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Rheology of Macromolecular Systems

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I. INTRODUCTION

AS the paper by Zimm (p. 123) shows, mechanical energy can be stored in a flexible macromolecular network at elastic equilibrium because of the configurational restrictions imposed on it by an external deformation. The resulting rubber-like elasticity and its characteristic dependence on temperature and cross-linking density are familiar and intuitively reasonable phenomena. Less familiar is the fact that elastic energy can be stored in a macromolecular system *without* cross-links when it is subjected to steady-state flow; this elasticity is manifested in solutions of either flexible or rigid molecules and even at high dilution. In flow, of course, mechanical energy is also continuously dissipated as heat. In some cases, the energy storage is masked by the dissipation and is difficult to detect; in others, including numerous systems of biological interest, the stored energy is obvious as seen, for example, in elastic recoil after cessation of flow.

The presence of stored elastic energy is usually associated with non-Newtonian character of the flow; the apparent steady-flow viscosity falls with increasing shear rate. Moreover, the elastic strain (i.e., that part of the deformation which is recoverable after removal of stress) may not be directly proportional to shear stress, so that the elasticity may be non-Hookean. The province of rheology should include the description and explanation of these nonlinear relationships, as well as the simultaneous appearance of viscosity and elasticity. Nevertheless, for sufficiently small stresses, the deviations from Newtonian flow and Hookean elasticity can be made negligible, and most of the present discussion is restricted to such conditions, corresponding to so-called linear viscoelastic behavior. Although nonlinear phenomena are certainly important and potentially valuable sources of information, they are less well understood and are omitted for the sake of brevity.

With this simplification, a rheological description of the concomitant viscous and elastic behavior of a macromolecular system involves the following quantities:

(a) The steady-flow viscosity, $\eta = \mathfrak{T}/\dot{\gamma}$, where \mathfrak{T} is the shear stress and $\dot{\gamma}$ the rate of shear. The energy dissipated per cc per sec in flow is $\eta\dot{\gamma}^2$.

(b) The steady-state compliance, $J = \gamma_e/\mathfrak{T}$, where γ_e is the elastic strain. The energy stored per cc is $J\mathfrak{T}^2/2$.

(c) Various parameters representing characteristic times. For example, the ratio of energy stored to energy dissipated per second has the dimensions of time ($= J\eta/2$). The terminal relaxation time for a macro-

molecular solution, τ_1 , is usually also of the order of $J\eta$. The time required to attain steady-state flow under constant stress is approximately τ_1 ; after cessation of flow, the stored energy is dissipated by relaxation processes within an interval which is also of the order of τ_1 . For a complete description of the approach to steady-state flow and of the course of relaxation, as well as of other time-dependent rheological processes, a spectrum of relaxation times is usually required.

From experimental measurements of stored energy and of the rate of approach to steady-state flow, or from equivalent information about response to oscillating stresses, conclusions can be drawn regarding the ease of motion of macromolecular segments through their surroundings and the nature of long-range coupling between molecules, as illustrated by the examples which follow.

II. ENERGY STORAGE IN STEADY-STATE FLOW

The storage of energy in very dilute solutions during flow can be attributed qualitatively to the departure from random orientation, familiar from discussions of streaming birefringence, which leads to a decrease in the entropy content in the steady state. The complete rheological behavior can be predicted by considering the interactions between the frictional forces imposed on solute molecules by the flowing solvent and their own Brownian motions, as calculated by Kirkwood and Auer¹ for thin rigid rods and by Rouse² and Zimm³ for flexible coils. The results correspond mathematically to the mechanical models in Fig. 1, where the solvent viscosity η_s is shown added to various viscosity contributions from the solute. For rods, one of the solute contributions behaves as though in series with an elastic spring; for coils, there is an infinite series of solute contributions, each in series with a spring. The magnitudes of some of the model components are given in Table I in terms of the solution viscosity, η , the molecu-

TABLE I. Rheological characteristics of macromolecular solutions.

