

A hierarchical multi-mode MSF model for long-chain branched polymer melts part II: multiaxial extensional flows

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Abstract In part I, a novel hierarchical multi-mode molecular stress function (HMMSF) model for long-chain branched (LCB) polymer melts has been proposed, which implements the basic ideas of (i) the pom-pom model, (ii) hierarchical relaxation, (iii) dynamic dilution, and (iv) interchain pressure. Here, the capability of this approach is demonstrated in modelling the extensional viscosity data of a broadly distributed long-chain branched polymer melt in uniaxial, equibiaxial, and planar extensional deformations with only a single non-linear parameter, the dilution modulus, which quantifies the fraction of dynamically diluted chain segments.

Keywords Molecular stress function model · Biaxial flow · Multiaxial extensional flow · Polyethylene · Polymer melt · Elongational flow

Introduction

The simple-term modelling of the extensional viscosity of polymers in general and their strain hardening behaviour in particular are of great importance for polymer

processing (Gupta 2002; Meissner and Hostettler 1994; Narimissa et al. 2014; Padmanabhan and Macosko 1997; Revenu et al. 1993; Sampers and Leblans 1988; Soon et al. 2009). The occurrence of multiaxial extensional deformation is manifested in tubular film inflation, blow moulding, and vacuum moulding polymer processing techniques (Takahashi et al. 1993). However, the measurement of the extensional viscosity in biaxial deformations at controlled rheological conditions is a challenging task, and thus far, it has been reported in limited studies: bubble inflation technique was established by Denson and co-workers (Denson and Hylton 1980; Denson and Gallo 1971); sheet stretching technique was developed by Meissner and co-workers (1981; 1982); axisymmetric stagnation flow was applied by Winter, Macosko, Bennett, van Aken, and Janeschitz-Kriegl (Van Aken and Janeschitz-Kriegl 1980; Van Aken and Janeschitz-Kriegl 1981; Winter et al. 1979); and lubricated squeezing extensional rheometer was introduced by Chatraei et al. (1981), and advanced by others (Kashyap and Venerus 2010). Laun and Schuch (1989) modified the tensile creep rheometer (Cogswell-Münstedt-type rheometer (Münstedt 1979)) by means of replacing the cylindrically shaped specimen with a tubelike sample to measure the planar elongational viscosity of polyethylene melts. They managed to keep the diameter of the tube-like samples constant through pumping oil from a syringe into the core of the tube. Nguyen et al. (2015) employed similar modifications in their filament stretching rheometer to investigate the planar extensional viscosity of polystyrene solutions. Hachmann (1996) and Hachmann and Meissner (2003) combined the application of metal belts for the uniaxial extensional flow measurement at elevated temperatures, with the use of rotary

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clamps at ambient condition in order to perform equibiaxial and planar extensional measurements up to 350 °C.

According to Stephenson (1980) and Meissner et al. (1982), the classification of multiaxial extensional flow at constant volume is defined based on a Cartesian coordinate system by

$$\dot{\varepsilon}_{11} \equiv \dot{\varepsilon}_0 \geq \dot{\varepsilon}_{22} \geq \dot{\varepsilon}_{33} = -(\dot{\varepsilon}_{11} + \dot{\varepsilon}_{22}) \quad (1)$$

Here, $\dot{\varepsilon}_0$ denotes the constant Hencky strain rate, and $\dot{\varepsilon}_{ij}$ are the components of the strain rate tensor. When the shear rate components are absent ($i \neq j$), the multiaxial extensional strain rate tensor becomes,

$$D(t) = \dot{\varepsilon}_0 h(t) \begin{pmatrix} 1 & 0 & 0 \\ 0 & m & 0 \\ 0 & 0 & -(1+m) \end{pmatrix} \quad (2)$$

where $m = \dot{\varepsilon}_{22}/\dot{\varepsilon}_{11}$ is the test parameter corresponding to the mode of extensional deformation and $h(t)$ is the unit step function. The values of m in uniaxial (simple), equibiaxial, and planar extensions are -0.5 , 1 , and 0 , respectively. Although Demarmels and Meissner (Demarmels and Meissner 1985) conducted the only study where m was a time-dependent parameter, i.e., $m = m(t) \neq \text{const.}$, this parameter has been considered constant and independent of time in the rest of the extensional rheological studies thus far.

