

# Effect of Additives on the Degradation of Acrylamide–Acrylic Acid Copolymer in Aqueous Solution

HOUCHANG KHERADMAND, JEANNE FRANÇOIS,\* *Institut Charles Sadron, CRM, Université Louis Pasteur, 67083 Strasbourg–Cedex, France*, and VERONIQUE PLAZANET, *Total Compagnie Française des Pétroles, Centre de Recherches de Beauplan, 78470 St-Rémy lès Chevreuse, France*

## Synopsis

This paper presents the results of a systematic study of the effect of different additives on the degradation of acrylamide–acrylic acid copolymers at high temperature. Under conditions of current applications in enhanced oil recovery (without oxygen and in the presence of ferrous ions), the effects of sodium azide, sequestrant DTPA, and isobutanol have been separately tested. It is shown that DTPA enhances degradation when ferrous ions are present. A new process of stabilization which may be efficient in most of the conditions is proposed.

## INTRODUCTION

In a recent work, we have studied under different conditions the degradation of an acrylamide–sodium acrylate copolymer, industrially prepared by photocopolymerization<sup>1</sup>: in the presence or absence of oxygen and ions of transition metals ( $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Cu}^+$ , and  $\text{Cu}^{++}$ ). In the absence of oxygen, no loss of viscosity was measured and the molecular weight remains constant for periods of several months. Degradation is observed in the presence of oxygen and also in deaerated solutions if transition ions are present, the reaction rate being much higher in the second case. In all the cases, the positive effect of the purification of the polymer sample leads to attribution of the degradation to low molecular weight impurities: More precisely, residues (*methyl benzoate and benzyle*) arising from the photolysis of the polymerization catalyst (*benzyl dimethyl ketal*) have been found in the sample. Methyl benzoate is assumed to be decomposed by transition ions or oxygen and the resulting radicals are able to attack the polymer chain, this reaction being favored or hindered by the complexation state of the ion.

Different additives have been recognized for reducing the degradation of such polymers<sup>2–4</sup> and their efficiency depends on the conditions of their industrial use. If one considers these polyelectrolytes as stiffening agents in the tertiary oil recovery process, the additives must be particularly efficient in the absence of oxygen and in the presence of ferrous ions. The addition of

\*To whom all correspondence should be addressed.

sodium azide ( $\text{NaN}_3$ ), isopropanol, and sequestrant (DTPA) has been proposed to stabilize the solutions of the same acrylamide–sodium acrylate copolymer under such conditions.<sup>5</sup> In this work we have studied the influence of each of these compounds separately and the effect of the addition of their mixture at different compositions. The efficiency of these compounds on the stability in the presence of oxygen is also discussed and some comparisons with another copolymer obtained by hydrolysis are given. On another hand, we propose a new efficient and simpler method to avoid degradation.

## EXPERIMENTAL

### Materials

The industrial sample of acrylamide–sodium acrylate copolymer (copolymer C) was prepared by photocopolymerization.<sup>6</sup> Its weight average molecular weight is  $6 \times 10^6$ ; its acrylate content is 17% as measured by  $^{13}\text{C}$ -NMR and potentiometric titration.<sup>7</sup> In this work, it was used without purification.

The second polymer sample was Pusher 700, polyacrylamide hydrolyzed at 35% and of same order of molecular weight.

### Preparation of the Solutions

The desoxygenated solutions ( $\text{O}_2 < 5$  ppb) have been prepared directly in an air-tight Ubbelohde viscosimeter by using a special device already described.<sup>1</sup>

### Experimental Techniques

The capillary diameter of the Ubbelohde viscosimeter was 0.9 mm and the flowing time was measured with a chronometer. The flowing time is  $32 \pm 0.02$  s at  $25^\circ\text{C}$ , under a slight argon pressure. The average shear rate is approximately  $1500 \text{ s}^{-1}$ . This viscosimeter was put in a thermostated oil bath regulated at  $\pm 0.05^\circ\text{C}$ .

