Concentration Dependence of the Viscosity and Viscoelasticity of Polymer Solutions: Application of the Theory of Muthukumar and Freed

Ken A. Dill*

Department of Chemistry, B-017, University of California—San Diego, La Jolla, California 92093. *Received October 11, 1979*

ABSTRACT: Recently, Muthukumar and Freed have proposed a theory for the concentration dependence of several viscoelastic properties of polymer solutions. Using data taken from monodisperse solutions of T2 DNA, we have made some tests of the theory. We have found that their theory correctly predicts the concentration dependence of the primary relaxation time. The Huggins constant which can be calculated from their theory is also in good agreement with available experimental data on these solutions. If, in addition, we adopt the simple phenomenological model of Klotz and Zimm which relates creep-recovery parameters to relaxation times, we can make predictions about the concentration dependence of retardation times and recoils. Although some of these predictions are less reliable, nevertheless the corrections are all in the right direction, and the theoretically predicted slopes of the linear concentration dependences are all within a factor of 2 of the experimental values.

Much previous attention has been given to relaxation times of polymer solutions. When extrapolated to zero concentration, these can be used to determine polymer molecular weights, based on the beads-springs theory of polymer dynamics.[1,2] One application has been the measurement of molecular weights of very large DNA molecules from relaxation and retardation times.[3-6] Much less attention has been given to the concentration dependence, at low concentration, of these relaxation times, in part because of the formidable difficulties in dealing with the theory for a concentration-dependent hydrodynamic interaction. However, recently Muthukumar and Freed[7] have proposed such a theory (hereafter referred to as MF) of the first-order concentration dependence of the viscosity and viscoelastic parameters. Here we present a range of data, all taken on highly monodisperse solutions[4,6] of DNA molecules from bacteriophage T2, which show quite good agreement with their theory. We have not done an extensive test of their theory. However we show that their value of the Huggins constant is correct, as is the slope, A, of the concentration dependence of the primary relaxation time. They predict A to be linearly dependent upon intrinsic viscosity, and we show indirect evidence which agrees with this. Combining the MF theory with a perturbation theory of Klotz and Zimm,[8] which relates creep-recovery dynamics to relaxation times, we can also make predictions about the concentration dependence of creep-recovery parameters such as the retardation times and primary recoil.

Relaxation Times

The theory of Muthukumar and Freed[7] predicts that the first-order concentration dependence of the individual relaxation times will be

$$\tau_p = \tau_p^{0}(1 + cAp^{-1/2} + ...) \tag{1}$$

where, in a Θ solvent

$$A = \frac{\pi N_a l^2}{2M_a}\left(\frac{l}{3}\right)^{1/2}\left(\frac{nl}{2\pi}\right) \tag{2}$$

and

$$\tau_p^{0} = \tau_1^{0} p^{-3/2} \tag{3}$$

Here c is the polymer concentration, N_a is Avogadro's number, l is the effective Kuhn length in the beads-springs model, n is the number of Kuhn-length monomers, and M_a is the molecular weight of a monomer.

The monomer molecular weight, M_a, is just M/n, where M is the molecular weight of the chain. In addition, we can use the Flory relation for a Gaussian chain[1]

$$(nl^2)^{3/2} = \frac{[\eta]M}{2.843 \times 10^{23}} \tag{4}$$

to simplify

$$A = 0.7665[\eta] \tag{5}$$

(Note that this particularly simple form is expected to be valid only for Θ solvents.)

In order to compare theory with experiment, we need the intrinsic viscosity. It is possible to calculate it for T2 DNA in an assumed Θ solvent, by using the light scattering data of Hays, Magar, and Zimm.[9] Thus we get

$$[\eta] = 3.42 \times 10^4 \text{ cm}^3/\text{g} \tag{6}$$

where we take the molecular weight to be 1.26×10^8 daltons.[4] Indeed this value of intrinsic viscosity is quite close to the value of 3.51×10^4 cm^3/g of Bowen and Zimm,[4] which was measured in a solvent containing 0.06 M Na$^+$. Thus the calculation for A is reasonably independent of our choice of solvent, so we use the Θ solvent value for consistency. Therefore, for T2 DNA, the MF theory prediction is $A = 2.62 \times 10^4$ cm^3/g. In Figure 1, we show the experimental concentration dependence of the primary relaxation time, divided by its zero-concentration value. The data are taken from the flow birefringence relaxation studies of Thompson and Gill[10] and Adam and Zimm[11] and the shear-stress relaxation measurements of Dill.[6] The linear least-squares best-fit line is shown in the figure and has a slope of 2.66×10^4 cm^3/g, in excellent agreement with the theory.

