

Effect of Molecular Weight, Polydispersity and Monomer of Linear Homopolymer Melts on the Intrinsic Mechanical Nonlinearity ${}^3Q_0(\omega)$ in MAOS

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ABSTRACT

A large variety of linear mono- and polydisperse homopolymer melts have been investigated with Fourier transformation rheology (FT rheology) to quantify their nonlinear mechanical behaviour under medium amplitude oscillatory shear (MAOS). Master curves of the zero-strain nonlinearity ${}^3Q_0(\omega)$ have been created, and are examined for their dependence on molecular weight, molecular weight distribution and monomer.

INTRODUCTION

The widespread interest in the linear and nonlinear mechanical behaviour of complex fluids established large amplitude oscillatory shear (LAOS) as a well-accepted test method. Oscillatory shear tests lead to a broad spectrum of mechanical responses of viscoelastic materials by varying excitation frequency ($\omega_1/2\pi$), strain amplitude (γ_0), and temperature independently. There are several methods to analyse the results of LAOS tests³, one of which is the use of Fourier transformation (FT). This offers the possibility to transform the raw stress time data from oscillatory shear into a frequency spectrum, where higher harmonics of the excitation frequency can be identified and quantified. The intensity of higher harmonics I_n changes as a function of strain amplitude γ_0 and excitation frequency $\omega_1/2\pi$, where a nonlinear mechanical behaviour results in an increase of the odd harmonics of the shear

stress at $3\omega_1/2\pi$, $5\omega_1/2\pi$, etc. The third harmonic intensity I_3 was chosen as a measure for nonlinearity in several publications, for example by Hyun et al.¹ who investigated the relative ratio $I_{3/1}(\gamma_0, \omega) \equiv I_3/I_1$ within a magnitude spectra of stress versus frequency with regard to branched structures and long chain branching. At medium strain amplitudes (medium amplitude oscillatory shear, MAOS) a scaling of $I_{3/1} \propto \gamma_0^2$ can be found in experiments. This region typically starts at $I_{3/1} \approx 10^{-4}$ - 10^{-3} for polymer melts.

THEORY

The time dependent shear stress $\sigma(t)$ can be derived from Newton's law in combination with a Taylor series of the shear rate dependent viscosity $\eta(\dot{\gamma})$:²

$$\begin{aligned} \sigma(t) = & \underbrace{\eta_0 i \omega_1 \gamma_0}_{I_1 \propto \omega_1 \gamma_0} e^{i\omega_1 t} + \underbrace{c_1 i^3 \omega_1^3 \gamma_0^3}_{I_3 \propto \omega_1^3 \gamma_0^3} e^{i3\omega_1 t} \\ & + \underbrace{c_2 i^5 \omega_1^5 \gamma_0^5}_{I_5 \propto \omega_1^5 \gamma_0^5} e^{i5\omega_1 t} + \dots \end{aligned} \quad (1)$$

Fourier transformation of the time-dependent stress should consequently consist of peak signals at the odd higher harmonics of the excitation frequency $\omega_1/2\pi$ in the frequency spectrum. To partly compensate experimental variations, I_3 is normalized to I_1 which results in an intensive property $I_{3/1}$. This enhances reproducibility in a way that

experimental errors, as for example inhomogeneity of the sample or improper loading and trimming, are mainly compensated, since they equally influence the different harmonic intensities. A quadratic scaling of $I_{3/1} \propto \gamma_0^2$ is expected from Eq. 1

The nonlinear parameter ${}^3Q(\omega, \gamma_0)$ and the intrinsic nonlinearity ${}^3Q_0(\omega)$ were defined by Hyun et al.¹ as follows:

$${}^3Q(\omega) \equiv \frac{I_{3/1}}{\gamma_0^2} \quad (2)$$

$$\lim_{\gamma_0 \rightarrow 0} {}^3Q(\omega, \gamma_0) \equiv {}^3Q_0(\omega) \quad (3)$$

The intrinsic nonlinearity ${}^3Q_0(\omega)$ is expected to be a function of molecular weight and the measurement temperature. With the use of the time-temperature superposition (TTS) principle, intrinsic nonlinear master curves can be generated in analogy to linear

master curves, using the same WLF parameters^{1,4}. The TTS principle is expected to be applicable for the intrinsic nonlinearity, since it is a back-extrapolation of 3Q to the linear viscoelastic regime (Eq. 3). The general procedure to obtain nonlinear master curves is illustrated schematically in Fig. 1.

