Linear and non-linear shear rheology of marginally entangled ring polymers: a non-equilibrium molecular dynamics study

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ABSTRACT

Atomistic simulations of ring polymer melts under equilibrium conditions have been proven very useful in extracting scaling laws for the conformational and transport properties (chain center-of-mass diffusion coefficient and zero-shear-rate viscosity) of this unique class of polymers in the crossover regime around the entanglement molecular weight M_e [1]. In combination with a detailed geometric analysis, these atomistic simulations have also helped tremendously characterize topological constraints in such systems developing due to ring-ring but also ring-linear threading (in the presence of any remaining linear impurities) and their connection with the slow relaxation modes observed experimentally [2].

In the present work, we extend the study to nonequilibrium conditions by investigating in a systematic way the flow behavior of ring polymers and its dependence on molecular weight, using as a model system poly(ethylene oxide) (PEO). We have conducted detailed nonequilibrium molecular dynamics (NEMD) simulations of pure ring and pure linear PEO melts under shear flow over a wide range of shear rates covering both the linear and nonlinear regime using the p-SLLOD equations of motion [3]. Through these simulations, we have been able to compute the relevant viscometric functions (shear viscosity and first and second normal stress coefficients) as a function of applied shear rate and molecular weight of the melt. The results are compared to those of the pure linear analogues at the same flow conditions. In addition, selected configurations from the NEMD trajectories have been subjected to a detailed geometric analysis [2] to provide information on the effect of flow on the degree of ring-ring threading, and thus on the nature of topological constraints in melts of non-concatenated ring polymers, given the tendency of rings to penetrate each other and form a network.

REFERENCES

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