In the linear-viscoelastic regime, the extensional stress $\sigma^0(t)$ in terms of the elongational strain rate tensor (Eq. 2) is given as

$$\sigma^0(t) = 2(2+m)\dot{\varepsilon}_0 \int_0^t G^0(t-t') dt' = 2(2+m)\dot{\varepsilon}_0 \eta^0(t) \quad (3)$$

$\eta^0(t)$ is the linear-viscoelastic transient shear viscosity with the limiting case of the zero shear viscosity $\eta_0 = \eta^0(t \rightarrow \infty)$ (Hachmann and Meissner 2003), and $G^0(t)$ is the linear-viscoelastic shear relaxation modulus. $2(2+m)$ is the extensional flow-dependent coefficient of $\eta^0(t)$ which is 3 (Trouton ratio) for uniaxial, 6 for equibiaxial, and 4 and 2 for planar extensions. For comparison of multiaxial flows, Stephenson (1980) and Meissner et al. (1982) introduced a reduced extensional viscosity $\mu(t)$,

$$\mu(t) = \frac{\sigma(t)}{2(2+m)\dot{\varepsilon}_0} \quad (4)$$

which, in the linear viscoelastic regime, reduces to

$$\mu^0(t) = \eta^0(t) \quad (5)$$

Hence, the transient extensional viscosities of uniaxial, equibiaxial, and planar flows, are $\mu_u(t)$, $\mu_e(t)$, $\mu_{p1}(t)$, and $\mu_{p2}(t)$, respectively,

$$\mu_u(t) = \sigma_u(t)/3\dot{\varepsilon}_0 \quad (6)$$

$$\mu_e(t) = \sigma_e(t)/6\dot{\varepsilon}_0 \quad (7)$$

$$\mu_{p1}(t) = \sigma_{p1}(t)/4\dot{\varepsilon}_0 \quad (8)$$

$$\mu_{p2}(t) = \sigma_{p2}(t)/2\dot{\varepsilon}_0 \quad (9)$$

The importance of planar deformations is on account of the presentation of two material functions as a result of one test. This mode of extensional flow features extensional viscosities in the direction of flow (μ_{p1}), and in the cross direction of flow (μ_{p2}) (Hachmann and Meissner 2003). μ_{p2} is sometimes called the “cross viscosity”. Hachmann and Meissner showed that for LDPE and HDPE samples, μ_{p1} demonstrates strain hardening (similar to μ_u), i.e., $\mu_{p1} > \eta^0$, while μ_{p2} shows strain softening ($\mu_{p2} < \eta^0$), and μ_e initially strain softening followed by strain hardening.

The constitutive modelling of multiaxial behaviour of polymer melts has been an intellectually challenging endeavour for polymer rheologists. The K-BKZ integral constitutive equation (Bernstein et al. 1963; Kaye 1962) is an over 50-year-old model which has demonstrated promising results in the prediction of shear and elongational deformation of polymeric systems (Tanner 1988). However, Samurkas et al. (1989) showed that the K-BKZ model is incapable of describing both strain softening in shear and extreme strain hardening in planar flows at the same time, when its damping function (Wagner 1976) is measured from either of those deformations. In the case of equibiaxial extensional flow, there have been very limited publications (Chatraei et al. 1981; Khan et al., 1987; Nishioka et al. 2000; Soskey and Winter 1985) available as compared to the elongational flow studies. Takahashi et al. (1993) showed that the deviation of the stress growth coefficient from the low strain rate asymptotes in all types of extensional flow is expected when considering chain stretch in multiaxial deformation. Wagner et al. (1998) predicted the extensional rheological behaviour of linear and LCB polyethylene melts based on the Doi-Edwards theory (Doi and Edwards 1986) and the molecular stress function model of Wagner and Schaeffer (1992; 1993). Sugimoto et al. (2001) modelled the equibiaxial extensional viscosity of polypropylene (containing small amounts of polyethylene) using the strain hardening nonlinearity parameter (Hingmann and Marczinke 1994; Ishizuka and Koyama 1980; Takahashi et al. 1993), as well as the extensional model proposed by Osaki et al. (1999) which is based on the constitutive equations of the pom-pom model (McLeish and Larson 1998).

