Kinetic gelation of the polyacrylamide–glyoxal system

A. Omari
Laboratoire MASTER, ENSCPB, 33405 Talence Cedex, France
(Received 10 May 1993; revised 22 October 1993)

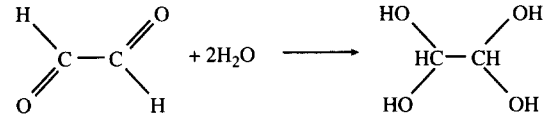
In aqueous solutions many polymers may be gelled by adding an appropriate cross-linking agent, and the system that is obtained is usually characterized by using rheological measurements. Among the most investigated properties of such systems is their gelation kinetics. In this work we deal with a system where the polymer is a nonionic polyacrylamide and the cross-linking agent is glyoxal. We focus our study in particular on the gelation kinetics by following the change in elastic modulus under given experimental conditions. In an alkaline medium and at low temperatures, the bond formation rate is found to follow certain power laws with relation to both polymer and glyoxal concentration. However, at an alkaline pH and at sufficiently high temperatures, the system loses its gelled structure due to a 'parasitic' chemical reaction. This reaction may be eliminated by reducing the pH to an acid value, but at the same time the gelation kinetics become modified as the complexation process is then different from the alkaline case.

(Keywords: polyacrylamide–glyoxal; gel kinetics; elastic modulus)

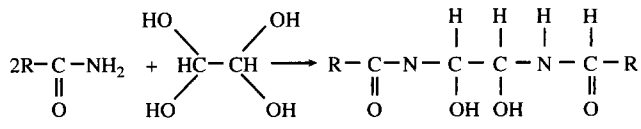
INTRODUCTION

In the last few years many experimental studies have dealt with polymeric gels. These have been of several kinds and have differed in the particular processes of formation. The most common ones are those obtained solely through temperature variation or by polymerization processing or, of course, by the addition of a cross-linking agent to the polymer solutions. The rheological behaviour of the gel is usually interpreted on the basis of the species that are formed[1–5]. In numerous applications such as, for example, in the oilfield industry, the most important property of water-soluble polymer gels is their gelation kinetics which dictates use of the particular system conditions[6,7]. Such kinetics are expressed in terms of the rate of bond formation, which not only depends on the polymer and cross-linker concentrations, but also on the prevailing physico-chemical conditions. For several of these investigated polymer gels, this rate dependency on concentration has been found to follow a power-law relationship and various numerical values of the relevant exponents are available in the literature[8–10]. These exponents are of course dependent on the system of interest, and therefore on the reactions occurring during cross-link formation.

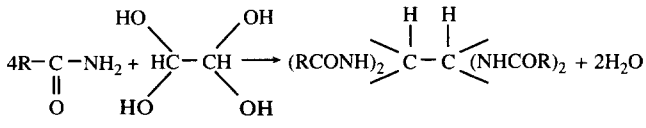
The goal of this present work is to study the gelation kinetics of a new system, consisting of a nonionic polyacrylamide of a high mean molecular weight and glyoxal, which is used as the cross-linking agent. This is done by following the time course of the change in the elastic modulus G' of the polyacrylamide solutions, after addition of the cross-linking agent, by using a Carri-Med rheometer. The overlapping polymer concentration was determined as a preliminary datum from viscometric measurements and has been found to be close to $c^* = 1300$ ppm. Subsequently, all experiments were performed with polymer concentrations higher than c^*. Indeed, as indicated from both phase diagram[10] and thermodynamic predictions[11] no gel formation would be expected when the polymer concentration is below c^*. The glyoxal used here is a dialdehyde monomer which is hydrated in aqueous solution as follows:



Although less common in dilute solutions, other polymerized forms (especially those containing dimer structures) also exist in equilibrium with the monomer[12] and under certain conditions the glyoxal hydrates give glycolate ions as a consequence of the Cannizzaro reaction. When reacting with the primary amides of the polyacrylamide, the glyoxal hydrates link polymer chains together to form a polymer network. As can be seen below, this cross-linking reaction involves only two primary amides at a neutral or a slightly basic pH, while a condensation reaction, involving four primary amides, takes place in an acidic medium[13]:



(in neutral or alkaline medium)



(in acidic medium)

0032-3861/94/10/2148–05

In the next section we shall present and discuss the influence of several factors on the gelation kinetics of this system. The main parameters of interest here are the polyacrylamide and glyoxal concentrations, and also the temperature, pH, and the amount of added neutral salt.

