Stress Relaxation in Linear Polymer Solutions after Stepwise Decrease of Shear Rate

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ABSTRACT: Shear stress relaxation in linear polystyrene solutions after a stepwise decrease of shear rate from a value of $\dot{\gamma}_1$ to a lower value $\dot{\gamma}_2$ was observed with an R-17 Weissenberg rheogoniometer. The experimental results in the region of low shear rates agreed well with the theory of linear viscoelasticity. In nonlinear regions, it was found that the initial parts of the relative relaxation curves compose a single line independent of $\dot{\gamma}_2$ if $\dot{\gamma}_1$ is kept constant. The behavior is consistent with that of stress development after a stepwise increase of shear rate, reported previously. It was concluded that the quasi-network structure of polymer solutions has a stability and the structure change occurs with a time lag.

Introduction

In highly concentrated solutions of linear polymers, the polymer coils are extensively entangled with each other. In steady shear flow, those molecules are more or less stretched and rotate around their centers of gravity. During the process, the entanglements are transferred from one molecule to another. If the shear rates are low enough, viscoelastic properties of the solutions can be well explained by assuming that the polymer solution has a quasi-network structure having an effective density of entanglements.[1-5] The effective density of entanglements is independent of shear rate if the shear rate is low enough, i.e., in the linear region. If the shear rates are high, i.e., in nonlinear regions, the effective density of entanglements may vary with shear rate but is constant if the solution is at a steady state. That is, it is assumed that all interactions working between polymer molecules are represented by a number of effective entanglement points. In principle, it is sure that other effects such as chain stretching, orientation, etc. cannot be neglected in a discussion of the nonlinear viscoelastic properties of linear polymers. In practice, however, we remark that at least the shear rate dependence of concentrated linear polymer solutions can be well explained by the theory of Graessley, in which only the change in entanglement density is taken into account. Nonlinear phenomena under steady shear flows, therefore, may well be explained if we take into account changes in the effective entanglement density with shear rate.

In nonlinear transient phenomena, such as stress development or stress relaxation, however, the effective density of entanglements changes not only with the strength of the stimulus but also with time after the external stimulus is given to the solution. In previous papers on stress development phenomena, it was pointed out that the structure of polymer solutions has a stability so that the change of structure may occur with a time lag.[6-8]

In stress relaxations, too, the effective density of entanglements may change not only with the strength of the stimulus but also with time. Nonlinear stress relaxation experiments have been studied by many workers for different types of deformation.[2,3,6,9-12] The structure of the polymer solution may change with time in different ways, depending on the type of deformation. In step-strain type experiments, in which a certain strain is instantly given to a sample at $t = 0$, the structure may change gradually with time from the equilibrium one to another structure and again return to the equilibrium structure. The structure at the initial stage of observation is not clear. On the other hand, in stress relaxation after cessation of a steady shear flow, the initial structure (effective entanglement density) is determined by the shear rate and the structure changes toward the equilibrium structure.

The purpose of this work is to discuss the shear stress relaxation phenomena after an instant decrease of shear rate from $\dot{\gamma}_1$ to $\dot{\gamma}_2$, taking into account the change in the structure of the polymer solution.

Theory

Let us suppose that a polymer solution flowing at a shear rate $\dot{\gamma}$ is instantly stopped at $t = 0$. Then the shear stress in the solution relaxes from a steady-state value $P_{12}(\dot{\gamma})$ to zero with time (shear stress relaxation after cessation of steady shear flow $P_{12}^{r}(t|\dot{\gamma})$). If we define the transient viscosity during stress relaxation by $\eta^{r}(t|\dot{\gamma}) \equiv P_{12}^{r}(t|\dot{\gamma})/\dot{\gamma}$, $\eta^{r}(t|\dot{\gamma})$ decreases with time from a steady value $\eta(\dot{\gamma})$ to zero. Likewise, if the shear rate under which a polymer solution is flowing is instantly changed from a value $\dot{\gamma}_1$ to a lower value $\dot{\gamma}_2$ at $t = 0$, the shear stress in the solution changes with time from $P_{12}(\dot{\gamma}_1)$ to $P_{12}(\dot{\gamma}_2)$ (transient shear stress $P_{12}^{r}(t|\dot{\gamma}_1 \rightarrow \dot{\gamma}_2)$). In this case, if we define the excess transient viscosity $\eta^{r}(t|\dot{\gamma}_1 \rightarrow \dot{\gamma}_2)$ by