In more recent attempts by Wagner and co-workers (2004; 2001; 2003), the multiaxial extensional viscosity of LCB melts were predicted by the MSF model utilizing two nonlinear material parameters which signify the ratio of the number of all entangled chain segments to the number of (backbone) chain segments stretched (parameter β), and the square of the maximum relative stretch of the chain segments determining the steady-state value of the extensional viscosity (parameter f_{\max}^2). Ianniruberto and Marrucci (2012) extended the Doi-Edwards theory for entangled linear polymers to LCB polymers in the case of fast elongational flows. They showed that due to the alignment of the branched molecules during flow, branched molecules reshape to linear architecture, and hence, the behaviour of star and pom-pom polymers resemble to that of linear polymers at extensional rates greater than the reciprocal of the Rouse time. Masubuchi and co-workers (2014) performed primitive chain network simulations to investigate the molecular motion under elongational flow. They demonstrated reasonable agreement between simulations and elongational viscosity data of monodisperse linear and pom-pom branched polystyrene, and they concluded that the branch point withdrawal is the dominant mechanism of backbone relaxation under the flow.

In part I of this research (Narimissa et al. 2015), we proposed a hierarchical multimode stress function (HMMSF) model for the elongational viscosity of LCB melts implementing the basic ideas of the pom-pom model, hierarchical relaxation, dynamic dilution, and interchain pressure. In the HMMSF model, the branch point withdrawal mechanism is replaced by the assumption of the balance of backbone stretch by the interchain pressure. This model demonstrated excellent agreement with elongational viscosity data of different LCB polymer melts investigated via three different extensional rheometers at a wide range of strain rates based exclusively on their linear-viscoelastic characterization, and features only a single non-linear material parameter, the dilution modulus G_D . The aim of this study is to extend the applicability of the HMMSF model to multiaxial extensional viscosity data of an LCB melt.

Hierarchical multi-mode MSF model

The stress tensor of the hierarchical multi-mode molecular stress function (HMMSF) model is given as

$$\sigma(t) = \sum_i \int_{-\infty}^{+\infty} \frac{\partial G_i(t-t')}{\partial t'} f_i^2(t, t') \mathbf{S}_{DE}^{IA}(t, t') dt' \quad (10)$$

$\mathbf{S}_{DE}^{IA}(t, t')$ is the Doi and Edwards (DE) orientation tensor assuming an independent alignment (IA) of tube segments (Doi and Edwards 1986), and $f_i(t, t')$ represent the molecular stress functions of each relaxation mode i characterized by the

partial relaxation moduli $G_i(t)$. The molecular stress functions $f_i(t, t')$ are inverse proportional to the relative tube diameters. Note that while orientation of chain segments is described by \mathbf{S}_{DE}^{IA} , which is proportional to the second order orientation tensor, stretch is assumed to be isotropic (Narimissa et al. 2015). The relaxation modulus $G(t)$ of a polymer can be represented by discrete Maxwell modes $\{g_i, \tau_i\}$,

$$G(t) = \sum_{i=1}^n G_i(t) = \sum_{i=1}^n g_i \exp(-t/\tau_i) \quad (11)$$

During the relaxation process, there are two relaxation regimes: “permanent dilution” and “dynamic dilution.” Permanent dilution occurs due to the presence of oligomeric chains and un-entangled or marginally entangled (fluctuating) chain ends. Dynamic dilution refers to the dynamic dilation of the tube diameter of the non-relaxed chains through the solvent effect of the already relaxed ones, which does not only affect the linear-viscoelastic properties but has also an effect on chain stretch, due to the dilation of the tube diameter. The onset of dynamic dilution occurs when the relaxation process has reached the dilution modulus $G_D \leq G_N^0$. As outlined by Narimissa et al. (2015), the dilution modulus is a free parameter of the model, which needs to be fitted to non-linear viscoelastic experimental evidence, since the mass fraction of oligomeric chains and un-entangled or marginally entangled chain ends is not known a priori. The mass fraction w_i of a dynamically diluted chain segment with relaxation time $\tau_i > \tau_D$ is determined by considering the ratio of the relaxation modulus at time $t = \tau_i$ to the dilution modulus $G_D = G(t = \tau_D)$, while chain segments characterized by relaxation times $\tau_i < \tau_D$ are considered to be permanently diluted and their weight fractions are fixed at $w_i = 1$,

$$w_i^2 = \frac{G(t = \tau_i)}{G_D} = \frac{1}{G_D} \sum_{j=1}^n g_j \exp(-\tau_i/\tau_j) \quad \text{for } \tau_i > \tau_D$$

$$w_i^2 = 1 \quad \text{for } \tau_i < \tau_D \quad (12)$$

Thus, the dilution modulus quantifies the fraction of dynamically diluted chain segments. It is assumed that the value of w_i obtained at $t = \tau_i$ can be attributed to the chain segments with relaxation time τ_i . The evolution equation for the molecular stress function of each mode is given as

$$\frac{\partial f_i}{\partial t} = f_i(\mathbf{K} : \mathbf{S}) - \frac{f_i - 1}{\tau_i} \left(1 - \frac{2}{3} w_i^2 \right) - \frac{2}{3} \frac{f_i^2 (f_i^3 - 1)}{3 \tau_i} w_i^2 \quad (13)$$

