

Aspects of Crosslinking Sulfonated Polyacrylamides from Rheological Studies on Their Gels

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ABSTRACT: Crosslinking of sulfonated polyacrylamide by zirconium requires some acrylate sites on polymer chain, and a schematic reaction is proposed to describe this process. Moreover, gelation kinetics is found to be fairly proportional to polymer acrylate site content. On the other hand, decreasing sulfonation level or solvent salt concentration is shown to result in increasing the system gelation, and an explanation of such behavior is attempted. Furthermore, we find that gelation kinetic is highly dependent on zirconium concentration in an unusual manner. So, for a given polymer sample, a maximum of zirconium concentration exists above which gelation kinetic decreases until it vanishes. This behavior is interpreted by existence of a background reaction where highly stable zirconium complexes are formed. This reaction indeed competes against the polymer cross-linking process and zirconium concentration increases.

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INTRODUCTION

Various water soluble polymers are extensively used in many industrial fields. In oil field applications such as the enhancement of oil recovery, they are used as viscosifying or gelling products.¹ Hence, the selected polymer should satisfy the reservoir conditions, including temperature, salinity, and other physicochemical parameters in addition to the cost, of course. Polyacrylamide is a commonly used polymer, and numerous investigations have been devoted to it. When it is used under hostile reservoir conditions; i.e., high temperature and hard salinity, it undergoes thermal degradation and hydrolysis to end in precipitation by divalent ions, resulting in the loss of rheological properties. So, one way to avoid these limitations is to reinforce the polymer chain structure by substitution or grafting of an appropriate chemical species on the backbone. Previous studies have already demonstrated that sulfonation of

polyacrylamide permits achievement of this aim.^{2,3} The modified polymer then becomes a polyelectrolyte when the sulfonation level is sufficiently high. Therefore, in salt-free medium, the reduced specific viscosity increases the polymer concentration lowers. For a similar purpose, i.e., to minimize polymer precipitation and segregation phenomena, polystyrene has been sulfonated by different means^{4,5} and was characterized in various solvents^{6,7} containing different cations. Agarwal et al.⁷ have found that variation of the intrinsic viscosity comparatively to the unsulfonated polymer one $[\eta]/[\eta]_0$ depends on the solvent dielectric constant value ϵ . So, at low dielectric constant, intrinsic viscosity decreases as the level of sulfonation increases but depends on the counter ion nature. This behavior was attributed to intramolecular cross-links or to a decrease of the distance of pair segments. These authors have also shown that all contraction ratios lie on a master curve, which follows the equation

$$[\eta]/[\eta]_0 = f(\xi) \quad (1)$$

with $\xi = A_s A_a X$.

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A_s and A_a are the solvent and counterion factors, respectively, and X stands for fractional substitution. For high values of ϵ , the ratio above has been found as an increasing function of the sulfonation level, while it behaves relatively insensitive to the counter ion used. Working on sulfonated polyacrylamide in synthetic sea water, Noik and Audibert⁸ have observed, however, that relative viscosity decreases slightly with sulfonation level. It should be noticed that although only a few samples of the same molecular weight have been tested, these authors also studied the high ionic strength used, inducing screening effects.

Polyacrylamide undergoes hydrolysis if the temperature or the pH increases. In this process, acrylamide monomers are converted to acrylate units following a well-known chemical reaction.⁹ The conversion rate may be determined by several methods, including nuclear magnetic resonance (NMR), ionic exchange titration, or ammonia analysis; but results were found somewhat, depending on the technique used.¹⁰ Nevertheless, polyacrylamide intrinsic viscosity increases as hydrolysis proceeds. More precisely, it follows the equation below, which is a Fox-Flory-like type,⁹ where D_H is the degree of hydrolysis, and B is the number on the carbon atoms backbone:

$$[\eta]^{5/3} - [\eta] = D_H^2 * \left(\frac{B}{4}\right)^{5/2} \quad (2)$$

D_H depends on temperature, pH, and time process. So even if hydrolysis is initially very fast, it decreases gradually and finally reaches an asymptotic plateau value. A plausible explanation of such an effect is electrostatic shielding of remaining amide groups by the created acrylate groups toward OH^- ions. Indeed, hydrolysis at a given stage was observed to be higher as the concentration of free salt increases.¹⁰

