and thereby indistinguishable from it in the "infinite" chain. For example, C_3(1,4-1,4-1,4-MM*M*) is equivalent to C_3(4,1-4,1-4,1-M*M*M), C_2(1,4-1,4-4,1-MS*M*M) is equivalent to C_2(1,4-4,1-4,1-M*M*SM), and so on.
(27) A. E. Tonelli, *Macromolecules*, **12**, 255-256 (1979).
(28) R. C. Ferguson, *J. Polym. Sci., Part A*, **2**, 4735-4741 (1964).
(29) T. Okada and T. Ikushige, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2059-2063 (1976).
(30) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, 1969, p 280.
(31) A. E. Tonelli, unpublished calculations.
(32) M. M. Coleman and E. G. Brame, *Rubber Chem. Technol.*, **51**, 668-76 (1978).
(33) J. I. Cunneen and W. F. Watson in "Macromolecular Syntheses", Collect. Vol. 1, J. A. Moore, Ed., Wiley, New York, 1977, p 245.
(34) W. R. Sorenson and T. W. Campbell in "Preparative Methods of Polymer Chemistry", 2nd ed., Interscience, New York, 1968, p 316, expt. 260.
(35) For example, calculations show that the C-C bond in the sequence $-SO_2-CH_2-CHR-SO_2-$ prefers the trans conformation, which maximizes the distance between sulfones; see A. H. Fawcett and K. J. Ivin, *Polymer*, **16**, 569-572 (1975).
(36) R. E. Cais and F. A. Bovey, *Macromolecules*, **10**, 757-762 (1977).
(37) J. E. Hazell and K. J. Ivin, *Trans. Faraday Soc.*, **58**, 342-349 (1962).
(38) M. Iino, H. H. Thoi, S. Shioya, and M. Matsuda, *Macromolecules*, **12**, 160-161 (1979).

Dynamics of Polymer Solutions. 1. Theory for an Instrument

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ABSTRACT: We present the theory for an instrument which can measure several parameters of the viscoelasticity of dilute solutions of very large polymer molecules. In previous work on solutions of large DNA molecules, we used retardation times, measured by creep recovery, to get the molecular weight of the largest such molecules in solution. We have now added the capability to measure stress relaxations, the theory for which is described here. In the following paper, we show that by combining creep-recovery and strain-relaxation measurements it is possible to get information about the molecular-weight distribution of large polymer molecules in the solution.

The viscoelastic behavior of dilute polymer solutions gives much information about the sizes of the polymer molecules and their distribution. With very large molecules the relaxation times are long and viscoelasticity is easy to measure; such is the case with large DNA. Herein we describe the theory for an instrument which can make a variety of viscoelastic measurements on dilute DNA solutions. We believe it will be of value to both biologists and rheologists. For example, with a simpler instrument our lab and others have measured one viscoelastic parameter—the longest retardation time—and used it for getting information about the size and structure of chromosomal DNA in viruses,[1] bacteria,[2] and eukaryotes.[3] Those experiments, called creep-recovery experiments, give primarily information about the largest molecules in the solution. Here, and in the following paper, we show that by adding the capability to measure shear-stress relaxation as well it is possible to get information about the distribution of sizes of those molecules. This now allows us to study natural populations of DNA sizes, biological mechanisms of DNA damage, and physical mechanisms of damage such as radiation or shear degradation in flow. For rheological studies, DNA is in some ways an ideal polymer. Each molecule is biologically synthesized to have the same molecular weight. Therefore, in physical studies of solutions of DNA from an appropriate source, molecular-weight distribution need not complicate the rheology. Here we present the theory for a general rheological instrument for DNA solutions with which we can measure specific viscosity, creep recovery, and shear-stress-relaxation dynamics on the same solution. With it we can study viscoelastic properties and molecular-weight distributions of DNA solutions. Elsewhere we present a detailed description of the instrument[4] and experimental results.[5]

Instrument Description

The DNA solution is in a cylindrical glass chamber. Concentric with the cylindrical chamber and suspended in the solution is a plastic rotor containing a metal ring at the bottom. An external electromagnetic field produces eddy currents in the ring which turn the rotor, thus applying a shear stress to the solution. This "windup" of the rotor prepares for either of two kinds of experiment (see Figure 1). Also during this windup, the applied stress is fixed and we can measure the strain rate, so that we can get the solution viscosity. Some of the applied energy is stored in the "elastic" entropy of the molecules as they are stretched from their equilibrium configuration by the shear. So now at the time we call $t = 0$, the molecules are allowed to relax, causing either (1) a relaxation of the strain in the solution or (2) a relaxation of the shear stress in the solution. Relaxation of the strain—a creep-recovery experiment—is accomplished by turning off the externally-applied drive field, allowing the rotor to be governed by the solution dynamics alone. The molecules relax, pulling the rotor in the reverse direction. The angular velocity of the rotor decays exponentially, which we follow with an optical system. In the relaxation of the shear stress—a stress relaxation—the rotor angular position, $\theta(t)$, as monitored by the optical system, is held fixed at θ_0 by servo electronics which apply a restoring torque, $T = -k(\theta(t) - \theta_0)$, to the rotor if the angular position deviates from θ_0. As the molecules relax, the shear stress in the solution, and the electromagnetically-applied torque which balances it, decay exponentially to zero. It is this torque that we measure in this case.

