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Polymer Vol. 36 No. 4, pp. 815-819, 1995

0032-3861/95/$10.00+0.00

Rheological study of the gelation kinetics of the scleroglucan–zirconium system

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(Received 25 February 1994; revised 22 June 1994)

The formation kinetics of scleroglucan–zirconium gels was studied using rheological measurements. It was possible to determine such kinetics by following the change in solution elastic modulus as a function of time. Gelation kinetics was found to increase vs. polymer concentration according to a power law function. In contrast, when zirconium concentration was increased, gelation kinetics was found to increase, reaching a critical value and then decreasing drastically. On the other hand, the influence of temperature showed that the crosslinkage process was endothermic ($W_A \approx 33\,\mathrm{kJ\,mol^{-1}}$). The last parameter studied was the pH. Our results clearly demonstrate that gelation was enhanced by pH elevation. So, despite the complicated zirconium chemistry, an explanation of observed behaviour was attempted on the basis of the presumed formed species.

(Keywords: rheology; gelation kinetics; zirconium)

INTRODUCTION

In past years, polymer gels have been extensively investigated because of their great interest in both the theoretical field[1] and in numerous industrial applications[2,3]. For example, the permeability of oil reservoirs may be modified by means of *in situ* gelation processes in additional oil recovery[4,5]. Therefore, gelation kinetics has been the principal property investigated because of its dependence on the prevailing physicochemical conditions. Various techniques, including n.m.r.[6], rheology[7] and microscopy[8], have been used to follow gel formation, and explanations of the observed behaviour were usually given on the basis of reactions involved in the gelation process. The main group of polymeric gels is those obtained by adding an appropriate crosslinking agent to semidilute solutions of a given polymer. Transition metals are often used for this purpose[9].

In the present work, we focus our study on the gelation kinetics of a weak polymeric gel. The polymer chosen is a neutral polysaccharide, scleroglucan[10]. It is a linear but relatively rigid polymer with weight-average molecular weight close to 3×10^6. The crosslinking agent is zirconium which, in aqueous solution, exists in complexed polymeric forms except under particular conditions (high acidity, i.e. $[\mathrm{H}^+] = 1$–$2\,\mathrm{M}$, and low concentrations, i.e. $<5 \times 10^{-4}\,\mathrm{M}$) where its monomeric species are predominant[11]. For intermediate conditions, the zirconium hydrates undergo polymerization and hydrolysis as described below[3,12]:

$$x[\mathrm{Zr(H_2O)_8}]^{4+} \leftrightarrow [\mathrm{Zr}_x(\mathrm{OH})_y(\mathrm{H_2O})_{(8x-2y)}]^{(4x-y)+} + y\mathrm{H_3O^+} \qquad (1)$$

For intermediate zirconium concentrations in highly acidic medium, n.m.r. and spectrophotometry studies reveal that the main polymeric species is a cyclic tetramer with a hydration number of four[13-15]. The hydrolysis reaction has been reported to be enhanced as pH value increases[11]. In other respects, zirconium reacts with oxyacids to form complex species with varying stability[11]. So, crosslinkage between $\mathrm{Zr^{4+}}$, or its polymeric forms, and polymer is fundamentally a ligand exchange process. During this crosslinking reaction, some ligands of zirconium complexes are replaced by oxygen coming from the polymer hydroxyl groups, as given by equation (2) in a simplified manner:

$$\mathrm{Zr}_x(\mathrm{L})_n + m\mathrm{P(OH)} + m(\mathrm{H_2O}) \leftrightarrow \mathrm{Zr}_x(\mathrm{PO})_m(\mathrm{L})_{n-m} + m\mathrm{L} + m\mathrm{H_3O^+} \qquad (2)$$

In this unbalanced reaction, P(OH) represents the polymer complexation sites, L is a ligand, and the coefficient m is a whole number greater than 1. When L represents $\mathrm{H_2O}$ or $\mathrm{OH^-}$, the ligand exchange is a relatively rapid process. This exchange should, however, be much slower when L is an organic ligand. In any case, the ligand exchange/crosslinking reaction is an equilibrium process, consequently the gelation proceeds only when zirconium–polymer crosslinking complexes are more thermodynamically stable than zirconium–ligand complexes. It should be emphasized that crosslink formation resulting from organic ligand exchange should lead to a decrease in the pH of the solution (reaction (2)).

