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Experimental considerations on the step shear strain in polymer melts: sources of error and windows of confidence

Huagui Zhang, Khalid Lamnawar,
Abderrahim Maazouz, João M. Maia

Abstract Shear step strain experiments with various strain amplitudes have been performed on poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) melts using both stress-controlled and strain-controlled rheometers. Firstly, the onset of the rheological nonlinearity, i.e., nonlinear stress damping behavior, occurring after a large step strain is found to be a phenomenological consequence of an abrupt stress decline within the transient period of strain actuation. Such a feature, analogous to the stress overshoot in a fast startup shear with sufficiently high rates, is interpreted based on theoretical frameworks concerning chain disentanglement/re-entanglement arising from chain retraction. Furthermore, this work infers that full technical considerations in step strain experiments are indispensable for acquisition of accurate stress relaxation data, as some common but easily overlooked technical problems are influential, probably introducing errors. For instance, a too long finite rise time and a stress overload enable to hinder the nonlinearity onset in the transient period, resulting in inaccurate experimental data. In this

sense, the stress-controlled rheometer is advantageous relative to the strain-controlled one, although the inertia in the stress-controlled mode incurs a strain overshoot effect. Nevertheless, the amplitude-dependent strain overshoot offers a very subtle effect on the stress damping behavior. Moreover, transducer compliance problems need to be taken into account, especially for high stiffness polymers. Overall, the effects of such technical factors are dictated by their ability to influence the chain stretching/retraction and the disentanglement. A well-considered experimental methodology is necessary to achieve confidence windows in step strain experiments for analysis accuracy.

Keywords Step strain · Relaxation behavior · Nonlinear rheology · Transient period · Stress damping · Disentanglement/re-entanglement theory · Melt and polymer solutions

Introduction

Stress relaxation after a step strain, especially with high strain amplitudes, is quite an important measurement tool for stress modulus determinations of materials either the neat polymers or the blends/composites (Dealy and Larson 2006; Filipe et al. 2006; Silva et al. 2007). Nevertheless, it is a question whether a “step strain” is a real step strain and whether the “instantaneous” is real instantaneous. Despite of the eminent progress in modern rheometers, it is still impossible to impose experimentally a perfect step strain, instead, a finite rise time, t_0 , is required in practice to actuate a desired strain, since the rotational rheometer components and the fluid have inertia and cannot be instantaneously accelerated. To the best of our knowledge, not enough attention has been paid to the transient period of the strain imposition (Laun 1978; Vrentas and Graessley 1981, 1982). The main open questions are what

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happens to the actual strain variation in the transient period when a prescribed “step” amplitude is being imposed and whether the data in that period are utilizable. Meanwhile, if the experimental data at short times are unreliable, what is the confidence window of the data for stress relaxation modulus?

Hence, researchers should care about the experimental problems and the data accuracy analysis in the step strain experiments, especially in the transient period where the strain is actuated. In fact, some few papers have been dedicated to the technical limitations and the experimental data analysis, wherein several factors have been mentioned to be influential in the relaxation modulus measurement (Venerus 2005; Gevgilili and Kalyon 2001). They are finite rise time (imperfect strain history), wall slip, transducer compliance, strain inhomogeneity, etc.

In a typical step strain experiment, upon a sudden shear deformation γ_0 , the decay of the shear stress $\sigma(t)$ is measured versus time, which is universally expressed in a function of stress relaxation modulus $G(\gamma_0, t)$ via:

$$G(\gamma_0, t) = \sigma(t)/\gamma_0 \quad (1)$$

When the imposed shear strain is small enough, $G(\gamma_0, t)$ becomes strain independent, equaling to the linear relaxation modulus $G(t)$. In the case of a large strain, $G(\gamma_0, t)$ is typically separable above a characteristic time, t_c , into a strain-dependent function $h(\gamma_0)$ and a time-dependent linear relaxation modulus $G(t)$, i.e.:

$$G(\gamma_0, t) = G(t)h(\gamma_0) \quad (2)$$

$h(\gamma_0)$ is the so-called damping function, which is used to describe the rheological nonlinearity. For such damping function, Rolon-Garrido and Wagner (2009) have recently published a review paper addressing its theoretical background and the physical interpretation. The characteristic time t_c is the onset time of the time-strain separability, which is predicted to be of the same order of the Rouse relaxation time of the tested polymer chains according to the original tube model of Doi and Edwards (1986), a theory improved from the first work of de Gennes (1971). Nevertheless, most experimental findings indicate that t_c is closer to the order of the longest reptation relaxation time, τ_{rep} . The progressively evolved tube theories described the nonlinear features of stress relaxation process based on a concept of chain retraction upon affine deformation and consequent convective chain release (CCR) and finally loss of entanglements between chains (Marrucci 1996; Ianniruberto and Marrucci 2014; Graham et al. 2003). This is conceptually equivalent to the disentanglement by formation of a network strand proposed by Wagner and Meissner (1980), as well as a recent picture of force imbalance and elastic breakup proposed by Wang et al. (2007, 2013). In other works, refined theories have been developed for entangled polymer melts and concentrated solutions that include

mechanisms like chain retraction, CCR, disentanglement/re-entanglement, etc. More importantly, the rheological nonlinearity is so far also argued to be related to tube dilation and monomeric friction ζ reduction upon large flows (Ianniruberto and Marrucci 2014; Sussman and Schweizer 2012; Yaoita et al. 2012). Based on abundant literature, a consensus might be inferred that the nonlinear rheological features of the entangled polymers are relevant to chain disentanglement, i.e., tube dilation, resulting from chain retraction/stretching under large external deformations.

It is worthy of noticing that above the characteristic time, t_c , the stress relaxation moduli obtained at different strains become independent of strain amplitude and are superimposable by vertical shifting. Below t_c , more exactly during the transient period, one common feature being observed for large strains (Vrentas and Graessley 1982) is that the shear relaxation modulus (or shear stress) immediately experiences a rapid decline after the step strain imposition before returning to the normal relaxation shape. Nevertheless, most of the previous studies on the nonlinear relaxation behavior more often focus on the long-time behavior of the damping function, omitting or discarding the experimental data in the transient period (Vrentas and Graessley 1982; Stadler et al. 2008; Ferri and Greco 2006; Silva et al. 2007). That is, the rapid decline of $G(\gamma_0, t)$ in the short time period are neglected in most literature. Many of them attributed the data in this short period to be a result of the technical problems such as imperfect strain history (Vrentas and Graessley 1982; Venerus et al. 1990).

In some cases, however, data for short times (e.g., from 0.01 s) with the rapid $G(\gamma_0, t)$ decline included have been published. For instance, in the work of Archer and coworkers (Islam et al. 2001; Juliani and Archer 2001; Archer et al. 2002) concerning nonlinear shear relaxation of entangled polymer solutions, features of the rapid $G(\gamma_0, t)$ drop at short times were clearly displayed, although no particular explanation was given for them. Their step shear experiments were performed using a stress controlled rheometer (i.e., Anton Paar Physica Modular Compact Rheometer (MCR300)) equipped with stainless steel cone-and-plate fixtures, with the nonlinear step strains being imposed, as claimed by the authors, in less than 0.1 s for their materials. In their cases, they argued that it was appropriate to consider the imposed deformation as a step strain since the terminal relaxation time of the materials exceeded the strain imposition times by more than an order of magnitude. It is worthy of mentioning that both strain- and stress-controlled rheometers have been employed for step shear strain experiments, with the stress-controlled type being reported in the literature as popular as the strain-controlled one (Venerus 2005). The difference between these two types with regard to the step strain will be specified below. Recently, Wang and coworkers (Wang et al. 2006; Boukany and Wang 2009; Boukany et al. 2009) drew closer attention to characteristics like fast declining of shear stress in the transient period

and demonstrated that it is a result of nonquiescent relaxation behavior after large step strain with the aid of particle tracking velocimetric (PTV) technique. As explained by the authors, previous studies based on step strain experiments typically reported the relaxation data in a literal way in the form of the damping function, but with the more important data involving the actual time-dependent startup shear stress in the transient period omitted. They attributed the origin of the ultra strain softening around the t_c to be interfacial yielding and interfacial failure (i.e., chain disentanglement) after large deformation.

In fact, discarding or omitting the data of the short time period in analysis is partially for the reason to exclude the possible effect introduced by the finite time of strain imposition, or in other words, the imperfect strain history as well as the effect of instrument response times (Vrentas and Graessley 1981, 1982; Venerus et al. 1990). From this standpoint, for data reliability sake, a “rule of thumb” in the literature is to skip the data before $10 t_0$ (Dealy and Larson 2006; Rolon-Garrido and Wagner 2009), with t_0 being the finite rise time. Indeed, such common practice of simply ignoring the first $10 t_0$ of the relaxation data was demonstrated to be not valid for materials where the relaxation time is of the same order of magnitude of the ramp time (Flory and McKenna 2004). Here one question arises: does the rapid relaxation modulus $G(t, \gamma)$ decline that occurs immediately after the step strain result from a technical reason like the imperfect strain history or is it from a molecular reason like chain disentanglement, as proposed by Wang et al. (2007)? In the present study, we attempt to shed light on the short time period of a stress relaxation measurement after a step strain using both stress-controlled and strain-controlled rheometers.

To this end, emphasis is given to the possible origins of the onset of the rheological nonlinearity and its relations to some common technical problems that might generate errors. Hence, some pertinent originalities in this work are as follows: (1) to assess the comparability between stress-controlled and strain-controlled rheometers involving step strain experiments; (2) to check whether the data in the transient period can be taken into account or not. If not, what is the confidence window of the reliable data?; (3) to address some sources of error during a step strain experiment and define experimental protocols to obtain enough analysis accuracy; and (4) to reveal the underlying theoretical mechanisms behind the effects of the relevant experimental factors on the nonlinearity emergence and the experimental data reliability.

