Comparison of Ring and Linear Polyethylene from Molecular Dynamics Simulations

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The conformational and dynamical properties of macromolecular melts are strongly affected by topological constraints. The extent to which the constraints become dominant depends on various polymer parameters, such as molecular weight and architecture. In this regard, the conformational characteristics and dynamics of linear polymers have been studied extensively experimentally and theoretically.[1] It has been confirmed that their conformational properties in a melt are identical to those of unperturbed chains.[2,3] With respect to their dynamics, a transition occurs from an isotropic motion, described by the Rouse model,[1] to a locally anisotropic motion induced by the noncrossability of neighboring chains when the molecular weight exceeds a certain value. The latter dynamics may be approximated by the reptation theoretical model,[4] as confirmed by computer simulations[5−7] and experiments.[8−10] In the conventional reptation model, the presence of the chain ends plays a dominant role in relaxation process of a linear polymer in a melt. For other polymer architectures such as polymer rings, which obviously have no ends, different relaxation processes have to be expected. A new model of a ring polymer in a gel, a so-called "lattice animal", was proposed,[11] and experiments of ring polymers in linear matrices[12] and linear polymers in ring matrices[13] were performed. In various rheological measurements,[14−16] it was found that the viscosity of rings beyond a certain molecular weight exhibit a molecular weight dependence similar to that of linear molecules. The predicted entanglement molecular weight is higher than that of comparable linear molecules. However, no conclusive experimental results have been obtained so far, since the synthesis of unknotted and nonconcatenated "pure" ring polymers remains an unresolved issue.[14] Recently, Monte Carlo simulation studies[17−20] on ring polymers in a melt have been performed exploiting the bond-fluctuation model. These simulations exhibit a severe influence of topological constraints on polymer conformations as well as their dynamics. However, ring polymers are predicted to show a higher diffusion constant compared to their linear counterparts,[17] in apparent disagreement with experimental results.[21] Moreover, such models do not easily provide insight into the detailed structural changes on a very local scale of a few monomers. Thus, a comprehensive understanding of the structure and dynamics of real ring polymers with realistic topological constraints at experimental densities is missing. In this Communication, we present molecular dynamics simulation results on linear and ring polyethylene molecules in a melt. A well-confirmed atomistic force field of polyethylene[22,23] is applied in a constant temperature and constant pressure simulation algorithm. A united atom model is used to describe the

methylene and methyl groups which interact via a Lennard-Jones potential.[22,23] The temperature is kept at 509 K by Nosé−Hoover chains[24] and the pressure at 1 atm. The lengths of the polymers vary from 40 carbon atoms up to 300 carbons. In contrast to previous coarse-grained simulations, the constant pressure algorithm yields an adjustment of the density with increasing length of the polymers; i.e., it accounts for changes of the free volume due to chain-end effects. Thus, the current simulations closely resemble the experimental situation. In addition, phantom chain Brownian dynamics (BD) simulations[3] were performed to compare the chain conformations in the melt to those in a Θ solvent.

To measure the average size of a polymer, we use the mean-square radius of gyration $\langle R_g^2 \rangle$. Results for various chain lengths are given in Table 1 and presented in Figure 1. Consistent with other simulations of ring polymers,[17−20] we obtain a distinctly different dependence of the radius of gyration on the number of carbon atoms. The relation $\langle R_g^2 \rangle \sim N^{2\nu}$ yields the exponent $\nu_L \approx 0.53$ for linear PE chains and $\nu_R \approx 0.45$ for ring PE molecules ($N > 100$). The latter is consistent with recent experimental results on PDMS rings.[25] Therefore, topological constraints lead to more compact structures for the rings than the linear molecules. The value ν_L for linear polyethylenes exceeds the value for an ideal freely jointed linear chain in a Θ solvent. This is a consequence of the intrinsic stiffness (persistence length) of PE chains.[26] The BD simulations confirm this conclusion because they provide almost identical radii of gyration and exponents. At the same time, the BD simulations of rings confirm the considerable shrinkage of the ring polymers in a melt as compared with the unperturbed chains. Considering the dependence of the density on molecular weight, our simulations yield an increase of density for linear polymers with increasing number of carbon atoms, as shown in Table 1 and Figure 1. In contrast, the ring systems assume an almost size-independent density. For large molecular weights, the linear polymers and the rings seem to approach the same limiting density.

