# Stress Overshoot of Polymer Solutions at High Rates of Shear

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**ABSTRACT:** Overshoot of shear stress,  $\sigma$ , and the first normal stress difference,  $N_1$ , in shear flow were investigated for polystyrene solutions. The magnitudes of shear corresponding to these stresses,  $\gamma_{\sigma m}$  and  $\gamma_{\rm Nm}$ , for entangled as well as nonentangled solutions were universal functions of  $\dot{\gamma}\tau_{\rm eq}$ , respectively, and  $\gamma_{\rm Nm}$  was approximately equal to  $2\gamma_{\sigma m}$  at any rate of shear,  $\dot{\gamma}$ . Here  $\tau_{\rm eq} = \tau_{\rm R}$  for nonentangled systems and  $\tau_{\rm eq} = 2\tau_{\rm R}$  for entangled systems, where  $\tau_{\rm R}$  is the longest Rouse relaxation time evaluated from the dynamic viscoelasticity at high frequencies. Only concentrated solutions exhibited stress overshoot at low reduced rates of shear,  $\dot{\gamma}\tau_{\rm eq} < 1$ . The behavior at very low rates,  $\dot{\gamma}\tau_{\rm eq} < 0.2$ , was consistent with the Doi–Edwards tube model theory for entangled polymers. At high rates,  $\dot{\gamma}\tau_{\rm eq} > 1$ ,  $\gamma_{\sigma m}$  and  $\gamma_{\rm Nm}$  were approximately proportional to  $\dot{\gamma}\tau_{\rm eq}$ . At very high rates of shear, the peak of  $\sigma$  is located at  $t = \tau_{\rm R}$ , possibly indicating that the polymer chain shrinks with a characteristic time  $\tau_{\rm R}$  in dilute solutions. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 1917–1925, 2000 **Keywords:** polymer solution; entanglement; tube model; Rouse model; stress overshoot

#### **INTRODUCTION**

One of the important rheological phenomena of polymeric liquids is the stress overshoot at the start of shear flow with sufficiently high rate of shear,  $\dot{\gamma}$ : the shear stress,  $\sigma$ , and the first normal stress difference,  $N_1$ , increase with time, pass through a maximum, and level off at long times.<sup>1</sup> Provided that  $\dot{\gamma}$  is not too high, the magnitude of shear corresponding to the maximum of  $\sigma$ ,  $\gamma_{\sigma m}$ , is about 2 to 3 and is independent of  $\dot{\gamma}$ . The strain corresponding to the maximum of  $N_1$ ,  $\gamma_{\rm Nm}$ , is approximately twice as large as  $\gamma_{\sigma m}$ .

These features may be described with a K-BKZ constitutive model<sup>2,3</sup> with an appropriate memory function. The memory function can be derived from the strain-dependent relaxation modulus,

 $G(t, \gamma)$ , as far as shear deformation is concerned. The data of  $\sigma$  and  $N_1$  in shear flow are actually in fair agreement with ones derived from the K-BKZ model and the memory function determined from data of  $G(t, \gamma)$ . This is factorized as

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

at times longer than a certain characteristic time,  $\tau_{\rm k}$ , for entangled polymer systems where G(t) is the relaxation modulus at the limit of zero strain and the damping function,  $h(\gamma)$ , is a decreasing function of magnitude of shear,  $\gamma$ .<sup>4</sup> Assuming that the damping function is an exponential function of  $\gamma$ ,

$$h(\gamma) = \exp(-\alpha\gamma) \tag{2}$$

one can derive the strains at the maxima of  $\sigma$  and  $N_1$  as

$$\gamma_{\sigma m} = \frac{1}{\alpha}, \quad \gamma_{Nm} = \frac{2}{\alpha}$$
 (3)

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in accord with the features mentioned above.

These results could be interpreted in terms of the tube model theory of Doi and Edwards.<sup>5</sup> The theory gives a constitutive equation equivalent to a K-BKZ model, a relaxation modulus factorable as eq 1, and a damping function in fair agreement with observed ones. The flow field tends to extend and orient the flexible polymer chain in entanglement network. The Doi–Edwards theory states that the equilibration rate of the chain contour length is much higher than the relaxation rate of the orientation so that the chain keeps its equilibrium contour length in flow fields of moderate rate. The chains are oriented to the flow direction but are not extended and this unbalanced deformation of chain gives rise to the nonlinear effect.

