Title	A New Type of Apparatus for Stress Relaxation Measurement under Large Deformation (Special Issue on Polymer Chemistry, VIII)
Author(s)	Tamura, Mikio; Kurata, Michio; Osaki, Kunihiro; Einaga, Yoshiyuki; Kimura, Sinichi
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1971), 49(2): 43-52
Issue Date	1971-09-21
URL	http://hdl.handle.net/2433/76362
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 49, No. 2, 1971

A New Type of Apparatus for Stress Relaxation Measurement under Large Deformation

Mikio TAMURA*, Michio KURATA**, Kunihiro OSAKI**,
Yoshiyuki EINAGA**, and Sinichi KIMURA*

Received April 7, 1971

A new type of apparatus was devised for measuring the stress relaxation of viscoelastic fluids under large deformation. The measurable range of the relaxation modulus was from 10^{-1} to 10^{6} dyne/cm^2. The design and performance of the apparatus were described as well as some typical results obtained for polystyrene solutions in chlorinated diphenyl.

I. INTRODUCTION

Experimental studies recently performed on the non-linear viscoelasticity of polymer solutions include measurements of non-Newtonian viscosity,[1] large amplitude sinusoidal oscillation,[2] sinusoidal oscillation superimposed on steady shear,[3,4] stress growth at the beginning of steady shear and stress relaxation after the sudden stop of steady shear.[5] However, a more fundamental measurement will be that of the stress relaxation under large deformation, for it provides the most direct information on the distribution of various relaxation mechanisms existing in materials. In fact, in the limit of small deformation, the relaxation modulus gives the relaxation spectrum to the first approximation. Thus, in this series of study, we intend to obtain a systematic information on the non-linear relaxation phenomena of polymer solutions as functions of temperature, polymer molecular weight, concentration and so on.

A number of apparatus have so far been devised for measurements of the stress relaxation under tensile deformation, but few for measurements under torsional deformation. Furthermore, application of the latter apparatus has been restricted, in the case of polymer solutions, within the linear range of viscoelasticity.[6,7] We devised a new apparatus for measuring the relaxation modulus of polymer solutions under large torsional deformation. This paper describes its design and performance.

II. APPARATUS

a. Design: The apparatus is schematically shown in Fig. 1 (a). A sample (11) is placed in a gap between two platens. The top one (10) is of a conical shape and is attached to an upper shaft (9). This shaft is suspended with a steel torsion wire

---

* 田村幹雄, 木村慎一: Laboratory of Physical Chemistry, Department of Industrial Chemistry, Kyoto University, Kyoto.

