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Rheology of ring polymer melts: From linear contaminants to ring/linear blends

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Ring polymers remain a major challenge to our current understanding of polymer dynamics. Experimental results are difficult to interpret because of the uncertainty in the purity and dispersity of the sample. Using both equilibrium and non-equilibrium molecular dynamics simulations we have systematically investigated the structure, dynamics and rheology of perfectly controlled ring/linear polymer blends with chains of such length and flexibility that the number of entanglements is up to about 14 per chain, which is comparable to experimental systems examined in the literature. The smallest concentration at which linear contaminants increase the zero-shear viscosity of a ring polymer melt of these chain lengths by 10% is approximately one-fifth of their overlap concentration. When the two architectures are present in equal amounts the viscosity of the blend is approximately twice as large as that of the pure linear melt. At this concentration the diffusion coefficient of the rings is found to decrease dramatically, while the static and dynamic properties of the linear polymers are mostly unaffected. Our results are supported by a primitive path analysis.

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While much has been learned about linear and branched polymers [1, 2], a comparable understanding of ring or cyclic polymers is lacking. Ring polymers, as they do not have free ends, represent the simplest model system where reptation is completely suppressed. Also, mitochondrial and plasmid DNA are usually cyclic, and melts of rings are considered highly relevant model systems to understand chromatin folding in the cell nucleus [3, 4]. This makes ring polymers perfect test cases for both fundamental polymer and bio physics.

Early experimental studies on pure ring polymer melts gave inconsistent results most likely because the samples were contaminated with linear chains [5–7]. Also the existence of self-knots could not be controlled. More recently experiments have been conducted [8] based on new characterization and purification techniques [9, 10]. For melts of nonconcatenated polystyrene rings with molecular weight (MW) to entanglement MW ratios of 9.2 and 11.3, where the entanglement MW is 17500 g/mol, Kapnistos et al. [8] reported that the stress relaxation modulus, $G(t)$, follows a power-law decay with no sign of a rubbery plateau. The authors used scaling arguments to show $G(t) \sim t^{-2/5}$, a result in agreement with the data up to the terminal time. Milner and Newhall [11] introduced the “diffusion of centrality” concept and mapped the ring conformations to annealed tree-like structures and found a similar prediction of $G(t) \sim t^{-1/2}$.

Kapnistos et al. [8] also reported that the smallest concentration of linear contaminants that affects the rheology of the ring melt is almost two decades below the overlap concentration of the linear chains. Despite the synthetic effort, the characterization and control of the experimental systems including polydispersity, knotting, concatenation and linear contaminants is far from perfect. Because of this, computer simulations of optimized models, which by now easily reach effective experimental molecular weights, are perfect to test concepts for precisely defined systems under well-controlled conditions. Our own recent simulations [12] of a melt of nonconcatenated and unknotted ring polymers have shown that $G(t) \sim t^{-\alpha}$ with $\alpha$ decreasing from 0.5 to 0.45 with increasing chain length.

Here we employ molecular dynamics (MD) simulations to study the structure, dynamics and rheology of ring/linear polymer blends of equal chain length. We consider two lengths of $N = 200$ and 400 monomers per chain. For the model used here the entanglement length of a melt of linear polymers is $N_e = 28 \pm 1$ [13] which corresponds to $N/N_e \approx 7.1$ and 14.3 entanglements per chain. For this a bond bending potential along the chains is introduced, leading to a Kuhn length of $l_k \approx 2.79 \sigma$ [13], $\sigma$ being the unit of length. $N_e$ is determined by a primitive path analysis [13, 14], which is known to yield $N_e$ values which properly reproduce rheological data [15, 16]. Our systems are perfectly monodisperse, unknotted and nonconcatenated, allowing for a rather stringent test of currently discussed concepts. Previous simulations of such mixtures have only considered short chain lengths and did not measure any rheological properties [17, 18]. While different polymer melts can be related to each other by the $N/N_e$ ratio, we note that for the present comparison to experiment [8] also the ratio of the Kuhn length and the packing length $l_k/p$ are not that different, namely 6.5 for our simulation model [13] and 3.8 for a polystyrene melt [19].

