

Viscoelastic Properties of Macromolecules in Dilute Solution

John D. Ferry

Department of Chemistry and Rheology Research Center, University of Wisconsin, Madison, Wisconsin 53706

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It is well known that dissolving as little as 1% of a high polymer (*e.g.*, polystyrene) in a solvent (*e.g.*, benzene) can easily double the viscosity of the latter, and measurements of such viscosity increases are made by the hundreds daily in the plastics and rubber industries to monitor molecular weights and other characteristics. It can be easily understood that the viscosity increment corresponds to extra dissipation of energy in flow as the long threadlike polymer molecules swirl around in the viscous medium.

It is less well recognized that even a very dilute solution of a high polymer also possesses elasticity, *i.e.*, is viscoelastic. This effect is best observed and described by the response of the solution to small oscillating shearing deformations, as illustrated in Figure 1. If a sinusoidally varying shear stress (tangential force per unit area) is applied to an elastic solid, it responds with a strain (tangent of deformation angle) exactly in phase with the stress and always proportional to it, following Hooke's law of elastic deformation. If the subject of the experiment is a viscous liquid, on the other hand, the rate of strain is proportional to the stress, following Newton's law of viscous flow. Then if the strain is a sine function, the rate of strain is a cosine, so the strain and stress are 90° out of phase. For a material with *both* viscous and elastic character, the phase difference between stress and strain is somewhere between 0 and 90°, as shown in Figure 1, and the stress can be decomposed into two components in phase and in quadrature with the strain (lower graph); the mathematics is exactly analogous to that used in treating alternating current circuits.

In the theory of elasticity, the ratio of shear stress to strain for small deformations is the shear modulus (G). The ratios of in-phase and out-of-phase stresses to the strain in Figure 1 are the storage modulus (G') and loss modulus (G''), respectively. The former is a measure of energy stored and recovered in a cycle of deformation; the latter, of energy dissipated as heat. In mathematical form, if the strain γ is a sine function of time

$$\gamma = \gamma_0 \sin \omega t \quad (1)$$

The stress σ is given by

$$\sigma = \gamma_0(G' \sin \omega t + G'' \cos \omega t) \quad (2)$$

where γ_0 is the peak strain and ω the radian frequency (2π times the frequency in hertz). Both moduli G' and G'' may be expected to depend on ω .

There was at first skepticism as to whether a very dilute polymer solution could have elasticity. In a concentrated solution like rubber cement where the threadlike molecules tangle, they can be imagined as hooking together somehow to transmit an elastic force, but how could elastic energy be stored at high dilution where the molecules are floating around independently? Nevertheless, existence of elasticity was clearly shown in 1948 by experiments of Mason and Baker,¹ who subjected solutions with polymer concentrations as low as 0.1% to oscillating deformations at frequencies of the order of 10^4 Hz.

Theory for Threadlike Molecules

Kirkwood² showed in 1949 that the elasticity observed by Mason and Baker could be understood as arising from interaction between Brownian motion of the macromolecules and hydrodynamic torques imposed by the flowing solvent. Stated in another way, the distribution of the many possible configurations which a contorted flexible macromolecular thread can and does assume will be perturbed by motion of the solvent; the new distribution is less probable and corresponds to a decrease in entropy, hence an increase in free energy which is stored (elastic) energy.

To apply the principle specifically to threadlike molecules, it was necessary to adopt a simplified molecular model, now generally known by the term bead-spring, as illustrated in Figure 2. The molecule is arbitrarily divided into N submolecules of equal length; in the figure, $N = 4$, but for useful results it should be considerably larger. The frictional interaction with the solvent medium is supposed to be concentrated at the junctions between the submolecules (the beads) while the energy storage is due to perturbation of the configurational distributions of the submolecules themselves (the entropy springs). The model is not so unrealistic as it may first appear, since for some purposes the value of N does not influence the final results as long as it is fairly large. Based on this model, the theories of Rouse³ in 1953 and Zimm⁴ in 1956 predict the frequency dependence of G' and G'' in terms of molecular parameters.