Light scattering experiments were made with a home built apparatus<sup>8</sup> (wavelength =  $6320 \text{ \AA}$ ), for diffusion angle  $\theta$  varying between  $30$  and  $150^\circ$ . The values of weight average molecular weight  $M_w$  was obtained from the extrapolation of the scattered intensity at  $\theta = 0$  and polymer concentration  $c = 0$ . We used values of refractive index increment  $dn/dc$  obtained in a previous work.<sup>9</sup>

GPC analyses were performed at low pressure with a large column of Sepharose 2B and 4B from Pharmacia and a refractometric detection.

## RESULTS AND DISCUSSION

Most of our experiments were carried out under conditions of high temperature ( $T = 80^\circ\text{C}$ ) and salinity ( $\text{NaCl} = 5000$  ppm). The polymer concentration is that currently used in the application (1000 ppm) and  $\text{pH} = 6.5$ . In some cases, no  $\text{NaCl}$  has been added.

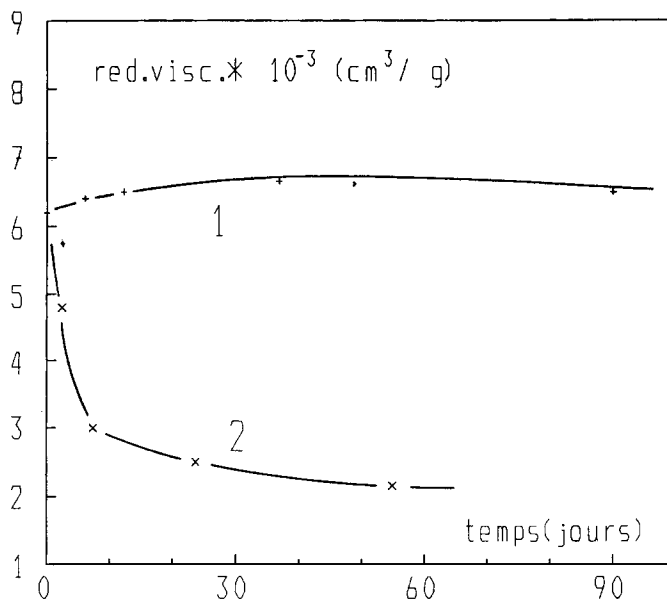


Fig. 1. Effect of sodium azide on the stability of P 700 in the presence of oxygen:  $T = 80^{\circ}\text{C}$ ,  $\text{NaCl} = 5000 \text{ ppm}$ ,  $c_p = 1000 \text{ ppm}$ , curves 1 and 2 with 0 and 65 ppm  $\text{NaN}_3$ , respectively.

### Addition of Sodium Azide

Sodium azide has been proposed as stabilizing agent for three reasons:

- (i) It is able to complex  $\text{Fe}^{+++}$  ions,<sup>10</sup> which are often assumed to be responsible for the degradation of hydrosoluble polymers in solution.<sup>4</sup>
- (ii) The  $\text{N}_3^-$  ion behaves as  $\text{Br}^-$  or  $\text{I}^-$  and acts as free radical scavenger<sup>10-14</sup> due to its low ionization power. Catherin and Marchal<sup>4</sup> suggest that  $\text{N}_3^-$  could reduce hydroperoxides.
- (iii) This salt is well known for its bacteriostatic properties.

The addition of 65 ppm of sodium azide has not changed the degradation rate of the polymer C, either in the presence of oxygen or in desoxygenated solutions containing 5 ppm of  $\text{Fe}^{++}$ .

Contrarily,  $\text{NaN}_3$  used in the same concentration is efficient in the case of oxygenated solutions of polymer P 700, as can be seen in Figure 1 and already shown in Ref. 15. The difference between these two polymers confirms that the mechanism of degradation is not the same. We have already shown that the chemical scheme proposed by Catherin and Marchal<sup>4</sup> (decomposition of hydroperoxides by  $\text{Fe}^{+++}$  ions) could explain the degradation of P 700 but not that of copolymer C. We have indeed detected the presence of iron and hydroperoxides in the industrial sample of P 700, which is not the case of copolymer C.

### Addition of Sequestrant DTPA

In the presence of oxygen, the addition of DTPA does not modify the degradation kinetics. The most interesting result is obtained for deaerated solutions which contain transition ions.

