Hydrolysis of polyacrylamide and acrylic acid–acrylamide copolymers at neutral pH and high temperature

Houchang Kheradmand and Jeanne François*
Institut Charles Sadron, CRM, Université Louis Pasteur, 6 rue Boussingault, 67083 Strasbourg, France

and Véronique Plazanet
Total, Compagnie Française des Pétroles, Centre de Recherche de Beauplan, Route de Versailles, 78470 St-Remy les Chevreuse, France
(Received 26 June 1987; accepted 5 November 1987)

The hydrolysis of acrylamide–acrylic acid copolymers has been studied as a function of pH and of the initial composition of the samples. Our experimental results confirm the intramolecular catalysis by neighbouring undissociated carboxylate groups for $3 < \mathrm{pH} < 5$, as already demonstrated by Smets *et al.*, and the catalysis of OH^- ions with autoretarded kinetics for $\mathrm{pH} > 11$. In the range of neutral pH, the observed kinetics cannot be simply explained by the superposition of these two mechanisms. Nevertheless, some empirical laws can be established from experimental data. A simulation based on a Monte Carlo method is proposed in order to predict the hydrolysis of these copolymers in different conditions.

(Keywords: hydrolysis; kinetics; polyacrylamide; acrylic acid–acrylamide copolymers; Monte Carlo method)

INTRODUCTION

Partially hydrolysed polyacrylamide or acrylic acid–acrylamide copolymers are among the most water-soluble polymers used in the chemical tertiary oil recovery process. The changes with time of the viscosity of their aqueous solutions are due to hydrolysis of the amide groups and to chemical degradation[1,2]. The first modification, which enhances the polyelectrolytic character, can lead to an increase or decrease of the viscosity according to the nature of the ions present in the medium and to the range of effective charge of the polymer that is reached during the ageing. Chemical degradation, in dilute solution, is generally expected to decrease the viscosity. The prediction of the evolution of the thickening solution properties in the long term need good knowledge of the mechanisms and kinetics of hydrolysis and degradation.

The present paper deals with the hydrolysis kinetics in the range of neutral pH for which few reliable data are available. It is well known that base hydrolysis of polyacrylamide obeys autoretarded kinetics due to the electrostatic repulsion between the anionic reagent and the polymeric substrate[3-5]. In the range of slightly acid pH ($3 < \mathrm{pH} < 5$), Smets and Hesbain[6] have demonstrated a mechanism of intramolecular catalysis by neighbouring carboxylate groups that are not dissociated. Some experimental work has dealt with hydrolysis of initially partially modified polyacrylamide in the pH range ($4 < \mathrm{pH} < 10$) corresponding to the conditions of industrial applications. Nevertheless, the mechanisms of the reaction have not been elucidated or discussed and the experiments were not carried out under conditions appropriate to the interpretation of the results[1,2].

We will present a systematic experimental study of the hydrolysis of homopolyacrylamide and its copolymers with acrylic acid as a function of pH and initial carboxylate content, at high temperature ($75°\mathrm{C} < T < 95°\mathrm{C}$).

A model for the mechanisms will be proposed, which takes into account the retarding and accelerating effects of the neighbouring already-modified groups according to their dissociation state and their distribution along the chain.

EXPERIMENTAL METHODS

We used five samples of acrylamide–acrylic acid copolymers synthesized by photopolymerization[7], namely A, B, C, D and E with carboxylate contents equal to 0, 7, 17, 27 and 37% respectively[8]. Their molecular weight M_w is approximately 6×10^6. Sample P700 is a partially hydrolysed polyacrylamide (33%) of $M_w = 7 \times 10^6$.

The polymer solutions were prepared 48 h before use and homogenized at room temperature by slow stirring. The initial pH, $\mathrm{pH_i}$, is adjusted by addition of HCl or NaOH solutions. The solutions, contained in carefully closed Erlenmeyer flasks, are put in a hot-air bath thermostatted at ±1°C. At different intervals of time, 20 $\mathrm{cm^3}$ of solution are pipetted, cooled at room temperature and stirred with a large excess of cationic resin. The composition of the copolymer is then determined by potentiometric titration using a pH meter (Metrohm 605), a glass microelectrode (Metrohm E125) and a microburette (Dosimat 645). The titration operations and data treatment are automated through a program established by Truong[9]. The equivalent volume is determined by the method of Wolf[10].

---

* To whom correspondence should be addressed

0032-3861/88/050860-11$03.00

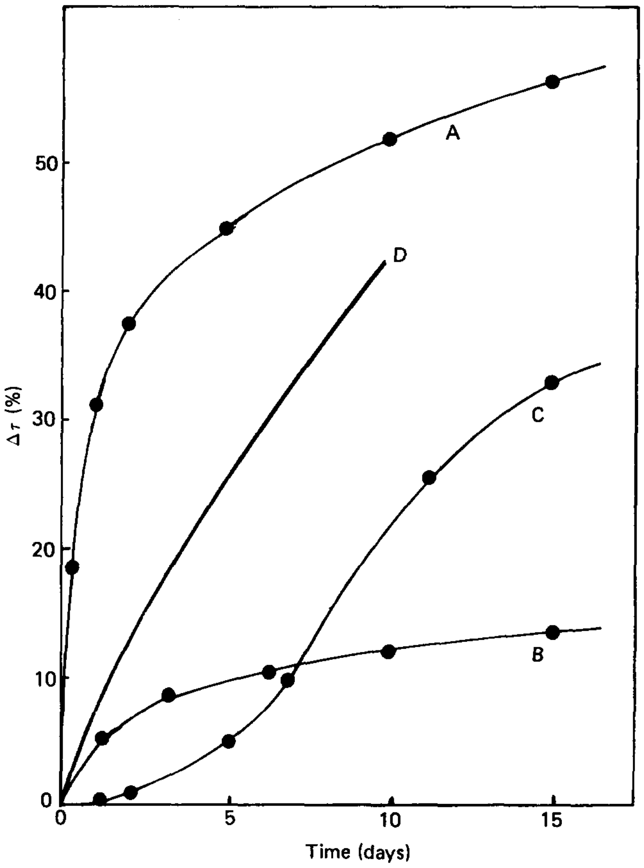

Figure 1 Hydrolysis kinetics of polyacrylamide A at 80°C ($c = 8 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$) for initial pH 11.85 (curve A), 7.55 (curve B) and 3.75 (curve C); curve D is calculated from data of alkaline hydrolysis for pH 11.85 (see text)

EXPERIMENTAL RESULTS

Hydrolysis of unhydrolysed polyacrylamide

Figure 1 shows the hydrolysis kinetics of polyacrylamide A at 80°C, for a polymer concentration $c_p = 810\,\mathrm{ppm}$ or $1.14 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$ and for three different initial pH values. The features of the kinetic curves clearly confirm the autoaccelerated (for $\mathrm{pH_i} = 3.75$) and autoretarded (for $\mathrm{pH_i} = 11.85$) character of the reaction, according to the previous experimental studies[3-6]. In our experiments we have not used buffers and a variation of pH due to the formation of NH_3 in solution is then registered, as already found in works of Muller *et al.*[1,2]. The variations of pH for the same experimental conditions as those of *Figure 1* are given in *Table 1*. When $\mathrm{pH_i}$ is lower than 8, an increase of pH is observed, the inverse effect being found for high values of $\mathrm{pH_i}$. We will show in the 'Discussion' that such variations can easily be predicted quantitatively by taking into account the different ionic equilibria that take place in solutions during reaction. The increase of pH with time explains the form of the curve C ($\mathrm{pH_i} = 3.75$) of *Figure 1*, which presents a slow step after 15 days reaction following the acceleration step.

If we consider the initial reaction rate, it appears that it decreases with decreasing $\mathrm{pH_i}$. Qualitatively speaking, this behaviour suggests that the hydrolysis is catalysed by OH^- ions at least in the initial step when the accelerating effect of COOH groups cannot be present. By adjusting our experimental results by polynomials of degree 3 or 4, we have determined the values of the initial rates k_0 for each studied $\mathrm{pH_i}$. We have found 2.48×10^{-6}, 4.62×10^{-5} and 6.72×10^{-4} ($\mathrm{mol^{-1}\,h^{-1}}$) at $\mathrm{pH_i}$ 3.75, 7.55 and 11.85 respectively. If the hydrolysis was catalysed by OH^- and H^+ ions, the kinetic expression should be that generally assumed for low-molecular-weight amides[11,12]:

$$-\frac{d[A]}{[A]dt} = k_H[H^+] + k_{OH}[OH^-] \qquad (1)$$

where [A] is the concentration of amide groups. If catalysis by OH^- is predominant:

$$k_0 = -\frac{d[A]}{[A]dt} = k_{OH}[OH^-] \qquad (2)$$

and the initial rate is expected to vary as $[OH^-]$. The experimental values of k_0 do not follow this law. An analogous behaviour is described in ref. 12 for an acrylic acid–*p*-nitroacrylamide copolymer and is attributed to intramolecular catalysis by undissociated COOH groups. However, for $\mathrm{pH} > 7$, the degree of dissociation of carboxylic groups is near 1 and this type of catalysis should become negligible. From relation (2), the ratio of k_0 values for $\mathrm{pH_i} = 11.85$ and $\mathrm{pH_i} = 7.55$ is 2×10^4 while the experimental ratio is 14. On the other hand, we have calculated the hydrolysis kinetics expected, for these two $\mathrm{pH_i}$, from the data of refs. 3 and 4 established at high pH ($\mathrm{pH} > 13$) where OH^- ions only are responsible for the reaction. For $\mathrm{pH_i} = 7.55$, one finds a k_0 value 10^4 times lower than that measured. The curve calculated for $\mathrm{pH_i} = 11.85$ is also very different from the experimental curve (see *Figure 1*). Consequently, it clearly appears that hydrolysis of polyacrylamide cannot simply be interpreted in terms of catalysis by OH^-, although these ions probably play a role since the rate is dependent on their concentration. Secondly it seems that auto-acceleration for $\mathrm{pH} < 7$ must be taken into consideration.