RESULTS AND DISCUSSION

As mentioned above, after the preparation of each solution, the rheological properties are measured at various times until the gelation process is complete. The quantity measured is the elastic modulus G' under dynamic oscillatory shear flow conditions *versus* the frequency ω in the linear region. *Figure 1* shows typical $G'(\omega)$ curves for a given solution at four different stages of gelation. First, it can be observed that, as the time increases, the elastic modulus also increases and the Hookean plateau becomes more extended. This is a consequence of bond creation modifying the system topology which gradually loses its solution condition to become more solid-like. More precisely, at the beginning of the complexation process, the elastic modulus is greatly influenced in the low-frequency regime. This is due to the fact that, at this stage, only a very few junctions per chain are created. In consequence, only the longer macromolecular relaxation times, which govern the system's mechanical response at low frequencies, are influenced. When, however, the complexation has sufficiently advanced, the characteristic relaxation time spectrum is substantially changed, and this, in turn, induces a change in the system behaviour over a larger part of the frequency range[14].

Having said this, it should be added that the G' values used thereafter to follow the system's gelation are those corresponding to a frequency equal to 1 Hz.

Influence of concentration

For this purpose, the polymer concentration c_p is first fixed at 3000 ppm, while the glyoxal concentration c_g is varied from 25 to 100 ppm. At each value of c_g, the

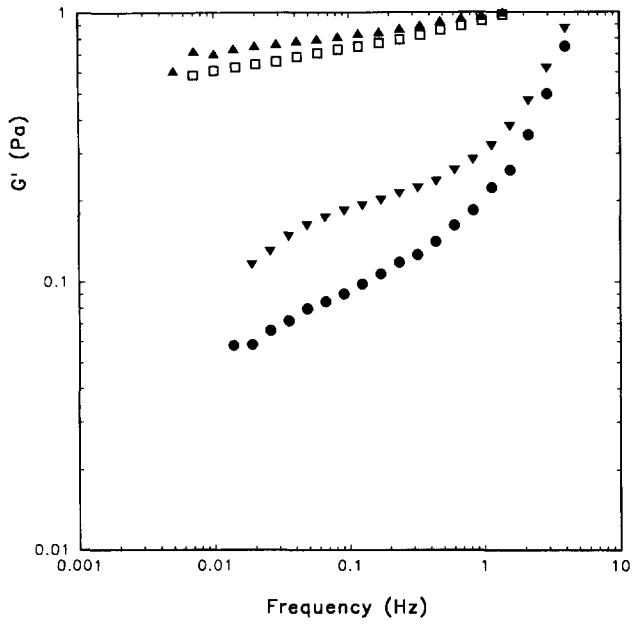


Figure 1 Plots of G' *versus* frequency at four different stages of gelation, with $c_p = 3000$ ppm, $c_g = 100$ ppm, pH = 8, and $T = 30°C$: (●) 22.5; (▼) 26; (□) 44 and; (▲) 92 h

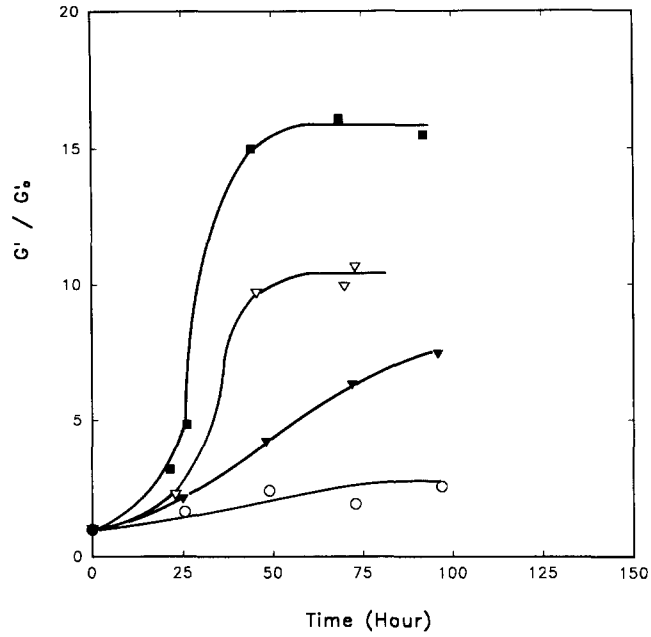


Figure 2 Change in the ratio G'/G'_0 during gelation as a function of time, with $c_p = 3000$ ppm, pH = 8, and $T = 30°C$, measured for various values of c_g: (○) 25; (▼) 50; (▽) 75 and; (■) 100 ppm

