Interactions between aluminium ions and acrylic acid–acrylamide copolymers in aqueous solution: 3. Influence of ionic strength on gelation and phase separation

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Phase separation and gelation of the aqueous solutions of acrylamide–acrylic acid copolymers in the presence of aluminium chloride are studied as a function of pH and ionic strength. At pH 7, only phase separation is observed as a flocculation of aluminium hydroxide particles by polymer bridges, but because of their small positive residual charge the phenomenon is partially due to electrostatic interactions and consequently depends on the ionic strength of the solution. At pH 5, gelation attributed to the presence of polycations Al_{13}^{3+} occurs for values of the polymer charge which increase with increasing ionic strength. A qualitative model is proposed to define the conditions and the limits of gelation in such systems.

(Keywords: gelation; phase separation; acrylamide–acrylic acid copolymers; aluminium ions; aluminium hydroxide)

INTRODUCTION

In previous work[1,2], we have discussed some aspects of the interactions between acrylic acid–acrylamide copolymers and the different species of aluminium ions in aqueous solution. We have evaluated, using ^{27}Al n.m.r., the fraction of Al bound on the polymer as a function of pH (pH < 5). The experiments show that this fraction passes through two maxima, at pH 4.2 and 4.7, which correspond to the fixation of mononuclear ions ($Al(H_2O)_6^{3+}$) and polynuclear ions $Al_{13}(OH)_{28}(H_2O)_8^{3+}$, under conditions favouring the formation of these last species. A simple model of association equilibria gives a rather good account of such results and shows that the extent of this binding is never negligible even for weakly charged polymers.

The strong interactions between multivalent ions and polyelectrolytes are well known to lead to phase separation or gelation. In a second step[2] we have studied the phase diagrams of this system in free monovalent salt solutions, as a function of the copolymer composition, focusing our attention on two pH ranges. (1) At around pH 5, where Al polyions are present, the most striking fact is the existence of a gel phase for samples of low carboxylate content ($\tau \approx 1.5\%$) while for $\tau > 5\%$ only loss of viscosity followed by demixing is observed. (2) At around pH 7, $AlCl_3$ solutions contain only aluminium hydroxide particles which are expected to be uncharged and to interact with polymer through hydrogen bonds. In fact, phase separation also occurs for low Al contents and the strong dependence of the stability on the polymer charge suggests that this phenomenon is at least partially due to electrostatic interactions.

The purpose of the present paper is to complete and explain these previous observations by considering the effect of ionic strength, performing complementary studies such as electrophoretic measurements and microscopic observations and by discussing the observed behaviour in the light of new information recently obtained about the size and charge of aluminium species present in $AlCl_3$ solutions[3,4].

EXPERIMENTAL

Samples

Four polymer samples, AD10, AD17, AD27 and AD37, were supplied by Rhone-Poulenc and were prepared by photocopolymerization of acrylamide and sodium acrylate[5]. Their acrylate contents (τ), measured by potentiometry, elemental analysis and ^{13}C n.m.r., were 1.5, 7, 17 and 27%, respectively[6]. The molecular weight, M_w, of the four samples was approximately 5×10^6.

Preparation of the solutions

$AlCl_3$ solutions of given concentrations ($0 < C_a < 20$ ppm) were neutralized by addition of small volumes of NaOH solutions with concentration 10 times higher, the neutralization ratio ranging between 0 and 3. The neutralized solutions were slightly stirred and used before 15 days' ageing.

The industrial polymer samples were sodium salts of acrylamide–acrylic acid copolymer. Their solutions at a given concentration were homogenized by slow stirring at room temperature for at least 1 day and the pH was adjusted by addition of HCl 0.1 N. In order to avoid inhomogeneities due to strong interactions between the

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two compounds, for given concentrations C_p and C_a, the solutions were obtained by mixing two equal volumes of a polymer solution of $2C_p$ concentration and a $AlCl_3$ solution of $2C_a$ concentration, each being adjusted to the same pH.

To study the influence of monovalent salts on polymer–aluminium interaction, we prepared solutions in the same manner and used 20 g l^{-1} of NaCl solution as the solvent instead of pure water.

Turbidimetry

The turbidity of the solutions was measured with a spectrophotometer UV 240 Shimadzu, at 700 nm. As shown previously[2], the C_a dependence of the turbidity of solutions at given C_p presents an abrupt change for C_a^* and above this value the system is considered to present phase separation.

Viscometry

The viscosity measurements were performed with a low shear viscometer Contraves LS30 equipped with the system 2T2T (Φ = 11 mm, L = 20 mm, e = 1 mm) and thermostatted at 25°C. The measurements were carried out on the supernatant phase.

Measurement of elastic modulus

The elastic modulus of swollen gels was measured in unidirectional compression. The apparatus was built in our laboratory and includes an HBM amplifier coupled to a force transducer for the measurement of very small static loads (the maximum nominal load being 5 g for tension or compression). The force transducer could move perpendicularly to the gel surface by micrometric steps with the help of a Micro Controle translator. The gel was contained in a glass cell (Φ = 2.5 cm, h = 1 cm) and thermostatted at 25°C.

Electrophoresis

A Rank Bros. apparatus was used, consisting of a flat cell (e = 1 mm, L = 10 mm) containing the solution, kept at constant temperature (25°C). Two platinum electrodes applied a d.c. field up to 100 V. The cell was illuminated with a lamp allowing observation of the moving particles and their velocity was determined by means of a video camera and a TV monitor.

Optical microscopy

A Zeiss Photo MiII microscope allowed micrographs to be made, usually at 327 × and 815 × magnification, from $Al(OH)_3$ species in the absence or presence of polymers.

RESULTS

pH 7

The characteristics (weight average molecular weight $\bar{M}_{wa}$, radius of gyration R_{ga} and average number per litre n_a) of the $Al(OH)_3$ particles, which are slightly positively charged, are given in *Figure 1* as a function of Al concentration[3]. At pH 7, the four polymer samples are nearly completely dissociated and from previous studies[7,8], one can deduce the following limits for their radius of gyration R_g in the concentration range C_p 100–1000 ppm: 4000–2300 Å for AD10; 4900–3400 Å for AD17; 5500–3700 Å for AD27; 5800–3900 Å for AD37. In NaCl (20 g l^{-1}) solution, the following constant values can be used: R_{gp} = 1500, 1700, 1900 and 2000 Å for AD10, AD17, AD27 and AD37 respectively.