Here, \mathbf{K} is the deformation rate tensor, \mathbf{S} the second order orientation tensor, and $f_i(\mathbf{K} : \mathbf{S})$ is the average increase of length per unit length of a tube segment with the starting conditions $f_i(t = t', t) = 1$. The second term on the right hand side models stretch relaxation along the backbone tube, and the third term takes into account the interchain pressure perpendicular to the tube direction. The interchain pressure is reduced by tube

dilation, which is caused by dynamic dilution of chain segments and leads to an effective increase of the tube diameter relaxation time $3\tau_i$ to $3\tau_i/w_i^2$ (Narimissa et al. 2015). Thus, the HMMSF model consists of the multi-mode stress equation, a set of evolution equations for the molecular stresses f_i , and a hierarchical procedure to evaluate the effect of dynamic dilution with only one free non-linear parameter, the dilution modulus G_D .

We now demonstrate the applicability of the HMMSF model predictions not only to uniaxial but also to the equibiaxial and planar modes of extensional deformation.

Comparison of HMMSF model predictions and multiaxial extensional viscosity data

The extensional rheological modellings of this study were conducted on a well-characterized low density polyethylene (Lupolen 1810H) melt previously characterized and tested by Hachmann (1996) and Hachmann and Meissner (2003). Table 1 displays the weight average molecular weight (M_w), number average molecular weight (M_n), polydispersity index (M_w/M_n), melting temperature (T_m), room temperature density (ρ_{RT}), testing temperature density (ρ_T), zero shear viscosity at testing temperature (η_0), melt flow index (MFI), activation energy (E_a), dilution modulus G_D obtained by fitting of the extensional data, and the linear-viscoelastic relaxation spectrum of Lupolen 1810H at testing temperature.

The multiaxial extensional rheological measurements were performed by Hachmann (1996). The uniaxial extensional measurements of the samples were conducted by the commercial form of Meissner rheometer manufactured by Rheometric Scientific, and named Rheometrics Melt Extensional Rheometer (RME) (Meissner and Hostettler 1994). The equibiaxial and planar elongational measurements were performed after applying new directional arrangements to the metal belts of the RME clamps, i.e., in a circle for equibiaxial tests and in a rectangle for planar tests. The details of the modified version of the RME are described elsewhere (Hachmann and Meissner 2003). Thus far, this set of uniaxial, equibiaxial, and planar viscosity data can be regarded as the most reliable data set for multiaxial flow.

We compare the multiaxial extensional viscosity data of Hachmann (1996) with the predictions of the HMMSF model, as defined by the equation of stress (Eq. 10), the set of evolution equations for the molecular stress functions (Eq. 12), and the hierarchical procedure to evaluate the effect of dynamic dilution with only one free non-linear parameter, the dilution modulus (Eq. 13).

The symbols in Fig. 1 present the uniaxial, equibiaxial, and planar transient viscosities (μ_u , μ_e , μ_{p1} , and μ_{p2} , respectively) of LDPE at 150 °C. The predictions of the HMMSF model are illustrated by the use of continuous lines in this figure. The

Table 1 Characterization of LDPE.

Characteristics	LDPE
Product	Lupolen 1810H
Producer	BASF
M_w [g/mol]	188,000
M_n [g/mol]	16,600
M_w/M_n	11.3
T_m [°C]	110
T [°C]	150
ρ_{RT} [g/cm ³]	0.917
ρ_T [g/cm ³]	0.778
η_0 (@ T) [kPa.s]	65
MFI [g/10 min]	1.2
E_a [kJ/mol]	58.6
G_D [Pa]	1.5E + 04
Rheometer	Meissner-type (Hachmann and Meissner 2003)

