



The further understanding of chain topology effect on the properties of single polymer in good solvent: Special behaviors of single tadpole chain

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ABSTRACT

Chain topology strongly affects the static and dynamic properties of polymer melts and polymers in dilute solution. For different chain architectures, such as ring and linear polymers, the molecular size and the diffusion behavior are different. To further understand the chain topology effect on the static and dynamic properties of polymers, we focus on the tadpole polymer which consists of a cyclic chain attached with one or more linear tails. It is found that both the number and the length of linear tails play important roles on the properties of the tadpole polymers in dilute solution. For the tadpole polymers with fixed linear tail length and number, with increasing the degree of polymerization of tadpole polymers, a transition from linear-like to ring-like behavior is observed for both the static and dynamic properties. By studying the radii of gyration for different chains, we define a ratio of the number of monomers in linear tails (N_{tail}) to the total degree of polymerization (N), and found that when the ratio N_{tail}/N is more than about 0.73, tadpole chains behave as linear chains, while, when N_{tail}/N is less than about 0.29, they behave as ring chains. This result will be helpful in further understanding of the chain topology dependence on the static and dynamic properties of polymer in dilute solution. Furthermore, the tadpole polymers behave as what Zimm theory expected before they deviate from the linear-like regime, or after they reach the ring-like regime, however, in the intermediate regime, the behavior of tadpole polymer does not show what Zimm model expected.

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1. Introduction

Polymers may have different chain architectures, such as linear chains, ring chains, star chains, and dendrimer chains. As is well known that the chain topology strongly influences the static and dynamic properties of polymer chains. However, it is difficult to synthesize polymers with well controlled chain architectures in the past years. With the improvement of synthetic technology, it becomes easier for experimenters [1–3] to synthesize these well controlled complex polymers, which makes possible for scientists to study the properties of polymer chains with different architectures. The effect of chain topology on the static and dynamic properties of polymers has attracted a lot of attentions [4–11]. As we know, the molecular size and the diffusion behavior of ring chains show big difference from those of linear chains [11]. To further understand the chain topological effect, we focus on the tadpole chain which is composed by a ring block and one or more linear blocks (Fig. 1). There are both ring blocks and linear blocks in tadpole chains, and the behaviors of these chains will be considerably interesting.

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In recent years, tadpole polymers attract a lot of attentions [12–14] due to their special chain architectures. Li et al. [14] have shown that the tadpole architecture has a direct impact on the crystallization of the constitutive components. The tadpole architecture also plays an important role in the lyotropic behavior of an amphiphilic macrocrown ether [12] and in the pharmacological properties of cyclic and linear analogs obtained by similar ways [13]. However, until now, we have not seen any work concerning the chain topology effect of tadpole chains on the static and dynamic properties of their solutions. The investigation of the behaviors of single tadpole chain will be helpful in further understanding the chain topology dependence on the static and dynamic properties of polymer in dilute solution. In this work, single tadpole polymer in good solvent is investigated using molecular dynamics simulation method. We give model and simulation details in Section 2, and the results and discussion in Section 3. Finally, summarization of our results is present in Section 4.

2. Model and simulation details

The static and dynamic properties of single tadpole polymer in good solvent are investigated by molecular dynamics (MD) method to show the chain topology effect on the properties of single chain

