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ORIGINAL CONTRIBUTION

On the universality in the extensional rheology of monodisperse polymer melts and oligomer dilutions thereof

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Abstract

The startup and steady extensional viscosities were measured on two narrow molar mass distributed (NMMD) poly(methyl methacrylates) (PMMA) diluted in 57% 2.1 kg/mole oligomer methyl methacrylates. The oligomer is short enough to be random configured and un-entangled though it is still a Kuhn chain. The weight-based average molecular weights of the PMMAs are 86 kg/mole and 270 kg/mole with polydispersites of 1.08 and 1.09 respectively. The extensional viscosities were in theoretical agreement with a constant 'interchain pressure' model, representing the maximal level of strain hardening in a Kuhn fluid. This has been observed for similar (styrene) oligomer diluted NMMD polystyrenes before, when the styrene oligomers were Kuhn chains. The original 'interchain pressure' model by Marrucci and Ianniruberto (Macromolecules 37(10):3934–3942, 2004), represents the minimal level of strain hardening in a Kuhn fluid. It has been shown previously to predict the extensional viscosities of NMMD polystyrene melts, and it is also in agreement with the extensional viscosities of the 86 kg/mole NMMD PMMA melt as well.

Keywords Poly(methyl methacrylates) · Monodisperse polymer melts · Oligomer dilutions · Extensional rheology · Interchain pressure

Introduction

The physics of polymer melt flow is still not established. Of particular importance is the modelling of flow of molten polymers in a production process. In this case, constitutive equations, capable of continuum mechanical simulations of the complex flow of molten polymers, are needed. To obtain experimental information of the flow physics of polymer melts, efforts have been put into flow measurement on particular monodisperse polymer systems. These are the theoretical simplest systems as they only contain one length of polymers. Particular uniaxial extension has been of interest due to its sensitivity to change in the material's property and composition. The extension of a nearly monodisperse polymer melt was initiated by Vinogradov et al. (1975). They measured the startup of uniaxial extensional stress of narrow molar mass distributed (NMMD) polyisoprenes. The samples failed at Hencky strain values at about and below 2 limiting its theoretical impact. In an effort to understand the flow dynamics of entangled monodisperse polymer system, Bhattacharjee et al. (2002) measured the steady extensional stress on NMMD polystyrene solutions. Bach et al. (2003a), likewise, measured it on NMMD polystyrene melts, showing substantially less strain hardening than the solutions. Further, Nielsen et al. (2009) observed that the startup of (uniaxial) extensional stresses on NMMD polyisoprene showed stress values in-between polystyrene melts and solutions. A similar behaviour has been observed for a NMMD poly(n-butyl acrylate) (Sridhar et al. 2014). To understand the difference between the flow behaviour of polymer melts and solutions, Huang et al. (2013) measured the startup and steady extensional viscosities of polystyrene diluted in styrene oligomer. When the oligomer had at least two Kuhn segments, i.e. was a Kuhn chain, the dilution showed the same behaviour in extensional stresses as NMMD polyisoprene and poly(n-butyl acrylate). If not, the dilutions behaved as a solvent based system. The extensional stress in polymers solutions and melts differs fundamentally. The diluent has to

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Table 1 NMMD poly(methyl methacrylates) (PMMA) and oligomer methyl methacrylates (OMMA) molecular weights from Wingstrand et al. (2015)

Name	M_w	M_w/M_n
OMMA2k	2.1 kg/mole	1.22
PMMA86k	86 kg/mole	1.08
PMMA270k	270 kg/mole	1.09

be a Kuhn chain for the diluted polymer to behave similar to polymer melts. Currently, it seems as the extensional stresses in undiluted NMMD polystyrene are somewhat unique, compared to the similar measurements on NMMD PI and poly(n-butyl acrylate) melts, as wells dissolved polymer systems. The extensional stresses are considerably lower in the undiluted NMMD polystyrene measurements. Notice that the original extensional measurements on NMMD polystyrenes by Bach et al. (2003a), using a filament stretching rheometer (Sridhar et al. 1991; Bach et al. 2003b), have been reproduced by independent researchers using (Luap et al. 2005) a Meissner rheometer (Meissner and Hostettler 1994). Here, we will study the extensional viscosities in NMMD poly(methyl methacrylate) (PMMA), both as pure melt and oligomer dilutions. We will present new extensional stress measurement on oligomer dilutions NMMD PMMA. Compared with the similar measurement in Wingstrand et al. (2015), we measure in a wider range of extensional rates.