Hydrolysis of acrylic acid–acrylamide copolymers

pH <6. In order definitely to confirm the acceleration due to the undissociated carboxylic groups, we have reproduced the experiments described by Smets and Hesbain[6]. They compared the hydrolysis kinetics of an unneutralized copolymer at its own pH (called internal H^+) to that of polyacrylamide at the same pH obtained by addition of HCl (called external H^+), the concentration of amide groups being identical in the two experiments. Our results given in *Figure 2* for $\mathrm{pH_i} = 3.75$ are in complete agreement with those of Smets and Hesbain. The initial reaction rate for copolymer C is approximately 100 times higher than that obtained for copolymer A.

One can then deduce that for the whole pH range where

Table 1 Variations in pH for experimental conditions in *Figure 1*

Time (h)	pH	pH	pH
0	3.75	7.55	11.85
24	3.80	7.91	11.45
48	3.85	8.12	11.05
120	4.12	8.20	–
168	4.48	–	–
264	5.07	8.20	10.10
360	5.41	8.20	9.80

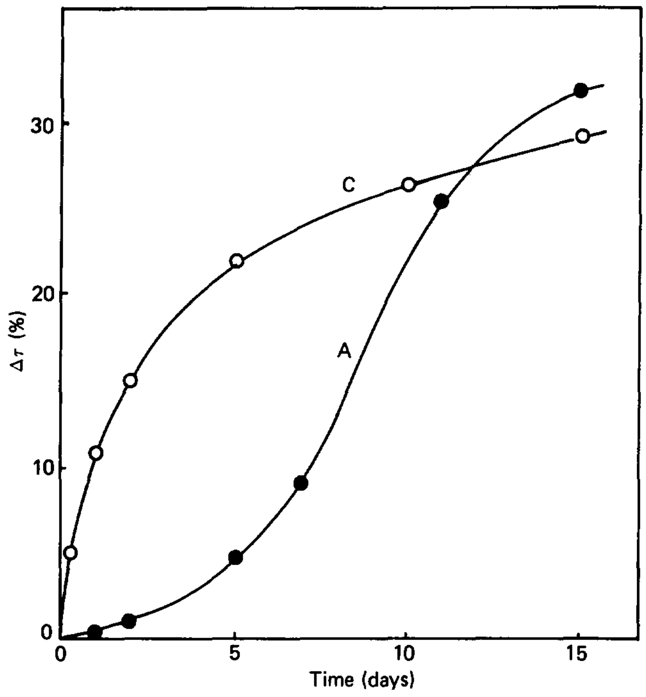

Figure 2 Comparison between hydrolysis kinetics of copolymer C and homopolyacrylamide A at the same initial pH (3.75), temperature (80°C) and amide group concentration (1.14×10^{-2} mol l^{-1})

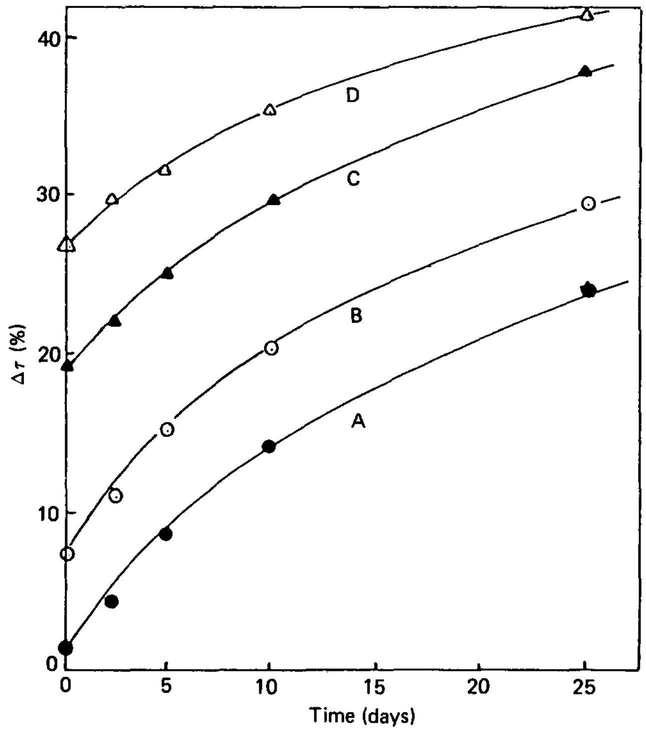

Figure 3 Hydrolysis kinetics of copolymers A, B, C and D at the same polymer concentration (10^{-3} g cm^{-3}), initial pH (6.5) and temperature (80°C)

carboxylate groups are not completely dissociated, intramolecular catalysis must be taken into account.

6<pH<8. We compare in *Figure 3* the hydrolysis kinetics of A, B, C and D at the same polymer concentration for $pH_i = 6.5$. The values of k_0 obtained from these results are 10^{-5}, 9.5×10^{-6}, 1.2×10^{-5} and 1.4×10^{-5} (mol^{-1} h^{-1}) for the four samples, respectively. This shows that the hydrolysis is slightly sensitive to the initial polymer composition, the effect of neighbouring groups being relatively low for such a pH. In fact, we will see later that this behaviour is due to the compensation of both effects, acceleration and retardation.

On the contrary, for $pH_i = 7.55$, the more hydrolysed the initial polymer, the lower the reaction rate (see *Figure 4*). At such a pH the carboxylate groups are highly dissociated and the accelerating effect is low. This observation, which can be explained by the effect of electrostatic repulsion as at high pH[3,5], suggests that, even if the reaction is not directly catalysed by OH^- ions, their presence in the neighbourhood of the reacting groups enhances the reactivity. This is consistent with the decrease of reaction rate by decreasing pH in the case of polyacrylamide.

pH>8. Figure 5 shows that the retarding effect of dissociated carboxylate groups is very pronounced at $pH_i = 11.85$.

These first results show that three ranges of pH can be distinguished:

(a) the range $3 < pH < 6$ where the accelerating effect of undissociated COOH groups will be predominant;

(b) the range $6 < pH < 7$ where in a first approximation the influence of neighbouring groups could be neglected; and

(c) the range $pH > 7$ where the main effect is that of dissociated carboxylate groups.

Detailed investigation of hydrolysis of copolymer C

Relation between hydrolysis and degradation. In other works[13,14], we study the degradation of the copolymer C under different conditions: in the absence or presence of oxygen and oxido-reductive ions. We observe polymer degradation in solution at 80°C when oxygen is present in

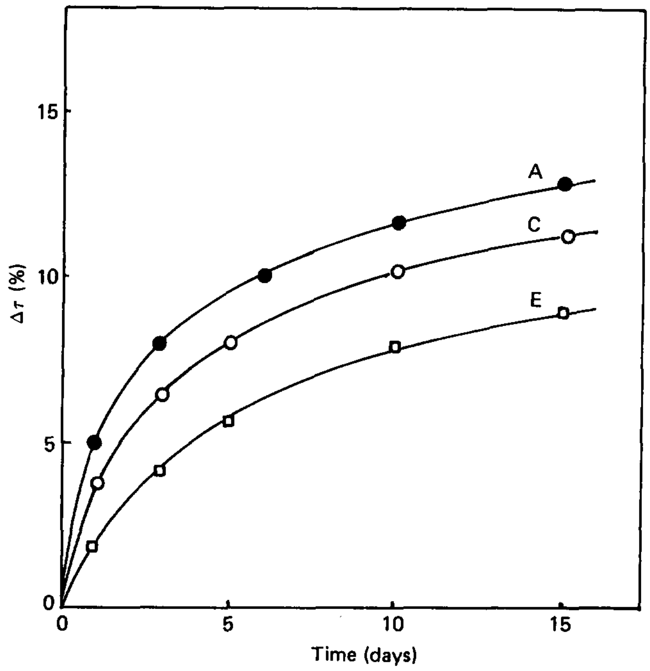

Figure 4 Hydrolysis kinetics of copolymers A, C and E at the same molar concentration of amide groups (1.14×10^{-2} mol l^{-1}), initial pH (7.55) and temperature (80°C)