** 倉田道夫, 尾崎邦宏, 榮永義之: Laboratory of Polymer Solutions, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

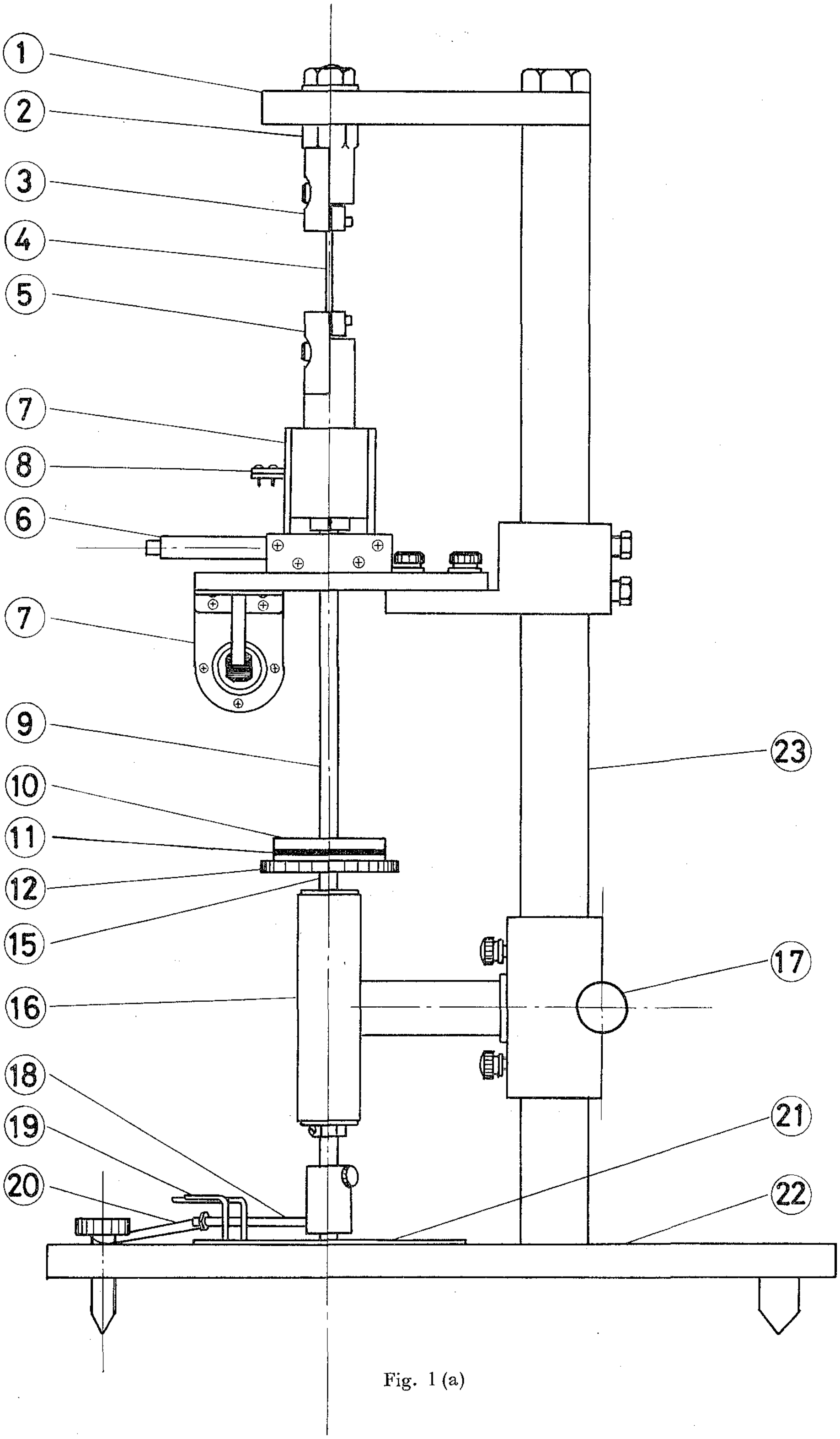

Fig. 1 (a)

(4) from an upper stay (1) which is fixed to a pole (23). The bottom platen (12) is of a disk type and is attached to a lower shaft (15). This shaft is supported through bearings by a lower stay (16) which can be driven up and down with a driving screw (17). The rotation angle of the lower shaft can be fixed by holding an arm (18) at the position of a pin (19) with the aid of a rubber band (20). The rotated angle is measured by a circular protractor (21) mounted on a base (22).

The upper shaft (9) has a needle (13) at its lower end, whose apex slightly sticks out through the cone surface as shown in Fig. 1 (b). The apex of the needle is inserted into a pin hole (14) hollowed at the center of the lower plate so that the cone and plate can be rotated around a common axis of rotation.

Figure 1(c) shows the details of an upper part of the apparatus. A mover or a core (8) of a transducer (7) is attached to the upper shaft (9). The twisted angle of the torsion wire (4) or the rotated angle of the cone is measured as a change in the voltage generated by the transducer.

The apparatus is installed in an air bath, in which the temperature is kept constant, in the range from room temperature to 80°, to within 0.2° at the sample position with a thermister regulator.

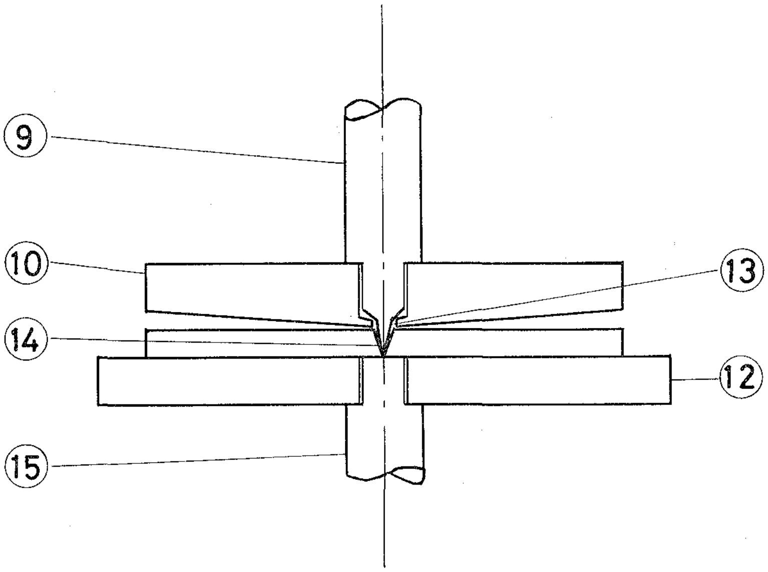

Fig. 1 (b)

Fig. 1 (a). A sketch of the apparatus. (1) upper stay; (2) upper jointer of a torsion wire; (3) and (5) metal fittings ; (4) torsion wire; (6) zero adjuster of transducer; (7) transducer; (8) core of transducer; (9) uppershaft; (10) cone; (11) sample; (12) disk; (15) lower shaft; (16) lower stay; (17) driving screw; (18) arm; (19) pins; (20) rubber band; (21) circular protractor; (22) stand; (23) pole.