$$\eta^{r}(t|\dot{\gamma}_1 \rightarrow \dot{\gamma}_2) \equiv \{P_{12}^{r}(t|\dot{\gamma}_1 \rightarrow \dot{\gamma}_2) - P_{12}(\dot{\gamma}_2)\}/(\dot{\gamma}_1 - \dot{\gamma}_2) \quad (1)$$

it decreases with time from a value $\{P_{12}(\dot{\gamma}_1) - P_{12}(\dot{\gamma}_2)\}/(\dot{\gamma}_1 - \dot{\gamma}_2)$ to zero.

In the linear region where both $\dot{\gamma}_1$ and $\dot{\gamma}_2$ are low enough, the shear stress can be expressed by using a memory function $\mu(t-t')$ or an aftereffect function $\phi(t-t')$, where t and t' are the present and past times, respectively. If we employ $\phi(t-t')$, the steady shear stress ($P_{12}(\dot{\gamma})$) and two types of transient shear stresses during stress relaxations ($P_{12}^{r}(t|\dot{\gamma})$ and $P_{12}^{r}(t|\dot{\gamma}_1 \rightarrow \dot{\gamma}_2)$) are respectively given by[2-4]

$$P_{12}(\dot{\gamma}) = \dot{\gamma}\cdot\eta(\dot{\gamma}) = \dot{\gamma}\int_{-\infty}^{t}\phi(t-t')\,dt' \quad (2)$$

$$P_{12}^{r}(t|\dot{\gamma}) = \dot{\gamma}\cdot\eta(t|\dot{\gamma}) = \dot{\gamma}\int_{-\infty}^{0}\phi(t-t')\,dt' \quad (3)$$

$$P_{12}^{r}(t|\dot{\gamma}_1 \rightarrow \dot{\gamma}_2) = \dot{\gamma}_1\int_{-\infty}^{0}\phi(t-t')\,dt' + \dot{\gamma}_2\int_{0}^{t}\phi(t-t')\,dt' \quad (4)$$

If $\phi(t-t')$ is independent of shear rate, eq 4 may be reformed into

$$P_{12}^{r}(t|\dot{\gamma}_1 \rightarrow \dot{\gamma}_2) = \dot{\gamma}_1\int_{-\infty}^{t}\phi(t-t')\,dt' - \dot{\gamma}_1\int_{0}^{t}\phi(t-t')\,dt' + \dot{\gamma}_2\int_{0}^{t}\phi(t-t')\,dt' = P_{12}(\dot{\gamma}_1) + (\dot{\gamma}_2 - \dot{\gamma}_1)\int_{0}^{t}\phi(t-t')\,dt' = (\dot{\gamma}_1 - \dot{\gamma}_2)\int_{-\infty}^{0}\phi(t-t')\,dt' + P_{12}(\dot{\gamma}_2) \quad (4')$$

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From eq 1–4, therefore, we have

$$\eta^r(t|\dot\gamma_1\rightarrow\dot\gamma_2) = \int_{-\infty}^{0}\phi(t-t')\,dt' = \eta^r(t|0) \qquad (5)$$

which is the limiting value of $\eta^r(t|\dot\gamma)$ at $\dot\gamma \rightarrow 0$.