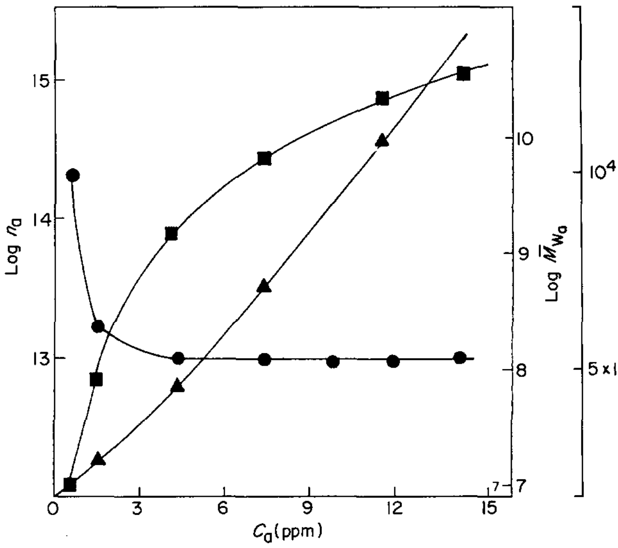


Figure 1 Characteristics of $Al(OH)_3$ species at pH 7: weight average molecular weight $\bar{M}_{wa}$ (■), radius of gyration R_{ga} (▲) and average number of particles per litre n_a (●) as a function of Al concentration C_a

Figures 2 to *5* summarize results obtained by turbidimetry and viscometry for polymer–$AlCl_3$ systems in pure water and NaCl (20 g l^{-1}) solutions. It is clear that NaCl prevents phase separation and loss of viscosity from occurring in the solution. This confirms that even at pH 7 the behaviour of such systems is partially due to electrostatic interactions. *Figures 4* and *5* show that the phase separation is related to a mechanism of flocculation through adsorption of polymer on $Al(OH)_3$ and interparticle bridging with the formation of large clusters. These clusters were found to be negatively charged in electrophoresis measurements. This means that they take the polymer charge as already described by Furusawa *et al.*[9] in a similar case of oppositely charged colloid and polymer (anionic latex with poly-L-lysine). Our results may be interpreted according to the scheme used by these authors[9] who only take into account electrostatic effects. In the absence of polymer the $Al(OH)_3$ particles are maintained in suspension by their electrostatic repulsion and the solutions are not turbid since the particle size is less than 20 000 Å. The addition of non-ionic polymer (unhydrolysed polyacrylamide) does not affect this stability because its adsorption does not change the particle charge. If the polymer is anionic, on increasing its concentration one observes a first step of flocculation due to the neutralization of the particles and a second step where the particles become negatively charged and are again stabilized. This stabilization effect is expected to require polymer concentration increasing with Al content and to be enhanced by increasing polymer charge (as observed in *Figure 2a*). This scheme may essentially be used in pure water. In the presence of NaCl, the screening out of the electrostatic interactions leads to an extension of the stabilization range in the phase diagram and to the disappearance of the restabilization effect at high polymer concentration (see *Figure 2b*). Nevertheless, even if such an electrostatic model explains most of our results well, one probably cannot neglect effects due to hydrogen bonds between

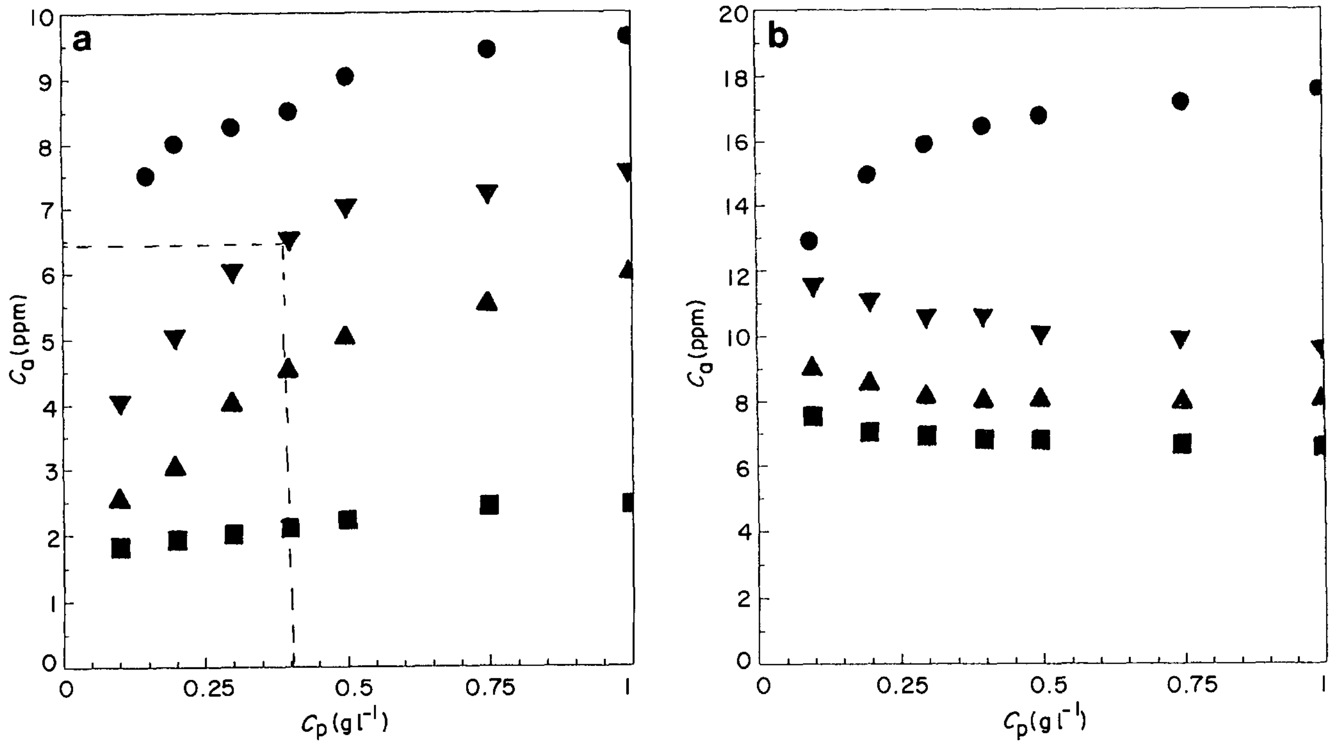


Figure 2 Results of turbidity measurements at pH 7 for AD17 (■), AD27 (▲), AD37 (▼) and AD10 (●) in the absence (a) and presence (b) of NaCl (20 g l^{-1})