Fig. 1 (b). A detailed sketch of the sample part. (9) upper shaft; (10) cone; (12) disk; (13) needle; (14) pin hole; (15) lower shaft.

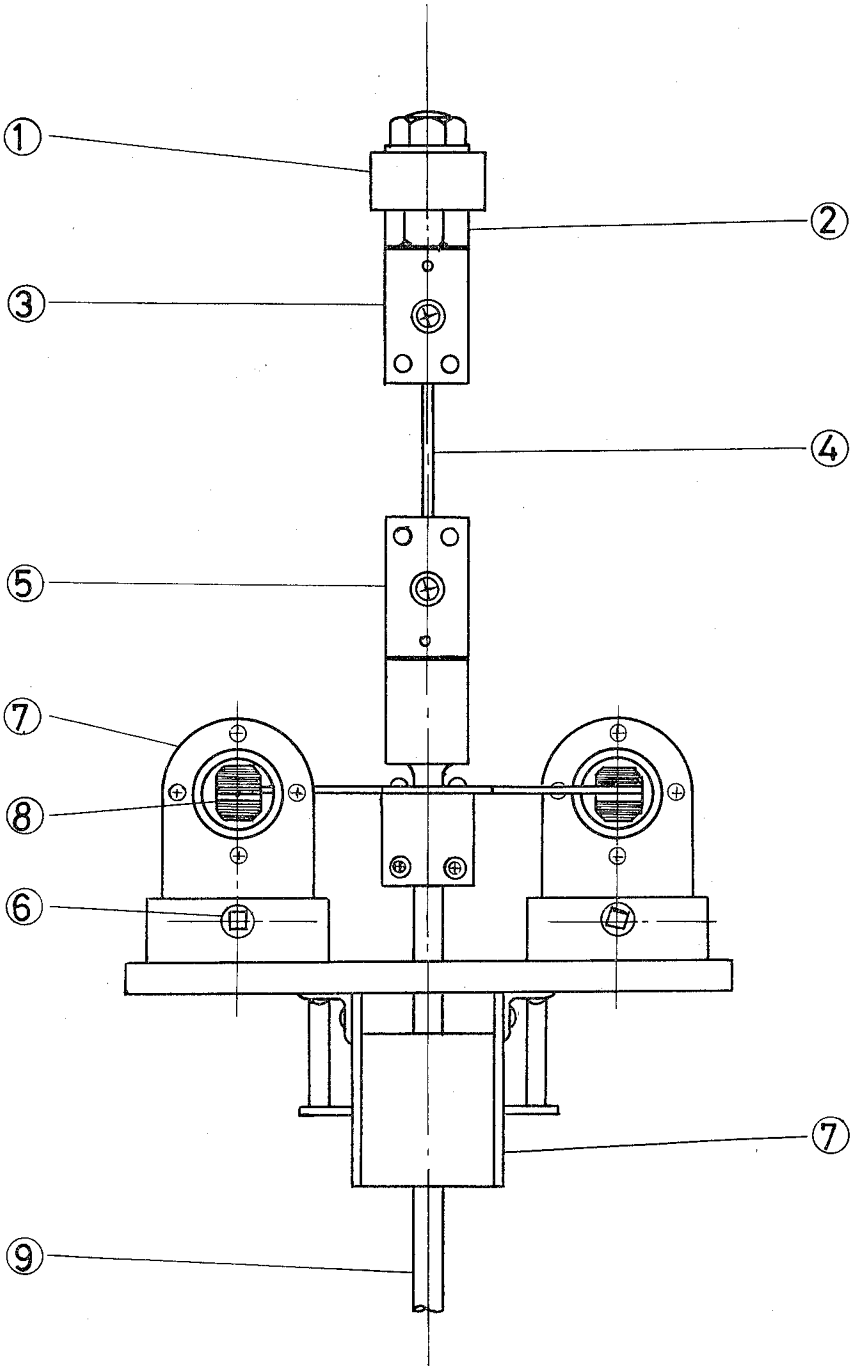

Fig. 1 (c). A detailed sketch of the upper part. (1) upper stay; (2) upper jointer; (3) and (5) metal fittings; (4) torsion wire; (6) zero adjuster; (7) transducer; (8) core; (9) upper shaft.

