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## Stress Relaxation of Polymer Solutions under Large Strain: Elastic Recovery after Partial Stress Relaxation

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Constrained elastic recovery of shear strain was measured after partial stress relaxation for a concentrated solution of polystyrene in chlorinated biphenyl. A constant torsional shear strain  $s$  was applied to the sample held in a cone-plate sample holder during the period of  $-t_1 < t < 0$ . Then the shear stress was removed by releasing the clamp tightening the cone so that the sample was allowed to undergo a torsional shear deformation by itself. The elastic recovery  $\gamma_R(t, t_1, s)$  was evaluated from the rotation angle of the cone measured as a function of time  $t$ . It increased and approached the ultimate value  $\gamma_R(\infty, t_1, s)$  more rapidly when the period of relaxation  $t_1$  was shorter. A large fraction of the original strain  $s$  was recovered only when the initial strain  $s$  as well as  $t_1$  was very small. The effects of varying  $t_1$  and  $s$  on  $\gamma_R(\infty, t_1, s)/s$  were similar to those on the strain-dependent relaxation modulus  $G(t_1, s)$  (=stress at  $t=0$  divided by  $s$ ). When  $t_1$  was longer than a certain time  $\tau'_k$ , the ratio  $r_R = [\gamma_R(\infty, t_1, s)/s] / \lim_{s \rightarrow 0} [\gamma_R(\infty, t_1, s)/s]$  was independent of  $t_1$  and was approximately equal to the ratio  $G(t_1, s) / \lim_{s \rightarrow 0} G(t_1, s)$  for large  $t_1$ . It was concluded that the internal state of the sample after the application of large strain  $s$  may be reorganized in the period of  $\tau'_k$  independent of  $s$  and the shear stress as well as the elastic recovery for  $t_1 > \tau'_k$  may be described by linear viscoelasticity if an effective strain  $s_e = sr_R$  is employed in the place of the actual strain  $s$ .

### INTRODUCTION

In previous papers of this series, we have studied the stress relaxation under large shear strain of a polymer solution and obtained the following results.<sup>1-3)</sup> The effect of large strain  $s$  on the strain-dependent relaxation modulus  $G(t, s)$  is described in a simple manner,<sup>1,2)</sup> the ratio  $G(t, s)/G(t, 0)$  is approximately unity in the range of  $t$  shorter than a certain time  $\tau_l$ , gradually decreases as  $t$  increases in an intermediate time scale of  $\tau_l < t < \tau_k$  and then becomes independent of  $t$  in the longer time scale. Here  $\tau_k$  is independent of  $s$  and the ratio  $G(t, s)/G(t, 0)$  for large value of  $s$  and for  $t > \tau_k$  is approximately proportional to  $I_D^{-0.83}$ , where  $I_D = s^2 + 3$  is the first invariant of the strain tensor. Thus the stress at long time scale increases with increasing strain only when  $s$  is small. For  $s$  value larger than about 3 shear units, the stress at long time scale is the smaller, the larger  $s$  is. Measurements of stress relaxation after application of double-step strain have revealed<sup>3)</sup> that the stress for very large strain may not be described with constitutive equations of single integral type based on

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a strain-dependent nor a strain-rate-dependent relaxation spectra.<sup>4,5)</sup> In the present study, we investigate the elastic recovery after a partial stress relaxation in order to investigate more details of the stress state in the process of stress relaxation under large strain. The measurement of elastic recovery, performed under shear stress-free condition, may be one of the typical methods for studying the stress state and may be compared with the measurement of relaxation modulus which is performed under another extreme condition of constant shape of the sample during the measurement.