Theory

The dynamical behavior of the DNA solution acting on the rotor can be described by the Rouse-Zimm beads-springs theory,[6] in which it is assumed that the friction of each polymer molecule with the solvent is localized at beads along the chain, and that springs, which model the configurational entropy of the chain, connect the beads. To treat the complete dynamics of the instrument, we must include rotor inertia, and we consider a solution

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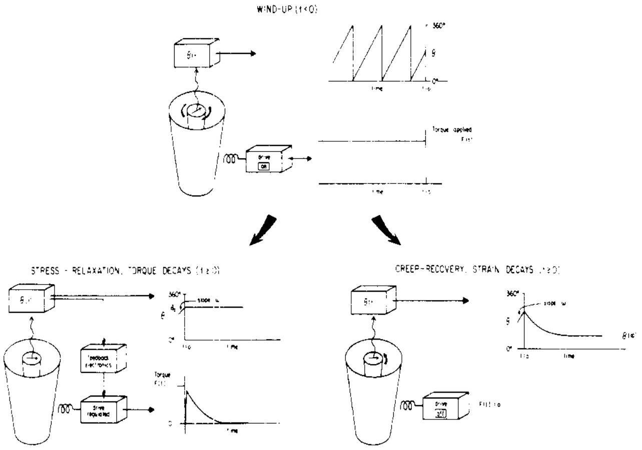

Figure 1. Creep recovery vs. stress relaxation.

containing subpopulations of molecules of different molecular weights. The simplest approach is to set up force balance equations, using phenomenological Maxwell elements (springs and dashpots), and then to substitute the molecular parameters from the Rouse–Zimm theory at a final stage of the calculations. This procedure has been successfully used before by Chapman et al.[7] and Klotz and Zimm.[8] The Maxwell element picture is shown in Figure 2. Each molecule has a spectrum of decay times arising from internal modes of relaxation. In addition, we assume the general case in which there is some distribution of discrete molecular weights in the solution, which we call species. Thus each Maxwell element, a spring in series with a dashpot, represents a single mode of relaxation of a single species of DNA molecules. We will discuss the generalized operation of the instrument, in which the Couette shearing chamber containing the polymer solution is effectively in the feedback loop of an operational amplifier, after the windup has been performed. There are then two limiting cases of interest. First, if the amplifier gain, A, is zero so that the force applied to the rotor is zero, then the rotor motion, $\theta(t)$, will follow the creep-recovery dynamics previously described by Klotz and Zimm.[8] In this case, all the springs and dashpots relax cooperatively until the rotor comes to a stop. In the second case, if we have set the amplifier gain to be very large ($A \to \infty$), then a force will be applied to hold $\theta(t) - \theta_0$ to be very small. Since the rotor does not move, each spring relaxes only against its own dashpot, producing a sum of independent forces which must be compensated by the electronics. Here, we follow the dynamics of $F(t)$.

To begin, we assume a solvent viscosity of η_0, and that the rotor has a radius r, cylindrical surface area a, and moment of inertia I. We consider a heterogeneous solution with $i = 1, 2, 3, ..., P$ various molecular weight species, each of which has $k = 1, 2, 3, ..., N$ internal modes of relaxation. Each Maxwell element has spring constant K_i and a viscous damping coefficient of η_{ik}. By definition, $\tau_{ik} = \eta_{ik}/K_i$, which is the stress-relaxation time constant of each Maxwell element. When there is no polymer, the only mechanical element is the dashpot representing the Newtonian solvent. In our concentric cylinder Couette apparatus, the gap between cylinders is sufficiently small that we can approximate the flow as a simple shear between parallel plates, separated by a distance d. Thus the force acting on the rotor due to the solvent alone is:

$$F_s = -\eta_0 a \frac{dv}{dz} = -\eta_0 \gamma \frac{d\theta}{dt} \tag{1}$$

where dv/dz is the shear rate in the gap, $d\theta/dt$ is the angular velocity of the rotor, and $\gamma = ar/d$. If it is necessary to account for deviations from ideal parallel plate shear, γ can simply be considered to be a geometric constant with units of square centimeters. The rotor angular position $\theta(t)$ is taken relative to some fixed angle θ_0, which we choose to be 0 for convenience. The other forces which act on the rotor are $F(t)$, due to the externally-applied magnetic field, and $F_{ik}(t)$ from each Maxwell element. For each Maxwell element, the force F_{ik} is the same as the force on the dashpot and the force in the spring

$$F_{ik} = -K_i \gamma \theta_{\text{spring}} = -\eta_{ik} \gamma \frac{d\theta_{\text{dashpot}}}{dt} \tag{2}$$

where the displacements due to the spring and the dashpot are parcelled according to[8]

$$\theta = \theta_{\text{spring}} + \theta_{\text{dashpot}} \tag{3}$$

so that

$$\frac{d\theta}{dt} = \frac{d\theta_{\text{sp}}}{dt} + \frac{d\theta_{\text{dash}}}{dt} \tag{4}$$

When we substitute the relations from eq 2, this becomes

$$\frac{d\theta}{dt} + \frac{1}{\gamma K_i} \frac{dF_{ik}}{dt} + \frac{1}{\gamma \eta_{ik}} F_{ik} = 0 \tag{5}$$

which is essentially the same as eq 2.12 of Klotz and Zimm.[8] The force balance equation for all the elements is

$$F_s + F + \sum_{i=1}^{P} \sum_{k=1}^{N} F_{ik} = \frac{I}{r} \frac{d^2\theta}{dt^2} \tag{6}$$

or, upon substitution of eq 1

$$\frac{\eta_0 \gamma}{\beta} \frac{d^2\theta}{dt^2} - \sum_{i,k} F_{ik} + \eta_0 \gamma \frac{d\theta}{dt} = F \tag{7}$$

where $\beta = r\eta_0\gamma/I$ is a measure of the rate at which the rotor motion decays in pure solvent alone.

