NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATION OF MARGINALLY ENTANGLED RING POLYMER MELTS AND RING-LINEAR POLYMER BLENDS

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ABSTRACT

Detailed molecular dynamics (MD) simulations and experimental studies with state-of-the-art techniques have been extremely useful in the last years in understanding the intriguing dynamic, transport and conformational properties of ring polymer melts, a unique class of polymer molecules that lack chain ends and whose dynamics cannot be described by well-established polymer theories such as reptation. Particular emphasis has been given to the equilibrium properties of ring polymer melts in the crossover region around the entanglement molecular weight M_e of the corresponding linear polymer, with very interesting results.[1] MD simulations in combination with a detailed geometric analysis[2,3] have also helped understand the role of topological constraints in such polymers associated with ring-ring and ring-linear (caused by remaining linear impurities) threading events, and the connection of these events with the slow relaxation modes observed in high molecular weight ring polymers.[3,4] In the present work, this study is extended to ring polymers under flow, as well as to ring-linear polymer blends. We present results from a systematic study of the flow behavior of ring-linear polymer blends both in the linear and nonlinear regime using as a model system poly(ethylene oxide) (PEO), a polymer that has been studied rather extensively in the literature. The flow simulations have been carried out with a very efficient Non-Equilibrium Molecular Dynamics (NEMD) algorithm based on the p-SLODD equations of motion for shear in the NVT ensemble, in conjunction with the Lees-Edwards boundary conditions.[5] Simulation results for the relevant viscometric functions (viscosity and first and second normal stress coefficients) of the simulated PEO pure ring and linear chains melts, and of the linear-ring blends are analyzed as a function of molecular weight and blend concentration in linear molecules. We also present results from a preliminary topological analysis of the simulated blends, which provides information for the effect of flow on the degree of topological coupling between linear and ring polymers and the structure of the underlying topological network formed under equilibrium conditions.

INTRODUCTION

The dynamic and rheological properties of polymers depend crucially not only on the chemistry but also on the molecular architecture of the constituent chains. For melts of linear polymers, important theories describing their segmental and terminal relaxation as well as their flow behavior include the Rouse model for unentangled melts (chain molecular weight M_w less than the characteristic entanglement molecular weight M_e) and the tube model for entangled ones (chain molecular weight M_w significantly higher than the characteristic entanglement molecular weight M_e). In the last years, a class of polymers whose dynamics and rheology have attracted the interest of many scientists is that of ring chains, mostly due to the importance of these structures in many complex biological processes,[6-10] as well as in biotechnology.[11-15] Due to their closed loop geometry, existing theories for linear chains do not directly apply to ring polymers. For example, the Rouse theory for linear polymers must be suitably adapted in order to apply to rings.[16] Several predictions of this modified, ring Rouse theory (e.g., for the dependence of chain conformation and diffusion on chain size) have been recently validated by experimental studies[17-19] and simulations.[16, 20]

In linear chains, as the M_w increases above M_e, strong topological constraints develop in the melt known as entanglements that substantially affect system dynamics and relaxation. In the same spirit, as the ring molecular weight increases, the conformational and dynamic properties of the ring polymer melt are expected to change. However, the tube model, which is based on stress release mechanisms through the motion of free chain ends, cannot describe the behavior of rings. Thus, recent theoretical models for rings have proposed[21-23] new scaling laws for their conformational and dynamical properties at equilibrium that differ significantly from those of the corresponding linear counterparts. These scaling laws have been validated by state-of-the-art simulations [22,24,25] and experimental measurements.[26]

The exploration of the rheological properties of ring polymers was initiated in the early 80's[27-29] when researchers managed to synthesize ring chains by anionic polymerization in very dilute solutions. However, several inconsistencies were observed in the published results, many of which are now believed to be due to significant contamination of the synthesized samples by linear counterparts. The problem of producing pure ring polymers was solved only recently with the help of Liquid Chromatography at the critical condition (LCCC) which helped reduce the percentage of linear chains down to 0.1%.[30] This led to the landmark work by Kapnistos et al.[31] who explored the stress relaxation of entangled ring polystyrene melts as a function of linear content and observed that even tiny amounts of linear contamination can have dramatic effects for their rheology (e.g., their stress relaxation modulus, which for rings does not exhibit a plateau but rather follows a power law behavior). More recently, Doi et al. [32] investigated the dependence of the zero-shear rate viscosity of highly purified ring polystyrene melts on M_w and found that ring melts follow the ring-Rouse model for M_w's up to $5M_e$. We recall that linear melts follow the Rouse model only for molecular weights lower than $1M_w$.

