

## A new non-linear Parameter for polymer melts, using FT-Rheology

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### ABSTRACT

The nonlinear coefficients  $Q(\gamma_0)$  and  $Q_0(\omega)$  obtained from the nonlinear response of monodisperse linear and comb polymer melts show a strong influence of the underlying molecular topology.  $Q(\gamma_0)$  and  $Q_0(\omega)$  can also be calculated using molecular stress function (MSF) and the pom-pom model for branched polymers.

### INTRODUCTION

Large Amplitude Oscillatory Shear (LAOS) is a test method for the characterization of complex fluids. Varying independently both strain amplitude ( $\gamma_0$ ) and frequency ( $\omega/2\pi$ ) allows to cover a broad spectrum of rheological responses with respect to time scales and involved non-linearity.<sup>1-3</sup> Moreover, it is experimentally relatively simple to generate LAOS flow, because oscillatory shear does not involve any sudden jump in either strain or strain rate. There are several methods to analyze the resulting torque data received from the LAOS test protocol: (1)  $G'$  and  $G''$  as a function of strain amplitude (2) Stress shape (stress vs. time) or Lissajous pattern (stress

vs. strain or stress vs. strain rate) (3) Fourier transform or decomposition into characteristic waveforms<sup>4</sup> (4) generalized “storage” and “loss” modulus when decomposing the nonlinear stress data (5) Chebyshev polynomials using decomposing stress data and further development of Chebyshev polynomials. An in depth overview with respect to LAOS tests and the related analysis can be found in a recent review article.<sup>3</sup>

The Fourier Transform (FT)-Rheology is perhaps the most sensitive method of those discussed above and a pre-request for further Chebyshev polynomials analysis. FT-Rheology converts the stress (torque) data of the time domain into frequency dependent spectra. FT-Rheology can quantify very weak signals of the generated higher harmonics. However, this method suffers from a rather complex interpretation due to multiple higher harmonics. Among the higher harmonics, the relative intensity of the third harmonic ( $I_{3/1} \equiv I(3\omega)/I(\omega)$ , where  $\omega/2\pi$  is the excitation frequency) is the most important towards quantifying the nonlinearity especially for polymer melts. So far there has been no systematic research

regarding the nonlinearity itself (especially,  $I_{3/1}$ ) with polymer melt systems as a function of topology. Therefore we investigated systematically the  $I_{3/1}$  value in a wide range of both strain amplitude ( $\gamma_0$ ) and frequency ( $\omega/2\pi$ ) for linear and comb polymers.<sup>5</sup> For this, we proposed a new nonlinear coefficient  $Q$  established from FT-Rheology under large amplitude oscillatory shear (LAOS). From the experimental observation of  $I_{3/1} \propto \gamma_0^2$  and related simulations, we defined  $Q(\omega, \gamma_0) \equiv I_{3/1} \propto \gamma_0^2$  as a new nonlinear coefficient, as well as the *zero-strain nonlinearity* or *intrinsic nonlinearity*  $\lim_{\gamma_0 \rightarrow 0} Q(\omega, \gamma_0)$ .  $Q_0$  is the asymptotic limiting and constant value of  $Q$  at small strain amplitude like the *zero-shear viscosity*. In this presentation, we introduce our recent experimental and simulation results of a new nonlinear coefficient  $Q$  for polymer melt systems.

## RESULTS AND DISCUSSION

### Definition of the nonlinear coefficients $Q$ and $Q_0$

The nonlinear shear stress response under LAOS flow can be expanded by a Fourier series with odd higher terms. From the ratio of two series, we can obtain the  $Q$  coefficient as follows:<sup>3,5</sup>

$$\begin{aligned} \frac{I_3}{I_1} &= \frac{\sqrt{(G'_{33}\gamma_0^3 + \dots)^2 + (G''_{33}\gamma_0^3 + \dots)^2}}{\sqrt{(G'_{11}\gamma_0 + \dots)^2 + (G''_{11}\gamma_0 + \dots)^2}} \\ &= \frac{\sqrt{G'_{33}{}^2\gamma_0^6 + G''_{33}{}^2\gamma_0^6 + O(\gamma_0^8)} \dots}{\sqrt{G'_{11}{}^2\gamma_0^2 + G''_{11}{}^2\gamma_0^2 + O(\gamma_0^4)} \dots} \quad (1) \\ &= \frac{\sqrt{G'_{33}{}^2 + G''_{33}{}^2 + O(\gamma_0^2)} \dots}{\sqrt{G'_{11}{}^2 + G''_{11}{}^2 + O(\gamma_0^2)} \dots} \times \frac{\gamma_0^3}{\gamma_0} \\ &= Q(\omega, \gamma_0) \cdot \gamma_0^2 \end{aligned}$$