The forces on the beads are described in terms of an $(N + 1) \times (N + 1)$ matrix, the eigenvalues of which are related to a sequence of characteristic

John D. Ferry was born in Dawson, Canada, in 1912. He received his A.B. and Ph.D. degrees from Stanford, and between these was a student at the University of London. He was a Junior Fellow of the Society of Fellows at Harvard. Since 1946 he has been on the chemistry staff of the University of Wisconsin, and from 1959 to 1967 was Department Chairman. In 1968 he was Visiting Lecturer at Kyoto University, Japan. Professor Ferry's research interests center on polymers and natural and synthetic macromolecules.

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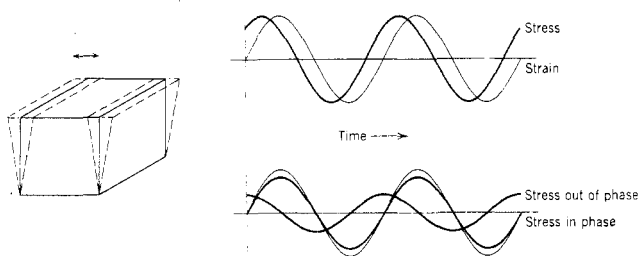


Figure 1. Time dependence of shear stress and strain when a viscoelastic medium is subjected to small sinusoidal deformations.

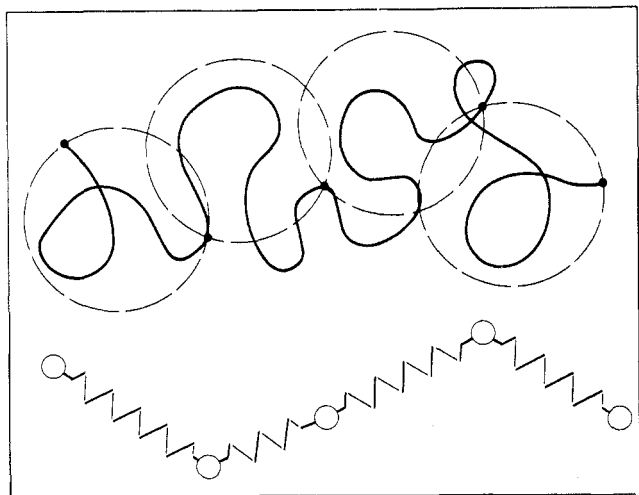


Figure 2. Representation of a flexible, linear thread-like molecule by the bead-spring model.

times τ_p which describe the motions of the whole molecule expressed by a sequence of normal modes. The storage and loss moduli are predicted to have the following frequency dependence.

$$[G'] = (RT/M) \sum_{p=1}^N \omega^2 \tau_p^2 / (1 + \omega^2 \tau_p^2) \quad (3)$$

$$[G''] = (RT/M) \sum_{p=1}^N \omega \tau_p / (1 + \omega^2 \tau_p^2) \quad (4)$$

In these equations, the brackets mean limiting ratios to concentration c (in grams of polymer per milliliter of solution) when extrapolated to infinite dilution; thus

$$[G'] = \lim(c \rightarrow 0) G'/c \quad (5)$$

$$[G''] = \lim(c \rightarrow 0) (G'' - \omega \eta_s)/c \quad (6)$$

In eq 6, η_s is the solvent viscosity; the solvent contribution to the loss modulus is subtracted from the total to give the polymer contribution. No subtraction is necessary in eq 5 because the solvent contributes no elasticity.