On the other hand, a controlled stress rheometer (Carri-Med CSL 100) has been used to follow the gelation kinetics of this system by measuring the modification of its rheological properties. It is well known from the theory of elasticity[16] that elastic modulus G' is proportional to the density of formed crosslinks ν as indicated by:

$$G' - G'_0 = q\nu kT \qquad (3)$$

where G'_0 is the elastic modulus of fresh polymer solution, kT is the Boltzmann factor and q is a coefficient which lies between 0.4 and 1 depending on the system under study.

It appears that measurement of elastic modulus must give information about the advance in crosslink formation. In this paper we present the influence of both polymer and zirconium concentration, in addition to pH and temperature, on the system gelation kinetics.

EXPERIMENTAL

Polymer solutions of defined concentration were obtained by dissolving various amounts of scleroglucan in synthetic seawater (30 g l^{-1} NaCl + 3 g l^{-1} $CaCl_2$). NaN_3 (400 ppm) was added to polymer solutions in order to prevent microbial degradation. The pH was then adjusted with aqueous HCl or NaOH solutions. Each polymer concentration used was many times greater than the overlapping concentration C^* ($\approx$200 ppm) so that no gelation would be obtained below C^*[17]. The zirconium sample used in this study was furnished by Zirtech (Midland, TX, USA). It was in the form of zirconium lactates in order to stabilize it. The zirconium concentration, C_{Zr}, is given in ZrO_2 equivalent concentration. The prepared samples were transferred to the rheometer as soon as the desired amount of zirconium was added to the polymer solution. Before the experiments, it was taken into account that the elastic modulus measurement should be done in the linear regime. Consequently, the change of sample G' was measured in the course of time at sufficiently low deformations, and all reported experiments were performed at a frequency of 1 Hz.

RESULTS AND DISCUSSION

In most cases, the sample elastic modulus increases rapidly and reaches a plateau, indicating that gel formation is over. Typical G' values of these gels due to the crosslinkability are found to be at most two times greater than their initial values, G'_0, which correspond to the fresh polymer solutions. *Figure 1* shows a typical plot of G' variation during the gelation process. Subsequently the gelation kinetics are determined from G' *versus* time curves in terms of their initial slopes. Indeed, when relation (3) is derived in respect of time, dG'/dt expresses the rate of crosslink creation at a given temperature. So, the influence of retained factors on the gelation kinetics has been examined in that way.

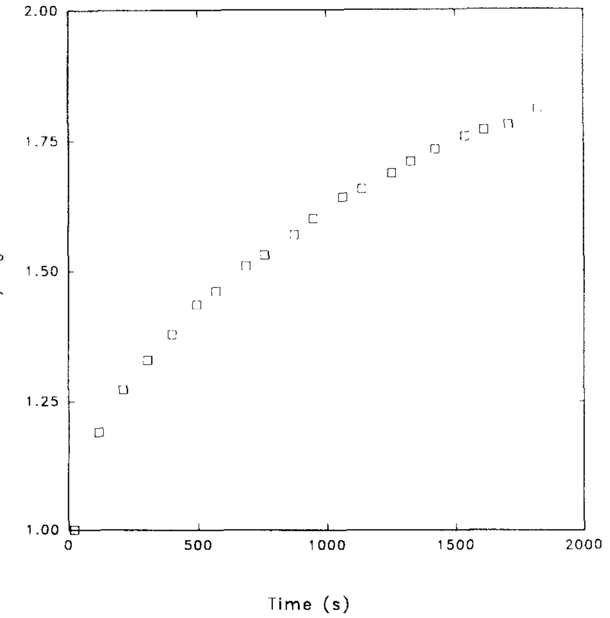

Figure 1 Typical plot of elastic modulus during system gelation when normalized by its initial value

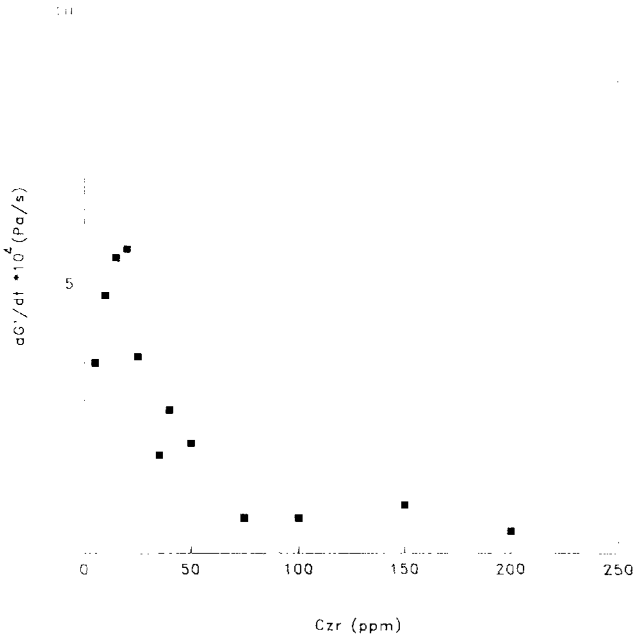

Figure 2 Gelation kinetics, dG'/dt, *versus* C_{Zr} at C_s = 1000 ppm, pH = 7 and T = 35°C

