

Interrupted shear flow of unentangled polystyrene melts

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Synopsis

Low molecular weight polystyrene melts were subjected to shearing flow which was periodically halted. Weak maxima in both the viscosity and normal stress were observed upon startup of the flow, notwithstanding the absence of entanglements. The strain associated with the viscosity maxima was independent of shear rate, and consistent with the overshoot strains for entangled polymers. The stress overshoots disappeared or were of weaker intensity when the flow was resumed after a brief interruption. For sufficiently long rest periods between flow, the original behavior was reproduced. The time scale for recovery of the maxima was about the same as that for relaxation of the stress from steady state flow. This differs from the behavior of entangled polymers.

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I. INTRODUCTION

Stress overshoots can be observed in any material whose structure can be disrupted by flow [White and Dickinson (1997); De Kee and Chan Man Fong (1994)]. Much attention has been given to stress overshoots and other transient phenomena accompanying shear flow of high molecular weight polymers [Vinogradov and Belkin (1965), Crawley and Graessley (1977); Laun (1978); Huia *et al.* (1999); Archer (1999)]. For melts and entangled solutions, overshoots of the shear stress and the normal force are considered to originate in the orientation and the subsequent decrease in the entanglement density of the chains [Graessley (1965); Porter and Johnson (1966); Wagner and Meissner (1980); Isono *et al.* (1997); Oakley *et al.* (1998)]. This transient flow behavior can be described empirically using Kaye–Bernstein–Kearsley–Zapas (K–BKZ) type constitutive equations [Menezes and Graessley (1982)]. Experimental and simulation results for the stress overshoot phenomenon are usually interpreted using some variation of the reptation model [Doi and Edwards (1986); Moore *et al.* (1999); Osaki *et al.* (1999, 2000a, 2000b, 2000c); Mead *et al.* (1998); Marrucci (1996)]. For entangled melts sheared at sufficiently high rates, a maximum is also observed in the normal stress [Menezes and Graessley (1982)], and this too is interpreted using the reptation model, modified to include chain stretching [Archer and Mhetar (1999); Pearson *et al.* (1991)].

Although stress overshoots are associated with non-Newtonian fluids [Lockyer and Walters (1976)], entanglements are not necessary for their occurrence. Unentangled chains can be stretched and oriented under the influence of flow, and thus exhibit transient flow effects. However, stress overshoots are not observed for low molecular polymers under the usual experimental conditions; the stress simply increases monotonically

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before leveling off at steady state. The difficulty of measuring the rheology of unentangled polymers in the nonlinear viscoelastic regime makes experimental results scarce and theoretical understanding limited. For example, the Rouse model, while useful if not entirely accurate in describing linear behavior [Ngai and Plazek (1995)], is invalid for large deformations [Larson (1988)]. Modifications to accommodate nonlinear effects have been proposed by Carl (1994) and by Dua and Cherayil (2000).

Experiments on polymer solutions often involve concentrations sufficient for coil overlap in order to facilitate mechanical measurements [Larson (1988)]. At sufficiently high rates of deformation ($> 10^8 \text{ s}^{-1}$, or approaching the rate of molecular rotation), even small molecule liquids can become non-Newtonian [Chynoweth and Michopoulos (1997); Cui *et al.* (1999)]. For linear molecular structures, this is associated with orientation by the flow field [Kioupis and Maninn (1999)]. In polymers, elasticity is a prerequisite for stress overshoots [Lockyer and Walters (1976); Bird *et al.* (1987); Larson (1988)], with transient phenomena related to inherent chain properties such as flexibility [Andrews *et al.* (1998); Noda and Hearst (1970); Moore *et al.* (1999); Osaki *et al.* (2000a, 2000b, 2000c)]. In polymer solutions, flow-induced alterations of the concentration fluctuations [Mani *et al.* (1992)] or even the phase diagram [Meyer *et al.* (1993); Chopra *et al.* (1999)] can contribute to transient stress phenomena.

