POLYSACCHARIDES

1. Introduction

Polysaccharides are naturally occurring polymers in which the repeat unit consists of monosaccharides linked through glycosidic linkages by a condensation-type reaction. Cellulose is a linear homopolymer made of β (1→4) D-glucose units. Figure 1 shows the cellulosic chains. Polysaccharides exist in plants, animals, or microbial worlds where their roles as energy storage or structural materials or as a source of biological activity are recognized. Books on this subject are listed in the General References.

Because of the presence of −OH groups, natural polysaccharides may be modified by chemical reactions, usually in heterogeneous phase to give derivatives with new specific properties. Industrial derivatives are mainly obtained from cellulose, starch, and chitin and chitosan, which are semicrystalline polymers. The presence of these −OH functional groups is the reason for its interaction with water molecules (hydrophilic character of oligo- and polysaccharides) and the intra- and interchain hydrogen-bond network formation, which plays a role in reactivity control, swelling, or dissolution rate.

2. Characterization and Structure

2.1. Extraction–Purification. The purification of polymeric molecules is often easier than for small molecules. It is relatively easy to separate small impurities from large molecules based on solubility, gel filtration, or by dialysis.

If the polymer is water soluble, as in many natural polysaccharides (algae, microbial), it is often a polyelectrolyte, containing uronic acid. It can be precipitated using a nonsolvent, eg, ethanol or isopropyl alcohol (in a ratio ∼ 1:1 water/alcohol) after clarification of the extract by filtration and addition of monovalent salt excess to exchange the multivalent counterions (1, 2). The presence of bivalent counterions left in the sample prevents redissolution after drying and they must be eliminated. With a strongly interacting polymer with calcium (eg, pectin), an oxalate is used as chelating agent.

Before extraction of polysaccharides from plants or woods, it is recommended to extract these materials with organic solvent (toluene, chloroform, methanol, etc) to remove pigments, waxes or oils; then, to eliminate lignin, a highly cross-linked polyaromatic compound, by chemical treatment (chlorite, ozone, sulfite, etc).

For neutral polymers, cellulose is excluded. Extraction can be performed using dimethyl sulfoxide (DMSO) (3), NaOH, or KOH at different concentrations. Over pH 12, alcoholate is formed on the −OH groups increasing the solubility of polysaccharides. When hemicelluloses have to be extracted from a plant source, KOH 24% or NaOH 18% are often used; these hydroxides produce swelling of the cellulosic matrix by rupturing hydrogen-bonding associations allowing better diffusion of other polymers (4).

The extract may contain different polysaccharides and it is useful to redissolve this material after a first purification and to perform steric exclusion chromatography in addition to a ion exchange chromatography before establishing

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the structure and characterization of the properties. This allows the separation of fractions with different average molecular weights and different average charge densities.

2.2. Nmr Spectroscopy. The structure can be established using proton (^{1}H) and ^{13}C nmr. Many examples are given in the literature (5, 6). Nuclear magnetic resonance is especially useful for analyzing polysaccharide with a regular structure. Under these conditions, it is necessary to control the conformation of the polymer. When a helical conformation exists like in xanthan or a regular conformation is stabilized by a hydrogen -bond network, eg, in hyaluronic acid sodium salt or hyaluronan (HA) or chitosan, it is essential to perform nmr at a temperature higher than T_m, the temperature for helix-coil conformational transition or high enough to disrupt the hydrogen-bonds. Mobility is recovered and the analysis is then quantitative. The ^{1}H nmr spectrum of a bacterial polysaccharide based on a two sugar repeat unit (HA) taken at 85°C in D_2O is discussed in Ref. 7. The influence of temperature was also investigated on different polysaccharides. On the ^{1}H nmr spectrum, the two anomeric H1 are identified as well as the acetyl of the *N*-acetyl-D-glucosamine unit. In addition, two different C=O signals appear in the range of 175 ppm due to the carboxylic group and the acetyl group. The attribution of all the signals were given (6). Nuclear magnetic resonance is also used to estimate the yield in substituents, the number of sugars in the repeat units, and for finding the anomery, as well as the position of linkage and the sequence (8–10).

2.3. Composition. The most usual method to determine the composition of a polysaccharide is the complete hydrolysis by heating the polysaccharide in acidic conditions (1*M* H_2SO_4) followed by neutralization with barium carbonate, or with 2*M* trifluoroacetic acid. This acid is volatile and easily eliminated after reaction (11,12). Nevertheless, no recommendation can be proposed *a priori*, especially, for heteropolysaccharides. The rate of hydrolysis of osidic linkage depends on the sugars involved: glycosidic bonds of deoxysugars and furanose sugars, eg, arabinose and fructose, are more fragile, whereas, the glycosidic bond of the uronic moiety is more stable. In the latter case, it is better to reduce the polymer before hydrolysis (13,14). Methanolysis is sometimes preferred to the simple acid hydrolysis, leading to methylglycoside derivatives (15).

The quantitative determination of sugar is achieved by high performance liquid chromatography (hplc) or gas chromatography (gc). The hplc method has the advantage of utilizing sugars directly, but each sugar can give two or more peaks corresponding to anomeric equilibrium. Reduction of the sugar gives the alditols and only one peak per sugar. The same occurs in gc, but, in addition, as sugars are not volatile, they must be transformed into alditol acetates by reduction and peracetylation to get a single peak per sugar in gc (16,17).

Methylation is often necessary to determine the primary structure of polysaccharides. It involves the complete conversion of all free hydroxyl groups in a polysaccharide into methoxyl groups ($-OH \rightarrow -O-CH_3$). The Hakomori procedure using DMSO, sodium hydride, and methyl iodide is the most useful (18). For significant results, methylation must be perfectly completed, then, the modified polysaccharide is fully hydrolyzed and the methylated sugars are separated by hplc (19). Usually, the methylated sugars are reacted alditol acetates and separated by gc combined with mass spectroscopy (20–23).

Partial hydrolysis with acid under mild conditions gives a mixture of oligosaccharides allowing the sequence of sugar units to be determined. The fragments permit the sequencing of the monosaccharide residues in the polysaccharides. The polysaccharide structure may also be obtained by the complementary use of specific enzymes.

2.4. Molecular Weight Determination and Viscosity. When the polysaccharide is perfectly water soluble it is easy to use steric exclusion chromatography (sec), but polysaccharides are rich in −OH groups that may form aggregates due to a network of hydrogen bonds that are often created by the conditions of isolation and drying of the pure polysaccharide. Filtration on porous membranes with small pores is needed (eg, diameter 0.2 μm). In addition, many natural polysaccharides carry ionic groups (eg, $-COO^-$, $-SO_3^-$, $-NH_3^+$) and become polyelectrolytes (24). This implies that the polymer has to be dissolved and eluted in an external 1:1 electrolyte (25). A multidetection experimental device in which a complete molecular weight distribution can be obtained without calibration was developed (2,26). This technique is essential for the determination of real molecular weight as well as hydrodynamic behavior from viscometric detection at very low concentration. An example of a chromatogram obtained with HA is given in Fig. 2. The three traces (concentration from the differential viscometer), light scattering taken at 90° (but also all the angular dependence is analyzed), and viscosity (from the capillary viscometer) are obtained using a GPCV -Alliance 2000 Waters instrument associated with a Dawn DSP MALLS from Wyatt. Using these data, one also obtains the differential molar mass distribution w(M) directly, because the dependence of the radius of gyration with the molar mass and the intrinsic viscosity $[\eta]$ is a function of the molar mass. From this last result, one obtains the Mark -Houwink parameters on the fractionated material.

Another important parameter is the intrinsic viscosity $[\eta]$ (expressed in mL/g). It can be obtained from sec directly, but also more usually it is determined in a separate experiment by extrapolation to zero polymer concentration of the reduced viscosity (η_{red}) of the polymeric solution plotted as a function of the polymer concentration (C g/mL) in accordance with the Huggins relation:

$$\eta_{red} = (\eta - \eta_0)/\eta_0\ C = [\eta] + k'[\eta]^2 C \qquad (1)$$

in which η is the viscosity of the polymer solution, η_0 is the viscosity of the solvent, and k' the Huggins constant.

In the dilute and semidilute regimes, the most important characteristic for application is the thickening character of solution that depends on the intrinsic viscosity, molecular weight, and concentration of the polymer at a given temperature and in a given solvent.

In these cases, the viscosity of a polymer solution at zero shear rate is directly described by the following relation (27):

$$\eta sp = C[\eta] + k'(C[\eta])^2 + B(C[\eta])^n \qquad (2)$$

with $\eta_{sp} = (\eta - \eta_0)/\eta_0$ is the specific viscosity of the polymer; C is the polymer concentration expresssed in grams per milliliter (g/mL). In this relation, B and n are two characteristics for the systems considered; $n = 3.4–4$ in the concentrated regime. Recently, such development was given in the following form:

$$\eta sp = C[\eta]\left(1 + k_1(C[n]) + k_2(C[n])^2 + k_3(C[n])^3\right) \tag{3}$$

in which $k_1 = 0.4$, $k_2 = k_1/2!$; $k_3 = k_1/3!$ (28). This relation is very important: it shows that the overlap parameter ($C\ [\eta]$) controls the viscosity of the solution at zero shear rate and allows prediction of this behavior; For a specific polymer, under given thermodynamic conditions, all the viscosity values for different polymer concentrations and molar masses appear on the same curve when plotted as a function of $C\ [\eta]$. The k_1 value represents the Huggins constant and for many completely water soluble polysaccharides, it equals 0.4. All deviations compared with this reference curve indicate interchain interaction or aggregation, eg, observed with galactomannan (29). The experiments can be performed using a capillary viscometer, but for a non-Newtonian solution a coaxial low shear viscometer is better.

There is an empiric relation between the intrinsic viscosity and the molecular weight of the polymer following the Mark-Houwink relationship:

$$[\eta] = K\ M_V^a \tag{4}$$

in which M_v is the viscometric-average molecular weight; K and a are two parameters depending on the polymer, the solvent, and the temperature.

