

Modified Bead-Spring Theory of Dilute Polymer Solutions. II. Effects of Polydispersity and Comparison with Experiment

A. E. EVERAGE, JR., and R. J. GORDON, *Department of Chemical Engineering, University of Florida, Gainesville, Florida 32601*

Synopsis

A constitutive equation, previously derived for dilute, monodisperse solutions of linear macromolecules, is extended to include polydisperse solutions. This result, which represents a coupling of continuum and molecular theory, realistically portrays the effects of molecular weight and molecular weight distribution on mechanical behavior. Intrinsic viscosity-shear rate data are well described, and with certain semiempirical modifications the equation also fits normal stress and dynamic viscosity data for slightly more concentrated solutions. Some unusual effects associated with the characterization of macromolecular degradation, in studies of turbulent drag reduction, are also explained.

INTRODUCTION

Dilute solution properties of linear macromolecules at small deformations have long been used for molecular characterization. For example, the Mark-Houwink-Sakurada¹ equation

$$[\eta]_0 = KM^a \quad (1)$$

relates the intrinsic viscosity at zero shear rate to the molecular weight M . The exponent a is a measure of polymer-solvent interaction, the well-known condition $a = 0.5$ corresponding to a theta solvent.¹ Increasing values of $(a - 0.5)$ are associated with increasingly better solvents.

This rather settled state of affairs with regard to low shear rate or small deformation properties contrasts sharply with the situation for finite deformations.²⁻⁵ The Rouse-Zimm bead-spring theories are a case in point: these theories provide an excellent description of small-amplitude, dynamic properties of dilute polymer solutions; but only with significant modification can they be used to describe such effects as the shear dependence of intrinsic viscosity.^{2,3}

Perusal of the polymer literature suggests that none of these modified molecular theories (which give reasonable predictions for finite deformations) are generally accepted. In addition, the theories are often unexpressible in explicit form; that is, an explicit relation between the stress tensor,

the flow field, and characteristic molecular properties (concentration, molecular weight, molecular weight distribution, etc.). This latter point limits their usefulness in the analysis of such phenomena as flow stability or turbulent drag reduction.

A number of explicit constitutive equations do exist, these being derived from continuum-mechanical considerations, and hence presumably apply to both concentrated and dilute polymer solutions. Although such equations can describe finite deformation behavior fairly accurately, the large number of associated phenomenologic constants detracts from their usefulness, especially with regard to polymer characterization. Thus, for many purposes, the available theories of the mechanical behavior of dilute polymer solutions are quite unsatisfactory.

CONSTITUTIVE EQUATION

We recently developed the following constitutive equation, using a combined continuum-molecular theory^{6,7}:

$$\boldsymbol{\tau} + \theta \frac{\mathfrak{D}\boldsymbol{\tau}}{\mathfrak{D}t} = 2 \frac{Nc}{M} kT\theta(1 - \epsilon)\mathbf{D} \quad (2)$$

$$\frac{\mathfrak{D}\boldsymbol{\tau}}{\mathfrak{D}t} \equiv \frac{\partial\boldsymbol{\tau}}{\partial t} + \mathbf{v} \cdot \nabla\boldsymbol{\tau} - \nabla\mathbf{v} \cdot \boldsymbol{\tau} - \dot{\mathbf{e}} \cdot \nabla\mathbf{v}^t + \epsilon\mathbf{D} \cdot \boldsymbol{\tau} + \epsilon\boldsymbol{\tau} \cdot \mathbf{D} \quad (3)$$

$$\mathbf{S} = -p\boldsymbol{\delta} + 2\eta_s\mathbf{D} + \boldsymbol{\tau} \quad (4)$$

where \mathbf{S} is the stress tensor, η_s is the solvent viscosity, θ is a relaxation time, k is Boltzmann's constant, T is the absolute temperature, and $\boldsymbol{\tau}$ is the contribution to \mathbf{S} from the polymer molecules.

These results represent a modification of the well-known dumbbell equations⁸ and reduce to those equations for $\epsilon = 0$.^{6,7} Here, ϵ is a constant which arises from the continuum aspects of our theory and consequently does not have a specific molecular interpretation. Physically, $\epsilon\mathbf{D} \cdot \mathbf{r}$ may be interpreted as the difference between the actual rate of change of the end-to-end vector \mathbf{r} of a linear macromolecule, and that rate of change as calculated from the simplified dumbbell model. This point is discussed more fully in reference 6. The value of ϵ is subject to the restriction

$$0 \leq \epsilon < 1. \quad (5)$$

Equations (2) to (4) have been shown to describe qualitatively many properties of dilute polymer solutions.⁷ Here, we generalize these expressions to account for polydispersity and present comparisons of the corresponding predictions with experimental data. The results are encouraging and clearly demonstrate the advantages and utility of this new constitutive model.