In pioneering work on entangled polymer solutions, Huppler *et al.* (1967) and Stratton and Butcher (1973) carried out interrupted shear flow experiments, and found that the magnitude of the stress overshoot increased with the duration of the rest interval prior to resumption of steady shearing. They attributed the effect to re-entanglement of chains disentangled during the prior shearing. A few studies addressed entangled polymer melts [Dealy and Tsang (1981); Dealy and Soong (1984)]; Madonia (1970)], with the phenomena again ascribed to disentanglement and re-entanglement [Tadmor and Gogos (1979)]. The maximum in the stress overshoot is found to occur at shear strains in the range of 2–3 [Bird *et al.* (1987)], independent of the duration of the rest period [Menezes and Graessley (1982)].

In this article we describe interrupted shear flow experiments on low molecular weight polystyrene melts. By carrying out the experiments at low temperature, the transients are slow enough to be measured. We contrast the observed behavior with that of entangled polymers.

II. EXPERIMENT

Two linear, atactic polystyrenes (PS) (Scientific Polymer Products), with respective molecular weights, M , equal to 3680 (PS3) and 13 700 (PS13) daltons and polydispersities of 1.1, were studied. They were molded under vacuum to form disks with a thickness of $\sim 1.5 \text{ mm}$. As discussed below, our measured steady state recoverable compliances are in agreement with literature values for J_S^0 ; this provides evidence of the absence of any high molecular weight tail in the molecular weight distribution of these materials.

Interrupted flow measurements [Huppler *et al.* (1967); Stratton and Butcher (1973)] were carried out with various time delays using an ARES (Rheometric Scientific Instruments) rheometer. Prior to each experiment, the samples were presheared (0.01 rad/s) at an elevated temperature ($\sim 130^\circ\text{C}$), then allowed to relax for 1 h at the measurement temperature. Shear rates were in the range from 0.001 to 0.2 rad/s.

A parallel plate geometry (sample radii and gaps were ~ 6 and 1.3 mm, respectively) was used. A cone and plate would be preferred, since the shear rate is constant along the radius. However, the active nature of the force rebalance transducer (FRT) [Niemiec *et al.* (1996); Zapas *et al.* (1989)] coupled with the low compliance of the PS samples for

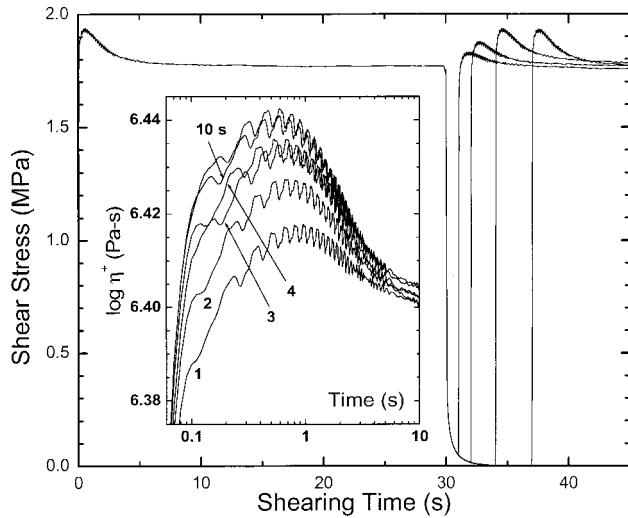


FIG. 1. Transient shear stress for PS3 ($\dot{\gamma} = 0.7$ rad/s and $T = 90$ °C) from a fully relaxed condition and following intermittent cessation of the flow. The inset shows the stress growth curves after the indicated rest periods (in s). The high frequency oscillations are due to the active nature of the FRT, as discussed in the text.

temperatures close to the glass transition, T_g , caused a high frequency resonance oscillation in the FRT [McKenna (1999)]. This was minimized by use of parallel plates, although correction for the distribution of shear rates was then necessary. This was done for the steady state viscosity and first normal stress coefficient using the Weissenberg-Rabinowitsch formula [Bird *et al.* (1987)]. For the transient, interrupted flow experiments, however, we report the apparent shear rate.