In the asymptotic limit of the small-strain amplitudes (medium amplitude oscillatory shear, MAOS), we thus can obtain the *zero-strain nonlinearity* or *intrinsic nonlinearity*,  $Q_0(\omega)$

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$$\begin{aligned} Q_0(\omega) &= \lim_{\gamma_0 \rightarrow 0} Q(\omega, \gamma_0) \\ &= \lim_{\gamma_0 \rightarrow 0} \frac{\sqrt{G'_{33}{}^2 + G''_{33}{}^2 + O(\gamma_0^2)} \dots}{\sqrt{G'_{11}{}^2 + G''_{11}{}^2 + O(\gamma_0^2)} \dots} \quad (2) \\ &= \frac{\sqrt{G'_{33}{}^2(\omega) + G''_{33}{}^2(\omega)}}{\sqrt{G'_{11}{}^2(\omega) + G''_{11}{}^2(\omega)}} = \frac{|G_{33}^*(\omega)|}{|G_{11}^*(\omega)|} \end{aligned}$$

For the specific case of Doi-Edwards model for entangled polymer systems, we can find:

$$\lim_{\omega \rightarrow 0} Q_0(\omega) \rightarrow \frac{1}{3} (\tau_d \omega)^2 \propto \omega^2 \quad (3)$$

Therefore, a quadratic scaling in the low frequency limit can be assumed for the nonlinear coefficient  $Q_0(\omega)$ .<sup>6</sup>

### $Q_0(\omega)$ and $Q(\omega, \gamma_0)$ of linear and comb PS melt

In Fig. 1, the values of  $Q_0$  for the linear and comb PS samples are plotted at a reference temperature of  $T_{\text{ref}} = 190$  °C. The data for the monodisperse linear PS as a function of frequency displays a single local peak value and terminal quadratic behavior ( $Q_0 \propto \omega^2$ ) at low frequencies (Fig. 1b). For the linear PS,  $Q_0(\omega)$  has one peak value. In the case of the comb PS sample with unentangled branch chains (C622, see at top of Fig. 1),  $Q_0(\omega)$  displays a similar shape as a function of frequency (with one maximum value and a terminal regime ( $Q_0 \propto \omega^2$ )). For the comb PS with entangled side branches (C632 and C642, see at top of Fig. 1),  $Q_0(\omega)$  has two peak values, one corresponding to the branches' disentanglement at higher frequencies and the second arising from backbone relaxation at lower frequencies (Fig. 1a). As a consequence of having en-

tangled branches, the maximum value of  $Q_0$  can be associated with the backbone relaxation ( $Q_{0,b}$ ) and is much lower than that of the comb PS with unentangled branches (C622). As the entangled branch chain length becomes longer, the value of  $Q_{0,b}$  drops progressively and the frequency dependence becomes narrower and sharper (see Fig. 1b).