Finally, we include the feedback loop,

$$F = A\theta + B \frac{d\theta}{dt} \tag{8}$$

where we allow sufficient generality to include a stabilizing velocity feedback, $B\ d\theta/dt$. The initial conditions are:

$$\theta(0^-) = 0 \tag{9a}$$

$$\frac{d\theta(0^-)}{dt} = \omega \tag{9b}$$

$$\frac{d^2\theta(0^-)}{dt^2} = 0 \tag{9c}$$

$$\frac{dF_{ik}(0^-)}{dt} = 0 \tag{9d}$$

$$F_{ik}(0^-) = -\gamma\omega\eta_{ik}(1 - e^{-t_w/\tau_{ik}}) \tag{10}$$

These initial conditions require some elaboration. The individual forces just prior to $t = 0$ depend on how fast and how long the stretching has been applied during what we call "windup". For either retardation or relaxation mode, prior to $t = 0$, we must drive the rotor to stretch the molecules. If we maintain this torque for a long time—relative to the τ_{ik} of interest—we call the windup "steady state". Alternatively, we can maintain the torque only briefly, and these we call "twitch" windups. For these extremes and the various windup conditions between them, we can solve for the initial conditions, and this is done in the Appendix. We now solve eq 5, 7, and 8 by first Laplace transforming them to:

$$s\tilde{\theta}(s) + \frac{1}{\gamma K_i}\left(s + \frac{1}{\tau_{ik}}\right)\tilde{F}_{ik}(s) = -\omega\tau_{ik}(1 - e^{-t_{\mathrm{w}}/\tau_{ik}}) \qquad (11)$$

$$\gamma\eta_0 s\left[\frac{1}{\beta}s + 1\right]\tilde{\theta}(s) - \sum_{i,k}\tilde{F}_{ik}(s) - \tilde{F}(s) = \frac{I\omega}{r} \qquad (12)$$

$$\tilde{F}(s) = (A + sB)\tilde{\theta}(s) \qquad (13)$$

where s is the transform variable, and $\tilde{\theta}(s)$, $\tilde{F}_{ik}(s)$, and $\tilde{F}(s)$ are the Laplace transforms of $\theta(t)$, $F_{ik}(t)$, and $F(t)$, respectively. Note that in the transform domain we could allow A (loop gain) and B (velocity gain) to be complex functions rather than constants. This is of practical interest since the electronics necessarily has some high-frequency attenuation. The simplest model for this inherent (low-pass) filtering would be:

$$A(s) = \frac{A}{\tau_A s + 1}$$

$$B(s) = \frac{B}{\tau_B s + 1} \qquad (14)$$

where τ_A and τ_B are constants of the electronics. These would reduce to the appropriate constants, A and B, when τ_A and τ_B are small, as they are in our instrument.

Now from eq 11 we have:

$$\tilde{F}_{ik}(s) = \frac{-\gamma\omega\eta_{ik}(1 - e^{-t_{\mathrm{w}}/\tau_{ik}}) - \gamma s K_i\tilde{\theta}(s)}{s + (1/\tau_{ik})} \qquad (15)$$

Substituting eq 15 and 13 into eq 12 gives:

$$\tilde{\theta}(s) = \frac{\dfrac{I}{r}\omega - \gamma\omega\displaystyle\sum_{i,k}\frac{\eta_{ik}(1 - e^{-t_{\mathrm{w}}/\tau_{ik}})}{s + (1/\tau_{ik})}}{\gamma\eta_0 s\left(\dfrac{s}{\beta} + 1\right) + s\gamma\displaystyle\sum_{i,k}\frac{K_i}{s + (1/\tau_{ik})} - (A + sB)} \qquad (16)$$

We simplify this by multiplying the numerator and denominator by

$$\beta\prod_{i=1}^{P}\prod_{k=1}^{N}\left(s + \frac{1}{\tau_{ik}}\right) = \beta\left(s + \frac{1}{\tau_{11}}\right)\left(s + \frac{1}{\tau_{12}}\right)\left(s + \frac{1}{\tau_{21}}\right)\ldots\left(s + \frac{1}{\tau_{PN}}\right) \qquad (17)$$

to get

$$\tilde{\theta}(s) = \left[\gamma\eta_0\omega\prod_{i,k}\left(s + \frac{1}{\tau_{ik}}\right) - \gamma\omega\beta\sum_{i,k}\eta_{ik}(1 - e^{-t_{\mathrm{w}}/\tau_{ik}})\prod_{\substack{j\neq i,\\ k\neq m}}\left(s + \frac{1}{\tau_{jm}}\right)\right]\Bigg/\left[\gamma\eta_0 s(s + \beta)\prod_{j,m}\left(s + \frac{1}{\tau_{jm}}\right) + \beta s\gamma\sum_{i,k}K_i\prod_{\substack{j\neq i,\\ m\neq k}}\left(s + \frac{1}{\tau_{jm}}\right) - \beta(A + sB)\prod_{i,k}\left(s + \frac{1}{\tau_{ik}}\right)\right] \qquad (18)$$

We can get $\tilde{F}(s)$ easily from this, using eq 13.

