The Nonlinear Response of a Polydisperse Polymer Solution to Step Strain Deformations

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ABSTRACT: The rheological behavior of a concentrated solution of well-characterized, broad molecular weight distribution polystyrene in step strain flows is examined at large deformations. Mechanical and optical techniques are used to obtain the full stress tensor in terms of the shear stress, first normal stress difference, and second normal stress difference. Stress relaxation data on this novel system in single- and double-step strain flows over a wide range of shear strains are presented. Direct comparisons to data on a similar system having a narrow molecular weight distribution are made illustrating the effects of polydispersity on nonlinear rheological behavior. The new data set is also used to evaluate the reptation model and K-BKZ theory.

I. Introduction

The rheological behavior of entangled polymeric liquids is characterized by complex relaxation mechanisms determined to a large extent by the length and architecture of the chain molecules making up the system. Polymeric liquids of commercial interest often have a relatively broad distribution of chain lengths or a broad molecular weight distribution. For such systems, polymer dynamics involve a complex and poorly understood interplay of intra- and interchain relaxation mechanisms having a broad distribution of time scales.

While the effects of polydispersity on the linear viscoelastic response of linear polymers have received considerable attention,[1] fewer studies systematically address the question of how nonlinear rheology is influenced by molecular weight distribution. It is well-known that polydispersity can have a pronounced effect on the shear rate dependence of the steady viscosity[2] and can even cause qualitative changes in polymer flows.[3] However, in these and other examples, the role(s) played by polydispersity in the manifestation of these effects is (are) difficult to assess.

A particularly useful tool for probing relaxation dynamics is step strain deformations in shear flow. Numerous investigations on the rheology of entangled polymer liquids in step shear strain flows have been carried out on systems having both narrow and broad molecular weight distributions. For narrow molecular weight distribution polymers, solutions of linear chain polymers are often used while, for broad molecular weight distribution systems, polymer melts are often considered that are also often branched chain polymers. It appears, however, that stress relaxation data have not been reported that allow the influence of polydispersity on the nonlinear rheological response of linear chain polymers to be systematically examined.

The objective of this investigation is to fill this void by presenting and interpreting stress relaxation data from single- and double-step strain deformations of a *well-characterized*, broad molecular weight distribution polymer solution. This fluid is similar to a concentrated solution of narrow molecular weight distribution polystyrene for which extensive single- and double-step strain data have been published. In the remainder of this first section, we shall briefly summarize material functions and rheological consistency relations arising in step strain flows and review previous work relevant to this investigation. In the following section, the test fluid and rheological methods used to characterize the full stress tensor in step strain flows are described. In the third section, experimental results for the broad molecular weight distribution polystyrene solution are presented and compared to published data for the narrow molecular weight distribution system. The conclusions of this investigation are presented in the last section.

Single- and double step strain experiments are an invaluable tool for the investigation of nonlinear viscoelasticity in entangled polymeric systems. In a single-step strain experiment, a strain γ is imposed at $t = 0$, and the shear stress σ, first normal stress difference N_1, and second normal stress difference N_2 can be measured as a functions of time and strain. The shear stress relaxation modulus $G(\gamma,t)$ is defined by

$$G(\gamma,t) = \frac{\sigma(\gamma,t)}{\gamma} \tag{1}$$

and the damping function by

$$h(\gamma) = \frac{G(\gamma,t)}{G(t)} \tag{2}$$

where $G(t) = G(\gamma \rightarrow 0,t)$ is the shear stress relaxation modulus of linear viscoelasticity. Measurements of N_2 in single-step strain flows are quite rare and are usually reported in terms of a ratio to N_1

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$$g(\gamma) = -\frac{N_2(\gamma,t)}{N_1(\gamma,t)} \qquad (3)$$

In general, $h(\gamma)$ and $g(\gamma)$ can also be functions of time depending on the type of polymer liquid, the strain level and the time interval during which the functions are evaluated.

The well-known reptation model of Doi and Edwards[4] suggests that the damping function $h(\gamma)$ is independent of time for sufficiently large times. According to the reptation picture, $h(\gamma)$ is a manifestation of the relatively fast retraction process by which a stretched chain returns to its equilibrium length. The slower process of reptation within the deformed tube is assumed to take place with the chain at its equilibrium length giving rise to the time-dependent function $G(t)$. Thus, the time-strain factorability of $G(\gamma,t)$ as given in eq 2 should be displayed after the process of retraction is complete. This behavior is typically observed for linear, narrow molecular weight distribution systems at times greater than an empirically determined time τ_k; for branched and/or broad molecular weight distribution systems for essentially all observable times. Values of τ_k are believed to represent time required for a chain in a deformed tube to retract to its equilibrium contour length. The reptation, or tube model, also suggests that the ratio of normal stress differences $g(\gamma)$ defined in eq 3 is independent of time. It should be noted that use of the independent alignment approximation[4] (IAA) has a rather minor effect on the damping function $h(\gamma)$ and a somewhat pronounced effect on the magnitude of the normal stress difference ratio $g(\gamma)$. It is finally noted that use of the IAA causes predictions of the reptation model to coincide with those of the well-known K-BKZ model,[5,6] a widely used single-integral rheological constitutive equation.