The present study concerns gels obtained by adding an external cross-linking agent to sulfonated polyacrylamide solutions. The cross-linking agent is zirconium, which, from a chemistry point of view, is complicated. Generally, this transition metal in aqueous medium undergoes hydrolysis and hydration and forms polynuclear species.^{11,12,13} Monomeric forms exist only in very dilute regime ($<10^{-4}M$) and in high acidity ($[\text{H}^+] = 1-2M$). Moreover, zirconium is known to react with oxyacids to form complexes of different shapes and stabilities,¹⁴ so it is usually commer-

cialized in a stabilized form. Under some conditions, when these complexes and the polymer are brought together, a ligand exchange may occur. This, then, results in a polymer cross-linking reaction in which complexes of higher thermodynamic stability are built up. For this particular system, it will be discussed in more detail in the following Experimental Section. In this work, we will focus on the gelation of the sulfonated polyacrylamide-zirconium system as a function of various parameters. This gelation is studied by following changes in the rheological properties of the system. It is well known from the theory of elasticity¹⁵ that formation of polymer-polymer bonds leads to an increase of the elastic modulus G of the medium. Far from the reaction onset and assuming that cross-linking takes place randomly, we have

$$G(t) - G_0 = \nu kT \quad (3)$$

G_0 corresponds to the uncross-linked polymer solution; ν is the density of created bonds, which contributes effectively to the system elasticity; and kT represents the Boltzmann factor. The parameter q , which lies between 0.4 and 1, is introduced here to take into account, among other contributions, the relative mean square end-to-end distance of a polymeric strand between two successive bonds in respect to the mean square end-to-end distance of the same strand if it is not constrained¹⁶; so it accounts somehow for the cross-link chemical nature. Hereafter, q will be taken equal to unity. Also, when derived in respect to time, the relation above [eq. (3)] shows that the rate of intermolecular bond formation or the gelation process is directly proportional to the slope of the G versus t curve. In oscillatory shear experiments, when frequency is sufficiently low, we have $\omega\tau < 1$, G should equal the elastic shear modulus G' , with τ being the longest relaxation time of the formed species. By this way, gelation of the system under interest can be investigated, keeping in mind that the above relation is rigorously valid only for uniform networks.

EXPERIMENTAL

Unless otherwise stated, the solvent used is a 5 g/L NaCl brine, which contains 400 ppm NaN_3 in order to prevent microbial degradation of the polymer. Numerous samples of sulfonated polyacrylamide have been studied. The counter ion is sodium, and its mean weight molecular weight is close to $8 \cdot 10^6$. Also, some of them have been

submitted to hydrolysis by setting the pH of the polymer solution to 11 and storing it at 60°C during a predetermined time. Thereafter, hydrolysis was stopped by bringing the temperature to the ambient and the pH to 7. Samples are then freeze-dried, and the polymer acrylate content is determined by NMR. Therefore, each sample is hereafter identified as $H_{x,y}$ where x represents the sulfonation level, while y stands for the acrylate content. The polymer concentration C_p was set at 5000 ppm, which is much greater than the overlapping concentration C^* . After adjusting the solution pH to 7, a given amount of zirconium was added, and the sample was stored at 60°C. The zirconium used here is a zirconium-lactate complex furnished by Zirtech (Midland, Texas, U.S.A.). In the remainder of this article, zirconium concentration C_{Zr} is given in ZrO_2 equivalent. After sample preparation, gelation is allowed to proceed, and rheological measurements are carried out with sampling at regular time intervals by the means of an imposed stress rheometer, Carri-Med CSL 100. As mentioned before, the shear elastic modulus measurements should be performed in the linear regime and at sufficiently low frequency in order to fulfill the requirements listed in the Experimental Section. Therefore, in the present study, all measurements were done at a frequency of 1 Hz since it was observed to still verify the $\omega\tau < 1$ condition. In the Results and Discussion Section, we present and discuss the influence of acrylate and sulfonate content of polymer. Influence of other parameters, such as

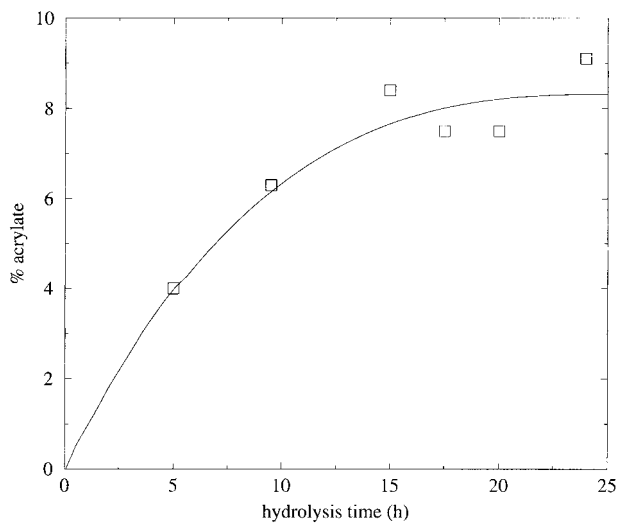


Figure 1 Measurement of acrylate percentage versus hydrolysis time.