b: Method of measurement : A measurement of stress relaxation is performed as follows. At first, set a sample on the lower platen, and lift the platen up to the right position with the driving screw. At this position, the apex of the needle is to be almost in contact with the bottom of the pin hole as shown in Fig. 1(b). It is also essential that the sample fully fills the gap between the cone and disk. Next, insert two pins in suitable holes which are arranged circularly on the base stand, and fix the arm of the lower shaft at the position of one of the pins with the aid of a rubber band. After the whole system attaind equilibrium, this pin is removed and the lower shaft is rotated almost instantaneously to the position of the second pin by the force of the rubber band. Thus, the sample is put in a sheared state. The rotation angle Θ of the disk is of course equal to the angle between two pin positions. The upper platen is also rotated by an angle θ due to the rigidity of the sample, which can be recorded by the transducer. If the torsion wire is suitably chosen, the rotated angle of the cone is kept negligible in comparison with that of the disk, and the relaxation modulus $G(t)$ can be evaluated by the equation

$$G(t) = (3k\phi/2\pi R^3\Theta)\theta(t) \tag{1}$$

where k is the coefficient of torsion of the steel wire, R is the radius of the lower disk, and ϕ is the angle between the cone and the disk.

c. Some details of the apparatus : For successful use of this apparatus, it is most important to prevent a slippage of the torsion wire at the joints, (3) and (5) in Fig. 1(a). For the purpose, a drill rod as the torsion wire was connected by its both ends with metal fittings by welding and was carefully tempered. Then, the top end of this piece was fixed to the upper stay with a jointer (2) and the bottom end to the upper shaft with a screw and a pin. Diameters of the used drill rods were 1.6, 2.0 and 3.0 mm. Their torsional coefficients were 1.396×10^7, 3.519×10^7 and 1.673×10^8 dyne·cm/radian, respectively, as determined from the frequency in a free oscillation in which a plate with a known moment of inertia was used as a pendulum.

The rotation axes of the cone and disk were put in coincidence with the aid of the needle-pin hole system shown in Fig. 1(b). Of course, such a needle as this complicates the geometry of the gap between two platens. But, the effect was practically negligible, for that part was so small compared with the total volume of the gap. The frictional effect between the needle and pin hole was also found to be negligible in a preliminary test.

The sample was held in the gap by its self-adhesion and viscosity. The angle between two platens was 3 degrees, and the diameters of the used disks were 3 and 5 cm.

The rotated angle of the cone was measured in the range from 10^{-5} to 1 degrees by the system consisting of a transducer, mV converter and recorder. The transducer was designed as to detect the rotating motion of the upper shaft alone, but not the translational. The measurable range of the relaxation modulus was from 10^6 to 10^{-1} dyne/cm², when the above combinations of torsion wire, cone and disk were used.

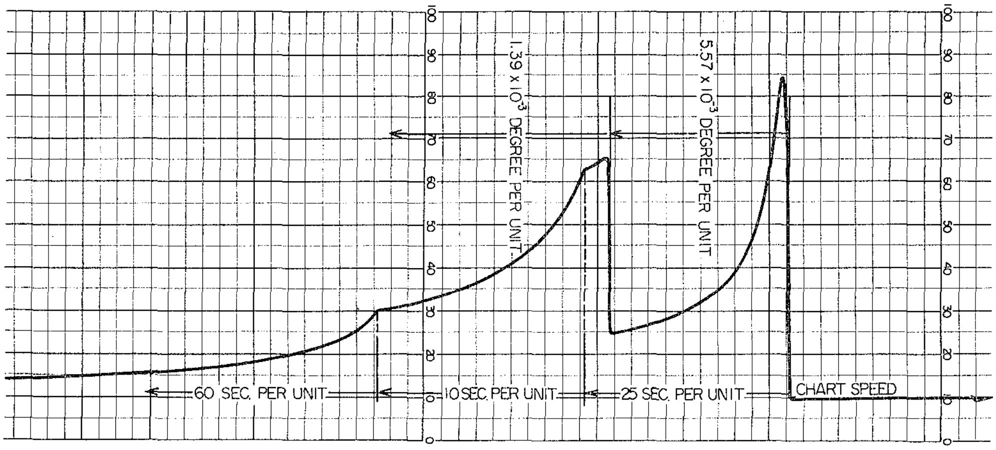

Fig. 2. A recorded chart of the rotated angle of the upper platen, cone. Sample; 20% solution of polystyrene in chlorinated diphenyl. Temperature; 33.5°C.