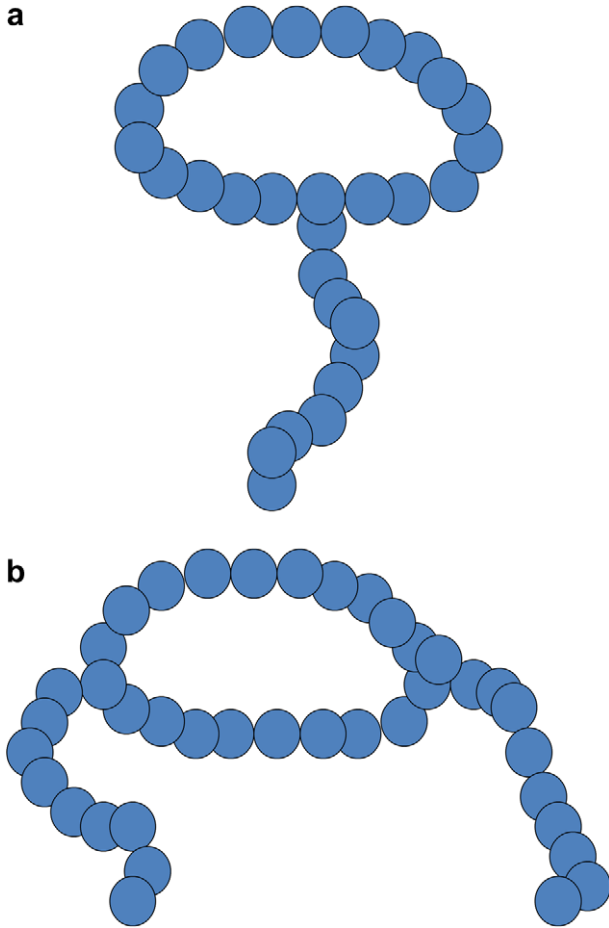


Fig. 1. The sketches of tadpole polymer. (a) One-tail tadpole polymer; (b) two-tail tadpole polymer.

in solvent. The tadpole architecture is easy to be constructed and the hydrodynamic interaction is easy to be employed by MD method. The program used in the simulation is compiled by us. In order to testify the validity of this software, the program was firstly used to study the dynamic and static properties of linear chains, and the results are in agreement with those from Ref. [15], which are shown in Ref. [11]. For the tadpole chains, there is a truncated Lennard–Jones [15–17] interaction U_{LJ} for the embodiment of volume exclusive effect where the cutoff diameter is $r_c = 2^{1/6}\sigma$ for the computational efficiency, and FENE potential [15,16] U_{fene} is introduced for the backbone potential whose parameters are selected according to literature [11], i.e., $k = 7.0$ and $R_0 = 2.0\sigma$.

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] & \text{for } r < r_c \\ 0 & \text{for } r \geq r_c \end{cases} \quad (1)$$

and

$$U_{fene}(r) = -\frac{k}{2} R_0^2 \ln \left(1 - \frac{r^2}{R_0^2} \right) \quad (2)$$

The reduced units are introduced for convenience, where σ , ϵ and μ (the mass of a solvent particle) are set to unity, and time is measured in unit of $\tau_{LJ} = (\mu\sigma^2/\epsilon)^{1/2}$. The mass of a monomer particle is double as that of a solvent particle. The side length of simulation box is fixed to 16.8σ with periodic boundary condition, therefore, the simulation box contains 4096 particles, and the number density is 0.864. The degree of polymerization of tadpole polymer we

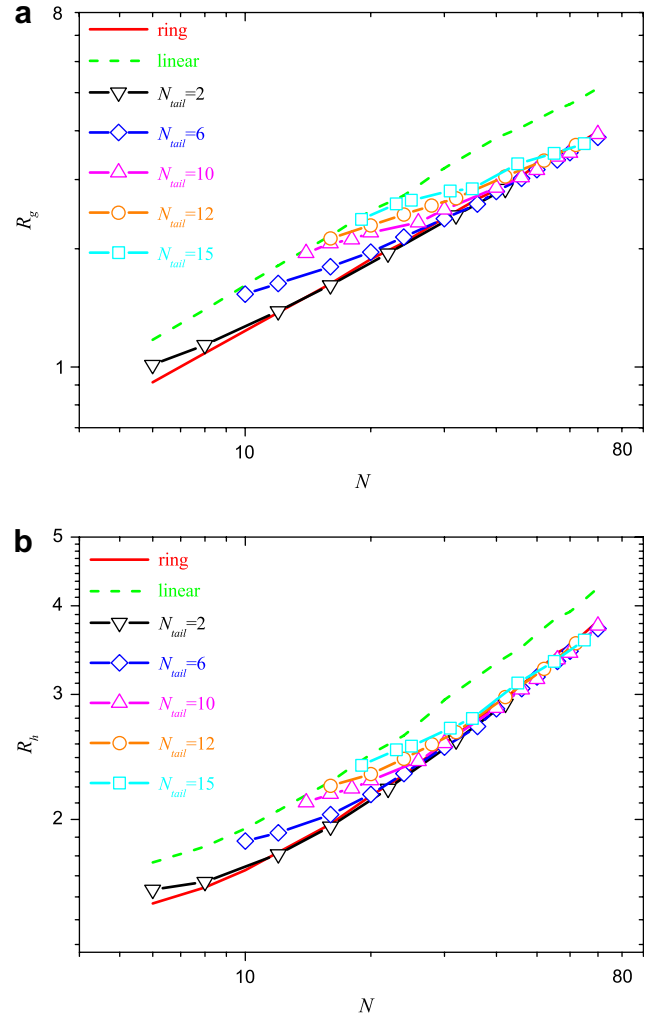


Fig. 2. The radius of gyration R_g (a) and the hydrodynamic radius R_h (b) for one-tail tadpole polymers as functions of polymerization degree N . Corresponding data of linear (dashed line) and ring (solid line) are introduced from Ref. [11]. Different symbols with corresponding lines denote the tadpole chains with different tail lengths.

