

dedicated to Professor K. Walters on his seventieth Birthday

MODELING NONLINEAR RHEOLOGY OF POLYDISPERSE POLYMER MELTS

M.H. WAGNER*

Polymertechnik/Polymerphysik, TU Berlin
Fasanenstr. 90, D-10623 Berlin, GERMANY
e-mail: manfred.wagner@tu-berlin.de

Melt rheology of polydisperse polymers is reviewed with special emphasis on the separation of effects of chain orientation and chain stretch, as described consistently by the Molecular Stress Function (MSF) theory. Based on energy balance considerations, first the Free Energy of a tube segment with a strain-dependent tube diameter is established, and it is demonstrated that the molecular stress is a function of the orientational free energy under these conditions. Then constraint release is introduced as a dissipative process, which modifies the energy balance of tube deformation, and leads to a strain-dependent evolution equation for the molecular stress function. For simple shear and extensional flows, the predictions of the MSF model consisting of a history integral for the stress tensor and a differential evolution equation for the molecular stress function with only one (extensional flows) or two (shear flow) nonlinear material parameters, are in excellent agreement with experimental data of HDPE, LDPE, LLDPE, PS, and PP melts. 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.

Key words: linear polymer melts, long-chain branched polymer melts, molecular stress function theory, orientation, stretch strain energy function, extensional flow, shear flow.

1. Introduction

In spite of considerable progress made in recent years in understanding the dynamics of macromolecular systems, there are still considerable challenges in understanding the melt rheology of “simple” homopolymers like PE or PS, which are produced commercially by the millions of tons. In this review, three specific issues will be considered:

- Why is it that polydisperse linear and long-chain branched polymer melts show a strain-hardening behavior which is qualitatively (so not quantitatively) similar in all aspects?
- Why is the slope of the elongational viscosity after inception of strain-hardening higher for branched melts than for linear melts (Wagner, 1999), and how can we quantify this effect?
- Why do long-chain branched polymer melts show a reversible or “BKZ” behavior in double-step shear strain experiments, while the behavior of linear melts is irreversible (Wagner and Ehrecke, 1998)?

We are not concerned here with the linear-viscoelastic properties of polymer melts and their relation to molecular weight and molecular weight distribution, where based on the concept of reptation (de Gennes, 1974) considerable progress has been made in recent years. We are rather concerned with the nonlinear rheology of polydisperse melts, which still poses tremendous challenges both experimentally and theoretically.

2. Tube models and chain stretch

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 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

* To whom correspondence should be addressed

remains constant and equal to its equilibrium value (Doi and Edwards, 1978; 1986). The main contribution to the extra stress tensor $\mathbf{s}(t)$ is then given by the orientation of the tube segments due to the flow. The resulting constitutive equation is of the single integral form

$$\mathbf{s}(t) = \int_{-\infty}^t m(t-t') \mathbf{S}_{\text{DE}}^{\text{IA}}(t') dt', \quad (2.1)$$

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

$$\mathbf{S}_{\text{DE}}^{\text{IA}} \equiv 5 \left\langle \frac{\mathbf{u}' \mathbf{u}'}{u'^2} \right\rangle_o = 5 \mathbf{S} \quad (2.2)$$

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

$$\langle \cdot \rangle_o \equiv \frac{1}{4\pi} \oint [\cdot] \sin \theta_o d\theta_o d\phi_o, \quad (2.3)$$

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

$$\mathbf{u}' = \mathbf{F}_t^{-1} \cdot \mathbf{u}. \quad (2.4)$$

Consequently, the DE model does not account for any strain hardening in extensional flows (Figs 1 and 2). It does, however, predict the separability of time and strain effects in the nonlinear stress relaxation modulus $G(t, \gamma_o) = G(t)h(\gamma_o)$, which is observed even for polydisperse polymer melts over several decades of relaxation time.

