

# Novel Rheological Model for the Gelation Kinetics of Ionic Polysaccharides

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## Synopsis

Homogeneous networks of an ionic polysaccharide (namely pectate) in the presence of divalent ions were prepared *in situ* by proper procedure and the kinetics of the gel formation was studied by means of a coaxial cylinder rheometer in oscillatory flow conditions. The stress response was expanded in a Fourier series and the variation of the components of the fundamental harmonic with time during the gelation process were examined. A model is proposed for the correlation between kinetic parameters such as the concentration of the species active during the gel formation and the rheological parameters that can be experimentally determined, like  $G'$  and  $G''$ . Considerations are developed concerning the mechanism that governs the gelation process under dynamic conditions.

## INTRODUCTION

One of the most important properties of polysaccharides, from the standpoint of the biochemical function and of the industrial utilization, is their ability to form hydrated, crosslinked networks. In contrast to synthetic polymer gels, the crosslink formation does not occur through covalent bonds, but by cooperative noncovalent association of chain segments into extended junction zones of regular chain conformation, largely resembling that found in the solid state.<sup>1</sup> To achieve an expanded, hydrated network, rather than a solid precipitate, however, the system must also incorporate interconnecting regions of partial conformational disorder.

In the case of biopolymer networks, since the gel formation involves physical rather than covalent crosslinks, it is difficult to quantify unambiguously the number of crosslinks that are formed; moreover, the crosslinks themselves may also be transient in nature. In these respects, biopolymer networks share many features with synthetic systems such as polyacrylamide in the presence of Cr(III) and polydimethylsiloxanes, or temporary networks of ionomer systems where interchain bonding is noncovalent.<sup>2</sup>

From the experimental standpoint, structural information on networks has been mostly inferred from dynamic measurements and derived rheological quantities such as the complex modulus  $G^*$  and its elastic and viscous components,  $G'$  and  $G''$ , whereas the theoretical interpretation of most of the past research has been confined to a verification of the theory of rubber elasticity.

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Several of these studies<sup>3-6</sup> have been carried out on synthetic polymers, in which authors have focused attention on the evolution of the elastic modulus with the extent of the crosslinking reaction. On the other side, little attempt can be found in literature to correlate kinetic parameters (such as the concentration of the species that are active during the various steps of the gelation process) with the rheological parameters that can be experimentally determined, like  $G'$  and  $G''$ . Much attention has been given in the work of this laboratory on the thermodynamics of conformational, aggregational changes of ionic polysaccharides induced by specific ions. Since those changes are currently believed to be the macromolecular basis of the gelation phenomena that many of those systems are able to produce, in previous works<sup>7-8</sup> we tried to prove experimentally a correlation between the (macroscopic) rheological parameters of the gelation process and the relevant thermodynamic quantities of the conformational changes of two natural polyuronates, i.e., alginate and pectate. For practical reasons, we found it expedient to measure the rheological parameters as a function of time (i.e., the kinetics) during a chemically controlled process of *in situ* gel formation (see below).

In the case of alginate gels, the gelation process has its origin in a capacity of the polysaccharide molecules to specifically bind ions accompanied by conformational/aggregational changes. It has been shown<sup>1</sup> that calcium ions bind preferentially to guluronate blocks (G-blocks); the crosslinking then involves lateral association of guluronate segments of two different chains to form ordered junction zones. The divalent ions, cooperatively bound during the process, occupy the electronegative cavities ("egg-box" model). The junctions among these dimeric units then give origin to an elastic gel. Pectate gelation in the presence of calcium ions is reminiscent of the behavior of alginates, also because the galacturonic acid blocks in pectate are near mirror images of the G-blocks of the alginates. Thus, as for alginates, crosslinking of pectate chains is proposed<sup>1</sup> to occur by the egg-box model.

The successful comparison of the temperature dependence of the rheological "kinetic" parameters with the measured enthalpy changes of conformational transition<sup>7-8</sup> has clearly indicated that the origin of the elasticity of the ion-induced polyuronate gels is mainly enthalpic, at variance with the essentially entropic nature of the covalently linked, rubber-type gels and as already suggested by Andresen and Smidsrød several years ago.<sup>9</sup>

The present rheological work is aimed at proposing a more detailed, albeit phenomenological, kinetic model for the formation of ionic polysaccharide gels (namely pectate) in the presence of Ca(II) and a correlation between kinetic concentrations and rheological quantities.

## EXPERIMENTAL

### Materials

Sodium pectate was a Sigma product, Cat. No. P-3889 (Sigma Chem. Co., USA). D-glucono- $\delta$ -lactone was a Sigma product, Cat. No. G-4750, grade IX; the reagents for the preparation of calcium-ethylenediaminetetraacetic acid (EDTA) complex were of analytical grade and used without further purification.

Bidistilled water was used throughout. The temperature control (stability  $\pm 0.2^\circ\text{C}$ ) was achieved by external circulating liquid.

The polysaccharide gels were formed in presence of divalent ions following the procedure described by Toft et al.<sup>10</sup> The homogeneous release of divalent ions in a solution containing soluble polysaccharide chains was accomplished by adding D-glucono- $\delta$ -lactone, which hydrolyzes to gluconic acid and dissociates, lowering the pH. Under these conditions, the binding equilibrium of the  $[\text{CaEDTA}]^{++}$  complex is shifted towards the formation of free calcium ions in solution. The molecular ratio of total calcium-to-polymer repeating units,  $R$ , was 0.17 in all cases. The polymer concentration,  $C_p$ , was always  $2 \times 10^{-2}$  (mole uronate) $\text{L}^{-1}$ . Sodium chloride 0.1M as supporting electrolyte was used throughout.