studied in this work is not more than 70 to eliminate the finite size effect [15] and to ensure the polymer solution is in the dilute region. The static properties (such as radius of gyration R_g , hydrodynamic radius R_h , and static structure factors $S(k)$) and the dynamic properties (such as diffusion coefficient of mass center of polymer D_{cm} , relaxation time τ for the polymer chain diffusing its own size, and the dynamic structure factors $S(k,t)$) are evaluated according to the following equations [11,15]. The static properties are calculated from the average of 36,000 samples and the dynamic ones are calculated from the average of 1795 samples. Because of the large number of samples, the standard errors are small enough to ensure the reliability of the simulation. Take mean square radius of gyration as example, whose relative error is between 0.109% and 0.207%. Therefore, to preserve better visual presentation, we only give the data points in the figures without error bars.

$$\langle R_g^2 \rangle = \frac{1}{2N^2} \sum_{m=1}^N \sum_{n=1}^N \langle (\vec{r}_n - \vec{r}_m)^2 \rangle \quad (3)$$

$$\left\langle \frac{1}{R_h} \right\rangle = \frac{1}{N^2} \sum_{m \neq n} \left\langle \frac{1}{r_{mn}} \right\rangle, \quad (4)$$

where \vec{r}_n is the position vector of the n -th monomer, and r_{mn} is the distance between the m -th and the n -th monomer.

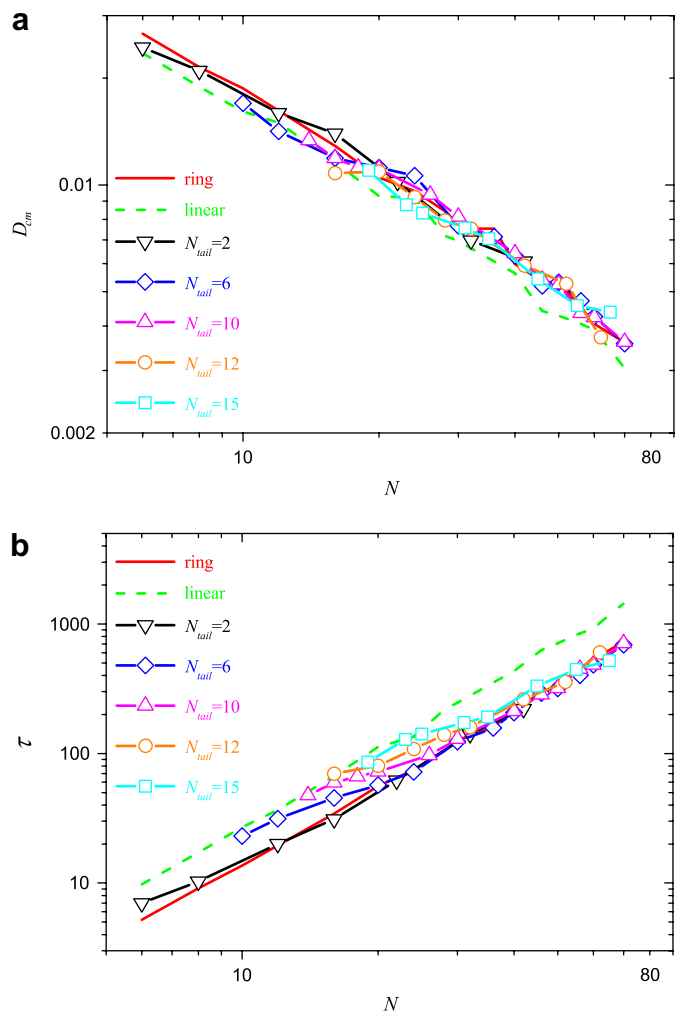


Fig. 3. The diffusive coefficient D_{cm} (a) and the relaxation time τ (b) for one-tail tadpole polymers as functions of polymerization degree N . The meaning of symbols and lines are the same as in Fig. 1.

