

Dimension of ring polymers in bulk studied by Monte-Carlo simulation and self-consistent theory

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We studied equilibrium conformations of ring polymers in melt over the wide range of segment number N of up to 4096 with Monte-Carlo simulation and obtained N dependence of radius of gyration of chains R_g . The simulation model used is bond fluctuation model (BFM), where polymer segments bear excluded volume; however, the excluded volume effect vanishes at $N \rightarrow \infty$, and linear polymer can be regarded as an ideal chain. Simulation for ring polymers in melt was performed, and the ν value in the relationship $R_g \propto N^\nu$ is decreased gradually with increasing N , and finally it reaches the limiting value, $1/3$, in the range of $N \geq 1536$, i.e., $R_g \propto N^{1/3}$. We confirmed that the simulation result is consistent with that of the self-consistent theory including the topological effect and the osmotic pressure of ring polymers. Moreover, the averaged chain conformation of ring polymers in equilibrium state was given in the BFM. In small N region, the segment density of each molecule near the center of mass of the molecule is decreased with increasing N . In large N region the decrease is suppressed, and the density is found to be kept constant without showing N dependence. This means that ring polymer molecules do not segregate from the other molecules even if ring polymers in melt have the relationship $\nu = 1/3$. Considerably smaller dimensions of ring polymers at high molecular weight are due to their inherent nature of having no chain ends, and hence they have less-entangled conformations. © 2009 American Institute of Physics. [doi:10.1063/1.3247190]

I. INTRODUCTION

Ring polymers are interesting and puzzling materials for mathematical, theoretical, and experimental scientists because ring polymers do not have chain ends. Conformations of linear and ring polymers in melt have been studied with theoretical,^{1–8} simulational,^{9–17} and experimental^{18–23} methods. The radius of gyration of polymer molecule, R_g , can be scaled with the segment number of the molecule N in the general form as

$$R_g \sim N^\nu, \quad (1)$$

where ν is Flory's scaling exponent.^{4,5} The ν value for linear polymers in melt is $1/2$, where the polymer chains can be regarded as an ideal chain whose thickness is zero or whose excluded volume effect is screened completely. The trajectory of linear polymers in melt can be described as a random walk with step number N . The chain crossing is allowed because of a random walk, which was suggested by Rouse,^{24,25} and hence this model is called "phantom chain model" (PCM). The chain conformation of linear polymer in melt have been studied and explained successfully with the PCM since a random walk is permitted and the excluded

volume effects of chains vanish. On the other hand, conformations for ring polymers in melt do not fit the model based on the PCM because the chain ends are connected. This fact implies that the excluded volume effect of ring polymer chains in melt may not be zero because of the topological effect. In fact, the Θ -temperatures for diluted ring polymers are apparently lower than those of linear polymers.^{22,23,26–29} To understand the difference in physical properties between ring polymers and linear chains, topological effect of ring polymers should be considered.

ν for linear polymers in melt were obtained with neutron scattering experiment by Benoit *et al.*¹⁸ and Kirste *et al.*,¹⁹ and the ν values were determined to be 0.5. These facts indicate that the excluded volume effect of linear polymer in melt is screened completely and linear polymer chain can be treated as an ideal chain. Arrighi *et al.*²⁰ reported that the ν value for ring polymers in melt is also 0.42 with neutron scattering experiment, though the molecular weights of the ring polymers are fairly low as $M < 10k$, and moreover the amount of linear contamination was not clarified. Takano and co-workers^{21–23} synthesized ring polymer samples with molecular weight as high as $M < 573k$. According to their detailed separation and characterization by size-exclusion chromatography and liquid chromatography at the critical condition, it has been found that the amount of linear con-

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tamination is 4% or less. They measured R_g of ring polymers in melt by small angle neutron scattering, and the exponent ν was obtained as 0.34.²²