Experimental section

Materials

Poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) supplied by ARKEMA were used in this

study. Main material characteristics of these polymers are listed in Table 1. More information of the polymers' characterization could be found in our earlier work (Zhang et al. 2012, 2013).

Sample preparation for rheological measurements

All the polymers were dried at 80 °C under vacuum to remove any moisture before use. Specimens of round disk ($\phi=25$ mm) for rheological measurements were prepared by compression molding at 180 °C with a pressure of 200 bar between two Teflon films to obtain a smooth surface. All samples were prepared under identical processing conditions to eliminate sample-to-sample errors. To eliminate the possible effect of surface orientation brought about by the compression molding, all the disks were annealed at 80 °C under vacuum for at least 24 h before measurements.

Small-amplitude oscillatory shear measurements

Linear viscoelastic behavior of neat polymer melts has been measured at different temperatures using a stress-controlled rotational rheometer DHR-2 (Discovery Hybrid Rheometer, TA instrument) with a parallel plate geometry (diameter $\phi=25$ mm). During all the rheological experiments, nitrogen purging was maintained throughout the tests to avoid the potential degradation and oxidation of the polymers.

Stress relaxation measurement after a single step strain

Both types of stress-controlled rotational rheometer, DHR-2, and strain-controlled rotational rheometer, ARES (Advanced Rheometrics Expansion System, Rheometric Scientific, Inc.), were employed for step strain experiments. The polymer systems involved are PMMA, PVDF melts, with measurements done in a parallel plate geometry at 200 °C.

Experimental considerations for shear step strain

Cone-and-plate or parallel plate fixture?

Commonly, a cone-and-plate fixture is preferred to be used for step strain experiments thanks to its strain homogeneity. However, the obtainable maximum strain is very small, though beyond the linear viscoelastic region. The strain is limited by the maximum angular displacement θ_{\max} for a given cone angle α as $\gamma_{\max}=\theta_{\max}/\alpha$, especially for the strain-controlled rheometer. Hence, variation of the strain is available by changing the cone angle, which needs different fixtures. Another limitation for the cone-and-plate fixture, especially the small cone, is the potential high axial compliance that may be encountered against the stiffness of the rheometer in comparison to the parallel plate fixture (Alcoutlabi et al. 2009). Using

Table 1 Characteristics of the investigated polymers

Samples	Trademark/supplier	T_c (°C) ^a	T_g (°C) ^a	T_m (°C) ^a	M_w^b (g/mol)	M_w/M_n^b	Ea (kJ/mol) ^c
PVDF	Kynar 720/ARKEMA	136	-42	170	210,000	2.0	59
PMMA	V825T/ARKEMA	–	114	–	95,000	2.1	169

^a Measured in our laboratory by a TA Instruments Q20 DSC at a heating and cooling rate of 10 °C/min under N₂

^b Determined in our laboratory by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as the eluent for PMMA and dimethylformamide (DMF) for PVDF

^c Energy of activation of the viscous flow (Ea) obtained from $\ln\eta_0$ plotted versus $1/T$ within a temperature range of 180 °C < T < 240 °C

a parallel plate fixture, the maximum strain obtainable can be extended to a much larger amplitude by the varying gap, while the sensitivity to gap errors can be reduced (Soskey and Winter 1984; Stadler et al. 2008). For instance, using a Rheometrics dynamics spectrometer (RDS), Soskey and Winter (1984) were able to increase the strain to a very large value of 25 for low-density polyethylene (LDPE) in their experiments. Using a Bohlin CVOR stress-controlled rotational rheometer with parallel plate fixture, Stadler et al. (2008) carried out their step strain experiments of polypropylene to a large amplitude of 70.

The main problem in the parallel plate fixture is associated with the strain nonhomogeneity along the radial direction. This requires a correction for the determination of the relaxation modulus of large strains. Soskey and Winter (1984) proposed a correction method for the $G(t, \gamma_0)$ by incorporating a term calculated from the double-logarithmic derivative of the apparent relaxation modulus $G_{app}(t, \gamma_0)$ with respect to the deformation via

$$G(t, \gamma_0) = G_a(t, \gamma_0) \left(1 + \frac{1}{4} \frac{\partial \lg G_a(t, \gamma_0)}{\partial \lg \gamma_0} \right) \quad (3)$$

At low strains, γ_0 , the correction factor $d \lg G_a(t, \gamma_0) / d \lg \gamma_0$ in the right term of Eq. 3 approaches zero. At larger strains, the factor becomes increasingly negative. In the present study, the maximum strain involved is no more than 5.0 for the PMMA and the PVDF melts, in which cases the actual $G(t, \gamma_0)$ was evaluated to be only 10~15 % negatively deviated from the apparent one, $G_a(t, \gamma_0)$. This is not very significant compared to the ~50 % in the studies of Soskey and Winter (1984) and Stadler et al. (2008) for their very large strains (i.e., 25 and 70, respectively). For simplicity purposes, the measured $G(t, \gamma_0)$ are directly used for discussion as apparent relaxation modulus in this work.

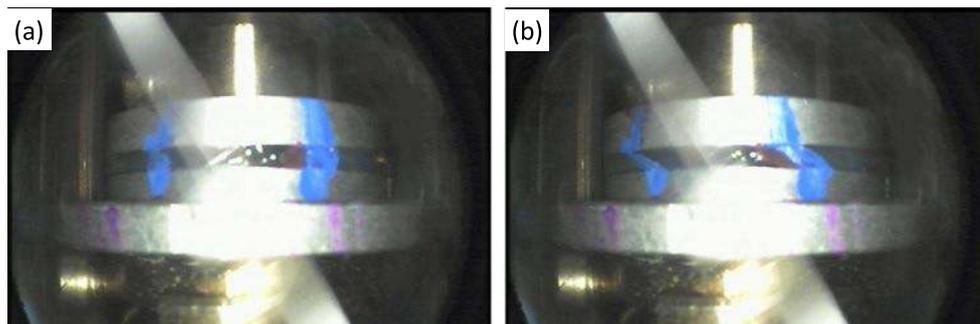
Wall slip

One of the most important experimental artifacts and error sources in large step strain measurements comes from wall slip occurring due to entanglement loss at the interface between polymer melt and plate metal (Gevgilili and Kalyon

2001; Rolon-Garrido and Wagner 2009). It is worth noting that the anomalous loss of $G(t, \gamma_0)$ observed in some cases where the damping function $h(\gamma_0)$ is categorized into type C, that is, $h(\gamma_0)$ is lower than the DE tube model prediction, was hitherto believed to be consequence of wall slip (Rolon-Garrido and Wagner 2009). To avoid or minimize such experimental problems, some care must be taken in performing the experiments. One preferred practice is to equilibrate the samples at the measured temperature for sufficient time before testing, for the sake of increasing the adhesion between the polymers and the metal plates. Besides, disposable aluminum plates have been demonstrated to be better than stainless steel ones for polymer adhesion, partially due to its unmirror-like polished surface (Ferri and Greco 2006; Gevgilili and Kalyon 2001). Meanwhile, the aluminum plates are able to be scratched in order to increase the surface roughness, thus decreasing the interfacial tension between the metal and the polymer and enhancing adhesion. Note that an interesting tactic, as executed by Gevgilili and Kalyon (2001), to document whether or not wall slip happens during the step strain experiments, is to use a straight-line marker line. Specifically, in this work, the straight marker line was placed perpendicular to the parallel plates, covering the edges of the fixtures and the edge surface of the specimen before the step strain was imposed (Fig. 1a). During the imposition of the shear strain, the motion of the fixture and the resulting deformation of the specimen at its edge were continuously monitored and recorded with the cameras installed inside the rheometer.

In Fig. 1 that shows an example of PVDF melt before and after a step strain of 5.0 being imposed, the marker line continuity at the metal/polymer melt interface holds during the imposition of the strain. In principle, if wall slip happens during the imposition of a step strain, the marker line should experience a discontinuity at the metal/polymer interface. The line continuity in this work indicates that wall slip was not occurring; in these experiments, we allowed sufficient time for thermal equilibration before running a test and disposable aluminum plates were employed. In addition, it was reported that a minimum shear stress of 10^5 Pa is needed for the onset of wall slip in a polymer melt (Lee et al. 2009). In our work, the shear stress is limited to be around 6.5×10^4 Pa due to the limitation of the instrument compliance. It is necessary to

Fig. 1 Images of the PVDF melt in a step strain experiment with a commanded strain at T200 °C: **a** before step strain; **b** after a step strain of 5.0. Continuity of the straight marker line indicates no wall slip



mention that we have also checked the wall slip problem according to the method of Yoshimura-Prud'homme (1998) by rerunning experiments with varied gap heights. The experimental data obtained therein are basically reproducible for a given strain amplitude, implying no wall slip.

Minimization of finite rise time

In the rheometer, the strain is ramped up to the desired value over a very short, nevertheless measurable, period of finite rise time, t_0 (or somewhere named Δt). With regard to this point, a number of previous studies have been carried out concerning the finite rise time effect from both experiment and theory (Laun 1978; Wagner and Ehrecke 1998; Kolkka et al. 1991). The time required depends on the magnitude of the step, the power of the actuator, the control settings, and the stiffness of the material. The typical response time is in the order of 10 ms for a 10 mrad step. As such, finite rise time has been argued to be the origin of the damping behavior of stress relaxation in some literature (e.g., Venerus 2005), and one of the aims in this work is to clarify the question that whether the rise time does affect the damping behavior.

Transducer compliance effect

One more subtle but critical problem that needs to be taken into account in step strain experiments is transducer compliance because of its finite stiffness, which may affect the transient stress measurements. Upon imposition, some of the strain may deform the sample, and some of the strain may deform the shaft, depending on the shaft and sample compliance. Ideally, the sample deformation in the melt is relatively larger than the shaft displacement, and the relative error associated with the measurement is negligible. However, this error becomes significant when very stiff samples are tested, and the shaft displacement is approximately equal to the total displacement.