$$\tilde{\theta}(S) = \frac{-\omega\begin{vmatrix} -1/\beta & -1 & -1 & -1 & \ldots & -1 \\ 0 & -\dfrac{1}{A + sB} & 0 & 0 & \ldots & 0 \\ \tau_1(1 - e^{-t_{\mathrm{w}}/\tau_1}) & 0 & E(s + \dfrac{1}{\tau_1}) & 0 & \ldots & 0 \\ \tau_2(1 - e^{-t_{\mathrm{w}}/\tau_2}) & 0 & 0 & E(s + \dfrac{1}{\tau_2}) & \ldots & 0 \\ \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & \cdot & & \cdot \\ \tau_N(1 - e^{-t_{\mathrm{w}}/\tau_N}) & 0 & 0 & 0 & \ldots & E(s + \dfrac{1}{\tau_N}) \end{vmatrix}}{s\begin{vmatrix} (\dfrac{1}{\beta}s + 1) & -1 & -1 & -1 & \ldots & -1 \\ \dfrac{1}{\gamma\eta_0 s} & -\dfrac{1}{A + sB} & 0 & 0 & \ldots & 0 \\ 1 & 0 & E(s + \dfrac{1}{\tau_1}) & 0 & \ldots & 0 \\ 1 & 0 & 0 & E(s + \dfrac{1}{\tau_2}) & \ldots & 0 \\ \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & \cdot & & \cdot \\ 1 & 0 & 0 & 0 & \ldots & E(s + \dfrac{1}{\tau_N}) \end{vmatrix}} \qquad (19)$$

We briefly consider the specific conditions of monodispersity ($i = 1$), in order to draw parallels with the determinant notation of Klotz and Zimm,[8] and to elucidate the features of the solution to the equations. The determinant is given in eq 19, where

$$E = \sum_{k=1}^{N}\tau_k/\eta_{\mathrm{sp}} \qquad (20)$$

and

$$\eta_{\mathrm{sp}} = \frac{1}{\eta_0}\sum_{k=1}^{N}\eta_k \qquad (21)$$

We can see first that the upper left-hand element of the

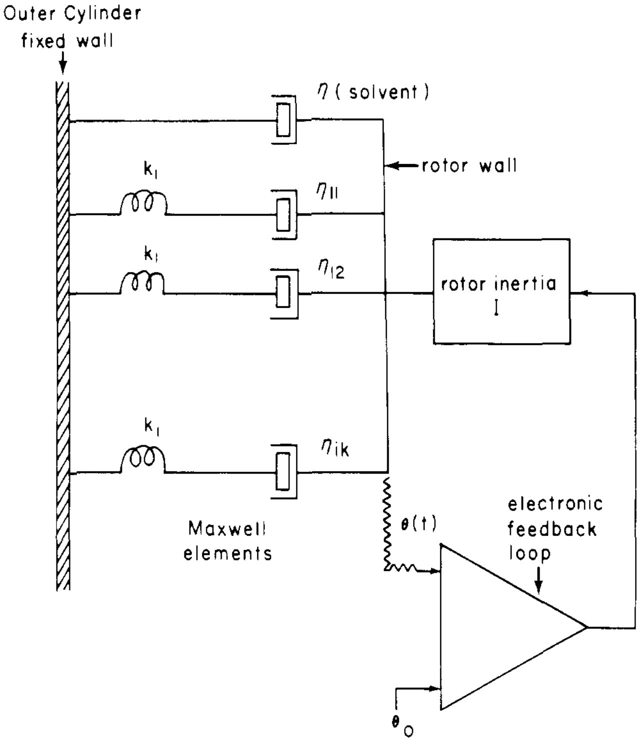

Figure 2. Maxwell element representation of viscoelastic experiments on polymer solutions.

determinant gives us the time dependence of the rotor motion in solvent alone, during a creep-recovery experiment:

$$\tilde{\theta}(s) = \frac{\omega}{s(s + \beta)} \tag{22}$$

so

$$\theta(t) = \frac{\omega}{\beta}(1 - e^{-\beta t}) \tag{23}$$

Next, when $A, B \neq 0$, the upper left 2×2 determinant is the response of the rotor to just the solvent, but now for a relaxation experiment:

$$\tilde{\theta}(s) = \frac{\omega}{s(s + \beta) - \frac{r}{I}(A + sB)} \tag{24}$$

The corresponding force is

$$\tilde{F}(s) = \frac{(A + sB)\omega}{s(s + \beta) - \frac{r}{I}(A + sB)} \tag{25}$$

Since A and B are set to be large under stress-relaxation conditions

$$F(t) = -\frac{I\omega}{r}\delta(t) \tag{26}$$

where $\delta(t)$ is the unit impulse at time $t = 0$.

The negative sign here indicates that the instantaneous torque applied at $t = 0$ must be in the opposite direction to the torque applied before $t = 0$. This counteracts the inertia in order to stop the rotor at a fixed position, $\theta(t) = 0$. In order that $\theta(t) = 0$, $\tilde{\theta}(s)$ must be zero, which can be seen to be the case if A is large in eq 24.