The elastic recovery of polymer solutions has mainly been studied in regard to the stress state in steady shear flow. Lodge showed that the stress tensor and the refractive index tensor are essentially equivalent in steady shear flow of an elastic liquid derived from a simple entanglement model.<sup>6)</sup> This result indicated that the stress tensor gives information on the elastic deformation of the polymer chains and that the stress state of polymer concentrates in steady flow may be simulated by assuming an elastic deformation of a rubberlike solid. Philippoff *et al.* measured the shear stress, the normal stress and the flow birefringence of polymer solutions in steady shear flow and revealed that the stress components as well as the flow birefringence are described by assuming an elastic strain of a hypothetical elastic material.<sup>7-9)</sup> This hypothetical strain, called recoverable strain by Philippoff *et al.*, is related to the stored energy in the elastic liquid and is the deformation of the elastic element in terms of a three-dimensional Maxwell model.<sup>10)</sup> It was asserted that the recoverable strain is equal to the ultimate elastic recovery on removal of the shear stress after sudden stop of steady shear flow.<sup>7-9)</sup> However, Lodge proved that the ultimate elastic recovery is a half of the recoverable strain at the limit of zero rate of shear.<sup>11)</sup> Actually the ratio (ultimate elastic recovery)/(recoverable strain) was found to be approximately 1/2 at small rate of shear<sup>12)</sup> but larger than 1/2 in the range of rate of shear sufficiently large to cause the non-linear effect and even to exceed 1 at very high rate of shear.<sup>13)</sup> At the present stage, both of these two quantities may be employed in the studies of elastic behavior of polymer solutions. The ultimate elastic recovery was employed by Vinogradov *et al.* as a measure of the internal strain in the process of stress growth at the beginning of shear flow.<sup>14)</sup> They defined an energy to break the entanglement network and showed that the energy is related to the non-Newtonian viscosity of the polymer solution. The measurement of elastic recovery after a partial stress relaxation has not been reported as far as the authors are informed.

## EXPERIMENTAL

The constrained elastic recovery after a partial stress relaxation we are concerned with is defined as follows. A shear strain  $s$  is applied to the sample at time  $t = -t_1$  and the shape of the sample is kept constant until  $t = 0$  as illustrated in Fig. 1. Accordingly, a shear stress as well as normal stresses is generated in the sample and gradually decreases while the shape is kept constant. In the case of free elastic recovery, in which all the components of the remaining stress are removed for  $t > 0$ , the elastic recovery of the shear strain may be accompanied with an elongational deformation.<sup>11)</sup> In the present case of the constrained elastic recovery, the shear

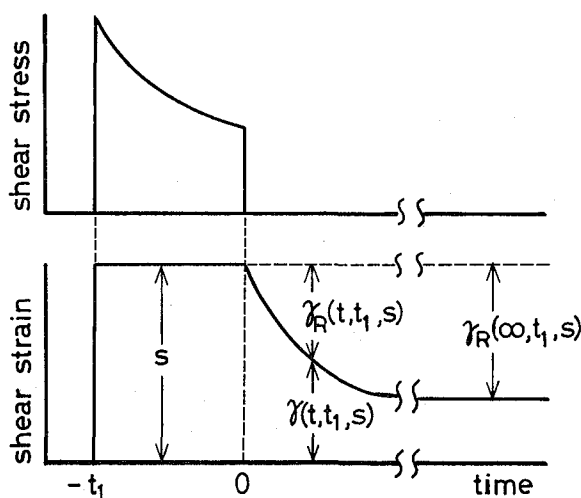


Fig. 1. Illustration of constrained elastic recovery. Shear strain  $s$  is applied for period of  $-t_1 < t < 0$ . Then shear stress is removed so that only deformation in shear is allowed.  $\gamma(t, t_1, s)$  represents shear strain at time  $t$  in reference to original state.  $\gamma_R(t, t_1, s)$  and  $\gamma_R(\infty, t_1, s)$  are elastic recovery at time  $t$  and ultimate elastic recovery, respectively.

stress is made zero for  $t > 0$  by allowing only the shear deformation; normal stresses are spontaneously adjusted by the wall of the apparatus so that the elongational deformation may not occur. The shear strain for  $t > 0$  relative to the original shape is denoted as  $\gamma(t, t_1, s)$  and the elastic recovery is defined by  $\gamma_R(t, t_1, s) = s - \gamma(t, t_1, s)$ . The ultimate elastic recovery is given by  $\gamma_R(\infty, t_1, s) = \lim_{t \rightarrow \infty} \gamma_R(t, t_1, s)$ .

