Correlation of Stress Data in Viscoelastic Polymer Solutions

MICHAEL C. WILLIAMS

University of California, Berkeley, California

In earlier papers (*10* to *12*) an approximate molecular theory was developed for the stresses in concentrated polymer solutions. The present objective is to verify some of the resulting predictions, and to indicate how this theory and others can be used as guides for correlating experimental data.

MOLECULAR THEORY

By a summation of forces between all polymer segments in solution, it is possible to arrive at a general expression for the total stress tensor **P** as displayed in Table 1. Details of the derivation, and important literature references, are cited in previous works. All dilute-solution theories (DST) make the approximation that interpolymer interactions are unimportant and the term preceded by n^2 can be dropped. This is valid when the polymer molecule concentration n is small and when the spatially averaged forces ∇V between pairs of molecules are negligible. Differences between the different DST's lie in how the intramolecular term preceded by n is evaluated. Retention of this term plus $\mathbf{P}_o$ always leads to the prediction of a characteristic fluid relaxation time λ of the type shown in Table 1. Variations from model to model cause K_{dil} to differ, but the dependence of λ on M and c is always the same and fixed by the dilute-solution limitation. An important consequence of this is the implication that viscoelastic properties, such as non-Newtonian viscosity and normal stress can be correlated over wide ranges of c, M, and shear rate γ by certain reduced variables which incorporate c, M, and $\eta_o(c, M)$ in a certain way. This has been verified experimentally (*8*, *9*) even for cases wherein specific molecular models do not supply a satisfactory quantitative description of the shear dependency.

The concentrated-solution theory (CST) is based on the assumption that, for some range of c and M, the intramolecular term is negligible compared with the intermolecular one. This might occur in part owing to an increase of n, but primarily because the average forces between molecules become dominant. In this case, a different dependence of λ on c, M, and $\eta_o(c, M)$ appears; this is also shown in Table 1. Unfortunately, the arguments leading to this λ rule out the determination of K_{conc}. Nonetheless a significantly different set of reduced variables is implied for such materials. This indeed resolves a number of reports (*11*) wherein the DST predictions failed to correlate data.

EXPERIMENTAL VARIFICATION

The older observations which tend to support the CST have already been reviewed (*11*) and need not be repeated. These dealt separately with the factors of c and M for correlation purposes, but were complicated by the lack of polymer samples which were monodisperse or well characterized in molecular weight. Recently, such samples have become available and new work has been reported from various laboratories. These appear to give additional strong support for the CST predictions, and will be discussed here.

Graessley and co-workers (*2*) obtained non-Newtonian viscosity data on monodisperse polystyrenes in *n*-butyl benzene, covering a range of concentration from 20 to 55% and molecular weight from 97,200 to 2.4×10^6. Plots of $\eta(\gamma)/\eta_o$ vs. γ were shifted along the γ axis until all coincided on a master curve; each such shift determined an experimental relaxation time for that fluid, λ_{exp}. The superposition of these data was excellent, verifying that a single mechanism of molecular response was dominant. A critical test of the CST can now be made by computing $\lambda_{exp}/\lambda_{dil}$, where λ_{dil} is chosen for convenience to be the Rouse value (*2*). This ratio should be constant over ranges of c and M if any DST applies, and equal to $K/cM \cdot F(c) \approx K/cM$ if CST applies (see Table 1). A plot of $\lambda_{exp}/\lambda_{dil}$ vs. cM is therefore presented in Figure 1, where it is seen to exhibit distinctly non DST behavior. The function is not quite hyperbolic, as suggested by CST, but is almost so. This shows that concentrated behavior is characteristic of a wide range of the parameter cM; dilute behavior may be extremely difficult to attain when M is large.