In a previous paper,[8] the transient shear stress in shear rate jump experiments ($\dot\gamma_1 < \dot\gamma_2$), $P_{12}{}^d(t|\dot\gamma_1\rightarrow\dot\gamma_2)$ was observed and the excess transient viscosity $\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2)$, defined by

$$\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2) \equiv \{P_{12}{}^d(t|\dot\gamma_1\rightarrow\dot\gamma_2) - P_{12}(\dot\gamma_1)\}/(\dot\gamma_2 - \dot\gamma_1) \qquad (6)$$

was discussed. (In the previous paper,[8] $\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2)$ was denoted by $\eta^e(t|\dot\gamma_1\rightarrow\dot\gamma_2)$.) In the linear region, the following relationship was experimentally confirmed:

$$\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2) = \int_0^t\phi(t-t')\,dt' = \eta^d(t|0) \qquad (7)$$

where the transient viscosity $\eta^d(t|\dot\gamma)$ is related to the transient shear stress observed after onset of a steady shear flow $P_{12}{}^d(t|\dot\gamma)$ by $\eta^d(t|\dot\gamma) \equiv P_{12}{}^d(t|\dot\gamma)/\dot\gamma$.

Moreover, if we define the negative excess transient viscosity relative to the first steady-state viscosity by

$$\eta^{-r}(t|\dot\gamma_1\rightarrow\dot\gamma_2) \equiv \{P_{12}(\dot\gamma_1) - P_{12}{}^r(t|\dot\gamma_1\rightarrow\dot\gamma_2)\}/(\dot\gamma_1 - \dot\gamma_2) \qquad (8)$$

it should be

$$\eta^{-r}(t|\dot\gamma_1\rightarrow\dot\gamma_2) = \int_0^t\phi(t-t')\,dt' = \eta^d(t|0) \qquad (9)$$

From eq 5, 7, and 9, we have the following relationship in the linear region:

$$\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2) = \eta^d(t|0) = \eta^{-r}(t|\dot\gamma_1\rightarrow\dot\gamma_2)$$
$$(=\eta^\circ - \eta^r(t|0)) \qquad (10)$$

where η° is the zero-shear viscosity ($\equiv\eta(0)$).

In the nonlinear region, the aftereffect function should vary with shear rate as $\phi(t-t'|\dot\gamma)$. If the effects of two external stimuli were additive in the nonlinear region, eq 4 should be written as

$$P_{12}{}^r(t|\dot\gamma_1\rightarrow\dot\gamma_2) = \dot\gamma_1\int_{-\infty}^{0}\phi(t-t'|\dot\gamma_1)\,dt' + \dot\gamma_2\int_0^t\phi(t-t'|\dot\gamma_2)\,dt' \qquad (11)$$

The transient stresses observed after the cessation and onset of steady shear flow, $P_{12}{}^r(t|\dot\gamma)$ and $P_{12}{}^d(t|\dot\gamma)$, are likewise given by

$$P_{12}{}^r(t|\dot\gamma) = \dot\gamma\int_{-\infty}^{0}\phi(t-t'|\dot\gamma)\,dt'$$

$$P_{12}{}^d(t|\dot\gamma) = \dot\gamma\int_0^t\phi(t-t'|\dot\gamma)\,dt'$$

Thus, if the effects of two stimuli were additive, we should have

$$P_{12}{}^r(t|\dot\gamma_1\rightarrow\dot\gamma_2) = P_{12}{}^r(t|\dot\gamma_1) + P_{12}{}^d(t|\dot\gamma_2) \qquad (12)$$

It was already pointed out in the previous paper[8] on stress development experiments that the effects of external stimuli are not additive in nonlinear regions. In the stress relaxation, too, the relationship in eq 12 would not hold in nonlinear regions. (The relationship in eq 10 cannot hold even if eq 12 were valid.)

Moreover, it was also pointed out in the previous paper that the structure of solution has a stability so that the structure change would occur with a time lag. The solution may keep the same aftereffect function as at $\dot\gamma$, $\phi(t-t'|\dot\gamma)$, during a certain period of time after a stepwise change of shear rate. Then, in nonlinear regions, the following relationships corresponding to eq 10

$$\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2) = \eta^{-r}(t|\dot\gamma_1\rightarrow\dot\gamma_2) = \int_0^t\phi(t-t'|\dot\gamma_1)\,dt' \qquad (13)$$

would hold at the beginning of stress relaxation as long as $\dot\gamma_1$ is kept constant.