In double-step strain flows, a strain of γ_1 is imposed at $t = 0$ followed by a second step strain imposed at $t = t_1$ giving a total strain of γ_2. Relaxation of the shear stress (σ) and two normal stress differences (N_1 and N_2) are measured for $t > t_1$. Reversing double step strain flows ($\gamma_2 < \gamma_1$) have been found to be particularly useful for discriminating various constitutive equations.[7−14] For example, it has been argued that the tube model with the IAA (or K-BKZ model) is unable to describe flows with strain reversal while a more rigorous tube model for double step strain flows proposed by Doi does not suffer from this shortcoming.[7] Similar to previous studies, we focus on two reversing double step flows: one where $\gamma_2 = \gamma_1/2$, which will be referred to as a type B flow, and one where $\gamma_2 = 0$, which will be referred to as a type C flow.

Many of the predictions derived from the reptation model both with and without the IAA can be written in terms of *rheological consistency relations*. This designation is often made because for a given model or theory, a material function for a particular flow can be related to one or more material functions from different flows. For example, the shear stress prediction from Doi's model[7] for type C double step strain flows can be written in terms of shear stresses from single step strain flows as follows

$$\sigma(\gamma_1,0,t,t_1) = -[\sigma(\gamma_1,t - t_1) - A(\gamma_1)\sigma(\gamma_1,t)] \qquad (5)$$

where $A(\gamma_1)$ is a correction introduced by Doi that equals one when the IAA is made. For type B flows a consistency relation involving N_1 is given by

$$N_1\left(\gamma_1,\frac{\gamma_1}{2},t,t_1\right) = N_1\left(\frac{\gamma_1}{2},t - t_1\right) - C(\gamma_1)N_1\left(\frac{\gamma_1}{2},t\right) \qquad (6)$$

For $C(\gamma_1) = 0$, N_1 following the second step strain is predicted to be independent of the duration of the first step strain (t_1) and equal to N_1 for a single-step strain flow of $\gamma_1/2$. The tube model prediction of Doi gives $C(\gamma_1)$ that is approximately zero; with the IAA, $C(\gamma_1)$ is identically zero.[13] It is noted that $C(\gamma_1)$ for the irreversible network rupture model of Wagner[15] is given by

$$C(\gamma_1) = \left[1 - \frac{h(\gamma_1)}{h(\gamma_1/2)}\right] \qquad (7)$$

A consistency relationship identical to eq 6 is also predicted by the tube model for the second normal stress difference;[14] however, the usual form of Wagner's INR model predicts zero N_2.

A rheological consistency relation for type C double-step strain flows, involving the ratio of the first normal stress difference and shear stress, given by

$$\frac{N_1(\gamma_1,0,t,t_1)}{\sigma(\gamma_1,0,t,t_1)} = -\gamma_1 \qquad (8)$$

is known as the Osaki−Lodge relation.[13] This consistency relation is satisfied by a rather general class of fluid models that includes the Doi−Edwards, K-BKZ and INR models. For $t_1 \to \infty$, eq 8 gives the well-known Lodge-Meissner consistency relation single-step strain flows.

To report N_2 measurements in double-step strain flows, we introduce the ratio

$$\Psi = -\frac{N_2(\gamma_1,\gamma_2,t,t_1)}{N_1(\gamma_1,\gamma_2,t,t_1)} \qquad (9)$$

In both type B and type C flows, the normal stress ratio is predicted by the tube model to be independent of both t and t_1.

In a series of recent papers,[12−14,16] the response of a relatively narrow molecular weight distribution polystyrene solution in single- and double-step strain flows was reported and compared with the predictions of the reptation model with and without the IAA. In single step strain flows, $G(\gamma,t)$ was found to be independent of time for times greater than three seconds ($\tau_k \sim 3$ s) and the damping function $h(\gamma)$ to be in good agreement with the prediction of the tube model. The normal stress difference ratio $g(\gamma)$ was found to increase slightly with time and fall between the predictions of the reptation model with and without the IAA. In reversing double-step strain flows, the rigorous (without IAA) reptation model was found to be incapable of describing observed behavior, particularly for situations when t_1, $t - t_1 \leq \tau_k$. As expected, the consistency relation in eq 8 was found to hold for all times and values of t_1. Equation 6, with $C(\gamma_1) = 0$, was not consistent with experimental data, while the prediction of the INR model given in eq 7 was found to be in qualitative agreement.