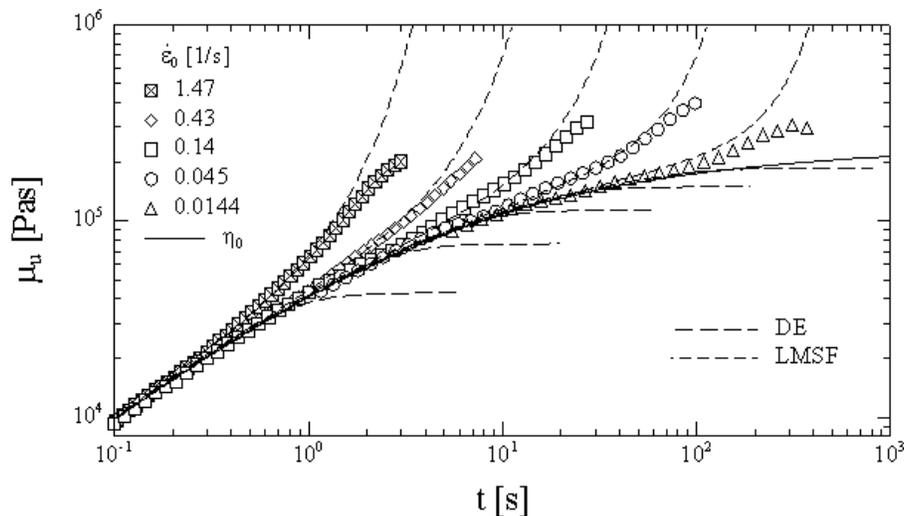
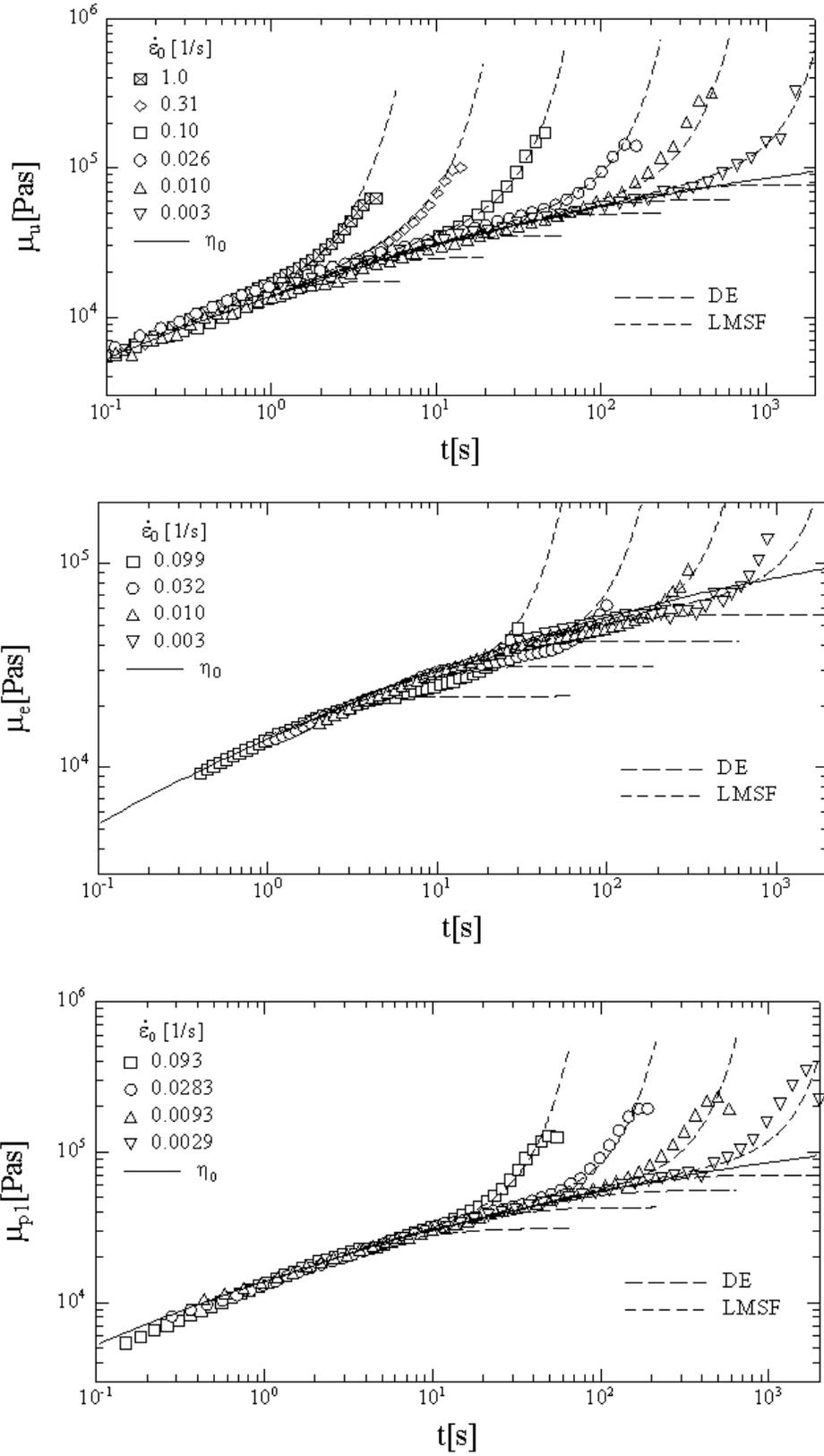


Fig.1. Uniaxial viscosity μ_u of a polydisperse linear PS melt (Bastian, 2001). Comparison of experimental data (symbols) to predictions of DE and LMSF (zero parameter) model.



