

## Polydisperse Polymers: Relations Among Molecular Weight Distribution, Stress Relaxation, and Distribution of Relaxation Times

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### Synopsis

Relaxation times in polydisperse polymers were calculated on the basis of more realistic viscosity mixing rules than have previously been used. These relaxation times and mixing rules are in turn used to calculate viscoelastic functions such as stress relaxation following sudden straining or steady shearing. Inversion of these functions provides an accurate way to estimate the molecular weight distribution. This method is useful for insoluble or otherwise intractable polymers.

### INTRODUCTION

Previous studies by Menefee and Peticolas<sup>1</sup> and Peticolas<sup>2,3</sup> indicated that it is possible to write approximate expressions for the stress relaxation of bulk polydisperse, amorphous polymers above their glass transition temperature and to invert these expressions to obtain the molecular weight distribution. Mathematical difficulties encountered in that work necessitated a simplified treatment that was not altogether satisfactory. The present paper gives a more exact and complete treatment of the relation between stress relaxation and molecular weight distribution and provides new and simple interconversions between the distribution of relaxation times and the distribution of molecular weights. These relations should be of practical value for the characterization of many polymers, particularly those that are insoluble or otherwise intractable.

### EFFECT OF ENTANGLEMENTS ON THE RELAXATION TIME

For a free-draining polymer, the relaxation time of the  $p$ th normal mode was given by Rouse<sup>4</sup> as

$$\tau_p = \frac{b^2 f_0}{24 kT} csc^2 \frac{p\pi}{2(N+1)} \cong \frac{b^2 f_0 M^2}{6\pi^2 kT M_s^2 p^2} \quad (1)$$

where  $b$  is the r.m.s. average of the length of a submolecule,  $M_s$  is the molecular weight of a submolecule,  $f_0$  is the submolecule friction factor,  $N$

is the number of submolecules in the entire molecule, and  $M$  is the molecular weight of the entire molecule. The submolecule friction factor is related to the monomeric friction coefficient  $\zeta_0$  by the expression

$$f_0 = q\zeta_0 \quad (2)$$

where  $q$  is the number of monomers in a submolecule. For a monodisperse polymer solution, Rouse gave for the real part of the complex viscosity

$$\eta = \eta_s + \frac{cRT}{M} \sum_{p=1}^N \frac{\tau_p}{1 + \omega^2\tau_p^2} \quad (3)$$

where  $\eta_s$  is the solvent viscosity;  $c$  is the polymer concentration in g/cc, and  $\omega$  is the angular frequency of dynamic oscillation.

In the absence of entanglements, the unknown friction factor  $f_0$  and the mean square length  $b^2$  in eq. (1) are eliminated by summing eq. (3) with  $\omega = 0$  to find  $\eta_0$ , then solving for  $b^2f_0$ . To sum, the following identity is used:

$$\sum_{p=1}^N \csc^2 \frac{p\pi}{2(N+1)} = \frac{2}{3} N(N+2). \quad (4)$$

Using  $b^2f_0$  thus found in eq. (1) yields for  $\tau$

$$\tau_p = \frac{3(\eta_0 - \eta_s)M}{2cRT N(N+2)} \csc^2 \frac{p\pi}{2(N+1)}. \quad (5)$$

For  $N$  large enough so that  $\csc^2 \frac{p\pi}{2(N+1)} \cong \frac{4N^2}{p^2\pi^2}$ ,

$$\tau_p = \frac{6(\eta_0 - \eta_s)M}{cRT\pi^2 p^2}. \quad (6)$$

Since there is no solvent, the free-draining results should be applicable to bulk polymers. This extension to the bulk case is feasible only because the relaxation times are determined in terms of the bulk viscosity:

$$\tau_p = \frac{6\eta_0 M}{\pi^2 cRT p^2}. \quad (7)$$

At low molecular weights, the viscosity  $\eta_0$  of a monodisperse bulk polymer is proportional to  $M^\alpha$ , where  $\alpha$  is between 0.8 and 1.8.<sup>5</sup> At a higher molecular weight  $M_c$ , uninhibited molecular movement ceases and the coiling molecules interfere with each other through temporary entanglements.<sup>6,7,8</sup> This causes the viscosity to depend on a much higher power of molecular weight, between 3 and 4, but usually taken to be 3.4. Ferry<sup>9</sup> gives the following description of the effect of molecular weight on the friction factor:

"The well-known fact that, experimentally,  $\eta/M$  is not constant implies that the average friction coefficient  $f_0$  changes with molecular weight; it increases with  $M$ , presumably because the loosening effect of free molecular

ends is gradually eliminated. Eventually, with increasing  $M$ , the effect of free ends disappears asymptotically, being proportional to  $1/M$ . Qualitatively, when the molecular ends are far enough apart, the average polymer segment is oblivious of their existence. Then  $f_0$  should become independent of molecular weight, and there is good experimental evidence that it does. Meanwhile, entanglement coupling has set in, so  $\eta/M$  is still not constant, but for a different reason: the frictional resistance to long-range motions, which primarily determine  $\eta$  as well as the viscoelastic behavior at long times, is strongly influenced by the entanglements. But the shorter range modes of motion are oblivious of the entanglements, and are governed by an  $f_0$  which is independent of  $M$ ."

By a purely empirical argument, Ferry, Landel, and Williams<sup>8</sup> modified the friction factor in eq. (1) to take into account the entanglement effect. They assumed that when the mode number  $p$  is greater than  $p_e = M/2M_e$ , the friction factor is  $f_0$ ; when  $p$  is less, the friction factor becomes equal to  $f$ , given by the following expression for monodisperse polymers:

$$\frac{f}{f_0} = \left( \frac{M}{2M_e} \right)^{2.4} \quad (8)$$

In this hypothesis,  $M_e$  is the molecular weight of segments long enough to be involved in entanglements. The assumption has been made that  $M_c = 2M_e$ , although Porter, MacKnight, and Johnson<sup>10</sup> have shown that there may be no such simple equivalence at all. However, we will retain this particular assumption since no great error is introduced in practical situations.

For reasons of internal consistency that appear when considering the rubbery modulus as derived from expressions for stress relaxation following sudden straining, it is necessary to modify the Ferry, Landel, and Williams assumption that the critical mode  $p_e$  occurs at  $M/2M_e$ . As will be shown later, in order for the rubbery modulus to be equal to  $cRT/M_e$ , consistent with rubber elasticity theory, the critical mode index must be  $p_e = M/M_e$ . In agreement with this new definition of  $p_e$ , we also use a revised expression for  $f/f_0$ :

$$\frac{f}{f_0} = \left( \frac{M}{M_e} \right)^{2.4} \quad (9)$$

For most situations of interest, the molecular weight is so high that this alteration of the Ferry, Landel, and Williams definition of  $p_e$  and of  $f$  makes no difference whatever.

For a monodisperse polymer, the relaxation time (including entanglements) can be converted to macroscopic variables by a method analogous to the development of eq. (5) or eq. (6). We have

$$\eta_0 = \frac{cRT}{M} \left[ \sum_{p=1}^{p_e} \frac{b^2 f_0}{24kT} \left( \frac{f}{f_0} \right) \csc^2 \frac{p\pi}{2(N+1)} + \sum_{p_e}^N \frac{b^2 f_0}{24kT} \csc^2 \frac{p\pi}{2(N+1)} \right], \quad (10)$$

or, on rearranging the sums,

$$\eta_0 = \frac{cRT}{M} \frac{b^2 f_0}{24kT} \left[ \left( \frac{f}{f_0} - 1 \right) \sum_{p=1}^{p_e} \csc^2 \frac{p\pi}{2(N+1)} + \sum_{p=1}^N \csc^2 \frac{p\pi}{2(N+1)} \right]. \quad (11)$$