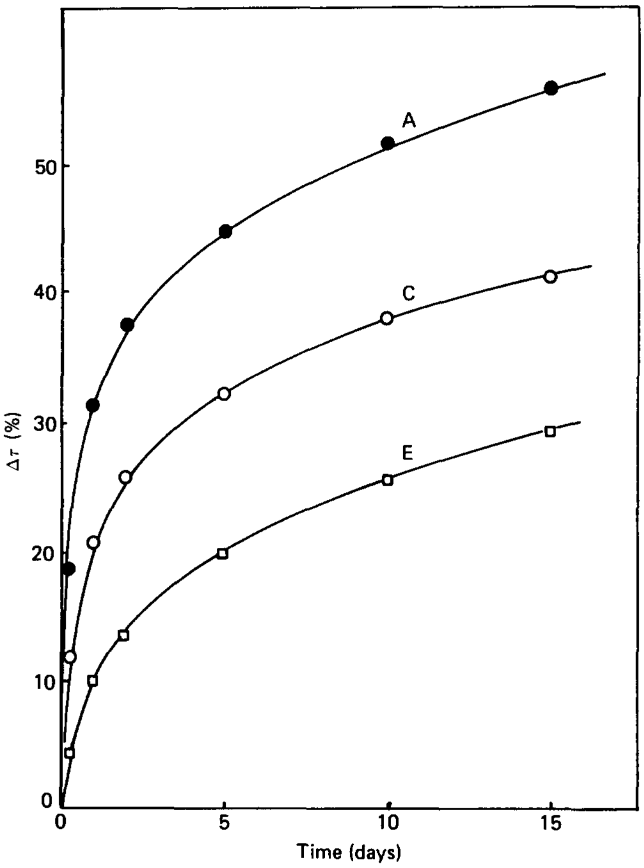

Figure 5 Hydrolysis kinetics of copolymers A, C and E at the same molar concentration of amide groups (1.14×10^{-2} mol l^{-1}), initial pH (11.85) and temperature (80°C)

solution, while the molecular weight of the polymer remains constant for a long time (several months) when the solutions are perfectly deaerated. Moreover, this degradation phenomenon can be avoided by a careful purification of the sample. Most of our hydrolysis studies have been carried out under conditions where degradation occurs simultaneously. But in *Figure 6* we compare the hydrolysis kinetics of copolymer C when degradation does not occur. It appears that the loss of viscosity arising from degradation has a slight increasing effect on the hydrolysis rate. We have also observed an influence of isobutanol, which can be added as a stabilizing agent. It should be useful to verify if the hydrolysis rate is really dependent on molecular weight for a given polymer concentration.

pH effect. We have reported in *Figure 7* the variation of the initial reaction rate k_0 as a function of pH_i. A minimum is observed for $pH_i = 7$. Let us recall that k_0 is a decreasing function of pH_i for polyacrylamide. The minimum is then expected to appear only above a given initial carboxylate content τ_i, and to be shifted towards high pH values when τ_i increases.

Temperature effect. Different results dealing with the variation of k_0 with temperature are gathered in *Figure 8*. Two comments can be made:

(a) For pH 7, where hydrolysis depends slightly on τ_i, one notes a good agreement between our results and those of Muller[1,2].

(b) In a first approximation, the activation energy does not seem to depend strongly on the pH and consequently on the reaction mechanism.

A more systematic study at different pH values would be necessary; however, we will use a mean value of the activation energy and consider this value as independent of pH, in a first approach.

Effect of the distribution of monomers on the chain

In recent work[5,8], we have compared by ^{13}C n.m.r. the distribution of the monomer units of acrylic acid–acrylamide copolymers prepared by copolymeriza-

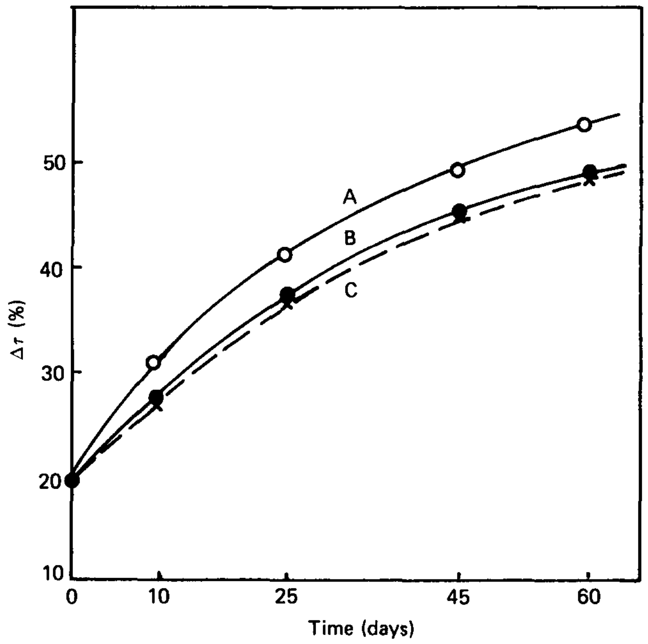

Figure 6 Hydrolysis kinetics of copolymer C ($pH_i = 6.5$, $T = 80°C$, $c = 10^{-3}$ g cm^{-3}) in the presence of oxygen (curve A), in the absence of oxygen (curve B) and after polymer purification with oxygen (curve C)

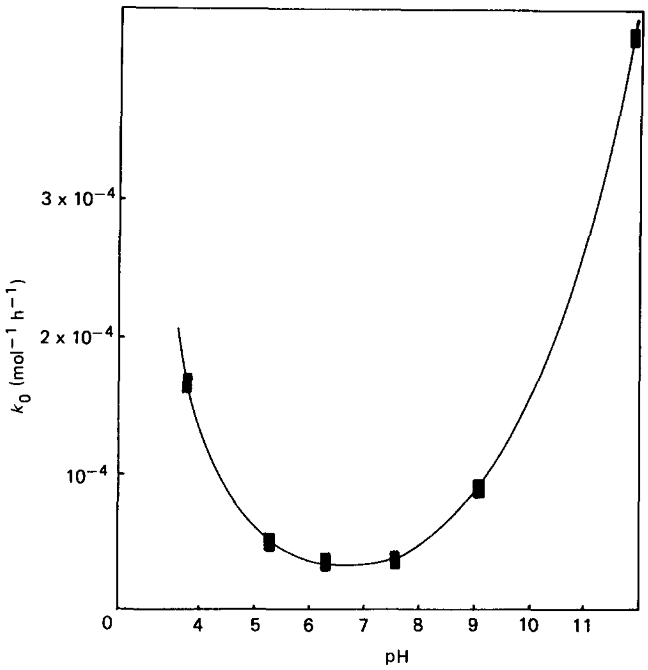

Figure 7 Variation of the initial rate constant k_0 of the hydrolysis of copolymer C as a function of pH ($c = 10^{-3}$ g cm^{-3}, $T = 80°C$)

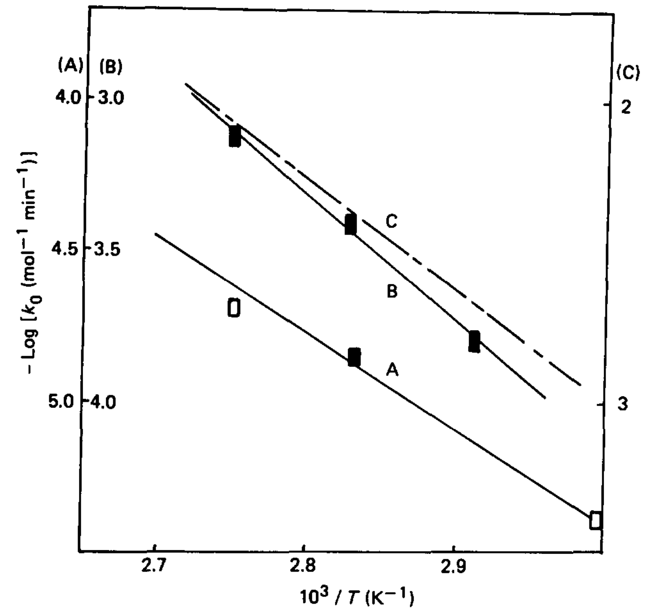

Figure 8 Dependences of the initial rate constant with temperature for different pH values: curve A, pH = 7, initial degree of hydrolysis 35%, (□) results of ref. 2, (■) our results for copolymer E; curve B, pH = 11.85, our results for copolymer C; curve C, pH = 13.4, curve obtained from refs. 3 and 5

tion or by hydrolysis of the parent polyacrylamide. We showed that the mean length of acrylamide and acrylate sequences is always higher in true copolymers (whatever the pH of the polymerization) than that obtained by alkaline hydrolysis. In this type of reaction, where the nature of neighbouring groups plays an important role, the distribution of monomer units is expected to be a driving factor.

In the range of low pH, intramolecular catalysis requires that the catalytic COOH group is the nearest neighbour of the reacting amide function[15]. As shown later, it is easy to construct a model taking into account the monomer unit distribution.