measured G' is normalized by its initial value, G'_0, and is then plotted against time (see *Figure 2*). This figure shows that G'/G'_0 varies as an increasing function of the time before it reaches a plateau. The increasing portions of these curves may be used to calculate the rate of bond creation. Indeed, from the theory of elasticity[15–17] the network modulus G' is related to the bond density ε by the following relationship:

$$G' = G'_0 + q\varepsilon kT \tag{1}$$

where kT is the Boltzmann factor and q is a coefficient which depends on the cross-link functionality, and must lie between 0.4 and 1. It should be emphasized that only those tie-points which effectively contribute in increasing the medium elasticity are taken into account when obtaining the above relationship. Moreover, its validity is restricted to the case where bond density is regular. This implies that the use of this relationship is only convenient far from the start of gelation where only individual clusters are present in the medium. When this relationship is expressed in terms of time, it is evident that the progress of the complexation process, or the rate of bond creation, $d\varepsilon/dt$, may be calculated from the slope of the elastic modulus in the linear growth region. *Figure 3* shows that this slope (expressed in Pa h^{-1}), is a power-law function of the glyoxal concentration.

In addition to this information, the plateau values that are finally obtained for G' may be used to determine the number of the bonds formed at the end of complexation by using equation (1). If the parameter q is taken as being equal to unity, the number of bonds formed per macromolecule is found to be close to 14, 9, 6 and 2, for 100, 75, 50 and 25 ppm of glyoxal, respectively. This indicates that we are beyond the number of bonds required for gel formation to occur (i.e. one bond per macromolecule) in all cases.

In the same way, when the polyacrylamide concentration varies, while maintaining the glyoxal concentration at a fixed value ($c_g = 100$ ppm), the rate of bond formation, expressed as in *Figure 3*, increases as the polymer

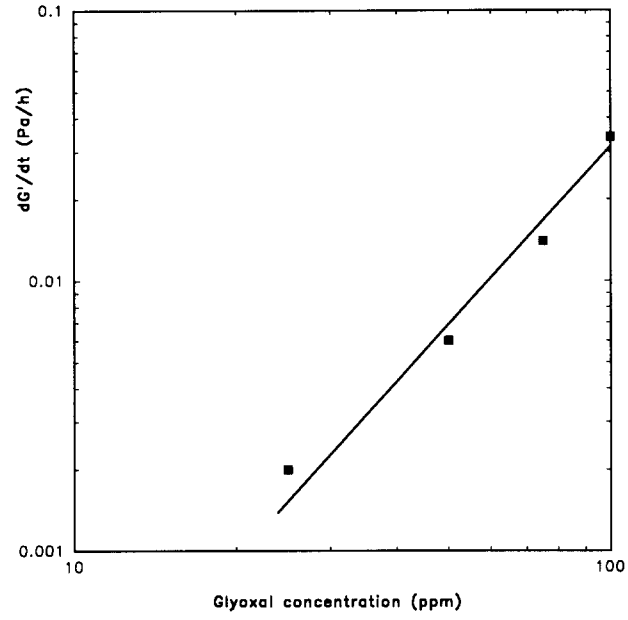


Figure 3 G' slope variation *versus* glyoxal concentration for $c_p = 3000$ ppm, pH = 8, and $T = 30°C$

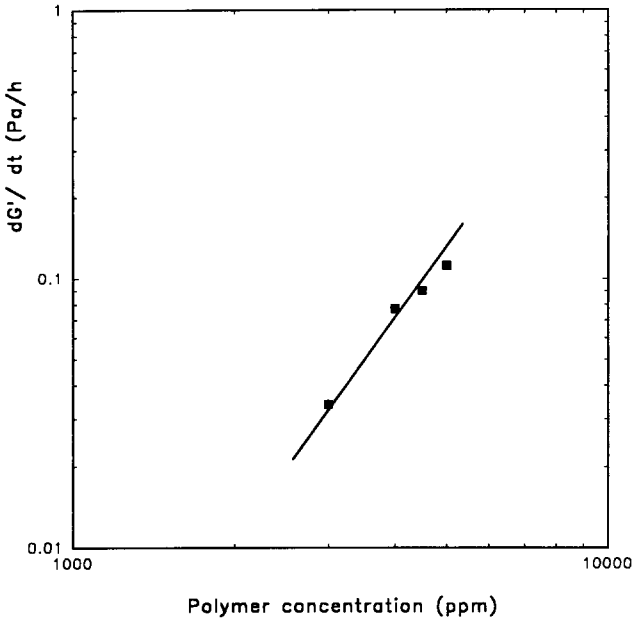


Figure 4 G' slope variation *versus* polymer concentration for $c_g = 100$ ppm, pH = 8 and $T = 30°C$