Experiments were performed for a 20% solution of polystyrene in Aroclor 1248 with an apparatus mentioned below. The polystyrene was the standard sample 14a from Pressure Chemical Company and Aroclor 1248 was a mixture of chlorinated biphenyl of various degrees of chlorination from Monsanto Chemical Company. The polymer solution has been employed for measurements of strain-dependent relaxation modulus<sup>1-3)</sup> and stress relaxation after cessation of steady shear flow.<sup>15)</sup> It has been revealed that the mechanical behavior of this sample is described with linear viscoelasticity if the shear strain is smaller than about 1 and that the viscosity and the maximum relaxation time are approximately  $4.3 \times 10^6$  poise and  $7.5 \times 10^2$  sec, respectively, at  $35^\circ$  at which the present study was performed.<sup>1-3,15)</sup> The initial strain  $s$  was varied from 0.619 to 23.27 and the elastic recovery was measured after stress relaxation of various periods  $t_1$  ranging from 10 to 1000 sec for each  $s$  value.

#### APPARATUS

**Design:** The elastic recovery was measured with an apparatus illustrated in Fig. 2. This is a modification of an apparatus of cone-and-plate type used for measurements of strain-dependent relaxation modulus.<sup>16)</sup> The system of torsion wire and differential transformer for the detection of stress was replaced with an assembly

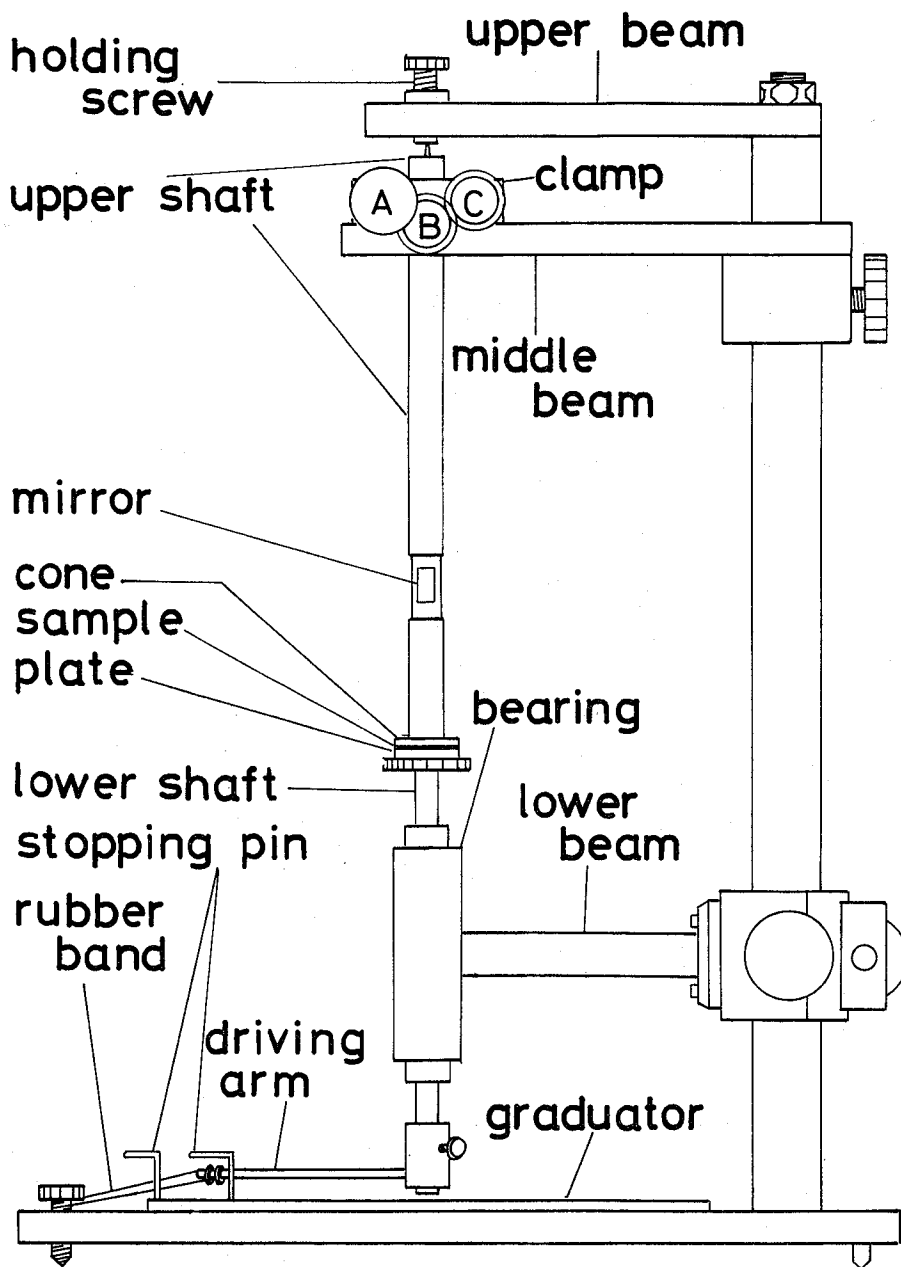


Fig. 2. Apparatus for measurement of constrained elastic recovery.