POLYDISPERSITY CORRECTION

It is assumed that eq. (2) applies to each molecular weight fraction, the total contribution to \mathbf{S} being the sum over all fractions. Thus, we have

$$\tau_i + \theta_i \frac{\mathfrak{D}\tau_i}{\mathfrak{D}t} = \frac{2Nc_i}{M_i} kT\theta_i(1 - \epsilon_i)\mathbf{D} \quad (6)$$

$$\mathbf{S} = -p \delta + 2\eta_s \mathbf{D} + \Sigma \tau_i \quad (7)$$

where i refers to a particular molecular weight species. The summation in eq. (7) may be converted to an integration via an appropriate molecular weight distribution. For this purpose, we employ the Schulz-Zimm distribution,^{5,9-13} namely,

$$dn = \left(\frac{z+2}{M_w}\right)^{z+1} \left(\frac{M^z}{z!}\right) \exp\left\{-\frac{(z+2)}{M_w} M\right\} dM \quad (8)$$

where dn is the fraction of molecules with molecular weights in the range $M, M + dM$; M_n and M_w are number- and weight-average molecular weight, respectively; and z is defined by

$$\frac{z+2}{z+1} = \frac{M_w}{M_n} \quad (9)$$

The z values may range from -1 to infinity, corresponding to $M_w/M_n \rightarrow \infty$ and $M_w/M_n \rightarrow 1$; $z = 0$ yields the commonly observed most probable distribution of molecular weights ($M_w/M_n = 2$), while negative z values are required to characterize the broader distributions common to most free-radical polymerizations.

MODEL PREDICTIONS AND COMPARISON WITH EXPERIMENT

Intrinsic Viscosity

The development of eqs. (2) to (9) was based on the supposition that intermolecular interactions are negligible. The intrinsic viscosity, representing a viscometric parameter extrapolated to infinite dilution, would thus seem to be an especially pertinent measure with which to compare the predictions of our model. These may be expressed in the form

$$[\eta]/[\eta]_0 = \frac{1}{1 + B\beta^2} = 1 - B\beta^2 + \dots \quad (10)$$

$$B = \frac{\epsilon(2 - \epsilon)}{(1 - \epsilon)^2}$$

for monodisperse solutions, and in the form

$$[\eta]/[\eta]_0 = \frac{\left(\frac{z+2}{M_w}\right)^{z+a+2}}{\Gamma(z+a+2)} \int_0^\infty \left(\frac{M^{z+a+1}}{1+B\beta^2}\right) \exp\left\{-\frac{(z+2)}{M_w} M\right\} dM \quad (11)$$

$$[\eta]_0 = \frac{KM_w^a \Gamma(z+a+2)}{(z+2)^a (z+1)!} \quad (12)$$

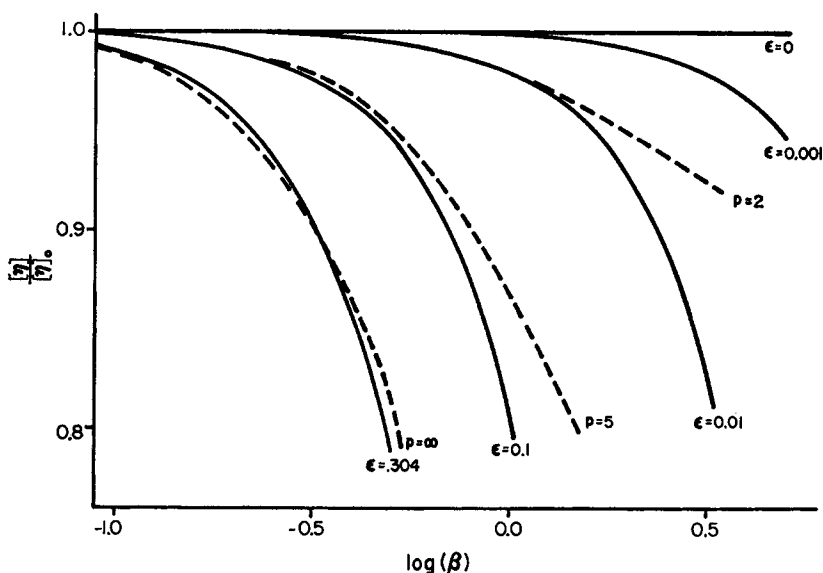


Fig. 1. Plot of $[\eta]/[\eta]_0$ vs. $\log(\beta)$: (—) theoretical prediction for monodisperse solutions; (---) theoretical prediction for rigid ellipsoid model with axial ratio p as indicated.

for polydisperse solutions. β , often referred to as the "generalized shear rate,"⁵ is equal to $[\eta]_0 M \eta_s G / NkT$. In the derivation of eqs. (11) and (12), we have used the relation

$$\theta_i = \frac{\eta_s [\eta]_{0i} M_i}{NkT(1 - \epsilon_i)} = \frac{\eta_s K M_i^{1+a}}{NkT(1 - \epsilon_i)} \quad (13)$$

which may easily be obtained from eqs. (1) to (4). In addition, the Mark-Houwink-Sakurada constants K and a were assumed to be independent of molecular weight (strictly speaking, this is only true for a theta solvent^{13,14}). There seems to be ample precedent for this assumption.^{5,9,13}

To illustrate the predicted results, eqs. (10) and (11) have been plotted in Figures (1) to (3). Figure 1 shows the influence of ϵ (which might aptly be called a "non-Newtonian parameter") on the $[\eta]/[\eta]_0$ -versus- β relationship for monodisperse solutions. Clearly, larger values of ϵ result in an earlier departure from the Newtonian behavior predicted by the elastic dumbbell model ($\epsilon = 0$). Also plotted in Figure 1 are the results of the rigid ellipsoid model^{5,15} for various values of the axial ratio p . This model has been used with some success by Suzuki, Kotaka, and Inagaki.⁵ The figure indicates that the two theories agree closely for low values of β . At high rates of shear, the rigid ellipsoid model predicts a nonzero asymptotic value for $[\eta]/[\eta]_0$, in agreement with experimental results. Our model, however, predicts a zero value for this limit. This deficiency is apparently common to many molecular theories.¹⁶