$$6D_{cm}t = \langle (\vec{r}_{cm}(t) - \vec{r}_{cm}(0))^2 \rangle \quad (5)$$

$$\tau = R_g^2 / (6D_{cm}) \quad (6)$$

where $\vec{r}_{cm}(t)$ is the position vector of the polymer chain mass center at time t .

$$S(k) = N^{-1} \sum_{mn} \langle \exp(i\vec{k} \cdot [\vec{r}_m - \vec{r}_n]) \rangle = N^{-1} \sum_{ij} \frac{\sin(k|r_m - r_n|)}{k|r_m - r_n|} \quad (7)$$

$$S(k, t) = N^{-1} \sum_{mn} \langle \exp\{i\vec{k} \cdot [\vec{r}_m(t) - \vec{r}_n(0)]\} \rangle = N^{-1} \sum_{mn} \frac{\sin(k|r_m(t) - r_n(0)|)}{k|r_m(t) - r_n(0)|} \quad (8)$$

where \vec{k} is a wave vector.

3. Results and discussion

The static properties (radius of gyration R_g and hydrodynamic radius R_h) and the dynamic properties (diffusive coefficient D_{cm} ,

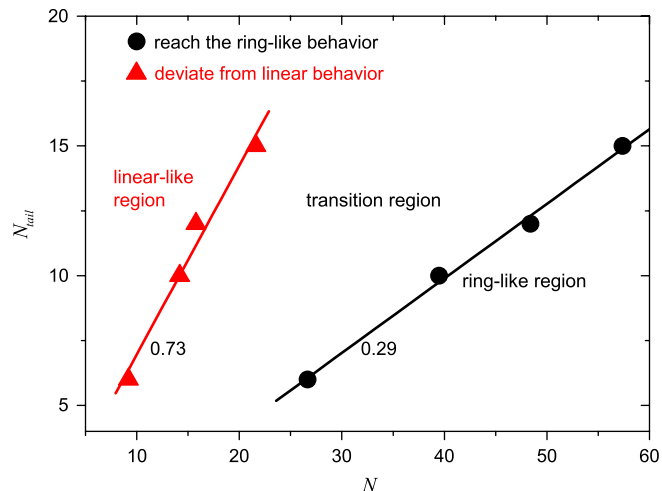


Fig. 4. The transition point of N_{shift} against N_{tail} . Circles denote the shifting point of tadpole chains deviating from linear-like behavior, and triangles denote that the tadpole chains start showing the ring-like behavior.

relaxation time τ and dynamic structure factor) of tadpole polymers at fixed linear tail length for different degrees of polymerization are obtained and shown in Figs. 2 and 3. For comparison, the relevant data for linear and ring polymers are introduced, where the data of