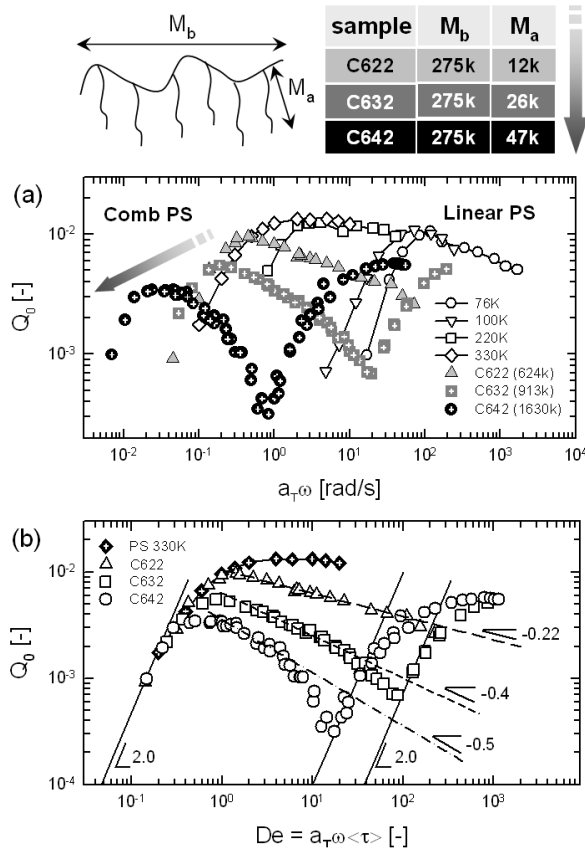


Figure 1. (a)  $Q_0$  for linear PS (76k, 100k, 220k, 330k) and PS combs (C622, C632 and C642) at  $T_{ref} = 190$  °C. (b)  $Q_0$  is plotted against Deborah number ( $De = a_r \omega \langle \tau \rangle$ ) of linear PS 330K and PS combs (C622, C632 and C642) at  $T_{ref} = 190$  °C.<sup>3</sup>

In the case of the comb PS series (C622, C632 and C642), the volume fraction of the backbone chain decreases as the side branch length increases. From the viewpoint of dynamic tube dilution, the fully-relaxed side-branches act as an effective solvent for the unrelaxed backbone chain. The increasing length of the side branches has a similar

effect to decreasing the concentration of the main backbone chain in a viscous solvent. Quantitative measurement of  $Q_0(\omega)$  can thus effectively probe frequency dependence in the relaxation processes associated with disentanglement for a range of polymer melts.

Wagner et al.<sup>6</sup> calculated  $Q_0(\omega)$  from a constitutive analysis based on a general single integral constitutive equation, which includes the Doi-Edwards (DE) model without and with independent alignment assumption (DE IA) as well as the molecular stress function (MSF) model. The  $Q_0(\omega)$  calculated from MSF model strongly depends on the difference ( $\alpha - \beta$ ) between the orientational effect (parameter  $\alpha$ ) according to the DE and DE IA model and the stretching effect (parameter  $\beta$ ) of the strain measure as obtained by the MSF model. Both DE and DE IA models describe the experimental data qualitative but not quantitative.

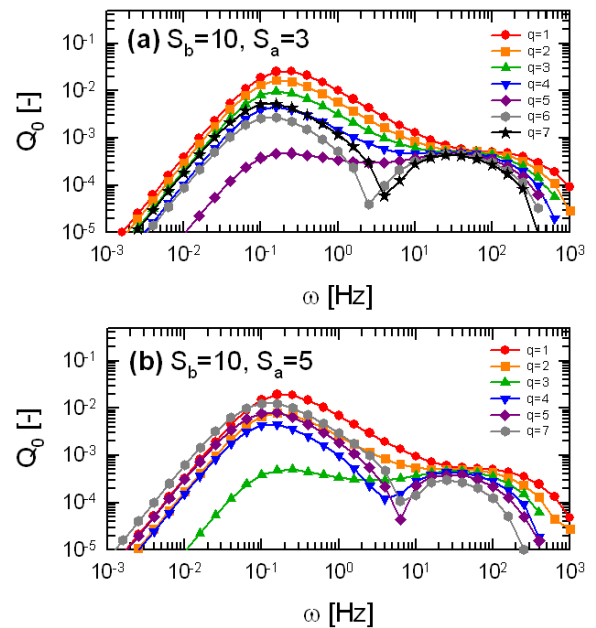


Figure 2.  $Q_0(\omega)$  from LAOS simulations over a wide frequency range ( $10^{-3} \sim 10^3$  Hz) for a single mode Pom-Pom model at various arm numbers ( $q$ ) with (a)  $S_b=5, S_a=1$  and (b)  $S_b=10, S_a=5$ .<sup>8</sup>