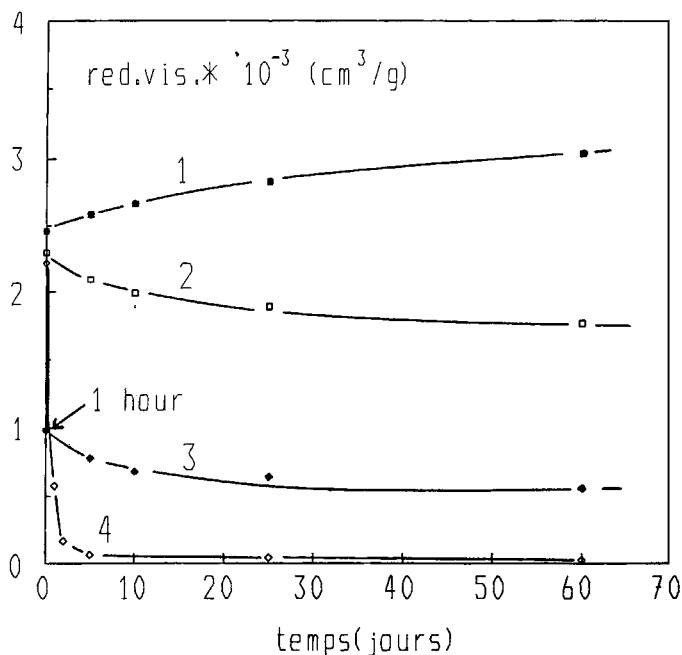


Fig. 2. Effect of different ions on the stability of copolymer C:  $T = 80^{\circ}\text{C}$ ,  $\text{NaCl} = 5000$  ppm,  $c_p = 1000$  ppm,  $\text{O}_2 < 5$  ppb; (1) without divalent cations; (2, 3, and 4) with 5 ppm of  $\text{Ca}^{++}$ ,  $\text{Fe}^{++}$ , and  $\text{Cu}^{++}$ , respectively (previous results).<sup>1</sup>

We briefly recall the behaviors observed in the absence of sequestrant. In Figure 2, we have reported the evolution of reduced viscosity  $\eta_{\text{red}}$  as previously obtained<sup>1</sup> for copolymer C in the absence of oxygen and in the presence of 5 ppm of  $\text{Ca}^{++}$  or  $\text{Fe}^{++}$  or  $\text{Cu}^{++}$ :

- In the absence of divalent cations, no degradation occurs even with the unpurified polymer sample (curve 1).
- The addition of  $\text{Ca}^{++}$ , which has no oxidation–reduction power, does not induce significant molecular weight decreases.<sup>1</sup> The slight change of reduced viscosity is only due to the high screening effect of electrostatic charges (curve 2).
- With  $\text{Fe}^{++}$ , which is a reducing ion, a very fast degradation is observed (curve 3). After an aging time of 1 h,  $\eta_{\text{red}}$  is only  $1000 \text{ cm}^3 \text{ g}^{-1}$  while the initial  $\eta_{\text{red}}$  value is  $2500 \text{ cm}^3 \text{ g}^{-1}$ . A quasi-instantaneous decrease of  $M_w$  has also been measured.<sup>1</sup>
- The addition of an oxidizing ion such as  $\text{Cu}^{++}$  leads to a more important degradation than  $\text{Fe}^{++}$  but the first step is slower (curve 4).

The addition of a sequestrant is expected to modify as well the screening effects as the oxidation–reduction reactions. In order to well understand this double role, we have performed a first series of experiments with copolymer C: the variation of  $\eta_{\text{red}}$  has been measured after 1 h aging as a function of DTPA concentration without divalent cations and in the presence of  $\text{Ca}^{++}$  or  $\text{Fe}^{++}$  (5 ppm). For these measurements, no NaCl has been added in order to amplify