The relaxation times τ_p are determined by the molecular weight (M) and certain other molecular characteristics. They depend also on a "hydrodynamic interaction parameter" h^* which is a measure of the hydrodynamic drag forces between beads and may be thought of very roughly as the effective ratio of bead size to average distance between neighboring beads. The longest relaxation time τ_1 is related to measurable quantities by

$$\tau_1 = [\eta] \eta_s M / RT S_1 \quad (7)$$

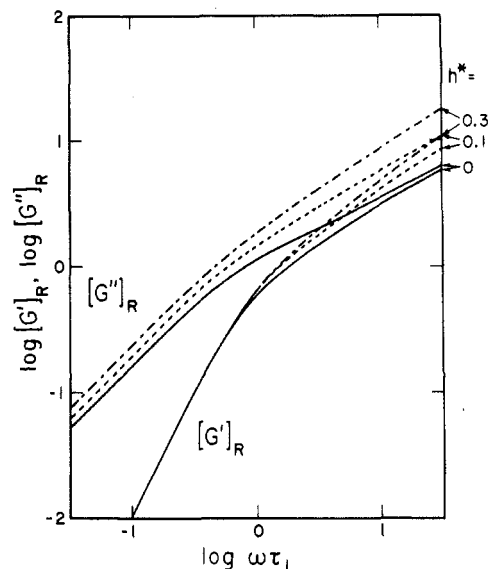


Figure 3. Dimensionless shear moduli $[G']_R$ and $[G'']_R$ plotted logarithmically against dimensionless frequency $\omega \tau_1$, as calculated from Zimm theory with exact eigenvalues evaluated by Lodge and Wu, for $N = 200$ and three values of h^* as indicated.

in which the intrinsic viscosity $[\eta]$ is defined by the familiar equation

$$[\eta] = \lim(c \rightarrow 0) (\eta - \eta_s) / \eta_s c \quad (8)$$

where η is the viscosity of the solution; also, $[\eta]$ is the low-frequency limiting value of $[G'']/\omega \eta_s$; and

$$S_1 = \sum_{p=1}^N \tau_p / \tau_1 \quad (9)$$

The longest time τ_1 corresponds to a mode of motion in which the ends of the molecule are going in opposite directions; the others correspond to more complicated modes with increasing numbers of nodal points. Sequences of τ_p were obtained from approximate eigenvalue solutions for certain specific values of h^* by Rouse,³ Zimm,⁴ and Tschoegl.⁵ Recently, exact eigenvalue solutions have been obtained by Lodge and Wu⁶ for various combinations of h^* and N , and the frequency dependences have been calculated. (The choice of N is without influence unless it is small and/or the frequency is high.)

Examples of storage and loss moduli calculated in this way from eq 3 and 4 are shown in Figure 3. The moduli $[G']_R$ and $[G'']_R$ are dimensionless quantities defined as $[G']M/RT$ and $[G'']M/RT$, respectively, the abscissa is the dimensionless frequency $\omega \tau_1$, and both scales are logarithmic. The plot shows two characteristic frequency zones. For $\omega < \tau_1^{-1}$, $[G']$ and $[G'']$ are proportional to ω^2 and ω , respectively, and $[G'] \ll [G'']$. In this regime, all possible configurational changes occur within a period of cyclic deformation. For $\omega > \tau_1^{-1}$, $[G']$ and $[G'']$ increase less rapidly than with the first power of ω , and are similar in magnitude; in this regime, with increasing frequency, the shrinking period encompasses fewer and fewer of the motional modes. At still higher frequencies than shown, the model becomes inadequate because the fictitious subdivision into submolecules

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cannot describe short-range motions. For N large, the only adjustable parameter in the theory is h^* , all others being experimentally accessible.

It has been assumed that the polymer has uniform molecular weight, and comparisons with experimental measurements are restricted to data on polymer samples with high molecular weights and very narrow molecular weight distributions.