The intrinsic nonlinearity ${}^3Q_0(De)$ can be predicted by constitutive pom-pom and molecular stress function (MSF) models. Asymptotical simplifications of single mode versions of these models result in the following equations:

$${}^3Q_0(De) = \frac{1}{2\pi} \frac{(1-2.5Z^{-1})De^2}{1+10Z^{-1}De^3} \text{ for } Z > 2.5 \quad (4)$$

$${}^3Q_0(De) = \frac{3}{2} \left(\alpha - \frac{\beta}{10} \right) \frac{De^2}{1+6De^2} \quad (5)$$

Where Eq. 4 is the result from the single mode pom-pom model and Eq. 5 is the result from the single mode MSF model, with $\alpha =$

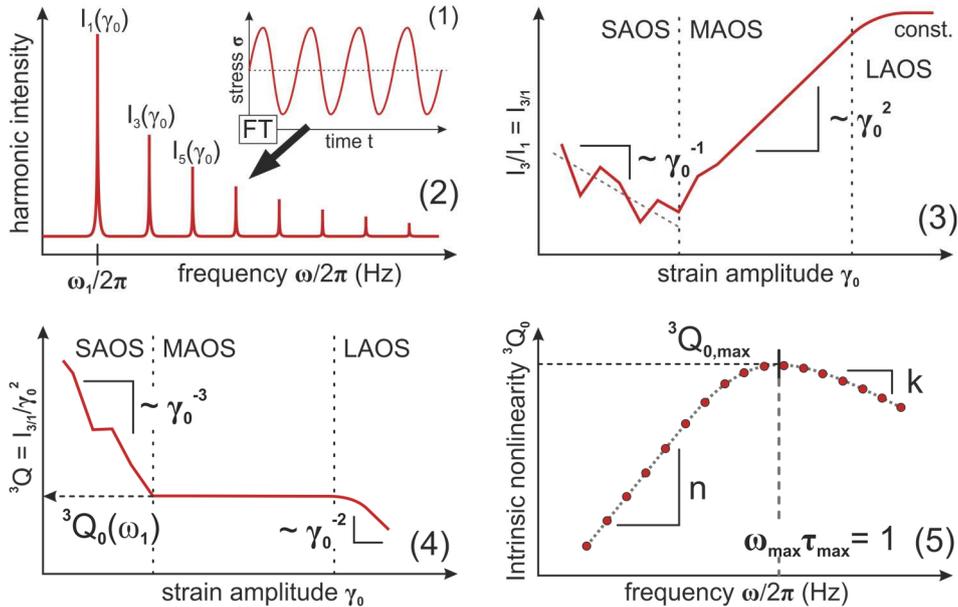


Figure 1. Scheme of a five-step procedure from raw data (1) to nonlinear master curve (5).

(1) Nonlinear stress time data of an oscillatory shear experiment. (2) After Fourier transformation of the time data, a magnitude frequency spectrum with odd higher harmonics can be obtained. (3) The ratio $I_{3/1}(\gamma_0, \omega_1)$ of the first and third harmonic is proportional to γ_0^2 in the MAOS region. (4) Extrapolation of ${}^3Q(\gamma_0, \omega_1)$ to small amplitudes gives the intrinsic nonlinearity ${}^3Q_0(\omega_1)$. (5) A nonlinear master curve can be created by plotting several ${}^3Q_0(\omega_1)$ values of different excitation frequencies, which are shifted to a reference temperature, utilizing the TTS principle.

5/21 and $\alpha = 1.0$ for linear polymer topologies.

A comparison between Eq. 4 and 5 shows that a general equation could predict the intrinsic nonlinearity as

$${}^3Q_0(De) = a \frac{De^2}{1+bDe^{2+k}} \quad (6)$$

Where a , b and k are the material characteristics that might depend on the monomer type, molecular weight and/or polydispersity.

