Influence of iron salts on the photooxidation of poly(N-vinylpyrrolidone) in aqueous solution

Fatima Hassouna [a,b,1], Gilles Mailhot [a,b,*], Sandrine Morlat-Thérias [a,b], Jean-Luc Gardette [a,b]

[a] Clermont université, Université Blaise Pascal, Laboratoire de Photochimie Moléculaire et Macromoléculaire, BP 10448, F-63000 Clermont-Ferrand, France
[b] CNRS, UMR 6505, BP 80026, F-63171 Aubière, France

ABSTRACT

This article reports on the effect of UV–vis radiation ($\lambda \geq 300$ nm) on the degradation of poly(N-vinylpyrrolidone) PVP photoinduced by Fe(III) in aqueous solution and in the presence of oxygen. The formation of oxidation products was followed by infrared analysis of deposits obtained after evaporation of water and by UV–vis analysis of the irradiated polymer solutions. Size exclusion chromatography (SEC) was used for monitoring the variations of molar weight and intrinsic viscosity with irradiation time. Total organic carbon (TOC) measurements were performed with the aim of checking the mineralisation of aqueous solutions.

Depending on the concentration of Fe(III), the concentration of PVP and the pH of the solution, we were able to show that the photooxidation of PVP leads to a chain scission and to a cross-linking mechanism, contrary to photooxidation of PVP in the absence of Fe(III) which only involves a mechanism of chain scission. A mechanism of PVP photooxidation until its possible mineralisation is proposed, taking into account the concentration of Fe(III) in the solution.

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1. Introduction

Because of its unique chemical and physical properties, Poly(N-vinylpyrrolidone) (PVP) has found significant use in pharmaceuticals, cosmetics (hairsprays), medicine (blood plasma extender), construction industry (in plywood, sealing composites, etc.), textiles, paper, detergents, etc. [1,2]. After use, depending on its domain of application, this polymer can be discharged as dilute aqueous solutions or into solid waste disposal systems. Effluents entering aqueous wastewater streams may enter the environment directly. Like the majority of synthetic polymers, PVP is not sensitive to biodegradation [3] so its fate in the environment is uncertain. Moreover, due to its water solubility, PVP has received less attention in the media than packaging plastics, which visibly litter the countryside and contribute to landfill overload.

The degradation of PVP in the environment may take place through several paths. Among the different abiotic degradation processes, solar irradiation is one of the main factors responsible for pollutant degradation in the aquatic environment. In a recent paper [4], we reported work on the photooxidation of poly(N-vinylpyrrolidone) (PVP) under long wavelengths ($\lambda \geq 300$ nm) in solid state and in aqueous solution. Based on the results of photooxidation, a mechanism accounting for the main routes of oxidation can be proposed.

The photochemical evolution of PVP under oxidative conditions under long wavelengths ($\lambda \geq 300$ nm) involves two types of hydroperoxides. The oxidation path, leading to scission of the macromolecular chain, involves the formation of a tertiary hydroperoxide, whereas in the path involving the formation of a secondary product, the decomposition of these hydroperoxides leads only to bond scission of the pyrrolidone ring.

If we examine the role of water in the orientation of the photooxidation mechanism, we notice that in the solid state, the rate of formed unsaturation is higher than in aqueous solution. The ratio between unsaturations and cyclic imides is higher in the solid state. There is thus a significant influence of the medium on the PVP degradation mechanism.

In this paper, we have investigated the influence of Fe(III) salts, which is a transition metal naturally present in the aquatic compartments, on the photochemical behaviour of PVP in aqueous solution. The influence of Fe(III) chloride on the photodegradation under 254 nm irradiation of PVP aqueous solution has been studied by Kaczmarek et al. [5]. The efficiency of FeCl$_3$ on the rate of photooxidation was compared with the effect caused by H$_2$O$_2$. It was concluded that the photo-oxidative degradation of PVP was accelerated by either FeCl$_3$ or H$_2$O$_2$. However, $^\bullet$OH and $^\bullet$OOH radicals,

which are generated from the decomposition of H_2O_2, were more efficient accelerating agents than $Cl^\bullet$ radicals. Moreover, the high concentration of carbonyl groups detected by IR spectroscopy is in favour of efficient Norrish I and II type reactions leading to a fast decomposition of PVP. A relatively high amount of gel was formed in PVP solution in the presence of H_2O_2, which points out that in this case recombination of macroradicals dominates the disproportionation or reaction between small radicals and macroradicals. It seems that in the presence of H_2O_2, the occurrence of ring opening reaction in PVP is more likely and the macroradicals formed in this process also take part in the termination of degradation. Interestingly, both the competing and opposing reactions of chain scission and cross-linking are efficiently accelerated for PVP irradiated in H_2O_2 solution compared to pure PVP.

In previous works, the photodegradation of pollutants induced by Fe(III) has been reported [6–8]. It has been revealed that the attack by $^\bullet OH$ radicals arising from Fe(III) species in the excited state is a very efficient process. Indeed, Fe(III) aquacomplexes can absorb solar light and undergo a photoredox process giving rise to Fe(II) and hydroxyl radicals [9,10]. Among the Fe(III) aquo-complexes, $Fe(OH)^{2+}$ (which refers to $[Fe(H_2O)_5(OH)]^{2+}$) is photolysed with the highest quantum yield [10] according to the following reaction:

$$Fe(OH)^{2+} \xrightarrow[H_2O]{h\nu} Fe^{2+} + {}^\bullet OH \tag{1}$$
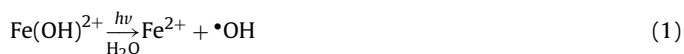
Hydroxyl radicals are known to be very reactive species, reacting with most organic substrates with rate constants that are limited by diffusion. The photodegradation of pollutants induced by Fe(III) [11,12] has been previously investigated and in all cases, it has been concluded that it was a useful process for the elimination of pollutants in water.

The present work deals with the photodegradation of PVP in aqueous solution induced by Fe(III) aquacomplexes until it is completely mineralised. The role of Fe(III) species is discussed and a mechanism of PVP degradation is proposed.