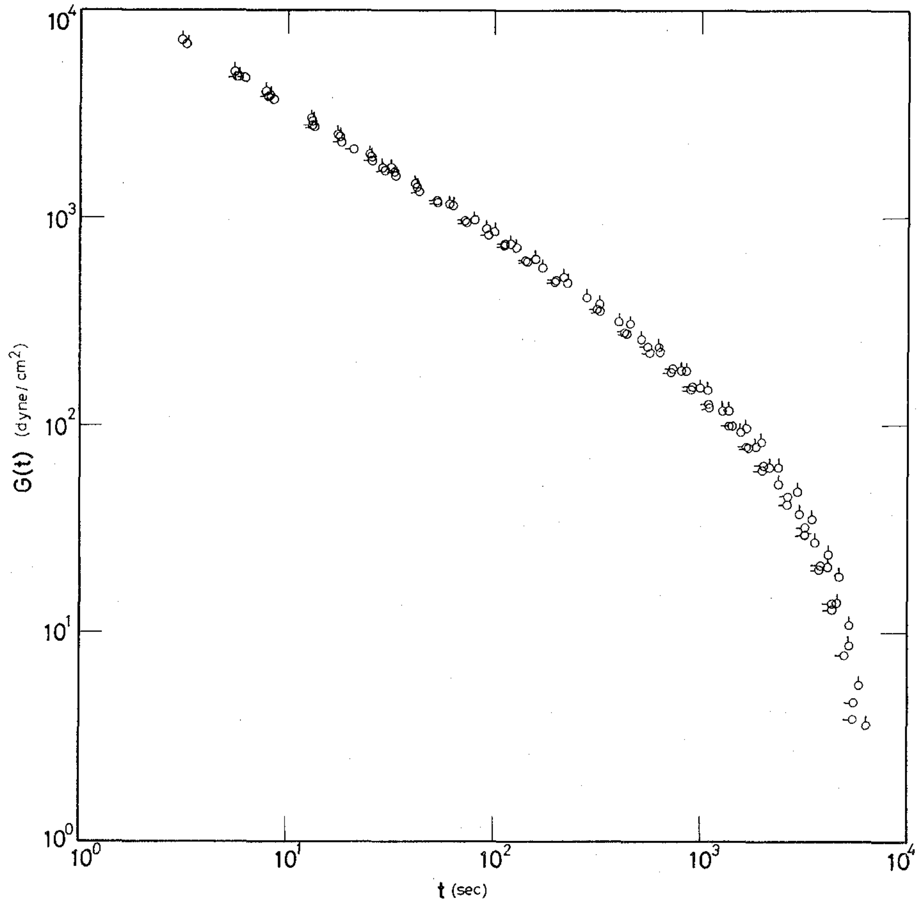

Fig. 3. Relaxation modulus of a 20% solution of polystyrene under a strain of 334%. Pip left; $k=3.519\times10^7$ dyne·cm/radian, $R=1.5$ cm. Pip up; $k=1.673\times10^8$ dyne·cm/radian, $R=2.5$ cm.

III. MEASUREMENTS

In order to test the accuracy of this apparatus, measurements were made on a 20% solution of polystyrene in chlorinated diphenyl. The viscosity average molecular weight of the polymer was 1.00×10^6. Figure 2 shows the results of a stress relaxation measurement in which a torsion wire of 2 mm diameter and a pair of cone and disk, both of 3 cm diameter, were used, and a strain of 334% was given. In the chart, the rotated angle of the cone was recorded as a function of time. The left peak and two break points of the curve were due to a change in sensitivity and in chart speed of the recorder, respectively. The right peak represents the real maximum of the rotated angle of the cone. Its height and position slightly depended on the speed, with which the disk was rotated or the strain was imposed on the sample. The effect, however,