The important thing is that polysaccharides usually deviate from synthetic flexible polymers. It is seen that even in θ conditions, the "a" exponent of the Mark-Houwink relation is never equal to 0.5, excluding, eg, the direct use of the Flory-Fox relation. So, a wormlike chain model was proposed sometime ago to interpret the data from intrinsic viscosity and radius of gyration as a function of molar masses for polysaccharides. For neutral polysaccharides, one assumes that θ conditions are approached as the χ parameter (interaction polymer–solvent) is near 0.5 (30). Theoretically, the persistence length L_p of a chain and the molar mass impact directly on the radius of gyration R_g and the intrinsic viscosity $[\eta]$ on the basis of the wormlike chain model in θ conditions (31):

$$R_g^2 = L\ L_p/3 - L_p^2 + 2\ L_p^3 L - 2(L_p^4/L^2)[1 - \exp(-L/L_p)] \tag{5}$$

in which L is the contour length calculated from the chemical structure and the molar mass. For high molar masses, one can limit the analysis to the first right term of equation 5. The intrinsic viscosity is given by

$$[\eta] = \Phi(M, L_p, d)(M_L/2L_p)^{-3/2}\ M^{1/2} \tag{6}$$

with d, the hydrodynamic diameter and M_L the mass per unit length of the chain that is known as soon as the local structure is known (32).

For charged polysaccharides, the treatment proposed following Odijk (33–35) and later Reed (36), included an electrostatic contribution to L_p, called L_e; then, the treatment is applied with $L_t = L_p + L_e$. A second term is for the electrostatic excluded volume and is calculated easily. The treatment using homemade software may be applied for a given charge density, a given ionic concentration, and a given chemical structure to deduce L_p. In fact, L_p is also equal to the value of L_t extrapolated to infinite salt concentration, considering complete screening of the electrostatic interaction (37–39).

2.5. Rheology of Solutions and Gels. Rheology of polysaccharides in solution is of great interest on fundamental and applied points of view; the solutions even at low polymer concentration are often non-Newtonian due to the stiffness of the polysaccharides that depresses the critical overlap concentration ($C^* \sim [\eta]^{-1}$) and imposes strict control of the experimental conditions adopted. The main relations relating viscosity to molar mass and polymer concentration at zero shear rate are expressed by equations 3 and 4.

Two types of experiments are usually performed in direct relation with the fundamental properties of the systems. Polysaccharides are usually good thickeners, which means that, when dissolved in a solvent, they increase its viscosity. This effect is reflected by the viscosity that depends on the polymer concentration, molar mass, stiffness of the polymer, temperature, shear rate adopted, and the composition of the solvent (ionic concentration in aqueous medium, nature of the ions, pH). The first type of experiment concerns the flow experiments to determine the viscosity as a function of the shear rate (γ). Due to the chain characteristics, the flow curves usually show a non-Newtonian character, which is characterized by a critical shear rate γ_c over which the viscosity decreases when the shear rate increases. The first part of the curve is called the Newtonian plateau where the viscosity is independent of γ; it is the domain where the viscosity has to be measured to determine the intrinsic viscosity discussed previously. The critical shear rate γ_c decreases when the molar mass increases or when the polymer concentration increases (27,40). In the semidilute regime, the chains overlap progressively, and entanglements are formed giving a larger dependency of the specific viscosity with $C[\eta]$, the overlap parameter (41,42). As soon as loose interactions exist in solution, as frequently observed with polysaccharides in aqueous medium, the limit slope n (eq. 2) is $> 3.4–4$ and increases progressively with the increase of the interactions (29). An example of curve is given in Fig. 3.

The second series of experiments involves the dynamic measurements. A sinusoidal deformation is imposed to the solution in a large range of frequencies, and the response is a complex modulus decomposed in an in-phase response (G' reflecting the elastic character) and out off-phase response (G'' reflecting the viscous response). This study allows for the analysis of the viscoelastic behavior of a polymeric solution. For a given concentration, when the viscosity is high enough a plane-cone viscometer is used for both types of experiments (flow and dynamic). For a solution, at low frequency, G'' is larger than G', but over a critical frequency ω_o, G' becomes larger than G'' corresponding to the presence of entanglements, transitory cross-link points (Fig. 4). The parameter ω_o is displaced to a lower frequency when the polymer concentration and/or molar mass increase; at the same time, the value of $G'(\omega_o)$ increases. For a complete solution of linear polymers,

shifts along the two axis make it possible to plot a master curve, ie, all the points are on the same reference curve. This was clearly obtained for xanthan (40) and for hyaluronan (42).

Dynamic experiments are also performed on gels when they are not too strong; otherwise, calibrated pieces of gel are tested in compression with a tensile machine for very low degree of strain to avoid solvent expulsion (43).

3. Plant Polysaccharides

Polysaccharides from vegetal biomass are present in a large number of renewable polymers and have been used for a long time in many industrial applications; but many other sources exist, eg, bacteria, animals, fungi. The main polysaccharides for large-scale utilization are cellulose and starch (44–46). There is much literature available on the morphologies and three-dimensional (3D) structure of these polymers.

Cellulose is the main structural polymer in wood representing ~50% of the dried matter. In agricultural resources, (normally cellulose represents 35–75% of the dried matter depending on the source; eg, for cotton, the values are 90 and 99%). Cellulose is a very organized fibrous structure that is the bases for the majority of applications, eg, as paper fabrication or reinforcement of composite materials (Fig. 5) (47). Fibrils from primary cell walls eg, beet residue, can be dissociated and used as thickening suspension to promote gellike behavior (44,46). On the other hand, starch constitutes a reserve polysaccharide organized in a granular structure and consists of two polymers, amylase and amylopectin (Fig. 6) (48,49). These are semicrystalline polymers based, respectively, on β(1→4)-D-glucose repeat unit for cellulose and α(1→4)-D-glucose for linear amylose and α(1→4) and α(1→6)-D-glucose units for highly branched amylopectin, respectively.

Derivatization may be used to extend the areas of application for these natural polymer. Nevertheless, their relative lack of solubility, and their high degree of organization lead usually to heterogeneous chemical modifications (50–52). Heterogeneity of the substitution gives poor reproducibility of the samples obtained and depends also on the sources of polymers. Due to this problem, a large variety of parameters relating the degree of substitution and molecular weight to the physical properties, eg, viscosity, can be found in the literature.

The supramolecular structure of the initial materials is a very important point. The swelling and/or dissolution in different conditions depend on the morphology of the native substrate. As it is well known, cellulose in cellulosic fibers and amylose/amylopectin in the starch granules are tightly packed in a more or less regular organization depending on their source, but also on the presence of other additional components. Then, the accessibility of the reactive groups (−OH) will depend on this supramolecular structure in addition to the degree of crystallinity (diffusion control of the reactants) and on the intra- or interchain hydrogen bonds giving a modulation of the −OH groups reactivity. This is why cellulose as well as starch are not thermoplastic. Starch needs the presence of water or glycerol as plasticizer to be processed. Only a complete destructurating by complete dissolution will avoid the memory effect of the original state of

structure organization in order to obtain a regular chemical modifications. This was very clearly demonstrated on carboxymethylcellulose and methylcellulose prepared on laboratory scale (53). The two main characteristics of cellulose and starch derivatives are the distribution in molecular weight, or the weight-average degree of polymerization DP_w or weight-average molecular weight M_w and the average degree of substitution represented by DS (DS = average number of substituents per glucose unit; $0 < DS < 3$). Generally, the polysaccharide solutions used contain aggregates of molecules that perturb the molecular weight determination; thus, only a viscosity test is performed at a given polymer concentration to allow comparison between different samples.

3.1. Cellulose and Derivatives. The solid state of cellulose was investigated for many years and demonstrated the complexity of the 3D structure of this natural polymer (54–57). The fibrillar structure is essential for applications in textile, paper industry, or reinforcement of composites in concurrence with glass fibers (58–61). New continuous cellulosic fibers were produced with the development of new direct solvents for cellulose, eg, *N*-morpholine *N*-oxide (MMNO) (62–66). Regenerated lyocell fibers with original physical characteristics were produced by Courtauld company. Bacterial cellulose produced by *Xanthamonas campestris* bacteria is also available, but is still too expensive for large-scale applications (57).

Dissolving natural cellulose to determine its molecular weight is delicate. One of the most powerful solvents is cupriethylenediamine for which the Mark-Houwink parameters, that relate the intrinsic viscosity to the molecular weight ($[\eta] = KM^{\alpha}$) were determined (see Table 1) (67–75). Some authors previously prepared cellulose derivatives, eg, nitrocellulose or cellulose tricarbanilate, to determine the molecular weight and molecular weight distribution assuming no polymer degradation (Table 2) (76).

Chemical modifications of cellulose (Fig. 1) are very useful in order to develop improved solubility in organic or aqueous solvents or to obtain new thermoplastic materials (44). For this development, the degree of substitution is a very important parameter as well as the chemical structure of the substituent.

Molecularly dispersed solutions are obtained when −OH groups involved in the hydrogen-bond network are substituted avoiding cooperative interchain hydrogen bonding resulting in aggregation. But also it can be shown that the distribution of the substituents along the chain (depending on the morphology of the initial substrate) is important to control the physicochemical properties. This point has been discussed for methylcellulose (53). This also explains why some derivatives having the same average molecular weight and the same average DS have completely different behaviors. Recent studies have been done on selective cellulose functionalization obtaining regioselectively substituted esters and ethers (50).

Among the large variety of cellulose derivatives, two main groups of products can be prepared depending on the type of substituent of the −OH groups of the polymer: cellulose esters and cellulose ethers. Worldwide, $\sim 1.4 \times 10^6$ t/year of cellulosic dissolving pulp are used in the production of cellulose esters, whereas 5.4×10^5 t/year are used in the production of cellulose ethers. Cellulose esters are obtained by reaction of the −OH groups of cellulose with inorganic or

organic acids. Organic cellulose esters are the most important product, but an important inorganic ester is cellulose nitrate.

Cellulose xanthate is produced as an intermediate in viscose process, even though it is not generally used as a final product. The viscose process to produce regenerated cellulosic fibers is progressively decreasing in importance because of the cost and the degree of pollution of this technology. Cellulose xanthate was proposed for selective flocculation of minerals (77).

Nitration was investigated in the author's laboratory using the reagent HNO_3/ Ac_2O/AcOH with different relative composition. The objective was to obtain a cellulose derivative having good solubility in organic solvents and representative of the initial cellulose to test the mechanism of depolymerization by a strong acid and enzyme (76). The molecular weight distribution was tested by sec in tetrahydrofuran (THF) as the solvent using the universal calibration and the Mark-Houwink relation (78):

$$[\eta] = 1.5\, M_{\mathrm{w}}^{1.01} \tag{7}$$

Usually, nitration of cellulose is performed on bleached linters and highly purified chemical grade wood pulp; the industrial nitration process is produced by a system of nitric acid, sulfuric acid, and water. The optimal nitrating mixture is 1:2:2, respectively. Cellulose nitrate is a white, odorless, and tasteless substance. Its characteristics, eg, its solubility and its uses are dependent on the degree of substitution. Typical solvents are ethanol, methanol, esters, ethers, or ketones. They are stable in cold and hot water, aromatic and aliphatic hydrocarbons, and oils. Nevertheless it is not resistant to alkalies and strong acids. Its principal uses are as explosives, lacquers, celluloid, and plastic compounds (79–81).