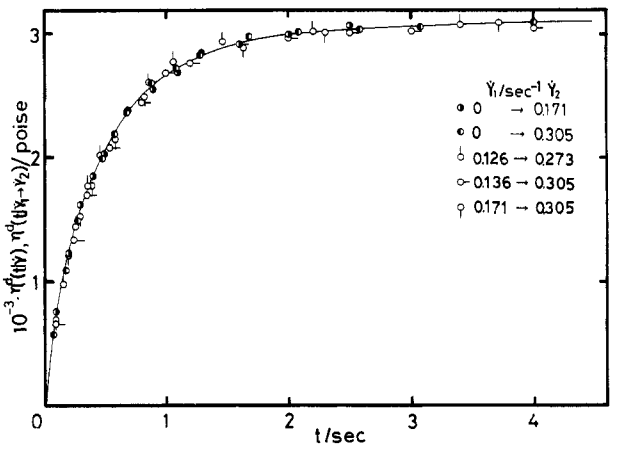

Figure 1. Experimental transient viscosities in the stress development experiments in the linear region. Half-filled circles show the data after onset of steady shear flow ($\eta^d(t|\dot\gamma)$). Open circles show the data after a stepwise increase of shear rate ($\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2)$). The shear rates are denoted in the figure.

Experimental Section

A linear polystyrene, F-128 (Toyo Soda Manufacturing Co. Ltd.), which has a weight-average molecular weight 1.26×10^6 and a narrow molecular weight distribution, was dissolved in a poor solvent, dioctyl phthalate (13%). The zero-shear viscosity η° of this solution at 50.0 °C was 3.15×10^3 P.

The transient shear stress after a stepwise change of shear rate from $\dot\gamma_1$ to $\dot\gamma_2$, $\{P_{12}{}^r(t|\dot\gamma_1\rightarrow\dot\gamma_2)$ if $\dot\gamma_1 > \dot\gamma_2$, and $P_{12}{}^d(t|\dot\gamma_1\rightarrow\dot\gamma_2)$ if $\dot\gamma_1 < \dot\gamma_2\}$ was observed by a Type R-17 Weissenberg rheogoniometer (Sangamo Controls Ltd.) equipped with a gap-servo system. Ordinary stress development and relaxation experiments in the cases of $0 \rightarrow \dot\gamma$ and $\dot\gamma \rightarrow 0$, respectively, were also carried out for reference. The drive unit of the R-17 instrument was modified to actuarize such stepwise changes of shear rate by using a Type 121-10-10 double-clutch unit (Miki Pulley Co. Ltd.). The details of the modification of the drive unit have already been reported.[8] A cone with a 4° angle and 5-cm diameter was used. The temperature was kept at 50.0 ± 0.1 °C. The transient shear stresses were continuously recorded on an electromagnetic recorder. The reliability of measurements with the Type R-17 rheogoniometer was confirmed by oscillation and other experiments as reported previously.[14-16] It was also confirmed that shear stresses in a Newtonian simple fluid after a stepwise change of shear rates reach steady values within the switching time of the modified drive unit (40 ms at the maximum load).

Results and Discussion

The transient viscosities in stress developments $\eta^d(t|\dot\gamma)$ in the region of low $\dot\gamma$ compose a single line independent of $\dot\gamma$ as reported in previous papers. The data in the linear region are shown by half-filled circles and the master curve of $\eta^d(t|0)$ is shown by a solid line in Figure 1. The excess transient viscosity $\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2)$ in the linear region calculated from eq 6, using the experimental $P_{12}{}^d(t|\dot\gamma_1\rightarrow\dot\gamma_2)$ and $P_{12}(\dot\gamma_1)$ data is also shown by open circles in Figure 1. It can be observed that $\eta^d(t|\dot\gamma_1\rightarrow\dot\gamma_2)$ agrees well with $\eta^d(t|0)$ if shear rates are low enough, as reported in the previous paper.[8]

