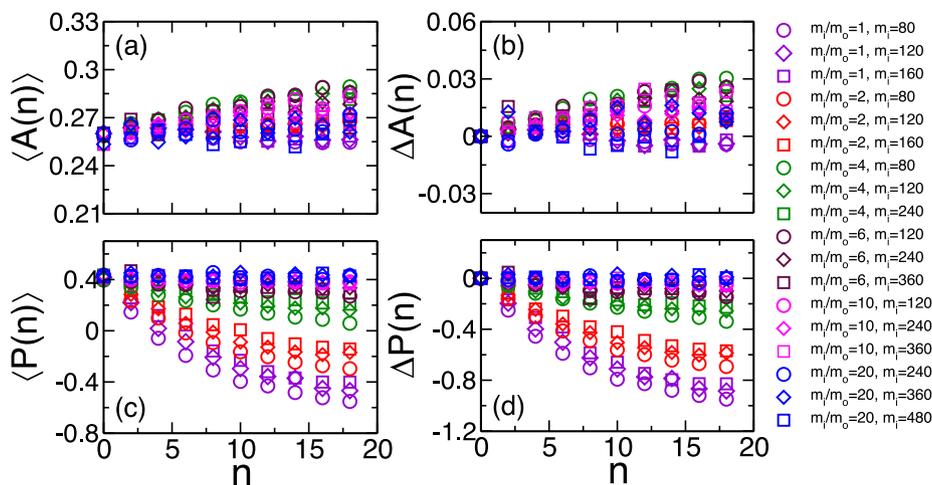


Fig. 7. The mean asphericity (a), $\langle A(n) \rangle$, and the mean prolateness (c), $\langle P(n) \rangle$, of the inner rings in polymer catenanes of Case II as a function of number of the outer rings, n . Note that the case of $n = 0$ is the isolated ring polymer. Changes of values of the mean asphericity, $\Delta A = \langle A(n) \rangle - \langle A(n=0) \rangle$, and the mean prolateness, $\Delta P = \langle P(n) \rangle - \langle P(n=0) \rangle$, of the inner rings in polymer catenanes from those of the same rings in isolation as a function of number of the outer rings in the catenanes of Case II, n , are shown in (b) and (d), respectively.

in Case I (see Fig. 4). Nevertheless, one can notice that for the same catenane presence of the excluded volume interactions between the outer rings makes the inner ring more oblate than that in Case I, where the excluded volume interactions between the outer rings are absent. To further illustrate role of excluded volume interactions between the outer rings in modifying shape properties of the inner rings, Fig. 8 shows ratios of the average eigenvalues $\langle \lambda_1 \rangle / \langle \lambda_3 \rangle$ and $\langle \lambda_1 \rangle / \langle \lambda_2 \rangle$ of the gyration tensor for the inner rings from several selected types of polymer catenanes of both Case I and Case II, in which the inner rings are concatenated with n outer rings. It is seen that there is a gradual increase of $\langle \lambda_1 \rangle / \langle \lambda_3 \rangle$ and decay of $\langle \lambda_1 \rangle / \langle \lambda_2 \rangle$ with increasing n . Consistent with results given in Figs. 4 and 7, this means that the inner rings in those catenanes with $m_i/m_o = 1, 2, 6$ become more oblate when there are more outer rings being concatenated with them in polymers. We note that even for those catenanes with $m_i/m_o = 1$, where shape changes of the inner rings are the most pronounced, $\langle \lambda_1 \rangle / \langle \lambda_2 \rangle$ still remains larger than unity. Furthermore, in those catenanes with presence of excluded volume interactions between the outer rings, changes of ratios of the average eigenvalues are more pronounced than those in Case I. This clearly demonstrates specific role of the excluded volume interactions between the outer rings in modifying shape properties of the inner rings. However, for those catenanes with $m_i/m_o = 20$, the ratios of the average eigenvalues remain approximately unchanged, suggesting that effect of the outer rings on shape of the inner rings dies away when their molecular weight gets relatively small.