### Methods

The apparatus used for dynamic tests was the torsionally oscillating rheometer (Haake RV 100, measuring device CV 100), mounted with a coaxial sensor system ZB 15 (Couette type). During the tests, while the outer cup is driven, the inner cylinder is mechanically positioned and centered by an air bearing. Top and bottom surfaces are recessed to minimize end effects. To reduce the destructive effects of the measurements on the forming gel structure, the cup was forced to oscillate with an amplitude of 0.175 rad; this value resulted to be the lowest compatible with measurable stresses, especially in the first time interval of the tests. The oscillation frequency at which measurements were carried out (0.314 rad/s) was sufficiently high to allow for neglecting the stress variation occurring during one cycle as a consequence of the gelation process.

In general, when the response of a rheometer to tests in oscillatory flow conditions is recorded in a stress-strain plane, elliptic Lissajous figures are obtained. Such figures correspond to real ellipses when the materials under examination exhibit a linear viscoelastic behavior, of which polymeric solutions can be taken as a typical example. On the other hand, when concentrated disperse systems undergo dynamic tests, even at small amplitudes, skewed Lissajous figures are usually obtained. Such a nonlinear viscoelastic behavior can be ascribed to the presence of aggregation structures in the disperse phase and to the consequent anisotropy of the system.

When a linear viscoelastic response is obtained, the determination of the complex viscosity  $\eta^*$  (or the complex modulus  $G^*$ ) and its viscous and elastic components  $\eta'$  and  $\eta''$  (or  $G''$  and  $G'$ , respectively) can be directly accomplished by the analysis of the corresponding Lissajous figures.

Calibration of the apparatus was performed by carrying out measurements on Newtonian fluids under the same experimental conditions utilized for the dynamic tests on gels, to evaluate both the response linearity of these systems under the selected operative conditions and the inertial effects due to the instrument and the fluid.

Having verified the effective linearity in the response for Newtonian systems and hence limited the analysis to the consideration of the fundamental harmonic alone, it has been possible to develop a standard procedure for the correction of the inertial effects to be applied in the data-reduction section. Although some theoretical procedures are available for the correction of the inertial effects,

they are generally complex and, in many cases, only approximated solutions can be obtained. The empirical procedure applied in this work was an easier task to perform and allowed for obtaining the inertial correction factors from experimental tests carried out on systems differing in viscosity and density.

### Theory

Most of the past research efforts in the area of gels and networks has been focused on studying the physicochemical nature of the crosslinking mechanism. In spite of the nonequilibrium character of most gels, thermodynamic approaches such as differential scanning calorimetry, equilibrium dialysis, optical rotatory dispersion, and ionic activity have been largely applied as sources of information about gels and gelling processes. On the other hand, few papers have appeared with the purpose of relating aspects of network structure to rheological behavior during the gelation process.

Starting from the fundamental works of Flory<sup>11-12</sup> and Stockmayer,<sup>13</sup> which appeared in the 1940s and have been and still are considered as the basis for the formulation of different theories of gelation, many papers have recently appeared in which the concentration dependence of the modulus of physically crosslinked gels is discussed in terms of classic theory of rubber elasticity. From the standpoint of the mechanism of gel formation, very few attempts to formulate a relation between kinetic and rheological parameters have been carried out. In a recent work<sup>14</sup> concerning the formation of a polyacrylamide gel in the presence of Cr(III) ions, Prud'homme et al. suggest the hypothesis that the maximum slope of the  $G'(t)$  curve, i.e., the maximum value of the  $G'$  derivative with time  $(dG'/dt)_{\max}$ , is a reliable measure of the rate of crosslink formation during gelation, if  $G'(t)$  is considered proportional to the crosslink density, according to the classical theory of rubber elasticity. Similar considerations can be drawn from the work of Roscoe<sup>15</sup>; the model proposed by the author on the basis of some simplifying assumptions suggests a correlation between the kinetics of the increase in the  $G'$  values and the increase in the number of the crosslinks, from a general point of view. In both papers, however, no hypothesis regarding the functional dependence of  $G'$  on time is formulated.

Aim of what follows is to present a kinetic model for the formation of a gel in the presence of ions and to correlate the concentration of the species that are active during the various steps of the process with the rheological parameters that can be experimentally determined, like the elastic and viscous components of the modulus,  $G'$  and  $G''$ , respectively.

The mechanism assumed to be a basis for the proposed model implies an initial phase characterized by the presence of the polymer in solution and a controlled release of ions. These conditions gradually lead to the formation of an ion-mediated ordered conformation, which can be thought of as composed of segments of chain faced in an ordered way and forced into such position by the presence of suitable cations. If such ordered species is indicated with  $B$ , and the initial species, which can be assumed to be monomeric and disordered, is indicated with  $A$ , it is possible to assume for the first step of the gel formation a condition of conformational equilibrium, which in general will read



In excess of free ions, the equilibrium is governed only by the initial polymer concentration;  $a$  is the number of associating (disordered) chains.