At higher rates of shear, the strains at the maxima of stress,  $\gamma_{om}$  and  $\gamma_{Nm}$ , are not independent of  $\dot{\gamma}$  any more but increase with  $\dot{\gamma}$ . The increase with  $\dot{\gamma}$  is probably related to the extension of flexible molecules at high rates of shear. The strains,  $\gamma_{om}$  and  $\gamma_{Nm}$ , corresponding to the maxima of stresses are reported to be universal functions of  $\dot{\gamma}\tau_{\rm R}$ .<sup>6</sup> Here  $\tau_{\rm R}$  is the longest Rouse relaxation time evaluated from the viscosity and molecular weight for well entangled systems. It is supposed to be related to the equilibration time of contour length proposed in the tube model theory.

Similar increase of  $\gamma_{\sigma m}$  and  $\gamma_{Nm}$  is observed for slightly entangled or nonentangled polymeric systems, for which the concept of the entangled system may not be applied. The longest Rouse relaxation time can be evaluated from the complex modulus measured at sufficiently high frequencies for dilute solutions as well as for entangled systems.<sup>7</sup> For nonentangled polymeric systems, linear viscoelastic behavior is described with dilute solution theory with good approximation. The Rouse model theory<sup>8</sup> is usually applicable in the case of solutions in good solvents and/or of moderate concentrations.<sup>9</sup> The maximum relaxation time of viscoelasticity must be related to the shape change of chain as well as of orientation. For entangled systems, we can borrow the idea of Doi-Edwards theory that the chain contour length varies as that of a Rouse model moving in the tube. We assume that the viscoelastic behavior at the high frequency region next to the rubbery plateau zone, characterized by a power law variation of storage modulus with frequency, is a manifestation of the Rouse chain in the entangled system.<sup>7</sup> Thus, we can determine the longest Rouse relaxation time from the complex modulus in the power law region for entangled as well as

$M/10^{4}$	$c/{ m g~cm^{-3}}$	$M/M_e$	
289	0.01	0.63	
824	0.01	1.80	
42.7	0.10	2.37	
70.6	0.10	3.9	
109	0.10	6.1	
	$\frac{M/10^4}{289}\\824\\42.7\\70.6\\109$	$\begin{array}{ccc} M/10^4 & c/{\rm g~cm^{-3}} \\ \\ 289 & 0.01 \\ 824 & 0.01 \\ 42.7 & 0.10 \\ 70.6 & 0.10 \\ 109 & 0.10 \\ \end{array}$	

nonentangled systems. Such information of linear viscoelasticity, although known for a long time, has not been explicitly used in analyzing the behavior of nonlinear viscoelasticity. The purpose of this study is to examine the nature of stress overshoot of polymer solutions of various degrees of entanglement based on data of well-defined characteristic time.

In this regards, Kinouchi et al. observed two maxima in shear stress for a solution of polymer with bimodal molecular weight distribution, which included a slight amount of polymer with very high molecular weight.<sup>10</sup> The behavior is not consistent with the Doi–Edwards model and Osaki et al. pointed out the possibility of high extension of the high M component.<sup>11</sup> Stress overshoot of such polymer blends will be reported in the following paper.

#### EXPERIMENTAL

## Materials

The test solutions are described in Table I. Polystyrene samples with sharp molecular weight distributions were purchased from Toso Co., Ltd. The solvent, tricresyl phosphate was purchased from Nakarai Chemicals Co. and used as supplied. The solvent is a good solvent for polystyrene and the theta temperature, if any, is lower than 40 °C. Weighed amounts of polymer and solvent were homogeneously mixed by addition of dichloromethane and the latter was removed completely at 50 °C and lowered pressure. Solutions with relatively high molecular weights and low concentrations are to represent the high Mcomponents in the succeeding study of blends. Those with low molecular weights and high concentrations are meant to be the matrix.

For rough estimate of the degree of entanglement, following equation for entanglement molecular weight,  $M_{\rm e}$ , was used.

$$(c/g \text{ cm}^{-3})^{1.4} M_e(c) = 7300 \text{ g mol}^{-1}$$
 (4)

where c is the concentration. This equation was obtained for polystyrene in chlorinated biphenyl  $^{12}$  and may not be the best for polystyrene in tricresyl phosphate. Since some preliminary data for the latter were consistent with this equation, we used it for definiteness. The number of entanglements,  $M/M_{\rm e}$ , are shown in the table. Some of the solutions belong to nonentangled  $(M/M_{\rm e} < 2)$  or hardly entangled polymeric systems  $(M/M_{\rm e}$  not much larger than 2).

