Monte Carlo study of catenated ring polymers

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Monte Carlo simulations of isolated ring polymers and pairs of catenated ring polymers were done on a simple cubic lattice. Differences in static and dynamic properties of these systems are presented and discussed.

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Many experimental results concerning isolated ring polymers and pairs of catenated ring polymers have recently been published[1–7]. However, the theory of cyclic macromolecules is still incomplete[1,2]. In order to develop the theory of properties of concentrated ring systems and melts[8–10], we studied dilute systems containing cyclic polymers.

There is discussion about the properties of ring polymers, and the presence of topological constraints, such as knots and/or catenated chains, is suspected in some cases. The influence of self-knotting on the properties of isolated cyclic chains and melts was recently studied[8,9] by means of the Monte Carlo method. We employed a similar Monte Carlo method to study the influence of catenation on the properties of dilute ring systems.

Dynamic Monte Carlo simulations of catenated polymer ring systems were performed. Model ring macromolecules were confined to a simple cubic lattice. The procedures of growth, equilibration and simulation have been described in detail elsewhere[8,9]. Basically, both rings forming a catenated pair are simultaneously subjected to growth and equilibration. The initial ring contains eight beads. The topology of the system is not changed during this process. A pair of rings was then simulated by the dynamic Monte Carlo method. A classical set of local micromodifications was used[8,11]: (i) two-bond kink motions; (ii) three-bond kink motions; and (iii) three-bond crankshaft motions. A time unit consisted of an attempt of all three motions per chain bead, on average. Changes of conformation were accepted, accounting for the excluded volume and topological restrictions. No long-range interactions were introduced (i.e. all systems under consideration are athermal). The topology of the system was preserved during a simulation run because the set of local motions preserves the bond cutting.

We studied ring chains of various lengths, with number of beads $N=10$, 20, 40, 60, 80, 100, 200, 400 and 800, in a Monte Carlo box with edges changing from 10 to 100 (the edge should be a few times greater than the radius of gyration). Periodic boundary conditions were used. A pair of catenated rings consists of two chains of identical length N. In addition to catenanes we simulated a single isolated polymer ring with length N in the same range in order to compare properties with this simple system.

Static properties of a polymer chain are usually described by the mean-square diameter $\langle d^2 \rangle$ (mean square distance between beads 1 and $N/2$) and the mean-square radius of gyration $\langle S^2 \rangle$. Both these parameters should exhibit scaling behaviour. In the case of the pair of catenated rings we observed the following scaling relations: $\langle d^2 \rangle_c \approx N^{1.174 \pm 0.003}$ and $\langle S^2 \rangle_c \approx N^{1.181 \pm 0.003}$. These scalings are valid for sufficiently long chains ($N>60$). Crude extrapolation of the ratio $\langle d^2 \rangle_c / \langle S^2 \rangle_c$ leads to the value of 0.30 in the limit of an infinite chain. For a single uncatenated chain $\langle d^2 \rangle_i \approx N^{1.180 \pm 0.008}$ and $\langle S^2 \rangle_i \approx N^{1.186 \pm 0.002}$ (for $N>60$) and their ratio $\langle d^2 \rangle_i / \langle S^2 \rangle_i$ approaches the value of 0.30 (for chain lengths $N>60$).

Simulation results concerning the static properties of all systems under consideration are presented in *Table 1*. The size of catenated rings is distorted by a topological constraint, catenation. The size of a catenated ring polymer is greater than a single ring polymer because the presence of the topological constraint (catenation) increases the excluded volume. After a short induction period the relative difference in size does not change a lot with increasing chain length ($\langle d^2 \rangle_i / \langle d^2 \rangle_c = 0.84$ and $\langle S^2 \rangle_i / \langle S^2 \rangle_c = 0.88$ for $N=800$), but one can expect that in the limit of infinite chain the dimensions and shape of the catenated polymer ring are the same as those of a single ring. A similar effect was observed in the simulation of isolated self-knotted rings[8,9].

