

RHEOLOGY OF INDUSTRIAL
POLYSACCHARIDES

PT. 2

元



图书馆

Chapter 4

Rheology of polysaccharide systems

4.1 Introduction

The transport properties and, specifically, the rheological behavior of real and complex materials such as polysaccharide systems can be significantly affected by several factors, mainly related to molecular and supermolecular features. Most of these factors are common to all polymeric systems, as they have universal character; others are peculiar to carbohydrate polymers. If we bear in mind the concepts discussed in §1.4, we can easily imagine for polysaccharides a variety of structural conditions much wider than that generally observed for synthetic polymers. On both molecular and supermolecular scales, polysaccharides possess special characteristics that reflect specific behavior so that different classes of materials can be identified.

Let us consider the molecular scale first: at this level, the polymer backbone and its related features, such as its length in solution, shape, stiffness and the eventual presence of ionizable groups, play a major role in determining the macroscopic properties of the system, including its rheology. Many of these molecular parameters correlate among themselves (e.g. chain stiffness and length); others must be combined with external factors such as, for instance, the characteristics of the solvent medium. These latter may, in turn, exert an influence on the conformation adopted by the macromolecule in the medium itself, as well as on the possibility of forming supermolecular structures. In other words, changes in ionic strength, the nature of counterions, temperature or other solvent parameters may induce a conformational transition, thus modifying the hydrodynamic resistance of the macromolecule to flow. Also, if the polymer concentration is high enough, the variations described above may promote structural changes at a supermolecular level and, accordingly, modifications in the rheological behavior. Before leaving this brief comment on solvent characteristics we must mention the viscosity although,

in the case of polysaccharides, its contribution to the viscosity of the whole system can be neglected, water being commonly employed as a solvent for these biopolymers.

We now focus our attention on another parameter that is of primary importance in controlling the structural and, hence, the rheological properties of polysaccharide systems: the polymer concentration C . In sufficiently dilute solutions, the hydrodynamic interactions among the chains play a secondary part with respect to those occurring intramolecularly or with the solvent molecules. Each single macromolecule may be viewed as immersed in a viscous continuum, thus affording its individual contribution to the macroscopic behavior of the system. In concentrated regimes, every chain is at least surrounded by other chains, if not in close contact; this implies that all the possible configurations accessible to a single chain in its Brownian fluctuation are greatly reduced by virtue of topological constraints represented by other polymer molecules.

Starting from these fundamental ideas, several different kinds of molecular theories have been proposed for modeling polymeric fluids. For instance, if we refer to a permanent network of chemically crosslinked chains, then concentrated polymer solutions can be viewed as temporary *entanglement networks*. According to this physical model, the impossibility for the chains to cross each other by cutting through their backbones is converted into the concept of entanglement. Entanglements then play the role of temporary crosslinks and constitute the physical junctions that are continuously disrupted and reformed among the chains.

A somewhat different picture of concentrated polymeric systems is given by *reptation models*. Here, each macromolecule is confined in a tube-like region, whose contours vary with time, being settled by the surrounding chains. In place of the localized entanglements among neighboring chains or chain segments, the tube walls exert a continuous and uniform constraint through the repulsive potential, which keeps the chain close to the tube axis. The chain is effectively hindered in its lateral motion and the only way a molecule can move is by diffusion along the tube. It is a wriggling, snake-like motion and the process has the aptly descriptive name of reptation. This apparently one-dimensional process does not imply that the diffusion is not isotropic in three-dimensional space because, as the chain moves randomly back and forth in the tube, its ends, alternatively, are free to choose any direction in space.

Now, if the polymer chains have flexible backbones, the spatial configurations of two adjacent molecules are not correlated: the mutual interactions are given only by the temporary entanglements that may set up and break down between two chain segments or, according to reptation theories, by the contribution that each molecule affords the contour of the tube-like region where a molecule is confined. Conversely, if the chains are rigid and can be treated as long rods, the relative orientation of each given rod is still random, so that the whole system appears to be isotropic. There are situations, however, where this is no longer valid. Indeed, a critical polymer concentration exists, that marks the formation of a *liquid crystalline phase*, in

which a preferred direction of molecule orientations takes place. Under these conditions, the structure of the system is made up of randomly oriented domains of anisotropic regions embedded in an isotropic phase. Further increases in concentration lead to a totally anisotropic system. In a shear regime, the domains orient themselves in the flow direction and, depending on the type of flow, they deform and, eventually, the domain structure can be destroyed. It should now be clear that the orientation and modification processes of the domain structure are fundamental in governing the rheological behavior of polymer liquid crystals. In passing, we must remark that, in a condition of domain total breakdown, the scale order of the orientation process induced by flow is again molecular so that the macroscopic behavior approximates that of concentrated polymer solutions.