	Thin rigid rods (Kirkwood and Auer ^a)	Flexible free-draining coils (Rouse ^b)
G_1	$3cRT/5M$	cRT/M
η_P	$(\eta - \eta_s)/4$...
η_1	$3(\eta - \eta_s)/4$	$6(\eta - \eta_s)/\pi^2$
J (very dilute)	$3M[\eta]^2c/20RT$	$2M[\eta]^2c/5RT$
J (concentrated)	^c	$2M/5cRT$

^a Reference 1.^b Reference 2.^c Rigid rods will not form a concentrated disordered solution, preferring thermodynamically to distribute themselves between a dilute disordered and a very concentrated ordered phase.^{4,5}

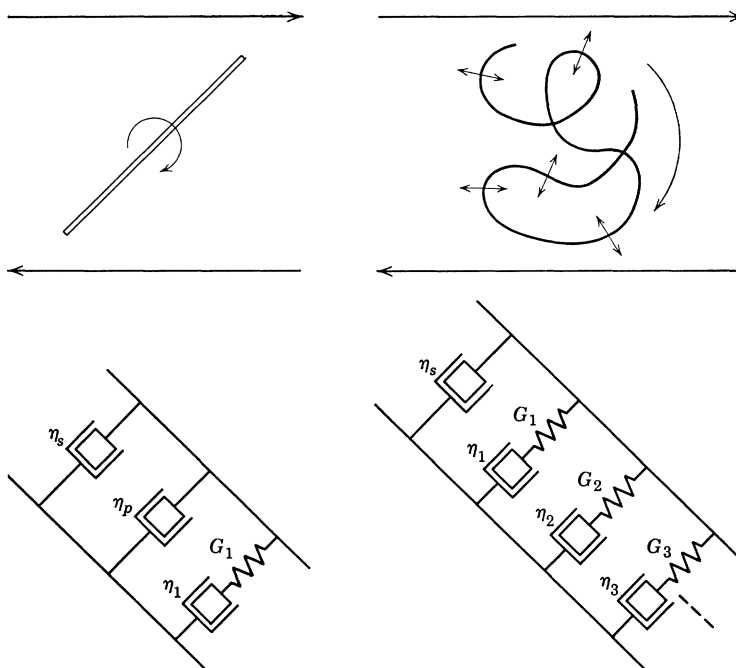


FIG. 1. Mechanical models corresponding to theoretical viscoelastic behavior of dilute rigid rods and flexible coils (below); schematic hydrodynamics (above).

lar weight, M , and the concentration, c (in g/cc). The values for rigid ellipsoids^{6,7} are quite similar to those for rigid rods, and those for coils with internal hydrodynamic interaction³ are somewhat similar to those for the free-draining type. Of course, the portrayal of a mechanical model is not an essential feature, but it aids visualization. The terminal relaxation time (for rods, the only relaxation time) is $\tau_1 = \eta_1/G_1$.

Table I also gives the steady-state compliance for these systems. In very dilute solutions, it is proportional to the square of the intrinsic viscosity $[\eta]$ (expressed here in cc/g) and to the molecular weight. It is interesting that the values for rods and coils differ only by a minor numerical factor. In concentrated solutions (defined by the condition that $\eta \gg \eta_s$), J depends on the molecular weight only; if there are different macromolecular components, it is weighted strongly by those of highest molecular weight.⁸

Under the low stresses which would be necessary to avoid extreme non-Newtonian and non-Hookean effects, the magnitude of the stored elastic energy is quite small. For example, a dilute solution of tobacco mosaic virus⁹ flowing under a shear stress of 10 dyne/cm² would store 25 cal/mole of solute; one of hyaluronic acid¹⁰ (molecular weight 500 000), 0.25 cal/mole. At a concentration of 1%, the terminal relaxation times for these systems are calculated to be of the order of 10^{-3} and 10^{-4} sec, respectively, which are so short as to preclude direct experimental observation of a transient elasticity; macroscopic elastic recoil would be vitiated by the inertia of the solvent. The elasticity could be measured by dynamic experiments, however, as described in the following section. By contrast, the behavior of a concen-

trated solution of flexible coils may be illustrated by a 2% solution of the sodium salt of DNA, which¹¹ under a shear stress of 100 dyne/cm² would store about 200 cal/mole. (Sodium DNA molecules are of course not very flexible, but in concentrated solution exhibit some flexibility which may arise from hinges where the helix is unraveled for short distances.) The elastic shear would amount to about 50%, and the terminal relaxation time is calculated to be of the order of 1000 sec, so a substantial slow elastic recoil is readily observable following cessation of flow. It should be emphasized that to obtain such elastic effects, familiar in various biological systems (mucous and gelatinous secretions, slime molds), it is not necessary to have any linkages between the macromolecules or a netted gel structure.