Materials and characterisation

Materials

We particular investigate the extensional viscosity of two NMMD PMMA oligomer dilutions at the same concentration. It involves a (43% weight fraction) 86 kg/mole and a 270 kg/mole PMMA diluted in 2.1 kg/mole oligomer methyl methacrylates (OMMA). The polydispersites M_w/M_n were measured to 1.08 and 1.09 for the 86 kg/mole and 270 kg/mole PMMA polymers, respectively. The polydispersity of the OMMA was 1.22. The average molecular weights are weight-based, i.e. M_w. M_n is the mole-based average molecular weight. The PMMA polymers are the same materials as in Wingstrand et al. (2015), and the molecular weights were measured by Wingstrand et al. (2015) as well (listed in Table 1), using size exclusion chromatography (SEC). The weight fraction of the PMMA in the oligomer dilutions, θ (Table 2), were confirmed by the peak areas of the bimodal curve in the SEC. The glass transition temperatures, T_g, were measured by differential scanning calorimetry (DSC). About 4 mg of the sample was positioned in a hermeneutic pan using a TA Q1000 with a heating of 10 °C/minute. All materials were prepared and samples shaped using the procedures described in Wingstrand et al. (2015).

Mechanical spectroscopy

The PMMA270k/OMMA2k blend (see Table 2) and PMMA86k melt (see Table 2) were characterised with mechanical spectroscopy by Wingstrand et al. (2015). The mechanical spectroscopy of the samples, under N_2 atmosphere, were measured using an Ares G2 rheometer from TA instruments. The small amplitude oscillatory shear measurements were performed using an 8-mm plate-plate geometry with a gap of about 0.8 mm. All measurements where time temperature shifted to a temperature of 150 °C. The same procedure was applied to the PMMA86k/OMMA2k blend (see Table 2) here.

To quantify the small amplitude oscillatory shear measurements by linear viscoelasticity, the memory function, $M(t-t')$, from Baumgaertel, Schausberg and Winter (BSW) (Baumgaertel et al. 1990; Baumgaertel and Winter 1992), is used here. It was given as follows:

$$M(t-t') = \int_0^\infty \frac{H(\tau)}{\tau^2} e^{(-(t-t')/\tau)} d\tau, \tag{1}$$

$$H(\tau) = n_e G_N^0 \left[\left(\frac{\tau}{\tau_d}\right)^{n_e} + \left(\frac{\tau}{\tau_c}\right)^{-n_g} \right] h(1-\tau/\tau_d). \tag{2}$$

$h(x)$ is the Heaviside step function where t and t' are the present and past time respectively. τ_d is the maximal

Table 2 Linear viscoelastic parameters of the poly(methyl methacrylates) (PMMA) melt and blends at 150 °C

Melts	θ	G_N^0	τ_d	τ_c	Z	N_K/Z	T_g
PMMA86k	1	1150 kPa	550 s	0.15 s	15.9	9	122.8 °C
PMMA86k/OMMA2k	0.43	130 kPa	5.6 s	0.02 s	6.8	20.9	90.4 °C
PMMA270k/OMMA2k	0.43	130 kPa	1000 s	0.04 s	21.5	20.9	108.6 °C