The first sum may be expanded and summed for large  $N$ , and the second sum evaluated using eq. (4). This procedure yields the close approximation

$$\eta_0 = \frac{cRTb^2 f_0 M}{36kTM_s^2} \left[ \frac{f}{f_0} \left( 1 + \frac{2M_s}{M} + \frac{M_s^2}{2MM_e} \right) - \frac{M_s^2}{2MM_e} \right] \quad (12)$$

where  $M/M_s$  has been substituted for  $N$  (the maximum number of possible modes). Combining eqs. (1) and (12) yields the following relaxation times for monodisperse polymers of molecular weight  $M$ :

$$\tau_p = \frac{3\eta_0(f/f_0)M_s^2}{2cRTM\phi} \csc^2 \frac{p\pi}{2\left(\frac{M}{M_s} + 1\right)} \quad p \leq p_e \quad (13)$$

and

$$\tau_p' = \frac{3\eta_0 M_s^2}{2cRTM\phi} \csc^2 \frac{p\pi}{2\left(\frac{M}{M_s} + 1\right)} \quad p > p_e \quad (14)$$

where

$$\phi = \frac{f}{f_0} \left( 1 + \frac{2M_s}{M} + \frac{M_s^2}{2MM_e} \right) - \frac{M_s^2}{2MM_e}. \quad (15)$$

If  $M_s \ll M$ ,  $\phi$  reduces to  $f/f_0$ , and if the first term of the expansion of  $\csc^2 p\pi/2(N+1)$  is used, the relaxation times become identical to those given by Ferry, Landel, and Williams<sup>8</sup>:

$$\tau_p = \frac{6\eta_0 M}{\pi^2 cRT p^2} \quad p \leq p_e \quad (16)$$

and

$$\tau_p' = \frac{6\eta_0 M}{\pi^2 \frac{f}{f_0} cRT p^2} \quad p > p_e. \quad (17)$$

### INCORPORATION OF POLYDISPERSITY

When dealing with polydisperse linear polymers, the viscosity expressions used so far have to be modified to include an additional summing over the molecular species present. That is, one sums over the viscosity contributions of the normal modes of each molecule and then sums the contributions of all molecules. How this should best be done is still not completely

certain. The simplest mixing rule is a linear mixing of viscosities by weight fractions:

$$\eta_0 = \sum_i w_i \sum_{p=1}^N \eta_{pi} = \sum_i w_i \sum_{p=1}^N G_{pi} \tau_{pi}. \quad (18)$$

Here we have incorporated the familiar expression  $G_{pi} \tau_{pi} = \eta_{pi}$  where  $G_{pi}$ , the modulus of the  $p$ th mode of the  $i$ th molecule, is taken to be  $cRT/M_i$ . The mixing rule of eq. (18) is most valid for mixtures in dilute solution for which the molecular weight dependence of viscosity is nearly first power. For bulk polymers, the molecular weight dependence is not linear, at least above the critical molecular weight  $M_c$ . Taking the commonly accepted relationship  $\eta = AM_w^B$  for bulk polymers and  $\eta_i = AM_i^B$  for monodisperse polymers ( $A$  is a constant for the particular polymer and  $B$  is normally close to 3.4), we then have a second mixing rule based on the relation  $M_w = \sum_i w_i M_i$ :

$$\eta^{\frac{1}{B}} = \sum_i w_i \left( \sum_{p=1}^N \eta_{pi} \right)^{\frac{1}{B}} = \sum_i w_i \left( \sum_{p=1}^N G_{pi} \tau_{pi} \right)^{\frac{1}{B}}. \quad (19)$$

According to what has been said of the friction factor, mixing relations should reflect some dependence on the critical molecular weight  $M_c$ . For example, a possible mixing rule which takes into account the fact that molecules below a molecular weight  $M_c$  will not entangle is the following:

$$\eta = \underbrace{\sum_i w_i \eta_i}_{M < M_c} + \underbrace{\left( \sum_i w_i \eta_i^{\frac{1}{B}} \right)^B}_{M > M_c} \quad (20)$$

or

$$\eta = \underbrace{\sum_i w_i \left( \sum_{p=1}^{M_i/M_c} G_{pi} \tau_{pi}' \right)}_{M < M_c} + \underbrace{\left( \sum_i w_i \left( \sum_{p=1}^{M_i/M_c} G_{pi} \tau_{pi} + \sum_{p=M_i/M_c}^{M_i/M_c} G_{pi} \tau_{pi} \right)^{\frac{1}{B}} \right)^B}_{M > M_c}. \quad (21)$$

As Eq. (21) shows, this mixing rule involves a linear weighting of viscosity contributions from small molecules and a  $1/B$  power weighting of contributions from all modes in molecules of higher molecular weight. By a simple change, this rule may be converted to a form that incorporates nearly all the main features peculiar to polydisperse systems of linear molecules. This change involves removal of the high-mode contributions of long molecules from the  $1/B$  weighting and placing them with the linear weighting. This is justified by their not appearing specifically in the

entanglement process and therefore being counted simply as separate low molecular weight species. This final mixing rule is therefore

$$\eta = \underbrace{\sum_i w_i \left( \sum_{p=1}^{M_i/M_s} G_{pi} \tau_{pi}' \right)}_{M_i < M_c} + \underbrace{\sum_i w_i \left( \sum_{p=M_i/M_s}^{M_i/M_s} G_{pi} \tau_{pi}' \right)}_{M_i > M_c} + \left[ \sum_i w_i \left( \sum_{p=1}^{M_i/M_s} G_{pi} \tau_{pi}' \right)^{\frac{1}{B}} \right]^B. \quad (22)$$

Although the mixing expression of eq. (22) is fairly comprehensive, its use is rendered somewhat difficult by the necessity for knowing something about the molecular weight distribution. For this reason, the simpler expressions of eqs. (18) or (19) will often have to suffice, although sometimes the use of a known distribution or a general approximation may be possible.

Conti and Gigli<sup>11</sup> have discussed other weighting rules besides the one used here which involves weight fractions. The proper mixing methods can be determined ultimately by using the method of blends,<sup>12</sup> but so far no comprehensive study has been made. Some account might also be taken of the suggestion of Chomppf and Prins<sup>13</sup> that the friction factor be variable along the length of a molecule.

### Relaxation Times Using a Linear Mixing Rule

To average for polydispersity using the linear mixing rule, eq. (18), we insert a relaxation time equivalent to that of eq. (1), and use  $G_{pi} = cRT/M_i$  and  $N_i = M_i/M_s$ :

$$\eta_0 = \sum_i w_i \sum_{p=1}^{N_i} \frac{cRT}{M_i} \frac{b^2 f_0}{24kT} \csc^2 \frac{p\pi}{2(N_i + 1)} = \frac{2cRT}{3M_s^2} \left( \frac{b^2 f_0}{24kT} \right) \sum_i w_i (M_i + 2M_s) \quad (23)$$

$$= \frac{2cRT}{3M_s^2} \left( \frac{b^2 f_0}{24kT} \right) (M_w + 2M_s). \quad (24)$$

Solving for  $b^2 f_0/24kT$  and reinserting it into eq. (1), we find

$$\tau_{pi} = \frac{3\eta_0 M_s^2}{2cRT(M_w + 2M_s)} \csc^2 \frac{p\pi}{2\left(\frac{M_i}{M_s} + 1\right)} \quad (25)$$

$$\cong \frac{6\eta_0 M_i^2}{\pi^2 cRT(M_w + 2M_s)p^2} \cong \frac{6\eta_0 M_i^2}{\pi^2 cRT M_w p^2}. \quad (26)$$

Equation (23) shows that this procedure is equivalent to combining viscosities as a linear function of molecular weight, a procedure not valid

for bulk mixing. The relaxation times given by eq. (26) are, however, commonly used in stress relaxation calculations.<sup>1</sup> Since the individual frictional properties of a segment are averaged out by using the overall viscosity, there is a fortuitous compensation that leads to an essentially correct dependence of  $\tau_{pi}$  on  $M$  in eq. (26).

