Creep Behavior of Polymer Solutions. I. A New Type of Apparatus for Creep and Creep Recovery

Kunihiro Osaki,[1a,b] **Yoshiyuki Einaga,**[1b] **Michio Kurata,**[1b] **and Mikio Tamura**[1c]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan, and Department of Industrial Chemistry, Kyoto University, Sakyo, Kyoto 606, Japan.
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ABSTRACT: A new type of apparatus was devised for measuring the creep as well as the creep recovery of a viscoelastic material whose viscosity lies between 10^4 and 10^8 P. The apparatus is very similar to the torsion creep apparatus of Plazek, but is simpler in design. The torsion wire is suspended by a thin thread at its top. The measurement of creep recovery is performed at the end of the creep measurement by releasing the torque due to the twist of the torsion wire on the thread. A brief review of various existing methods of determination of the steady-shear compliance is given, and the need for obtaining unambiguous results in measurement of creep recovery and for elucidating the slow deformation characteristics of polymer solutions is emphasized.

Slow deformation of viscoelastic materials can be described by two parameters, viscosity, η, and steady-shear compliance, J_e. In the case of polymers or concentrated polymer solutions, a large quantity of data on viscosity has been accumulated.[2] The dependence of viscosity on temperature, concentration, molecular weight, and even on molecular structure has been studied and partially interpreted on a theoretical basis. On the other hand, relatively few data exist on the steady-shear compliance. This may be due to difficulties in measurement.

It was realized recently that the steady-shear compliance is a convenient parameter for describing the molecular mechanism of slow deformation of polymers. Several measurements have been performed on polymers and polymer solutions by various investigators using different methods. However, as shown in the next section, the large discrepancies in these results may be due not only to the difference in the nature of the materials but more probably to the inadequacy of some of the methods employed. With the new type of creep apparatus described in this paper, it is possible to determine the steady-shear compliance of polymer solutions from creep-recovery measurements with considerable accuracy.

Short Review of the Measurement of J_e

J_e from Creep and Creep Recovery. The steady-shear compliance is the recoverable part of the creep compliance $J(t)$ at a sufficiently long time t, and it may be best evaluated from creep recovery. However, it is rather difficult, in the case of soft materials, to measure the creep recovery with high precision.[3] Thus, precise measurement has been restricted so far to hard materials of $J_e < 10^{-6}$. This may be due mainly to the difficulty in eliminating mechanical friction in the apparatus. In addition, existing instruments are fairly complicated in design and have not yet come into wide use.

Also, the steady-shear compliance can be estimated from the creep compliance $J(t)$. The determination is based on the relation

$$J(t) = J_g + (J_e - J_g)\psi(t)/\psi(\infty) + t/\eta \qquad (1)$$

where J_g is the glass compliance and $\psi(t)$ is the creep function. The steady-shear compliance J_e can be obtained from $J(t)$ as

$$J_e = \lim_{t \to \infty} [J(t) - t/\eta] \qquad (2)$$

In applying eq 2, it, of course, is essential to measure $J(t)$ at a time t, long enough for $[J(t) - t/\eta]$ to be much smaller than $J(t)$ or t/η. Accordingly, a slight error involved in the measurement of $J(t)$ causes a large error in the estimate of J_e. Several methods of extrapolation have been devised to attain the limit in eq 2,[4] and they are currently in use.

J_e from Dynamic Compliance. According to the phenomenological theory of linear viscoelasticity, the steady-shear compliance is obtainable from the dynamic compliance $J'(\omega)$ as

$$J_e = \lim_{\omega \to 0} J'(\omega) \qquad (3)$$

This relation, however, can be applied only to very soft materials. In the case of hard materials, it is required to measure $J'(\omega)$ at frequency ω too low to be practical.

J_e from Relaxation Modulus. The phenomenological theory of linear viscoelasticity leads to[5]

$$J_e = \int_0^\infty tG(t)\mathrm{d}t/\eta^2 \qquad (4)$$

where $G(t)$ is the relaxation modulus. This method does not give J_e directly from measured values but requires numerical integration of the data. It can be applied to hard materials for which the measurement of stress relaxation is performed with high precision.