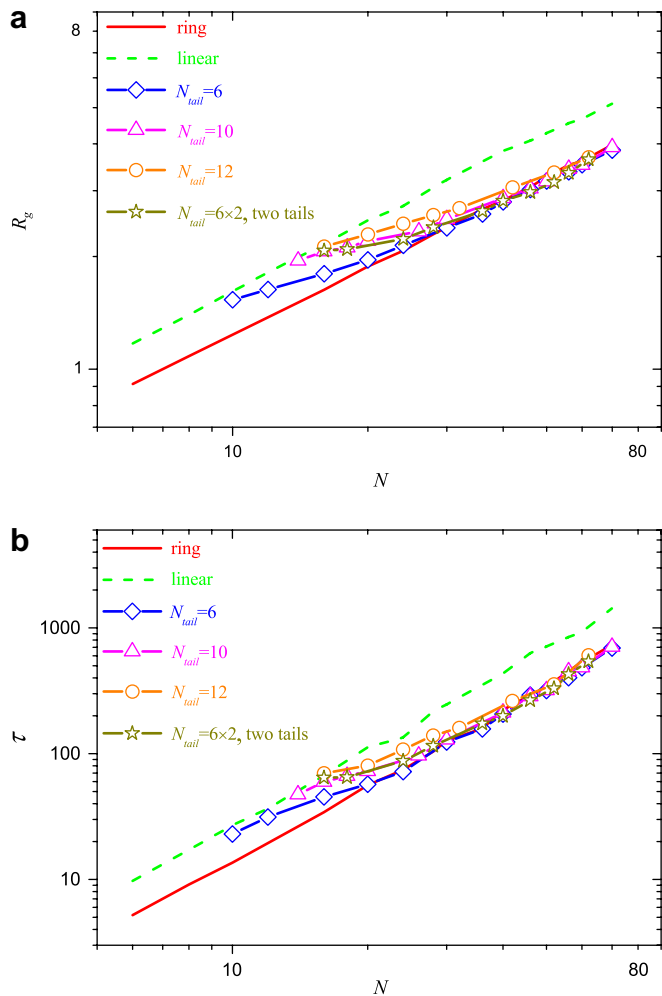


Fig. 5. The radius of gyration R_g (a) and the relaxation time τ (b) for tadpole polymers with one or two tails as functions of polymerization degree N . Different symbols denote the tadpole polymers with different tail lengths.

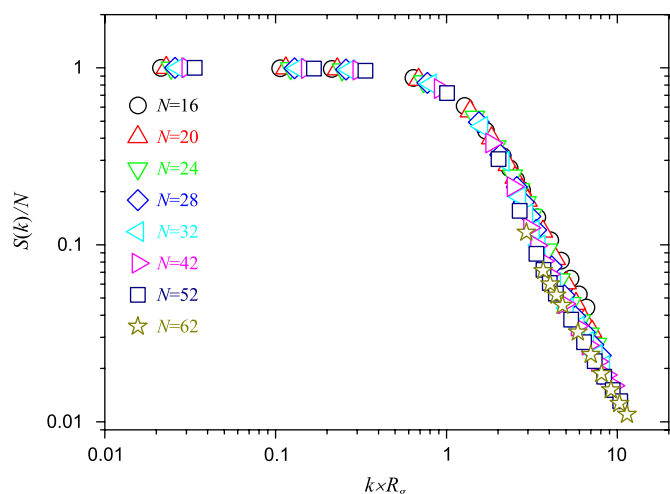


Fig. 6. The static structure factor $S(k)/N$ as a function of $k \times R_g$ for one-tail tadpole chains with $N_{\text{tail}} = 12$. Different symbols mean the polymer chain with different degrees of polymerization.

these chains whose polymerization degree is less than 50, refer to Ref. [11]. For the same polymerization degree, tadpole chains with longer linear tails have larger size, slower diffusion, and longer relaxation time than those with shorter linear tails. For the tadpole chains with fixed length of linear tail, as the increase of polymerization degree N , tadpole polymers have increased sizes and diffuse slowly. As is shown in Figs. 2 and 3, there is a transition from linear-like to ring-like behavior for both the static and dynamic properties of the tadpole chains. Furthermore, it is seen that the length of linear tail affects the transition behavior of one-tail tadpole

polymers greatly, i.e., it is more difficult for the tadpole chains with longer linear tails to deviate from the linear-like behavior or reach the ring-like behavior. Therefore, the ring-like behavior or linear-like behavior of tadpole chain depends on the concentration of ring part or linear part in the tadpole polymers. When the tadpole polymers behave as linear chains, they have bigger size and diffuse slower, while if the tadpole polymers behave as ring chains, they have smaller size and diffuse faster.

According to the static and the dynamic properties of these tadpole polymers, we can define a ratio N_{tail}/N to distinguish the ring-like behavior or linear-like behavior of tadpole chains, where N_{tail} is the polymerization degree of linear tail and N the polymerization degree of tadpole polymer. Fig. 4 shows the approximate relationship between N_{tail} and N , where the triangle points denote that the tadpole chains start deviating from linear-like behavior and the circle points denote that the tadpole chains reach ring-like behavior. This figure is obtained based on the radii of gyration of tadpole chains compared with those of linear or ring chains (for different properties, there is a slight difference in the shifting points). When N_{tail}/N is more than about 0.73, the tadpole chains behave as linear chains; and when N_{tail}/N is less than about 0.29, they behave as ring chains. Furthermore, in the intermediate regime, the relationship between radii of gyration and N of tadpole polymers shows a transition from linear-like to ring-like regime. This may be helpful for the understanding of what has been produced when polymer chains with complex architectures are synthesized.