Incidentally, when the relaxation time of eq. (26) is used to determine elastic compliance by the relation

$$J_e = \frac{1}{\eta_0^2} \sum_i w_i \sum_{p=1}^{N_i} G_{pi} \tau_{pi}^2, \quad (27)$$

the usual result<sup>14</sup> is obtained:

$$J_e = \frac{2}{5cRT} \frac{M_z M_{z+1}}{M_w}. \quad (28)$$

To perform the summations required to obtain eqs. (24) and (26), use was made of eq. (4). If eq. (25) is used in eq. (27) to determine  $J_e$ , the required summation can be carried out by using the identity

$$\sum_{p=1}^{N_i} \csc^4 \frac{p\pi}{2(N_i + 1)} = \frac{4}{45} [2(N_i + 1)^4 + 5(N_i + 1)^2 - 7]. \quad (29)$$

This yields, for the first two terms of the elastic compliance,

$$J_e = \frac{2}{5cRT} \frac{M_z}{M_w} (M_{z+1} + 4M_s). \quad (30)$$

Although the second term is normally ignorable, the use of a nonzero value for  $M_s$  has the effect of introducing a kind of stiffness to the chain. This is known from other considerations, since a polymer molecule in which  $M_s = 0$  would be completely flexible and would show no glass transition-dependent behavior at short times.

### Relaxation Times Using Nonlinear Mixing Rules

Leaving aside the linear mixing rule, we now use the full mixing expression of eq. (22) to derive relaxation times. Taking the relaxation times to be like those of eq. (1), except including the entanglement factor  $f/f_0$ , we have

$$\tau_{pi} = \frac{b^2 f_0}{24kT} \left( \frac{f}{f_0} \right) \csc^2 \frac{p\pi}{2(N_i + 1)} \cong \frac{b^2 f_0}{6\pi^2 k T M_s^2} \left( \frac{f}{f_0} \right) \left( \frac{M_i^2}{p^2} \right) \quad p \leq p_e \quad (31)$$

and

$$\tau_{pi}' = \frac{b^2 f_0}{24kT} \csc^2 \frac{p\pi}{2(N_i + 1)} \cong \frac{b^2 f_0}{6\pi^2 k T M_s^2} \left( \frac{M_i^2}{p^2} \right) \quad p > p_e. \quad (32)$$

The factor  $f/f_0$  is taken to be  $(M_w/M_e)^{2.4}$ , our modification of the form for polydisperse polymers proposed by Ferry, Landel, and Williams.<sup>8</sup> However, as we shall see later, there is reason to believe that  $f/f_0$  should

have some dependence on the molecular weight of each molecule and not just on an overall average. In any event, putting these expressions into eq. (22), along with the modulus  $G_{pi} = cRT/M_i$ , we obtain

$$\eta = cRTK \underbrace{\sum_i w_i M_i \left( \sum_{p=1}^{M_i/M_e} \frac{1}{p^2} \right)}_{M < M_e} + cRTK \left[ \sum_i w_i M_i \left( \sum_{p=M_i/M_e}^{M_i/M_e} \frac{1}{p^2} \right) + \frac{f}{f_0} \left( \sum_i w_i M_i^{\frac{1}{B}} \left( \sum_{p=1}^{M_i/M_e} \frac{1}{p^2} \right)^{\frac{1}{B}} \right)^B \right]_{M > M_e} \quad (33)$$

where we have let  $K = b^2 f_0 / 6 \pi^2 k T M_s^2$ . The first sum may be written in terms of the cumulative weight distribution  $W_c$  as follows:

$$\underbrace{\sum_i w_i M_i}_{M_i < M_e} = \int_0^{M_e} M W(M) dM = M_w W_c \quad (34)$$

where  $W_c$  represents in this instance the cumulative weight-average molecular weight distribution up to a molecular weight  $M_e$ . The main problem is that of evaluating the term

$$\underbrace{\left( \sum_i w_i M_i^{\frac{1}{B}} \left( \sum_{p=1}^{M_i/M_e} \frac{1}{p^2} \right)^{\frac{1}{B}} \right)^B}_{M_i > M_e}$$

Without much overall error we can perform the summation over  $p$  as though  $M_i/M_e \rightarrow \infty$ , obtaining the usual result  $\pi^2/6$ . We now designate the other sum as

$$M^* = \left( \sum_i w_i M_i^{\frac{1}{B}} \right)^B \quad (35)$$

It is more intractable and requires a specific form for the molecular weight distribution for its evaluation. In integral form,  $M^*$  becomes

$$M^* = \left( \int_{M_e}^{\infty} M^{\frac{1}{B}} W(M) dM \right)^B \quad (36)$$

If we assume a Schulz-type molecular weight distribution of the form

$$W(M) = a M^b e^{-cM} \quad (37)$$

and run the integral of eq. (36) from 0 to  $\infty$ , the result is very nearly

$$M^* \cong 0.647 M_w + 0.353 M_n \quad (38)$$

Making the lower limit of the integral  $M_e$  instead of 0 complicates matters by bringing in an incomplete gamma function; the error of omission is unlikely to be very great in any case, especially if  $M_e < M_n$ . Hence, we will not be far wrong in most cases in using eq. (38) for  $M^*$ . We can now solve eq. (33) for  $K$ , as follows:

$$\eta_0 = cRTK \frac{\pi^2}{6} W_c M_w + cRTK \frac{\pi^2}{6} \left( \frac{f}{f_0} \right) (0.647 M_w + 0.353 M_n) \quad (39)$$



whence

$$K = 6\eta_0 / \pi^2 cRTM_w \left[ W_c + \frac{f}{f_0} \left( 0.647 + 0.353 \frac{M_n}{M_w} \right) \right]. \quad (40)$$

This  $K$ , inserted into the relaxation time expressions of eqs. (31) and (32), yields

$$\tau_{pt} = 6\eta_0 \left( \frac{f}{f_0} \right) M_i^2 / \pi^2 cRTM_w \left[ W_c + \frac{f}{f_0} \left( 0.647 + 0.353 \frac{M_n}{M_w} \right) \right] p^2 \quad (41)$$

and

$$\tau_{pi}' = 6\eta_0 M_i^2 / \pi^2 cRTM_w \left[ W_c + \frac{f}{f_0} \left( 0.647 + 0.353 \frac{M_n}{M_w} \right) \right] p^2. \quad (42)$$

### STRESS RELAXATION RELATIONS

For monodisperse whole linear polymers the relaxation of stress after cessation of steady-state shearing is obtained by summing the stress contributions of the various modes of motion:

$$\frac{\sigma(t)}{\dot{\epsilon}_0} = \sum_{p=1}^N G_p \tau_p e^{-t/\tau_p} \quad (43)$$

where  $\sigma(t)$  is the stress at time  $t$  and  $\dot{\epsilon}_0$  is the shear rate before relaxation begins. Allowing for entanglements by analogy to eq. (10), we have

$$\frac{\sigma(t)}{\dot{\epsilon}_0} = \sum_{p=1}^{M/M_e} G_p \tau_p e^{-t/\tau_p} + \sum_{p=M/M_e}^{M/M_s} G_p \tau_p' e^{-t/\tau_p'} \quad (44)$$

where  $G_p = cRT/M$ , and  $\tau_p$  and  $\tau_p'$  are given by eqs. (13) and (14), respectively, or, for the simplification that  $M_s \ll M$ , by eqs. (16) and (17). Written in full, the expression for stress relaxation after cessation of steady shear becomes

$$\begin{aligned} \frac{\sigma(t)}{\dot{\epsilon}_0} = \frac{6\eta_0}{\pi^2} \left[ \sum_{p=1}^{M/M_e} \frac{1}{p^2} \exp \left( -\frac{\pi^2 cRT p^2 t}{6\eta_0 M} \right) \right. \\ \left. + \sum_{p=M/M_e}^{M/M_s} \frac{(M_e/M)^{2.4}}{p^2} \exp \left( -\frac{\pi^2 cRT p^2 t}{6\eta_0 M (M_e/M)^{2.4}} \right) \right]. \quad (45) \end{aligned}$$

When  $t = 0$ , eqs. (44) and (45) reduce to  $\sigma(t = 0)/\dot{\epsilon}_0 = \eta_0$ .