J_e from Normal Stress. This method is based on the

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(1) (a) Foreign Research Fellow at the Department of Chemistry, University of Wisconsin, in 1970–1971; (b) Institute for Chemical Research, Kyoto University; (c) Department of Industrial Chemistry, Kyoto University.

(2) See, for example, G. C. Berry and T. G Fox, *Advan. Polym. Sci.*, 5, 261 (1968).

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phenomenological theory for large deformation of viscoelastic fluids.[6] From the principal normal-stress difference ($\sigma_{11} - \sigma_{22}$) and the shear stress σ_{12} in steady-shear flow with the rate of shear κ, one can evaluate J_e as

$$J_e = {}^1\!/_2 \lim_{\kappa \to 0} (\sigma_{11} - \sigma_{22})/\sigma_{12}^2 \qquad (5)$$

Since the normal stress can not be measured at present in hard materials of $\eta > 10^4$ P, this method can be applied only to very fluid materials.

Examples of the Results. Several measurements of the steady-shear compliance have been performed on concentrated solutions of polymers with narrow distributions of molecular weight. Two types of dependence of J_e on molecular weight M and concentration c have been reported

$$J_e \propto M/c \qquad (6a)$$

$$J_e \propto 1/c^2, \text{ independent of } M \qquad (6b)$$

Type 6a was observed in the creep measurement of solutions of polyisobutylene in cetane[7] and of poly(vinyl acetate) in diethyl phthalate.[8] The same type of result was obtained by measurement of the dynamic compliance[9] of polystyrene solutions in chlorinated diphenyl. On the other hand, the measurement of the normal stress in steady-shear flow[10] of polystyrene solutions in toluene gave type 6b.

In the case of undiluted polymers, J_e was proportional to M based on the creep of poly(vinyl acetate).[8] On the other hand, J_e was a slightly increasing function of molecular weight based on the relaxation modulus of polystyrene[5,11] and poly(α-methylstyrene),[12] while J_e was a constant or even a decreasing function of molecular weight based on the creep of poly(α-methylstyrene)[13] and polystyrene[14] and on the dynamic compliance of polystyrene.[15] The differences in these results may be due to differences in materials or in the range of concentration investigated. However, it is obvious that some of the methods used for evaluating J_e involve ambiguity or arbitrariness in extrapolation of the data or in numerical integration. The difference in the results obtained from the same polymer, polystyrene or poly(α-methylstyrene), may be due to this arbitrariness.

Apparatus for Creep and Creep Recovery

Design of the Apparatus. The new type of apparatus described here is designed to measure the creep as well as the creep recovery of moderately hard materials. The apparatus is essentially the same as the torsion creep apparatus of Plazek[8a] as far as the creep measurement is concerned. The difference lies in the measurement of creep recovery. The structure of the apparatus is shown schematically in Figure 1. More details of the three principal parts are shown in Figure 2.

The main part of the apparatus consists of parallel disks between which the sample is held, a steel wire which suspends the upper plate, and a silk thread which suspends the steel wire. The silk thread is attached to a supporting rod at the upper end. A disk-shaped sample (P) is placed between two metal disks (O and Q). The lower disk (Q) can be driven up and down with a driving screw (R). The upper disk (O) is attached to a metal rod (K, lower rod) and this rod is suspended with a steel wire (I). The wire is again suspended with a thread (B) through a rod (C, upper rod) and the upper end of the thread is fixed to a supporting rod (A). Thus all the rotating parts (upper disk, lower rod, steel wire, and upper rod) are suspended as a whole from the thread (B) when the two clamps (D) and (L) are opened. The lower rod and the upper disk can be fixed to a supporting plate (N) with the clamp (L). The upper rod can be fixed with the clamp (D) to a rotatable plate (E) which is mounted on a supporting plate (H) through a bearing (F). The plate (E), with the upper rod (C), can be fixed to the supporting plate (H) at an arbitrarily rotated position. By opening the clamp (D), the upper rod returns to the

