Relaxation Times of Polystyrene

G. H. WEST

The maximum relaxation times of a series of polystyrenes of narrow molecular weight distribution were determined from stress relaxation after steady shear flow at 227°C in a cone-and-plate system. The results obtained were found to differ significantly from previous investigations conducted at 100°C. The maximum relaxation times of two heterogeneous polystyrenes were determined in a similar way and it was found that agreement with experiment could be obtained if it is assumed that relaxation times of the components are additive on a weight basis.

THE viscoelastic behaviour of polymers is frequently interpreted using a model consisting of m Maxwell elements connected in parallel. When this system is subjected to a simple shear deformation the behaviour of each element is characterized by a shear modulus G and a relaxation time τ where the latter represents the time for a steady stress imposed on the element to decay by a factor $1/e$ when the stress is removed. The resultant behaviour of the m elements is given by[1]:

$$\sigma(t)/\dot{\gamma} = G_1\tau_1 \exp(-t/\tau_1) + \ldots\ldots G_m\tau_m \exp(-t/\tau_m) \tag{1}$$

where $\sigma(t)$ represents the shear stress at time t after cessation of shear and $\dot{\gamma}$ is the shear rate imposed. This equation implies that the material possesses a definite maximum relaxation time τ_m and the validity of this assumption has been discussed by Tobolsky and Murakami[2]. These authors concluded that an application of equation (1) to stress relaxation data for both monodisperse and polydisperse polystyrenes between 100° and 125°C yielded significant discrete relaxation times τ_m and τ_{m-1}. These relaxation times were shown to be meaningful by, amongst other methods, the lack of agreement between the predictions of equation (1) and a continuous distribution of relxation times; the closeness of the fit obtained when higher relaxation times obtained from equation (1) are compared with a known discrete distribution based on the Rouse theory[4]; and the linearity resulting when log $[\sigma(t)/\dot{\gamma}]$ and log $[\sigma(t)/\dot{\gamma} - G_m\tau_m \exp(-t/\tau_m)]$ are plotted against t. τ_m is obtained from the linear portion of the former plot and τ_{m-1} from the linear portion of the latter. By an application of this procedure to a range of monodisperse polystyrenes it was found by Tobolsky, Alkonis and Akovali[3] that τ_m was proportional to the molecular weight to the power of 4·0.

Predictions of stress relaxation behaviour in polymers can be obtained by an application of the Rouse-Bueche theory[4,5] and the Ferry, Landel and Williams modification of this theory[6]. The polymer molecule is considered to be divided into N sub-molecules which are subjected to both a Brownian motion and a perturbation from a Gaussian distribution due to local friction caused by shear flow. The hydrodynamic forces due to the shear flow are concentrated on the junctions between the sub-molecules and are characterized by a friction coefficient. The motion of these junctions is described through a transformation of coordinates as the sum of a series of cooperatives modes. Each mode represents motion away from a configuration in which the segments lie along the molecular contour and in the limit the number of modes must equal the number of sub-molecules. Each mode corresponds to a discrete contribution to the relaxation spectrum and it can be shown that:

$$\tau_m \propto M^2\zeta_0 \tag{2}$$

where M is the molecular weight of the polymer, assumed to be monodisperse and ζ_o the monomeric friction coefficient. The significance of maximum relaxation time (τ_m) on the basis of these concepts lies in its characterization of the behaviour of the sub-molecule. In the original Rouse-Bueche theory it was assumed that ζ_o was independent of molecular weight while in the modification of Ferry, Landel and Williams a 2·4 power proportionality between ζ_o and molecular weight was introduced resulting in a 2·0 and 4·4 power proportionality respectively between τ_m and molecular weight. It is thus seen that the latter treatment predicts a molecular weight dependence of the maximum relaxation time for monodisperse polystyrene which is reasonably close agreement with the experimental data so far available.

The influence of polydispersity on the maximum relaxation time will now be considered. It will be assumed that the relaxation time of a heterogeneous polymer can be obtained from the relaxation times of the homogeneous components using a suitable integration technique. The commonest forms of the latter are based on the number of molecules of each component present or on their relative weights. The respective relaxation times τ^N_m and τ^W_m are then given by:

$$\tau^N_m = \sum n_i\tau_{mi} / \sum n_i \tag{3}$$

$$\tau^W_m = \sum w_i\tau_{mi} \tag{4}$$

where n_i, w_i, and τ_{mi} are the number of molecules, weight fraction and maximum relaxation time of species i respectively. Alternative expressions relating to higher moments of composition could also have been employed but the relations given above represent the two simplest cases. An application of the modified Rouse-Bueche theory[7,8] where ζ_o is a function of molecular weight results in a correction to equations (3) and (4) to take into account the change in friction coefficient between the blend and the homogeneous polymer. The corrected equations are given by:

$$\tau^N_m = \sum n_i\tau_{mi}(\zeta_{ob}/\zeta_{oi}) / \sum n_i \tag{5}$$

$$\tau^W_m = \sum w_i\tau_{mi}(\zeta_{ob}/\zeta_{oi}) \tag{6}$$

where ζ_{ob} and ζ_{oi} are the monomeric friction coefficients for species i in the blend and in the homogeneous polymer respectively. At the present time no detailed consideration of the relaxation times of polydisperse materials has been made on this basis. One of the objects of the current investigations was to determine how the maximum relaxation time of a polydisperse material depends on the molecular weight distribution.

EXPERIMENTAL

For measurements of stress relaxation after steady shear flow an R.17 Weissenberg Rheogoneometer, fitted with a 4° angle, 2·5 cm diameter, cone-and-plate system, was employed. In this instrument the sample is contained in the gap between a rotating cone and a stationary plate and the shear stress generated in the sample by the rotation is measured by determining the deflection of the torsion bar to which the upper plate is rigidly attached. The lower cone is rotated by means of a motor and gearbox driving through an electromagnetic clutch, the purpose of which is to enable the cone to attain a given speed and to stop in an interval of time of the order of milliseconds.

The clutch consists of two discs of high permeability metal, each containing a coil winding and friction pad, mounted on either side of a clutch disc of the same metal. This clutch disc is fixed to a horizontal shaft which carries the drive to the cone. One of the outer discs is mounted on a shaft continuously driven by the motor and gearbox unit and the other is rigidly fixed to the casting. When the coil winding of the disc on the drive shaft is energized, the clutch disc disengages the drive to the cone and when this coil is de-energized and the coil winding on the rigid disc energized, the clutch disengages from the drive and engages the brake disc which arrests the rotation. It was found that in the original design the switching circuit for the clutch was such that a significant time (of the order of 70 milliseconds) elapsed between the disengagement of the drive and the application of the brake and this often caused a spurious shape of relaxation curve. The introduction of a reed switching unit in conjunction with a smoothed D.C. supply to the clutch resulted in a significantly improved clutch characteristic with the elimination of this effect.

Measurements of stress relaxation were conducted under conditions such that the rotation of the cone was reduced to a minimum during recovery. This was accomplished by the use of a 0·25 in diameter torsion bar which gave a maximum angular deflection of the cone of 2×10^{-4} radians at the shear rates at which measurements were taken. This corresponds to a value of shear recovery of $3{\cdot}0\times10^{-3}$ for a 4° cone. The ultimate shear recovery of the samples in the absence of restraining forces can be predicted in terms of the stresses generated in the sample during steady shear flow by an application of the Lodge theory of liquids[9]. On this basis, if P_{11} and P_{22} are defined as the normal force generated in the liquid in the direction of flow and along the axis of rotation respectively, the ultimate shear recovery s is given by:

$$s=\tfrac{1}{2}[(P_{11}-P_{22})/\sigma] \tag{7}$$

Substituting appropriate values of $(P_{11}-P_{22})$ and σ, the former being obtained from steady state normal force measurements, it is found that s

is of the order of 1 to 5 for shear rates employed. As the shear recovery in the stress relaxation measurements is negligible compared with this value, the influence of recoil can be ignored in these studies.

The samples employed in the investigation comprised four narrow distribution polystyrenes and two polydisperse materials. The weight and number average molecular weights of the polystyrenes $\overline{M}_w$ and $\overline{M}_n$ (respectively) are shown in *Table 1*. The samples M1 to M4 possess weight to number average molecular weight ratios of 1·2 or less while P1 has the molecular weight distribution curve (determined by us using gel permeation chromatography) shown in *Figure 1*. Sample P2 was formed by mixing samples M1 and M4 in such proportions that a material of the same weight average molecular weigth ($\overline{M}_w$) as P1 was obtained. P2 thus possesses a bi-modal distribution.