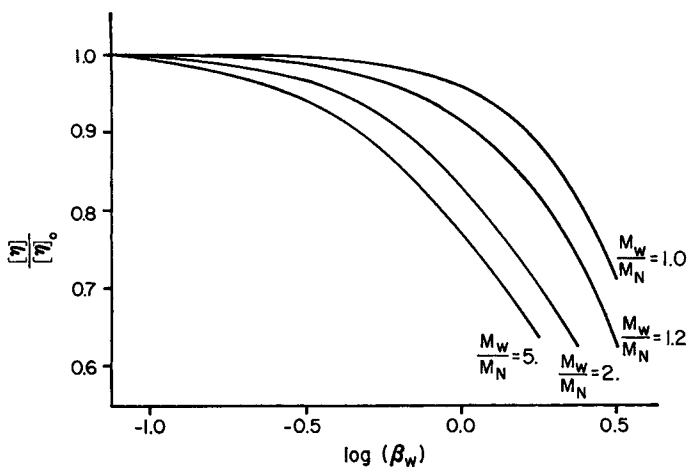


Fig. 2. Plot of $[\eta]/[\eta]_0$ vs. $\log(\beta_w)$ for polydisperse solutions with molecular weight distributions as indicated.

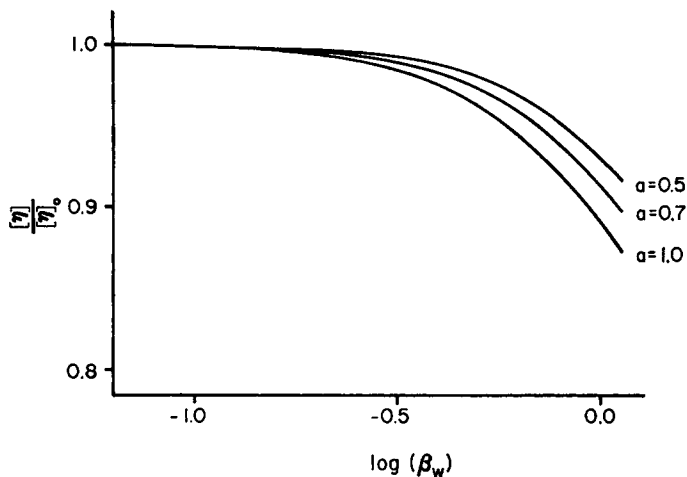


Fig. 3. Plot of $[\eta]/[\eta]_0$ vs. $\log(\beta_w)$ for values of a as indicated.

Figure 2 illustrates the effects of polydispersity. Here, we have used the typical values $K = 10 \times 10^{-5}$ dl/g, $a = 0.7$, $T = 25^\circ\text{C}$, $M_w = 1.2 \times 10^6$, $\eta_s = 0.005$ P, and $\epsilon = 0.02$. These results demonstrate that the more polydisperse solutions show pronounced non-Newtonian behavior at lower values of β_w ($\beta_w = [\eta]_0 M_w \eta_s G / NkT$) and exhibit a smaller (negative) slope in the high shear rate region. Both effects have been observed experimentally for concentrated polymer solutions and melts.¹⁰

The effect of polymer-solvent interaction (as characterized by the Mark-Houwink-Sakurada exponent a) on the $[\eta]/[\eta]_0$ -versus- β_w relation is illustrated in Figure 3. Here, we have chosen the same values for K , T , M_w , η_s , and ϵ as in Figure 2; Z is equal to 4.0. From a qualitative viewpoint,

TABLE I
Effect of Molecular Weight and Solvent Power on ϵ

Polymer	Solvent	Temp., °C	Molec- ular weight, $\times 10^{-6}$	$[\eta]_0$, dl/g	$\alpha\eta^3$	$\epsilon, \times 10^3$
Polystyrene	benzene	30	6.0	11.65	5.85	0.93
	Aroclor	40	6.0	4.50	2.26	0.55
	benzene	30	3.16	7.04	4.96	1.26
Poly(α -methylstyrene)	benzene	30	7.14	13.50	6.31	2.63
	toluene	25	0.69	1.49	—	25.9
	toluene	25	1.24	2.44	—	6.06
	toluene	25	1.82	3.175	—	2.74

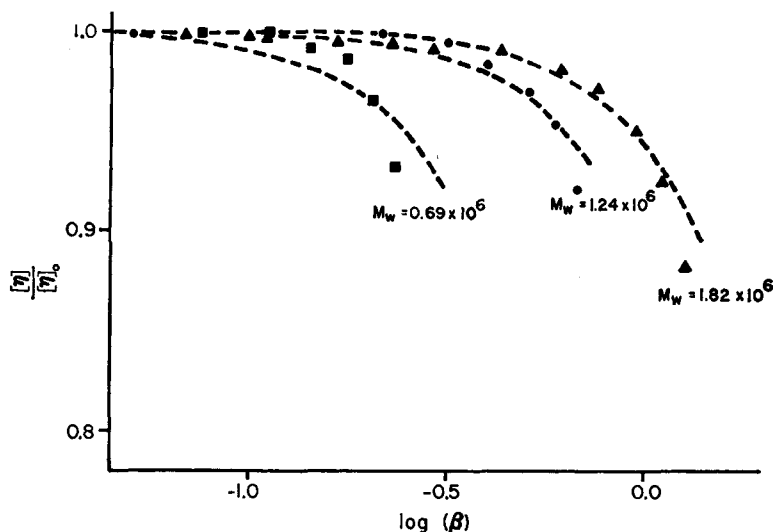


Fig. 4. Plot of $[\eta]/[\eta]_0$ vs. $\log(\beta)$ for various molecular weights of poly(α -methylstyrene) in toluene;⁵ (-----) theoretical prediction for monodisperse solutions.

these results also agree quite nicely with generally accepted experimental behavior.^{4,5,13}

The remainder of this section is devoted to a comparison of eqs. (10) and (11) with experiment. Our objectives are an examination of the predictive ability of our theory, and some qualitative insight into the molecular weight and solvent power dependence of ϵ .