For polydisperse polymers, the stress relaxation expressions are beset with the same difficulties encountered in averaging for viscosity. Because of similarities in structure of the expressions for viscosity and steady-shear stress relaxation, we can consider three kinds of mixing rules for stress relaxation by analogy to eqs. (18), (19), and (22):

$$\frac{\sigma(t)}{\dot{\epsilon}_0} = \sum_i w_i \sum_{p=1}^{N_i} G_{pi} \tau_{pi} e^{-t/\tau_{pi}}, \quad (46)$$

$$\frac{\sigma(t)}{\dot{\epsilon}_0} = \left[ \sum_i w_i \left( \sum_{p=1}^{N_i} G_{pi} \tau_{pi} e^{-t/\tau_{pi}} \right)^{\frac{1}{B}} \right]^B \quad (47)$$

and

$$\frac{\sigma(t)}{\dot{\epsilon}_0} = \underbrace{\sum_i w_i \sum_{p=1}^{Ni} G_{pi} \tau_{pi}' e^{-t/\tau_{pi}'}}_{M < M_c} + \underbrace{\sum_i w_i \sum_{p=M_i/M_c}^{M_i/M_s} G_{pi} \tau_{pi}' e^{-t/\tau_{pi}'}}_{M > M_c} + \left[ \sum_i w_i \left( \sum_{p=1}^{M_i/M_c} G_{pi} \tau_{pi}' e^{-t/\tau_{pi}'} \right)^{\frac{1}{B}} \right]^B \quad (48)$$

Of the relations, only eq. (46) has been used to any extent, although the others are more realistic representations. For monodisperse polymers, all these expressions reduce to the form of eq. (43). The use of eq. (46) implies that entanglement effects are not considered in detail, but rather are lumped into the expression by the fact that  $\tau_{pi}$  contains  $\eta_0$ , as shown by eq. (26). Writing eq. (46) as it has been applied before,<sup>1</sup> we have

$$\varphi(t) = \frac{\sigma(t)}{\dot{\epsilon}_0} = \frac{cRT}{a^2} \sum_i w_i M_i \sum_{p=1}^{M_i/M_s} \frac{1}{p^2} \exp\left(-\frac{a^2 p^2 t}{M_i^2}\right) \quad (49)$$

where

$$a^2 = \frac{\pi^2 cRT M_w}{6\eta_0} \quad (50)$$

In terms of a continuous weight distribution of molecular weights, eq. (49) becomes

$$\varphi(t) = \frac{cRT}{a^2} \int_0^\infty MW(M) \sum_{p=1}^{M/M_s} \frac{1}{p^2} \exp\left(-\frac{a^2 p^2 t}{M^2}\right) dM. \quad (51)$$

This expression has been used for determining  $W(M)$  from stress relaxation data<sup>1</sup> and will be discussed further later. The expression is also the suitable one for polymers with no entanglements; that is, those with molecular weights less than  $M_c$  or  $2M_c$ .

To incorporate the details of the entanglement process, we use eq. (48) along with the relaxation times from eqs. (41) and (42) and the modulus  $G_{pi} = cRT/M_i$ . The result, for stress relaxation after steady-state shearing, is

$$\varphi(t) = \frac{cRT}{a^2 g^2} \left\{ \underbrace{\sum_i w_i M_i \sum_{p=1}^{M_i/M_s} \frac{1}{p^2} e^{-\frac{ta^2 g^2 p^2}{M_i^2}}}_{M < M_c} + \underbrace{\sum_i w_i M_i \sum_{p=M_i/M_c}^{M_i/M_s} \frac{1}{p^2} e^{-\frac{ta^2 g^2 p^2}{M_i^2}}}_{M > M_c} \right. \\ \left. + \frac{f}{f_0} \left[ \underbrace{\sum_i w_i M_i^{\frac{1}{3.4}} \left( \sum_{p=1}^{M_i/M_c} \frac{1}{p^2} e^{-\frac{ta^2 g^2 p^2}{(f/f_0) M_i^2}} \right)^{\frac{1}{3.4}}}_{M > M_c} \right]^{3.4} \right\} \quad (52)$$

where

$$a^2 = \frac{\pi^2 c R T M_w}{6 \eta_0} \quad (53)$$

$$g^2 = W_c + \frac{f}{f_0} \left( 0.647 + 0.353 \frac{M_n}{M_w} \right) \quad (54)$$

and

$$\frac{f}{f_0} = \left( \frac{M_w}{M_e} \right)^{2.4} \quad (55)$$

where  $W_c$  is defined by Eq. 34 as  $M_w^{-1} \int_0^{M_c} M W(M) dM$ . If needed, eq. (52) can easily be written for a continuous distribution of molecular weights.

The discussion so far has dealt with stress relaxation after steady shearing, most commonly performed on fluid polymers. However, stress relaxation following sudden straining is the usual relaxation measurement for solid polymers, or even viscous fluids. For monodisperse amorphous linear polymers, the appropriate phenomenologic representation is

$$G(t) = \frac{\sigma(t)}{\epsilon_0} = \sum_{p=1}^N G_p \exp(-t/\tau_p). \quad (56)$$

This expression, when  $\tau_p$  is written out, becomes

$$G(t) = \frac{cRT}{M} \sum_{p=1}^{M/M_s} \exp\left(-\frac{\pi^2 c R T}{G \eta_0 M} p^2 t\right) \quad (57)$$

where we have taken  $G_p = cRT/M$ . The glassy modulus can be found by setting  $t = 0$ , which yields

$$G_0 = \frac{cRT}{M_s} \quad (58)$$

There is no rubbery plateau or rubbery flow region, since there are no entanglements. Equation (56) can also be derived by differentiating eq. (43) according to the relation<sup>15</sup>:

$$G(t) = -\frac{d}{dt} \left[ \frac{\sigma(t)}{\epsilon_0} \right]. \quad (59)$$

When entanglements do exist, for  $M > M_c$ , we find, by differentiating eq. (44) with respect to time,

$$G(t) = \sum_{p=1}^{M/M_e} G_p \exp(-t/\tau_p) + \sum_{p=M/M_e}^{M/M_s} G_p \exp(-t/\tau_p') \quad (60)$$

or, written more fully,

$$G(t) = \frac{cRT}{M} \left[ \sum_{p=1}^{M/M_e} \exp\left(-\frac{\pi^2 cRT p^2 t}{6\eta_0 M}\right) + \sum_{p=M/M_e}^{M/M_s} \exp\left(-\frac{\pi^2 cRT p^2 t}{6\eta_0 M (M_e/M)^{2.4}}\right) \right]. \quad (61)$$

The glassy modulus,  $G_0$ , is again found by taking  $t = 0$ , and is the same as that given by eq. (58). In this case there is a rubbery modulus, which is found by summing only the first term of eq. (61) with  $t = 0$ ,

$$G_e = \frac{cRT}{M_e}. \quad (62)$$

It is this relation that dictates the critical mode number,  $p_e$ , as discussed previously. Equation (61) will be used later when comparing calculated and experimental results.

The incorporation of polydispersity into the sudden-strain stress relaxation modulus expressions brings in some difficulty. From the form of eq. (56), we can see that each term of the sum over  $p$  is weighted only by  $G_p = cRT/M$ . Hence, depending on the time, each term can contribute strongly to  $G(t)$ . This means that for a polydisperse polymer at very short times, the problem of how to weight the low molecular weight species will become important. We therefore turn immediately to the most inclusive form of the steady shear relaxation, eq. (48) or its alternate form eq. (52), and differentiate it to obtain  $G(t)$ :

$$G(t) = \sum_i w_i \underbrace{\sum_{p=1}^{M_i/M_s} G_{pi} \exp(-t/\tau_{pi}')}_{M < M_e} + \sum_i w_i \underbrace{\sum_{p=M_i/M_e}^{M_i/M_s} G_{pi} \exp(-t/\tau_{pi}')}_{M > M_e} + \left[ \sum_i w_i \left( \sum_{p=1}^{M_i/M_e} G_{pi} \tau_{pi} \exp(-t/\tau_{pi}) \right)^{\frac{1}{3.4}} \right]^{2.4} \times \left[ \sum_i w_i \left( \sum_{p=1}^{M_i/M_e} G_{pi} \tau_{pi} \exp(-t/\tau_{pi}) \right)^{-\frac{2.4}{3.4}} \left( \sum_{p=1}^{M_i/M_e} G_{pi} \exp(-t/\tau_{pi}) \right) \right] \quad (63)$$

$M > M_e$

where  $\tau_{pi}$  is given by eq. (41) for  $p \leq M/M_e$ ,  $\tau_{pi}'$  is given by eq. (42) for  $p > M/M_e$ , and  $G_{pi} = cRT/M_i$ .

