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Rheological Behavior of Polysaccharides Aqueous Systems

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I. INTRODUCTION

The relevance of rheology to polysaccharide studies concerns both their practical and their fundamental aspects.

The capacity of polysaccharides to extensively modify the rheology of aqueous media into which they are introduced, even at fairly low concentrations, is the basis of their “functional properties” as thickening and gelling agents. It is also involved in many other types of applications, such as encapsulation, controlled release, etc. Some degree of rheological characterization is essential in particular to evaluate the potential uses of a polysaccharide as extracted from a natural source or subsequently modified.

On the other hand, rheology provides precious tools to explore and understand the properties of polysaccharides in aqueous systems. The rheological behavior of polymer systems manifests the underlying structure of the systems. In the simplest case, that of polymer solutions, viscosity is directly related to fundamental molecular properties (molecular conformation, molecular weight and molecular weight distribution, intramolecular and intermolecular interactions). In the case of more structured polymer systems, gels, for example, their viscoelastic properties are related to supramolecular organization. Although the relation between structure and rheological properties subsequently becomes more complex and less direct, rheology allows us to probe the structure of the systems at different scales, in conditions where other physical methods are impossible or difficult to use. Rheological techniques are especially useful to monitor and to probe structural changes in the systems, such as gelation or phase separation processes.

Polymer rheology, which has been thoroughly studied and set up on firm theoretical foundations, provides a general frame for the investigation and the interpretation of the rheological behavior of polysaccharide systems. However, usually the parallel cannot be drawn very far into the details, particularly on quantitative grounds, as the following short discussion will make clear.

A remarkable variety of physical chemical properties reflect the structural diversity of polysaccharides. Even chemically related polysaccharides can behave quite differently in aqueous media, and, furthermore, in a way which strongly depends on solvent conditions. The same applies by way of consequence to their rheological properties.

Polysaccharides are seldom homopolymers; in most cases, their backbones comprise several types of sugar monomers linked in sequences which, when indeed not totally unknown, are not characterized in detail. The “heteropolymeric” character is responsible for the capacity of many polysaccharides to form gels in certain conditions. Moreover, polysaccharides are often branched polymers; the degree and pattern of branching, the lengths of the side chains, their composition itself in many cases, are generally ill defined. Among the polysaccharides that behave on the whole as linear homopolymers from a rheological point of view, many can be nevertheless grafted with short side chains, in which the number, length, and distribution along the backbone do play an important role in their properties. On the other hand, the presence of a few of sugar heteromonomers inserted along an otherwise uniform linear sequence has a strong effect on the conformation of the chain and its physical chemical behavior. Such limited structural differences often result in a large variety of rheological properties, which can be observed among polysaccharides as belonging to the same chemical class but arising from different biological origins.

Extraction, purification, and fractionation processes are another source of structural diversity. First, some polysaccharide or protein impurities, the nature and quantity of which depend on the purification procedure, are likely to remain in the sample. Their presence has been found to deeply affect the properties of the polysaccharide under consideration, or can be suspected to do so. Supposing this problem is solved, because in the initial material the polysaccharide of interest certainly presents some degree of structural heterogeneity of natural origin, the

exact composition and structure of the purified sample will depend on the way it has been prepared. This is the very consequence of the selectivity of the extraction and fractionation operations themselves. Finally, chemical modifications of the polysaccharide are likely to occur during the preparation of the sample, giving rise to an artifactual heterogeneity; an example is backbone hydrolysis and partial demethylation of pectins during their extraction and purification. Indeed, many different samples may be obtained with as many preparation procedures! As a result, purified polysaccharide samples generally show at the same time very large polydispersity, i.e., they contain macromolecules with widely different molecular weights and polymolecularity—they contain chains with qualitatively similar compositions, but differing in their quantitative compositions and in their structures. With much work, polysaccharide fractions with relatively narrow polydispersity can be obtained (to be used as molecular weight standards, for example), but in most cases, it is practically impossible to avoid some degree of polymolecularity.