As an illustrative representation, Figs. 9 and 10 show, for two kinds of polymer catenanes of Case II in terms of m_i/m_o , typical conformation snapshots of catenanes and average segment density distributions of the inner and outer rings on three planes ($z = 0, y = 0, x = 0$) in the corresponding system of principal axes. Here the axes, x, y, z , are parallel to the three principal axes of decreasing values of the corresponding eigenvalues, $\lambda_1, \lambda_2, \lambda_3$, for the average instantaneous radius of gyration tensor. Specifically, Fig. 9 is for polymer catenanes with $m_i/m_o = 1$, $m_i = 160$, and $n = 2, 18$. Comparing segment density distributions of the inner rings on plane $z = 0$ in Fig. 9 ($n = 2$ (b) and $n = 18$ (b)), one can clearly see that, with increasing number of the outer rings, the inner ring becomes significantly swollen and furthermore confined within a ‘ring’-shaped tube, where the segments of the inner ring distribute inhomogeneously. The inhomogeneous distribution of segment density of the inner ring in this ‘ring’-shaped tube is due to an ellipsoid nature of the inner ring shape on plane $z = 0$, as indicated by a fact of $\langle \lambda_1 \rangle / \langle \lambda_2 \rangle > 1$ shown in Fig. 8. In addition, by comparing segment density distributions of the outer rings in Fig. 9, we find

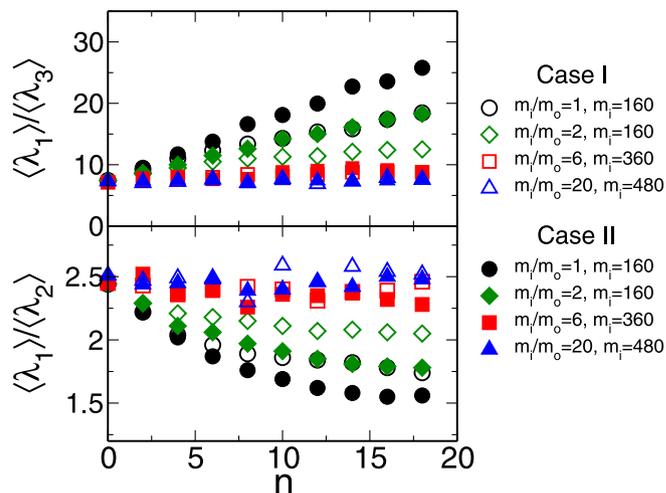


Fig. 8. Ratios of the average eigenvalues $\langle \lambda_1 \rangle / \langle \lambda_3 \rangle$ and $\langle \lambda_1 \rangle / \langle \lambda_2 \rangle$ of the gyration tensor for the inner rings of polymer catenanes of both Case I (open symbols) and Case II (solid symbols) composed of varying number of the outer rings, n .

that presence of excluded volume interactions between the outer rings leads to more segregation of them in catenane of $n = 18$ away from the center of mass of the catenane. In contrast, as shown in Fig. 10, all of these above-mentioned ‘structured’ segment density distributions become much weaker in catenanes with $m_i/m_o = 20$.

Considering above-mentioned role of the outer rings in regulating the inner ring conformations, it is instructive to learn some basic properties of conformation and packing structure of the outer rings in catenanes. To that end, we investigate how the outer rings distribute along contour of the inner ring. Fig. 11 represents the average distance, $\langle d_{\text{com},o} \rangle$, between centers of mass of any two nearest neighboring outer rings as a function of their number, n , in selected examples of catenane. In Fig. 11, $\langle d_{\text{com},o} \rangle$ is rescaled by root of mean-squared radius of gyration of the outer rings, $\bar{R}_{g,o} = \sqrt{\langle R_{g,o}^2 \rangle}$. We note that, as seen in the inset of Fig. 11, $\bar{R}_{g,o}$ is of a constant value, it is both n -independent and irrelevant to whether the excluded volume interactions between the outer rings are present or not. From Fig. 11, one can see that $\langle d_{\text{com},o} \rangle / \bar{R}_{g,o}$ decreases as n increases in each catenane, meaning a denser packing of the outer rings along contour of the inner rings when