Deutsch and Dinder¹² proposed the bond fluctuation model (BFM), where polymer chains show the excluded volume. Shaffer¹⁵ studied the effects of chain topology with BFM. If the averaged total segment concentration φ is assigned to be 0.5, the ν value for linear polymers is 0.5 so that the excluded volume effect vanishes. Brown and Szamel^{13,14} also obtained ν for ring polymers in melt with BFM as 0.42 in the range of $100 \leq N \leq 500$. Muller *et al.*^{16,17} investigated the topological effect in ring polymers, and they concluded that the self-consistent theory⁶ and BFM for ring polymers in melt give the same result, $\nu=2/5$ with $\varphi=0.5$ at $N \rightarrow \infty$. We studied the topological effect of ring polymers in melt in the range of $10 \leq N \leq 1000$ with BFM,⁹ found that the ν value reaches 0.365 at $N=1000$, and concluded that the ν value for ring polymers in melt might be in the range of $1/3 \leq \nu \ll 0.365$ at $N \rightarrow \infty$. Very recently, Vettorel *et al.*^{30,31} studied the dimension of ring polymers in melt by a Monte-Carlo simulation allowing even nonlocal moves. The algorithm consists of the following moves of segments: (a) crankshaft rotation, (b) wedge flip, and (c) kink translocation. Here (a) and (b) are local, while (c) is not. It was shown that with the nonlocal moves, the relaxation time is reduced by about 90%. Finally, they obtained $\nu=1/3$ in the large N region, $N \approx 10\,000$. However, the validity of such nonlocal moves still remains open.

Since segment number N was not large enough in the previous studies,^{9,13,14,16,17} we try to obtain the ν value directly with BFM in large N region in this paper. Thus the motivation of this study is to clarify the reason for the difference in chain dimension between the predictions and the experimental results for ring polymers in melt. In this study, ν for ring polymers in melt is obtained by the Monte-Carlo simulations at large molecular weight limit, and the ν value is also evaluated with a self-consistent theory including the topological effect of ring polymers.

II. SIMULATION MODEL

The simulation model used is BFM,^{12–15} of which the simulation algorithm was explained in detail in the previous paper.⁹ A polymer molecule in BFM is composed of segments and bonds, and N is the number of segments in a molecule. Each segment is located at a simple cubic lattice point, and a lattice point should not be shared among segments. Since bond crossing and overlapping of segments are inhibited, a polymer chain in BFM bears excluded volume and is not a “phantom chain.” $\langle R_g^2 \rangle$ can be related with N as^{4,5}

$$\langle R_g^2 \rangle \propto N^{2\nu}. \quad (2)$$

In Equation (2), the exponent ν was obtained to be 0.5 for linear polymers from BFM (Ref. 13) at $\varphi=0.5$, where φ is the averaged total segment density in the lattice. The value of 0.5 for φ actually corresponds to melt density of linear polymers, where the excluded volume effects are screened. Simulations for ring polymers in the previous paper and the present study were performed with the condition of $\varphi=0.5$.

TABLE I. Simulation parameters and the simulated results (Ref. 9) at $\varphi=0.5$. N : number of segments of a polymer molecule; L : size of the cubic lattice; and $\langle R_g^2 \rangle$: averaged mean square radius of gyration.

N	L	$\langle R_g^2 \rangle$
10	100	2.08
16	64	3.32
20	100	4.13
32	64	6.50
50	100	9.90
64	64	12.43
100	100	18.70
128	64	23.27
200	100	34.32
256	64	43.05
400	100	61.03
500	100	74.12
512	64	74.71
600	60	85.04
700	70	97.80
800	100	106.91
1000	100	122.64

Table I shows the simulation parameters and the results reported in the previous paper.⁹ To avoid self-knots and concatenations, ring polymer chains were folded many times, and initial conformations were set in highly compact state, in keeping with the BFM rule. 1000 was set as the maximum N for ring polymers in the melt with which the simulation can be finished in a realistic time. The highly compact conformation is not the best one as a initial state because the relaxation velocity was slow and enormous Monte-Carlo steps (MCS) was required to untangle the initial conformation of the ring polymers at high N . To break down this problem, the new algorithm was developed in this study for preparing initial conformation of ring polymers in melt. The following list is its procedure.

- (1) A ring polymer whose segment number is N was defined in a three dimensional space and relaxed in a dilute condition with BFM rule. The ring polymer was set without self-knots and concatenations.
- (2) The ring polymer chain was shrunken and restricted in a sphere whose volume is $2N$. The segment density of the polymer in the sphere is 0.5, which is the same density as in melt. The BFM rule was also kept in this process.
- (3) The restricted ring polymer was released in the simulation space one after another until the total segment density reached $\varphi=0.5$. The release positions were selected randomly in the space. Each spherical vacant space for the releasing was prepared in the lattice with the BFM rule, and the loops were isolated from the other. At the initial state of the addition, each molecule in the space acted as if it was an isolated polymer chain and eventually it swelled.
- (4) Top 10% of ring polymers in terms of R_g^2 values were replaced with the restricted polymers. Excess swollen molecules were replaced in this procedure.