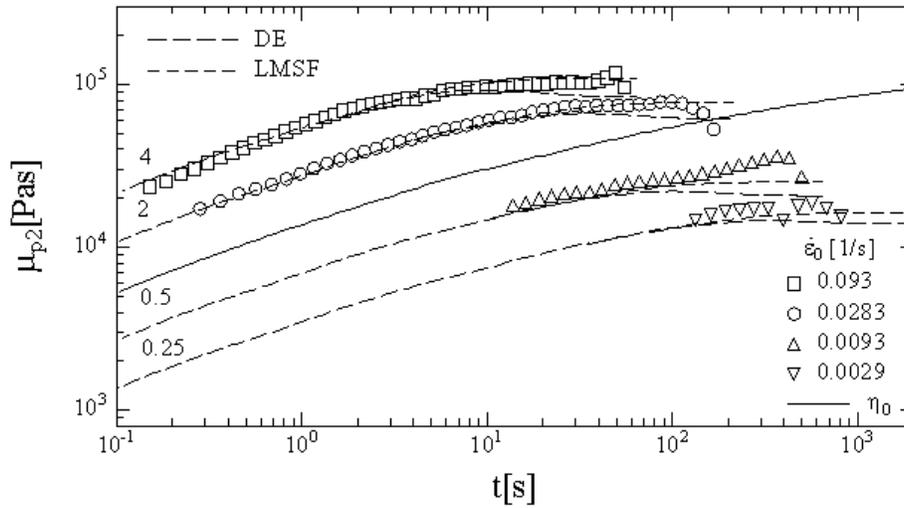


Fig.2. Uniaxial (μ_u), equibiaxial (μ_e), and planar (μ_{p1}, μ_{p2}) viscosities of a HDPE melt. Comparison of experimental data (symbols) to predictions of DE and LMSF (zero parameter) models (Bastian, 2001).

Doi and Edwards (1986) incorporated a stretch process with a stretch λ of the tube segments due to the flow in order to explain the discrepancies of the DE theory at start-up of shear and extensional flows. Pre-averaging the stretch, i.e. assuming that the stretch is uniform along the chain contour length and an explicit function $\lambda(t)$ of the observation time, which operates on the orientational configuration resulting from the integration over the strain history, the extra stress tensor is given by

$$s(t) = \lambda^2(t) \int_{-\infty}^t m(t-t') S_{DE}^{IA}(t') dt'. \quad (2.5)$$

Equation (2.5) generated the necessity to find stretch evolution equations, and a vast variety of concepts based on different kinetic ideas have been proposed in recent years. Models of this type invariably lead to rate-dependent tube stretch, and to obtain agreement with experimental data of polydisperse polymer melts, multi-mode formulations with an excessive number of empirical fit parameters are needed.

While in models with rate-dependent tube stretch, the tube diameter is invariably assumed to stay constant and equal to its equilibrium value a_o , tube stretch can also be introduced by the assumption of a strain-dependent tube diameter, as first suggested by Marrucci and de Cindio (1980). In this way, also the pre-averaging of the stretch can be avoided, which is inherently present in models based on Eq.(2.5) or its differential approximations, and which might be the root cause for the need of a large number of nonlinear parameters.

A generalized tube model with strain-dependent tube diameter was presented by Wagner and Schaeffer (1992; 1993; 1994). In the Molecular Stress Function (MSF) theory, 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_o . Taking into account that the tube diameter a represents the mean field of the surrounding chains, it is assumed that the tube diameter is independent of the orientation of tube segments. The extra stress is then given as

$$s(t) = \int_{-\infty}^t m(t-t') f^2 S_{DE}^{IA}(t') dt' \quad (2.6)$$

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

$$f = a_o/a. \quad (2.7)$$

In contrast to Eq.(2.5), tube stretch in Eq.(2.6) does not depend on the observation time t , but depends on the strain history, i.e. for time-dependent strain histories, tube stretch varies along the tube.

