ANALYSIS OF MEDIUM AMPLITUDE OSCILLATORY SHEAR (MAOS)

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Studying the mechanical response of nearly monodisperse linear and comb polystyrene (PS) melts to medium amplitude oscillatory shear (MAOS), Hyun and Wilhelm (2009) identified two important scaling relations: (1) The relative intensity $I_{3/1}$ of the 3rd harmonic compared to the 1st harmonic scales with the strain amplitude according to γ_0^2. Consequently, a new nonlinear coefficient $Q \equiv I_{3/1}/\gamma_0^2$ as well as the so-called intrinsic nonlinearity $Q_0 \equiv \lim_{\gamma_0 \to 0} Q$ were introduced. (2) In the terminal relaxation regime, the intrinsic nonlinearity $Q_0(\omega)$ scales with ω^2, and was found to be a very sensitive measure regarding molecular topology by identifying and separating relaxation processes in model branched polymers. A constitutive analysis based on a general single integral constitutive equation, which includes the Doi-Edwards model without (DE) and with independent alignment assumption (DE IA) as well as the molecular stress function (MSF) model, confirms both scaling relations. We show that the nonlinear viscoelastic moduli can be expressed as sums of their linear-viscolelastic counterparts at frequencies of ω, 2ω, and 3ω. The absolute value of $Q_0(\omega)$ depends on the difference $(\alpha - \beta)$ between the 3rd order orientational effect (parameter α) according to the DE or DE IA model and the 2nd order isotropic stretching effect (parameter β) according to the MSF model. When comparing MAOS data to constitutive models, the apparent values of $Q_0(\omega)$ measured in parallel-plate geometry have to be rescaled in order to take the non-uniform shear deformation into account. Both the DE and DE IA model fail to describe the experimental data. The data of four linear PS melts are quantitatively described by the MSF model with nonlinear parameters $\alpha = 5/21$ (corresponding to the DE IA model) and $\beta = 0.12$ in the terminal relaxation regime. For the comb polymers, with the same orientational parameter of $\alpha = 5/21$, a stretch parameter of $\beta = 0.14$ for a polymer with unentangled branches, and of $\beta = 0.18$ for two polymers with entangled branches are found. However, the model predicts a plateau at the level of the maximum of the experimental data, while the experimental values of Q_0 decrease with increasing frequency. For the comb polymers with entangled branches, a minimum in Q_0 is observed, and a second increase of Q_0 at higher frequencies, which correspond to the terminal relaxation times of the branches. Surprisingly, these features can be modelled quantitatively if only the terminal relaxation modes of the backbone, and, if present, the branches are assumed to deforming non-affinely and responding to the nonlinearity. The shorter modes seem to be deforming affinely and are excited only in the regime of finite linear viscoelasticity. We are presently not aware of any molecular mechanism that could explain this behaviour.