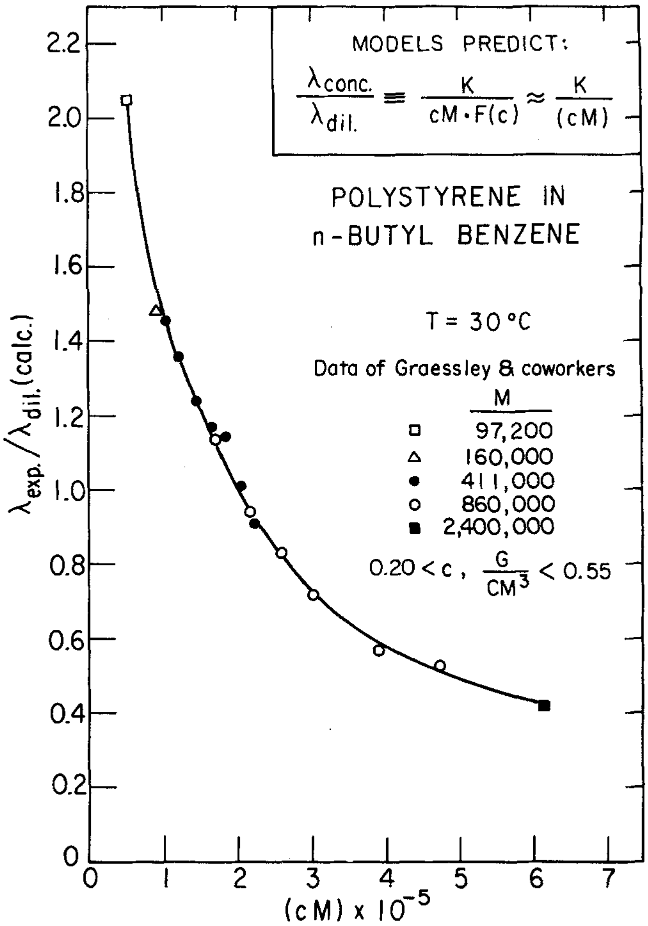

Fig. 1. Experimentally determined relaxation times λ_{exp}, referred to calculated times λ_{dil} based on Rouse dilute-solution theory, shown as a function of cM. Here, c = polymer concentration in grams per cubic centimeter and M = polymer molecular weight. Data taken from reference (2).

It has recently been noted that the parameter cM appears to correlate a wide variety of data. Ferry and coworkers (5) in plotting $G'(\omega)$ and $G''(\omega)$ for concentrated DNA and polystyrene solutions, found these two curves to intersect twice; this never occurs in dilute solutions. The spacing between intersections, $\Delta \equiv \log \omega_1/\omega_2$, was a function of cM and vanished at a critical value $(cM)_c$. Even for nominally dilute solutions, Holmes and Ferry (3) found that the dimensionless steady state shear compliance $(cRT/M)J_e$, given by $(\Sigma \lambda_i^2)/(\Sigma \lambda_i)^2$ in every DST, have changed smoothly from the Zimm value to the Rouse value as a function of cM.

It is most interesting that O'Reilly and co-workers have obtained rheological correlations for polymer melts, polydimethyl siloxane (7), and polystyrene (6), that resemble Graessley's in their dependence on M. This is surely not coincidental; it has long been known that mechanical properties of melts and concentrated solutions are qualitatively similar. Indeed, the general expression for **P** in Table 1 also applies to melts, and it is quite likely that an appropriate evaluation of the n^2 term would lead to results which resemble the CST predictions of $\lambda(M)$.

