8TH PACIFIC RIM CONFERENCE ON RHEOLOGY, May 15-19, 2023

VISCOELASTIC PROPERTIES OF BIDISPERSE LINEAR POLYMERS UNDER ELONGATIONAL FLOW

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ABSTRACT

The Doi−Edwards tube model, coupled with relaxation mechanisms, such as reptation, contour length fluctuation, and constraint release, allows us to quantitatively predict the linear viscoelastic properties of entangled polymers. However, for nonlinear elongational flows, large discrepancies between theoretical predictions based on the tube model and experimental results still persist. This is, for example, the case for the experimentally observed strong qualitative differences in extensional flow of entangled polystyrene (PS) melts and solutions, characterized by the same number of entanglements and exhibiting the same linear viscoelastic behaviour.[1] The cause of this non-universality is usually attributed either to a monomeric friction reduction or to an interchain pressure effect.

In this work, we investigate the extensional flow behaviour of binary blends of linear polymers, in order to further understand the role of the molecular environment on the stretch state of a probe chain. For this purpose, we measured the nonlinear extensional responses of different polystyrene (PS) chains, both in the monodisperse and bidisperse state, and systematically vary the concentration and the molar mass of the chains, to obtain different interactions between the long chains and their molecular environment. This allows us to highlight scaling relationships for describing the steady-state elongational viscosity.[2,3,4]

Our data confirm that the linear evolution of the steady-state extensional viscosity with the molar mass, that was first observed by Bach et al.[5] for melts, can be extended to polymeric solutions. The results also show that the steady-state extensional viscosity of bidisperse systems follow a simple mixing rule only if both components are stretching.[3]

While in a previous work, we found that all polystyrene long chains diluted in a short, non-stretching short chain matrix (with molar mass higher than 9 kg/mol) exhibit different transient strain hardening properties but the same apparent steady-state elongational viscosity; i.e., the long chains reach the same final stretch state,[5] we explore here the behaviour of these long

chains diluted in even shorter matrices, as it is expected that too short chains enhance the strain hardening of the long component.[6] By varying the composition of our solutions, we further quantify this effect.

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