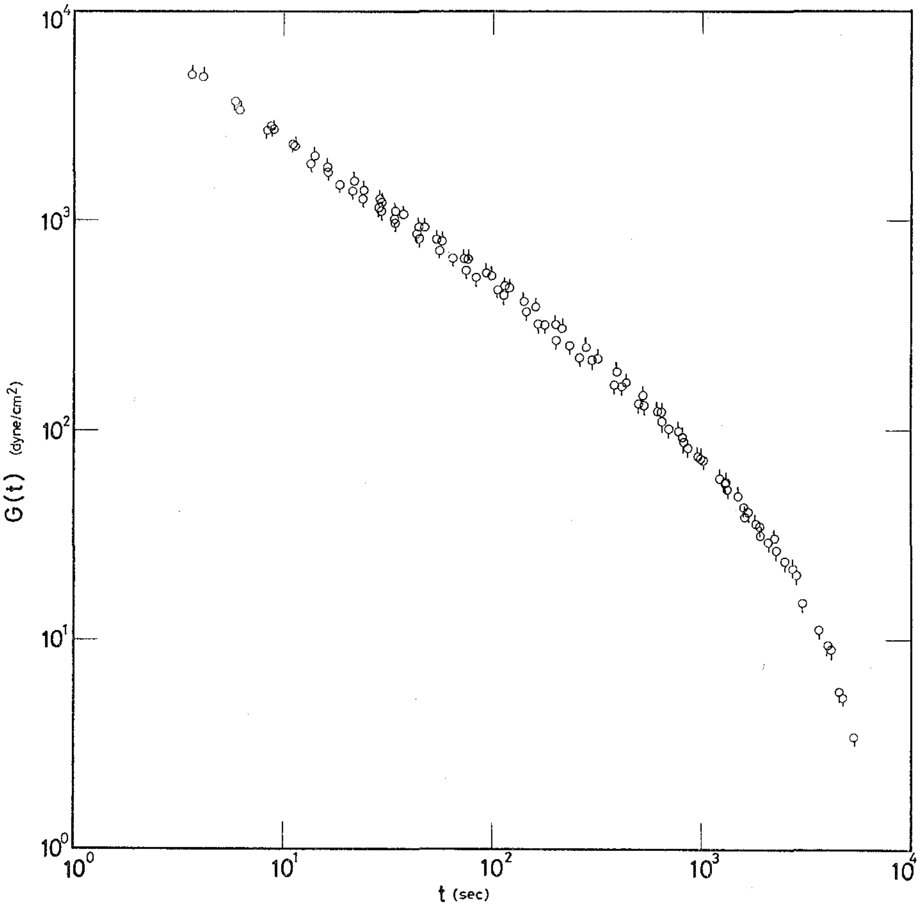

Fig. 4. Relaxation modulus under a strain of 668%. Pip down; $k=1.673 \times 10^8$ dyne·cm/radian, $R=1.5$ cm. Sample and other symbols are the same as those in Fig. 3.

disappeared after two or three seconds elapsed, and a stress relaxation curve characteristic of the sample was obtained with the aid of Eq. (1). The results are shown in Fig. 3 by the circles with pip left. The similar measurements were repeated on the same sample under the same strain using another combination of torsion wire and platens, *i.e.* a wire of 3 mm diameter and platens of 5 cm diameter. The results are also shown in Fig. 3 by the circles with pip up. Agreement between these two series of data was satisfactory to within a error of 5%.

In order to study the effect of the imposed strain on the stress relaxation curve, measurements were carried out on the same sample under the strains of 668% and 1340%. The results are shown in Figs. 4 and 5. Three relaxation curves obtained under the strains of 334%, 668% and 1340% are summarized in Fig. 6. The relaxation curve shifted downwards almost in parallel to each other as the imposed strain

