DYNAMIC MONTE CARLO SIMULATION OF A MELT OF RING POLYMERS

by

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Over the past several years we have done a set of dynamic Monte Carlo simulations on lattice models of a melt of linear polymer chains,[1,2] which casts doubts on the physical model behind the popular reptation theory of polymer melt dynamics[3,4]. We have also formulated an alternative theory of polymer melts using the insights obtained from these simulations[5,6]. While reptation theory has had reasonable success in explaining the dynamic properties of linear polymer melts it has not been as successful in explaining the dynamic properties of melts of ring polymers. Ring polymers diffuse more rapidly and have a lower viscosity[7] than linear polymers of the same molecular weight. The reptation model leads to the opposite conclusions[8].

We have now done a set of dynamic Monte Carlo simulations on melts of monodispersed ring polymers. We view these simulations as computational experiments to enable us to better understand the dynamics of polymers melts.

Model and Method

The dynamic Monte Carlo simulations on melts of ring polymers were done in the same way as our previous simulations of melts of linear polymers[1,2] (these references should be consulted for further details). We used a simple cubic lattice in a Monte Carlo box with cyclic boundary conditions, large enough that finite size box effects can be safely neglected.

A chain consists of n adjacent distinct lattice sites (beads) connected in a closed ring by n bonds. No two beads, whether from the same chain or different chains can occupy the same lattice site. No micromodification (see below) will be allowed which passes two chain segments through each other. Hence, the model includes all excluded volume effects. Other than this hard core repulsion there is no interaction between the beads, hence the system is athermal.

Briefly, the simulation is performed in the following steps: *i)* We start out with a set of smallest possible sized rings. These are then randomly grown and randomly modified (see below) until the rings have all reached the desired size. As we add bonds to the chain the ring is never opened up so that there is no chance for the rings to concatenate or for knotted rings to form. The micromodifications used were the same as for linear chains[1c] (two-and-three-bond jumps and 90° crankshafts) with the obvious exception of end modifications. These modifications are made randomly in accord with the standard Monte Carlo algorithm. It should be noted that this set of micromodifications spans the set of all modifications possible on a simple cubic lattice. Step *i)* is completed when each chain has attained the desired degree of polymerization n at the final density of $\phi=0.5$ (where ϕ is defined as the fraction of occupied lattice sites. At this time the rings are already partially equilibrated. *ii)* We then performed an equilibration run by repeating our basic micromodifications. Since we could not use the very efficient reptation algorithm for our equilibration of rings as we did for linear chains the equilibration run took considerably longer. *iii)* We then performed our simulation saving the trajectory for subsequent calculation of various averages. A Monte Carlo time unit was one attempt, on average, for

each bead in the Monte Carlo box to undergo each of the possible modifications. These simulations were continued until the mean square center of mass displacement was greater than 10 mean square radii of gyration, $<S^2>$, for n = 100, 216, 392; about $4<S^2>$ for n = 800 and approximately $<S^2>$ for n = 1536.

Equilibrium Results

Historically the average size of a polymer has been used to obtain information about the kind of statistics which describes the polymeric system under different conditions. We used two different measures of the size of rings - the mean square radius of gyration, $<S^2>$, and the mean square diameter, $<d^2>$ (this is the mean square distance between bead 1 and n/2, and is to be compared with the mean square end to end distance of linear chains $<R^2>$). The results are tabulated in Table I along with a comparison of the ring data with the analogous data for linear chains taken from Ref. (1C). As the degree of polymerization increases the ratios depart more and more from Gaussian statistics - the rings are smaller than Gaussian statistics would predict. This is most easily seen by obtaining how the size scales with n using the data in Table I:

$$<d^2>rings \sim n^{0.84}$$

$$<S^2>rings \sim n^{0.88}$$

which can be compared to the Gaussian result obtained[1C] for linear melts:

$$<R^2>linear \sim n^{0.99}$$

$$<S^2>linear \sim n^{1.02}$$

TABLE I   Equilibrium Properties

n	$<d^2>$	$<S^2>$	$<S^2>/<d^2>$	$\dfrac{<S^2>rings}{<S^2>linear^a}$	$\dfrac{<d^2>rings}{<R^2>linear^a}$
100	46.9± 0.4	15.15±0.07	0.323	0.492	0.250
216	92.2± 2.8	30.9 ±0.3	0.335	0.458	0.223
392	151.8± 7.8	52.0 ± 1.3	0.342	0.418	0.212
800	282 ±22	95.0 ± 3.1	0.338	0.370	0.197
1536	460 ±49	168.4 ± 5.4	0.359	0.334	0.170

^{a}The values of $<S^2>linear$ and $<R^2>linear$ are from Ref. 1C. The values for n which were not simulated in Ref. 1C (e.g. n=1536) were obtained by a fit to the simulations.