The transient viscosities $\eta^r(t|\dot\gamma)$ after cessation of steady shear flow at sufficiently low $\dot\gamma$ are shown by half-filled circles in Figure 2. It can be observed that $\eta^r(t|\dot\gamma)$ also compose a single line independent of $\dot\gamma$ if $\dot\gamma$ is low enough. In this figure, the excess transient viscosity in stress re-

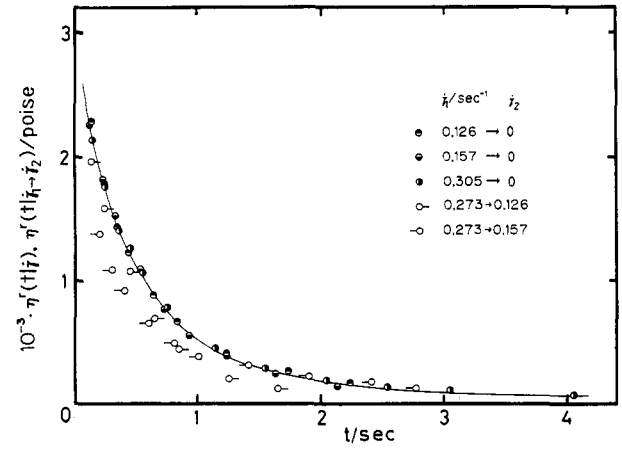

Figure 2. Experimental transient viscosities in the stress relaxation experiments in the linear region. Half-filled circles show the data after cessation of steady shear flow ($\eta^r(t|\dot{\gamma})$). Open circles show the data after a stepwise decrease of shear rate ($\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$). The shear rates are denoted in the figure.

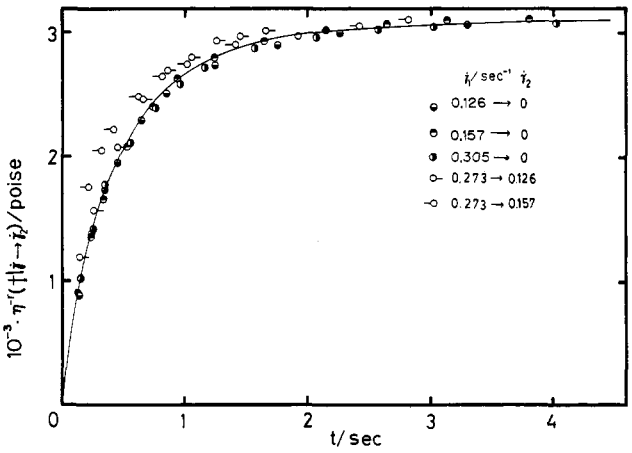

Figure 3. Comparison between transient viscosities in stress development ($\eta^d(t|0)$) and stress relaxation ($\eta^{-r}(t|\dot{\gamma}_1\to\dot{\gamma}_2)$) in the linear region. The solid line denotes the master curve in stress development, while the circles denote the data in stress relaxation. The shear rates are denoted in the figure.

laxation $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ calculated from eq 1 using the experimental $P_{12}{}^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ and $P_{12}(\dot{\gamma}_2)$ data is also shown by open circles. The $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ data are somewhat scattered and the agreement of $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ with $\eta^r(t|0)$ is not so good as the agreement between $\eta^d(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ and $\eta^d(t|0)$. If shear rates are low, measurements of stresses in stress relaxation are much more difficult than in stress development because of low stress values. The ambiguity in the experimental $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ data in Figure 2 may be about 10%. Here, we conclude that $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ also agrees with $\eta^r(t|0)$ in the linear region.

In Figure 3, the data in Figure 2 are replotted in the form of $\eta^{-r}(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ vs. time together with the master curve of $\eta^d(t|0)$. The agreement between $\eta^{-r}(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ and $\eta^d(t|0)$ is satisfactory, as predicted in eq 10. From these results, it can be concluded that the effects of stimuli in the linear region are additive even in transient phenomena. That is, the Boltzmann superposition principle is experimentally confirmed in transient phenomena.