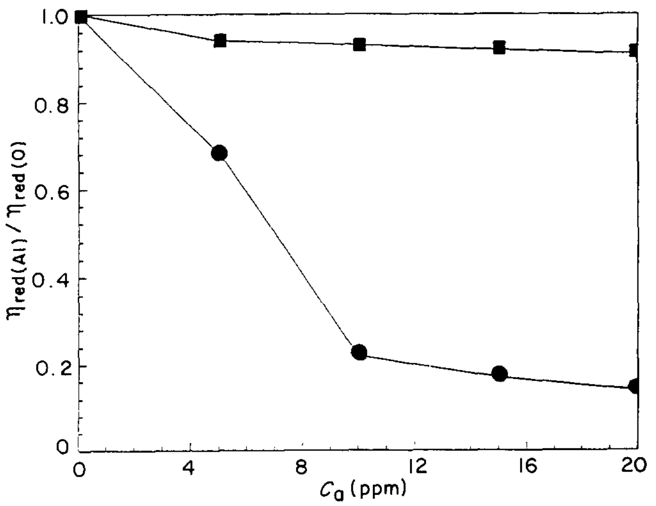
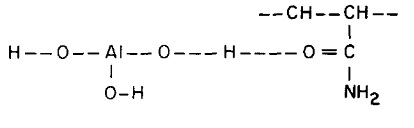


Figure 3 Variation of the ratio of the reduced viscosities $\eta_{red(Al)}/\eta_{red(O)}$ *versus* Al concentration at pH 7 in the absence (●) and presence (■) of NaCl (20 g l^{-1})

hydroxyl groups of $Al(OH)_3$ and amide groups of polyacrylamide, whose existence was well demonstrated in studies dealing with the adsorption of polyacrylamide on kaolinite[10,11]:



$$\mathrm{H{-}O{-}\underset{\displaystyle O{-}H}{Al}{-}O\cdots H\cdots O{=}\overset{\displaystyle -CH-CH-}{\underset{\displaystyle NH_2}{C}}}$$

pH 5

The composition of $AlCl_3$ solution neutralized around pH 5 has been extensively studied. The most striking fact is the existence of polycation species in equilibrium with mononuclear ions and non-ionic $Al(OH)_3$ particles. The

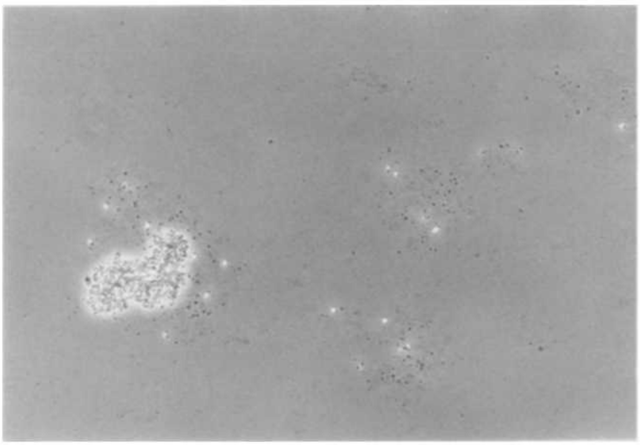


Figure 4 $Al(OH)_3$ particles at pH 7 (Al_{tot} = 60 ppm) (×408)

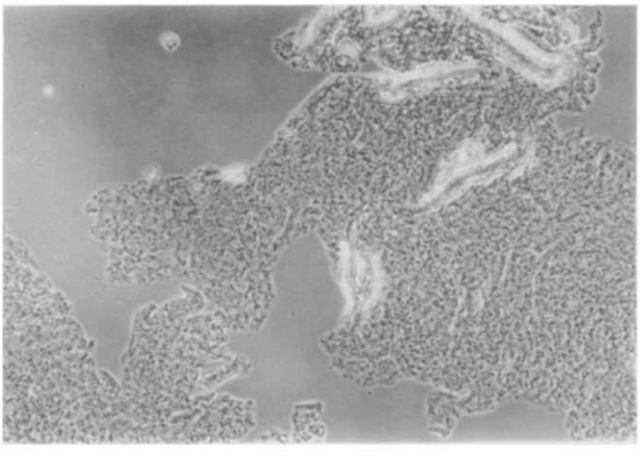


Figure 5 Cluster of $Al(OH)_3$ particles in the presence of polymer at pH 7 (Al_{tot} = 30 ppm, AD17 250 ppm) (×164)

Table 1 Molar fraction (%) of Al species for pH close to 5

Concentration (ppm)	pH	Al^{3+}	$Al(OH)^{2+}$	$Al(OH)^+$	$13Al_{13}$	$Al(OH)_3$
5	4.8	14	4	80	0.1	0
	5	6	3	76	12	0
	5.2	2	1	65	15	16
27	4.8	4.6	1.6	26	64	0
	5	1.2	0.5	17	26	54
	5.2	0.5	0	12	12	75

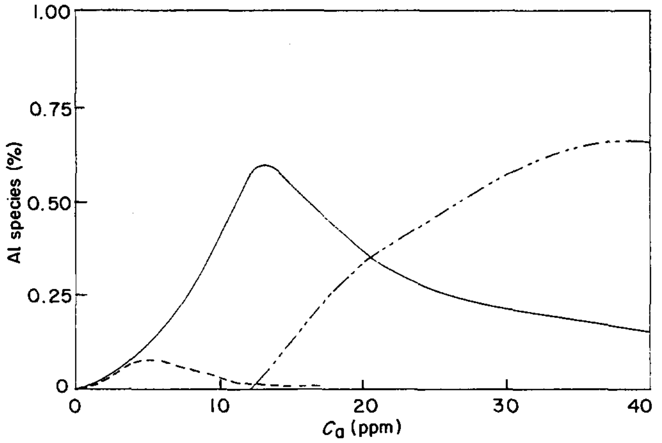


Figure 6 Distribution of the different Al species (in %) at pH 5: Al^{3+} (---); Al_{13}^{3+} (———); $Al(OH)_3$ (—-—)

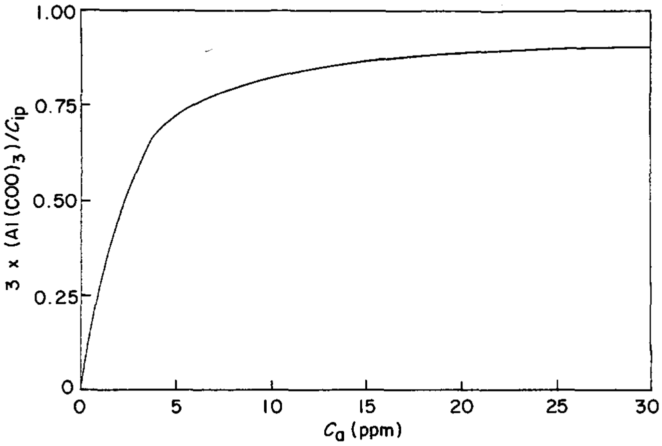


Figure 7 Calculated variation of the fraction of 'bound' carboxylate groups as a function of Al concentration (for 250 ppm of AD10)

following formula seems to be well established for the polycations: $Al_{13}(OH)_{28}(H_2O)_8^{3+}$.