Our results are in agreement with the simulation of Pakula and Geyler[9] on a melt of ring polymers who obtain

$$<S^2>rings \sim n^{0.9}$$

using a very different simulation method.

Before discussing the possible origin of the smaller ring dimensions we should note the ratio $<S^2>/<d^2>$ in Table I is in reasonable agreement with the Gaussian statistics result that

$$<S^2>rings/<d^2>rings = 1/3,$$

despite the fact that melts of rings are clearly not Gaussian.

Our simulation is in reasonable agreement with the Flory-like mean field treatment of Cater and Deutsch[10] which gives

$$<d^2>rings \sim n^{4/5}$$

in three dimensions. They presented an argument for rings having a statistics intermediate between that for a collapsed chain ($n^{2/3}$) and a Gaussian chain. They assume along with Flory that excluded volume interactions are fully screened. However, the fact that concatenated rings are not allowed enforces a topological constraint on the system. Many of the ring configurations which would be allowed for a Gaussian ring (ring in a θ solvent) are disallowed because they would lead to concatenated rings. The more extended the ring structure, the larger the number of configurations which are disallowed. Hence the set of configurations which must be averaged over to obtain the average properties of a ring in a melt has a smaller number of extended configurations than would be the case for a set obeying Gaussian statistics.

Dynamic Properties

The self diffusion constant, D, and the terminal relaxation time of the mean square diameter (the longest internal relaxation time for a ring), τ_R, were obtained from the simulation as in Ref. (1) and are listed in Table II. One should note that to run the simulations long enough to

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TABLE II   Transport Properties

n	n/n_e	D	τ_R
100	0.21	1.14×10^{-3}	1.15×10^3
216	0.46	4.56×10^{-4}	7.5×10^3
392	0.83	1.88×10^{-4}	3.02×10^4
800	1.17	$(8 \times 10^{-5})^a$	1.33×10^5
1536	3.3	-------	-------

^{a} This value is an upper bound estimation of the diffusion constant (See Ref. 1C).

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obtain the transport properties for the n - 1536 melt are beyond present computational capabilities. The scaling behavior of the dynamic quantities with respect to degree of polymerization was obtained from the data in Table II as

$$D \sim n^{-1.5} \text{ and } \tau_R \sim n^{2.4}.$$

This scaling behavior suggests that the rings are not yet in the fully entangled regime but are rather in the crossover regime between Rouse and entangled.

We can show that our simulated melts are in the crossover regime in another way by evaluating the average number of entanglements per ring. To obtain this from our data we use an expression for the chain length dependence of a chain in a melt [derived in Ref. (5)]

$$D(n) = \frac{d_o}{n(1+n/n_e)}$$

where n_e is the entanglement length (average number of monomer units between entanglements) and d_o is a monomeric friction constant. Fitting this expression to the data in column 2 of Table II gives n_e(rings) - 470. This should be compared to our simulated value of n_e(linear) - 130 obtained under the same conditions[1C,2]. Hence, the ratio

$$n_e(\text{rings})/n_e(\text{linear}) - 3.6$$

which is in reasonable agreement with the experimental value for the ratio of approximately 5 obtained for polybutadiene[7]. The mean number of entanglements per ring, n/n_e, is given in of Table II. It is apparent that even the n - 1536 ring melt is in the crossover regime and at least twice that length would be required to obtain fully entangled melt behavior.

This dramatic decrease in the number of entanglements of a ring when compared to a linear polymer of the same molecular weight is an important feature in the dynamics of ring melts. The fact that rings are more compact than linear chains, as discussed in the previous section, is undoubtedly a contributing factor. However, it seems unlikely, considering the rather small differences between the simulated size of the rings and that predicted using Gaussian statistics, that this can be the major cause. We suggest that the cause is in the dynamics of entanglements. If one thinks of an entangled ring moving in any (arbitrary) direction it is apparent that many fewer of the contacts with other chains will act to retard this motion than would be the case for a linear polymer with the same number of contacts with other polymer chains. Hence, even though the number of contacts with other polymers is almost as large for ring polymers as it is for linear ones the number that are actually retarding the motion is much smaller. It is those contacts which retard the motion of the polymer which act as entanglements, hence, rings having a smaller number of effective contacts, are less entangled than linear polymers.

Lastly, although it is not surprising considering the small number of entanglements in our simulated ring melts, an examination of the trajectories of ring motion shows no evidence for reptation-like motion of rings.

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