2. Materials and methods

2.1. Materials

All reagents were of the purest grade commercially available and were used without further purification.

Poly(N-vinylpyrrolidone) (PVP) sample was supplied by Scientific Polymer Products. The average molar weight of the polymer was $360,000\,g\,mol^{-1}$. Ferric perchlorate nonahydrate $(Fe(ClO_4)_3 \cdot 9H_2O; >97\%)$ was a Fluka product kept in a dessicator. Hydroxylamine chlorhydrate and ferrozine (3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid, sodium salt, 97%) were purchased from Aldrich.

Water was purified by a Millipore Ultra-Pure System $(\rho = 18.2\,M\Omega\,cm)$. PVP solutions of 6.25% $(62.5\,mg\,mL^{-1})$, 1.25% $(12.5\,mg\,mL^{-1})$ and 0.1% $(1.0\,mg\,mL^{-1})$ of wt.% were prepared by dissolving PVP into deionised water with mild stirring overnight at room temperature. The natural pH of aqueous solutions of PVP was around 4.2. Acidified solution (pH 3.1) was obtained by adding drops of diluted $HClO_4$. $HClO_4$ was chosen for acidifying the aqueous solution because ClO_4^- is far less reactive and photosensitizer than Cl^-, and is the counter anion of the ferric salt used. No buffer was used in order to avoid any contamination of the solution and any interaction with iron.

Solutions with iron were prepared by dissolving $Fe(ClO_4)_3$ in PVP aqueous solutions. The pH of the solution changed from 4.2 to 3.1 or 4.2 to 2.95 after the addition to PVP aqueous solution ($[PVP] = 62.5\,mg\,mL^{-1}$) of $Fe(ClO_4)_3$ at a concentration of $6 \times 10^{-4}\,mol\,L^{-1}$ or $1.2 \times 10^{-3}\,mol\,L^{-1}$, respectively. Solutions with

hydrogen peroxide were prepared by adding different concentrations of H_2O_2 (10^{-1}, 10^{-2}, 10^{-3}, 1.2×10^{-3} and $6 \times 10^{-4}\,mol\,L^{-1}$) into PVP aqueous solutions ($[PVP] = 62.5\,mg\,mL^{-1}$).

Relatively concentrated polymer solution (6.25%) was chosen in order to follow the chemical modifications of the irradiated solutions by IR analysis of deposits on ZnSe windows. FTIR transmission spectra were recorded for thin deposits of oxidised samples of PVP, which were obtained by evaporation of aliquots of irradiated aqueous solution of PVP. The samples were dried at room temperature for 24 h.

Unless otherwise noted, our experiments were performed with $[PVP] = 62.5\,mg\,mL^{-1}$ (6.25%) and $[Fe(III)] = 6 \times 10^{-4}\,mol\,L^{-1}$.

2.2. Irradiation

PVP aqueous solutions were irradiated in a SEPAP 14/24 unit at $20\,°C$. The chamber is an elliptical reactor equipped with one medium-pressure mercury lamp (Mazda MA 400) in vertical position at one focal axis of the chamber. Wavelengths below 300 nm were filtered by a glass envelope. At the second focal axis of the chamber, the aqueous solution of PVP was placed in a Pyrex reactor cooled by water circulation. The temperature of the solution was maintained at $20\,°C$ in order to avoid water evaporation.

2.3. Chemical and spectrophotometric analysis

Fe(II) concentration was determined by complexometry with *ortho*-phenanthroline, using $\varepsilon_{510} = 1.118 \times 10^4\,L\,mol^{-1}\,cm^{-1}$ for Fe(II)-phenanthroline complex [13]. Total iron concentration was determined after reduction of Fe(III) species with a solution of hydroxylamine chlorhydrate $(3\,mol\,L^{-1})$ prepared by dissolution of 104.25 mg in a 500 mL flask into 200 mL 32% HCl and then completed with distilled water. Ferrozine forms a strong coloured complex with Fe(II). In a 5 mL flask were added 0.25 mL sample, 1.5 mL water and 0.5 mL of hydroxylamine solution $(3\,mol\,L^{-1})$. After stirring vigorously and waiting for 10 min, it was added 0.5 mL of ferrozine $(0.02\,mol\,L^{-1})$, 1 mL ammonium acetate buffer 0.1 N and water to complete to 5 mL. After stirring, absorbance was measured at 562 nm. The accuracy of the method is $\pm 0.1\,\mu mol\,L^{-1}$.

Infrared spectra were recorded with a Nicolet 760-FTIR spectrometer, working with OMNIC Software. Spectra were obtained using 32 scans summation and $4\,cm^{-1}$ resolution. The thickness (e, in μm) of the non-photooxidised samples was calibrated by measuring the absorbance (OD) at $1370\,cm^{-1}$, which corresponds to a vibrational band of (C–H) bending mode. The thickness dependence of the absorbance obeyed the equation $OD = 0.0175 \times e$. UV–vis spectra of solutions were recorded on a Cary 3 double beam spectrophotometer (Varian).

The variations of molar weight, viscosity and molar weight distribution (polydispersity index, Mw/Mn) were measured by size exclusion chromatography (SEC) using a Viscotek chromatograph working with a differential refractometer detection (Viscotek VE 3580), a viscometer detector (Viscotek TriSec Model 270) and a linear column (TSK/Ref: GMPWXL). The analyses were performed with $NaNO_3$ $0.1\,mol\,L^{-1}/CH_3CN$ (80/20) as eluent at a flow rate of $0.7\,mL\,min^{-1}$. The equipment was calibrated with PEO standards. Molar weight distributions were calculated with OMNISEC Software.

