Unraveling of Long Entangled and Unentangled Polymers in Fast Extensional Flow

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Using molecular dynamics, Brownian dynamics, and "kink dynamics" simulations, along with experimental data, we find that long polymer chains in fast extensional flow do not reach steady-state stress when polymer strands are fully stretched within tube segments, but only upon complete unraveling of the chain, in disagreement with the standard tube model. Strands are found to unravel through folded states, wherein highly stretched strands connected by kinks, or fold points, bear most of the stress. This process occurs universally at high stresses in polymer solutions, melts, and glasses, and is responsible for the final stages of strain hardening seen in extensional flows in all these states, regardless of whether the polymer is entangled or not.