A potential anomaly concerning normal force data measured using a FRT, due to gap changes at large torques [Niemiec *et al.* (1996); Zapas *et al.* (1989)], was not significant here. Corroborating experiments were carried out on a Bohlin VOR, which does not use a FRT. Very similar overshoot phenomena were observed. However, the Bohlin rheometer relies on a belt drive, which generally leads to lower quality data.

An absence of flow instabilities, such as melt fracture, striations, or material exuding from the gap, was affirmed primarily by visual inspection, both during and after the testing. Archer *et al.* (1997) reported “fracture phenomena” in unentangled PS sheared at sufficiently high shear stresses. The consequence was a dramatic decrease in apparent shear stress, accompanied by bubble and cavity formation in the sample. We were able to observe, at least in part, similar effects at very high shear rates. The results reported herein are restricted to lower shear rates (≤ 0.2 rad/s), for which sample integrity was maintained and the shear stress data behaved well.

The terminal viscosities and recoverable compliance, $J_r(t)$, for PS13 were determined directly from the recovery after steady state creep, using a magnetic-bearing creep apparatus [Plazek (1968)]. The steady state recoverable compliance, defined as $J_S^0 = \lim_{t \rightarrow \infty} J_r(t)$, was determined at several temperatures in the range from $T_g + 5$ to $T_g + 45$.

III. RESULTS

The transient stress for PS3 sheared at 0.7 rad/s is shown in Fig. 1. The temperature is 90 °C, which is 18.9 °C above its T_g [Santangelo and Roland (1998)], falling within the

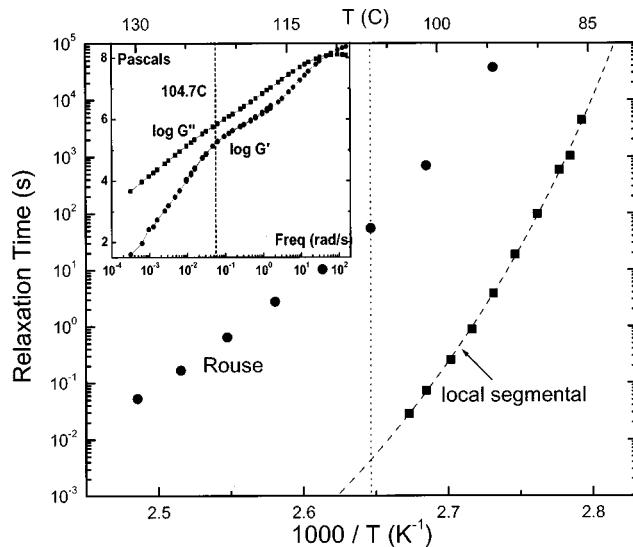


FIG. 2. Segmental relaxation times for PS13 (■), defined as the inverse of the frequency of the maximum in the dynamic loss modulus. The vertical dotted line denotes the temperature of the transient experiments on PS13. Also shown is the longest Rouse time (●), calculated as the product of the zero-shear viscosity and the steady state recoverable compliance. The inset shows the dynamic moduli as a function of frequency at 104.7 °C. The vertical line indicates the reciprocal of the time at which the overshoot is observed at 0.14 rad/s shear rate.

glass–liquid transition zone. Although the critical molecular weight associated with entanglement effects in polystyrene ($M_c = 33\,000$ daltons [Ferry (1980)]) is a factor of 10 larger than the molecular weight of PS3, there is a maximum in its shear stress. This peak stress is about 10% above the steady state level. This is significantly weaker than the stress overshoot observed for entangled polymers, although the latter is shear rate dependent [Bird *et al.* (1987)]. If the shearing is interrupted for a short time, this peak for PS3 is absent or of reduced magnitude upon resumption of the flow.

The inset of Fig. 1 shows the growth of the stress maximum for various rest periods between shearing. The strain associated with the overshoot appears to be independent of shear history. The location of the maximum cannot be accurately determined due to partial overlapping with the servomotor's rise time. Note also that there are oscillations in the data, which have previously been observed [Archer *et al.* (1997)], and herein are, at least in part, a transducer artifact [Niemiec *et al.* (1996); Zapas *et al.* (1989); Osaki *et al.* (2000a, 2000b)]. We can minimize these to some extent by going to higher temperature; however, the stress overshoot for PS3 then occurs at too short a time to be observed.

