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Uniaxial and Equibiaxial Elongations of Polymer Melts: Molecular Origin of the Differences under Start-up Deformation

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Experiment indicates that uniaxial elongation shows strain hardening whereas, for a certain range of shear rates, equibiaxial elongation shows strain softening. To understand the molecular origin of this behaviour, we simulate the dynamics of entangled polymer chains under deformation using the Primitive Chain Network model. For the molecular insights obtained from the model to be relevant for the understanding of experimental data, the model must at least be able to describe the data from start-up experiments for uniaxial and equibiaxial deformations at constant elongation rates. We find that the model can satisfactorily reproduce the experimental data for both uniaxial and equibiaxial deformation using only two parameters and both of them can be obtained by fitting the linear rheology data. Having established this, we calculate the time (or equivalently, the strain) dependence the segment orientation, chain stretch and the number of entanglements from the simulations. For the strain rates studied, the time dependence of the chain stretch and the number of entanglements for both uniaxial and the biaxial deformations are similar. However, the segment orientation at a certain strain was found to be significantly larger for uniaxial deformations. We then use the Mead-Larson-Doi (MLD) decoupling approximation to calculate the time-dependent stress from the three molecular quantities. Although the MLD approximation is quantitatively deficient, it is adequate to capture the trend in the variation of the start-up viscosity upon varying the deformation rate. Hence, using this approximation, we can confirm that the difference in the segment orientation under uniaxial and equibiaxial deformation is sufficient to explain the experimentally observed difference between the two deformations, i.e., strain hardening for uniaxial versus strain softening for equibiaxial elongations at intermediate strain rates.