Total organic carbon (TOC) in aqueous solution was measured using a Total Organic Carbon analyzer Shimadzu model TOC-5050A. The Shimadzu TOC-5050A is capable of performing total carbon (TC) analyses by combustion and inorganic carbon (IC) analyses by oxidation in 25% H_3PO_4 solution. TOC measurements were obtained by calculating the difference between TC and IC measurements. Calibration curves within the range of $0–500\,mg\,L^{-1}$ for TC and $0–100\,mg\,L^{-1}$ for IC were obtained using potassium hydrogen phthalate for total carbon and sodium hydro-
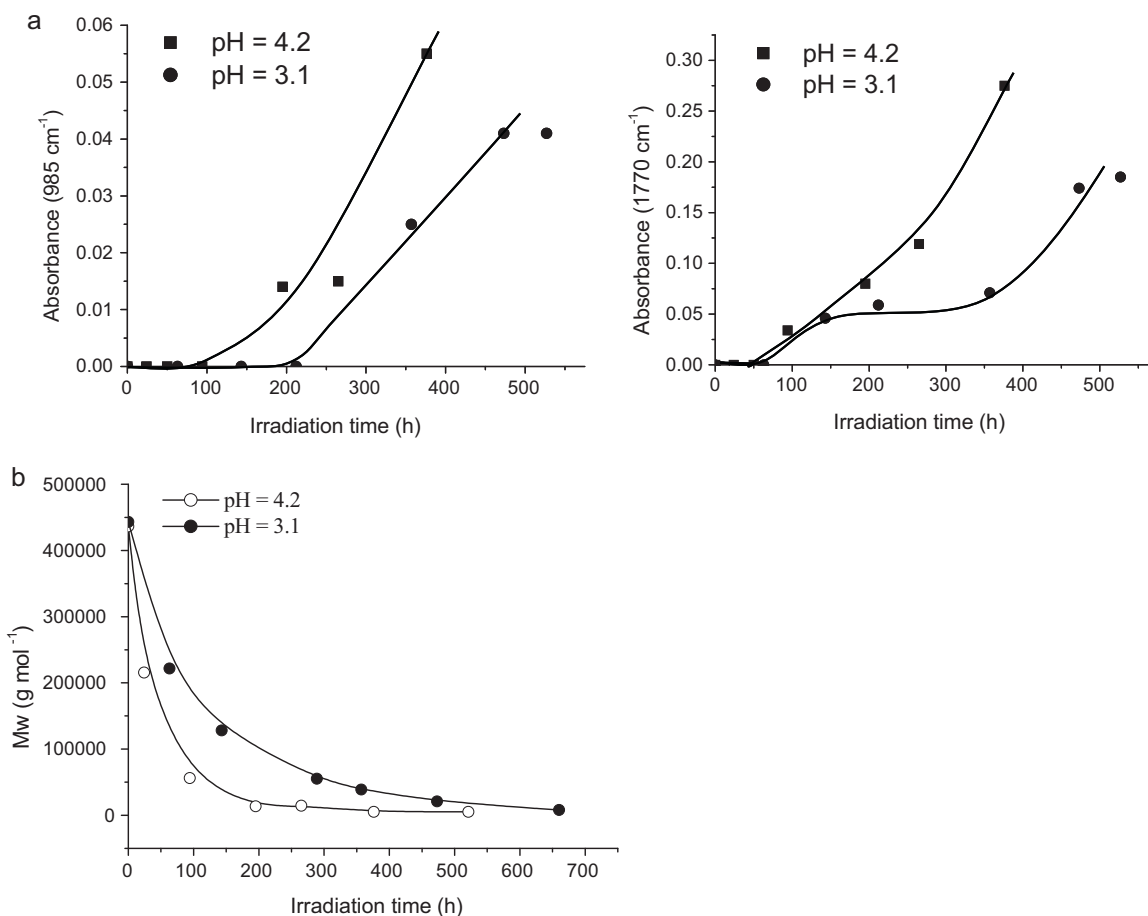
Fig. 1. (a) Evolution of absorbance at 1770, and 985 cm^{-1}, of PVP aqueous solutions as a function of irradiation time, pH $_{initial}$ = 4.2 and 3.1, [PVP] = 62.5 mg mL^{-1}. (b) Evolution of PVP molar weight (Mw) as a function of irradiation time for PVP aqueous solutions at pH 4.2 and 3.1, [PVP] = 62.5 mg mL^{-1}.

gen carbonate with potassium carbonate for inorganic carbon.

The insoluble fraction of the samples was evaluated by gravimetric measurements for different times of irradiation. After each exposure time of PVP aqueous solution, the solutions were filtered and the insoluble fractions were dried outdoors. The films obtained were then put into a glass phial with water, a solvent of PVP. The amount of water was adjusted in order to obtain the same specific concentration for all the mixtures; typically M_{total}/V_{water} = 3.5 mg mL^{-1}. The phials were then hermetically sealed and hidden from the daylight for 96 h. The gel obtained was dried until constant weight. The gel fraction is defined as the ratio between the weight of the dry gel ($M_{insoluble}$) and the weight of PVP (M_{total}).

$$\text{Gel fraction} (G_f) = \frac{[M_{insoluble}]}{[M_{total}]}$$

3. Results and discussion

Firstly, before approaching the study of the photooxidation of PVP aqueous solution in presence of Fe(III) (pH 3.1), the PVP photooxidation was studied at the same pH but without Fe(III). The solution was acidified with HClO$_4$ in order to study the effect of the pH on the photooxidation of PVP aqueous solution before investigating the effect of the Fe(III). Indeed, during the dissolution of Fe(ClO$_4$)$_3$, perchloric acid is formed in the aqueous solution. Moreover, a dark experiment at room temperature with PVP and Fe(III) in aqueous solution was performed. No degradation of PVP and no interaction between PVP and Fe(III) were observed after few days.

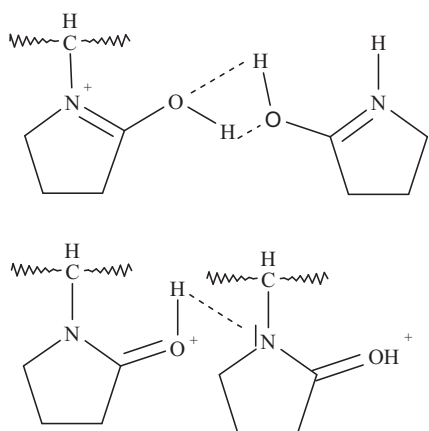### 3.1. Photooxidation of PVP aqueous solution at pH $_{initial}$ = 3.1

3.1.1. PVP aqueous solution in the presence of perchloric acid

The IR spectrum of PVP deposit obtained from aqueous solution in presence of HClO$_4$ shows two new absorption bands at 1095 and 620 cm^{-1} compared to IR spectrum of natural PVP aqueous solution. The intensity of these two bands increases with the concentration of HClO$_4$. The same bands were observed in the spectrum of HClO$_4$. These two bands are thus part from ClO$_4^-$ vibrations.