The molecular weights are listed in Table 1. The weight fraction of the largest polymer chains in the polymer/oligomer blend is θ. The values of $n_e = 0.2$ and $n_g = 0.7$. The remaining relevant parameters are obtained from mechanical spectroscopical measurements, as shown in Fig. 1, fitting the relevant parameters in the BSW model (2) (Rasmussen et al. 2000). The parameters for the PMMA270k/OMMA2k blend were obtained by Rasmussen and Huang (2017). The values $M_k = 0.6$ kg/mole and $M_e = 5.4$ kg/mole have been used in the calculation of the number of Kuhn steps, N_K, and the number of entanglements, Z, respectively relaxation time and τ_c is the characteristic relaxation time of the glassy modes. G_N^0 is the plateau modulus. As in Rasmussen and Huang (2017), we use the fixed values of $n_e = 0.2$ and $n_g = 0.7$ for all PMMA samples. The remaining three linear viscoelastic parameters are obtained by fitting the measured mechanical spectroscopic data to the BSW model (Rasmussen et al. 2000). The parameters for the PMMA270k/OMMA2k blend were obtained by Rasmussen and Huang (2017). The mechanical spectroscopic measurements for the PMMA86k melt (from Wingstrand et al. 2015) and the PMMA86k/OMMA2k blend with the corresponding fittings are shown in Fig. 1.

Extensional measurements

The extension measurements on the PMMA blends were performed using an in-house developed filament stretching rheometer (FSR) (Bach et al. 2003b; Marin et al. 2013). The PMMA blends were moulded into cylindrical-shaped samples with initial diameter, D_i, of 5.4 mm and heights, L_i, of 1.5–2.5 mm. $D(t)$ is the central diameter. The samples were pre-stretched to a central diameter, D_0, in the range of 2.5–5.2 mm, with a rate considerably slower than the inverse of the largest relaxation time (of the particular sample). The Hencky strain is calculated as $\epsilon(t) = -2\ln(D(t)/D_0)$ and the extensional viscosity as $\eta_E^+ = (\sigma_{zz} - \sigma_{rr})/\dot{\epsilon}_0$. σ_{zz} and σ_{rr} are the axial (the drawing direction) and radial components of the stress tensor, σ, respectively. $\dot{\epsilon}_0$ is the (constant) applied extensional rate, defined as $\dot{\epsilon} = d\epsilon/dt$. The sample is stress relaxed before the initiation of the stretch (at $t = 0$). At small values of the Hencky strain, pre-stretched strain and aspect ratio a shear contribution may add to the measured extensional viscosity. We have used the stress correction formula from Rasmussen et al. (2010) to obtain the correct, ideally within 3%, initial extensional viscosities in these cases. All the extension measurements were time-temperature shifted to 150 °C.

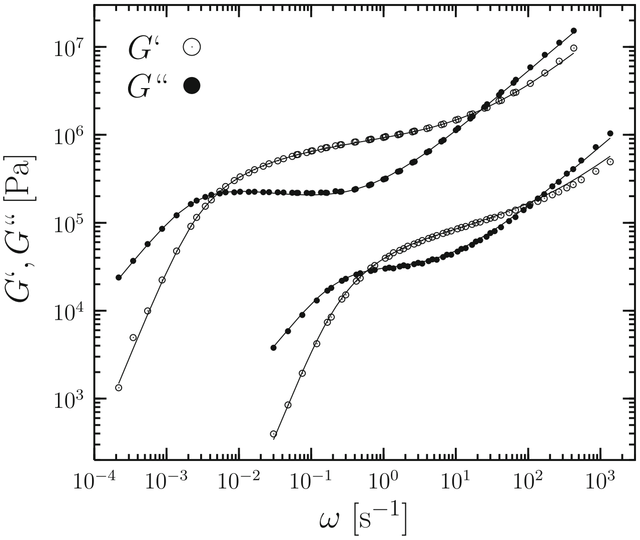

Fig. 1 Loss, G'' (open circles; ∘) and storage moduli, G' (bullets; •), both as a function of the angular frequency ω measured at 150 °C for the $\theta = 0.43$ (43%) PMMA86k/OMMA2k blend and PMMA86k melt. The solid lines (——) are the least-square fittings to the BSW model in Eq. 2