Experimental Measurements on Linear Threadlike Molecules

In very dilute solution, the elastic contribution of the polymeric solute is masked by the viscosity of the solvent unless very sensitive measurements can be made; the phase difference between stress and strain in Figure 1 is only slightly less than 90° . Over the years, measurements have been pushed to lower and lower concentrations until the extrapolations to infinite dilution expressed by eq 5 and 6 could be performed. Viscoelasticity was measured by the writer or his associates at a concentration of 15% polymer⁷ in 1942; at 4%⁸ in 1950; at 1%⁹ in 1961; but extrapolation was still not possible. The first successful extrapolation to infinite dilution for comparison with theoretical curves such as Figure 3 was made by Tanaka and collaborators in 1965,¹⁰ from concentrations as low as 0.1%. The values of $[G']$ and $[G'']$ agreed quantitatively with the predictions of the original Zimm theory for strong hydrodynamic interaction, corresponding to h^* about 0.25, for two polymers dissolved in Θ solvents. (A Θ solvent is a rather poor solvent in which the average distance between any two points on the molecule is proportional to the square root of the number of bonds between them, corresponding to random walk statistics.) The range of frequencies was, however, rather narrow.

More recently, a new experimental method suggested by Birnboim¹¹ and developed by Schrag¹² has made possible measurements which can be extrapolated to infinite dilution over a wider range of frequencies and solvent viscosities. This multiple-lumped resonator consists of a stack of five cylinders machined from a single piece of low-loss aluminum alloy (the "five-story pagoda"), immersed in the solution to be measured, and excited in torsional oscillations with very small amplitude at five different resonant frequencies. With two resonators, a frequency range of 60- to 80-fold can be covered. An example of data is shown in Figure 4 for a high molecular weight polystyrene sample¹³ in two Θ solvents with quite different viscosities; since τ_1 is proportional to η_s in eq 7 and the universal abscissa in the theory is $\omega\tau_1$, a plot against $\log \omega\eta_s$ should make data in both solvents fall on the same pair of curves, and it does. The agreement with the Zimm theory (*i.e.*, with $h^* = 0.25$) is excellent with no adjustable parameters.

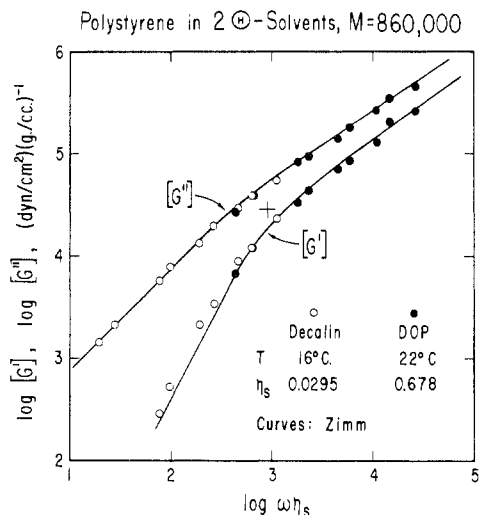


Figure 4. Measured intrinsic shear moduli plotted logarithmically against $\omega\eta_s$ for polystyrene with molecular weight 0.86×10^6 in two Θ solvents: open circles, decalin; black circles; bis(2-ethylhexyl) phthalate (DOP). Curves drawn from Zimm theory ($h^* = 0.25$, N very large). At the cross, $\omega = \tau_1^{-1}$ and the ordinate is RT/M .

Evidently the bead-spring model is quite satisfactory so long as the frequency does not go much higher than $10\tau_1^{-1}$ for molecular weights greater than 10^5 (the higher the molecular weight, the broader the satisfactory frequency range). Two important corollaries are: the frictional resistance to motions comes entirely from the surrounding solvent so the molecule is behaving like a limp thread without internal stiffness, and the detailed chemical structure of the polymer has no influence on its behavior. Indeed, results of measurements on polystyrene,¹³ poly(α -methylstyrene),¹⁴ polybutadiene,¹⁵ and poly(dimethylsiloxane)¹⁶ all look the same. (At higher frequencies, however, specific differences appear as will be mentioned below.)

In "good" solvents as contrasted with Θ solvents, the shape of the frequency dependence of $[G']$ and $[G'']$ is somewhat different, but quantitative agreement with the theory is still obtained by choosing an appropriate value of h^* .¹³⁻¹⁶

Branched Threadlike Molecules

Although the behavior in the frequency range we are discussing is oblivious of detailed chemical structure, it is strongly influenced by the long-range connectivity of the polymer molecule, as illustrated by results with branched polymers such as stars (with arms radiating from a central point) and combs (with arms spaced along a central backbone). The basic theory for stars was developed by Zimm and Kilb¹⁷ in 1959 by use of the bead-spring model; it has recently been evaluated with exact eigenvalues by Osaki and Schrag,¹⁸ and Osaki¹⁹ has also extended it to combs with certain specific geometries.

