Predicting the viscoelastic response of entangled polymer melts and concentrated polymer solutions

It has been about a decade ago that undershoots in the transient viscosity of polymer solutions, when startup shear flow is applied, were observed for the first time and more recent rheological measurements further illustrate that such a dumping behavior is absent in the transient normal stress coefficients (Ref. 1). Furthermore, the steady-state extensional viscosity of dense polymeric liquids in fast elongational flows is known to be peculiar in the sense that for entangled polymer melts it monotonically decreases – whereas for concentrated polymer solutions it increases – with increasing strain rate beyond the inverse Rouse time.

We have solved the Curtiss-Bird model (that we coin the tumbling-snake model), a bead-link chain kinetic theory for entangled polymer melts and concentrated solution, via the use Brownian Dynamics simulations (Ref. 2) and demonstrated that it has the necessary capacity to qualitatively predict the appearance of undershoots in the transient viscosity at large shear rates under startup shear and its absence in the normal stress coefficients of concentrated polymeric solutions (Fig. 1), when supplemented by a non-constant link-tension coefficient that we relate to the nematic order parameter (Refs. 1,3). The observed phenomena are attributed to the tumbling behaviour of the links, triggered by rotational fluctuations, on top of reptation. Naturally such a dumping behaviour should be absent in elongation flows, without any further adjustments (Refs. 4-5). In addition, by having the friction tensor increasingly becoming isotropic at large strain rates as the polymer concentration decreases, the model (Ref. 4) is seen to capture the experimentally observed behaviour noted in the steady-state extensional viscosity (Fig. 2). Overall, our work demonstrates the capacity of the tumbling-snake model to improve our microscopic understanding of the rheology of entangled polymer melts and concentrated polymer solutions (Refs. 1-4).

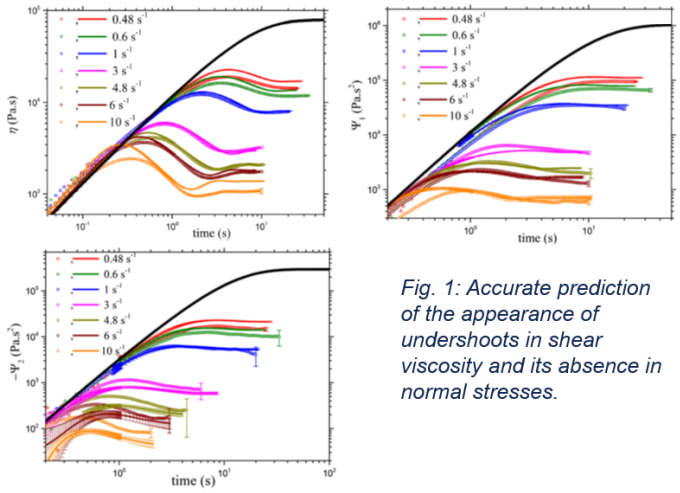

Fig. 1: Accurate prediction of the appearance of undershoots in shear viscosity and its absence in normal stresses.

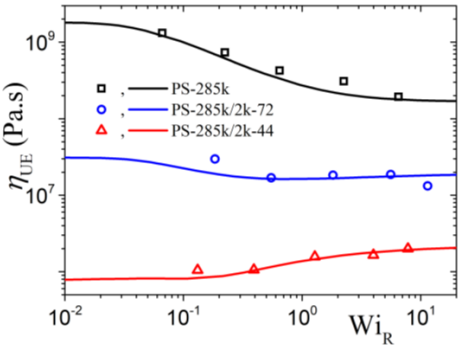

Fig. 2: We manage to accurately predict the increase of the steady-state extensional viscosity for concentrated polymer solutions it increases with increasing strain rate beyond the inverse Rouse time

References

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