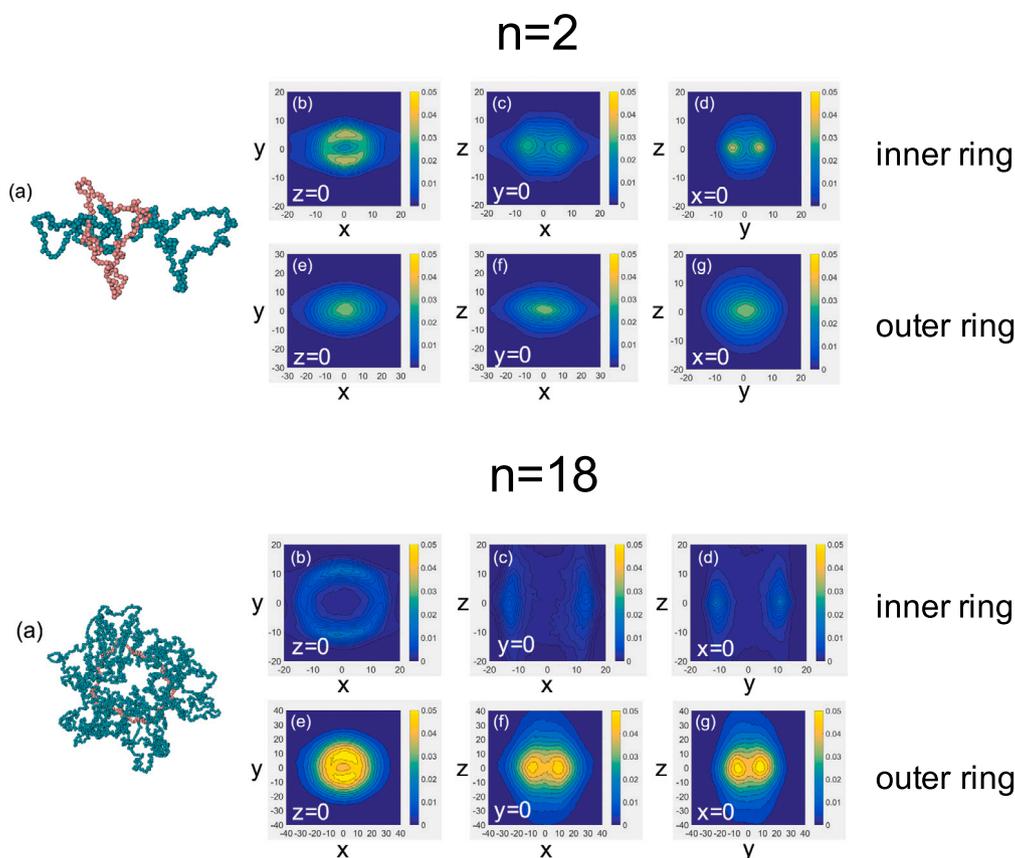


Fig. 9. Typical snapshots of catenane conformations and average segment density distributions of the inner ring and outer rings on cross-sections in the system of principal axes of the catenanes of Case II with $m_i/m_o = 1$, $m_i = 160$, and $n = 2, 18$. In polymer snapshots, red segments are from the inner ring, while green segments are from the outer rings. The axes, x, y, z , are parallel to the three principal axes of a decreasing values of the corresponding eigenvalues. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

there are more outer rings. Furthermore, presence of excluded volume interactions between the outer rings results in a less dense packing of them.

4. Discussion

One of key findings given in Section 3 is the gradual swelling of the inner ring when it is topologically interlocked with an increasing number of the outer rings in a catenane. All in all, the equilibrium size of the inner ring in the catenane is essentially determined by a requirement that the free energy of the whole catenane gets minimized. Therefore, if the free energy, $F(R_g)$, of any given catenane shown Fig. 1 with the instantaneous radius of gyration of the inner ring, R_g , as variable, could be derived or constructed, one would make a quantitative prediction about the mean-squared radius of gyration of the inner rings, $\langle R_g^2 \rangle$, which then can be compared to computer simulation results in Section 3. Unfortunately, it is extremely difficult to describe the topology catenation mathematically, which hinders an analytical formulation of the free energy. To able to proceed analysis, consequently, we only pursue a qualitative interpretation in the following.

To that end, we look into effects of topological catenation on physical features of the catenane molecule. Physically, there are mainly two unique features introduced into a catenane by the catenation topology. First, because the outer ring and the inner one are topologically interlocked and thus cannot cross each other, translational motion of the outer rings is strongly compressed for a fixed center of mass of the whole polymer catenane. Nevertheless, the outer rings can gain relatively more translational entropy when the inner ring gets swollen,

when the outer rings are able to access larger volume of space. On the other hand, swelling of the inner ring leads to a decrease of its own conformational entropy. For a catenane molecule, therefore, it is a delicate balance of these two entropic effects that plays a key role in the equilibrium conformation of the inner ring. As expected, when an increasing number of outer rings being interlocked with the inner ring, entropy gain from the outer rings becomes more dominant. Therefore, maximizing entropy of the whole system requires a swelling of the inner ring to some extent to get more translational entropy of the outer rings by sacrificing conformational entropy of the inner one. Second, due to the same reason of chain topology in a catenane, segments from the outer rings unavoidably have a density distribution within the occupying space of the inner rings. Also, the outer ring polymers distribute along chain backbone of the inner ring in the catenane. These facts enhance probability of a direct contact of segments from the outer rings in space. Consequently, interaction energy between the outer rings must contribute to the total free energy of the system and thus plays another key role in equilibrium conformation of the inner ring.

