

Degradation of Acrylamide–Sodium Acrylate Copolymer in Aqueous Solution

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INTRODUCTION

Partially hydrolyzed polyacrylamide or acrylic acid–acrylamide copolymers are currently the most widely used control polymers for secondary and tertiary oil recovery.¹ Increasing interest in this class of polymers has stimulated investigations of their stability which have been reported, dealing particularly with the role of oxygen and salts or oxides of iron.^{2,3} Different ways to avoid degradation have been studied, such as addition of formaldehyde or hydrosulfite.^{3–6} But generally the chemical process remains undetermined because degradation is first investigated by measurements of global properties, viscosity, screen factor, or permeability and secondly by using industrial samples containing unidentified impurities.

It has been shown that a partially hydrolyzed polyacrylamide becomes stable at high temperature in the presence of oxygen when it is purified by precipitation in methanol but the nature of the impurities eliminated in this treatment and the origin of the degradation has not been elucidated.⁷ In another work, Catherin and Marchal^{8,9} have compared the degradative process of industrial samples and carefully prepared and purified samples; they have deduced from this comparison that the process of degradation of polyacrylamide is the decomposition of chain hydroperoxides by ferric ions. These authors predict a more important degradation when the polymer solution contains ferrous ions in absence of oxygen.

In this article, we study the degradation of an acrylamide–sodium acrylate copolymer, industrially prepared by photopolymerization,¹⁰ under different conditions: in the presence or absence of oxygen and ions of transition metals. The mechanism is discussed from the analysis of the impurities, the effect of purification, and the comparison with the behavior of another commercial polymer. In all cases the degradation is studied by viscosimetry but in many cases the results are confirmed or made more precise by gel chromatography and light-scattering experiments.

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EXPERIMENTAL

Materials

Most of our experiments were carried out on an industrial sample of sodium acrylate-acrylamide copolymer prepared by photopolymerization¹⁰ (copolymer C of molecular weight = $6 \cdot 10^6$). Its acrylate content is $17 \pm 1\%$ as measured by ¹³C NMR and potentiometric titration.¹¹ Its purification was achieved by precipitation in a methanol-ethanol mixture.

The second studied sample was P700, polyacrylamide hydrolyzed at 35% and of same order of molecular weight.

Preparation of the Solutions

For studies in presence of oxygen, polymer solutions were prepared 48 h prior to their use in simple carefully closed erlenmeyers and homogenized at room temperature by slow stirring. The solutions are kept in a hot-air bath thermostated at $\pm 1^\circ\text{C}$. At different time intervals, a given volume is pipetted and the solution is studied by viscosimetry, light scattering, and by gel permeation chromatography (GPC) in some cases.

For studies in absence of oxygen we used the device represented in Figure 1, which allows preparation and maintenance of concentrated solutions of polymer, ferrous chloride, or other additives and mixtures of different compositions.

First, one liter of water or brine (0.1M NaCl) and weighted quantities of polymer and Cl_2Fe are introduced in calibrated vessels A, B, and C, respectively. The perfect desoxygenation of water or brine is obtained after 7 to 10 cycles of freezing and melting under vacuum. The measurements of oxygen content is made in vessel E with K 7540 Chemetrics ampoules. Given volumes of desoxygenated water ($\text{O}_2 < 5$ ppb) are then transferred through pipe p in vessels B and C by applying a slight argon pressure. The concentrated polymer solution is homogenized by slow stirring for 48 h at room tempera-

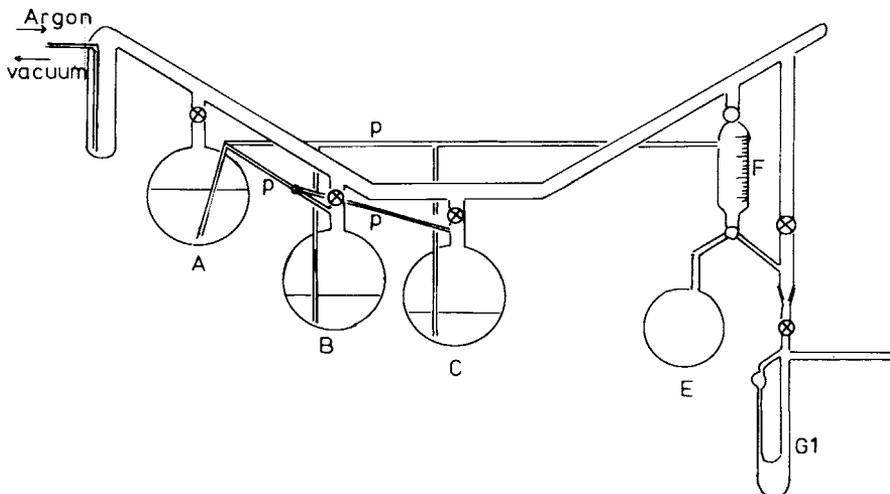


Fig. 1. Scheme of the device used for the preparation of free oxygen solutions.

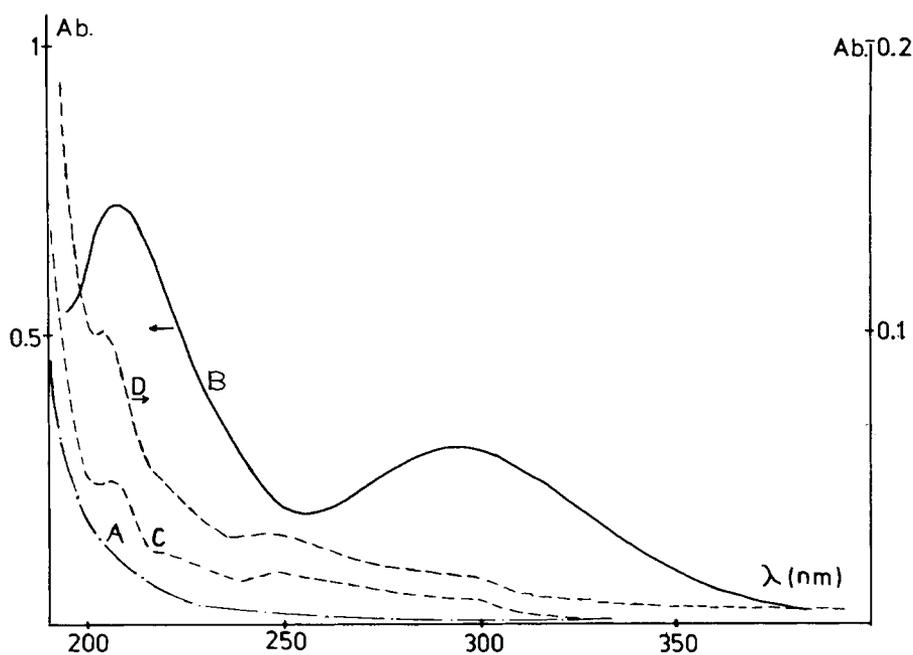


Fig. 2. UV absorption spectra of Cl_3Fe (B), and Cl_2Fe (A, C, D) solutions (see text).

