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

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Abstract

Detailed molecular dynamics (MD) simulations and experimental studies have helped tremendously in the last years to understand the intriguing dynamic, transport and conformational properties of ring polymer melts (stress relaxation moduli, chain center-of-mass diffusion coefficient, zero-shear-rate viscosity, normal stresses coefficients, radii-of-gyration tensor), a unique class of polymers 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 rings 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 nature of topological constraints in such polymers that are connected with ring-ring and ring-linear (caused by remaining linear impurities) threading events. This state-of-the art analysis has opened the way to a better understanding of the equilibrium dynamics of ring polymers because it also made clear the connection between threading events and the slow relaxation modes observed in high molecular weight ring polymers [3, 4].

In the present work, we extend this study to mixtures of marginally entangled linear and ring polymers, addressing also the effect of flow on their dynamics. We will present results from a systematic study of the flow behavior of ring-linear polymer blends both in the linear and highly 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 state-of-the-art Non-Equilibrium Molecular Dynamics (NEMD) algorithm employing the p-SLODD equations of motion in the NVT ensemble for a shear flow in conjunction with the Lees-Edwards boundary conditions [5].

Simulation results will be presented and discussed for the relevant viscometric functions (viscosity and first and second normal stress coefficients) of the simulated PEO blends and will be discussed as a function of molecular weight and concentration in linear molecules. We will 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. The effect of the flow to the relaxation time spectrum will also be discussed.

References

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