TABLE II. Simulation parameters and the calculated results. The parameters used are the same as in Table I, while M denotes the number of molecules of each system.

N	M	L	$\langle R_g^2 \rangle$
1024	128	64	127.8
1536	85	64	164.9
2048	64	64	193.6
3072	42	64	250.0
4096	32	64	303.1

Table II shows the parameters and results obtained in this study. The simulation was executed on the simple cubic lattice, which has L^3 lattice points and the three dimensional periodic boundary conditions. Most of the computations adapted in this study were executed on the Central Computing System, Linux cluster system, hosted by High Energy Accelerator Research Organization. We estimated that it took 3 months to reach an equilibrium state at $N=4096$ for each calculation with an Intel Xeon Processor. After the relaxation time, averaged $\langle R_g^2 \rangle$ and their sample variances were calculated. Two independent simulations were performed for every set of parameters, and the two results agreed reasonably well. It is clear that the simulation results show good stability and do not depend on the initial conformation of a ring polymer chain. The results shown in Table II are their average.

III. RESULTS AND DISCUSSION

A. Simulation

Figure 1 shows $\langle R_g^2 \rangle$ dependence on MCS for ring and linear polymers in melt. The values of $\langle R_g^2 \rangle$ for ring polymers over the wide range of N up to 4096 were obtained with the new algorithm. As clearly shown in Fig. 1, $\langle R_g^2 \rangle$ increases rapidly with MCS at the beginning, indicating that ring polymer chains were invaded into the other polymer molecule territory.

$\langle R_g^2 \rangle$ thus obtained are double logarithmically plotted against N in comparison with linear counterpart in Fig. 2. Here the main issue is the N dependence of $\langle R_g^2 \rangle$ at large N limit, referring to the simulation results obtained in the previous paper,⁹ in which the largest N adopted was 1000. The data for linear chains as a reference state should be noted first. Filled circles in the range of $32 \leq N \leq 512$ were fitted to a line with its slope, 2ν , of 1.02; it gives approximately 1/2 for ν , which is a well-known result and has been reported.⁹ Thus the excluded volume effect of a linear polymer chain is screened, and it can be treated as an ideal chain in this system; therefore we can discuss the topological effect of ring polymers in melt.

On the other hand, it is obvious that the open circles in Fig. 2, for ring polymers in melt, cannot be fitted with a straight line over the wide range of N but has N dependence. At small N limit, data can be fitted into a line with slope of 0.94, which gives a ν of 0.47, while at large N limit, the slope is found to be 0.66, corresponding to ν value of $0.33 \approx 1/3$. Cates and Deutsch⁶ reported that ring polymers in melt have a ν value between 1/2 and 1/3. They suggested

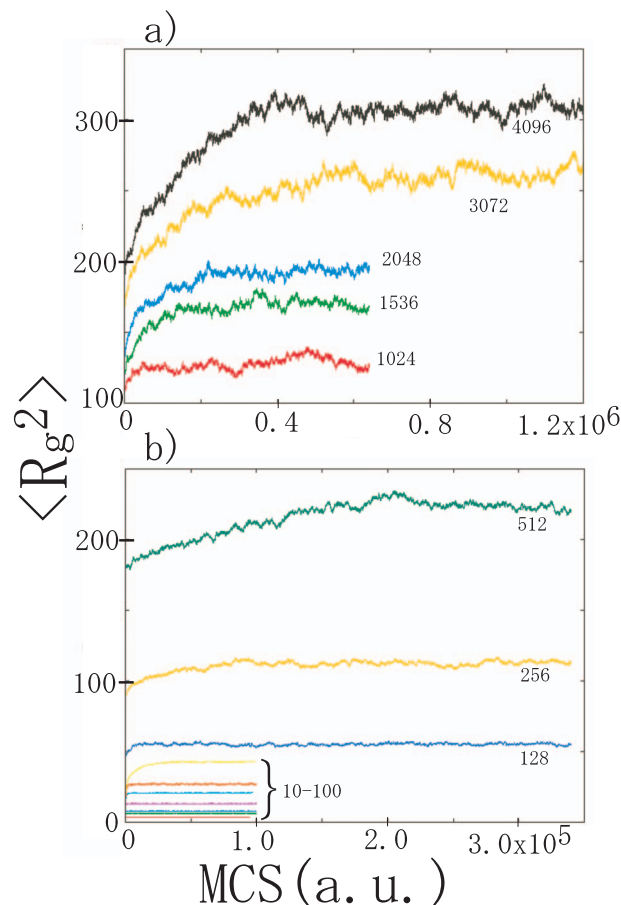


FIG. 1. Variation in averaged mean square radius of gyration $\langle R_g^2 \rangle$ vs MCS for (a) ring and (b) linear polymers in melt. Numbers associated with curves denote N .