Under higher stresses, substantial amounts of energy may be stored, but the complications of nonlinear effects prevent making numerical estimates. With a high degree of orientation, the structure of the system may be completely changed by the appearance of ordered phases,^{4,5} and the changes may be irreversible as in the secretion of silk.¹² These phenomena may give some hint of the nature of rheological processes in protoplasm.¹³

III. ENERGY STORAGE AND DISSIPATION IN OSCILLATING MOTIONS

When a stress is applied to a macromolecular system, a finite time of the order of τ_1 is required for the stored energy to build up to its steady-state value. The changes during this transient period are determined by the characteristic relaxation times, or relaxation spectrum, mentioned in Sec. I. Equivalent information about the relaxation times can be obtained, often more easily, by subjecting the system to a sinusoidally oscillating shear

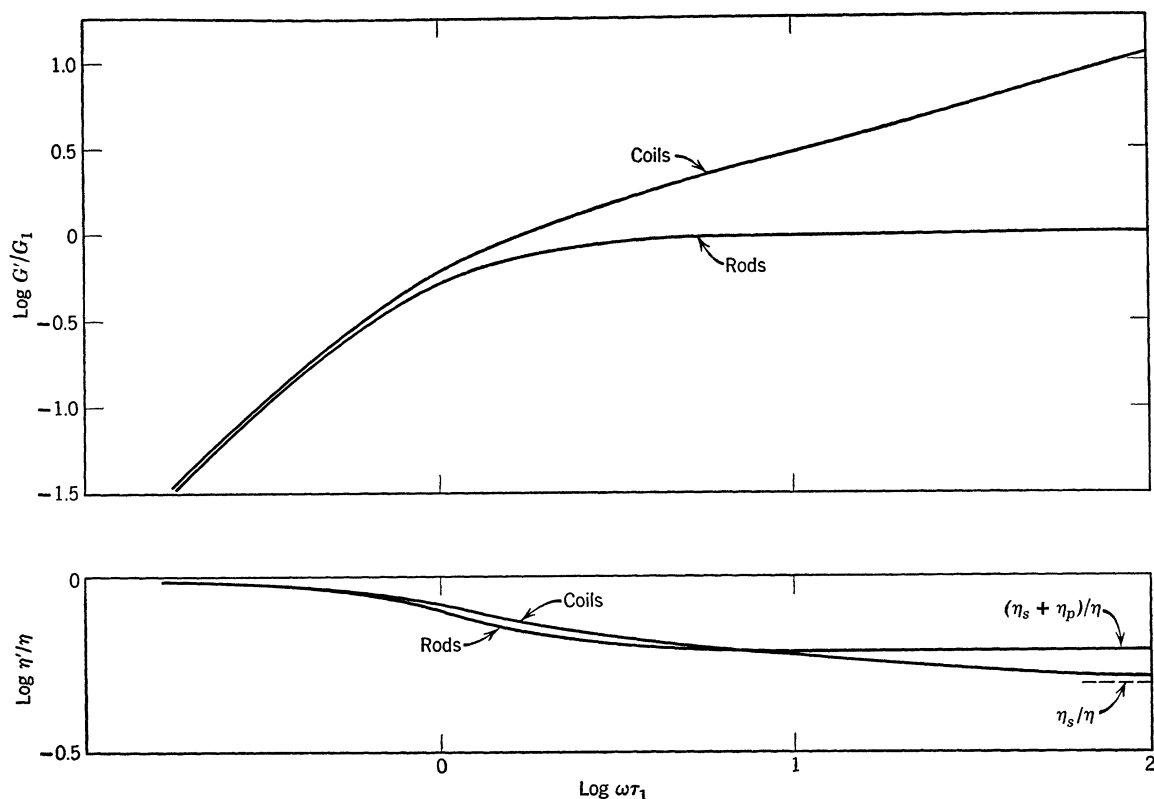


FIG. 2. Predicted frequency dependence of the dynamic storage modulus G' and the real part of the complex dynamic viscosity η' , for dilute rigid rods and free-draining flexible coils, at concentrations such that $\eta = 2\eta_s$.

stress. Here some of the energy is stored and released each cycle, and some is dissipated. The respective values (for a given peak strain) are proportional to the storage modulus G' and the real part of the dynamic viscosity η' , which are defined as the stress divided by those components of strain and rate of strain, respectively, in phase with the stress. Although it is doubtful whether any rhythmic biological processes can be approximated by this pattern, sinusoidal experiments are very useful for deducing the rates of molecular rearrangements.