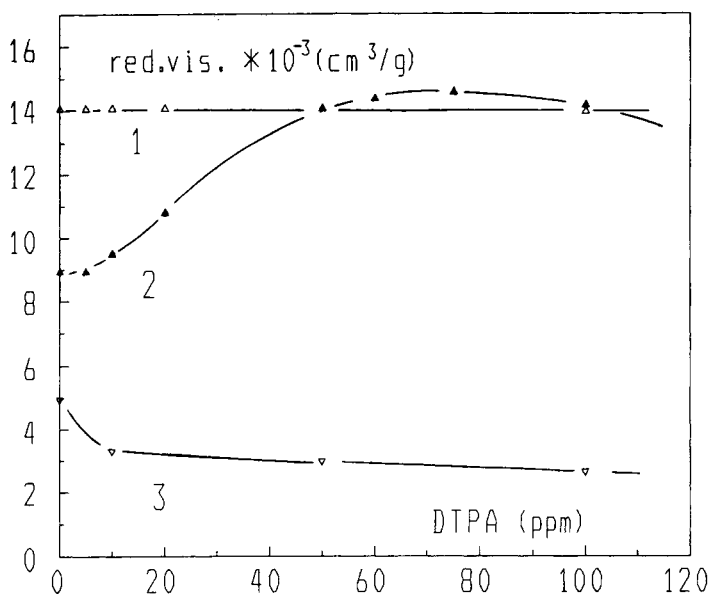


Fig. 3. Reduced viscosity of copolymer C measured after 1 h aging as a function of DTPA concentration without NaCl:  $T = 80^{\circ}\text{C}$ ,  $\text{O}_2 < 5$  ppb; (1) without divalent cations; (2 and 3) with 5 ppm of  $\text{Ca}^{++}$  and  $\text{Fe}^{++}$ , respectively.

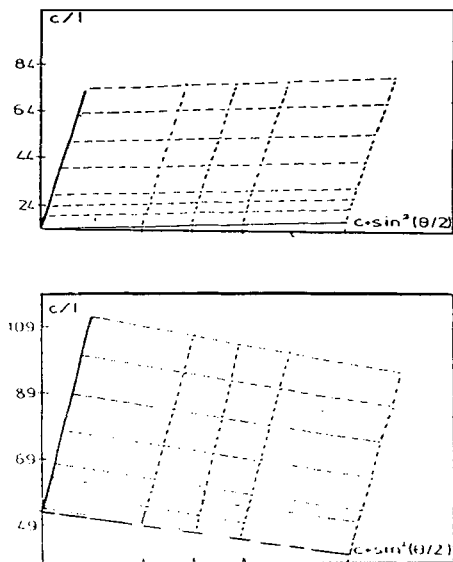


Fig. 4. Zimm plots of copolymer C after degradation for 1 h:  $T = 80^{\circ}\text{C}$ ,  $\text{O}_2 < 5$  ppb, NaCl (5000 ppm) added for light scattering measurements; (1) 5 ppm of  $\text{Fe}^{++}$ ; (2) 5 ppm of  $\text{Fe}^{++}$  and 100 ppm of DTPA.

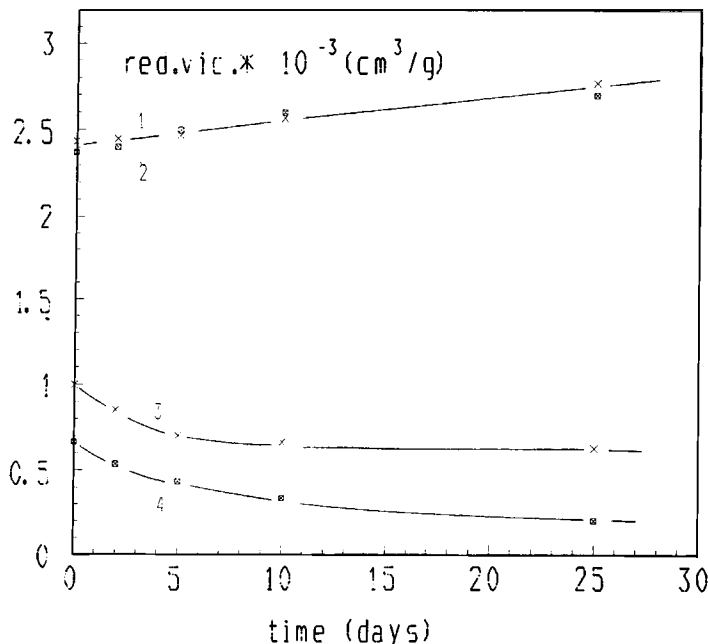


Fig. 5. Variation of reduced viscosity of copolymer C with time:  $T = 80^\circ\text{C}$ ,  $\text{O}_2 < 5$  ppb,  $\text{NaCl} = 5000$  ppm,  $c_p = 1000$  ppm; (1) without divalent cation and DTPA; (2) with 100 ppm of DTPA; (3) with 5 ppm of  $\text{Fe}^{++}$ ; (4) with 100 ppm of DTPA and 5 ppm of  $\text{Fe}^{++}$ .