of upper shaft and clamp for the present purpose of measuring the constrained elastic recovery. See the previous report for the detailed dimensions and materials of various parts.<sup>16)</sup>

The sample holder is made of a disk plate and a cone with its apex on the surface of the plate. The plate is attached to the top of a lower shaft, which is supported by a bearing and may be rotated freely. At the bottom of the shaft is attached a

driving arm which is employed to give rise to a sudden rotation of the lower shaft by a given angle with the help of a rubber band and two stopping pins set in holes on a graduated. The lower shaft assembly may be driven up and down by moving a lower beam supporting the bearing. The cone is attached to the bottom of an upper shaft. Steel needles are glued in the holes at both ends of the upper shaft. The point of the needle at the bottom sits on the top of the lower shaft through holes at the centers of cone and plate.<sup>16)</sup> The point of the upper needle is held by a holding screw. The compressive force from the holding screw may be adjusted so that the upper shaft may be rotated with a very small frictional resistance in the absence of sample fluid. The upper surface of the lower shaft and the lower surface of the holding screw, which are in contact with the needles, are made of very hard drill rods in order to decrease frictional resistance. A mirror is glued at about the middle of the upper shaft. The direction of the shaft is detected with a spot of light reflected by the mirror and can be determined to the precision of  $0.01^\circ$  with the distance 60 cm between the mirror and a scale. The upper shaft may be gripped on flattened surfaces near its upper end with a clamp whose clamping part consists of two brass blocks of variable distances. Each block is driven with two screws inside connected respectively to a knob A and a gear C coupled to the knob through a gear B. The clamp may be released within 0.1 sec by rotating the knob quickly by hand.

**Method of Measurement:** In measuring the elastic recovery after partial stress relaxation, one tightens the upper shaft with the clamp, lowers the lower shaft assembly, spreads the sample over the plate and raises the shaft up to the proper height, where the apex of the cone lies on the surface of the plate, with the use of a micrometer.<sup>16)</sup> One loosens the clamp, adjusts the holding screw so that the upper shaft may rotate as freely as possible without missing the proper axis of rotation. Then one hangs a rubber band between a stopper on the base and the driving bar attached to the lower shaft, rotates the lower shaft so that the rubber band is stretched and stops the bar with a pin standing in one of the holes on the graduated. The excess sample squeezed out of the gap between the cone and the plate is wiped off and the whole apparatus is covered with a thermostated box.

After a thermal and mechanical equilibrium is attained, the lower shaft is rotated quickly by a preset angle corresponding to a shear strain  $s$  of the sample by removing the pin holding the bar and allowing the bar to be dragged by the rubber band up to another stopping pin set in a proper hole on the graduated. After a period  $t_1$  of stress relaxation, the clamp holding the upper shaft is quickly released and the rotation angle thereafter of the upper shaft is measured. The strain may be obtained by dividing the rotation angle of the cone by the gap angle between surfaces of cone and plate.

**Preliminary Tests:** Reproducibility of the results obtained with this apparatus was examined with the use of solutions of a thermally polymerized polystyrene (viscosity-average molecular weight  $\cong 10^6$ ) in Aroclor 1248. The main cause of scattering of data was revealed to be the frictional resistance at supporting points of the upper shaft. This was avoided with the use of very hard materials for the needles at the ends of the shaft and for the parts in contact with the points of needles. In this case the upper shaft can be held in the proper position with a very small compressive force from the holding screw and it can be rotated very lightly in the absence

of the sample fluid. Under this condition the results of measurements were well reproducible. Various rise time up to 1 sec of the initial strain did not affect the elastic recovery measured after 10 sec or longer period of stress relaxation. It was possible to keep the rise time below approximately 0.1 sec for a polymer solution of viscosity  $10^7$  poise just by using a bundle of rubber bands. The moment of inertia of the upper shaft assembly,  $109 \text{ g}\cdot\text{cm}^2$  in our case, was not likely to be the source of large error.<sup>17)</sup> Measured results of the ultimate elastic recovery in the case of small initial strain were compatible with another viscoelastic quantity obtained in the range of linear viscoelasticity (See Fig. 5).