Noda and co-workers¹⁷ have studied the effect of molecular weight on the $[\eta]/[\eta]_0$ -versus- β relationship. The solutions investigated were various molecular weights of poly(α -methylstyrene) in toluene, with *very sharp distributions* ($M_w/M_n < 1.01$). Their results are plotted in Figure 4. Equation (10) was compared with these data (dashed lines in Fig. 4) by determining the value of ϵ that gave the "best looking" fit. Values of ϵ thus obtained are tabulated in Table I. We see that the theory describes

the data fairly well for the lowest molecular weight fraction, and very well for the higher fractions. Note that the lower molecular weights exhibit non-Newtonian effects earlier (i.e., smaller β), thus implying a decrease in ϵ with increasing molecular weight. Noda et al. explain these results as a manifestation of chain rigidity (or "internal viscosity") which becomes increasingly important for short chain lengths.¹⁷ Inasmuch as our theory takes no account of such an effect, it is significant that the agreement of theory and experiment improves at larger molecular weights.

The $[\eta]$ -versus- β_w relations for polystyrene fractions in various solvents have been reported by Suzuki, Kotaka, and Inagaki.⁵ Their data for four solutions are plotted in Figures 5 and 6. Figure 5 illustrates the effect

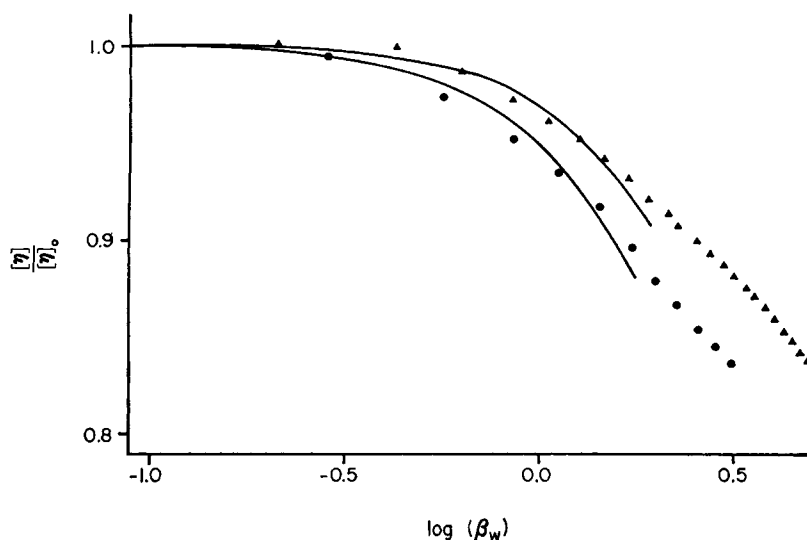


Fig. 5. Plot of $[\eta]/[\eta]_0$ vs. $\log(\beta_w)$ for solutions of polystyrene ($M_w = 6.0 \times 10^6$) in benzene (●) and Aroclor⁵ (▲); (—) theoretical prediction for polydisperse solutions.

of solvent power on $[\eta]/[\eta]_0$ -versus- β_w , a "powerful" solvent being a very good one for the particular polymer species in question. The solutions are polystyrene ($M_w = 6.0 \times 10^6$, $M_w/M_n = 1.22$) in benzene, a good solvent, and Aroclor 1248 (Monsanto Company), a fair solvent. The hydrodynamic expansion factors are $\alpha_\eta^3 = 5.85$ and 2.26 for benzene and Aroclor, respectively. The predictions of eq. (11) are represented by the solid lines. Here, literature values of a ($=0.77$ for benzene,¹ 0.64 for Aroclor¹⁸) were used, and K ($=7.145 \times 10^{-5}$ dl/g for benzene, 2.109×10^{-4} for Aroclor) was obtained from eq. (12), using experimental values of $[\eta]_0$. Values of ϵ were determined via a nonlinear least-squares computer program (supplied through the courtesy of Professor A. W. Westerberg) and are tabulated in Table I. As is apparent from the figure, eq. (11) fits the data quite well for low to moderate values of β .

Figure 6 illustrates the effects of molecular weight on $[\eta]/[\eta]_0$ -versus- β_w for two fractions of polystyrene ($M_w = 3.16 \times 10^6$, $M_w = 7.14 \times 10^6$) in benzene. The distribution widths for these fractions were not given, thus precluding the application of eq. (11) to the data. In this case, we decided to use eq. (10) (for monodisperse solutions), primarily to gain some insight into the molecular weight dependence of ϵ . Again, values of ϵ were determined which gave the best-looking fit to the data. The resulting predictions are given by the dashed lines in the figure, and the corresponding values of ϵ are tabulated in Table I.