Especially when the response time of the transducer is comparable to the characteristic time of the viscoelastic fluid being tested, the measured response involves both the rheological response of the fluid and the mechanical response of

the rheometer (Dutcher and Venerus 2008). Indeed, a number of works have reported with regard to the transducer compliance effect on step strain flows, where torsional and axial compliances are involved (Vrentas and Graessley 1981; Venerus et al. 1990; Venerus 2005; Schweizer and Bardow 2006). To evaluate its effect, criteria have been developed based on the comparison between transducer response time and the characteristic relaxation time and/or chain retraction time of polymer liquids. The sample stiffness/compliance is related to both the modulus and geometry of the sample. Although measurements can be taken close to the limit, one must be aware that accuracy may be affected.

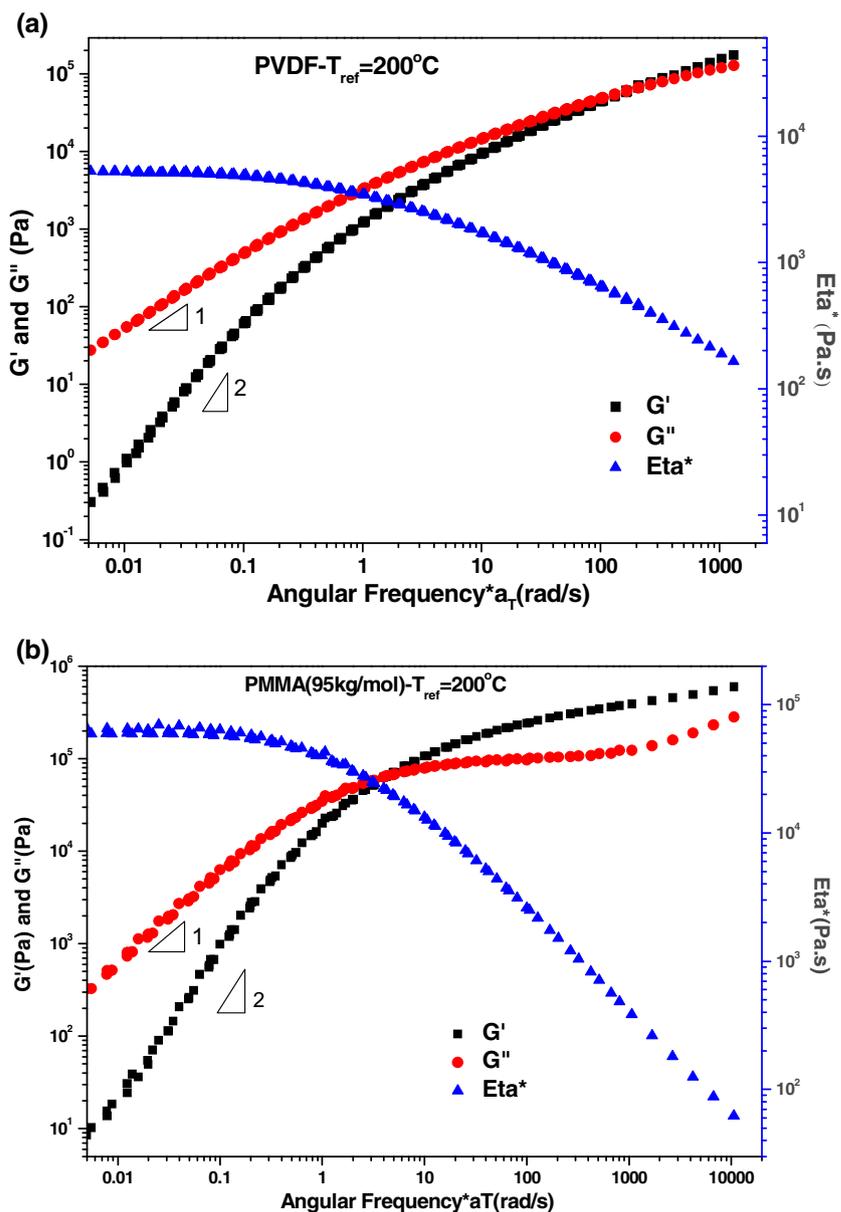
Results and discussion

Linear viscoelasticity (LVE) of polymers

Linear viscoelastic properties of neat polymers were determined by small-amplitude oscillatory shear (SAOS) measurements at different temperatures ranging from 180 to 240 °C. Master curves of storage modulus (G'), loss modulus (G''), and dynamic viscosity (η^*) of these neat polymers are produced via time-temperature superposition at a reference temperature of 200 °C, as shown in Fig. 2. Zero shear viscosity, η_0 , of these polymers are determined by fitting the Carreau model to the viscosity curve versus angular frequency. Methods to determine the plateau modulus G_N^0 of PMMA and PVDF have been addressed in our earlier work (Zhang et al. 2012). The entanglement molecular weights, M_e , are evaluated from G_N^0 by the relation of $M_e = \rho RT / G_N^0$. Weighted average terminal relaxation times, τ_{0w} , are determined from the Cole-Cole curve ($\eta'' \sim \eta'$), taken as the order of reptation time, τ_{rep} . Furthermore, the Rouse relaxation times, τ_R , can be estimated according to (Dealy and Larson 2006):

$$\tau_R = \frac{6M_w\eta_0}{\pi^2\rho RT} \left(\frac{M_c}{M_w} \right)^{2.4} \quad (4)$$

Fig. 2 Master curves of G' , G'' , and η^* as a function of angular frequency produced at the reference temperature of 200 °C for **a** PVDF melt and **b** PMMA melt



where ρ is the density, R is the universal gas constant, T is the temperature in Kelvin unit, and M_c is the critical molecular weight for a viscosity satisfying $M_c = 2M_e$. The main characteristic material parameters of these two PMMA and PVDF melts are listed in Table 2.

Transient period in step strain: reason of the nonlinear stress damping

Shedding light on the experimental data within the very short initial time window of the step strain, for the PMMA melt as shown in Fig. 3, one can observe that indeed it is in the transient period where the “step strain” is actuated that finds the underlying reason for the rheological nonlinearity (stress damping behavior). In the short-time window of the PMMA

melt, the relaxation modulus $G(t, \gamma_0)$ at strains no more than 50 % undergoes a smooth decrease with time, similar to the linear relaxation modulus $G(t)$ at a very small deformation. However, strains higher than 50 % portray a quite different picture, with $G(t, \gamma_0)$ experiencing a sharp decline at a critical time before returning back to the classical shape as linear relaxation, that is, so-called stress kink. The data indicates that this onset of nonlinearity systematically shifts to shorter times as the imposed strain amplitude is increased. Meanwhile, the $G(t, \gamma_0)$ decline becomes larger as well, which is consistent with the experimental results of Boukany et al. (2009). Distinctly depicted in the figure, the onset of the $G(t, \gamma_0)$ rapid decline corresponds to a sudden jump of the stress, experienced with a shape somewhat like an “overshoot” before reaching a plateau. It is also denoted by an

Table 2 Characteristic parameters of PMMA and PVDF

Polymer	ρ (g/cm ³) at 200 °C	η_0 (Pa s) at 200 °C	G_N^0 (Pa)	M_e (g/mol)	τ_{rep} (s) at 200 °C	τ_R (s) at 200 °C
PMMA	1.097	6.4×10^4	3.6×10^5	1.2×10^4	~ 0.96	$\sim 3.1 \times 10^{-2}$
PVDF	1.471	4.0×10^3	6.5×10^5	8.9×10^3	~ 0.18	$\sim 4.7 \times 10^{-3}$

inflection of the strain profile before going into a faster increment in the transient period. Note that for comparison and easy reading purposes, in the figure, the different strain amplitudes are normalized to a steady value. Here, the sudden jump or the “overshoot” of the stress is analogous to the stress overshoot feature happening in a shear startup at sufficiently high rates. Moreover, the “overshoot” amplitude increases with the imposed strain. From a phenomenological viewpoint, the sudden decline of the stress and the inflection of strain seem to be the reasons for the ultrafast decline of the $G(t, \gamma_0)$ at the very short time period.

From a theoretical viewpoint, the onset of rheological nonlinearity must be associated with flow-induced chain disentanglement according to the relevant theories. For example, the Doi-Edwards tube model (1986) discerns chain excess orientation and stretching under large deformation. The chain retraction process within the tube after the affine deformation dictates the nonlinearity in step strain experiments. The theory was refined by Marrucci (1996) and coworkers (Ianniruberto and Marrucci 2014) with the well-known CCR mechanism, arguing that the flow-induced convection of chains relative to each other results in loss of entanglements between chains. It is reasoned that the stress damping behavior that was caused by the chain retraction process happens only when there is not enough time for the chains to relax upon a large perfect “step” deformation. The chains are stretched affinely, and an ultrafast relaxation of chain retraction back to its equilibrium tube contour length occurs after the step deformation. That means that the “step” strain should be imposed within a time lower than the relaxation time of the polymer. In case the time is much too high, the ultrafast relaxation of chain retraction (it is also called as contour length relaxation by Doi-Edwards) does not occur.

Likewise, other scenarios, for example, Wang’s force imbalance model (Wang et al. 2007) and Sussman-Schweizer’s self-consistent microscopic dynamic theory (Sussman and Schweizer 2012) also predict chain disentanglement upon large deformations. Thus, even though intensive debates still exist in the literature, chain disentanglement (i.e., tube breaking) or decrease of topological entanglement in number per chain (i.e., tube dilation) seems to be the most convincing factors behind the rapid stress decline (or ultrafast relaxation) after a large step strain. This flow-induced disentanglement/re-entanglement effect has also been confirmed to be the reason of stress overshoot in startup shear experiments of

polymer melts (Roy and Roland 2013). Despite its variation with strain amplitude, we find in our case that the onset of the rheological nonlinearity happens at a time in the order of Rouse relaxation time, and the time-strain separability occurs at a time order of the reptation relaxation time (Zhang et al. 2014).

