Hydrolysis of sodium-2-acrylamido-2-methylpropanesulfonate copolymers at elevated temperature in aqueous solution via ^{13}C n.m.r. spectroscopy

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The stability of sodium-2-acrylamido-2-methylpropanesulfonate (P), copolymerized with acrylamide (M) or acrylic acid (A), towards amide hydrolysis at >100°C is examined. Two copolymers, with average structural sequences of MMMP (polymer I) and APAP (polymer II), were aged at high temperature in 0.1 N NaCl and the hydrolysis monitored by integration of carbonyl resonances. M hydrolysis in polymer I at pH 8 (energy of activation = 85.9 kJ mol^{-1}) is 10 times greater at 150°C than at 120°C and is unaffected by the presence of P. P hydrolysis occurs in two steps for both polymers at 150°C. The initial hydrolysis rate increases dramatically after half of the P units are hydrolysed. Intramolecular P hydrolysis catalysed by an adjacent dissociated carboxylate in A is proposed to explain the rapid hydrolysis. Nearby Ps prohibit this hydrolysis. The initial P hydrolysis rate in polymer II is enhanced five times on decreasing the pH from 8 to 6 due to decreased Coulombic repulsion between hydroxide and the polymer. At pH 8 and 150°C, P in polymer II is two times more stable than in polymer I lasting 9 days before complete hydrolysis occurs.

(Keywords: hydrolysis; kinetics; copolymers)

INTRODUCTION

Acrylamide-based polymers and copolymers are commonly used by oil industries for enhanced oil recovery (EOR) technologies[1]. At elevated temperatures in hard brine, these polymers are unstable due to hydrolysis of the amide group to carboxylate. The formation of carboxylate complexes with magnesium and calcium ions can lead to polymer precipitation reducing its useful lifetime[2,3].

Polyacrylamide hydrolysis has received much attention[2,4–9]. Initially, the rate is second order depending on the acrylamide (M) and hydroxide concentrations. At low pH (<7) undissociated neighbouring acid groups act as internal catalyst towards M hydrolysis[4]. At pH > 7 there are two opposing effects on the hydrolysis rate as the pH is increased: one tends to increase the rate due to the greater number of hydroxide ions, whilst the other one tends to lower the rate as the net negative charge on the polymer increases (formation of negatively charged carboxylate residues)[5]. There is a limiting degree of M hydrolysis at a given temperature[2]. A 'safe' temperature limit for most saline solutions, to avoid precipitation due to divalent cations, was established at around 82°C[2].

Copolymers of M with other monomers have been synthesized[10–19] in an effort to raise this limit. Doe *et al.*[15] found that copolymers of *N*-vinylpyrrolidone (Vp) and M have improved stability towards precipitation by divalent cations at elevated temperatures with respect to polyacrylamides. Vp protects M toward hydrolysis. The equilibrium concentration of acrylic acid (A) units in Vp–M copolymers after ageing at a fixed temperature was significantly lower than that for polyacrylamide and proportional to the Vp content.

Dexter and Ryles[20] incorporated sodium 2-acrylamido-2-methylpropanesulfonate (P) units into acrylamide polymers and found, up to 120°C, an apparent decrease in the rate of M hydrolysis (at pH 9), which was proportional to the amount of P present. However, Moradi-Araghi *et al.*[21] found that M–P copolymer does not protect M against thermal hydrolysis with consequent precipitation in hard brines. They also hypothesized that P hydrolysis occurs above 120°C.

Many polymers with P residues have been commercialized in recent years for EOR applications. What are their upper temperature limits? Is M hydrolysis affected by P? How easily does P hydrolyse? In an effort to answer these questions, the hydrolysis of two P copolymers above 120°C was investigated by a technique which detects microstructure.

EXPERIMENTAL

Materials

Acrylamide (Aldrich) and 2-acrylamido-2-methylpropanesulfonic acid (Fluka) were purified by recrystallization from methanol, and vacuum dried at room temperature. Acrylic acid (Fluka) was purified by vacuum distillation. Potassium persulfate (Aldrich) was recrystallized twice from distilled water.