At very low frequencies, η' approaches the ordinary steady-flow viscosity η , and G' approaches zero. However, the limiting value of $G'/(\omega\eta')^2$, where ω is the radian frequency, remains finite at vanishing ω and is in fact the steady-state compliance J . With increasing frequency, G' increases and η' decreases monotonically. These changes correspond to the obvious expectation in the mechanical models of Fig. 1 that with increasing frequency the motions will occur more in the springs and less in the dashpots. On a molecular scale, they mean that, as the period of oscillation is shortened, there is less opportunity for Brownian motion (rigid rotatory diffusion for rods, configurational rearrangements for coils) to erase the orientation imposed by the external deformations.

The characteristic frequency dependence expected for two simple cases is shown in Fig. 2, calculated for dilute

solutions at a concentration such that $\eta = 2\eta_s$. For rigid rods,¹ there is a single relaxation time; G' should approach a limiting high-frequency value of G_1 , and η' should approach $\eta_s + \eta_p$ (cf. Fig. 1 and Table I). Measurements of transverse wave propagation in solutions of rod-like intermediate polymers of fibrinogen are in rough agreement with this prediction.¹⁴ For free-draining flexible coils,² there is a spectrum of relaxation times reflecting various degrees of cooperation between neighboring segments in configurational rearrangements; η' should decrease and G' increase more gradually with increasing frequency, following slopes of -0.5 and 0.5 , respectively, on a doubly logarithmic plot, as the motions responding within the period of oscillation become restricted to shorter range cooperation. Eventually η' should approach η_s , and G' should attain a very high value of the order of the rigidity of a hard glass multiplied by the volume fraction of solute (this limit, which is not taken into account in the theories quoted,^{2,3} corresponds to complete lack of configurational rearrangement within the period of oscillation, and is probably of no relevance to biological conditions). At present there are no data of this sort on polymers of biological origin; measurements on dilute solutions of synthetic polymers follow the general course shown in Fig. 2, although a somewhat different slope would be expected because of hydrodynamic interaction.³

Concentrated, rather than dilute, solutions are of primary interest in biological systems. Here the frequency dependence of dynamic mechanical behavior is more complicated, as shown in Fig. 3 for a 1.2% solution of sodium DNA.¹¹ Although the coils of this polymer have perhaps only moderate flexibility, the behavior follows a well-established pattern common to many flexibly coiling polymers of high molecular weight in concentrated solution.¹⁵ There is an intermediate frequency range in which η' falls steeply and G' changes relatively little. This is associated with long-range coupling phenomena which cause the motions of one molecule to influence those of others separated by considerable distances but connected by some kind of chain of entanglements or coupling points.

The intermediate region—often called the plateau zone—lies between two extreme regions where the mechanical behavior is dominated by quite different physical processes. At high frequencies (corresponding to short times in transient experiments), the relaxation times are determined by the local friction of a short coil segment moving through its surroundings, oblivious of long-range coupling. The frequency dependence of G' and η' follows the Rouse theory for free-draining flexible coils, and from it the magnitude of the local friction can be calculated (Sec. IV). At low frequencies (corresponding to long transient times), the relaxation times are determined by the long-range coupling, which in turn is reflected in the steady-flow viscosity (Sec. V).

All the oscillatory phenomena described here relate to macroscopic deformation in shear. High-frequency measurements of G' and η' can be made by wave-propagation experiments provided shear waves are employed. In most sonic and ultrasonic wave-propagation experiments, however, the waves are longitudinal and the deformation is a combination of shear plus bulk compression. The energy storage is almost entirely due to the compression, in which, for a polymeric solution, the solute would play a minor role.