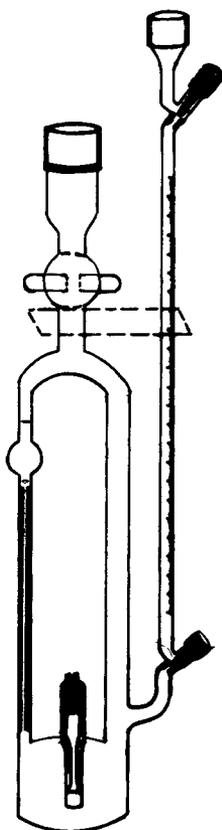


Fig. 3. Scheme of the device used to simultaneous conductivity and viscosity measurements in absence of oxygen.

ture. Given volumes of polymer solution and of water or brine (measured in the graduated flask F) were successively introduced through pipe p' in the measurement device G, in order to obtain the given polymer concentration. After 5 h required for homogeneity the calculated volume of Cl_2Fe solution can be added.

Two types of measurement devices G were used. The device G_1 (Fig. 1) is an Ubbelohde viscosimeter with a spectroscopic cell laterally sealed. The stopcock is large enough (10 mm) to make the device air-tight for several months as it can be checked by ultraviolet (UV) spectroscopy. In Figure 2 we show that the UV spectrum of a Cl_2Fe solution aged in this device (curve A) does not present the absorption peaks characteristics of ferric chloride at 220 and 300 nm^{12} (curve B). In a solution of the same concentration prepared by boiling and argon injection and kept in air-tight flasks, the formation of ferric ions is observed (see curves C and D of Fig. 2). The device G_2 (Fig. 3) allows simultaneous measurements of conductivity and viscosity of polymer solutions as a function of Cl_2Fe concentration, small volumes of salt being added from the graduated tube T.

The same device was also used for the preparation of all the solutions in absence of oxygen for instance for the study of the catalyst residues.

Experimental Techniques

Most of the viscosity measurements were performed with the device G_1 . The capillary diameter was 0.9 mm and the flowing time was measured with a chronometer (accuracy ± 0.01 s). The flowing time is 32 ± 0.01 s at 25°C , under a slight argon pressure. The average shear rate is approximately 1500 s^{-1} . This viscosimeter was put in a thermostated oil bath regulated at $\pm 0.05^\circ\text{C}$. For some studies carried out in the presence of air, the measurements were made with the automatic viscosimeter Fica with a shear rate of 100 s^{-1} . Most of our experiments where the molecular weight of the polymer is higher than 10^6 correspond to the non-Newtonian regime.

The spectroscopic investigations were performed with a Shimadzu UV 240 spectrophotometer.

Light-scattering experiments were made with a home built apparatus¹³ (wave length = 6320 Å), for diffusion angle θ varying between 30 and 150° . The values of weight average molecular weight M_w and radius of gyration R_g were obtained from the extrapolation of the scattered intensity at $\theta = 0$ and polymer concentration $c = 0$ and from the slope of the $P(\theta) = f(\sin \theta/2)$ curves for $30^\circ < \theta < 60^\circ$, respectively. We used values of refractive index increment dn/dc obtained in a previous work.¹⁴

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

For the titration of the peroxide functions in copolymer C, we used the method proposed by Catherin.⁹ Hydroperoxides or peroxides are reduced by Fe^{II} and the complex formed between Fe^{III} and ammonium thiocyanate is detected by colorimetry ($\lambda = 475 \text{ nm}$). With a copolymer C solution (1%) we have not detected peroxides by this very sensitive method. This shows that the content in active oxygen in this sample is lower than $1.8 \cdot 10^{-7} \text{ mol/L}$ while

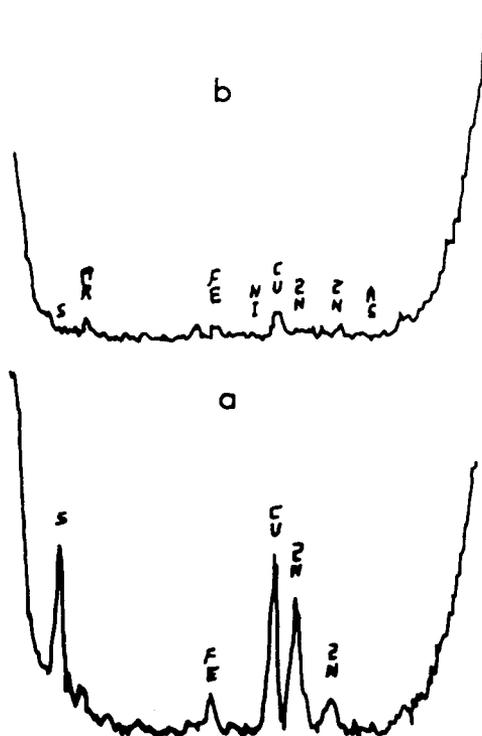


Fig. 4. X fluorescence diagrams of P700 (a) and copolymer C (b).

Catherin has measured for other commercial polymers (particularly P700) contents ranging between 1 and 2×10^{-6} mol/L.

The mineral impurities in the polymer samples were analyzed by elemental analysis, atomic absorption, and X fluorescence. It was found that P 700 contains 10.2% of sodium carbonate and the X fluorescence diagram of the dried powder represented in Figure 4 shows the presence of different metals. The supernatant of a dialyzed solution of copolymer C at 1% does not contain ions or metals detectable by atomic absorption. This is consistent with the X fluorescence diagram of the powder (see Fig. 4).

The organic impurities in copolymer C sample were detected by using gas chromatography (Apparatus Hewlett Packard 5880 equipped with a capillary column of crosslinked phase SE54 and 25 m of length). The analyses were carried out either directly on a dilute aqueous polymer solution (0.5 g/L) or on the supernatant of a more concentrated dialyzed solution (10 g/L) or after extraction by methanol and ether (1% of acrylic acid and 4 ppm of methyl benzoate have been detected by this method).