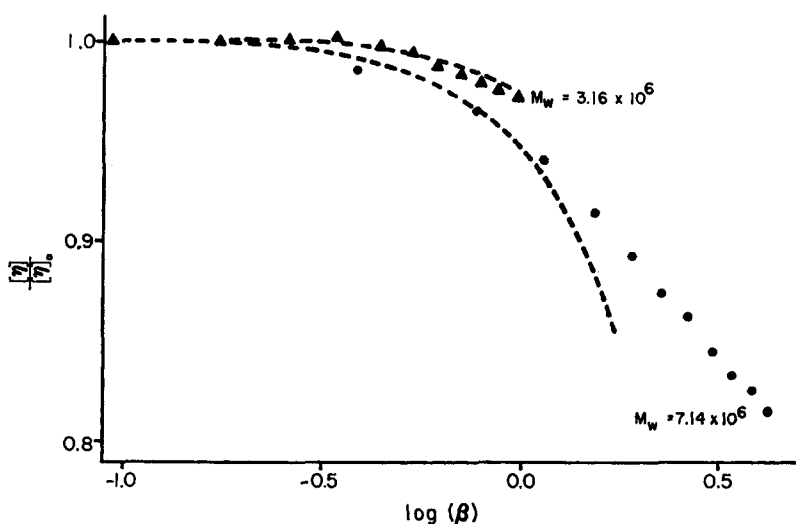


Fig. 6. Plot of $[\eta]/[\eta]_0$ vs. $\log(\beta_w)$ for solutions of polystyrene in benzene:⁵ (●) $M_w = 7.14 \times 10^6$; (▲) $M_w = 3.16 \times 10^6$; (----) theoretical prediction for monodisperse solutions.

Turning to Table I, we see that ϵ is an increasing function of solvent power for the polystyrene-benzene-Aroclor system. In addition, ϵ decreases with M for poly(α -methylstyrene) and increases with M for polystyrene. As noted earlier, the decrease in ϵ for poly(α -methylstyrene) with increasing M may be a manifestation of chain rigidity. The increase of ϵ with M for polystyrene, which has greater segmental flexibility, is probably the more typical behavior of linear macromolecules.

In summary, our theory seems to portray in a fairly accurate manner—for low values of β —the intrinsic viscosity-shear rate behavior of flexible linear macromolecules, as a function of molecular weight, molecular weight distribution, and polymer-solvent interaction. The non-Newtonian parameter ϵ increases with solvent power for a given molecular weight, at least for the polystyrene-benzene-Aroclor system. (Note that α_η^3 increases with M in a good solvent.) The molecular weight dependence of ϵ is still somewhat unclear.

Relation to Rouse Theory

Equations (2) to (4) lead to the following predictions for the dynamic storage and loss moduli:

$$G_{R'}' = \frac{M}{cRT} G' = \frac{(1 - \epsilon)\omega_R^2}{1 + \omega_R^2} \quad (14)$$

$$G_{R''}'' = \frac{M}{cRT} (G'' - \omega\eta_s) = \frac{(1 - \epsilon)\omega_R}{1 + \omega_R^2} \quad (15)$$

where $\omega_R = \theta\omega$ and R is the gas law constant (Nk). These expressions are identical in form, with the exception of the factor $(1 - \epsilon)$, to the Rouse or Zimm theory predictions for the case of a *single* "submolecule".³ In Figure 7 we have plotted eqs. (14) and (15) for $\epsilon = 0.01$, along with the

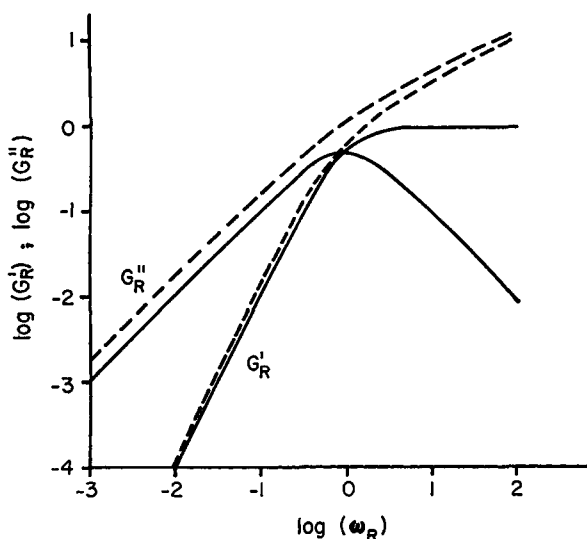


Fig. 7. Theoretical prediction of $\log(G_{R'}')$ and $\log(G_{R''}''')$ vs. $\log(\omega_R)$: (-----) Rouse theory; (—) present monodisperse theory.

results from the Rouse theory (for P submolecules, as $P \rightarrow \infty$ ³). The theories agree quite well for low values of ω_R , but diverge drastically as ω_R increases above 1. This behavior is to be expected, as a consequence of the single relaxation time in our model, and indicates quite clearly that to describe small amplitude, dynamic data over wide ranges of frequency, eqs. (2) to (4) must be generalized to a *multibead model* (with a large number of relaxation times³).

Complex Viscosity, Normal Stresses

With the exception of intrinsic viscosity, very few rheological measurements of truly "dilute" polymer solutions have been reported. In order to utilize measurements of several rheological properties over wide ranges of

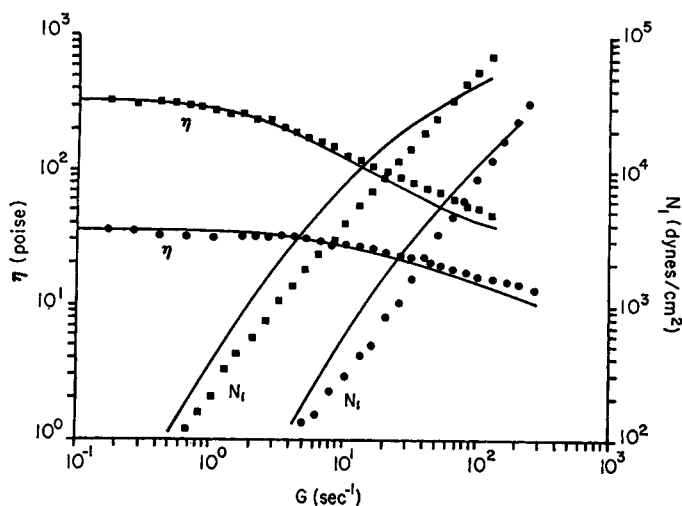


Fig. 8. Plot of η and N_1 vs. G for polystyrene in Aroclor:¹⁹ experimental results for (●) $c = 0.0144$ g/cc and (■) $c = 0.036$ g/cc; (—) theoretical prediction for poly-disperse solutions.

