# The Rheology of Linear and Long-chain Branched Polymer Melts

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**Summary:** By generalising the Doi-Edwards tube model to the Molecular Stress Function theory, the non-linear rheology of polymer melts can be described quantitatively. The strain-hardening of linear polymer melts in extensional flows can be accounted for by a strain energy function, which reflects the increase of strain energy due to tube squeeze. In comparison to linear polymer melts, long-chain branched polymer melts show enhanced strain-hardening. This is due to the fact that while the backbone of the branched macromolecule is stretched by deformation, side chains are compressed. It is demonstrated that the experimentally observed slope of the elongational viscosity after inception of strain-hardening depends on the ratio $\beta$ of total molar mass to backbone molar mass as predicted by the model. The steady-state (plateau) value of the elongational viscosity depends on the maximum relative stretch, $f^2_{MAX}$, which can be supported by chain segments and which represents the maximum elastic energy storable in the polymeric system.

**Keywords:** Doi-Edwards tube model; extensional viscosity; Molecular Stress Function (MSF) model; strain energy; strain-dependent tube diameter

## Introduction

Constitutive equations describing the non-linear rheological behavior of polymer melts have been a subject of focus due to their important role in providing a logical picture of the molecular structure of the polymer as well as their importance in designing and optimizing polymer processing. Most of the current theoretical work in rheology is devoted to the development of precise constitutive equations with parameters that are in some way or other obtainable through the microstructural properties of polymer melts, and it is the purpose of this paper to present a survey of the development of a highly successful class of microstructural integro-differential constitutive equations based on the now classical tube model of Doi and Edwards [1].

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### The Tube Model

To reduce the intricacies of a many body system, intermolecular interaction of concentrated systems of linear polymer chains is modeled by the tube concept: The mesh of constraints caused by surrounding chains confines the macromolecular test chain laterally to a tubelike region. Doi and Edwards (DE) assumed that the diameter $a_0$ of the tube is not changed even by large non-linear deformations, or equivalently that the tension in the deformed macromolecular chain remains constant and equal to its equilibrium value [1]. The main contribution to the extra stress tensor $\boldsymbol{\sigma}(t)$ is then given by the orientation of the tube segments due to the flow. The resulting constitutive equation is of the single integral form,

$$\boldsymbol{\sigma}(t) = \int_{-\infty}^{t} \mathrm{m}(t-t')\mathbf{S}^{\mathrm{IA}}_{\mathrm{DE}}(t')dt' \qquad (1)$$

if the tube segments are assumed to align independently of each other in the flow field (the ''Independent Alignment (IA)''

approximation). The strain measure is given by

$$\boldsymbol{S}_{\mathrm{DE}}^{\mathrm{IA}} \equiv 5\left\langle \frac{\mathbf{u}'\mathbf{u}'}{u'^2} \right\rangle_{\mathrm{o}} = 5\boldsymbol{S} \tag{2}$$

where $\boldsymbol{S}$ is the second order orientation tensor. The bracket denotes an average over an isotropic distribution of unit vectors $\boldsymbol{u}$ and can be expressed as a surface integral over the unit sphere,

$$\langle\rangle_{\mathrm{o}} \equiv \frac{1}{4\pi} \oiint [\,] \sin\theta_{\mathrm{o}} d\theta_{\mathrm{o}} d\varphi_{\mathrm{o}} \tag{3}$$

$u'$ is the length of the deformed vector $\boldsymbol{u}'$, which is calculated from the affine deformation hypothesis (with $\boldsymbol{F}_t^{-1}$ as the deformation gradient tensor) as

$$\boldsymbol{u}' = \boldsymbol{F}_t^{-1} \cdot \boldsymbol{u} \tag{4}$$

In the DE model, stress results from chain orientation only, and there is no chain stretch. Consequently, the DE model doesnot account for any strain hardening in extensional flows (Fig. 1). It does, however, predict the separability of time and strain effects in the nonlinear stress relaxation modulus, which is observed even for polydisperse polymer melts over several decades of relaxation time.

#### Tube Model with Chain Stretch

For monodisperse polymer melts, the Doi-Edwards strain measures seemed to give an acceptable description of material behavior in step-shear experiments for times greater than the equilibration time. For fast deformations and for polydisperse linear and branched polymer melts, on the other hand, although time-deformation separability often works over most or even the entire (experimentally attainable) time range, the measured stresses in shear and extensional flows are often much higher than predicted by the Doi-Edwards strain measure [1–4], which is a signature of considerable chain stretch.