#### Measurements

A standard rheometer (ARES; Rheometrics Scientific Far East) was used for all the measurements. The complex modulus was measured with a parallel plate fixture. Radii of 25 mm and 8 mm were used depending on the temperature. Dynamic measurements were performed over a temperature range from -40 °C to 30 °C and the data were reduced to a reference temperature, 0 °C, with the method of reduced variables.<sup>13</sup> The shift factor,  $a_{\rm T}$ , was determined by comparing the loss tangent, tan  $\delta$ , at various temperatures. The reduction of tan  $\delta$  was always attainable with high precision. Then the components of complex modulus,  $G'(\omega)$  and  $G''(\omega)$ , were reduced. Good reduction was attained with introduction of a slight vertical shift factor,  $b_{\rm T}$ .<sup>1</sup> Master curves represent the plots of  $G'(\omega)/b_{\rm T}$  and  $G''(\omega)/b_{\rm T}$  against  $\omega a_{\rm T}$ .

Shear stress,  $\sigma$ , and the first normal stress difference,  $N_1$ , at constant rate of shear,  $\dot{\gamma}$ , were measured as a function of time of flow, t. Cone and plate of 25 mm radii and 6 ° cone angle were used. Measurements were performed at 0 °C and a few lower temperatures. The results at lower temperatures were reduced to the reference temperature, 0 °C; reduced stresses

$$\sigma/b_T$$
 and  $N_1/b_T$  (5)

were regarded as functions of reduced time,  $t/a_{\rm T}$ , at a reduced rate of shear  $\dot{\gamma} a_{\rm T}$ . Here the shift factors,  $a_{\rm T}$  and  $b_{\rm T}$ , from the dynamic measurements were employed.

#### RESULTS

#### **Complex Modulus and Characteristic Times**

The storage modulus, G', and the loss modulus, G'', for solution f288-01 are plotted against the



**Figure 1.** Complex modulus, G' and G'', for polystyrene solution f288-01 reduced to reference temperature, 0 °C. Thin solid lines represent fitting curves. Dashed lines: spring-beads term, eq 6, plus viscous term, eq 7. Thick lines: additional term, eq 8.

angular frequency,  $\omega$ , in Figure 1. The result is typical of dilute solution of flexible polymers in good solvent.<sup>9</sup> G' and G" are proportional to  $\omega^2$ and  $\omega$ , respectively, at the limit of low  $\omega$ , and are proportional to  $\omega^{1/2}$  and  $\omega$ , at high  $\omega$ . Except at very low frequencies, the data can be fitted with an equation of bead-spring theory plus a viscous term (dashed lines). The equation for the beadspring theory reads

$$G' + iG'' = \frac{cRT}{M} \sum_{p=1}^{N} \frac{i\omega\tau_p}{1 + i\omega\tau_p}$$
$$\tau_p = \frac{\tau_R}{p^a}$$
(6)

It is known that the equation of Rouse theory  $(a = 2)^8$  is a good approximation for good solvent systems.<sup>9</sup> The data of Figure 1 were fitted with a = 1.95. The viscous term represents the viscous behavior at high frequencies.

$$G'' = \omega \eta_{\text{inf}} \text{ (high frequencies)}$$
(7)

Here adjustable parameters  $\tau_{\rm R}$  (=0.25s) and  $\eta_{\rm inf}$  (=0.42 Pas) were determined through curve fitting at high frequencies ( $\omega > 10 \text{ s}^{-1}$  in this case).

Code	η/Pa s	$ au_R/{ m s}$	$cRTM^{-1}$ /Pa	$\eta_{\rm inf}/{\rm Pa~s}$	$ au_a/{ m s}$	$G_a$ /Pa
f288-01	4.2	0.25	7.8	0.42	1	1
f850-01	20.6	2.16	2.7	0.45	6.5	1.7
f40-10	190	0.06	531	0.8	0.27	400
f80-10	1100	0.16	320	1.0	2.35	$(G_N = 1400 \text{ Pa})^*$
f128-10	5000	0.39	208	1.2	15.0	$(G_N = 1300 \text{ Pa})^*$

**Table II.** Characteristic Parameters at 0 °C

\* Additional term cannot be written as eq 8.