II. Experimental Considerations

The system studied was a 12 wt % solution of polystyrene in tricresyl phosphate. The solution was prepared from a series of narrow molecular weight distribution polystyrenes (supplied

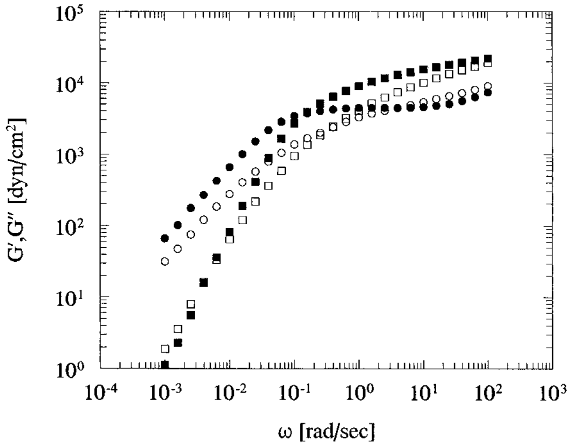

Figure 1. Shear storage G' (squares) and loss G'' (circles) moduli for PSB (open) and PSN(filled) polystyrene solutions.

Table 1. Composition of Broad Molecular Weight Distribution Polystyrene

$M_w \times 10^{-6}$	M_w/M_n	wt %
14.4	1.3	1.0
6.50	1.2	4.0
3.94	1.06	14.0
1.92	1.25	33.0
0.942	1.06	25.0
0.400	1.02	15.5
0.208	1.05	5.5
0.091	1.04	1.5
0.048	1.05	0.4
0.024	1.04	0.1

Table 2. Comparison of Polystyrene/Tricresyl Phosphate Solutions

quantity	PSN	PSB
polystyrene wt %	12	12
test temp (°C)	23	25
$M_w \times 10^{-6}$	1.9	1.9
M_w/M_n	1.25	2.9
$\eta_0 \times 10^{-3}$ (P)	67.5	33.5
τ_m (s)	15	40

by Pressure Chemical Co.) in the proportions shown in Table 1. The resulting weight-average molecular weight M_w is estimated to be 1.9×10^6 and the number-average molecular weight M_n is estimated to be 0.66×10^6. Hence, the ratio M_w/M_n, which gives a measure of the polydispersity of the polymer system, has a value of 2.9, a value typical of commercial polystyrenes. Wasserman and Graessley[1] used a similar polystyrene blend to study polydispersity effects on the linear viscoelasticity of melts. A comparison of this broad molecular weight distribution solution, hereafter designated as PSB, and the narrow molecular weight distribution solution considered in previous studies, designated as PSN, is shown in Table 2.

Mechanical rheological measurements of σ and N_1 were made on a Rheometrics Mechanical Spectrometer (RMS-800) at 25 °C. Cone and plate fixtures with different cone angles and diameters were used to ensure the effects of imperfect step strains and transducer compliance were avoided.[13] All reported second normal stress difference N_2 data were obtained using the optical technique described in Brown et al.[16] Comparisons of mechanical and optical data collected on the PSN liquid indicated a high degree of consistency between the two techniques.

Shear storage and loss moduli data obtained from small amplitude oscillatory flow for the narrow and broad molecular weight distribution solutions are compared in Figure 1. As expected,[17] the transition between the plateau and terminal regions is more distinct for PSN compared with PSB. From these data for PSB, we estimate the zero-shear rate viscosity η_o to be 3.4×10^4 P and the mean relaxation time τ_m to be 40 s. The linear viscoelastic properties of PSB and PSN fluids are compared in Table 2. The larger than expected differences in η_o and τ_m values shown in Table 2 are most likely explained by the difficulties encountered in estimating these quantities for broad molecular weight distribution polymers.