Note that while S is related directly to the deformation history via Eq.(2.4), 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 a solution of an evolution equation derived from an energy balance argument (Wagner *et al.*, 2001).

3. The molecular stress function theory for linear melts

Based on prior work of de Gennes (1974) and Marrucci and Hermans (1980), the molecular stress function f for linear melts is related to a strain-energy function w_{MSF} of the form

$$\frac{w_{MSF}}{3kT} = (f^2 - I). \quad (3.1)$$

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 (Wagner *et al.*, 2001). f^2 is found as solution of the evolution equation (with velocity gradient κ and plateau modulus G_N^o)

$$\frac{I}{3kT} \frac{\partial w_{MSF}}{\partial t} = \kappa : \frac{s}{5G_N^o} = f^2 (\kappa : S), \quad (3.2)$$

to be
$$f^2 = e^{\langle \ln u' \rangle_o}, \quad (3.3)$$

i.e. f^2 is an exponential of the orientational free energy $3kT \langle \ln u' \rangle_o$. Note that by use of Eq.(3.3), the strain energy function of Eq.(3.1) can be expressed as

$$\frac{w_{LMSF}}{3kT} = \langle \ln u' \rangle_o + f^2 - \ln f^2 - I, \quad (3.4)$$

i.e. as sum of orientational free energy and stretch energy. The part of the strain energy due to chain stretch has the desired properties, namely a minimum at equilibrium ($f^2 = I$) and a quadratic dependence on f in the vicinity of equilibrium.

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 (LMSF model), as exemplified in Figs 1 and 2 (Bastian, 2001).

Now constraint release (CR) is introduced as a dissipative process (Wagner *et al.*, 2001), which modifies the energy balance of tube deformation, and leads to a strain-dependent evolution equation for the

molecular stress function of the form

$$\frac{\partial f^2}{\partial t} = f^2 \left[(\kappa : \mathbf{S}) - \frac{I}{f^2 - 1} CR \right]. \quad (3.5)$$

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

$$CR = a_1 (f^2 - 1)^2 \sqrt{\mathbf{D}^2 : \mathbf{S}} + a_2 (f^2 - 1)^2 \sqrt{|\mathbf{W} \cdot \mathbf{D} : \mathbf{S}|}, \quad (3.6)$$

with \mathbf{D} and \mathbf{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 a simple shear flow, both the parameters a_1 and a_2 are of relevance. The evolution equation for the molecular stress function of linear melts in extensional flows is given by

$$\frac{\partial f^2}{\partial t} = \mathfrak{E}^2 \left[\begin{array}{l} S_{11} + mS_{22} - (1+m)S_{33} \\ -a_1 (f^2 - 1) \sqrt{S_{11} + m^2 S_{22} + (1+m)^2 S_{33}} \end{array} \right] \quad (3.7)$$

where the parameter $m (-1/2 \leq m \leq 1)$ describes the type of extensional flow, and \mathfrak{E} is the largest extension rate. S_{ii} are the components of the orientation tensor \mathbf{S} . The parameter a_1 can be expressed in terms of f_{MAX}^2 as

$$a_1 = \frac{I}{f_{MAX}^2 - 1}. \quad (3.8)$$

f_{MAX}^2 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 the polymer melt rheology of linear polymers in irrotational flows. Note that although dissipative constraint release is a rate process, integration of Eq.(3.7) leads to a molecular stress function f which is deformation dependent (Wagner *et al.*, 2001).

4. The molecular stress function theory for long-chain branched melts

The simplest model of a section of a long-chain branched macromolecule consists of one chain segment oriented in the direction of the tube defined by the “backbone” of the macromolecule, and one or more side chains representing $\beta - 1$ crosslinked chain segments (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 (Wagner *et al.*, 2003).

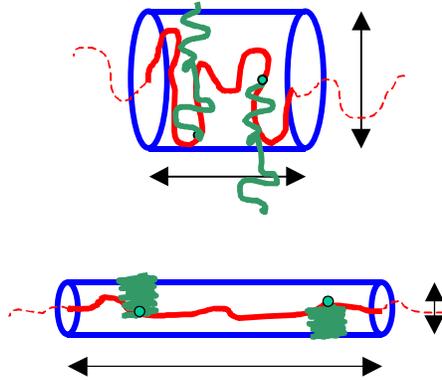


Fig.3. Tube segment of a long-chain branched polymer molecule before and after deformation: one chain segment is stretched, while side chain segments are compressed (Wagner *et al.*, 2003).