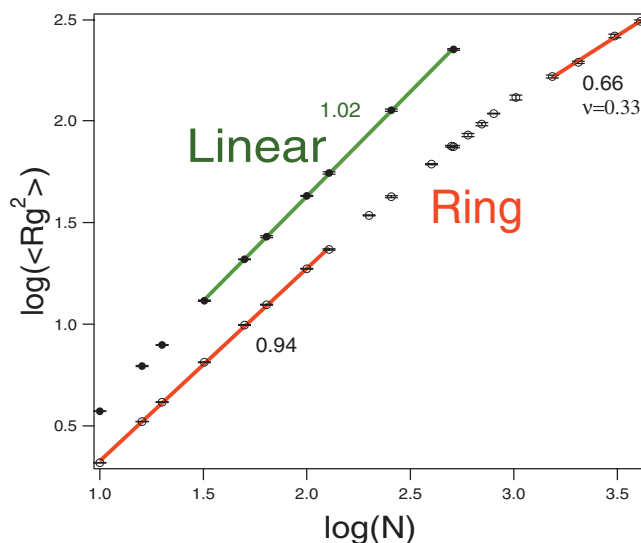


FIG. 2. Double-logarithmic plots of $\langle R_g^2 \rangle$ and N for linear and ring polymers in melt. The numbers are the magnitude of the slopes are 2ν values. The error bars represent 2σ , where σ^2 is the standard deviation in evaluating $\langle R_g^2 \rangle$, as shown in Fig. 1. The magnitude of the slopes and ν values for ring polymers in high N region are shown. Data points for $\log N \leq 3.0$ were obtained in the previous work (Ref. 9), while those at higher $N (> 10^3)$ were given in the present study.

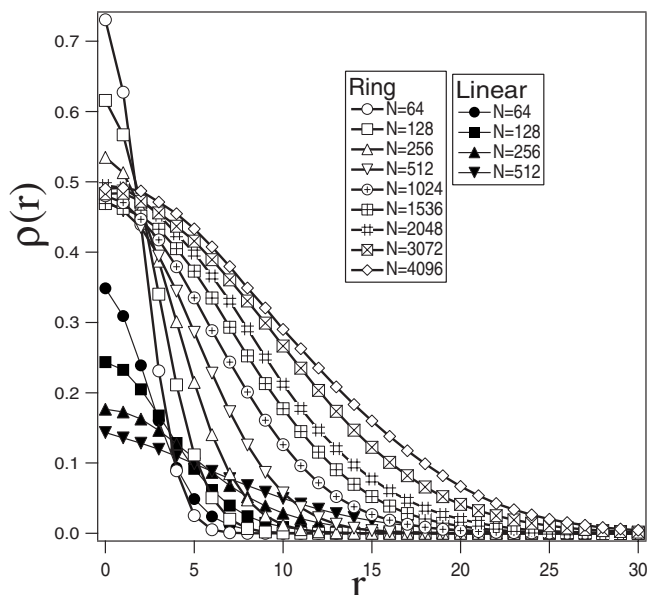


FIG. 3. Variation in segment density $\rho(r)$ of a polymer molecule in melt with the distance r to each segment is from the center of mass of the molecule. The averaged total segment density of this system is set to be 1.0.

that if ring polymer coils segregate from the other molecules completely, ring polymer in melt has the exponent of $1/3$. However, their self-consistent theory indicated that ring polymer in melt at $N \rightarrow \infty$ has the exponent of $2/5$. In the previous paper⁹ we reported that the ring polymer in melt is squeezed by the surrounding ring polymers and the ν value reaches 0.365 at $N=1000$ and concluded that ν has the limiting value of $1/3$, i.e., ν is in the range of $1/3 \leq \nu \ll 0.365$ for ring polymers in melt at $N \rightarrow \infty$.