Constitutive models

A variety of models considering the flow of polymer systems have been published in the recent years, meant to predict the fluid mechanics of polymer systems in general (Yaoita et al. 2012; Park et al. 2012; Andreev et al. 2013). Concerning monodisperse polymer melts system (Doi and Edwards 1978, 1986) initiated the constitutive modelling with a model based on pure orientational stress. The idea of chain stretch was introduced by Marrucci and co-workers (Marrucci and de Cindio 1980; Marrucci and Grizzuti 1988). All the following suggested constitutive equations were based on a chain stretch. It is generally accepted and shown in both shear (Osaki et al. 2000; Menezes and Graessley 1982; Takahashi et al. 1993) and extension (Bhattacharjee et al. 2002) that the strain hardening in the flow depends on the Rouse time, τ_R, all suggesting a dependence of the Rouse time as the square of the number of entanglements, Z. Particular concerning monodisperse systems, to explain the transition from melts to solutions, the interchain pressure (Wagner 2014) and monomeric friction (Yaoita et al. 2012; Ianniruberto et al. 2012) have been considered. None of the referred models, and any other according to our knowledge, seems to be able to address the differences in NMMD melt uniaxial extensional behaviour.

Here, we will analyse the extensional viscosities using on the molecular stress function (MSF) constitutive framework (Wagner et al. 2005; Wagner and Rolón-Garrido 2010; Wagner et al. 2018). In the MSF constitutive framework, the components, σ_{ij}, of the stress tensor were defined as follows:

$$\sigma_{\mathrm{ij}} = \int_{-\infty}^{t} M(t-t') f(\boldsymbol{x}, t, t')^2 5 \times \left\langle \frac{[\mathbf{E}(\boldsymbol{x}, t, t') \cdot \mathbf{u}][\mathbf{E}(\boldsymbol{x}, t, t') \cdot \mathbf{u}]}{|\mathbf{E}(\boldsymbol{x}, t, t') \cdot \mathbf{u}|^2} \right\rangle dt' \quad (3)$$

with an initial value of the molecular stress function of $f(\boldsymbol{x}, t', t') = 1$. Here, $\mathbf{E}(\boldsymbol{x}, t, t')$ is the displacement gradient tensor. Its components are defined as $E_{\mathrm{ij}}(\boldsymbol{x}, t, t') = \partial x_{\mathrm{i}}/\partial x_{\mathrm{j}'}$, $\mathrm{i} = 1, 2, 3$ and $\mathrm{j} = 1, 2, 3$. $\boldsymbol{x} = (x_1, x_2, x_3)$ and (x_1', x_2', x_3') are the Cartesian coordinates of the same particle in the present, t, and past time, t', respectively. All angular brackets are unit sphere integral, given as $\langle \ldots \rangle =$

$1/(4\pi)\int_{|\mathbf{u}|=1}\ldots d\mathbf{u}$. $\mathbf{u}$ is the unit vector. The analytical solution of all involved unit sphere integrals can be found in Urakawa et al. (1995).

Here, we will particularly consider two constitutive models. Both are based on the interchain pressure (Marrucci and Ianniruberto 2004). Marrucci and Ianniruberto (2004) suggested that in a monodisperse polymer melt, the interchain pressure increases as the chains extend. This effectively reduces the strain hardening to a minimum level. Rasmussen and Huang (2014) suggested that in an oligomer dilution, the oligomer Kuhn chain will be in a random configuration imposing a constant interchain pressure on the long polymers. This maximised the strain hardening in a structured (i.e. Kuhn) fluid. In a MSF framework (Wagner et al. 2005), the interchain pressure stretch evolution is given as follows:

$$\frac{\partial}{\partial t} f(\boldsymbol{x},t,t') = f(\boldsymbol{x},t,t')\left[\frac{\partial}{\partial t}\left\langle \ln\left|\mathbf{E}(\boldsymbol{x},t,t')\cdot\mathbf{u}\right|\right\rangle - \frac{f(\boldsymbol{x},t,t')}{3\tau_R}\left(f(\boldsymbol{x},t,t')^3-1\right)\right]. \tag{4}$$

for the model suggested by Marrucci and Ianniruberto (2004), and

$$\frac{\partial}{\partial t} f(\boldsymbol{x},t,t') = f(\boldsymbol{x},t,t')\left[\frac{\partial}{\partial t}\left\langle \ln\left|\mathbf{E}(\boldsymbol{x},t,t')\cdot\mathbf{u}\right|\right\rangle - \frac{1}{\tau_R}\left(c(f(t,t'))f(\boldsymbol{x},t,t')-1\right)\right] \tag{5}$$

in the case of the constant 'interchain pressure' (Rasmussen and Huang 2014). These depend on the Rouse time, τ_R. In the latter one, Rasmussen and Huang (2014) used the transition to a maximum extensibility as the relative Padé (Cohen 1991) inverse Langevin function as suggested by Ye and Sridhar (2005):

$$c(f) = \frac{(3-f^2/\lambda_{\max}^2)(1-1/\lambda_{\max}^2)}{(3-1/\lambda_{\max}^2)(1-f^2/\lambda_{\max}^2)}. \tag{6}$$