In the range of very high pH ($\mathrm{pH} > 13$), the catalyst is not the neighbouring group but the OH^- ions, and the hydrolysis process is generally characterized by three decreasing rate constants for reacting groups that have zero, one or two already-modified neighbours respectively[16-20]. Sawant and Morawetz[4] have found a mean reaction rate lower for the polymer obtained by hydrolysis than for copolymers, and explained this result by the higher percentage of acrylamide-centred triads (BAB) of poor reactivity in products of alkaline hydrolysis, as later confirmed by Truong *et al.*[5,8]. Sawant and Morawetz, however, suggest that this model of three constants could be replaced by an analysis analogous to that generally adopted for the interpretation of potentiometric titration of polyelectrolytes, by taking into account the mean charge of the polyion. Such a treatment of the kinetics of the polymer chemical modification had already been proposed by Katchalsky *et al.*[21] in order to explain the alkaline hydrolysis of the pectin[22].

Since our results show that OH^- ions do not directly catalyse the reaction (at least in a first-order reaction) for $\mathrm{pH} < 13$, we could expect a lower influence of the monomer distribution. *Figure 9* shows that the copolymer E has a higher hydrolysis rate for $\mathrm{pH_i} = 11.85$ than P700, whose degree of hydrolysis is lower, a result in agreement with the observations of Sawant and Morawetz. But for a lower $\mathrm{pH_i}$ (7.55), the difference was not detectable. This justifies for the range $\mathrm{pH} < 9$, where we will limit our calculations, a model derived from the assumptions of Katchalsky *et al.*[21].

INTERPRETATION AND DISCUSSION

Preliminary remarks and model

Our experimental results are consistent with the mechanisms already proposed: intramolecular catalysis by undissociated COOH groups, for low pH, and kinetics retarded by the presence of charged functions along the chain for higher pH. Nevertheless, for $7 < \mathrm{pH} < 11$, one cannot interpret the results in terms of a first-order catalysis by OH^- ions. However, it is clear that pH plays a role but we are not able to specify the mechanism.

In the case of low-molecular-weight compounds, this type of behaviour is explained by the formation of an intermediate species and a kinetic expression is proposed[11]:

$$k_a[\mathrm{A}] = k_{\mathrm{OH}}[\mathrm{OH}^-][\mathrm{A}] + k_{\mathrm{A}}[\mathrm{A}] \qquad (3)$$

where k_a is the apparent hydrolysis constant and k_{A} is the rate constant for the formation of the intermediate species. In *Figure 10* we have plotted $\log k_0$ as a function of $\mathrm{pH_i}$, by considering the cases where the catalysis by COOH cannot occur (initial step of unhydrolysed polymer and $\mathrm{pH_i} > 7$ for copolymers). The linear variation observed for each polymer is not consistent with relation (3) since $\log k_a$ is expected to reach a plateau ($\log k_{\mathrm{A}}$) when pH decreases. The possible formation of

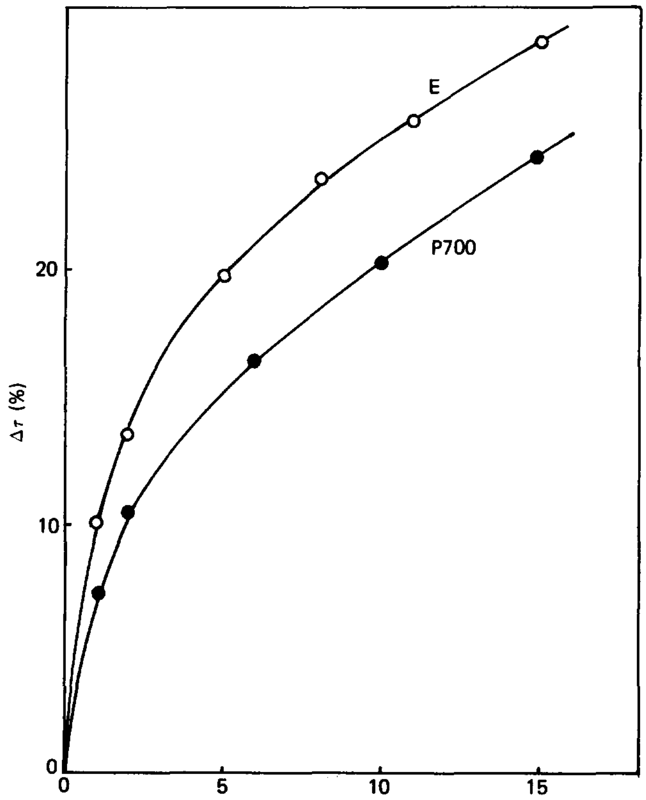

Figure 9 Comparison between hydrolysis kinetics of copolymer E and P700 at the same pH (11.85), molar concentration of amide functions (1.14×10^{-2} mol l^{-1}) and temperature (80°C)

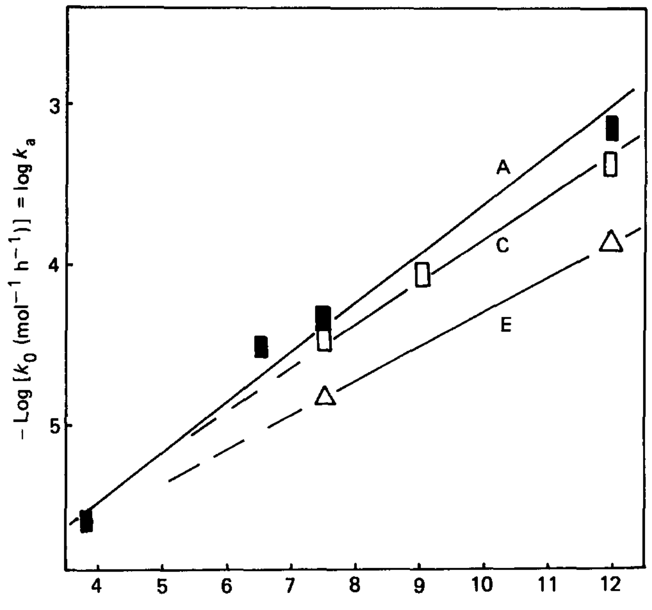

Figure 10 Logarithmic variation of the initial rate constant for copolymers A, C and E as a function of initial pH

imides has also been proposed for polyacrylamide[6]. However, by using the same experimental techniques as Sawant and Morawetz[4], we have not identified imide functions, at least for copolymers. In fact, these authors show that only two neighbouring head-to-head monomers can form imides (4% at maximum). Although the detailed mechanisms have not been elucidated, the main purpose of our work is to obtain semiempirical laws able to predict the hydrolysis kinetics. Then, we will propose the following simple model, for $3<\mathrm{pH}<9$. We will consider two types of reacting monomer units:

(a) units that have an undissociated neighbouring group that catalyses the reaction with a rate constant k_H independent of pH (X units); and

(b) other units (Y units) whose hydrolysis rate depends on pH according to the semiempirical law obtained from the results of *Figure 10* and by using the analogy made by Katchalsky *et al.*[21] between hydrolysis and neutralization of polyelectrolytes:

$$\log k_a = \log k_{a0} + \mathrm{pH}[C_A - C_B\alpha\tau - C_C(\alpha\tau)^2] \qquad (4)$$

In this expression, $\log k_{a0} + \mathrm{pH}\, C_A$ represents the variation of the rate constant with pH for the initial step of hydrolysis of polyacrylamide. The terms $C_B\alpha\tau$ and $C_C(\alpha\tau)^2$ correspond to the retarding effect when the charge ($\alpha\tau$) increases, α being the degree of dissociation of the carboxylate groups.

Then, for a degree of polymerization N, at time t, the number N_X of X units is:

$$N_X = N_{AB}(1-\alpha) \qquad (5)$$

where N_{AB} is the number of AB diads. The probability of finding such a diad at $t=0$ is determined by the method of preparation of the polymer and varies during reaction according to the preponderant mechanism. The number of Y units is simply $N_Y = (N - N_X)$ and all these units will be assumed to have the same probability of reacting, with a rate constant which depends on the pH.

The modelling of the hydrolysis kinetics requires, at each time, knowledge of the value of α and the distribution of the monomer units.

Variations of degree of dissociation α and pH during reaction

The pH of the reacting medium is determined by the three dissociation equilibria of water, polyacid and NH_3 formed during reaction, with respective constants K_e, K_a and K_b. It is well known that for a polyacid K_a decreases on increasing α. The expression for pK_a contains a term for the electrostatic free energy[23]:

$$pK_a = pK_0 + 0.434\Delta G_{elec}/kT \qquad (6)$$

The prediction of the variation of ΔG_{elec} as a function of α has been the object of many theoretical works based on models of either uniform spherical distribution of the charges[23,24], or Gaussian coil[25,26] or rigid rod[27-29]. In fact, the bad agreement with the experimental results has led to the introduction of neighbouring-group effects, as in the hydrolysis reaction[30]. More empirically, Mandel[31] has proposed representing the pK_a variations by simple polynomials:

$$pK_a = pK_0 + \Phi_1\alpha + \Phi_2\alpha^2 \qquad (7)$$

Truong[8] has recently carried out a systematic study of the potentiometric titration of acrylic acid–acrylamide copolymers. He obtained the following expressions, where pK_0 and Φ_1 depend on polymer composition:

$$pK_0 = 4.5 + 2.1\tau \qquad \Phi_1 = 2.2\tau \qquad \Phi_2 = 0.45 \qquad (8)$$

At time zero of the hydrolysis reaction, the concentration of carboxylate groups is:

$$c_0 = c\tau_0 \qquad (9)$$

if c is the molar concentration of polymer and τ_0 the initial carboxylate content; there is no NH_3 in solution but to reach the desired $\mathrm{pH_i}$, HCl or NaOH must be added to the solution. Their amounts are determined from the relation of dissociation equilibrium of the polyacid by using expressions (7), (8) and (9). The dissociation state of the polymer and the concentration of ions in solution are well known at time zero.