In the Molecular Stress Function (MSF) model of Wagner and coworkers [2,5–13], tube stretch is caused by the ''squeeze'' of the surrounding polymer chains, leading to a reduction of the tube diameter $a$ from its equilibrium value $a_0$. Taking into account that the tube diameter $a$ represents the mean field of the surrounding chains and its associated strain energy, it is assumed that the tube diameter is independent of the orientation of tube segments.

The stress is then given as

$$\boldsymbol{\sigma}(t) = -p\mathbf{I} + \int_{-\infty}^{t} \mathrm{m}(t-t') f^2 \mathbf{S}_{\mathrm{DE}}^{\mathrm{IA}}(t,t') dt' \tag{5}$$

where the molecular stress function $f$ is the inverse of the relative tube diameter,

$$f(t,t') = a_o / a(t,t') \tag{6}$$

It is important to note that tube stretch in Eq. (6) does not only depend on the observation time $t$, but also on the strain history, i.e. for time-dependent strain histories, tube stretch varies along the tube. The dependence on $t$ and $t'$ is dropped in the following.

Note that while $\boldsymbol{S}_{\mathrm{DE}}^{\mathrm{IA}}$ is related directly to the deformation history via Eq. (4), no a priori dynamics of the internal variable $f$ is prescribed in the MSF model. Rather, $f^2$ is assumed to be directly related to the strain energy stored in the polymeric system, and is determined as solution of an evolution equation derived from an energy balance argument [2].

Based on prior work of de Gennes [14], and Marrucci et. al. [15,16], the molecular stress function $f$ for linear melts is related to a strain-energy function $w_{MSF}$ of the form

$$\frac{w_{MSF}}{\mathbf{3}k_B T} = (f^2 - 1) \tag{7}$$

Neglecting dissipative constraint release, i.e. considering the hyper-elastic limit, the power input of the stress tensor into the polymer system is equal to the increase of the strain energy by tube deformation [2]. $f^2$ is found as solution of the evolution equation (with velocity gradient $\boldsymbol{\kappa}$ and plateau modulus $G_N^0$)

$$\frac{1}{3k_B T} \frac{dw_{MSF}}{dt} = \boldsymbol{\kappa} : \frac{\boldsymbol{\sigma}}{5G_N^o} = f^2(\boldsymbol{\kappa} : \mathbf{S}) \tag{8}$$

 