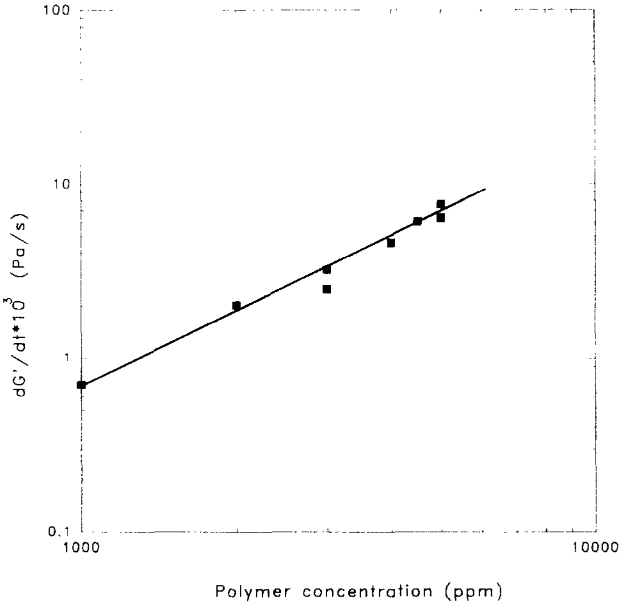

Figure 3 Variation of gelation kinetics with polymer concentration at C_{Zr} = 25 ppm, pH = 7 and T = 35°C

Influence of concentrations

Figure 2 shows the change in gelation kinetics as zirconium concentration, C_{Zr}, increases. It is clear that, starting from zero, the gelation kinetics increases as C_{Zr} increases and passes through a maximum before undergoing a drastic decrease. For higher zirconium concentrations, no gel formation is observed. Moreover, the plateau value obtained at the end of gelation, $G' - G'_0$ (which may be called the gel strength), shows an identical variation when plotted against C_{Zr} (data not shown). The behaviour of the present system is unusual when compared to that of systems with simpler chemistry, in which gelation kinetics is found to follow a power law dependence on the crosslinker concentration[7,18]. To explain such observations, we advance the following hypothesis: during the cross-linkage process some lactate ligands dissociate from the zirconium complex before their substitution by polymer oxygen hydroxyl groups. This explanation is supported by the fact that, in the presence of ligands which form with Zr complexes of higher stability, the gelation kinetics is found to be slower (data not yet published). Similar results were obtained with the Cr^{3+}–polyacrylamide system[19]. On the other hand, the crosslinkage reaction competes with formation of higher zirconium polymeric species as C_{Zr} increases. In this manner, the critical zirconium concentration (≈30 ppm), beyond which gelation kinetics decreases, must correspond to the onset of formation of very large polymeric species. These species are then less reactive towards the polymer macromolecules in addition to possible hindrance effects reducing the build-up of crosslinks. The obtained value of the critical zirconium concentration must, however, depend on the polymer concentration and physicochemical conditions.

In the same way, the influence of scleroglucan concentrations, C_s, on gelation kinetics is investigated. In the previous pH and temperature conditions, C_s varies from 1000 to 5000 ppm while C_{Zr} is maintained at a fixed value ($C_{Zr} = 25$ ppm). As shown in *Figure 3*, we find that the gelation kinetics is an increasing power law function of C_s, i.e. $dG'/dt \cong C_s^{1.4}$. This behaviour is usually observed for several systems[2,7,18]. For most polymeric gels, the corresponding exponents to polymer concentration are rarely whole, owing to the complex nature of macromolecular solutions. This exponent is essentially sensitive to the structure and the conformation of the considered polymer, since cooperative phenomena play an important role in gel formation. Values reported in the literature for relatively rigid polymers are commonly small when compared to those obtained for highly flexible polymers[7,18]. For example, this exponent is close to 2.7 for polyacrylamide with different crosslinkers, while it equals 2/3 for the hydroxypropylguar–titanium system[2].