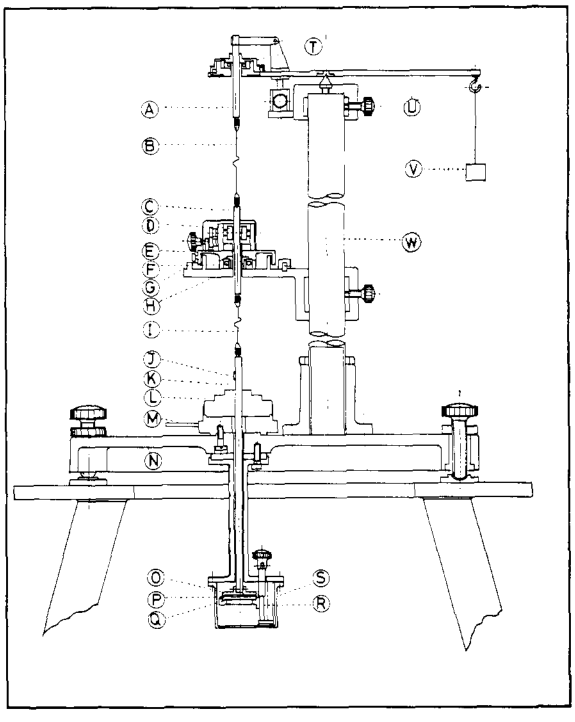

Figure 1. A sketch of the apparatus for creep and creep recovery: (A) supporting rod, (B) thread, (C) upper rod, (D) upper clamp, (E) rotating plate, (F) bearing, (G) graduator, (H) supporting plate, (I) steel wire, (J) mirror, (K) lower rod, (L) lower clamp, (M) arm, (N) supporting plate, (O) upper disk, (P) sample, (Q) lower disk, (R) driving screw, (S) metal cylinder, (T) rotating plate, (U) balancing arm, (V) counterweight, (W) pole.

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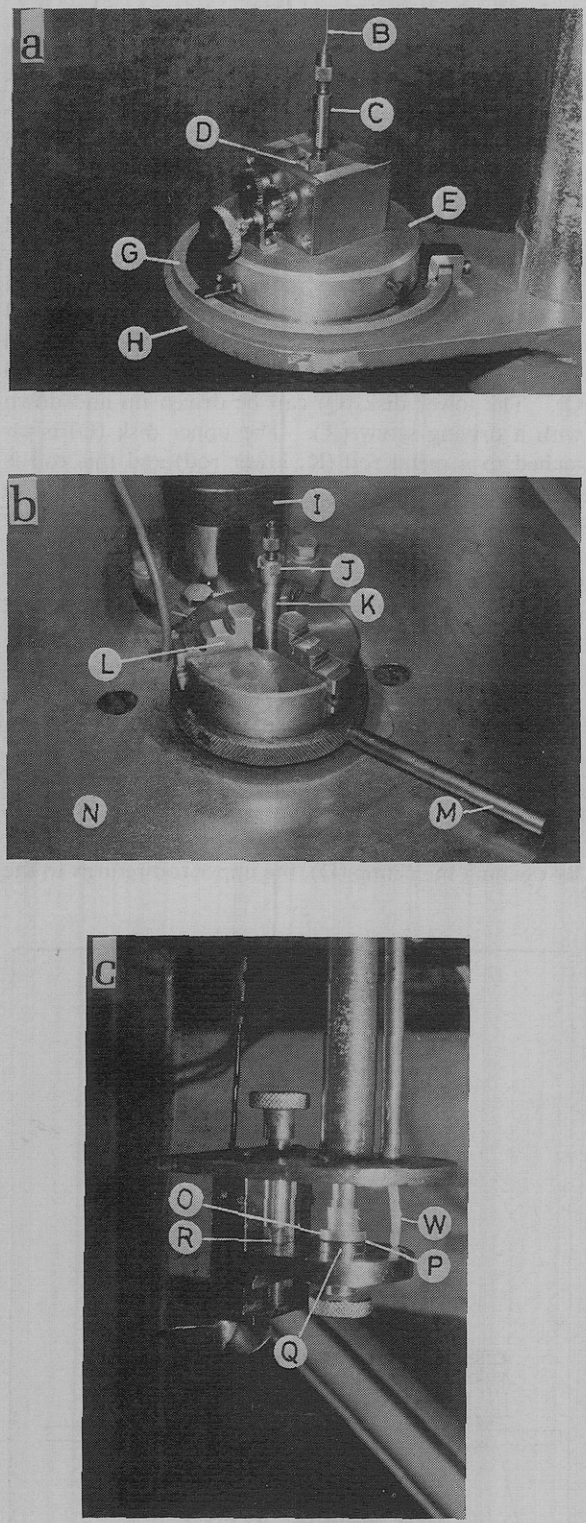