At time t of the reaction, the concentration of carboxylate groups becomes:

$$c_t = c\tau_t \qquad (10)$$

where τ_t is the new carboxylate group content and the NH_3 concentration is:

$$c_N = c(\tau_t - \tau_0) \qquad (11)$$

By taking into account the different equilibria and writing the electro-neutrality relation, it is then easy to calculate the variations of pH and concentrations of each ionic species as a function of t or τ_t.

In *Figure 11*, we show the good agreement between the experimental and calculated variations of $\mathrm{pH} = f(\tau_t)$ for the hydrolysis of copolymer C. The formation of NH_3 in solution explains well the increase of pH for low $\mathrm{pH_i}$ and its decrease for high $\mathrm{pH_i}$. For $\mathrm{pH_i} = 9$, the pH is expected to change with a minimum in the variation curve, as observed. On the other hand, this agreement justifies using the pK_0, Φ_1 and Φ_2 values in the next calculation of the hydrolysis kinetics.

Hydrolysis kinetics

The problem is to determine at each time t the concentrations of X and Y units which depend on τ, α and on the chain statistics. We will first consider the case of

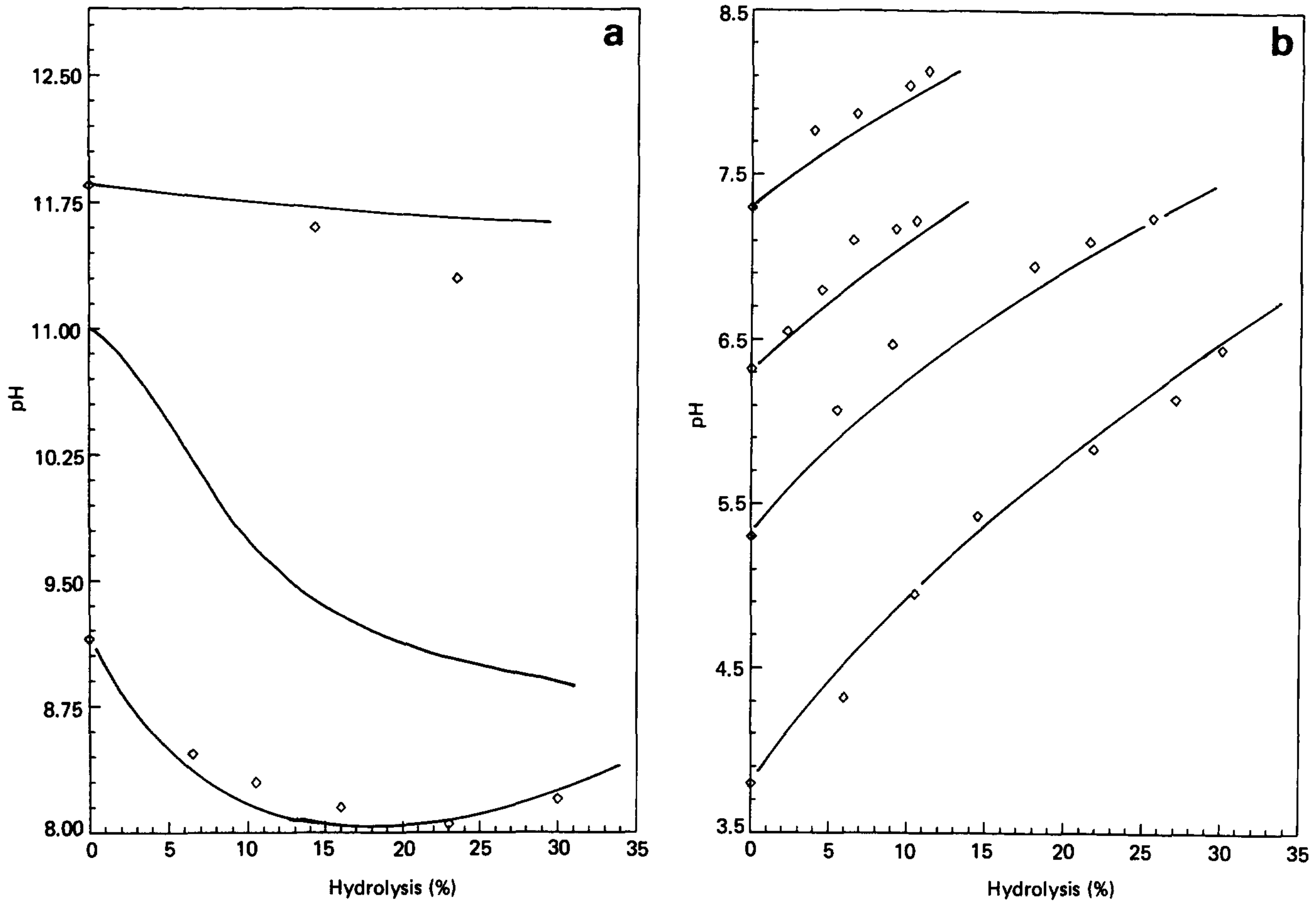

Figure 11 Comparison between the experimental and calculated variations of pH as a function of degree of hydrolysis during hydrolysis of copolymer C ($T = 80°C$; molar concentration of amide groups $= 1.14 \times 10^{-2} \mathrm{mol\,l^{-1}}$), for different values of initial pH

polyacrylamide, for which the chain statistics have no influence on the initial reaction step.

Unhydrolysed polyacrylamide. The program we have developed can be described as follows. Let us consider a polymer chain with degree of polymerization N. At time $t = 0$, only Y units are present on the chain and their rate constant $k_{a(t=0)}$ is defined by relation (4) with $\tau = 0$.

At time $t = \Delta t_1$, Δt_1 being the time necessary to transform one unit whose position is determined by the random function of the computer. $(1 - \alpha)$ functions of type X are created. Then α and pH are calculated as explained above and a new value of k_a is determined.

At time $t = \Delta t_1 + \Delta t_2$, with $\Delta t_2 = \beta \Delta t_1 N/(N - 1)$, a new Y unit randomly chosen is transformed and $Z'(1 - \alpha)/(N - 1)$ units X are transformed. Here β is introduced to take into account the variation of k_a and Z' is the ratio $k_h/k_{a(t=0)}$; α, τ, pH and k_a are calculated.

At all other times corresponding to the transformation of one Y unit new values of α, pH and k_a are calculated, the number of X units that must be transformed in the next step is deduced and their position is randomly determined as well as that of unit Y. It is also easy to determine the chain statistics by calculating the number of acrylamide and acrylic acid monomers in sequences of length n.

From the straight lines of *Figure 10*, one can calculate the empirical values of the constants in relation (4):

$$\log k_{a0} = -6.5 \qquad C_A = 0.3$$

$$C_B = 0.105 \qquad C_C = 0.15$$

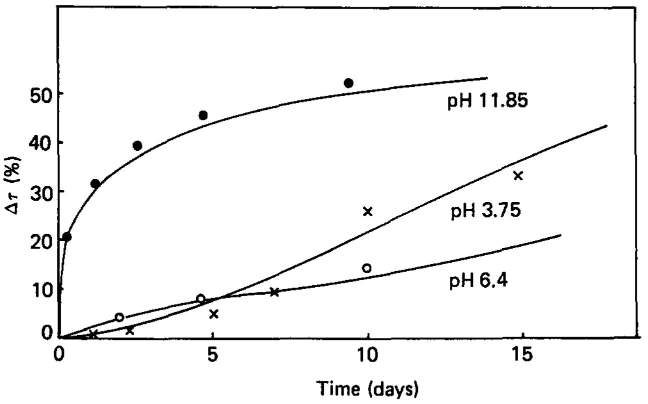

Figure 12 Comparison between experimental and calculated ($Z = 150$) hydrolysis kinetics of polyacrylamide A for different initial pH ($T = 80°C$; $c = 10^{-3}\,\mathrm{g\,cm^{-3}}$)

Figure 2 gives the order of magnitude of Z, the value of the ratio Z' for pH $= 3.75$; we will consider values of Z between 50 and 150.

The results of 100 experiments are averaged.

Two types of calculations were performed: at variable pH in order to compare calculated predictions and experiments, and at constant pH to establish more general predictions.