3.1.2. Photooxidation process

During photooxidation of PVP aqueous solution in presence of oxygen at 20 °C (pH 3.1), chemical modifications of PVP were followed by IR analysis. Deposits, of about 20 μm, were obtained by casting from aqueous irradiated solutions onto ZnSe wafers. After evaporation of water, the thickness of the deposits was determined by IR. The general evolution of the IR spectra of PVP upon irradiation at pH 3.1 in aqueous solution is comparable to that of PVP aqueous solution at pH 4.2 [4]. Furthermore, the stoechiometries of the different photoproducts are identical. The pH of the solution decreased weakly during irradiation, from 3.1 to 3.0 after 300 h.

Kinetics of photoproducts formation at pH 4.2 and 3.1 were compared by studying the evolution of the absorbance measured at 1770 cm^{-1} (succinimide rings), and 985 cm^{-1} (unsaturations) (Fig. 1a). These rates are slower at pH 3.1 than at pH 4.2. At pH 3.1, an induction period of around 50 h is observed before the detection of photoproducts. This indicates that the rate of photooxidation of PVP decreases in the presence of HClO$_4$.

Scheme 1. Possible hydrogen bonds to be formed between PVP chains in acidic solution (pH 3.1).

The evolution of average molar weights of PVP in aqueous solution (pH 3.1) during the photooxidation was characterized by SEC and compared with the trend observed at pH 4.2 (Fig. 1b). A decrease of the molar weight was observed during the irradiation, which implies a mechanism of chain scission, but the decrease of molar weight was faster when the initial pH of the solution was 4.2 rather than 3.1. This means that the mechanism of chain scissions slowed down in the presence of HClO$_4$. This result is in agreement with the evolution of IR spectra commented previously.

One explanation of the slower photooxidation of PVP in presence of HClO$_4$ is that in relatively acidic solution, protonation of PVP takes place on the oxygen atom, whereas protonation on the nitrogen atom would destroy the conjugation [14]. Indeed, PVP can be considered as a Lewis polybase [15] and the electronic configuration of the polymer after protonation is consequently modified. Interactions by hydrogen bonding can take place between PVP macromolecular chains. The same behaviour was observed when carboxylic acids or polyacids were added to the PVP aqueous solution [15–17] (Scheme 1).

3.2. Photooxidation of PVP aqueous solution in the presence of Fe(III)

3.2.1. IR analysis

After dissolution of Fe(III) in PVP aqueous solution, the pH of the solution decreased from 4.2 to 3.2. Irradiation of this solution led to important modifications of IR spectra obtained on deposits of aliquots of the polymer aqueous solution on ZnSe plate.

Several absorption bands were observed from the beginning of irradiation (Fig. 2). Absorption bands corresponding to succinimide ring (1770 and 820 cm^{-1}) appeared from the first 8 h of irradiation while absorption bands corresponding to unsaturations (1060, 985 and 785 cm^{-1}) were observed after an induction period of 25 h. These absorption bands are similar to those observed during the photooxidation of PVP aqueous solution in absence of Fe(III), which indicates that the oxidation products are identical. Furthermore, the photoproducts of PVP in water in presence and in absence of Fe(III) represent the same percentage as a function of degraded PVP. As a contrary, it is important to note that the pH increased from 3.2 to 3.4 after 400 h of photoageing and reached the value of 3.8 after 500 h. The pH of the aqueous solution PVP/Fe(III) tends to increase during the irradiation contrary to the behaviour under irradiation of the PVP aqueous solution in absence of Fe(III). This observation has an important consequence on the speciation of iron species present in aqueous solution.
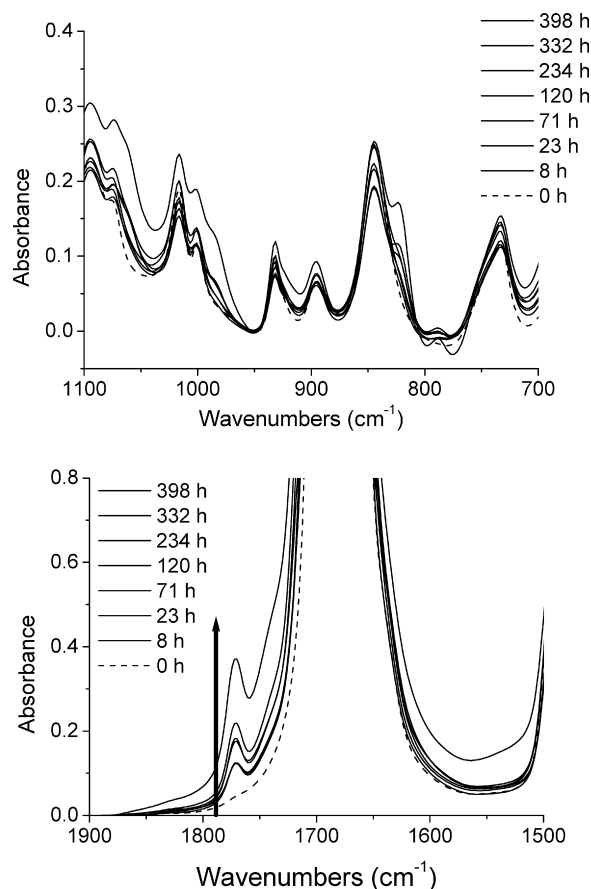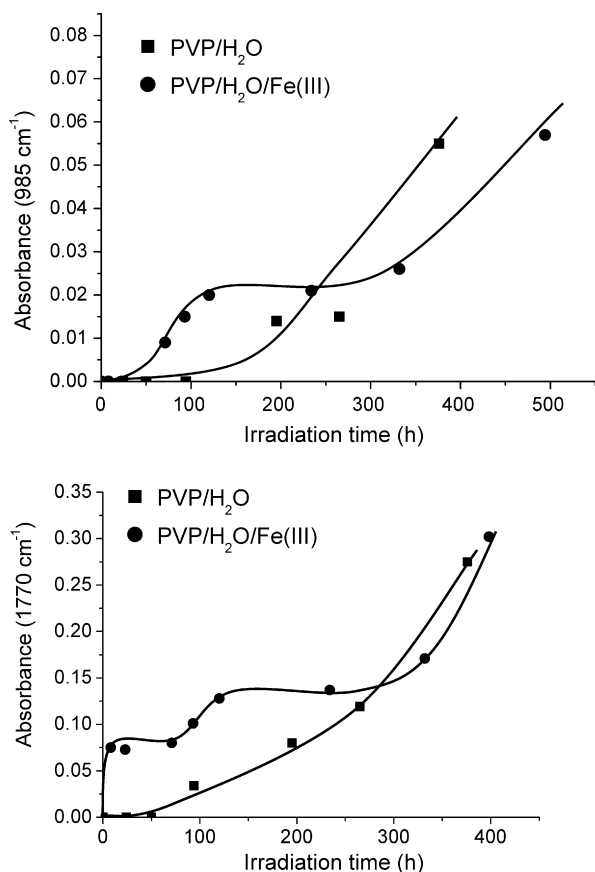

