Effects of Topological Constraint on the Relaxation of a Single Ring Polymer

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ブラウン動力学シミュレーションを用いて, 結び目をもつ環状高分子の緩和を調べた. 環状高分子は鎖に沿った並進対称性を持つため, セグメントの相対位置の平衡状態での時間相関関数から波数ごとに緩和率が計算できる. 排除体積効果のある線状高分子の p 番目に遅い緩和率 λ_p はスケーリング則 $\lambda_p \propto (p/N)^{2.2}$ が成り立つことが知られている. 自明な結び目を持つ高分子の波数 p に対する緩和率分布は $\lambda_{p=1} \propto (1/N)^{2.18}$, $\lambda_{p>1} \propto (p/N)^{2.21}$ と振るまい, べき乗則の指数は同じであるが, 振幅は $p=1$ と $p>1$ で異なっていた. これは自明な結び目においても, トポロジー拘束が緩和率分布に影響を与えていることを示している. 三葉結び目を持つ高分子では, 最も遅い緩和を与える波数は $p=1$ ではなく $p=2$ であった. また自明な結び目の緩和率に比べ, $p=1$ では値は大きく, $p>1$ では値が小さくなった.

1 Introduction

The effects of topological constraints caused by the entanglement of polymers on the properties of polymer systems have attracted much attention. Especially, the static properties of a single knotted ring polymer, which is one of self-entangled systems, have been well studied[1]. In contrast, there have been few studies on its dynamic properties[2]. In this study, the effects of the topological constraints on the dynamic properties of a single knotted ring polymer are studied by Brownian dynamics simulations. The distribution of relaxation rates are estimated for a ring polymer with the trivial knot and the trefoil knot and the effects of the topological constraints on the relaxation rate distribution are clarified.

2 Model and Relaxation Rate

The Brownian dynamics simulations of a bead-spring model of a single ring polymer of N segments with the excluded volume interaction are performed. The hydrodynamics interaction is not taken into account. For the ring polymer, each relaxation rate is associated with a wave number p, because the ring polymer has the translational invariance along the polymer chain. The relaxation rates are estimated for each wave number p by the least square fit of data of an autocorrelation function $C(p:t)$ to the double

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exponential function. Here,

$$C(p:t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} C(i,j:t)\mathrm{e}^{-i\frac{2\pi}{N}p(i-j)} \tag{1}$$

and $C(i,j:t)$ denotes the equilibrium time-correlation function of the positions of the ith and the jth segments relative to the center of mass of the polymer. In the following, only the smallest relaxation rate λ_p for each wave number p is considered.

3 Result and Discussion

Figure 1 shows log-log plots of λ_p versus p/N for the trivial knot (a) and the trefoil knot (b). For the trivial knot, the relaxation rate distribution appears to satisfy $\lambda_{p=1} \propto (1/N)^{2.18}$ and $\lambda_{p>1} \propto (p/N)^{2.21}$. These exponents are similar to that of a linear polymer chain[3][4]. In the case of a linear polymer chain, the pth slowest relaxation rate λ_p behave as $\lambda_p \propto (p/N)^{2.2}$. It should be noted that even in the case of the trivial knot the topological effect can be seen as the difference between the amplitude of the power law dependences of $\lambda_{p=1}$ on $1/N$ and $\lambda_{p>1}$ on p/N, because there appears no such difference for a linear polymer chains. For the trefoil knot, it is characteristic that not $p = 1$ but $p = 2$ corresponds to the slowest relaxation mode for each N. In comparison with the relaxation rate for the trivial knot, it is clearly seen the relaxation rates for the trefoil knot are larger for $p = 1$, and smaller for $p > 1$.

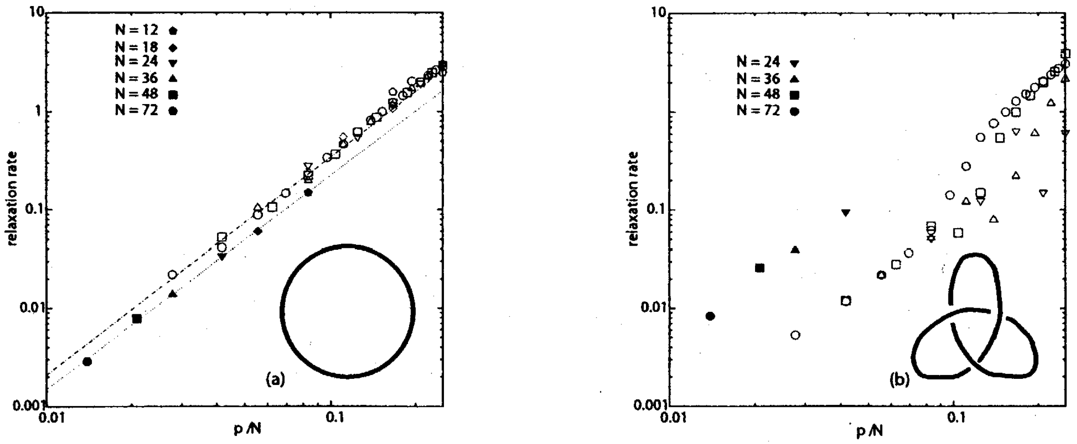

Figure 1: Log-log plots of λ_p versus p/N for the trivial knot(a) and the trefoil knot(b), respectively. The relaxation rates are denoted the black symbol for $p = 1$ and the white symbol for $p > 1$. The solid lines are given by the linear least square fit.

References

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