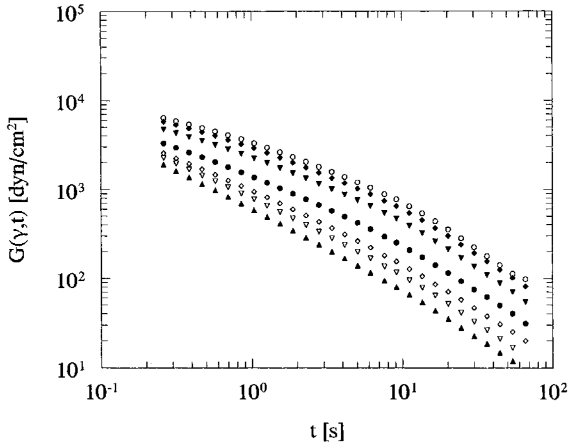

Figure 2. Stress relaxation modulus of PSB for the following strains: 0.25 (○); 1.0 (◆); 2.0 (▼); 4.0 (●); 6.0 (◇); 8.0 (▽); 10.0 (▲).

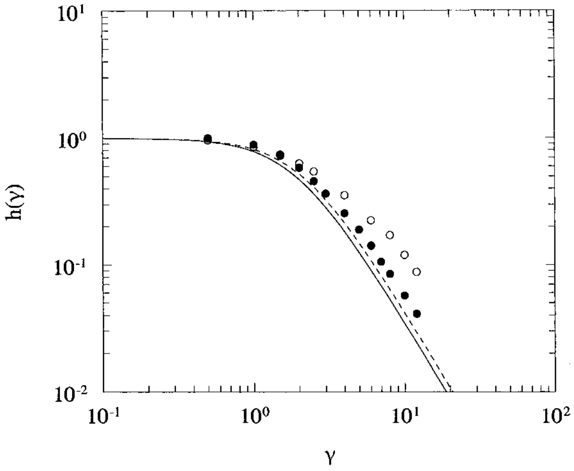

Figure 3. Comparison of damping functions for PSB (open) and PSN (filled) polystyrene solutions. Also shown are reptation model predictions without IAA (solid line) and with IAA (dashed line).

III. Results and Discussion

Single-step strain experiments were carried out on the PSB fluid at strains ranging from 0.25 to 12. Shear stress results are shown in Figure 2 as stress relaxation modulus vs time. From the data shown in this figure it appears that $G(\gamma,t)$ can be factored into strain- and time-dependent functions over most of the times accessible in the experiment. This behavior is markedly different from the PSN fluid,[12] where rather distinct regions of factorable and nonfactorable behavior are displayed, but similar to what has been found for several polydisperse melts.[18,19] It seems reasonable that polydispersity would have such an effect due to the distribution of chain lengths and, thus, relaxation times, causing a smearing out of otherwise distinct relaxation mechanisms.

Values of the damping function $h(\gamma)$ defined in eq 2 for PSB and PSN fluids are compared with the prediction of the reptation model in Figure 3. We note that good agreement between $h(\gamma)$ data and reptation model predictions are found for a wide range of linear, narrow

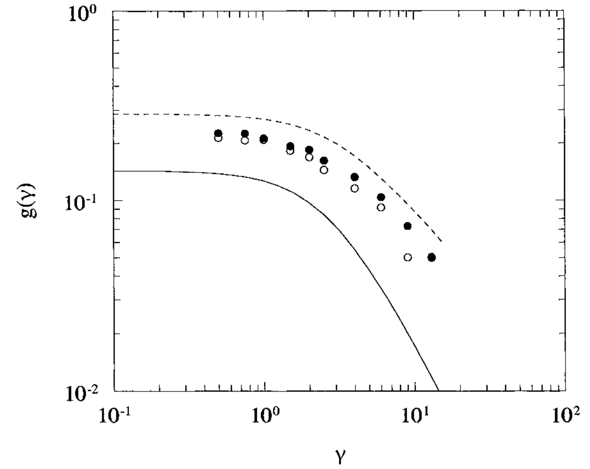

Figure 4. Comparison of normal stress difference ratio for PSB (open) and PSN (filled) polystyrene solutions. Also shown are reptation model predictions without IAA (solid line) and with IAA (dashed line).

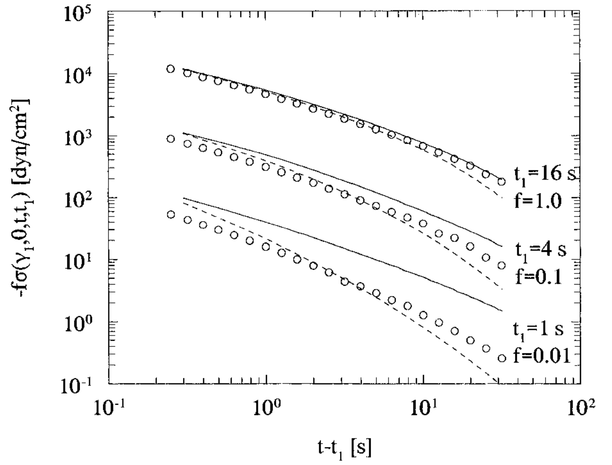

Figure 5. Shear stress relaxation for PSB in type C double-step strain flow with $\gamma_1 = 4$, $\gamma_2 = 0$ for three values of t_1 scaled by the factor f as shown. Experimental data are represented by symbols (○) and reptation model predictions, eq 5, without IAA by a solid line and with IAA by a dashed line.