EXPERIMENTAL RESULTS

Most of our experiments were carried out under conditions of high temperature ($T = 80^\circ\text{C}$) and salinity ($\text{NaCl} = 5$ g/L). The polymer concentration is that currently used in the application (1 g/L) with a pH = 6.5. Sodium azide (NaN_3) (65 ppm) is added as bacteriostatic agent in order to facilitate the

TABLE I

	Time (days)				
	0	5	10	25	60
η_{red} (cm^3g^{-1})	2420	2560	2680	2800	2920
$M_w \times 10^{-6}$	5.5	5.6	5.3	5.3	5.4

light-scattering experiments. We will show that this salt does not play a significant role in the degradation process.

Without Oxygen and Salts of Transition Metals

Table I shows that copolymer C is not degraded in absence of oxygen or salts of transition metals. A slight increase of reduced viscosity (η_{red}) is observed which can easily be interpreted as a modification of the hydrolysis degree.¹⁵⁻¹⁸ In another work, we discuss the hydrolysis kinetics of these copolymers and propose a mechanism of reaction for the range of neutral pH.¹⁵⁻¹⁸ In absence of NaN_3 , the same evolution of viscosity was obtained.

The good stability of copolymer C in desoxygenated solutions shows that the industrial sample does not contain impurities able to thermally form active free radicals. The same behavior has also been observed with another commercial sample.¹⁹ Catherin and Marchal^{8,9} have suggested that the reduction reaction of metal residues (Fe^{II}) on chain peroxides could induce degradation in absence of oxygen. This type of mechanism does not take place with the investigated polymer sample: this is consistent with the results of the impurities analysis which has not revealed peroxide or transition metal.

In Presence of Oxygen and Without Salts of Transition Metals

In Figure 5(a) we have reported the evolution of reduced viscosity of solutions of unpurified copolymer C in the presence of oxygen (curve 1). The abrupt change of η_{red} is correlated to a decrease of molecular weight [Fig. 5(b)]. Curve 2 of Figure 5(a) shows that the purification of the sample strongly reduces the degradation. This result, in agreement with the observations of Muller⁷ on P 700 sample, clearly indicates that the degradation is due to the oxidation of impurities contained in the sample. Different mechanisms can be proposed:

1. Catherin and Marchal^{8,9} have observed a degradation of purified commercial samples of polyacrylamide and attributed this phenomenon to the decomposition of chain hydroperoxides by traces of Fe^{III} contained in water used as solvent or from the glass walls. At first in the case of copolymer C the absence of degradation with the purified sample shows that if Fe^{III} is responsible for the reaction it must be contained in polymer powder. Secondly, our titrations do not reveal either Fe^{III} nor peroxides in the dried sample and the concentrations of these species are necessarily lower than the detection limits of the techniques: less than $1.3 \cdot 10^{-6}$ mole of hydroperoxide and $7 \cdot 10^{-7}$ mol of Fe by monomer. If one considers the degradation kinetics obtained by Catherin^{8,9} with samples containing 10 to 100 times more Fe and

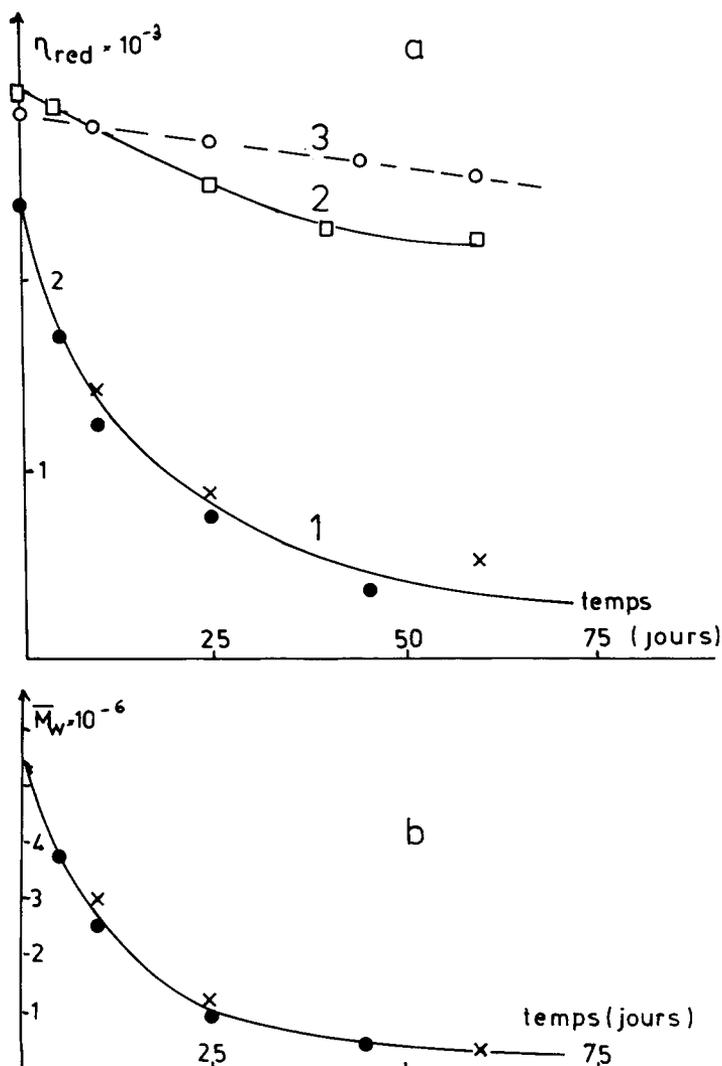


Fig. 5. Degradation in the presence of oxygen; unpurified sample of copolymer C: viscosity (a1) and light-scattering results (b); (●, X two different experiments); purified samples: viscosity results for copolymer (a2) and P700 (a3).

hydroperoxides, it is impossible to explain the behavior of copolymer C by the same mechanism.

2. Catherin and Marchal also suggest that formaldehyde generally considered as a stabilizing agent^{3,5} of polyacrylamide in aqueous solution could, on the contrary, promote degradation, in particular in presence of metallic ions and hydroperoxides. They assume that in a first step the formation of formaldehyde is due to the oxidation of residues of acrylamide or methanol in samples purified by precipitation in this solvent. Then the purification leading to an increase of methanol content should also enhance the degradation. The inverse effect of purification has been observed and we will not consider this mechanism in the case of copolymer C.