the purely electrostatic effects. In Figure 3, it appears that the addition of DTPA on pure polymer solution induces a very slight decrease of  $\eta_{\text{red}}$ : The sequestrant, in the absence of other salts, has only a screening effect (curve 1). When  $\text{Ca}^{++}$  is present in the solution, one observes an increase of  $\eta_{\text{red}}$  by increasing the DTPA concentration. The progressive complexation of  $\text{Ca}^{++}$  ions by DTPA reduces their screening effect and the initial expansion of the polymer (without any added salt) is recovered when the amount of DTPA is large enough to complexate all the  $\text{Ca}^{++}$  ions (70 ppm of DTPA for 5 ppm of  $\text{Ca}^{++}$ ). A behavior completely different is observed with  $\text{Fe}^{++}$  (see curve 3):  $\eta_{\text{red}}$  becomes a decreasing function of DTPA concentration. On another hand, the  $M_w$  values measured by light scattering are  $2.7 \times 10^6$  and  $7 \times 10^5$  in the absence and presence of DTPA, respectively (see Zimm plots of Fig. 4). Such a result shows that, in the presence of a reducing ion which is able to induce the polymer degradation, the addition of a sequestrant is not convenient. In our previous work, we have suggested that benzyl residues play a role by complexing  $\text{Fe}^{++}$  ions and changing their oxidation-reduction potential and consequently their ability to decompose methyl benzoate. The evolutions observed in the presence of DTPA confirm such an hypothesis: Its influence can be very important on the degradation phenomenon while its role on the electrostatic interactions is negligible.

In a second series of experiments carried out on solutions containing 5000 ppm of  $\text{NaCl}$  (without  $\text{O}_2$ ), we studied the degradation kinetics for longer aging times. The results are reported in Figures 5 ( $\eta_{\text{red}}$ ), 6 ( $M_w$ ), and 7 (GPC

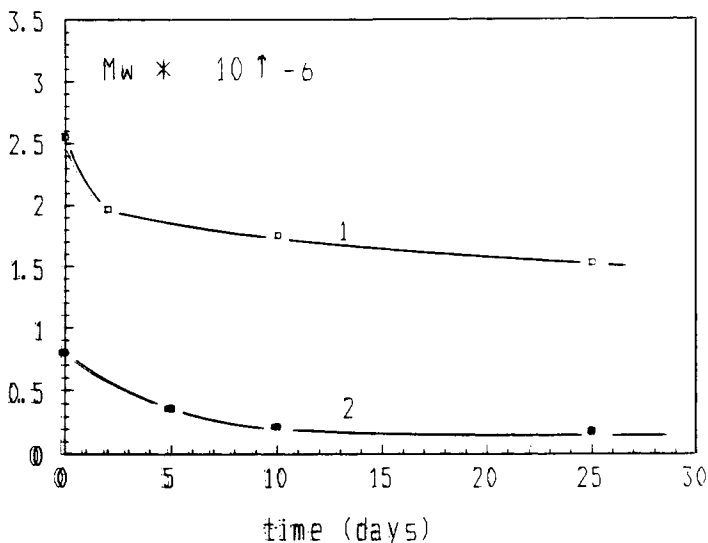


Fig. 6. Variation of molecular weight of copolymer C with time:  $T = 80^{\circ}\text{C}$ ,  $\text{O}_2 < 5$  ppb,  $\text{NaCl} = 5000$  ppm,  $c_p = 1000$  ppm; (1) with 5 ppm of  $\text{Fe}^{++}$ ; (2) with 5 ppm of  $\text{Fe}^{++}$  and 100 ppm of DTPA.

chromatograms). It can be seen that:

- (i) One hundred parts per million of DTPA have no influence on the stability of copolymer C (curve 1, Fig. 5). The slight increase of viscosity is simply due to the hydrolysis of amide groups, which progressively enhances the polyelectrolyte character of the polymer and consequently its expansion.<sup>1,16</sup>
- (ii) As pointed out above, the addition of DTPA strongly increases the degradation due to  $\text{Fe}^{++}$  ions and after 25 days aging the solution viscosity becomes very low (curve 2, Figs. 5, 6, and 7).
- (iii) Contrarily, it is interesting to note that DTPA reduces the degradation for an oxidizing ion such as  $\text{Cu}^{++}$ . With 50 ppm of DTPA, the viscosity remains constant for at least 10 days (curve 3, Fig. 5).

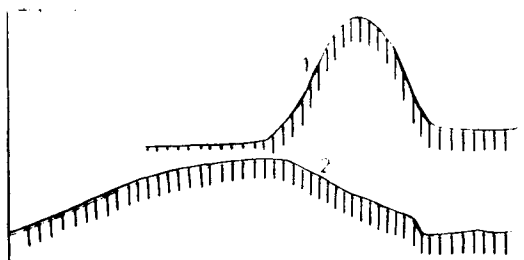


Fig. 7. GPC chromatograms of copolymer C after 90 days aging at  $80^{\circ}\text{C}$ ,  $\text{O}_2 < 5$  ppb,  $\text{NaCl} = 5000$  ppm,  $c_p = 1000$  ppm; (1) with 5 ppm of  $\text{Fe}^{++}$ ; (2) with 5 ppm of  $\text{Fe}^{++}$  and 100 ppm of DTPA.

We can at first conclude that the commercial DTPA sample does not contain impurities able to induce degradation since its addition has no effect on the presence or absence of oxygen when the solutions do not contain transition ions. Secondly, DTPA plays a role when the degradation is due to the presence of transition ions by changing their oxidation-reduction potential by complexation. In the case of reducing ions ( $\text{Fe}^{++}$ ), it enhances the phenomenon; in the case of oxidizing ions, it depresses the degradation.

### Addition of Isobutanol

It is well known that alcohols can reduce the degradation of polymers in solution by acting as agents of free radical tranfert<sup>3</sup> and by formation of less active free radicals.

For copolymer C, in the presence of oxygen, the addition of isobutanol has a slight decreasing effect on the degradation rate, as shown in Figure 8. Nevertheless, under such conditions a complete stabilization requires too high amounts of this additive.

In the case of free oxygen solutions containing 5 ppm of  $\text{Fe}^{++}$ , 6000 ppm of isobutanol is sufficient to obtain a constant viscosity for at least 2 months. This result leads to predict that the amount of isobutanol able to stabilize the solutions which also contain DTPA should be higher than that required in its absence, if the present ion is reducing.

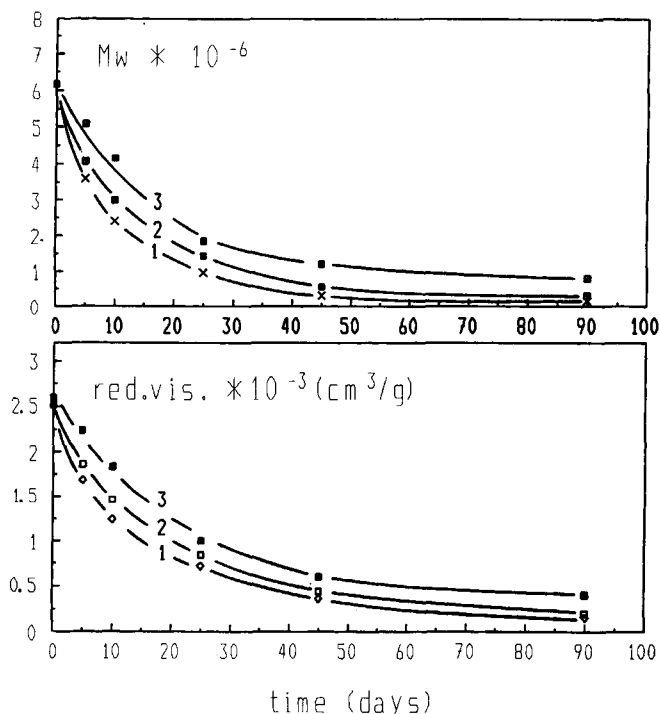


Fig. 8. Effect of isobutanol on the stability of copolymer C in the presence of oxygen:  $T = 80^\circ\text{C}$ ,  $\text{NaCl} = 5000$  ppm,  $c_p = 1000$  ppm, (1, 2, and 3) with 0, 1000, and 6000 ppm of isobutanol, respectively.