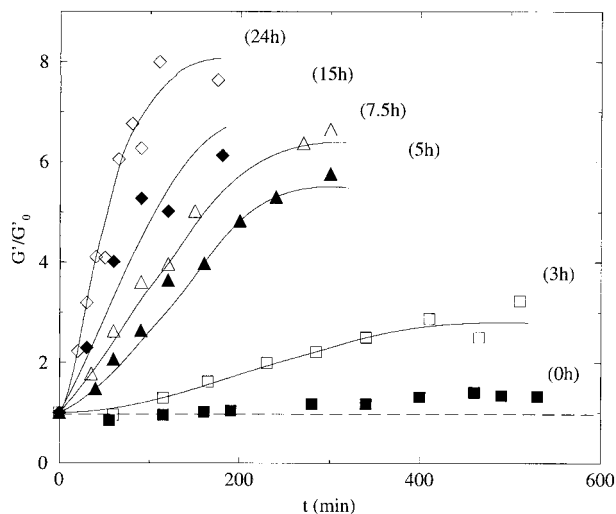


Figure 2 Evolution of shear modulus versus gelation time for several hydrolysis times. The initial sample is H13,0.

ionic strength and zirconium concentration, are also investigated.

RESULTS AND DISCUSSION

We start with unhydrolyzed polyacrylamide polymer samples, whose sulfonation level varies from 5 to 100%, while zirconium concentration is fixed at 200 ppm. For such samples, no gelation has been detected during the overall observation time (many days). This suggests that neither sulfonate groups nor amide groups take part in the formation of polymer-zirconium complexes.

We further submit the sample labelled as H13,0 (13% sulfonate groups and 0% acrylate content) to hydrolysis and determine the percentage of created acrylate sites following the procedure described above. When the percentage of acrylate is plotted against hydrolysis time (Fig. 1), the resulting curve shows a shape similar to that already observed by Maurer et al.¹⁰ Although physicochemical conditions are not the same. Gelation of such hydrolyzed polymers solutions is then allowed to occur for the same value of C_{Zr} . Results obtained are shown in Figure 2, where hydrolysis time is indicated between brackets. Thus, it appears clearly that the presence of acrylate sites on the polymer chain is needed for zirconium-polymer gel formation. Moreover, gelation is improved by the density of acrylate units both in terms of gelation kinetic and strength of formed gels (the reached plateau value). This is more

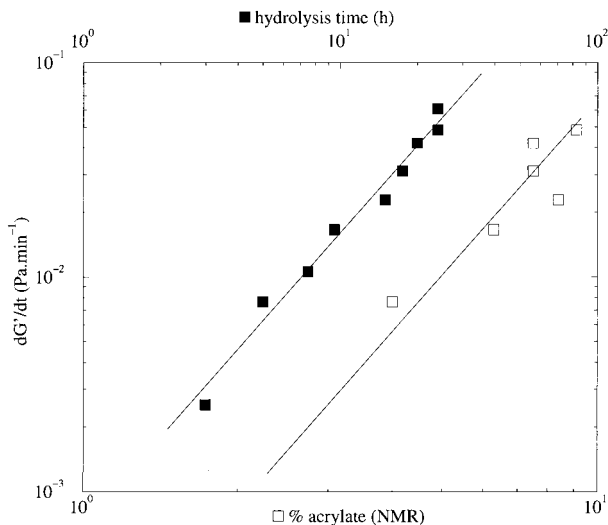
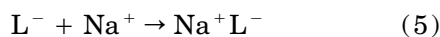
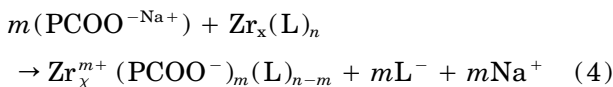


Figure 3 Plot of gelation kinetic (dG'/dt) as a function of hydrolysis time (■) and measured acrylate percentage (□). Other conditions are the same as in Figure 2.