Fig. 2. FTIR spectra of deposits obtained from a PVP aqueous solution in the presence of Fe(III) during photooxidation (pH 3.2, [PVP] = 62.5 mg mL^{-1}, [Fe(III)] = 6 × 10^{-4} mol L^{-1}).

3.2.2. Kinetics of photooxidation

The variations of absorbance at 1770 and 985 cm^{-1} as a function of irradiation time of PVP aqueous solution are plotted in Fig. 3. These results show that in the presence of Fe(III), the rate of formation of the photoproducts is faster during the first hours of irradiation. The degradation kinetics in the presence of Fe(III) allow confirming the correlations of the absorption bands at 1770 and 820 cm^{-1} assigned to succinimide rings [4] as well as unsaturations at 785 and 985 cm^{-1}. Indeed, oxidation products corresponding to the unsaturations appear after an induction period of 25 h and the oxidation products corresponding to the succinimide rings are detected from the beginning of the irradiation. In the absence of Fe(III), the different photoproducts can be observed beginning after 50–80 h of irradiation. In presence of Fe(III), during the first hours of irradiation, the rate of formation of the photoproducts is significant. Indeed, as shown in a previous article devoted to the influence of Fe(III) on the photodegradation of PEO [18], the monomeric species Fe(OH)$^{2+}$ are predominant in aqueous solution at pHs between 2.5 and 5.0, and can be considered as the most important source of •OH radicals production (reaction 1) under exposure to light.

The concentration of Fe(II) was also measured all along the irradiation. The results show a very fast increase in the concentration of Fe(II) at the beginning of the irradiation, which mainly results from the photoredox process of Fe(OH)$^{2+}$ species. Fe(III) is mainly transformed into Fe(II) and the formation of •OH is maximum. Then, Fe(II) concentration reaches a constant value corresponding to a photostationary equilibrium between Fe(III) and Fe(II) in the presence of organic compounds ([Fe(II)] ≈ 5.5 × 10^{-4} mol L^{-1} at the
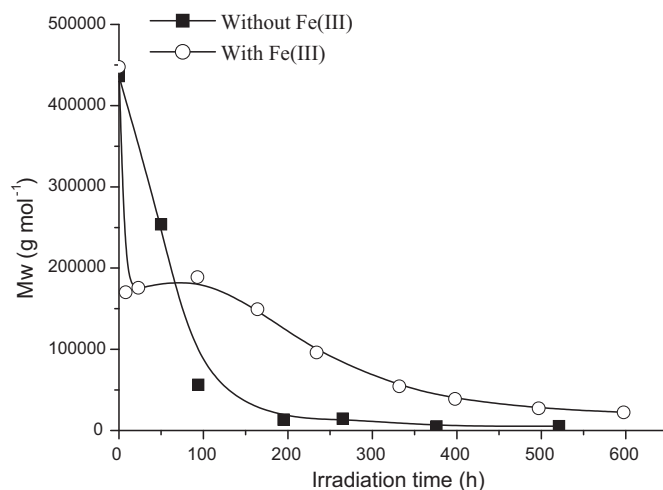
Fig. 3. Evolution of absorbance at 1770 and 985 cm^{-1}, of PVP aqueous solution as a function of irradiation time in presence of Fe(III) (pH$_{initial}$ = 3.1, [PVP] = 62.5 mg mL^{-1}, [Fe(III)] = 6 × 10^{-4} mol L^{-1}).

Fig. 4. Evolution of PVP molar weight (Mw) as a function of irradiation time in the presence and in the absence of iron ([Fe(III)] = 6 × 10^{-4} mol L^{-1}, [PVP] = 62.5 mg mL^{-1}).

competition between a mechanism of chain scissions and cross-linking in which an equilibrium is established.

3.3. Influence of Fe(III) concentration

The influence of Fe(III) concentration on the photooxidation of PVP in water was followed by IR spectroscopy, UV–vis spectrophotometry and by SEC analyses for two concentrations of Fe(III): 6 × 10^{-4} and 1.2 × 10^{-3} mol L^{-1}. The increase of Fe(III) concentration from 6 × 10^{-4} to 1.2 × 10^{-3} mol L^{-1} in PVP aqueous solution ([PVP] = 62.5 mg mL^{-1}) leads to the formation of hydrogel after 350 h of irradiation. This hydrogel was not observed for concentration of Fe(III) equal to 6 × 10^{-4} mol L^{-1}.