One more source of complexity in the behavior of polysaccharide systems is the special nature of the solvent—water—and the delicate balance between chain–chain and chain–solvent interactions (hydrogen bonding, hydrophobic interaction, ionic interactions). Small changes in ionic strength or ionic composition, and limited shifts of temperature can induce a change in the physical nature of the system, e.g., a transition from the state of a macromolecular solution to that of a gel, causing a drastic modification of its rheological behavior.

The polydisperse and polymolecular character of polysaccharides, as they are available in practice, and the fact that their macromolecular structure is generally only quite vaguely known put severe limitations to the quantitative application of polymer rheology theories, whereas their structural diversity and complexity give rise to an extremely rich phenomenology, which largely gives rise to their functional versatility. However, *within a defined physical state*, the rheological behaviors of polysaccharide/(aqueous) solvent systems are amenable to a general pattern, and they essentially differ on quantitative grounds. Structural differences mainly show in the conditions controlling the shift from one physical state to the other (from the solution to the gel and conversely, or from the solution to the dispersion or to the precipitate in phase separating systems). Accordingly, on one hand, theoretical considerations will be kept to a minimum in this chapter. On the other hand, the rheology-relevant specific features pertinent to the different classes of polysaccharides will not be surveyed. Our intention is neither to scan the different classes of polysaccharides, nor to draw a panorama of the application of different rheological techniques in this field; several valuable books and extensive reviews, written along these lines, are available and will be quoted in due place. We shall instead consider the main types of polysaccharide aqueous systems, and show schematically how rheological studies can provide an insight into their organization, focusing more on the common features than on the specific properties of each polysaccharide. The main types of polysaccharide systems that are encountered in the appli-

cations can be distributed schematically in three classes: solutions, gels, and polysaccharide/polysaccharide (or polysaccharide/protein) mixtures in aqueous media. The last class comprises an extremely broad spectrum of systems ranging from mixed solutions to complex structured multiphase systems. Biopolymers, even differing little in composition or structure, are in effect generally incompatible in aqueous media. As a consequence, the simultaneous presence of two polysaccharides (or of a polysaccharide and a protein) in the system results in a variety of microstructures through phase separation processes. These processes can interfere or combine with gelation processes in a way that is highly dependent on the details of the structure of the biopolymers and on the experimental conditions. This gives rise to a fascinating variety of morphologies at different spatial scales, and, among other applications, allows “tuning” the rheological behavior of the systems to suit specific requirements. In spite of the theoretical and practical interest of polysaccharide mixtures, we shall restrict this chapter to simple solutions and gels, the rheology of which marks out the field of the behaviors of polysaccharide aqueous systems. Only shear deformation will be considered. Finally, the discussion of viscoelasticity will be limited to the linear domain.

II. POLYSACCHARIDE SOLUTIONS: GENERAL REMARKS

True polymer solutions are defined by the conjunction of the two following characteristics: (1) they are thermodynamically stable systems; (2) only physical interactions exist between the coils—hydrodynamic interactions and topological constraints which develop above a critical concentration (coil overlap concentration).

Rheology of polymer solutions has been extensively studied and thorough theoretical treatments are available, at least for linear neutral chains. This provides a frame to understand the rheology of polysaccharide solutions. However, because of polydispersity, polymolecularity, and molecular interactions, departures from polymer laws are often observed.

In particular, obtaining true polysaccharide solutions is often not trivial. Polysaccharides are well-known to manifest a strong propensity to associate via hydrogen bonds, because of the abundance of hydroxyl groups. This is indeed the basis of the gelling properties of polysaccharides such as amylose and amylopectin, agarose, etc. but reversible and/or irreversible association occurs also in many other cases, although it does not lead to gel formation in usual observation conditions. In any event, solubilization of polysaccharides is always difficult when the concentration is not low. Aggregation and incomplete solubilization result in the presence of microgels of more or less swollen particles in the system. The system is then actually no longer a solution, but a suspension in a polymer solution. These problems increase with polysaccharide concentration, with the consequence that polysaccharide solutions can be prepared in practice only up to rather limited concentrations. In many cases, the range of con-

centrations over which the rheological behavior can be studied is moreover limited on the lower side because of relatively low M_w , hence low viscosity and low viscoelasticity that would require high sensitivity instruments to be measured. Few *systematic* rheological studies have been carried out on polysaccharide solutions (with the exception of cellulose derivatives) for the above reasons, and also because of the tedious extraction, purification, and fractionation operations necessary to obtain polysaccharide samples suitable for quantitative characterization.