Recent work of Bottero *et al.*[12–14] shows that the fraction of polynuclear species in moderately aged solutions (10–15 days) is an increasing function of concentration. We have confirmed this result and typical composition diagrams are given in Figures 2 and 3 of ref. 2 for $C_a = 2 \times 10^{-4}$ and 10^{-3} mol l^{-1}. It is also known that the onset of $Al(OH)_3$ formation, for the same ageing time, is shifted *versus* low pH by increasing concentration. In *Table 1* compositions are compared of $AlCl_3$ solutions neutralized (15 days aged) at three pH values around pH 5 for $C_a = 2 \times 10^{-4}$ mol l^{-1} (5 ppm) and 10^{-3} mol l^{-1} (27 ppm). This table shows how much the composition of the system varies with very low pH changes.

Figure 6 shows the molar fraction of Al^{3+}, Al_{13}^{3+} and $Al(OH)_3$ as a function of Al_{tot} for pH 5. The disappearance of the polynuclear ions with ageing time was studied by ^{27}Al n.m.r. Our results[1] confirm those of Turner[15] and show that the solution can be considered as free from these species after 6 months ageing.

The ionization of the copolymers is ruled by the classical dissociation equilibrium, with a constant K_a which depends on the neutralization degree α, carboxylate content τ, and ionic strength.

In previous work, we tried to evaluate the interactions between polymer and Al by calculating the fraction of aluminium bound to the polymer by hydrolysis equilibria of aluminium, dissociation equilibrium of COOH and association equilibria.

This calculation was based on different hypotheses. (i) Uniform distribution of the carboxylate groups and Al species in bulk: this assumption can only be correct if $C_p > C_p^*$ (C_p^* being the critical concentration of chain overlapping), since in isolated coils the true concentration is $\sim C_p^*$ and the concentration of Al ions is higher in the vicinity of the polymer than the average concentration in the bulk. We have obtained[1] a good agreement with the results of our model and n.m.r. experiments for $C_p > C_p^*$. (ii) Preponderance of associations of carboxylate groups with trivalent Al cations: Al^{3+} and Al_{13}^{3+}. We have assumed that in each case, the main equilibrium corresponds to the association of three carboxylate groups per trivalent Al ion. (iii) $Al(OH)_3$ species are not taken into account. Then for pH 7, where they are predominant, the interaction is predicted to fall to zero.

An example of the results is given in *Figure 7*, which shows that the major part of the carboxylate groups is associated in $Al(COO)_3$ for Al concentrations higher than 5 ppm.

Two important precautions have been taken in these studies. (1) In order to avoid inhomogeneities arising from a high local aluminium concentration, we have not added small volumes of concentrated solutions of $AlCl_3$ to polymer solutions. Instead, we have mixed two solutions with concentrations two times higher than the desired solutions. (2) Since very slight changes of pH induce important shifts in the composition of $AlCl_3$ solutions, the pH was adjusted in both solutions of $AlCl_3$ and polymer before mixing. Moreover, the $AlCl_3$ solutions have been aged at the given pH for 10–15 days, under conditions where their compositions are well known from previous ^{27}Al n.m.r. studies. The importance of this precaution is also easily understood. If the $AlCl_3$

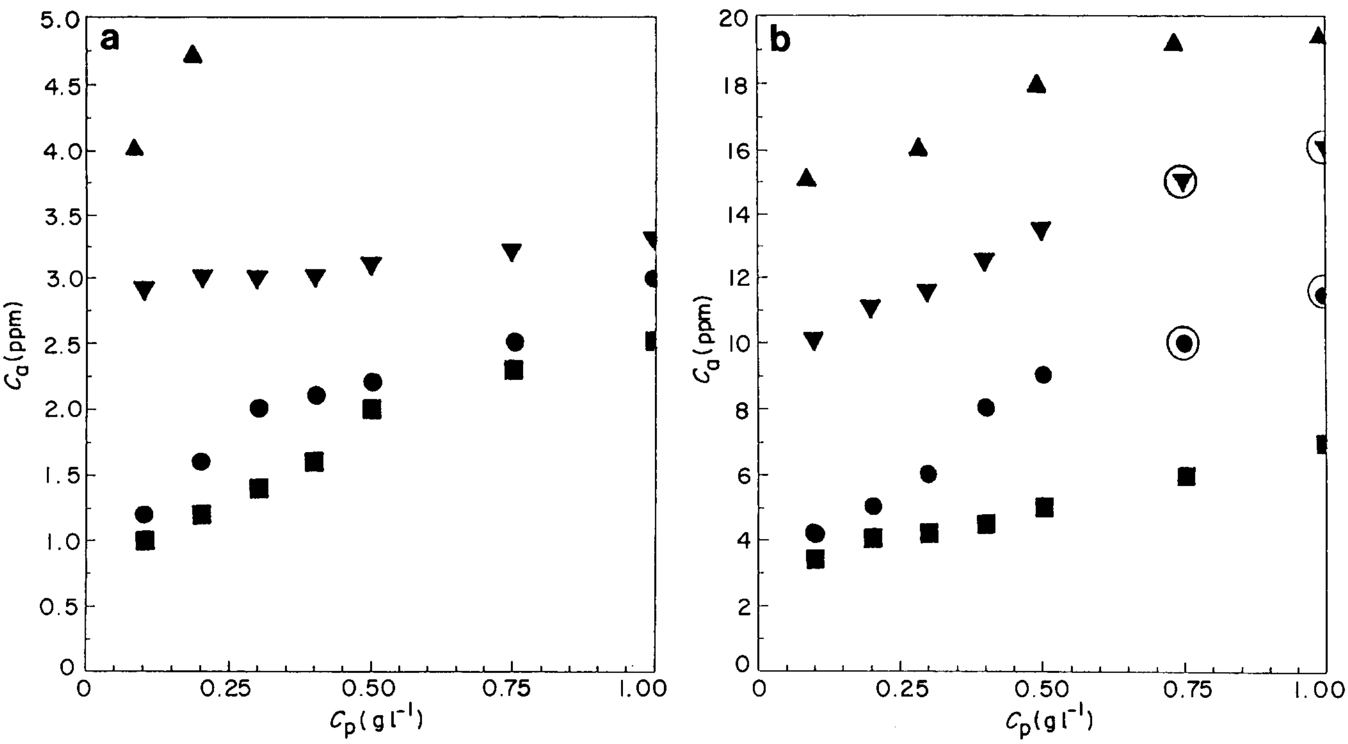


Figure 8 Results of turbidity measurements at pH 5 for AD17 (■), AD27 (●), AD37 (▼) and AD10 (▲), in the absence (a) and presence (b) of NaCl (20 g l^{-1}). Circled symbols represent a phase near to gel