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

$$\frac{w_{\text{MSF}}}{3kT} = \frac{1}{\beta}(f^2 - 1) + \frac{\beta - 1}{\beta} \left(1 - \frac{1}{f^2} \right). \quad (4.1)$$

Note that in the vicinity of $f^2 = 1$, this strain energy function is well behaved, as Eq.(4.1) reduces to Eq.(3.1).

The parameter β has values $\beta \geq 1$, with $\beta = 1$ for linear melts. For $\beta = 2$, excellent agreement with experimental data of a long-chain branched (radiation-crosslinked) PP melt is found (Fig.4). Note that the increase in elongational viscosity is steeper for long-chain branched melts than for linear melts.

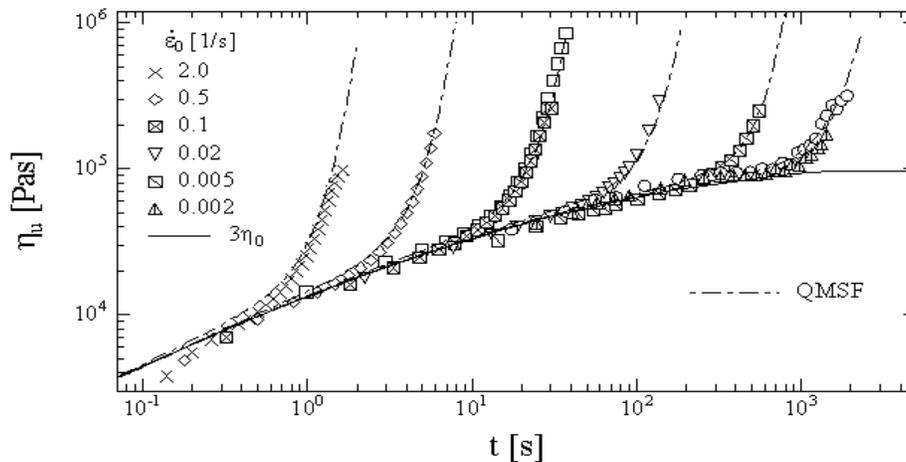


Fig.4. Uniaxial viscosity η_u of a long-chain branched PP melt (Bastian, 2001). Comparison of experimental data (symbols) to predictions of the MSF model with $\beta = 2$ (QMSF model).

Introducing again constraint release as a nonlinear 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

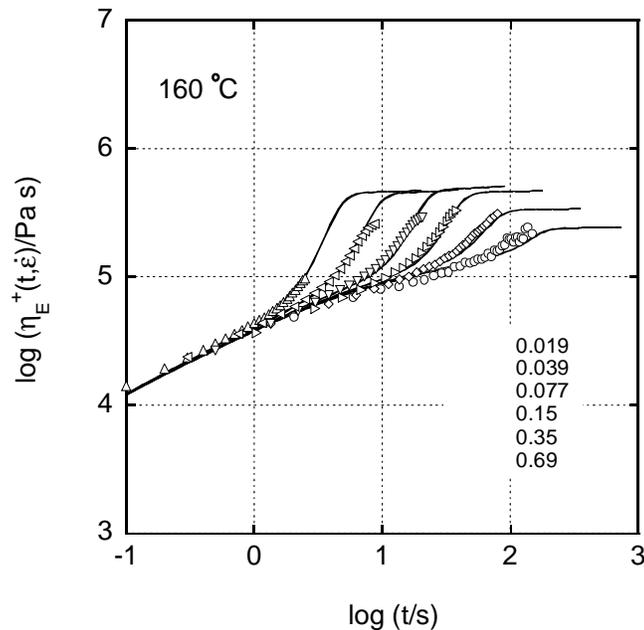
$$\frac{\partial f^2}{\partial t} = \frac{\beta f^2}{1 + \frac{\beta-1}{f^4}} \left[(\kappa : S) - \frac{1}{f^2-1} CR \right]. \quad (4.2)$$

The evolution equation for the molecular stress function in constant strain-rate extensional flows is then given by

$$\frac{\partial f^2}{\partial t} = \frac{\beta f^2}{1 + \frac{\beta-1}{f^4}} \left[\begin{array}{l} S_{11} + mS_{22} - (1+m)S_{33} \\ - \frac{f^2-1}{f_{MAX}^2-1} \sqrt{S_{11} + m^2 S_{22} + (1+m)^2 S_{33}} \end{array} \right]. \quad (4.3)$$

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 the elongational flow (the “side chains”), and only part of the chain segments is stretched (the “backbone”). In the multi-chain segmental MSF model developed 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) (Wagner *et al.*, 2003).