molecular weight distribution polymer systems.[20] The damping function data for PSB show a less pronounced dependence on strain and are well above the tube model prediction. At large strains, the solid and dashed lines as well as the PSN data have a slope of minus 2.0, while the PSB data have a slope of approximately minus 1.5. Similar results have been reported for polydisperse melts of polystyrene and low-density polyethylene.[18,19] These data may be rationalized by noting that the strong strain thinning predicted by the tube model is only manifested after complete retraction. In the polydisperse case, long chains may only be partially retracted while short chains are reptating; on average, the response is then less severely strain thinning than predicted by the tube model.

Second normal stress data for PSB and PSN fluids are compared with predictions of the tube model in Figure 4. The normal stress difference ratio $g(\gamma)$ was approximately independent of time, and the values shown in Figure 4 were determined from time averages. It seems reasonable to conclude that the ratio of the second to first normal stress difference is not sensitive to polydispersity for linear polymers. While the damping function, $h(\gamma)$, is a strong function of time for $t < t_k$, the normal stress ratio function $g(\gamma)$ is neither predicted nor observed to be strongly affected by incomplete chain retraction.[16] It is not surprising then that mixing of reptation and retraction by polydispersity does not affect the strain-dependent normal stress ratio. Most steady shear N_2 data on polydisperse fluids have not shown shear thinning of the normal stress ratio. This is probably due to the fact that the underlying strain-thinning character exhibited in Figure 4 is broadened by the distribution of relaxation processes in steady-state measurements on polydisperse samples. Since most steady-state N_2 measurements have covered a limited shear rate range, any shear thinning in Ψ may have been obscured. By decoupling time- and strain-dependent responses, these step strain data reveal that $g(\gamma)$ is a fundamentally strain-thinning function in linear polymers, even in the presence of polydispersity. More recently, Magda and co-workers have observed shear thinning of Ψ in steady-state measurements on monodisperse polystyrene solutions.[21]

Figure 5 shows the relaxation of shear stress for a type C double step strain flow where $\gamma_1 = 4$ and $\gamma_2 = 0$, at three t_1 values. At t_1 is increased, the rate of stress relaxation is decreased and, as expected, approaches the behavior of a single step strain flow as t_1 becomes comparable to the longest relaxation time of the fluid. The behavior of PSB shown in Figure 5 is similar to what was observed for PSN[12] although the t_1-dependence appears to be more pronounced for the broad molecular weight system. Shear stress predictions from the tube model, eq 5, are also shown in Figure 5. For $\gamma_1 = 4$, as is the case in Figure 5, $A(\gamma_1) \simeq 0.49$. From this figure, it appears that neither model is capable of describing the experimental results for the two smaller values of $t_1 = 1$ and 4 s and that reasonable agreement is observed for $t_1 = 16$ s. These results are again similar to what was found for the PSN fluid, except that the predictions of Doi's model were somewhat better. This is not surprising given the fact that, in a strict sense, the tube model is applicable only to monodisperse polymer systems.

We now consider the consistency relation for double-step strain flows with $\gamma_2 = 0$, eq 8, which suggests that the ratio N_1/σ is independent of t_1 and t and equal to $-\gamma_1$. Experimental values of this ratio are plotted in Figure 6 vs $t - t_1$ for three values of t_1 (1, 4, and 16 s) represented by different symbols. The solid lines shown in Figure 6 are single-step strain results ($t_1 \rightarrow \infty$) and indicate that the Lodge–Meissner relation is satisfied by the PSB fluid. From the double step strain data shown in Figure 6 it appears that, within experimental limits, the consistency relation in eq 8 is satisfied. This is consistent with the results obtained on the PSN fluid; these two data sets are the only published confirmations of the Osaki–Lodge consistency relation.[13]

Relaxation of N_2 in terms of the ratio to N_1, Ψ, defined in eq 9, for type C double-step strain flows are shown in Figure 7 and compared to the predictions of the tube model with and without the IAA. Given the semblance in the normal stress difference ratio in single-step strain flow for the PSB and PSN fluids shown in Figure 4, it is not surprising that the data shown in Figure 7 for PSB are quite similar to results obtained for PSN[14] in this flow. As was found for PSN, for small t_1, the magnitude of Ψ can lie well outside the envelope of the tube model predictions with and without the IAA. The double-step strain data shown in Figure 7 indicate that