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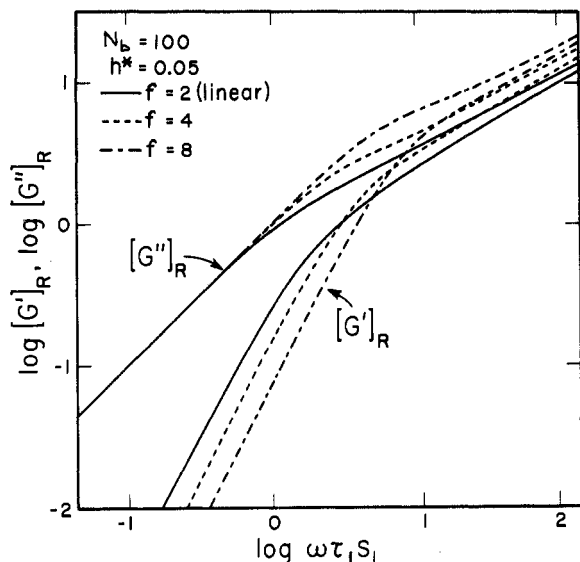


Figure 5. Frequency dependence of $[G']_R$ and $[G'']_R$ for linear, four-arm star, and eight-arm star molecules calculated from the Zimm-Kilb theory with the exact eigenvalues of Osaki and Schrag, taking $h^* = 0.05$ and N_b (i.e., submolecules per arm) = 100. Abscissa is $\omega\tau_1 S_1$, where $S_1 = \sum(\tau_p/\tau_1)$.

For a star with f arms of equal length, the odd-numbered relaxation times are f -degenerate. This alters the shape of the frequency dependence of $[G']$ and $[G'']$ as illustrated in Figure 5; a "bump" appears in both curves at frequencies a little above τ_1^{-1} . Also, the storage modulus $[G']$ is smaller at low frequencies; this is associated with the fact that τ_1 is smaller for a branched molecule than for a linear molecule of the same molecular weight. (In Figure 5, the abscissa scale is normalized to make $[G'']$ coincide at low frequencies for the different species; there are various ways of displaying comparisons.)

An example of experimental data is shown in Figure 6 for a star polystyrene with nine arms in two Θ solvents.²⁰ The agreement with the theory is very good, with h^* chosen as 0.40. Again, the bead-spring model is satisfactory and the energy storage can be attributed to entropy changes caused by perturbation of configurational distributions.

However, current measurements on stars and combs with larger numbers of branches reveal more complicated behavior which is not yet understood; the relaxation times are longer than would be expected from the Zimm-Kilb theory, and the frictional resistance may be abnormally high near the center of such a molecule where the branches are crowded together.

In any case, viscoelastic properties in very dilute solution seem to be more strongly influenced by branching than are most other physical properties, and may eventually serve to characterize the degree and type of branching, which at present can be deduced only from rather indirect evidence.

Behavior at High Frequencies

At higher frequencies than shown in Figures 3-6, the bead-spring model fails because the molecule responds with configurational changes at such short range that they fall within the fictitious submolec-