Other ordered forms can be adopted by polysaccharide systems, which require the alignment and interaction of two or more chain segments, usually with long regions of regular covalent sequence. Often, such regions are terminated by changes in sequence which are incompatible with the ordered association. An important consequence of these interruptions is that a single chain can pass through several chain associations, each involving a different partner, with the result that a three-dimensional network, or *gel structure*, is set up. For polysaccharides, relevant forces to intermolecular associations are hydrogen bonding, Coulombic, dipole-dipole, van der Waals, charge transfer and hydrophobic interactions. These secondary interactions are individually weak and their number and position can, and do, fluctuate with time and temperature. Transitory interchain connections provided by such forces, if uniformly distributed throughout the system, are ineffective in producing a *physical gel*. In contrast, if the interchain forces act cooperatively so that a sufficient number of adjacent segments are involved in the formation of extended *junction zones*, then the permanency of the interconnections is enormously enhanced and clusters of molecules dispersed in a continuous phase can be formed, even at low polymer concentration C . Increasing C over a threshold value will eventually lead to a continuous three-dimensional network, where the *junction zones* play the part of the point crosslinks in covalent gels. The continuity of the structure then reaches macroscopic dimensions and possesses a degree of permanency that confers to the system the solid-like properties characteristic of physical gels.

Nevertheless, substantial differences exist between the structures of physical gels and of covalently crosslinked networks. Firstly, the former contain large amounts of solvent and are prepared by crosslinking in the presence of the solvent itself. Second, physical gels are not homogeneous over the entire distance scale, and frequently a specific and intricate hierarchy of structure can be distinguished within the system. Various levels of heterogeneity are encountered in non-covalently crosslinked networks, depending on the different mechanisms of chain association, the extension of the *junction zones* and their distribution through the system.

It is then a daunting if not impossible task to develop a systematic understanding and

classification of something so complex as polysaccharide physical gels on the mere basis of their structural differences. On the other hand, rheology may be helpful in providing a first rough classification of gels into two major categories: the *strong* and the *weak gels*. Under small deformation conditions, the mechanical spectra of strong gels approximate closely to solid-like behavior. When subjected to large deformation or continuous flow conditions, the gel network ruptures into smaller gel regions with discontinuity surfaces running throughout the system. The flow conditions then become heterogeneous. This is not the case for weak gels, which may flow homogeneously, even under continuous shear conditions. They exhibit marked non-Newtonian properties, strictly connected to the progressive disruption of the network into smaller flow units as the shear rate is increased.

Let us go further in considering the interplay between physical gelation and solubility. Physical gelation is intrinsically connected with the formation of junction zones, which can be regarded as separate insoluble regions distributed in a soluble matrix. The stability and macroscopic integrity of the gel strongly depend on the balance between polymer-polymer and polymer-solvent interactions. When polymer aggregation is favored, segregation into two phases may take place or interchain association may be restricted to small *microgel* clusters dispersed in a macromolecular solution.

Microgel formation is not the only way in which polysaccharide dispersions can be obtained. Sometimes the attempt to dissolve a high crystalline native polymer results in a system made up of swollen particles suspended in a continuous medium. Whatever the case, the rheological behavior of disperse systems depends on the volume fraction of the disperse phase, the rigidity of the particles and the rheological properties of the continuous phase. At high disperse phase concentrations, microgel and particle dispersions display solid-like behavior at low stresses and their rheological properties cannot be easily distinguished from those of weak gels.

In concluding this brief survey we must mention *mixed* and *filled gels* which, although to all outward appearances are very complex, show rheological features not far from those of the other structured systems described above.

4.2 Dilute solutions

As a start, let us consider polymer solutions where the dissolved chains do not interact among themselves and only intramolecular hydrodynamic interactions may occur. This condition is encountered only at very low values of polymer concentration C , i.e. for C tending to zero. *Infinitely dilute solutions* of flexible macromolecules may be viewed as systems in which islands of polymeric coils are scattered in the sea of a liquid solvent and almost never impinge

or interpenetrate; in other words, the individual coils are well separated from one another and are free to move independently. When a shear field is applied to such systems, the flow behavior of each single molecule is not affected by the presence of any other molecule at all, and the total rheological response of the solution can be considered as the sum of the individual contributions of the molecules.

Increasing C gradually leads to an increase in the statistical probability of intermolecular interactions: the collision of islands becomes more frequent and causes the chain to overlap or interpenetrate in a complex fashion. To picture this situation we can assume a physical model in which each polymer coil and the solvent bound to it are associated to a hydrodynamic impenetrable sphere. Consequently, it is possible to set an *a priori* upper boundary of the dilute region as that condition where the polymeric spheres begin to touch one another throughout the solution. The corresponding C value, usually designated as C^* , is the so-called *coil overlap concentration*.