Now we focus on the influence of linear tail numbers on the properties of tadpole polymers. The radius of gyration and relaxation time of two-tail tadpole polymer, whose linear tail length is $N_{\text{tail}} = 6 \times 2$, are studied and compared with one-tail tadpole chain of $N_{\text{tail}} = 6, 10$ or 12. As is shown in Fig. 5, the behavior of two-tail tadpole chain with $N_{\text{tail}} = 6 \times 2$ is in agreement with one-tail

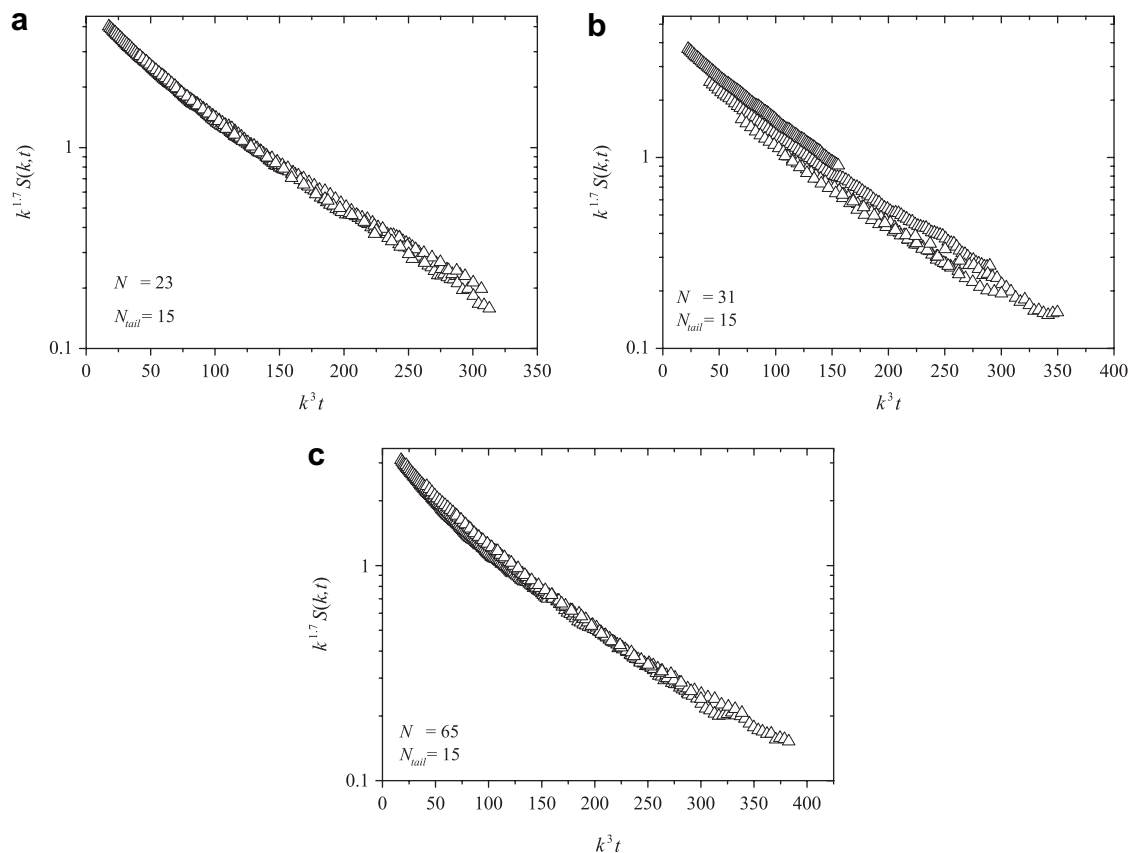


Fig. 7. The dynamic structure factor timed by $k^{1/2}$ as a function of time t , where $1/R_g \ll k \ll 1/b$, $0 < t < 70$ and $S(k, t) \geq 0.05$ for one-tail tadpole chains with $N_{\text{tail}} = 15$ when polymerization degree $N = 23$ (a), 31 (b) and 65 (c), where b is the microscopic length of monomer size.