a)



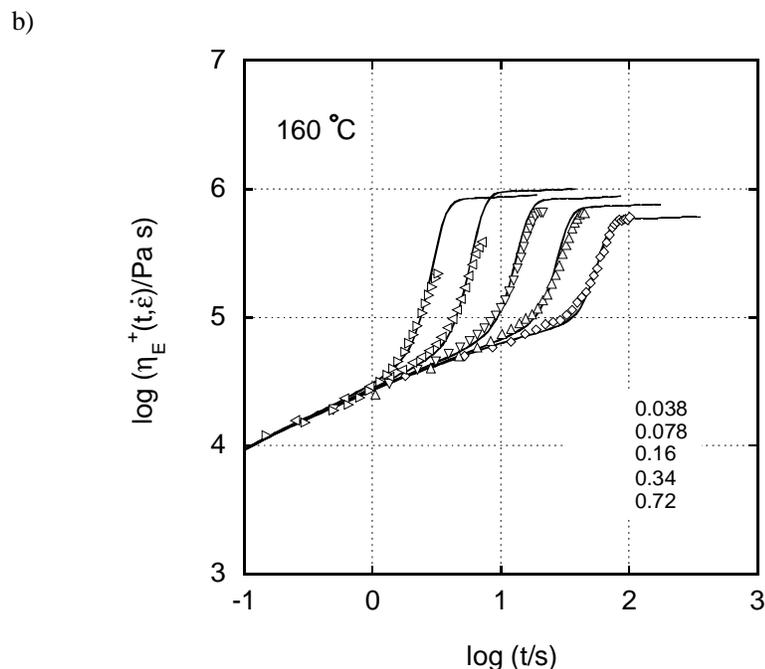


Fig.5. Elongational viscosity data (symbols) of LDPE melts and predictions by MSF model (Wagner *et al.*, 2003):

a) LDPE tubular-o: $\beta = 2$ and $f_{MAX}^2 = 30$; b) LDPE autoclave-O: $\beta = 4$ and $f_{MAX}^2 = 80$.

5. Comparison of MSF predictions to the elongational and shear rheology of model branched polystyrene melts

It is difficult if not impossible to derive the parameter β from the topology of randomly branched LDPE; therefore we have treated β (Wagner *et al.*, 2003) as a fit parameter (the only one in the hyperelastic limit). However, in the meantime we have analysed the nonlinear rheology of comb shaped model polystyrene melts investigated by Hepperle (2003) and Münstedt, and we find that indeed, β 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 (Wagner *et al.*, 2004): Following the basic idea of the MSF model proposed by Wagner *et al.* (2003), we assume simplistically that all grafted side chains will be increasingly compressed onto the backbone during the elongational deformation. Then the parameter β is obtained as the 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

$$\beta = \frac{M_n}{M_{n,bb}} = \frac{1}{1 - \Phi_{n,br}}. \quad (5.1)$$

For linear polymers, naturally $\beta = 1$ is obtained from Eq.(5.1).

As exemplified in Fig.6, 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_{MAX}^2 is the same for all relaxation times of the terminal zone of the relaxation spectrum.