In Case I, the outer rings do not interact with each other in that the excluded volume interactions between segments from different outer rings are switched off. So, the conformation properties of the inner rings can be seen as approximately controlled by purely entropic effects, i.e., the above-mentioned first effect. As discussed above, indeed a gradual increase of the swelling degree, f_{sw} , as the number of outer rings, n , increases has been confirmed in computer simulation results shown in Fig. 2 for Case I. Situations become different in those catenanes where the excluded volume interactions between the outer rings are present (Case II). On one hand, invading of the outer ring segments inside the region of inner ring can generate an effect of volume exclusion,

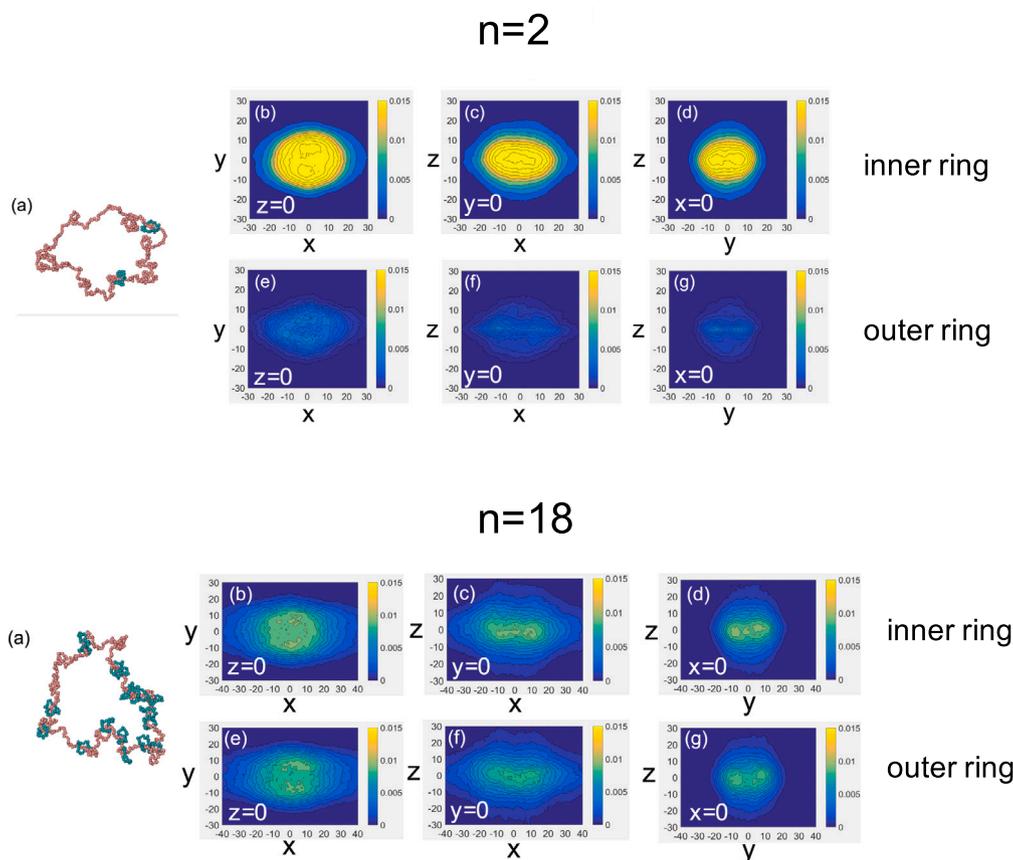


Fig. 10. Typical snapshots of catenane conformations and average segment density distributions of inner ring and outer rings on cross-sections in the system of principal axes of the catenanes of Case II with $m_i/m_o = 20$, $m_i = 480$, and $n = 2, 18$. In polymer snapshots, red segments are from the inner ring, while green segments are from the outer rings. The axes, x, y, z , are parallel to the three principal axes of a decreasing values of the corresponding eigenvalues. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