Influential factors concerning nonlinearity in stress damping

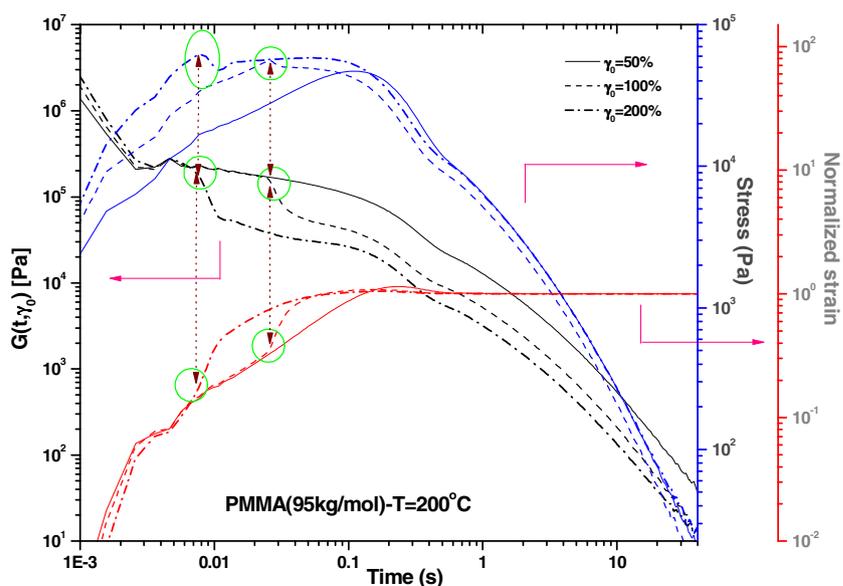
In this section, we attempt to address here some factors that are commonly encountered during a step strain experiment and may cause error on both the onset of the nonlinearity and its data accuracy analysis.

Difference between stress- and strain-controlled mode

It is well known that the rheological measurements in the linear viscoelastic regime are independent of measurement rheometers: strain controlled (typically with separate motor/transducer systems) and stress controlled (combined motor/transducer systems). However, in the nonlinear viscoelastic regime where the effect of strain becomes significant, the question arises whether differences exist between these two types of rheometers on the nonlinear stress relaxation measurements. In a stress-controlled rheometer, as the controlled input signal is stress, a relatively large inertia effect is expected in a step strain experiment since a time lag is needed for the conversion from stress signal to strain signal. On the contrary, strain-controlled rheometer directly controls the deformation (or rate of deformation) as the input signal and measures the stress signal using the separated torque transducer, which decreases inertia significantly and makes it a better potential tool for step strain experiments.

Figure 4 shows the same step strain experiments performed on the same PMMA melt using both strain-controlled (ARES) and stress-controlled rheometers (DHR-2). We see in Fig. 4a that nearly no stress damping (i.e., the $G(t, \gamma_0)$ almost superposed together) and no strain dependency exist in the PMMA melts measured in the ARES, even though the strain is increased to a very large amplitude. This is in contrast to the obvious nonlinearity (i.e., strong stress damping) observed in the same PMMA melts measured in DHR (Fig. 3). So, the question is then why is there no evident rheological nonlinearity in the ARES rheometer.

Fig. 3 Nonlinear relaxation modulus $G(t, \gamma_0)$ (black), stress $\sigma(t)$ (blue), and normalized strain (red) versus time for PMMA ($M_w=95$ kg/mol) after different step strains: $\gamma_0=50\%$ (solid); $\gamma_0=100\%$ (dash); $\gamma_0=200\%$ (dash dot) measured in DHR



For this, we turn our attention to the transient period at deformation startup. As indicated in Fig. 4b, contrary to the monotonous increment observed in the strain-controlled rheometer (i.e., ARES), the actual strain varies in multisteps in the DHR, beginning with a very fast first increase in less than 3 ms. Then, it slowly increases to reach the set strain value before 0.1 s. Moreover, a strain overshoot is observed in the DHR after reaching the commanded amplitude, the effect of which will be discussed in the following section. Meanwhile, the finite rise time t_0 seems to shift to smaller values as the imposed amplitude is increased. In other words, at high imposed strain amplitudes, the DHR needs shorter times than the ARES to startup the desired strain, even though it is a stress-controlled instrument, subject to higher inertia. Thus, from this aspect, the DHR is more advantageous in inducing chain retraction upon fast stretching.

Furthermore, Fig. 4c indicates that the stress in DHR grows at a much faster rate than the ARES for a given strain amplitude. According to the tube model, the shear stress is directly proportional to the amount of chain stretching upon a fast enough shear rate (e.g., $\dot{\gamma} > 1/\tau_{rep}$) that allows no reptation relaxation. Chain retraction happens along with a rapid decline in the shear stress. In addition, in Wang's picture (Wang et al. 2007), it is the fact that the retraction force reaches the entanglement force that results in the rapid decline of the shear stress, as a manifestation of elastic yielding. The disappearance of the nonlinear stress damping in ARES in our case of the PMMA melt is probably attributed to the rather slow strain and stress rising rates and the relatively low shear stress value in the transient period. The mild shear conditions encountered in such PMMA cases in the ARES did not satisfy the requirements of fully affine stretching to bring about chain retraction process and/or massive disentanglements of PMMA chains. Obviously, the apparent shear rate in the actuation period of a

large "step" strain, approximated as $\dot{\gamma}_0 = \gamma_0/t_0$ with t_0 as the rise time, is significantly higher in the DHR than in the ARES for the PMMA melt. Because of this, the nonlinear stress damping behavior that should occur along with the first ultra-fast relaxation process of chain retraction fails to appear for the PMMA melt in ARES. In this sense, one can conclude that the DHR-2 takes some advantages over the ARES on generating the desired strain within a short time due to its more rapid ramp-up of the strain and the stress.

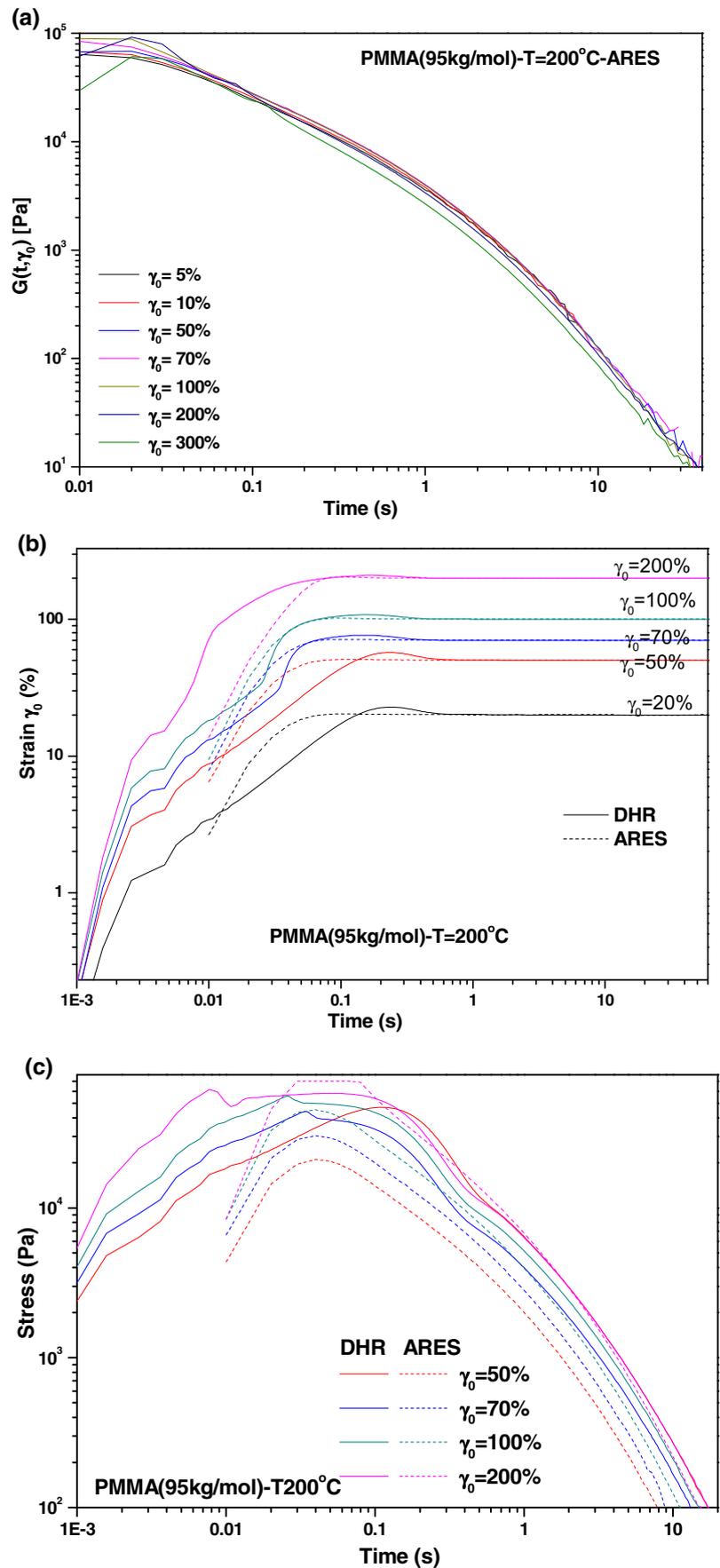
In addition, as also argued by Stadler et al. (2008), some advantages of stress-controlled over strain-controlled rheometers on performing step strain experiments are as follows:

- (i) The maximum strain obtainable in a stress-controlled rheometer is only limited by the material response and by the maximum force which can be applied. However, in strain-controlled rheometers, the deformation in step shear is limited by the maximum angular displacement of 0.5 rad.
- (ii) Direct imposition of a high strain in a very short time period would lead to high forces, which might damage the rheometer, whereas in a stress-controlled rheometer, the step strain is imposed by acting a maximum stress until the desired deformation is reached.
- (iii) The ARES uses separate transducers, each of which has limited torque ranges, at least in the version available for this work, which easily causes noisy data when the torque is very low.

