

Topological Effect in Ring Polymers Studied by Monte Carlo Simulation

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Abstract

We studied equilibrium conformations of ring polymers in the melt over the wide range of segment number, N , up to 1000 by the Monte-Carlo simulation method and the bond fluctuation model (BFM), and obtained Flory's scaling exponent ν and the radial distribution function of segments. It is clear that ν for ring polymers is decreased with N , and ν goes down to 0.365 when N reaches 1000, whose value is smaller than the theoretically-predicted one, i.e., $2/5$. Ring polymer chains in the melt are squeezed both by their own topological effect and the compression effect by the neighboring ring polymer coils, and they are perturbation chains in the melt. The difference in our study and the theory is that the estimation of topological entropy loss in ring polymers was ignored in the theoretical prediction, while it has been taken into consideration in this study. If polymer coils repel each other in the melt at $N \rightarrow \infty$, they have the limiting ν value of $1/3$, and we conclude that ν is in the range $1/3 \leq \nu \ll 0.365$ when the molecular weight of a ring polymer is high enough.

バルクにおけるリングポリマーの拡がりをモンテカルロシミュレーション法を用いて検討した。フローリの指数 ν とセグメントの分布を、Bond Fluctuation Model (BFM) を使って広い範囲のセグメント数 ($10 \leq N \leq 1000$) で求めた。シミュレーションの結果、 ν は N の増加とともに減少し $N = 1000$ で $\nu = 0.365$ まで低下することがわかり、これらは理論予測である $\nu = 2/5$ よりも小さい。リングポリマーのバルクにおける拡がり、末端がないトポロジーによる自分自身による拘束と隣接するリングポリマーとの相互作用の二つによって非摂動鎖よりも小さく、かつ、分子量依存性を示すことがわかった。セグメントの分布について求めたところ、リングポリマーのセグメント数が無限大の条件では、 $\nu \rightarrow 1/3$ を持つことが考えられることから、 $1/3 \leq \nu \ll 0.365$ が得られ、実験結果をよく説明することが分かった。理論予測は、リングポリマーのトポロジーによるエントロピー低下を十分に考慮していなかったため、本研究の結果と理論予測の結果に差が生じていると結論できる。

1 Introduction

Ring polymers are interesting materials for experimental and theoretical scientists, because they do not have chain ends. Cates and Deutsch¹⁾ studied Flory's scaling exponent ν theoretically, and reported that ring polymers in the melt have a certain ν value between $1/2$ and $1/3$. If the ν value is $1/2$, segments in ring polymer chains are Gaussian, while ring polymer chains segregate from the other molecules when the ν value is $1/3$. Takano²⁾ studied ν for ring polymers in the melt with the neutron and light scattering experiments, and obtained that the ν value for ring polymers is 0.34. The motivation of this study is to solve the gap of the ν value between the theoretical predictions and the experimental results for ring polymers in the melt, and ν for ring polymers is obtained by the Monte-Carlo simulations.

2 Simulation Method

Simulation model we used is BFM^{3, 4)}. To avoid making self-knots and concatenations of ring polymers, the loops were isolated from the other and has trivial shape. Scott Shaffer⁵⁾ reported that the excluded volume effect of linear polymer in the melt is screened if half of the

lattice points are occupied by segments. The simulations for ring polymers in this study were performed with the same condition as linear polymers. After the relaxation time, a hundred snapshots were acquired and the averaged square of radius of gyration, $\langle R_g^2 \rangle$, of polymer chains were calculated from them.

3 Results and Discussion

Fig.1 shows the dependence of ν for ring polymers on N . It is apparent that ν for ring polymers becomes smaller as N increases. Cates et.al.¹⁾ reported that ν for ring polymers is $2/5$, which was derived from the self-consistent theory. ν for ring polymers obtained in this study in high N region is smaller than $2/5$, for example, ν is 0.365 at $N = 1000$. Since the segment distribution of rings is more compact than those of linears, and ν for rings depends on N . The ring polymer chain in the bulk cannot be categorized as a Gaussian chain.

To obtain averaged chain shapes of ring polymers (a) in the melt and (b) non-self-avoiding walk (non-SAW), 80 snapshots of the system at long intervals were obtained. The segment distribution for (a) is almost the same as that of (b), but the distributions for (b) are a little broader than those for (a). The passage of (b) is random walk whose the start and finish segments must be at the same location. The polymer coils for (a) are squeezed by the neighboring squeezed molecules, and the force of the squeezing is increased with increasing N .

We estimated and analyzed ν for ring polymers in the melt at $N \rightarrow \infty$, $\nu_{\infty, \text{ring}}$. Cates et.al.¹⁾ suggested that $\nu_{\infty, \text{ring}}$ is intermediate between $1/2$ (Gaussian) and $1/3$ (segregated), and the relationship, $\nu_{\infty, \text{ring}} = 2/5$, was obtained from the self-consistent theory under the requirement of free energy minimum. The free energy was composed of the enthalpic and entropic terms which are the volume of the overlap with neighboring rings and the entropic gap between Gaussian- and real-chain shapes, respectively. But the increased topological entropy loss with increasing N was not taken into account in their study. Ring polymers in the melt are squeezed by two effects, i.e., their own topological effect and the compression effect from the neighboring ring polymers. We regard that $\nu_{\infty, \text{ring}}$ is larger than $1/3$, because ring polymer coils are not segregated completely. We can propose that ν value for ring polymers have the following relationship at high N larger than 1000:

$$1/3 \leq \nu_{\infty, \text{ring}} \ll 0.365. \quad (1)$$

The result of this study supports the result of neutron scattering experiments²⁾. The detail of this study have been published⁶⁾.

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References

- 1) M. E. Cates and J. M. Deutsch, *J. Physique* **47**, 2121 (1986).
- 2) Atsushi Takano, *Polym. Prepr. Jpn.* **56**(2), 2424 (2007).
- 3) Scotto Brown and Grzegorz Szamel, *J. Chem. Phys.* **108**, 4705 (1998).
- 4) Scotto Brown and Grzegorz Szamel, *J. Chem. Phys.* **109**, 6184 (1998).
- 5) J. Scott Shaffer, *J. Chem. Phys.* **105**, 761 (1995).
- 6) Jiro Suzuki, Atsushi Takano and Yushu Matsushita, *J. Chem. Phys.* **129**, 034903 (2008).

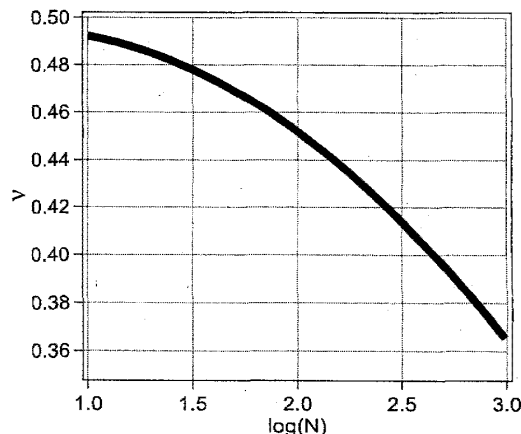


Figure 1: ν for ring polymers in the melt vs $\log(N)$.