Examples of $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ in the experiments of stress relaxation from various $\dot{\gamma}_1$ to lower values of $\dot{\gamma}_2$ in the nonlinear regions are shown in Figure 4. The $\eta^r(t|\dot{\gamma})$ data in the linear and nonlinear regions are also shown in this figure for comparison. It is clear from this figure that data of either $\eta^r(t|\dot{\gamma})$ or $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ do not compose a single line but are different with different shear rates if shear rates

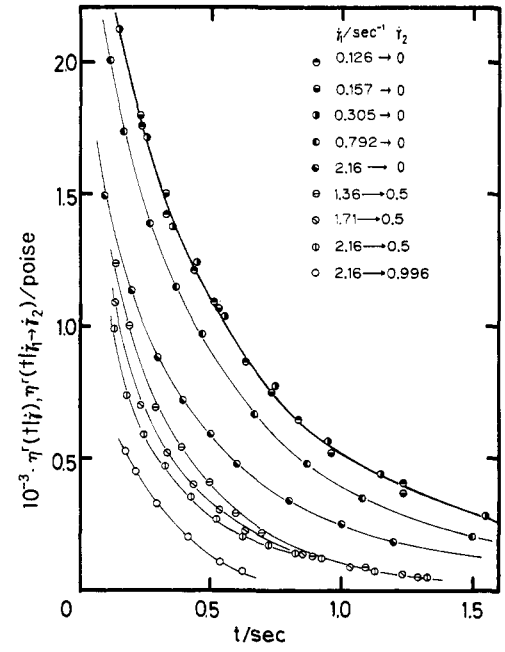

Figure 4. Experimental transient viscosities $\eta^r(t|\dot{\gamma})$ and $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ in nonlinear regions. The data in the linear region are shown by a thick solid line. The shear rates are denoted in the figure.

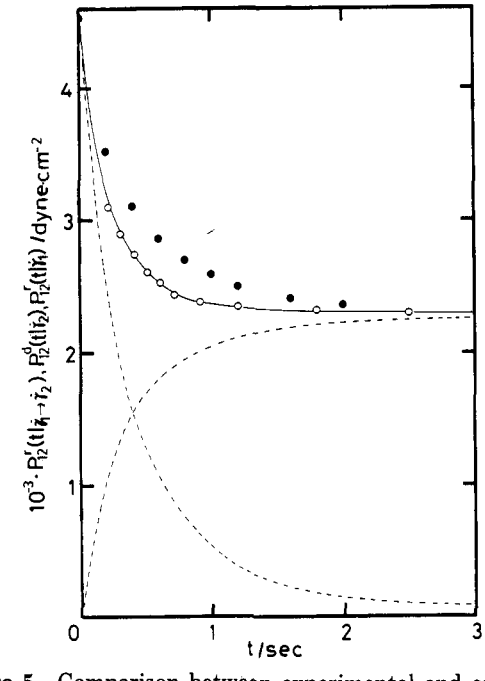

Figure 5. Comparison between experimental and calculated values of transient shear stress $P_{12}{}^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ after a stepwise decrease of shear rate in nonlinear regions. Open circles denote the experimental data while closed circles denote the calculated values of eq 12. Dotted lines denote the data of transient shear stress after the onset and cessation of steady shear flow. $P_{12}{}^d(t|\dot{\gamma}_2)$ and $P_{12}{}^r(t|\dot{\gamma}_1)$, used in the calculation. Shear rates: $\dot{\gamma}_1 = 2.16\ s^{-1}$, $\dot{\gamma}_2 = 0.792\ s^{-1}$.

are high. However, it may be pointed out that not only $\eta^r(t|\dot{\gamma})$ (see Figure 4 in ref 4) but also $\eta^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ converge on a single line at long times if $\dot{\gamma}_2$ is kept constant ($\dot{\gamma}_2 = 0.5\ s^{-1}$). At the end of the transition the structure of the solution may be determined by the steady shear rate $\dot{\gamma}_2$.