Organic esters from different types of organic acids can be produced but, in practice only the cellulose esters obtained from aliphatic carboxylic acids between two and four carbon atoms are produced industrially. Cellulose acetate represents $> 90\%$ of the market.

The raw materials used in the acetate production are usually cotton linters with an α-cellulose content $\sim 99\%$, and celluloses from wood pulp. The process of acetylation may be performed in a homogeneous system using glacial acetic acid and methylene chloride as a solvent or in a heterogeneous system with acetic anhydride in an inert suspension medium, eg, toluene, benzene, or carbon tetrachloride. Cellulose acetates are white, amorphous, nontoxic, odorless, tasteless, and less flammable than nitrocellulose. Depending on acetyl content, cellulose acetate is soluble in different organic solvents or water. They are resistant to weak acids and are largely stable in mineral, fatty oils, and petroleum.

In the case of acetate propionate or acetate butyrate mixed ester production, only esterification in a homogeneous system is carried out. The esterification mixture consists of anhydrides of acetic and propionic acid or of acetic and butyric acid respectively. For these cellulose mixed esters, physical properties depend on the content in acetyl groups and propionyl or butyryl groups (see Table 3 for properties). Results on the density, melting point, water absorption, relative humidity, or solubility vary over a wide range composition and can be

obtained by ^{1}H nmr. Properties of acetate and mixed acetates used as molding compounds are presented in Table 3.

The major outlets for cellulose acetates are in textile fibers and cigarette filter tows, mainly in the form of secondary acetate (83).

Cellulose ethers are obtained by substitution of $-OH$ groups by ether groups. These compounds, depending on the substituent, can be soluble in water or organic solvents.

Approximately 300,000 t/year of carboxymethylcellulose are produced each year (79). It is a water soluble polymer when it is in sodium salt form (when $DS > 0.5$). It is produced by reaction of the alkalicellulose with sodium chloroacetate or chloroacetic acid (84) or sodium in liquid nitrogen (85–87). On a laboratory scale, soluble carboxyme (CMC) with DS varying from 0.5 up to 3 has been produced in the author's laboratory. The typical raw materials for the cellulose ethers production are wood pulp or cotton linters.

Carboxymethylcellulose sodium salt is a white, odorless, and nontoxic solid. Viscosities range from 10 to $> 50{,}000$ mPa s for 2% aqueous solutions. The DS of commercial samples may be between 0.3 and 1.2, although clear and fiber-free CMC solutions require a minimum DS value of ~ 0.5. These CMC solutions often show thixotropic behavior, which decreases when CMC is more uniformly substituted (88,89). The viscosity of aqueous solutions varies as a function of pH, showing a maximum at pH 6–7. This is related to the polyelectrolyte properties of these water soluble derivatives. The role of the charge density on the solution properties (activity of counterions, pK, etc) was thoroughly examined in the author's laboratory (24).

Properties of CMC are a hydrophilic character, high viscosity in diluted solutions (thickener), good film formation, inocuity, and excellent behavior as protecting colloids and adhesives. Its field of applications is very wide, ie, in the textile industry, the paper industry, paint, drilling muds, detergents, the food industry, cosmetics, pharmaceuticals, agriculture, and in the building sector.

As studied, CMC can be also cross-linked with epichlorydrine or formol (90,91) to obtain cation-exchanger gels or membranes that can be used, eg, in the purification of black liquors from pulping processes.

Other than sodium carboxymethylcellulose, other mixed ethers exists on the market, eg, carboxymethylhydroxyethylcellulose (CMHEC), which is used as drilling muds or completion fluids and carboxymethylmethylcellulose (CMMC) used as a binder and as an adhesive for tobacco sheets (92).

Methylcellulose (MC) is produced as is carboxymethylcellulose by the Williamson synthesis. Other hydroxyalkyl derivatives or mixed ethers are hydroxyethyl methyl cellulose (HEMC), hydroxypropyl methyl cellulose (HPMC), hydroxybutyl methyl cellulose (HBMC), ethyl methyl cellulose (EMC), and carboxymethyl methyl cellulose (CMMC).

Methylcellulose is prepared by the reaction of alkali cellulose with methyl chloride. Purification of methylcellulose and its hydroxyalkyl derivatives (propyl HPMC and butyl HBMC modifications) is achieved after removal of volatile distillates and washing out with hot water, because these products are insoluble in hot water. Methylcellulose is a white to slightly off-white, essentially odorless and tasteless powder. The solubility of methylcellulose varies as a function of

degree of substitution. In fact, commercial methylcellulose is divided in two types of products according to DS. The MC product with a degree of substitution between 1.4 and 2.0 is soluble in cold water, whereas lower substituted materials are soluble in dilute alkali. methylcellulose is also soluble in ethanol, acetone, ethyl acetate, benzene, and toluene for a higher DS and form gels at specific temperatures when heated (93). Gelation temperature is also influenced by the rate of heating, shear, and additives, especially salts. Salts and additives modify the gelation temperature, depending on concentration and nature of cation and anion (94).

The mechanism of gelation has been examined as it is related to the distribution of substituents along the chain. Two steps in the gelation mechanism were demonstrated and especially the first clear gel was related to the existence of block of highly substituted glucose units (53,95,96). The phase diagram was determined and it was shown that MC in water has a lower critical solution temperature (LCST) $\sim 30^{\circ}$C. Methylcelluloses have excellent water retention properties. On the basis of their properties, methylcelluloses can be used as additives in adhesives, agricultural chemicals, ceramics, construction products, cosmetics, foods, leather, paints, paper products, and pharmaceuticals (79).

The two main types of commercial hydroxyalkylcelluloses are hydroxyethylcellulose (HEC) and hydroxypropylcellulose (HPC). The HEC product is produced in larger amounts, $\sim 60{,}000$ t/year. Other mixed ethers exist, eg, hydroxyethylhydroxypropyl cellulose (HEHPC), and carboxymethylhydroxyethylcellulose (CMHEC). Both HEC and HPC are synthesized by reaction of alkali cellulose with ethylene oxide or propylene oxide, respectively, in a slurry process in an organic medium. In the case of HPC, it is possible to use liquid propylene oxide as a medium of reaction; after etherification the crude product is purified by washing with hot water. The HEC product is soluble in cold and hot water or some mixtures of water and water-miscible organic solvents. The nonionic chemical structure and its solubility in both cold and hot water are the main advantages for the utilization of HEC. Hydroxyethylcellulose is used as a thickener, binder, stabilizer, film former, and protective colloid in cosmetics, pharmaceutical, and in the fabrication of latex.

Hydroxypropylcellulose has a thermal gel point like MC and is thermoplastic. Due to its high level of substitution (molar substitution, MS ~ 4) and its remarkable hydrophobic character, it is soluble in a number of organic solvents as well as water. It is used as stabilizer, coating, and protective colloid in food, pharmacy, cosmetics, inks, and paint removers. Many books discuss the structure and reactivity of cellulosic materials and preparation of their derivatives or regenerated form (44,50–52,97,98).

3.2. Starch and Derivatives. The starch granule dimensions depend on the sources as well as the composition (amylose yield) and degree of cristallinity. The molecular structure of the polysaccharides in the starch granules consist of linear (1→4)- D-glucose chain, the amylose. Amylose is a flexible polymer having a relatively low thickening power; its molecular weight seems to remain relatively low (< 1 million). The second major component is a highly grafted polymer, amylopectin. It is a very compact molecule with a very high molecular weight, 10−100 millions have been cited in the literature. Also, in some materials a

third category exists, a slightly grafted amylose called the intermediate material (48,49,99).

The main techniques for characterizing starch molecules consist of iodine or butanol complex formation to estimate the fraction of linear amylose (100). A colored complex is formed whose wavelength of absorption is characteristic of the length of the helicoidal segments involved in the complex formed with iodine. This technique was previously examined on different starches. The second important characteristic is the molecular weight, or better, the molecular weight distribution. It is often difficult to solubilize starch in aqueous solution. One recently investigated the sec of starch in aqueous systems containing some DMSO or KOH (101–103). It was shown that amylopectin has a low solubility whatever the solvent used. The determination of the molecular weights can be performed using the empiric relation relating the intrinsic viscosity to the viscometric average molecular weight. Some parameters are given in Table 1.

Currently, starch is used in industry as native starch, gelatinized starch, modified starch, or as partially or totally degraded starch (83). First, the characteristics of the products depend on the parent starch sample.

Chemical modifications of starch produce esters and ethers, the same as in the case of cellulose (104,105). Starch esters are synthesized by reaction of a carboxylic acid, an acyl chloride, or an acid anhydride with the hydroxyl groups of amylose or amylopectin chains. As in the case of cellulose derivatives, there are organic and inorganic esters depending on the origin of the substituent.

Acetate of starch is the most important ester industrially produced. Commercial products are traditionally low substituted derivatives ($DS < 0.3$). In this range of DS, it is possible to produce derivatives, preserving the granule structure, to purify by washing with water and to recover by centrifugation or filtration. The acetylating agent is commonly acetic anhydride in aqueous medium in the presence of dilute sodium hydroxide. The principal uses are in food (paste clarity and viscosity stability), and in the pharmaceutical and textile industries (warp sizing, finishing operations). Another class of acetylated starches are those obtained with a degree of substitution of 2–3. Their solubility and thermoplasticity permit their utilization as materials (106–110). A series of acetates of amylose and amylopectins with different DS were prepared materials in the absence of organic solvent (108). From this study, one investigated the hydrophobic character of the polymers (no freezing water remains in the materials for $DS > 1.7$). At the same time, the glass transition temperature T_g stabilizes $\sim 150^{\circ}C$. These polymers were proposed for the preparation of hydrophobic thermoplastic materials or to coat hydrophilic films. Even up to $DS \sim 3$, the polymers remain biodegradable (110).

Synthesis of longer chain organic esters (C_3–C_{18}) have been carried out on a laboratory scale, but have not yet been produced industrially because at present they are not profitable (106,111–114). Starch can be etherified by reaction of an alkyl halide or an epoxy in alkaline medium. Depending on the substituent, it is possible to obtain anionic, hydroxyalkyl, and cationic products. The two main types of hydroxyalkyl ethers industrially produced are hydroxyethyl starch and hydroxypropyl starch. These compounds are synthesized by reaction of ethylene oxide or propylene oxide, respectively, with starch under alkaline conditions. For water-soluble derivatives, when the product is dissolved,

retrogradation of the starch chains is inhibited, resulting in a more fluid paste with improved clarity, viscosity stability, freeze–thaw stability, and cohesiveness.