## RESULTS AND DISCUSSIONS

**Time Dependence of Elastic Recovery:** Typical results of elastic recovery  $\gamma_R(t, t_1, s)$  for the 20% solution of polystyrene 14a in Aroclor 1248 are shown in Figs. 3 and 4 representing a small and a large initial strain  $s$ , respectively. In these figures  $\gamma_R(t, t_1, s)$  for various relaxing periods  $t_1$  are plotted against the time  $t$  of elastic recovery. In Fig. 3, almost all of the initial strain is recovered if  $t_1$  is not very large ( $\leq 20$  sec). As  $t_1$  increases,  $\gamma_R(t, t_1, s)$  decreases and after 1000 sec of stress relaxation, the ultimate elastic recovery is less than 1/10 of the initial strain. It may be noted that a large part of the ultimate recovery is attained in a short time when  $t_1$  is small while the elastic recovery proceeds rather slowly when  $t_1$  is large. These results may be reasonable in view of the linear viscoelasticity relations for this sample.

The result for a large initial strain as shown in Fig. 4 is qualitatively similar to that for a small strain. However, it is evident that the elastic recovery is a much smaller fraction of the initial strain in Fig. 4 even when  $t_1$  is small. For example, the elastic recovery approaches the final value rapidly but the ultimate elastic recovery is only about 1/4 of  $s$  even for  $t_1=10$  sec. The elastic recovery proceeds more slowly and the ultimate elastic recovery becomes smaller for larger period  $t_1$ .

**Ultimate Elastic Recovery:** Fig. 5 gives plots of the relative ultimate elastic

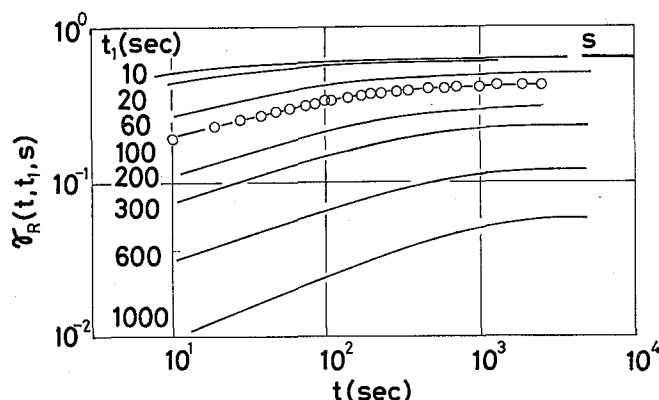


Fig. 3. Elastic recovery  $\gamma_R(t, t_1, s)$  plotted against time  $t$  for 20% polystyrene solution in chlorinated biphenyl at  $35^\circ$ . Initial strain  $s=0.619$  is shown with thick line and periods of stress relaxation  $t_1$  are indicated.

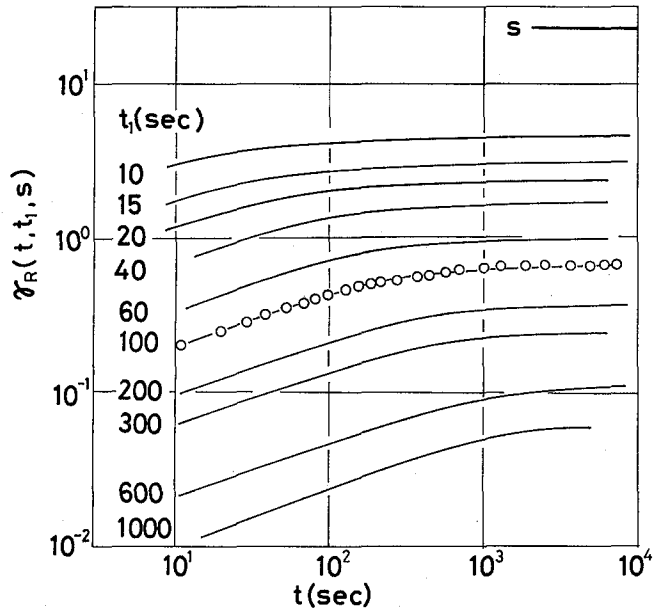


Fig. 4. Elastic recovery  $\gamma_R(t, t_1, s)$  plotted against time  $t$  for 20% polystyrene solution in chlorinated biphenyl at 35°. Initial strain  $s=23.27$  is shown with thick line and periods of stress relaxation  $t_1$  are indicated.