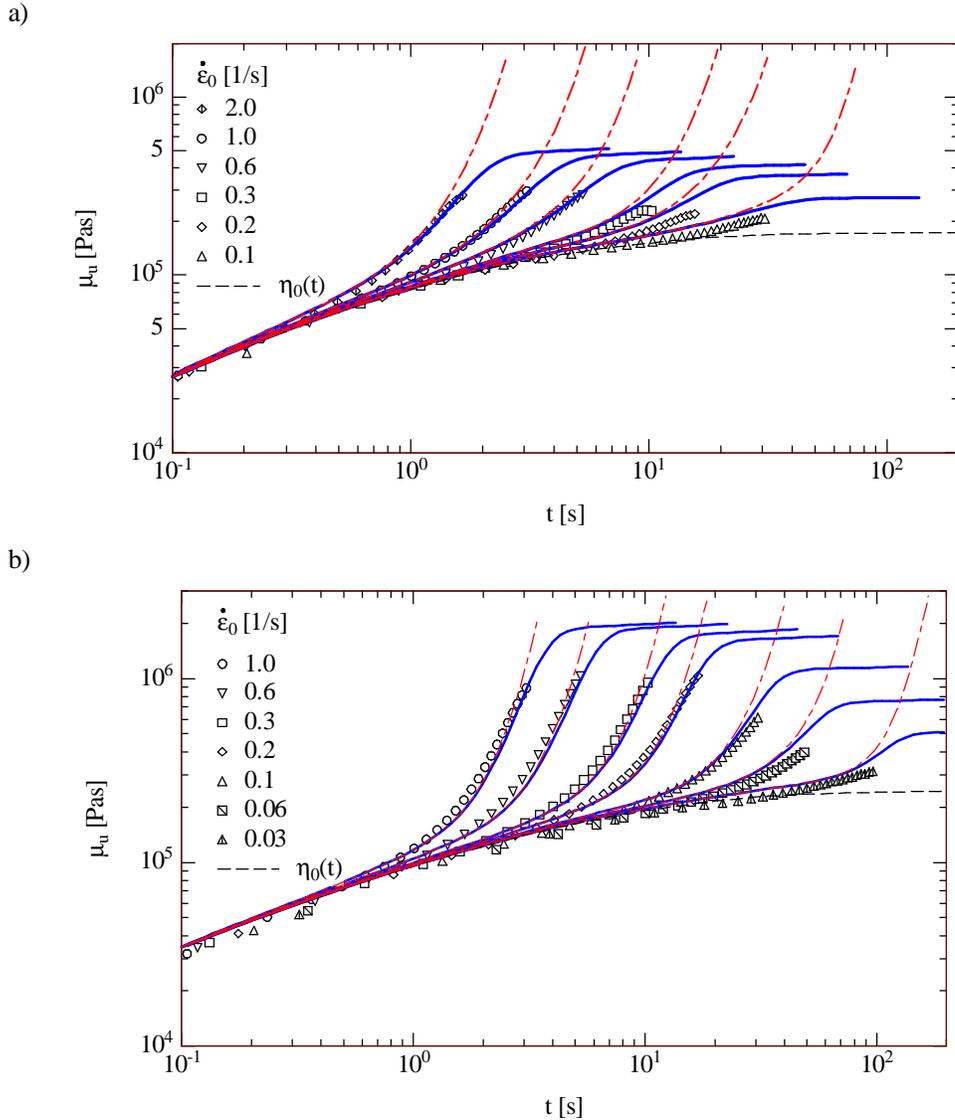


Fig.6. Comparison of elongational viscosity data (symbols) of two branched PS melts to predictions (lines) of MSF theory (Wagner *et al.*, 2004).

a) PS 80-0.6G-22: $\Phi_{n,br} = 0.14$, $\beta = 1.2$; dotted line: $f_{MAX}^2 \rightarrow \infty$, solid line $f_{MAX}^2 = 25$;

b) PS 70-3.2G-22: $\Phi_{n,br} = 0.5$, $\beta = 2.0$; dotted line: $f_{MAX}^2 \rightarrow \infty$, solid line $f_{MAX}^2 = 80$.

The shear damping function of model branched PS melts was measured by nonlinear shear relaxation experiments (Hepperle, 2003). Although the shear strain range investigated was limited to $\gamma < 5$, this is the important shear strain range determining the shear stress in steady shear-rate flows. As is well known, branching also has significant influence on the shear strain behavior, although the effect is usually much smaller than in extensional flows (Wagner *et al.*, 2004): melts with high side chain mass fractions show

substantially less shear damping than melts with low side chain mass fractions, and for shear strains up to 5, their shear damping functions are close to the hyper-elastic or “BKZ” limit, i.e., the dissipative effect of constraint release is very small (Fig.7a). This agrees with earlier investigations of Wagner and Ehrecke (1998) demonstrating that a LDPE melt shows a reversible (or BKZ) behavior in double-step shear strain experiments in contrast to a (linear) polyisobutene melt, which showed an “irreversible” behavior. With decreasing side chain mass fraction, the shear damping behavior of the model branched polystyrene melts approaches the behavior of linear polystyrene (PS-r-95), and the influence of the parameter a_2 describing the additional dissipative constraint release due to rotational flow becomes important (Fig.7b).