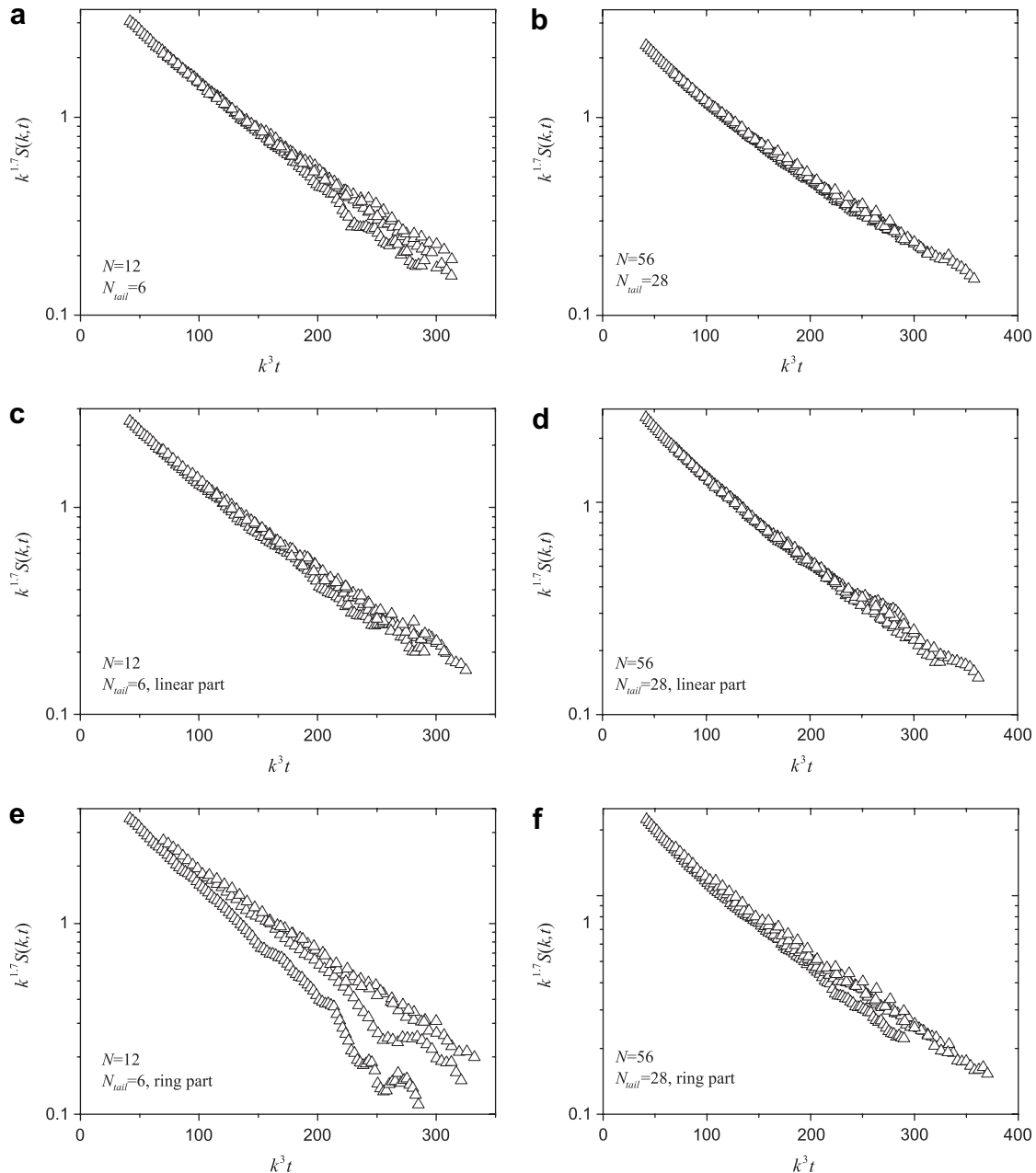


Fig. 8. The dynamic structure factor of the whole tadpole chain (a and b), the linear part (c and d), and the ring part (e and f) timed by $k^{1/\nu}$ as a function of time t , where $1/R_g \ll k \ll 1/b$, $0 < t < 70$ and $S(k,t) \geq 0.05$ for one-tail tadpole chains with $N_{\text{tail}}/N = 0.5$ and $N = 12$ (a,c and e) or 56 (b,d and f).

tadpole chain with neither $N_{\text{tail}} = 6$ nor $N_{\text{tail}} = 12$, but with $N_{\text{tail}} = 10$. At fixed length of linear tails, increasing the number of linear tails will decrease the size and the relaxation time of tadpole polymers and make it easier for tadpole chain to deviate from the linear-like behavior regime or reach the ring-like behavior regime. Therefore, for the tadpole polymers, both the length and the number of linear tails affect the properties of tadpole polymer in dilute solution greatly.