concentration increases (see *Figure 4*). Moreover, this rate is also found to have a power-law dependence on the polymer concentration. Overall, the rate of change of the bond density ε may be written as:

$$d\varepsilon/dt = Kc_g^{2.1}c_p^{2.7} \quad (2)$$

where K is a fixed parameter for the system and temperature of interest.

The cross-linker concentration exponent, which is ~ 2, indicates that the determining step in this complex cross-linking reaction is second-order in nature. Therefore, we can assume that two glyoxal monomers are involved in this step. In this case, links of cyclic structure, where the nitrogens of the primary amides are fully substituted, build up. In the following steps, these links are then subjected to rearrangement and breakage before they take the definitive form shown in the reaction scheme given above. We must recall that in dilute solution both monomer and dimer hydrate forms of glyoxal can coexist in an equilibrium state, as was emphasized in the Introduction. The exponent is otherwise close to that found for the polyacrylamide–chromium system[8], while it equals 4/3 for the hydroxypropyl guar (HPG)–titanium[9] and 1 for the scleroglucan–zirconium[10] systems. As far as the c_p exponent is concerned, its value is higher than 2, probably due to cooperative phenomena in the polymer network. (It must however be rigorously equal to 2 when only acrylamide monomers are used in the experiments.) In other respects, this exponent is essentially sensitive to the structure and conformation of the polymer chains. Therefore, as the polymer stiffness is reduced (for example, when electrostatic interactions are investigated by adding a certain quantity of a neutral salt to an ionic polymer solution) the crosslinkage is enhanced and hence the polymer concentration exponent increases[8]. For relatively rigid polymers, such as polysaccharides, the usual exponent values are significantly lower, and different numerical values have been reported in the literature[8–10].

An additional point of interest is that the density of the bonds, when calculated at the end of the complexation reaction, is insensitive to the polymer concentration under the present conditions. This simply indicates that the crosslinkable polymeric sites are much more numerous than the glyoxal hydrate molecules for all of the polymer concentrations studies. It should be noted that if the cross-linking agent is present in excess, this bond density should depend on polymer concentration in a power-law fashion. In this case the exponent involved should be equal to that of the polymer entanglement density, $3\nu/(3\nu - 1)$, which reaches the value of 2.25 for a linear polymer in a good solvent and in the semidilute region, with ν being the excluded volume parameter[14].

Influence of temperature

Figure 5 shows the influence of temperature on the gelation of the system when the glyoxal concentration is maintained at 50 ppm, while the other conditions remain

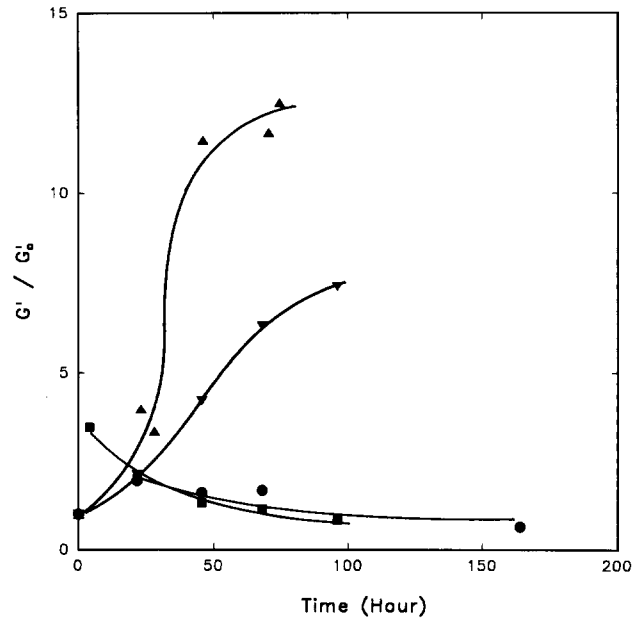


Figure 5 Influence of temperature on gelation kinetics for $c_p = 3000$ ppm, $c_g = 50$ ppm, and pH = 8: (▲) 23; (▼) 30; (●) 40°C and; (■) 47°C