Effect of strain overshoot

As shown in Fig. 4b, the strain overshoots before moving back to the prescribed value for the stress-controlled rheometer.

Fig. 4 **a** Nonlinear shear relaxation modulus $G(t, \gamma_0)$ of PMMA melt ($M_w=95$ kg/mol) at various strain magnitudes obtained in ARES; **b** actual strain variation in transient period of the PMMA melt at several given amplitudes imposed by DHR and ARES, respectively; and **c** corresponding stress variation versus time in the transient period experienced in DHR and ARES, respectively



This is due to the inevitable inertia effect between the strain detection and the stress imposition during operation of the stress-controlled rheometer, different from that of the strain-controlled one. The obvious question is then whether such strain overshoot encountered in the stress-controlled rheometer affects the final relaxation behavior. Therefore, we quantitatively determine some important parameters regarding such strain overshoot, such as the finite rise time t_0 , the stable time t_{st} , i.e., the time that the strain return from the overshoot to its steady level, as shown in the schematic in Fig. 5. In addition, an overshoot error, $\Delta\gamma\%$, is defined as $\Delta\gamma\% = (\gamma_{max} - \gamma_0) / \gamma_0 \times 100\%$, with γ_0 as the prescribed amplitude and γ_{max} as the peak value at the overshoot. Table 3 lists the values of these parameters for the PVDF and PMMA melts obtained at different imposed strain amplitudes. It is clear that such strain overshoot varies with the imposed strain amplitude and the dependence is more pronounced for the PMMA melt than the PVDF.

Figure 6a implies that the strain undergoes a maximum overshoot at an intermediate amplitude lower than unity for the PMMA melt, but higher for PVDF. Thereafter, as the imposed amplitude is increased, the strain overshoot diminishes. Evidently, the stiffer PMMA melt suffered more from the strain overshoot effect than the PVDF melt. To evaluate its effect on the relaxation modulus, we normalize the actual strain to the steady level and superpose the relaxation modulus $G(t, \gamma_0)$ of different strains together in a function of $G(t, \gamma_0) / h(\gamma_0)$ at a long time period. In this way, as shown in Fig. 6b, one can see clearly that the strain overshoot zone corresponds to a region where the $G(t, \gamma_0)$ undergoes a small twist or kink, though their amplitudes are not deemed to have quantitative correlations with each other.

To verify if such small twist in the $G(t, \gamma_0)$ is the direct consequence of the strain overshoot problem and to check if this effect influences the relaxation data at long times, we

display the ensemble results of the DHR and the ARES in Fig. 7 at a constant strain amplitude of 100%. In contrast to the DHR, in the ARES, no twist or kink emerges in the stress or the $G(t, \gamma_0)$ curves as it experiences no strain overshoot. For the stress-controlled rheometer, despite the small twist generated in the stress and the $G(t, \gamma_0)$ curves arising from the strain overshoot, $G(t, \gamma_0)$ gets over the small twist and returns back to the normal shape of the stress relaxation. Hence, the strain overshoot effect on the long time experimental data is very subtle. For accuracy, we suggest that only the data at a time long enough, that is, beyond the strain overshoot zone, is used for the analysis as we did in our recent work (Zhang et al. 2014) and as some earlier studies also suggest (Stadler et al. 2008; Ferri and Greco 2006).

However, we retain an idea that the small twist/kink shown here is very likely to develop into a “break-off” feature when the entanglement of the tested polymer is weak enough, especially in semidilute polymer solutions and low entanglement density melts. For example, we recently observed that in PMMA ($M_w = 95$ kg/mol)/dimethylformamide (DMF) solutions with low and medium concentrations ranging from unentangled to lightly entangled regimes, the stress in the transient period undergoes a break-off, i.e., a sharp jump to zero, before returning to normal stress relaxation. The results will be published elsewhere. This sudden stress break-off characteristic might be more associated with the quite low polymer entanglement density in the boundary of unentangled regime, rather than the strain overshoot effect.

Effect of finite rise time

As experimentally shown above, the actual strain pattern generated by the rheometer in response to a command of a step strain is not exactly a perfect step function. A finite rise time t_0 is required for the motor to rotate the plate to achieve

Fig. 5 Schematic of strain overshoot in a step strain experiment performed in a stress-controlled rheometer

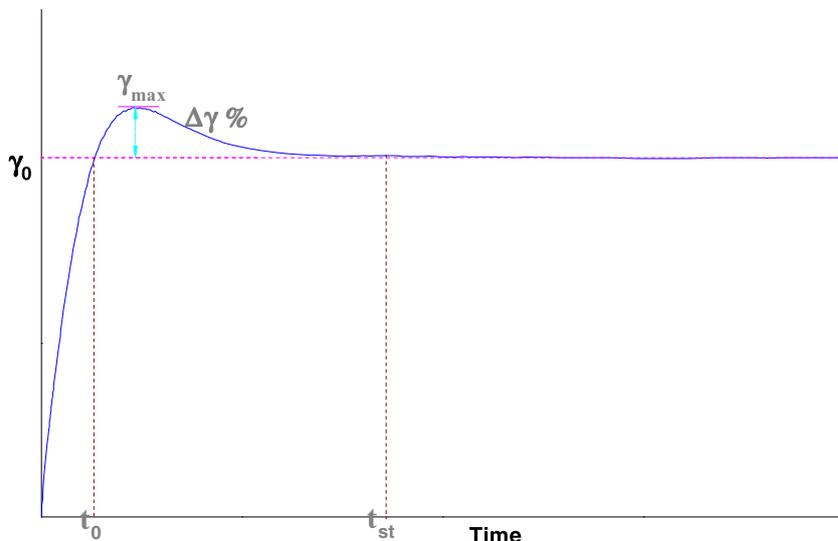


Table 3 Some parameters regarding strain overshoot extracted in an actual strain profile

Strain	Rise time, t_0 (ms)	Stable time, t_{st} (ms)	Overshoot error, %
PVDF-T=200 °C-DHR			
0.05	29	124	4.56
0.3	29	129	4.47
1	29	143	4.20
1.75	27	117	5.44
2.58	32	140	5.39
4.4	59	139	2.74
5	49	134	2.28
PMMA-T=200 °C-DHR			
0.01	133	450	13.5
0.2	133	560	14.2
0.5	133	560	14.3
0.7	64	440	9.4
1	65	460	8.1
2	75	480	4.8
2.87	66	480	3.2

the prescribed strain. The effect of such finite rise time on the stress relaxation result has been addressed in some earlier studies (Venerus 2005; Laun 1978; Kolkka et al. 1991). It has been reported that the imperfect step strain history cannot be excluded from having influence on the experimental anomalies, e.g., type C behavior with damping function lower than the DE prediction. A common realization in the literature is that the finite rise time effect makes the step-strain data achieved in the transient period out of confidence. In particular, Laun (1978) has proposed a procedure to correct the relaxation modulus data within the short time period by incorporating a factor with regard to the nonzero rise time effect. To avoid the initial transient imperfect “step” effect, a “rule of thumb” in the literature is that only the relaxation data at times $t > 10 t_0$ can be considered meaningful to represent the true behavior of the melt (Dealy and Larson 2006; Rolon-Garrido and Wagner 2009). Another earlier statement is that useful information about the relaxation functions can be obtained only if the mean relaxation time τ_m of the material is substantially greater than the rise time t_0 (Vrentas and Graessley 1981).

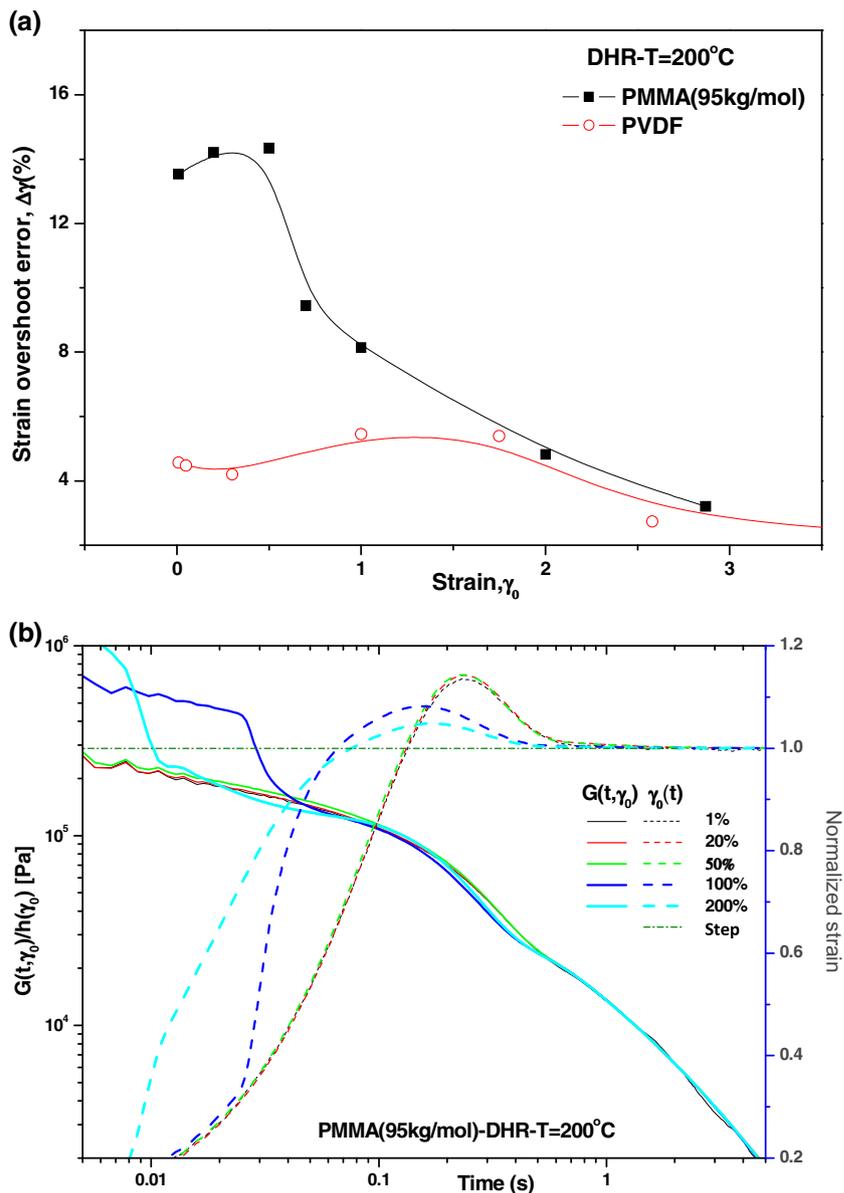
Back to the purpose of checking the nonzero rise time effect on the onset of rheological nonlinearity, we carried out step strain experiments using different rise times t_0 . Figure 8a shows in a semilogarithm term the actual strain profile versus time as actuated with different prescribed rise times t_0 ranging from 0.01 to 1.0 s for a $\gamma_0=200$ %. Apparently, as the t_0 is increased, the strain overshoot is greatly reduced. Indeed, the actual strain rise time fails to meet the stringently prescribed transient time value like $t_0=0.01$ s in light of the instrument limitations and precision. The corresponding stress and relaxation modulus generated thereby clearly display a significant