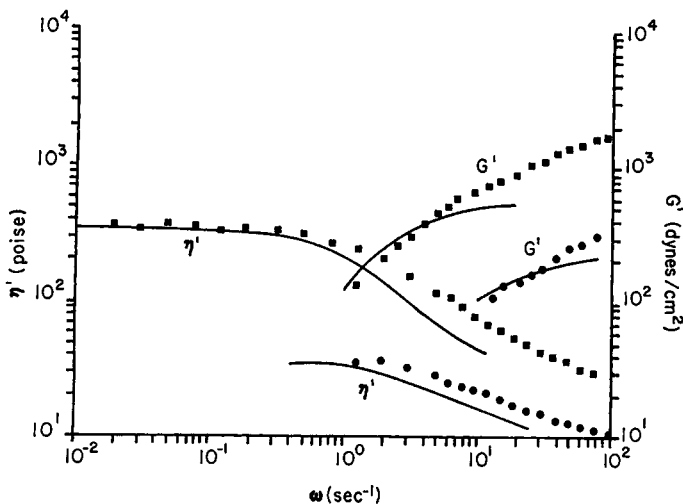


Fig. 9. Plot of η' and G' vs. ω for polystyrene in Aroclor:¹⁹ experimental results for (●) $c = 0.0144$ g/cc and (■) $c = 0.036$ g/cc; (—) theoretical prediction for poly-disperse solutions.

shear rate (for a single polymer solution), we must be prepared to relax somewhat the restriction of negligible intermolecular interaction.

Ashare¹⁹ has recently published some careful measurements of non-Newtonian viscosity, primary normal stress difference, dynamic viscosity, and dynamic storage modulus for several solutions of polystyrene in Aroclor. His results for $M_w = 1.8 \times 10^6$, $M_w/M_n = 1.2$, and $c = 0.0144$ and 0.036 g/cc are plotted in Figures 8 and 9. These data must certainly

reflect some effects of intermolecular interaction, and at concentration levels of well over 1%, it is not clear whether or not such effects are negligible.

Nevertheless, our model was compared with Ashare's results, and it was found that good agreement could be obtained if η_s in the theoretical equations were replaced throughout by a variable, $\hat{\eta}$. In other words, *the effects of intermolecular interaction could be accounted for by assuming that the solvent is effectively "thickened" by the factor $\hat{\eta}/\eta_s$* . The Mark-Houwink-Sakurada constants, however, still refer to the actual solvent.

It was also found necessary to consider the molecular weight dependence of ϵ (clearly, ϵ would be anticipated to depend on M). This was assumed of the form

$$B = \frac{\epsilon(2 - \epsilon)}{(1 - \epsilon)^2} = \gamma M^\sigma \quad (16)$$

as suggested, *e.g.*, by Suzuki, Kotaka, and Inagaki.⁵

With these substitutions, the expressions for η , N_1 , N_2 , η' and G' ($= \omega\eta''$) are found to be:

$$\eta = \hat{\eta} + \frac{c\hat{\eta}K}{(z+1)!} \left(\frac{z+2}{M_w}\right)^{z+2} \int_0^\infty \frac{M^{z+a+1}}{1 + \gamma \left(\frac{\hat{\eta}KGM^{1+a+\sigma/2}}{NkT}\right)^2} \times \exp\left\{-\frac{(z+2)}{M_w} M\right\} dM \quad (17)$$

$$N_1 = \frac{2c(G\hat{\eta}K)^2}{NkT(z+1)!} \left(\frac{z+2}{M_w}\right)^{z+2} \int_0^\infty \frac{M^{z+2a+2}(1 + \gamma M^\sigma)^{1/2}}{1 + \gamma \left[\frac{\hat{\eta}KGM^{1+a+\sigma/2}}{NkT}\right]^2} \times \exp\left\{-\frac{(z+2)}{M_w} M\right\} dM \quad (18)$$

$$N_2 = \frac{-c(G\hat{\eta}K)^2}{NkT(z+1)!} \left(\frac{z+2}{M_w}\right)^{z+2} \int_0^\infty \frac{M^{z+2a+2}\{(1 + \gamma M^\sigma)^{1/2} - 1\}}{1 + \gamma \left[\frac{\hat{\eta}KGM^{1+a+\sigma/2}}{NkT}\right]^2} \times \exp\left\{-\frac{(z+2)}{M_w} M\right\} dM \quad (19)$$

$$\eta' = \hat{\eta} + \frac{c\hat{\eta}K}{(z+1)!} \left(\frac{z+2}{M_w}\right)^{z+2} \int_0^\infty \frac{M^{z+a+1}}{1 + (1 + \gamma M^\sigma) \left[\frac{\hat{\eta}K\omega M^{1+a}}{NkT}\right]^2} \times \exp\left\{-\frac{(z+2)}{M_w} M\right\} dM \quad (20)$$

