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Evolution of chain conformation and entanglements as related to the origin of stress overshoot during startup shear of entangled polymer melts ZHEN-GANG WANG, California Institute of Technology, YUYUAN LU, LIJIA AN, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, SHI-QING WANG, University of Akron — Using Brownian Dynamics simulation, we determine the chain orientation and stretching and their connection to stress overshoot in an entangled polymer melt undergoing startup shear at rates lower than the reciprocal of the Rouse time yet higher than the reciprocal reptation time. In this regime, the prevailing tube theory envisions little chain stretching and monotonic increase of the radius of gyration to a saturated value, and attributes the stress overshoot to excessive chain orientation. In contrast, our results reveal that there is significant chain stretching which persists well beyond the Rouse time and contributes substantially to the initial stress growth. In particular, stress overshoot is found to be primarily due to chain retraction after considerable stretching rather than chain over-orientation. The coil size shows non-monotonic dependence on the strain. Furthermore, up to many Rouse times, the relaxation of the initial entanglements is slower than that under the quiescent condition. These results point to fundamental deficiencies in the molecular picture of the tube model for startup shear.

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