Dynamic dilution exponent in monodisperse entangled polymer solutions

We study and model the linear viscoelastic properties of several entangled semi-dilute and concentrated solutions of linear chains of different molar masses and at different concentrations dissolved in their oligomers. We discuss the dilution effect of the oligomers on the entangled long chains. In particular, we investigate the influence of both concentration and molar mass on the value of the effective dynamic dilution exponent determined from the level of the storage plateau at low and intermediate frequencies. We show that the experimental results can be quantitatively explained by considering the tension re-equilibration process along the chains, in agreement with van Ruymbeke et al. (Macromol., 2014), i.e., by considering that the real dilution exponent $\alpha$ is always equal to 1, while larger values of the dilution exponent ($1 < \alpha < 1.3$) found experimentally are attributed to the enhanced relaxation of the long chain extremities. Then we discuss the influence of the polymer concentration on the terminal relaxation time of the solutions and how this can be modelled by the enhanced contour length fluctuation process (CR-CLF). We point out that this larger dilution effect is not only a function of concentration but also depends on the molar mass of the chains. While the proposed approach successfully explains the viscoelastic properties of a large number of semi-dilute solutions of polymers in their own oligomers, important discrepancies are found for semi-dilute entangled polymers in small-molecule theta or good solvents. Possible explanations for the differences between these sample sets are proposed, based on the comparison of their viscoelastic behavior.