Having demonstrated the effect in this very low molecular weight sample, we carried out the same experiments on PS13. While still unentangled, its higher molecular weight provides more separation from the glassy zone, facilitating measurements. Local segmental relaxation times measured for PS13 over a range of temperatures are displayed in Fig. 2. At the measurement temperature used for the transient experiments described below, segmental relaxation is too fast to observe in the experimental window of our mechanical spectrometer. Extrapolation of the data in Fig. 2 indicates a segmental relaxation of time of ~ 0.004 s at 104.7 °C.

Figure 3 shows representative results for the shear stress growth coefficient, $\eta^+(t)$, measured for PS13 during interrupted flow. The data were obtained at a shear rate $\dot{\gamma}$

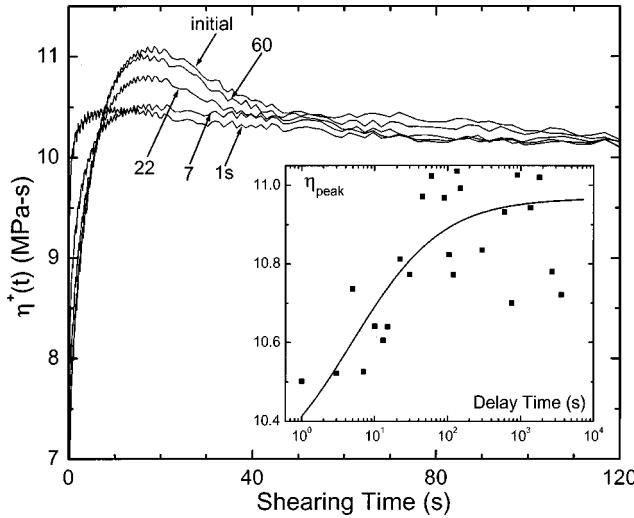


FIG. 3. Representative transient viscosities measured for PS13 at a shear rate of 0.14 rad/s and $T = 104.7^\circ\text{C}$ upon initial startup and after resumption of flow following intervals of the durations indicated. In the inset, the height of the overshoot is displayed as a function of this delay period. The curve through the data is a visual aid only.

$\dot{\gamma} = 0.14 \text{ rad/s}$ and a temperature of 104.7°C , which is 17.1°C above T_g [Santangelo and Roland, (1998)]. A maximum is observed in the transient viscosity, which at $\dot{\gamma} = 0.14 \text{ rad/s}$ has a magnitude again about 11% larger than the steady state value of η . The stress overshoot disappears when the interrupted flow is resumed immediately. As shown in the inset of Fig. 3, the magnitude of the peak is completely recovered for sufficiently long rest intervals ($\sim 100 \text{ s}$). The position of the maximum is invariant to rest time, occurring at a shear strain ($= \dot{\gamma} \times t$) equal to 2.5 ± 0.2 .

In Fig. 4 is shown the first normal stress coefficient, $\Psi^+(t)$, measured under the same conditions as the transient viscosity data in Fig. 3. There is an apparent minimum in $\Psi^+(t)$, since the normal stress from the previous shearing has not completely relaxed. More interesting is the weak, broad maximum at longer times. The magnitude of this peak is only a few percent greater than the steady state value of Ψ^+ . It is also obscured to some extent by noise in the measurements, including oscillations, which are also observed in entangled solutions [Bird *et al.* (1987); Meissner (1972)]. In light of this, and since the transient data are not corrected for the distribution in $\dot{\gamma}$, we eschew a quantitative analysis. In the inset of Fig. 4 are shown selected curves, on an expanded scale, in the region of the maximum. The peak in $\Psi^+(t)$ occurs at several units of shear strain, which is significantly greater than strain associated with the shear stress maximum.