the same as in *Figure 2*. It appears that an increase in temperature results in a decrease in both the gelation kinetics and the density of the bonds that are produced. Moreover, when the temperature is greater than 30°C, the elastic modulus, after first increasing, then undergoes a significant decrease as the temperature rises. To explain this behaviour, we propose the existence of an equilibrium involving the following two reactions, which compete with each other in opposite ways: (i) intermolecular bond formation involving the glyoxal in its hydrated forms and (ii) the Cannizzaro reaction, where the glyoxal is converted to glycolate in an alkaline medium[13]. Therefore, as the temperature increases, the equilibrium shifts away from bond formation, and hence the gelation process is restricted. In addition, at sufficiently high temperatures, the cross-linkers previously involved in bond formation are progressively disengaged, thus leading to gel destruction and a fall in the elastic modulus. Furthermore, as will be shown below, no gel destruction is observed when the Cannizzaro reaction is removed. In any case, the temperature must be held below 50.4°C, which is the temperature of glyoxal evaporation. Other experiments performed at 40°C with various glyoxal concentrations (data not shown) indicate, as would be expected, that this behaviour is established for the whole glyoxal concentration range which is being considered, except that its appearance is delayed by the c_g increase.

Influence of pH

In order to examine the influence of pH on the gelation kinetics, the system's elastic modulus change is followed at 40°C and for the same c_g range, but at a slightly acid pH, i.e. 6.85. The results obtained are then compared to those previously obtained at pH = 8. For the sake of simplicity, only the results corresponding to $c_g = 100$ ppm are presented in *Figure 6*. It can be seen that bringing the pH to an acid value results in two separate modifications of the elastic modulus curve: first, the network destruction observed at an alkaline pH disappears, and secondly, the G' slope in the ascending region is found to decrease. To explain the first effect we again propose the Cannizzaro reaction. Indeed, this reaction, which in an alkaline medium acts in an opposite way to bond formation and leads to network destruction, is now completely inhibited at acid pH levels. Consequently, the gel structure is preserved. The second effect that is observed may, however, arise from the following contributions:

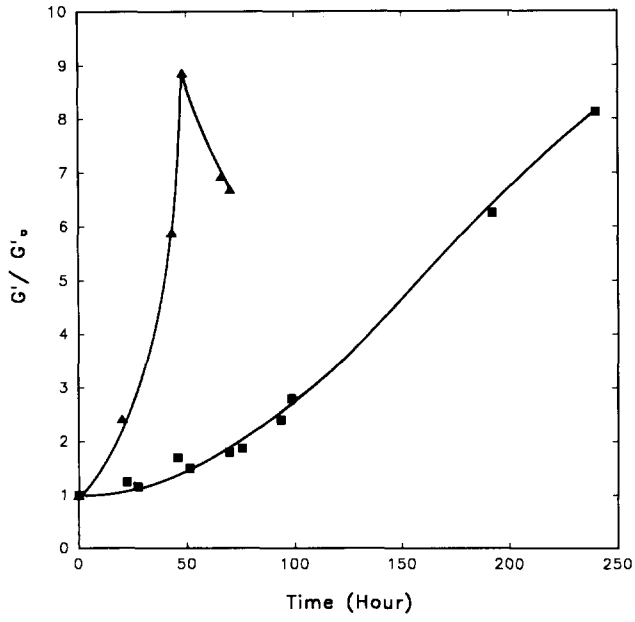


Figure 6 Change in the ratio G'/G'_0 during gelation as a function of time, with $c_p = 3000$ ppm, $c_g = 100$ ppm, and $T = 40$°C, measured at acid and alkaline pH: (■) = 6.85 and; (▲) pH = 8