Finally, consider the 3×3 determinant from the upper left-hand corner of eq 19. Now the polymer in the solution is modeled with only a single Maxwell element of time constant τ. This makes the general nature of the model evident, without the complicating details. In this case:

$$\tilde{\theta}(s) = \frac{\omega E\left(s + \frac{1}{\tau}\right) - \beta\tau\omega(1 - e^{-t_{\mathrm{w}}/\tau})}{Es(s + \beta)\left(s + \frac{1}{\tau}\right) + \beta s - \frac{Er}{I}(A + sB)\left(s + \frac{1}{\tau}\right)} \tag{27}$$

Assuming creep-recovery conditions, $A = B = 0$, and $\eta_{\mathrm{sp}} \ll 1$ and ignoring inertia (β large), this reduces to

$$\tilde{\theta}(s) = \frac{-\tau\omega(1 - e^{-t_{\mathrm{w}}/\tau})}{Es\left(s + \frac{1}{\tau}\right)} \tag{28}$$

or

$$\theta(t) = \frac{-\omega}{E}\tau^2(1 - e^{-t_{\mathrm{w}}/\tau})[1 - e^{-t/\tau}] \tag{29}$$

which is identical with the single Maxwell element creep-recovery result of Chapman et al.[7] for steady-state wind-ups.

Now consider stress-relaxation conditions. A is large, and we need make no assumptions about η_{sp} to reduce eq 27 to:

$$\tilde{\theta}(s) = \frac{\gamma\eta_0\omega\tau(1 - e^{-t_{\mathrm{w}}/\tau})}{E(A + sB)\left(s + \frac{1}{\tau}\right)} - \frac{I\omega}{r(A + sB)} \tag{30}$$

which again approaches zero as A is made large. Of more interest is

$$\tilde{F}(s) = \frac{\gamma\eta_0\omega\tau(1 - e^{-t_{\mathrm{w}}/\tau})}{E\left(s + \frac{1}{\tau}\right)} - \frac{\omega I}{r} \tag{31}$$

which transforms to

$$F(t) = \frac{\gamma\eta_0\tau\omega}{E}(e^{-t/\tau})(1 - e^{-t_{\mathrm{w}}/\tau}) - \frac{\omega I}{r}\delta(t) \tag{32}$$

where $\tau/E = \eta_{\mathrm{sp}}$ for these single Maxwell elements.

Note that this means if we have applied forward torque prior to $t = 0$, then at $t = 0$ we must apply reverse torque to counteract the inertia, but in addition a forward torque is then required to balance the relaxing molecules. Furthermore, the required holding torque decays exponentially to zero, and the time constant τ is just the relaxation time of the Maxwell element. An advantage of these stress relaxations is the fact that the inertia and the relaxation processes act independently; the results are more complicated for creep recovery. Further comparison of eq 28–29 with 31–32 shows an interesting difference between the two types of experiment. If inertia is ignored, the operator $\gamma\eta_0$ (d/dt) will convert the creep-recovery result to the stress-relaxation result. This does more than convert from units of angular position to shear force, it also divides out one factor of τ from the amplitude of the exponential. Thus the amplitude of the stress-relaxation exponential is less sensitive to τ than is a creep-recovery exponential.

The more complete results for a heterogeneous solution, including all the relaxation modes, can be obtained by reducing eq 18 to a simpler form when A and B are large:

$$\tilde{F}(s) = \gamma\omega \sum_{i=1}^{P} \sum_{k=1}^{N} \frac{\eta_{ik}(1 - e^{-t_{\mathrm{w}}/\tau_{ik}})}{s + \frac{1}{\tau_{ik}}} - \frac{I\omega}{r} \tag{33}$$

so

$$F(t) = \gamma\omega \sum_{i,k} \eta_{ik} e^{-t/\tau_{ik}}(1 - e^{-t_w/\tau_{ik}}) - \frac{I\omega}{r}\delta(t) \qquad (34)$$

We can see that the total force exerted on the rotor by the molecules is just the sum of the $N \times P$ independent Maxwell element forces. It can be shown that this is the simple result we would expect if the inertial element in Figure 2 were simply replaced by a fixed wall at time $t = 0$. Now we consider the two limiting windup cases of eq 34: steady state

$$F(t) = \gamma\omega \sum_{i,k} \eta_{ik} e^{-t/\tau_{ik}} - \frac{I\omega}{r}\delta(t) \qquad (35)$$

and twitch

$$F(t) = \gamma\Delta\theta \sum_{i,k} K_i e^{-t/\tau_{ik}} - \frac{I\omega}{r}\delta(t) \qquad (36)$$

Not only do twitch windups emphasize spring-like behavior, as we noted before, but also the amplitudes of the twitch exponentials are independent of the mode index, k. The interesting implications of this become more evident if we introduce the molecular parameters corresponding to the Maxwell element components. We do this by using the result of the beads-and-springs theory:[6]

$$\tau_{ik} = \frac{M_i \eta_0 [\eta]_i \lambda_1'}{RTS_1 \lambda_k'} \qquad (37)$$

where R = the gas constant, T = the absolute temperature, M_i = the molecular weight of the ith species, $[\eta]_i$ = the intrinsic viscosity of the ith species, and λ_1', λ_k' = eigenvalues from the theory, modified by the Peterlin parameter, ϵ. We take $\epsilon = 0.1$, which corresponds for DNA to a solvent containing 0.2 M Na^+. These values can be found elsewhere.[9,10]

$$S_1 = \nu\lambda_1' \sum_{k=1}^{\infty} \frac{1}{\lambda_k'} \qquad (38)$$

where ν is a theoretical degeneracy factor ($\nu = 1$ for linear chains; $\nu = 2$ for circular chains). It can be shown that the Maxwell element constants must be separated as follows:[8]

$$\eta_{ik} = \frac{\eta_0 C_i [\eta]_i \lambda_1' \nu}{S_1 \lambda_k'} \qquad (39)$$

and therefore

$$K_i = \frac{RTC_i}{M_i} \qquad (40)$$

where C_i = the weight concentration of the ith species. This leads us to the conclusion that

$$F(t) = \frac{\gamma\omega\eta_0\nu}{S_1} \sum_i C_i[\eta]_i \sum_k \left(\frac{\lambda_1'}{\lambda_k'}\right) e^{-t/\tau_{ik}}(1 - e^{-t_w/\tau_{ik}}) \qquad (41)$$