III. SOLUTIONS OF NONCHARGED CHAINS

A. The Isolated Polymer Coil

A typical polymer molecule is a long, flexible or semiflexible chain that can adopt in solution any configuration compatible with its fixed bond lengths and angles and other possible steric restrictions. The set of these spatially and temporally fluctuating configurations defines the equilibrium statistical conformation of the polymer coil in the solvent. The polymer coil is a swollen structure; the volume occupied by the monomers accounts only for a small fraction of the total volume pervaded by the coil; monomer density decreases from the center of gravity of the coil to its periphery. If the volume of the chain itself is neglected, and if steric and physical chemical interactions between monomers or between monomers and solvent molecules are absent, the spatial distribution of the monomers (or of the chain segments) within the coil would be Gaussian ("random coil"). The volume of the Gaussian coil depends only on the length (or the molecular weight M) of the chain, and on the size b_0 of the monomer. In real polymer molecules, bond angles are fixed and there are steric and energetic restrictions to rotations, resulting in a less-flexible chain (nonfreely jointed chain). Nevertheless, polymer molecules can still be treated as an equivalent Gaussian chain by replacing as statistical units the monomers by segments comprising n monomers; the rigidity of the backbone will be reflected in the length $b = nb_0$ of the statistical elements the articulation of which forms the chain. This length b (twice the "persistence length" L_p) can be directly determined from small angle neutron or small-angle X-ray scattering experiments. An appropriate chain stiffness parameter is the ratio of the contour length L of the chain to the length b of the statistical element: for a given polymer, chain flexibility increases with the molecular weight. A ratio $L/b > 10$ would be required for the polymer conformation to be regarded as a coil; this corresponds to M higher than some limiting value M_c . Most polysaccharides are relatively stiff chains, with statistical element length of ~ 10 nm and $M_c \sim 3 \times 10^4$.

N , being the number of statistical elements of the chain, the average square end-to-end distance of the equivalent Gaussian chain is $\bar{L}_0^2 = b^2 N = kM$. The diameter of the coil will be equal to $b\sqrt{N}$, its radius of gyration $(\bar{R}_g^2)_0^{1/2}$ such as $(\bar{R}_g^2)_0 = \bar{L}_0^2/6$; the average monomer (or segment) density within the coil will decrease as $N^{-1/2}$.

The coil volume is actually somewhat larger than that of the equivalent Gaussian coil, because two segments

distant along the chain cannot occupy the same volume element at the same time when approaching each other, as a consequence of their finite volume. This is the so-called "excluded volume interaction." On the other hand, there are always attractive and repulsive monomer/monomer and monomer/solvent interactions. The balance between these interactions will result in coil contraction or coil expansion. Whereas backbone rigidity and molecular weight are intrinsic characteristics of the polymer chain considered, this balance depends on solvent "quality" (the chemical nature of the solvent and the temperature). The effective "excluded volume" will therefore depend on solvent and temperature. In "good" solvent conditions, the chain configuration is more expanded, because solvation of chain segments increases excluded volume; then, its average square end-to-end distance will be $\bar{L}^2 > \bar{L}_0^2$ and can be written as:

$$\bar{L}^2 = b^2 N^{2\nu}; \quad \text{with } \nu \geq 0.5 \quad (1)$$

Parameter ν is the exponent of the radius of gyration–molecular weight relationship of the coil ($R_g \propto M^\nu$), its value depending on chain flexibility: obviously, $\nu = 1$ for fully extended rigid chains, and $\nu = 1/3$ for compact spheres. For polymer coils, ν lies of course in between these two limiting values. However, it depends not only on the more or less flexible character of the backbone, but also on polymer–solvent interactions, which govern coil expansion. Exponent ν has the value of 0.5 for Gaussian chains, as we have seen; for typical flexible polymers in good solvents, it is close to 0.6. In "bad" solvent conditions, attraction between chain segments dominates and causes coil collapse: the coil contracts, forming a dense particle ($\nu \rightarrow 1/3$), which eventually precipitates from the solution. Somewhere in between these two situations, repulsion between chain segments can be exactly compensated for by attraction; such solvent conditions are called " Θ conditions" or " Θ solvent." In Θ conditions, the polymer coil behaves indeed as if it were actually Gaussian and has its "unperturbed" dimension $\bar{L}_0^2 = b^2 N$ ($\nu = 0.5$).

It is classical to express coil dimension as:

$$\bar{L}^2 = \alpha_L^2 \bar{L}_0^2, \quad \text{or } \bar{R}_g^2 = \alpha_g^2 (\bar{R}_g^2)_0 \quad (1b)$$

α_L^2 or α_g^2 , called the expansion factor of the polymer, is equal to 1 in Θ conditions and >1 in good solvents. Because the probability that one segment comes to take the place already occupied by another increases with N , the expansion factor increases with the molecular weight of the polymer. It is a complicated function of L , b , ν , and of the second virial coefficient A_2 of the polymer in the solution [1].

B. Solutions of Noncharged Chains at Finite Concentrations: The Three Concentration Regimes

Three concentration domains can be distinguished in solutions of polymers with molecular weights above the critical value M_c .

1. Dilute Regime ($c < c^*$)

In a very dilute solution, the volume available to each polymer molecule is much higher than that of the individual coil. The coils remain statistically far from each other, and encounters are infrequent. The coils maintain the dimensions of the isolated chain. This situation prevails up to the critical overlap concentration c^* , at which the coils fill the volume of the solution. The volume of each coil being proportional to $(\bar{R}_g^2)^{3/2} = (1/6)^{3/2}(\bar{L}^2)^{3/2}$,

$$c^* \propto M/(\bar{L}^2)^{3/2} \propto N^{1-3\nu} \quad (2)$$

2. Semidilute Regime ($c^* < c < c^{**}$)

When polymer concentration is increased above c^* , there is a progressive interpenetration of the coils, concomitant with a contraction of their individual volume. Coil contraction is a result of the progressive screening off of the “excluded volume interaction”: as a result of interpenetration, segments of “foreign” chains interpose themselves between segments belonging to the same chain. The solution becomes a transient network of entangled chains, an entanglement being the topological constraint corresponding to a point of contact between two chains, and being due to the fact that the chains cannot cross each other. A given polymer with $M > M_c$ statistically contracts a determined number of entanglements at a given concentration $c > c^*$, but, because of chain conformation fluctuations, these entanglements continuously unfasten to be reformed on other points along the chain contour; their lifetime is very short. If $M < M_c$, the length of the chain is shorter than the minimum distance required between entanglement points. An alternative view [2] is to consider the system as equivalent to a cage between the rails of which one given chain has to reptate along its own contour in order to move away; the chain is confined within a tube, the diameter of which is the mesh size of the temporary network.

In the semidilute domain, the mesh size ζ of the network (average distance between entanglement coupling) and the size of the coil decrease as concentration increases. ζ^2 measures the mean square end-to-end distance of the chain segment comprised between two successive entanglement points along one chain. The chain segment thus defined, made up of g statistical elements, constitutes a “blob,” and a chain of N/g blobs forms the polymer molecule. The excluded volume interaction between two adjacent blobs along the chain being screened off by an interposed foreign chain, the chain of blobs is Gaussian, so that the mean square end-to-end distance a polymer chain can be written: $\bar{L}^2 = \zeta^2 N/g$. Within the blob, on the contrary, the excluded volume interaction is effective and $\zeta^2 = b^2 g^{2\nu}$. Scaling laws give [3]: $\zeta \propto c^{\nu/1-3\nu}$ and $\bar{L}^2 \propto c^{2\nu-1/1-3\nu}$.

In the semidilute regime, there are two characteristic lengths in the system: the size of the coil—as the coils still retain some degree of individuality—and the entanglement spacing (or size of the blob).