$\lambda_{\max}$ is the maximal relative stretch. These two functional for the molecular stress function depends solely on the rouse time and a maximal relative stretch. A transition in these two functionals has as yet not been suggested, to describe a continuous transition from oligomer dilutions to pure melt systems. The maximal relative stretch is limiting the molecular stress function, in Eq. 5, to below this value. This avoids the divergence of the steady extensional stress. The stretch is the square root of the number of Kuhn steps between entanglements, N_e, for the particular polymer, given as follows:

$$\lambda_{\max} = \sqrt{N_e} = \sqrt{N_K/Z}. \tag{7}$$

$N_K = M_w/M_K$ is the number of Kuhn steps in the polymer chain where M_K is the Kuhn step molecular weight. It is expected to be independent of the degree of the oligomer dilution, θ. As in Rasmussen and Huang (2017), we will use the M_K value of atactic PMMA of 0.6 kg/mole (Fetters et al. 2007). Both PMMAs were synthesized (Wingstrand et al. 2015) by living anionic polymerisation using the same initiator giving the same tacticity, although the stereoisomeric structures of involved PMMAs are not clearly defined. A linear dependency on the number of entanglements with the concentration, $Z = M_w(\theta/M_e)$, is expected. As in Rasmussen and Huang (2014), we use the value of the entanglement molecular weight M_e of 5.4 kg/mole for both involved PMMA melts. The value of 5.4 kg/mole for M_e lies between the 5 and 6 kg/mole given by Wingstrand et al. (2015). This interval was based on the assumption of identical mechanical spectroscopic data with the same number of entanglements. A comparison with NMMD polystyrenes was made, with the assumption of an entanglement molecular weight of 13.3 kg/mole for polystyrene.

Results and discussion

The Rouse time, scaled relative to the relaxation time, depends on the number of entanglement. In Rasmussen and Huang (2017), the Rouse time was fitted to a set of extensional viscosities measured using the same 270k NMMD PMMA as the one here though diluted in 56% 3.5 kg/mole OMMA. With an expected squared dependency of the Rouse time on the entanglement number, a relation of

$$\tau_d/\tau_R = 50\cdot(Z/22)^2 \tag{8}$$

were obtained. We use the same relation her. Notice the proportionality factor (here of 50 for PMMA) is not identical to the corresponding values for other polymers (Rasmussen 2015).

In Figs. 2 and 3 the extensional measurements on the two oligomer dilutions are presented, showing the extensional viscosities as a function of the time at increasing extensional rates from the right to the left curves. The Rouse times, τ_R, have been marked on the figures by the arrows on the time axis. This represents the shift between an extensional flow dominated by pure configurational orientations at large time scales, and the strain hardening occurring at fast flows. We have added the corresponding theoretical model predictions to the experiments for the constant interchain pressure with (i.e. $\lambda_{max}^2 = 20.9$) and without (i.e. an infinite value of λ_{max}) the maximal extensibility, applying the Eqs. 5 and 6. These are the solid and dashed lines in the figures respectively. Due to the different polymer lengths in the two samples the Rouse time, relative to the relaxation time, is a factor of 10 different to each other. A good agreement between the models based on the constant interchain pressure assumption has been obtained in the