effect of the rise time on the rheological nonlinearity onset, as shown in Fig. 8b. The signature of the nonlinearity onset, i.e., the stress overshoot and the rapid decline of $G(t, \gamma_0)$, becomes weaker as t_0 is increased, that is to say, the value of $G(t, \gamma_0)$ at a given t is slightly increased. Eventually, when t_0 exceeds 0.1 s (an order of $\tau_{rep}/10$), the sudden jump of the stress does not appear any more (i.e., the overshoot disappears), staying at a higher level than that with short t_0 . Correspondingly, the relaxation modulus in such cases undergoes no steep decline, with only a small sharp decreasing front at the beginning of the relaxation behavior as does in the shear stress. In other words, to get meaningful information about rheological nonlinearity, the rise time t_0 should be as short as possible. A too high t_0 gives no onset of rheological nonlinearity. This is to say that the “rule of thumb” which considered the relaxation data at times $t > 10 t_0$, while meaningful, cannot be always true if t_0 is too high, for example, far from the mean relaxation time of the material. Conversely, the early criterion of Vrentas and Graessley (1981) that $t_0 \ll \tau_m$ might make the most sense.

Indeed, it is not difficult to understand the physics, as the onset of the rheological nonlinearity is considered to be a result of chain retraction accompanying by *convective constraint release* (CCR) upon an affine deformation, according to the tube models. The prerequisite for such chain retraction and CCR to happen is that the strain rate should be rapid enough that chains cannot relax in time via the normal reptation mechanism. In other words, only if the flow rate exceeds the inverse of the reptation time τ_{rep} , is the test chain forced to deform affinely, with chain segments largely oriented and affinely stretched beyond its equilibrium tube contour length. In response to such suddenly rapid and large deformation, the chain retracts within the tube to its original length, and simultaneously, the constraints on the test chain are convectively released (i.e., CCR) as the neighboring matrix chains affinely deform and relax by the same mechanisms. Flow convection of matrix chains past the test chain decays the constraints imposed on the test chain by releasing entanglements between chains, i.e., entanglement loss or entanglement density decrement, which corresponds to the so-called tube dilation of the test chain. Chain retraction upon full stretching and the constraint release at a rate dictated by the rate of the imposed flow then occur. As this is the case, the nonlinearity feature, i.e., the sudden decline of the shear stress, as an evidence of chain retraction, depends on the strain rate imposed to the material particularly within the strain imposition period. Here, as the rise time t_0 is increased, the shear rate in the transient period, $\dot{\gamma}_0 = \gamma_0/t_0$, decreases. Thus, the chain is less oriented and stretched, thus produces a lower degree of chain retraction and less CCR, therefore, less entanglement reduction. That is why the nonlinearity feature is weakened as t_0 is raised.

In conclusion, to get meaningful information on the rheological nonlinearity in the relaxation modulus curve, it is

Fig. 6 **a** Errors of strain overshoot versus strain amplitude imposed for the polymer melts at 200 °C in DHR; **b** superposed relaxation modulus and normalized strain profile versus time in the case of PMMA melt with different strain amplitudes



necessary to let the “step strain” instantaneously generated be as perfect a step function as possible, which is not surprising. That is, t_0 should be as short as possible, at least not exceed one tenth of the mean relaxation time of the material, though this is quite a challenging task in practice. As indicated in some studies (Juliani and Archer 2001), one strength that a stress-controlled rheometer offers is the possibility that a nonlinear step strain could be imposed in less than 0.1 s for even a very high stiffness polymer system.

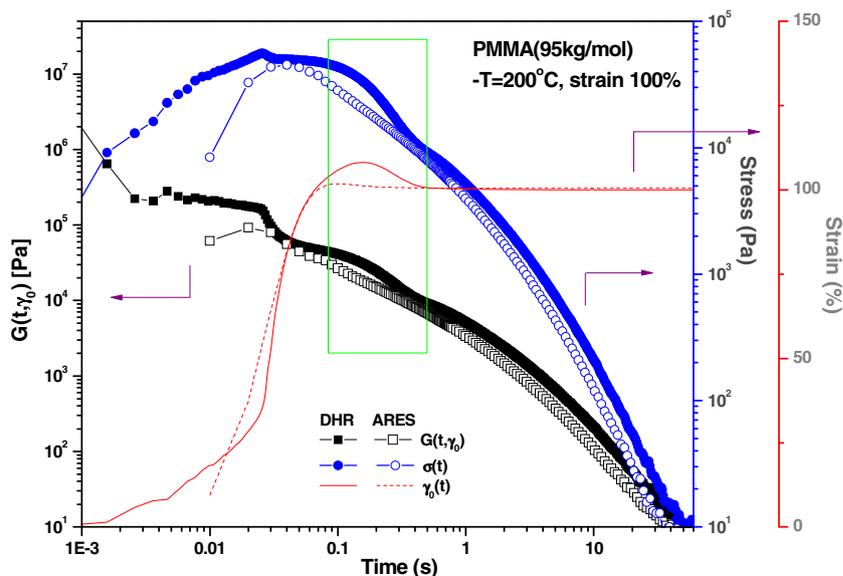
Effect of stress overload

In step strain experiments, nonlinear stress relaxation behavior of the test fluid is often measured to a very large strain amplitude, somewhere up to 20 or even higher (Soskey and

Winter 1984; Stadler et al. 2008). In such cases, if the test fluid is sufficiently stiff, the shear stress in response to the too large deformation amplitude makes it very easy to reach the transducer limitations that cause stress overload in the transient period. Therefore, considering that the stress overload encountered at large strains may cause some effects on the relaxation data concerning the rheological nonlinearity, caution must be exercised regarding this technical problem. In fact, stress overload arising from transducer limitation was already perceived in the early study of Soskey and Winter (1984) to be a potentially important factor, but not enough attention was given to it, and its effect has yet to be studied in detail.

To examine its effect on the experimental data, especially regarding the onset of rheological nonlinearity, i.e., stress damping behavior, step strain experiments were systematically

Fig. 7 One example of strain overshoot in stress-controlled rheometer (DHR) as compared to strain-controlled mode (ARES) for PMMA (95 kg/mol) at a step strain of 100 %