It is obvious from Fig. 4 that the peak in $\Psi^+(t)$ is recovered in a time shorter than required for relaxation of the normal force after shearing is stopped. To the contrary, the overshoot in the shear stress recovers over a time span roughly equivalent to the stress relaxation time upon cessation of the shearing. These relaxation curves are displayed in Fig. 5. Not only the recovery of the peak in $\Psi^+(t)$, but also the rate of the normal stress decay, are substantially faster than the corresponding processes for the shear stress.

The data in Figs. 3 and 4 were obtained at a shear rate ($= 0.14 \text{ rad/s}$) for which the behavior is non-Newtonian. This can be seen from Fig. 6, which shows the steady state viscosity and normal stress coefficient for PS13 as a function of $\dot{\gamma}$, again at

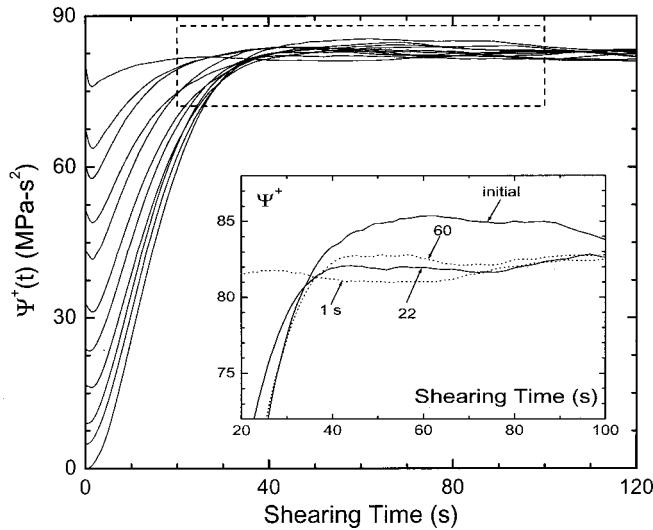


FIG. 4. First normal stress growth coefficient measured for PS13 at a shear rate of 0.14 rad/s and $T = 104.7^\circ\text{C}$ upon initial startup (lowest curve) and after resumption of flow following delay intervals of 1 (uppermost curve), 3, 5, 7, 10, 15, 22, 30, 45, and 60 s. The stress has not fully recovered prior to restart of the shearing. There is a systematic increase in the (weak) maximum with rest time, although the data are too noisy for quantitative analysis. Selected data from the boxed region are shown in the inset on an expanded scale.

$T = 104.7^\circ\text{C}$. The ratio of the maximum in the shear stress to its steady state value is an increasing function of shear rate, while the strain at which the peak $\eta^+(t)$ occurs is independent of $\dot{\gamma}$. At shear rates below $\sim 10^{-2}$ rad/s, no peak is observed in either $\eta^+(t)$ or $\Psi^+(t)$.

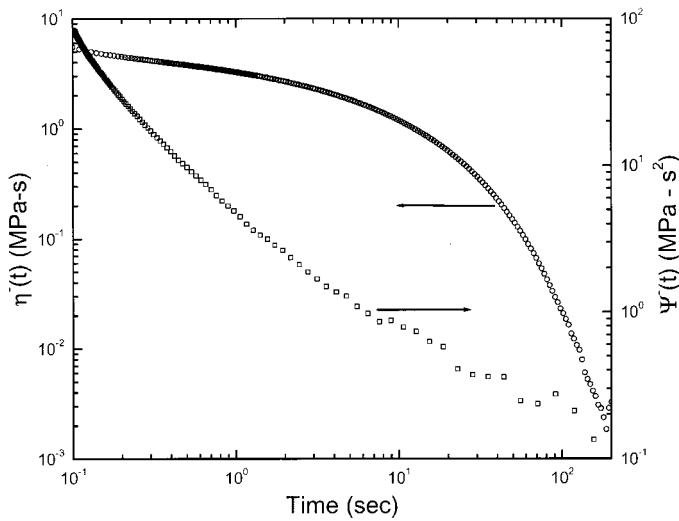


FIG. 5. Relaxation of shear and first normal stresses for PS13 after cessation from steady state shearing at 0.14 rad/s and $T = 104.7^\circ\text{C}$.