RESULTS

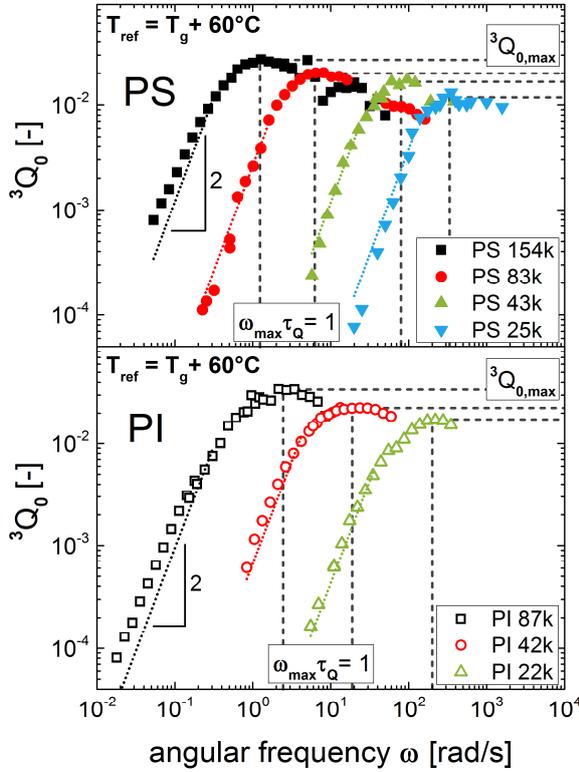


Figure 2. Nonlinear master curves of low PDI polystyrene (PS) and *cis*-1,4-polyisoprene (PI).

Nonlinear master curves of a broad variety of linear homopolymers with a low PDI < 1.1 were investigated with respect to molecular weight and monomer (Fig. 2). These nonlinear master curves showed a scaling of $\lim_{\omega \rightarrow 0} {}^3Q_0(\omega) \propto \omega^n$ with typically $n = 2 \pm 0.4$. A characteristic feature of all

nonlinear master curves is the appearance of a global maximum ${}^3Q_{0,\max} \propto Z^{0.35}$ (entanglement number $Z = M_w/M_e$). The nonlinear relaxation time τ_Q is calculated via $\tau_Q \omega = 1$ at the maximum ${}^3Q_{0,\max}$ and is within experimental limits, similar to the longest relaxation time τ_0 , obtained from respective linear master curves. This similarity between nonlinear and linear relaxation times shows that they can be associated with similar molecular dynamics and processes. For further analysis with respect to the pom-pom and MSF constitutive models, as well as the proposed general Eq. 6, all nonlinear master curves are plotted against the Deborah number, $De = \omega \tau_0$ (Fig. 3).

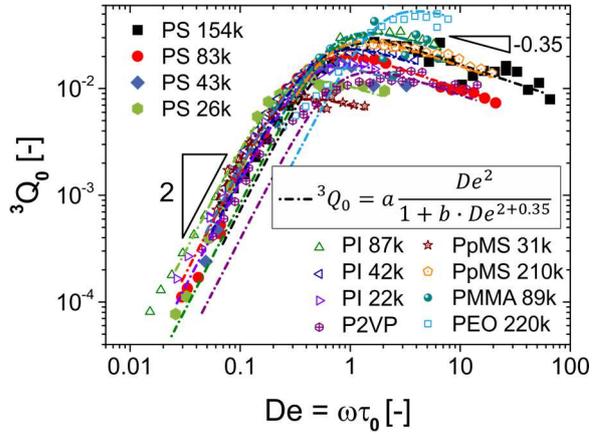


Figure 3. Nonlinear master curves of monodisperse (PDI ≤ 1.07) linear melts and related fits via Eq. 6.

The obtained picture can be compared with the predictions of the constitutive model theories and Eq. 6. Fitting Eq. 6 to the experimentally obtained nonlinear master curves yielded the parameters a and b , which were plotted against the number of entanglements Z (Fig. 4). A weak scaling law, related to the entanglement number Z for a and b , was found for all investigated polymers, $a = AZ^{0.5}$ and $b = BZ^{-1}$. In a next step, an iteration of Eq. 6 with the new scaling laws for a and b , was fitted on the experimental data with respective entanglement numbers for Z and resulted average values for A and B .