Figure 2. Detailed view of the important parts: (a) B–H, (b) I–N, (c) O–R.

state directly suspended by the thread. A mirror (J) is attached to the lower rod (K). The rotation angle of this rod and the upper disk (O) is determined by measuring the position of a spot of reflected light on a scale.

The lowest part of the apparatus is covered with a metal cylinder (S) and is held in a thermostated bath. The temperature of the bath is controlled by a thermistor and the thermistor head is attached to the lower disk (Q). Accuracy of ±0.1° is achieved at the position of the sample if the temperature is in the range $-30 \sim +80°$.

The top part of the apparatus is complicated in structure as seen in Figure 1. This part is equipped with a balancing arm (U) and a plate (T). The latter is mounted on the arm through a bearing and can be rotated to an arbitrary angle. The uppermost part of the thread is attached to the center of the plate (T). All the rotating parts can be balanced with a counterweight (V) through the arm, so that the tension of the wire and the thread may be controlled. The plate (T) was equipped to give various angles of rotation to the upper end of the thread at the beginning of creep recovery measurement and to test the effect of rigidity of the thread on the creep recovery. However, as will be mentioned later, this feature was found to be unnecessary provided that an appropriate silk thread was used.

Principle of Measurement of Creep and Creep Recovery. A creep measurement is performed as follows. At first, open all the clamps, so that all the rotating parts are suspended from the thread, and wait for the rotating parts to come to rest in an equilibrium position. Then, fix the upper rod and the lower rod, respectively, with the clamps. Set the sample on the lower disk, and lift the disk up to a suitable position with the driving screw. At this position, it is essential that the sample fully fills the gap between two disks. The length l of the sample is then measured by a microscope. Next, the upper rod is rotated to a suitable angle Θ and fixed at that angle. In this way the steel wire as well as the thread are twisted by an angle Θ. Finally the lower rod is made free by opening the lower clamp and the rotation angle $\theta(t)$ of the lower rod is measured from time to time. If the angle θ is sufficiently smaller than Θ, the creep compliance $J(t)$ is given by the equation

$$J(t) = (\pi r^4/2lk\Theta)\theta(t) \qquad (7)$$

where r is the radius of the sample and k is the coefficient of torsion of the steel wire.

To start the creep recovery measurement, one releases the upper rod instantaneously by opening the clamp at some moment t_1 during the measurement of the creep. Then most of the twisting angle of the wire and thread ($= \Theta$) disappears, and only a small part corresponding to $\theta(t_1)$ is redistributed to the wire and thread according to their rigidity. If the rigidity of the thread is low enough, the torque imposed on the sample will be released almost instantaneously. Thus, in this case, the upper plate is rotated by a torque which is attributed only to the elastic strain remaining in the sample. The creep recovery $R(t,t_1)$ is obtained from the rotating angles of the upper plate at the times t_1 and $(t + t_1)$ as

$$R(t,t_1) = (\pi r^4/2lk\Theta)[\theta(t_1) - \theta(t + t_1)] \qquad (8)$$

If t_1 is large enough, the steady-shear compliance J_e is obtained from $R(t,t_1)$ as

$$J_e = \lim_{t,t_1 \to \infty} R(t,t_1) \qquad (9)$$

Some Details of the Apparatus. For successful use of this apparatus, it is most important to satisfy the following conditions. (i) Neither the upper rod nor the lower rod moves by opening and closing the upper clamp or the lower one; that is, all the rotating parts (thread, upper rod, wire, lower rod and upper plate) have the same center of rotation as those of the clamps and the lower plate. (ii) The upper disk or the lower rod does not change its center of rotation by rotating the upper rod. In other words, the trosion wire is straight. (iii) The rigidity of the thread is low enough. (iv) The dimension of the sample is suitably chosen.