From this assumption, it follows that the initial concentration of the  $B$  species, indicated with  $B_0$ , is given by

$$B_0 = \kappa[(C_p/n) - B_0]^a \quad (1)$$

where  $\kappa$  is the equilibrium constant,  $C_p$  is the polymer concentration, and  $n$  is the number of chain monomers in the cooperative unit.<sup>16</sup>

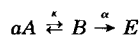
For conditions of low conversion ( $B_0 \ll C_p/n$ )

$$B_0 \simeq \kappa C_p^a/n^a \quad (2)$$

In a following step, the formation of a tridimensional network of the chain segments ordered in the ion-mediated structure starts to build up. These ordered segments, via the formation of a number of junctions, give origin to some wall-to-wall "connectivity lines," thus contributing to the increase of the elastic modulus. This mechanical model of statistical origin is known as the percolation model.<sup>8,17</sup> The percolation is a concept widely used in statistical physics for characterizing the behavior of a group of objects not completely connected together. In the case of the structure of a forming network, its significance is evident: only when the wall-to-wall connectivity is reached is the network able to bear a stress. As the connectivity grows up (i.e., the number of junctions connecting the ordered segments from wall to wall becomes larger), the elastic modulus  $G'$  increases. In other words,  $G'$  depends on the number of junctions that generates the connectivity lines.

However, not all the junctions among the chains or, to say, the individual sequences of the egg-box type between any two chain segments result in an increment of  $G'$ ; among all possible junctions, only those that lead to the connectivity lines can be considered as responsible for the increment in the value of  $G'$ . Hence, from the ordered conformation species  $B$ , represented by segments of chain faced in an ordered way and present at an initial concentration  $B_0$ , originates a whole series of junctions, among which there are those we can define as "effective" in terms of the gel elastic resistance.

If  $E$  is the concentration of the effective junctions, and if the gelation process is carried out under limiting conditions of no-shear or, at least, under conditions in which the applied deformations are negligible, the phases of the process described above become:



where  $\alpha$  is the first-order rate constant of the transformation process of the  $B$  species into the "effective"  $E$  species.

The evolution of the network with time is hence described by a system of differential equations

$$dB/dt' = -\alpha B \quad (3)$$

$$dE/dt' = \alpha B \quad (4)$$

The use of  $t'$  as the time variable indicates that the initial time of the gelation process does not coincide with the time  $t$  of the experiment. In general, during gel-forming processes like those considered here, the increase of  $G'$  becomes appreciable only after a time interval  $t_c$ , which can be defined, according to other authors' observations,<sup>14-15</sup> as an induction time.

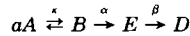
Upon integration of eqs. (3) and (4) with the boundary conditions that, at the instant  $t' = 0$ , the concentration of the  $B$  species must be equal to  $B_0$ , one gets:

$$B = B_0 \exp(-\alpha t') \quad (5)$$

$$E = B_0 [1 - \exp(-\alpha t')] \quad (6)$$

This model has a rigorous validity only under nondestructive working conditions, in which it can be assumed that no breakdown of the connectivity lines occurs. On the contrary, in each dynamic test some destructive effects due to the actual shear conditions are present. Hence, it is necessary to take into account the processes that lead to the effective junctions breakdown and therefore to the formation of "flow units"  $D$ , constituted by chains linked in a different way and consequently having different dimensions.

The scheme of the consecutive processes can be then modified as follows:



where  $\beta$  is the rate constant of the network breakdown process, assumed to be of the first order.

The system of differential equations reported above therefore becomes

$$dB/dt' = -\alpha B \quad (3)$$

$$dE/dt' = \alpha B - \beta E \quad (7)$$

$$dD/dt' = \beta E \quad (8)$$

Integration of eqs. (3), (7), and (8) with the boundary conditions that, at the time  $t' = 0$ , the concentration of the  $E$  species must be equal to 0 gives

$$B = B_0 \exp(-\alpha t') \quad (5)$$

$$E = \alpha B_0 / (\alpha - \beta) [\exp(-\beta t') - \exp(-\alpha t')] \quad (9)$$

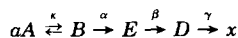
$$D = B_0 [1 - \beta \exp(-\alpha t') / (\beta - \alpha) + \alpha \exp(-\beta t') / (\beta - \alpha)] \quad (10)$$

From the expression of  $E$  [eq. (9)] it can be seen that the concentration of the  $E$  species reaches a maximum value at time  $t'_{mE} = [1/(\beta - \alpha)] \ln(\beta/\alpha)$ . From the expression of  $D$  [eq. (10)] it is also evident that, for  $t' \rightarrow \infty$ , the concentration of the  $D$  species tends to the maximum value  $B_0$  with a monotonic path.

By operating under highly destructive conditions, further degradations of the system can be obtained, resulting in the reduction of the  $D$  species into different flow units of smaller dimensions, whose contribution to the viscous

component can be considered negligible if compared with that due to the  $D$  species.

If these small flow units are cumulatively identified as the  $x$  species, the final scheme can be hypothesized as follows:



where  $\gamma$  is the first-order rate constant for the process that leads to the complete breakdown of the network.<sup>18</sup>

Taking into account the last consecutive reaction, the differential equation (8) for the description of the course of the concentration of the  $D$  species with time becomes

$$dD/dt' = \beta E - \gamma D \quad (11)$$

Upon integration of eqs. (3), (7), and (11) with the boundary conditions that, at  $t' = 0$ , the concentrations of the species  $E$  and  $D$  must be equal to 0, one finally gets

$$B = B_0 \exp(-\alpha t') \quad (5)$$

$$E = \alpha B_0 / (\beta - \alpha) [\exp(-\alpha t') - \exp(-\beta t')] \quad (9)$$

$$D = \alpha \beta B_0 \left\{ \exp(-\gamma t') / [(\gamma - \alpha)(\gamma - \beta)] + \exp(-\alpha t') / [(\gamma - \alpha)(\beta - \alpha)] - \exp(-\beta t') / [(\gamma - \beta)(\beta - \alpha)] \right\} \quad (12)$$

$$\chi = \alpha \beta \gamma B_0 \left\{ \exp(-\beta t') / [\beta(\beta - \alpha)(\gamma - \beta)] - \exp(-\alpha t') / [\alpha(\beta - \alpha)(\gamma - \alpha)] - \exp(-\gamma t') / [\gamma(\gamma - \alpha)(\gamma - \beta)] \right\} \quad (13)$$

