

SHORT COMMUNICATION

## Stress Relaxation of Polymer Solutions under Large Strain

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(Received May 10, 1971)

**KEY WORDS** Stress Relaxation / Torsional Shear / Nonlinear Viscoelasticity / Terminal Relaxation Time / Cone-Plate / Polymer Solution / Polystyrene /

In the framework of linear viscoelasticity, the stress relaxation curve as a function of time represents the so-called relaxation spectrum to the first approximation and provides direct information on the distribution of various relaxation mechanisms in test material. This feature will not be greatly altered in the study of nonlinear viscoelasticity of polymer solutions. Studies of stress relaxation of solutions under large strain should provide important information on the nature of nonlinear viscoelastic phenomena.

A few measurements have been taken on the stress relaxation of polymer solutions.<sup>1,2</sup> However they were all confined to a range of relatively small values of strains because of the limited capacity of the apparatus used. Thus, in this series of studies, we devised a new apparatus for measuring the relaxation modulus of polymer solutions under large torsional shear, and carried out systematic measurements on polystyrene solutions in chlorinated diphenyl, varying the strain, temperature, polymer molecular weight, and concentration. This communication presents a typical result obtained for the effect of strain on the relaxation modulus.

The apparatus is of the cone-plate type, a sample being held in a gap between the upper cone and lower plate. The cone is suspended with a steel torsion wire from a stationary stay.

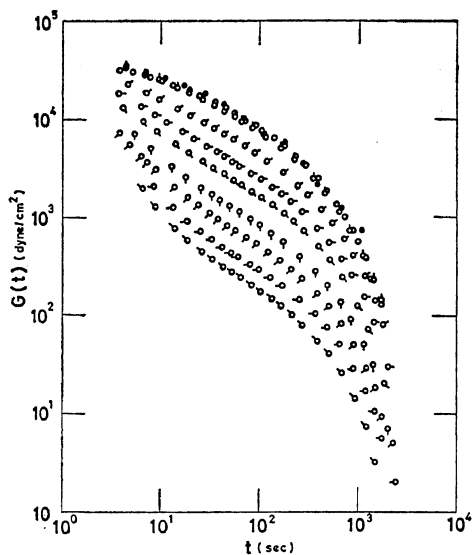
To measure the relaxation modulus  $G(t)$  of the sample, the lower plate is rotated almost instantaneously to a given angle  $\theta$  and remains set there during the taking of stress-relaxation measurements. The rigidity of the sample causes rotation of the cone which is recorded by a transducer. If the torsion wire is suitably chosen, the rotated angle  $\theta$  of the cone is kept negligibly small compared with that of the plate  $\Theta$ , and the relaxation modulus  $G(t)$  can be evaluated by the equation,

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

where  $k$  is the torsional coefficient of the steel wire,  $R$  is the radius of the plate, and  $\phi$  is the angle between the cone and plate. Details of the apparatus used will be published elsewhere.<sup>3</sup> The measurable range of  $G(t)$  was from  $10^6$  to  $10^{-1}$  dyn/cm<sup>2</sup>.

A series of measurements were made on a 20-% solution of narrow-distribution polystyrene in chlorinated diphenyl at 33.5°C under various magnitudes of strain. The weight-average molecular weight of the polymer was  $1.80 \times 10^6$  and its ratio to the number-average molecular weight was 1.25. Figure 1 shows the stress relaxation curves obtained under various strains. Under strains of 0.41 and 1.87 units, the relaxation curves were in agreement with each other

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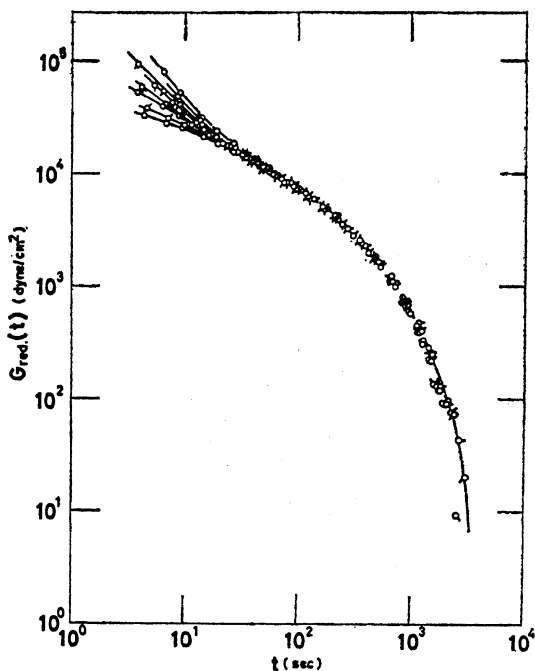


**Figure 1.** Stress relaxation curves for a 20-% solution of narrow-distribution polystyrene in chlorinated diphenyl (Aroclor 1248). The values of strain: open circles without pip, 0.41; pip up, 1.87; pips with directions of successive clockwise 45° rotations correspond to 3.34, 5.22, 6.68, 10.0, 13.4, 18.7, and 25.4 in the strain unit, respectively. Black circles represent the values of  $G(t)$  calculated from our previous data of linear creep measurements.

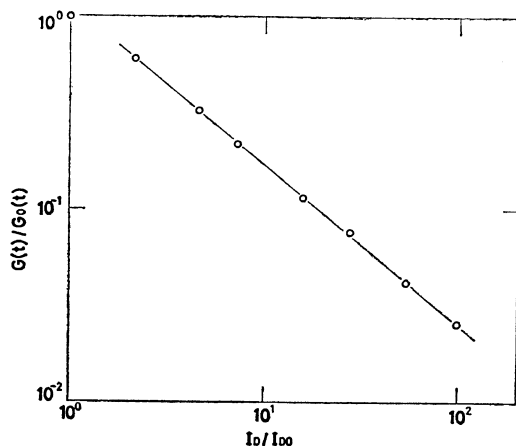
and they were consistent with the values converted from our previous data on creep compliance.<sup>4</sup> In other words, these strain values were in the linear range of viscoelasticity.

As the strain was increased beyond about 2 strain units, the relaxation moduli became strain-dependent, but the terminal relaxation time remained unaffected. All relaxation curves retained the same shape in the region of relatively long time scale and they were able to be superimposed on a single curve by making vertical shifts alone. Figure 2 illustrates this statement, where the relaxation curve for the strain of 1.87 units was chosen as the reference. On the other hand, in the region of relatively short time scale, each relaxation curve displayed an upward turn at an almost constant time scale  $\tau_k$ .

The effect of strain on the relaxation modulus may be conveniently characterized by the vertical shift which was made in Figure 2. The value of  $G(t)/G_0(t)$  was found to be related to the first invariant of the strain tensor,  $I_D$ , in terms of the following equation:



**Figure 2.** Effect of the strain on the shape of the relaxation curve. Symbols are the same as in Figure 1.



**Figure 3.** The vertical shift factor,  $G(t)/G_0(t)$ , plotted against the first invariant of the strain tensor,  $I_D/I_{D0}$ .

$$G(t)/G_0(t) = K(I_D/I_{D0})^{0.83} \quad (2)$$

Here  $K$  is a constant and the subscript 0 attached to  $G$  and  $I_D$  denotes the values for the reference strain. Figure 3 illustrates this finding.

The effects of polymer molecular weight, concentration and temperature on the relaxation modulus will be discussed in later communications.

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