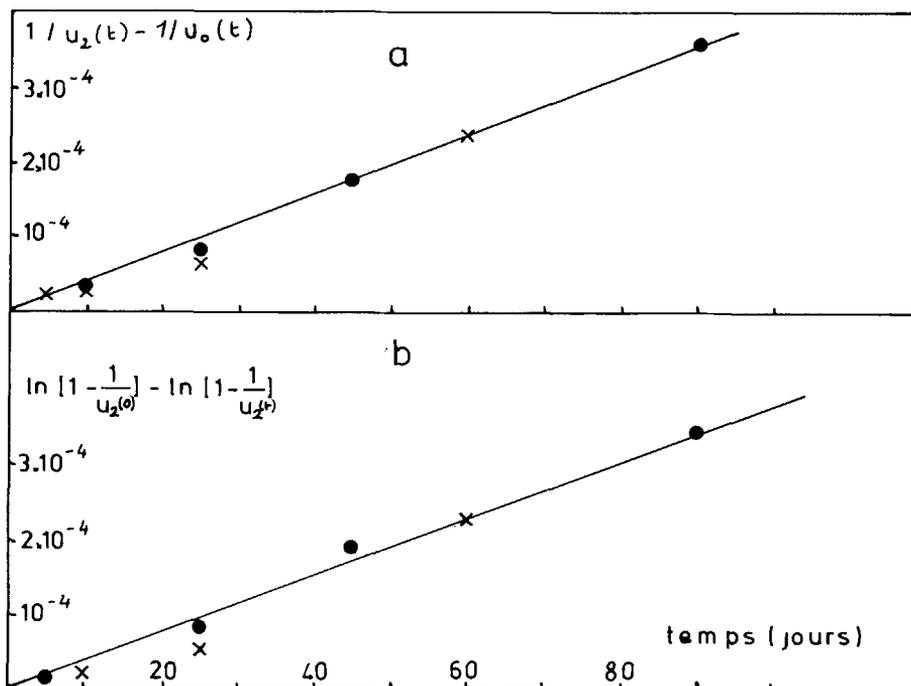


Fig. 6. Kinetics of degradation of copolymer C in the presence of oxygen (see text).

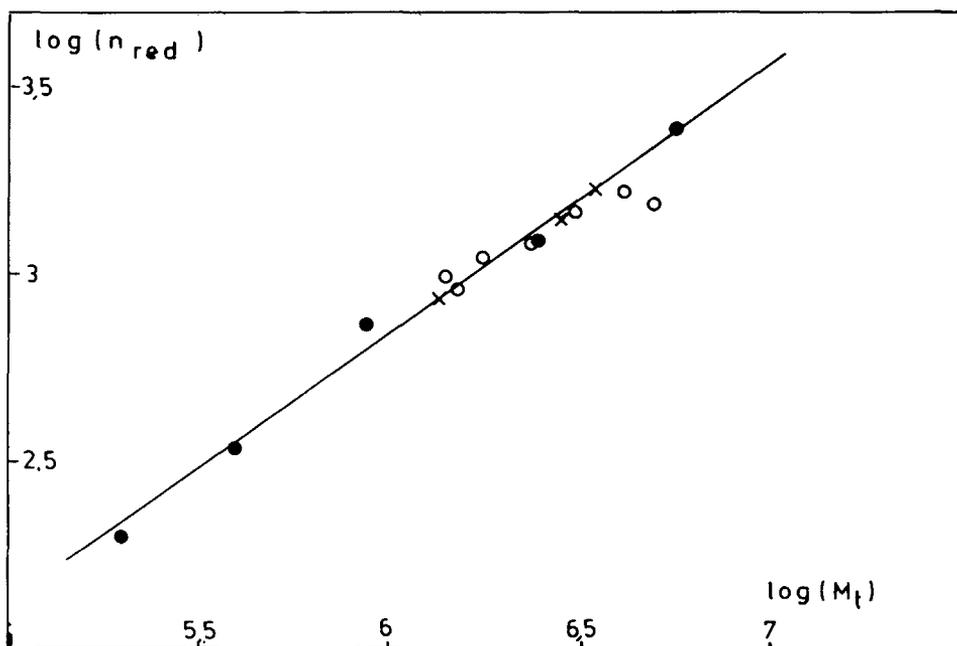


Fig. 7. Molecular weight dependence of reduced viscosity of copolymer C degraded in the presence of oxygen (O, X); reference data of Schwartz and François¹⁴ (●).

3. The degradation of copolymer C in the presence of oxygen is probably due to the impurity identified by gas chromatography: methyl benzoate which is one of the products of the photolysis of the polymerization catalyst, benzyl dimethylacetal.^{10,20,21} This residue, thermally stable in absence of oxygen could be oxidated and the product of oxidation could be unstable at high temperature. As discussed later we are not able to define the mechanism.

From results of Figure 5, we have calculated the variations of $1/u_2(t)$ and $\ln(1 - u_2(0)) - \ln(1 - u_2(t))$ (where $u_2(0)$ and $u_2(t)$ are the weight-average degree of polymerization at times zero and t , respectively). If the degradation is a random process of link breaking, linear variations of these functions are expected.²²⁻²⁵ As shown in Figure 6, this is the case for the degradation of copolymer C. Moreover, we have plotted in Figure 7 the variations of η_{red} with M_w , both parameters being measured at different aging times. These variations do not significantly differ from the reference data obtained by Schwartz and Francois¹⁴ with fractions of partially hydrolyzed polyacrylamide, from viscosity measurements performed with the same type of capillary viscosimeter and taking into account the change of hydrolysis degree. We can conclude that the degradation of copolymer C in the presence of oxygen leads to the formation of short linear chain. In fact, crosslinking effects during degradation generally do not occur in the range of concentration used in our study.^{22,23}