In Figure 5, the experimental $P_{12}{}^r(t|\dot{\gamma}_1\to\dot{\gamma}_2)$ data in the nonlinear region are compared with the sum of $P_{12}{}^r(t|\dot{\gamma}_1)$ and $P_{12}{}^d(t|\dot{\gamma}_2)$ as predicted by eq 12. The $P_{12}{}^r(t|\dot{\gamma}_1)$ and $P_{12}{}^d(t|\dot{\gamma}_2)$ data used in the calculation are also shown in

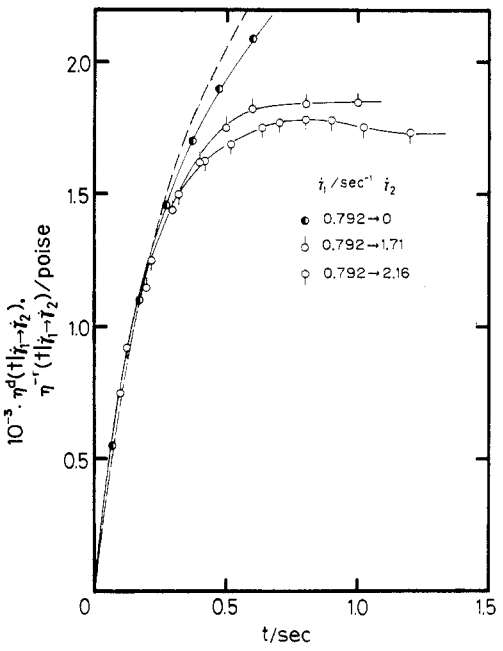

Figure 6. Comparison between transient viscosities in stress development and stress relaxation in nonlinear regions. The broken line denotes the master curve of $\eta^{d}(t|0)$. The shear rates are denoted in the figure.

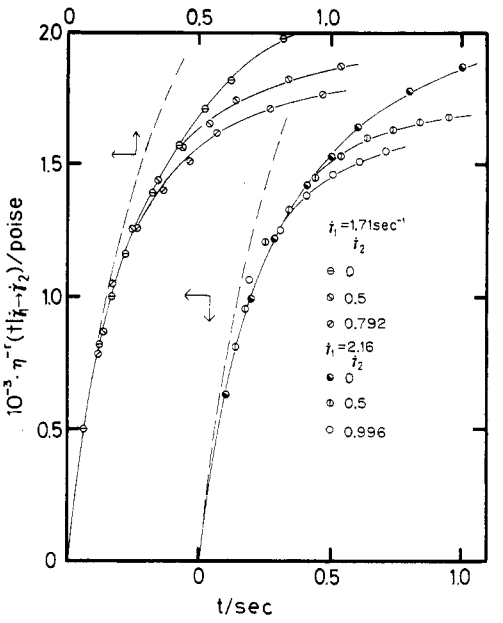

Figure 7. Experimental data of $\eta^{-r}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ in nonlinear regions. The broken line denotes the master curve of $\eta^{d}(t|0)$. The shear rates are denoted in the figure.

this figure. It is clear that the relationship in eq 12 does not hold in the nonlinear region.

For the purpose of observing the initial parts of the stress relaxations clearly, the data in Figure 4 were recalculated into the negative excess transient viscosity $\eta^{-r}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ using eq 8. The values of $\eta^{-r}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ thus obtained are shown in Figures 6 and 7. In Figure 6, $\eta^{d}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ in shear rate jump experiments ($\dot{\gamma}_1 < \dot{\gamma}_2$) are also shown for comparison. It can be observed in these figures that the $\eta^{-r}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ data compose a single line independent of $\dot{\gamma}_2$, up to ca. 0.4 s, if $\dot{\gamma}_1$ is kept constant. Moreover, the $\eta^{-r}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ and $\eta^{d}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ data agree with each other if the first shear rates $\dot{\gamma}_1$ are the same, as predicted from eq 13. The data in Figures 6 and 7 support the conclusion that the quasi-network structure of polymer solutions has a stability and remains unchanged for a certain period of time after the shear rate is changed from one value to some other value. In the present model, the slopes of $\eta^{d}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ and $\eta^{-r}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ should become lower with increasing $\dot{\gamma}_1$. The present experimental data support this speculation.