The topological constraint that a ring must remain unknotted and nonconcatenated leads to nontrivial behavior even for the static properties of a melt or concentrated solution of rings. Rings are found to be approximately Gaussian at short chain lengths, while for larger lengths the nonconcatenation dominates the conformational statistics. Cates even for the static properties of a melt or concentrated solution of rings. Rings are found to be approximately Gaussian not that different, namely 6.5 for our simulation model [13] and 3.8 for a polystyrene melt [19].

While much has been learned about linear and branched polymers [1, 2], a comparable understanding of ring or cyclic polymers is lacking. Ring polymers, as they do not have free ends, represent the simplest model system where reptation is completely suppressed. Also, mitochondrial and plasmid DNA are usually cyclic, and melts of rings are considered highly relevant model systems to understand chromatin folding in the cell nucleus [3, 4]. This makes ring polymers perfect test cases for both fundamental polymer and bio physics.
Results for the mean-square gyration radius for the rings and linear chains normalized by their respective pure melt values are shown in Fig. 2(a). For the rings with $N = 200$, $\langle R_g^2 \rangle$ is found to increase with increasing linear concentration. At $\phi_{\text{linear}} \approx 0.96$, $\langle R_g^2 \rangle = 45.3 \pm 2.2 \sigma^2$, which is 1.5 times larger than the value of the pure ring melt. For a Gaussian ring $\langle R_g^2 \rangle = Nl/12 = 45.2 \sigma^2$, where $l$ is the average bond length. For the rings with $\phi_{\text{linear}} \approx 0.96$ the static structure function scales as $S(q) \sim q^{-2}$ for $2\pi/(R_g^2)^{1/2} < q < 2\pi/l$, even though the rings cannot sample the whole conformational space of a Gaussian ring [31]. For the $N = 400$ systems a similar swelling behavior is found for the rings. The linear chains are found to be Gaussian for all combinations of $N$ and $\phi_{\text{linear}}$. At small values of $\phi_{\text{linear}}$ the rings are partially collapsed as discussed above. As the fraction of linear chains increases, the size of the rings grows because it is entropically favorable for the linear chains to thread the rings. At infinite dilution the nonconcatenation constraint vanishes and the rings are found to be multiply-threaded and nearly Gaussian [17, 31, 32].

The diffusion coefficients, $D$, which are determined by the long-time behavior of the mean-square displacement of the center-of-mass of the chains, are shown in Fig. 2(b). The diffusivity of the rings for both values of $N$ is found to steadily decrease with increasing fraction of linear chains until a dramatic decrease is observed. With the overlap concentration of linear chains being $c^* = \phi_{\text{linear}}\rho = N/(4/3)\pi (R_g^2)^{3/2}$, this transition corresponds to approximately $0.1\rho = 1.5c^*$ for $N = 200$ and $0.04\rho = 0.9c^*$ for $N = 400$. For $N = 400$ the diffusion coefficient of the rings at $\phi_{\text{linear}} = 0.5$ is reduced by a factor of about 75 compared to the pure ring melt. While the linear chains clearly restrict the motion of the rings, the motion of the linear chains for both values of $N$ is largely independent of the blend composition, which is consistent with early experimental results [33].

Linear chains have free ends and undergo reptation independently of whether the surrounding chains are rings or linear, and accordingly their diffusion is found to be independent of $\phi_{\text{linear}}$. Rings in a pure melt do not reptate like linear chains. As linear chains are added to the ring melt, the rings become threaded and the nature of their motion changes. A threaded ring can only diffuse through the release of threads. For a one-thread situation Mills et al. [34] have shown that the diffusion coefficient of the ring is $D \sim N_{\text{ring}}^{-1}N_{\text{linear}}^{-1}$. At high fractions of linear chains the rings become multiply-threaded and their diffusion is severely hindered. In this regime the motion of a ring monomer is coupled to the motion of surrounding linear chains. This implies Rouse dynamics for the ring with a monomer relaxation time governed by the reptation relaxation of the linear chains, leading to a relaxation time scaling of $N_{\text{ring}}^2N_{\text{linear}}^3$. This argument is due to Graessley [35] and predicts $D \sim N_{\text{ring}}^{-1}N_{\text{linear}}^{-3}$.