When we set  $t = 0$  in eq. (63), we obtain for the glassy modulus  $G_0$

$$G_0 = \frac{cRT}{M_s} + \frac{cRT}{M_e} \left[ \underbrace{\left( \sum_i w_i M_i^{\frac{1}{3.4}} \right)^{2.4} \left( \sum_i w_i M_i^{-\frac{2.4}{3.4}} \right)}_{M > M_e} - 1 \right]. \quad (64)$$

The second term in this expression will be small, so that essentially  $G_0 = cRT/M_s$ , a result identical with that for a monodisperse polymer, although eq. (64) does bring in a weak molecular weight dependence.

### COMPARISON OF EXPERIMENTAL AND CALCULATED RELAXATION MODULUS

A useful material for testing relaxation expressions is an early NBS polyisobutylene sample on which stress relaxation data were obtained by Tobolsky and Catsiff.<sup>16</sup> Marvin and Oser<sup>17</sup> compared the experimental results at 25°C with a curve calculated from their ladder model equations. Results for  $G(t)$  calculated from the ladder model are shown as the dashed line in Figure 1. Using the same data, eq. (61) was used to calculate the solid line on Figure 1. As seen, the agreement with experiment of both Marvin and Oser's curve and that of eq. (61) is fairly good, with eq. (61) being considerably easier to use than the ladder equations. Parameters used in eq. (61) were  $M = 1.03 \times 10^6$ ;  $M_c = 2M_e = 17,100$  (ref. 5);  $cRT/M_e = 2.65 \times 10^6$  dynes/cm<sup>2</sup>;  $cRT/M = 2.20 \times 10^4$  dynes/cm<sup>2</sup>;  $M/M_e = 117$ ;  $cRT/M_s = 1.207 \times 10^{10}$  dynes/cm<sup>2</sup>;  $M/M_s = (cRT/M_s)(M/cRT) = 5.49 \times 10^5$ .

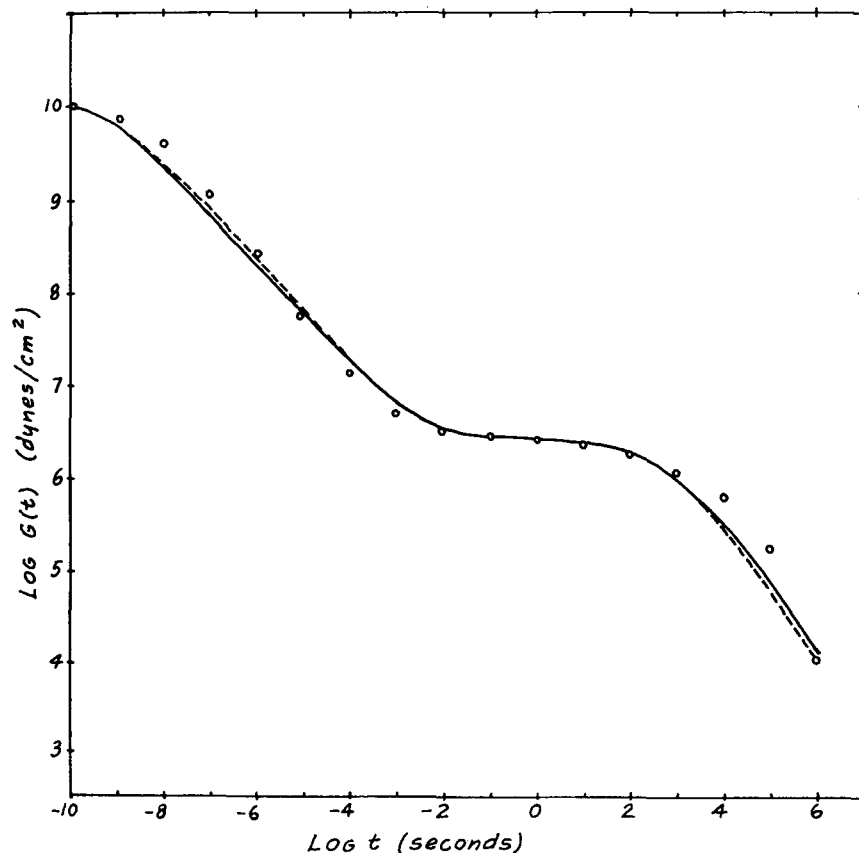


Fig. 1. Relaxation modulus  $G(t)$  of NBS polyisobutylene: Circles, experimental data of Tobolsky and Catsiff<sup>21</sup>; dashed line,  $G(t)$  calculated using ladder model equations of Marvin and Oser<sup>20</sup>; solid line,  $G(t)$  calculated using eq. (61) of this paper.

In spite of the nominally good agreement between calculations and experiment, three problems remain. First, in the viscous flow region (at times longer than those of the rubbery plateau), the agreement is poor because of inadequate incorporation of the molecular weight distribution (MWD). We will shortly show how this apparent defect can be turned to advantage to give a good idea of the MWD if it is not known. Second, the slope of the relaxation modulus in the glass transition region is not correct. The Rouse-based theory predicts a slope of  $-1/2$  on a  $\log G(t)$ -versus- $\log t$  plot, and experiment favors a steeper slope of  $-2/3$  to  $-3/4$ . If the Zimm relaxation times<sup>17</sup> are used, this slope will become  $-2/3$ .<sup>19</sup> Rather than say, however, that the deviation from a slope of  $-1/2$  is due to hydrodynamic interactions (the Zimm nonfree-draining case) between small segments, Ferry prefers to attribute it to the failure of the concept of an average friction coefficient. The same problem may be present to some extent in the later flow region, where a theory by Graessley<sup>20</sup> gives a slope of  $-0.82$  to the high shear rate portion of  $\log \eta(\dot{\epsilon})$  versus  $\log \dot{\epsilon}$ . These questions are still pending.

The third problem is exemplified by an objection made by Tobolsky<sup>21</sup> to the use of the Rouse theory in the glassy region. He correctly states that the kind of elasticity exhibited in this region is not entropic in nature, as the whole derivation based on Rouse theory dictates. This can be seen from two observations. First, if  $M_s$  is calculated from the relation  $G_0 = cRT/M_s$ , it turns out to be 1.8 for polyisobutylene, an absurdly low molecular weight for a statistical segment. Also, the glassy plateau is weakly inversely temperature dependent, and *not* directly proportional. This objection does not necessarily interfere with the use of the Rouse approach isothermally, because the exact definition of a segment is never specifically needed. Tobolsky and Aklonis<sup>22</sup> have suggested a modification of the Rouse theory for this region that would throw most of the deformation energy into rotational modes rather than entropic deformation modes. Their formulation for the glassy region is

$$G_\sigma(t) = G_0 \sum_{p=1}^N \frac{1}{N} \exp\left(-\frac{tp^2}{N^2\tau_1}\right) \quad (65)$$

where  $N$  is the number of torsional oscillators in the linear molecule, though the actual value is not too critical. At this stage,  $\tau_1$  has to be determined experimentally. If we incorporate this rotational contribution into eq. (61) for  $G(t)$  of a monodisperse linear amorphous polymer, we have

$$G(t) = \frac{cRT}{M} \left[ \sum_{p=1}^{M/M_e} \exp\left(-\frac{\pi^2 cRT p^2 t}{6\eta_0 M}\right) + \sum_{p=M/M_e}^{M/M_s} \exp\left(-\frac{\pi^2 cRT p^2 t}{6\eta_0 M (M_e/M)^{2.4}}\right) \right] + \frac{1}{N} \left( G_0 - \frac{cRT}{M_s} \right) \sum_{p=1}^N \exp\left(-\frac{p^2 t}{N^2 \tau_1}\right) \quad (66)$$

where  $M_s$  is redefined as a more realistic segment length, which could presumably be determined from temperature studies of  $G(t)$  versus  $t$ . Since the contribution of each mode in Tobolsky's development has a form identical to the original Rouse-like formulation, there is no need to carry along parallel developments in the present work.

### DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION FROM STRESS RELAXATION

Two assumptions are basic to most approaches that attempt a determination of the distribution of molecular weights from experimental stress relaxation information. They are (1) the establishment of a mixing rule and (2) some assumption regarding the molecular weight dependence of the entanglement friction factor  $f/f_0$ . Over the years, one relation for the viscosity of bulk polymers has been fairly well established:

$$\eta = AM_w^{3.4}. \quad (67)$$

The coefficient  $A$  depends on the polymer type, the temperature, and the shear rate. The exponent 3.4 has this value only at low shear rates and decreases at higher shear rates. There is usually some variability in the 3.4 value anyway, from polymer to polymer, but we shall take this as the average. From eq. (67), we would expect that the same dependence would hold for the  $i$ th monodisperse fraction of a mixture:

$$\eta_i = AM_i^{3.4}. \quad (68)$$

Thus, combining eqs. (67) and (68), we obtain

$$\eta = \left( \sum_i w_i \eta_i^{\frac{1}{3.4}} \right)^{3.4}. \quad (69)$$

This is the nonlinear mixing rule discussed before. It has been reasonably well verified as a suitable mixing rule for bulk polymers by the method of blends.<sup>12</sup>

#### Linear Mixing

In spite of the presence of more exact mixing rules, especially eq. (69), most work done so far to relate MWD to stress relaxation has been based on a linear mixing rule of the form

$$\eta = \sum_i w_i \eta_i \quad (70)$$

which is known<sup>1</sup> not to be true except for dilute solutions, a case we are not considering here. There is good reason why we would prefer to work with linear mixing, and it is illustrated by the following derivation. Let us take the basic steady-flow stress relaxation expression derived from Rouse relaxation behavior, using linear mixing<sup>1</sup>:

$$\varphi(t) = \frac{\sigma(t)}{\dot{\epsilon}_0} = \frac{cRT}{a^2} \int_0^\infty MW(M) \sum_{p=1}^{M/M_e} \frac{1}{p^2} \exp\left(-\frac{a^2 p^2 t}{M^2}\right) dM. \quad (71)$$

If for the present we ignore the influence of modes greater than unity (not a drastic assumption, it turns out) and write out  $\varphi(t)$  in terms of a relaxation distribution, we have

$$\varphi(t) = \int_0^\infty H(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau = \frac{cRT}{a^2} \int_0^\infty MW(M) \exp\left(-\frac{a^2 t}{M^2}\right) dM. \quad (72)$$

Now, since  $\tau = M^2/a^2$ , we have  $MdM = 1/2 a^2 d\tau$ . Putting this value of  $MdM$  into the right-hand integral of eq. (72), we obtain

$$\int_0^\infty H(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau = \frac{cRT}{2} \int_0^\infty W(M) \exp\left(-\frac{t}{\tau}\right) d\tau \quad (73)$$

which leads immediately to

$$W(M) = \frac{2}{cRT} H(\tau), \quad M = a\sqrt{t}. \quad (74)$$

The simplicity of this expression is easily apparent, and even though its correctness may be questionable in detail, it shows the close relationship that exists between  $H(\tau)$  and  $W(M)$ , a fact that has been observed experimentally many times.

Actually, a result very similar to this was obtained by Watkins, Spangler, and McKannan,<sup>23</sup> who were the first to make a calculation of MWD from stress relaxation. We will not reproduce their somewhat unwieldy argument, but will give a derivation based on the above method. First, consider the original Rouse-like relaxation times, from eq. (1):

$$\tau_p = \frac{b^2 f_0 M^2}{6\pi^2 k T M_s^2 \rho^2}. \quad (75)$$

As before, the assumption is made that the friction factor  $f_0$  should be replaced by another factor that shows molecular weight dependence. We shall give it the form

$$f_0 \rightarrow f_0 \left(\frac{M}{M_e}\right)^\beta \quad (76)$$

by analogy to a similar expression used in preceding developments. Thus, we have

$$\tau_p = \frac{b^2 f_0 M^{\beta+2}}{6\pi^2 k T M_s^2 M_e^\beta \rho^2} = \frac{KM^{\beta+2}}{\rho^2}. \quad (77)$$

Using this expression along with  $G_p = cRT/M$ , we have, following the linear mixing rule,

$$\varphi(t) = \int_0^\infty W(M) \left( \sum_{p=1}^{M/M_e} G_p \tau_p \exp\left(-\frac{t}{\tau_p}\right) \right) dM. \quad (78)$$



Again assuming only the first mode to be important, we obtain

$$\varphi(t) = \int_0^\infty H(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau = KcRT \int_0^\infty M^{\beta+1} W(M) \exp\left(-\frac{t}{KM^{\beta+2}}\right) dM. \quad (79)$$

Taking  $\tau = KM^{\beta+2}$ , we have

$$d\tau = (\beta + 2)KM^{\beta+1}dM.$$

Substituting this into eq. (79) and equating under the integrals gives the final result

$$W(M) = \frac{\beta + 2}{cRT} H(\tau), \quad M = \left(\frac{\tau}{K}\right)^{\frac{1}{\beta+2}}. \quad (80)$$

Watkins et al. eliminated the  $K$  in eq. (80) by adopting the approximation

$$M = M_w \left(\frac{\tau}{\tau_w}\right)^{\frac{1}{\beta+2}},$$

where both  $M_w$  and  $\tau_w$  are assumed to occur at similar points in their respective distributions. They found that the best value for  $\beta$  is 1.5 rather than the 2.4 used by Ferry, Landel, and Williams<sup>8</sup> for a related friction factor problem. Watkins' results for poly(methyl methacrylate) were quite reasonable, indicating that this semiempirical approach has merit.

In a more elaborate development, Menefee and Peticolas<sup>1</sup> inverted the original linear mixing relation of eq. (71) and obtained  $W(M)$  as a function of  $\varphi(t)$  rather than  $H(\tau)$ . If all the modes in  $p$  are retained, it is found that no simple association can be made between the  $\tau$  of the relaxation distribution integral and the multiple  $\tau$  values in the integral over molecular weight. Menefee and Peticolas therefore performed an initial inversion based on a theorem of Moebius to get rid of the modal sum over  $p$  and then a second inversion of the resulting Laplace transform expression to obtain  $W(M)$ . The Moebius inversion of eq. (71) gives

$$\int_0^\infty MW(M) \exp\left(-\frac{a^2t}{M^2}\right) dM = \frac{\pi^2 M_w}{6} \sum_{n=1}^\infty \frac{\mu(n)}{n^2} \varphi(n^2t) \quad (81)$$

and the final result is

$$W(M) = \frac{2}{cRT} \lim_{\nu \rightarrow \infty} \left[ \frac{(-1)^\nu}{\nu!} \nu^{\nu+1} t^{\nu-1} \sum_{n=1}^\infty \frac{\mu(n)}{n^{2-2\nu}} \frac{d^\nu \varphi(\nu n^2 t)}{d(\nu n^2 t)} \right] \quad (82)$$

where

$$M = \left( \frac{\pi^2 cRT M_w t}{6\eta_0} \right)^{1/2} = at^{1/2}. \quad (83)$$

The  $\mu$ 's are the Moebius  $\mu$ -function terms, defined as equal to +1 if  $n$  is 1 or if  $n$  is factorable into an even number of unlike primes, equal to -1 if  $n$  is factorable into an odd number of unlike primes, and equal to zero for all other  $n$  values. For example, the first few terms for  $\mu(n)$  are 1, -1, -1, 0, -1, +1, -1, 0, 0, etc.

Equation (82) can be cast into a more compact form as follows:

$$W(M) = \frac{2}{cRT} \sum_{n=1}^{\infty} \mu(n) H(n^2\tau) \quad M = a\tau^{1/2}. \quad (84)$$

For the first few terms we have then

$$W(M) = \frac{2}{cRT} [H(\tau) - H(4\tau) - H(9\tau) \dots] \quad M = a\tau^{1/2}. \quad (85)$$

Taking only the first term on the right side gives eq. (74).