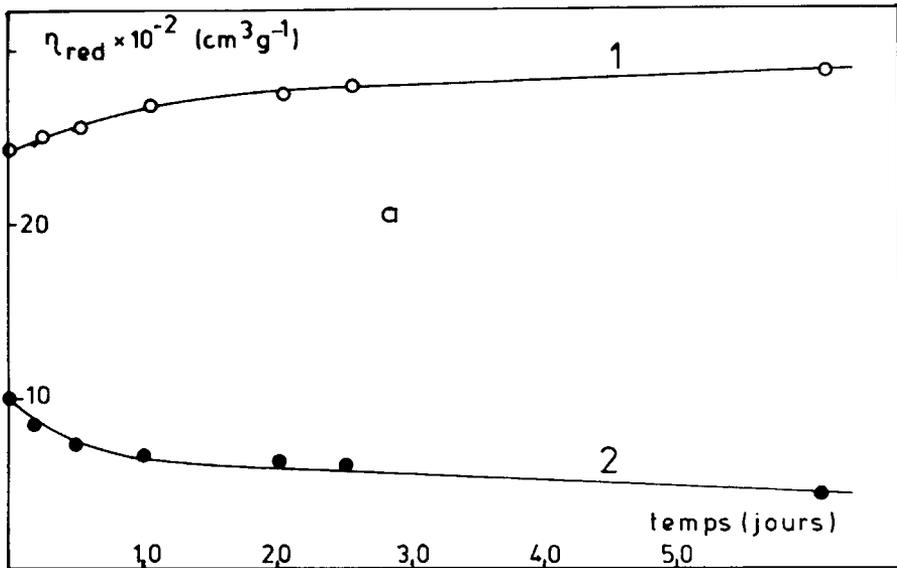
In Absence of Oxygen and with Salts of Transition Metals

With Ferrous Chloride. In Figure 8(a), we compare the evolutions of reduced viscosity of free oxygen solutions of copolymer C with and without 5 ppm of Fe^{2+} . The main observation is the abrupt decrease of η_{red} after 15 minutes of aging time in presence of Fe^{2+} . As confirmed by the variations of molecular weight [Fig. 8(b)] and by the Zimm plots of Figure 9, a quasi-instantaneous degradation of copolymer C occurs followed by a much slower reaction. The confirmation of viscosity measurements by light-scattering experiments is important since such a viscosity change could be attributed to a strong interaction between polyanions and Fe^{2+} which is expected to induce a decrease of the dimensions of the macromolecular coil.²⁶

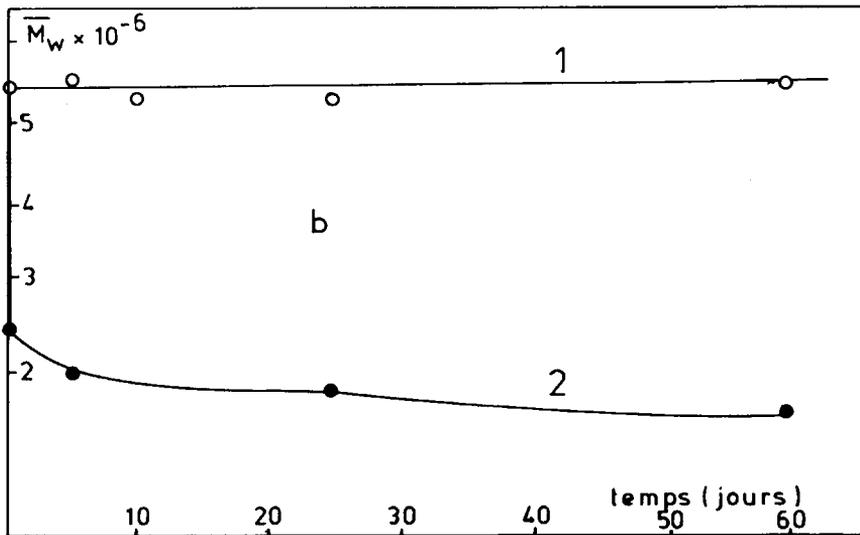
We have represented the variations of η_{red} measured after 1 h as a function of the concentration of Fe^{2+} (< 5 ppm) in Figure 10. The reaction rate increases by increasing concentration in Fe^{2+} and 5 ppm do not correspond to an excess of Fe^{2+} with respect to the species with which it reacts.

With the purified sample we have not observed degradation under the same experimental conditions. This result leads us to eliminate, among the possible different processes, the mechanism including the decomposition of chain peroxides by Fe^{2+} . This conclusion is probably specific to the sample under investigation. Indeed the purified sample of P700 is degraded in the presence of Fe^{2+} . This is consistent with the hypothesis of Catherin and Marchal,^{8,9} who have detected hydroperoxides in this sample. No influence of NaN_3 has been observed.

With Other Metal Chlorides. The above results show that the addition of reducing ions induces the degradation of copolymer C in the absence of oxygen. Here we compare the effects of other cations: Ca^{2+} which has no oxidation-reduction power; Cu^+ and Fe^{2+} which are reductants; Cu^{2+} and



(a)



(b)

Fig. 8. Degradation of copolymer C in free oxygen solutions without (1) and with added Fe^{2+} ions (5 ppm) (2); viscosity (a) and light-scattering results (b).

Fe^{3+} which are oxidants. The results of this comparison are gathered in Figure 11 and Table II. It appears:

1. As expected, the addition of Ca^{2+} does not induce degradation, \bar{M}_w remaining approximately constant during 60 days (Table II). A slight decrease of viscosity is observed instead of the increase obtained in the absence of Ca^{2+} . This shows that under these experimental conditions (in excess of NaCl), the interaction between polyion and divalent cations cannot be responsible for a

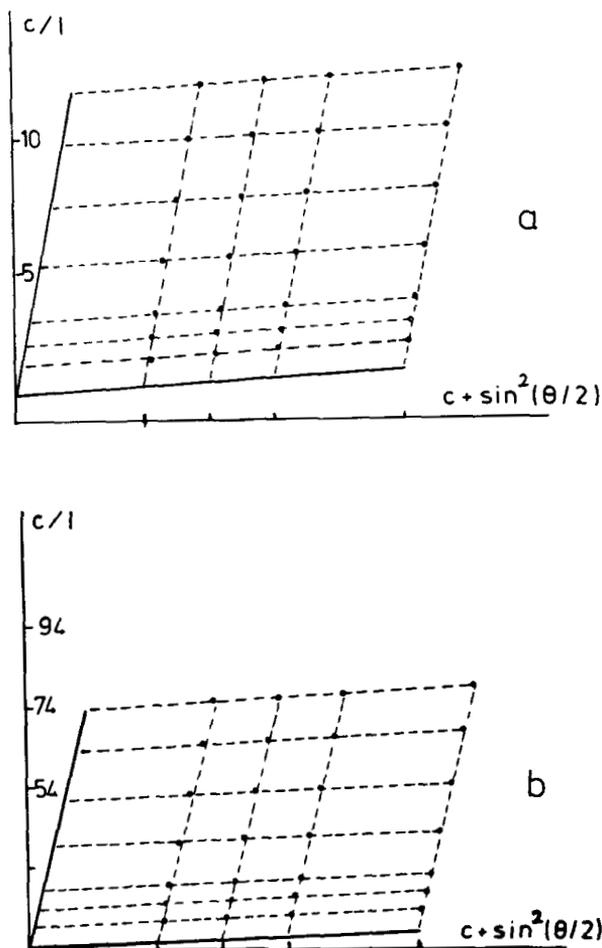


Fig. 9. Light-scattering Zimm plots of copolymer C; (a) undegraded sample; (b) after 1 h in free oxygen solution in the presence of 5 ppm of Fe^{2+} .

high viscosity loss. In another work,¹⁹ we show by conductimetry that the interactions of transition ions with copolymer C are not much stronger than that of alkaline earth ions, and changes in the viscosity of the same order of magnitude with the different types of ions could be expected.