TABLE 1. STRESS APPROXIMATIONS

Theory of stress in polymeric liquids	Predicted λ
General:	
$\mathbf{P} = \mathbf{P}_o + n\Sigma <\mathbf{R}\nabla U> + \frac{n^2}{2} <\mathbf{r}\nabla V>$	— —
Dilute approximation:	
$\mathbf{P} = \mathbf{P}_o + n\Sigma <\mathbf{R}\nabla U>$	$K_{\text{dil}} \left[\frac{M(\eta_o - \eta_s)}{c}\right]$
Concentrated approximation:	
$\mathbf{P} = \mathbf{P}_o$ .... $+ \frac{n^2}{2} <\mathbf{r}\nabla V>$	$K_{\text{conc}} \left[\frac{(\eta_o - \eta_s)}{c^2 F(c)}\right]$

Note $\frac{\lambda_{\text{conc}}}{\lambda_{\text{dil}}} = \frac{K}{cM \cdot F(c)} \approx \frac{K}{cM}$

STRESS-RATIO CORRELATIONS

A failing of the CST in its present form is its inability to describe accurately the dependence of **P** on c, M, and shear rate γ. The latter weakness is shared by nearly all molecular models.

Experimental evidence, however, shows that certain stress ratios are relatively insensitive to shear; one such ratio is $G(\gamma) \equiv (\text{shear stress})^2/(\text{normal stress})$. A variety of literature data suggest that the general shape of the $G(\gamma)$ curve resembles Figure 2. The limit G_o which represents second-order fluid behavior, is difficult to achieve experimentally, and characterizes a shear range of little significance in processing applications. Most available data would suggest that $G(\gamma)$ is an increasing function of γ, but this appears to represent a transition region between G_o and a higher plateau G_1. This second plateau is rarely reached in the laboratory but is in the shear range of industrial importance. Apparently G_1 can be about one order larger than G_o, but in general $G(\gamma)$ undergoes changes of magnitude far less than the components $P_{ij}(\gamma)$.

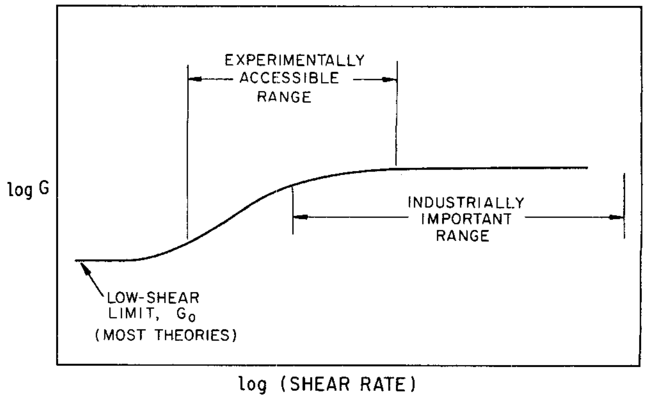

Fig. 2. General shape of $G(\gamma)$ function, as suggested by shear-dependent stress data on a variety of polymer solutions.

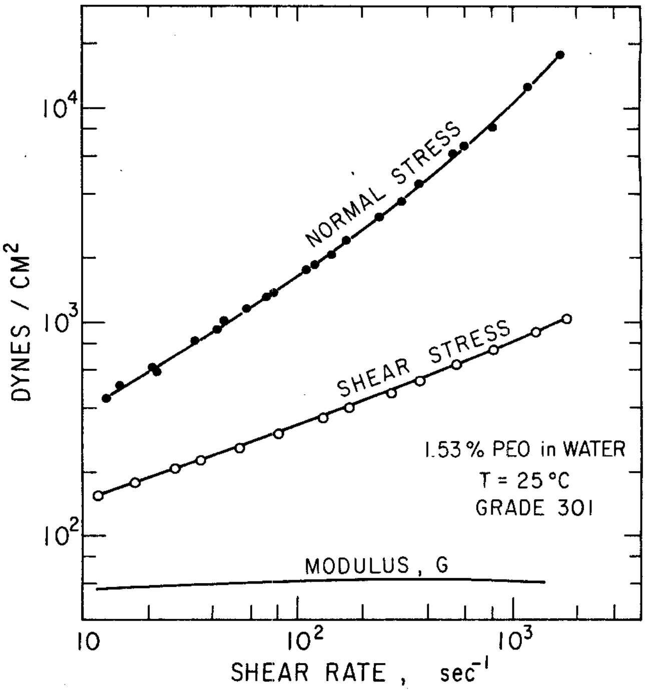

Fig. 3. Shear-dependent stress functions for a 1.53% aqueous solution of polyethylene oxide, from reference 13. The normal stress represents the slope of the logarithmic radial stress profile in cone-and-plate device, $P_{11} + P_{22} - 2P_{33}$.