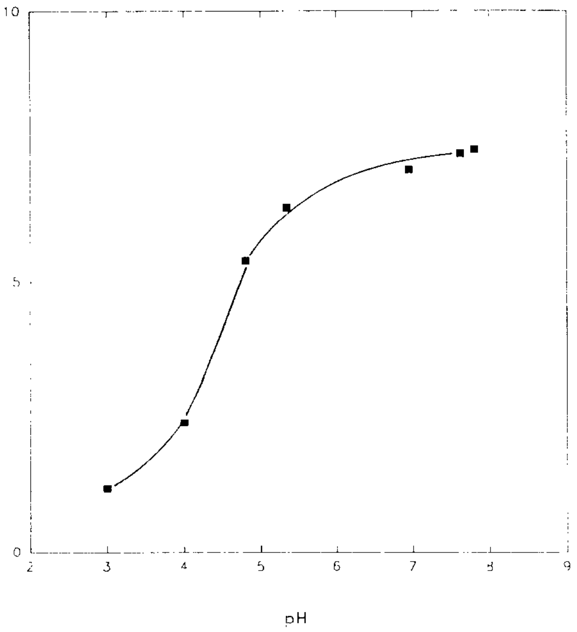

Figure 4 Influence of initial pH on gelation kinetics for $C_s = 1000$ ppm, $C_{Zr} = 25$ ppm and $T = 35°C$

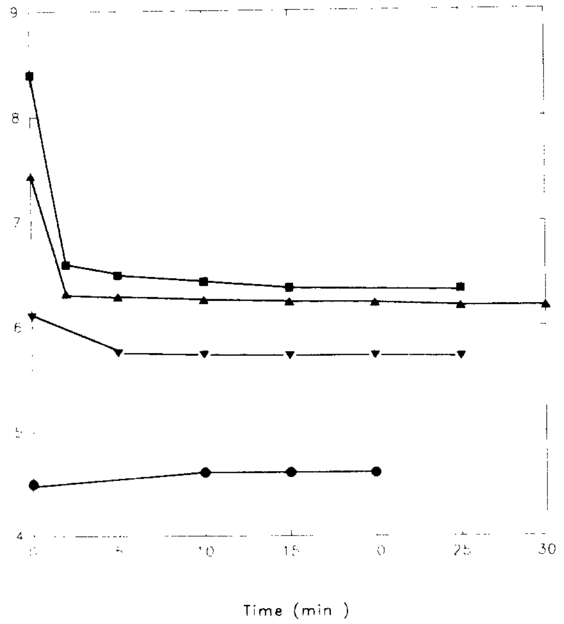

Figure 5 Variation of sample pH during gelation

Influence of pH

In this section the influence of initial sample pH on the gelation kinetics is examined. In our experiments, we follow in the course of time the changes of both the sample elastic modulus and pH. The variation of gelation kinetics with initial sample pH and the change in pH during gelation are shown in *Figures 4* and *5*, respectively. It appears that gelation kinetics is an increasing function of initial pH but seems to reach a plateau above a critical pH value, pH*. This critical value is close to the equilibrium pH of zirconium lactate at the considered concentration (≅5.7). Although the chemistry of zirconium is greatly influenced by pH in a complicated manner, we suggest that the noticed effects of pH on the gelation kinetics are a consequence of the following contributions.

(i) Examination of the crosslinking (reaction (2)) shows that increase in pH should be expressed in gel formation enhancement.

(ii) The equilibrium reactions between zirconium lactate and lactic acid (a weak acid) are displaced for the benefit of the dissociated lactate form as pH increases. This contribution by yielding of the lower stability zirconium lactate of course goes in the same way as (i).

(iii) In contrast, and as we emphasized before, the zirconium hydrolysis is increased by increasing pH value. This should be a delaying factor on gelation since the electrical charge of zirconium species is lower (see equation (1)).

The crosslinking reaction results then from competition between these contributions.