This is the general form—for any windup but ignoring inertia—for the situation in which our applied torque balances the relaxing molecules by holding the rotor in a fixed position. It is possible to show that under twitch conditions the amplitude of this stress decay is related to the shear modulus, G, of the solution as follows:

$$F(0)_{\text{twitch}} = \gamma(\Delta\theta)G = at_w K_0 G \qquad (42)$$

As an aside, and as a check on eq 41, we note the following. Hassager and Bird[12] have shown theoretically that the area under a steady-state stress-relaxation curve should be directly related to the first normal stress difference of a polymer solution. The normal stress differences are material properties of the polymer and are independent of the type of flow. They show that

$$\sigma_1 = \tau_{xx} - \tau_{yy} = 2K_0 \int_0^{\infty} \frac{F(t)}{a}\, \mathrm{d}t \qquad (43)$$

where σ_1 = the first normal stress difference, τ_{xx}, τ_{yy} = the normal stresses, K_0 = the shear rate applied during windup, and $F(t)/a$ is the relaxation of stress after cessation of steady shearing flow between parallel plates. Since our couette device approximates parallel plate flow, it is possible to compare our result with theirs if we let $K_0 = \gamma\omega/a$, we ignore inertia, and we substitute eq 41 into 43:

$$\sigma_1 = \frac{2S_2 K_0^2 \eta_0^2 \nu}{S_1^2 RT} \sum_{i=1}^{P} C_i M_i [\eta]_i^2 \qquad (44)$$

where

$$S_2 = \nu \sum_k \left(\frac{\lambda_1'}{\lambda_k'}\right)^2 \qquad (45)$$

This result agrees with that found elsewhere for σ_1.[13]

We can make a direct comparison of the stress-relaxation and strain-relaxation results as follows. For strain relaxations ($A = B = 0$), Klotz and Zimm[8] have shown that eq 18 reduces to

$$\theta(t) = \frac{\omega\eta_{sp}\nu}{S_1\langle\tau_1\rangle\eta_{rel}} \sum_{i=1}^{P} f_i \tau_{i1}^2 \sum_{k=1}^{N} \left(\frac{\lambda_1'}{\lambda_k'}\right)^2 e^{-\lambda_k' t/\lambda_1'\tau_{i1}}[1 - e^{-\lambda_k' t_w/\lambda_1'\tau_{i1}}] \qquad (46)$$

(note that we have appended the t_w dependence to their expression), where they have set $\theta(\infty) = 0$, and f_i is the number fraction of molecules of species i:

$$f_i = \frac{C_i/M_i}{\sum_{j=1}^{P} C_j/M_j} \qquad (47)$$

$$f_i L = (N_a)\frac{C_i}{M_i} \qquad (48)$$

L is the total number of molecules per unit volume, and N_a is Avogardo's number. Also

$$\langle\tau_1\rangle = \sum_{i=1}^{P} f_i \tau_{i1} \qquad (49)$$

For stress relaxations, using relations 47 and 48 above, eq 41 becomes

$$F(t) = \gamma\omega k_B T\nu L \sum_{i=1}^{P} f_i \tau_{i1} \sum_{k=1}^{N} \left(\frac{\lambda_1'}{\lambda_k'}\right) e^{-\lambda_k' t/\lambda_1'\tau_{i1}}[1 - e^{-\lambda_k' t_w/\lambda_1'\tau_{i1}}] \qquad (50)$$

where k_B is the Boltzmann constant. We can see that in a creep-recovery experiment $\theta(t)$ decays as a sum of exponentials and that in a stress-relaxation experiment $F(t)$ is similarly a sum of exponentials. In the limit of zero concentration, the retardation times are equal to the stress-relaxation times, and these time constants depend on molecular weight to a power of about 1.5–1.8. The notable difference between eq 46 and 50 is that the relative amplitudes of the exponentials are different. A strain-relaxation curve is primarily a single exponential curve corresponding to the relaxation of the largest molecular species in solution. Relative to this, a stress-relaxation curve includes larger amplitudes of the faster-relaxing species. Furthermore, as we will show in the following paper,[9] the faster relaxing species are even further emphasized by shortening the windup time of the experiment. Since each of these kinds of experiment differently weights the relaxations of different molecular size components of the DNA in solution, it is then possible in principle to extract as least crude information about the molecular-weight distribution of these large molecules. In the following paper, we also show how the data from these various experiments can be combined to give the concentrations C_i of the various species of molecular weight M_i.

Discussion

We have presented the theory for a general viscoelastic instrument with which we can measure most of the low-frequency shear-stress properties of dilute solutions of large DNA molecules. Judicious choice of the experimental conditions for several experiments performed on the same solution leads to a large number of measurable parameters. In the following paper we show how they can be combined into a series of moment equations, which can be solved to yield simple information about the molecular weight distribution of the DNA in the solution. Thus this instrument, the detailed design of which is described in ref 4, should be useful for the study of many of the rheological parameters of solutions of very large polymer molecules, such as chromosome-sized DNA.