To investigate the local conformational properties, the static structure factors represented by Kratky plots for $N = 300$ are compared in Figure 2. Linear PEs exhibit a self-similar structure which is not perturbed by the topological effect of the dense polymer melt, except a very small difference for $q > 0.3/\text{Å}$, as shown by the comparison between the MD (thin solid line) and BD (thin dashed line) results. For rings, the structure factor of unperturbed molecules (bold dashed line) exhibits a small peak indicative of correlations on the length scale of a few nanometers, in qualitative agreement with the experimental results on polystyrene rings in dilute solutions.[27] For the melt of ring PEs, the structure factor (bold solid line) around this peak region shows a considerable increase as compared with the unperturbed ring. Moreover, while the structure factors of unperturbed rings and linear chains agree well for $q > 0.3/\text{Å}$, the structure factor of the rings in the melt exhibits a minimum followed by a pronounced second maximum around $q \approx 1.2/\text{Å}$ (double-bump structure). The second maximum corresponds to the nearest intermolecular distances in the melt chains but is much weaker for the linear PE melt. Therefore, this double-bump structure indicates that the topological effects of densely packed ring polymers result in conformational perturbations in the form of increased compact loop-like local conformations. Since the conformational statistics of trans and gauge states are nearly

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Table 1. Relevant Simulation Parameters and Results[a]

		linear				ring			
	M	ρ [g/cm^3]	$\langle R_g^2 \rangle^{1/2}_{MD}$ [Å]	$\langle R_g^2 \rangle^{1/2}_{BD}$ [Å]	D_N [Å^2/ps]	ρ [g/cm^3]	$\langle R_g^2 \rangle^{1/2}_{MD}$ [Å]	$\langle R_g^2 \rangle^{1/2}_{BD}$ [Å]	D_N [Å^2/ps]
C$_{40}$	30	0.720	9.01		0.104	0.760	6.26		0.082
C$_{50}$	30	0.730	10.42	10.52	0.076	0.763	7.30	7.54	0.064
C$_{60}$	30	0.736	11.56		0.060	0.764	8.22		0.054
C$_{100}$	30	0.750	15.96	16.05	0.024	0.766	10.98	11.56	0.028
C$_{150}$	40	0.757	20.19	20.39	0.012	0.767	13.46	14.54	0.018
C$_{200}$	40	0.761	23.38	24.18	0.0066	0.768	15.41	17.00	0.013
C$_{300}$	70	0.770	29.18	29.91	0.0029	0.773	18.38	20.95	0.0078

[a] M = number of polymer chains in the melt; ρ = density; $\langle R_g^2 \rangle$ = mean-square radius of gyration; D_N = diffusion coefficients. MD corresponds to PE chains in a melt and BD to a phantom PE chain.
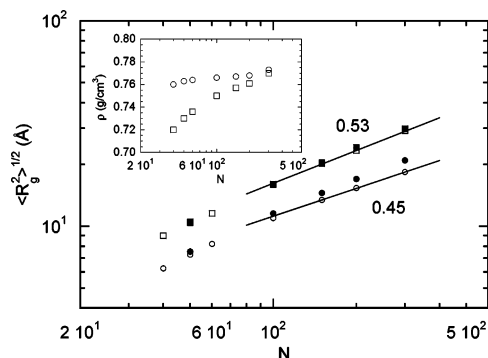