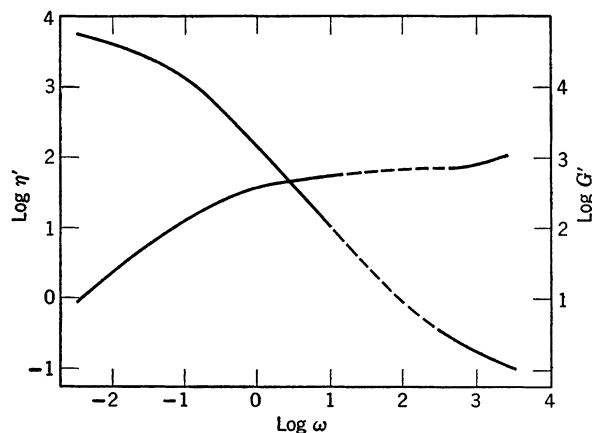


FIG. 3. Observed frequency dependence of G' (ascending curve) and η' (descending curve) in a 1.2% solution of sodium DNA.¹¹

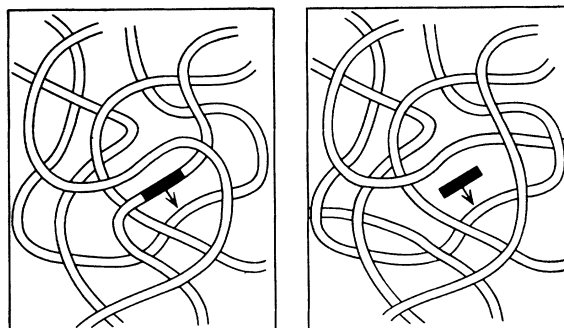


FIG. 4. Schematic representation of translational friction for a unit of a macromolecular chain (left) and a small foreign molecule in a macromolecular matrix (right).

IV. LOCAL MOLECULAR FRICTION

The frictional forces encountered by a short segment of a flexible coil as it pushes its way through its surroundings in a concentrated solution are very complicated but can, on the average, be described by a friction coefficient per monomer unit, ζ_0 , which is force per unit velocity. This represents the same sort of translatory friction which a foreign molecule encounters in diffusion (Fig. 4). For certain soft synthetic polymers (with no diluent present), it has been possible to compare the friction coefficient per monomer unit of the wriggling chain, calculated from rheological measurements such as those in Fig. 3, with the friction coefficient of a foreign molecule similar in size to the monomer unit, obtained from diffusion measurements where only a trace of the foreign component is present.¹⁶ They are actually of similar magnitude—for example, in polyisobutylene at 25°C, 4.5×10^{-5} dyne sec/cm for the chain unit, and 3.8×10^{-5} for a pentane molecule.

The friction coefficient reflects a sort of local viscosity which involves pushing aside solvent molecules together with short segments of other polymer coils in the immediate vicinity. A very crude estimate of the effective local viscosity η_e can be obtained from Stokes' law ($\zeta_0 = 6\pi\eta_e r$), taking r as the radius of a sphere with the volume of a monomer unit. When the solution is not highly concentrated, the limited information available indicates that η_e is not far from the solvent viscosity,¹⁷ and is thus much smaller than the macroscopic steady-flow viscosity. With increasing polymer concentration, ζ_0 and η_e increase rapidly, but not nearly as rapidly as does the macroscopic viscosity η . The most extreme divergence is reached in an undiluted soft polymer; for the polyisobutylene quoted above, for example, η_e is about 70 poises and η is 10^{10} . For sufficiently high molecular weights, ζ_0 and η_e are independent of molecular weight, since the local motions are oblivious of the distant ends of the macromolecules. But η increases very rapidly with molecular weight, often with the 3.4 power.¹⁸

It is evident that the effective local viscosity encountered in translatory friction of a foreign molecule