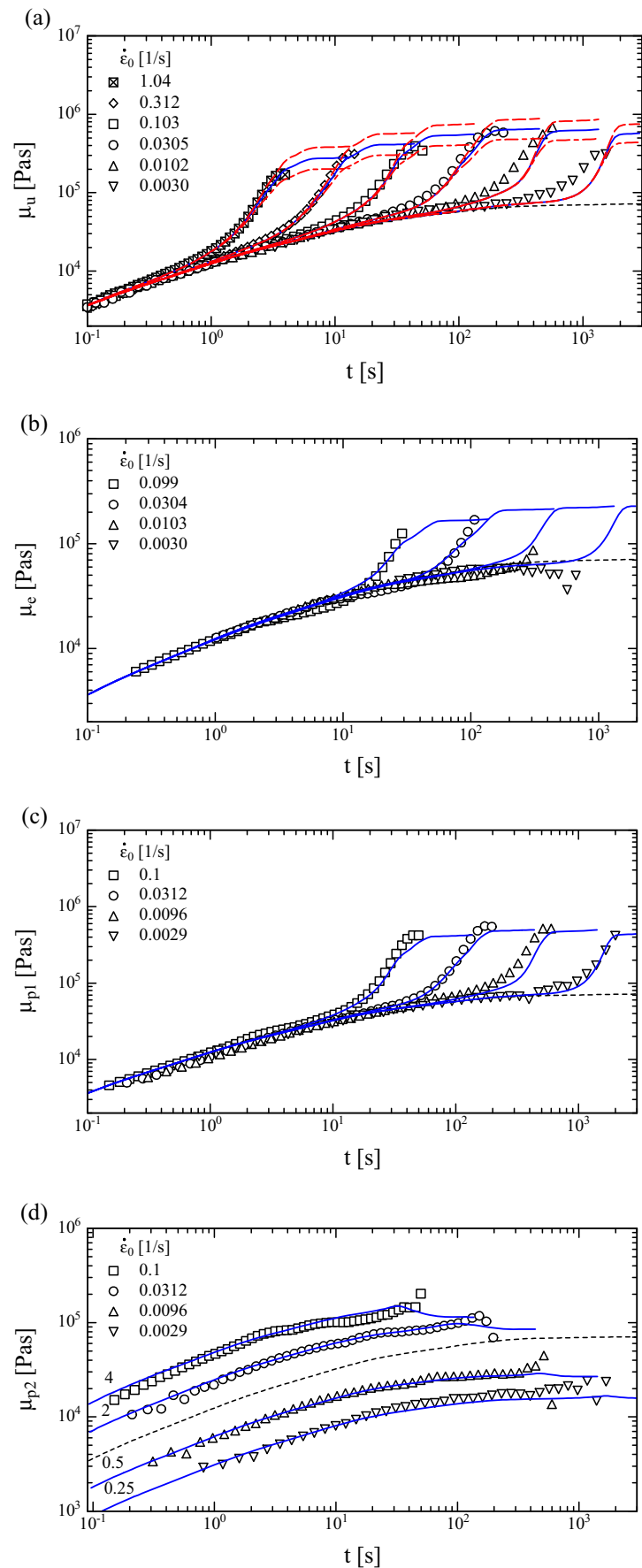
Relaxation spectrum at T		
i	g_i [Pa]	τ_i [s]
1	3.000E-01	5.0E + 03
2	4.587E + 00	1.0E + 03
3	2.746E + 02	1.0E + 02
4	2.578E + 03	1.0E + 01
5	9.797E + 03	1.0E + 00
6	2.968E + 04	1.0E − 01
7	5.202E + 04	1.0E − 02

HMMSF model shows a very good agreement with the uniaxial extensional viscosity of LDPE during the strain hardening regime and its transition to the steady-state extensional viscosity (Fig. 1). The slight under-prediction of the uniaxial extensional viscosity at $\dot{\epsilon} = 0.003$ and 0.0102 s^{-1} could be due to the experimental errors as the result of limited extension of the relaxation spectrum of LDPE, and consequently the underestimation of the weight of the longest relaxation time, which leads to an inaccurate prediction of the elongational viscosity of the polymer at low strain rates. According to Wagner et al. (2001) the “spurious strain hardening” at low Hencky rates may also be caused by the miniscule force signal transmitted by the polymer to the force transducer which is not distinguishable from the lower limit of the force transducer.

Figure 1a demonstrates also the sensitivity of the HMMSF model predictions with respect to the value of the dilution modulus G_D by increasing G_D from the optimal value of $G_D = 1.5\text{E} + 4$ Pa by a factor of 2 ($G_D = 3.0\text{E} + 4$ Pa), or decreasing G_D by a factor of 0.5 ($G_D = 0.75\text{E} + 4$ Pa).