As a rule when simple models are assumed, this sketch is only a rough approximation of the real physical state of the system. Two major criticisms can be made of it: the first is that, having an open structure, actual polymer coils start interpenetrating as soon as the solution leaves the state of infinite dilution; the second, far more important, is that this model is unsuitable for the description of rigid elongated macromolecule solutions. More sophisticated and complete models have also been developed, in which each segment-segment interaction among all different chains has been mediated on a statistical basis. These treatments are necessarily complex in their expressions as they must take into account all possible factors that contribute to the chain conformation which, for flexible random coils, fluctuates continuously under Brownian motion. Thus, despite the high degree of approximation involved, the impenetrable sphere model constitutes an easy and useful tool that is widely adopted in the current polymer literature.

From the simple considerations developed above, we can now conclude that all the possible states for a system between infinite dilution and C^* may be generically defined as *dilute solutions*. In the corresponding range of C , the single macromolecules afford their individual contribution to the rheological properties of the system, independently of the imposed shear regime (laminar, turbulent or extensional). What this does imply is that, under a given flow condition, the quantitative or qualitative differences in rheological behavior can be ascribed to distinct molecular characteristics.

Let us consider, for instance, a continuous laminar flow: in the case of rigid rodlike molecules the motion induces a progressive orientation of the chain along the lines of the shear field whereas, for flexible chains, this orientation effect combines with a stretching of the coils. It is easy to imagine that these different mechanisms imply different dependences of the material functions η , N_1 and N_2 upon the applied shear rate $\dot{\gamma}$. Other structural features play a

role in determining the flow properties of a system, and a notable example can be found in turbulent regimes, where long-chain flexible linear backbones have important characteristics for good drag reducing agents.

4.2.1 Steady shear viscosity

Until recent times, dilute polymer solutions attracted only occasional interest in rheological studies. From the standpoint of industrial research, the lack of experimental work can be explained by considering that the industrialist, for obvious reasons, is driven by a pragmatic motivation: the limited possibility of exploitation of these systems.

Frequently, when dealing with the rheological behavior in shear flow conditions of dilute solutions, one is tempted to treat it as Newtonian. Although this approximation can be justified for many practical industrial purposes, it is no longer valid for a basic analysis of the system properties on a molecular scale. Indeed, even very dilute polysaccharide solutions exhibit an apparent viscosity that depends on shear rate and, in analogy with synthetic polymers, this effect is greater for rigid macromolecules.

The experimental observations on the non-Newtonian behavior of dilute solutions that can be found in literature mainly concern the study of the material function $\eta(\dot{\gamma})$ under steady simple shear flow. It is instructive to start the examination of a series of selected examples by considering two bacterial polysaccharides that belong to the conformational class of rigid rods: schizophyllan and scleroglucan. These extracellular homoglucons dissolve in water as molecules made up of three linear chains wound in a rodlike triple helix (also called a *triplex*). When dissolved in dimethylsulfoxide (DMSO) or in $\text{NaOH} \geq 0.1 \text{ M}$, the helices dissociate and the individual chains assume random coil configurations. Clearly, these two conformations give rise to different rheological behaviors in solution, easily discernible even at low C . Let us consider Fig. 4.1 (a), which shows shear viscosity data for a series of dilute aqueous solutions of schizophyllan triple helices [1]. Even though the C range is not much extended towards high dilutions, we can observe that all systems are shear-thinning. Such behavior may be viewed as being of modest proportions but, even for the lowest C value, we can calculate a twofold change in viscosity over two decades of $\dot{\gamma}$. The shear-thinning behavior is associated with the progressive orientation of the triple helices in the shear field as $\dot{\gamma}$ is increased. When the full orientation of the molecules is attained, we can expect these solutions to reach the upper Newtonian plateau, characterized by the constant infinite-shear-rate viscosity η_{∞} . In the case of Fig. 4.1, the highest applied shear rate is too low to predict the existence of this second Newtonian region.

Contrary to aqueous solutions, this polysaccharide in the random coil conformation (DMSO) shows a Newtonian character, which is verified up to the highest C in the entire range

of $\dot{\gamma}$, as depicted in Fig. 4.1 (b) [1]. This Newtonian behavior is expected for single flexible random coils that show far less anisotropy and shear orientation than the rigid helices. Analogous results have been obtained for scleroglucan in $\text{NaOH} \geq 0.1 \text{ M}$ [2].

