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Importance of chain tumbling and finite extension on the start-up and relaxation behavior of transient networks[1] MICHELLE SING, Massachusetts Inst of Tech-MIT, ZHEN-GANG WANG, California Institute of Technology, GARETH MCKINLEY, BRADLEY OLSEN, Massachusetts Inst of Tech-MIT — Associative polymer networks are ubiquitous in tissue and biomedical engineering. However, the particular molecular attributes that contribute to the macroscopic behavior like shear thinning, self-healing, and yield stress are less well known. Here we incorporate chemical kinetics in the the Smoluchowski Equation capable of modeling the full network chain end-to-end distance distribution while tracking the fraction of looped, bridged, and dangling chains in the gel. In steady shear, we see the development of non-monotonic flow instabilities when the rate of chain association and dissociation are slower than the rate of chain relaxation. These instabilities arise due to a combination of chain finite extensibility and tumbling. During start-up of steady shear, the combination of these two phenomena also results in stress overshoots followed by multiple damped oscillations toward steady-state. The timescale of chain relaxation after the cessation of shear is dominated by the chain kinetics of association and dissociation as a function of the fraction of dangling chains present at any time post-shear.

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Michelle Sing
Massachusetts Inst of Tech-MIT

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