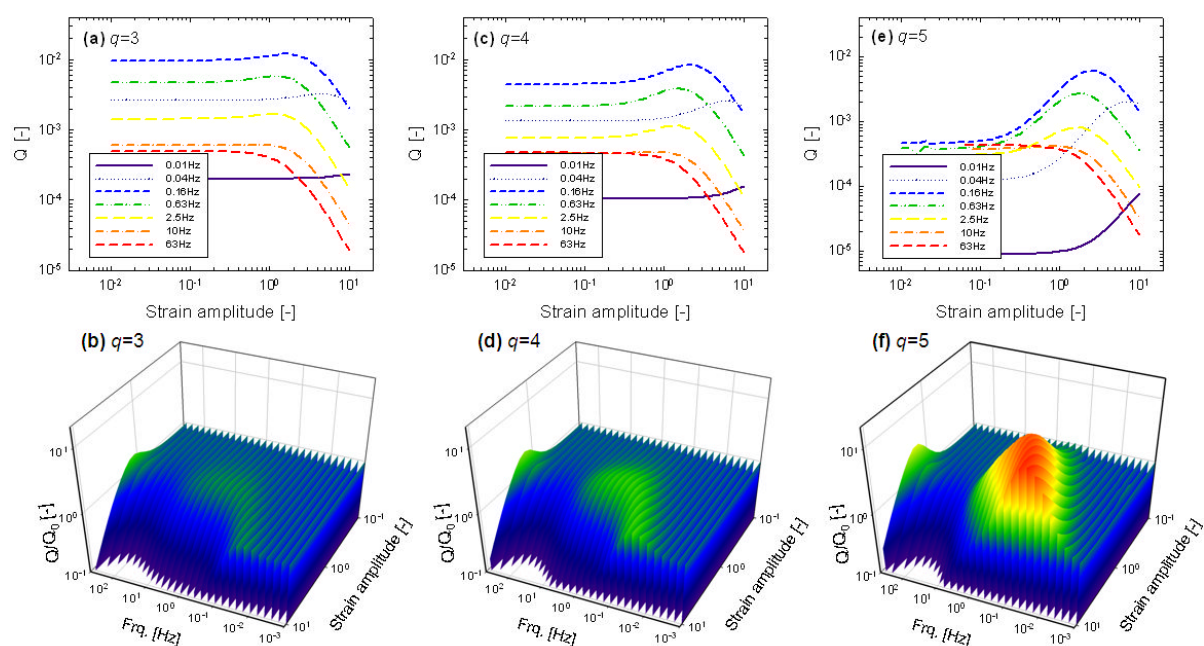


Figure 3. (a)  $Q$  and (b) normalized  $Q/Q_0$  as a function of strain amplitude at various frequencies for single mode Pom-pom model with  $S_b=10$ ,  $S_a=3$ ,  $q=3$ . (c)  $Q$  and (d) normalized  $Q/Q_0$  as a function of strain amplitude at various frequencies for single mode Pom-pom model with  $S_b=10$ ,  $S_b=3$ ,  $q=4$ . (e)  $Q$  and (f) normalized  $Q/Q_0$  as a function of strain amplitude at various frequencies for single mode Pom-pom model with  $S_b=10$ ,  $S_b=3$ ,  $q=5$ .<sup>8</sup>

The linear PS melts are described by MSF model with  $\alpha=5/21$  and  $\beta=0.14$ , and  $\alpha=5/21$  and  $\beta=0.14$  for the comb PS with untangled branches and  $\alpha=5/21$  and  $\beta=0.18$  for the comb PS with entangled branches are found.

It is concluded that chain stretch is an essential ingredient in constitutive modeling of the polymer melts. The behavior of the coefficient  $Q$  with increasing strain amplitude is also investigated at a fixed frequency. For monodisperse linear PS melts,  $Q$  decreases as the strain amplitude increases at various frequencies [ $Q(\gamma_0)$  decreasing]. By contrast, the value of  $Q(\gamma_0)$  for the comb PS sample with entangled side branches (C642) increases as the strain amplitude increases [ $Q(\gamma_0)$  increasing]. A strong influence of the molecular topology on these nonlinear parameters ( $Q$  and  $Q_0$ ) was found from experi-

ments and constitutive equations. The coefficient  $Q_0(\omega)$  opens up the possibility for quantitative comparisons between experiments and simulations under nonlinear oscillatory shear. It is worth mentioning that the simulations are substantially faster than the complex synthesis of low but long branched monodisperse homopolymers<sup>7</sup> therefore allowing to optimize the planned chemical structures prior to synthesis.