From a conceptual point of view, an interesting system to study is that of blends of linear and ring chains. For example, Halverson et al.[33] carried out coarse-grained equilibrium molecular dynamics (MD) simulations of entangled ring-linear monodisperse melts and observed that the zero-shear rate viscosity as a function of the linear contamination exhibits a maximum at φ_{linear} = 50%. Also, Yan et al. have studied pure ring chains, pure linear chains and blends thereof using as model system polystyrene. The viscosity of linear chains came out to be higher than the viscosity of rings, and in addition they conformed the findings of Halverson et al., as the system with 85 % linear chains exhibited a higher viscosity than the corresponding linear chain melt.

In the present study, we use NEMD simulations in atomistic detail to study the flow behavior of ring PEO melts and how this compares to the corresponding behavior of linear PEO melts. We also address blends of ring and linear PEO and how their shear rheology changes as a function of the concentration of the melt in linear chains. Because of the atomistic nature of our simulations, our study here is limited to relatively short PEO melts, below and above the characteristic entanglement molecular weight M_e. Nevertheless, very useful results are obtained concerning the shear rheology of the pure rings and of their blends with linear, and how these compare with the predictions of the ring Rouse theory. We discuss all of them in the next sections of this extended abstract.

SYSTEM STUDIED AND SIMULATION DETAILS

As already mentioned, in the present study we focused on three types of PEO melts: a) pure ring, b) pure linear, and c) blends of ring and linear. The chemical structure of the rings is $-CH_2-O-(CH_2-CH_2-O)_n-CH_2-$ and of the linear chains $CH_3-O-(CH_2-CH_2-O)_n-CH_3$, with n representing the degree of polymerization (number of monomers per chain). We have executed simulations for three different values of n (equal to 29, 40, and 120) which correspond to molecular weights (equal to 1322 g/mol, 1846 g/mol and 5326 g/mol, respectively, and practically the same between the two architectures) below and above the M_e value for linear PEO which is approximately

2,200 g/mol. We have denoted the three systems as PEO-1k, PEO-2k and PEO-5k, respectively. In Table1, we report several technical details concerning the simulated pure PEO melts.

Table 1. *Some technical details (such as molecular weight and number of chain molecules) of the pure PEO melts simulated in this work.*

System	M_W (g/mol)	Number of molecules
R-1k	1320	3750
R-2k	1844	3125
R-5k	5324	1458
L-1k	1322	3750
L-2k	1846	3750
L-5k	5326	1920

For the PEO blends, the simulated systems contained from 1300 to 7300 chains depending on the imposed shear rate. The lower the shear rate, the greater the number of chains in the simulation cell (to reduce statistical error). The blend systems simulated are the PEO-2k and PEO-5k at three levels of contamination in linear molecules corresponding to φ_{linear} (= number fraction of linear chains) equal to 20%, 50% and 70%.

Table 2. *Some technical details (molecular weight, percentage of linear molecules, total number of chains) of the PEO blends simulated in this work.*

M_W	φ_{linear}	Number of molecules
PEO-2k	20%	1300-7300
PEO-2k	50%	1300-7300
PEO-2k	70%	1300-7300
PEO-5k	20%	900-1920
PEO-5k	50%	900-1920
PEO-5k	70%	900-1920

Before the NEMD simulations, we conducted long equilibrium MD simulations in the NPT statistical ensemble at temperature T = 363 K and pressure P = 1 atm with the modified united-atom TrAPPE forcefield of Fischer et al.[34,35] using the GROMACS[36] software to obtain fully equilibrated configurations which were used as input for the subsequent flow simulations.

The flow simulations under steady shear were executed by implementing the p-SLLOD algorithm[5] in conjunction with the Lees-Edwards boundary conditions[37] in LAMMPS.[38] Intermolecular and intramolecular interactions were described using the same forcefield as in the equilibrium MD simulations. The simulations were carried out in the NVT ensemble (again at T = 363 K) with the Nosé-Hoover thermostat. The equations of motion were integrated using the reversible Reference Propagator Algorithm (r-Respa)[39] with three different time steps.

RESULTS AND DISCUSSION

In the present work we focused on the dependence of the steady-state shear viscosity on applied shear rate for ring and linear polymer melts, for the three different melts considered (PEO-1k, PEO-2k, PEO-5k). For clarity, we normalized the shear rate with the terminal orientational relaxation time τ_R^{ring} of the pure ring melt under equilibrium conditions which gave rise to the corresponding Weissenberg number Wi_R defined as $Wi_R = \tau_R^{ring} \, \dot{\gamma}$. For all different M_W melts, we observed the typical characteristic behavior of the shear viscosity with shear rate already known for linear polymer melts:

a) At low shear rates, the viscosity is constant defining what we know as the Newtonian plateau. b) At higher shear rates, the viscosity starts decreasing, exhibiting what we know from the corresponding behavior of linear polymers as shear thinning behavior. c) At even higher shear rates, we enter the highly nonlinear regime where the viscosity drops rapidly with applied shear rate.