Viscosity (Huggins Constant)

The viscosity of a polymer solution is given by:

$$\eta = \eta_0(1 + [\eta]c + k_h[\eta]^2c^2 + ...) \tag{7}$$

Also

$$\frac{\eta_{sp}}{c} = \frac{\eta - \eta_0}{c\eta_0} = [\eta] + k_h[\eta]^2c + ... \tag{8}$$

where η_0 is the solvent viscosity, and k_h is the Huggins constant. Thus the slope of $(\eta_{sp}/c)/(\eta_{sp}/c)_{c=0}$ versus con-

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*Address correspondence to this author at the Department of Chemistry, Stanford University, Stanford, California 94305.

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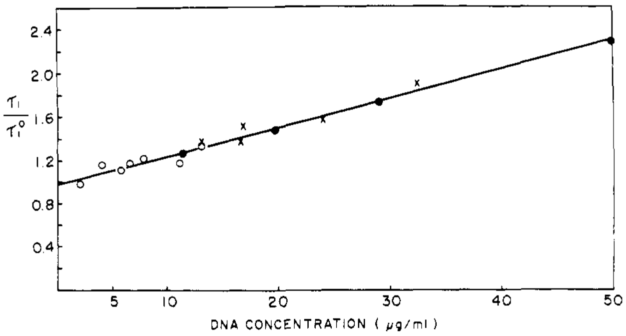

Figure 1. Concentration dependence of primary relaxation time, τ_1; τ_1^0 is the value at zero concentration: data from Thompson and Gill[10] (●), Adam and Zimm[4] (○), and Dill[6] (×). The linear least-squares best-fit slope is 2.66 × 10^4 cm^3/g.

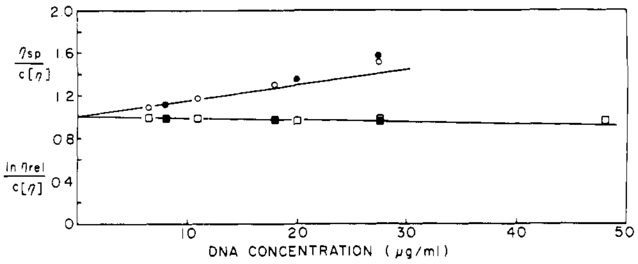

Figure 2. Dependence of zero-shear, steady-state viscosity on concentration: circles are $\eta_{sp}/c[\eta]$, squares are (ln η_{rel})/$c[\eta]$; data of Bowen and Zimm[4] (■,●) and Crothers and Zimm[12] (□,○). The linear least-squares slope through (ln η_{rel})/$c[\eta]$ δ_{rel})/$c[\eta]$ gives a Huggins constant of 0.475.

centration is equal to $k_h[\eta]$ at low concentrations. The MF theory predicts that:

$$k_h[\eta] = \frac{A \sum_{p=1}^{N} p^{-1/2}\tau_p^0}{\sum_p \tau_p^0} \tag{9}$$

For long chains, these sums can be approximated by the Riemann zeta function, so that:

$$k_h[\eta] = A\,\frac{\zeta(2)}{\zeta(3/2)} = 1.65 \times 10^4 \text{ cm}^3/\text{g} \tag{10}$$

Thus, this gives k_h = 0.482. In Figure 2 we show the combined data from experiments of Crothers and Zimm[12] and of Bowen and Zimm.[4] Crothers and Zimm took their data at a low shear stress at which the viscosity is Newtonian, and Bowen and Zimm extrapolated to zero shear stress.