From the proposed scheme, it follows that also the concentration of the  $D$  species passes through a maximum at a time  $t'_{mD}$ , which results to be greater than  $t'_{mE}$  and corresponds to the root of the equation

$$\gamma(\beta - \alpha) \exp(-\gamma t'_{mD}) + \alpha(\gamma - \beta) \exp(-\alpha t'_{mD}) - \beta(\gamma - \alpha) \exp(-\beta t'_{mD}) = 0 \quad (14)$$

The theoretical approach considered herein describes the kinetics of the buildup and breakdown processes of different species that have been assumed to be present in the system during the gelation procedure. Figure 1 shows a schematic representation of the profiles of the concentrations of the rheologically active species,  $D$  and  $E$ , as a function of time under the different kinetic conditions considered (ranging from nondestructive conditions up to highly destructive ones).

To step further to develop a rheological model able to describe the change of the complex modulus  $G^*$  and its components  $G'$  and  $G''$  with time, it is necessary to make some hypotheses on the nature of the species effectively active from a rheological point of view, and on the correlations between  $G'$  and  $G''$  and the concentration of these same species. With the aim of defining a simple functional dependence of the rheological variables on time, and to limit

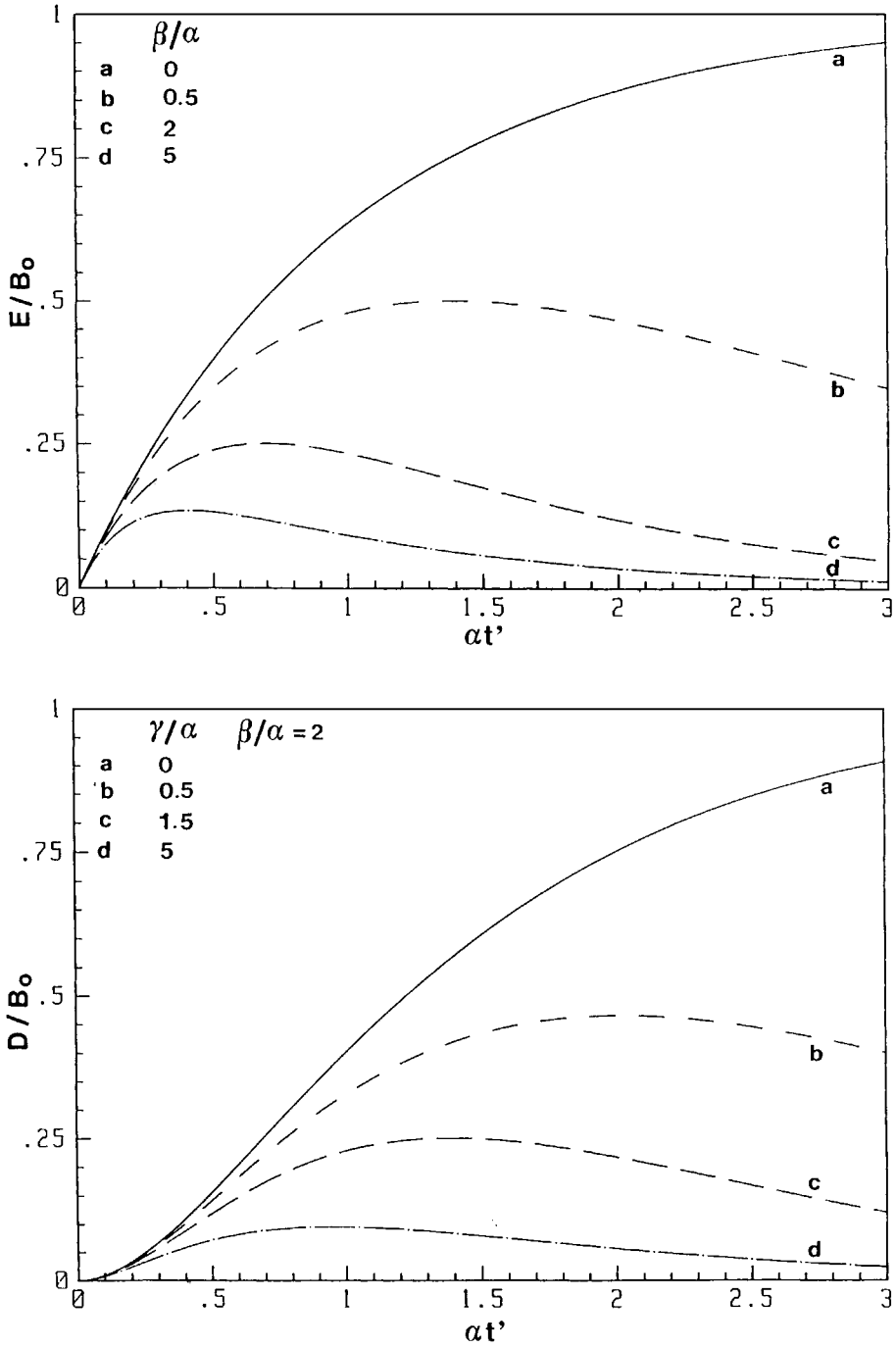


Fig. 1. Concentration of the rheologically active species  $E$  (top) and  $D$  (bottom) vs. time for different kinetic conditions.



the number of the involved parameters and the degree of correlation among them, it is useful to assume a unique correlation between  $G'$  and the concentration of  $E$ , and between  $G''$  and the concentration of  $D$ , respectively. In other words, it is assumed that the contribution to the elastic component of the modulus  $G'$ , due to the efficient junctions,  $E$ , is predominant over all other contributions from the different species present in the system, in particular of  $D$ . On the other hand, the viscous component is assumed to depend mainly on the concentration of the bigger flow units of the  $D$  type.