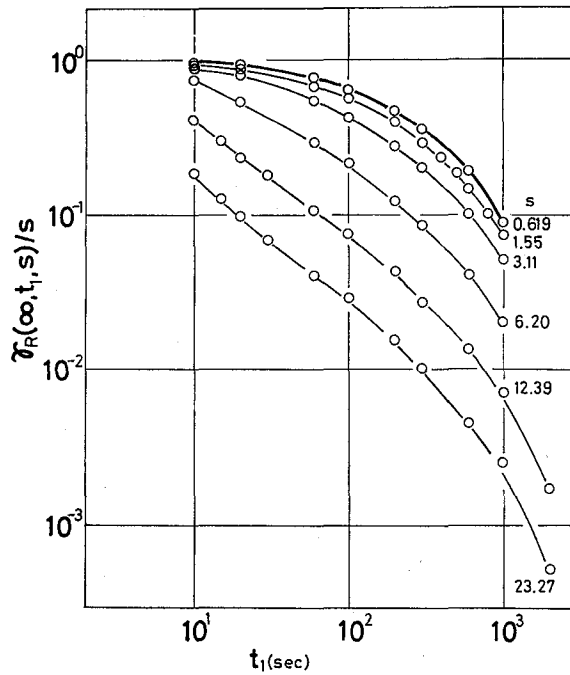


Fig. 5. Relative ultimate elastic recovery  $\gamma_R(\infty, t_1, s)/s$  plotted against period of stress relaxation  $t_1$  for 20% polystyrene solution in chlorinated biphenyl at 35°. Initial strains  $s$  are indicated. Thick solid line represents result obtained from  $\tilde{\eta}(t)$  with Eqs. 2 and 3 at the limit of  $s \rightarrow 0$ .



recovery  $\gamma_R(\infty, t_1, s)/s$  vs. the period of relaxation  $t_1$  with a double logarithmic scale for various initial strains  $s$ . In the cases of small  $s$  values,  $\gamma_R(\infty, t_1, s)/s$  is approximately 1 at 10 sec and decreases as  $t_1$  increases. In these cases, data points lie on convex curves and  $\log \gamma_R(\infty, t_1, s)/s$  decreases with increasing rates of decrease as  $\log t_1$  increases. In the cases of the largest two initial strains, on the other hand,  $\gamma_R(\infty, t_1, s)/s$  is much smaller than 1 at  $t_1=10$  sec and curves exhibit inflection points, *i.e.*,  $\log \gamma_R(\infty, t_1, s)/s$  as functions of  $\log t_1$  exhibit minimum rates of decrease around  $t_1=100$  sec.

At the limit of small strain, the elastic recovery may be calculated from a linear viscoelasticity relation

$$\gamma_R(t, t_1, s)/s = 1 - \int_{-t_1}^0 G(t' + t_1) [dJ(t - t') / dt'] dt' \quad (1)$$

where  $G(t)$  and  $J(t)$  are the relaxation modulus and the creep compliance, respectively. The ultimate elastic recovery may be given by

$$\gamma_R(\infty, t_1, s)/s = (1/\eta^0) \int_{t_1}^{\infty} G(t) dt \quad (2)$$

where  $\eta^0$  is the zero-shear viscosity. The integral in Eq. 2 may be evaluated from  $G(t)$  but it is also related to the shear stress after sudden cessation of a steady shear flow as

$$\tilde{\eta}(t) = \int_t^{\infty} G(t') dt' \quad (3)$$

where  $\tilde{\eta}(t)$  is the ratio of the shear stress to the rate of shear after a period  $t$  following cessation of steady shear flow of low rate of shear.<sup>18)</sup> An experimental result for  $\tilde{\eta}(t_1)/\eta$  is shown in Fig. 5 with a thick line.<sup>15)</sup> This is in good agreement with the result of  $\gamma_R(\infty, t_1, r)/s$  for  $s=0.619$  indicating that the results of the two types of experiments are consistent with each other in view of the phenomenological theory of linear viscoelasticity. Since the measurement of the elastic recovery is easier when  $s$  becomes larger, the agreement shown above suggests good precision of the present data over the whole range of  $s$  studied.