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Polymer synthesis

Poly(acrylamide-*co*-sodium-2-acrylamido-2-methylpropanesulfonate) (polymer I) was synthesized following the procedure already reported[11]. Acrylamide (15 g, 0.211 mol), 2-acrylamido-2-methylpropanesulfonic acid (18.6 g, 0.09 mol), NaOH (3.6 g, 0.09 mol) and deionized water (350 ml) were introduced into a 1 litre round bottom flask. The flask was maintained under mechanical stirring at 5°C until dissolution of the reagents. The pH was finally adjusted to 9 by addition of aqueous NaOH. The resulting solution was purged with nitrogen for 20 min and warmed to 30°C with a thermostatically controlled bath. Potassium persulfate (0.081 g in 10 ml water) was then injected into the solution through a rubber septum. After 4 h of stirring, 350 ml of deionized water was introduced into the reaction flask and the resulting solution poured into a large excess of acetone. The polymer was collected by filtration and further purified twice by dissolution (in water) and precipitation (acetone). The purified polymer was dried under vacuum at 50°C (80% yield). Poly(acrylic acid-*co*-sodium-2-acrylamido-2-methylpropanesulfonate) (polymer II) was synthesized as reported previously[22]. Acrylic acid (11 ml, 0.15 mol), 2-acrylamido-2-methylpropanesulfonic acid (37.3 g, 0.18 mol), NaOH (13.2 g, 0.33 mol), potassium persulfate (0.081 g) and 400 ml of deionized water were used.

Sample preparation

Polymeric solutions 2% (w/w) were prepared with 0.1 N NaCl in 25 ml glass tubes and sealed with screw caps. The pH was adjusted to the desired value with aqueous HCl or aqueous NaOH prior to the samples being placed in a convection oven with temperature control (± 3°C).

Polymer characterization

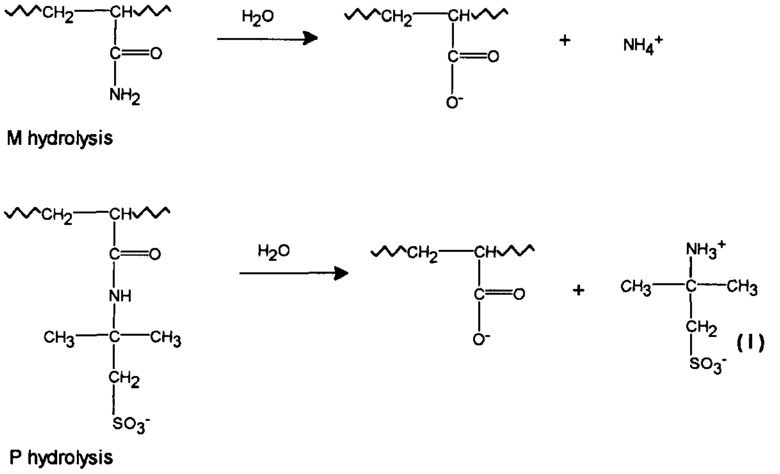
Copolymer compositions were determined from ^{13}C n.m.r. spectra collected at 75.47 MHz on a Bruker CXP-300 spectrometer using 10 mm spinning samples at 28°C. Chemical shifts were referenced externally to dioxane in water set at 67.0 ppm. Deuterium field lock stabilization was not used. Usually 20 000 scans were averaged with 45° radio frequency pulse, 2 s cycle delay, and continuous proton broad band decoupling. The nuclear Overhauser enhancement (NOE) factors for the carbonyl carbons of M, A and P are very similar[9,23]. Longitudinal relaxation ($T_1 < 2.5$ s) is complete for all carbons using the parameters above [9,22]. Thus, although the ^{13}C n.m.r. spectra were collected with NOE, in the interest of time, the relative areas of all the carbonyl resonances used to quantify hydrolysis are quantitative. This was confirmed by comparing spectra collected with and without NOE. N.m.r. integrals are generally accurate to within $\pm 15\%$ if good signal-to-noise ratios and resolution are obtained. This was the maximum error in precision obtained on integrating carbonyl resonances for repeated analysis of several samples.

The weight average molecular weight (M_w) was determined using 0.1 N NaCl solutions (25°C) by light scattering measurements and by measuring the specific refractive index increment (dn/dc). For polymer I dn/dc = 0.192 and $M_w = 2.3 \times 10^6$ g mol^{-1} and for polymer II dn/dc = 0.207 and $M_w = 1.8 \times 10^6$ g mol^{-1}. Light scattering experiments were performed with a DAWN F instrument, from Wyatt Corporation, using a He–Ne (632.8 nm) laser. Scattered light was detected by a set of photodiodes at angles (θ) between 26° and 128°. M_w values were obtained by extrapolating the scattered intensity to $\theta = 0$ and zero polymer concentration. dn/dc values were obtained with an OPTILAB 903 interferometric refractometer using a light source at 632.8 nm.