TABLE II
Model Parameters Used in Prediction of η , N_1 , N_2 , η' ,
and G' for Polystyrene in Aroclor

Concentration, g/cc	η_0 , P	η_s , P	$\hat{\eta}$, P	γ	σ
0.0144	35.	3.	7.38	9.39×10^{-30}	4.41
0.036	335.	3.	32.3	4.48×10^{-21}	3.08

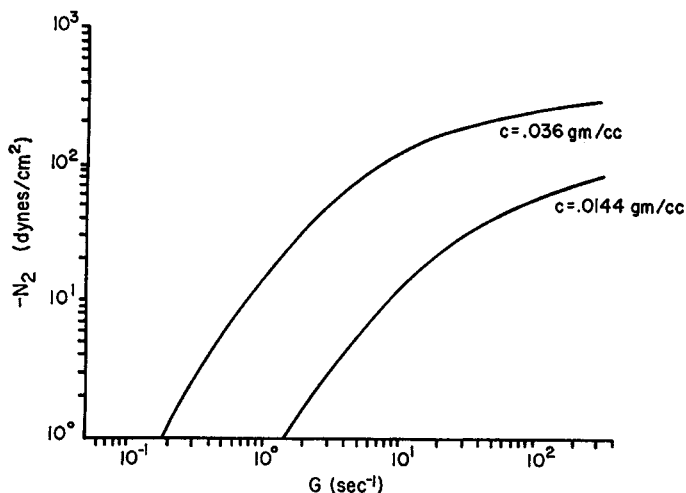


Fig. 10. Theoretical prediction of N_2 vs. G for polydisperse solutions.

$$G' = \frac{c(\omega\hat{\eta}K)^2}{NkT(z+1)!} \left(\frac{z+2}{M_w}\right)^{z+2} \int_0^\infty \frac{M^{z+2a+2}(1+\gamma M^\sigma)^{1/2}}{1+(1+\gamma M^\sigma) \left[\frac{\hat{\eta}K\omega M^{1+a}}{NkT}\right]^2} \times \exp\left\{-\frac{(z+2)}{M_w} M\right\} dM \quad (21)$$

Literature values of K and a for the polystyrene-Aroclor system were used ($K = 2.63 \times 10^{-4}$ dl/g, $a = 0.64^{18}$), and $\hat{\eta}$ was obtained directly from eq. (22):

$$\eta_0 = \hat{\eta} + \frac{c\hat{\eta}K(M_w)^a \Gamma(z+a+2)}{(z+2)^a (z+1)!} \quad (22)$$

where η_0 is the experimental zero-shear viscosity; γ and σ were evaluated by curve fitting eq. (17) to the experimental viscosity data, using the previously mentioned nonlinear least-squares analysis. Values of all parameters are listed in Table II. These values were then used to calculate N_1 , N_2 , η' , and G' ; the results are represented by the solid lines in Figures 8 to 10.

As is evident from these curves, the overall fit of our model to the data is fair to good. The viscosity data are well described, except at the higher shear rates. The normal stress predictions are somewhat high, except at high shear rates, where they cross the experimental curves. The η' and G' results dip below the data as ω increases, the predictions for G' being somewhat superior to those for η' , as anticipated from Figure 7 (recall, $\eta' = G''/\omega$). It should be emphasized that the overall predictions of our model could have been improved had we chosen to fit all four functions simultaneously. However, a more severe test of the model is obtained by fitting viscosity data exclusively and then predicting N_1 , η' , and G' .

Calculated values of N_2 have been plotted in Figure 10; experimental results were not available. Note that N_2 is *negative* and much smaller in magnitude than N_1 , in agreement with most available data.^{20,21}

Weissenberg Number

The so-called "elasticity" of a polymer solution may be characterized by the dimensionless Weissenberg number, $N_{ws} = N_1/(\eta - \eta_s)G$, where G is the shear rate.²² Experimentally, N_{ws} is known to increase (i.e., more elastic behavior) with molecular weight, breadth of molecular weight dis-

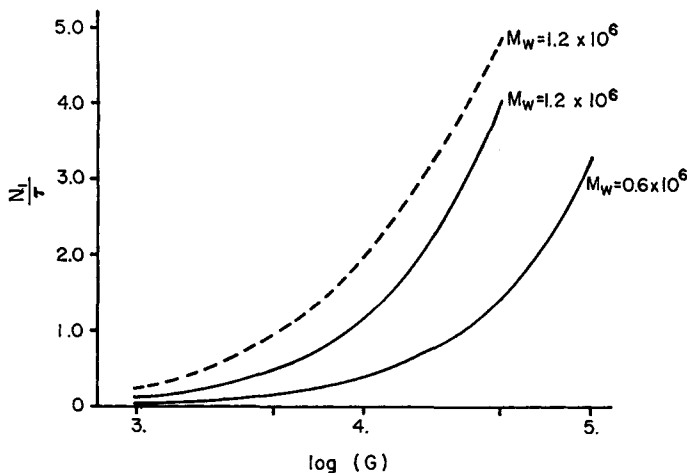


Fig. 11. Theoretical prediction of N_1/τ vs. $\log(G)$ for indicated molecular weights: (-----) $M_w/M_n = 5.0$; (—) $M_w/M_n = 1.2$.

tribution, and shear rate.²³ As illustrated in Figure 11, our theory predicts precisely this behavior, offering one more example, we feel, of the essential correctness of the constitutive equation. (In Fig. 11, the values chosen for the parameters were $K = 10 \times 10^{-5}$ dl/g, $\alpha = 0.7$, $\eta_s = 0.005$ P, and $\epsilon = 0.02$).