**Addition of Isobutanol + DTPA**

Since addition of DTPA is inefficient and that of isobutanol slightly efficient on the degradation in the presence of oxygen, it was not interesting to study the effect of their mixture under these conditions. The results concerning the degradation in free oxygen solutions containing 5 ppm of  $Fe^{++}$  are reported in Figure 9. As expected, in the presence of 100 ppm of DTPA, 10,000 ppm of isobutanol are required to avoid degradation for a period of 90 days.

From this series of experiments it appears that:

- In the presence of oxygen neither  $NaN_3$  nor DTPA nor isobutanol can significantly reduce the degradation of copolymer C, at low enough concentration.
- In the presence of transition ions for free oxygen solutions, the addition of DTPA could be efficient only in the case of oxidizing ions.
- If the ions are reducing, one can use an alcohol such as isobutanol, but the addition of a sequestrant must be avoided. As a matter of fact, in the case where the aqueous solutions of polymer are used in an oil recovery process (low amount of  $O_2$  and presence of ferrous ions), the method proposed in Ref. 5 does not seem to be well adapted since the effects of the two additives are not complementary but opposite.

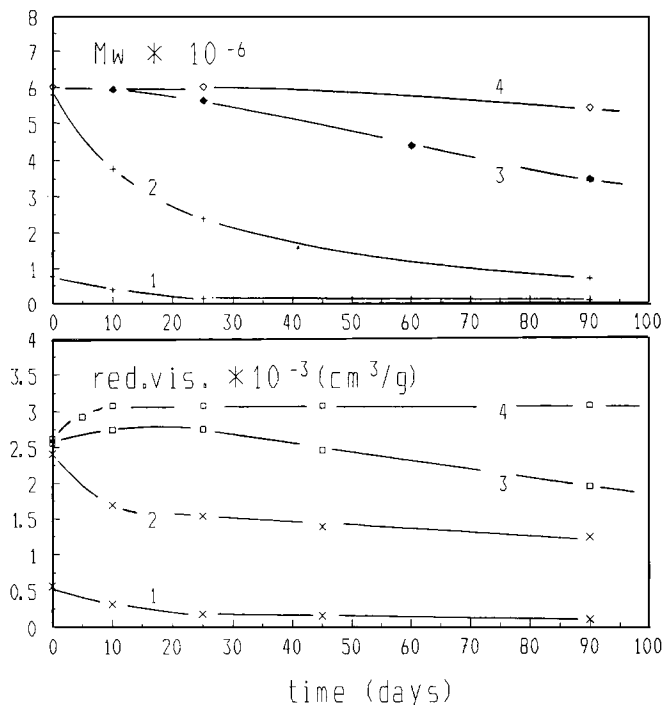


Fig. 9. Effect of isobutanol on the stability of copolymer C in the presence of DTPA (100 ppm):  $T = 80^{\circ}C$ ,  $O_2 < 5$  ppb,  $NaCl = 5000$  ppm,  $c_p = 1000$  ppm; (1, 2, 3, and 4) with 0, 3000, 6000, and 10000 ppm of isobutanol.