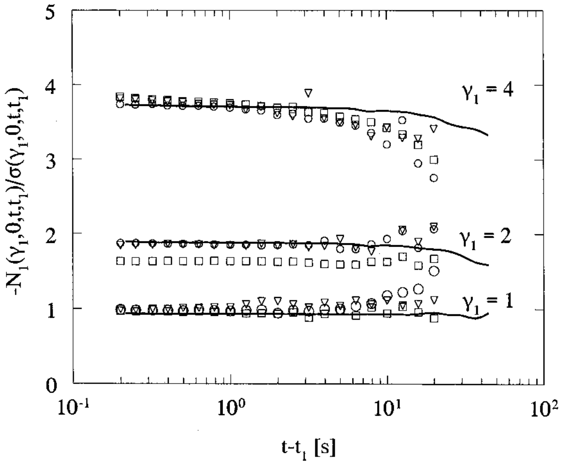

Figure 6. Evaluation of the Osaki–Lodge relation, eq 8, for type C double-step strain flows at values of γ_1 indicated for three values of t_1 (s): 1 (□); 4 (○); 16 (▽). Heavy solid lines are for $t_1 \to \infty$.

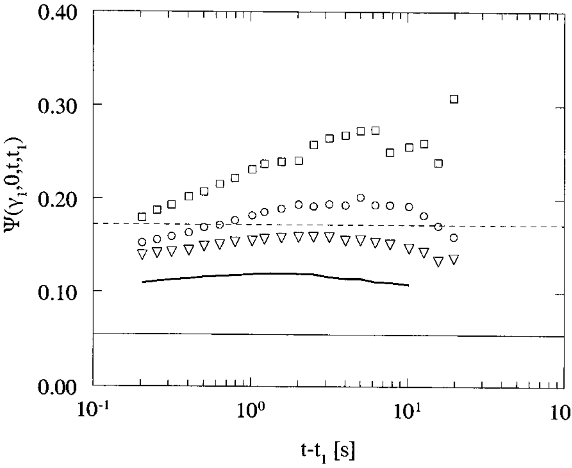

Figure 7. Normal stress difference ratio in type C double-step strain flow with $\gamma_1 = 4$, $\gamma_2 = 0$ for three values of t_1 (s): 1 (□); 4 (○); 16 (▽). Heavy solid line is for $t_1 \to \infty$. Also shown are reptation model predictions without IAA (solid line) and with IAA (dashed line).

Ψ decreases with t_1 and slightly with time ($t - t_1$), also similar to the PSN results.[14] Any dependence of Ψ on t_1 or $t - t_1$ is at variance with tube model predictions; however, this observation is consistent with a suggestion made by Osaki et al.[8] based on N_3/σ data (where $N_3 = N_1 + N_2$) on a fluid similar to PSN. If one accepts the Osaki–Lodge relation, eq 8, then $N_3/\sigma = -\gamma_1(1 - \Psi)$. Osaki et al.[10] have also reported N_3/σ for two broad molecular weight distribution polybutadiene melts and found N_3/σ was independent of time for the linear polymer and decreased with time for the branched polymer.

The second consistency relation to be evaluated is for type B flows given in eq 6. $N_1(\gamma_1,\gamma_1/2,t,t_1)$ data for three values of t_1 (1, 4, and 16 s) indicated by different symbols are compared with single-step $N_1(\gamma_1/2,t - t_1)$ (solid line) data in Figures 8–10. The strain following the first step, γ_1, is 2, 4, and 8 for Figures 8, 9, and 10, respectively. The data shown in these figures do not, in general, support the consistency relation given by the reptation model or K-BKZ theory in eq 6 where $C(\gamma_1) = 0$. In other words, the relaxation of $N_1(\gamma_1,\gamma_1/2,t,t_1)$ is *not* independent of t_1 and does not coincide with $N_1(\gamma_1/2,t - t_1)$. It also appears that the observed deviations from the consistency relation in eq 6 with $C(\gamma_1) = 0$ increase with increasing γ_1, consistent with the prediction for INR theory for $C(\gamma_1)$ given in eq 7. The failure of the consistency relation in eq 6 with $C(\gamma_1) = 0$ for PSB is