Drag Reduction and Elongational Viscosity

It has been suggested²⁴⁻²⁶ that turbulent drag reduction is a consequence of the unusually high elongational viscosity exhibited by dilute polymer solutions.²⁷ For example, Bakewell's work (as discussed by Seyer and Metzner²⁴) indicates that the turbulent eddy structure near a pipe wall may be considered as a transient "stretching" motion, and hence large values of elongational viscosity $\bar{\eta}$ (a measure of resistance to stretching^{24,28}) would tend ultimately to lower the drag.

We recently published a study of the molecular weight-time dependence of $\bar{\eta}$, after the inception of steady elongational flow in an initially unstressed fluid.²⁸ This result, for monodisperse solutions, dramatically illustrated the sensitivity of elongational viscosity to molecular weight. Here, we extend the analysis to polydisperse solutions, in order to examine the effects of molecular weight distribution on $\bar{\eta}$.

The results of Paterson and Abernathy²⁵ suggest that macromolecular degradation in poly(ethylene oxide) solutions may be pictured somewhat as illustrated in Figure 12. Here, the Schulz-Zimm distribution is plotted for $z = 1.0$ and various values of M_n . Thus, an initially broad distribution ($M_n = 1.0 \times 10^6$) is preferentially degraded at its high molecular weight end, resulting in successive shifts to distributions similar to those illustrated for $M_n = 5.0 \times 10^5$, 2.5×10^5 , and 1.0×10^5 . The effect of this degradation process on elongational viscosity may readily be determined for our model. For the case of sudden inception of steady elongational flow of constant stretch rate Γ , in an initially unstressed fluid, we find

$$\frac{\bar{\eta}}{3(\eta_0 - \eta_s)} = \left(\frac{z+2}{M_w}\right)^{z+a+2} \int_0^\infty \frac{M^{z+a+1} \exp\left\{-\frac{(z+2)}{M_w} M\right\}}{[1 - 2\theta(1 - \epsilon)\Gamma][1 + \theta(1 - \epsilon)\Gamma]} \times \left\{1 - \frac{2}{3} [1 + \theta(1 - \epsilon)\Gamma] \exp\left[-(1 - 2\theta(1 - \epsilon)\Gamma) \frac{t}{\theta}\right] - \frac{1}{3} [1 - 2\theta(1 - \epsilon)\Gamma] \exp\left[-(1 + \theta(1 - \epsilon)\Gamma) \frac{t}{\theta}\right]\right\} dM. \quad (23)$$

TABLE III
Effect of Molecular Weight Distribution on Intrinsic
Viscosity and Elongational Viscosity

$M_n, \times 10^{-5}$	$M_w, \times 10^{-5}$	$[\eta]_0, \text{ dl/g}$	$\bar{\eta}/3(\eta_0 - \eta_s)$ ($\Gamma = 2000 \text{ sec}^{-1}$, $t = 0.008 \text{ sec}$)
1.00	1.50	1.33	1.02
2.50	3.75	2.71	23.2
5.00	7.50	4.65	10800.
10.0	15.0	7.98	312000.

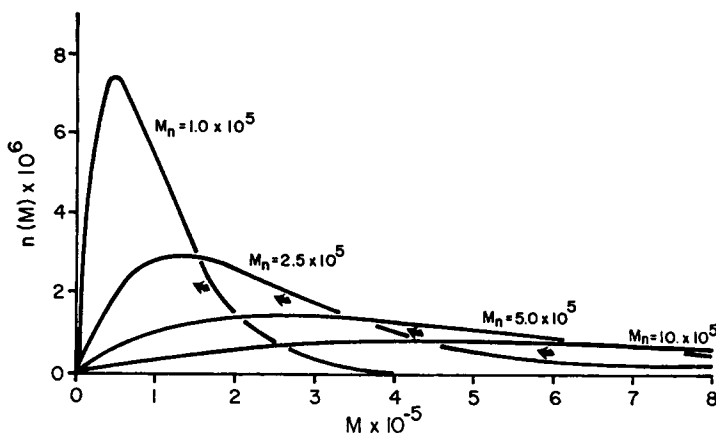


Fig. 12. Schulz-Zimm distribution $n(M)$ vs. molecular weight for $z = 1.0$ and various number-averaged molecular weights.

In Table III we have listed values of $\bar{\eta}/3(\eta_0 - \eta_s)$ and $[\eta]_0$, for the series of molecular weight distributions illustrated in Figure 12. These values correspond to $K = 1.25 \times 10^{-4}$, $a = 0.78$, $\eta_s = 0.81$ cP, $t = 0.008$ sec, and $\epsilon = 0.4$, the values used in our earlier study of monodisperse solutions.²⁸ It is clear that the shifts in molecular weight distribution lead to large changes in $\bar{\eta}$, but only minor changes in $[\eta]_0$. This would explain the findings of Paterson and Abernathy²⁵ and Eichstadt²⁹ that a polymer solution may show large decreases in drag-reducing ability due to shear degradation, but only insignificant changes in intrinsic viscosity.

SUMMARY

A constitutive equation, previously derived for dilute, monodisperse solutions of linear macromolecules, has been extended to account for polydispersity. This result, which represents a coupling of ideas from continuum mechanics and molecular theory, realistically portrays the effects of molecular weight, molecular weight distribution, and polymer-solvent interaction on mechanical behavior. By introducing the concept of "effective solvent viscosity" to account for intermolecular interactions, the theory may also be applied to moderately concentrated solutions. A number of examples of the utility of the theory are presented.

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