3.3.1. IR analysis
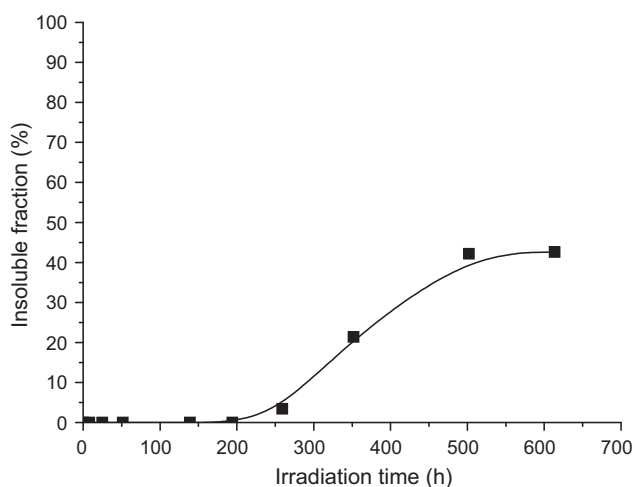
The presence of Fe(III) at a concentration of 1.2 × 10^{-3} mol L^{-1} in PVP aqueous solution leads to the decrease of the pH of the solution from 4.2 to 2.9. IR analysis did not show any evolution of PVP between 0 and 300 h of irradiation, which means that the presence of iron with higher concentration slows down considerably the appearance of the photoproducts as imides and unsaturations. It is important to note that after 350 h of photoageing, the solution became a hydrogel. The pH of the solution evolved during the photooxidation, it increased from 2.9 to 3.2 after 400 h of irradiation.

3.3.2. UV–vis analysis

The UV–vis spectra of PVP aqueous solution irradiated in the presence of Fe(III) (1.2 × 10^{-3} mol L^{-1}) showed mainly the disappearance of the absorption band at 297 nm corresponding to the transformation of Fe(III) to Fe(II). There were no significant changes in the absorption spectra of PVP in aqueous solution during 350 h of irradiation. After 350 h, the polymer in solution was a hydrogel and consequently it was not possible to continue its characterization by UV–vis spectrophotometry.

3.3.3. Hydrogel characterization

The cross-linking of PVP in aqueous solution was investigated by monitoring the insoluble fraction generated during irradiation. The nature of the hydrogel formed was also determined, namely reversible or permanent. The evolution of the insoluble fraction upon irradiation is represented in Fig. 5. During the first 200 h of irradiation, no insoluble fraction was measured. After that, an insoluble network of polymer appeared. The ratio of the insoluble part increased up to a plateau corresponding to 45% of insoluble fraction.

plateau), as reported in a previous study on PEO photodegradation [18]. This photostationary equilibrium can be explained by a photocatalytic cycle between Fe(III) and Fe(II) species [18].

The second phase of the kinetic curves of the photooxidation of PVP aqueous solution in presence of Fe(III) (between 100 h and 300 h) (Fig. 3) corresponds to a slowing down of the rate of formation of the photoproducts. This can be explained by the presence, after the first period where Fe(OH)$^{2+}$ is photodegraded, of a photocatalytic cycle of Fe(III)/Fe(II) in which radical species ($^\bullet$OH) are formed regularly in much smaller amount. This second phase can correspond also to the induction observed in the experiment without iron. After 350 h, the formation rate of the photoproducts increases again and resembles the kinetics obtained in the absence of iron. Iron has no more photochemical impact in the phototransformation of PVP.

3.2.3. SEC analysis

The changes provoked by the irradiation of PVP aqueous solution in the presence of Fe(III) (Fig. 4) can be characterized by the decrease in average molar weights, which implies several chain scissions. The decrease of molar weights is faster during the first hours of irradiation in presence of Fe(III). This result clearly shows the photoinductive effect of Fe(III) due to the production of $^\bullet$OH under irradiation. The mechanism of chain scissions is thus accelerated in presence of Fe(III). Between 8 and 100 h of irradiation, the average molar weight is almost constant. The invariance of the average molar weight can be correlated with the kinetics of formation of the photoproducts which show the same slow-down after 8 h of irradiation. This phenomenon can be attributed to the strong decrease of $^\bullet$OH hydroxyl radical production and/or to the

Fig. 5. Evolution of the insoluble fraction as a function of irradiation time ([PVP] = 62.5 mg mL^{-1}, [Fe(III)] = 1.2 × 10^{-3} mol L^{-1}, pH $_{initial}$ = 2.9).

In order to determine the nature of the insoluble fraction, several tests were carried out. Indeed, several types of interactions can be at the origin of the formation of hydrogels. The cross-linking can proceed through the formation of covalent bonds involving the macroradical reactivity, through the formation of hydrogen bonds between the molecules of polymer or through iron chelation by the polymeric matrix. To elucidate the nature of the PVP cross-linking and the eventual involvement of iron species, three tests were performed: heating test, ferrozine test and the effect of H$_2$O$_2$.

3.3.4. Heating test

Heating a reversible hydrogel leads to the breaking of hydrogen bonds and consequently makes the polymer soluble, which constitutes a simple test. For that purpose, 0.81 g of the hydrogel was placed in 10 mL of ultra-pure water. The mixture was warmed at 80 °C hermetically during 10 h. After filtration of the mixture, the totality of the insoluble fraction was recovered. This result shows that the hydrogen bonds are not at the origin of the hydrogel formation.

3.3.5. Ferrozine test

The hypothesis according to which Fe(III) or Fe(II) was in interaction with photooxidized PVP leading to the formation of the reversible hydrogel was not dismissed even though this hypothesis remains not very probable. Indeed, UV–vis spectra recorded at various extents of the photochemical ageing did not show any absorption band which could correspond to the formation of a complex between iron and photooxidized PVP. Furthermore, chemical functions such as carboxylates or alcoholates susceptible to chelate iron were not observed by IR.

Nevertheless, a test that could allow us to definitively throw back the hypothesis of possible interaction of the photooxidised PVP with Fe(II) or Fe(III) was performed. This test consisted in a quantitative determination of the total iron using ferrozine, a very strong complexing agent of iron, in the hydrogel obtained after 500 h of irradiation. Indeed, if iron was responsible for the formation of the hydrogel by interaction with photooxidized PVP, the ferrozine would make PVP soluble again in water, since it can complex iron. However, the totality of the iron was recovered after this quantitative determination (1.2 × 10^{-3} mol L^{-1}) and the hydrogel was not dissolved in the aqueous solution in spite of drastic conditions of pH used in this titration of iron.