A piano wire with 0.2 mm diameter and 1 m length was used as the torsion wire, which was not straightened by the weight of the lower rod and the upper disk (about 100 g). In order to straighten the wire it is tempered with an electric current after it is installed in the apparatus. The coefficient of torsion of the wire was checked occasionally by suspending a plate with a known moment of inertia and by counting the frequency of the free oscillation. The frequency was not dependent on the amplitude of the oscillation up to an amplitude of $\pm 360°$ nor on a tension on the wire of greater than 20 g. No change in the coefficient of torsion of the wire was observed during operation over a 6-month period. The error attributable to the coefficient of torsion of the wire was lower than 0.1%. When the torsion wire was straight, it was not very difficult to set the center of the rotating parts at the center of the clamps. Thus conditions (i) and (ii) can be satisfied.

A single silk thread of 1 m length was used as the suspending thread. Twisted threads were not used, because the relation between the twisting angle and the torque was not reproducible and sometimes the torque was unexpectedly large. The rigidity of a single silk thread had no effect on the creep recovery. The rotation of the top of the thread by several tens of degrees before the creep measurement did not influence the result of creep recovery irrespective of the hardness of the sample. The thread did not seem to change its length during the period of creep recovery if the sample had a viscosity higher than 5×10^3 P.

The sample is fully filled between two metal disks and held by its self-adhesion and viscosity. The diameter of the disk can be varied from 1 to 4 cm. The distance between the disks or the thickness of the sample are adjustable. However, the evaluation of the thickness includes a possible error of 0.03 mm, so a thickness larger than 1 mm is advisable. On the other hand, the diameter of the sample can not be measured accurately enough if the thickness is large. When the thickness exceeds 3 mm, an error larger than 0.1 mm in the diameter is expected. Therefore it is important to choose a suitable diameter of the disk depending on the properties of test samples, and also to keep the thickness of the sample between 1 to 2 mm.

The rotation angle of the upper plate can be measured to a precision of 0.005° with the mirror-lamp scale system. Since the angle increases very rapidly in the first 5 sec of the creep, it can not be measured in this period. For accurate measurement it is necessary to choose a suitable combination of the dimension of the sample and the twisting angle Θ of the wire, so that the spot of light on the scale moves with a suitable speed. In addition, the twisting angle Θ of the wire must be sufficiently large compared to the rotation angle θ so that the diminution of the torque of the wire can be ignored.

As the result of all these restrictions the sample must have the viscosity somewhere between 5×10^3 and 1×10^8 P. The lower limit of the viscosity is mainly due to the dimension of the sample.

The upper limit is due to the smallness of the rotation angle of the disk. This limitation may be avoided by the use of a thicker wire. However a heavy disk will be required for straightening a thick wire and such a disk cannot be suspended by a thin thread. In the present design of the apparatus, the balancing arm and the rotatory plate are installed at the top as shown in Figure 1. The balancing arm was equipped to give a constant tension on the thread and the torsion wire. However, it was found in preliminary tests that the wire constant was independent of the tension if a weight of over 20 g was applied to a piano wire of 0.2 mm diameter. The results of creep and creep recovery did not depend on whether the rotating part was balanced with a counterweight or not.

The rotatory plate to which the top of the thread is attached is designed to compensate for the slight twist of the thread at the beginning of creep recovery. The twisting angle Θ in the wire cancels that in the thread. However the twist θ which is due to the creep of the sample is not cancelled out, but remains in the thread. This angle may be compensated for by rotating the plate, to which the upper end of the thread is attached, by the angle θ, prior to opening the upper clamp at the top of the steel wire. However, it was found that the remaining torque in the thread was so small that the