Hydroxyethyl starch is used in papermaking, textile manufacturing, the medical, and pharmaceutical industries. Hydroxypropyl starch is used in the food industry, textile and paper products, building materials, cosmetics, and pharmaceuticals (115).

Cationic starches are obtained by reaction of starch with reagents containing amino, imino, ammonium, and sulfonium groups (116). The two main types of commercial products are the tertiary amino and quaternary ammonium starch ethers. Among the reagents that can add quaternary ammonium groups to starch probably the most popular is the 2,3-epoxypropyltrimethylammonium chloride. Different DSs were prepared and tested for their role in adsorption on calcium carbonate in relation with the mechanisms of dispersion and flocculation of small particles (117,118).

The key factor in the usefulness of these products is their affinity for negatively charged substrates. For that reason, cationic starches are used in papermaking. When they are used as a wet-end additive, affinity between the positively charged cationic starch and the negatively charged cellulose fibers results in almost complete and irreversible absorption of starch. They are also used in surface sizing and coating binders. Other applications are in textiles, flocculation, detergents, cosmetics, oil wells, adhesives, and photographic films (116).

Starch was also cross-linked with difunctional reagents; it reinforces the granule integrity and improves film properties. Cross-linking is employed when a stable and high viscosity starch paste is needed (119).

3.3. Other Plant Polysaccharides. Hemicelluloses constitute a series of polysaccharides associated with cellulose in plants; in wood, hemicelluloses represent $\sim 25\%$ in weight in addition of lignin and cellulose (120). The composition of hemicelluloses depends on the source: deciduous trees (hardwoods) have mainly glucuronoxylan; coniferous trees (softwoods) yield more glucomannans, *O*-acetylgalactoglucomannans, and xylans have both arabinofuranosyl and 4-*O*-methylgalacturonic side chains. Some softwoods also have a significant amount of arabinogalactan (as larch wood). Hemicelluloses from annual plants (eg, cereals crops) are mainly of the xylan type. The structure has been reviewed (121) and it is clear that they represent a large variety of molecules. There are no important applications for hemicelluloses extracted from plants.

Pectins are located in the middle lamella and primary cell walls of the plant tissues. Pectins are extracted from apple marks and citrus peels. They consist primarily of 1,4-linked α-D-galacturonic units or their methyl esters with some interruption by the rhamnogalacturonan region kinking the linear polygalacturonic backbone (122). They also contain branched chains composed of neutral sugars, eg, galactose or arabinose. These neutral sugars amount to 10–15% of the pectic dried weight and are concentrated in blocks called the hairy region (123).

Pectins exist with different degrees of esterification (DE), $\sim 70\%$ in nature depending on the age of the source and on the presence of enzymes (causing blockwise or random distribution of free carboxylic groups); if DE $< 50\%$, they

are made insolubilize by calcium association; the use of chelating agent (oxalate) is needed for extraction. Alkaline treatment also has a role in the deesterification; it produces a random hydrolysis of the ester groups.

Pectins with a high degree of esterification form thermoreversible gels in acidic conditions and in the presence of 60 wt% saccharose (124).

The interaction between calcium ions and carboxyl groups of the pectins forms gels when the DE is $< 50\%$; the interaction with calcium is very cooperative due to the stereochemistry of the 1,4-linked monomeric galacturonic units leading to the formation of a polar cavity that can be occupied by calcium or related cations. The mechanism of interaction is described by the eggbox model. A series of galacturonic acid oligomers was investigated to test the minimum carboxylic group necessary to get a stable junction in the same way as performed by Kohn (125–127). A two-step process goes to gelation: first dimer formation for $DP > 10$ (or $5\,Ca^{2+}$) followed by aggregation forming junction zones (128–131).

Ability to gel can be determined from the dependence of viscosity as a function of counterions added; at a given polymer concentration, the critical amount of cations at gel point is directly related to the distribution of carboxyl groups along the chain (132). It was also shown that the divalent counterions form gels with a sequence of affinity $Ba > Sr > Ca$, but Mg forms neither gels nor dimers. The interaction with counterions, as well as change in conformation, were identified by X-rays (133) and by circular dichroism (CD) (129). Recently, one discussed the role of the conditions of extraction of pectins from sugar beets and potatoes and the relation to their physical properties (gelling character) (134,135).

Galactomannans are neutral polysaccharides isolated from seeds (carob, guar, locust bean, and tara) (136). The main chain is made of [→4)-β-D-Man-(1] (Man = mannose M) with different degrees of substitution on *O*-6 with α-D-galactopyranosyl units (G). The composition (or M/G ratio) is easily determined by ^{1}H nmr.

The solubility of the galactomannan depends on the ratio M/G and on the distribution of galactose units along the mannan chain, the larger is the galactose content, the higher is the solubility in water. The ratio M/G varies from 1:1 to 1:5 in *Mimosa scrabella* to locust bean gum, respectively. In addition, the rheological properties of solution depend on M/G due to an increase of loose interchain interactions when the G content decreases (137–140). It is known that cooperative interactions may be stabilized between xanthan and galactomannan depending on the conformation of xanthan (helical or coiled). Two types of gels can be identified; one $\sim 20^\circ$C involving disordered xanthan and galactomannan whatever its content in galactose; the second one, $\sim 60^\circ$C, engages helical xanthan and it is the usual gel identified when these two polymers are mixed. Different types of complexes were predicted by molecular modeling (141–148). Molecular modeling was applied for the determination of the persistence length of a galactomannan model for which $M/G \approx 1$ (149). Good agreement was obtained between the experimental sec determination and calculated values; L_p was found in the range of 9.5 nm. The role of the microstructure of the polymer (random or blockwise distribution of galactose, content of galactose) was also analyzed by molecular modeling (150). Galactomannan is a linear neutral

polysaccharide whose solubility is relatively low. It has been modified to increase the solubility by oxidation with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (151); hydroxypropyl- and hydroxylethyl-galactomannans can also be prepared.

Glucomannans were also obtained from seeds or roots. The structure is a random arrangement of [→4)-β-D-Glc-(1] and [→4)-β-D-Man-(1]. The ratio Glc/Man depends on the source and varies from 1:1 in Iris bulbs to 1:5 in certain gymnosperms. Konjac glucomannan is developed mainly in Japan for food applications (152,153). In addition, the polysaccharides contain acetyl substituents that play a large role in the physical properties. Aceyl groups favor solubility, but their hydrolysis allow gelation based on cooperative interchain interaction (154,155). Glucomannans also form gels when complexed with xanthan or carrageenan (156–159). It was demonstrate that optimum rigidity of the mixed gel occurs for 40 wt% konjac for a xanthan–glucomannan mixture (160).

4. Animal Polysaccharide: Chitin

Chitin is one of the most important natural polymers constituting the shells of crustaceans and also the cell walls of many fungi. Commercial chitin is mainly extracted from shrimps and crabs. It can be found with various average DA values ranging from the fully acetylated to the totally deacetylated products. With the higher degree of acetylation, this polymer is soluble in very few solvents, which limits its applications. But, after partial deacetylation, when the degree of acetylation of chitin is $< 50\%$ (the polymer is named chitosan), it becomes water soluble in aqueous acidic conditions. Usually, the reaction is performed under heterogeneous conditions. Chitin is a semicrystalline polymer. The residual acetyl substituent distribution depends on the source of chitin, on the conditions of deacetylation, and on the degree of residual acetylation. It is clear that the solubility of these polymers must directly depend on the average degree of acetylation, but also on the distribution of the acetyl groups along the chains.

This polymer is of great importance for many applications in agriculture, water purification, biomedical application, and cosmetics. Much information can be found in general books (161–165). Chitin and chitosan are good film-forming polymers; in addition chitosan is a chelating polymer for which the mechanism was previously described (166–168). Chitosan is also the only cationic pseudonatural polysaccharide. It can be used as thickener, suspending agent, flocculating polymers to recover proteins, to concentrate dispersed particules or to purify water (Tables 4 and 5).

In the past few years, experimental work has been developed to characterize the chitosan molecular structure in connection with the physical properties in solution. The determination of the degree of acetylation, as well as its molecular weight, is under discussion at present, but much work is performed due to the great importance of these characteristics on the physical properties of the polymer.The determination of the chitin content in natural sources is also important to evaluate a new substrate in the objective to produce chitin.

Dissolving chitosan is performed in acid conditions (169,170) and one proposed the following solvent as giving less aggregation and better solubility:

0.3*M* AcOH/0.2*M* AcONa. From such solutions the Mark-Houwink parameters from eq. 8 were determined at 25°C and discussed

$$[\eta] = KM^a \tag{8}$$

Results are given in Table 6. The molar masses determined from viscosity are now much lower than those obtained with the coefficient proposed by previous authors, but is in perfect agreement with the data obtained by sec more recently (172,173). The nature of the aggregates formed in chitosan solution was also discussed; it seems that hydrogen bonds and hydrophobic interactions favor association in solution (174).

The molecular weight distribution was established by gel-permeation chromatography equipped with three detectors in line. Using specific columns and solvent, the molecular weight distributions on various samples of chitosan with different DA were obtained. Using the model developed in the author's laboratory, the interpretation of the experimental results gives not only the average molecular weights, but also the L_p. Independently, molecular modeling was performed to predict the stiffness of chitin and chitosan for different degrees of acetylation and also for different distributions of the substituents. It is confirmed that L_p varies from 9 nm for DA = 0 to 12 nm for DA = 50% remaining unchanged for chitin. These results agree with experimental results (175,176).

Different techniques have been proposed to evaluate the average degree of acetylation of chitosan (DA), including ir (177), ^{13}C solid-state nmr (178), potentiometric titration (179), ^{1}H liquid-state nmr (180), or elemental analysis. However, some experimental difficulties arise in each technique. A technique that can provide an evaluation of the *N*-acetyl is needed and one that is used is the ^{15}N CP–MAS nmr technique (178). As in polysaccharides, the ^{15}N nucleus is only present in chitin and chitosan, this technique appears very promising for evaluating the *N*-acetyl content, without any strong purification processes, and in the absence of proteins.

Native chitin itself is known to be insoluble in polar solvents, due to extensive intermolecular hydrogen bonding, however, it dissolves in the aprotic system *N*,*N*-dimethylacetamide–5% LiCl. In aqueous cold alkali, chitin also dissolves and behaves as a macromolecular solution (181). Then, when temperature increases, a sol–gel transition was observed. From the phase diagram, a LCST was located at $T = 30°C$ (1% concentration).