Looking at the system as a network can be readily extended to the case where low-energy physical chemical interactions develop between chains in the regions of entanglements, giving rise to junction zones. Junction

zones exhibit lifetimes much larger than that of entanglements. The system then has shifted from the state of an entangled solution to that of a “physical gel” (cf. Section VII). The difference between the characteristics of the two types of systems is primarily a difference in degree, and not in nature. However, the establishment of such junction zones generally involves a change in the conformation of the chains, which lose their character of “random” coils. (cf. Section VII).

3. Concentrated Regime ($c > c^{**}$)

At certain concentrations $c^{**} > c^*$, the coils reach their Θ dimension; the excluded volume interaction is completely screened off. Above c^{**} , coils will shrink no more; the polymer solution becomes an entanglement network where the chains have completely lost their individual character. The only characteristic length in the system is now the mesh size ζ of the network, which continues to decrease as concentration increases, tending toward its limit value b in the melt.

IV. THE CASE OF POLYELECTROLYTES

A polyelectrolyte is a flexible polymer electrically charged because its structure includes monomers bearing ionizable groups with charges of the same sign. Many polysaccharides, such as alginates, low-methoxyl pectins, carrageenans, etc., are anionic polyelectrolytes, negatively charged at pH values above the pK of ionization of their acid groups. The only commonly found cationic polysaccharide is chitosan.

The distinctive feature of polyelectrolytes is that the conformation of the macromolecule depends sharply on the ionic strength of the solvent, because the range of the electrostatic interaction decreases as ionic concentration increases. The Debye screening length $\kappa^{-1} \propto I^{-1/2}$, where I is the ionic strength, classically measures the range of the electrostatic interaction in simple electrolyte solutions. In the case of polyelectrolyte solutions, the polymer itself, because of its proper charge and of the counterions surrounding its charged groups, as well as the salt dissolved in the solvent, both contribute to electrostatic screening. The Debye length is now $\kappa^2 = \kappa_p^2 + \kappa_s^2$, where the indices p and s refer to the polymer and to the small ions contributions (including the counterions of the polyion), respectively. Thus, the conformation depends on both the polymer and the salt concentrations; $\kappa_p^2 \propto f c_p$, where c_p is the concentration of the polyelectrolyte and f is the fraction of charged monomers in its chain. However, the effective contribution of the polymer is generally lower than expected from its theoretical charge density, as a result of the binding of counterions on the macroion. Ion binding (“condensation”) results from strong attraction of counterions by the polyelectrolyte when its charge density is high; the ionic atmosphere surrounding the fixed charges can then differ widely from that of the Debye–Hückel approximation.

Obviously, electrostatic repulsion between the charged segments of the polyelectrolyte will favor more expanded conformations of the chain than if excluded volume effect were the only long-range interaction existing between chain

segments. Thus, the ionized polyelectrolyte will exhibit larger mean-square end-to-end length and radius of gyration values than the uncharged chain would have in good solvent. This can be accounted for by introducing an electrostatic contribution to the persistence length of the chain (see, for example, Ref. [4]). In very dilute salt-free solutions, the macromolecule tends to adopt an extended rodlike conformation in order to minimize the electrostatic contribution to the free energy of the chain; then, $\bar{L}^2 \approx L \alpha N$. As I increases, electrostatic interaction between charged segments is progressively screened off. At moderate values of I the chain conformation resumes a spherical symmetry, but with a larger radius of gyration than the equivalent uncharged chain in the same solvent, and at higher values of I , the dimension of the coil approaches that of the uncharged chain.

Even a very schematic analysis of the effect of coulombic repulsion of ionized groups on polymer conformation would be beyond the scope of this chapter. The reader can refer to Refs. [5,6] for a thorough theoretical treatment. Many points about the behavior of polyelectrolytes remain indeed unclear. Therefore, we shall just point out here a few remarks of practical importance.