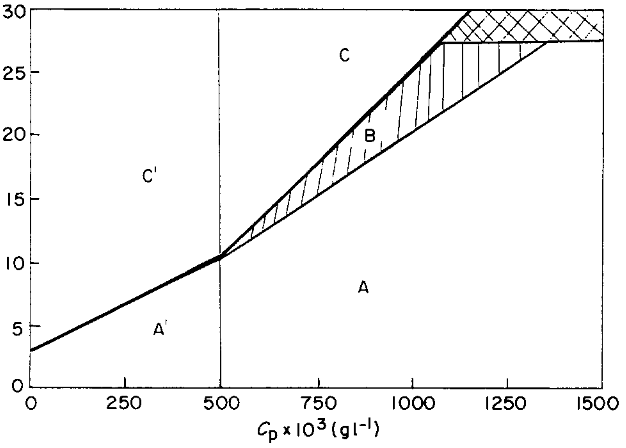


Figure 9 Phase diagram of AD27/AlCl$_3$ system in the presence of NaCl (20 g l^{-1}). The shaded area corresponds to flocculation by Al(OH)$_3$. See text for discussion of phases

and polymer solutions are taken at their own pH (low for AlCl$_3$ and around 8 for polymer, as reported in a recent work dealing with gelation of the same copolymers by chromium ions[16]) an intermediate pH, related to the different acidic-basic reactions, is obtained in a first fast step. After this the pH slowly reaches a value of around 5 and the kinetics effects on the nature and fraction of the different species of Al become very important. In such a method of preparation, uncertainty always remains about the ionic or non-ionic species which can interact with the polymer. In our procedure, we have systematically verified that the pH in the mixture is very near that of the initial solutions.

Phase diagrams from turbidimetry and visual observations of gel formation. In pure water (see *Figure 8*), for $\tau > 7\%$ only phase separation occurs for very low C_a values, due to polymer association with mononuclear ions Al^{3+}. For a less charged polymer such as AD10, the phase diagram presents a gelation domain for $C_p > C_p^*$ and for C_a concentration range where Al_{13}^{7+} is predominant[2].

In the presence of NaCl (20 g l^{-1}), the behaviours are different. Polymer AD10 does not form gels in the same range of composition as in pure water. A phase separation is observed for values of C_a higher than in pure water, which correspond to the formation of the non-ionic species (compare *Figures 6* and *8*). The same behaviour is also obtained for AD17 with lower values of C_a^*. With AD27 and AD37, we again find $C_p > C_p^*$ gelation domains inside the same type of diagram as for AD10 in pure water (see *Figure 9*). Gelation begins for both polymers for $C_p = 0.5$ g l^{-1} near the calculated C_p^* (using the relation $[\eta]C_p^* = 1$ we find that $C_p^* = 0.47$ g l^{-1} for AD27 and 0.4 g l^{-1} for AD37).

For $C_p^* < C_p < 6C_p^*$, these gels are formed with syneresis effect and then it is sometimes difficult to distinguish phase separation and gelation. Our criterion is the increase of viscosity with C_a in domain A of *Figure 9*. Phase separation is indeed always preceded by a viscosity decrease. The same difficulty exists for the upper limit of the gel domain. Nevertheless, we have been able to obtain the phase diagram for AD27 (*Figure 9*) with approximate limits: A = transparent solutions (increase of viscosity by increasing C_a); A′ = transparent solutions (decrease of viscosity by increasing C_a); B = gelation with slight syneresis effect, the range corresponds to the presence of polynuclear Al ions; C = phase separation due to the presence of non-ionic Al species; C′ = phase separation due to the presence of mononuclear Al ions. Such a diagram shows that gelation is due to Al polyions; this is confirmed by two other observations. (i) Gelation is not observed with neutralized AlCl$_3$ solutions aged for

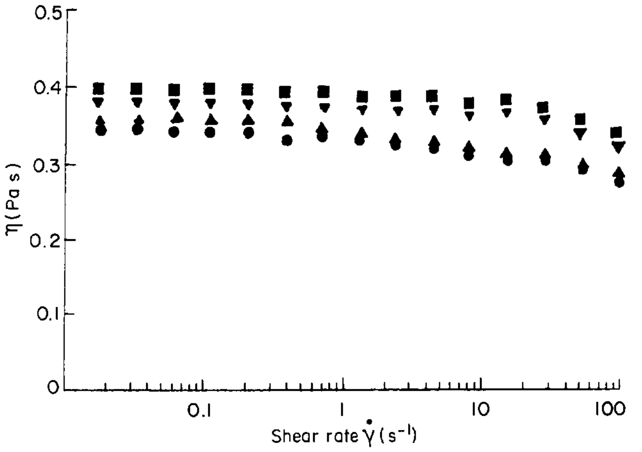


Figure 10 Variation of viscosity of AD17 solution (1000 ppm) at pH 5 in the presence of NaCl (20 g l^{-1}) and 0 (■), 5 (▼), 10 (▲) and 20 ppm (●) of Al

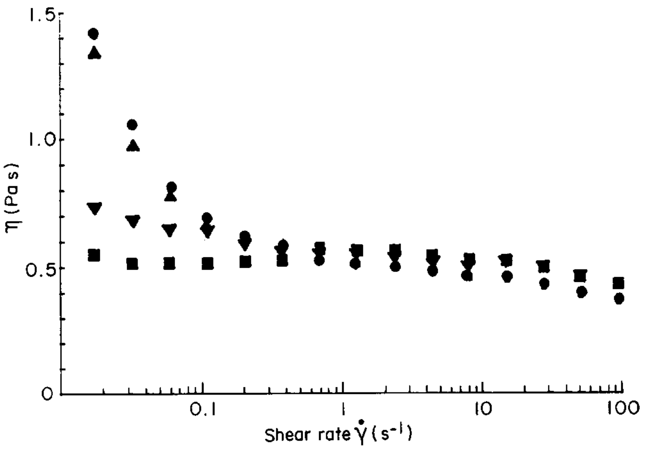


Figure 11 Variation of viscosity of AD37 solution (1000 ppm) at pH 5 in the presence of NaCl (20 g l^{-1}) and 0 (■), 5 (▼), 10 (▲) and 20 ppm (●) of Al

more than 2 months, and it has been shown[1,15] that Al_{13}^{3+} ions are absent from these solutions. (ii) For high polymer concentrations at pH 5, gelation is not possible because it requires an amount of Al_{13}^{3+} which cannot be reached due to the solubility limit of Al. As shown in *Table 1*, this amount can be obtained by a slight decrease of pH; gels without syneresis have been prepared under such conditions, as far good stoichiometry is respected (see Discussion).

Viscometry. We have measured the viscosity of the polymer solutions ($C_p = 1$ g l^{-1}) in the presence of aluminium and 20 g l^{-1} of NaCl, the shear rate varying between 10^{-2} and 100 s^{-1}.