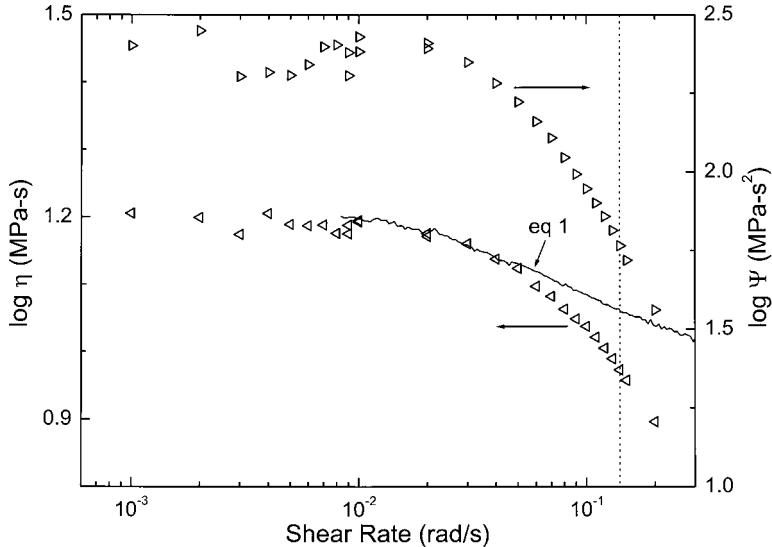


FIG. 6. Steady state values for the viscosity (\triangleleft) and first normal stress coefficient (\triangleright) of PS13 at $T = 104.7^\circ\text{C}$. The data were corrected for the nonconstant shear rate. Deviations from Newtonian behavior occur at $\sim 0.03 \text{ rad/s}$ for both quantities. The vertical dotted line is the shear rate corresponding to the data in Figs. 2 and 3. The viscosities calculated using the Geissle relation (solid curve) are included.

An empirical equation, suggested by Gleissle (1980) for entangled polymers, relates the steady state viscosity to the transient viscosity measured during approach to steady state at the limiting shear rate $\dot{\gamma} \rightarrow 0$.

$$\lim_{\dot{\gamma} \rightarrow 0} \eta^+(t, \dot{\gamma})|_{t=1} = \dot{\gamma} = \eta_{ss}(\dot{\gamma}). \quad (1)$$

The subscript denotes that the startup viscosity is taken at a shearing time equal to the reciprocal of the corresponding shear rate. Good agreement with Eq. (1) has been reported for several high molecular weight polymers [Gleissle (1980); Laun (1986)]. However, as seen in Fig. 6, the Gleissle relation substantially overestimates the steady shear viscosity for PS13, at least for $\dot{\gamma}$ more than a half decade into the non-Newtonian regime.

From the values of the viscosity and first normal stress coefficient in the zero-shear rate regime, we can calculate the steady state recoverable compliance [Bird *et al.* (1987)],

$$J_S^0 = \frac{\Psi}{2\eta_0^2}. \quad (2)$$

This can be compared to the value obtained from integration of the stress relaxation following cessation of flow (Fig. 5), using the formula of Stratton and Butcher (1973)

$$J_s^0 = \int_0^\infty \eta^-(t) dt / \eta_0^2. \quad (3)$$

The results are shown in Fig. 7, along with the compliance determined directly by steady state creep/recovery measurements. The determinations are in good mutual agreement. Note that J_S^0 exhibits a substantial temperature dependence. As first reported by Plazek and O'Rourke (1971), for low molecular weight polymers, the steady state compliance decreases