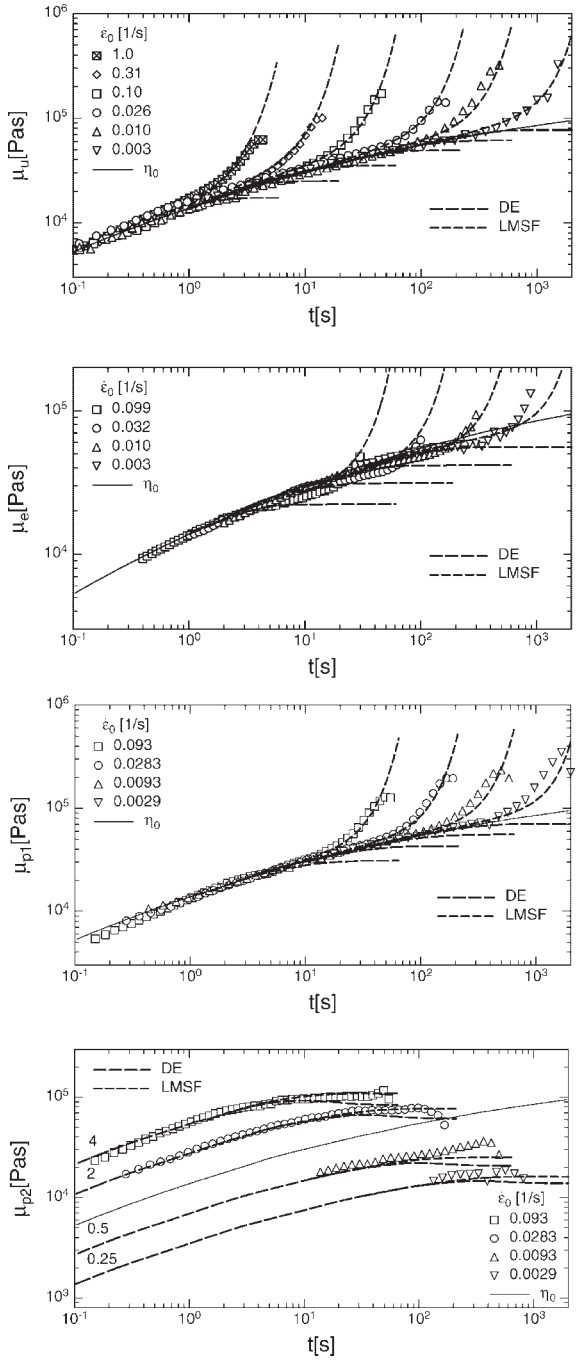


***Figure 1.***
Uniaxial ($\mu_u$), equibiaxial ($\mu_e$), and planar ($\mu_{p1}$, $\mu_{p2}$) viscosities of a HDPE at $T = 150\ ^\circ C$. Viscosities are normalized with respect to the zero-shear viscosity. Comparison of experimental data (symbols) to predictions of DE and LMSF (zero parameter) models.

 

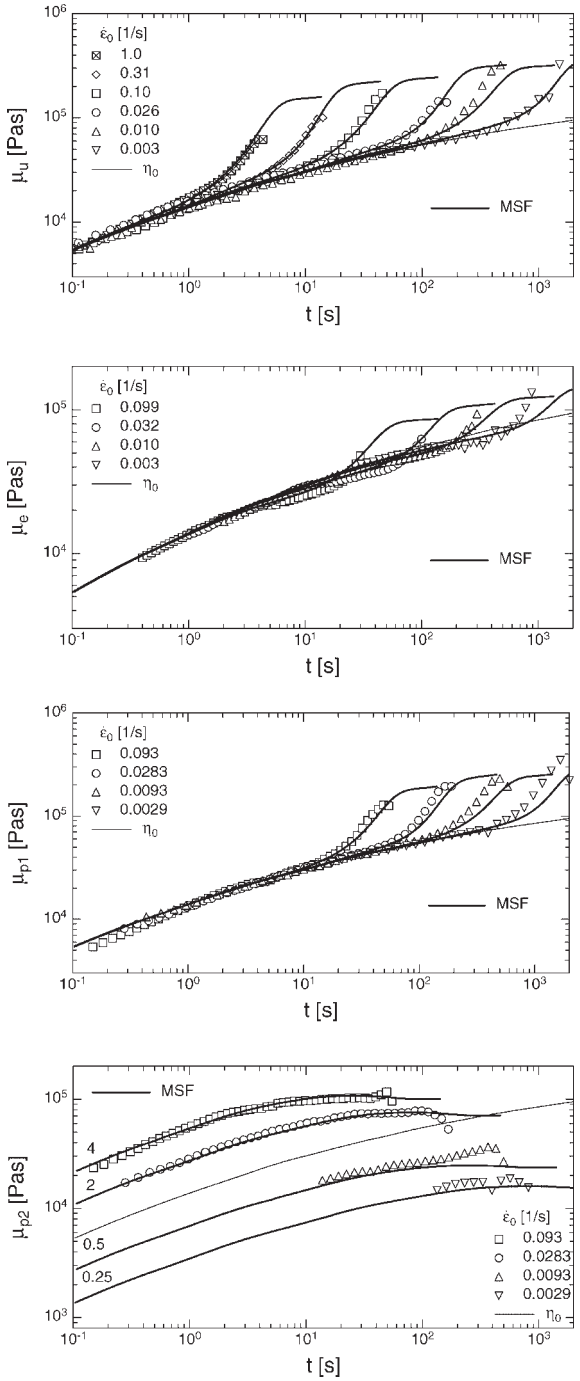


***Figure 2.***
Uniaxial ($\mu_u$), equibiaxial ($\mu_e$), and planar ($\mu_{p1}$, $\mu_{p2}$) viscosities of a HDPE melt. Viscosities are normalized with respect to the zero-shear viscosity. Comparison of experiment to predictions of the MSF model with dissipative constraint release. $f^2_{MAX} = 49$.

 

to be

$$f^2 = e^{\langle \ln u' \rangle_0} \tag{9}$$

i.e. $f^2$ is an exponential of the orientational free energy $3k_BT\langle \ln u' \rangle_0$. $\frac{d}{dt}$ indicates the material time derivative.

Predictions of the MSF model are in excellent agreement with the onset of strain-hardening in uniaxial, equibiaxial and planar extension of polydisperse linear polymer melts (the so-called LMSF model), as exemplified in Fig. 1 [2].