In the theory as presented here, we have based our formulas on the easily visualized Maxwell element model of viscoelasticity. It is well-known, however, that this model is mathematically equivalent to the constitutive equations of linear viscoelasticity theory; see, for example, Ferry,[11] Chapter 1, eq 7a and 30. Thus this discussion is of general applicability. We preferred the use of the Maxwell model because of the simpler physical framework it provides for the incorporation of inertial effects of the rotor and of the feedback loop.

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Appendix: Initial Conditions

In this section, we derive the initial conditions, eq 9 and 10, for any windup. We assume that an external force step function is applied at time $t = -t_w$. We must then solve eq 5 and 7, in order to get the values of the parameters at time $t = 0^-$, just prior to the relaxation. Just before the windup, we have

$$\theta(-t_w^-) = \frac{d\theta(-t_w^-)}{dt} = \frac{d^2\theta(-t_w^-)}{dt^2} = F_{ik}(-t_w^-) = \frac{dF_{ik}(-t_w^-)}{dt} = 0 \quad (A.1)$$

We use the same Laplace transform procedure as was used to get eq 11–16, except that there is no analogy to eq 13 which describes the feedback loop. This feedback is not switched into the circuit until $t = 0$. Therefore, the windup is described by

$$\tilde{\theta}(s) = \frac{\tilde{F}(s)}{\gamma\eta_0 s\left[\frac{1}{\beta}s + 1\right] + s\gamma\sum_{i,k}\frac{K_i}{s + 1/\tau_{ik}}} \quad (A.2)$$

where $\tilde{F}(s)$ is just the Laplace transform of the applied force function. For steady-state windups, which correspond to low frequencies, the left-hand side of the denominator dominates, so long as $\sum_{i,k}\eta_{ik} \ll \eta_0$ or $\eta_{sp} \ll 1$, which we have assumed to be true. Furthermore, at high frequencies (short twitches) the left-hand side becomes even more dominant. Physically, this is just a consequence of the inability of the longer modes and larger molecules to deform quickly at high frequencies. Thus by assuming infinite dilution, eq A.2 reduces to

$$\tilde{\theta}(s) = \frac{\tilde{F}(s)}{\gamma\eta_0 s\left[\frac{1}{\beta}s + 1\right]} \quad (A.3)$$

For a step applied at time $t = -t_w$, we can transform eq A.3 to get

$$d\theta/dt = \omega[1 - e^{-\beta(t+t_w)}] \quad (A.4)$$

where we have put $\omega = F_0/\eta_0\gamma$. This gives the initial condition

$$d\theta(0^-)/dt = \omega(1 - e^{-\beta t_w}) \quad (A.5)$$

and similarly

$$d^2\theta(0^-)/dt^2 = \beta\omega e^{-\beta t_w} \quad (A.6)$$

Since $\theta(0^-)$ is arbitrary, we now redefine it to be zero, by appropriate choice of $\theta(-t_w^-)$. If we assume that the moment of inertia is small, such that $\beta t_w \gg 1$, then the initial conditions simplify to

$$\theta(0^-) = \frac{d^2\theta(0^-)}{dt^2} = 0 \quad (A.7a)$$

$$d\theta/dt = \omega \quad (A.7b)$$

This is a reasonably good assumption. For many of our experiments, which are done in high viscosity glycerol–water solvents, β is typically greater than 10 s^{-1}. For solvents the viscosity of water, $\beta \simeq 1$ s^{-1}. In our present instrument, it is impractical to perform windups shorter than a few seconds, so that this condition is usually met. Now combining eq 5 and A.7b, we can get

$$F_{ik}(0^-) = -\gamma\omega K_i \int_{-t_w}^{0} e^{-(t+t_w)/\tau_{ik}}\,dt \quad (A.8)$$

which reduces to eq 10. Under the two limiting conditions of windup—twitch and steady state—we get different initial conditions for $F_{ik}(0^-)$

$$\lim_{t_w\to\infty} F_{ik}(0^-) = -\gamma\omega\eta_{ik} \quad (A.9)$$

which is the steady-state assumption of Klotz and Zimm.[7] Also, since

$$\lim_{t_w\to 0}(1 - e^{-t_w/\tau_{ik}}) = t_w/\tau_{ik} \quad (A.10)$$

then

$$\lim_{t_w\to 0} F_{ik}(0^-) = F_i(0^-) = -\gamma\Delta\theta K_i \quad (A.11)$$

where $\Delta\theta = \omega t_w$ is the total windup angle. Thus, under twitch conditions spring behavior dominates, while under steady-state conditions dashpot behavior dominates the windup.

References and Notes

(1) B. Bowen and B. Zimm, *Biophys. Chem.*, 7, 235 (1978).
(2) L. Klotz and B. Zimm, *J. Mol. Biol.*, 72, 779 (1972).
(3) R. Kavenoff, L. Klotz, and B. Zimm, *Cold Spring Harbor Symp. Quant. Biol.*, 38, 1 (1973).
(4) M. Troll, K. Dill, and B. Zimm, *Macromolecules*, part 3, this issue.
(5) K. Dill, *Macromolecules*, part 4, this issue.