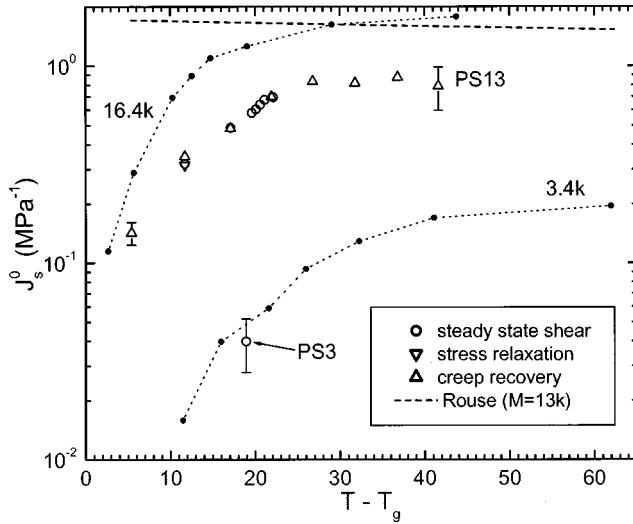


FIG. 7. Steady state recoverable compliance measured for PS13 using Eqs. (2) (\circ) and (3) (∇), and directly from steady state creep/recovery experiments (Δ). The dashed line at the top is calculated for PS13 using Eq. (4). The value obtained for PS3 from Eq. (2) is included, along with data from Plazek and O'Rourke (1971) for polystyrenes having $M = 16\,400$ and $3\,400$ daltons respectively (—·—).

with decreasing temperature as T_g is approached. This differs from the Rouse model for unentangled melts [Ferry (1980)], according to which

$$J_S^0 = \frac{2}{5} \frac{M}{\rho RT}, \quad (4)$$

where RT has its usual significance. The density (in g/ml) of polystyrene is given by [Plazek and O'Rourke (1971)]

$$\rho = \left(0.767 + 5.5 \times 10^{-4} T + 6.43 \times 10^{-2} \frac{T}{M} \right)^{-1}. \quad (5)$$

The Rouse prediction for PS13 is included in Fig. 7, along with literature data for two unentangled polystyrenes having similar molecular weights. The agreement of our results with the latter attests to the absence of a high molecular weight fraction in the PS13, which even in low concentrations would give a high value for J_S^0 [Plazek and O'Rourke (1971), Ngai *et al.* (1987); Ngai *et al.* (1997)]. This means that the overshoot phenomena described herein are likewise not an artifact of high molecular weight contaminants.

The longest Rouse relaxation time is related to the product of the steady state recoverable compliance and the zero-shear viscosity [Ferry 1980],

$$\tau_R = 0.66 J_S^0 \eta_0. \quad (6)$$

This quantity, plotted in Fig. 2, indicates that our overshoot phenomenon must involve the chain modes. Osaki *et al.* (2000a) reported that solutions of barely entangled chains exhibit a stress overshoot when the shear rate exceeds the inverse of the longest Rouse relaxation time. For the PS13 at 104.7°C , the minimum shear rate associated with a

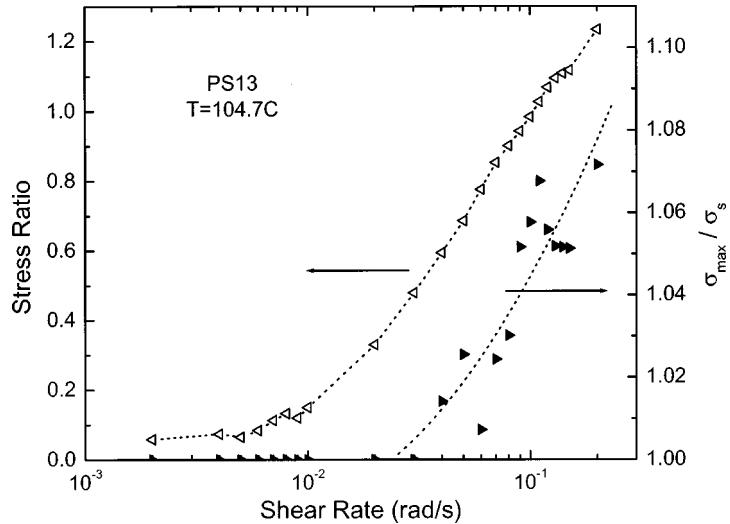


FIG. 8. Shear rate dependence of the stress ratio, defined as the ratio of the steady state values of the first normal stress and the shear stress, and of the ratio of the peak in the viscosity to the steady state viscosity. Both increase markedly at shear rates beyond the Newtonian regime.

stress overshoot was in the range of 0.01–0.04 rad/s. This is consistent with $\tau_R^{-1} = 0.018 \text{ s}^{-1}$ (see Fig. 2). Of course, the utility of the Rouse model is limited, as evident in Fig. 7.