The best-fit slope through the combined data of ln η_{rel}/c is −0.086 × 10^4 cm^3/g, which gives a Huggins constant of 0.475. The Huggins constant from the Crothers and Zimm[12] data alone is 0.45, and for a large number of DNAs, an earlier study of Eigner and Doty found k_h = 0.5 ± 0.2.[13] Thus here also we consider the agreement of the experiments with theory to be quite good.

Creep Recovery (Retardation Times)

Klotz and Zimm[8] have shown that to first order in concentration, retardation times, τ_{cr}, can be related to relaxation times as follows:

$$\tau_{cr_p} = \frac{\tau_p}{\left(1 + \frac{\tau_p}{\sum_p \tau_p}\eta_{sp}\right)} \tag{11}$$

so that for the primary retardation time:

$$\tau_{cr_1} = \frac{\tau_1^0(1 + cA)}{1 + \frac{c[\eta]}{S_1}} \simeq \left(\tau_1^0\left[1 + c\left(A - \frac{[\eta]}{S_1}\right)\right]\right) \tag{12}$$

to first order in concentration, where $S_1 = (1/\tau_1)\sum\tau_p$ = 2.612. Thus the slope of τ_{cr_1}/τ_1^0 with respect to concentration is A' where:

$$A' = A - \frac{[\eta]}{S_1} = 1.31 \times 10^4 \text{ cm}^3/\text{g} \tag{13}$$

To this we can compare the measured values of the primary creep-recovery times of the data of Bowen and Zimm,[4] from which the slope is A' = 1.60 × 10^4 cm^3/g. (Note that if we use the value of S_1 = 2.041, given by Bowen and Zimm,[4] then A' = 0.944 × 10^4 cm^3/g, which deviates substantially from A'_{exptl}.)

In several previous experimental studies, reduced relaxation and retardation time variables have been reported.[4,6,10] The slopes of these are simple to justify with the use of the above expressions for A or A' and $[\eta]$. For example, the relaxation time data of Thompson and Gill[10] show that the slope of τ_1/η_{rel} vs. concentration is −0.88 × 10^4 cm^3/g ($\eta_{rel} = 1 + \eta_{sp}$). We can calculate that:

$$\frac{\tau_1}{\eta_{rel}} = \frac{\tau_1^0(1 + cA)}{1 + c[\eta]} \simeq \tau_1^0[1 + c(A - [\eta])] \tag{14}$$

which gives a predicted slope of

$$A - [\eta] = -0.80 \times 10^4 \text{ cm}^3/\text{g} \tag{15}$$

Using the same procedure, we can show that $\tau_1 c[\eta]/\eta_{sp}$ should be practically independent of concentration, since here the appropriate slope is $A - k_h[\eta]$ which is small. This particular form of reduced variable, $\tau_1 c[\eta]/\eta_{sp}$, is even more effective for reducing the concentration dependence of retardation times. In this case, the slope of the concentration plot ($A' - k_h[\eta]$) is equal to zero, within experimental error, so long as the values for η_{sp}/c have been taken at or extrapolated to zero shear stress.

Molecular Weight Dependence of A'

The MF theory predicts that A and $[\eta]$ should both have the same molecular weight dependence. It is well-known[1] that $[\eta] \sim M^\alpha$, where α = 0.5 for a Gaussian coil, and α is in the range of 0.66–0.70 for DNA in 0.2 M simple salt.[12,13] Data are available with which it is possible to test this. We assume the validity of eq 11. Retardation times have been measured on solutions of DNA of various molecular weights. In several such cases, the concentration dependence has been published.[3-5,14,15] We have calculated A' values from four of these. In the remaining studies,[5,15] the concentrations used were so small, and the range of concentrations was so small, that it was impossible to discern a particular nonzero slope. The four values of A' are plotted in Figure 3. For the largest DNA's, from *E. coli* and *B. subtilis* bacteria, the errors in the measurement of $[\eta]$ and A' are large. Thus the line in Figure 3 is drawn through the two points we take to be the most reliable, and this corresponds to a molecular weight exponent of 0.61. Therefore, in these solvents for which $[\eta] \sim M^{0.66}$, this small collection of data gives $A' \sim M^{0.61}$. Within experimental error, this suggests that the molecular weight dependences of A' and $[\eta]$ are the same. Thus it is at least plausible that A, too, should have the same molecular weight dependence, as is predicted by the MF theory (eq 5).