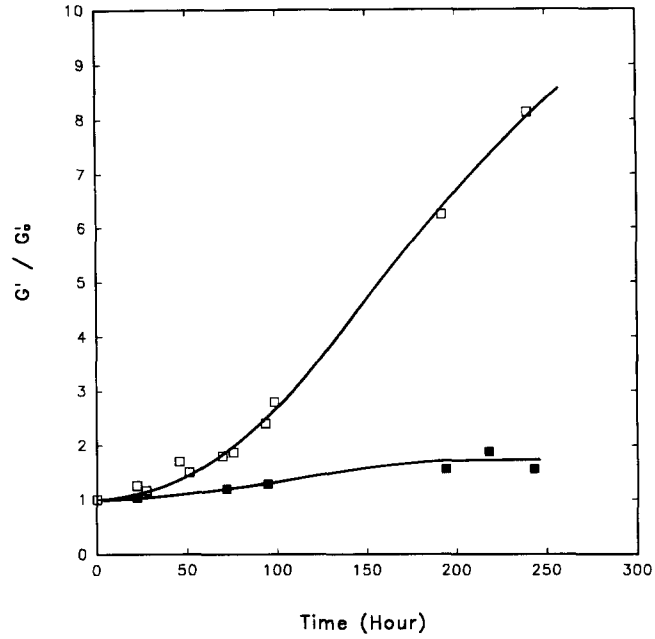


Figure 7 Comparison of gelation kinetic at two different NaCl concentrations for $c_p = 3000$ ppm, $c_g = 100$ ppm and $T = 40$°C: (□) 0 and; (■) 50 g l^{-1}

(a) On the one hand, as pointed out previously, the complexation process is different depending on whether the pH is alkaline or not. In an acidic medium, the polymer chains are linked by a condensation reaction, and each bond involves four close primary amides, while bond formation in an alkaline medium involves only two. Hence, complexation should be slower and more sensitive to store hindrance effects at acid pH values[13].

(b) On the other hand, after adjusting the pH to 6.85, a phosphate salt buffer is used which means that some quantity of free ions is introduced into the medium. Since the nucleophilic attacks arising during bond formation are prevented by free ions, this would, in part, explain the low bond formation rate in acidic media. Furthermore, a subsequent neutral salt (NaCl) addition leads to a decrease in both the gelation kinetics and in the final plateau bond density (see *Figure 7*).

CONCLUSIONS

Rheological measurements show that gel formation can occur when glyoxal is added to semidilute polyacrylamide solutions. The gelation kinetics and the gel strength are found to be dependent on the polymer concentration, the concentration of cross-linking agent, and the prevailing physico-chemical conditions. Therefore, the system gelation depends on whether the pH is alkaline or acid, since the cross-linking process is different in either case. In addition, in terms of temperature, in an alkaline medium, a temperature increase is found to restrict gel formation

and even to inhibit it at sufficiently high values, as a result of the Cannizaro reaction. However, at acid pH levels this last reaction does not occur, and hence no gel destruction is observed. Finally, this system is not suitable for those applications in which the pH is alkaline or when the temperature is excessively high.

ACKNOWLEDGEMENT

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

REFERENCES

1 Pezeron, E., Ricard, A., Lafuma, F. and Audebert, R. *Macromolecules* 1987, **21**, 2430
2 Kramer, J., Prud'homme, R. K., Wiltzius, P. and Knoll, S. *Colloid Polym. Sci.* 1988, **266**, 145
3 Moldenaers, P., Mewis, J. and Berghmans, H. *Rheol. Acta Prog. Trends Rheol. II* 1988, 420
4 Venkataraman, S. K. and Winter, H. H. *Rheol. Acta* 1990, **29**, 423
5 Allain, C. and Salome, L. *Macromolecules* 1990, **23**, 981
6 Zaitoun, A., Rahbari, R. and Kohler, N. 66th Annual Conference of the Society of Petroleum Engineers, Dallas, paper SPE 22785, 1991, 263
7 Zaitoun, A., Kohler, N. and Guerrini, Y. International Symposium on Oilfield Chemistry, Houston, paper SPE 18501, 1989, 379
8 Prud'homme, R. K. 4th Symposium on Enhanced Oil Recovery (EOR), Tulsa, paper SPE/DOE 12640, 1984, 121
9 Clark, P. E. and Barkat, O. SPE Meeting, Morgantown, paper SPE 19331, 1989, 231
10 Han, M. *PhD Thesis*, University of Rouen, 1992
11 Menjivar, J. A. *Adv. Chem. Ser.* 1986, **13**, 210
12 Kliegman, J. M., Whipple, E. B., Ruta, M. and Barnes, R. K. *J. Org. Chem.* 1972, **37**, 1276
13 'Glyoxal', Technical Document, Hoechst, Paris, France
14 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979
15 Flory, P. J. 'Principles of Polymer Chemistry', 11th Edn, Cornell University Press, Ithaca, 1981
16 Pearson, D. S. and Graessley, W. W. *Macromolecules* 1980, **13**, 1001
17 Laurent, J. L., Janmey, P. A. and Ferry, J. D. *J. Rheol.* 1980, **24**, 87