The plateau G_1 can be reached easily for some materials. Data published earlier (13) on polyethylene oxide solutions are reworked in Figure 3. The stresses clearly represent high-order behavior, so the $G(\gamma)$ function is not G_0 but rather G_1. In passing, it should be noted that the stresses are not power law in character; such a feature is not essential for $G(\gamma)$ to be independent of shear.

Since $G(\gamma)$ is found to be such a convenient parameter for correlating shear dependent stress data, the next objective is to predict its dependence on c and M. The DST predicts $G_o \sim c/M$ and the CST suggests $G_o \sim c^2$. Kotaka and co-workers (4) extrapolated their data on concentrated polydisperse polystyrene solutions to show $G_o \sim c^2$, independent of $\overline{M}$. O'Reilly and co-workers (6, 7) obtained analogous results for polymer melts: J_e (proportional to $1/G_o$) was independent of $\overline{M}$ for polydisperse silicones and monodisperse polystyrene.

This success of CST with $G_o(c, M)$ motivates use of the c^2 factor also with G_1. As shown in Figure 4 this works very well with G_1 for polyethylene oxide solutions (*13*). G_1 also seems to have some M dependence which is not predicted by any existing theories. Based on fragmentary data (*4, 13*) it appears that $G_1/c^2\overline{M}_n$ may correlate c and M effects for linear polymers at high shear.

Because G_o is independent of M, and G_1 is not strongly sensitive to M, one is prompted to speculate that the magnitude of G/c^2 is characteristic of molecular structure. A survey of the literature indicates that, other things being nearly equal, $G(\gamma)/c^2$ is larger for solutions of polymers whose molecular structure would be termed *stiff* or *rigid*. That is, all cellulosics have values of G/c^2 higher than all polystyrenes. This is an interpretation which meshes surprisingly well with the usage of G as a modulus of rigidity for liquids, in the continuum mechanics.

Factors of polymer-solvent interaction are also significant but very complex. Some limited data suggest that $G(\gamma)$ increases with solvent viscosity η_s (roughly linearly). This effect is entirely unexpected on the basis of DST, which can be used to show that J_e should be independent of solvent viscosity. Furthermore, there are experimental data on J_e showing it to be independent of η_s (*1*); this may, however, reflect a state of insufficient concentration. The role of the solvent, involving both η_s and the thermodynamics of good vs. poor solvents, is under continuing investigation.