Macromolecules **1980**, *13*, 432-436

(6) B. Zimm, *J. Chem. Phys.*, 24, 269 (1956).
(7) R. Chapman, L. Klotz, D. Thompson, and B. Zimm, *Macromolecules*, **2**, 637 (1969).
(8) L. Klotz and B. Zimm, *Macromolecules*, **5**, 471 (1972).
(9) K. Dill and B. Zimm, *Macromolecules*, part 2, this issue.
(10) V. Bloomfield and B. Zimm, *J. Chem. Phys.*, **44**, 315 (1966).
(11) J. Ferry, "Viscoelastic Properties of Polymers", Wiley, New York, 1970.
(12) O. Hassager and R. Bird, Rheology Research Center Report, University of Wisconsin, 1971, RRC 9.
(13) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, 1971.

Dynamics of Polymer Solutions. 2. The Determination of Molecular Weight Distribution by Viscoelasticity

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ABSTRACT: Viscoelastic measurements on dilute solutions of large polymer molecules are useful for determining the molecular weight of the largest molecules in a solution. Here we show that it is also possible to get information about the distribution of molecular weights. This can be done either with strain-relaxation data, with stress-relaxation data, or both. We have described such instruments in the preceding paper and elsewhere. Such information is particularly useful for the study of very large DNA molecules, for which other physical techniques are not available.

When chromosome-sized DNA molecules are extracted from cells, there may be several species of different molecular weights present in the solution. This may be due to the natural distribution of DNA sizes in the cells, or it may be due to degradation. A change in the molecular weight distribution could result from natural biological processes, from extraction procedures or shear degradation, or from externally induced damage from sources such as radiation or harmful reagents. For these very large DNA molecules, it has only recently been possible to measure the molecular weight of the largest such molecules in solution.[1-3] This has been done by the measurement of viscosity and creep-recovery dynamics.[4] In the preceding paper, hereinafter referred to as paper 1,[5] we describe a modified instrument which can additionally measure stress-relaxation dynamics. Depending on which experiments or combination of experiments are performed on a DNA solution, we measure several parameters such as relaxation times and exponential amplitudes. Here we show how those parameters can be combined to give not only the molecular weight of the DNA, but also a few of the higher moments of the molecular weight distribution. We present the equations for strain relaxations alone, for stress relaxations alone, and for both together. The most detailed information, of course, should result from the combination.

Table I
Eigenvalues[a]

k	λ_k' ($h = \infty$)	λ_k^* ($h = 1.812$)
1	5.0076	2.3224
2	16.258	7.9142
3	31.343	15.897
4	49.719	26.072
5	70.832	38.239
6	94.599	52.366
7	120.56	68.287
S_1	2.211	2.041
S_2	1.143	1.126
S_3	1.035	1.035

[a] Note the λ_k^* are the eigenvalues for T2 DNA with partial draining. The λ_k' are eigenvalues for nondraining DNA, molecules much larger than T2 DNA.

Creep Recoveries (Strain Relaxations)

In a creep-recovery experiment, we apply a shear stress to the solution by applying torque to a rotor therein. The torque is then removed so that the rotor is allowed to recoil freely. In this way the elastic component of the strain is recovered. We follow the rotor angle, $\theta(t)$, which is a measure of the strain-relaxation dynamics, and is governed by[4,5]

$$\theta(t) = \frac{\omega\eta_{\mathrm{sp}}\nu}{S_1\langle\tau_1\rangle\eta_{\mathrm{rel}}}\sum_{i=1}^{P} f_i\tau^2{}_{i1}\sum_{k=1}^{N}\left(\frac{\lambda_1'}{\lambda_k'}\right)^2 e^{-\lambda_k't/\lambda_1'\tau_{i1}}(1 - e^{-\lambda_k't_{\mathrm{w}}/\lambda_1'\tau_{i1}}) \tag{1}$$

where the notation here and throughout is the same as that in paper 1. Note that prior to relaxation, the time during which this shear stress is applied is called the "windup", t_{w}. If the windup is long ($t_{\mathrm{w}} \rightarrow \infty$), it is called "steady state"; if it is short ($t_{\mathrm{w}} \rightarrow 0$), it is called a "twitch";

$$\Gamma = \theta(0) = \frac{\omega\eta_{\mathrm{sp}}\nu}{\eta_{\mathrm{rel}}S_1\langle\tau_1\rangle}\sum_i f_i\tau_{i1}{}^2\sum_k\left(\frac{\lambda_1'}{\lambda_k'}\right)^2[1 - e^{-\lambda_k't_{\mathrm{w}}/\lambda_1'\tau_{i1}}] \tag{2}$$

which simplifies to

$$\Gamma = \frac{\omega\eta_{\mathrm{sp}}\langle\tau_1{}^2\rangle S_2}{\eta_{\mathrm{rel}}\langle\tau_1\rangle S_1} \tag{3}$$

for steady-state windups. S_1 and S_2 are constants given in Table I. Under twitch conditions, eq 2 simplifies to

$$\Gamma = (\Delta\theta)\eta_{\mathrm{sp}}/\eta_{\mathrm{rel}} \tag{4}$$

where $\Delta\theta = \omega t_{\mathrm{w}}$. Therefore by rearranging eq 4, we can get η_{sp} directly from a twitch experiment:

$$\eta_{\mathrm{sp}} = \frac{\Gamma/\Delta\theta}{1 - \Gamma/\Delta\theta} \tag{5}$$

There are other parameters we can get easily from retardation curves. Because of the $\tau_{ik}{}^2$ weighting of the exponentials in eq 1, $\theta(t)$ will be predominantly comprised of the exponential of longest time constant, τ_{11}. Therefore a semilog plot of the curve yields a straight line at long times, $t > \tau$.[2,3] The slope of that line gives $-1/\tau_{11}$, and the

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