Controlled chemical modifications of chitosan were developed taking advantage of the $-NH_2$ function on the C2 position of the monomeric unit. Such modifications result in derivatives water soluble in all pH ranges. The following groups were introduced: $-COO^-$, $-NR_3^+$ (182–184). Other modifications were performed to get amphiphilic polymers by the introduction of alkyl chains. Interesting associative systems were obtained going to gelation when 4% C12 alkyl chains were introduced (185,186). Selective interactions are developed for cyclodextrin-grafted chitosan, which interact with adamantane grafted chitosan to form a network (187–189).

Interesting developments are related to drug release and encapsulation based on polyelectrolyte complexation. Due to the cationic charge of chitosan

in acidic conditions, complexes are formed with alginate or polygalacturonic acid (190) and hyaluronic acid (179,191). Layer by layer capsules were also prepared involving chitosan sulfate (192) or synthetic polyelectrolyte (193).

5. Seaweed Polysaccharides

Algae are an important sources of polysaccharides with different structures. Different groups of algae are recognized: green algae (Chlorophycea), red algae (Rhodophycea), and brown algae (Phaeophycea); only the last two are used on an industrial scale (194). Many different polysaccharides may be extracted, but alginates and carrageenans are the more developed especially as physical gel forming (195); fucoidans also are now under investigation due to the importance of sulfated polysaccharides for biological applications (194,197).

5.1. Alginates. Alginates are cell-wall constituents of brown algae (Phaeophycota). Some 32,000–39,000 t of alginic acid/year are extracted worldwide. The main producers are Scotland, Norway, China, the United States, with smaller amounts being produced in Japan, Chile, and France. Alginates are linear copolymers of α-L-guluronate (G) and α-D-mannuronate (M), also called polyuronides; their gelling properties are derived from the cooperative binding of divalent cations on the G blocks in the eggbox model (similar to the model proposed for gelation of low methoxyl pectins). The mechanical properties of the gels increases when the content in guluronate increases (Fig. 7).

The ability to form gel depends on the divalent counterions with a sequence:

$$\mathrm{Ba} > \mathrm{Sr} > \mathrm{Ca}$$

when the Mg counterion forms neither a gel nor a dimer. This sequence can be established in a dilute solution using viscosity measurement as shown in Fig. 8. The mechanism of association was demonstrated by Kohn (127), using a series of oligomers of galacturonic, guluronic, and mannuronic acids. It was demonstrated that dimers were formed for $\mathrm{DP} > 10$ with galacturonic (pectins) and guluronic (alginates) acids.

Alginate behaves as a polyelectrolyte in the presence of monovalent counterions and in $0.1\,M$ NaCl; the intrinsic viscosity permits the determination of the viscosity-average molar mass (199). In the presence of Ca counterions, a dimer is formed before aggregation and gelation (202).

Alginate is often use now for encapsulation of pharmaceuticals, bacteria, or yeasts in biotechnological processes. Beads of gel are formed by the dripping technique: drops of alginate solution added in $1\,M$ $CaCl_2$ solution form beads that are washed in water after a few hours of maturation. Smaller and more regular particles can be obtained by emulsification (201,202). The porosity of these gels is also smaller than for that obtained by the dripping method.

5.2. Carrageenans and Agarose. These polysaccharides represented a family of alternating AB type copolymers with different degrees of sulfation. Agarose is the neutral polymer form. They are extracted from red algae. They

consist of alternating (1→3)-β-D-galactose and (1→4)-α-(3,6)anhydro-D-galactose or -α-(3,6)anhydro-L-galactose (in agarose).

Agarose, κ- and ι- carrageenans are recognized as gelling polymers; the conditions of gelation, as well as the mechanism of gelation, were abundantly discussed in the literature. The gels are thermoreversible based on hydrogen-bond stabilized conformation. Gelation is based on the formation of double helices that associate forming an aggregate or a junction zone that is the basis of the network formation. The two-step gelation has been clearly demonstrated. Gelation and melting of the gel present a hysteresis in temperature directly related with the degree of aggregation of double helices and on the charge density of the polymers (203–205). The rigidity of the gels follows the same trend; it was established as a sequence of solubility:

$$\text{agarose} < \kappa - \text{carrageenan} < \iota - \text{carrageenan} < \lambda - \text{carrageenan}$$

following the order of sulfate density:

$$\text{no sulfate} < 1 \text{ sulfate} < 2 \text{ sulfates} < 3 \text{ sulfates}$$

The stiffness of the gels formed in the presence of K^+ counterions varies in the following order:

$$\text{Agarose} > \kappa - \text{carrageenan} > \iota - \text{carrageenan}$$

The polymer λ-carrageenan, has three sulfate groups per dimer and no anhydro-galactose. It never forms neither gels nor a helical conformation.

The κ-carrageenan is especially known to form strong thermoreversible gels in the presence of monovalent counterions following the sequence:

$$Rb^+ > K^+ > Cs^+ > Na^+ > Li^+ \sim NH_4^+$$

It has been established that the same counterions promote coil–helix transitions (based on ion pair formation) and are involved in the gel formation (206). A gel can be considered as a 3D network stabilized by junction zones resulting from a microphase separation of stiff double helices. The local stiffness of the double helices favors the cooperative association, which is the basis of gelation (207–209). The stabilities of the conformation (double helix→coil transition) and that of gel (gel → sol transition) were established by a phase diagram relating the total ionic concentration to the inverse of the temperature of transition (209) (Fig. 9).

The mechanical properties of the gels formed in the presence of different counterions follow the same order: A Rb–carrageenan gel has a higher modulus and a higher melting temperature than Na–carrageenan gel. The molecular weight also plays a role on the elastic modulus, which increases up to a limit $\sim M\sim$250,000 (210). The mechanism of gelation in two steps is described in Ref. 209.

In the series of anions, a characteristic behavior was observed with I^-; it stabilizes the double helix, but prevents gelation (208, 211–213).

Hysteresis in the presence of KCl appears $\sim Cp = 7.5 \times 10^{-3}$ M (209), but only in 0.2 M NaI (211); the width of the hyteresis at a given total ionic concentration (C_T) is much larger in KCl corresponding to a larger degree of aggregation (ie, stabilization) of the double helices. The hysteresis obtained by DSC is shown in Fig. 10 for κ-carrageenans in presence of KCl (214).

κ-Carrageenan was examined in dynamic experiments; in 0.1 M NaI, for 10 g/L, κ- carrageenan behaves as a viscous solution at 20°C, but gives a gellike behavior in 0.1 M KCl (even for 1 g/L) in relation with the affinity for K^+ counterions (Fig. 11). This shows that NaI prevents aggregation and gelation (214). Table 7 gives some values obtained on gels formed in the presence of different salts.

5.3. Fucans and Fucoidans. Fucoidan is a polysaccharide that is rich in fucose and found mainly in brown seaweed (215). Various samples differing in molecular weight, carbohydrate composition, and number of sulfate groups were extracted from seaweeds collected from various regions of the Russian Far-East coast of the Pacific ocean. Their phase behavior in aqueous solutions, interactions with proteins, and oppositely charged polysaccharides were studied. Gels were characterized by means of oscillation rheology.

Fucoidans dissolved in water caused only a notable increase in viscosity. A transfer into the gel state was not observed up to the concentration of 25 wt%. It was established that a sol–gel transition was induced by the addition of glycerol or butanediol in aqueous solutions containing a high molecular weight fucoidan, while ethylene and propane glycol did not have such ability. The gel formation in the presence of the mentioned polyols is explicable on the basis of a change in the solvent quality and of cross-linking of neighboring polysaccharide molecules by polyol molecules via hydrogen bonds. Mixed gels of fucoidans were prepared with a helical protein, gelatin. The fucoidan addition made the gels softer. The interactions between polysaccharide and protein molecules depended on the pH of aqueous solutions relative to the isoelectric point of gelatin.

A globular protein, bovine serum albumin (BSA), when mixed with fucoidans, gave viscoelastic solutions. The effect was governed by electrostatic interactions. Anticoagulant properties of fucoidan were established by thrombin inhibition mediated via plasma antithrombin III. Immunostimulating activity of fucoidan from brown algae was also reported (215).

6. Microbial Polysaccharides

Fungi and bacteria are sources of polysaccharides, and especially of exopolysaccharides, which can be produced in a culture medium on an industrial scale. They have become a source of new additives for cosmetic or food applications, but also for biological activity. Many of them are now in development and a review was recently published (5,7). Many of these polysaccharides are water soluble and able to compete with natural polysaccharides described before (alginates, carrageenans, galacto- and glucomannans, chitosans, pectins), especially in the area of food additives. Many books discuss on these applications (216-226).

Bacterial polysaccharides are the most important for application. They consist in a large variety of polymers biosynthesized by bacteria. Their chemical structures, and also their physical properties in solution or in the solid state may vary in a large extent; they often contain uronic acid and then become polyelectrolytes (222). Actually, for industrial purposes, many new polysaccharides are developed from bacteria. Exocellular polysaccharides are produced on a large scale by the usual techniques of microbiology and fermentation. This procedure allows good control of the characteristics of the polymers and the purification of the polysaccharides more easily than from other natural sources (223–225). Extension of such production also allows for cost reduction and extends the range of applications. A good example is the HA previously produced by extraction from an animal source, but in which some fraction of proteins remained ie, not separated from Na. Here the bacterial HA can be prepared in a very pure form (42).

From a general point of view, these polysaccharides are especially important in the area of water soluble polymers. They play an important role as thickening, gelling, emulsifying, hydrating, film forming, and suspending polymers. Especially important is the fact that some polysaccharides give physical gels in well-defined thermodynamic conditions. They constitute a very important class of materials in food, cosmetics, or pharmaceutical applications. In Table 8, some of the most important microbial polysaccharides and their sources are listed.

The author's laboratory has developed specific methods for the purification of the polysaccharides, which are usually isolated under their sodium salt forms by precipitation from aqueous solution with ethanol or isopropyl alcohal. This step is most important for obtaining reproducible experimental characteristics. In fact, due to the presence of many $-OH$ groups in the molecule, the polysaccharides have a tendency to form cooperative intra- and interchain hydrogen bonds causing some insolubility, or at least the presence of aggregates, when solutions are prepared. Due to their stereoregularity, they are often able to adopt a helical conformation in solution. Their ordered conformation has a semirigid character and its stability depends on temperature and ionic concentration if the polysaccharide structure contains uronic acid unit or ionic substituents. Details on the chemical structure of bacterial polysaccharides were given previously by Lindberg (226,227) or Dutton (228).