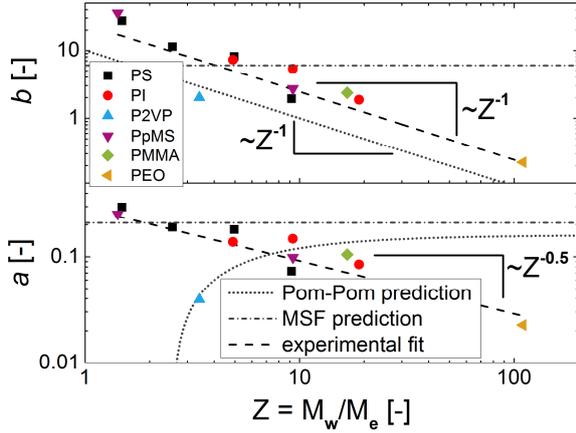


Figure 4. Parameters a and b from Eq. 6 for polymer samples with $\text{PDI} \leq 1.16$, along with predictions from the pom-pom constitutive model (pointed line) and MSF model (point-dashed lines) as a function of Z . Dashed lines indicate the power law behaviour of each parameter from the experiment.

$${}^3Q_0(De) = AZ^{-0.5} \frac{De^2}{1+BZ^{-1}De^{2+0.35}} \quad (7)$$

$${}^3Q_0(De) = 0.32Z^{-0.5} \frac{De^2}{1+33.8Z^{-1}De^{2+0.35}} \quad (8)$$

$${}^3Q_{0,max}(Z) \approx 0.01Z^{0.35} \quad (9)$$

Eq. 8 approximately describes all monodisperse, linear homopolymer melts, independent of chemical composition within the investigated samples. Figure 5 shows predictions from the pom-pom and MSF model with experimental data and the here presented semiempiric Eq. 8 in comparison. For low frequencies, all three methods depict the expected scaling of 2, but for high frequencies, only the semiempiric expression is able to describe the full behavior of the experimental data.

In conclusion, it was experimentally shown that a and b do not depend on the monomer for monodisperses, linear homopolymers, but rather only on the entanglement number Z . Therefore, Eq. 8 seems to be a unifying quantification of nonlinear shear under MAOS conditions for these kinds of polymer melts.

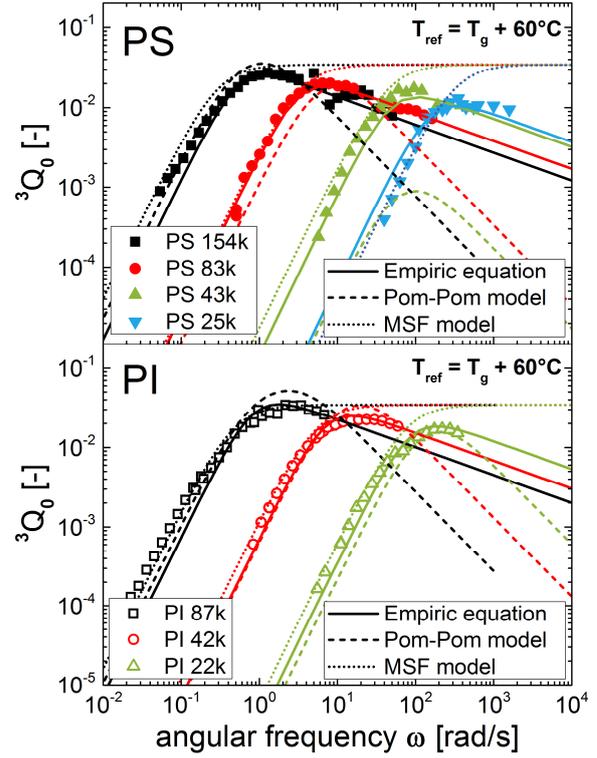


Figure 5. Predictions of the pom-pom and MSF model, measured data and the here presented semiempiric Eq. 8.

Several nonlinear master curves were obtained for polymer samples with varying polydispersities (Fig. 6).