Since its conformation strongly depends on its own concentration c , as well as on salt concentration c_s , the phase diagram of a polyelectrolyte is more complex than that of neutral polymers. An example of such a diagram is shown on Fig. 1. Because the macromolecule is highly expanded, the coil overlap concentration c^* is extremely low at low and intermediate salt concentrations. Below c^* , the situation is in fact complex. At low salt concentrations, the polyelectrolyte is in its extended conformation (DR regime of Fig. 1), far different from that of a neutral polymer, and furthermore, there are strong intermolecular interactions. However, for large enough salt concentra-

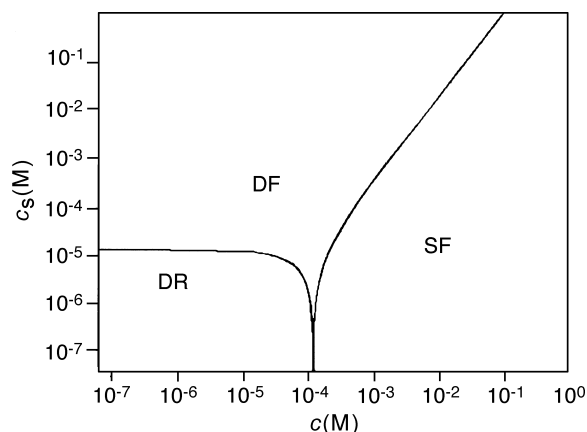


Figure 1 Theoretical phase diagram for an aqueous polyelectrolyte solution (molar concentration c) in presence of added salt (molar concentration c_s). DR: dilute rodlike regime. DF: dilute regime of flexible conformation. SF: semi-dilute regime. The diagram has been calculated for a chain with $N = 3350$ monomers, an average number of monomers between charges $A = 5$, and $Nb/A = 3$, where A is the actual extended length of the chain. Reproduced from Dobrynin et al. [5].

tion, the chain becomes flexible at all polyelectrolyte concentrations (DF regime). The conformation is then analogous to that of the neutral chain in good solvent, but the expansion factor is controlled by the electrostatic screening length, which depends on both c and c_s . Above c^* (SF regime), the chain is likewise flexible, but now the classical excluded volume interaction screening effect of neutral polymers combines with the electrostatic screening effect in governing the expansion factor. Whereas both effects depend on c , the contribution of the latter decreases as c_s increases, and at high enough salt concentrations the situation becomes similar to that for the neutral chain. Because at low and intermediate ionic strength values, polyelectrolyte dimension is strongly dependent on its concentration, the semidilute regime is very wide; it can extend over three or four polymer concentration decades.

The extremely low values of c^* and the existence of strong intermolecular interactions for $c < c^*$ make the experimental characterization of the isolated macromolecule difficult at low and intermediate c_s values. At large salt concentrations, experimental problems also arise, because the added salts affect solvent quality, independently of their electrostatic screening effect; actually, many flexible neutral water-soluble polymers approach unperturbed (Θ) dimensions as salt concentration increases; they eventually even precipitate (“salting out”). The density of charges along the chain, i.e., the relative number of monomers bearing ionizable groups and the degree of ionization are the primary intrinsic characteristics of the chain affecting polyelectrolyte expansion. Theories take into account an average value for charge density; they introduce, e.g., an average number of monomers between charges. But the distribution of the charged groups along the chain also plays a role: the repulsion between a pair of charges is likely to have a larger effect on the overall conformation when the charges are distant along the chain than when they are adjacent. In the case of polysaccharides, charge distribution is neither even nor random along the chain, and is generally completely unknown; it is susceptible to considerable variation for a given polysaccharide with a given average charge density.

V. FLOW BEHAVIOR OF POLYSACCHARIDE SOLUTIONS

A. Origin of Rheological Properties of Polymer Solutions

In the dilute regime, Newtonian flow behavior and absence of viscoelasticity are generally observable in practical conditions, at least for noncharged polymers,* because statistically, macromolecules are spatially and temporally noncorrelated. Nevertheless, in principle, polymer coils are able to deform when submitted to velocity gradients, and to recover their equilibrium conformation after cessation of

*As we shall see later, this is not the case for dilute polyelectrolyte solutions in low added salt conditions, because of long-range electrostatic interactions.

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