6.1. Xanthan. Xanthan was the first bacterial polysaccharide produced by the strain *X. campestris* and developed on a large scale. Xanthan is a semirigid polymer for which, in the native conformation, a persistence length was found ~ 40 nm. It was demonstrated that when the native form is heated to coil conformation (with a much lower stiffness) and renatured by cooling, the conformation is changed (229). This can be represented as follows:

Native xanthan	$\longrightarrow$	Denatured xanthan	$\leftrightarrow$	Renaturated xanthan
Single helix	Irreversible	Coil	Reversible	Double helix

This renaturated conformation was obtained in dilute solution and is stiffer ($L_p = 160$ nm), but shorter, with the viscosity being usually higher than that of the native form. The large persistence length explains why the viscosity in solution is much larger compared with other polymers. It also explains the stability of viscosity in the presence of external salt (230–234).

The weight-average molecular weight can be determined by viscometry; it was also established by the Mark-Houwink relation (eq. 159) in $0.1\,M$ NaCl at 25°C and a zero shear rate (27):

$$[\eta]\ \mathrm{ml/g} = 1.7 \times 10^{-4}\mathrm{M}^{1.14} \tag{9}$$

The large exponent in this relation prove the stiffness of the polymer.

Now, xanthan has many industrial applications due to its suspending character (stabilizer of solid suspensions or foams), its pseudoplastic and thickening properties, and good, stable rheological properties as a function of pH, temperature, and salt concentration. It was first used for tertiary oil recovery. Xanthan is accepted as a food additives by U.S. Food and Drug Administration (FDA) regulation and European authorities under the reference E 415. In this area of applications, it is mainly used as stabilizer of emuosions, and suspensions and as a thickener. It has a good stability during sterilization. It can be associated with other different biopolymers, eg, carrageenans, alginates, pectins, gelatin, galactomannans. The specific complex formed in the presence of galactomannans was previously mentioned.

6.2. Gellan. Gellan is produced by the bacteria *Sphingomonas elodea*. The native gellan as produced by the bacteria contains four sugar repeat units and two additional substituents (acetyl and L-glyceryl). After fermentation, chemical treatment takes off the substituents to produce the commercial polymer, Gelrite (235). A new product commercialized by Kelco in 1998 (now CP Kelco, part of the JM Huber Corporation), is Kelcogel LT100, a high acyl gellan giving soft and elastic thermoreversible gels applied for food applications: dressings, jellies, milk puddings, dairy, and food beverages. More recently, CP Kelco introduces KELCOGEL(R) HS-B gellan gum, a unique hydrocolloid system made with gellan gum that has been specially designed to provide suspension of soy, cocoa, and minerals in ready-to-drink neutral pH soy-based beverages. Gellan also shows synergism with other polymers, eg, gelatin or gum arabic.

The mechanism of gelation of deacylated gellan was examined and is shown as a two-step process similar to the mechanism proposed for κ-carrageenan (236,237). Deacylated gellan adopts an ordered conformation in double helix in salt excess and the temperature for conformational change, T_m, increases when the salt concentration increases as is usual for stereoregular polyelectrolytes. The helical conformation is more stable in presence of divalent counterions, but no ionic selectivity appears among monovalent counterions (Li, Na, K, (TMA) tetramethylammonium) on one side and among divalent counterions (Ca, Mg) on the other side. When the salt and polysaccharide concentrations increase, the double helices interact to give a physical gel with a strong ionic selectivity. The sequence of selectivity is

$$K^+ > Na^+ > Li^+$$

The K^+ ion promotes the gel formation and gives the higher elastic modulus. The behavior of this polymer, and especially the two-step mechanism of gelation appear to be similar to what is observed for κ-carrageenan.

Rhamsan and wellan have molecular backbones similar to that of gellan and constitue the "gellan family". They were compared for conformation and physical properties recently (238,239).

6.3. Succinoglycans. Succinoglycansare are produced by many soil bacteria of the species *Pseudomonas*, *Rhizobium*, *Agrobacterium*, and *Alcaligenes*. These polysaccharides have a general chemical structure based on height sugar repeat units (D-glucose/ D-galactose ratio equals 7:1). Different substituents are also present in the molecule, eg, acetyl, succinyl, and pyruvyl groups depending on the strain and on the conditions of fermentation or isolation (5,240,241).

It was first produced on a large scale by Shell Cy from the strain *Pseudomonas* sp. NCIB 11592 and later by Rhodia from *Agrobacterium tumefaciens* I-736 under the trade name Rheozan. It has a thickening behavior like that of xanthan with some specific uses because of its larger stability in acidic conditions. It is a thickener used in detergents and toilet bowl cleaners. As many bacterial polysaccharides, succinoglycan, whatever its origin, is water soluble, and since it is stereoregular, it adopts a single-chain helical conformation at least in dilute solution. This ordered conformation was demonstrated from the existence of a conformational transition induced by temperature change using optical rotation, nmr, calorimetry, viscosity, conductivity. As shown by the different techniques, the conformational transition is reversible and very cooperative at least in presence of some salt excess (240). The stability of the ordered conformation depends on the salt concentration in solution as usual for charged polysaccharides. On both sides of the transition, the stiffness is completely different: in the helical conformation, the chain behaves as a semirigid chain having an intrinsic Lp estimated to 35 nm and becomes more flexible at a higher temperature in the coiled conformation with $Lp \sim 5$ nm. The persistence length in the helical conformation was confirmed by atomic force microscopy from the analysis of chain curvature (242).

6.4. Hyaluronan. Hyaluronan (hyaluronic acid, sodium) becomes a very important polysaccharide from a microbacterial source. The chemical structure of hyaluronan is that of a linear polyelectrolyte based on β1-4 D-glucuronic acid (GlcA) and β1-3 D-*N* acetylglucosamin (GlcNAc) repeat unit (243). In fact, the existence of an ordered conformation in solution that is stabilized by a hydrogen bond becomes mobile when a temperature increase was proposed. Its semirigid character was characterized by a $Lp = 8.5$ nm at 25°C and confirmed by molecular modeling (42,244–248). These bonds can be released also in the presence of NaOH (249) or urea. In the solid state, hyaluronan forms a semicrystalline structure and different types of helexes were discussed.

One characteristic of a polyacid is its intrinsic pK value (pK_0). This value can be obtained from the pH metric neutralization curves of a solution of the acid form of HA (obtained from cation-exchange resin). This measurement allows

the determination of the apparent pK (pK_a) of the carboxylic group, taking into account the degree of autodissociation α_H, and the degree of neutralization α_N:

$$pK_a = pH + \log[(1 - \alpha_T)/\alpha_T] = pK_0 + \Delta pK \text{ (e.s.)} \quad (10)$$

where $\alpha_T = \alpha_N + \alpha_H$ equals the fraction of ionized carboxylic groups. From experimental data, the extrapolation to a null dissociation degree α_T gives $pK_0 = 2.9 \pm 0.1$ as usually found on polycarboxylic acid in the absence of the specific interaction involving the carboxylic groups. An important role of HA is for moisture retention recommended for cosmetic applications (248,249).

The parameters K and a are known as the Mark-Houwink parameters in the equation $[\eta] = KM^a$; in the range $4 \times 10^5 < M < 1.5 \times 10^6$ and in the sec conditions (0.1 M $NaNO_3$, 30°C), one gets, respectively, $K = 0.0336$ and $a = 0.79$ when $[\eta]$ is expressed in milliliters per gram (mL/g).

Hyaluronan is a very biocompatible polysaccharide and now it is often used for biomedical applications from which comes viscosuplementation, based on its good viscoelastic properties and semirigid character (250–253). Films are also developed for tissue engineering. A complex with polycation is also proposed for control release (191).

An important derivative is obtained by chemical cross-linkage of HA allowing a large modification of the rheological behavior of the solutions. This derivative was introduced by Balazs for medical applications in viscosupplementation in arthrosis treatment (254).

Specific oxidation of HA was completed using TEMPO. This radical mediated oxidation on the C6 position of the *N*-acetyl unit of HA was studied at pH 10.2 and temperature of 0°C with NaOCl as the primary oxidant (255).

New methods for chemical derivatization of HA are now in progress in different laboratories.

6.5. Curdlan. The best example of fungal polysaccharides is the $\beta(1 \rightarrow 3)$ glucans (curdlan) and branched $\beta(1 \rightarrow 3)$ glucans with few $\beta(1 \rightarrow 6)$ glucose units as side groups from which is scleroglucan; they often form a triple helical conformation with a tendency to give a physical gel (256-258). Studies on scleroglucan, lentinan, schizophillan, which have similar structure, are described in the literature. The solubility increases in alkaline conditions, but over pH 12, an irreversible triple helix–coil transition is observed. Many of these glucans were claimed to be antitumoral. Scleroglucan was oxidized with periodate giving a new polyelectrolyte.

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Table 1. **Mark-Houwink Parameters for Cellulose, Starch, and a Few Derivatives**

Polymer	Solvent	T,°C	$K\,10^3$, mL/g	a	References
cellulose	cupriethylenediamine	25	13.3	0.905	67
cellulose	cupriethylenediamine	25	10.1	0.9	68
cellulose	cupriethylenediamine	25	7.62	0.936	69
sodium carboxymethylcellulose	aqueous NaCl (0.1 M)	25	12.3	0.91	70
methylcellulose	water	25	316	0.55	71
methylcellulose	water	20	280	0.55	72
amylose	DMSO	25	15.1	0.70	73
amylose	DMSO	25	30.6	0.64	74
amylose	water	20	13.2	0.68	75
amylose	aq. KOH (0.15 M)	25	8.36	0.77	73

Table 2. **Nitration of Cellulose**[a]

Nitration composition	50:25:25[b]	43:25:32[b]	66:0:34[b]
N%	13.3	13.8	13.98
DS	2.9	2.93	2.96
M_w (LS)	1,300,000	1,410,000	1,400,000
M_w (sec)	1,085,000	1,307,000	1,456,000
M_w/M_n	1.68	1.82	2.14

[a]Ref. 76.
[b]% compostion $HNO_3/Ac_2O/AcOH$.

Table 3. **Properties of Acetate and Mixed Esters as Molding Compounds**[a]

Characteristics	Acetate	Acetate propionate	Acetate butyrate
melting point, °C	230	190	140
compression molding, mp, °C	127–216	129–204	129–199
injection molding, mp, °C	168–255	168–268	168–249
specific gravity, g/cm^3	1.22–1.34	1.17–1.24	1.15–1.22
refractive index	1.46–1.50	1.46–1.49	1.46–1.49
tensile strength, MPa	12.1–62.1	13.8–53.8	17.9–47.6
elongation, %	6–70	29–100	44–88
tensile modulus, 10^2 MPa	4.48–27.6	4.14–14.8	3.44–13.8
thermal expansion, 10^{-3} %/°C)	8–18	11–17	11–17

[a]Ref. 82.