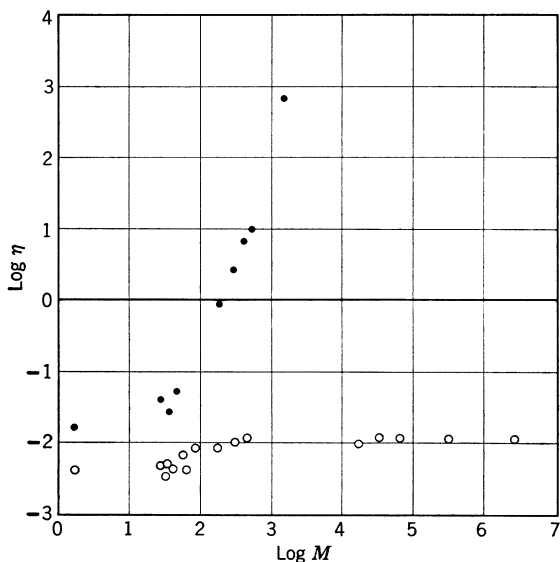


FIG. 5. Local effective viscosities of small organic molecules in soft rubber (black points) and in water (open circles), plotted against their molecular weights on a doubly logarithmic scale (after F. Grün²²).

should increase continuously with molecular size as its motion involves increasingly long-range cooperation of the coil segments which rearrange around it. When the size reaches a magnitude such that long-range coupling affects its motion, there should be a large increase in η_e , and eventually for macroscopic dimensions of the moving particle η_e must approach η .

There are some fragmentary examples of a striking dependence of local effective viscosity on the size of a moving particle, derived from measurements of centrifugation and diffusion in matrices of flexible coils. Bushy stunt virus molecules sedimented in an approximately 0.1% solution of sodium DNA encountered an effective viscosity only 20% higher than that of the solvent, in studies by Schachman and Harrington,¹⁹ while much larger polystyrene latex particles encountered a viscosity higher by a factor of 30. A size dependence for the effective viscosity of latex particles of different diameters sedimenting through concentrated sodium-polyacrylate solutions has been found by Ferry and Morton.²⁰ Diffusion of sucrose in concentrated aqueous solutions of polyvinyl pyrrolidone, studied by Nishijima and Oster,²¹ showed that the local effective viscosity encountered by the sucrose was independent of the molecular weight of the polymer and far smaller than the macroscopic viscosity. Finally, measurements of diffusion of various organic compounds, with molecular weights ranging up to 1000, in undiluted soft rubber enabled Grün²² and Kuhn²³ to calculate effective local viscosities which increased very rapidly with molecular size, as shown in Fig. 5. (The figure also shows effective viscosities calculated from diffusion measurements in water, which, by contrast, simply correspond to the

macroscopic viscosity of water over the whole molecular-weight range.)

The magnitude so fall relaxation times reflecting configurational changes of the sort described by the Rouse theory are proportional to ζ_0 . With increasing temperature, ζ_0 falls and the relaxation spectrum shifts to shorter times without changing its shape; curves such as those in Fig. 3 shift to higher frequencies without changing their shapes. For biological systems, temperature changes are probably much less important than concentration changes. With a decrease in polymer concentration, which might arise from osmotic flow, ζ_0 could drop sharply, speeding up all molecular rearrangements and conceivably allowing stored mechanical energy to be dissipated or to accomplish macroscopic movements.

V. LONG-RANGE COUPLING PHENOMENA

The plateau zone in Fig. 3, observed in all high molecular-weight polymers in concentrated solution or the undiluted state, represents qualitatively the behavior to be expected if the macromolecules were coupled together quite strongly, though slipping to some extent, at widely separated points.²⁴ The same concept of long-range coupling explains another widely observed phenomenon in the dependence of the steady-flow viscosity on molecular weight.²⁵ A doubly logarithmic plot of viscosity against molecular weight or degree of polymerization shows a sharply increased slope above a critical value of the abscissa, which in typical cases corresponds to $M = 10\,000$ to $50\,000$ (Fig. 6). The long-range coupling cannot, in general, be attributed to secondary bonding at loci of attraction, because it appears in nonpolar polymers which are quite homogeneous in chemical composition. It is apparently re-

