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Rheology of Entangled Polymer Melts: Recent Results from Molecular Dynamics Simulations

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Models for the rheology of entangled polymers, based on the "tube" model are now open to investigation by molecular dynamics simulations using the Kremer-Grest "pearl necklace" model of polymers. Here, we present extensive molecular dynamics simulations of the dynamics and stress in entangled melts of branched polymers and of "binary blends" of diluted long probe chains entangled with a matrix of shorter chains. Direct evidence of "hierarchical relaxation" is obtained in diffusion of asymmetric star polymers, wherein the rate of slow diffusion of the branch point is controlled by the much faster motion of the attached arm. In studies of binary blends, the ratio of their lengths is varied over a wide range to cover the crossover from the chain reptation regime to tube Rouse motion regime of the long probe chains. Reducing the matrix chain length results in a faster decay of the dynamic structure factor of the probe chains, in good agreement with recent Neutron Spin Echo experiments. The diffusion of the long chains, measured by the mean square displacements of the monomers and the centers of mass of the chains, demonstrates a systematic speed-up relative to the pure reptation behavior expected for monodisperse melts of sufficiently long polymers. On the other hand, the diffusion of the matrix chains is only weakly perturbed by the diluted long probe chains. The simulation results are qualitatively consistent with the theoretical predictions based on constraint release Rouse model, but a detailed comparison reveals the existence of a broad distribution of the disentanglement rates, which is partly confirmed by an analysis of the packing and diffusion of the matrix chains in the tube region of the probe chains. A coarse-grained simulation model based on the tube Rouse motion model with incorporation of the probability distribution of the tube segment jump rates is developed and shows results qualitatively consistent with the fine scale molecular dynamics simulations.

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