The two tests described above have shown that the hydrogel formed after irradiation of PVP aqueous solution in the presence of Fe(III) (1.2 × 10^{-3} mol L^{-1}) was not reversible. Neither the

hydrogen bonds nor the iron were responsible for the cross-linking of the polymer. This suggests that the formation of an hydrogel in presence of Fe(III) was probably due to intermolecular covalent bonds. Indeed, Fe(OH)$^{2+}$ were the dominant species in moderately acidic aqueous solution (pH 2.9). The production of hydroxyl radicals •OH during initial periods of irradiation was very important as the concentration of Fe(III) was very high (1.2 × 10^{-3} mol L^{-1}). In PVP aqueous solution, hydroxyl radicals lead to the formation of macroalkyl radicals by the abstraction of hydrogen atom from macromolecules at backbone or on the pyrrolidone ring [4]. The macroradicals are likely to form covalent bond in an intermolecular cross-linking process, which involves recombination of radicals coming from two different macromolecules [19]. So, according to Fig. 5, the insoluble fraction for this concentration of Fe(III) during the first 200 h of irradiation is not observed. After that, the insoluble fraction increases very quickly and reaches a limit value corresponding to maximal insolubility, which suggests the presence of a cross-linked network in the polymeric matrix.

The photooxidation of PVP aqueous solution with two different concentrations of iron gives an evidence of the influence of the Fe(III) concentration. When the concentration of Fe(III) is more important (1.2 × 10^{-3} mol L^{-1}), the photoageing leads to the formation of a hydrogel while for a Fe(III) concentration of 6 × 10^{-4} mol L^{-1}, a mechanism of PVP degradation by chain scissions is predominant. In order to confirm the intervention of hydroxyl radicals (•OH) formed by direct photolyse of Fe(OH)$^{2+}$ in the process of cross-linking of the polymer, aqueous solutions of PVP were irradiated in the presence of H$_2$O$_2$, which can be considered as another photochemical source of hydroxyl radicals.

3.3.6. Effect of H$_2$O$_2$

The photooxidation of PVP aqueous solution in the presence of H$_2$O$_2$ at different concentrations (10^{-1}, 10^{-2}, 10^{-3}, 6 × 10^{-4} mol L^{-1}) was investigated. Irradiation of PVP aqueous solution in presence of 10^{-1} mol L^{-1} of H$_2$O$_2$ led to the appearance of three absorption bands, 785, 985 and 1060 cm^{-1} after only 10 h of irradiation. The absorption bands corresponding to succinimide rings (820 and 1770 cm^{-1}) were not observed. After 10 h of irradiation, a hydrogel was formed. A deposit could be obtained by drying this hydrogel, but the IR spectra of the sample was too noisy. To obtain IR spectra of the hydrogel, the dry hydrogel was immersed in liquid nitrogen and crushed in a mortar to reduce it into powder. From this powder, KBr pellets were prepared. The IR spectra obtained from these pellets showed the absorption bands at 785, 985 and 1060 cm^{-1}, while the bands at 820 and 1770 cm^{-1} were very weak.

UV–vis analysis did not show any evolution during the irradiation, which can be explained by the fact that the accumulation of unsaturated products is not significant. The pH of the aqueous solution remained constant during the first 10 h of irradiation. These experimental results (IR, UV–vis, pH measures) can be correlated. They show that the process leading to the formation of oxidation products is minor although photoproducts were observed by IR analysis.

The characterization of the hydrogel by measurement of the insoluble fraction as a function of irradiation time is presented in Fig. 6. At the highest concentration of H$_2$O$_2$ (10^{-1} mol L^{-1}) and after only 10 h of irradiation, 46% of the polymer became insoluble. After 13 h, the rate of insoluble fraction was maximal (67%) while from 100 h of irradiation a beginning of dissolution of the hydrogel was observed. At lower concentration of H$_2$O$_2$ (10^{-2} mol L^{-1}), the insoluble fraction of the polymer did not represent more than 20% and a complete dissolution was observed after 60 h of irradiation. When the concentration of H$_2$O$_2$ was divided by 10, the maximal rate of insoluble fraction decreased from 67% to 18%. Indeed, when the concentration of H$_2$O$_2$ decreased, the quantity of hydroxyl radicals
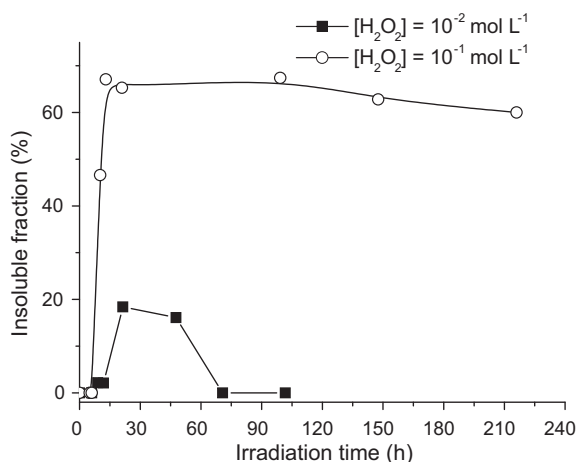
Fig. 6. Evolution of the insoluble fraction as a function of irradiation time ($[PVP] = 62.5 \, mg \, mL^{-1}$, $[H_2O_2] = 10^{-1}$ and $10^{-2} \, mol \, L^{-1}$).

Fig. 7. TOC evolution of PVP aqueous solution during the irradiation, $[PVP] = 0.1 \, mg \, mL^{-1}$, $[(Fe(III))] = 6 \times 10^{-4} \, mol \, L^{-1}$, pH 3.1.

formed by direct photolysis of H_2O_2 also decreased. These results suggest that hydroxyl radicals are responsible for the formation of the hydrogel. Furthermore, photoproducts previously observed during the irradiation of PVP in the water are not formed in a significant manner.