RESULTS AND DISCUSSION

Polymer I

Ageing of polymer I solutions was performed at 90, 120 and 150°C. Ammonium ions formed by M hydrolysis buffer the pH at 8 within 1 day (> 110°C) from the initial imposed 5.5 pH. The extent of M and P hydrolysis was determined by ^{13}C n.m.r. spectroscopy using the integration regions A (186.0, 183.0), M (182.0, 179.5), P (177.5, 175.5). The two hydrolysis reactions involved during ageing are reported in *Scheme 1*. The quantitative conversion (in mol%) of amide carbonyl carbons (of M and P) into carboxylate carbons (of A) are shown in *Figures 1*, *2* and *3* for polymer I at 90, 120 and 150°C, respectively. The conversion of M to A with time is



Scheme 1

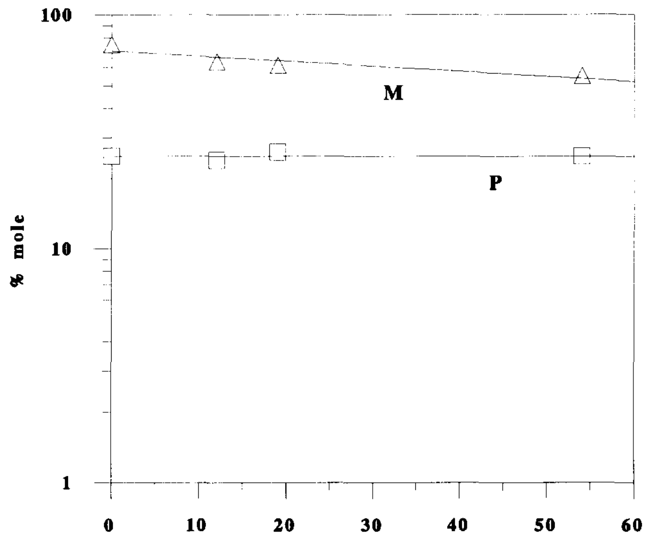


Figure 1 Hydrolysis of polymer I at 90°C and pH 8. M hydrolysis rate $k=0.0030$ days^{-1}. No P hydrolysis

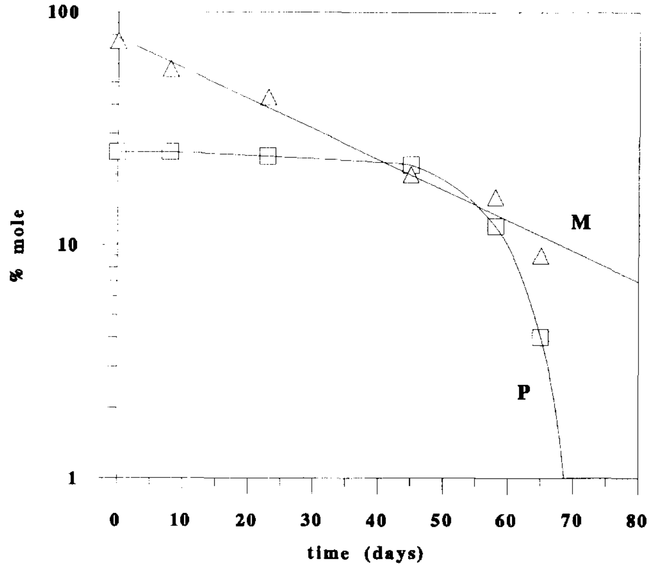


Figure 2 Hydrolysis of polymer I at 120°C and pH 8. M hydrolysis rate $k=0.030$ days^{-1}