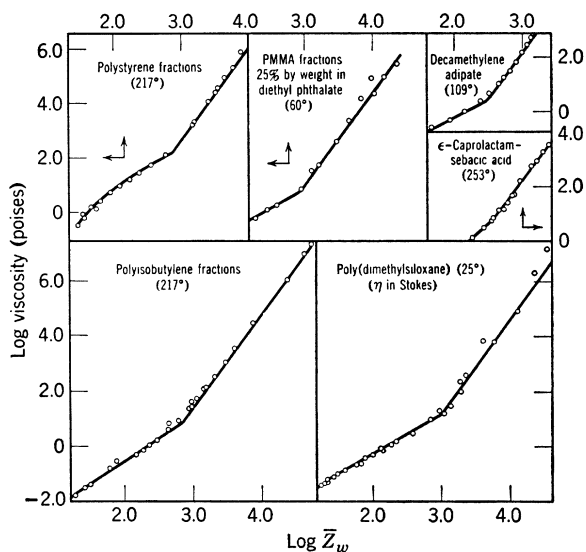


FIG. 6. Doubly logarithmic plots of viscosity against degree of polymerization for several types of synthetic polymers, showing proportionality to the 3.4 power of degree of polymerization or molecular weight above a critical value (after Fox and Loshaek¹⁸).

lated to the expectation that a molecule, in its long-range contour, will form a complete loop enclosing similar loops of other molecules,²⁶ but the topological requirements are not clear. Its influence increases with increasing molecular stiffness, as evidenced by comparing synthetic vinyl polymers, cellulose derivatives, and DNA.¹¹

The terminal relaxation time in a concentrated solution is determined by the long-range coupling, and the extent to which motions of one molecule can influence others, through chains of mutual entanglement. Since the steady-flow viscosity is also dominated by the coupling, however, the order of magnitude of τ_1 can still be estimated by the product $J\eta$.

Quite different from the above topological kind of coupling are the stronger linkages which cause some concentrated polymer solutions to gel. Here bonds of considerable permanence are formed, and the resulting network has no finite viscosity. It has no equilibrium elasticity either; under constant stress it continues to deform indefinitely at a very small and steadily decreasing rate. The spectrum of relaxation times extends indefinitely to long times, probably reflecting a mutual influence between molecular motions which extends throughout the system, communicated through the linkages. This is manifested, for low-frequency oscillating motions, by a very slight decrease in G' with decreasing frequency together with an increase in η' apparently without limit, as illustrated in Fig. 7 for a gel of polyvinyl chloride.¹⁷ In some gels, the linkages are probably very small crystalline regions, tying together handfuls of flexible strands,²⁷ growth of the crystallites being limited by some kind of structural heterogeneity along the macromolecular chain. In others, there may be local secondary bonding of specific chemical groups.²⁸ As an extreme case, primary chemical bonds may join the macromolecules into a network, as proposed for gels of denatured serum albumin^{29,30} and fibrin clots formed with fibrin-stabilizing factor.^{31,32} Thus, while a netted structure is not essential to the storage of elastic energy

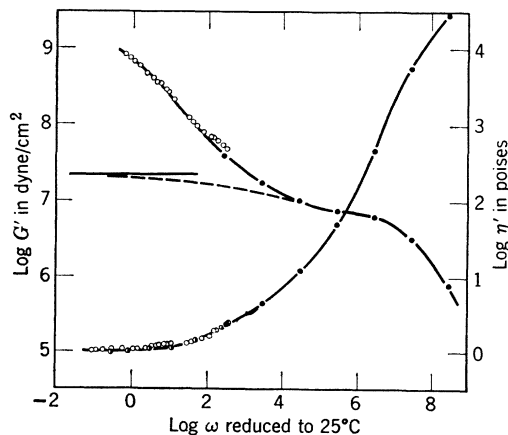


Fig. 7. Frequency dependence of G' and η' for a 10% gel of polyvinyl chloride in dimethyl thianthrene.¹⁷

under stress, it plays an important role when it is present.

The nature of molecular responses to very slow external motions in such networks, involving cooperation among widely separated network strands, is poorly understood. But if the strands between the linkage points are flexible macromolecular chains, the responses to rapid motions will be oblivious of the linkages and their rates will be governed by the local friction coefficient just as in the examples discussed in Sec. IV.

Changes in the consistency of protoplasm¹³ suggest that within it network linkages are sometimes formed and sometimes broken. Such structural modifications should not affect responses to rapid motions but would enormously alter the relative storage and dissipation of energy in slow motions. Correspondingly, they should markedly influence frictional resistance to translation of large particles while leaving the resistance to small molecules essentially unchanged.

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