In an experimental verification of some of the preceding developments, Peticolas<sup>2</sup> took only the first approximation to eq. (81), in the form

$$\frac{1}{M_w} \int_M^{\infty} MW(M) dM \cong \frac{\pi^2}{6} \sum_{n=1}^{\infty} \frac{\mu(n)}{n^2} \varphi(n^2t) \quad M = at^{1/2}. \quad (86)$$

Using the fact that the cumulative Z-distribution is defined as

$$Z_c = \frac{1}{M_w} \int_0^M MW(M) dM. \quad (87)$$

Equation (86) can be written as

$$Z_c(M) \cong 1 - \frac{\pi^2}{6} \sum_{n=1}^{\infty} \frac{\mu(n)}{n^2} \varphi(n^2t) \quad M = at^{1/2}. \quad (88)$$

In this form, Peticolas<sup>2</sup> found good agreement with experimental data for a linear polyethylene, but poor agreement with data for a polystyrene.

### Nonlinear Mixing

Once a mixing rule has been adopted, it seems probable that most of the remaining problem lies in how the entanglement factor  $f$  is handled. Ferry, Landel, and Williams<sup>8</sup> adopted the relation

$$f = f_0 \left( \frac{M_w}{2M_e} \right)^{2.4} \quad (89)$$

which reduces to  $f_0(M/2M_e)^{2.4}$  for monodisperse polymers. For polydisperse polymers, this expression has the disadvantage that it includes no details of the entanglement process. That is, one would expect that the friction factor would depend both on  $M_i$ , the individual molecular weight, and some average  $\langle M \rangle_f$  of the whole polymer. We recall that Watkins et al.<sup>23</sup> found a 1.5 power dependence on  $M_i$  of the friction factor. Hence, using as before  $M_e$  instead of  $2M_e$ , a general form of the friction factor might be taken as

$$f = f_0 \left( \frac{\langle M \rangle_f}{M_e} \right)^{2.4} \left( \frac{M_i}{\langle M \rangle_f} \right)^\alpha \quad (90)$$

where  $\alpha$  is an adjustable parameter denoting the sensitivity of  $f$  to the individual molecule and may have some relationship to the corresponding friction factor in dilute solutions, where average properties become less important. In actual fact, we would expect the true form of a friction factor to be much more complex than that shown by eq. (90), though it expresses the main points. Ferry et al.<sup>8</sup> have taken  $\langle M \rangle_f = M_w$  and  $\alpha = 0$ , so we may also consider this substitution of  $M_w$  for  $\langle M \rangle_f$ , though we retain a nonzero  $\alpha$ :

$$f = f_0 \left( \frac{M_w}{M_e} \right)^{2.4} \left( \frac{M_i}{M_w} \right)^\alpha. \quad (91)$$

The following relations will be taken as a starting point for an analysis similar to that leading to eq. (52), except that we ignore higher modes and low molecular weights:

$$\tau_{pi} = \frac{b^2 f}{6\pi^2 k T M_s^2} \frac{M_i^2}{p^2} \quad (92)$$

$$G_{pi} = \frac{cRT}{M_i} \quad (93)$$

$$\eta = A M_w^{3.4} \quad (94)$$

$$\eta^{1/3.4} = \sum_i w_i \eta_i^{1/3.4} \quad (95)$$

Summing the viscosity expression

$$\eta^{1/3.4} = \sum_i w_i \left( \sum_{p=1}^{M_i/M_e} G_{pi} \tau_{pi} \right)^{1/3.4} \quad (96)$$

allows us to eliminate the unknown factors in  $\tau_{pi}$  with the result

$$\tau_{pi} = \frac{6\eta M_i^{2+\alpha}}{\pi^2 c R T M_w^\alpha M^* p^2} = \frac{K M_i^{2+\alpha}}{p^2} \quad (97)$$

where

$$M^* = M_w^{-\alpha} \left( \sum_i w_i M_i^{1+\alpha/3.4} \right)^{3.4}. \quad (98)$$

The steady-flow stress relaxation then becomes

$$\varphi(t) = \frac{6\eta}{\pi^2 M_w^\alpha M^*} \left[ \sum_i w_i M_i^{1+\alpha/3.4} \left( \sum_{p=1}^{M_i/M_e} \frac{1}{p^2} \exp\left(-\frac{t}{\tau_{pi}}\right) \right)^{1/3.4} \right]^{3.4} \quad (99)$$

or, in integral form,

$$\varphi(t) = \frac{6\eta}{\pi^2 M_w^\alpha M^*} \left[ \int_0^\infty M^{1+\alpha/3.4} W(M) \left( \sum_{p=1}^{M/M_e} \frac{1}{p^2} \exp\left(-\frac{t}{\tau_p}\right) \right)^{1/3.4} dM \right]^{3.4} \quad (100)$$

where

$$\tau_p = \frac{6\eta M^{2+\alpha}}{\pi^2 c R T M_w^\alpha M^* p^2} = \frac{K M^{2+\alpha}}{p^2}. \tag{101}$$

By defining another distribution function,  $F(\tau)$ , we can write eq. (100) as

$$\begin{aligned} [\varphi(t)]^{3.4} &= \phi(t) = \int_0^\infty F(\tau) \exp(-t/\tau) d\tau \\ &= \left(\frac{6\eta}{\pi^2 M_w^\alpha M^*}\right)^{1/3.4} \int_0^\infty M^{1+\alpha/3.4} W(M) \left[ \sum_{p=1}^{M/M_e} \frac{1}{p^2} \exp\left(-\frac{t}{\tau_p}\right) \right]^{1/3.4} \\ &\qquad \qquad \qquad \times dM. \end{aligned} \tag{102}$$

The sum over  $p$  may be written out and expanded in the form

$$\left[ e^{-t/\tau_1} \left( 1 + \frac{1}{4} e^{-\frac{3t}{\tau_1}} + \frac{1}{9} e^{-\frac{8t}{\tau_1}} + \dots \right) \right]^{1/3.4},$$

yielding

$$\begin{aligned} \phi(t) &= \left(\frac{6\eta}{\pi^2 M_w^\alpha M^*}\right)^{1/3.4} \int_0^\infty M^{1+\alpha/3.4} W(M) \left[ \exp\left(-\frac{t}{3.4\tau_1}\right) \right. \\ &\quad + 0.0735 \exp\left(-\frac{3.294t}{\tau_1}\right) - 0.00649 \exp\left(-\frac{6.294t}{\tau_1}\right) + \\ &\quad \left. 0.0327 \exp\left(-\frac{8.294t}{\tau_1}\right) + \dots \right] dM. \end{aligned} \tag{103}$$

This may be cast into a shortened form as follows:

$$\begin{aligned} \phi(t) &= \left(\frac{6\eta}{\pi^2 M_w^\alpha M^*}\right)^{1/3.4} [I(t) + 0.0735I(11.2t) \\ &\quad - 0.00649I(21.4t) + 0.0327I(28.2t) + \dots] \end{aligned} \tag{104}$$

where we have set

$$I(t) = \int_0^\infty M^{1+\alpha/3.4} W(M) \exp\left(-\frac{t}{3.4\tau_1}\right) dM. \tag{105}$$

Hence, the inversion may be carried out by solving for  $I(t)$  and resubstituting appropriate terms:

$$\begin{aligned} \left(\frac{6\eta}{\pi^2 M_w^\alpha M^*}\right)^{1/3.4} I(t) &= \phi(t) - 0.0735\phi(11.2t) \\ &\quad + 0.00649\phi(21.4t) - 0.0327\phi(28.2t) + \dots \end{aligned} \tag{106}$$

We can now make use of the following property of the distribution function:

$$\phi(nt) = \int_0^\infty F(\tau) \exp\left(-\frac{nt}{\tau}\right) d\tau = n \int_0^\infty F(n\tau) \exp\left(-\frac{t}{\tau}\right) d\tau. \tag{107}$$

This may be used to reduce eq. (106) to the form

$$\begin{aligned} \left(\frac{6\eta}{\pi^2 M_w^\alpha M^*}\right)^{\frac{1}{3.4}} \int_0^\infty M^{\frac{1+\alpha}{3.4}} W(M) \exp\left(-\frac{t}{3.4\tau_1}\right) dM \\ = \int_0^\infty [F(\tau) - 0.823F(11.2\tau) + 0.1389F(21.4\tau) \\ - 0.922F(28.2\tau)] \exp\left(-\frac{t}{\tau}\right) d\tau. \end{aligned} \quad (108)$$