Now dissipative constraint release (CR) is introduced as a dissipative process [2], which modifies the energy balance of tube deformation, and leads to a strain-dependent evolution equation for the molecular stress function of the form

$$\frac{df^2}{dt} = f^2\left[(\boldsymbol{\kappa} : \mathbf{S}) - \frac{1}{f^2 - 1}CR\right] \tag{10}$$

Constraint release is considered to be the consequence of different convection mechanisms for tube orientation and tube-cross section, and for constant strain-rate flows can be expressed as

$$CR = a_1(f^2 - 1)^2\sqrt{\mathbf{D}^2 : \mathbf{S}} + a_2(f^2 - 1)^2\sqrt{|\mathbf{W} \cdot \mathbf{D} : \mathbf{S}|} \tag{11}$$

with **D** and **W** being the rate of deformation and rate of rotation tensor, respectively. The non-linear material parameters verify $a_1 \geq 0$ and $a_2 \geq 0$. Note that in extensional flows, constraint release depends only on the parameter $a_1$, while in simple shear flow, both the parameters $a_1$ and $a_2$ are of relevance. We restrict discussion here to extensional deformations. The evolution equation for the molecular stress function of linear melts in extensional flows is given by

$$\frac{df^2}{dt} = \dot{\varepsilon}f^2\Big[S_{11} + mS_{22} - (1+m)S_{33}. - a_1(f^2 - 1) \times \sqrt{S_{11} + m^2S_{22} + (1+m)^2S_{33}}\Big] \tag{12}$$

where the parameter m $(-1/2 \leq m \leq 1)$ describes the type of extensional flow, and $\dot{\varepsilon}$ is the largest extension rate. $S_{ii}$ are the components of the orientation tensor $\boldsymbol{S}$. At large strains, a maximum $f^2 = f^2_{MAX}$ is reached and $df^2/dt = 0$. Hence, the parameter $a_1$ can be expressed in terms of $f^2_{MAX}$ as

$$a_1 = \frac{1}{f^2_{MAX} - 1} \tag{13}$$

$f^2_{MAX}$ governs the steady-state value of the viscosity in extensional flows, and corresponds to the maximum of storable elastic energy. It is the only non-linear material parameter of the theory for describing polymer melt rheology of linear polymers in irrotational flows. The level of agreement between experiments in different extensional deformation modes and theory for a linear polyethylene melt is demonstrated in Fig. 2 [2].

### The MSF Model for Long-Chain Branched Melts

The most simple model of a tube section of a long-chain branched macromolecule containing $\beta$ entanglements consists of one chain segment representing one entanglement oriented in the direction of the tube (the ''backbone'' of the macromolecule), and one or more side chains representing $\beta - 1$ entanglements (Fig. 3). Note that a side chain can contain more than one chain segment, depending on the length of the side chain relative to the entanglement length. Thus, according to this model, chain segments fall into two distinct categories: either they belong to the backbone and are stretched by deformation, or they do not belong to the backbone and are compressed by deformation [10].

When the tube is stretched, one segment is extended, while $\beta - 1$ are compressed, leading to a total strain energy of

$$\frac{w_{MSF}}{3kT} = \frac{1}{\beta}(f^2 - 1) + \frac{(\beta - 1)}{\beta}\left(1 - \frac{1}{f^2}\right) \tag{14}$$

The parameter $\beta$ has values $\beta \geq 1$, with $\beta = 1$ for linear melts. For $\beta = 2$ (the so-called QMSF model), excellent agreement with experimental data of a long-chain

 

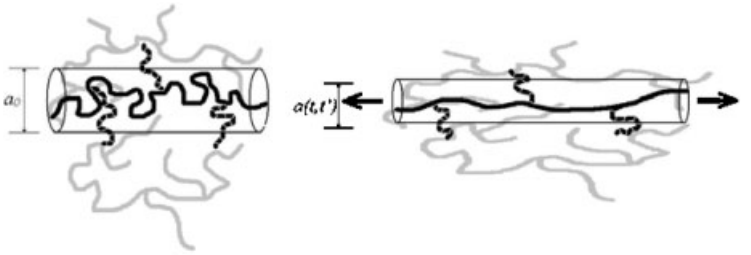


***Figure 3.***
Tube segment of a long-chain branched polymer molecule before and after deformation: one chain segment is stretched, while side chain segments are compressed.

branched (radiation-crosslinked) polypropylene melt is found (Fig. 4). Note that the increase in elongational viscosity is steeper for long-chain branched melts than for linear melts.