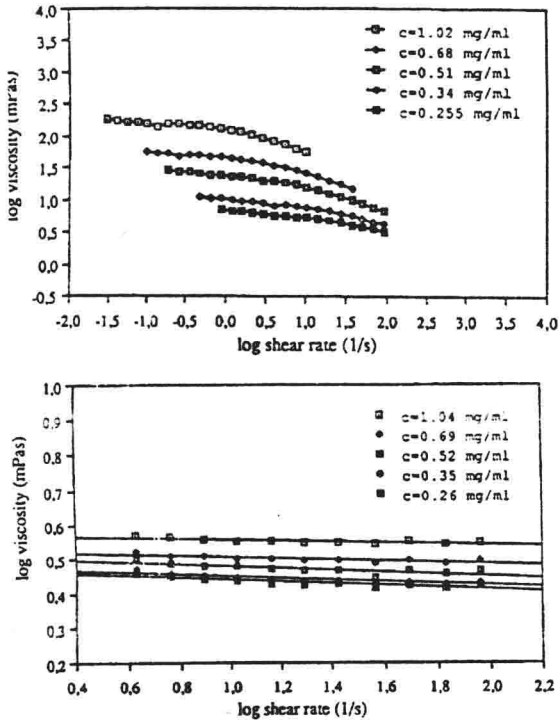


Fig. 4.1. Shear viscosity data for schizophyllan solution in (a) (top) water and (b) (bottom) DMSO. $T = 20^\circ\text{C}$. From [1] (with permission of Steinkopff Verlag).

The second example concerns a microbial polysaccharide which does not need further introduction: xanthan gum. There has been much discussion in the literature as to whether xanthan in salted aqueous solutions has a single or a double-stranded helical structure. The strandness appears to depend on bacterial origin, thermal history, post-fermentation processing and degree of acetate and/or pyruvate substitution in the side chains [3-9]. Nevertheless, data from several different techniques indicate that xanthan conformation can be modeled as a worm-like coil [10]. Let us consider the first four η - $\dot{\gamma}$ curves reported in Fig. 4.2, which belong to the dilute regime for xanthan in 0.1 M NaCl [11]. In the range of $\dot{\gamma}$ explored, obtained with capillary viscometers and covering three decades, we can observe that, even for the lowest C ($2.5 \cdot 10^{-3} \text{ g/dl}$), data demonstrate the existence of a lower Newtonian plateau, followed by the shear-thinning zone. Other papers are available in the literature, in which the

corresponding flow curves seem to approach the second Newtonian region [12-15].

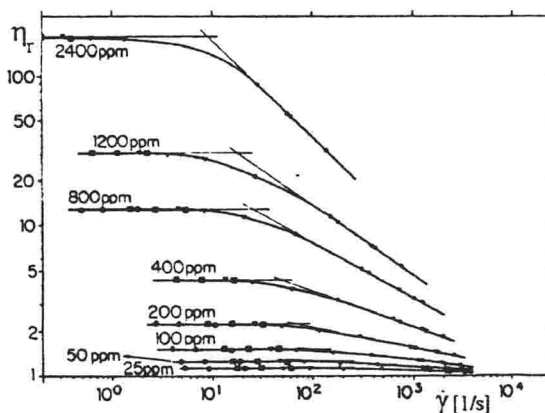


Fig. 4.2. Viscosity-shear rate curves for xanthan solutions in 0.1 M NaCl at different polymer concentrations. $T = 30^\circ\text{C}$. From [11] (with permission of the American Institute of Physics).

The sensitivity of viscosity η to ionic strength I is typical of polyelectrolytes, which normally exhibit high viscosities at low I , due to an expanded chain conformation caused by charge-charge repulsions. Such repulsions are screened at higher I , leading to a more compact conformation and, hence, lower viscosities. This trend is confirmed for xanthan by a comparison of viscosity data from different authors reported in Fig. 4.3, in a η - τ coordinate system [11,13,16]. Also, the transition from Newtonian to shear-thinning behavior takes place at a critical shear stress τ_c , which is a function of the ionic strength but does not depend upon polymer concentration. This is evident from data in 0.1 M NaCl in Fig. 4.3 (a) and (b), and can be expected from data in distilled water (Fig. 4.3 (a)), although data in the Newtonian region are not available for these systems.

Xanthan solutions in 0.1 M NaCl are suitable systems for obtaining a variety of experimental data on which academic scientists may speculate with molecular interpretations. Different solvent conditions, however, can be of interest for industrial evaluations and applications of this polysaccharide. We know, for instance, that xanthan is of potential use in polymer flooding and permeability modification of oil containing formations. Rheological comparisons of polymer batches under solvent conditions used in oil fields already constitute routine quality performance tests in oil companies prior to pilot polymer flooding experiments. The solvent system usually utilized is synthetic seawater, in which the selected salt composition is close to that of the injection water of the corresponding oil field.