Table 1. Characterization of polystyrenes

Sample	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$
M1	1·04	0·84
M2	1·87	1·76
M3	2·60	2·43
M4	4·11	3·88
P1	2·54	0·97
P2	2·57	1·37

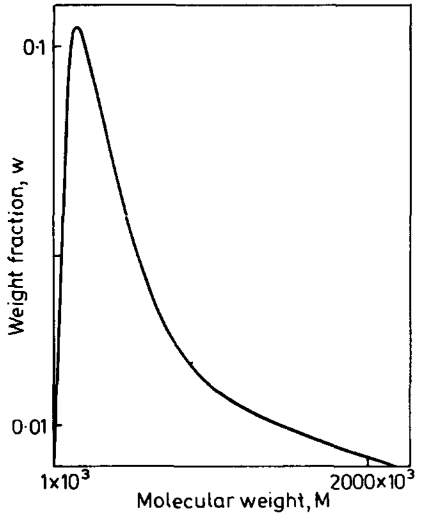

Figure 1—Molecular weight distribution of polydisperse polystyrene sample P1

RESULTS

The stress relaxation measurements for these materials at 227°C are shown in *Figure 2*. For all samples except M1 the relaxation curves were obtained after the imposition of a steady shear rate of 1·42 sec^{-1}. In the case of M1, to attain sufficient accuracy, it was necessary to carry out measurements at 18·0 sec^{-1} shear rate but experiments indicated that the form of the relaxation curve is, to an approximation, independent of shear rate. It is seen that, except at the shortest times, the relaxation data plotted in the form of log $\sigma\ (t)/\dot{\gamma}$ versus t can be represented by a straight line and hence, on the basis of equation (1), it appears that the maximum relaxation time τ_m dominates the relaxation characteristics. It is interesting to note that this conclusion applies equally to both the narrow distribution and polydisperse materials.

From measurements of the slope of the linear portion of the log $\sigma\ (t)/\dot{\gamma}$ versus t plot the maximum relaxation time (τ_m) can be calculated from the equation:

$$\text{slope} = -1/2{\cdot}303\,\tau_m \tag{8}$$

The values of τ_m obtained are shown in *Table 2*. *Figure 3* shows values of log τ_m and log $\overline{M}_w$ plotted for all samples.

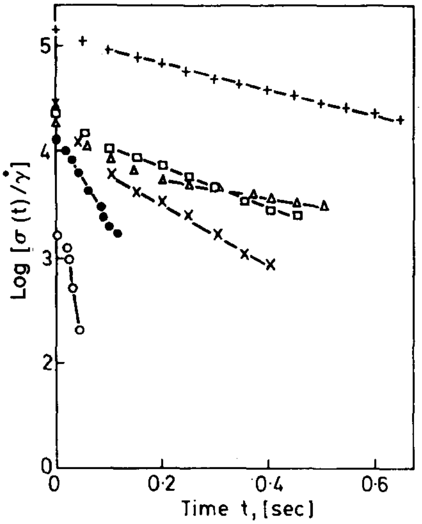

Figure 2—Stress relaxation—Plots of log $[\sigma(t)/\dot{\gamma}]$ as a function of time for narrow and wide distribution polystyrene samples

Sample	M1	M2	M3	M4	P1	P2
Symbol	○	●	×	+	△	□

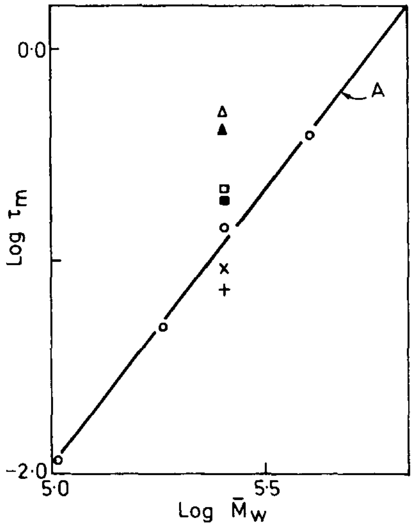

Figure 3—Values of maximum relaxation time for narrow and wide distribution polystyrene samples

Sample	M1–M4	P1	P2
Experimental value	○	△	□
Calculated τ_m^N	—	+	×
τ_m^W	—	▲	■

[Equation of line A:
$\tau_m = 2{\cdot}14 \times 10^{-15}(\overline{M}_w)^{2{\cdot}54}$]

DISCUSSION

From *Figure 2* it can be seen that both the polydisperse samples possess a well defined maximum relaxation time in the same way as the monodisperse material[2] and the contribution due to lower order relaxations is small. This may be due to the relatively high temperature at which the measurements were conducted for under these conditions the molecules can be expected to possess a high degree of flexibility with a resultant inter-molecular coordination which might suppress the characteristics of the individual molecular components present, in favour of some form of averaged behaviour.

