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Nonlinear shear rheology of unentangled and entangled linear polymer melts

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In a recent work [1], we proposed a new approach based on the shear slit model [2] to describe the nonlinear shear rheology of unentangled linear polymer melts. Our model involves the concept of shear strands, which represent the confinement effect induced by nonlinear shear flow on polymer chains. Within this molecular picture, we see the overshoot observed in the stress growth coefficient as a transition from the linear envelope to the steady regime**,** triggered by the progressive confinement of chains. By assuming that the chain confinement initiates at the time corresponding to the boundary between affine and non-affine deformation of chain, quantitative agreement was obtained between the experimental data and the predicted curves.

We extend this approach, initially applicable to chains with very few entanglements, to describe the flow characteristics of entangled polymer melts. In this case, the disentanglement process is expected to influence the confinement of the chain. To understand this influence, we performed new nonlinear shear measurements on polymer melts of different molar masses, ranging from poorly entangled to well entangled state. The confinement of the chains is studied by examining successive step rates with different applied shear rates. Interesting properties are pointed out. In particular, it is found that the importance of the overshoot strongly varies, depending on the sample history. These experimental results are then used to discuss the corresponding entanglement state of the chains as well as their confinement level. Based on these results, we extend our model and determine the characteristic times which govern the transient regime in presence of entanglements.

References:

[1] M. Dalne, et al., under review, Macromolecules ***2025***

[2] D. Parisi, et al., Macromolecules, ***2021*** *54 (6)*