Setting

$$\tau = 3.4\tau_1 = 3.4 KM^{\alpha+2} = \left(\frac{3.4(6\eta)}{\pi^2 cRT M_w^\alpha M^*}\right) M^{\alpha+2} \quad (109)$$

we can reduce eq. (108) in the same way that eq. (79) was handled, with the final result

$$\begin{aligned} M^{\frac{2.4}{3.4}} W(M) = (2 + \alpha) \left(\frac{3.4}{cRT\tau}\right)^{\frac{1}{3.4}} \tau [F(\tau) - 0.823F(11.2\tau) \\ + 0.1389F(21.4\tau) - 0.922F(28.2\tau) + \dots] \end{aligned} \quad (110)$$

where

$$M = \left(\frac{\pi^2 cRT M_w^\alpha M^*}{20.4 \eta}\right)^{\frac{1}{\alpha+2}} \tau^{\frac{1}{\alpha+2}}. \quad (111)$$

$F(\tau)$  can be determined by standard inversion methods from

$$\begin{aligned} \phi(t) = [\varphi(t)]^{\frac{1}{3.4}} = \int_0^\infty F(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau \\ = \int_{-\infty}^\infty \tau F(\tau) \exp\left(-\frac{t}{\tau}\right) d \ln \tau. \end{aligned} \quad (112)$$

Under usual circumstances, an adequate expression for  $W(M)$  should be obtainable from eq. (110) by using only the first term of the distribution function:

$$M^{2.4/3.4} W(M) \cong (2 + \alpha) \left(\frac{3.4}{cRT\tau}\right)^{\frac{1}{3.4}} \tau F(\tau). \quad (113)$$

The only snag to the use of the above expressions is the necessity for knowing  $M^*$  from eq. (98), which itself depends on the molecular weight distribution. For a Schulz distribution given in eq. (37),  $M^*$  may be evaluated approximately:

$$M^* = M_w - \frac{1}{2} (1 + \alpha) \left(1 - \frac{1 + \alpha}{3.4}\right) (M_w - M_n). \quad (114)$$

It is unfortunately not possible to perform a bootstrap calculation and use a first approximation  $W(M)$  to determine a value for  $M^*$ , and so on.

This is because of an identity involving eqs. (98) and (108) (with  $t = 0$ ). Hence, as eq. (114) indicates, some knowledge of an additional molecular parameter such as  $M_n$  is necessary, though fortunately the shape of  $W(M)$  is not greatly sensitive to  $M^*$  (or vice versa).

Using the experimental data of Fujita and Ninomiya<sup>24,25</sup> for a polystyrene sample at 135°C, we have computed  $W(M)$  for three values of  $\alpha$ : 1.0, 1.5, and 2.0. First, their experimental stress relaxation data, obtained as  $E(t)$ , was converted to  $G(t)$  by dividing by 3. It was then integrated to determine  $\varphi(t)$  and  $\eta_0$ .  $M_w$  was computed from  $\eta_0$  using the relation given by Fox and Loshaek.<sup>5,26</sup>  $M^*$  was calculated from eq. (114),

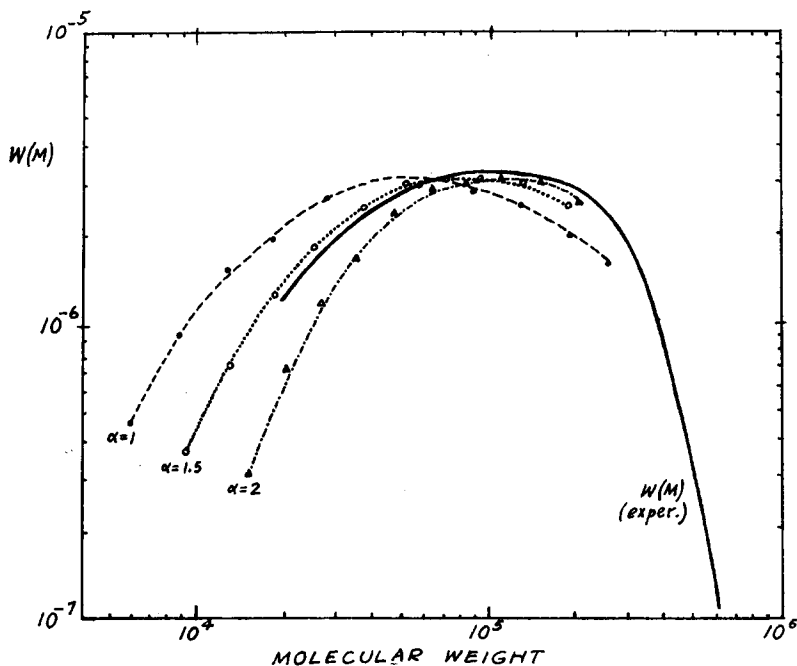


Fig. 2. Comparison of experimental weight distribution of molecular weight with that calculated from stress relaxation: Solid lines, experimental data from Fujita and Ninomiya<sup>24,25</sup>; broken lines, calculations made using eq. (113) of this paper.

using the most probable molecular weight distribution for the polystyrene, for which  $M_w = 2M_n$ . The parameters needed to calculate  $W(M)$  are then  $M_w = 3.57 \times 10^5$ ;  $\eta_0 = 6.58 \times 10^8$  poises; and  $cRT = 3.415 \times 10^{10}$  cgs units.  $F(\tau)$  was calculated from  $\phi(t) = [\varphi(t)]^{1/2.4}$  by the second-order approximation method of Schwarzl and Staverman.<sup>27</sup>

Of the three values for  $\alpha$  chosen, the results for  $\alpha = 1.5$  (Watkins' original value<sup>23</sup>) were best, as shown in Figure 2, where the calculated curve is compared with Fujita and Ninomiya's experimental values<sup>25</sup> for  $W(M)$ . Although the agreement is not perfect between the  $W(M)$  from stress relaxation and that measured experimentally, it is reasonable in

view of improvements that might be made in choosing  $\alpha$ , making better calculations to obtain  $F(\tau)$ , and perhaps improving the experimental stress relaxation and MWD curves. The unusual variation in  $W(M)$  shown by the method of Fujita and Ninomiya<sup>28</sup> at low molecular weights is eliminated, and also the present method meets Chomppf's criterion<sup>13</sup> that a suitable stress relaxation theory for polydisperse polymers must be based on a correct description of the relaxation behavior of a monodisperse polymer.

In examining the calculated and observed MWD in Figure 2, we note that the agreement might apparently be improved if  $\alpha$  were permitted to increase from 1.5 at lower molecular weights to 2 or possibly 2.4 at higher molecular weights. This is reminiscent of the observation by Graessley<sup>29</sup> that a nonuniform friction coefficient might be required to describe entanglement coupling in polydisperse systems. In this connection, it would be desirable to invert Graessley's viscoelastic theory<sup>29</sup> to obtain MWD along the lines of the present paper. How best to proceed in this direction is, however, not clear at this time.

### SUMMARY

By averaging molecular properties according to whether a segment is capable of participating in entanglements or not, it is possible to modify Rouse-based viscoelastic theory to give good experimental agreement for stress relaxation following sudden straining or steady shearing, and also to invert the stress relaxation relations to calculate molecular weight distribution from the terminal relaxation data of amorphous linear polymers.

Central results of this paper are the following:

**Monodisperse Polymers.** Relaxation times: eqs. (13) and (14), or (16) and (17); stress relaxation after steady flow: eq. (45); stress relaxation after sudden strain: eq. (61).

**Polydisperse Polymers.** (a) Linear mixing rule [eq. (18)]—relaxation times: eqs. (15) and (14), or (16) and (17); stress relaxation after steady shear: eqs. (49) or (51); MWD from relaxation distribution eqs. (74), (80), or (85).

(b) Nonlinear mixing rule [eqs. (19) (simplest) or (22)]—relaxation times: eqs. (41) and (42); stress relaxation after steady shear: eq. (52ff); stress relaxation after sudden strain: eq. (63); MWD from relaxation distribution: eq. (113).

These results provide usable methods for describing the relaxation behavior and determining the MWD for linear amorphous polymers within the framework of Rouse-type normal coordinate theory. Further improvements may be made by way of introducing chain branching and crosslinking, as well as by incorporating methods for dealing with semicrystalline polymers.

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