

Shear thinning of unentangled flexible polymer liquids

Experimentally, it is well known that the Rouse model gives a superb description of the concentration dependence of terminal relaxation time, terminal modulus, zero shear-rate viscosity, and diffusion coefficient of semidilute unentangled polyelectrolyte solutions. However, such solutions exhibit shear thinning of the apparent viscosity when the shear rate exceeds the reciprocal of the terminal relaxation time, which is not immediately anticipated by the Rouse model. We present a simple calculation based on the Rouse model for the dependence of the apparent viscosity η on shear rate $\dot{\gamma}$ in steady shear. The derived power law $\eta \sim \dot{\gamma}^{-1/2}$ applies to nearly monodisperse unentangled polymer melts and polymer solutions that have a high enough concentration so that chains overlap, but have low enough concentration that they are not entangled.

We find that the predicted power law agrees nicely with data on unentangled polymer melts and semidilute unentangled solutions of polyelectrolytes. The exponent $1/2$ means the empirical Cox-Merz rule applies to Rouse chains. This potentially has far-reaching consequences for entangled polymer melts, for which motion of a Rouse chain confined to a tube describes dynamics.