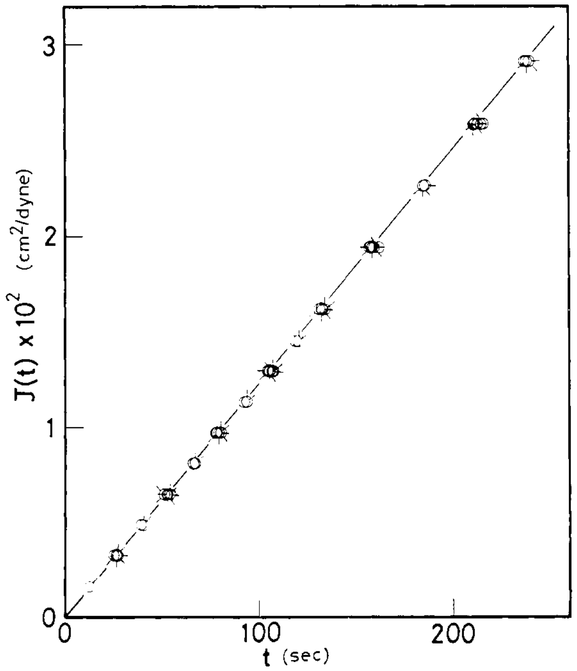

Figure 3. Creep compliance of silicon oil at 27° with various combinations of twisting angle and two directions of rotation: pip up, $\Theta = 320°$ and counterclockwise rotation (+); successive 45° rotations clockwise correspond to 320° (−), 160° (+), 160° (−), 80° (+), 80° (−), 40° (+), and 40° (−), respectively.

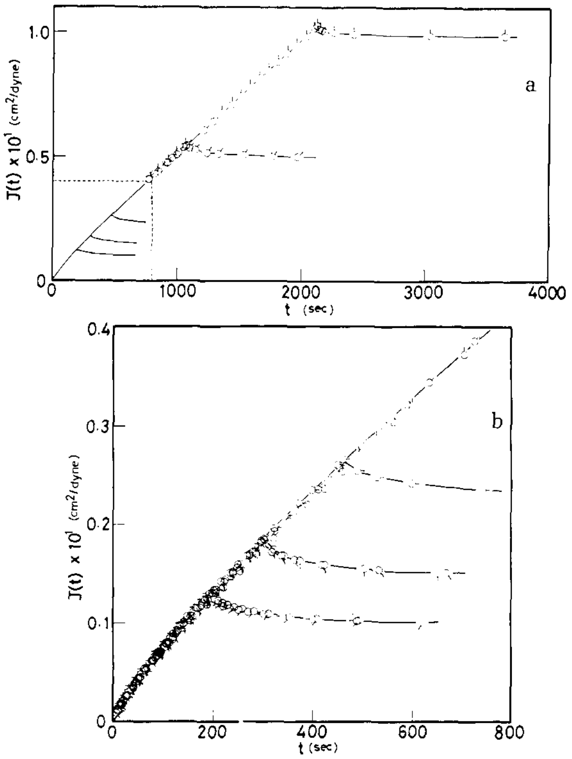

Figure 4. (a) Creep compliance of a 12% solution of polystyrene in chlorinated diphenyl at 30°. An enlarged figure of the part enclosed with the dashed line is shown in Figure 4b. Various directions of pips represent the conditions of measurement: pip up, r = 2.005 cm, l = 0.28 mm, Θ = 320° (−); pip up to right, r = 2.005 cm, l = 0.88 mm, Θ = 160° (−). (b) The enlarged figure of the short time part of Figure 4a. Various directions of pips represent the conditions of measurement: pip up, pip up to right are the same as Figure 4a; pip right, r = 1.005 cm, l = 0.47 mm, Θ = 160° (−); pip down to right, r = 1.505 cm, l = 1.38 mm, Θ = 40° (−); pip down, r = 1.505 cm, l = 1.38 mm, Θ = 80° (+); pip down to left, r = 1.505 cm, l = 1.38 mm, Θ = 160° (+); pip left, r = 1.505 cm, l = 1.38 mm, Θ = 160° (−).

results of creep recovery were not influenced by rotating the upper part of the thread by a few tens of degrees prior to opening the middle clamp.

These results show that two parts in the top of the apparatus, the balancing arm and the rotary plate, are unnecessary. It may be best to simply fix the uppermost part of the thread to a fixed arm.