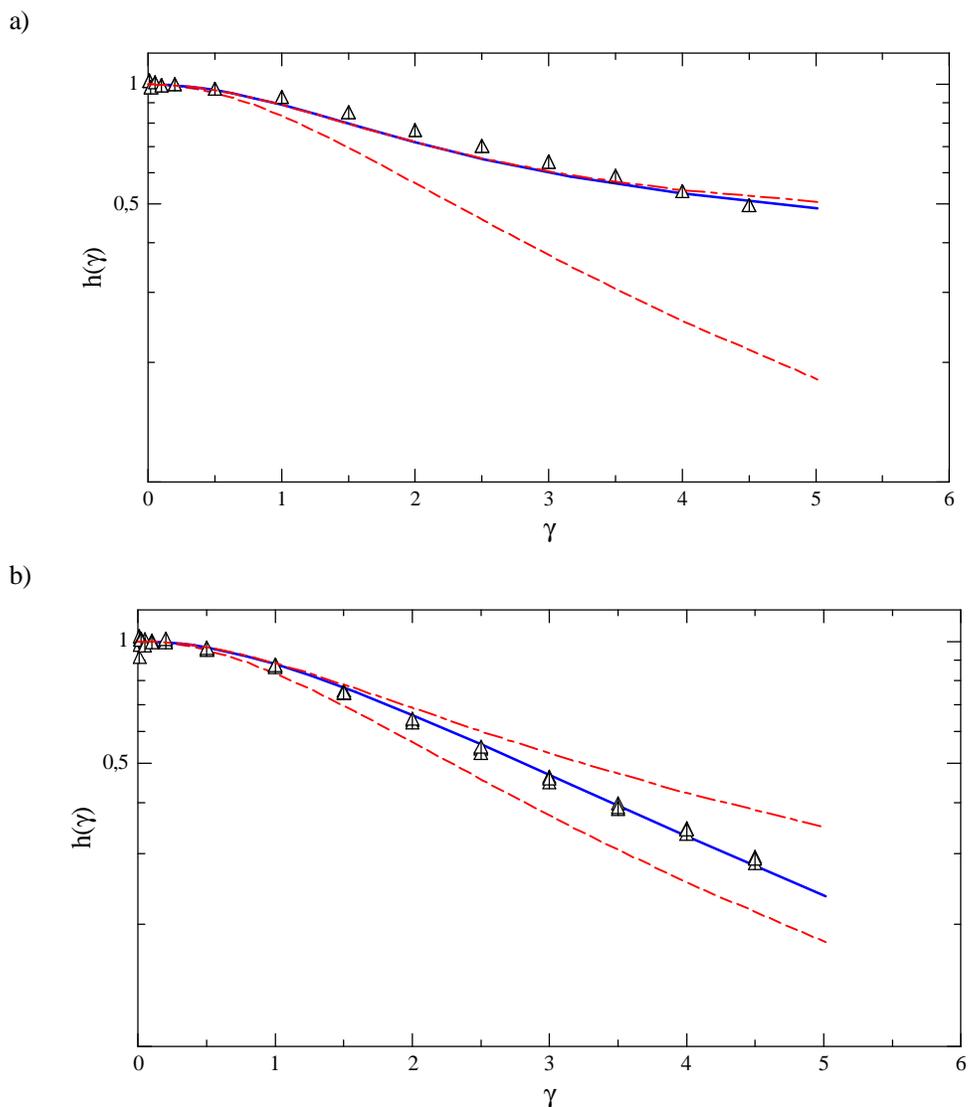


Fig. 7. Comparison of shear damping function data (symbols) of two PS melts to predictions of MSF theory (Wagner *et al.*, 2004); upper dotted line is the prediction assuming no constraint release (i.e., $f_{MAX}^2 \rightarrow \infty$, $a_2 = 0$); lower dotted line indicates predictions of Doi-Edwards (IAA) theory, i.e., $f_{MAX}^2 \equiv 1$.

a) branched PS 70-3.2G-22: full line is the prediction of MSF model with parameters $\beta = 2$, $f_{MAX}^2 = 80$ and $a_2 = 0$;

b) linear PS-r-95: full line is the prediction of MSF model with parameters $\beta = 1$, $f_{MAX}^2 = 6$ and $a_2 = 0.4$.

Conclusions

Returning to the three specific issues concerning the rheology of linear and long-chain branched polymer melts mentioned in the introduction, we can state that:

- 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 (Wagner *et al.*, 2001).
- 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 (Wagner *et al.*, 2003; 2004).
- Long-chain branched polymer melts show a reversible or “BKZ” behavior in double-step shear strain experiments, because dissipative constraint release occurs only at higher shear strains, in contrast to linear melts, where dissipation starts already at smaller shear strains (Wagner *et al.*, 2004).

Challenges in nonlinear rheology which still remain to be studied are, to mention just a few, the relations between macromolecular architecture of homopolymers and the nonlinear parameters f_{MAX}^2 and a_2 of the MSF theory, as well as modeling the nonlinear rheology of blends of linear and long-chain branched polymers.

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Received: April 28, 2005