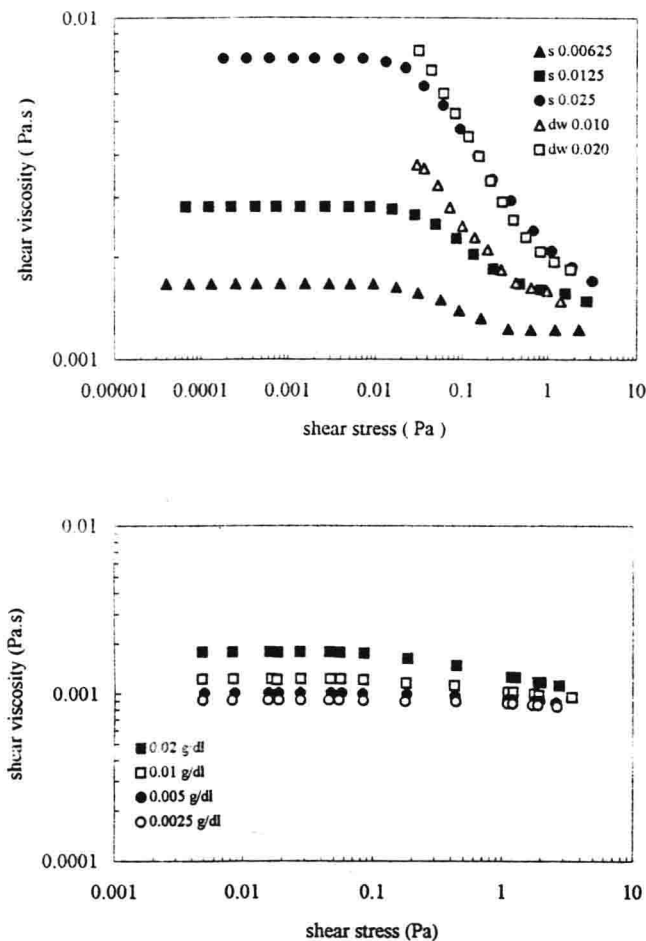


Fig. 4.3. Viscosity vs. shear stress for xanthan in 0.1 M NaCl and distilled water at different polymer concentrations. (a) (top) Filled symbols: data for salt solutions from [13], open symbols: data for distilled water from [16]. (b) (bottom) Data for salt solutions from [11]. Concentrations are expressed in % w/w.

One example of experimental work carried out to examine the influence of salinity on the rheological properties of xanthan solutions is reported in Fig. 4.4, where only the first three curves (from bottom) refer to the dilute regime [17]. Provided we do not rely on data at $\dot{\gamma} = 1 \text{ s}^{-1}$ (accuracy problems arise in the measurement of such low η values), the curves show a Newtonian plateau followed by a power-law region, a trend very similar to those discussed before.

Succinoglycan is another extracellular polysaccharide of possible use in enhanced oil recovery (EOR). A number of experimental data suggest that succinoglycan, like xanthan, can adopt an ordered, rigid helical conformation with partial lateral aggregation in water and aqueous NaCl solutions [18,19]. In fact, the uncharged backbone should be rather stiff because of the 1,4 and 1,3 enchainment of GlcP and GalP residues, and the terminal portion of its side arms may be also conformationally stiffened by the presence of two consecutive 1,3-linked β -D-GlcP residues bearing two fixed charges. The rheological properties of succinoglycan dilute solutions are quite similar to those exhibited by xanthan under the same experimental conditions [20].

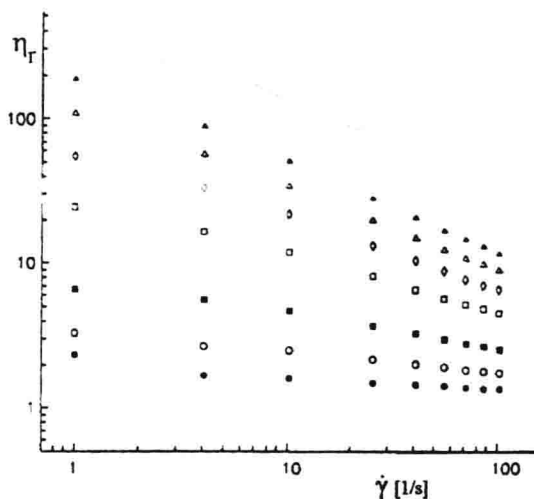


Fig. 4.4. Relative viscosity vs. shear rate for xanthan in synthetic seawater at different concentrations: (●) 0.05% w/w, (○) 0.1%, (■) 0.2%, other symbols refer to concentrated regime. $T = 20^{\circ}\text{C}$. From [17] (with permission of Elsevier Science Publishers B.V.).

We now make passing reference to polysaccharides that behave as more or less stiffened random coils in solution. Hydroxypropyl guar gum (HPG) is a synthetic derivative of guar galactomannan, obtained by reaction of the native polymer with propylene oxide in the presence of an alkaline catalyst. It finds extensive use in food, textile, printing and oil industries as a thickening agent. As we can see from the first three curves (from bottom) of Fig. 4.5, HPG dilute solutions exhibit Newtonian behavior in the entire shear rate range explored (three decades) [21]. Analogous considerations have been drawn by Sharman et al. on dilute solutions of galactomannans extracted from various sources [22].