Table 1 Static properties of the ring systems (subscripts c and i represent catenated ring polymer and isolated ring polymer, respectively)

N^a	$\langle d^2 \rangle_c$	$\langle S^2 \rangle_c$	$\langle S^2 \rangle_c / \langle d^2 \rangle_c$	$\langle d^2 \rangle_i$	$\langle S^2 \rangle_i$	$\langle S^2 \rangle_i / \langle d^2 \rangle_i$
10	6.79	1.67	0.260	5.01	1.43	0.285
20	13.77	3.88	0.282	11.56	3.31	0.287
40	30.21	8.72	0.289	24.27	7.47	0.308
60	48.53	13.96	0.288	40.52	12.26	0.303
80	67.10	19.71	0.295	58.46	17.33	0.296
100	86.22	25.49	0.296	74.73	22.51	0.301
200	195.4	57.65	0.295	175.1	50.98	0.291
400	444.9	130.5	0.293	382.3	117.1	0.307
800	1005	299.7	0.298	872.0	264.8	0.304

[a] N denotes length of one ring chain. A catenated pair consists of two chains each of length N

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Table 2 Dynamic properties of the ring systems (subscripts c and i represent catenated ring polymer and isolated ring polymer, respectively)

N^a	$D_c \times 10^3$	$(\tau_d)_c$	$D_i \times 10^3$	$(\tau_d)_i$
10	1.701	464.3	53.9	4.042
20	8.910	73.23	30.0	19.98
40	8.210	254.0	15.97	101.8
60	5.364	491.0	10.06	214.4
80	4.229	924.9	7.759	447.6
100	3.335	1267	6.212	698.0
200	1.940	5013	3.148	2761
400	1.035	24 594	1.555	10 598
800	0.559	109 840	0.796	44 325

[a] N denotes length of one ring chain. A catenated pair consists of two chains each of length N

These results compare well with other data. According to off-lattice Monte Carlo simulations of an isolated, freely jointed ring polymer[12], $\langle d^2 \rangle$ and $\langle S^2 \rangle \approx N^{1.18}$; their ratio is close to 0.30 in the range of N from 80 to 300 and approaches a value of 0.293 for the infinite chain. Monte Carlo simulations of a model cyclic chain confined to a diamond lattice[13] lead to the scaling law $\langle S^2 \rangle \approx N^{1.218}$. The exponents obtained by Reiter[14] in Monte Carlo simulations of cyclic chains on cubic lattice (using a different algorithm) were 1.174 and 1.194 for $\langle d^2 \rangle$ and $\langle S^2 \rangle$ respectively. Experiments concerning cyclic polystyrene in toluene[3] give the scaling relation $\langle S^2 \rangle \approx N^{1.13}$ for the concentration extrapolated to zero.

The dynamic properties of ring polymers are presented in terms of the diffusion constant D and the longest relaxation time τ_d. The diffusion constant was calculated from the centre-of-mass mean-square displacement $g_{cm}(t) = \langle [\mathbf{r}_{cm}(t) - \mathbf{r}_{cm}(0)]^2 \rangle$, where $\mathbf{r}_{cm}(t)$ is the centre-of-mass vector at time t, according to Einstein's formula $D = g_{cm}(t)/6t$. Calculations of the diffusion constant were made in a similar way as for linear chains[8], for displacements greater than $2\langle S^2 \rangle$ (for times greater than the longest relaxation time), which corresponds to free diffusive motion. The longest relaxation time τ_d can be extracted from the diameter autocorrelation function $g_d = \langle \mathbf{d}(t) \cdot \mathbf{d}(0) \rangle / \langle d^2 \rangle$. As usual we assumed that $g_d \approx \exp(-t/\tau_d)$. The fit was made in the window $0.75 < g_d < 0.25$, where $g_d(t)$ was linear for all systems under consideration. Results concerning the dynamic properties of ring polymer systems are presented in *Table 2*.

In the case of the isolated ring polymer, the diffusion constant D_i obeys the scaling law $D_i \approx N^{-0.99 \pm 0.01}$ for all longer chains ($N > 60$). This can be seen in *Figure 1* where the diffusion constant D_i is plotted *versus* number of segments in a chain N in a log–log plot. In the case of the pair of catenated rings, the diffusion constant D_c increases for chains with $N < 40$. This is an artefact caused by the lattice approximation (for $N = 8$ no motion is allowed and $D_c = 0$). A similar phenomenon was observed in the case of self-knotted ring polymers simulated on the same lattice and by the same method[8,9]. For longer chains ($N > 60$), D_c scales as $N^{-0.87 \pm 0.01}$.