The equations proposed for the concentration dependence of  $G'$  and  $G''$  are the following

$$G' = \kappa' E^m \quad (15)$$

$$G'' = \kappa'' D^n \quad (16)$$

The simple functional dependence of the power law type resembles those of other equations found in the literature; e.g., for disperse concentrated systems,<sup>19-20</sup> various types of parameters, such as the yield stress  $\tau_0$  and the limit value of the modulus,  $G'_0$ , follow this scaling dependence on the concentration of the disperse phase. In those cases, the rheological quantities  $\tau_0$  and  $G'_0$  are also connected to the formation of temporary junctions and, through them, to the onset of a tridimensional network, in analogy to what has been suggested for the gels and their  $G'$  values. In the case of  $\tau_0$  and  $G'_0$ , the power law exponent, determined by comparison with the experimental data, generally falls between 2 and 3. In the present case, the value of the exponents  $m$  and  $n$  of eq. (15) and (16), respectively, can be determined only by numerical fit of the experimental data.

## RESULTS AND DISCUSSION

For all the calcium-pectate systems examined, the initial rheological response is linear and elliptic Lissajous figures are obtained. Only after a time interval, or induction period, the variation of the shear stress with time differs appreciably from the simple sinusoidal one; this produces in skewed Lissajous figures varying in shape and dimensions with time (see Fig. 2).

The stress response was expanded in a Fourier series to evaluate the amplitude and the phase angle of the fundamental as well as the higher-order harmonics.

To discuss the results in terms of linear viscoelasticity, it should be possible to limit considerations to the elastic and viscous components of the fundamental harmonic ( $G'$  and  $G''$ ). If the analysis of the viscoelastic behavior is confined to the fundamental harmonic, the approximation introduced can be evaluated by comparing the maximum amplitude of the fundamental vibration with those of the higher-order harmonics, and then determining the accuracy obtained in the description of the Lissajous figure or of the variation of stress with time by using the fundamental harmonic alone. In general, for the systems examined, the amplitudes of the even harmonics are within the range of the experimental error and are negligibly small if compared with the odd ones. The ratio between the second and the fundamental harmonic is, generally, lower than 0.03. Thus,

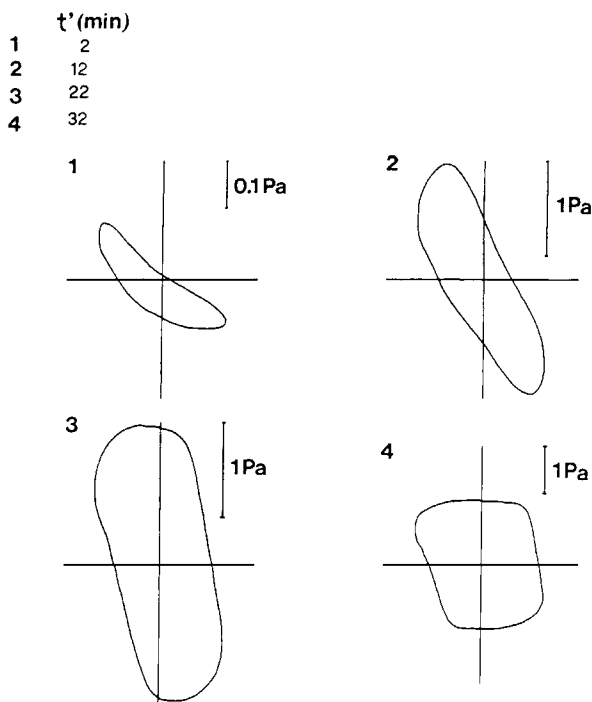


Fig. 2. Lissajous figures obtained at different times during the gelation process for the system Ca(II)/pectate at 25°C.

it follows that only the fundamental vibration and the higher odd harmonics (third and fifth) are significant for the description of the dynamic behavior of the systems studied here. As a matter of fact, a reasonable limit of significance for the ratios between the higher order harmonics and the fundamental one can be set equal to 0.03.

A typical plot of the higher odd harmonics vs. time is reported in Figure 3; it is evident from this figure that the behavior of the system examined becomes increasingly nonlinear with time.

In Figure 4, the experimental record of the vibration of the bob is plotted as a function of time and compared with calculated waves obtained by synthesis of the components corresponding to the fundamental vibration and to the relevant harmonics, determined as a result of the harmonic analysis. The synthetic wave obtained as the sum of the odd harmonics approaches the experimental one rather closely, but a still acceptable degree of approximation is given by the fundamental harmonic alone.