Number of terms in eq 6 was N = 500 in the fitting but did not affect the result if higher values were chosen. The same  $\tau_{\rm R}$  value was obtained with a more convenient method described in the Appendix. For representing the data at lower frequencies, an additional term was necessary (thick lines).

$$G' + iG'' = G_a \frac{i\omega\tau_a}{1 + i\omega\tau_a} \tag{8}$$

The parameters were determined as  $G_{\rm a} = 1$  Pa and  $\tau_{\rm a} = 1$  s. The result is essentially in accord with the early ones by Ferry et al.<sup>9</sup> The fitting parameters and the viscosity,  $\eta$ , are listed in Table II. The result for f850-01 was qualitatively the same. Since the high frequency data are determined by concentration and not affected by molecular weight,  $\eta_{\rm inf}$  is essentially the same for f288-01 and f128-01 and  $\tau_{\rm R}$  is approximately proportional to the square of molecular weight.

For f40-10 a good fitting was attained with the same procedure. Obtained parameters were  $\tau_{\rm R} = 0.06 \text{ s}$ ,  $\eta_{\rm inf} = 0.8 \text{ Pa s}$ ,  $\tau_{\rm a} = 0.27 \text{ s}$ , and  $G_{\rm a} = 400$  Pa. The modulus of the additional term, 400 Pa, is comparable with that for the term of p = 1 in eq 6, 531 Pa, and is dominant at long times but it is not large enough to invoke the feature of rubbery plateau zone characteristic of entangled system. This feature is consistent with the low  $M/M_{\rm e}$  value given in Table I.

Solutions f80-10 and f128-10 exhibited clear features of entangled systems. Since the high frequency behavior ( $\omega > 100 \text{ s}^{-1}$ ) is qualitatively the same as that shown in Figure 1, the  $\tau_{\rm R}$  and  $\eta_{\rm inf}$  values were readily evaluated. The additional term corresponds to the rubbery plateau zone and cannot be written as simple as eq 8. We do not give the details since it is not the subject of this study. The plateau modulus,  $G_{\rm N}$ , the value of G' at the inflection point of the curve of  $\log G'$  versus

log  $\omega$ , is shown in Table II. The longest relaxation time,  $\tau_a$ , is also shown.

#### **Steady Shear Flow**

The steady shear viscosity,  $\eta$  ( $\dot{\gamma}$ ), and the first normal stress coefficient,  $\Psi_1(\dot{\gamma}) = N_1/\dot{\gamma}^2$ , for f288-01 are shown in Figure 2. Curves represent the magnitude of the complex viscosity,  $\eta^*(\omega)$ , and  $2A_G(\omega) = 2G'/\omega^2$ , respectively, plotted against  $\omega$ . These should agree with  $\eta$  ( $\dot{\gamma}$ ) and  $\Psi_1(\dot{\gamma})$ , respectively, at the limit of  $\dot{\gamma}$ ,  $\omega \to 0$ . At high rates of shear, the data for steady shear are higher than the corresponding linear viscoelastic quantities. The Cox–Merz rule<sup>14</sup> stating the correspondence of  $\eta$  ( $\dot{\gamma}$ ) and  $\eta^*(\omega)$  is not applicable in this case, and also for f850-01 and f40-10, in contrast with the case of entangled systems. The



**Figure 2.** Viscosity,  $\eta(\dot{\gamma})$  and first normal stress coefficient,  $\Psi_1(\dot{\gamma})$ , in steady shear for polystyrene solution f288-01 at 0 °C. Curves represent magnitude of complex viscosity,  $\eta^*(\omega)$ , and  $2A_G(\omega)$ .

results for f80-10 and f128-10 are not shown since these are similar to widely known results. The Cox–Merz rule was a good approximation, for example.

# Stress Growth from Rest for Concentrated Solutions

The shear stress,  $\sigma(t)$ , and the first normal stress difference,  $N_1(t)$ , at various rates of shear,  $\dot{\gamma}$ , are shown in Figure 3 for the entangled solution, f128-10. Measurements were performed at -10 °C as well as at 0 °C and the data were reduced to 0 °C. The stresses are represented by following functions.

$$\eta^{+}(t) = \frac{\sigma}{\dot{\gamma}} \tag{9}$$

and

$$\Psi_1^+(t) = \frac{N_1}{\dot{\gamma}^2}$$
(10)

These may be called the growth functions of viscosity and the first normal stress coefficient, respectively. The abscissa, t, implies the reduced time of shear flow after rest state.

