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Role of the Energy Conversion Factor in Flow Birefringence and Polymer Crystal Network Formation

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Shearing a high-density polyethylene (HDPE) melt stretches chains in the high molecular weight tail of the molecular weight distribution. Size exclusion chromatography data in that tail are fit to $\exp(-M/M_{max})$ to estimate the volume fraction of chains E that get stretched at a given shear rate, that exceeds the reciprocal of their Rouse time. Hence, a sheared polymer melt undergoes de Gennes' first-order coil-stretch transition; the longest chains are stretched and coexist with shorter chains that are only partially oriented. We find that E is proportional to the measured birefringence at each shear rate. While the applied specific work (W) seems to be the control variable for acceleration of nucleation kinetics at intermediate shear rates, that is not the case for low or high shear rates. Shear rates from 1 - 70 s^{-1} were applied to form a network of crystal precursors that stabilize the melt, resulting in W levels of up to 60 MPa by varying the shearing time. A flow-induced nucleation model is applied based on Flory's entropy reduction model and Hoffman and Lauritzen's isothermal heterogeneous nucleation model. We find that the acceleration in crystallization after shear plotted as a function of EW collapses all data to the same curve, making the volume fraction of chains E that get stretched the effective energy conversion factor. The critical crystal nucleus volume V* is quantified using the model and found to increase with temperature in the range of 122°C ≤ T_C ≤ 126°C. We find the quiescent V* = 7.5 – 10.4 nm^3, containing 23 – 37 Kuhn monomers of HDPE. The sheared V* is 2/3 of the quiescent V* at all temperatures and shearing conditions thus far explored.