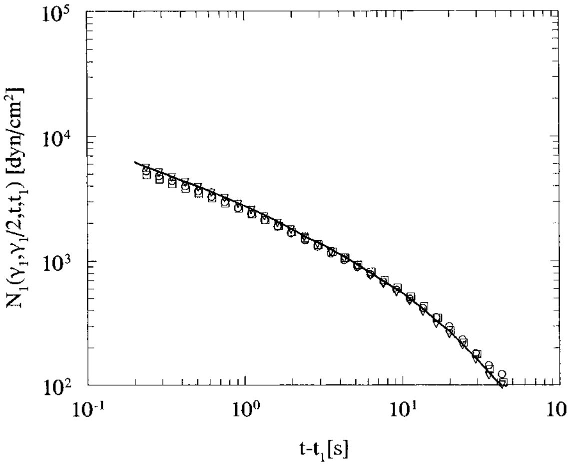

Figure 8. Evaluation of the consistency relation in eq 6 in type B double-step strain flows with $\gamma_1 = 2\gamma_2 = 2$ for three values of t_1 (s): 1 (□); 4 (○); 16 (▽). Heavy solid line is for single step strain flow with strain of 1.

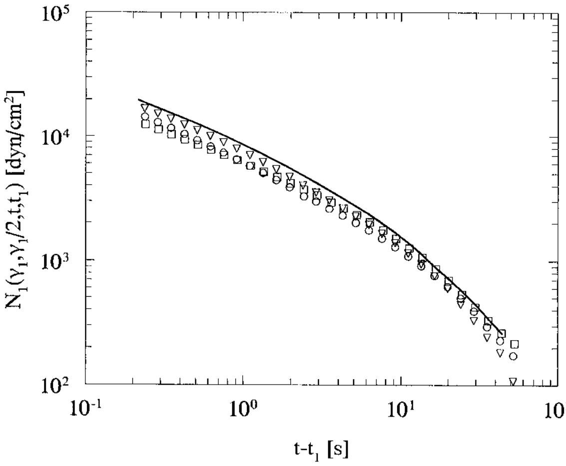

Figure 9. Evaluation of the consistency relation in eq 6 in type B double-step strain flows with $\gamma_1 = 2\gamma_2 = 4$ for three values of t_1 (s): 1 (□); 4 (○); 16 (▽). Heavy solid line is for single step strain flow with strain of 2.

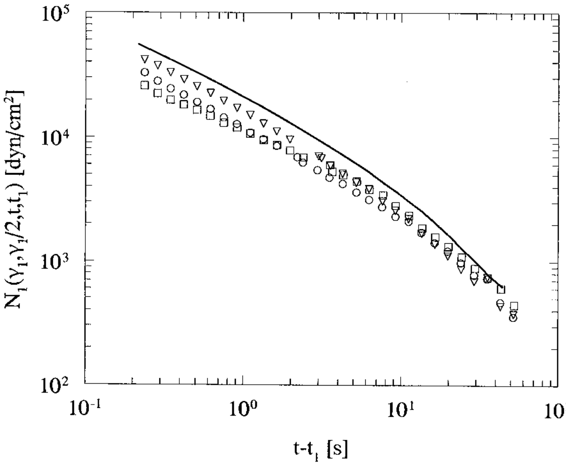

Figure 10. Evaluation of the consistency relation in eq 6 in type B double-step strain flows with $\gamma_1 = 2\gamma_2 = 8$ for three values of t_1 (s): 1 (□); 4 (○); 16 (▽). Heavy solid line is for single step strain flow with strain of 4.

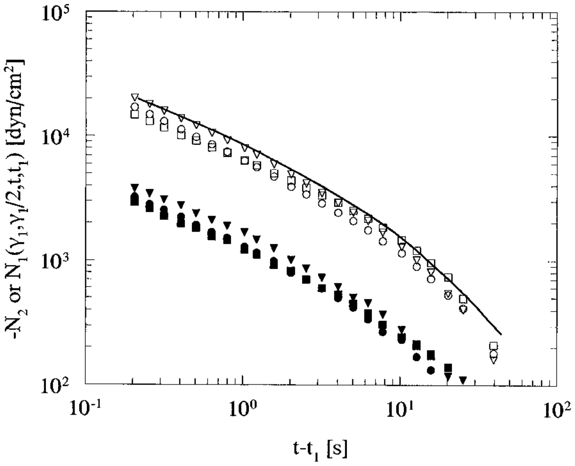

Figure 11. Normal stress difference data from optical method in type B double-step strain flows with $\gamma_1 = 2\gamma_2 = 4$ for three values of t_1 (s): 1 (□), 4 (○), and 16 (▽) for N_1; 1 (■), 4 (●), and 16 (▼) for $-N_2$. Heavy solid line is mechanically measured N_1 for single step strain flow with strain of 2.