Dashed curves at the top represent the prediction of the second order-fluid theory (equivalent to linear viscoelasticity theory for shear stress)<sup>15</sup> with the use of the relaxation spectrum obtained from complex modulus. At very small strains, all the data should lie on the dashed line. At small strains, approximately  $1.5 < \gamma (= \dot{\gamma}t)$ , the stresses are well described by the second order theory at any rate of shear,  $\dot{\gamma}$ . Deviation seems to appear at a certain value of strain rather than at a certain time. At high rates of shear, stress overshoot is observed for  $\eta^+$  as well as for  $\Psi_1^+$ . The time corresponding to the maximum of  $\Psi_1^+$  is about twice that for  $\eta^+$ . The time decreases with increasing  $\dot{\gamma}$ . At very high rates of shear a stress undershoot was observed for  $\eta^+$  as well as for  $\Psi_1^+$ . These are well known features for entangled systems as mentioned earlier.<sup>6</sup> At the rates higher than shown here, the sample deformed in irregular manners at an early stage of measurement.

The result for f80-10 is similar to that for f128-10. For f40-10, a hardly entangled concentrated solution, a similar result was obtained in narrower range of rate of shear. The flow became



**Figure 3.** Functions  $\eta^+(t)$  and  $\Psi_1^+(t)$  for polystyrene solution f128-10 reduced to reference temperature, 0 °C. Solid lines represent results at various rates of shear (in s<sup>-1</sup>); from top, 0.058 (only for  $\eta^+$ ), 0.10, 0.25, 0.40, 0.63, 1.0, 1.74, 2.9, and 5.8. Dashed lines represent calculated results with second-order viscoelasticity theory.

unstable before marked stress overshoot was detected.

#### Stress Growth from Rest for Dilute Solutions

Stress growth for sample f288-01, a dilute solution with no entanglement effect, is shown in



**Figure 4.** Functions  $\eta^+(t)$  and  $\Psi_1^+(t)$  for polystyrene solution f288-01 reduced to reference temperature, 0 °C. Ordinate of upper panel is expanded. Solid lines represent results at various rates of shear (in s<sup>-1</sup>); from top, 1.0 (only for  $\eta^+$ ), 2.0 (only for  $\eta^+$ ), 4.0, 8.0, 11.8, 16.8, 23.5, 30, 42, 60, 90, and 126. Dashed lines represent calculated results with second-order viscoelasticity theory.

Figure 4. The data were obtained at 0 °C, -10 °C, and -20 °C. Note that the ordinate axis for the upper panel is expanded in this figure; the deviation from the linear viscoelasticity behavior, the dashed curve, at short times may seem large but is less than 20%. In contrast with the entangled system,  $\eta^+$  as well as  $\Psi_1^+$  at various rates of shear increase along the dashed curves for the second order theory up to a certain time; about 0.1 s for  $\eta^+$  and 0.2 s for  $\Psi_1^+$ .

Shortly after the appearance of the nonlinear behavior,  $\eta^+$  and  $\Psi_1^+$ , respectively, exhibit maxima. As  $\dot{\gamma}$  increases, the maxima tend to approach certain times, respectively. The times corresponding to the maxima will be discussed later. The overshoot is followed by an undershoot for  $\dot{\gamma} > 16.8 \text{ s}^{-1}$ . For  $\dot{\gamma} < 50 \text{s}^{-1}$ , the stresses level off and steady values of viscosity and normal stress difference can be determined. At higher rates of shear, the stresses keep on increasing and steady state is not attained. At still higher rates of shear, over  $108 \text{ s}^{-1}$ , overshoot occurs at shorter times. After the undershoot and slow increase, the stresses begin to increase very rapidly at a certain time (thick line). The sudden fast increase following the slow increase was quite reproducible and the same curves were obtained in repeated experiments.

Qualitatively the same result was obtained for f850-01.

## DISCUSSION

#### Strains at the Peak Stresses

Magnitudes of shear,  $\gamma_{\sigma m}$  and  $\gamma_{Nm}$ , corresponding to the peaks of shear stress and the first normal stress difference, respectively, are plotted against a reduced rate of shear,  $\dot{\gamma}\tau_{\rm R}$ , in Figure 5. The crosses (x and +) represent dilute solutions; other marks, concentrated solutions; filled marks, entangled solutions. The raw value of rate of shear,  $\dot{\gamma}$ , for each point may be estimated by consulting the  $\tau_{\rm R}$  values in Table II. The upper bound of  $\dot{\gamma}$  for each sample corresponds to the highest rate of shear for which a steady state is attained at long times. The lower bound represents the lowest rate of shear for appearance of stress overshoot. The use of the longest relaxation time,  $\tau_{\rm a}$ , instead of  $\tau_{\rm R}$ for making reduced rate of shear does not lead us to any meaningful figure as discussed below.