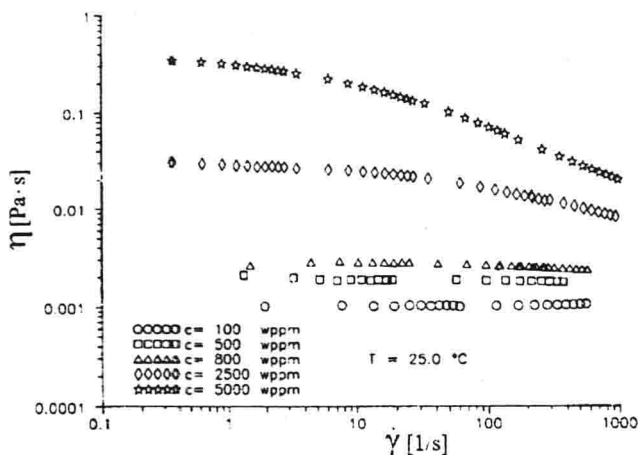


Fig. 4.5. The shear viscosity of HPG aqueous solutions as a function of shear rate for various concentrations. From [21] (with permission of Steinkopff Verlag).

Brownsey and coworkers have found that both acetylated and deacetylated geilan gum form true molecular solutions in 90% DMSO at concentrations less than 0.4 g/dl. As a consequence of the coiled shape adopted by the macromolecule in this solvent, the correspondent solutions are characterized by an extended lower Newtonian plateau, up to $C = 0.39$ g/dl [23]. Further evidence of the role played by chain flexibility on the non-Newtonian properties of dilute solutions comes from dextran, the archetype of 'true' random coil polysaccharides. For dextran systems, in fact, the lower Newtonian plateau extends to elevated $\dot{\gamma}$ values, even for high molecular weight samples [24,25].

4.2.2 Normal stresses

Even if we expect that normal stress effects may arise also in dilute polymer solutions as a direct consequence of η dependence on $\dot{\gamma}$, the available experimental information is quite limited, particularly for polysaccharides. Three main reasons may be put forward to explain this fact:

- normal stresses are material functions usually ignored by people from outside the academic world;
- there is an objective difficulty in gathering reliable experimental data for N_1 , and especially N_2 , deriving mainly from the characteristics of most accessible commercial rheometers;
- even when rheometers capable of determining N_1 and N_2 are available, potential sources of errors lie in instrument sensitivity and inertial effects. In fact, inertial corrections often are higher than the experimental value itself.

It is probably true to say that there are only two examples in the literature concerning normal stresses of dilute polysaccharide solutions. The first is an experimental work carried out by Bewersdorff and Singh on xanthan [15]. Figure 4.6 contains the first normal stress difference N_1 together with the shear stress τ vs. the shear rate $\dot{\gamma}$ for xanthan in the dilute regime (up to $C = 0.01$ g/dl). In the whole range measured, the dependence of N_1 on $\dot{\gamma}$ follows a power-law relationship, with exponents ranging between 1.75 and 2. If we compare the profiles of N_1 and τ , what we observe are unexpected high values of the stress ratio ($N_1/2\tau$). This is a definite indication that the study of normal stress effects in dilute polysaccharide solutions is at its very beginning, and further investigations should be promoted to confirm these first results.

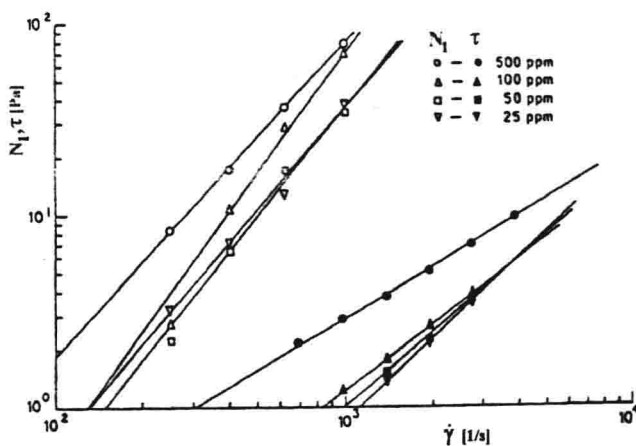


Fig. 4.6. First normal stress difference and shear stress vs. shear rate for xanthan aqueous solutions at different polymer concentrations. From [15] (with permission of Steinkopff Verlag).