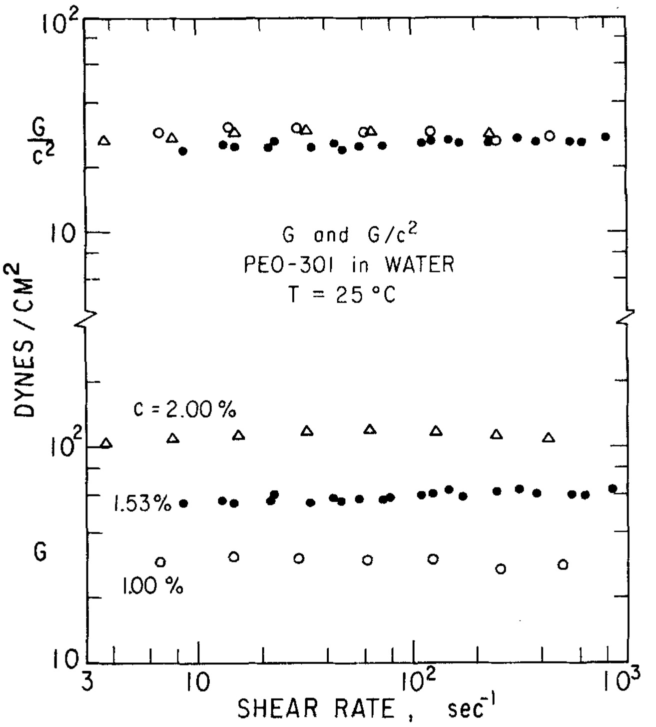

Fig. 4. Concentration dependence of high-shear plateau G_1 for polyethylene oxide solutions, $\overline{M} \approx 4 \times 10^6$. From the upper portion of this figure, we find that $G_1 \sim c^2$.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Financial support came also from the National Science Foundation. The author is grateful to Professor W. W. Graessley of Northwestern for making his results available prior to publication, and to K. S. Gandhi who performed many calculations which were the basis of much of the discussion in this article.

NOTATION

c = polymer concentration, g./cc.
$F(c)$ = thermodynamic function in CST
G = (shear stress)^2/(normal stress) as measured in steady laminar shear flow, dynes/sq.cm.
G_o, G_1 = low and high shear plateau values of G, dynes/sq.cm.
J_e = steady state shear compliance, sq.cm./dyne
K_{dil}, K_{conc} = coefficients in relaxation times, sec.^{2}mole/g. sq.cm. and sec.^{2}/g./cm.^{5}, respectively
K = $K_{\text{conc}}/K_{\text{dil}}$
M, $\overline{M}_n$ = molecular weight and number-average molecular weight, g./mole
n = concentration of polymer molecules, cm.$^{-3}$
$\mathbf{P}$, P_{ij} = total stress tensor and its ij component, dynes/sq.cm.
$\mathbf{P}_o$ = contribution of solvent and isotropic external pressures to $\mathbf{P}$, dynes/sq.cm.
$\mathbf{r}$ = vector position between polymer centers of mass, referred to molecular center, cm.
$\mathbf{R}$ = vector separation of segments in a single polymer molecule, cm.
∇U = force between polymer segments, gradient of intramolecular potential, dynes
∇V = force between polymer molecules, gradient of intermolecular potential, dynes

Greek Letters

γ = shear rate in steady laminar shear flow, sec.$^{-1}$
Δ = logarithmic spacing, along frequency axis, between two intersections of G', G'' curves
η, η_o, η_s = non-Newtonian viscosity, its low-shear limit, and solvent viscosity, g./cm. sec.
λ = relaxation times; sec.
λ_{exp}, λ_{dil}, λ_{conc} = times determined by experiment, by DST, and by CST, respectively, sec.
ω = radian frequency of an oscillatory shear experiment, sec.$^{-1}$

LITERATURE CITED

1. Ferry, J. D., Private Communication (July, 1967).
2. Graessley, W. W., R. L. Hazelton, and L. R. Lindeman, *Trans. Soc. Rheol.*, **11** (1967).
3. Holmes, L. A., and J. D. Ferry, *J. Polymer Sci.* **C16** (1967).
4. Kotaka, T., M. Kurata, and M. Tamura, *Rheol. Acta*, **2**, 179 (1962).
5. Meyer, H. H., W. F. Pfeiffer, and J. D. Ferry, *Biopolymers*, **5**, 123 (1967); J. D. Ferry, *J. Polymer Sci.*, **C15**, 307 (1966).
6. O'Reilly, J. M., and W. M. Prest, *Rheol. Bull.*, **35**, No. 2 (1966).
7. *Ibid.*, **36**, No. 1 (1967).
8. Osaki, K., K. Tanaka, M. Kurata, and M. Tamura, *J. Phys. Chem.*, **70**, 2271 (1966).
9. *Ibid.*, 516.
10. Williams, M. C., *AIChE J.*, **12**, 1064 (1966).
11. *Ibid.*, **13**, 534 (1967).
12. *Ibid.*, 955 (1967).
13. *Ibid.*, **11**, 467 (1965).