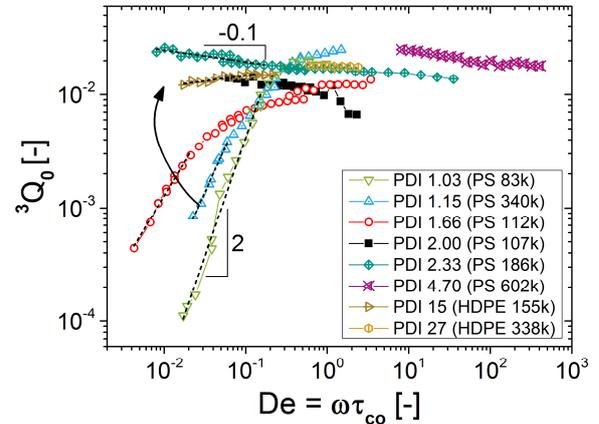


Figure 6. Nonlinear master curves of linear polymer melts with different PDI.

With increasing PDI, the slope of ${}^3Q_0(De)$ for low frequencies decreases. From the multi mode MSF prediction, a scaling of 2 is expected for very low frequencies, within the terminal regime of respective linear master

curves. In our experiments the slope levels off at a constant value, which equals ${}^3Q_{0,\max}$, within the measured frequency range and accessible intensity range of $I_{3/1}(\gamma_0)$ for samples with a PDI > 2. Our data show a dependence of the low frequency scaling ${}^3Q_0(De) \propto De^n$ on the PDI. The following empiric equation can describe this observation with a minimum set of parameters at $De = 0.02$, where the scaling of $n = 2$ for monodisperse samples (PDI=1) is still given (see also Fig. 7).

$$n = 2\text{PDI}^{-2.2} \quad (10)$$

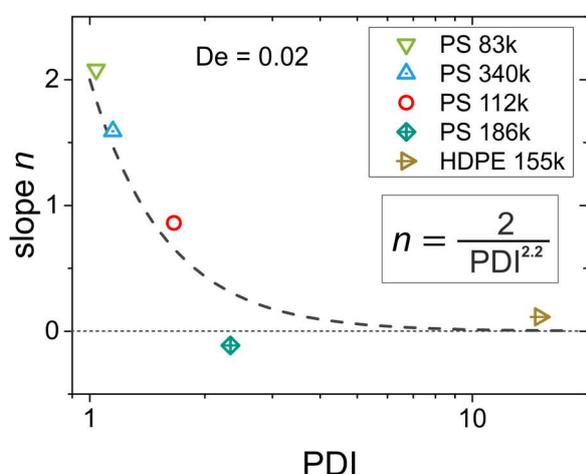


Figure 7. Scaling exponents n from ${}^3Q_0(De) \propto De^n$ for $De = 0.02$ as a function of the PDI.

CONCLUSION

The intrinsic nonlinearity ${}^3Q_0(\omega)$ was quantified with medium oscillatory shear (MAOS) measurements in combination with model calculations, i.e. predictions from the pom-pom and molecular stress function (MSF) constitutive models. Linear homopolymer melt model systems have been synthesized for this task with varying molecular weight, chemical composition, and polydispersity. For these samples, nonlinear master curves of ${}^3Q_0(\omega)$ have been created via the TTS principle, utilizing WLF parameters acquired from respective linear master curves. It was observed that all nonlinear master curves of low PDI samples

(PDI < 1.1) show a scaling of 2 for low frequencies (${}^3Q_0 \propto \omega^2$), until a maximum ${}^3Q_{0,\max}$ is reached. This result was also predicted by the pom-pom and MSF models. For high frequencies, it was experimentally found that ${}^3Q_0(\omega)$ scales with ${}^3Q_0 \propto \omega^{-0.35}$, which is in between the predicted values of the pom-pom ($\propto \omega^{-1}$) and MSF (constant plateau) models. A general equation, derived from simplified single mode pom-pom and MSF models was able to describe the experimentally obtained nonlinear master curves of linear homopolymer melts with a low PDI, independent of the investigated monomer. Polymer melts with a PDI > 1.1 revealed a scaling of ${}^3Q_0 \propto \omega^n$ at low frequencies, where $n = 2/\text{PDI}^{2.2}$ for a fixed Deborah number of 0.02. Model predictions from the multi mode MSF model for high PDI polymers expect a scaling of 2 at very low frequencies, again. This prediction, however, is currently not accessible experimentally due to potentially very high measurement temperatures in addition to an instrument sensitivity that is not available at the moment.

ACKNOWLEDGMENTS

The here presented results have also been published in Ref. 2.

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