It may be noted in Fig. 5 that the curve for a large  $s$  value is not similar to that for the stress after cessation of the steady shear flow at any rate of shear<sup>15)</sup> but to the plot of  $G(t_1, s)$  vs.  $t_1$  where  $G(t_1, s)$  is the strain-dependent relaxation modulus studied before.<sup>1,2)</sup>

**Comparison with Strain-Dependent Relaxation Modulus:** It has been reported for this polymer solution that the ratio  $G(t, s)/G(t)$  is independent of  $t$  when  $t > \tau_k$ , where  $\tau_k$  is a time independent of  $s$  and is about 15% of the maximum relaxation time  $\tau_m$ .<sup>1)</sup> In this range of time scale,  $G(t, s)/G(t)$  is proportional to  $s^{-1.66}$  when  $s$  is large. Since  $\gamma_R(\infty, t_1, s)/s$  as a function of  $t_1$  is similar in shape to  $G(t, s)$  as a function of  $t$ , we will examine if the same type of the effect of varying  $s$  as mentioned above is observed for the ultimate elastic recovery. In Fig. 5 the slope of the curve for large  $s$  value is relatively small in an intermediate time scale ( $=10^2$  sec) and any curve in the range of longer time scale seems to be superimposed on that for the smallest  $s$  value by a parallel shift along the ordinate. The result of parallel shift is shown in

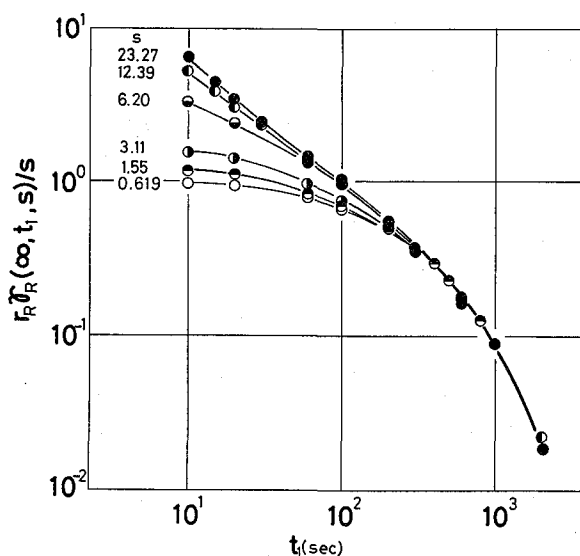


Fig. 6. Reduced plot of relative ultimate elastic recovery  $\gamma_R(\infty, t_1, s)/s$  vs. period of stress relaxation  $t_1$ . Reduction factor  $\tau_R$  is determined with  $\tau_R = [\gamma_R(\infty, t_1, s)/s] / [\lim_{s \rightarrow 0} \gamma_R(\infty, t_1, s)/s]$  at  $t_1 = 1000$  sec.

Fig. 6, where  $\tau_R$  represents the amount of vertical shift which may be defined by

$$\tau_R = [\gamma_R(\infty, t_1, s)/s] / \lim_{s \rightarrow 0} [\gamma_R(\infty, t_1, s)/s] \quad (t_1: \text{large}) \quad (4)$$

since  $\gamma_R(\infty, t_1, s)/s$  for the smallest  $s$  value studied is in agreement with its limiting value at  $s \rightarrow 0$  within experimental error. The value of  $\tau_R$  in Fig. 6 was determined at  $t_1 = 1000$  sec. It may be obvious that  $\tau_R$  is approximately independent of  $t_1$ , i.e.,  $\gamma_R(\infty, t_1, s)/s$  for various values of  $s$  can be superimposed by the parallel shift in the range of  $t_1$  larger than approximately 200 sec. This critical value of  $t_1$  ( $\equiv \tau'_k$ ) is much smaller than the maximum relaxation time and is close to  $\tau_k$ , which is a little larger than 100 sec for this sample at  $35^\circ$ , defined in regard to the strain-dependent relaxation modulus.<sup>1)</sup>

The shift factor  $\tau_R$  is plotted against the initial strain  $s$  in Fig. 7 together with the shift factor for the strain-dependent relaxation modulus  $\tau_G$ :<sup>1)</sup>

$$\tau_G = G(t, s)/G(t) \quad (t > \tau_k) \quad (5)$$

Apparently the shift factor  $\tau_R$  as a function of  $s$  is very close to  $\tau_G$ , although the former is slightly larger than the latter in the range of  $s$  where non-linear effect is evident. When  $s$  is very large,  $\tau_R$  varies as proportional to  $s^{-1.66}$ . This proportionality is in parallel with that reported for  $\tau_G$ .<sup>1)</sup> Thus the effect of large strain may be to depress the ultimate elastic recovery and the shear stress in a very similar manner.