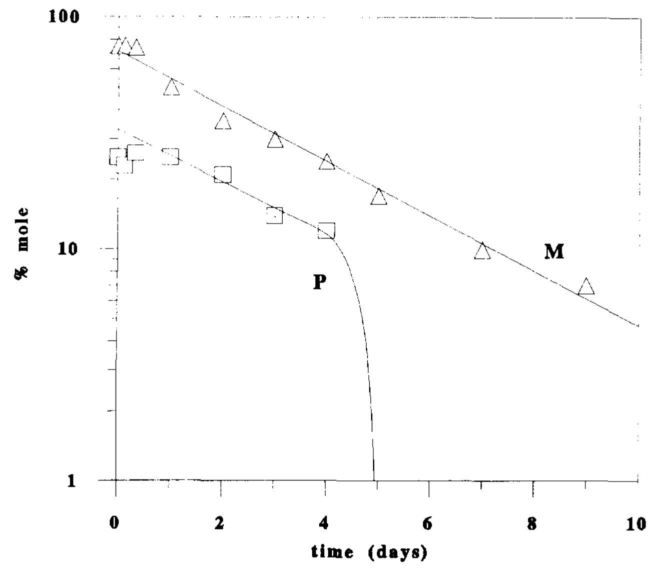


Figure 3 Hydrolysis of polymer I at 150°C and pH 8. M hydrolysis rate $k=0.27$ days^{-1}

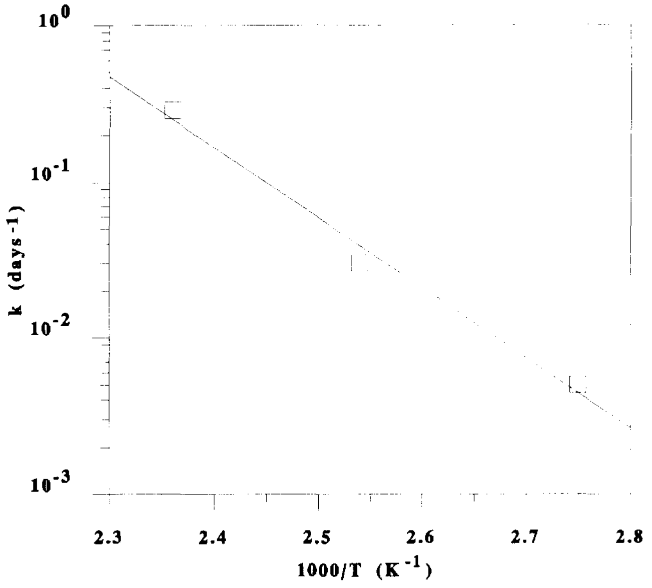


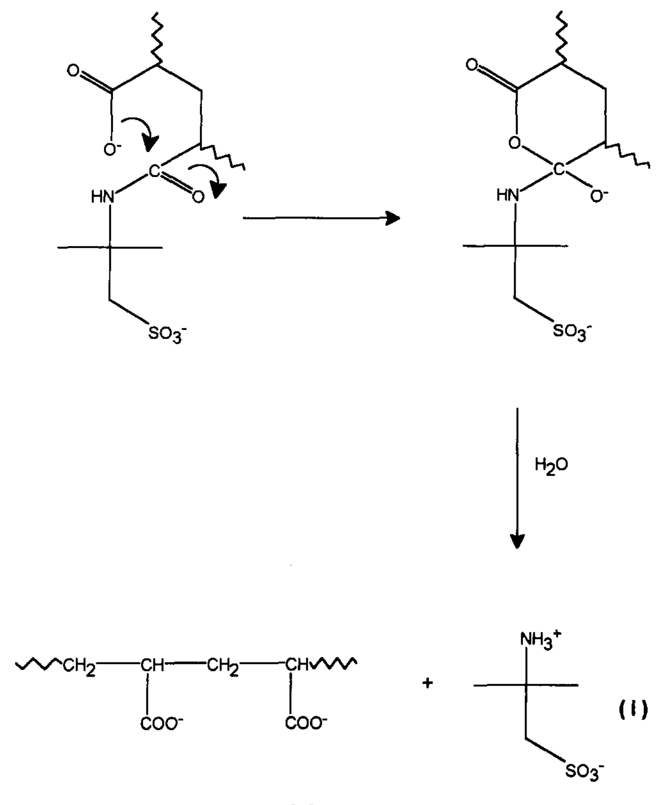
Figure 4 Arrhenius plot for M hydrolysis in polymer I at pH 8. Energy of activation = 85.9 kJ mol^{-1}