Measurement with the Apparatus. In order to test the accuracy of this apparatus, measurements were made on two samples—silicone oil and a 12% solution of polystyrene (M_v = 10^6) in chlorinated diphenyl. The former is a nonelastic liquid and the latter is a highly elastic liquid. In Figure 3 the results of a creep measurement for silicone oil at 27° are shown. The creep compliance of silicone oil was measured at various twisting angles of the steel wire (40∼320°) and at two directions of rotation. If conditions (i) or (ii) shown in the previous section are violated, the values of creep compliance will depend on the direction of rotation of the upper disk. But the creep compliances obtained under various conditions were in good agreement with each other. Moreover the creep compliances were found to be proportional to time for this nonelastic liquid. These results showed that the apparatus was operated in good condition. The viscosity value obtained was 8.23 × 10^3 P which was very near to the value 8.3 × 10^3 P obtained by the falling ball method. No creep recovery was observed for this material.

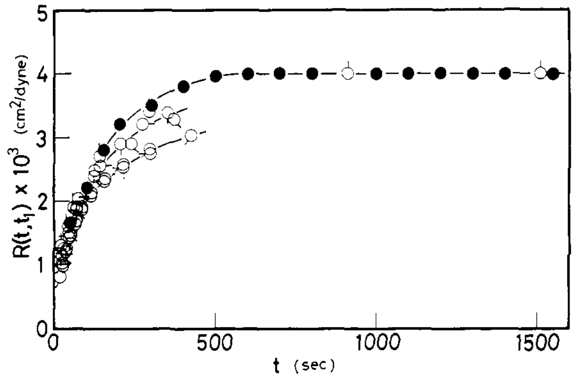

Figure 5. Creep recovery of a 12% solution of polystyrene in chlorinated diphenyl at 30°: creep recoveries after various creep times are shown. Creep times are 2114.2, 461.5, 302.9, 297.2, 199.1, and 191.3 sec, respectively, from top to bottom. Symbols are the same as in Figure 4. Black circles represent $J(t) - t/\eta$.

The results obtained for the polystyrene solution at 30° are shown in Figure 4a. In Figure 4b the results at short times are enlarged. The creep compliances measured with various twisting angles of the torsion wire and various dimensions of the samples are plotted against time. The radius of the sample was varied from 15 to 20 mm and the thickness from 0.28 to 1.38 mm. Obviously, curves for creep compliances measured under different conditions were in agreement with each other. Maximum scattering of the data was about 5% which was probably due to the error in determination of the thickness of the sample. Better agreement is obtained if the data corresponding to the thickness, 0.28 mm, are excluded. This suggests that use of such a small thickness is rather inadequate. The result of the creep recovery for the same solution is shown in Figure 5. The creep recoveries $R(t,t_1)$ obtained with different twisting angles and different dimensions of the samples are in good agreement when time t_1 of the start of the creep recovery is kept approxi-

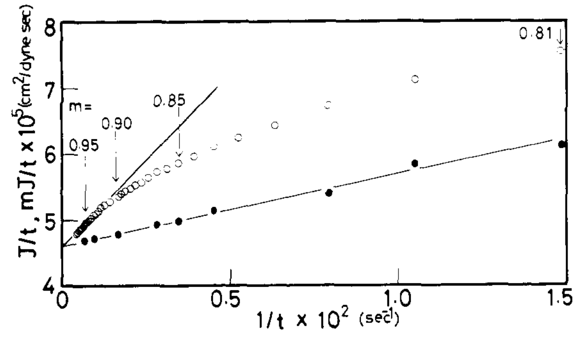

Figure 6. Ninomiya's extrapolation method on a 12% solution of polystyrene in chlorinated diphenyl. Open circles and black circles represent J/t and mJ/t, respectively. The intercept and the slope of the heavy line are $1/\eta$ and J_e, respectively, determined from creep recovery and creep measurement.

mately constant. In Figure 5, the quantity $J(t) - t/\eta$ is shown by black circles, which should be equal to the creep recovery started at sufficiently long time, *i.e.*

$$\lim_{t_1 \to \infty} R(t,t_1)$$

In fact, the creep recovery at $t_1 = 2114.2$ sec was in good agreement with $J(t) - t/\eta$. These results show that the rigidity of the thread can be ignored and that the creep as well as creep recovery of moderately soft materials can be satisfactorily measured by this apparatus.