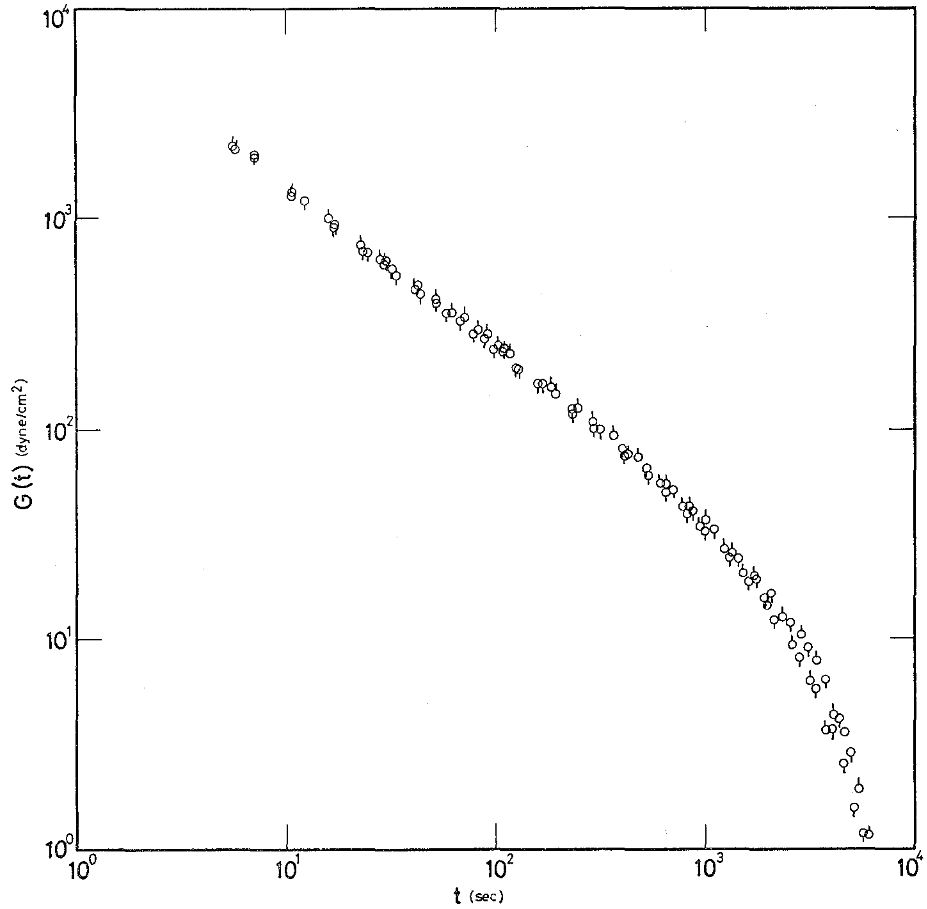

Fig. 5. Relaxation modulus under a strain of 1340%. Sample and symbols are the same as those in Fig. 4.

was increased, though a slight change in shape was observed in the range of relatively short times.

The similar measurements as above were also performed on a 15% solution of a narrow-distribution polystyrene in chlorinated diphenyl at 30°, whose weight-average molecular weight was 1.80×10^6. The results are shown in Fig. 7, where four curves represent the data obtained under strains of 187, 334, 668 and 1340%. These curves of the stress relaxation were considerably steep in comparison with those for the former example with a broader distribution, and the inflection of the curve became quite distinct under the highest strain at a short time.

Further studies are now in progress in our laboratories, and the results will be published elsewhere.

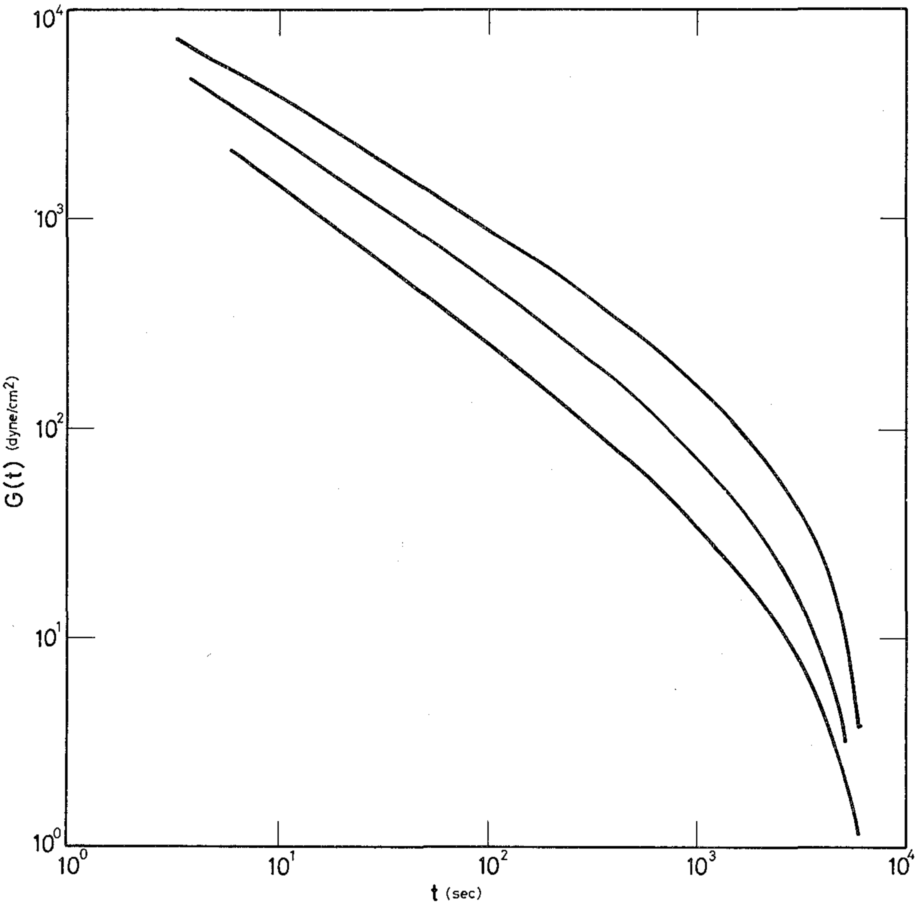

Fig. 6. Effect of imposed strain on the relaxation curves. From top to bottom; strains of 334, 668 and 1340%.