Static and dynamic structure factors of tadpole chains are also studied. For convenience, we only discuss the structure factors of one-tail tadpole polymers. The static structure factors of one-tail tadpole chains with $N_{\text{tail}} = 12$ are shown in Fig. 6. A qualitatively static scale exponent is obtained for radius of gyration from the static structure factors for $k \times R_g > 1$, [11,18] i.e., $\nu = 0.580$ for polymer chain with $N = 16$, and $\nu = 0.584$ for polymer chain with $N = 62$. As we know, the static scale exponent is slightly decreased when the

topology changes from linear chain to ring chain [11]. In this work, the static scale exponents decrease slightly with increasing N at fixed tail length until it reaches the ring-like regime, which also shows the transition from linear to ring behavior for the tadpole polymers.

As is proved in Refs. [11,15,18], the dynamic structure factors obey the following relationship for $R_g^{-1} \ll k \ll a^{-1}$ at the same range of time,

$$S(k,t) = k^{-1/\nu} f(k^z t) \quad \text{where } z = \begin{cases} 3.0 & \text{for Zimm case} \\ 2 + \frac{1}{\nu} & \text{for Rouse case} \end{cases} \quad (9)$$

Accordingly, $S(k,t) \times k^{1/\nu}$ is plotted as a function of $k^z \times t$ in Figs. 7 and 8. For one-tail tadpole chains with $N_{\text{tail}} = 15$, we obtain almost overlap lines for Zimm model either in linear-like regime or ring-like regime just as simple linear or ring chain (Fig. 7a and c). However, in the intermediate regime, tadpole chains show Zimm-

like behavior only for the polymers with considerably high polymerization degree, while those with low polymerization degree deviate from the Zimm model greatly (Fig. 7b). It has been proved that with the same polymerization degree, ring chain has the smaller size and diffuses faster than that of the linear chain [11]. For the tadpole polymer chains, ring and linear blocks are connected by the covalent bond, so the diffusion behavior of ring part (or linear part) should be affected by the linear part (or ring part). In order to explain the abnormal phenomena of tadpole polymers in the intermediate region, the dynamic behaviors of the linear part and ring part of tadpole polymer are investigated, respectively. As shown in Fig. 8, when we fix the ratio of $N_{\text{tail}}/N = 0.5$, with the polymerization degree N increasing, tadpole chains gradually behave as Zimm model as we expected (Fig. 8a and b). Furthermore, the linear block (Fig. 8c and d) starts showing Zimm-like behavior for lower polymerization degree than the corresponding ring part (Fig. 8e and f), i.e., the ring part is affected easily by the linear part. However, with the increase of polymerization degree, the difference in diffusion for chains with different architectures is getting smaller and smaller [11]. Therefore, due to the difference in diffusion of ring and linear chain, tadpole chains with small N deviate from Zimm behavior, but as increasing N , the small difference of diffusion coefficient between linear part and ring part leads to the Zimm diffusion model of tadpole polymers. These results will be helpful for experimentalists to investigate the properties of tadpole polymers as Refs. [19–21] do.

4. Summary

Chain topology strongly affects the static and dynamic properties of single polymer in dilute solution. To further understand the chain topology effect, we investigated tadpole polymer which consists of a cyclic chain attached with one or more linear tails. Due to the complex chain topology, tadpole chains behave more complex than linear chains or ring chains. It is found that both the number of the linear tails and the length of each tail play important roles on the static and dynamic properties of the tadpole polymers. For the same polymerization degree of tadpole polymers, tadpole chains with longer linear tails have larger size, smaller diffusion coefficient, and longer relaxation time. For the same polymerization degree of linear tail(s), tadpole polymers with more linear tail numbers have smaller size, bigger diffusion coefficient, and shorter relaxation time. Moreover, a transition from linear-like

to ring-like behavior for both the static and the dynamic properties of the tadpole chain is found as the polymerization degree increasing. Furthermore, the tadpole polymers behave as what Zimm theory expected before they deviate from the linear-like regime, or after they reach the ring-like regime, however, in the intermediate regime, due to the big difference in diffusion of small ring and linear chain, tadpole chains with small N deviate from Zimm behavior, but as increasing N , the small difference in diffusion of big ring and linear chains leads to the Zimm model behavior of tadpole polymers.

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