Table 4. **Main Applications of Chitin and Chitosan**

Industry	Applications
agriculture	defensive mechanism in plants
	stimulation of growth
	seed coating
	frost protection
	time release of fertilizers, nutrients, etc, into the soil
water and waste treatment	flocculant to clarify water (drinking water, pools)
	removal of metal ions
	ecological polymer (eliminate synthetic polymers)
	reduce odors
food and beverages	not digestible by human (dietary fiber)
	bind lipids (reduce cholesterol)
	preservative
	thickener and stabilizer for sauces
	protective, fungi static, antibacterial coating for fruits
cosmetics and toiletries	maintain skin moisture
	treat acne
	improve suppleness of hair
	reduce static electricity in hair
	tone skin
	oral care (toothpaste, chewing gum)
biopharmaceutics	immunologic
	antitumoral
	hemostatic and anticoagulant
	cicatrizant
	bacteriostatic

Table 5. **Applications and Properties of Chitosan**

Potential biomedical applications	Main characteristics
surgical suture	biocompatible
dental implant	biodegradable
artificial skin	renewable
rebuilding bone	film forming
corneal contact lenses	
time release drugs for animals and humans	
encapsulating material	

Table 6. **Mark-Houwink Parameters Predicted for the Wormlike Chain Model from Sec Experiments on Homogeneous and Heterogeneous Samples**[a]

DA (%)	K	a
0–3	0.079	0.796
12	0.074	0.800
22–24	0.0695	0.81
40	0.0634	0.823
56–61	0.0574	0.825

[a]Ref. 177.

Table 7. **Dynamic Moduli of Gels Obtained for κ-Carrageenan in the Presence of Different External 1-1 Salts**[a,b]

Salt tested	G',Pa	G'',Pa
KCl[c]	57.45	3.15
TMACl[d]	≈ 0	0.1
NaI[d]	4.026	4.87

[a]Ref. 214.
[b]General condition Cs = 0.1 *M* salt; frequency 0.5 Hz; 20°C.
[c]Cp = 1 g/L.
[d]Cp = 10 g/L.

Table 8. **Major Microbial Polysaccharides and Their Sources**

Polysaccharides	Structures	Organisms
		BACTERIA
alginate (also from algae)	linear, different M/G ratios	*azobacter, pseudomonas*
cellulose (also from plants)	linear $\beta(1 \rightarrow 4)$ -D-glucan	*acetobacter xylinium, agrobacterium*
curdlan	linear $\beta(1 \rightarrow 3)$ -D-glucan	*agrobacterium, alcaligenes*
gellan	linear, heteropolysaccharide with variable substituents	*sphingomonas*
rhamsan	two sugars branched for every four sugars with variable substituents	*alcaligenes*
welan	one sugar branched for every four sugars with variable substituents	*alcaligenes*
polyglucuronic acid	linear, $\beta(1 \rightarrow 4)$ -D-glucuronan with variable substituents	*Rhizobium meliloti mutant*
hyaluronic acid (also from animals)	linear (AB) copolymer	*streptococcus*
xanthan	three sugars branched for every two sugars with variable substituents	*X. campestris*
succinoglycan	four sugars branched for every four sugars with variable substituents	*alcaligenes, agrobacterium, rhizobium*
emulsan	heteropolysaccharide	*acinetobacter*
dextran (also with isolated enzymes)	branched $\alpha(1 \rightarrow 3)$, $\alpha(1 \rightarrow 6)$ -D-glucan	*Leuconostoc mesenteroides*, streptococcus
levan	branched $\beta(2 \rightarrow 6)$, $\beta(2 \rightarrow 1)$-D-fructan	*pseudomonas, zymomonas, bacillus*
different polysaccharides	heteropolysaccharide with galactose, glucose, rhamnose	*lactic bacteria*
		FUNGI
pullulan	linear $\alpha(1 \rightarrow 4)$,$\alpha(1 \rightarrow 6)$ in 2:1 ratio	*aureobasidium*
scleroglucan	linear, one glucose branched $\beta(1 \rightarrow 6)$ for every three glucoses linked $\beta(1 \rightarrow 3)$	*sclerotium*
schizophylan	linear, one glucose branched $\beta(1 \rightarrow 6)$ for every three glucoses linked $\beta(1 \rightarrow 3)$	*schizophyllum*
lentinan	linear, two glucose branches for every five glucose units	*lentinus*

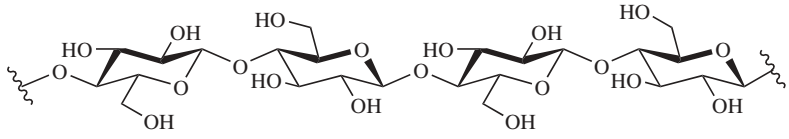

Fig. 1. Cellulosic chain showing the linear homopolymer structure made of β-(1→4)-D-glucose units.

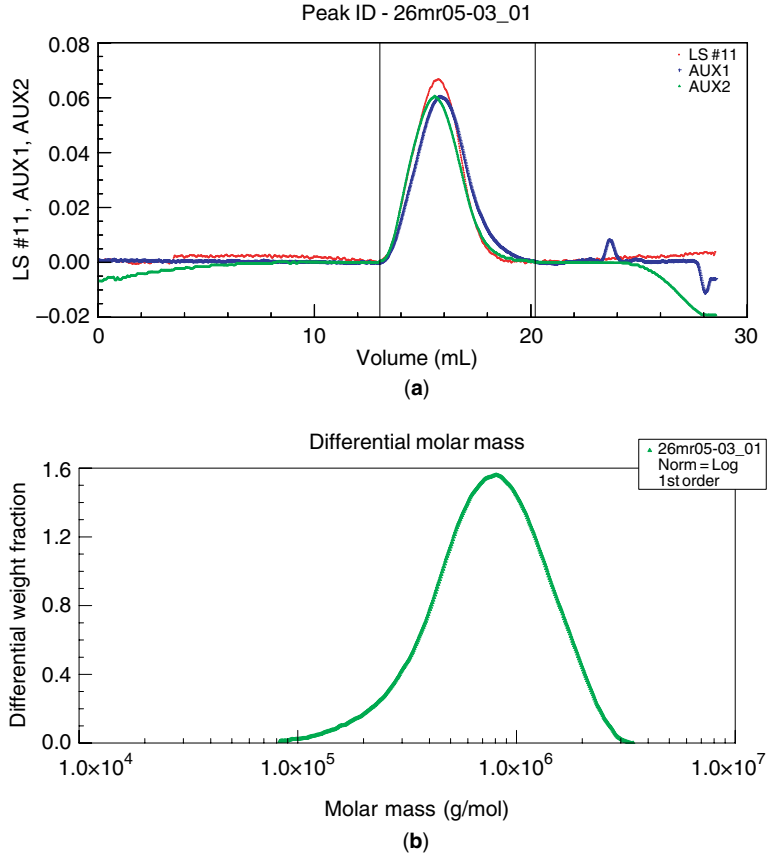

Fig. 2. The sec chromatograms (**a**) and molecular weight distribution (**b**) of HA in 0.1 *M* $NaNO_3$ at 30°C using a triple detection.

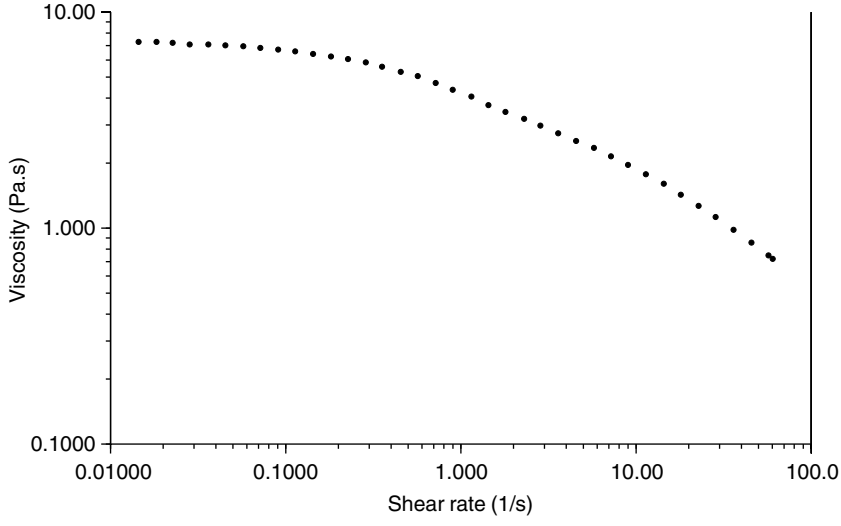

Fig. 3. Flow experiment on HA solution (Cp = 10 g/L in 0.15 *M* NaCl at 25°C).

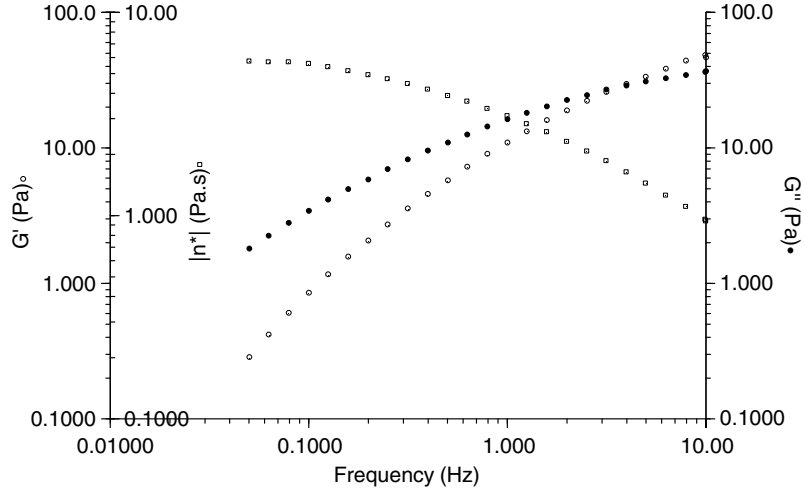

Fig. 4. Dynamic experiment for HA solution ((Cp = 10 g/L in 0.15 *M* NaCl at 25°C). Elastic modulus *G*′o; Viscous modulus *G*″ •; Complex viscosity $|\eta^*|$.