At pH 5, the viscosity of AD17 and AD10 solutions falls for any values of Al concentration (see *Figure 10*). In pure water, we observed the same behaviour for AD17[2] while AD10 was characterized by an increasing viscosity (due to the crosslinking phenomenon) for low values of shear rate. As pointed out above, these results are very useful for establishing phase diagrams.

In contrast with our previous work in pure water, we note for AD27 and AD37 solutions that the viscosity increases with increasing Al concentration, for shear rates $\gamma < 0.2$ s^{-1} (see *Figure 11*). This effect disappears for $\gamma > 1$ s^{-1}. The formation of networks (or finite gel) can explain this behaviour. Each network is a macroscopic entity made from association of macromolecular chains, so its dimensions (R_g) and relaxation times (T_r) will be very high. Thus the viscosity will increase for shear rates $\dot{\gamma} < 1/T_r$, while for $\dot{\gamma} > 1/T_r$ the network cannot come back to its initial conformation and will be distorted and the viscosity will break down.

Electrophoresis. To better understand the mechanism of ion fixation and to check the turbidity results, we have studied polymer solutions of a given concentration C_p with Al concentrations $C_a < C_a^*$ and $C_a > C_a^*$. (These experiments have been carried out in the absence of added monovalent salt to prevent any electrolysis phenomenon.) We used AD17 solutions at $C_p = 0.5$ g l^{-1} ($C_{ip} = 5 \times 10^{-4}$ mol l^{-1}). The turbidity measurements give a value of $C_a^* = 2.5$ ppm ($= 10^{-4}$ mol l^{-1}) (see *Figure 6*), so polymer solutions with Al concentrations equal to 1, 2.5 and 6 ppm have been investigated.

For $C_a = 1$ ppm ($= 4 \times 10^{-5}$ mol l^{-1} $< C_a^*$), we observe only a few Al–polymer complexes of very elongated form ($L \approx 0.6$ mm) and they are all negatively charged. For $C_a = C_a^* = 2.5$ ppm the number of complexes increases and they form loops with an average radius of 0.1 mm and the average charge remains weakly negative. When $C_a = 6$ ppm ($= 2.2 \times 10^{-4}$ mol l^{-1}), only dense and spherical particles ($\Phi \approx 10$ μm) can be seen and the average charge becomes positive. It turns out that C_a^* determined by turbidimetry corresponds to the appearance of macroscopic complexes of sufficient size and quantity to be detectable by turbidimetry, but the carboxylic groups are not completely neutralized by aluminium ions; this is not surprising because at C_a^*, C_{ip} ($= 5 \times 10^{-4}$ mol l^{-1}) $> 3C_a^*$ ($= 3 \times 10^{-4}$ ml l^{-1}).

For an aluminium concentration above $C_{ip}/3$, all the carboxylic groups might be neutralized ($C_a = 6$ ppm $= 2.2 \times 10^{-4}$ mol l^{-1}, $C_{ip}/3 = 1.7 \times 10^{-4}$ mol l^{-1}). This is only possible with trivalent Al ions (three carboxylic groups are compensated by one aluminium ion). We know that at pH 5 and $C_a \approx 5$ ppm, the Al^{3+} ions represent initially 10% of Al_{tot}. This amount should be insufficient to neutralize all the COO^- sites, if the polymer–Al^{3+} interaction was not strong enough to induce the displacement of all the ionic equilibria, favouring Al^{3+} formation.

This is an important result which confirms our electrostatic interaction model[1] where we supposed that $Al(OH)^{2+}$ and $Al(OH)_2^+$ do not bind to the polymer and each trivalent ion reacts with three carboxylic groups. But we can point out that there is not necessarily a complete polymer precipitation when Al^{3+} ions neutralize three COO^- groups. Effectively for $Al_{tot} = 6$ ppm all the carboxylic groups are neutralized, whereas in a recent work we found that for the same polymer and for $Al_{tot} = 20$ ppm only 30–50% of the polymer precipitates with complex formation. This site binding is due to the great concentration of Al^{3+} in the vicinity of the polyelectrolyte and the precipitation of polymer by aluminium bridging is a function of Al concentration. (It should be noted that a few Al–polymer complexes are formed, although at very low Al concentration, which must be due to the inhomogeneities of the solution. We cannot compare the charge of different complexes since the values of electrostatic charges are deduced from the

Table 2 Measurements of elastic modulus E_0 for AD10 in pure water. Values corresponding to COO^-, Al_{13}^{3+} and μ represent the number ($\times 10^{-18}$) of each species in one litre of the gel

C_p ($g\,l^{-1}$)	COO^-	C_a (ppm)	Al_{13}	Swelling ratio, Q	E_0 (Pa)	Number of junctions, μ
13.5	2.2	1200	100	46	490	9
13.5	2.2	1000	85	64	420	6
12	2	800	68	66	360	5
8.5	1.4	600	51	96	280	3
7.5	1.2	500	43	146	320	2
7.5	1.2	800	68	115	350	3

Table 3 Values of the ratio C_a^*/C_{ip} for the copolymers at 1000 ppm in water

Ion	AD60	AD37	AD27	AD17	AD10
Ca	2.73	5	∞	∞	∞
Al	–	0.07	0.1	0.2	–

velocity of the particles depending on their shape and average size, which are not well defined.

Measurement of elastic modulus. We have measured the elastic modulus E_0 in uniaxial compression of some gels made from AD10 polymer for different concentrations of aluminium and polymer, in the absence of NaCl. To obtain gels without syneresis, polymer concentration was higher than $5\,g\,l^{-1}$, and the aluminium solution was prepared under conditions (concentration, ageing time and pH) which nearly corresponded to a solution containing one Al_{13}^{3+} for three COO^-. This stoichiometry is deduced from our previous work, where we calculated (see above) that gelation occurs for one Al_{13}^{3+} for three COO^-. The elastic modulus of these gels is very weak (< 500 Pa) and reproducible results are obtained only if the gel samples are contained in a cell. The influence of cell dimensions has been checked, and it was found to be negligible in our case.

Theories of Flory[17] dealing with the elasticity of polymer networks allow calculation of the number of flexible chains and the number of junctions. In the case of swollen gel, the following relation can be used[18]:

$$\sigma = \frac{\nu A k T Q^{2/3} h^{2/3} (\lambda - \lambda^{-2})}{V_{gel}} \qquad (3)$$

where σ = stress in uniaxial compression ($N\,m^{-2}$), ν = total number of elastic chains in gel, k = Boltzman constant, T = absolute temperature, Q = swelling ratio, λ = deformation ratio and V_{gel} = gel volume. A and $h^{2/3}$ (called the memory term) are constants depending on gel structure, and there are many discussions about their values (varying between 0.5 and 1).