The zero-shear viscosity computed as $\eta_0 = \int_0^\infty G(t)dt$ is shown as a function of $\phi_{\text{linear}}$ in Fig. 2(c). A striking result is the clear indication that the smallest concentration at which linear contaminants alter the viscosity of a ring melt considerably (about 10%) for the chain lengths considered here is $\phi_{\text{linear}} \approx 1/100$ or $c^*/5$ with a strong increase around $c^*$. This threshold concentration is roughly consistent with the change in $D$ for the rings. We have confirmed our values of $\eta_0$ by conducting non-equilibrium MD simulations [36] where simple steady shear is imposed. For these
FIG. 2. (a) Mean-square gyration radii, (b) diffusion coefficients and (c) zero-shear viscosity versus $\phi_{\text{linear}}$. The overlap concentration of linear chains, $c^*$, is indicated for the two values of $N$. For the rings with $N = 200$ and 400, $\langle R^2_g \rangle_0 = 30.8$ and 52.9 $\sigma^2$, respectively, while for the linear chains $\langle R^2_g \rangle_0 = 88.9$ and 180.8 $\sigma^2$. Note that the horizontal axis is interrupted. Lines are drawn as a guide for the eye.
is entangled with are shown. Given the large number of entanglements at this composition, the dramatic decrease in the diffusivity of the rings and the increase in the blend viscosity in comparison to the pure ring melt value are easily understood.

The present work provides a complete scan of compositions of two different ring polymer/linear polymer melts for dynamical quantities such as viscosity and chain diffusion. One striking result is that the linear contaminants start significantly affecting the ring melt viscosity at a concentration well below their overlap concentration. This simulation result is in perfect qualitative agreement with the experimental observation of Ref. [8]: according to both simulation and experiment, there is clearly an effect below the overlap concentration. However, quantitatively we detect the onset of a viscosity change (10% increase for rings and linear chains with $N/N_e \approx 10$) at $\phi_{\text{linear}} \approx 0.01$, while Kapnistos et al. [8] reported a 2-fold viscosity increase in comparison to the “pure as currently possible rings” at a much smaller concentration of $\phi_{\text{linear}} = 0.0007$. To provide an intuitive picture of these concentrations one can estimate what would be the typical distances between chains. For $\phi_{\text{linear}} = 0.0007$ the typical distance between linear chains $(\rho/N)^{-1/3}$ would be about 66 $\sigma$ for $N = 200$ and 83 $\sigma$ for $N = 400$. The diameter $(2 \langle R_g^2 \rangle^{1/2})$ of the rings is about 11 $\sigma$ and 15 $\sigma$ and of the linear chains about 19 $\sigma$ and 27 $\sigma$, respectively. Thus two linear chains would be separated on average by about 4–5 ring diameters for $N = 200$, or by 4 ring diameters for $N = 400$. And, importantly, these rings would not be entangled since they are unconcatenated and have no free ends. At $\phi_{\text{linear}} = 0.01$, where our data indicate a 10% viscosity increase, distances and chain extensions are all rather similar. While the two works differ with respect to the onset concentration, fair agreement is found for the ratio of the pure linear melt viscosity to that of the (almost) pure ring melt as shown in the inset of Fig. 3 [8, 39]. Additionally, the simulation and experimental results for the dependence of $\eta_0/\eta_{\text{rings}}$ on $N/N_e$ are consistent not only with one another, but also with the theoretical framework of Ref. [8] and our previous result [12] which suggest a power law dependence with power close...
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