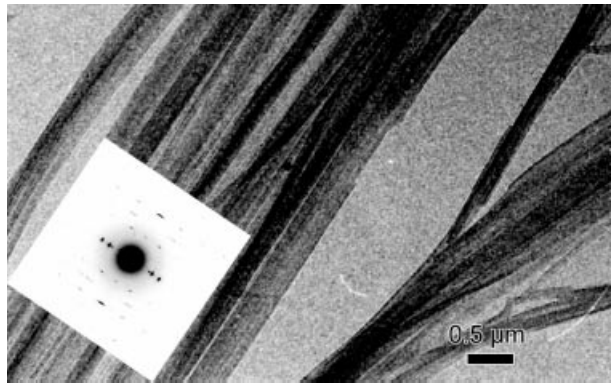

Fig. 5. Transmission electron micrograph of a parallel assembly of cellulose microfibrils in a thin cell wall fragment of the seaweed *Valonia ventricosa.* Insert: electron diffraction pattern recorded on 1 μ^2 of the specimen and revealing the perfect orientation and extreme crystallinity of this cellulose. [Photomicrography and electron diffraction pattern from the collection of H.Chanzy (CERMAV).]

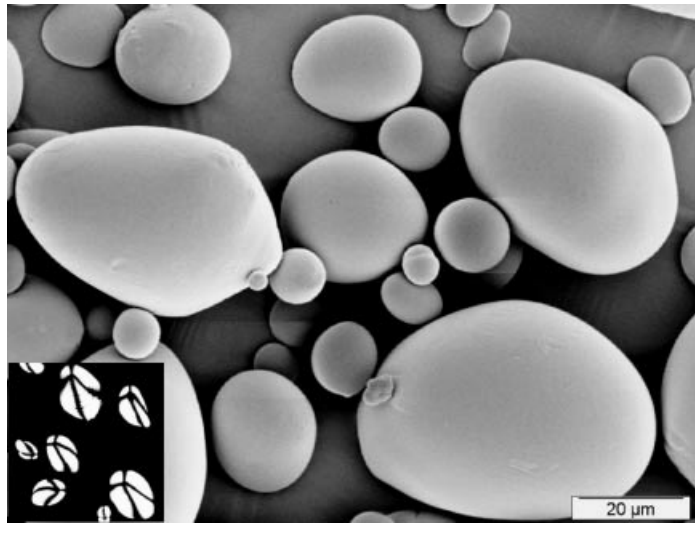

Fig. 6. Potato starch granules observed by scanning electronic microscopy (SEM). Insert: microscopy between crossed polarizers. [Micrography from the collection of D. Dupeyre and J-L. Putaux (CERMAV).]

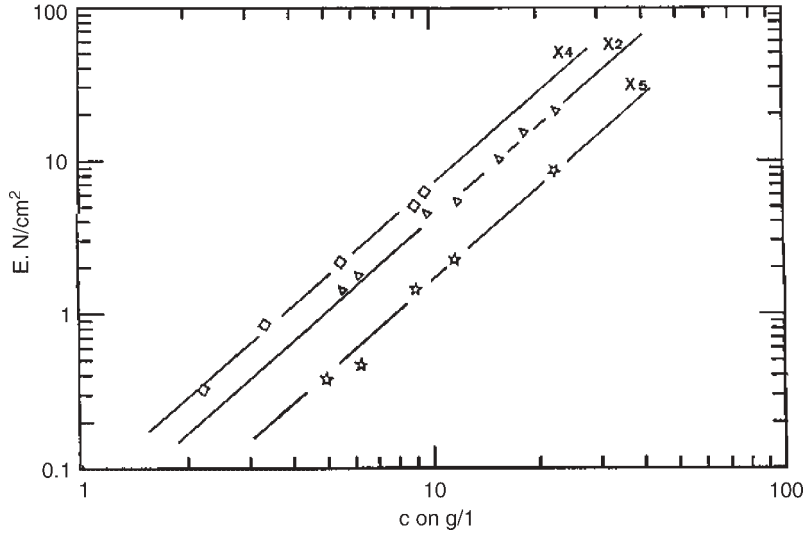

Fig. 7. Elastic modulus determined in compression as a function of polymer concentration for Ca–alginate gels with different M/G ratios. X2 M/G = 0.56; X4 M/G = 0.28; X5 M/G = 1.98 (198).

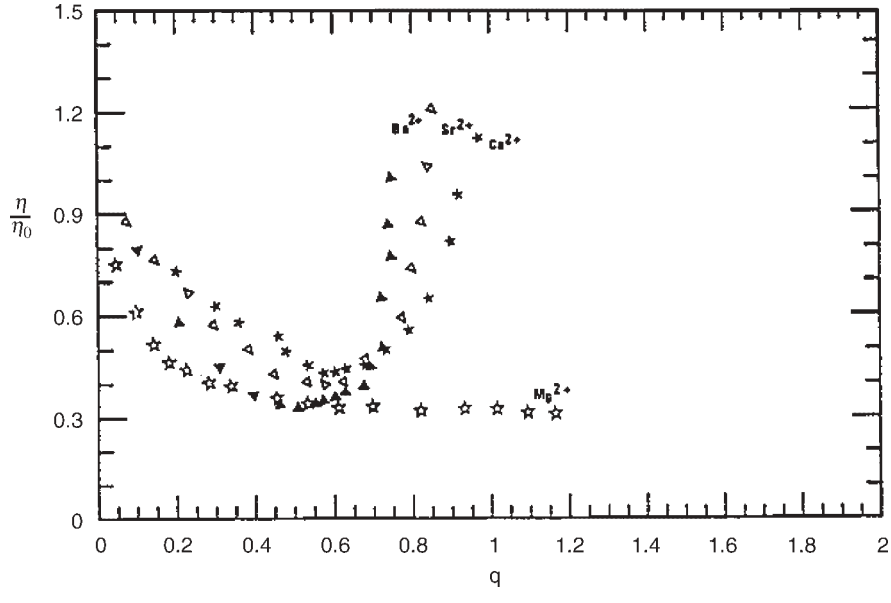

Fig. 8. Evolution of the relative viscosity for successive addition of divalent salt ($Cs = 5 \times 10^{-3}$ M) in dilute alginate solution (Cp = 0.6 g/L). $q = [Ca/2]/[-COO^-]$ (198).

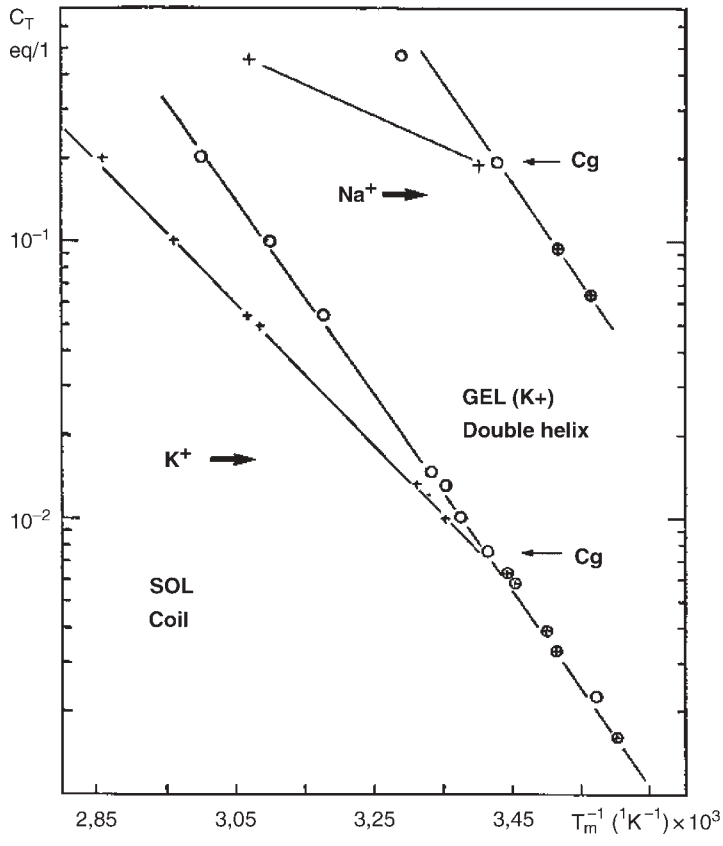

Fig. 9. Phase diagram for κ-carrageenan in K- and Na-salt forms. Inverse of the transition temperature (T_m) is given a function of the total ionic concentration (C_T) (209).

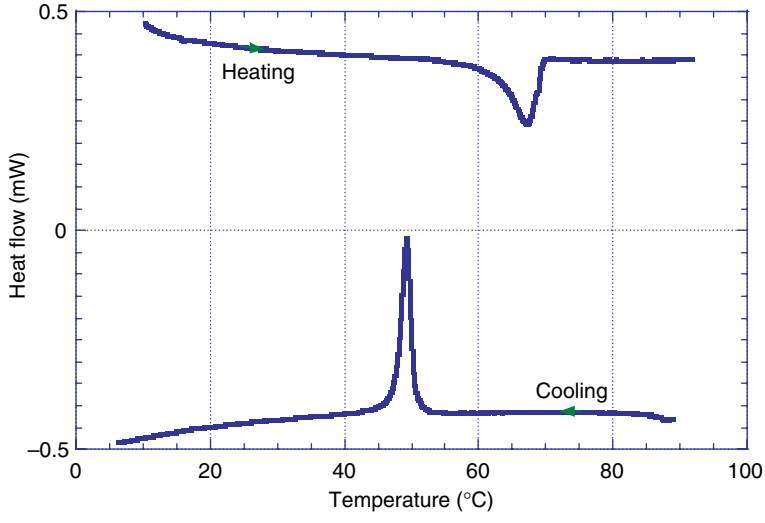

Fig. 10. Thermogram obtained for κ-carrageenan in 0.1 *M* KCl (Cp = 4 g/L) on heating and cooling ($\Delta T_m = 17°C$) (214).

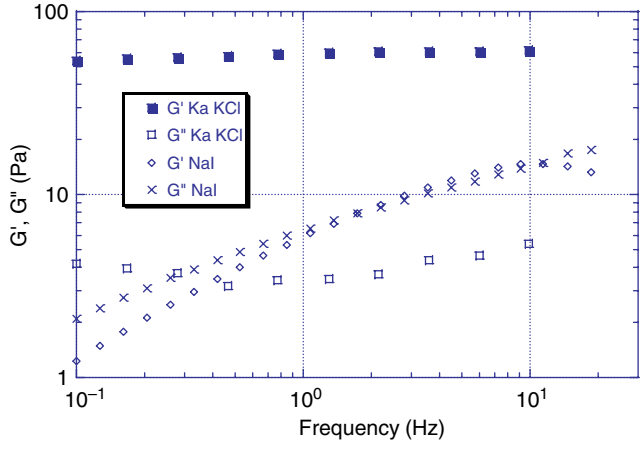

Fig. 11. Dynamic measurements on kappa-carrageenan as a function of the frequency in 0.1 *M* salt excess. G' ■ and G'' □ for Cp = 1 g/L in KCl; G' ◇ and G'' × for Cp = 10 g/L in NaI (214).