Recoil from a Creep-Recovery Experiment

In a creep-recovery experiment, the strain in the solution relaxes as a sum of exponentials, with total amplitude, Γ.

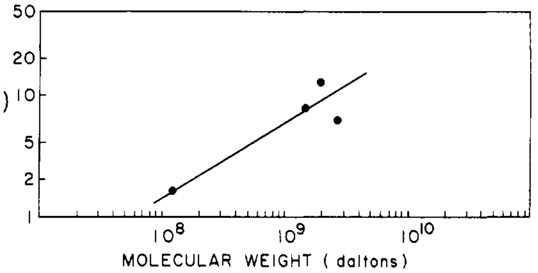

Figure 3. Molecular weight dependence of A', the slope of the concentration dependence of the primary retardation time. In order of increasing molecular weight, the points are from T2 DNA,[4] giant (13×) T2 DNA,[14] *B. subtilis*,[3] and *E. coli*.[3]

This is closely related to the shear compliance.[4] The primary contribution to that relaxation amplitude, Γ_1, is due to the slowest mode of the largest molecules. Thus, for example, Γ_1/Γ has been shown to be a measure of molecular weight heterogeneity,[16] and Γ_1 is a measure of the concentration of largest molecules.[4,8] Both Γ_1 and Γ have been shown to be dependent upon shear stress and concentration. Bowen and Zimm[4] have shown that the parameter $\Gamma_1/\kappa\tau_{cr_1}c$ where κ is the shear rate, when extrapolated to zero shear stress, shows a linear concentration dependence. It can be seen from their data that the slope of $\Gamma_1/\kappa\tau_{cr_1}c$ vs. concentration is -1.16×10^4 cm^3/g. In this case, combining the MF theory with the Klotz and Zimm approximation shows good agreement with experiment. Since[8]

$$\frac{\Gamma_1}{\kappa\tau_{cr_1}c} = \frac{\eta_{sp}}{c\eta_{rel}} \frac{\tau_{cr_1}}{\sum_p \tau_p} \qquad (16)$$

then if we take

$$\tau_{cr_1} = \tau_1^0(1 + cA') \qquad (17)$$

and

$$\sum \tau_{cr_p} = \tau_1^0 \sum_p p^{-3/2}(1 + cA'p^{-1/2}) \qquad (18)$$

then the predicted slope of $(\Gamma_1/\kappa\tau_{cr_1}c)/(\Gamma_1/\kappa\tau_{cr_1}c)_{c=0}$ will be

$$(k_h - 1)[\eta] + A'\left(1 - \frac{\zeta(2)}{\zeta(3/2)}\right) = -1.22 \times 10^4 \text{ cm}^3/\text{g} \qquad (19)$$

where $\zeta(t)$ is the Riemann zeta function.

By using the same procedure for $\Gamma/\kappa\tau_{cr_1}c$ we find the slope to be about the same as above, also negative. However, in this case we find the slope of $(\Gamma/\kappa\tau_{cr_1}c)_{exptl}/(\Gamma/\kappa\tau_{cr_1}c)_{c=0}$ to be -0.6×10^4, compared with the slope of $(\Gamma/\kappa\tau_{cr_1}c)_{theory}/(\Gamma/\kappa\tau_{cr_1}c)_{c=0}$ which is -1.3×10^4, not particularly close.

Summary

We have tested the theory of Muthukumar and Freed on the concentration dependence of viscosity and viscoelasticity in dilute polymer solutions. We have collected data only from studies of DNA and only from those studes for which the molecular weight distribution was extremely narrow.

We applied their theory for Θ solvents, since one of the formal constants (B) in their good-solvent theory cannot be evaluated in a simple way. Although the experiments were done in moderately good solvents, nevertheless we find their predictions of the Huggins constant and slope of primary relaxation time vs. concentration to be quite good. To relate creep-recovery parameters to relaxation times, we have used the phenomenological approximation of Klotz and Zimm. The combined theory gives reasonably good predictions for the concentration dependence of primary recoil, Γ_1, but predictions are not as good for total recoil, Γ, or for primary retardation time, τ_{cr_1}.

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References and Notes

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