PRIMITIVE CHAIN NETWORK SIMULATIONS FOR NON-LINEAR RHEOLOGY OF MONODISPERSE POLYSTYRENE MELTS WITH FRICTION CHANGE AND VIOLATION OF THE FLUCTUATION-DISSIPATION THEOREM

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To describe the elongational viscosity of concentrated polymers, the change in monomeric friction has been proposed and implemented in molecular models[1]. In these theories, the validity of the fluctuation-dissipation theorem (FDT) is implicitly assumed. However, FDT requires local equilibrium, which is inconsistent with the mechanism of friction change induced by a disturbed monomeric environment. Indeed, a recent analysis of data on Rouse melts by Watanabe et al.[2] demonstrates that FDT is violated under fast flow; the Brownian force intensity is almost independent of the flow rate, even though drag friction drastically decreases. In this study, Brownian simulations using a multi-chain slip-link model[3] were conducted for two monodisperse entangled polystyrene melts, for which non-linear shear and elongational rheology data are available in the literature. Two different friction reduction models[4,5] were examined, and the effect of switching FDT on and off was tested. The results demonstrate that irrespective of FDT, the two friction models examined can reasonably well reproduce the rheology, even with the same model parameters. This finding supports the use of molecular theories assuming the validity of FDT since the violation of FDT does not significantly affect the prediction of on-linear rheology.

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