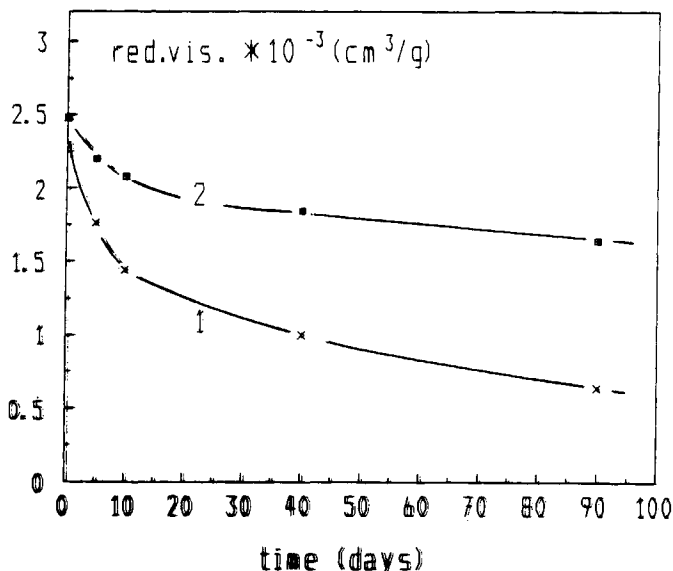


Fig. 10. Effect of acrylamide on the stability of copolymer C in the presence of oxygen:  $T = 80^{\circ}\text{C}$ ,  $\text{NaCl} = 5000 \text{ ppm}$ ,  $c_p = 1000 \text{ ppm}$ , (1 and 2) 0 and 50 ppm of acrylamide, respectively.

The purification of polymer samples, for instance, by washing them in methanol or methanol-ethanol mixture, could constitute another method for obtaining a good stability of their aqueous solutions.<sup>1</sup> This is not limited to the copolymer C prepared by photocopolymerization: Muller and Kohler<sup>15</sup> have indeed shown that the purification of P 700 (obtained by a classical radical polymerization of acrylamide and alkaline hydrolysis) allows one to

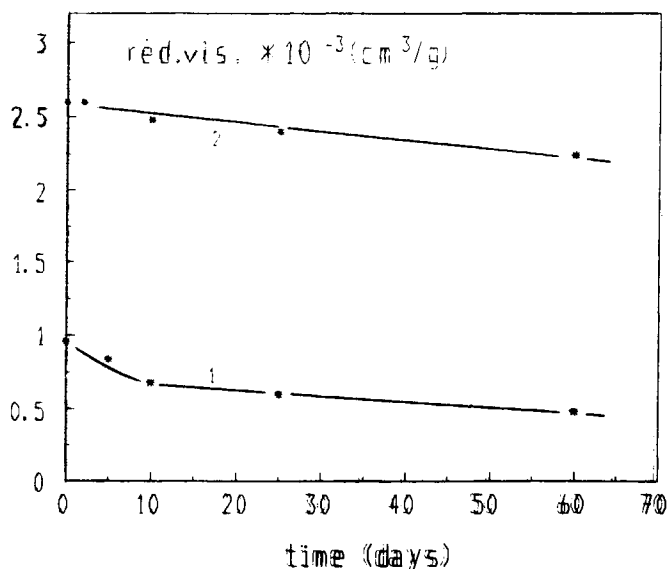


Fig. 11. Effect of acrylamide on the stability of copolymer C in absence of oxygen and with 5 ppm of  $\text{Fe}^{2+}$ :  $T = 80^{\circ}\text{C}$ ;  $\text{NaCl} = 5000 \text{ ppm}$ ,  $c_p = 1000 \text{ ppm}$ ; (1 and 2) with 0 and 50 ppm of acrylamide, respectively.

avoid degradation in the presence of oxygen. Such a method is perhaps too difficult and expensive.

We propose now the addition of acrylamide as stabilizing agent.

### Addition of Acrylamide

In Figures 10 and 11 we show the stabilizing effect of 50 ppm of acrylamide for copolymer C in solutions in the presence of oxygen and in free oxygen solutions containing 5 ppm of  $\text{Fe}^{++}$ , respectively: In the first case, we observe that 50 ppm of acrylamide is much more efficient than 6000 ppm of isobutanol. In the second case the fast initial degradation completely disappears and only a slow change of viscosity is observed. The same stability is obtained by using 10,000 ppm of isobutanol and 100 ppm of DTPA.

The free radicals formed by the reaction of  $\text{Fe}^{++}$  on the photochemical catalyst are used to initiate the polymerization of acrylamide and are no longer available to induce the copolymer degradation. It is obvious that the efficiency of the method is due to adequate ratios between the constants of the different possible reactions and further investigations should be necessary to determine the good amount of acrylamide according the conditions. We have found that this process is also efficient for P 700.

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