The swelling ratio has been determined by the method of Weiss *et al.*[19]:

$$Q = 1 + (G - 1) v_s / v_0 \qquad (4)$$

where v_s and v_0 = specific volume of the solvent and the dry gel respectively, ($v_s = 0.715\,cm^3\,g^{-1}$)[20] and G = swollen gel weight/dry gel weight.

To calculate the number of junctions μ, we make some assumptions: according to James and Guth[21], $A = 1$ and $h^{2/3} = 0.5$; the relation (3) can be used by assuming that the gel does not deswell by the applied force; the gels are tetrafunctionsl, i.e. the number of junctions[22] μ is 2ν. It should be noted that all these assumptions affect the value of μ by a factor near to unity, so by measuring the strain σ for low deformation ratio ($< 10\%$), we can deduce approximately the number of junctions μ.

In *Table 2*, one can compare the number of junctions, the calculated number of Al_{13} species and the number of carboxylate groups. We knew that each Al_{13} neutralizes three COO^- groups but had no way to determine whether they form intra- or intermolecular bridges. This study shows that the ratio Al_{13} number/junction number is very much lower than one and demonstrates that Al_{13} essentially forms intramolecular bridges.

DISCUSSION

These new results have confirmed our previous observations, that at pH ≈ 5, phase separation and gelation can occur in different ranges of the diagram according to the polymer composition and the ionic strength of the solution. We will try to draw some general qualitative laws of behaviour, although this system is particularly complex due to the nature of $AlCl_3$ solutions. We will distinguish two types of behaviour: phase separation *without* gelation; phase separation *and* gelation.

Phase separation without gelation

This behaviour is observed for $C_p < C_p^*$ in all cases and in the entire range of polymer concentrations in pure water for $\tau > 7\%$ and in NaCl ($20\,g\,l^{-1}$) for $\tau < 17\%$. This phase separation always corresponds to a loss of viscosity, and it is generally due to Al^{3+} ions, if one excepts the particular case of AD10 (for $20\,g\,l^{-1}$ of NaCl), where one observes in fact a flocculation of $Al(OH)_3$ particles.

It is interesting to compare the stability of these copolymers at pH 5 with respect to Al^{3+} with that observed at pH 7 in the presence of calcium (Ca^{2+})[23]: (i) for $C_p < C_p^*$ only copolymer AD60 ($\tau \approx 40\%$) precipitates with Ca^{2+}; (ii) for $C_p > C_p^*$, the copolymer stability is in the order AD10 $\gg$ AD17 $>$ AD27 $>$ AD37 $>$ AD60; for $\tau > 7\%$ the increase of polymer charge density leads to reduced stability, whereas we have observed the inverse effect with Al^{3+}; (iii) the addition of $20\,g\,l^{-1}$ of NaCl is sufficient to eliminate the precipitation of AD60 by Ca^{2+} and only induces a slight increase of C_a^* in the case of Al^{3+}.

We can compare the values C_a^*/C_{ip} for the two types of ion at a given polymer concentration (1000 ppm for instance) in pure water (see *Table 3*). This shows that C_a^*/C_{ip} is approximately 10% for Al^{3+} ions, while it is much higher for Ca^{2+} (5 for AD37). In the case of Ca^{2+}, it has been pointed out that precipitation of such polymers results from the contribution of two types of mechanism, called types H and L[24]. The first mechanism H, proposed by Flory[17], is analogous to the precipitation of non-ionic polymers at temperatures lower than the θ point. A θ salt concentration is defined and phase separation is attributed to a screening out of the electrostatic effect. This type of phase separation has been experimentally studied and occurs for high concentrations of monovalent salt (e.g. polyacrylic acid –NaCl[25]). The second mechanism L has been described[26] as due to counterion fixation and corresponds to the neutralization of a given fraction of polymer sites, this fraction being near to one (e.g. polyphosphate or polyacrylate–alkaline earth ions[27,28]). Precipitation is then expected for $C_a^*/C_{ip} \approx 0.5$ (for divalent cations) and $C_a^*/C_{ip} \approx 0.33$ (for trivalent cations).

For copolymers in the presence of Ca^{2+}, the first mechanism is predominant for $\tau < 30\%$ and the second one begins to play a role for $\tau > 30\%$ and the more concentrated the polymer solution the more important is the fixation effect[23]. This is attributed to the fact that for $C_p < C_p^*$ the interaction between a group $COOCa^+$ and a dissociated group COO^- is not sufficient to allow the formation of intramolecular loops. When C_p increases, the probability of formation of $CaCOO_2$ species by intermolecular bridges is higher, then the solubility decreases and the ratio C_a^*/C_{ip} decreases with increasing polymer concentration.

With Al^{3+} ions it is quite clear that the first mechanism can be eliminated and only Al^{3+} fixation is responsible for the phase separation (except for AD10). C_a^* is expected to vary as C_p (C_a^*/C_{ip} remaining constant). This is not exactly obtained in *Figure 8*: C_a^*/C_{ip} slightly decreases with C_p, then the contribution of intermolecular bridges cannot be neglected as for Ca^{2+}. If a given fraction of carboxylate groups must be neutralized at phase separation, it is expected that C_a^* increases with τ for a given polymer concentration and varies on a unique curve for all polymer samples ($\tau > 7\%$) with C_{ip}. This is consistent with our results in pure water and in the presence of salt. The number of associated species $Al(COO)_3$ is expected to decrease with addition of NaCl and more Al^{3+} is required to induce phase separation. Nevertheless, the values of C_a^*/C_{ip} are much lower than the expected value of 0.3, particularly for AD37.

As shown by our previous turbidimetry studies, phase titration and electrophoresis measurement, one must take into account the inhomogeneities in the solutions. On the other hand, viscometry shows that the chain is very collapsed and the intramolecular formation of loops must play an additional role in solubility reduction. In general, phase separation occurs when intramolecular associations are favoured with respect to intermolecular fixation and gels are expected in the reverse case.