Consequently, the analysis of the results can be carried out with good approximation on the basis of the values of the fundamental harmonic  $G^*$  and its viscous and elastic components  $G'$  and  $G''$ . Figure 5 shows an example of the behavior of these quantities as a function of the time of gelation for the system Ca(II)/pectate at 25°C. For all the samples examined, each rheological variable is an increasing function of time until it reaches a maximum value, after which it begins to decrease; this is due to the prevailing destructive action of the shear. The elastic component reaches its maximum before the maximum

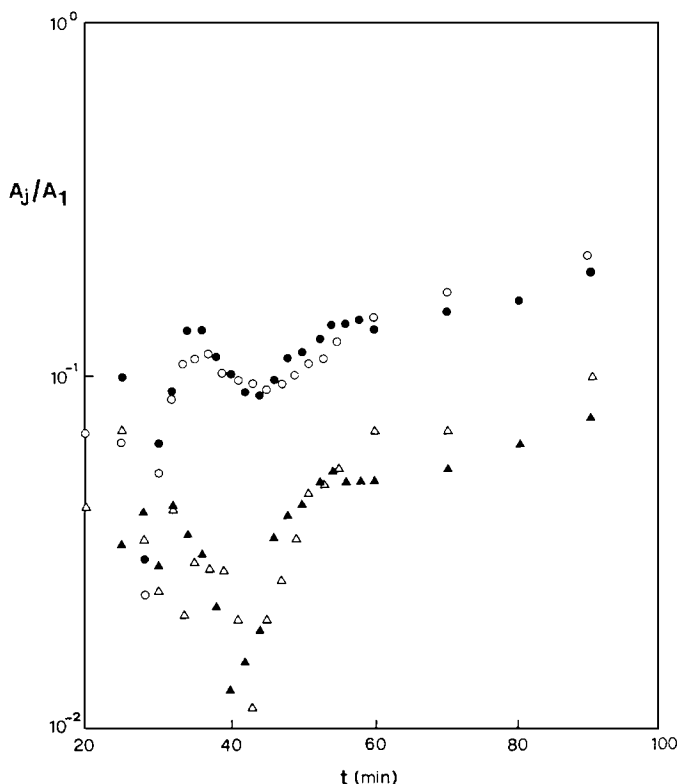


Fig. 3. Amplitude ratio of higher odd harmonics vs. time ( $A_3/A_1$ :  $\circ$ , 25°C;  $\bullet$ , 30°C;  $A_5/A_1$ :  $\Delta$ , 25°C;  $\blacktriangle$ , 30°C).

value of  $G''$  is reached, according to the results predicted by the model described in the previous paragraph. In particular, it is evident that the version that seems to be more suitable for the description of the gelation process is that relative to the shearing motion under highly destructive conditions, which results from combining eqs. (9), (12), (15), and (16). Several other experiments were carried out in different physical and chemical conditions, the same pattern was found in all cases.

The definition of the rheological model implies the determination of the values of the parameters; this can be performed more easily if the degree of correlation among the parameters is reduced. At the same time, it gets easier to compare the results that are obtained for the different systems. Accordingly, a preliminary parametrical study has been carried out on the values for the exponents  $m$  and  $n$  to operate a choice of the optimal set of values. Then, having kept these values fixed, it has been easier to determine the values for all the other parameters of the model.

The parametric study has been carried out on the data relative to the system Ca(II)/pectate at 25°C. In Figure 6, the comparison among different cases examined is carried out on the basis of the values relative to the normalized standard errors.

It is evident that the choice of the values  $m = 2$  and  $n = 1$  allows the best results to be attained. This set of values for the exponents turns out to be valid

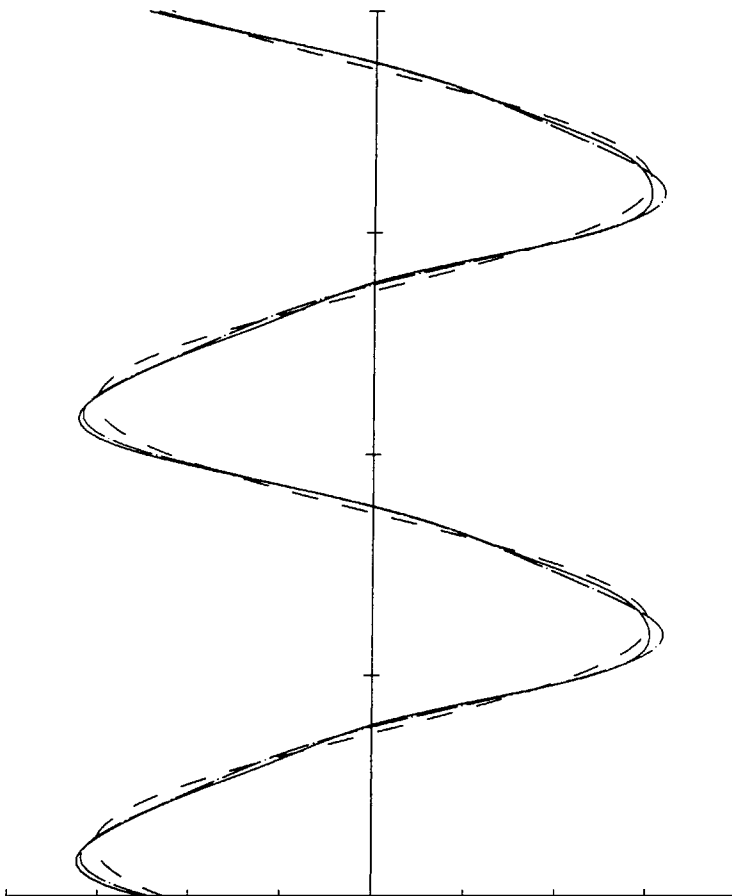


Fig. 4. Plot of the experimental vibration (—), the fundamental harmonic (---) and the synthetic wave (- · -) calculated as the sum of the odd harmonics against time for the system Ca(II)/pectate at 25°C ( $t' = 17$  min).

for all the systems experimentally examined in this work, the normalized standard error ranging between 0.037 and 0.052. Moreover, some successful tests using  $m = 2$  and  $n = 1$  performed on systems of extremely different nature such as polyacrylamide<sup>14</sup> and aluminum stearate<sup>15</sup> gels, characterized by totally different mechanism of the gelation process, show the excellent capability of fitting of the model.