Estimation of η and J_e. It was shown in the preceding section that two parameters characteristic of slow deformation, η and J_e, can be obtained with good precision by measuring creep and creep recovery. The same parameters often have been evaluated from creep data alone by applying the principle of eq 2. Ninomiya's method[4] is now widely used for that purpose. It consists of plotting two quantities J/t and mJ/t against $1/t$. Here m is the slope in the plot of log J *vs.* log t. The intercepts on the ordinate of these two plots, J/t *vs.* $1/t$ and mJ/t *vs.* $1/t$ should mutually coincide and give $1/\eta$. On the other hand the slope of the line for J/t at $1/t \to 0$ gives J_e. Usually the line for mJ/t is nearly parallel to the abscissa, and η is determined with reasonably good accuracy from the intercept of this line and the ordinate. The evaluation of J_e from the slope of the line for J/t is, however, subjected to a rather large error.

To illustrate the Ninomiya method, we replotted the data from the 12% solution of polystyrene in Figure 6, where open circles represent J/t and filled circles represent mJ/t plotted against $1/t$. The heavy straight line is drawn with the slope and intercept which are consistent with the values of J_e and η already established from the creep and creep recovery measurements. It is seen that all the data corresponding to $m > 0.9$ lie on this straight line. This indicates that reasonably correct estimates of η and J_e are obtainable from creep data alone if a sufficient number of the data $J(t)$ are available in the range of $m > 0.9$. On the contrary, if the data are restricted to the range $m \leqq 0.85$, a 20% error in J_e is unavoidable, and if $m \leqq 0.80$, a 10% error in η and a 50% error in J_e result.

In the paper of Ninomiya it is claimed that η and J_e can be estimated well from the data corresponding to $0.9 > m > 0.7$. Our data show that Ninomyiya's method is quite useful. However, it is to be stressed that the data with $m > 0.85$ are indispensible for accurate evaluation of J_e. Although the data are not reproduced here, we have some evidence that the shape of the curves in Ninomiya's plot depends on the kind of materials and thus the range of m necessary for a good estimation of J_e may depend on materials.

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Creep Behavior of Polymer Solutions. II. Steady-Shear Compliance of Concentrated Polystyrene Solutions

Yoshiyuki Einaga,[1a] Kunihiro Osaki,[1a,b] Michio Kurata,[1a] and Mikio Tamura[1c]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan, and
Department of Industrial Chemistry, Kyoto University, Sakyo, Kyoto 606, Japan.
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ABSTRACT: The steady-shear compliance J_e and the viscosity η were measured on concentrated solutions of narrow distribution polystyrene in chlorinated diphenyl with a new type of apparatus for measurement of creep and creep recovery. The range of molecular weight studied was $9.7 \times 10^4 \sim 1.8 \times 10^6$ and that of concentration was $0.1 \sim 0.6$ g/ml. The steady-shear compliance first increased with increasing concentration c, reached a maximum, and then decreased in proportion to c^{-3}. J_e was independent of molecular weight in the range of high concentration where it was proportional to c^{-3}. The maximum in J_e was lower and appeared at higher concentration if the molecular weight was lower. The concentration above which J_e obeyed the c^{-3} dependence was higher for lower molecular weight. The viscosity η was proportional to $M^{3.4}$ in the whole range of concentration. Thus, the entangled system for which the viscosity is proportional to the 3.4th power of molecular weight is further divided into two classes according to the behavior of J_e. Only in the highly entangled state does J_e become proportional to c^{-3} and independent of M. The assumption of uniform excess friction in the modified Rouse theory is not applicable to this highly entangled state of polystyrene.

As was pointed out in the preceding paper,[2] two types of dependence of the steady-shear compliance J_e on molecular weight M and concentration c have been reported for concentrated solutions of polymers, often on the same polymer–solvent system. They are

$$J_e \propto M/c \tag{1}$$

and

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(1) (a) Institute for Chemical Research, Kyoto University; (b) Foreign Research Fellow at the Department of Chemistry, University of Wisconsin, in 1970–1971; (c) Department of Industrial Chemistry, Kyoto University.

(2) K. Osaki, Y. Einaga, M. Kurata, and M. Tamura, *Macromolecules*, **4**, 82 (1971).