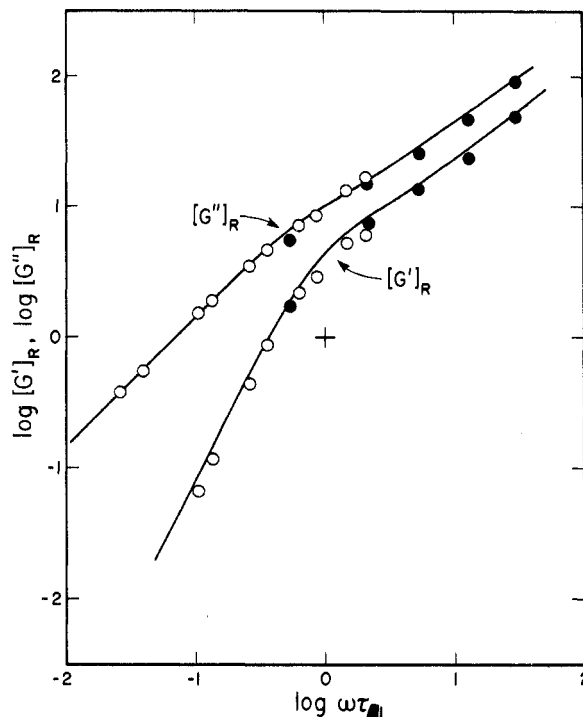


Figure 6. Measured values of $[G']_R$ and $[G'']_R$ plotted logarithmically against $\omega\tau_1$ for star polystyrene with an average of 8.7 arms in two Θ solvents: open circles, decalin; black circles, (bis(2-ethylhexyl) phthalate). Curves drawn from Zimm-Kilb theory with $f = 9$, $N_b = 100$, and $h^* = 0.40$. Cross as in Figure 4.

ules. The behavior can be studied experimentally by use of a solvent of high viscosity, since as pointed out in connection with Figure 4 a viscosity increase is equivalent to a frequency increase from the standpoint of the molecule. A different experimental method²¹ is required, and it is not so easy to extrapolate to infinite dilution, but at high frequencies the concentration dependence of viscoelastic properties is much less serious.

An example of data over an extended frequency range is shown in Figure 7 for a linear, high molecular weight polystyrene at a concentration of 1.5 g/dl in a chlorinated diphenyl solvent.²² Measurements at different temperatures have been combined by a plotting method which essentially takes into account the change in solvent viscosity with temperature; this change is enormous and so provides a very wide spread of effective frequencies. At the high-frequency end, the polymer contribution to loss modulus, $G'' - \omega\eta_s$, becomes directly proportional to frequency, and the storage modulus appears to approach a limiting value. Two characteristic parameters which describe this region are the ratio G'/v_2 , where v_2 is the volume fraction of polymer, and the ratio $(G'' - \omega\eta_s)/\omega\eta_{sc}$ extrapolated to infinite dilution, which is a high-frequency limiting intrinsic viscosity. Both these quantities appear to be independent of molecular weight but dependent on the specific chemical structure of the polymer; values are now available for polystyrene, poly(α -methylstyrene), and polybutadiene.²²⁻²⁴ Their physical significance is uncertain,

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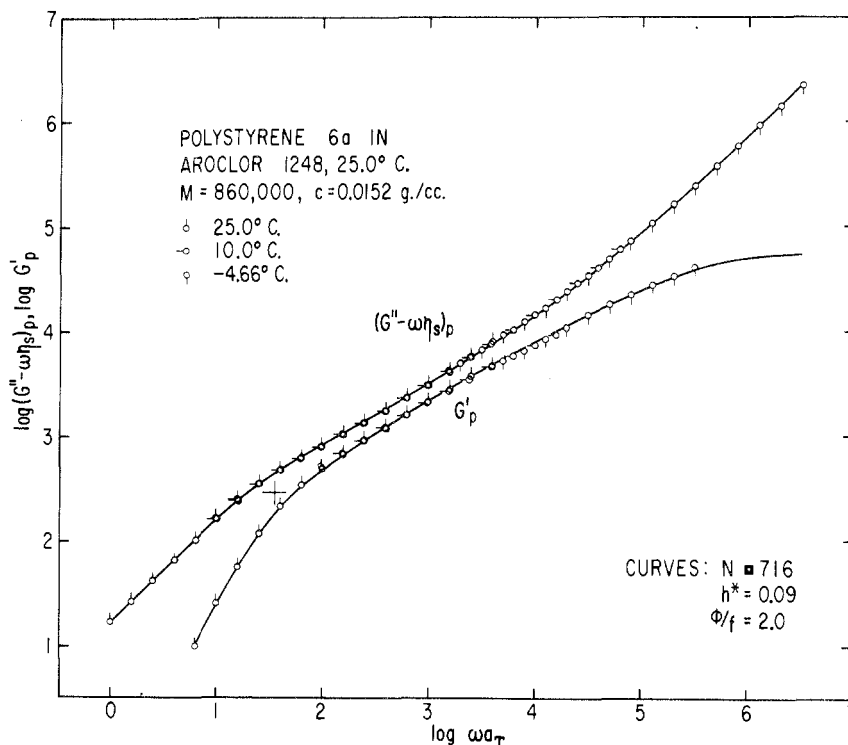