In the shear rate jump experiments,[6] the time t_c when the $\eta^{d}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$ curves begin to deviate from the universal line may be determined by the critical strain $\gamma_c = t_c(\dot{\gamma}_1-\dot{\gamma}_2)$. A critical strain may be needed to start a rupture of original quasi-network structure. In experiments with a stepwise decrease of shear rate, the time that the original structure at $\dot{\gamma}_1$ begins to change may be different from t_c since the relaxation process includes the formation of entanglements which may be determined by thermal diffusion of polymer molecules. Here, it should be noted that Dearly and Tsang[10] estimated the apparent relaxation time for reentanglement from $P_{12}^{r}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2)$.

In discussing the ordinary stress relaxations after addition of large step-strains, it may be more common and understandable to express the constitutive equation using the memory function which is given as a function of invariant of strain tensor.[11,12] The type of equation will read

$$P_{12}(t) = \int_0^\infty \mu(t-t'|\gamma(t)-\gamma(t'))\{\gamma(t)-\gamma(t')\}\,\mathrm{d}(t-t')$$

where $\gamma(t)$ is the strain at time t. In the stepwise changes of shear rate as in the present work, however, the relative strain is

$$\gamma(t)-\gamma(t') = \dot{\gamma}_2 t - \dot{\gamma}_1 t' \qquad \text{for } t-t' > t$$
$$= \dot{\gamma}_2(t-t') \qquad \text{for } 0 < t-t' < t$$

so that we may have

$$P_{12}(t|\dot{\gamma}_1\rightarrow\dot{\gamma}_2) = \int_t^\infty \mu(t-t'|\dot{\gamma}_2 t-\dot{\gamma}_1 t')(\dot{\gamma}_2 t-\dot{\gamma}_1 t')\,\mathrm{d}(t-t') + \int_0^t \mu(t-t'|\dot{\gamma}_2(t-t'))\dot{\gamma}_2(t-t')\,\mathrm{d}(t-t')$$

The memory function before changing the shear rate, $\mu(t-t'|\dot{\gamma}_2 t-\dot{\gamma}_1 t')$, becomes a function of the coming shear rate $\dot{\gamma}_2$. This type of theory, therefore, cannot be discussed in this paper.

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References and Notes

(1) Sakai, M.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1972**, *5*, 786.
(2) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*.
(3) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(4) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1002.
(5) Takahashi, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 2220.
(6) Kajiura, H.; Sakai, M.; Nagasawa, M. *Trans. Soc. Rheol.* **1974**, *18*(2), 323; **1976**, *20*(4), 575.
(7) Isono, Y.; Nagasawa, M. *Macromolecules* **1980**, *13*, 862.
(8) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1986**, *19*, 1217.
(9) Stratton, R. A.; Butcher, A. F. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1747.
(10) Dealy, J. M.; Tsang, W-M. K. W. *J. Appl. Polym. Sci.* **1981**, *26*, 1149.
(11) Osaki, K.; Kimura, S.; Kurata, M. *J. Rheol.* **1981**, *25*, 549.
(12) Menezes, E. V.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1817.
(13) Bernstein, B.; Kearsley, E. A.; Zapas, L. J. *Trans. Soc. Rheol.* **1963**, *7*, 391.
(14) Endo, H.; Nagasawa, M. *J. Polym. Sci., Part A-2* **1970**, *8*, 371.
(15) Sakai, M.; Fukaya, H.; Nagasawa, M. *Trans. Soc. Rheol.* **1972**, *16*(4), 635.
(16) Kajiura, H.; Endo, H.; Nagasawa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 2371.