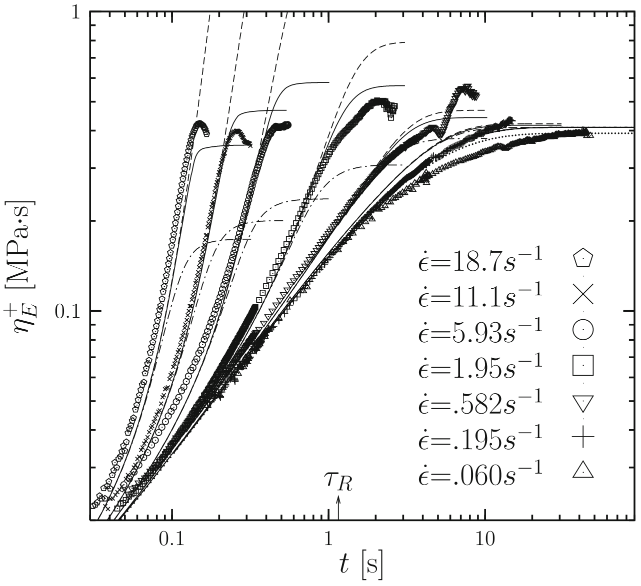

Fig. 2 The startup of extensional viscosity, η_E^+, as a function of time at 150 °C. The symbols are measurements on the (θ = 0.43) PMMA86k/OMMA2k blend (43% 86 kg/mole diluted in the 2.1 kg/mole oligomer). The dots ($\cdots$) are the linear viscoelastic extensional viscosity using Eq. 2 with the parameters listed in Table 2 . The solid lines (——) are the constant interchain pressure model Eq. 5 with a maximum extensibility of $\lambda^2_{\max}$=20.9. The dashed lines (- - -) are the corresponding predictions to the data from the Eq. 5 without a limit on the chain extensibility. The dashed-dotted lines (- · - · -) are the corresponding predictions to the data from the Eq. 4

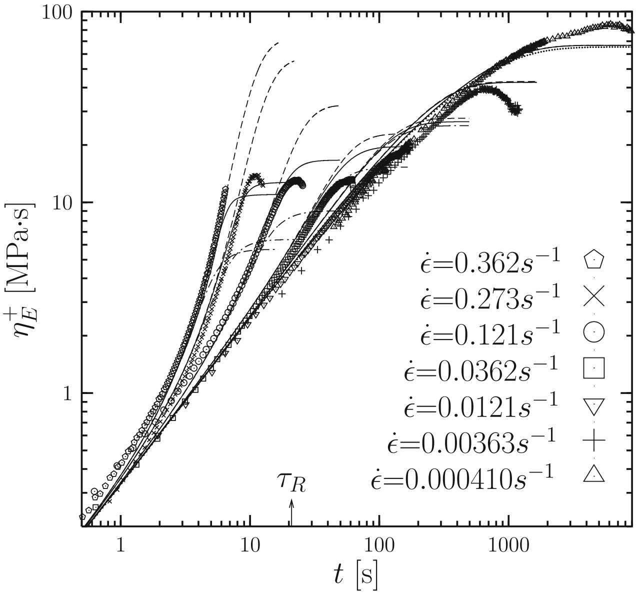

Fig. 3 The startup of extensional viscosity, η_E^+, as a function of time at 150 °C. The symbols are measurements on the (θ = 0.43) PMMA270k/OMMA2k blend (43% 270 kg/mole diluted in the 2.1 kg/mole oligomer). The dots ($\cdots$) are the linear viscoelastic extensional viscosity using Eq. 2 with the parameters listed in Table 2. The solid lines (——) are the constant interchain pressure model Eq. 5 with a maximum extensibility of $\lambda^2_{\max}$=20.9. The dashed lines (- - -) are the corresponding predictions to the data from the Eq. 5 without a limit on the chain extensibility. The dashed-dotted lines (- · · · · -) are the corresponding predictions to the data from the Eq. 4

startup of the extensional flow region, confirming both the use of the relation for the Rouse time and the constant interchain pressure, as a model for these diluted systems. With the use of the same oligomer concentration of 57% in the two OMMA dilution used here, they ideally have the same maximal extensibility with a λ_{max} value of about 4.6. With the use of the limit imposed by the chain extensibility the transition to extensional viscosity shows a maximal deviation of about 20% compared to the experiments. We have also added the model prediction from the Eq. 4, ideally expected to be a model for the flow behaviour of an undiluted monodisperse polymer melt, as suggested by Marrucci and Ianniruberto (2004). It is represented by Eq. 4. It is the dashed-dotted line in the Figs. 2 and 3. The model predictions stay as expected well below the experimental values. Equation 4 had been presented without a maximal extensibility. The inclusion of a maximal extensibility in this equation has currently not been relevant. At the extensional conditions presented in Figs. 2 and 3, steady levels of the viscosities will be lowered, somewhat, further below the experimental values if a maximal extensibility is included. Though it is not theoretically clear on how exactly it should be formulated.