Figure 7. Moduli G' and $G'' - \omega\eta_s$ plotted logarithmically against frequency reduced to 25° (actual data at three different temperatures as indicated), for polystyrene with molecular weight and concentration shown, in chlorinated biphenyl solvent. Curves drawn from Peterlin theory with parameters N , h^* , ϕ/f as indicated.

though the molecule may be thought of crudely as resembling a random coil of stiff wire with respect to very high frequency external forces. Analogous measurements can also be made at extremely high frequencies in solvents of lower viscosity,^{24,25} but these are very difficult and usually restricted to a comparatively narrow frequency range.

The entire frequency dependence of G' and $G'' - \omega\eta_s$ in Figure 7 can be described very well by a theory due to Peterlin,²⁶ in which the number of submolecules N in the bead-spring model is a dominant parameter together with another coefficient which reflects an additional source of energy dissipation;²⁷ the curves in Figure 7 are drawn in accordance with this theory. The number of monomer units per submolecule turns out to be independent of molecular weight and dependent on the chemical nature of the polymer. However, its physical significance is still not clear.

Rigid Rodlike Macromolecules

One of the classical problems in physical biochemistry is the appearance of non-Newtonian viscosity and flow birefringence in dilute solution of rigid rodlike macromolecules such as tobacco mosaic virus.²⁸ Because the rods develop a preferred orientation in steady flow, the viscosity falls with increasing shear rate²⁹ and the solution becomes increasingly birefringent.³⁰ In small oscillating deformations, visco-

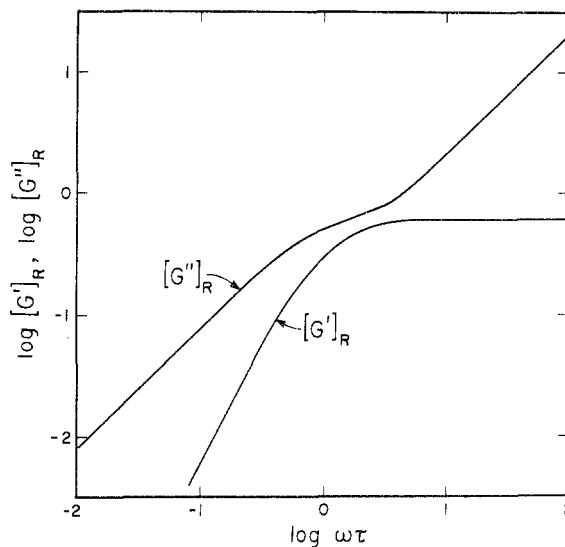


Figure 8. Frequency dependence of $[G']_R$ and $[G'']_R$ for a rigid rodlike macromolecule calculated from Kirkwood-Auer theory.

elasticity should be observed even though the rods are far apart at high dilution, because of the same interaction between Brownian motion and hydrodynamic torques as treated by Kirkwood.² Specific calculations by Kirkwood and Auer³¹ and Ullman³² for rodlike molecules predict the frequency dependence of $[G']$ and $[G'']$ illustrated in Figure 8. There is a single relaxation time which is related to the rotation of the rod end-over-end; in Ullman's calculation it is $\tau = \pi\eta_s L^3 / 18kT [\ln(2L/d) - x]$ where L and d are the length and diameter, respectively, of the rod, and x , a term of minor importance, is about 0.3.