2. In presence of Cu^+ , an initial decrease of molecular weight is observed, which is more important than that obtained with the approximately same molar concentration of Fe^{2+} (see Table II). This confirms that reducing ions play a role in the degradation process.

3. Curve 3 of Figure 11 corresponds to the variation of η_{red} with time when 5 ppm of Cu^{2+} are added in the polymer solution. This very important loss of viscosity is correlated to the decrease of molecular weight measured as well by light scattering (Table II) as by GPC (Fig. 12). The presence of oxidizing ions also influences the stability of the polymer. However the addition of Fe^{3+} leads to more complex phenomena. Indeed, in a first step, a phase separation is observed, with formation of microgels due to the formation of intermolecu-

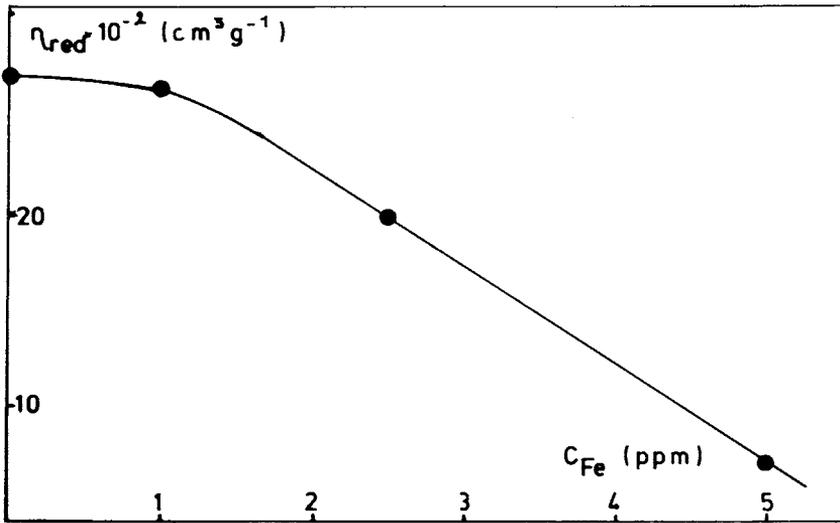


Fig. 10. Variation of the reduced viscosity of copolymer C measured after 1 h aging in free oxygen solution as a function of Fe^{2+} concentration.

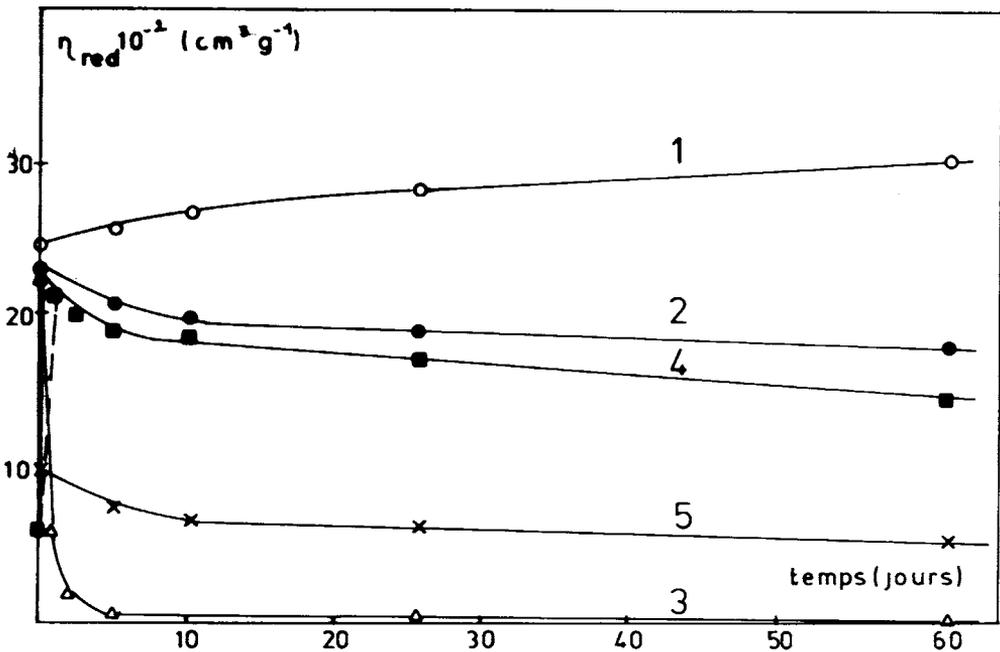


Fig. 11. Degradation of copolymer C in free oxygen solutions from viscosity results; curve 1: without added salts; curves 2, 3, 4, 5: with 5 ppm of Ca^{2+} , Cu^{2+} , Fe^{3+} , and Fe^{2+} , respectively.