(i) *Variable pH.* In *Figure 12*, one can see that this model gives a rather good account of the experimental results when the value of Z is 150. For $\mathrm{pH_i} = 3.75$, we have compared the calculated kinetics obtained by neglecting either acceleration effect ($Z = 1$) or pH variation (see *Figure 13*). It is then clear that the agreement with experimental results can only be obtained by taking into account both effects. The pH increase leads to the dissociation of the carboxylate groups and to a decrease of N_X. In their study of hydrolysis of copolymers in the same range of pH, Smets *et al.*[6] have observed a conversion limit, interpreted as an effect of stereoregularity of the chain on the intramolecular catalysis, which could require a particular conformation of the monomers bearing the catalytic and reacting functions. In their experiments, buffers were not used and variation of pH necessarily occurred, explaining at least partially the conversion limit. We have not taken into account this stereoregularity effect and more systematic studies should be performed, particularly dealing with the sequentiality of the transformed units. In our model, as seen later, the polymer hydrolysed at low pH by intramolecular catalysis could have long sequences of transformed units since only direct neighbouring is considered; if particular tacticity is also required, the sequences will be interrupted and the acceleration effect will become less important.

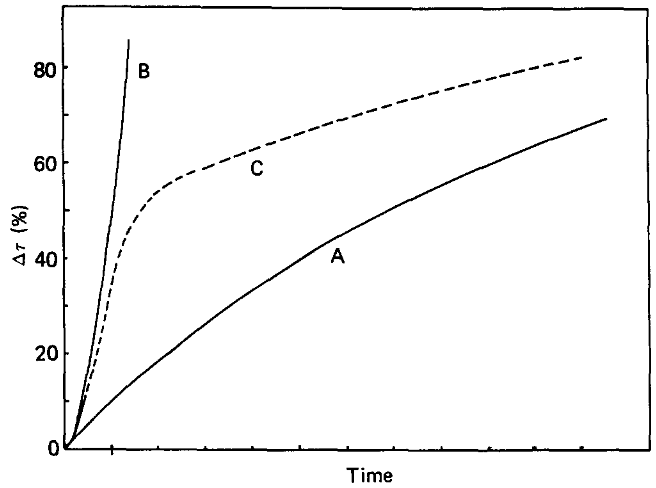

Figure 13 Hydrolysis kinetics of polyacrylamide A calculated for initial pH = 3.75 with different hypotheses: curve A, without acceleration; curve B, with acceleration but without pH variation; curve C, with acceleration and pH variation

(ii) *Constant pH*. In *Figure 14* some predictions of hydrolysis kinetics of polyacrylamide are given for different constant pH and three values of Z. These simulations correspond to a polymer concentration of $8 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$ and $T = 80°\mathrm{C}$.

The acceleration effect is significant for pH up to 7 and becomes negligible for higher pH. The variations of $(1-\alpha)$ and k_a reported in *Figure 15* allow us to understand the evolution of these kinetic curves.

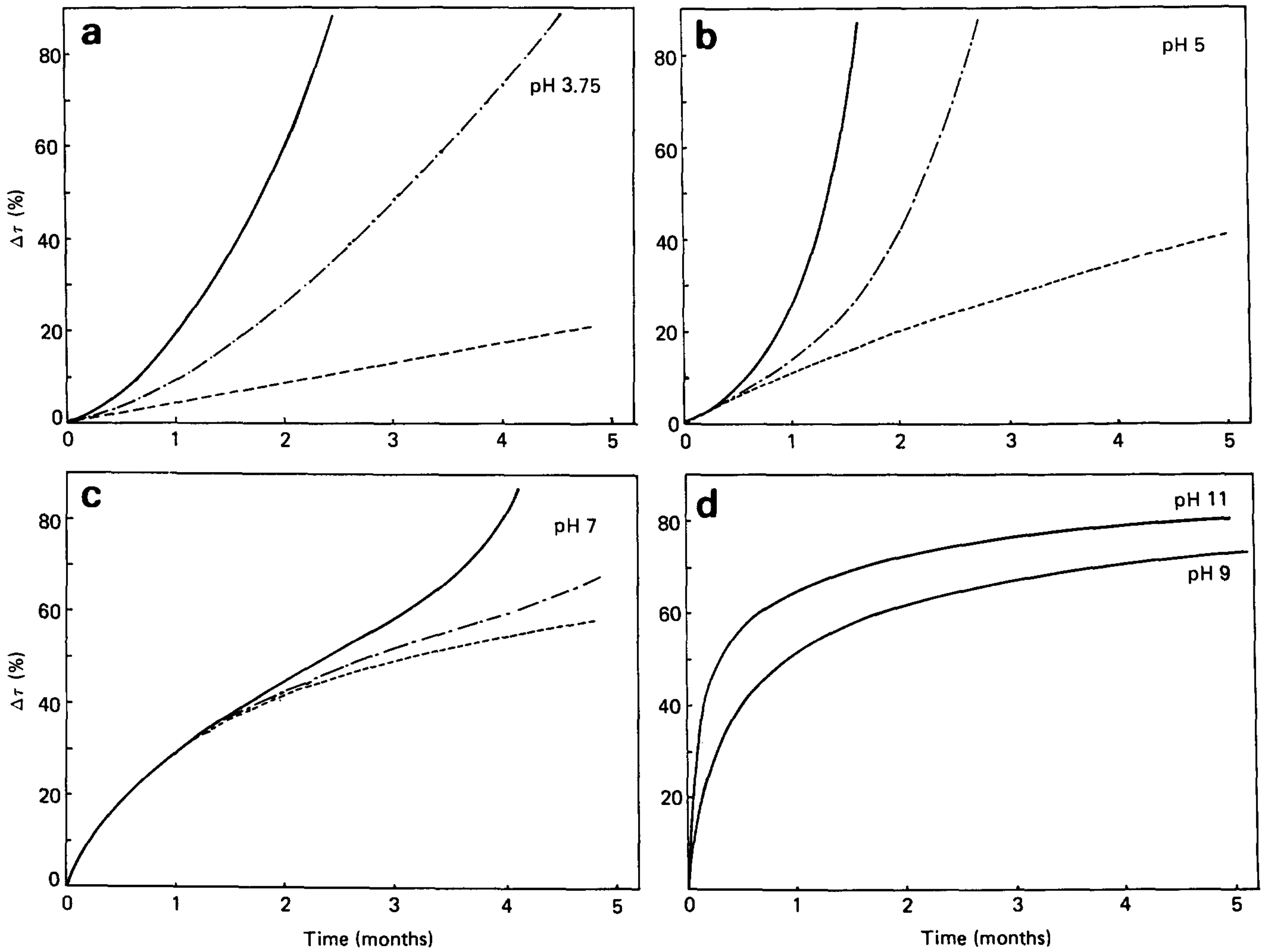

Figure 14 Predictions for hydrolysis kinetics of polyacrylamide at different constant pH ($T = 80°\mathrm{C}$; $c = 8 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$): (- - -) $Z = 1$, (-·-·-) $Z = 50$, (———) $Z = 150$

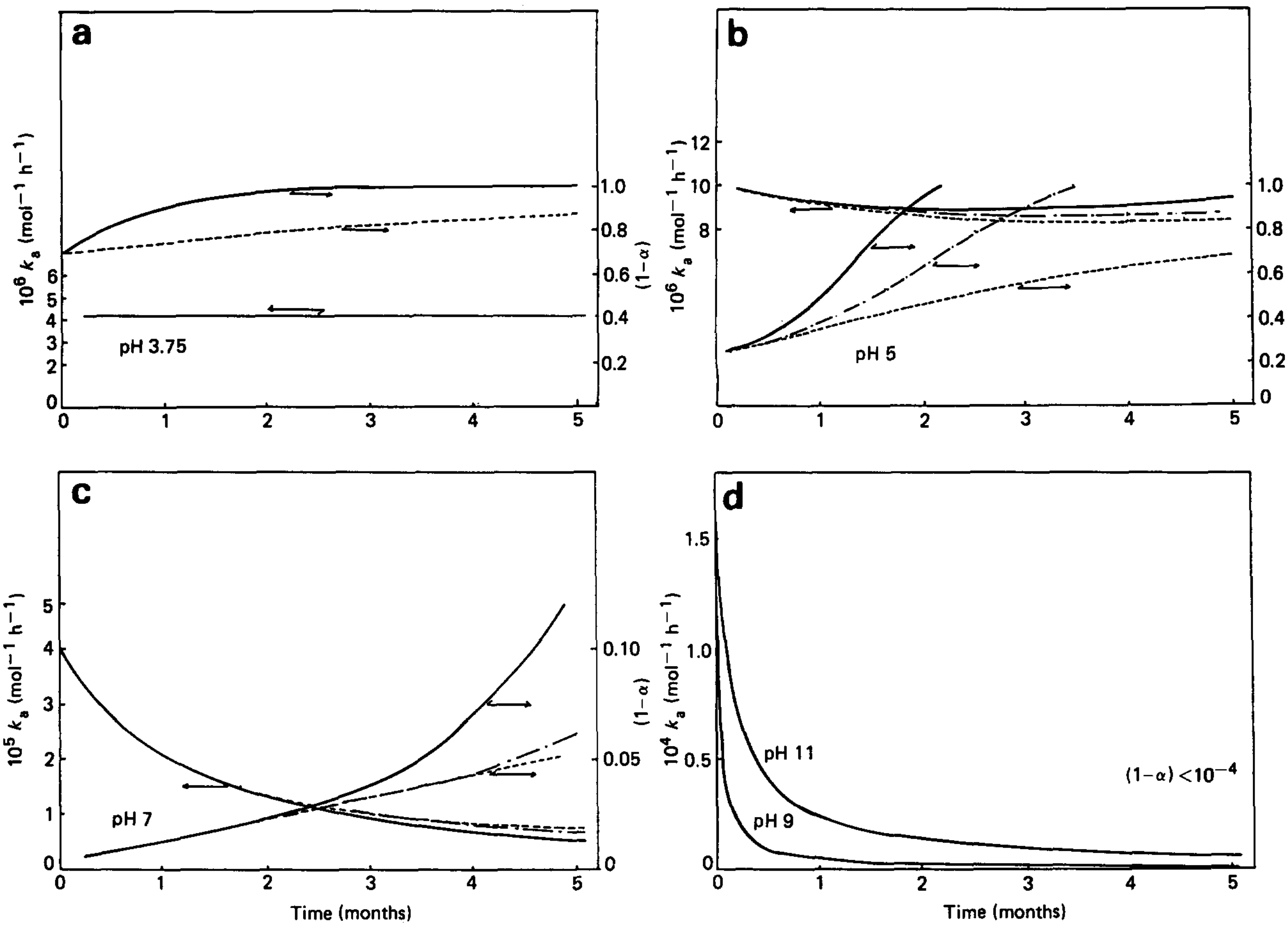

Figure 15 Calculated variations of k_a and $(1-\alpha)$ during hydrolysis of polyacrylamide (same conditions and symbols as in *Figure 14*)