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Measurements of viscoelasticity at finite concentrations have been made on solutions of such more or less rigid macromolecules as helical poly(γ -benzyl L-glutamate),³³ paramyosin from clam muscle,³⁴ and partially degraded deoxyribonucleic acid.³⁵ The low-frequency observations corresponded roughly to the left side of Figure 8 with a relaxation time of plausible magnitude, but at higher frequencies the behavior was intermediate between the predictions for rigid rods and flexible threads. Presumably, this result meant partial flexibility, although conclusions were limited by the presence of intermolecular interaction since the swirling rods must have been colliding at the finite concentration levels studied. Very recently, viscoelastic data on helical poly(benzyl glutamate) have been extrapolated to infinite dilution;¹⁶ the frequency dependence again reflects partial flexibility. It is hoped that such measurements will prove to be a more sensitive index of stiffness than any presently available, and that theories will be developed for quantitative evaluation.

Future Prospects and Applications

It is evident from the preceding paragraphs that several unsolved problems remain in understanding

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the motions of the macromolecular types currently being investigated through viscoelastic measurements. In addition, there are numerous other kinds of macromolecules whose dilute solution viscoelastic properties would be promising to study. These include block copolymers, whose configurations can be profoundly varied by changing solvents, polyelectrolytes, microgels, and a wide variety of biomacromolecules with different degrees of flexibility.

It might be expected that direct practical applications of viscoelastic measurements in very dilute solution would be almost nonexistent. However, the dramatic phenomenon of drag reduction in turbulent flow by exceedingly small polymer concentrations seems to be related to viscoelasticity and molecular deformation.^{36,37} Indirectly, applications are broad and important since understanding of polymer motions and flexibility in the simplest environment where the molecules are separated from each other is the first step toward interpreting their behavior in more concentrated systems including plastics, rubbers, textiles, and biological tissues.

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Reactions of Accelerated Carbon Ions and Atoms

Richard M. Lemmon

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

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How can a carbon-14 ion, accelerated by an electrostatic field, strike a benzene molecule in such a way as to yield a ¹⁴C-labeled benzene product? This is one of the intriguing questions that led us into studies of the chemical consequences of impinging a beam of carbon ions or atoms upon an organic target. From the standpoints of the statistician, the physicist, and the organic chemist the appearance of the benzene-¹⁴C seems an unlikely result—yet it happens. Along with recounting what we know about this ¹²C-¹⁴C replacement reaction, this Account will relate other factors that drew us into this field of research. Among them are that we wanted (1) to learn what we could about the carbon chemistry that takes place at energies beyond those reachable by thermal and photochemical techniques, (2) to look

for the possible appearance of new, that is to say, unknown, carbon compounds, and (3) to look into the possibility of obtaining useful amounts of labeled (tracer) organic compounds.

Carbon beam research may also have a relevance to chemical evolution and the origin of life. As is well known, Earth is steadily irradiated by high-energy carbon atoms in cosmic rays, and such irradiation was doubtless also taking place in prebiological times. It is quite possible that the emergence of life on our planet depended upon some key organic reaction or reactions that were promoted by the high-energy carbons. For any real understanding of this possibility we need to investigate energetic carbon reactions in our laboratories.

The "Hot-Atom" Chemistry of Carbon

Our research with carbon beams is closely related to the many studies that have been carried out in the recoil, or "hot-atom," chemistry of carbon. This research has followed the ultimate fate of an energetic carbon atom formed in a nuclear reaction that is

Richard M. Lemmon is a native of California, educated at Stanford University (A.B.), California Institute of Technology, and the University of California, Berkeley (Ph.D., 1949). He has held U. S. Public Health Service and Guggenheim fellowships, and has been a member of the Senior Staff of the Lawrence Berkeley Laboratory since 1951. His principal research activities are in radiation and hot atom chemistry and in chemical evolution.