The fitting of the experimental data with the model allowed for obtaining the values for the following adjustable parameters:  $\alpha$ ,  $\beta$ ,  $\gamma$  and for the combinations  $\kappa' B_0^2$  and  $\kappa'' B_0$ . The separate application of the model to systems at different temperatures has proved that the parameters  $\beta$  and  $\gamma$  do not vary appreciably with temperature. On the other hand,  $\alpha$ , the kinetic constant for the process that leads to the formation of the effective species, increases with temperature, and its dependence has been shown to be of the Arrhenius type:

$$\alpha = A_\alpha \exp(-E_\alpha/RT) \quad (17)$$

The products  $\kappa' B_0^2$  and  $\kappa'' B_0$  decrease with temperature; being  $\kappa'$  and  $\kappa''$  only

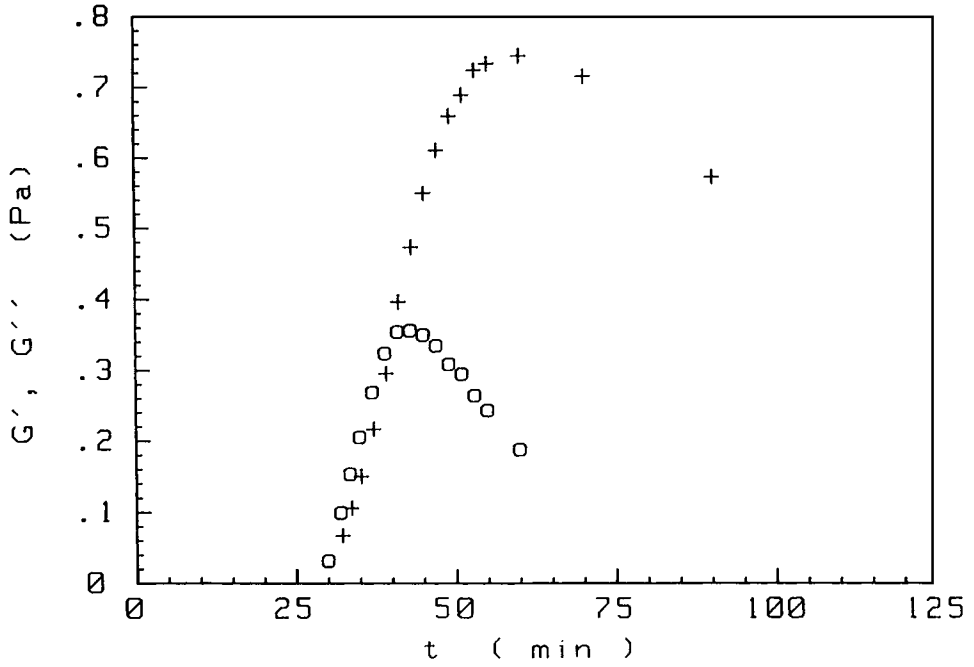


Fig. 5. Plots of  $G'$  (O) and  $G''$  (+) against time of gelation for the system Ca(II)/pectate at 25°C.

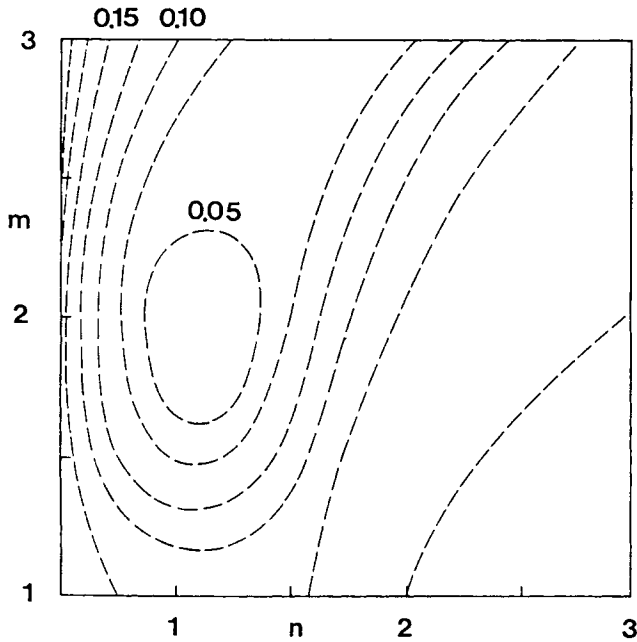


Fig. 6. Contour lines at constant normalized standard error for the system Ca(II)/pectate at 25°C.

scaling constants, this fact can be related with the dependence of  $B_0$  on temperature through<sup>21</sup>

$$B_0 = \kappa C_p^a / n^a = \kappa^* [\exp(-\Delta H^* / RT)] C_p^a \quad (18)$$

where  $\kappa^*$  includes both the scaling parameters and the entropic contributions, and  $\Delta H^*$  is the conformational enthalpy change for dynamic junction formation.