At pH = 3.75, $(1-\alpha)$ remains near to 1, the carboxylate groups are undissociated and intramolecular catalysis is the main process since k_a has a low value. The complete transformation will be reached after 2.5 months with $Z = 150$.

At pH = 5, the value of k_a is higher and $(1-\alpha)$ increases from 0.2 to 1, at the end of reaction. Then the kinetics resulting from both mechanisms (X and Y) are faster than for lower pH. Only 1.5 months of reaction are required to reach complete transformation.

At pH = 7, the initial rate is higher due to the increase of k_a and the effect of acceleration only appears at the end of reaction when $(1-\alpha)$ exceeds 0.04.

For pH > 7, the main process is hydrolysis retarded by the presence of charges along the chain, the value of $(1-\alpha)$ being zero and the value of k_a decreasing.

In *Figure 16* we give two examples of statistics of the distribution of monomer units as calculated from our model. We have plotted the fractions of acrylamide or acrylic acid contained in sequences of length *n* in the case where the reaction is not affected by the neighbouring effect (pH 7) and in the case where the reaction is essentially autoaccelerated (pH = 3.75). It is obvious that intramolecular catalysis favours the creation of long sequences of the two monomers. At high pH (> 13), it has already been shown that alkaline hydrolysis tends to isolate acrylic units[3,5]. Our hypothesis, according to which the hydrolysis of units of type Y depends only on the mean polymer charge and not on the nature of the neighbouring groups, leads for pH > 7 to Bernoullian statistics. The ability in our simulation method to

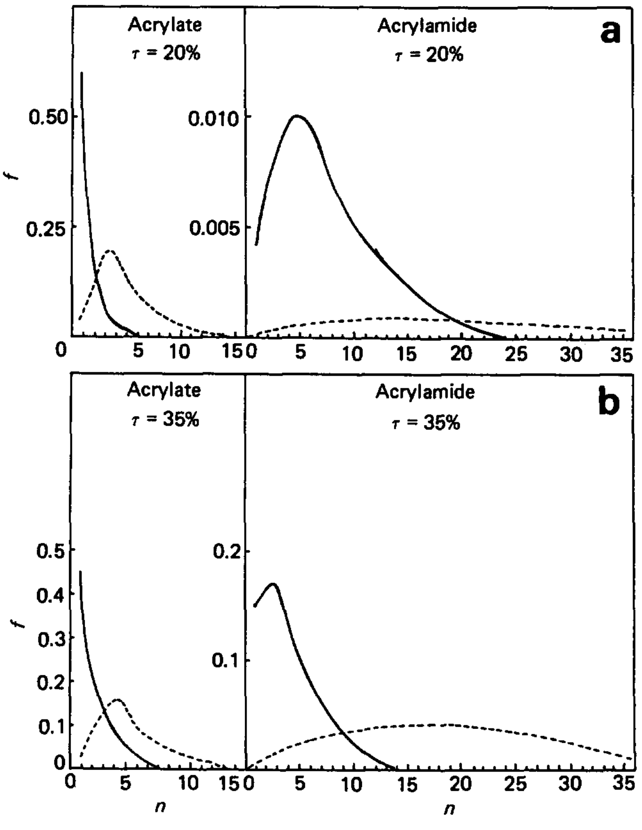

Figure 16 Statistics of monomer distribution after hydrolysis of polyacrylamide for two different values of τ: calculated without a neighbouring effect (Bernoullian statistics) (——) or by considering intramolecular catalysis (– – –)

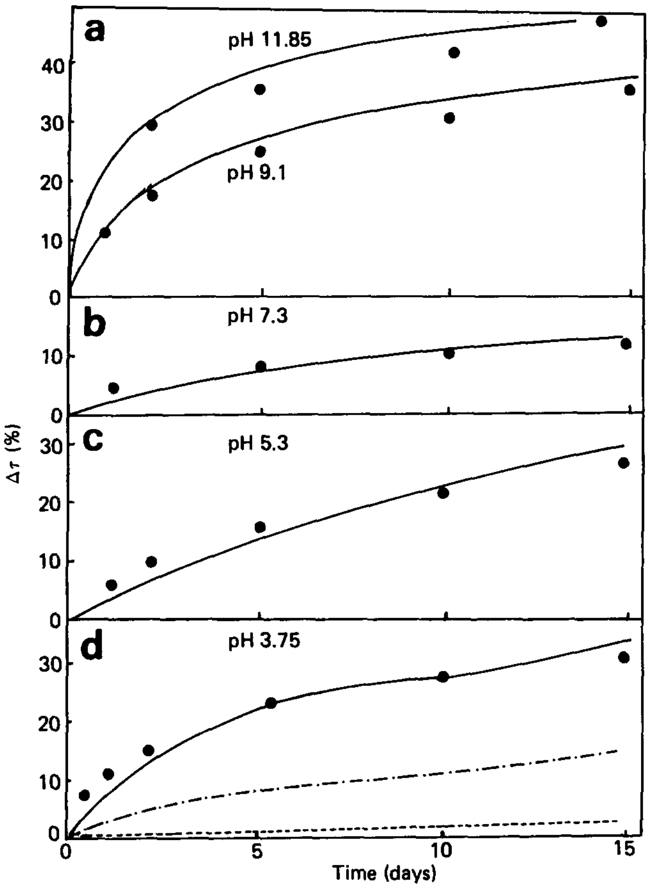

Figure 17 Hydrolysis kinetics of copolymer C ($T = 80°C$, $c = 10^{-3}$ g cm^{-3}) at different initial pH; comparison between experiments and predictions with $Z = 150$ (——), $Z = 50$ (-·-·-) and $Z = 1$ (---)

determine the distribution of the monomers according to the hydrolysis conditions is rather important since the sequentiality has been found to play an important role in the stability of these copolymers in aqueous solution in the presence of divalent cations[32,33]. The polymers hydrolysed at low pH are expected to be less stable than those prepared by alkaline hydrolysis.

Copolymers. The program described for polyacrylamide can be used but a preliminary step must be developed in order to take into account the initial monomer distribution. The probabilities of finding diads AA or BA in a copolymer are:

$$P_{AA} = \frac{r_A f_A / f_B}{1 + r_A f_A / f_B}$$

$$P_{BA} = \frac{1}{1 + r_A f_A / f_B}$$

where f_A and f_B are the molar fractions of acrylamide and acrylic acid and r_A is the copolymerization parameter of acrylamide. Then the first step of the calculation consists of generating a copolymer chain corresponding to these probabilities, obtained from different copolymerization studies[34–36]. In the case of copolymers of AD series, which have been prepared in alkaline medium, the value of r_A is 0.95[35].

(i) *Variable pH.* As shown in *Figure 17* our model also gives a rather good account of the experimental results for copolymer C at different pH$_i$, with the same value $Z = 150$ as for polyacrylamide. For pH$_i$ = 3.75 and 5, we have represented the kinetics calculated for $Z = 1$ (no acceleration) and $Z = 50$. The high discrepancies between the corresponding curves and the experimental points, particularly at pH$_i$ = 3.75, confirm the preponderance of intramolecular catalysis at low pH. The same agreement was found for the other investigated copolymers.

(ii) *Constant pH.* The predictions made from our model in the case where pH remains constant during the hydrolysis reaction of C ($c = 10^{-3}$ g cm^{-3}) at 80°C are represented in *Figure 18*. A faster reaction must be obtained at low pH since there is no slow initial step as for polyacrylamide, the acceleration effect occurring at $t = 0$. The total conversion will be obtained after 25 days and 1.2 months at pH = 3.75 and 5, respectively, while 2.5 and 1.5 months are required under the same conditions if the starting polymer is unhydrolysed. Inversely for high pH (> 7) the total reaction time is longer for copolymers than for polyacrylamide.