Introducing again constraint release as a non-linear dissipative process, which modifies the energy balance of tube deformation, leads to a strain-dependent evolution equation for the molecular stress function of the form

$$\frac{df^2}{dt} = \frac{\beta f^2}{1+\frac{\beta-1}{f^4}}\left[(\boldsymbol{\kappa}:\mathbf{S}) - \frac{1}{f^2-1}CR\right] \qquad (15)$$

Limiting discussion to extensional deformations, the evolution equation for the molecular stress function in constant strain-rate extensional flows is then given by

$$\frac{df^2}{dt} = \dot{\varepsilon}\frac{\beta f^2}{1+\frac{\beta-1}{f^4}}\left[S_{11}+mS_{22}-(1+m)S_{33} - \frac{f^2-1}{f^2_{MAX}-1}\sqrt{S_{11}+m^2S_{22}+(1+m)^2S_{33}}\right] \qquad (16)$$

The enhanced slope of elongational viscosity of long-chain branched polymer melts in comparison to linear melts is caused by the fact that a significant percentage of the chain segments of a long-chain branched molecule is compressed by elongational flow (the "side chains"), and only part

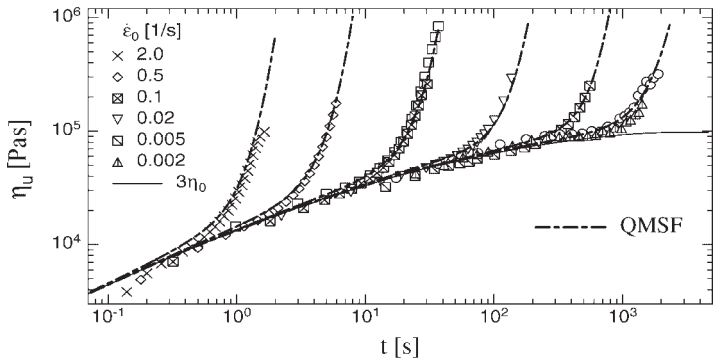


***Figure 4.***
Uniaxial viscosity $\eta_u$ of a long-chain branched PP melt. Comparison of experimental data (symbols) to predictions of the MSF model with $\beta = 2$ (QMSF model).

 

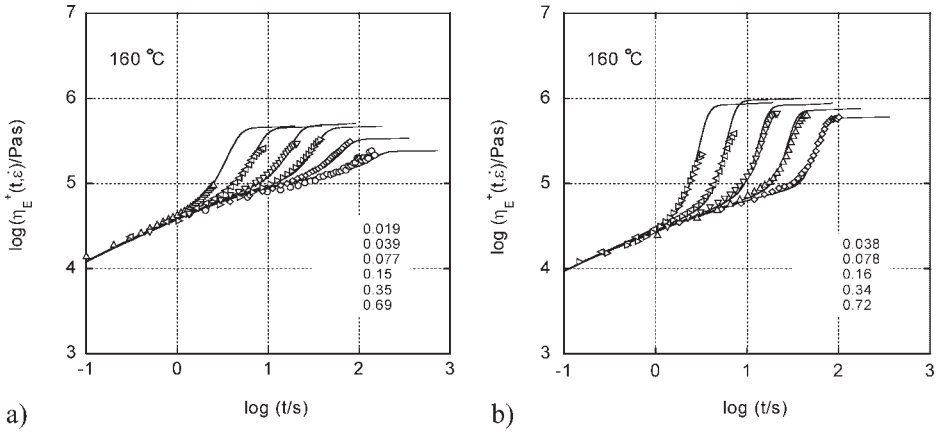


***Figure 5.***
Elongational viscosity data (symbols) of LDPE melts and predictions by MSF model. Parameters indicate elongation rates in units $s^{-1}$: a) LDPE produced by tubular process (Tubular-o): $\beta = 2$ and $f^2_{MAX} = 30$; b) LDPE produced by autoclave process (Autoclave-O): $\beta = 4$ and $f^2_{MAX} = 80$.