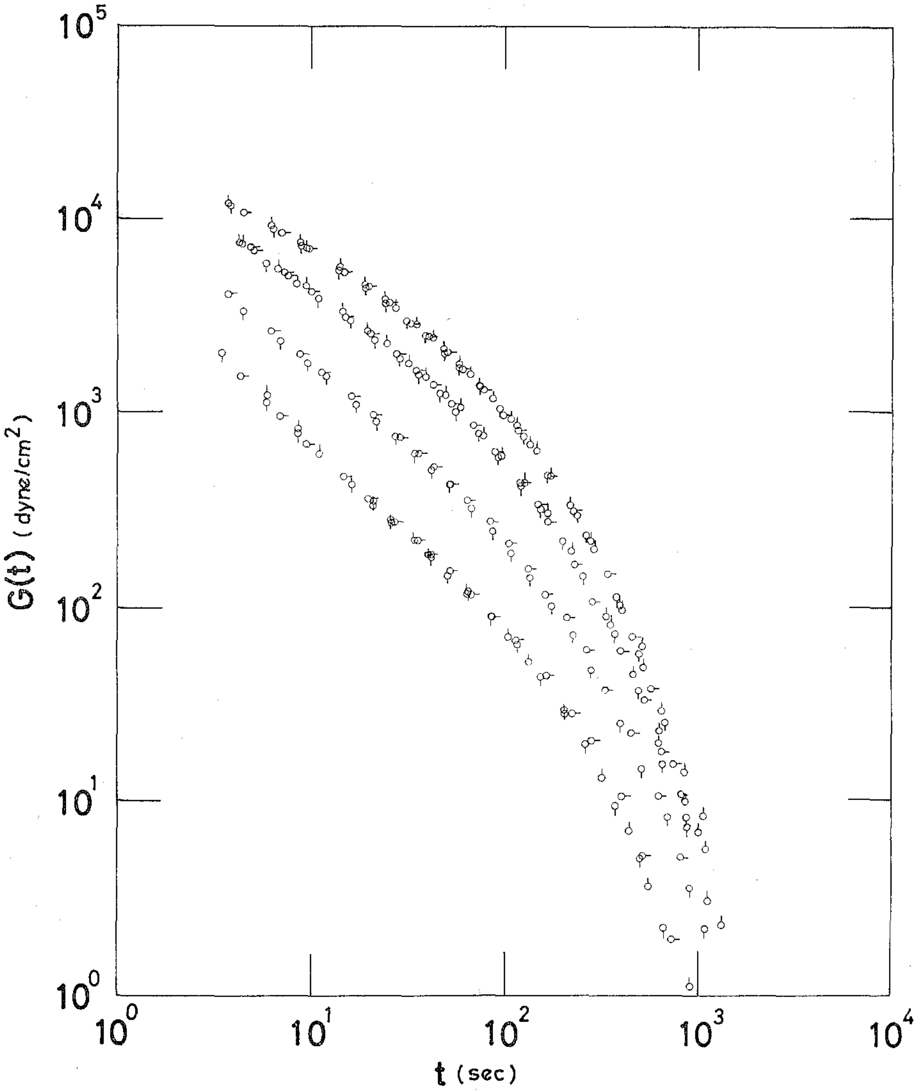

Fig. 7. Relaxation moduli of a 15% solution of a narrow-distribution polystyrene in chlorinated diphenyl. Imposed strains are 187, 334, 668 and 1340%, respectively, from top to bottom. Pip up: $k=1.673\times10^8$ dyne·cm/radian, $R=2.55$ cm. Pip right; $k=1.673\times10^8$, $R=1.5$. Pip down; $k=3.519\times10^7$, $R=1.5$.

REFERENCES

(1) For example, W. W. Graessley, *J. Chem. Phys.*, **47**, 1942 (1967).

(2) I. F. Macdonald, B. D. Marsh, and E. Ashare, *Chem. Eng. Sci.*, **24**, 1615 (1969).

(3) K. Osaki, M. Tamura, M. Kurata, and T. Kotaka, *J. Phys. Chem.*, **69**, 4183 (1965).

(4) H. C. Booij, *Rheol. Acta*, **5**, 215 (1966).

(5) J. D. Huppler, I. F. Macdonald, E. Ashare, T. W. Spriggs, and R. B. Bird, *Trans. Soc. Rheology*, **11**, 181 (1967).

(6) J. M. Watkins, R. D. Spangler, and E. C. Mckannan, *J. Appl. Phys.*, **27**, 685 (1956).

(7) C. Mussa, V. Tablins, and A. Nasini, *J. Appl. Polymer Sci.*, **5**, 574 (1961).