

Brownian dynamics simulations of dilute polymer chains with bending and torsional potentials

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The bead-spring model, which is extensively used for describing the linear viscoelastic properties of high molecular weight polymers, is justified through a coarse-graining approximation valid at long time and distance scales. At these scales, individual bonds corresponding to a single spring are assumed to relax quickly enough to sample their equilibrium configuration distribution. In fast flows or at high frequency, the number of bonds that can be successfully represented by a spring remains unclear. To understand this and the mechanism of energy dissipation at high frequencies, we carry out a Brownian dynamics study of a linear polymer chain with beads representing individual carbon atoms, stiff Fraenkel spring forces to maintain the distance between carbon atoms as 1.53 \AA , random Brownian force to represent the molecular motion of the continuum solvent, bending forces to maintain tetrahedral bonding, and realistic torsional forces to induce the chain to take on the preferred torsional configurations. With this model, we find that while the end-to-end vector autocorrelation function is in excellent agreement with the theoretical Rouse model predictions, the autocorrelation function of the bond orientation vectors which reflects the relaxation of the stress tensor, exhibits a decay rate that differs from Rouse predictions except near the longest relaxation time. We find that both the bending and torsional potentials suppress the contributions of fast relaxation times in the Rouse spectrum, bringing the relaxation of short chains (less than 50 bonds) closer to single exponential, in agreement with observations of birefringence relaxation made years ago by Shrag and coworkers (Lodge, T. P.; Miller, J. W.; Schrag, J. L. *J. Polym. Sci., Polym. Phys. Ed.*, **1982**, *20*, 1409). The results are in agreement with a recent model that invokes the notion of a “dynamical Kuhn length” that, because of torsional barriers to chain motion, can be longer than the ordinary static Kuhn length, leading to a loss of high frequency modes of relaxation (R.G. Larson, *Macromolecules*, *37*:5110-5114 2004).