obvious when gelation kinetic, which is represented here by dG'/dt , is plotted versus the percentage of created acrylate sites or time of hydrolysis (see Fig. 3). This kinetic seems to follow a power law dependence on determined acrylate percentage (close to proportionality; $\chi^{1.1}$). In the same figure, variation of gelation kinetic versus hydrolysis time is also represented for comparison. Reported values of pKa of carboxylate and sulfonate acids (4.5 and 3.5, respectively),⁸ are consistent with the previous observations. On the other hand, no noticed pH modification is observed as gelation proceeds. We can then reasonably think that sulfonated groups remain in their salt form while the less stable acrylate groups are involved in the polymer-zirconium complex formation. So we can assume that the cross-linking reaction of polymer by zirconium results in the formation of ionic type links by avoiding lactate ligands from initial zirconium complexes, which are then replaced by polymer acrylate groups. These reactions may be written schematically as follows:



where m should be an integer greater than unity to bridge polymer chains together. The second re-

action shows the subsequent formation of sodium lactate. To have a more precise opinion on the gelation process of our system, two polymer samples of different sulfonation level were used. These samples were hydrolyzed, and their acrylate content was determined to be 1%. Figure 4 shows that gelation is improved by decreasing sulfonation level. We then conclude that although sulfonated groups do not take part in the zirconium-polymer complexes, they influence their formation process. In our opinion, this influence is a consequence of the following contributions.

- 1) The steric hindrance effects are due to greater size of sulfonate groups when compared to that of acrylate or acrylamide, so increasing the polymer sulfonation level decreases the accessibility of acrylate sites, owing, therefore, to less gelation rate.
- 2) Because of the strong ionicity of the sulfonate groups, we may put forward their action on the stability of acrylate-zirconium complexes (deformation) by means of the electric field force that they generate, so decreasing this stability slows down the gelation kinetic of the system.

As emphasized in a previous section, sulfonation of polyacrylamide aims to increase its thermal stability and its resistance toward divalent cations contained in the reservoir brine, thus avoiding its precipitation. Consequently, in Influence of Salts Section, we will examine the influence of solvent composition on gelation kinetics.

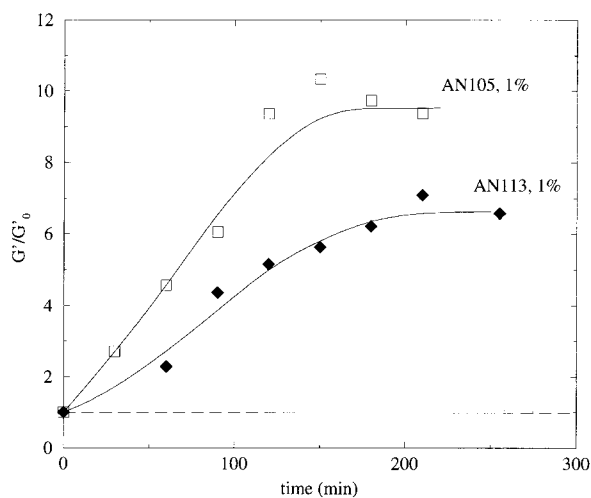


Figure 4 Influence of sulfonation level on gelation process: (□) sample H05,1; (◆) sample H13,1.

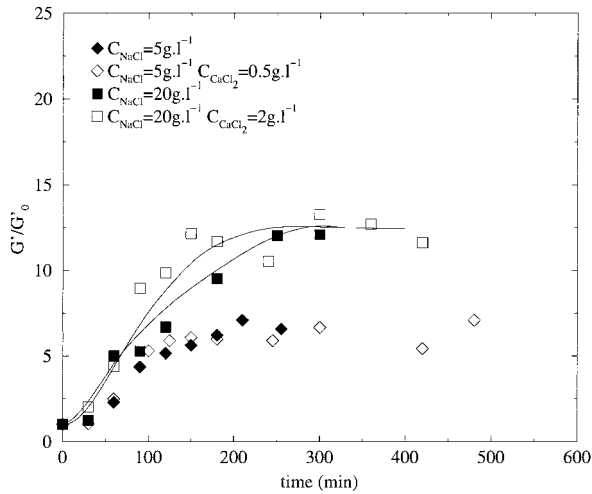


Figure 5 Influence of salt composition on gel characteristics for the sample H05,1.