Phase separation and gelation

Conditions of gelation. Experimental results show that gelation occurs if (1) $C_p > C_p^*$; (2) Al_{13}^{7+} ions are present; (3) polymer charge density has a critical value depending on the ionic strength. This allows us to formulate the main conditions for gelation. The probability of intermolecular contacts could be obtained for $C_p > C_p^*$. This is generally recognized as the main condition for the formation of physical gels[29] or gels obtained by ion complexation[30,31]. In our case, this is not sufficient since above C_p^*, solutions may or may not form gels according to the hydrolysis degree of the polymer. In fact in pure water C_p^* of AD37 is much lower than the C_p^* of AD10 and gelation should occur at lower concentration, but this is not the case. Here, we must remark that the gelating systems previously studied by other authors differ from ours in two aspects. (i) All the monomeric units play the same role with respect to the complexing ion (PVP–Cu^{II}[32], galactomannans–borate[30]) or in the physical gelation by intermolecular associations (the case of polystyrene or poly(vinyl alcohol). (ii) The polymer, initially uncharged, becomes charged by complexation. In our case, only some units (COO^- units) are able to bind a counterion. A major parameter is the distance between charges along the chain, r_{ii}, and our results lead us to formulate the following further condition: (4) r_{ii} must be in the same order of magnitude as the average distance r_{ij} between different chains. Thus if $r_{ii} < r_{ij}$, Al ions will more easily establish intramolecular bridges and the probability of crosslinking will be weak. This is the case in pure water for $\tau > 5\%$ in the dilute and semidilute regime. For AD10, r_{ii} is greater and becomes equivalent to r_{ij}. This leads to definition of a concentration of gelation C_p^{**} which is a function of τ.

This could be roughly understood from two different models for semidilute solutions of polyelectrolyte. If we consider the polyelectrolyte as a charged line[33] inside a cylindrical cell, it is easy to calculate C_p^{**} for AD10 ($2\,g\,l^{-1}$) and for AD17 ($20\,g\,l^{-1}$). This explains well that C_p^{**} should be much higher for copolymers of $\tau > 7\%$ than for AD10. Nevertheless it is not certain that this model is well adapted for very low values of τ.

If we consider an isotropic model of interpenetrating coils[34], the correlation length ξ is defined as for non-ionic polymers. (It is surely a better model for polymers with low charge density like AD10.) In this case the chain conformation is only slightly modified by addition of $AlCl_3$ and then C_p^* remains constant so condition 4 can be respected. For more charged polyelectrolyte, the coil expansion drastically decreases with addition of salt; this strongly reduces the intramolecular charge density and increases C_p^* value. Thus, condition 4 cannot be realized.

This condition also explains the influence of a large excess of NaCl ($Na^+/COO^- \approx 1000$) on gelation. In the calculation previously performed, we have neglected the following equilibrium:

$$-COONa \rightleftharpoons COO^- + Na^+ \qquad K_D$$

then

$$[COONa] = [COO^-][Na^+]/K_D \qquad (5)$$

so

$$[COONa] \propto [Na^+]$$

In a large excess of NaCl, the ratio of 'free' carboxylic groups decreases, and we will practically have a polymer with a lower hydrolysis ratio: the distance r_{ii} between free COO^- increases, and the polymer will take a Gaussian conformation. We have made this calculation again by introducing the additional relation (5) and found the same number of 'bound' carboxylate groups for AD27 in $20\,g\,l^{-1}$ of NaCl than for AD10 in pure water with $K_D = 0.03$. This explains well that gelation occurs for AD27 in $20\,g\,l^{-1}$ of NaCl as in AD10 in pure water. The same calculation applied to AD10 at high ionic strength predicts a very low number of COO^- available for interaction with Al, then the number of junctions is not sufficient to form a three-dimensional network.

Lower limit of gelation domain and elastic modulus. Some works deal with the comparison between lower and upper limits of gelation domain. The lower critical limit is assumed to correspond to the formation of one junction per chain according to the Flory[17] theory for the chemical network. This point of view has been applied with success in the case of galactomannans–borate systems[30]. Assuming that the bicomplexes may only be obtained by intermolecular bridging, the borax concentration required to reach the gel is found to scale as C_p^{-u}, u being given by $u = 1/(3v - 1)$. *Figure 9* of the present paper and Figure 5 of ref. 2 show that the concentration of Al_{13} at the lower gelation limit is an increasing function of C_p in contrast with such predictions. On the other hand, it was deduced from our measurements of E_0 that the number of effective junctions is much lower than the calculated number of Al_{13} bound on the polymer. We want to demonstrate that these apparently surprising results may be simply explained from the particular nature of the crosslinking agents—Al_{13} polyions characterized by a large size, a relatively low charge and purely electrostatic interaction with the carboxylate groups.

Let us assume that in a first step, most of the polyions participate to neutralize COO^- sites belonging to the same chain. A very simple calculation shows that this effect may occur without formation of loops and without significant chain conformation changes. Indeed, by assuming for AD10 the same molecular weight dependence of the radius of gyration R_g as for unhydrolysed polyacrylamide

$$R_g = 0.075 M_W^{0.65} \qquad (6)$$

one can calculate the average distance between three sites to be 30 Å. Then an Al_{13} ion ($\Phi = 38$ Å) could be fixed on three sites without loss of chain entropy and without syneresis, in contrast with Al^{3+} ions ($\Phi = 18$ Å). Then, in a second step, a few intermolecular bridges are sufficient to form a gel and the intermolecular bridging can only be efficient when the major part of the charged groups is neutralized to sufficiently decrease the electrostatic repulsion between chains. The concentration of Al_{13} necessary to obtain a gel is proportional to the number of carboxylate groups and consequently to C_p, as observed in the experiments. This hypothesis also explains the low E_0 values. More precisely, we can consider an isotrope model of interpenetrating coils[34] and compare the number of entanglement points and the effective junction number. By applying the de Gennes relation to determine the correlation length ξ (ξ being the size of a fictive coil of g monomers):

$$\xi = R_{G0}\left(\frac{C_p^*}{C_p}\right)^{0.75} \qquad (7)$$

where R_{G0} is the radius of gyration for $C_p \to 0$, given by relation (6) and

$$C_p^* = \frac{3}{4}\frac{M_W}{\pi N R_G^3} \qquad (8)$$

and by writing that

$$\xi = 0.075(gm)^{0.64} \qquad (9)$$

we find that the number of entanglement points (M_W/mg) is approximately six times higher than the junction number μ. So in our case the entanglement points are different from reticulation points, in contrast with other systems[30]. This confirms the hypothesis of physical reticulation of COO^- sites since it is clear that in an entanglement point the probability of finding two or more COO^- groups is very low due to electrostatic repulsion.

CONCLUSION

First we can conclude that our work reveals the high complexity of the interactions between aluminium ions and polyelectrolytes. One of the main difficulties arises from the complex nature of the ionic aluminium species and from their dependence on pH, concentration and time. Starting from low pH to pH 7, one can expect a precipitation phenomenon due to the formation of a neutral complex polymer–Al^{3+} gelation related to the presence of polymolecular ionic species of Al and flocculation of aluminium hydroxide by the charged polymer.

The gelation phenomenon at pH 5 is particularly interesting and our results seem to show that gelation is highly dependent on degree of hydrolysis of the polymer and salinity. We propose a model where, in a first step, the Al_{13} ions neutralize the carboxylate groups belonging to the same chain and form intermolecular bridges only when the electrostatic repulsion between chains is sufficiently reduced. These systems also present a rheostiffening behaviour which will be discussed in a forthcoming paper.

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