CONCLUSIONS

We have carried out some experimental investigations of hydrolysis of polyacrylamide and acrylamide–acrylic acid copolymers over a range of pH where the mechanism has not already been elucidated. Our results confirm the existence of intramolecular catalysis by undissociated neighbouring carboxylate groups at low pH. A second mechanism preponderant for $7 < \text{pH} < 13$ and leading to autoretarded kinetics resembles that already described for alkaline hydrolysis. Nevertheless, if the rate constant of this second mechanism increases with increasing concentration of OH$^-$, the observed variation is very different from that expected in first-order kinetics.

From these observations, we propose a model for the mechanism and a simulation method by computer which allow us to predict the hydrolysis kinetics for different experimental conditions and the statistics of the distribution of the monomer units.

Some points could be underlined: particularly, the influence of tacticity on intramolecular catalysis, the activation energy of the two types of reaction, and the range of validity of the treatment of autoretarded kinetics by using a constant rate depending on the mean charge density of the polyion in place of three constants according to the neighbours of the reacting group.

ACKNOWLEDGEMENTS

The authors are indebted to Dr J. C. Galin for fruitful discussions. This work has benefited from grants from Compagnie Française des Pétroles.

REFERENCES

1 Muller, G., Fenyo, J. C. and Selegny, E. J. *J. Appl. Sci.* 1980, **25**, 627
2 Muller, G. *Polym. Bull.* 1981, **5**, 31
3 Higuchi, M. and Senju, R. *Polymer* 1972, **3**, 370
4 Sawant, S. and Morawetz, H. *Macromolecules* 1984, **17**, 2427
5 Truong, N. D., Galin, J. C., François, J. and Pham, Q. T. *Polymer* 1986, **27**, 459
6 Smets, G. and Hesbain, A. M. *J. Polym. Sci.* 1959, **23**, 217
7 Boutin, J. and Contat, S. French Patent 249 217 issued to Rhône-Poulenc Ind., 1980
8 Truong, N. D., Galin, J. C., François, J. and Pham, Q. T. *Polymer* 1986, **27**, 467

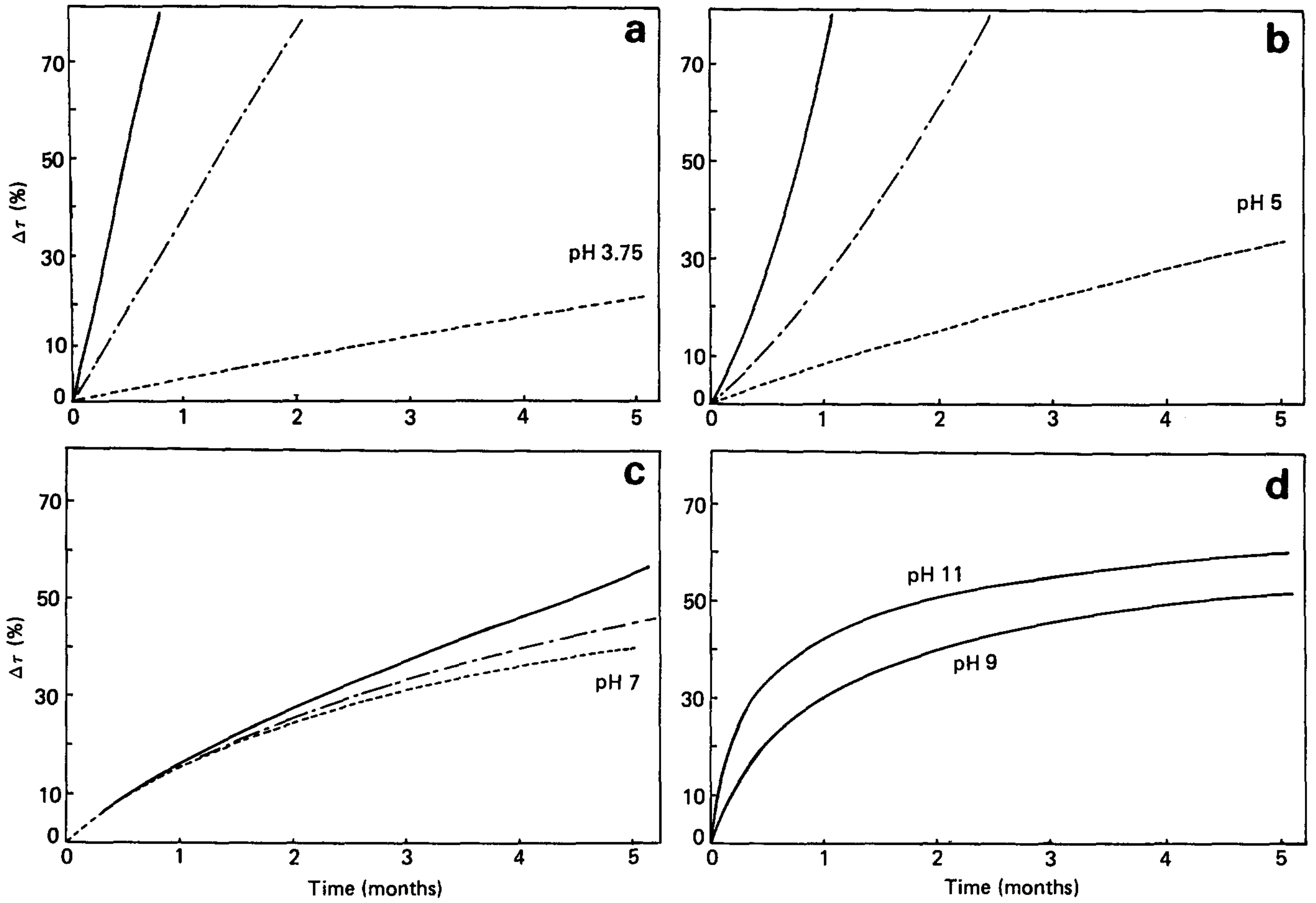

Figure 18 Predictions of hydrolysis kinetics of copolymer C at different constant pH ($T=80°\mathrm{C}$, $c=8\times10^{-4}\,\mathrm{g\,cm^{-3}}$) with $Z=1$ (– – –), $Z=50$ (–·–·–) and $Z=150$ (———)

9 Truong, N. D., Thesis, Strasbourg, 1984
10 Wolf, S. *J. Anal. Chem.* 1970, **13**, 250
11 Bruice, T. C. and Marquardt, F. H. *Org. Biol. Chem.* 1962, **5**, 365
12 Westhead, E. W. and Morawetz, H. *J. Chem. Phys.* 1958, **5**, 237
13 Kheradmand, H., François, J. and Plazanet, V. *J. Appl. Polym. Sci.* in press
14 François, J., Kheradmand, H., Plazanet, V., Murray, M. and Conrard, P. Proceedings of the National ACS Meeting, Anaheim, Sept. 1986
15 Bender, M. L., Chow, Y. L. and Chloupek, F. *J. Am. Chem. Soc.* 1958, **80**, 5380 and 5388
16 Fuoss, R. M., Watanabe, M. and Coleman, B. D. *J. Polym. Sci.* 1960, **5**, 48
17 Keller, J. B. *J. Chem. Phys.* 1962, **37**, 2584
18 Plate, N. A. and Noah, O. V. *Adv. Polym. Sci.* 1978, **31**, 133
19 Boucher, E. A. *Prog. Polym. Sci.* 1978, **6**, 63
20 Moens, J. and Smets, G. *J. Polym. Sci.* 1957, **13**, 931
21 Katchalsky, A. and Feitelson, J. *J. Polym. Sci.* 1954, **13**, 385
22 Deuel, H., Hutschnecker, P. and Solms, J. P. *Elektrochem.* 1953, **57**, 172
23 Overbeck, J. Th. *Bull. Soc. Chim. Belge* 1948, **57**, 154
24 Hermans, J. J. and Overbeck, J. Th. *Bull. Soc. Chim. Belge* 1948, **57**, 151
25 Harris, F. E. and Rice, S. A. *J. Polym. Sci.* (*B*) 1954, **15**, 151
26 Katchalsky, A. and Lifson, S. *J. Polym. Sci.* 1951, **11**, 151
27 Katchalsky, A., Shavit, N. and Eisenberg, H. *J. Polym. Sci.* 1954, **13**, 69
28 Lifson, S. and Katchalsky, A. *J. Polym. Sci.* 1954, **13**, 873
29 Kotin, L. and Nagasawa, M. *J. Chem. Phys.* 1962, **84**, 725
30 Sasaki, S. and Minakata, A. *Biophys. Chem.* 1980, **11**(2), 199
31 Mandel, M. *Eur. Polym. J.* 1970, **6**, 807
32 Truong, N. D., Galin, J. C., François, J. and Pham, Q. T. *Polym. Commun.* 1984, **25**, 208
33 Truong, N. D. and François, J. *Collect. Colloq. Semin.* 1984, **42**, 251
34 Cabaness, W. R., Yen-Chin-Lin, T. and Parkanyl, C. *J. Polym. Sci.* (*A1*) 1971, **9**, 251
35 Pontratnam, S. and Kapur, S. L. *Makromol. Chem.* 1977, **178**, 1029
36 Bourdais, J. *Bull. Soc. Chim. Fr.* 1955, 485