Influence of Salts

In order to study the influence of solvent salt content on the gelation kinetic, the sample H13,1 (13% sulfonated groups and 1% acrylate) was chosen. First, only the concentration of neutral salt NaCl was varied, while other conditions were kept the same as previously described. In a second step, the gelation system, when the solvent also contains CaCl₂, will be considered. All obtained results are brought together in Figure 5. It appears that as neutral salt is concerned, increase

of its concentration improves the gelation process. This influence may be explained by putting forward again that although sulfonate groups are not involved in zirconium-polymer complexes, they exert on them a perturbing force due to their high polarity. By increasing the salt concentration, these perturbation forces are lowered so the neutral salt screening effect induces a more efficient linking of zirconium to polymer chains. Moreover, this influence is pointed out since increase of salt concentration causes a decrease of viscosity of the fresh polymer solution. This may be seen somehow as an increase of the overlapping concentration or a decrease of polymer concentration. Similar influence was furthermore established on a less sulfonated polymer, H05,1, but was not as spectacular since the sulfonation level of such sample was relatively low. As mentioned previously, Figure 5 shows also how the presence of calcium influences the gelation process. As expected, the calcium divalent cation does not lead to any polymer precipitation; so it plays a similar role solely as the neutral salt, and the system gelation is improved. This effect is indeed more pronounced as the ionic strength of the medium increases. The involved polymer protection toward divalent ions has been also observed by Noik and Audibert,⁸ and they have attributed it to the presence of sulfonate groups. We agree with their explanation based on the fact that sulfonate groups the opposite of acrylate groups are located

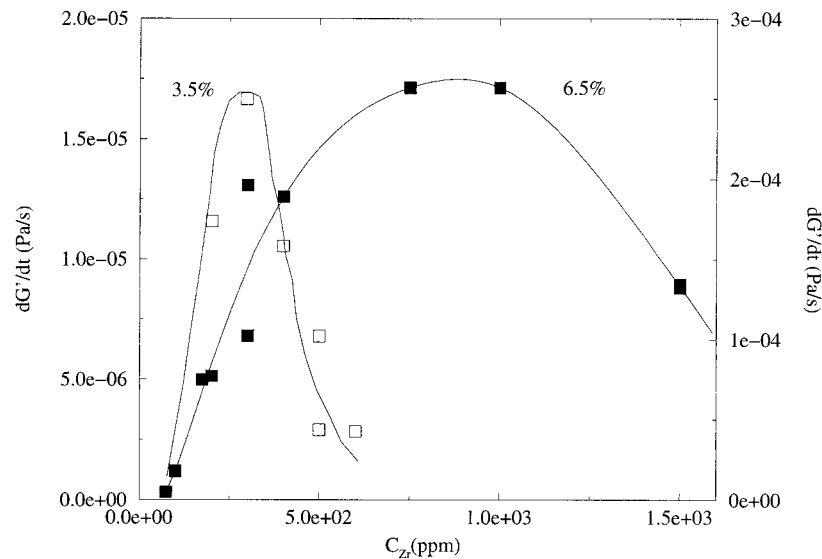


Figure 6 Effect of zirconium concentration on gelation kinetic for two hydrolyzed polymer samples: (□) 3.5%; (■) 6.5%.

far from the polymer backbone (seven chemical bonds). In this way, they form a shield that prevents acrylate sites from divalent ion attack.

Influence of Zirconium Concentration

The last parameter that is considered in this work is the cross-linker concentration C_{Zr} . The influence of such a parameter is investigated using two polymer samples whose sulfonation level is 13%. They differ, however, in their acrylate content (3.5 and 6.5%). The cross-linker concentration ranges from 25 to 1500 ppm, while polymer concentration is maintained constant at 5000 ppm. The results obtained are presented in Figure 6 in terms of dG'/dt versus C_{Zr} . We observe first that each curve is of the same shape, with the gelation kinetic increasing as C_{Zr} increases and passing through a maximum before it subsequently decreases. For much higher zirconium concentrations, all samples have been observed to return to a fluid state. This unusual behavior was reported earlier for the scleroglucan-zirconium system.¹⁷ We may notice, however, that the location of the maximum and its magnitude depend on the sample considered, i.e., on the acrylate content. An explanation of such phenomena rises from the nature of the cross-linking reaction itself. So the cross-linking process is due to a ligand exchange, leading to the formation of zirconium-polymer complexes, which are of higher stability than the zirconium-lactate ones. In fact, this reaction competes with another one, where polynuclear zirconium species may be formed. We think that those polynuclear species become more stable than the zirconium-polymer complexes above a critical zirconium concentration C_{Zr}^* . Since the stability of zirconium-polymer complexes depend on the number of acrylate groups involved, C_{Zr}^* increases with the acrylate content, thus explaining why the localization of the kinetic maximum varies from one sample to another.

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