Table 2. Observed maximum relaxation times of polystyrenes

Sample	τ_m (s)
M1	0·011
M2	0·050
M3	0·142
M4	0·396
P1	0·488
P2	0·209

The maximum relaxation times, given in *Table 2*, of the monodisperse samples can be represented as a function of molecular weight by the relation:

$$\tau_m = 2{\cdot}14 \times 10^{-15} (\overline{M}_w)^{2{\cdot}54} \tag{9}$$

This is shown in *Figure 3*. The value of the index of 2·54 is closer to the predictions of the Rouse-Bueche theory (index 2·0) than to the Ferry, Landel and Williams modification (index 4·4). Previous experimental work by Tobolsky, Aklonis and Akovali at 100°C gave a value of the index of 4·0 and it is possible that the discrepancy between this value and the current results is due to the difference in temperature at which the measurements were obtained.

The maximum relaxation times of the polydisperse materials can be interpreted according to the Rouse-Bueche theory on either the basis of an additive number or weight basis [equations (5) and (6)]. The investigation with narrow distribution materials showed that the Rouse-Bueche theory rather than the Ferry, Landel and Williams modification predicts results which are in closest agreement with the experimental data and hence the friction factor ratios in equations (5) and (6) will be assumed to be unity. If a general relation of the type $\tau_{m_i} = KM_i^a$ is used to describe the behaviour of a monodisperse polymer i where K and a are constants and M_i is the molecular weight, equations (5) and (6) can be written:

$$\tau_m^N = \frac{K\Sigma(n_i M_i)M_i^{a-1}}{\Sigma n_i} = \frac{K\Sigma w_i M_i^{a-1}}{\Sigma w_i/M_i} = K\overline{M}_n \Sigma w_i M_i^{a-1} \tag{10}$$

$$\tau_m^W = K\Sigma w_i M_i^{a-1} \tag{11}$$

Values of τ_m^N and τ_m^W for polydisperse samples P1 and P2 can thus be calculated employing the appropriate values of K and a. The samples employed to characterize the behaviour of the monodisperse material possess, in practice, a finite distribution of molecular weights as shown in *Table 1*, and thus the value of K and a will be dependent on whether $\overline{M}_w$ or $\overline{M}_n$ is employed to characterize the relaxation time behaviour of these materials. Values of K and a of $2{\cdot}14 \times 10^{-15}$ and 2·54 respectively were obtained by the use of the weight average molecular weight $\overline{M}_w$ and corresponding values of $2{\cdot}69 \times 10^{-15}$ and 2·54 were found for the number average molecular weight $\overline{M}_n$. It is probably more appropriate to employ the former values in equation (11) and the latter in equation (10) and in this case it is seen from the relaxation times obtained (given in *Table 3* and plotted in *Figure 3*), that while τ_m^N is considerably less than the corresponding experimental figure τ_m^w is in good agreement. It can thus be concluded that these experimental results can be satisfactorily explained by application of the Rouse-Bueche theory and the use of additivity of relaxation times on a weight basis.

Table 3. Predicted maximum relaxation times of polydisperse polystyrenes

Sample	$\Sigma w_i M_i^{a-1}$	τ_m^N	$\Sigma w_i M_i^a$	τ_m^W
P1	$2{\cdot}76 \times 10^8$	0·072	$1{\cdot}91 \times 10^{14}$	0·409
P2	$2{\cdot}47 \times 10^8$	0·090	$9{\cdot}32 \times 10^{13}$	0·199

It is interesting to compare these results with the corresponding behaviour of the zero shear viscosities of the materials. Experimentally it has been found by West[10] that this quantity is proportional to molecular weight to the power 3·1 at the temperature at which the stress relaxation measurements were performed, the latter being made under conditions of shear rate at which zero shear viscosities are applicable. The Rouse-Bueche theory predicts a 1·0 power proportionality and there appears to be no obvious explanation for this discrepancy. Bueche[11] however has predicted a proportionality of molecular weight to the power 3·5 from a consideration of the nature of entanglement couplings.

In conclusion it has been found that as the maximum relaxation time of a polydisperse material depends on the weight of the components present and their maximum relaxation times, some insight into the weight distribution of a polymer is available from stress relaxation measurements, particularly if the general type of distribution is known. The existence of a maximum relaxation time which greatly exceeds lower order relaxations is rather surprising and indicates that interactions between molecules are present to such an extent that the relaxation of the components are suppressed in favour of an overall response.

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Department of Polymer and Fibre Science,
University of Manchester Institute of Science and Technology,
Manchester

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