Figure 1. Radii of gyration for linear (open squares) and ring (open circles) PE molecules of various carbon numbers obtained by molecular dynamics simulations. For linear molecules the solid line shows the scaling $\langle R_g^2 \rangle^{1/2} \sim N^{0.53}$ and for rings $\langle R_g^2 \rangle^{1/2} \sim N^{0.45}$. The filled symbols correspond to the phantom chain simulations. Inset: variation of density with the number of carbon atoms.
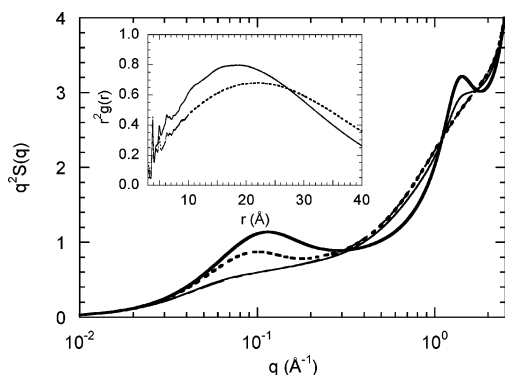

Figure 2. Single chain structure factors (Kratky plots) of linear (thin) and ring (bold) PE molecules with $N = 300$. The solid lines are obtained by MD simulations of melt chains and the dashed lines by BD simulations of phantom chains. The scattering vector q is given by $q = 4\pi \sin(\theta/2)/\lambda$, where λ is the wavelength and θ the scattering angle. The inset displays the intramolecular pair correlation functions for rings in a melt (solid line) and for phantom rings (dotted line).

identical, with the trans fractions of 0.62, for the simulated linear and ring PE molecules, we conclude that the shrinkage of the rings in the melt, by the formation of compact loops, is a unique long-range effect, unlike the conventional excluded-volume effect. In this regard, the very recent SANS experiments on PDMS ring melts are consistent with the simulation results.[28]

The intramolecular pair correlation functions for ring PEs with $N = 300$—shown in the inset of Figure 2—confirm our conclusions on compact local loop-like structures. The distributions are almost identical below 4 Å for the phantom and melt rings as well as the linear polymers, in agreement with the nearly identical trans and gauge states populations. However, the intrachain correlations increase significantly between 5 and 20 Å for the rings in a melt.
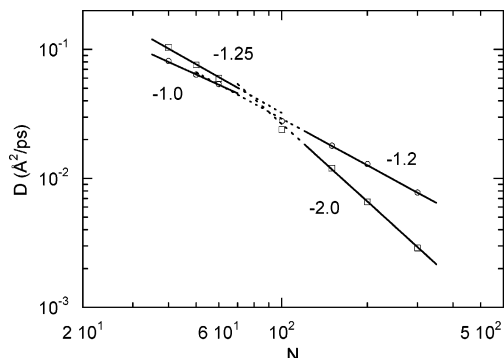

Figure 3. Center-of-mass diffusion constants as a function of the number of carbon atoms for linear chains (squares) and rings (circles).

Since the topology of a ring polymer is different from that of a linear polymer, different types of relaxation processes are to be expected in the motion of ring polymers. In Figure 3 the center-of-mass diffusion constants are shown as a function of the number of carbon atoms. There is a distinct difference in the molecular weight dependence between the linear chains and the rings. Low molecular weight linear PE chains move faster than rings due to the lower overall density, in agreement with simulations[29] and experiments.[21] This contrasts the result of previous Monte Carlo simulations performed under a constant volume approximation.[17] The chain length dependence of the ring diffusion coefficient is well described by $D \sim N^{-1}$ for these ring sizes, which corresponds to the behavior predicted by the Rouse model.[1] For larger rings ($N > 110$), we observe a transition to the dependence $D \sim N^{-1.2}$. A similar dependence is also seen in Monte Carlo simulations,[17,19,20] and this result will be discussed in detail below. The diffusion coefficients of the linear PE chains exhibit a much more pronounced chain length dependence. For short chains we find $D \sim N^{-1.25}$ followed by a transition to $D \sim N^{-2}$ for longer chains. The transition seems to be a consequence of entanglements. The onset of the entanglement effects occurs at chain lengths $N \approx 110$, slightly smaller than predicted by experiments,[9] possibly due to polydispersity in the samples used in experiments. A recent reconsideration of experimental diffusion coefficients lead to the dependence $D \sim N^{-2.4}$.[30] Similarly, previous computer simulations[7] seem to predict such a dependence. Such a strong dependence on chain length is not seen in our simulations of unimolecular systems. Since our chain lengths do not reach deeply into the entanglement regime, we cannot rule out a large slope. It seems, however, plausible that the small polydispersity in previous simulations and experiments may be responsible for this observation. This effect would then disappear as the polydispersity decreases and chain length increases as seen experimentally.[31]