In 1973, Jones and coworkers suggested a procedure for the indirect evaluation of normal stresses in dilute polyacrylamide and xanthan solutions [26]. The method requires experimental information on Taylor instabilities and the assumption of a rheological equation of state containing a limited number of material constants. The physical phenomenon that lies behind the theory is the suppression of toroidal vortices in Couette flow, obtained by the addition of small polymer amounts. Despite the arbitrary assumption of a constitutive equation and the difficulty of using this technique - which accounts for its low popularity with experimentalists - this procedure can make up for the lack of direct rheometrical measurements, due to the high sensitivity of instability and turbulence phenomena to concentrations of the order of ppm.

4.2.3 Dynamic viscoelastic moduli

It is universally agreed that mechanical spectra are basic elements for the analysis of the viscoelastic response of materials. Also, they provide a popular ground for the validation of models based on molecular theories, or derived from continuum mechanics principles.

When an oscillatory flow field is applied to a dilute polymer solution, and the imposed deformations are small enough to correspond to the usual restrictions of linear viscoelastic behavior, the energy storage per cycle depends on G' and is contributed by the polymeric solute molecules alone, whereas the energy dissipation depends on G'' , and has contribution from both solute and solvent. The relative contributions of the solute to G' and G'' depend on the extent to which the configuration changes, produced by Brownian motions, are correlated with the external forces.

Let us consider for simplicity the case of a linear flexible macromolecule. On a scale of atomic dimensions, the configurational motions must be accounted for by rotations around all the bonds in the chain backbone.

For very high frequencies of oscillation ω there will be no time for any internal rotation within a period of alternation, and the response of the polymer molecule will be limited to bending and stretching chemical bonds. At lower ω , regions of the chain not too far removed from each other have time to change their relative positions within a period of cyclic deformation; each coil deforms more easily. At very low frequencies, all possible configurational rearrangements occur within the period of a cycle: the coils deform so easily that the force in phase with displacement is negligible and G' vanishes compared to G'' .

Despite the manifest importance of experimental data, the lack of data parallels that of normal stresses. This contradiction is only an illusion. Indeed, to obtain measurable values of the viscoelastic quantities for dilute solutions we must either resort to high sensitivity instruments, or extend the effective frequency range towards extremely high values of ω . This can be attained only with specialized devices.

The only example of a mechanical spectrum referred to an individual system is that reported in Fig. 4.7 for xanthan in distilled water [27]. The authors have been able to gather data in the low frequency region, where the slopes of G' and G'' curves tend to 2 and 1, respectively.

Finally, in two interesting papers Carriere et al. underline how a recently designed rheometer, the so-called *multiple-lumped resonator*, permits measurements of the viscoelastic properties for schizophyllan solutions at sufficiently low concentrations and over a wide frequency range, to provide for extrapolation to infinite dilution [28].

Accordingly, useful information can be extracted from the polymer configuration in different solvent media.

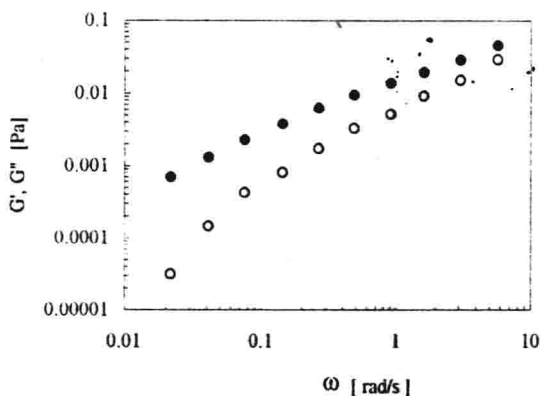


Fig. 4.7 Dynamic moduli for xanthan in distilled water. $C = 0.01\%$ w/w, $T = 25^\circ\text{C}$. (O) G' , (●) G'' . Data from [27].

4.2.4 Modeling the shear dependence of η

In the previous sections we have introduced a number of different examples to delineate the flow properties of dilute solutions under shear conditions. As the polymer concentration C is increased, the shear dependent behavior changes from Newtonian to shear-thinning. At the same time, viscoelastic characteristics begin to appear.

If our aim is to evaluate how the rheological properties can be influenced by C and other physical parameters such as pH, ionic strength and temperature, then we should attempt to fit experimental data with rheological models or, at least, with simple phenomenological equations. The analysis is then confined to obtaining a limited number of relevant parameters.

With the choice of a rheological model, expressed in tensorial notation, we can process an entire data base obtained for the shear dependence of different material functions. Moreover, if the model has been derived according to the classical rules of molecular rheology, it is also possible to draw some conclusions about the polymer shape in solution. Among the different constitutive equations derived from the kinetic theory approach [29,30], the models that may be regarded as promising candidates for describing and interpreting nonlinear properties, such as the shear rate dependence of η , are those based on the use of *finitely extensible nonlinear elastic* (FENE) connectors [31-38]. In fact, there is no doubt that not only the crudest model - the Hookean dumbbell model - but also more sophisticated and realistic models (say the Rouse and Zimm chainlike equations [39-40]) are inadequate to describe the shear viscosity function since spring connectors obey Hooke's law. The use of a

finitely extensible spring instead of the Hookean spring takes into account the salient feature of polymer molecules: their limited extensibility.