characterized by a single exponential decay, consistent with a first-order kinetic law. In this case pH is constant and the hydrolysis rate depends only on amide content: $-d[M]/dt = k[M]$. M hydrolysis in a polyacrylamide homopolymer at 80°C (pH 7.5) is about 10% in 15 days[5] which is similar to the 12% observed by us (*Figure 1*) in 12 days (pH 8, 90°C). Under these conditions no P hydrolysis occurred. The energy of activation for M hydrolysis in polymer I is calculated to be 85.9 kJ mol^{-1} based on hydrolysis rates at three temperatures (*Figure 4*). A value of 89.2 kJ mol^{-1} was obtained for polyacrylamide[3]. Thus, it is clear that P does not affect M hydrolysis. The M hydrolysis rate is enhanced 10 times on increasing the temperature by 30°C. M hydrolysis is nearly complete at the higher temperatures, in agreement with Moradi-Araghi observations[21] for the same kind of copolymer.

P hydrolysis occurs in two steps above 100°C. At 120°C the P content in the aged polymer remains almost constant for 55 days, then a rapid conversion to A is observed (*Figure 2*). At 150°C P hydrolysis occurs almost at the same rate as M hydrolysis up to about 4 days then hydrolysis becomes very rapid (*Figure 3*). This rapid change in P hydrolysis occurs in both cases when M is reduced to ~ 25 mol%.

Obviously there is more than one mechanism involved in P hydrolysis. The initial composition is 75 mol% M and 25 mol% P. Utilizing reactivity ratios ($r_1 = 1.02$ for M and $r_2 = 0.50$ for P) found by McCormick and Chen[12], under the same conditions used to synthesize polymer I, the mean sequence lengths were calculated ($\mu_M = 3.1$, $\mu_P = 1.2$). These lengths correspond to an average sequence MMMP-MMMP-. The prevalent triad centred on P is MPM.

In order to explain P hydrolysis we hypothesize that two kinds of mechanism are involved: an 'external' one due to direct attack by hydroxide ions, and an 'internal' one due to intramolecular catalysis by an adjacent A (*Scheme 2*). P hydrolysis at 120°C (*Figure 2*) starts when most of the Ms are transformed to A (about 2/3) allowing the internal mechanism to occur. At 120°C the direct attack of a hydroxide ion is retarded by the steric



Scheme 2

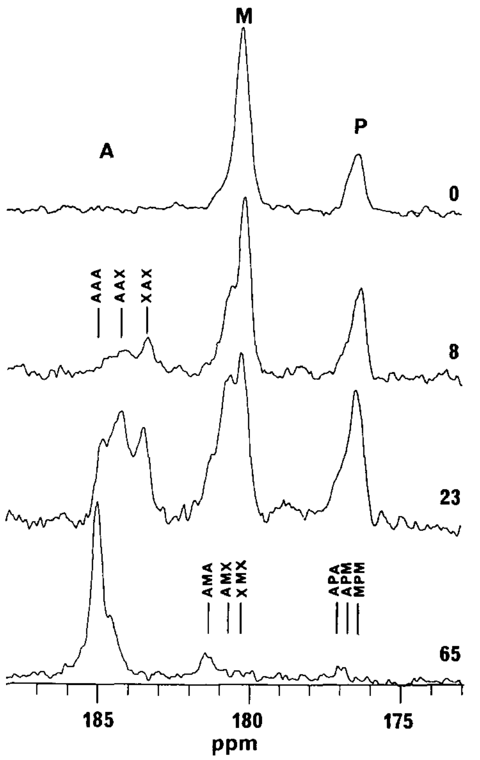


Figure 5 Partial ^{13}C n.m.r. spectra (carbonyl region) of polymer I ageing (in days) at 120°C and pH 8. X represents M or P

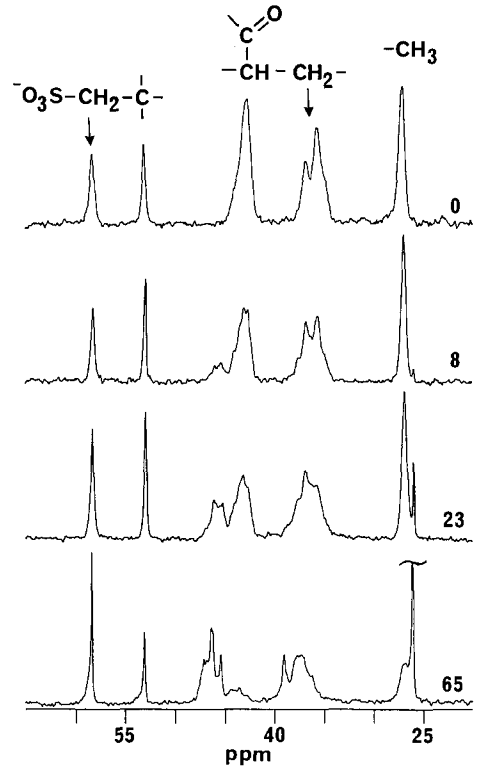


Figure 6 Partial ^{13}C n.m.r. spectra (aliphatic region) of polymer I ageing (in days) at 120°C and pH 8