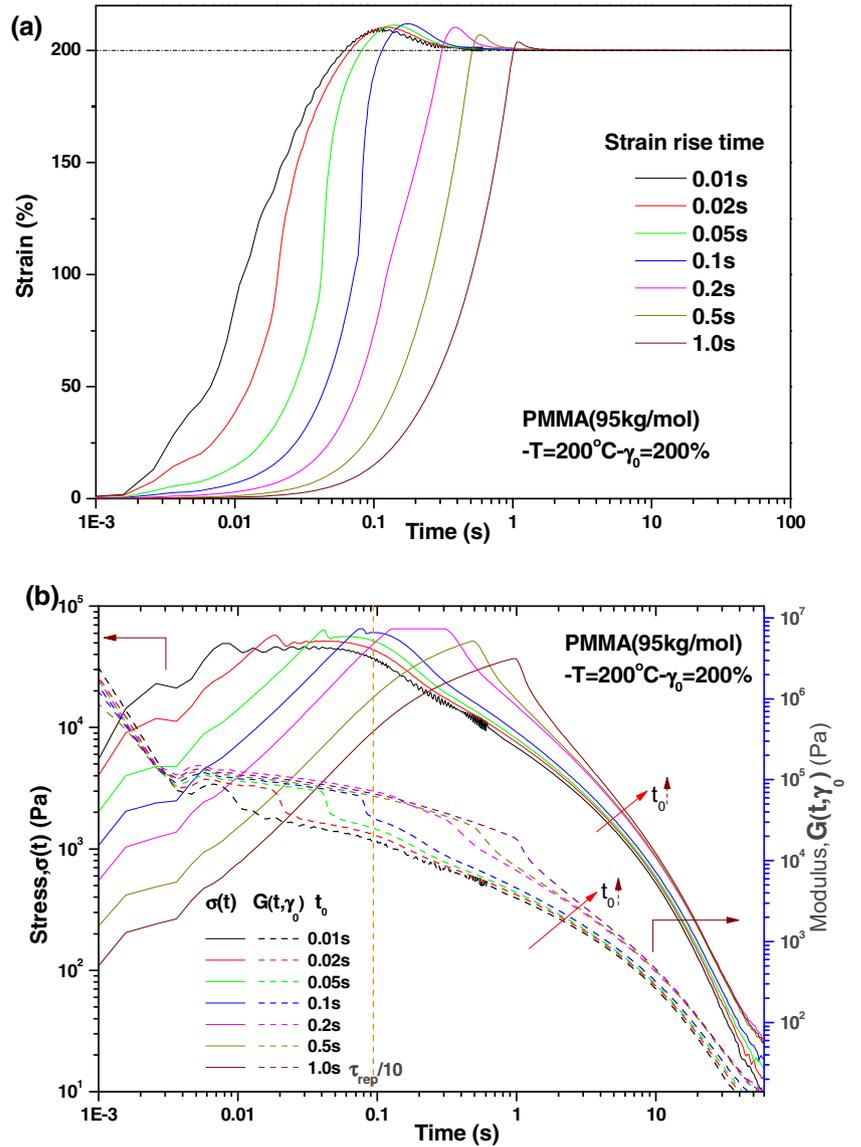
carried out at several relatively large strain amplitudes, where stress overload emerges. Both the stress-controlled (DHR) and strain-controlled (ARES) rheometers were used, and PMMA ($M_w=95$ kg/mol) was selected as an example. In the DHR (Fig. 9a), with imposition of a 300 % strain to the melt, it is surprising that the actual strain fails to reach the prescribed amplitude, with only 230 % being reached in a rise time t_0 longer than 1 s. The shear stress upon such imposition rapidly reaches a plateau value as the transducer is overloaded, and prevents further stress buildup. This plateau in stress lasts until the strain reaches the steady value. The corresponding relaxation modulus $G(t, \gamma_0)$ is shifted to a higher level relative to that of the 200 % strain amplitude. In normal circumstances of the nonlinear regime, the 200 % strain case is supposed to yield a higher $G(t, \gamma_0)$ than the 230 or 300 %. Undoubtedly, the stress overload due to the transducer limitation greatly affects the measured $G(t, \gamma_0)$. Only in some extreme cases of very large amplitudes reached within very short times can reliable data be obtained. In the strain-controlled rheometer (ARES), as shown in Fig. 9b, the stress gets to the overload state easier than the DHR, i.e., it occurs even at γ_0 as low as 200 %. This is due to the lower transducer limitation of this particular version of the ARES rheometer. Likewise, the stress overload in the ARES lets the imposed strain be reached in a longer t_0 . However, the relaxation modulus $G(t, \gamma_0)$ keeps going down to lower levels rather than shifting to higher levels, as in the DHR, as the strain amplitude is increased under the stress overload state. Despite this, it is quite clear that data collected under stress overload conditions either from stress-controlled or from strain-controlled rheometer are out of the confidence range.

With regard to the relaxation response difference between the stress- and the strain-controlled rheometers upon stress overloading, it is crucial to understand the working principle of these two types of rheometer in operating a step strain

experiment. In the strain-controlled mode, a strain displacement is applied by the motor, and the resulting torque (stress) is measured separately on the other side of the sample by an additional force transducer. The stress-controlled type machine employs a combined motor transducer system, in which the rotation of the drive shaft is realized from an electrical torque and the torque signal is directly calculated from the motor current (Lauger and Stettin 2010). At very high deformations, the strain-controlled rheometer by definition directly imposes a very large angular displacement within a transient time and thus may lead a very high force σ which could exceed the transducer limitation but is limited to the overloading state σ_m . Nevertheless, with the large imposed step strain γ_0 , the stress-controlled type handles the imposition of the step by performing a “creep test” with the maximum stress σ_m acting until the prescribed strain is reached (Stadler et al. 2008). Therefore, it is possible that in the strain-controlled mode, the real stress σ' of the material in response to the γ_0 is higher than the overloading value σ_m , and in the stress-controlled mode, the real strain γ' of the material in response to the σ_m may be lower than the prescribed value γ_0 . If this is the case, according to the relation $G(t, \gamma_0) = \sigma(t)/\gamma_0$, it is not difficult to anticipate that the stress-controlled type (e.g., DHR) might overestimate the relaxation modulus $G(t, \gamma_0)$, whereas the strain-controlled type (e.g., ARES) might underestimate the $G(t, \gamma_0)$ when the stress overload state is reached. Meanwhile, the rise time is no longer uniform for both stress-controlled and strain-controlled types when the stress obtains the overload level. Hence, in the step strain experiments of high molar mass and stiff materials, it is important to take into account the stress overload effect in their analysis of nonlinear relaxation.

One final issue is that, in addition to stress overload, transducer compliance, both axial and torsional, is able to affect mechanically the measured transient stress, especially with highly stiff materials. The criterion to evaluate the effects

Fig. 8 **a** Actual strain profile versus time with different prescribed strain rise times, t_0 ; **b** corresponding stress $\sigma(t)$ and relaxation modulus $G(t, \gamma_0)$ variation versus time with different rise times



is the comparison between the transducer response time and the response time of the tested fluid. In a rotational rheometer with parallel plate geometry (disk radius R and plate distance H), the torsional response time τ_T and axial response time τ_A of the transducer depend on the tested fluid and the transducer stiffness, which could be determined, respectively, by (Dutcher and Venerus 2008):

$$\tau_T = \frac{\pi\eta_0 R^4}{2K_T H} \quad (5)$$

and

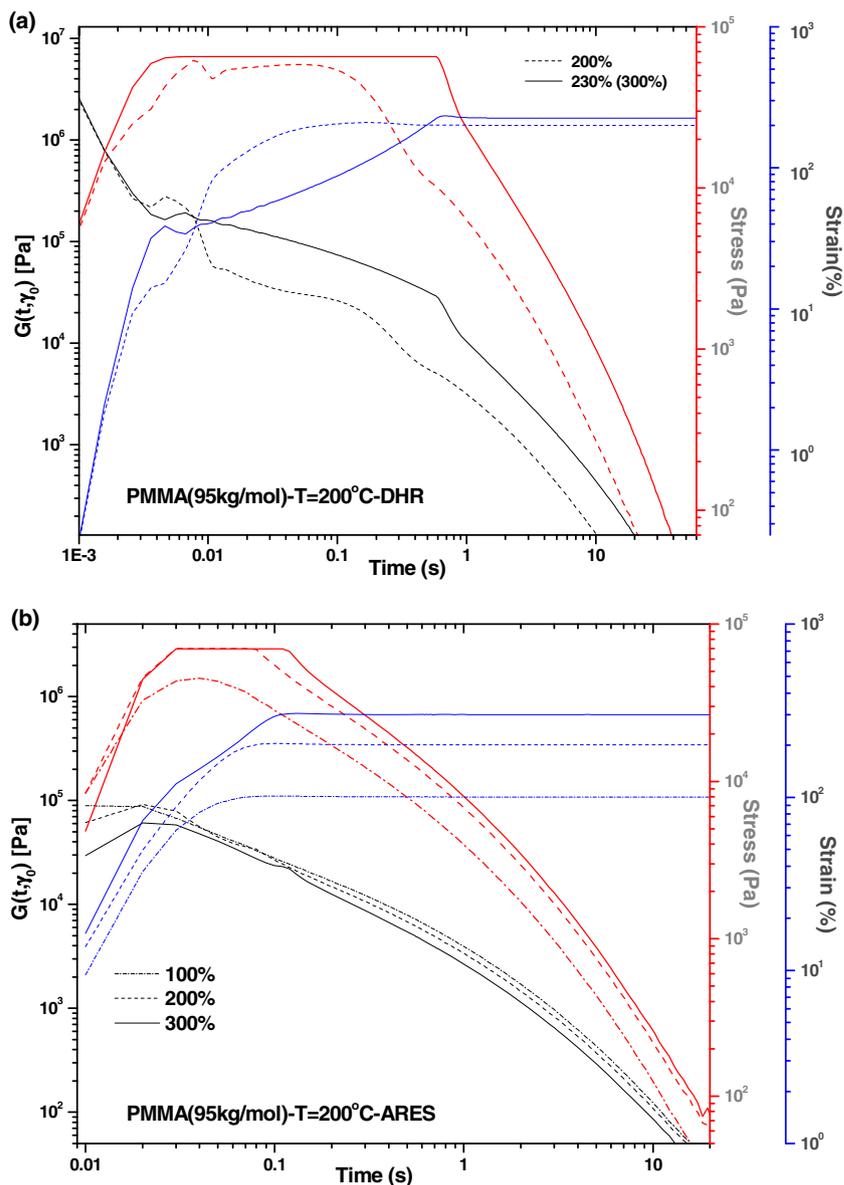
$$\tau_A = \frac{3\pi\eta_0 R^4}{2K_A H^3} \quad (6)$$

where η_0 is the zero shear viscosity of the tested fluid, and K_T , K_A are the torsional and axial stiffness of the transducer,

respectively. Since $H/R \ll 1$, as shown in Eqs. 5 and 6, the transducer compliance effects are more pronounced for transient normal stress measurement compared to transient shear stress. It is often assumed that the effects of axial transducer compliance, which are difficult to avoid in practice, can be ignored if one is only interested in shear stress measurements (Dutcher and Venerus 2008). However, it is well known that axial compliance dramatically affects transient normal stress measurement (Venerus 2005) and that it is only a few tenths of micrometers per Newton.