In the case where the concentration of H_2O_2 was between 10^{-3} and $6 \times 10^{-4} \, mol \, L^{-1}$, no hydrogel was formed during the irradiation. It was observed throughout the photooxidation course that no UV–vis absorption band appeared. Also, no bands corresponding to photoproducts were detected by IR over a period of 475 h. In addition, the pH of the solution remained constant and the average molar weight decreased only by 10% after 475 h.

As shown by the IR, UV–vis and SEC analysis, the presence of H_2O_2 at relatively low concentrations ($\leq 10^{-3} \, mol \, L^{-1}$) in PVP aqueous solution leads to a considerable decrease of the oxidation rate of the polymer. This indicates that H_2O_2 acts as a stabilizer at low concentration. A recent study showed that PVP is capable of forming a stable cyclic complex (during several months) with H_2O_2 by hydrogen bonds [20]. The formation of this complex when the concentration of H_2O_2 is lower could protect the polymer from the photochemical oxidation.

The immediate conclusions from these different experimental results concern the role of hydroxyl radicals in the formation of the hydrogel. Indeed, during the photooxidation of the PVP aqueous solution in the presence of relatively high concentration of H_2O_2 there is an important production of hydroxyl radicals generated by direct photolysis of H_2O_2. They abstract hydrogen atoms from macromolecules, thus macroradicals are formed. The most important reaction of macroalkyl radicals is the intermolecular cross-linking. Moreover, it is well known that only a small proportion of these radicals seems to evolve according to a mechanism of chain scissions [4].

3.4. Total organic carbon (TOC) concentration

TOC experiments were undertaken to prove the efficiency of Fe(III) salts in the elimination of PVP from the aqueous solution. Relatively diluted polymer solutions ($0.1 \, mg \, mL^{-1}$) were chosen in order to highlight the mineralisation process of the polymer. The evolution of organic carbon concentration in PVP aqueous solutions in the absence or in the presence of Fe(III) is illustrated in Fig. 7. In the presence of Fe(III) (pH 3.1), 70% of the TOC quickly disappeared during the first 40 h of irradiation but the total mineralisation of the polymer was not reached. Indeed, 13% of the organic carbon still remained in the aqueous solution after 118 h of irradiation. The
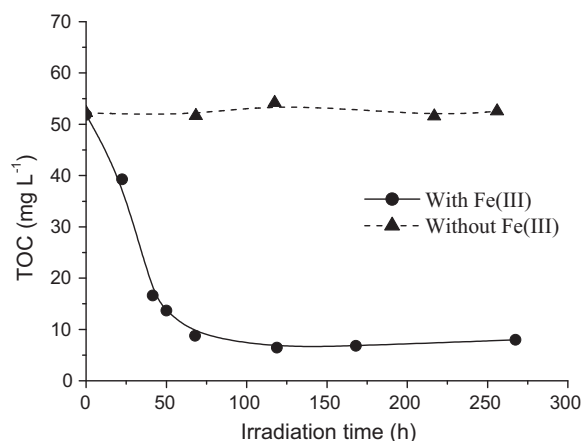
degradation products accumulated after 40 h are probably not or weakly photodegradable. On the contrary, in the absence of Fe(III), no decrease of the TOC was noticed after 270 h of irradiation. Therefore, the important mineralisation (87%) of PVP in presence of Fe(III) can be explained by the photoinductor effect of iron leading to the formation of hydroxyl radicals. In our experimental conditions, the presence of iron in PVP solutions gave an important mineralisation of PVP during photooxidation.

4. Conclusions

The present work illustrates the efficiency of PVP degradation in aqueous solution photoinduced by Fe(III). Through our study, we demonstrate that a couple Fe(III)- solar light can play an important role in the fate of PVP in water. According to the concentration of Fe(III), the concentration of PVP and the pH of the medium, photooxidation of PVP leads to a chain scission or to a cross-linking mechanism contrary to the photooxidation of PVP in the absence of Fe(III) where only the mechanism of chain scission was observed. Indeed, the influence of the presence of Fe(III) on the mechanism of photooxidation of PVP in relatively concentrated aqueous solution ($[PVP] = 62.5 \, mg \, mL^{-1}$) shows that:

- When Fe(III) is added at a concentration of $6 \times 10^{-4} \, mol \, L^{-1}$, iron is mainly present in the form of $Fe(OH)^{2+}$, which is the most photoreactive species in terms of $^\bullet OH$ radicals formation. In this case, hydroxyl radicals provoke the acceleration of the degradation process of the polymer by chain scissions.
- When the concentration of the Fe(III) is two times higher ($1.2 \times 10^{-3} \, mol \, L^{-1}$), the same iron species ($Fe(OH)^{2+}$) is present in aqueous solution but at higher concentration. In this case, the concentration of macroradical is also increased. So, the mechanism of cross-linking of the polymer is strongly favoured and the formation of a permanent hydrogel is observed. Effectively, the production of hydroxyl radicals is much more important during the first times of irradiation since the concentration of Fe(III) is higher. These radicals react with PVP macromolecular chains to give macroalkyl radicals that lead to the generation of cross-linked network. The formation of the hydrogel, therefore, is attributed to the recombination of macroalkyl radicals.

The incorporation of H_2O_2 into the PVP aqueous solution showed clearly the role of hydroxyl radicals in the formation of the hydrogel. The presence of H_2O_2 at high concentrations ($10^{-1} \, mol \, L^{-1}$), which is also a photochemical source of hydroxyl radicals leads to the formation of a hydrogel.

During this work, we also demonstrated that iron species present in aqueous solution can oxidise the PVP until its partial mineralisation. The addition of Fe(III) (6×10^{-4} mol L^{-1}) into PVP diluted aqueous solution (0.1 mg mL^{-1}) leads to a high mineralisation (87%) of the polymer.

The mechanism of photooxidation of PVP in aqueous solution in the presence of Fe(III) depends strongly on the ratio between the concentrations of PVP and of Fe(III). At lower concentration of Fe(III), the presence of iron accelerates the photooxidation of PVP by a mechanism of chain scission identical to that observed in aqueous solution without iron, showing mainly the formation of succinimide rings and unsaturations. At higher concentration of iron, the photochemical reaction leads to a mechanism of polycondensation of macromolecular chains until the formation of insoluble hydrogel.

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