The data points of  $\gamma_{\rm om}$  and  $\gamma_{\rm Nm}$ , respectively, for nonentangled systems approximately lie on single lines, which correspond to ones in Figure 6. The points for entangled systems systematically deviate from the lines. All the points can be brought on single lines if another reduced rate of shear,  $\dot{\gamma} \tau_{\rm eq}$ , is used for the abscissa (Fig. 6). Here we define

$$\tau_{\rm eq} = \tau_R \ ({\rm non-entangled})$$
 (11)



**Figure 5.** Magnitudes of shear corresponding to peaks of shear stress and first normal stress difference plotted against reduced rate of shear,  $\dot{\gamma}\tau_{\rm R}$ . Various marks represent test solutions;  $\times$ : f288-01, +: f850-01,  $\bigcirc$ : f40-10,  $\blacklozenge$ : f80-10,  $\blacksquare$ : f128-10.

$$\tau_{\rm eq} = 2\tau_R \; (\text{entangled}) \tag{12}$$

The result may be fortuitous. On the other hand, the factor 2 in eq 12 could be significant in the definition of characteristic time for the contour length equilibration.<sup>5</sup> Studies of eq 11 are needed for understanding the significance, or insignificance, of Figure 6.

The lines in Figure 6 are approximately expressed as

$$\gamma_{\sigma m} = 0.87 [1.59 + (\dot{\gamma}\tau_{\rm eq})^{2/3}]^{3/2}$$
(13)

$$\gamma_{Nm} = 2\gamma_{\sigma m} \tag{14}$$

It may be noted that at high rates of shear the maximum of  $\sigma$  appears at  $t = \tau_{\rm R}$  and that for  $N_1$  at  $t = 2 \tau_{\rm R}$ .

#### **Behavior of Entangled Solutions**

The data for entangled systems are located at relatively low reduced rates of shear. In the range  $0.2 < \dot{\gamma} \tau_{\rm eq}, \gamma_{\rm om}$  is almost independent of  $\dot{\gamma}$  and the overshoot of the normal stress difference is scarcely detected. These features are close to the prediction of the Doi–Edwards theory based on the assumption of equilibrated contour length.

The separability criterion, eq 1, for entangled polystyrene solutions led to an estimate that the contour length of polymer chain completely equilibrates in  $t = 4.5 \tau_{eq}$  after deformation.<sup>16</sup> One may expect that the chain keeps its equilibrium contour length in the flow of  $\dot{\gamma} < (4.5 \tau_{eq})^{-1}$ , which is consistent with the present observation at low  $\dot{\gamma}$ .

The concentrated systems became unstable at relatively low reduced rate of shear. However, the measurable range for one with the highest molecular weight, f128-10, extended up to  $\dot{\gamma}\tau_{\rm eq} = 3$  where  $\gamma_{\rm m}$  values are higher than the prediction of the Doi–Edwards model. The data points in the range of high  $\dot{\gamma}$  lie on the same curve as that for dilute solutions.

#### **Behavior of Nonentangled Solutions**

The stress overshoot is first detected at about  $\dot{\gamma}\tau_{\rm eq} = 1$  for dilute solutions. The magnitudes of shear corresponding to the maxima of stresses are approximately proportional to  $\dot{\gamma}\tau_{\rm eq}$  over almost whole range of measurements. The result can be qualitatively understood by assuming that the polymer chain extends in the flow field on one hand and shrinks with a characteristic time,  $\tau_{\rm eq} = \tau_{\rm R}$ , on the other hand. The assumption is not consistent with the Rouse model theory. The test of nonlinear models will be published elsewhere.



**Figure 6.** Magnitudes of shear corresponding to peaks of shear stress and first normal stress difference plotted against reduced rate of shear,  $\dot{\gamma}\tau_{\rm eq}$ . For marks, see Figure 5. Lines represent fitting functions, eq 13 and 14.