To obtain an averaged chain conformation of ring polymers in melt, 500 snapshots of the simulation systems at long intervals were acquired in the range of $64 \leq N \leq 4096$. Segment density $\rho(r)$ against the distance r from the center of mass of a polymer molecule was obtained. The segments on a noted molecule only were counted to estimate $\rho(r)$, that is, those on the other molecules were ignored. The $\rho(r)$ values for nine molecules with different N were averaged, and $\rho(r)$ is compared in Fig. 3 for each N . It should be noted that $\rho(r)=1.0$ corresponds to the averaged total segment density ρ_0 as a normalized value. The segment density at the center of mass of a ring polymer $\rho(0)$ is decreased with increasing N in the small N range, and this tendency is the same as that of linear polymers.

It is well established that segment distribution of an ideal linear polymer is Gaussian, the trajectory of the chain can be presented as a random walk, and the excluded volume effect is screened completely. The segment distribution for an ideal chain at $r=0$ should be decreased continuously with increasing N without the limiting value of N . However, the decrease in $\rho(0)$ with N is suppressed, and the value becomes independent of N in the large N region, i.e., $N \geq 1024$. The segment density of a ring molecule at $r=0$ in the high N region has the lower limit, and this fact brings the clear contrast between a linear and a ring polymer in melt. The $\langle R_g^2 \rangle$ value was increased with MCS at the beginning of the simulations, and polymer chains were swollen by the surrounding chains,

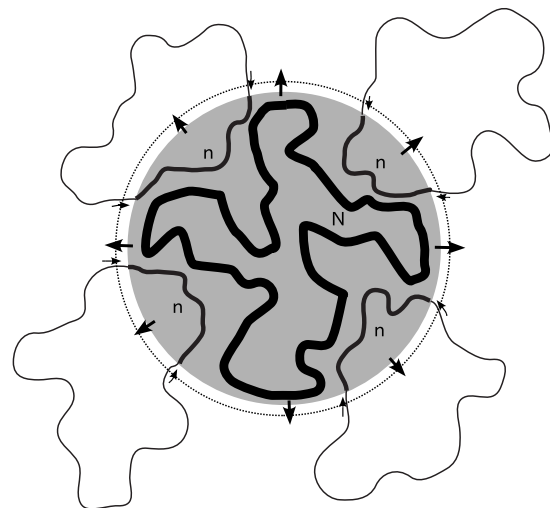


FIG. 4. Schematic illustration of a marked ring polymer (thick line) in Ψ (gray sphere) and the neighboring molecules. If the volume of Ψ is increased (thick arrows), the neighboring polymer chains are drawn into Ψ (thin arrows) to keep the total segment density constant in Ψ . The number of segments on each neighboring polymer in Ψ is n .

but the swelling of a polymer chain was restricted when it reaches the equilibrium state. The existence of the lower asymptomatic limit indicates that every ring polymer in melt has a core region, whose segment density is approximately $\rho(0) \approx \rho_0/2$. The core region is formed by the topological effect of the ring polymer architecture, i.e., the striking structure with no chain ends. Because of this feature, a ring polymer chain can less penetrate into the other molecules. To keep segment density constant, the ring polymer chain is squeezed by themselves instead of penetrating into the neighboring molecules. In other words, a ring polymer coil is squeezed by the surrounding polymer coils, which is also squeezed, but is still not segregated completely from the surroundings.

B. Self-consistent theory

Cates and Deutsch⁶ studied the ν value for ring polymers in melt with the self-consistent theory, and they yielded

$$\langle R_g \rangle \sim N^{2/5} \quad (3)$$

in three dimensions, but this prediction does not agree with our simulation result. They mentioned that rings in melt have some intermediate value between $\nu=1/2$ (Gaussian) and $\nu=1/3$ (segregated). The simulation result in the present work suggests that rings in melt do not segregate completely; nevertheless they show the relationship $\nu=1/3$. The gap between the prediction and the simulation result is discussed in this section.