hindrance and Coulombic repulsion of the dimethyl and sulfonate P groups, respectively. At 150°C, in the early stage (*Figure 3*), the elevated temperature is sufficient to permit the external mechanism. When most of the M units adjacent to P are hydrolysed, the rate increases due to the more efficient internal mechanism. Apparently, a nearby P unit impedes this mechanism (see below). In *Scheme 2* we propose that at the high ageing temperatures used here a COO^- group acts as catalyst whereas for M hydrolysis at lower temperatures (80°C) only a COOH group is thought to do this[4,5].

The carbonyl resonances from M, P and A can be subdivided into triads[6,9], or sequences of three monomer units (a unit with its two nearest neighbours). In *Figure 5* it can be seen that nearest neightbour A groups cause downfield shifts of the carbonyl resonances. X is used to represent M or P since the effect of M or P on the neighbouring carbonyl resonance appears to be equal. For example, the chemical shift of the carbonyl carbon arising from the M unit in the AMP triad appears to be equal to that in the AMM triad. Unfortunately the triad signals are not well resolved in the spectra obtained here.

P hydrolysis was also evidenced by the aliphatic ^{13}C resonances of P (*Figure 6*). The hydrolysed amine of P, 2-amino-2-methylpropanesulfonic acid in zwitterion form (I in *Scheme 1*), has narrower resonances than polymeric P. The methyl residue shifts 1.0 ppm upfield on hydrolysis. Aliphatic signals were not used to quantify hydrolysis for the spectra collected due to differences in NOE enhancement factors.

Polymer II

Hydrolysis of polymer II (50 mol% P, 50 mol% A) was studied at 150°C and at two pHs by integrating carbonyl regions [pH 6: A (184.0, 181.0), P (177.5, 176.0); pH 8: A (185.7, 183.0), P (178.0, 175.8)]. Reactivity ratios r_1 for A and r_2 for P are 0.740 and 0.187, respectively[22]. The product $r_1r_2 = 0.138$ indicates a strong tendency to produce the monomer sequence APAPAP.

The initial pH is unchanged on ageing since P hydrolysis produces a zwitterion (*Scheme 1*). A dramatic pH effect on P hydrolysis was found (*Figure 7*). The initial

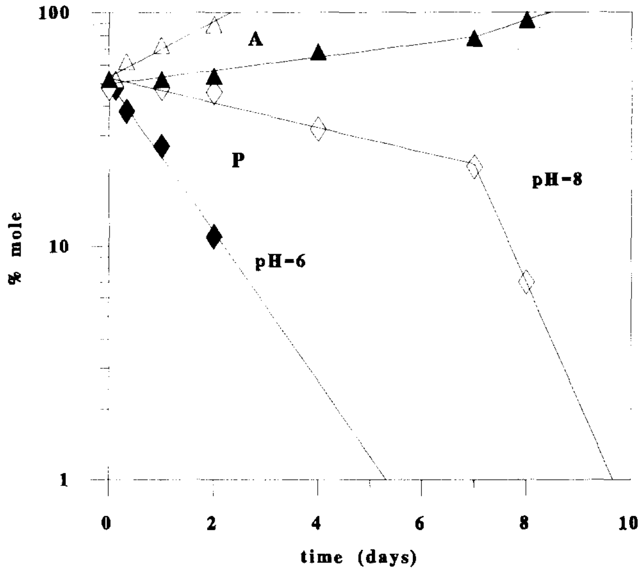


Figure 7 Hydrolysis of polymer II at 150°C. P hydrolysis rate: pH 6, $k=0.74$ days^{-1}; pH 8, $k=0.14$ days^{-1}