Figure 4 displays the mean-square displacements of the central monomers of linear PE chains (a) and the average over
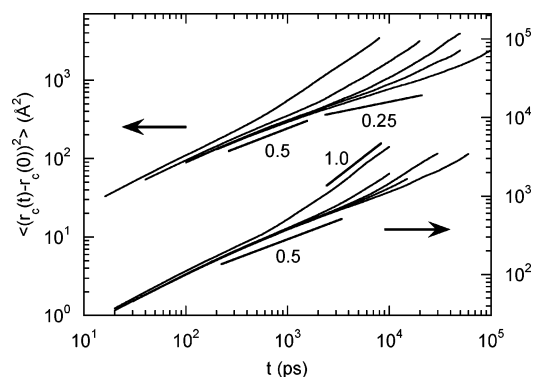
Figure 4. Mean-square displacements of the central monomers of linear PE molecules (top set of curves, left *y*-scale) and the average over all monomers for PE rings (bottom set of curves, right *y*-scale). The carbon atom numbers are $N = 50$, 100, 150, 200, and 300 (top to bottom).

all monomers of PE rings (b) for various chain lengths. Independent of chain length, the various mean-square displacements approach a linear time dependence for $t \rightarrow \infty$. At short times, the reduction in free volume with increasing chain length of the linear molecules leads to a shift of the mean-square displacement curves to larger times. For sufficiently long PE chains, the mean-square displacement exhibits a time range with a $t^{1/2}$ dependence as predicted by the Rouse model. Entanglement effects lead to a further slowdown of the monomer dynamics for the longest linear molecules visible by the time dependence t^{α} with α smaller than 1/2. Since the polymer density of the ring systems depends only weakly on their molecular weight, the mean-square displacements of the PE rings are almost identical at short times. In contrast to the linear PE molecules, there is no visible entanglement regime present. However, the changes in the conformational properties of the rings will naturally affect their dynamics in the unentangled melts. This is clearly seen by the particular carbon number dependence of the diffusion constant. At first sight, one might argue that compactification of the rings would lead to a faster dynamics, since the interaction with the surrounding of the interior of the more compact structure would be smaller. Thus, *D* should display a carbon number dependence with an exponent larger than -1.0, which obviously contradicts the simulation results of -1.2. On the other hand, since the shrinkage of the ring dimensions is achieved by compact loop formation, the dynamics of the monomers of such a loop will be highly cooperative, leading to a slowdown of the dynamics of the whole ring polymer. This seems consistent with the finding that the dynamics of the rings in the melt are slower than those of unperturbed rings, shown by the simulation data.

In conclusion, by studying an atomistic model of PE rings, we have observed that such rings collapse in a melt by comparing their radii of gyration with those of phantom chains. The collapse becomes more pronounced with increasing chain lengths, and the careful analysis of the intramolecular structure factors indicates that this is caused by compact loop formation in melt chains. The mean-square displacement of linear PE chains displays a clear transition to an entanglement dominated dynamics for chain lengths above $N = 110$. However, no such entanglement dynamics is observed for ring PE melts up to PE rings $C_{300}H_{600}$. We expect that the entanglement dynamics of PE rings in a melt will be seen for higher molecular weight

systems.[32] The details of such entanglement dynamics of ring polymers are not understood so far. Therefore, we hope that the results of our simulations, expected to be in almost quantitative agreement with experiments on PE melts, will stimulate and guide extensive investigations on ring polymer melts.

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