A close relative viscosity investigation of the equibiaxial deformation mode of LDPE reveals an undershoot ($\mu_e/\eta^0 < 1$) followed by a crossover ($\mu_e/\eta^0 = 1$), and eventually the strain hardening region (Hachmann and Meissner 2003). Figure 1b shows that the predictions of the HMMSF model are in

Fig. 1 Comparison of **a** uniaxial, **b** equibiaxial, as well as **c**, **d** planar transient viscosity data (symbols) of LDPE (Lupolen 1810H) melt characterized in Table 1 with predictions of the HMMSF model ($G_D = 1.5E + 4$ Pa, continuous lines). *Dotted line* indicates the linear-viscoelastic shear viscosity $\eta^0(t)$. **a** Also, HMMSF model predictions for $G_D = 3.0E + 4$ Pa and $G_D = 0.75E + 4$ Pa are presented by *dashed lines* and *dash-dotted lines*, respectively. **d** Factors 0.25, 0.5, 2, and 4 were applied on μ_{p2} data and predictions to separate the viscosities for the purpose of clarity



excellent quantitative agreement with the equibiaxial viscosity of LDPE. Moreover, our model presents a remarkably well prediction of planar extensional viscosity of LDPE in the direction of flow (μ_{p1}) in both qualitative and quantitative scales (Fig. 1c). The planar extensional viscosity in the direction of flow, μ_{p1} , exhibits noteworthy similarities with its uniaxial counterpart which was already noticed by Hachmann and Meissner (2003). In contrast to μ_{p1} , the cross viscosity of LDPE in the planar extension, μ_{p2} , does not display strain hardening behaviour, and in fact, Hachmann and Meissner (2003) stated that the relative cross viscosity of LDPE always shows undershoots ($\mu_{p2}/\eta^0 < 1$) except for the smallest Hencky rates (Fig. 1d). The predictions of the HMMSF model are also in good agreement with the cross viscosity of the planar extensional mode. We may add that the existence of small maxima in the μ_{p2} data can be inferred from the experiments at strain rates 0.0312 and 0.0096 1/s. These maxima, which are predicted by the HMMSF model, are due to the strain dependence of the difference $S_{22} - S_{33}$ of the orientation tensor components S_{22} and S_{33} , and are already predicted by the Doi-Edwards IA model (Wagner 1999). Only the intensity and location of the maxima in the time or strain domain are affected by the isotropic stretch.

Discussion and conclusions

In part I (Narimissa et al. 2015), a novel hierarchical multi-mode molecular stress function (HMMSF) model for long-chain branched (LCB) polymer melts was developed which implements the basic ideas of (i) the pom-pom model, (ii) hierarchical relaxation, (iii) dynamic dilution, and (iv) interchain pressure. It is based on the assumption that stretch and orientation are coupled, and stretch is implemented through a tube diameter which decreases with increasing deformation. Therefore, stretch and orientation of tube segments have the same dynamics as characterized by the linear-viscoelastic relaxation spectrum. In addition, a decrease of the tube diameter increases the interchain pressure which, in combination with the effect of dynamic dilution, sets a limit on the minimum tube segment diameter, and thereby the maximum stretch of the backbone chain segment for a given deformation rate. Dynamic dilution increases the tube diameter of the non-relaxed chains through the solvent effect of the already relaxed ones, which does not only affect the linear-viscoelastic properties but has also an effect on chain stretch, due to the reduction of the interchain pressure by dilation of tube diameter. The onset of dynamic dilution in a relaxation experiment occurs when the relaxation process has reached the dilution modulus $G_D \leq G_N^0$. The dilution modulus is a free parameter of the model, which needs to be fitted to non-linear viscoelastic experimental evidence, since the mass fraction of oligomeric chains

and un-entangled or marginally entangled chain ends, which cause permanent dilution, is not known a priori.

Here, we demonstrated that the HMMSF model, with only one free non-linear parameter, namely the dilution modulus G_D , is able to model the extensional viscosity data of a broadly distributed long-chain branched polymer melt in uniaxial, equibiaxial and planar deformation modes based exclusively on the linear-viscoelastic characterization. This shows that the fundamental concept of the HMMSF model, i.e. the coupling of anisotropic orientation as defined by the Doi-Edwards IA tensor S_{DE}^{IA} with isotropic stretch as expressed by the molecular stress functions f_i , is validated by comparison with experimental evidence in general biaxial flows.

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