The two models quantified in Eqs. 4 and 5 represent the minimal and maximal level of strain hardening in a Kuhn fluid, respectively. NMMD polystyrene melts follows the minimal level (Eq. 4). Intermediate behaviour has actually been observed in the extension of NMMD polystyrene dilutions with styrene oligomer concentration of 10% and 30% (Huang and Rasmussen 2017). At higher oligomer concentrations, shown at and above 47%, the assumption of the constant interchain pressure assumption (Eq. 5) seems to hold accurately. The involved styrene oligomers were all Kuhn chains without entanglements. The relation in (5) has been shown to be valid for a wide range of oligomer NMMD polystyrene dilutions (Huang and Rasmussen 2017) as well on bidisperse systems of polystyrene and polyisoprene, as long as the short chains are in random configurations. More surprisingly, agreement with the constant interchain pressure in Eq. 5 has been observed for NMMD polyisoprene (Rasmussen 2016) and poly(n-butyl acrylate) melts as well (Sridhar et al. 2014).

The use of the maximal extensibility seems to be valid for the diluted NMMD PMMA systems. Previously, the validity of the maximal extensibility has currently only been confirmed in bidisperse, including oligomer, polystyrene systems. Experimentally, it is a challenging task to measure the steady extensional viscosities, η_E (see Fig. 4), particularly for monodisperse polymer melt systems. The maximal extensibility has not been included in

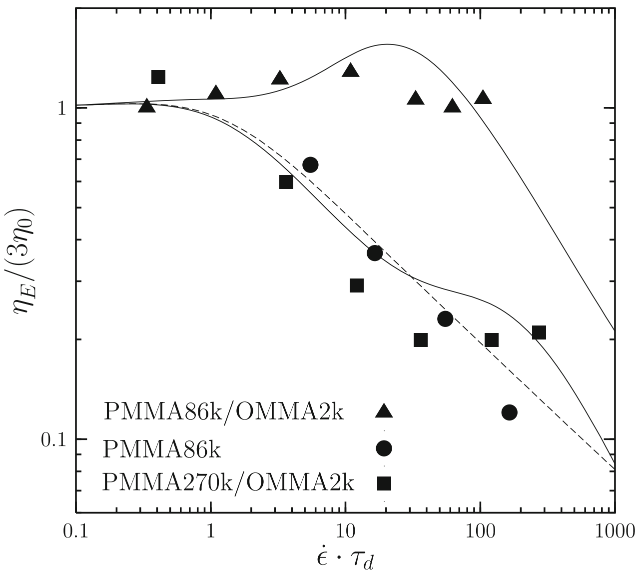

Fig. 4 Steady extensional viscosity, η_E, relative to the zero extensional rate viscositiy, $3\eta_0$, as a function of the extensional rate, $\dot{\epsilon}$, multiplied with the maximal relaxation time, τ_d. The solid lines (——) are the corresponding predictions to the PMMA270k/OMMA2k (triangles) and PMMA86k/OMMA2k data (boxes) using the constant interchain pressure model Eq. 5, both lines with a maximum extensibility of $\lambda^2_{\max}$=20.9. The dashed line (- - -) is the interchain pressure model from Eq. 4 corresponding predictions to the 86k NMMD PMMA melt data (bullets) from Morelly et al. (2019)

