

EFFECTS OF ARCHITECTURAL DISPERSITY ON THE LINEAR AND NONLINEAR RHEOLOGY OF EXACT COMBS

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The effects of the inherent architectural dispersity of exact polybutadiene combs, prepared using high-vacuum anionic synthesis [1], on their linear and nonlinear rheological behavior have been investigated experimentally. The combs under investigation are termed “exact” because the number and position of the branches on the backbone are, in principle, exactly known. Due to unavoidable imperfections in the synthesis, there are, apart from the main target combs, small fractions of other species present in the final melt. The effects of these “impurities” on the dynamics can in some cases be profound, as clearly exemplified by ring polymers [2]. In the literature, this type of imperfection of the melt and its possible effect on the dynamics is generally disregarded, meaning that one directly characterizes the melt as obtained from the chemists (e.g. [3,4]). In this work, we show that also for exact combs the effects of architectural dispersity can be significant.

The effects of architectural dispersity are investigated for both the linear viscoelastic properties and the nonlinear shear properties, namely stress relaxation and step rates. First the freshly synthesized melts are measured. Then the samples are fractionated using temperature gradient interaction chromatography (TGIC). And finally, the purified samples are measured and as such the effects of architectural dispersity on the linear and nonlinear flow dynamics of the exact combs is assessed. A strain-controlled rheometer (ARES-2KFRTN1, Rheometric Scientific) is used for all rheological measurements. Obtaining quantitatively meaningful results for nonlinear shear properties of polymer melts is difficult, mainly due to edge fracture. To enable us to obtain results in the nonlinear regime we adopted a design from literature, the so-called cone partitioned-plate [5,6]. We developed this geometry for the ARES rheometer in-house and tested it extensively. Nonlinear shear data on freshly synthesized and purified samples are obtained with this special geometry.

Concerning the linear viscoelastic properties, the typical hierarchical relaxation typical for combs (e.g. [4]) is observed for all samples. The fractionation improved the match between the experimental mastercurves obtained with standard time-temperature superposition and tube-based modelling (after [7]). Analysis of the chromatograms helped identifying possible structures of side-products. We also obtained a set of reliable nonlinear rheological data that provide guidelines for testing existing theories and rationalizing the response of these types of systems to fast deformations. This work suggests the importance of fractionation in understanding the physics of model branched polymers.

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