The dissociated lactate ligands from the crosslinkage reaction are used to displace the lactic acid equilibrium for $pH < pH^*$ while they serve to form zirconium lactate for $pH > pH^*$. This last effect, in addition to the zirconium hydrolysis, may explain the observed behaviour in alkaline medium. Lockhart *et al.*[5], studying gelation of Cr^{3+}–polyacrylamide solutions, have also shown that the gelation time decreases as sample pH increases from 3 to 6. Furthermore, the calculation of gelation time *versus* pH, using available values of equilibrium and kinetic constants of Cr^{3+} dimerization, appeared to be only in qualitative agreement with experimental results. To explain the observed quantitative discrepancy, they noticed that the pH increase promotes the formation of chromium hydroxide monomers. So, they hypothesized that since this reaction is a determinative one, these species should be more reactive towards polyacrylamide. Their results seem, however, to be in contradiction with those reported in the same paper and which indicate that chromium oligomers are accelerating the gelation rate. In our opinion, the degree of polyacrylamide hydrolysis may be put forward to explain the quantitative discrepancy involved above, which is indeed more pronounced at low pH values.

On the other hand, when the change in sample pH during gelation is considered, we remark that the recorded pH variation is of two different kinds depending on its initial value (cf. *Figure 5*). First, starting at high initial values ($pH > 6$) the sample pH undergoes a rapid decrease before it reaches a plateau. It is observed that the decrease is more marked as the initial pH value is high. This may be explained by following the argument given above. At these pH values, the crosslinkage process produces supplementary H_3O^+ ions with formation of lactate salts, but at the same time the pH decrease induces limitation in crosslinkage rate and then an equilibrium state is reached. The second type of behaviour observed is the slight increase of sample pH in the course of time when starting at a low level. At this pH value, only a few crosslinks are formed and the released lactates proceeding from gelation serve to displace the lactic acid equilibrium. The observed slight increase is probably due to the tendency of the system to reach the zirconium lactate equilibrium value ($pH \approx 5.7$).

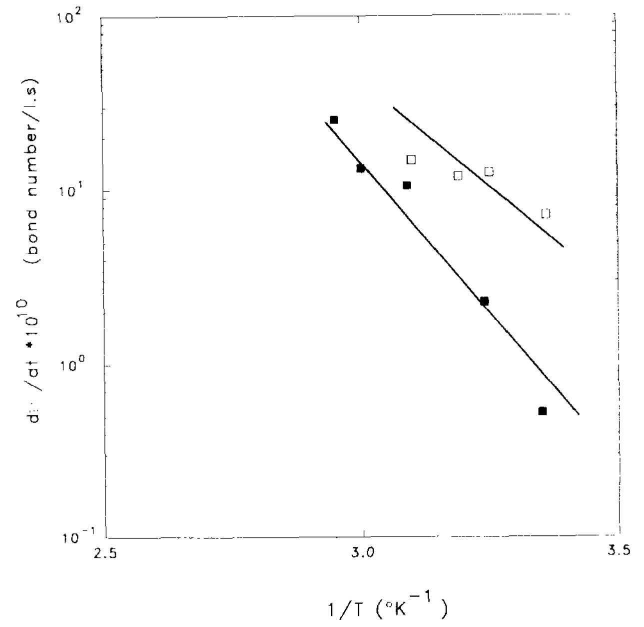

Figure 6 Influence of temperature on created bond density, dν/dt, at $C_{Zr} = 25$ ppm and pH = 7: ■, $C_s = 1000$ ppm; □, $C_s = 3000$ ppm

Influence of temperature

The last parameter investigated in this study is temperature. For this purpose two polymer concentrations are used. The results are plotted in semi-log coordinates (*Figure 6*). The quantity reported on the ordinate axis is the rate of bond creation, dν/dt, determined from equation (3), where the parameter q is taken as equal to unity. It clearly appears that the crosslinkage process is favoured when temperature increases. Moreover, this endothermic reaction follows the Arrhenius law; the shape remains the same when polymer concentration is modified. The activation energy determined from the slopes of the curves is found to be approximately $33\,kJ\,mol^{-1}$. This value is not too far from the one obtained by Devia and Sykes[14] ($\approx 55\,kJ\,mol^{-1}$), studying dissociation of zirconium tetrameric ions, although the conditions were not the same.

CONCLUSION

We have shown in this study that polymer gels obtained by means of zirconium addition exhibit a complex behaviour due to the zirconium chemistry. Except for the classic dependence on polymer concentration and temperature, the zirconium concentration and pH are found to have unusual effects on gelation kinetics. So, the obtained results are interpreted according to the available information about zirconium chemistry in the literature. However, we have to keep in mind that the published results were obtained under drastic conditions, namely a highly acidic medium and low concentration.

ACKNOWLEDGEMENT

This research was supported by the Association de Recherche sur les Techniques d'Exploitation du Pétrole (ARTEP), France.

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