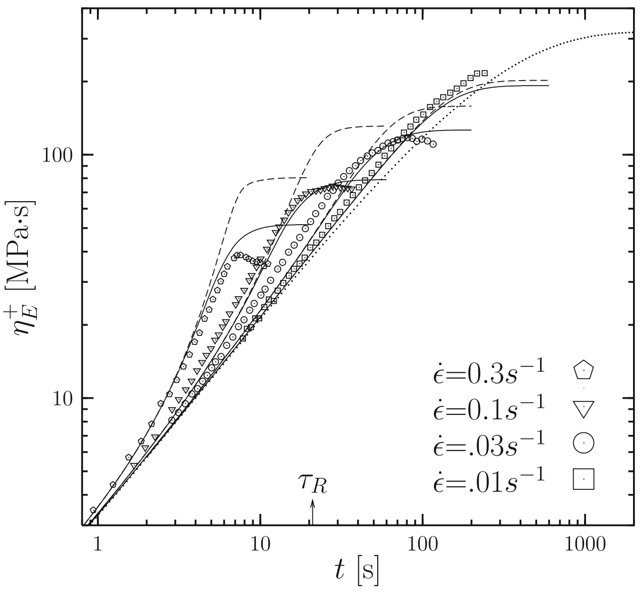

Fig. 5 The startup of extensional viscosity, η_E^+, as a function of time at 150 °C from Morelly et al. (2019). The dots (···) are the linear viscoelastic extensional viscosity using Eq. 2 with the parameters listed in Table 2. The solid lines (——) are the interchain pressure model from Eq. 4. The dashed lines (- - -) are the corresponding predictions to the data from Eq. 5 with the limit on the chain extensibility of $\lambda_{\max}$=3

Eq. 4, though the maximal extensibility is theoretically at its lowest value in (undiluted) monodisperse melts. Currently, in NMMD polystyrene melts, the measured extension rates have not been sufficiently high to create a significant effect of the inclusion of a maximal extensibility in Eq. 4. The extensional thickness in the steady viscosity, as seen here in Fig. 4 for the MMA86k/OMMA2k blend, is a commonly observed phenomenon in NMMD polymer melts, dilutions or solutions. The actual onset, or lack of it, depends on the particular sample as it is an effect of the strain hardening initiated at the Rouse time.

In Fig. 5, we have shown the measured startup of extensional viscosities by Morelly et al. (2019) on the undiluted 86k NMMD PMMA melt, measured at four different extensional rates. Morelly et al. (2019) measured the startup of extensional viscosities on the same PMMA batch as the one here, and used the same FSR as the one used here. The 86k NMMD PMMA has a number of entanglement of 15.9. This is in between the corresponding values for the two dilutions as seen in Table 2, having 6.8 and 21.5 entanglements, respectively. The arrow on the time axis in Fig. 5 is the Rouse time of the melt. Both interchain models quantified in Eqs. 4 and 5 have been added in the figure as well. The latter one with a maximal extensibility $\lambda_{\max}$ of 3, the ideal value for the undiluted PMMA. This is a value somewhat lower than the value of 4.7 for monodisperse polystyrene melts. As in NMMD polystyrene melts, the agreement seems to be in accordance with the idea of Marrucci and Ianniruberto (2004). Further, the measurements cannot be used to conclude on an effect of a potential maximal extensibility in the use of Eq. 4.

Summary and conclusion

We have measured the startup of uniaxial extensional viscosities and the steady viscosity on two oligomer diluted NMMD poly(methyl methacrylates), both diluted in 57% 2.1 kg/mole oligomer methyl methacrylate. Both dilutions, having 6.8 and 21.5 entanglements, were measured within broad ranges of extensional rates, below and above the Rouse time. Both extensional viscosity series follow a MSF constitutive model, based on a constant interchain pressure. It is a model for the flow of an idealised solution of a monodisperse polymer in a structured diluent (i.e. consisting of Kuhn chains), appearing in a random configuration. This is the maximal possible level of extensional strain hardening in an ideally structured fluid. The steady viscosities were in agreement with a finite chain extensibility of (undiluted) PMMA of 3, based on the Kuhn steps in one entanglement, and the assumption of an ideal dilution. Further, the uniaxial extensional viscosities measured by Morelly et al. (2019) on an undiluted NMMD poly(methyl methacrylate) melt, with 15.9 entanglement, follows the interchain pressure model by Marrucci and Ianniruberto (2004) representing the minimal hardening in a Kuhn fluid. Undiluted and oligomer methyl methacrylate diluted NMMD PMMA melts behave theoretically similar to NMMD polystyrenes systems.

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