**A Speculation on the Effect of Large Strain:** The result shown above indicates that the ultimate elastic recovery as well as the relaxation modulus may be separated into a strain-dependent and a time-dependent factors in the range of relatively long time scale. Let us define an effective strain  $s_e$  to represent the strain-dependent factor of the elastic recovery as follows.

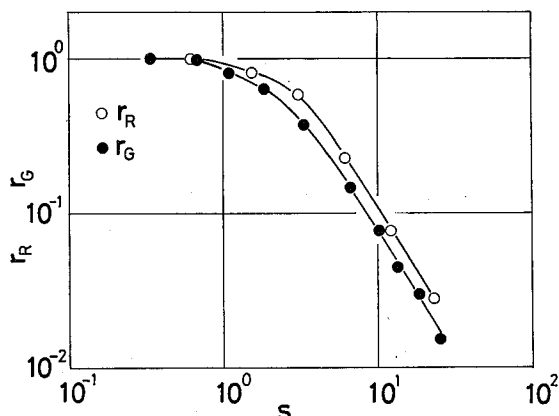


Fig. 7. Reduction factor  $r_R$  and  $r_G$  for ultimate elastic recovery and relaxation modulus, respectively, plotted against initial strain  $s$ .

$$\gamma_R(\infty, t_1, s) = s_e \lim_{s \rightarrow 0} \gamma_R(\infty, t_1, s)/s \quad (6)$$

In the range of very small  $s$  value where the linear viscoelasticity applies,  $s_e$  is equal to the actual strain  $s$ . When  $s$  is sufficiently large to originate non-linear behavior of  $\gamma_R(\infty, t_1, s)$ ,  $s_e$  is a function of  $t_1$  as well as of  $s$ ; it decreases with increasing  $t_1$  in the range  $t_1 < \tau'_k$ . However, in the range of longer time scale, it takes a value  $r_R s$  independent of  $t_1$ . Since the shear stress at  $t_1$  after the application of a strain  $s$  is given by  $\sigma(t_1, s) = sG(t_1, s)$ , it may be written in a form similar to Eq. 6 in terms of another parameter  $s'_e$ :

$$\sigma(t_1, s) = s'_e \lim_{s \rightarrow 0} \sigma(t_1, s)/s \quad (7)$$

Here  $s'_e$  may not be equal to  $s_e$  but it varies in a very similar manner as  $s_e$  does with varying  $t_1$  and  $s$ : it is equal to  $s$  for very small values of  $s$  and it is a decreasing function of  $t_1$  for large  $s$ . In the range of time scale  $t_1 > \tau_k$ , it takes a constant value  $r_G s$  approximately equal to  $r_R s$ , the value of  $s_e$  in the long time range.

These results indicate that dependences on  $t_1$  of the ultimate elastic recovery and of the shear stress can be described by the corresponding quantities  $\lim_{s \rightarrow 0} \gamma_R(\infty, t_1, s)/s$  and  $G(t_1)$ , respectively, in linear viscoelasticity in the range of  $t_1$  longer than  $\tau_k$  or  $\tau'_k$ . The strain-dependent factors for  $\gamma_R(\infty, t_1, s)$  and  $G(t_1, s)$  in this time scale are approximately identical with each other. Two quantities  $s'_e$  and  $s_e$  decrease from  $s$  to a common constant value in the period of  $t_1 < \tau_k$ . As pointed out in the introductory section,  $\gamma_R(\infty, t_1, s)$  and  $G(t, s)$  belong to two extreme conditions of measurements, which may give information on the internal state during stress relaxation. Since  $s_e$  approximately represents the strain dependence of these quantities, it may possibly represent the strain dependence of quantities measured under different conditions. So far we have not succeeded in applying the idea of the effective strain to the stress observed following the application of a double-step strain.<sup>3)</sup>

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