#### $Q_0(\omega)$ and $Q(\omega, \gamma_0)$ from Pom-Pom model

Additionally  $Q(\gamma_0)$  and  $Q_0(\omega)$  was calculated using the pom-pom model for branched polymers.<sup>8</sup> One of the main ideas of the pom-pom model is the separation of the two relaxation processes of stretch (fast) and orientation (slow) for the two branch points of the H-polymer.<sup>9</sup> Physically, the

separation is the consequence of entanglement dynamics. It is found that  $Q_0(\omega)$  can detect two different time scales at various topological conditions (the length of the backbone  $S_b$ , the length of the arm  $S_a$ , and the number of arms  $q$ ) (see Fig. 2).

Simulating the  $Q(\gamma_0)$  dependency both strain softening [ $Q(\gamma_0)$  decreasing] and strain overshoot [ $Q(\gamma_0)$  increasing] with increasing strain amplitude are found (see Fig. 3).

At the frequency corresponding to the backbone orientation relaxation,  $Q(\gamma_0)$  shows a strain overshoot and  $Q_0(\gamma_0)$  shows strain softening behavior at frequencies corresponding to stretch relaxation. With increasing number of arms, the strain overshoot becomes stronger and stronger and the onset of increasing  $Q$  appears at relative small strain amplitude.<sup>8</sup> The new nonlinear parameter  $Q$  and  $Q_0$  from FT-Rheology is promising to investigate the topology of homopolymer melt systems. Furthermore, it can be useful to characterize other polymer melt systems, e.g. polymer composites, polymer blends, and so on.

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#### REFERENCES

1. Dealy, J.M. and Wissbrun, K.F. (1990), "Melt rheology and its role in plastics processing: Theory and applications", Springer, New York.
2. Yosick, J.A., Giacomini, A.J. and Moldenaers, P. (1997), "A kinetic network model for nonlinear flow behavior of molten plastics in both shear and extension", *J. Non-Newtonian Fluid Mech.*, **70**, 103.
3. Hyun, K., Wilhelm, M., Klein, C.O., Cho, K.S., Nam, J.G., Ahn, K.H., Lee, S.J., Ewoldt, R.H. and McKinley, G.H. (2011), "A Review of Nonlinear Oscillatory Shear Tests: Analysis and Application of Large Amplitude Oscillatory Shear (LAOS)", *Prog. Polym. Sci.* (in press), DOI:10.1016/j.progpolymsci.2011.02.002.
4. Wilhelm, M. (2002), "Fourier-Transform Rheology", *Macromol. Mater. Eng.*, **287**, 83.
5. Hyun, K. and Wilhelm M. (2009), "Establishing a New Nonlinear Coefficient  $Q$  from FT-Rheology, first investigations on entangled linear and branched Polymer melts", *Macromolecules*, **42**, 411.
6. Wagner, M.H., Rolón-Garrido, V.H., Hyun, K. and Wilhelm, M. (2011), "Analysis of medium amplitude oscillatory shear data of entangled linear and model comb polymers", *J. Rheol.*, **55**, 495.
7. Kempf, M., Barroso, V.C., and Wilhelm, M. (2010), "Anionic Synthesis and Rheological Characterization of Poly(p-methylstyrene) Model Comb Architectures with a Defined and Very Low Degree of Long Chain Branching (LCB)", *Macromol. Rapid Commun.*, **31**, 2140.
8. Hyun, K. and Wilhelm, M. (2011), "Numerical Simulation results of the New Nonlinear Coefficient  $Q$  from FT-Rheology using a single mode Pom-Pom model", *J. Rheol.* (to be submitted).
9. Hoyle, D.M., Harlen, O.G., Auhl, D. and McLeish, T.C.B. (2009), "Non-linear step strain of branched polymer melts", *J. Rheol.*, **53**, 917.