To decouple the dynamics of the undesired axial and torsional motion of the transducer from the dynamic response of the fluid, one earlier criterion proposed by Vrentas and Graessley (1981) is that $\tau_A/\tau_d \ll 1$ and $\tau_T/\tau_d \ll 1$, where τ_d is the longest relaxation time. Later, Venerus (2005) suggested a more stern criterion by replacing τ_d with Rouse relaxation time, τ_R , that is, $\tau_A/\tau_R \ll 1$ and $\tau_T/\tau_R \ll 1$ should be

Fig. 9 Stress relaxation behavior of PMMA (95 kg/mol) melt after step strains where stress overload appears as measured in **a** DHR and **b** ARES rheometers



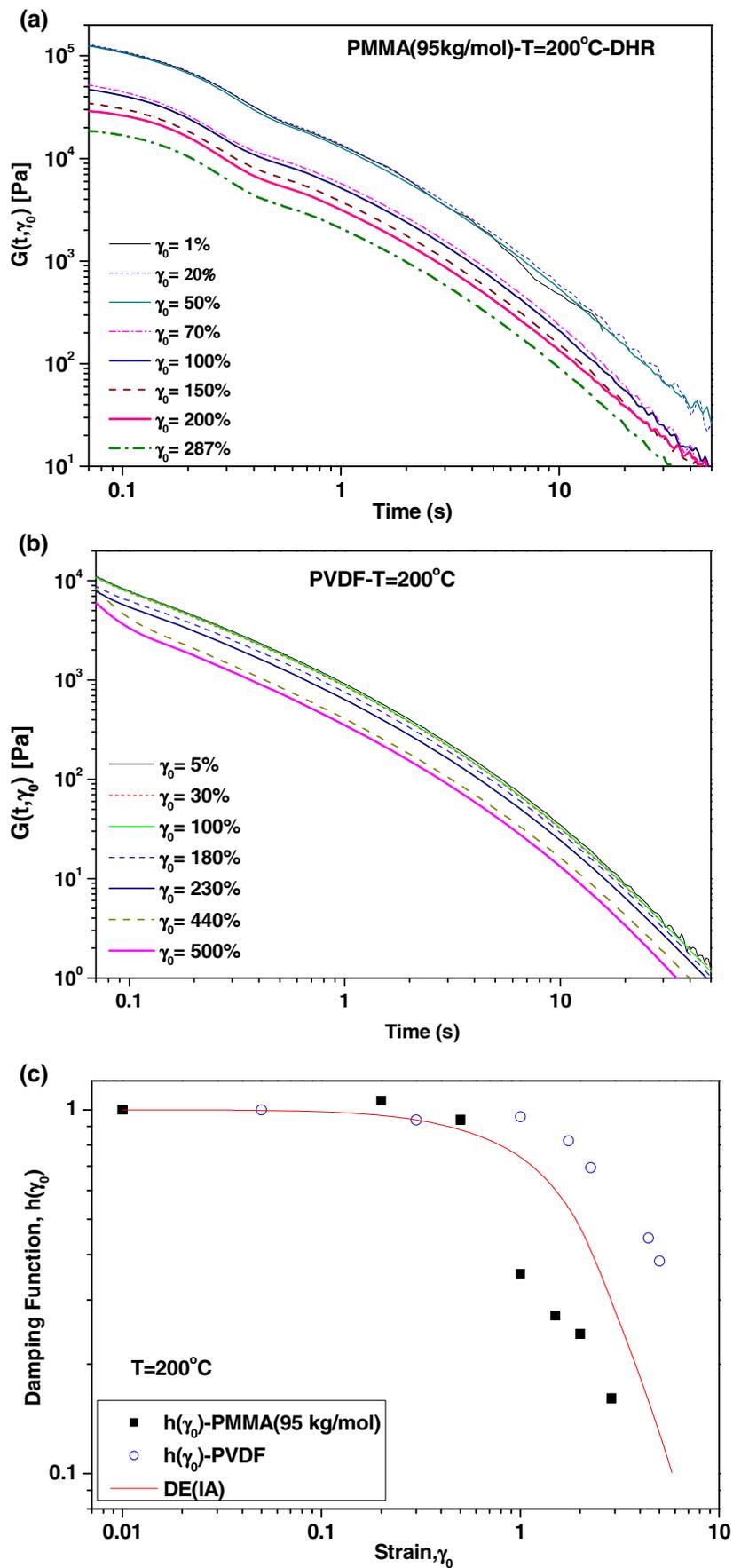
satisfied to exclude the effect of the transducer compliance from the stress relaxation data. For the DHR-2 rheometer, the torsional compliance is 2.02 mrad/N m, that is, the $K_T = 495$ N m/rad, thereby $\tau_T = 0.02$ s for the PMMA melt and $\tau_T = 3.0 \times 10^{-4}$ s for the PVDF melt as calculated based on Eq. 5. That means the criterion for torsional compliance, $\tau_T / \tau_R \ll 1$, is well satisfied.

Example of good experiments in step strain for rheological nonlinearity

As already mentioned, most work has focused more on the damping behavior determined in the long time period, i.e., the superimposable range. The experimental data in the transient period where a step strain experiment is actuated is often

omitted or deliberately excluded partially because of the many influential factors that may make sense in such short time period. However, it is argued that the rheological nonlinearity, that is, the stress damping behavior, is likely to originate from the normally omitted transient zone. In the previous sections, we have revealed in the transient period of strain imposition the underlying reasons of the nonlinearity and have addressed some of the key error factors. Here, we give examples of good step strain experiments achieved according to the experimental protocol and the confidence window as proposed before to avoid the error effects. Figure 10a, b shows (in a time window mostly used by researchers) the typical curves of stress relaxation modulus evolved versus time at varied step strain amplitudes for PMMA ($M_w = 95$ kg/mol) and PVDF melts, respectively.

Fig. 10 a, b Stress relaxation modulus $G(t, \gamma_0)$ versus time in a typical step-strain test obtained in DHR at 200 °C of PMMA melt and PVDF melt, respectively; and c their damping function $h(\gamma_0)$ versus strain



In the figure, stress damping behavior can be clearly observed above a critical strain amplitude, demonstrated as a feature of rheological nonlinearity. This is a direct consequence and expression of the sudden decline of the stress and the ultrafast decline of the relaxation modulus within the transient period window as shown in Fig. 3. Specifically, for a strain of no more than 50 %, the relaxation modulus $G(t, \gamma_0)$ undergoes a smooth decrease with time as linear relaxation modulus $G(t)$ at very small deformations. There is no difference between the stress relaxation behavior at amplitude $\gamma_0 = 50$ % and that at $\gamma_0 = 1$ %. In the range of high strain amplitudes, $G(t, \gamma_0)$ becomes strain dependent, decreasing in a nearly parallel way as the strain is further raised. In particular, at long times, the $G(t, \gamma_0)$ curves at different strains are superimposable. Such rheological nonlinearity is more often displayed in a term of time-independent damping function $h(\gamma_0)$ versus strain, as shown in Fig. 10c. Such damping function $h(\gamma_0)$ as defined $h(\gamma_0) \equiv G(t, \gamma_0)/G(t)$ is a normalized relaxation modulus determined in the superimposable time domain. $h(\gamma_0)$ in our case of PVDF melt can be classified into a type B according to Osaki's classification criterion using the universal prediction of Doi-Edwards tube model, i.e., $h(\gamma_0) = 1/(1 + 4\gamma_0^2/15)$, as reference. PMMA ($M_w = 95$ kg/mol) seems to belong to type A/C according to the criterion, (the validity of the criterion itself is still under dispute in the literature (Ravindranath and Wang 2007)). Obviously, the data shown in the most used long time window and the analysis given therein are dictated by the results of the transient period where onset of nonlinearity happens due to chain retraction and the disentanglements. Hence, any factors that are influential in the transient period need to be well considered in order to achieve reliable analysis accuracy of the nonlinear stress relaxations and damping behavior in a long time range.

Conclusions

Step shear strain, as one of the most important measurement for nonlinear rheology of viscoelastic liquids, is yet to be fully comprehended, especially regarding the rheological nonlinearity features of the stress damping behavior at high strains. Throughout this paper, we have demonstrated, based on PMMA and PVDF melts, that the onset of the nonlinearity is phenomenologically associated with an abrupt decline of the shear stress happening at a time before the characteristic relaxation time of the tested polymer. Meanwhile, a series of experimental factors, especially the technical problems during the transient period that the step strain is being actuated, is illustrated to be influential to the measured relaxation data. Some crucial technical problems presented in this work cover wall slip, strain overshoot, finite rise time, stress overload, and transducer compliance. All of these can and often will cause

errors or inconsistencies in the data analysis accuracy. Therefore, a confidence window needs to be defined. To that end, we tried to study and discuss physically the onset of the rheological nonlinearity under some theoretical frameworks like tube models incorporating the CCR mechanism.

Both stress- and strain-controlled rheometers were used for the step strain experiments of polymer melts, and their difference were investigated based on their distinct working principles. The strain overshoot arising from inertia effect in stress-controlled mode varies with strain, as it experiences a maximum before diminishing when the imposed strain amplitude is increased. The overshoot appears to subtly affect the relaxation modulus $G(t, \gamma_0)$ in the transient period, by producing a small twist, the effect of which on long time data however is negligible. In contrast, finite rise time, which is critical in affecting the nonlinearity onset, needs to be as short as possible, at least, not exceed one tenth of the relaxation time to get meaningful information. Moreover, the stress overload for highly viscous and stiff materials also produces inaccurate stress relaxation results, showing distinct effects in stress- and strain-controlled modes. These effects of the technical factors on the nonlinearity are greatly related to their influence on the onset of chain retraction/disentanglement upon affine deformation, which depends on the shear rate. The conclusions obtained in this study based on highly entangled polymers either in melt or in concentrated solutions might need some other complements for the case of solutions with low concentrations.

In summary, this paper belongs to a critical technical part of step strain experiments that aims to achieve reliable stress relaxation data and to define confidence windows. For this, experimental protocols with respectful cautions of some critical factors as mentioned in the present study have to be considered for accuracy and data validity.

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