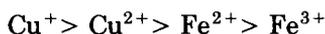
lar bridges by fixation of Fe^{3+} carboxylate groups. After one day, a homogeneous solution is again obtained according probably to a process described by Rosthauser et al.²⁸ for hydroxamic acid copolymers. Intramolecular bridges progressively take the place of intermolecular bridges and aggregates are partially destroyed. After this first step required to reach equilibrium state in

TABLE II

Ion (5 ppm)	0 Day	25 Days	60 Days
Ca^{2+}	$M_w = 5.2 \times 10^6$ $R_g = 2460 \text{ \AA}$ $A_2 = 3.4 \times 10^{-3}$	$M_w = 4.7 \times 10^6$ $R_g = 2300 \text{ \AA}$ $A_2 = 2.8 \times 10^{-3}$	$M_w = 4.5 \times 10^6$ $R_g = 2200 \text{ \AA}$ $A_2 = 2.4 \times 10^{-3}$
Cu^{2+}	$M_w = 7.5 \times 10^5$	—	—
Fe^{2+}	$M_w = 2.7 \times 10^6$ $R_g = 1670 \text{ \AA}$ $A_2 = 1.7 \times 10^{-3}$	$M_w = 1.7 \times 10^6$ $R_g = 1490 \text{ \AA}$ $A_2 = 8.4 \times 10^{-4}$	$M_w = 1.4 \times 10^6$ $R_g = 1217 \text{ \AA}$ $A_2 = 6.2 \times 10^{-4}$
Cu^{2+}	$M_w = 1.2 \times 10^6$ $R_g = 1081 \text{ \AA}$ $A_2 = 3.8 \times 10^{-3}$	$M_w = 4.7 \times 10^5$ — $A_2 = 1.7 \times 10^{-3}$	$M_w = 1.1 \times 10^5$ — $A_2 = -2 \times 10^{-3}$
Fe^{3+}	Phase Separation	$M_w = 4.1 \times 10^6$ $R_g = 2300 \text{ \AA}$ $A_2 = 1.7 \times 10^{-3}$	$M_w = 3 \times 10^6$ $R_g = 1900 \text{ \AA}$ —

solution, loss of viscosity and decrease of M_w are observed. The amplitudes of these variations are much lower than those obtained with Cu^{2+} . It is difficult to interpret these results in terms of difference in the oxidation-reduction potential of both ions. It seems that the fixation of the ions must be taken into account since it reduces the concentration of reactive ions.

The following order of catalysis activity of the studied ions in the degradation of copolymer C can be deduced from these experiments:



It is interesting to note that a different order was found in our experiments with P700: the oxidizing ions are more efficient than the reducing ions. This confirms that the degradation does not proceed by the same mechanism for these two samples.

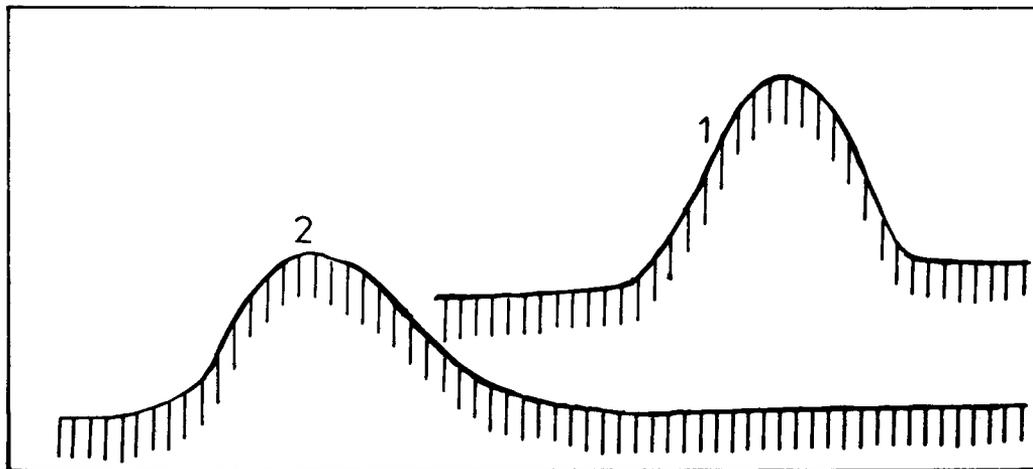


Fig. 12. GPC chromatograms of undegraded sample of copolymer C (1), and of the sample degraded in free oxygen solution in the presence of 5 ppm of Cu^{2+} (2) after 5 aging days.

DISCUSSION

In both cases where degradation of copolymer C occurs, it can be attributed to impurities contained in the polymer sample and which can be eliminated by precipitation in a methanol-ethanol mixture.

In the experimental part, we report results of analysis of this sample which contains very few impurities: we have only detected 1% of residual monomer (acrylic acid) and 4 ppm of methyl benzoate. We have reported in Figure 13 the reactional scheme of the photolysis of benzyl dimethyl cetal, used as photoinitiator in the polymerization of copolymer C. The reaction leads to the formation of intermediate reactive species according to a "cleavage" process of Norrish I type:²¹ benzoyl and α, α -dimethoxybenzyl radicals. The benzoyl radical plays the preponderant role in the polymerization initiation and can form benzoyl. The second radical leads, by decomposition, to the formation of methyl benzoate and to methyl radical, which either can participate in the initiation reaction, or by combination with benzoyl radical, also form methyl benzoate. Thus, it is not surprising to find methyl benzoate in the polymer sample and one also could expect the presence of benzyl in lower amount. Some spectroscopic measurements confirm this scheme: we have reported in Figure 14 the spectrum of a solution of benzyl dimethyl cetal at 50 ppm, with

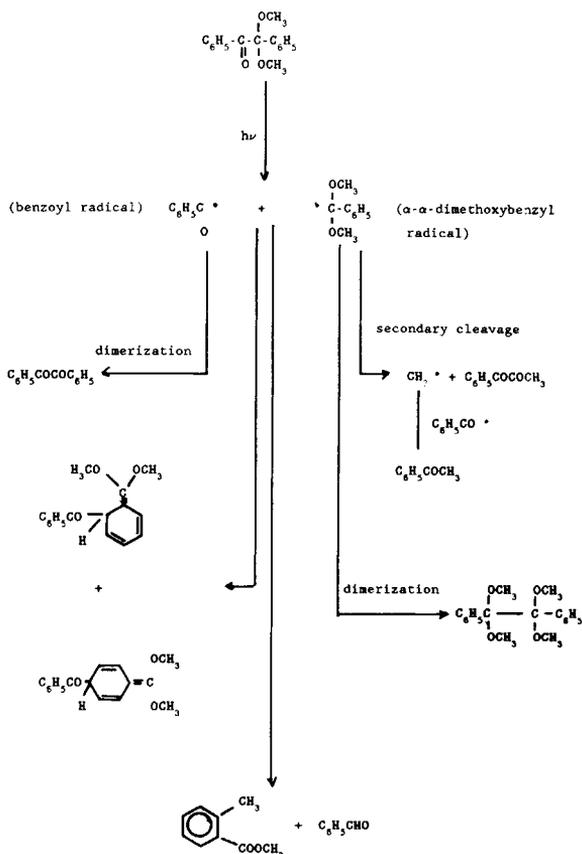


Fig. 13. Reactional scheme of the photolysis of benzyl dimethyl cetal from ref. 12.