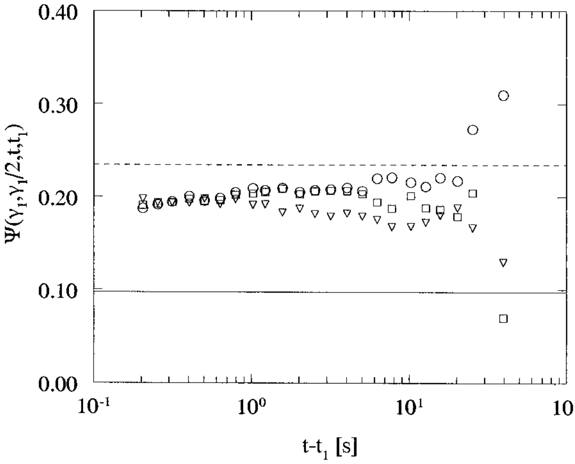

Figure 12. Normal stress difference ratio in type B double-step strain flow with $\gamma_1 = 2\gamma_2 = 4$ for three values of t_1 (s): 1 (□); 4 (○); 16 (▽). Solid line is for $t_1 \to \infty$. Also shown are reptation model predictions without IAA (solid line) and with IAA (dashed line).

similar to what was observed for PSN although deviations for the latter were more pronounced and showed a somewhat stronger dependence on t_1.[13] In addition, the deviations observed in PSN varied systematically with t_1, and were largely confined to times shorter than t_k, suggesting that incomplete retraction may play a significant role in explaining the failure of the consistency relation. Conversely, in Figures 8−10, the deviations from the consistency relation change their relative ordering with t_1 and occur throughout the relaxation process. Such qualitative changes in the mode by which the consistency relation fails may again result from a mixing of retraction and reptation within the polydisperse sample. The results in this study for PSB and the previous study on PSN are the only tests of the consistency relation given in eq 6; and both indicate that $C(\gamma_1) \neq 0$.

Figure 11 presents optical measurements of N_1 and N_2 in a type B flow with $\gamma_1 = 2\gamma_2 = 4$; these data may be compared with the mechanical N_1 results of Figure 9. To facilitate this comparison, the mechanical N_1 data for infinite t_1 are included in Figure 11. The mechanical and optical results are in extremely good agreement, including such details as the crossovers of the curves for various t_1. The N_2 data demonstrate that failure of the type B consistency relationship for second normal stress difference is qualitatively similar to the behavior of N_1: N_2 is not independent of t_1 in Type B flow. In fact, the t_1-dependence of both N_1 and N_2 is such that the normal stress ratio, Ψ, is basically independent of t_1, as shown in Figure 12. This fact is consistent with tube model predictions, and is qualitatively similar to previous observations in the PSN solution.[14]

IV. Summary

Stress relaxation data on a concentrated solution of well-characterized, broad molecular weight distribution polystyrene in step strain flows has been reported. Using a combination of mechanical and optical techniques, the shear stress, σ, and two normal stress differences, N_1 and N_2, have been measured in single- and double-step strain flows over a range of shear strains that probe well into the nonlinear regime.

Comparisons of the new data set for the broad molecular weight distribution polystyrene system to a previously published data set on a similar polystyrene solution, differing only in that the latter had a narrow molecular weight distribution, were made to examine the effects of polydispersity on nonlinear rheological behavior. The shear stress relaxation modulus measured in step strain flow showed, in contrast to the narrow molecular weight distribution system, time−strain factorability over a wide range of strain levels and times. Also, the strain dependence of the measured damping function was not as pronounced and above predictions of the tube model. On the other hand, the strain dependence of the ratio of normal stress differences was unaffected by polydispersity level.

Two double-step strain flows were conducted that involved flow reversal. Shear stress relaxation data for type C flows with $\gamma_1 = 4$ and $\gamma_2 = 0$ was compared to tube model predictions both with and without the IAA; both were unable to describe experimental results. The Osaki−Lodge relation for the ratio N_1/σ was evaluated for only the second time and found to be satisfied for the broad molecular weight distribution polystyrene system. For type B flows with $\gamma_2 = \gamma_1/2$, a consistency relation involving N_1 that follows from the K-BKZ theory and tube model was tested and found not to be in agreement with experiments, particularly at high strain levels. The second normal stress difference behaved in a similar manner in type B flow. Finally, the normal stress difference ratio N_2/N_1 was measured for type B and type C flows and found to have nearly the same behavior as for the narrow molecular weight distribution system.

The data on the novel polymer system considered in this study, in conjunction with data from previous studies, make possible a direct examination of polydispersity effects on the rheological behavior of entangled polymer liquids. Not surprisingly, polydispersity appears to smear out more distinct relaxation processes that can be clearly distinguished in narrow distribution polymers. It is hoped that the data presented in this paper can be used to test molecularly derived models that attempt to include polydispersity.

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