Given that the calculation of the stress tensor in atomistic NEMD simulations at very low shear rates (below $1/\tau_R^{ring}$) suffers from large statistical fluctuations, to compute the corresponding zero shear rate viscosity η_0 we fit our data to the Carreau Model:

$$\eta(\dot{\gamma}) = \eta_0 \left[1 + (\lambda \cdot \dot{\gamma})^2 \right]^{-p} \qquad (1)$$

In eq. (1), *p* is a characteristic exponent and *λ* a fitting parameter with units of time.

Using eq. (1) to compute η_0 proved very efficient and allowed us to reliably estimate the ratio $\eta_{0,L}/\eta_{0,R}$ of the zero shear rate viscosity of the ring melt to the corresponding zero shear rate viscosity of the linear analogue. Interestingly enough, for the PEO-1k, we found that $\eta_{0,L}/\eta_{0,R} = 1.0 \pm 0.2$. A similar result has been reported by Nam et al.[40] who studied experimentally the viscosity of short ring and linear PEO melts. We remind the reader that according to the Rouse model, the ratio $\eta_{0,L}/\eta_{0,R}$ is equal to 2. The reason for the deviation from the Rouse model should be sought to excess free volume phenomena present in the linear melts due to the presence of chain ends, which accelerate chain dynamics and, in turn, cause the viscosity to decrease. Clearly, as the chain length increases, these excess free volume phenomena will diminish, and the viscosity should be come closer to the prediction of the Rouse theory. Indeed, for the PEO-2k melt, the corresponding ratio comes out to be $\eta_{0,L}/\eta_{0,R} = 2.1 \pm 0.2$, a result which is fully consistent with the Rouse model. By furrher increasing M_w, entanglements start developing between chains in the linear melt which restrict their dynamics, thus we expect the viscosity of the linear melt to increase faster than the viscosity of the ring melt. Indeed, for PEO-5k (a marginally entangled melt), the ratio $\eta_{0,L}/\eta_{0,R}$ from our NEMD simulations comes out to be $\eta_{0,L}/\eta_{0,R} = 2.6 \pm 0.2$. Overall, we can say that according to our NEMD simulations, the ratio $\eta_{0,L}/\eta_{0,R}$ for very short PEO melts (well below M_e) starts from a value close to 1 and then increases smootthly with M_e reflecting the faster increase of the viscosity in the corresponding linear melt as inter-chain entanglements start developing between linear polymers.

Next, we turned our attention to the zero-shear rate viscosity of ring PEO melts contaminated with linear chains. The contamination of the ring in linear chains was controlled by specifying the number density of linear molecules in the mixture, φ_{linear}. We observed that η_0 increases smoothly with increasing φ_{linear}, which should be attributed to linear-ring threadings already investigated in the past by several researchers under equilibrium conditions. Indeed, as reported by Tsalikis et al.,[2] in a blend of ring-linear molecules, a linear chain can penetrate not only one but several ring molecules, thus strongly affecting dynamics. The effect becomes stronger with increasing molecular weight, causing a considerable increase in the viscosity of the melt. For example, Halverson et al. and Yan et al.[33,41] have reported that for high molecular weight rings, η_0 even goes through a maximum at a certain level of linear contamination. In our case, we always observed a monotonic increase of η_0 with φ_{linear} (and never a maximum). This might be due to the relatively low M_w of the PEO melts addressed here, and clearly deserves further investigation.

CONCLUSIONS

We have discussed our initial findings from an effort to use NEMD simulations to study the shear rheology of unentangled and marginally entangled ring PEO melts and how it compares with the shear rheology of the corresponding linear melts. We have also directed our analysis to ring melts contaminated with linear chains of the same molecular weight. For the shortest melt addressed here (PEO-1k), our NEMD simulation results for the relative viscosity between ring and linear PEO are consistent with the experimental measurements of Nam et al.[40]. The zero-shear rate viscosity of the simulated PEO ring melts presents a milder dependence on chain length compared to that of linear analogues, which is in very good agreement with theory (ring and linear Rouse model). The NEMD results for the linear-ring blends show that η_0 increases smoothly with degree of linear contamination. For all simulated ring-linear blends, our NEMD simulations do not suggest the presence of a maximum at an intermediate contamination. This does not agree with other experimental and simulation works which, however, addressed much higher molecular weight samples; it is an important issue which we plan to address in a future study.

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