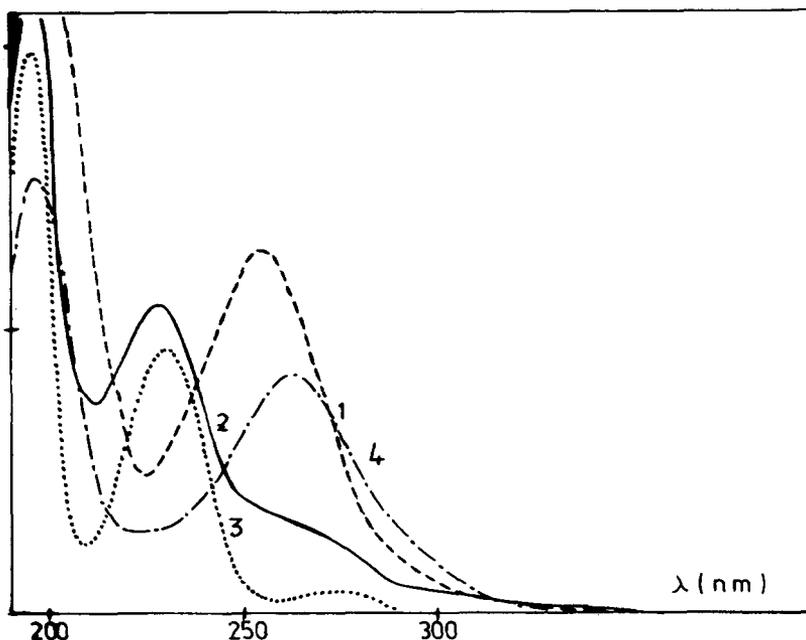


Fig. 14. UV absorption spectra of unirradiated (1) and irradiated solution of benzyl dimethyl cetal (50 ppm) (2), of methyl benzoate (3) and benzyl (4) solutions (50 ppm).

an absorption band at 255 nm, and the spectrum of the same solution irradiated by UV during 1 h, with a band at 228 nm and a shoulder at 265 nm. Comparison with the spectra of methyl benzoate and benzyl confirm that these two substances are the main products of the photolysis of benzyl dimethyl cetal (see Fig. 14).

The UV spectrum of a solution of benzyl dimethyl cetal heated several hours at 80°C in presence of ferrous ions and in absence of oxygen does not differ from that shown in Figure 14 (curve 1), for the unirradiated catalyst. A reaction of ferrous ions on residues of benzyl dimethyl cetal cannot be responsible for the polymer degradation. In Figure 15, are shown the spectra of the initiator solution irradiated during 1 h at 25°C and heated at 80°C during 30 min, after addition of 5 ppm of transition ions, Cu^+ , Cu^{2+} , and Fe^{2+} in absence of oxygen. The presence of reducing and oxidizing ions induces important changes in the spectrum: disappearance of the peak at 228 nm and increase of the absorption at 262.5 nm. This result clearly shows that oxidation-reduction reaction occurs between transition ions and products of the photolysis of the polymerization initiator.

Since methyl benzoate has been identified as main residue, we have studied, by UV spectroscopy, its behavior in the presence of ferrous ions. A slight change in the spectrum is observed, with the same decrease of absorption at 228 nm as previously described. If a very small amount of benzyl is added in the same solution, the spectrum modifications become more important (Fig. 16). One can deduce from these qualitative experiments that an oxidation-reduction of methyl benzoate with formation of free radicals could explain the degradation, with benzyl also playing a role. We have not found in literature

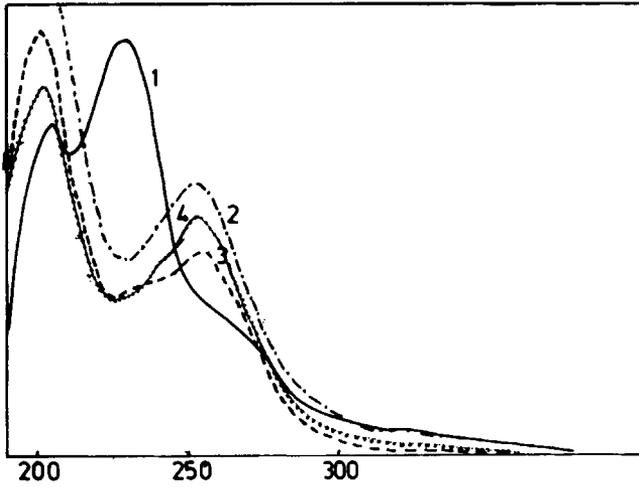


Fig. 15. UV absorption spectra of a benzyl dimethyl cetal heated at 80°C for 30 min in free oxygen solutions (50 ppm) without ions (1) and with 5 ppm of Cu^+ (2), Cu^{2+} , (3) and Fe^{2+} (4).

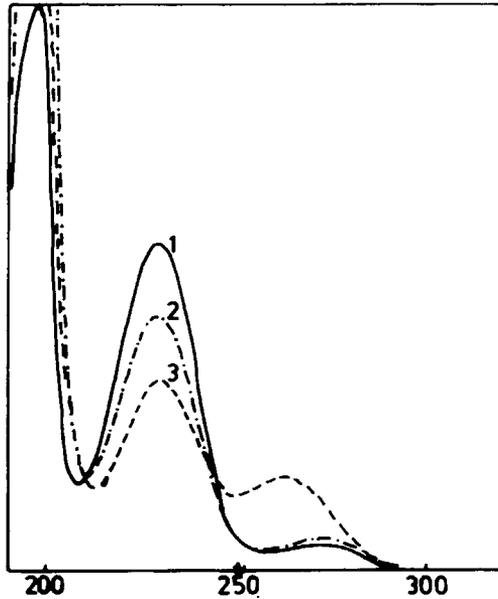


Fig. 16. UV absorption spectra of methyl benzoate in free oxygen solutions heated at 80°C for 30 min without additives (1) and in the presence of 5 ppm of Fe^{2+} (2) and 5 ppm of Fe^{2+} , and 5 ppm of benzyl (3).

any data dealing with possible reactions of methyl benzoate and transition ions.

We propose a speculative mechanism for the degradation of copolymer C by transition ions and in absence of oxygen, where benzyl is assumed to play a role by complexing the ions and changing their oxidation-reduction potential.

Some qualitative experiments led us to propose a mechanism whereby the decomposition of methyl benzoate by transition ions produces free radicals able to attack the polymer chain, such reaction being favored or hindered by the complexation state of the ion.

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