We try to confirm the simulation result with a modified self-consistent theory in three dimensions. Free energy per ring in melt can be estimated with the consideration of an osmotic pressure from the neighboring molecules and an entropic penalty of polymer chain conformations. The number of segments of a ring polymer molecule is N , while the radius of the dimension of a ring polymer molecule is R , which may be proportional to $\langle R_g \rangle$, and the domain of a target ring

polymer is defined as Ψ . Figure 4 is the schematic illustration of the noted ring polymers and its neighboring molecules. Averaged total segment concentration is set to be one, and local segment concentration is kept constant. Since a ring polymer does not have chain ends, each molecule is prevented from threading and starts to segregate from the other molecules to keep segment density constant. To realize the segregation, a ring molecule must be collapsed and hence large entropic penalty may be required. To prevent from the entropic penalty, the surrounding ring polymer chains are compelled to invade into Ψ , and the ring in Ψ is threaded and overlapped with a number of neighbors. To obtain free energy of ring polymers in melt, estimation of the restricted threading energy due to topological effect thus considered is important.

When the radius of Ψ , R , is increased, the neighboring ring chains are naturally drawn into Ψ . The volume of Ψ is $4\pi R^3/3$, and so the number of segments of the neighboring molecules in Ψ domain is $4\pi R^3/3 - N$. The surface area of Ψ is $4\pi R^2$, and the number of polymer chains drawn into Ψ , i.e., the number of chains crossing the surface of Ψ , is scaled as R^2 . Hence the number of segments of each chain drawn into Ψ , n , is scaled as

$$n \sim \frac{1}{R^2} \left(\frac{4\pi}{3} R^3 - N \right). \quad (4)$$

The chain length of each neighboring molecule drawn into Ψ is also scaled as n . If a ring chain is regarded as a molecular spring, the spring constant κ of the polymer molecule is scaled as

$$\kappa \sim \frac{T}{N}, \quad (5)$$

where T is temperature. The potential energy stored in each neighboring molecule is described as κn^2 , and then the restricted threading energy per ring, $F(N, R)_{\text{thr}}$, is estimated as

$$F(N, R)_{\text{thr}} \sim \kappa n^2 R^2 \quad (6)$$

$$\sim \frac{T}{N} \left[\frac{1}{R^2} \left(\frac{4\pi}{3} R^3 - N \right) \right]^2 R^2. \quad (7)$$

If the ring polymer is shrunken from unperturbed conformation, entropic penalty should be generated, and its contribution to the free energy $F(N, R)_{\text{ent}}$ for a ring chain is scaled⁴ as

$$F(N, R)_{\text{ent}} \sim k_b T \frac{N}{R^2}, \quad (8)$$

where k_b is the Boltzmann's constant. The difference in the entropy loss between linear and ring polymers upon squeezing may be small.⁶ Therefore, we can write the total free energy $F(N, R)$ for a ring polymer molecule in melt as in Eq. (10),

$$F(N, R) \sim F(N, R)_{\text{thr}} + F(N, R)_{\text{ent}} \quad (9)$$

$$\sim \frac{1}{N} \left[\frac{1}{R^2} \left(\frac{4\pi}{3} R^3 - N \right) \right]^2 R^2 + \frac{N}{R^2}. \quad (10)$$

The minimum value of the free energy for certain N will be given at $dF(N, R)/dR=0$, as is expressed in Eq. (11),

$$\frac{dF(N, R)}{dR} \sim \frac{64\pi^2 R^3}{9N} - \frac{4N}{R^3} - \frac{8\pi}{3} = 0. \quad (11)$$

From Eq. (11), R can be related with N as in Eq. (12),

$$R \sim N^{1/3}. \quad (12)$$

This relationship obtained from the modified self-consistent theory supports the simulation result. Namely, not only the simulation but the theory suggest that a ring polymer in melt has the relationship $R \propto N^{1/3}$ at large N limit even if the ring polymer is not segregated completely from the other molecules in melt.

IV. CONCLUSION

The main result obtained in this study is that the Flory's scaling exponent ν for ring polymers in melt is decreased with increasing N , and it reaches 1/3 in large N region, i.e.,

$$\langle R_g \rangle \propto N^{1/3}. \quad (13)$$

This relationship is also confirmed by the self-consistent theory. In short, even if a ring polymer chain is not segregated completely from the surrounding polymer chains, the ν value for the ring polymer in melt reaches 1/3. Moreover, the segment density at the center of a ring polymer molecule shows the lower limit $\rho(r=0) \approx \rho_0/2$, indicating that the distribution manner of a ring polymer chain in melt is quite different from that of a linear ideal chain as shown in Figs. 3 and 4. Thus the degree of interpenetration of a ring chain into the neighboring chains is apparently less than a linear chain with the same segment number; in other words, it is rather very weakly "segregated" in melt.

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