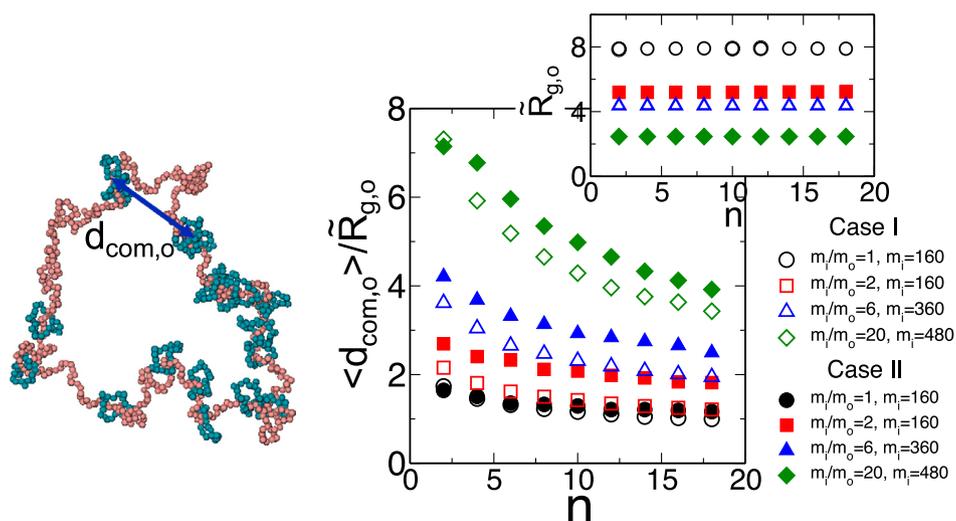


Fig. 11. The average distance between centers of mass of two nearest neighboring outer rings, $\langle d_{com,o} \rangle$, in unit of root of mean-squared radius of gyration of them, $\sqrt{R_{g,o}^2} = \sqrt{\langle R_{g,o}^2 \rangle}$, as a function of their numbers in catenanes, n . Inset: root of mean-squared radius of gyration of the outer rings in catenanes of both Case I (open symbols) and Case II (solid symbols) composed of varying number of the outer rings n .

i.e., they tend to occupy more space 'inside' the occupying region of the inner ring in order to decrease segment density in that region and thus decrease the interaction energy between them. Due to uncrossability of the outer rings through the inner ring, the volume exclusion from

the outer ring segments can also make the inner ring further swelling to some extent. This effect could be even more predominant in those cases where the molecular weights of the inner and outer rings are comparable. On the other hand, a decrease of direct contact of the outer

rings segments can be simply realized if the inner ring swells in a way that the outer rings are 'diluted' in the occupying space of the catenane. Therefore, in the same situation in terms of n and m_i/m_o , we expect that in Case II the inner ring can swell more compared to results in Case I.

Regarding effect of the topological catenation on the shape properties of the inner ring, we find that the inner ring becomes more and more oblate when it is simultaneously concatenated with an increasing number of the outer rings. And, this effect is more pronounced for those polymer catenanes with smaller m_i/m_o . They could be explained as following. As described previously, the inner ring can get gradually swollen if number of the outer rings, with which the former is topologically interlocked, increases. As expected, the inner ring conformation then become tighter due to the closing chain topology of ring, or, effectively, the inner ring becomes more semiflexible. Indeed, Alim et al. [40] have concluded from their simulation results and analytic calculations that a ring polymer with increasing semiflexibility exhibits more oblate conformation.

5. Conclusions

In this work, by considering a series of polymer catenanes, we have uncovered effect of the catenation topology upon static conformational properties of the inner ring polymer in the catenane. Topological catenation induced size and shape changes of the inner ring in a catenane compared to those of the same ring but in isolation have been revealed by molecular dynamics simulations. Two different cases are considered in this work. In Case I, the outer rings in a catenane do not interaction with each other, while the excluded volume interactions between the outer rings are present in Case II. Our simulations reveal that the inner ring in a catenane can get swollen to a varying extent compared to size of the same ring in isolation. It is concluded that in both Cases the swelling degree, f_{sw} , scales with respect to number of the outer rings in catenane, n , i.e., $f_{sw} = an^\alpha$ with a and α being predominantly dependent on molecular-weight ratio of the inner to outer rings. Furthermore, the inner ring swells more significantly in Case II than that in the same catenane of Case I. Concerning shape properties of the inner ring, simulation results conclude that the mean asphericity of the ring is increased slightly, while its mean prolateness changes remarkably. In detail, the inner ring gets more oblate in a catenane either with increasing number of the outer rings or enlarging the molecular-weight ratio of the inner to outer rings. In addition, compared with those catenanes of Case I, change of the mean prolateness of the inner rings is more pronounced when the excluded volume interactions between the outer rings are present. The corresponding changing profile of the mean prolateness of the inner ring from those of the isolated ring polymer as a function of the outer ring numbers are predominantly determined by the molecular-weight ratio of the inner to outer rings.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Guojie Zhang: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Software, Validation, Visualization, Writing - original draft, Writing - review & editing. **Jianguo Zhang:** Investigation, Formal analysis, Visualization, Writing - review & editing.

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