Analogous behaviour was observed for the longest relaxation times. The procedure for calculation of the relaxation time τ_d was described above. *Figure 2* presents the longest relaxation times τ_d *versus* the number of segments N in a log–log plot. For the catenated pair of rings τ_d decreases with increasing chain length for short chains. This effect is connected with the lattice restrictions, as discussed above. For longer chains ($N > 60$) it scales as $N^{2.02 \pm 0.03}$. For a single ring the scaling exponent is 2.08 ± 0.04. The ratio D_c/D_i increases with increasing chain length, approaching a value of 0.70 for $N = 800$. The ratio τ_i/τ_c does not change monotonically; for the longest chain its value is 0.40.

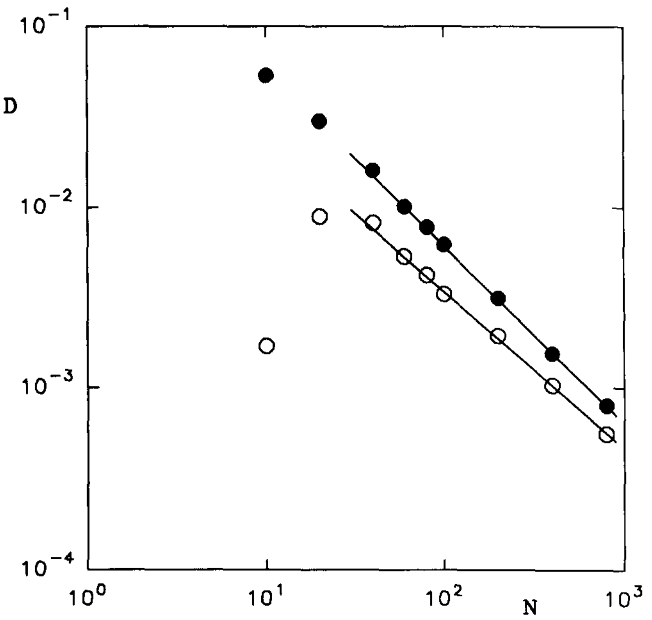

Figure 1 Log–log plot of diffusion constant D *versus* the number of segments in the ring polymer chain N: ○, pair of catenated rings; ●, single ring chain

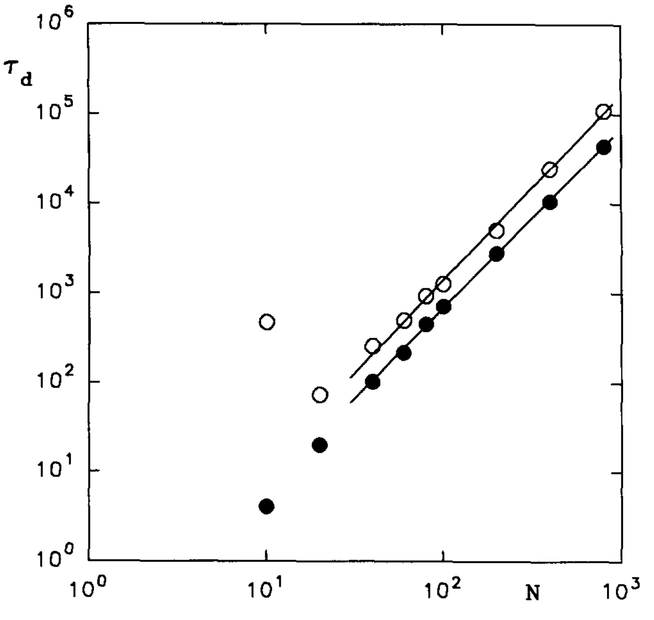

Figure 2 Log–log plot of the longest relaxation time τ_d *versus* the number of segments of the ring polymer chain N: ○, pair of catenated rings; ●, single ring chain

According to experiments, D scales approximately as $N^{-0.5}$ for polystyrene and polydimethylsiloxane rings[1,2]. This value is not close to the Rouse exponent because of the presence of hydrodynamic interactions in real solutions.

This work could easily be extended to the simulation of melts containing ring polymers, ring and linear polymers with (and without) self-knotting and catenation. We hope it will result in a good theory of polymer melt dynamics.

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