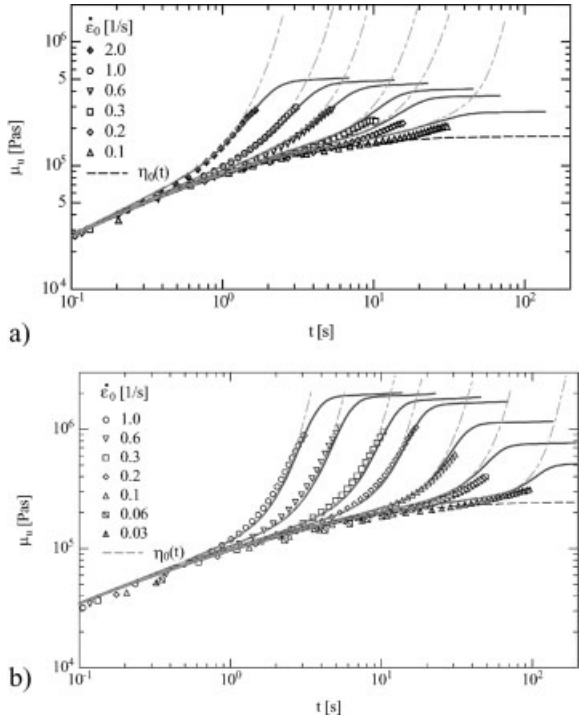


***Figure 6.***
Comparison of elongational viscosity data (symbols) of two branched PS melts to predictions (lines) of MSF theory. Viscosities are normalized with respect to the zero-shear viscosity. $\eta_0(t)$ indicates the start-up zero-shear viscosity. a) PS 80-0.6G-22: $\Phi_{n,br} = 0.14$, $\beta = 1.2$; dashed line: $f^2_{MAX} \to \infty$, solid line $f^2_{MAX} = 25$; b) PS 70-3.2G-22: $\Phi_{n,br} = 0.5$, $\beta = 2.0$; dashed line: $f^2_{MAX} \to \infty$, solid line $f^2_{MAX} = 80$.

 

of the chain segments is stretched (the "backbone"). In the multi-chain segmental MSF model described here, for one chain segment stretched, $\beta - 1$ chain segments are compressed. While for LDPE melts produced by the tubular polymerization processes typically values of $\beta = 2$ are found, more highly branched autoclave LDPE melts show values of $\beta = 3$ and even of $\beta = 4$ (Fig. 5) [10].

### Comparison of MSF Model Predictions to Elongational Rheology of Model Branched Polystyrene Melts

It is difficult if not impossible to derive the parameter $\beta$ from the topology of randomly branched LDPE; therefore $\beta$ was so far treated as a fit parameter (the only one in the hyper-elastic limit). However, from an analysis of the non-linear rheology of comb shaped model polystyrene melts, it was found that indeed, $\beta$ as derived from the topology of these model melts by assuming stretch of the backbone chain and compression of the side chains, is in quantitative agreement with experimental evidence seen in uniaxial extension [11]. The parameter $\beta$ can simply be obtained as ratio of the number average molar mass of the grafted polymer, $M_n$, to the number average molar mass $M_{n,bb}$ of the backbone, which can be expressed in terms of the number average mass fraction $\Phi_{n,br}$ of grafted side chains,

$$\beta = \frac{M_n}{M_{n,bb}} = \frac{1}{1 - \Phi_{n,br}} \tag{17}$$

For linear polymers, naturally $\beta = 1$ is obtained from Eq. (17).

As exemplified in Fig. 6 [11], agreement between predicted and observed slopes of the elongational viscosity after inception of strain-hardening is excellent for all model branched polystyrene melts investigated. Within the experimentally accessible window of elongation rates, time-strain separability of the measured elongational viscosities is observed. Also, as far as a maximum strain-hardening could be determined, the data are compatible with the implicit assumption of the MSF model that the material parameter $f^2_{MAX}$ is the same for all relaxation times of the terminal zone of the relaxation spectrum.

## Conclusion

A survey of the most recent and most successful constitutive equation in non-linear rheology shows the amount of progress made in recent decades. The microstructural MSF model shows excellent predictive capabilities for modeling the non-linear extensional and shear behavior (not discussed here in detail) of both linear and long-chain branched industrially important polymers. The concept of a strain-dependent tube diameter, which decreases with increasing deformation, explains consistently the strain hardening of linear as well as of long-chain branched polymer melts. The steeper slope of the elongational viscosity after inception of strain-hardening for branched melts in comparison to linear melts is due to the fact that in branched melts only a fraction ("the backbone") of chain segments is stretched, while side chains are compressed. Also, long-chain branched polymer melts show reversible or "K-BKZ" behavior in double-step strain experiments [17], because dissipative constraint release occurs only at higher strains, in contrast to linear melts, where dissipation starts already at smaller strains.

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