According to FENE model, macromolecules are idealized as elastic dumbbells, consisting of two spherical beads joined by a nonbendable spring. The force law for the spring in the model has the following form:

$$\underline{F} = \frac{HR}{1 - (R/R_0)^2} \quad \text{for } R \leq R_0 \quad (4.1)$$

where H is Hooke's law force constant and \underline{R} is the orientation vector which specifies the distance between the bead centers and the angular orientation of the dumbbell in space. Such a spring obeys Hooke's law for small extensions R , but becomes stiffer and stiffer when extended; furthermore, the spring cannot be extended beyond an upper limiting length R_0 .

Dumbbell and chain models can be modified and their descriptive capability upgraded. Other effects can be invoked to portray the dependence of η on $\dot{\gamma}$: hydrodynamic interactions, excluded volume, internal viscosity, etc.. The FENE spring modifications, however, are not only the most useful but also allow an interpretation of the model parameters in terms of molecular conformational characteristics.

In the derivation of the rheological equation of state for the FENE dumbbells we must introduce two *time constants* λ_H and λ_R , which account for the Hookean and rigid contributions, respectively:

$$\lambda_H = \frac{\zeta}{4H} \quad (4.2)$$

$$\lambda_R = \frac{\zeta R_0^2}{12kT} \quad (4.3)$$

where k is the Boltzmann constant and T is the absolute temperature. ζ in eqns. (4.2) and (4.3) is the *friction coefficient*, characterizing the hydrodynamic drag experienced by a single bead in motion through the solvent, and is given by the Stokes law:

$$\zeta = 6 \pi \eta_s r \quad (4.4)$$

where η_s is the viscosity of the solvent and r is the bead radius.

After some complex mathematics [31], we can get the shear rate dependence of the viscosity as follows:

$$\eta = \eta_s + \frac{3nkT\lambda_H}{b+5} \left[1 - \frac{9(8b+34)}{(b+5)(b+7)(b+9)(2b+7)} (\lambda_H \dot{\gamma})^2 + \dots \right] \quad (4.5)$$

In the above, n is the number of dumbbells per unit volume and is equal to CN_A/M , where C is the polymer concentration, M is the molecular weight and N_A is Avogadro's number. The extensibility parameter b is defined as:

$$b = \frac{3\lambda_R}{\lambda_H} = \frac{HR_0^2}{kT} \quad (4.6)$$

We must point out that eqn. (4.5) is an approximate expression, which holds only for small shear rates.

The FENE dumbbell applies to all different polymer shapes - from the elastic coil to the rigid chain - and, accordingly, the corresponding $\eta(\dot{\gamma})$ profiles can be described by varying the parameter b , as depicted in Fig. 4.8. When $b \rightarrow \infty$, eqn. (4.5) reduces to the Hookean dumbbell model:

$$\eta = \eta_s + nkT\lambda_H \quad (4.7)$$

whereas, for small b values, eqn. (4.5) approximates the behavior of a rigid dumbbell. For $b \rightarrow 0$, we obtain:

$$\eta = \eta_s + \frac{3}{5}nkT\lambda_H \left[1 - \frac{34}{245}(\lambda_H\dot{\gamma})^2 + \dots \right] \quad (4.8)$$

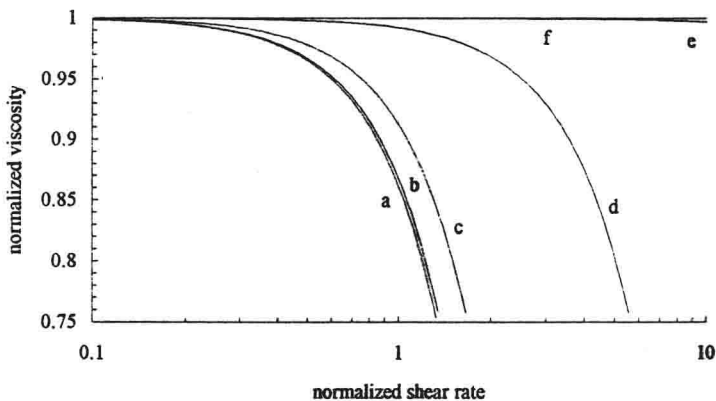


Fig. 4.8. Viscosity profiles predicted by the FENE dumbbell model (eqn. (4.5)) for different b values. a: $b=0$; b: $b=0.1$; c: $b=1$; d: $b=10$; e: $b=100$; f: Hookean dumbbell. Normalizing factors: $\eta_s + 3nkT\lambda_H/(b+5)$ for viscosity and λ_H for shear rate.