Since the stress overshoot reflects orientation of the unentangled chains, we expect a correlation between the magnitude of the overshoot and the chain elasticity. A measure of the latter is the stress ratio, defined as the steady state ratio of the normal stress to the shear stress, $\Psi \dot{\gamma} / \eta$ [Bird *et al.* (1987); Larson (1988)]. This quantity is plotted in Fig. 8 for various shear rates, along with the maximum in the relative magnitude of the transient stress, which is proportional to η_{\max}^+ / η . The development of an overshoot in the stress occurs at shear rates for which the stress ratio is significantly greater than zero, reflecting a significant degree of chain stretching.

IV. SUMMARY

The mechanism underlying the startup transients and recovery from interrupted flow described herein is orientation of the chains arising from their elasticity, and reflected in their nonzero recoverable compliance. While this means the phenomenon is general, and not restricted to entangled chains, for low molecular weight polymers it can only be measured fairly close to the glass temperature. At more conventional measurement temperatures, motion is too fast. The height of the observed overshoots in η^+ is small ($\sim 11\%$), relative to the steady state viscosity. This is much less than that found for entangled polymers. For entangled polymers the viscosity peak can equal the magnitude of the steady state value itself [Bird *et al.* (1973)]; all the ratios of these quantities depend on the shear rate [Bird *et al.* (1987)]. This difference between the overshoot behavior of short chains and entangled polymers is in accord with the magnitude of their recoverable compliances. In the high polymer limit, J_S^0 for polystyrene attains a value of $\sim 14 \text{ MPa}^{-1}$ [Plazek and O'Rourke (1971)], which is a factor of 20 higher than that for PS13 observed here.

The maximum in η^+ occurs at a product of the shear rate times the shearing time that is invariant to both the recovery time and the shear rate. For PS13, this critical strain is equal to 2.5 ± 0.2 , which interestingly is in the range of 2–3 generally observed for entangled polymers [Meissner (1972); Bird *et al.* (1987)]. The maximum only occurs, however, at shear rates beyond the inverse of the longest Rouse relaxation time (notwithstanding the failure of the Rouse model with respect to the temperature dependence of J_S^0 seen in Fig. 7).

The time scale for recovery of the shear stress peak (~ 100 s for PS13 at 104.7°C) is the same as the time for relaxation of the shear stress following cessation of flow (Fig. 5). This is in contrast with the behavior of entangled polymers, wherein recovery of the transient peak requires an order of magnitude longer time [Stratton and Butcher (1973)]. The difference is that, for entangled polymers, stress relaxation transpires at the reduced degree of entanglements brought about by the shearing flow. For the low molecular weight polymers herein, the two processes (overshoot recovery and stress decay) both involve only orientation. There are no entanglements and hence no change in the structure of the material during flow.

A weak maximum in the normal force is also observed for PS13 and, analogous to entangled polymers [Meissner (1972)], it appears at a higher strain than the peak in the shear stress. However, the intensity of the peak in $\Psi^+(t)$ relative to its steady state value is about a factor of 100 weaker than that found for high molecular weight polymers [Meissner (1972)].

Finally, it would be of interest to carry out rheo-optical measurements in the regime studied herein. The stress-optical law is valid for non-Newtonian steady state conditions [Janeschitz-Kriegel (1983)], although it breaks down during transient flow [Mott and Roland (1996)]. Birefringence data have been employed to extract the relative contribution of different relaxation modes to the dynamic mechanical spectrum of polymers [Read (1983); Inoue *et al.* (2000)]. Such an analysis is delicate, however, and depends sensitively on the assumptions used to deconvolute the various modes [Mott and Roland (1998); Roland and Mott 1999].

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