It has been possible to carry on a simultaneous fitting of all the experimental  $G'$  and  $G''$  data for all the systems examined by assuming for  $t_c$  the values obtained from the separated fittings and setting  $a = 2$ . If one considers the limited number of adjustable parameters (7) and the large amount of experimental data analyzed (270), the results are satisfactorily valid, as it can be inferred from the comparison between the experimental data and the theoretical curves reported for a sample case in Figure 7. The values for the parameters of the proposed model for the Ca-induced pectate gelation are reported below:

$$\begin{aligned} A_\alpha &= 81 \text{ min}^{-1}, E_\alpha = 16.8 \text{ kJ mole}^{-1} \\ \beta &= 0.0460 \text{ min}^{-1}, \gamma = 0.0438 \text{ min}^{-1} \\ \kappa'(\kappa^*)^2 &= 11.4 \text{ Pa mole}^{-1}, \kappa''\kappa^* = 6.15 \text{ Pa mole}^{-1} \\ \Delta H^* &= -16.8 \text{ kJ mole}^{-1} \end{aligned}$$

Among all the parameters listed above, an additional comment can be made on the value of  $\Delta H^*$ , which represents the enthalpy change for the conformational equilibrium and is obviously computed per mole of cooperative unit

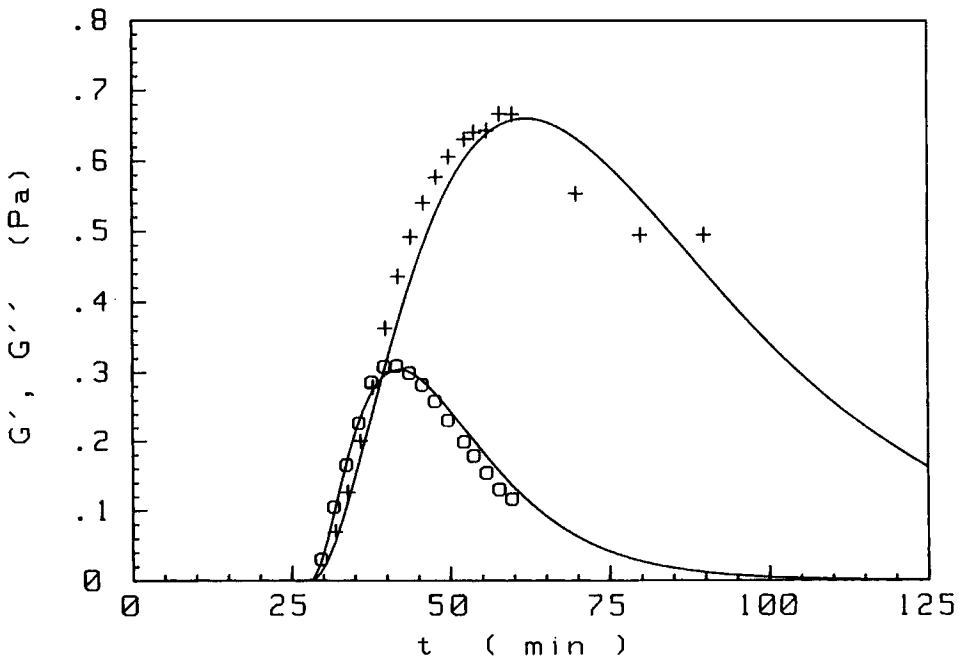


Fig. 7. Comparison between the experimental data of  $G'$  (O) and  $G''$  (+) and the calculated curves obtained for the system Ca(II)/pectate at 25°C.

involved. At the molecular level, the enthalpy change<sup>22</sup> of Ca(II)-induced conformational transition of an uronate monomer is about  $-3 \text{ kJ (mole sugar)}^{-1}$ ; consequently, it can be concluded that about three galacturonic units must cooperatively form a row, together with an opposing sequence of the same size, to specifically bind Ca(II) ions.

The identity of  $E_\alpha$  and  $-\Delta H^\ddagger$  might not be fortuitous. In fact, to achieve an optimal sequence of joints to form the wall-to-wall effective  $E_\alpha$  species, it could be necessary to break (cfr.  $E_\alpha = -\Delta H^\ddagger > 0$ ) an already formed junction which is, however, not connecting the line of force between the walls, and to reform it in a new but effective matching.

## CONCLUSIONS

The aim of this paper was the formulation of a model able to describe the gelation process of polysaccharide systems under different shear conditions. Consequently, some hypotheses concerning the mechanisms on molecular bases and the correlation between active species and rheological parameters have been formulated. The model hence derived turned out to be able to describe, from a phenomenological point of view, not only the behavior of these systems but also the behavior of systems characterized by a totally different nature; moreover, a further evidence of the validity of this model is given by the positive comparison of the values obtained for the activation enthalpy of the systems examined with those obtained for the same systems by other nonrheometrical techniques.

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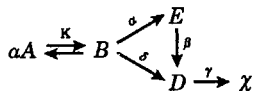
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16. For the case of the dimerization equilibrium that is known to take place for alginate and pectate calcium gels, the equation of  $B$  will read:

$$B = \frac{1}{2}(C_p/n) + (1/8\kappa) - \sqrt{(1/8\kappa)^2 + (C_p/n)(1/8\kappa)}$$

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18. Among the many more different models that might be conceived to describe the observed kinetics, a reasonable one could allow for direct interconversion of species  $B$  into  $D$ , with an additional rate constant for the process:



Such a model, as well as all the other possible ones, needs an additional fitting parameter (the kinetic constant), the introduction of which does not seem to be justified by the experimental data and, after all, by the success of the three kinetic parameter model described in the text.

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21. The approximated form of eq. (18) can be used in the present case since the fraction of  $C_p$  involved in binding with calcium is small ( $R = 0.17$ ). Moreover, the presence of substantial amount of supporting 1 : 1 electrolyte will make the  $\text{Na}^+$  concentration about 30 times larger than that of  $\text{Ca}^{++}$  and hence the  $\text{Na}^+/\text{Ca}^{++}$  competition will even more reduce the number of the calcium-linked  $B_0$  species.

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Received July 10, 1989

Accepted September 25, 1989