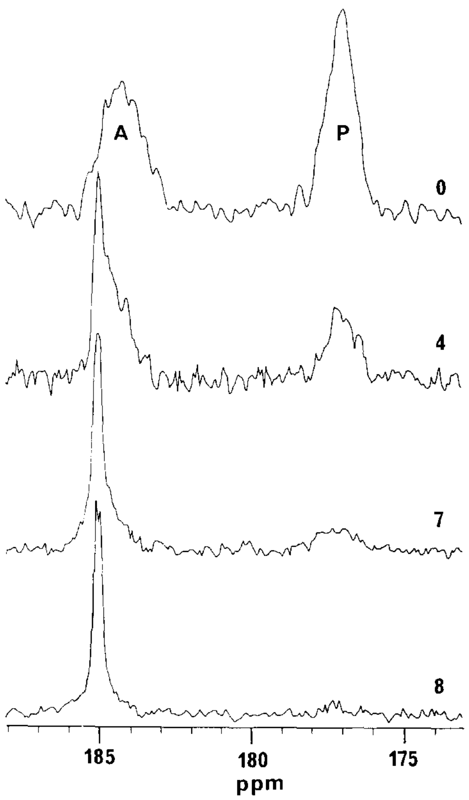


Figure 8 Partial ^{13}C n.m.r. spectra (carbonyl region) of polymer II ageing (in days) at 150°C and pH 8

rate of P hydrolysis at pH 6 ($k=7.4\times10^{-1}$ days^{-1}) is about five times faster than at pH 8 ($k=1.4\times10^{-1}$ days^{-1}). At pH 8 P hydrolysis is bimodal as found for polymer I.

Based on systematic studies of acrylamide hydrolysis it is known that the net negative polymer charge retards hydrolysis. This charge, in the present case, depends on the number of A and P groups. At the pHs used here all the sulfonate groups of P are ionized. The carboxylates of A are partially ionized at pH 6 and completely ionized at pH 8 (assuming pK_a between 5 and 6)[24].

Intramolecular hydrolysis accelerates hydrolysis and is independent of pH provided the microstructure around the group to be hydrolysed is correct. We theorize that intramolecular P hydrolysis occurs only when A is a nearest neighbour to P as discussed for polymer I. In addition, distant Ps are required. This follows from the observation that rapid hydrolysis occurs in polymer II at pH 8 only after half of the P units are consumed (*Figure 7*). Apparently, the initial rate of P hydrolysis at pH 6 is so similar to the rate due to the intramolecular mechanism that they are not distinguished. In order to verify this an A–P copolymer with smaller P content should be studied.

At pH 8 the net negative charge on the polymer is greater than at pH 6, since the carboxylate of A is more dissociated, and the direct attack by hydroxide ions is more difficult due to greater electrostatic repulsion. Thus, P hydrolysis is slower at pH 8 (*Figure 7*). The initial rate of P hydrolysis in polymer II at pH 8 is two times slower than for polymer I at the same pH. Polymer II has a greater P content and therefore more negative charge than polymer I.

Carbonyl resonance triads are not resolved for polymer II (*Figure 8*). This is probably due to an enhanced transverse relaxation caused by a decreased mobility of the polymer segments. P groups are sterically bulky and for this polymer (APAPAP) the P groups are close enough to cause a decreased mobility. Linewidths of the A resonance narrow considerably as the distance between P groups increases. A sharp signal is observed after 7 days when Ps are distant (*Figure 8*). This supports the idea that close P units favour a restricted polymer conformation which may prohibit the intramolecular hydrolysis mechanism.

CONCLUSIONS

^{13}C n.m.r. spectroscopy was used to examine the progressive changes in microstructure, caused by amide hydrolysis, which occur on ageing two copolymers of sodium-2-acrylamido-2-methylpropanesulfonate in 0.1 N NaCl. P hydrolysis was of special interest since P has been proposed to stabilize polyacrylamide for EOR in hostile environments. At pH = 8 and 150°C, P initially hydrolyses rather slowly for both polymers and then, after half of the Ps are consumed, rapid hydrolysis occurs. The initial rate of P hydrolysis increases as the pH decreases consistent with a decrease in electrostatic repulsion between the entering hydroxide ion and the charged polymer. Rapid P hydrolysis is attributed to intramolecular hydrolysis catalysed by a nearest neighbour A, which is suppressed by a nearby P. Unlike M hydrolysis, an ionized A carboxylate is thought to act as catalyst. M–P copolymers do not have optimum EOR properties for use in deep wells since hydrolysis is facile above 120°C.

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