

Dimension of ring polymers in bulk studied by Monte-Carlo simulation

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[Introduction] Ring polymers are interesting molecules for mathematical, theoretical and material scientists, because they do not have chain ends. The radius of gyration of polymer molecule, R_g , is scaled with the segment number of the molecule N in the general form as $R_g \sim N^\nu$, where ν is Flory's scaling exponent. The ν value for linear polymers in bulk is $1/2$, where the trajectory of linear polymers can be described as a random walk and the chain conformations can be explained with the “phantom chain model” (PCM), i.e., ideal-chain. On the other hand, conformations of ring polymers in bulk do not fit the model based on PCM, because their chain ends are connected. This fact tells that the excluded volume effect of ring polymers in bulk is not zero because of the topological effect. Takano and co-workers synthesized ring polymers with very small amount of linear polymer contamination[1]. The ν value for ring polymers in bulk obtained from the neutron scattering experiment is smaller[1] than those predicted by the self-consistent theory[2] and the simulations[3]. In this study, ν for ring polymers in bulk is investigated by a Monte-Carlo simulation at the large N limit and the result is compared with a self-consistent theory including the topological effect of ring polymers.

[Simulation] The simulation model used is bond-fluctuation model (BFM)[3]. A polymer molecule in BFM is composed of segments and bonds on a lattice. Since bond crossing and overlapping of segments are inhibited, a polymer chain in BFM bears excluded volume and therefore it is not a “phantom-chain”. The exponent ν is 0.5 for linear polymers from BFM at $\varphi = 0.5$, where φ is the averaged total segment density in the lattice. The value of 0.5 for φ corresponds to melt density of linear polymers, where the excluded volume effect is screened. Simulations for ring polymers were performed with the same condition of $\varphi = 0.5$. To avoid self-knots and concatenations of ring polymers, the loops were isolated from the other. The N dependence of averaged R_g^2 , $\langle R_g^2 \rangle$, was obtained in the range of $10 \leq N \leq 4096$.

[Results and Discussion] In Fig.1 $\langle R_g^2 \rangle$ for ring polymers are plotted double logarithmically against N in comparison with linear polymers. The data for linear polymers in the range of $32 \leq N \leq 512$

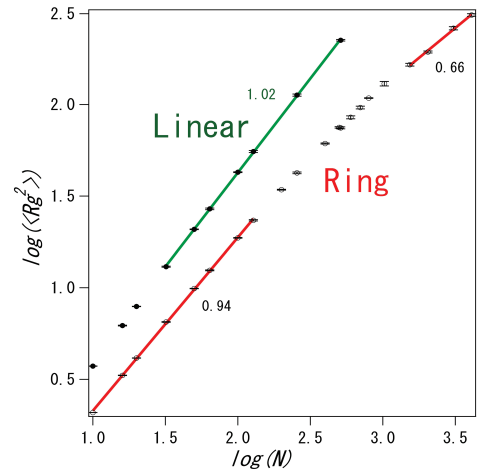


Fig.1 : Double-logarithmic plots of $\langle R_g^2 \rangle$ and N for linear and ring polymers in melt. The numbers as the magnitude of the slopes for linear and ring polymers are 2ν values.

were fitted to a line with its slope, 2ν , of 1.02; $\nu \approx 1/2$. The excluded volume effect of linear polymers is completely screened. The data for ring polymers cannot be fitted to a straight line over the wide range of N . In the small and large N limits, the slopes of the lines are 0.94 and 0.66, respectively. The ν value for ring polymers reaches $0.33 \approx 1/3$ at the large N limit. Self-density of segment $\rho(r)$ against the distance r from the center of mass of a polymer molecule was obtained. Segment distribution of PCM, i.e., a linear polymer in bulk, is Gaussian, and $\rho(0)$ should be decreased continuously with increasing N without the limiting value of N . It is found that $\rho(0)$ for ring polymers in the high N region, $N \geq 1024$, has the lower limit of $\rho(0) \approx \rho_0/2$, where ρ_0 is the averaged total segment density. The existence of the lower limit indicates that every ring polymer in bulk has a core region but is not segregated.

The ν value for ring polymers in bulk, $1/3$, does not agree with the theoretical prediction of $\nu = 2/5$ [2], therefore the simulation result was compared with a modified self-consistent theory. Free energy per ring in bulk can be estimated with the consideration of an osmotic pressure from the neighboring molecules i.e., the restricted threading energy per ring, $F(N, R)_{\text{thr}}$, and an entropic penalty of polymer chain conformations, $F(N, R)_{\text{ent}}$, where the radius of the dimension of polymer molecule is R , which is proportional to $\langle R_g \rangle$. The free energy $F(N, R)$ for a ring polymer in bulk is

$$F(N, R) \sim F(N, R)_{\text{thr}} - F(N, R)_{\text{ent}} \sim \frac{1}{N} \left[\frac{1}{R^2} \left(\frac{4\pi}{3} R^3 - N \right) \right]^2 R^2 + \frac{N}{R^2}.$$

The minimum value of the free energy for certain N is given at $\partial F(N, R)/\partial R = 0$, and thus the relationship, $R \sim N^{1/3}$, is obtained. The result from the modified self-consistent theory supports the simulation result in this study.

Not only the simulation but the theory suggest that a ring polymer in bulk has the relationship, $\langle R_g \rangle \propto N^{1/3}$, at the large N limit even if the ring polymer is not segregated completely from the other molecule in melt[4,5].

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