The solution f40-10 exhibits stress overshoot even at  $\dot{\gamma}\tau_{\rm eq} < 1$ . On the other hand, the variation of  $\gamma_{om}$  and  $\gamma_{\rm Nm}$  is different from that of entangled systems and seems like that of dilute solutions extrapolated to low rate of shear. Further studies on nonentangled concentrated solutions are in progress.

#### **Comparison with Published Result**

The result shown in Figure 5 is not in agreement with the same plot given by Menezes and Graess-ley.<sup>6</sup> They evaluated  $\tau_{\rm R}$  from the viscosity for well entangled systems according to eqs A4 through A8. The present data are in fair agreement with those of Menezes and Graessley if  $\tau_{\rm R}$  values are evaluated from the viscosity. For the present systems, we use the  $M_{\rm e}$  value from eq 4 and assume that

$$M_c = 2M_e \tag{15}$$

The values for the concentrated solutions, f40-10, f80-10, and f128-10, were about 2.5 times larger than  $\tau_{\rm R}$  values from the complex modulus. Still larger values were obtained with use of the formula for  $M_c$  given by Menezes and Graessley.<sup>6</sup> This method may be good for discussing the gross features such as the shape of curve in Figure 5 but may not be good for quantitative features like the precise position of the curve along the abscissa. The result varies with the choice of the equation for  $M_{\rm e}$  and the coefficient in eq 15. Also the assumption (eq A4), that the viscosity of nonentangled system is completely associated with the Rouse theory, is not very good as seen from the considerable contribution to viscosity from the additional term for the sample f850-01.

# CONCLUSION

Overshoot of shear stress and the first normal stress difference is observed for dilute polymer solutions as well as for entangled polymer systems. The magnitudes of shear corresponding to these stresses,  $\gamma_{om}$  and  $\gamma_{\rm Nm}$ , for various systems are, respectively, universal functions of  $\dot{\gamma}\tau_{\rm eq}$  if  $\tau_{\rm eq} = \tau_{\rm R}$  for nonentangled systems and  $\tau_{\rm eq} = 2\tau_{\rm R}$  for entangled systems. Here  $\tau_{\rm R}$  is the Rouse relaxation time evaluated from the dynamic viscoelasticity at high frequencies. Only entangled systems exhibit stress overshoot at low reduced rates

of shear,  $\dot{\gamma}\tau_{\rm eq} < 1$ . The behavior at very low rates,  $\dot{\gamma}\tau_{\rm eq} < 0.2$  is consistent with the Doi–Edwards tube model theory. At high rates,  $\dot{\gamma}\tau_{\rm eq} > 1$ ,  $\gamma_{\sigma m}$  and  $\gamma_{\rm Nm}$  are approximately proportional to  $\dot{\gamma}\tau_{\rm eq}$  indicating that the polymer chain shrinks with a characteristic time  $\tau_{\rm eq}$  in dilute solutions as well as in entangled solutions. The present observation will be employed in analyzing the stress overshoot of polymer blends in which a slight amount of polymer with very high molecular weight is included.

#### APPENDIX

#### Methods for $\tau_{R}$ Determination

According to the Rouse theory, the storage modulus in the power law region is approximated by

$$G'(\omega) = \frac{1.111cRT}{M} (\tau_R \omega)^{1/2}$$
(A1)

If the measured result is approximated by

$$G'(\omega) = a\,\omega^{1/2} \tag{A2}$$

the longest Rouse relaxation time,  $\tau_{\rm R}$ , is determined as

$$\tau_R = \left(\frac{aM}{1.111cRT}\right)^2 \tag{A3}$$

This method is applicable to entangled systems as well as to nonentangled systems.

The evaluation of  $\tau_{\rm R}$  from the viscosity,  $\eta$ , is based on the following assumptions.<sup>6</sup>

$$\tau_R = \frac{6M\eta}{\pi^2 cRT} \quad (M < M_c) \tag{A4}$$

$$\tau_R = \tau_R(M_c) \left(\frac{M}{M_c}\right)^2 \quad (M > M_c) \tag{A5}$$

$$\eta = \eta(M_c) \left(rac{M}{M_c}
ight)^{3.5} \quad (M > M_c) \qquad (A6)$$

Then

$$au_R = rac{6M\,\eta}{\pi^2 cR\,T} \left(rac{M_c}{M}
ight)^2$$

$$a = 0 \quad (M < M_c) \tag{A7}$$

$$a = 2.5 \quad (M > M_c)$$
 (A8)

The values from this method are always larger than the values from complex modulus.

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